# SATURATED HYDROCARBON POLYMERIC BINDER FOR ADVANCED SOLID PROPELLANTS

## TRIENNIAL REPORT

PERIOD COVERED: October 27, 1965
September 30, 1968

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100.

Report Edited By: James E. Potts

Contributors: A. C. Ashcraft, Jr.
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} UCC

Publication Date: October 31, 1968

Jet Propulsion Laboratory Contract No. 951210

Technically Managed By: H. E. Marsh, Jr. JPL

UNION CARBIDE CORPORATION
Chemicals and Plastics
Polymer Research and Development
Bound Brook, New Jersey

RE-ORDER NO. 68-607

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# TECHNICAL CONTENT STATEMENT

This report contains information prepared by Union Carbide Corporation, Chemicals and Plastics Operations Division, under J.P.L. subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology or the National Aeronautics and Space Administration.

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# I. OBJECTIVE

Union Carbide Corporation, Plastics Division, has agreed to provide, on a level of effort basis, assistance to the improved polymeric binder for advanced solid propellant and hybrid solid grains.

The desired binder shall meet the following general requirements:

1. The binder must principally consist of saturated aliphatic hydrocarbon, compatible with high energy oxidizers such as nitronium perchlorate and stable with ammonium perchlorate under heat-sterilization conditions and space environment.

2. The binder shall be compatible with powdered light metals or their hydrides for hybrid propellant applications.

3. The binder shall be a low temperature curing (below 100°F) polymer, which will cure within the time span of seven hours and seven days.

4. The prepolymer shall be a liquid at room temperature with a viscosity below 2500 centipoise, shall not crystallize on storage and shall have a low glass transition temperature.

5. The curing reaction shall proceed without evolution of by-products (i.e. an addition reaction).

Other, more detailed requirements are set forth in the contract.

## II. SUMMARY

### Part 1

Saturated, amorphous ethylene-neohexene copolymers containing terminal carboxylic acid groups have been made by free radical, high pressure polymerization using azobisisobutyronitrile (AIBN) as initiator and terminator of chain growth, followed by hydrolysis of the CN groups to COOH groups.

Copolymers in the required viscosity range (100-2500 cps) were prepared without difficulty. Amorphous, non-crystallizable polymer was obtained at a composition of 2.6 moles of ethylene per mole of neohexene. These products remain liquid (increasingly viscous) down to -70°F.

The acid functionality of the hydrolyzed copolymer is low due to the hybrid character of the initiator radicals produced by AIBN. One end group type (CN) hydrolyzes to COOH, the other (keteneimine) does not.

In spite of the low average functionality, this prepolymer was cured with formulations suggested by J.P.L., to yield soft, rubbery gels, apparently crosslinked and insoluble in organic solvents.

Molecular distillation is effective for producing fractions of these ethylene-neohexene copolymers in the molecular weight range of 200-800. The fractions so obtained have very narrow molecular weight distributions.

### Part 2

Ethylene-neohexene prepolymers were prepared using the organic peroxides succinic acid peroxide and glutaric acid peroxide. These initiators result in acid terminated prepolymers which are quite high in viscosity considering their molecular weights. Esterification of the acid end groups results in a decrease in viscosity, which is attributed to elimination of hydrogen bonding association. Molecular weight determinations in polar solvents such as tetrahydrofuran yield functionalities close to one COOH per molecule. Hydrogen atom chain transfer involving the peroxide initiators themselves is believed to be responsible for this.

## Part 3

Diethyl α, α'-azobis-isobutyrate has been prepared and its kinetics of thermal decomposition measured at 100°C. This initiator was then used for ethylene/neohexene copolymerizations. The products were saponified using potassium hydroxide in n-butanol, then acidified to give the carboxyl terminated products. Analysis of these products showed them to be monofunctional in COOH.

## Part 4

Dimethyl α,α'-azobisisobutyrate (DMAB) has been synthesized from readily available materials in a four step synthesis with an overall yield of 58%. This material was used as an initiator in the preparation of ethylene/neohexene copolymers. It decomposes with kinetics similar to both AIBN and DEAB to give free radicals and may be used interchangeably with either initiator.

The oxygen functionality of the prepolymer made with DMAB initiator was found to decrease with increasing batch reaction time, indicating a changing reaction environment. Further examination of these products demonstrated that after saponification and recovery of the acidified product, the COOH functionality was near 1.0 regardless of the $O_2$ functionality of the ester terminated precursor. These results were explained on the basis of chain transfer to methyl isobutyrate, a known decomposition product of DMAB and an active telogen.

A small, continuous, high pressure tube reactor was used to carry out a series of ethylene-neohexene copolymerizations using DMAB as the initiator. Larger quantities of copolymer could easily be made using this technique, however, upon hydrolysis of the resulting ester terminated copolymers, the carboxyl terminated products were monofunctional. These experiments demonstrated that even in the short residence times which exist in the tube reactor (1-2 minutes), radicals from DMAB have time to disproportionate extensively to yield methyl isobutyrate.

## Part 5

The synthesis of di-t-butyl α, α'-azobisisobutyrate (DTAB) was attempted in order to evaluate DTAB as an initiator. The synthesis failed but gave intermediates which proved to be useful later in the program (see Part 8).

## Part 6

A fundamentally different route to a prepolymer of higher functionality than attainable with DMAB or AIBN initiation was then examined. This route utilized the telomerization of ethylene/neohexene with $CCl_4$; initiated by a small quantity of a free radical initiator. Low molecular weight molecules result which have a chloride functional group upon one end and a trichloromethyl group on the other. These telomers were produced with functionalities approaching two in the batch stirred autoclave reactor. Telomerizations run in the continuous tubular reactor were less successful however, probably due to the telogen $CCl_4$ being used up in the reaction zone near the entrance of the reactor, with none being available in succeeding portions of the tube.

The terminal Cl and $CCl_3$ group proved to be difficult to efficiently convert into COOH groups. Hydrolysis of the $CCl_3$ groups using conditions which work well for non-polymeric substances failed when applied to the $CCl_4$ telomers of ethylene/neohexene.

## Part 7

Three symmetrical disulfides containing ester functionality were synthesized for use as telogens in the telomerization of ethylene with neohexene. The disulfides were: dimethyl α, α'-dithiodibutyrate, di-t-butyl α, α'-dithiobis isobutyrate , and dimethyl dithioglycolate

The disulfides prepared were found to be inhibitors rather than active chain transfer agents. The conversion to copolymer was very low and the sulfide functionalities of the products themselves were very low.

## Part 8

In order to circumvent the only serious problem encountered in the telomerization of ethylene/neohexene with $CCl_4$, namely the difficulty of converting the telomer functional groups to COOH, telogens were prepared which yield more reactive end groups. Bromotrichloromethane, bromoacetic acid, bromoisobutyric acid, and the t-butyl and methyl esters of α-bromoisobutyric acid were the telogens obtained for this purpose. The latter three compounds proved to be very useful in this respect, giving rise to telomer molecules having one bromide end group and one carboxyl or carboxylic ester end group.

These products were expected to be easier to convert to difunctional carboxyl terminated prepolymers than any products produced to date. Having one COOH group per molecule as a starting point, we planned to use the more reactive bromide group in various ways to obtain additional carboxylic acid functionality.

Model compound studies on 11-bromohendecanoic acid have demonstrated the feasibility of this approach for preparing dicarboxylic acids using three different reaction sequences.

Of the methods which were tried for converting the telomer terminal groups into carboxyl groups, one has yielded curable prepolymers. This method is based upon elimination of HBr from the telomer end groups, followed by oxidation of the resulting terminal double bond to give a carboxyl group. Complete conversion to the desired products in each step was required in order to realize the highest functionality in the final product.

The continuous feed equipment used on the tubular reactor (discussed in Parts 4 and 6) was adapted for use with the stirred autoclave previously used in batch copolymerizations and telomerizations. The continuous stirred autoclave reactor thus obtained allowed the production of telomers in longer continuous runs at pressures up to 20,000 psi. This reactor was subsequently modified by substitution of a reaction vessel of higher pressure rating, giving an upper limit of 35,000 psi. Telomers of the highest functionality yet obtained were prepared using this reactor and the telogen methyl α-bromoisobutyrate. The largest run completed to date in the continuous stirred autoclave reactor yielded 549 grams of telomer having a functionality of 1.05 bromides per molecule at a molecular weight of 883.

## Part 9

A new series of telomers was prepared having ethylene and propylene as comonomers and having $BrCCl_3$, α-bromo isobutyric acid and its t-butyl and methyl esters as the telogens. A combination of low viscosity and very low penetration temperature make these telomers very attractive as solid propellant binder precursors. Telomers were also prepared using three other α-olefin comonomers, butene-1, propene-1 and hexene-1, giving telomers with even lower penetration temperatures.

The low functionality caused by chain transfer to monomer in these runs remains the main obstacle to preparation of curable binders using these comonomers. A higher reactor pressure (greater than 35,000 psi) may allow attainment of higher functionalities or else fractionation of the chemically modified telomer may be necessary.

## Part 10

Analytical procedures for the analysis of ionomers and the comonomer distribution in copolymers were developed and applied to the ethylene/neohexene copolymers.

The new technique of gel permeation chromatography was used to determine the molecular weight distributions of ethylene/neohexene copolymers prepared by various methods. The ratio $\bar{M}_w/\bar{M}_n$ was found to be between 1.2 and 1.5 for the samples studied. The data accumulated in this study provide strong reasons for preferring molecular weight data obtained in polar solvents such as tetrahydrofuran, to similar data obtained when non-polar solvents are used.

Several factors which might adversely influence the attainment of satisfactory levels of carboxyl content in the prepolymer have been examined critically. The choice of solvent in the molecular weight determination had previously been found to be very critical. The titrimetric procedure for determining neutralization equivalent was found to be somewhat lacking in precision and accuracy and was altered. This had only a small effect on the measured value of N. E.

The possibility that polymeric anhydrides were being formed during sample work-up was tested using an available analytical determination for anhydrides. No evidence for the presence of anhydrides was found.

The monomer, neohexene, was analyzed by gas chromatography on a capillary column for the presence of chain transfer impurities--none were found.

Three methods for determining the glass transition temperature of liquid prepolymers were examined in order to select a convenient method for routine examination of samples. These methods consisted of 1) simply measuring the temperature at which a sample becomes a glassy solid in a manner analogous to determining a freezing point, 2) measurement of the temperature at which a weighted penetrometer needle begins to sink into the glassy polymer as it is allowed to warm up through $T_G$, and 3) measurement of the dynamic mechanical properties of the polymer using a torsion pendulum. Method (2) was found to be fast, reliable and more suitable for screening large numbers of samples than either of the other methods. In the molecular weight region of interest, the ethylene neohexene copolymers have a transition temperature near -50°C.

Column chromatography on silica gel was used to separate a carboxyl terminated ethylene/neohexene copolymer of 1.34 average functionality into fractions differing in functionality. These fractions were analyzed by thin layer chromatography on silica gel. The latter technique provided a rapid qualitative analysis of the functionality distribution of the various fractions, independent of molecular weight determination or functional group assay. The technique of thin layer chromatography as utilized in this program may be of general applicability for the analysis of other binder materials for functionality distribution.

Countercurrent distribution between dimethylformamide and pentane allowed preparative isolation of the difunctional component of a carboxyl terminated binder sample of low functionality.

## III. SCOPE OF PROJECT

The scope of the experimental program has been outlined in the work statement and performance schedule of the contract and must be viewed in relation to the level of effort permitted by the contract.

The technical approach which was adopted at the beginning of the project is described in the Introduction. Basic to this initial approach was the concept that terminally difunctional copolymers of ethylene could be prepared in the presence of a high concentration of initiator free radicals bearing the functional group desired or precursors from which the desired functional group could be obtained. The comonomer used in this initial approach was neohexene, and small batch copolymerizations in already existing high pressure reactors were run to quickly define the experimental conditions necessary to synthesize the required copolymers.

This approach has been subject to redefinition as new facts were generated and chemical principles elucidated during the course of the actual laboratory work. In particular the scope of the project was expanded to include 1) telomerization as a means for introducing the required functional groups and controlling the molecular weight of the resulting copolymers and also to include 2) an examination of the copolymers of ethylene with other α-olefins.

Major emphasis has been placed upon development of reliable methods for the characterization of the copolymers prepared, particularly in the area of functionality determination. The synthetic program has been primarily directed toward preparing copolymers with as high a terminal functionality as possible.

# IV. INTRODUCTION

The initial approach adopted by the Union Carbide Corporation's Plastics Division for the synthesis of the polymeric binder described in Part 1 of this report was based upon the high pressure, free radical copolymerization of ethylene with neohexene. Specific initiators and chain terminating agents were selected to place certain desired functional groups at the chain ends.

In order to achieve control over end group functionality in such a copolymer it was necessary that unwanted chain transfer agents be excluded from the system. The temperature must be kept well below 200°C to avoid chain transfer effects from the monomers themselves. The solvent must be chosen to maintain a homogeneous system during copolymerization and must not be a transfer agent.

The use of ethylene as the sole monomer under these conditions of polymerization will not yield an amorphous polymer, but rather a low molecular weight polyethylene, which is highly crystalline because of the very regular $CH_2$ sequence in the polyethylene chain. A comonomer is necessary to disrupt this regularity if the crystallinity of the product is to be avoided.

Neohexene (3,3-dimethylbutene-1) was selected as the comonomer of choice for the binder program for the following reasons: 1) The t-butyl groups derived from the neohexene monomer units were expected to be quite effective in disrupting the ordered $CH_2$ chain. 2) Neohexene was commercially available. 3) Neohexene posseses no allylic hydrogen atoms and is therefore not expected to give rise to chain transfer. 4) The reluctance of neohexene to homopolymerize except under forcing conditions greatly increases the ease of formation of random copolymers.

The type of functional group which is introduced at the ends of the copolymer chain is determined by the choice of free radical initiator used. It is preferable that the initiator be cleaved homolytically to two identical radicals, each bearing the desired functional group or a group which can be converted into the desired group without altering the rest of the copolymer.

The functional group of choice is the carboxylic acid group for the following reasons: (1) This group reacts readily with aziridines and epoxides at low temperatures to give cross links without evolution of by-products. (2) Among the functional groups which are known to react at low temperature the carboxyl group is the most inert to nitronium perchlorate.

Prior to the inception of this contract, Carbide had carried out preliminary copolymerization experiments which had yielded liquid copolymers having room temperature viscosities around 25,000 centipoise. These polymers were made using azobis isobutyro-nitrile (AIBN) as the initiator. From number average molecular weight and kjeldahl nitrogen analysis it was calculated that these samples contained on the average two nitrogen atoms per molecule. The samples also exhibited strong absorption at 4.46 μ in the infrared, the wave length associated with the CN band. Alkaline or acid hydrolysis of the CN groups to COOH was considered to be technically feasible.

Various alternate initiators for placing carboxyl groups on the polymer chains were reviewed with JPL personnel, including azobisisobutyronitrile (AIBN), azobis cyanovaleric acid, and succinic acid peroxide. AIBN was chosen as the initiator to be used in preparing prepolymer for initial evaluation. This choice was based on several considerations:

1. Preliminary copolymerizations using AIBN had given an apparent functionality of two.

2. Such copolymers containing CN groups had been successfully hydrolyzed, which eliminated the CN band in the infrared.

3. AIBN is a commercially available, reasonably priced initiator.

4. The fully hydrolyzed copolymer was believed to contain no functional groups other than carboxylic acid.

Part 1 of the technical discussion to follow describes and interprets the results obtained using this initial approach.

Succeeding Parts 2 through 5 describe the results obtained when other free radical initiators were used in place of AIBN in the procedure described above. Part 2 deals with polymerization in the presence of the diacyl peroxide initiators derived from succinic acid and glutaric acid, while Parts 3 and 4 deal with polymerizations conducted in the presence of the azoester initiators diethyl azobisisobutyrate (DEAB) and dimethyl azobisisobutyrate (DMAB).

Parts 6 through 9 deal with the preparation of the polymeric binder using a fundamentally different approach. In this approach an active chain transfer agent or telogen is added to the polymerization reaction mixture along with a comparatively small amount of a free radical initiator. The initiator serves to start free radical polymerization which results in growing polymer chains containing a functional group derived from the initiator at one end and an unpaired electron at the other end. Subsequently the growing polymer radical abstracts a functional group from the added telogen producing a terminated difunctional polymer radical, and a new radical derived from the telogen. This radical is capable of behaving like an initiator radical and giving rise to another growing polymer chain. The net result of this process of telomerization is that a low molecular weight polymer, or telomer, is formed, each molecule of which contains two functional groups derived from the telogen. A comparatively smaller number of molecules will be produced which contain a functional group derived from the initiator.

Part 6 deals with telomerizations in which carbon tetrachloride was used as the telogen. The functional groups produced in this case were Cl and $CCl_3$, and proved to be difficult to convert efficiently into carboxyl groups.

Part 7 deals with attempts to use disulfides containing ester functionality as chain transfer agents.

Part 8 describes the use of several bromine containing telogens to produce telomers of high terminal functionality. Methods whereby this functionality is converted into the required carboxyl functionality are also described.

In part 9 copolymers of ethylene with propylene and several other α-olefins are described. These were prepared by the telomerization method described in Part 8.

Part 10 describes special analytical methods developed during the course of this work. These methods were developed to measure comonomer content, functionality, low temperature properties, functionality distribution and molecular weight distribution of the copolymers produced in this program.

# V. TECHNICAL DISCUSSION, PART 1

## ETHYLENE/NEOHEXENE COPOLYMERS PREPARED WITH AIBN INITIATOR

### Contents

# PART 1

## ETHYLENE/NEOHEXENE COPOLYMERS PREPARED WITH AIBN INITIATOR

### A. Determination of Optimum Neohexene Level in Copolymer

A series of six copolymerization experiments were carried out at 90°C, using benzene as solvent and AIBN as initiator, in which the ratio of ethylene to neohexene in the charge was varied in order to determine the minimum amount of neohexene needed in the polymer to eliminate crystallinity. The resulting copolymers varied from crystalline waxes to fluid oils, depending on neohexene content.

A method for analysis of comonomer ratio in the copolymer was developed based upon nuclear magnetic resonance spectroscopy (N.M.R.). The method is described in detail in Part 10, Section B, of this report. The results of this analysis of the copolymers described above are given in Table I.

TABLE I

NMR ANALYSIS OF ETHYLENE/NEOHEXENE COPOLYMERS

| Sample 22EMS | Mol. Wt. Mn | 25°C Viscosity, cps | Wt. % Neohexene in Charge | Ethylene/ Neohexene Mol Ratio in Copolymer |
|---|---|---|---|---|
| 26 | 1212 | Wax | 47 | 8.0 |
| 27 | 1176 | Grease | 53 | 6.4 |
| 28 | 536 | Grease | 55 | 5.3 |
| 29 | 630 | Soft Grease | 60 | 4.9 |
| 32 | 424 | 1270 | 65 | 3.4 |
| 33 | 357 | 1195 | 70 | 2.6 |

Only samples thirty-two and thirty-three are suitable as amorphous binders; the other samples were partially crystalline. Sample thirty-two solidified at -69°F while sample thirty-three solidified at -76°F. Both samples thirty-two and thirty-three were in the viscosity range desired by J.P.L. (100-2500 cps).

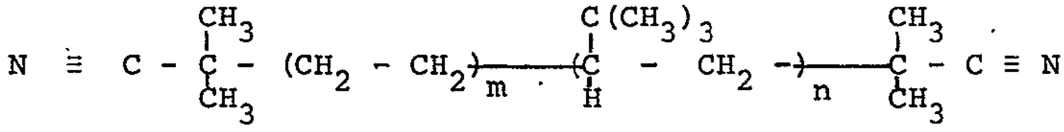
We have concluded from these results that the ethylene to neohexene molar ratio must be 3.4 or less in the final product in order to prevent crystallization of the copolymer. To achieve this molar ratio in the product, the comonomer charge to the reactor must contain at least 65 wt.% neohexene.

## B. Preparation of the Nitrile Terminated Prepolymer

The experiments shown in Table II were performed to determine the reproducibility of composition, molecular weight, viscosity and nitrogen functionality which could be obtained by performing the batch copolymerization in the same manner for five consecutive runs. These experiments were carried out in a 1.5 liter Magnedash high pressure autoclave. In continuous polymerization equipment where higher conversion rates would be desired, pressure would be higher than used here.

These five samples contained from fifty-six to sixty-one per cent neohexene and varied in molecular weight from 1083 to 1358. The nitrogen functionality varied from 1.93 to 2.50. From the observed viscosity - molecular weight data on samples five - eight, it is estimated that sample four should have a molecular weight around 1000 for a viscosity of 18,000 cps. This would result in a functionality of about two for sample four.

In the above runs it was assumed that the initiator, AIBN, dissociated into two cyanoisopropyl radicals and one molecule of $N_2$ and that both initiation and termination was accomplished by these radicals. The resulting copolymers should have the structure:



$$N \equiv C - \underset{CH_3}{\overset{CH_3}{C}} - (CH_2 - CH_2)_m - (\underset{H}{\overset{C(CH_3)_3}{C}} - CH_2 -)_n - \underset{CH_3}{\overset{CH_3}{C}} - C \equiv N \qquad \text{I}$$

Elemental analysis for nitrogen was used to compute the nitrile equivalent weight. The number average molecular weight was determined by vapor phase osmometry. Functionality is defined as the ratio between these two weights:

$$\text{Functionality} = \frac{\text{Number Average Molecular Wt.}}{\text{Equivalent Weight}}$$

Calculation of the nitrogen functionality by this method has given values near two for most of the AIBN initiated samples prepared, including those shown in Table II. These results support structure I for the prepolymer. As will be shown later, however, the nitrogen analysis cannot be used as a measure of the nitrile content.

## TABLE II

## PREPARATION OF ETHYLENE/NEOHEXENE COPOLYMERS

| Run No. 22EMS- | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| <u>Charge</u> | | | | | |
| Benzene, gms | 410 | 410 | 410 | 410 | 410 |
| Neohexene, gms | 625.5 | 625.5 | 625.5 | 625.5 | 625.5 |
| Wt. % on Monomers | 75 | 75 | 75 | 75 | 75 |
| AIBN, gms | 34 | 34 | 34 | 34 | 34 |
| <u>Reaction Conditions</u> | | | | | |
| Temperature °C | 90 | 90 | 90 | 90 | 90 |
| Pressure, psi | 7500 | 7500 | 7500 | 7500 | 7500 |
| Time, hours | 4.5 | 4.5 | 4.75 | 3.4 | 4.27 |
| <u>Production Data</u> | | | | | |
| Resin, gms | 116 | 105 | 97 | 110 | 97 |
| Conversion, % | 13.8 | 12.5 | 11.5 | 13.1 | 11.5 |
| Rate, %/hour | 3.1 | 2.8 | 2.4 | 3.9 | 2.7 |
| <u>Physical Properties</u> | | | | | |
| % Neohexene | 56 | 59 | 60 | 57 | 61 |
| Wt. % N, Kjeldahl | 2.74 | 2.57 | 2.52 | 2.61 | 2.47 |
| Mol. Wt. (Mechrolab Osmometer) | 1277 | 1197 | 1110 | 1086 | 1083 |
| Nitrogen Atoms/Polymer Chain | 2.50 | 2.20 | 2.00 | 2.02 | 1.93 |
| Brookfield Viscosity, 74°F cps | 18,500 | 31,250 | 25,500 | 24,400 | 25,200 |

## C. Hydrolysis of the Nitrile Terminated Prepolymer.

As initially prepared, the copolymers made with AIBN have no value in curable systems. It is necessary to convert the terminal CN groups into reactive functional groups such as -COOH or - $NH_2$, which can then be reacted with di- or tri-functional curing agents. For previously discussed reasons it was decided to hydrolyze the nitrile groups over to carboxyl groups.

It was found that, compared to model compounds, the nitrile groups in the copolymers were quite resistant to hydrolysis by mild conditions. However, by using more vigorous conditions we were able to completely hydrolyze the terminal CN groups. Carboxy terminated prepolymers were obtained by the following procedures:

1. The prepolymer is heated under autogenous pressure in a titanium lined rocker bomb in n-butanol solution in the presence of $H_2O$ and strong caustic. LiOH, NaOH and KOH were all effective. At 200°C a reaction time of twenty-four hours was needed to complete the reaction. Fifteen hours was inadequate to completely remove CN groups. At 150°C the reaction was much slower. These reaction times were prolonged by the poor agitation in the rocker bomb.

2. Hydrolysis can be effected at atmospheric pressure by passing steam through the prepolymer heated to 250°C in the presence of an excess of NaOH and with violent agitation.

3. Using a 1" duplex-dispersator (Premier Mills, Inc.) for agitation, hydrolysis can be effected at 110°C and atmospheric pressure in the presence of $H_2O$ and NaOH. Reaction times of forty-eight hours are required.

4. Acid hydrolysis has been effected by heating the polymer in the presence of an equal volume of 48% aq. HBr in a sealed Pyrex tube. At 150°C the reaction is complete in about twenty-four hours. At 200°C, a considerable amount of decarboxylation occurs.

Pivalonitrile, $(CH_3)_3$-C-CN, a model compound for the end group of the prepolymer, was hydrolyzed in heptane solution using 48% aq. HBr. After one hour in a rocking sealed tube at 150°C no trace of pivalonitrile remained and the required amount of pivalic acid was formed. No other products were observed.

During the course of this study a gas-liquid chromatographic method for the analysis of pivalonitrile, pivalic acid and other related compounds was developed and used.

Heptane solutions of both pivalic acid and nitrile were unchanged after heating at 150°C for twenty-four hours.

The kinetics of the hydrolysis of a sample of CN terminated ethylene - neohexene prepolymer was studied at 90°, 120°, and 150°C, using 48% aqueous HBr and neat polymer. Pseudo first order kinetics were found in all experiments. The following expression for rate constant was calculated from the rate constant data:

$$k = 8.44 \times 10^{10}\ e^{-22,600/1.987T}, \text{ where T is in } {}^{\circ}K$$

The time for 99% reaction at 200°C was calculated to be 1.5 hours. A sample of the prepolymer was subjected to hydrolysis with 48% aq. HBr at 200° for 16 hours. Hydrolysis was complete, however 2/3 of the COOH groups were lost by decarboxylation at this temperature.

Table III summarizes the significant data pertaining to the hydrolysis studies which were carried out.

## TABLE III

### HYDROLYSIS OF CN GROUPS IN PREPOLYMER

| SAMPLE | REAGENTS | EQUIPMENT | TEMPERATURE | TIME | RESULTS | NOTEBOOK REF. |
|---|---|---|---|---|---|---|
| 17-EMS-123 (0.64g) | 48% aq. HBr (50 ml) | Round bottomed flask<br>Vibromixer | Reflux ~100°C | 2 hrs. | CN band unchanged. | 7846-4-3 |
| 22-EMS-5 (2 ml) | 48% aq. HBr (2 ml) | Sealed Pyrex tube | 120°C | 53-1/2 hrs. | 28% of original CN remains. Strong COOH band. | SK-71 |
| 22-EMS-55-B. (11.39g) | 48% aq. HBr (2.40g) | Sealed Pyrex tube | 150°C | 16 hrs. | <2% CN remains. Strong COOH band. No evidence for decarboxylation. | SK-98-2 |
| 22-EMS-6 (8.27g) | 48% aq. HBr (10 ml) | Steel bomb with sealed Pyrex tube | 200°C | 16 hrs. | No CN remaining. Only 1/3 the expected amount of COOH. Much decarboxylation occurred. | 7864-64-2 |
| 17-EMS-105-B (120g) | NaOH (17g)<br>$H_2O$ (20 ml)<br>Butanol (75 ml<br>Dimethylformamide)(25 ml added after 48 hours) | Round bottomed flask, magnetic stirrer | 74° for 48 hrs. then: 68°C for 16 hrs. | | 66% of original CN remained after workup. | 5726-143 |
| 17-EMS-105-B (14.96g) | NaOH (4.8g)<br>$H_2O$ (2.4g)<br>Butanol (100 ml) | 1" Duplex Dispersator<br>Resin Kettle | 112°C | 48 hrs. | ~5% of original CN remained. | SK-57 |
| 22-EMS-7 (0.87g) | 17M aq. NaOH, .6 ml Butanol(1 ml) | Sealed Pyrex tube | 150°C | ? | Glass tube was weakened by caustic and exploded. Sample lost. | SK-83 |
| 22-EMS-7 (0.55g) | "<br>" | Sealed Kimax alkali resistant glass tube | 150°C | 17 hrs. | 96% of original CN remained. | SK-85 |
| 22-EMS-4 (25.0g) | NaOH (8g)<br>$H_2O$ (4 ml)<br>Butanol (100 ml) | Titanium lined steel bomb, autogenous pressure | 250°C | 15 hrs. | No CN band remaining in Product. Strong carboxyl band. Neutralization equivalent = 1015. No decarboxylation detected. | 7846-38-1 |
| 22-EMS-5 | NaOH (8g)<br>$H_2O$ (4 ml)<br>Butanol (100 ml) | " " | 200°C | 16 hrs. | No CN band remaining in product. Strong carboxyl band. Neutralization equivalent = 1187 as expected from CN content. | 7846-38-2 |

## D. Characteristics of the Carboxyl Terminated Prepolymers

The products obtained by the high-temperature, high pressure alkaline hydrolysis route (route 1, Section C) were viscous oils. Their color varied somewhat, depending upon the work-up procedure, but was usually a clear amber. Infrared spectroscopy demonstrated the absence of a significant amount of nitrile, less than 1% of the original amount. A broad intense carbonyl absorption at 1700 $cm.^{-1}$ confirmed the presence of carboxyl. These carboxyl groups were completely neutralized with sodium hydroxide to give the sodium salt of the polymer, a clear soft solid material, from which the carboxyl groups could be regenerated upon acidification.

Neutralization equivalents were run upon the various samples of carboxyl terminated prepolymer. The following unexpected result was obtained: In most cases the neutralization equivalent was quite close to the value of the number average molecular weight of the nitrile terminated precursor. This would seem to indicate a carboxyl functionality of only one per molecule. The carboxyl terminated prepolymers themselves were submitted for molecular weight determination. The results indicated that the molecular weights of the hydrolyzed products were similar to those of their nitrile precursors, and again the values were quite close to the neutralization equivalent.

At this point the question was raised: Is the nitrogen content of the nitrile terminated prepolymers truly a measure of the nitrile content? To answer this it was necessary to develop an independent analysis for nitrile.

Since infrared spectra had been obtained for all of the samples of nitrile terminated prepolymer, it was decided to calibrate the 2240 $cm.^{-1}$ (4.46μ) nitrile band, and use its intensity for nitrile assay.

A pure sample of pivalonitrile was obtained, and its infrared spectrum measured. A 5M solution in $CCl_4$ in a cell with a path length of 1.04 mils had an absorption at 2240 $cm.^{-1}$ of 0.1566. Thus the extinction coefficient is:

$$a = A/bc = \frac{0.1566}{1.04 \text{ mils} \times 5 \text{ moles/liter}} = 0.03013/\text{milxmoles/l}$$

By using this value, together with the known cell thickness used, the nitrile concentrations in all of the prepolymer samples were calculated from their infrared spectra. The results of these calculations are given in Table IV, together with other pertinent data for the prepolymers as well as for their hydrolyzed products.

## TABLE IV

### COMPARISON OF NITROGEN, NITRILE AND CARBOXYL FUNCTIONALITIES

| Sample Designation | $\overline{M}_n$[1] Nitrile Polymer | Nitrogen[2] Equivalent Weight | Avg. No. Nitrogens Per Chain | Nitrile[3] Equivalent Weight | Avg. No. Nitriles Per Chain | $\overline{M}_n$[1] of Carboxy Product | Neutralization Equivalent Wt. of Carboxy Product | Avg. No. COOH Per Chain |
|---|---|---|---|---|---|---|---|---|
| 105B | 811 | 293 | 2.77 | 874 | 0.93 | | Sample Supply Exhausted. | |
| 22EMS4 | 1270 | 511 | 2.50 | 1241 | 1.02 | | Sample Supply Exhausted. | |
| Composite | 811-1270 | 293-513 | >2 | - | - | 1559 | 1515 | 1.03 |
| 22EMS5 | 1197 | 552 | 2.16 | 1185 | 1.01 | 1239 | 1187 | 1.04 |
| 22EMS6 | 1110 | 556 | 2.0 | 1185 | 0.94 | 1193 | 1116 | 1.07 |
| 22EMS7 | 1086 | 537 | 2.02 | 1128 | 0.96 | 892 | 1027 | 0.87 |
| 22EMS8 | 1083 | 567 | 1.93 | 983 | 1.10 | 988 | 1144 | 0.86 |

[1] $\overline{M}_n$ = Number Avg. Mol. Wt. by Vapor Phase Osmometry
[2] Obtained from Kjeldhl Nitrogen Analysis
[3] Obtained from infrared analysis of Nitrile Concentration in polymer before hydrolysis
[4] Obtained from titration of hydrolyzed product with KOH/$C_2H_5OH$

A number of significant conclusions can be drawn from this set of data:

1. There exists no 1:1 correlation between the total nitrogen equivalent weight and the equivalent weight based upon the nitrile content as determined by infrared spectroscopy. In fact, as shown in Figure 1, and approximate correlation of 2:1 is found instead. This points out that our initial interpretation of the nitrogen analysis vs. molecular weight data as discussed earlier in this report, was premature. Nitrogen containing structures other than nitrile must be present, either in or associated with the polymer.

2. There is a very good 1:1 correlation between the nitrile equivalent weight and the number average molecular weight of the prepolymer. Thus, the nitrile functionality of the prepolymers is really one, rather than two as had been previously assumed.

3. No significant change has occurred in the polymer molecular weight as a result of the hydrolysis procedure.

4. The average carboxyl functionality of the hydrolyzed products is one.

5. The 1:2 correlation between equivalent weight based on total nitrogen and the molecular weight of the prepolymer before hydrolysis is valid but was misinterpreted.

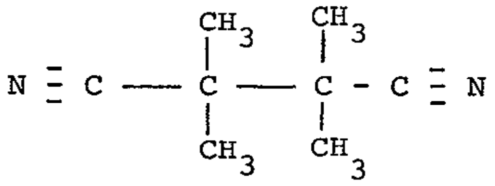
## E. Explanation for Observed Functionality of Hydrolyzed Copolymer

The data in Table Iv suggested that a nitrogen containing functional group other than CN was present in the copolymer as well as the CN group. The infrared spectra of numerous samples were scanned and the presence of a band at about 2000-2012 cm.$^{-1}$ characteristic of structures such as allenes, isocyanates and ketenes was detected. Keteneimines have been reported to absorb at 4.97-5.2 microns (1920-2012 cm.$^{-1}$).

Copolymer samples worked up by MeOH extraction (to remove tetramethyl succinodinitrile) or which had been subjected to temperatures of 150°C during solvent removal showed this absorption weakly or not at all. However, when care was taken during work up to avoid solvolysis or thermal abuse, strong absorbance near 2000-2015 cm.$^{-1}$ was observed.

The origin of this keteneimine structure in the polymer is attributed to the recently discovered fact that AIBN dissociates into radicals which have a significant amount of unpaired electron density localized around the nitrogen atom.

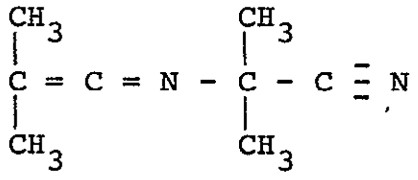
The major product resulting from thermal decomposition of AIBN in inert solvent media[1] is tetramethyl succinodinitrile (II).



$N\equiv C-C(CH_3)_2-C(CH_3)_2-C\equiv N$

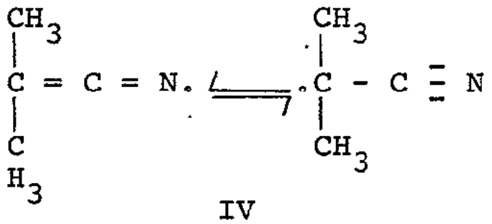
II

However, there are two routes to II. The first is direct recombination of two isobutyronitrile radicals at the tertiary carbon atoms to give II directly, which is a thermally stable material. The other mode of formation of II is via the thermally unstable keteneimine structure III.



$(CH_3)_2C=C=N-C(CH_3)_2-C\equiv N$

III

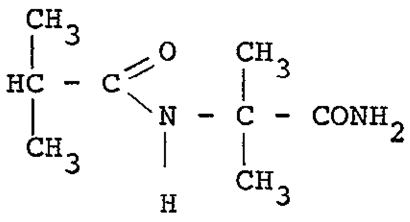


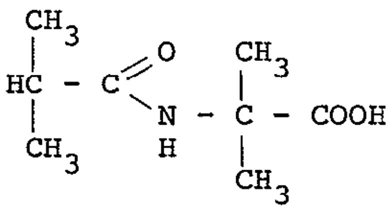
$(CH_3)_2C=C=N\cdot \rightleftharpoons \cdot C(CH_3)_2-C\equiv N$

IV

Which evidently arises by recombination of the two radicals shown in IV[2]. These are resonance structures of the same radical.

The intermediate III was detected spectroscopically[2,3] and derivatives isolated by extracting toluene solutions of decomposing AIBN with dilute HCl[3]. Products V and VI were obtained, which one would expect from hydrolysis of III.


V


VI

Structure III is converted to II; probably by reversible dissociation to IV followed by irreversible recombination to give II[4,5].

A reasonable explanation for the nitrogen functionality of two and the CN and COOH functionalities of about one is now possible. If radical structure IV reacts with either ethylene or a polymer chain radical as the keteneimine radical, a keteneimine chain end will result. If radical IV reacts as the isobutyronitrile radical a CN group is formed on the chain end.

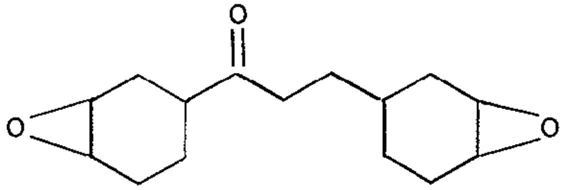
During alkaline hydrolysis of the copolymer the keteneimine groups are split off the chain, since the COOH polymer contains no nitrogen.

Depending on the proportion of keteneimine end groups in the original polymer, the carboxyl functionality of the hydrolyzed product can vary. The average functionality of about one COOH per molecule suggests that about 50% of the time radical IV reacts as a keteneimine radical and as an isobutyronitrile radical the other half of the time.

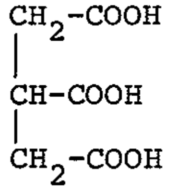
The labile character of the keteneimine "end" group suggests the possibility of rearranging it to an isobutyronitrile end group.

## F. Curing Studies on Hydrolyzed Copolymer

As recommended in our contract we have limited our curing studies to formulations based upon a reactive and well characterized diepoxide, together with a tricarboxylic acid to provide the necessary crosslink density. We selected EP-221 (I) and tricarballylic acid (II) for these preliminary formulations.



I



$$\begin{array}{l} CH_2\text{-COOH} \\ | \\ CH\text{-COOH} \\ | \\ CH_2\text{-COOH} \end{array}$$

II

The prepolymers examined were:

1. A composite sample, 7846-28R, of the hydrolyzed ethylene-neohexene copolymer (prepared with AIBN initiator) having a carboxyl equivalent weight of 1515 (Formulations 7-10) and

2. Butarez 2-CTL* having a carboxyl equivalent weight of 3010. (Formulations 1-6).

Chromium octoate was added to most of the formulations to increase the curing rate.

Since acid catalyzed homopolymerization of epoxides usually occurs as a side reaction, an excess of epoxide is often used to insure complete utilization of the carboxyl groups in the curing agent. Accordingly, we have studied formulations containing a ratio of 0.6 equivalents carboxyl to 1.0 equivalent epoxide as well as formulations containing the stoichiometric amount of the reactants. See Table V.

The curing studies were carried out in aluminum foil cups, first at room temperature, then at 80°C in a dry box with a nitrogen atmosphere. An arbitrary qualitative curing scale of 0-5 was developed to facilitate recording of data. This scale is given below Table V.

---

* A carboxy terminated liquid polybutadiene made by Phillips Chemical Company.

Comparing formulations one and two with three-six, one can readily see the importance of the chromium octoate catalyst, particularly for the initial room temperature cures. For this reason the catalyst was used in all the studies with our hydrolyzed product 7846-28R.

The addition of the tricarballylic acid had little effect on the final cured state attained in the Butarez formulations. However, use of this trifunctional acid component was necessary to obtain a fully cured product with our saturated carboxy terminated prepolymer. This is borne out in the solvent extraction studies. Formulations seven and eight without tricarballylic acid gave poor cures and were completely soluble in both hexane and toluene. Formulations nine and ten to which the tri-acid had been added gave much better cures, particularly in the case of formulation nine. This cured product was a flexible, fairly tough rubber containing 47% of gelled insoluble material.

## TABLE V

## PREPOLYMER CURING STUDIES

| Formulation | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Carboxyl Prepolymer | ← Butarez 2-CTL → | | | | | | ← 7846-28R → | | | |
| Wt. Prepolymer gms | ← 10 gms → | | | | | | 4.90 | 4.91 | 4.90 | 4.91 |
| Equivalents COOH | ← .00332 → | | | | | | 00324 | 00325 | 00324 | 00325 |
| Epoxide Used | ← Epoxide EP-221 → | | | | | | | | | |
| Wt. Epoxide Used | 0.45 | 0.73 | 0.42 | 0.71 | 1.63 | 2.67 | 0.46 | 0.79 | 1.63 | 2.66 |
| Equivalents Epoxide | .00356 | .00578 | .00332 | .00562 | .0129 | .0212 | .00364 | .00625 | .0129 | .0211 |
| Tricarballylic Acid, Wt. gms | 0 | 0 | 0 | 0 | 0.5 | 0.5 | 0 | 0 | 0.5 | 0.5 |
| Equivalents COOH | - | - | - | - | .0085 | .0085 | - | - | .0085 | .0085 |
| Chromium Octoate, gms | 0 | 0 | 0.11 | 0.13 | 0.11 | 0.14 | 0.10 | 0.15 | 0.14 | 0.10 |
| Ratio, COOH to Epoxide | 0.9 | 0.57 | 1.0 | 0.59 | 0.91 | 0.56 | 0.89 | 0.52 | 0.91 | 0.56 |
| Initial Cure at 25°C | ← 96 hrs. → | | | ← 70 hrs. → | | | ← 24 hrs. → | | | |
| | 0 | 0 | 3 | 2 | 1-2 | 1 | 0 | 0 | 0 | 0 |
| Intermediate Cure at 80°C | ← 24 hrs. → | | | | | | | | | |
| | 0 | 0 | 3-4 | 3 | 2 | 1-2 | 0 | 1 | 1-2 | 1-2 |
| Final Cure at 80°C | ← 120 hrs. → | | | | | | | | | |
| | 3 | 3 | 3-4 | 4 | 4 | 3 | 0 | 1 | 3-4 | 2-3 |
| Weight Percent Hexane Insolubles | — | — | — | — | — | — | 0 | 0 | 62 | 60 |
| Weight Percent Toluene Insolubles | — | — | — | — | — | — | 0 | 0 | 47 | 51 |

| Degree of Cure | Observation |
|---|---|
| 0 | - No detectable difference from starting mixtures |
| 1 | - Some thickening noted, but little penetration resistance |
| 2 | - Pronounced thickening, some resistance to penetration |
| 3 | - Flexible solid, pressure required to penetrate |
| 4 | - Hard solid, difficult to penetrate |
| 5 | - Very hard, brittle solid |

## G. Fractionation of an Ethylene-Neohexene Copolymer by Molecular Distillation

A blend of AIBN initiated ethylene-neohexene copolymer samples was prepared and designated 8134-20. Its composition is given in Table VI.

### TABLE VI

| Sample, 22-EMS# | 41 | 42 | 50 | 55-B | Composite |
|---|---|---|---|---|---|
| Wt. Used | 360.64 | 350.81 | 237.52 | 326.92 | 1275.89 |
| $M_n$ of Sample (ØH) | 407 | 309 | 354 | 517 | 384 |
| Moles Used | .886 | 1.136 | 0.627 | 0.631 | 3.325 |
| CN. Eq. Wt. (IR) | 350 | 315 | 371 | 501 | 373 |
| Eq. CN | 1.03 | 1.11 | .64 | .65 | 3.43 |
| Nitrogen Analysis | 6.85% | 6.63% | 6.19% | 5.10% | 6.28% |
| N. Eq. Wt. | 205 | 212 | 227 | 274 | 225 |
| Eq. Nitrogen | 1.79 | 1.69 | 1.05 | 1.19 | 5.72 |
| Functionality: | | | | | |
| N/Molecule | 1.97 | 1.46 | 1.56 | 1.42 | 1.70 |
| CN/Molecule | 1.16 | 0.98 | .96 | 1.03 | 1.03 |

The composite sample was itself submitted for analysis with the following results:

$M_n$ (THF) = 385 6.75 % Nitrogen (207 eq. wt.)
$M_n$ (ØH) = 393 .88 Oxygen (1820 eq. wt.)

The infrared spectrum of the composite sample showed a strong CN band at 2235 cm.$^{-1}$, A/mil = 0.0602*, and a strong keteneimine band at 2019 cm.$^{-1}$, A/mil = 0.153. An amide carbonyl band of moderate intensity at 1650 cm.$^{-1}$ was also observed. Using the $-C\equiv N$ calibration previously determined, the $C\equiv N$ equivalent weight is 431. This value shows that a considerable amount of keteneimine or other nitrogen functions are present.

Functionality, calculated from elemental + IR analysis:

1.85 N/molecule, 0.22 O/molecule, 0.91 CN/molecule

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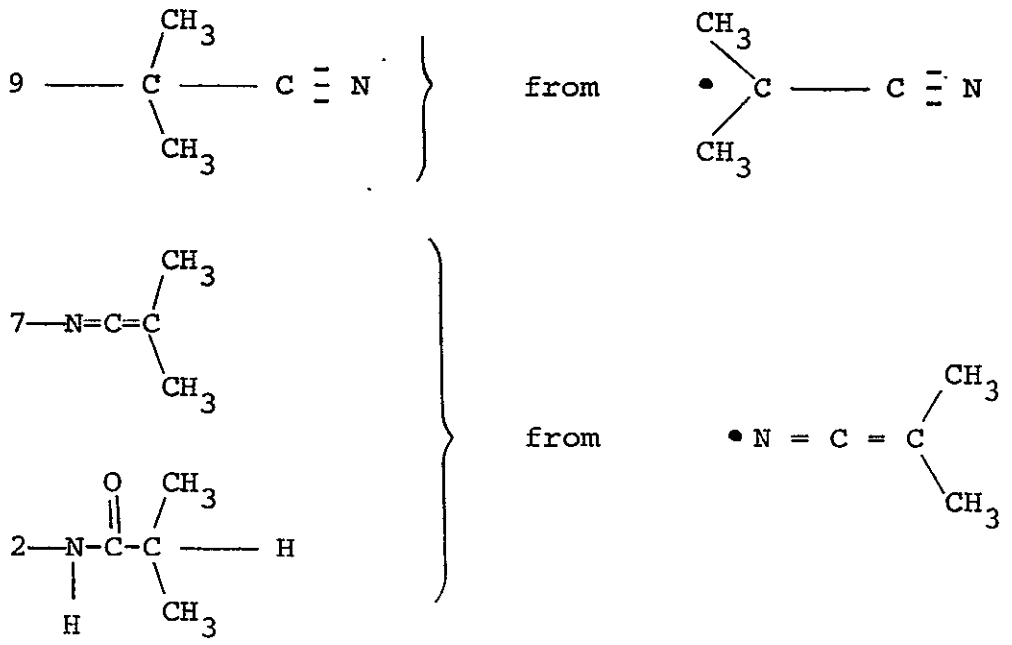
* Peak absorbance per mil of sample thickness

In a group of 10 average molecules, this pattern of functionality is best fit by the following distribution of end groups:



2 —— H (non-functional)  chain transfer or disproportionation?

20 end groups

The amide end groups can be derived from the keteneimine end groups by hydrolysis under very mild conditions.

1200 grams of this composite sample was hydrolyzed in the inconel autoclave at South Charleston using the following procedure:

| | | | |
|---|---|---|---|
| Charge: | 1200 g | 8134-20-1 | (3.127 moles) |
| | 1500 ml | n-butanol | |
| | 700 g | KOH | (12.51 eq.) |
| | 1000 ml | $H_2O$ | |

After 5-1/3 hours at 200°C/280 psi with stirring, an aliquot was removed and found to contain only a trace of $C\equiv N$ by IR. After a total of 20 hours under these conditions, the reactor was cooled to 70°C and dumped under nitrogen and worked up by acidification with 1000 ml conc. HCl, filtered through filter aid and evaporated as usual to give 1209 g dark amber oil, still containing some volatiles.

In an attempt to devolatilize this product by passing it through our molecular still, we found that a large portion of the product could be distilled. Five distillation fractions, 8134-28-1, 2, 3, 4 and 5 were obtained, and a residue product, 8134-28-6, with a total of 1070 g of material recovered. The other 139 g presumably being volatiles and transfer losses.

The molecular still we used was of the falling film type. Rotary wipers, having a downward impelling action, sweep the material to be distilled through a heated glass tube under vacuum. Volatile material evaporates and condenses upon a cold finger condenser in the center of the heated tube. Non-volatile residue is swept out of the heated zone and collected in a separate flask.

We use an oil diffusion pump with a mechanical fore pump. A dry ice-acetone cooled trap is placed between the still and the pumps. When no volatile materials are present, our system will attain a limiting pressure of about .3 microns. However, when material containing large amounts of solvent or other volatiles is being distilled, the pumping rate usually limits the pressure one can attain to 30-50 microns.

The crude hydrolyzed product was passed through the still at 150°C/50-100 microns. A residue and distillation fraction 1 was obtained. The residue was recycled through the still at 160-165°C/40-60 microns. Distillation fraction 2 and a residue were obtained. This process was repeated until five distillation fractions and a final residue were obtained. The distillation conditions and analytical data are summarized in Table VII.

Note particularly, the narrow molecular weight distribution exhibited by fractions 1 through 5, and the smoothly increasing molecular weight as the boiling point goes up and the distillation pressure goes down. A fractionation of functionality also is occurring, ranging from about one-half COOH per molecule, in the lowest boiling fraction to near monofunctionality in the higher boiling fractions. The residue had the highest functionality, of 1.24 COOH per molecule.

Because of the excess oxygen over that required by the COOH groups, it is likely that much of the residual nitrogen in these samples is in the form of an amide function. They could be formed by addition of water or butanol to the keteneimine structures present in the starting material.

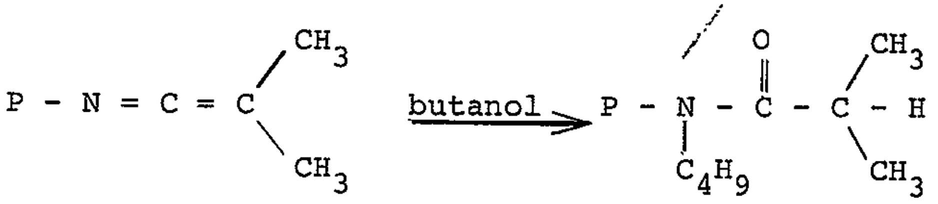
## TABLE VII

## SUMMARY OF DATA UPON POLYMER DISTILLATION FRACTIONS - EXPERIMENT 8134-20

| Sample | CN Starting Material | Distillation Fractions | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| B.p., °C | | 150 | 160-165 | 175-185 | 185-190 | 185-190 | Residue |
| Pressure, microns Hg | | 50-100 | 40-60 | 5-10 | 5-10 | 2-5 | - |
| Yield, gms | 1209 | 289 | 147 | 157 | 103 | 39 | 336 |
| Color | Straw | Lt. Amber | Amber | Reddish Amber | Tea Color | Tea Color | Black |
| Brookfield Viscosity, cps. at 22°C | - | 1,660 | 91,600 | 136,000 | 1,460,800 | - | 1,900,000 |
| Acid Number | - | 137 | 156 | 157 | 130 | 99 | 87 |
| Wt. % Nitrogen | 6.75 | 1.61 | 1.65 | 1.68 | 1.42 | 1.34 | .86 |
| Wt. % Oxygen | .88 | 12.75 | 12.14 | 11.00 | 9.97 | 8.73 | 6.28 |
| Neutralization Equivalent | - | 410 | 360 | 358 | 431 | 567 | 645 |
| Nitrogen Equivalent Wt. | 207 | 872 | 850 | 835 | 988 | 1048 | 1630 |
| Oxygen Equivalent Wt. | 1820 | 127 | 132 | 145 | 160 | 183 | 255 |
| $\bar{M}_n$ (v.p.o. in benzene) | 393 | 339 | 511 | 660 | 783 | 880 | 1370 |
| $\bar{M}_n$ (v.p.o. in THF) | 385 | 234 | 296 | 380 | 436 | 518 | 802 |
| $\bar{M}_w/\bar{M}_n$ (by gel-permeation chromatography in THF) | 1.4 | 1.07 | 1.08 | 1.08 | 1.08 | 1.06 | 1.16 |
| Functionality: | | | | | | | |
| 1. COOH per chain (benzene $M_n$) | .89 (CN/Chain) | .83 | 1.42 | 1.84 | 1.82 | 1.55 | 2.13 |
| 2. COOH per chain (THF M) | | .57 | .82 | 1.06 | 1.01 | .92 | 1.24 |
| 3. Nitrogen per chain (THF) | 1.86 | .27 | .35 | .45 | .44 | .50 | .49 |
| 4. Oxygen per chain (THF) | .211 | 1.84 | 2.24 | 2.62 | 2.73 | 2.84 | 3.14 |

### H. Residual Non-COOH Functionality in Hydrolyzed Products Derived from AIBN

In the preceding section we presented the analytical data obtained upon some molecular distillation fractions derived from a hydrolyzed copolymer prepared with AIBN initiator. In that discussion we interpreted the data to indicate the presence of oxygen containing functional groups other than carboxyl. The low nitrogen level remaining in these samples (between 1/4 and 1/2 nitrogen per molecule) suggested that at least part of the oxygen could be present in an amide structure derived from a ketoneimine end group by solvolysis:



P = polymer chain

However more excess oxygen was present than could be accounted for by this explanation.

Table VIII summarizes the earlier results and shows that there are about twice as many excess oxygen atoms per molecule as there are residual nitrogen atoms per molecule. The "composite sample" is simply a weighted average of the properties of the five distillation fractions and the residue. If all the nitrogen in this sample is present as amide, it contains only the average .8 COOH groups, .4 amide groups and .3 other oxygen functions (probably hydroxyl) per molecule. This adds up to a total of 1.5 functional groups per molecule for the whole hydrolyzed product. Fractions 5 and the residue are even higher in total functionality: both have 1.9 groups per molecule.

One must be quite cautious about taking this type of functionality determination too literally, because the quantities involved, especially the nitrogen analyses, are quite small. The usual accuracy quited for a nitrogen determination is ± .3%. Note that the nitrogen reported in these samples was between .27 for fraction 1 and .50 for fraction 5.

We have also analyzed some of the hydrolyzed AIBN products for double bond content using the Wijs Iodine monochloride titration method. For example, hydrolyzed 22-EMS-50 had a c = c equivalent weight of 1600, corresponding to about .23 c = c per molecule.

## TABLE VIII

## TOTAL FUNCTIONALITIES OF AIBN PRODUCTS

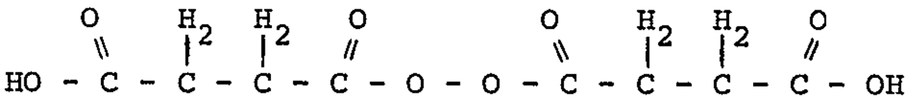
| Sample | CN Term. Precursor | Distillation Fractions | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | R | Comp. |
| gms. obtained | 1209 | 289 | 147 | 157 | 103 | 33 | 336 | 1070 |
| Wt. % O | .88 | 12.57 | 12.14 | 11.00 | 9.97 | 8.73 | 6.28 | 9.92 |
| Wt. % N | 6.75 | 1.61 | 1.65 | 1.68 | 1.42 | 1.34 | .86 | 1.35 |
| $\overline{M}$n (THF) | 385 | 234 | 296 | 380 | 436 | 518 | 802 | 372 |
| Neut. Eq. | - | 410 | 360 | 358 | 431 | 567 | 645 | 450 |
| Nit. Eq. Wt. | 207 | 872 | 850 | 835 | 988 | 1048 | 1630 | 1039 |
| Ox. Eq. Wt. | 1820 | 127 | 132 | 145 | 160 | 183 | 255 | 161 |
| CN Eq. Wt. | ~420 | - | - | - | - | - | - | - |
| COOH/mol. | - | .57 | .82 | 1.06 | 1.01 | .92 | 1.24 | .83 |
| N/mol. | 1.86 | .27 | .35 | .45 | .44 | .50 | .49 | .36 |
| O/mol. | .21 | 1.84 | 2.24 | 2.62 | 2.73 | 2.84 | 3.14 | 2.31 |
| non-COOH O/mol. | .21 | .70 | .60 | .50 | .71 | 1.00 | .66 | .65 |
| CN/mol. | ~.9 | - | - | - | - | - | - | - |
| Total* | - | 1.3 | 1.4 | 1.6 | 1.7 | 1.9 | 1.9 | 1.5 |

* See text for explanation

## V. TECHNICAL DISCUSSION, PART 2

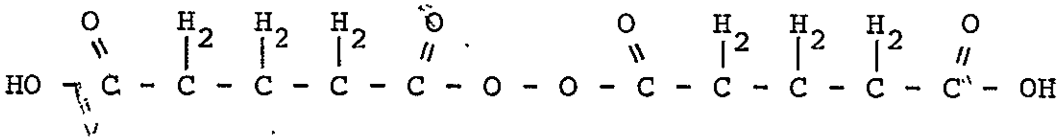
### PREPARATION OF ETHYLENE-NEOHEXENE PREPOLYMERS USING ORGANIC PEROXIDE INITIATORS

These experiments were carried out using succinic acid peroxide and glutaric acid peroxide. The former was obtained from the Lucidol Division of Wallace and Tiernan, Inc. while the latter was synthesized within the Corporation. Their structures are:



$$HO-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OH$$

Succinic Acid Peroxide (SAP)



$$HO-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OH$$

Glutaric Acid Peroxide (GAP)

These peroxides decompose at the peroxide linkage, eliminate $CO_2$ and form primary radicals, which initiate polymerization.

Tables IX and X list data for the preparation of GAP initiated prepolymers with tetrahydrofuran as solvent, and for two SAP runs made using dimethyl formamide and acetone as solvents. These initiators will not dissolve in benzene. Run 43 was made with GAP and DTDBA (dithio dibutyric acid) as a chain terminating agent.

The functionality of products 31, 34 and 38 were all low, regardless of whether the acid number or the oxygen analysis was used to compute the molecular weight equivalent to one carboxylic acid group. The product from run 35 contained nitrogen, indicating that this solvent is an active transfer agent. Run 36 gave only one gram of product.

## TABLE IX

## NEOHEXENE/ETHYLENE COPOLYMERS ACID PEROXIDE INITIATED RUNS

| Run No. 22 EMS- | 31 | 34 | 38 | 43 | 35 | 36 |
|---|---|---|---|---|---|---|
| **Initial Charge** | | | | | | |
| Solvent | THF | THF | THF | THF | DMF | Acetone |
| Solvent Wt., gms. | 50 | 74 | 43 | 38 | 62 | 98 |
| Neohexene, gms. | 635 | 255 | 426 | 426 | 364 | 125 |
| Neohexene Wt. % Monomers | 75 | 70 | 73 | 73 | 70 | 70 |
| Initiator | GAP | GAP | GAP | GAP | SAP | SAP |
| Wt. gms. | 3.8 | 7.4 | 9.3 | 4 | 6 | 2 |
| Ethylene, gms. | 211 | 109 | 158 | 158 | 156 | 53.4 |
| **Fed During Reaction** | | | | | | |
| Solvent, gms. | 268 | 670 | 329 | 721 | 571 | 882 |
| Initiator, gms. | 51 | 66 | 84 | 36 | 56 | 18 |
| DTDBA, gms. | -- | -- | -- | 34 | -- | -- |
| **Reaction Conditions** | | | | | | |
| Temperature, $^{\circ}C$ | 95 | 90 | 95 | 95 | 90 | 60 |
| Pressure, | | | | | | |
| Initial, psi | 4100 | 500 | 700 | 750 | 500 | 400 |
| Final, psi | 5300 | 2200 | 900 | 20,000 | 4300 | 6750 |
| Reaction Time, hrs. | 6.5 | 6.5 | 6.5 | 3.0 | 4.5 | 6.0 |
| **Productivity** | | | | | | |
| Yield, gms. | 155 | 120 | 168 | 105 | 35 | 1.0 |
| Conversion, % | 18.3 | 32.9 | 28.8 | 18.0 | 6.7 | 0.5 |
| Rate, % per hr. | 2.8 | 5.1 | 4.4 | 6.0 | 1.5 | 0.1 |

NOTES:
1. GAP = glutaric acid peroxide
2. SAP = succinic acid peroxide
3. THF = tetrahydrofuran
4. DMF = dimethyl formamide
5. Percent conversion is yield in grams divided by total weight of monomers charged times 100.

## TABLE X

## NEOHEXENE/EHTYLENE COPOLYMERS ACID PEROXIDE INITIATED RUNS

|  | 31 | 34 | 38 | 43 | 35 | 36 |
|---|---|---|---|---|---|---|
| **Physical Properties** |  |  |  |  |  |  |
| Mol. Wt. | 943 | 415 | 526 | 459 | 467 |  |
| Brookfield Vis., Centipoise, 25°C | 22.610 | 555 | 3105 | 816 | -- | Discarded |
| Sp. Vis. at 80°C | 0.022 | 0.017 | 0.017 | 0.015 | 0.016 |  |
| Acid Number | 54 | 103 | 53 | 96 | -- |  |
| Nitrogen, Wt. % | -- | -- | -- | -- | 3.41 |  |
| Carbon, Wt. % | 81.80 | 77.89 | 79.12 | 75.3 | -- |  |
| Hydrogen, Wt. % | 13.71 | 13.16 | 13.45 | 13.15 | -- |  |
| Oxygen, Wt. % | 4.94 | 8.49 | 7.86 | 8.09 | 7.71 |  |
| Sulfur, Wt. % | -- | -- | -- | 3.26 | -- |  |
| **Functionality** |  |  |  |  |  |  |
| By Acid No. | 0.91 | 0.76 | 0.5 | 0.79 | -- | -- |
| By $O_2$ Analysis | 1.46 | 1.10 | 1.29 | 1.16 | 0.56 | -- |
| **Description** | Lt. Yellow Heavy Oil | Yellow Oil | Yellow Oil | Yellow Oil | Dark Tan Oil | Tan Grease |

NOTES:
6. Specific Viscosity determined with 0.4% polymer in methyl cyclohexane at 80°C.
7. Acid Number defined as milligrams KOH per gram of polymer.
8. COOH functionality Run 43 derived from sulfur analysis 0.47.
DTDBA used as chain stopper.
9. $O_2$ functionality results from both ester and carboxyl groups from peroxide initiators.

The low functionality in these runs was attributed to solvent chain transfer effects primarily, although the possibility that these initiators might possess transfer activity was not ignored. It was decided to search for a solvent which would dissolve both the acid initiator and the polymer and not be an active transfer agent. A 50/50 mixture of benzene and tertiary butanol was found to dissolve DTDBA whereas benzene would not. However, no good solvent for SAP which was low in transfer activity was found.

Table XI lists those runs made with SAP initiator where the mixed benzene/t-BuOH solvent was used. Run 62 was made with all SAP charged initially and a solution of DTDBA charged during the reaction. A low yield indicated that the DTDBA acted as a retarder; 68% of the DTDBA was recovered unchanged. Run 64 was a repeat of 62 using one third more initiator. This tripled the yield compared to Run 62.

Run 66 utilized a slurry technique for feeding SAP. A 50/50 mixture of benzene/t-BuOH was used to slurry the SAP which was kept in suspension by cycling past the suction check of a high pressure injection pump using a Viking gear pump. The rupture disk on the pump blew which terminated the run. This was caused by a plugged feed line. However, this run gave 100 grams of product, which reflected the absence of DTDBA and the continual replenishment of initiator during the run.

Run 70 was a SAP slurry run similar to 66 except that the temperature was increased 10° to 110° and the initiator feed rate was doubled which halved the reaction time. The yield was 84 grams. In order to scale up this run safely it would be necessary to place the recycling slurry behind an explosion proof barricade and install remote control equipment. Scale up to a 2 gallon autoclave would necessitate recycling 2/3 of a pound of peroxide in slurry. The danger arises in injection the peroxide slurry with a high pressure piston pump. Crystals of peroxide might be detonated by friction if caught between the piston and cylinder walls.

Run 64 gave a gross product of molecular weight (benzene) 769 and Brookfield viscosity 27,000 cps at room temperature. The acid number was 170.4. This results in an apparent functionality of 2.34 acid groups per molecule. From a sulfur content of 12.69% (assuming one S atom per COOH group) the functionality was 3.05 COOH groups per molecule. This product later separated into two phases and was not further investigated.

## TABLE XI

### ETHYLENE-NEOHEXENE COPOLYMERS - SUCCINIC ACID PEROXIDE RUNS IN BENZENE-TERTIARY BUTANOL MIXED SOLVENT

| | 62 | 64 | 66 | 70 |
|---|---|---|---|---|
| Initial Charge | | | | |
| Solvent | 50/50 Benzene/t-BuOH | | | |
| Wt. gms. | 410 | 402 | 99 | 99 |
| Neohexene, gms. | 315 | 315 | 494 | 484 |
| Initiator | SAP | SAP | SAP | SAP |
| Wt. gms. | 21.6 | 30.2 | 5 | 5 |
| Ethylene, gms. | 116 | 116 | 1000psi at RT | 161 |
| Fed During Reaction | | | | |
| Solvent, gms. | 222 | 222 | 480 | 495 |
| Initiator, gms. | -- | -- | 51 | 45.5 |
| DTDBA, gms. | 22 | 22 | -- | -- |
| Reaction Conditions | | | | |
| Temperature, °C | 95 | 95 | 100 | 110 |
| Pressure, psig | | | | |
| Initial | 100 | 800 | 2225 | 850 |
| Final | Gage Plugged | 7700 | 15,000 | 16,000 |
| Reaction Time | 3.5 | 1.5 | 4.25 | 2.0 |
| Productivity | | | | |
| Yield, gms. | 7.0 | 22 | 104 | 84 |
| Conversion, % | 1.6 | 5.1 | 15.4 | 13 |
| Rate, %/hr. | 0.5 | 1.02 | 4.4 | 6.5 |

The following characterization data were obtained for the product from Run 66.

| | |
|---|---|
| Brookfield Viscosity | 238,000 cps |
| Molecular Weight in Chloroform | 1432 |
| Molecular Weight in THF | 1465 |
| Molecular Weight in Benzene | 2198 |
| Neutralization Equivalent | 1630 |

The functionality calculated from these data are:

$$F\ (\text{Benzene}) = \frac{2198}{1630} = 1.34\ \text{COOH groups/molecule}$$

$$F\ (\text{CHCl}_3) = \frac{1432}{1630} = 0.88\ \text{COOH groups/molecule}$$

$$F\ (\text{THF}) = \frac{1465}{1630} = 0.90\ \text{COOH groups/molecule}$$

This product was reacted with thionyl chloride to convert the COOH groups to COCl groups. This lowered the viscosity from 238,000 to 90,000 cps as a result of elimination of hydrogen bonding. The acid chloride was converted into the ester which reduced the viscosity to 12,000 cps. The drop from 238,000 cps to 12,000 cps illustrates the effect on viscosity of eliminating hydrogen bonding.

The following characterization data were obtained for the product from Run 70.

| | |
|---|---|
| Molecular Weight in Benzene | 1453 |
| Brookfield Viscosity | 87,500 cps |
| Oxygen Concentration | 6.65% |
| Acid Number | 76.8 |
| Neutralization Equivalent | 731 |

$$\text{Functionality} = \frac{1453}{731} = 1.98\ \text{COOH/molecule}$$

This product was further purified and resubmitted for molecular weight and acid number with the following results:

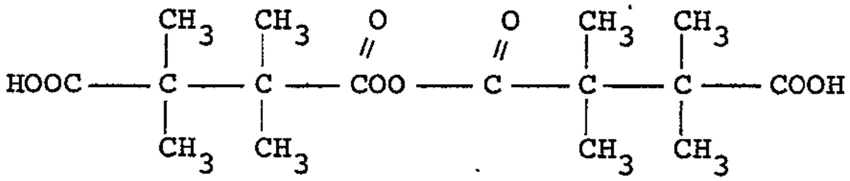
| | |
|---|---|
| Molecular Weight in Benzene | 1134 |
| Molecular Weight in THF | 791 |
| Neutralization Equivalent | 793 |

$$\text{Functionality (Benzene)} = \frac{1134}{793} = 1.43$$

$$\text{Functionality (THF)} = \frac{791}{793} = 0.999$$

The Brookfield Viscosity of this product was 87,500 cps, which is quite high for a material with a number average molecular weight of 791. To test the possibility that this anomaly is due to hydrogen bonding association the acid terminated product was esterified. Conventional Fischer esterification, with ethanol and p-toluene sulfonic acid did not proceed to completion; however, the partially esterified product had a viscosity of 8,000 cps. By thionyl chloride treatment followed by reacting the acid chloride with ethanol in the presence of pyridine the residual COOH groups were converted to $COOC_2H_5$. The viscosity of the esterified product was only 230 cps, which confirms the hypothesis that COOH association caused the high viscosity of the acid product. The number average molecular weight of the esterified product was 880, showing that no degradation of the product occurred.

The low functionality of the SAP initiated product made in mixed benzene/t-butanol suggests that SAP itself is a chain transfer agent. A desirable alternate catalyst is tetramethyl succinic acid peroxide.



$$HOOC-C(CH_3)_2-C(CH_3)_2-\overset{O}{\overset{\|}{C}}OO-\overset{O}{\overset{\|}{C}}-C(CH_3)_2-C(CH_3)_2-COOH$$

This initiator contains no hydrogen atoms alpha to a carboxyl group and is not likely to undergo chain transfer reactions. The precursor of this initiator, tetramethyl succinic acid is available.

# V. TECHNICAL DISCUSSION, PART 3

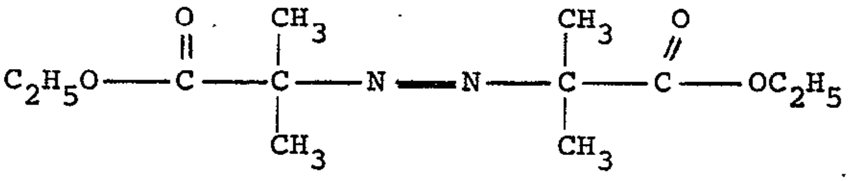
## ETHYLENE/NEOHEXENE COPOLYMERS PREPARED WITH DEAB INITIATOR

### Contents

## A. Preparation of Diethyl-α, α'-Azobis-isobutyrate Initiator and Measurement of Rate of Decomposition

### 1. Preparation

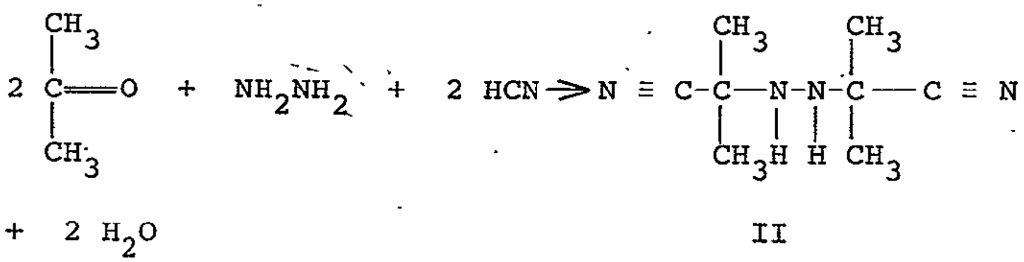
Diethyl-α, α'-azobis-isobutyrate (I) DEAB can be prepared by two routes at present.



$$C_2H_5O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

I

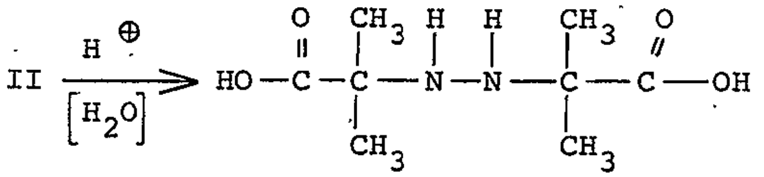
The first starts with the condensation of acetone with hydrazine in the presence of HCN to give α, α'-hydrazobis-isobutyronitrile, II.



$$2\,\overset{CH_3}{\underset{CH_3}{C}}{=}O + NH_2NH_2 + 2\,HCN \rightarrow N\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv N + 2\,H_2O$$

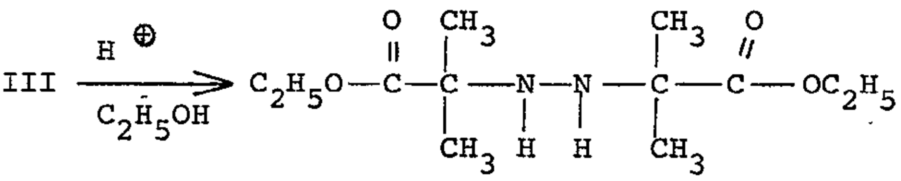
II

This material can be hydrolyzed to the dicarboxylic acid III and then esterified with ethanol to give the diethyl-α, α'-hydrazobis-isobutyrate, IV.



$$II \xrightarrow[{[H_2O]}]{H^{\oplus}} HO-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{N}-\overset{H}{N}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

III



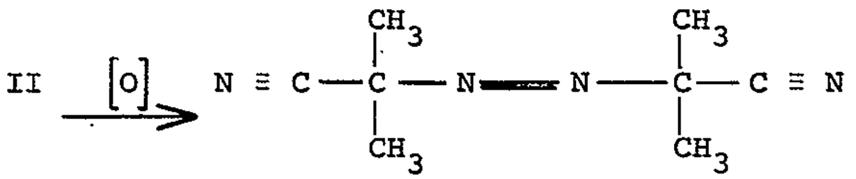
$$III \xrightarrow[C_2H_5OH]{H^{\oplus}} C_2H_5O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

IV

The hydrazoester IC can be oxidized to I by a variety of methods:

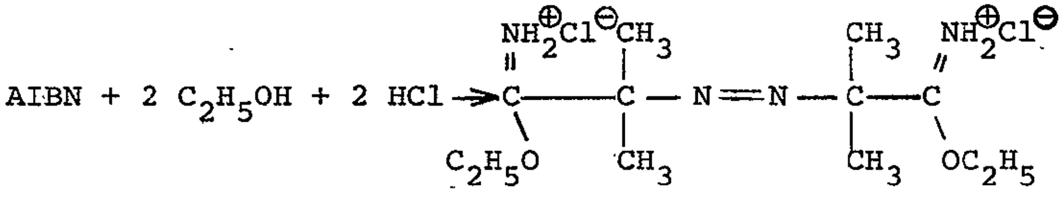
$$\mathrm{IV} \xrightarrow{[O]} \mathrm{I}$$

An alternate procedure is to oxidize II to give α, α'-azobis-isobutyronitrile (AIBN) and then react AIBN with HCl in anhydrous ethanol to give the iminoether hydrochloride V.



$$\mathrm{II} \xrightarrow{[O]} N\equiv C-C(CH_3)_2-N=N-C(CH_3)_2-C\equiv N$$

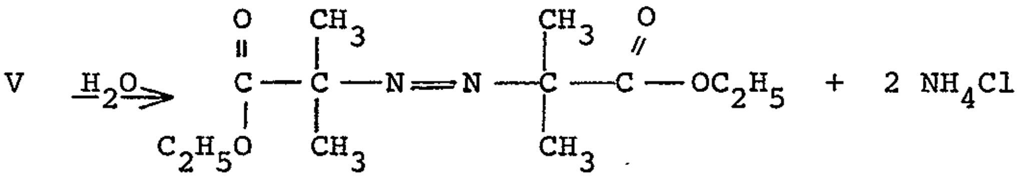
AIBN



$$\mathrm{AIBN} + 2\ C_2H_5OH + 2\ HCl \rightarrow (C_2H_5O)(NH_2^{\oplus}Cl^{\ominus}{=})C-C(CH_3)_2-N=N-C(CH_3)_2-C({=}NH_2^{\oplus}Cl^{\ominus})OC_2H_5$$

V

Mild hydrolysis of V gives I directly.



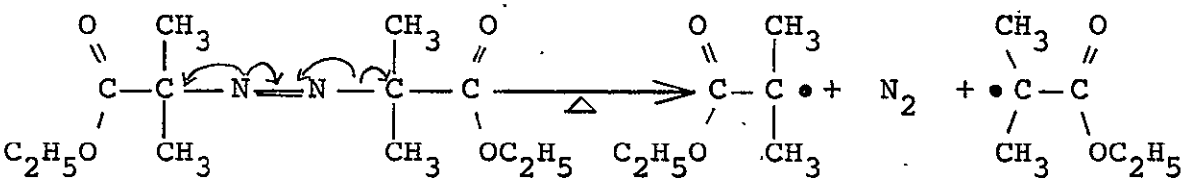
$$\mathrm{V} \xrightarrow{H_2O} C_2H_5O-C(=O)-C(CH_3)_2-N=N-C(CH_3)_2-C(=O)-OC_2H_5 + 2\ NH_4Cl$$

I

The procedure adopted was the latter, using commercially available AIBN. This provided I in two steps which are easily carried out in the laboratory. The former route is more economical for production purposes.

## 2. Rate of Decomposition of DEAB

Diethyl-α, α'-azobis-isobutyrate DEAB decomposes smoothly when heated to yield nitrogen gas and free radicals:



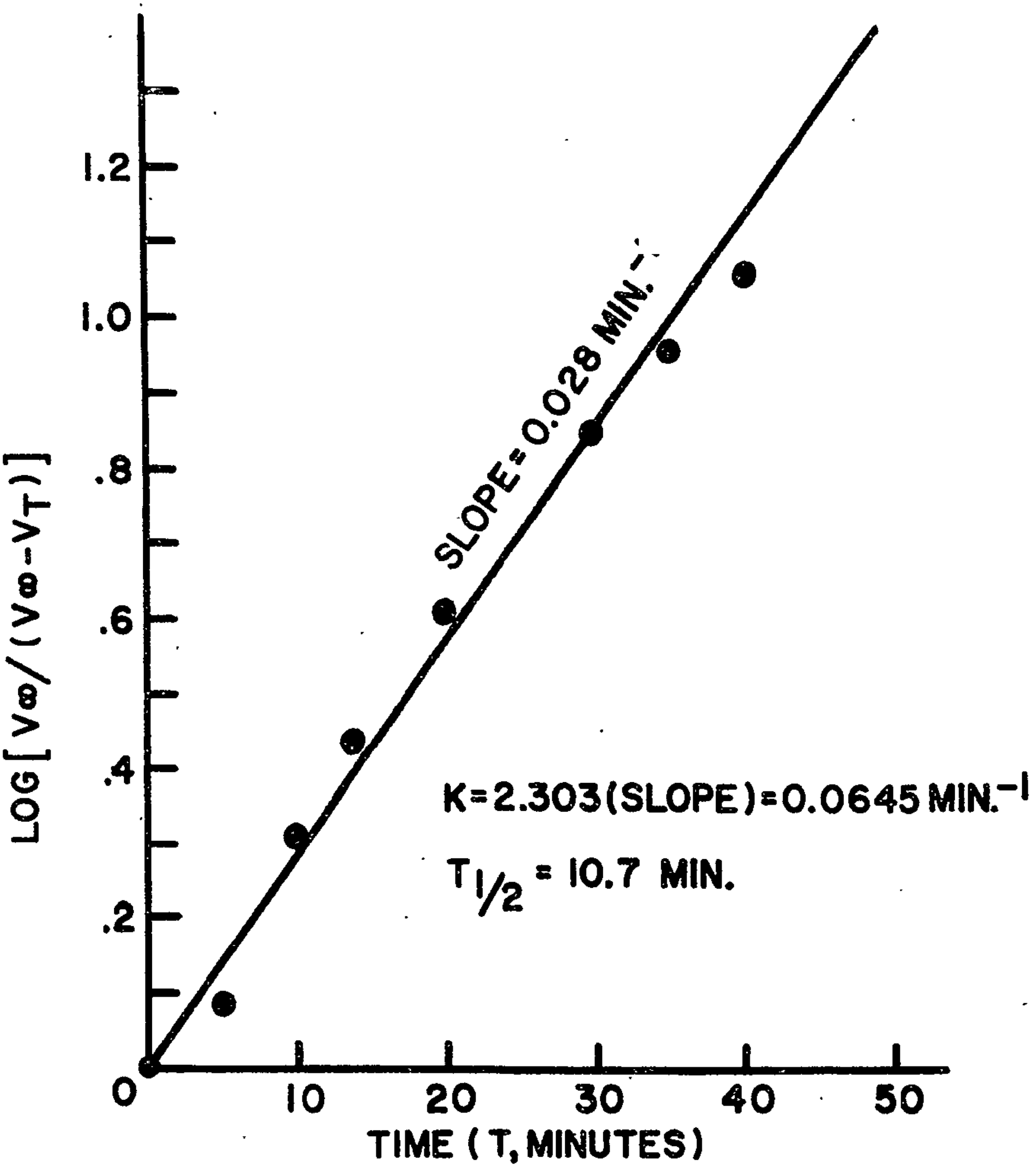
I

The carbethoxy group in the radical derived from structure I stabilizes the radical in much the same way as the CN group stabilizes the cyanoisopropyl radical derived from AIBN.

The kinetics of decomposition of I in xylene solution at 100°C was studied. The evolved nitrogen was collected in a gas burette and the volume, $V_t$, measured as a function of time. After the reaction had gone to completion the total volume of evolved nitrogen, $V_\infty$, was measured. At any time, t, the quantity $V_\infty - V_t$ represents the amount of nitrogen yet to be evolved and hence is proportional to the amount of I remaining in the reaction mixture. $V_\infty$ is proportional to the original amount of I, therefore the ratio, $[V_\infty - V_t] \div V_\infty$, represents the fraction of I remaining in the reaction mixture at time t. According to the usual kinetic procedure for first order reactions, a graph of the logarithm of the fraction of I remaining in the reaction mixture plotted versus time gives a straight line passing through the origin, with a slope of -K/2.303, where K is the first order rate constant.

Since $-\log [(V_\infty - V_t) \div V_\infty] = +\log [V_\infty \div (V_\infty - V_t)]$, we plotted the latter quantity versus time as shown in Figure 2. At 100°C the rate constant was 0.0645 reciprocal minutes and the half life was 10.7 minutes (compared with 7 minutes for AIBN).

FIGURE 1



KINETICS OF DECOMPOSITION OF
DIETHYL-α,α', AZOBIS-ISOBUTYRATE (DEAB)
IN XYLENE AT 100° C

## B. Ethylene-Neohexene Copolymers Prepared with DEAB

Table XII lists the reaction conditions used in preparing the first series of copolymers with the new catalyst. These were carried out in benzene at 90°C, a solvent in which all the components in the reaction are soluble, including DEAB. In order to traverse the molecular weight range of interest in this work, the catalyst concentration was varied as was the pressure.

As expected, the samples varied in viscosity and molecular weight from 200 cps to 2300 cps. In appearance they were pale yellow liquids. The end groups are esters.

The molecular weight of sample 99 was determined in two polar and one non-polar solvent with remarkable agreement. Hydrogen bonding is not a problem in the ester terminated products, which accounts for the agreement between molecular weight data in benzene and THF and also the observed low viscosities.

No ketene-acetal endgroups were detected.

Additional runs were then made to obtain larger quantities of copolymer, and also to study the effect of changes in other polymerization parameters. The results of these runs are shown in Table XIII. Figure 2 shows the viscosity-$\bar{M}_n$ relationship.

The temperature was changed from that employed for the earlier runs (90°C) to determine the effect of this variable upon the product obtained. The longer half-life of the DEAB at 80°C (~1.7 hours) required correspondingly longer times in order to efficiently utilize the initiator.

In run 22-EMS-136, DTDBA was used as a chain stopper, necessitating the use of the more polar benzene/t-butanol solvent mixture. Because of the thiobutyric acid end groups introduced by the chain stopper, this product had a neutralization equivalent of 1230 before hydrolysis of the ester end groups.

## TABLE XII

### ETHYLENE-NEOHEXENE COPOLYMERS PREPARED WITH DEAB

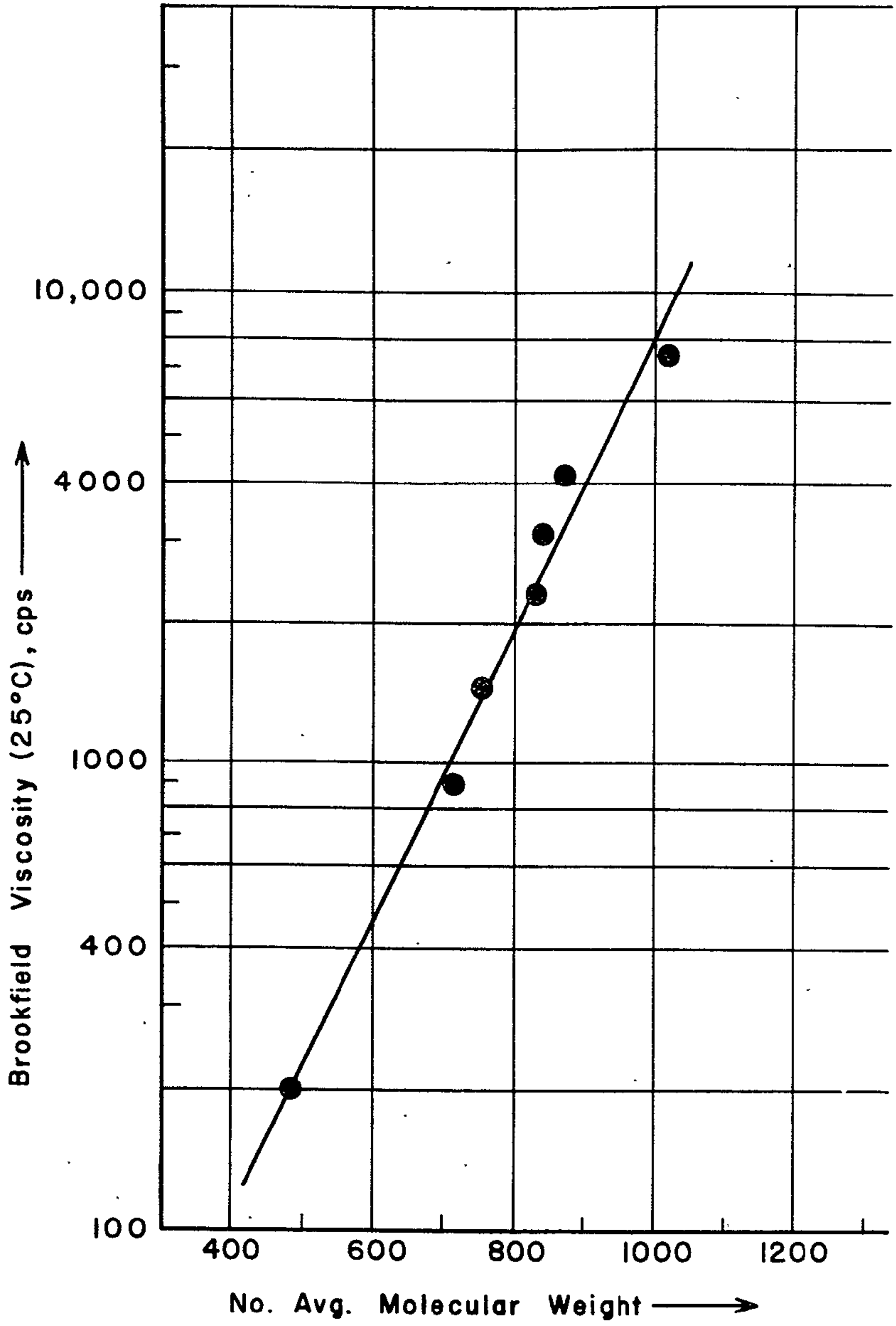
| Initial Charge | 99 | 108 | 109 |
|---|---|---|---|
| Benzene, wt. gms. | 30 | 65 | 12 |
| Neohexene, gms. | 472 | 527 | 591 |
| DEAB, gms. | 10 | 7.2 | 4.0 |
| Ethylene, gms. | 175 | 195 | 218 |
| **Fed During Reaction** | | | |
| Benzene, gms. | 270 | 195 | 145.6 |
| DEAB, gms. | 90 | 65 | 36.4 |
| **Reaction Conditions** | | | |
| Temperature, °C | 90 | 90 | 90 |
| Initial Pressure, psig | 990 | 1400 | 2800 |
| Final Pressure, psig | 2400 | 2675 | 3625 |
| Reaction Time, hrs. | 4.5 | 4.5 | 4.5 |
| **Productivity** | | | |
| Yield, gms. | 176 | 180 | 164 |
| % Conversion | 27.2 | 22.7 | 20.3 |
| Rate, % per hr. | 6.1 | 5.1 | 4.5 |
| **Physical Properties** | | | |
| Brookfield Viscosity, 25°, cps. | 203 | 898 | 2323 |
| No. Ave. Mol. Wt. in | | | |
| Benzene | 482 | 710 | 830 |
| $CHCl_3$ | 478 | | |
| THF | 484 | | |

## TABLE XIII

## ETHYLENE-NEOHEXENE COPOLYMERS PREPARED WITH DEAB

| | 22-EMS | | | 23-EMS | | |
|---|---|---|---|---|---|---|
| Run No. | 126 | 127 | 136 | 1 | 4 | 11 |
| Initial Charge | | | | | | |
| Solvent Used | Benzene | Benzene | 1/1 Benzene /t-Butanol | 1/1 Benzene /t-Butanol | Benzene | Benzene |
| Solvent, gms | 11.2 | 12.5 | 23.4 | 17.9 | 56.7 | 57.0 |
| Neohexene, gms | 543 | 605 | 457 | 462 | 2762 | 2782 |
| Ethylene, gms | 201 | 224 | 169 | 171 | 980 | 1035 |
| DEAB, gms | 3.7 | 4.1 | 4.1 | 3.2 | 19.0 | 20.2 |
| Fed During Reaction | | | | | | |
| Solvent, gms | 100.5 | 112.7 | 322.6 | 326.8 | 570.9 | 519.5 |
| DEAB, gms | 33.5 | 37.3 | 37.1 | 28.4 | 170.2 | 170.3 |
| DTDBA, gms | -- | -- | 19.8 | 29.2 | -- | -- |
| Reaction Conditions | | | | | | |
| Temperature, °C | 110 | 80 | 80 | 80 | 80 | 80 |
| Initial Pressure, psig | 600 | 3050 | 950 | 1000 | 1350 | 1485 |
| Final Pressure, psig | 2800 | 4000 | 950 | 1250 | 1075 | 1100 |
| Reaction Time, hrs. | 4.5 | 23.5 | 21.8 | 22.4 | 21.0 | 21.0 |
| Productivity | | | | | | |
| Yield, gms | 141 | 222 | 173 | 145 | 815 | 889 |
| % Conversion | 19.0 | 26.8 | 27.6 | 22.6 | 21.8 | 23.1 |
| Rate, % per hour | 4.2 | 1.1 | 1.3 | 1.0 | 1.04 | 1.1 |
| Physical Properties | | | | | | |
| Brookfield Viscosity, cps. | 1472 | 7430 | 1700 | 2550 | 3100 | 4070 |
| Molecular Wt. (Vapor Phase Osmometry in Benzene) | 751 | 1018 | -- | -- | 837 | 869 |
| Molecular Wt. (Vapor Phase Osmometry in tetrahydrofuran) | -- | -- | 548 | 552 | -- | -- |

FIGURE 2


10,000
4000
1000
400
100
400
600
800
1000
1200
Brookfield Viscosity (25°C), cps
No. Avg. Molecular Weight

## C. Hydrolysis of Terminal Ester Functions

The ester end groups are very easily hydrolyzed provided that care is taken upon work-up to avoid re-esterification. For solubility reasons, n-butanol is the preferred solvent. Both the copolymers and KOH will dissolve to a large extent in refluxing butanol. The key to the procedure is to completely remove all traces of butanol before the potassium salt of the polymer and the excess KOH are neutralized with HCl. Otherwise, extensive re-esterification will occur. Since the butyl ester is nearly indistinguishable from the ethyl ester at this molecular weight, re-esterification upon work-up has the same symtoms as incomplete hydrolysis during the reaction.

The procedure used in the hydrolysis of 23-EMS-11 is typical and is described in detail below.

### Hydrolysis of 23-EMS-11

Into a 2-l round bottomed flask fitted with a reflux condenser were placed 100 gms 23-EMS-11 (a nearly colorless, slightly cloudy syrup), 100 gms KOH and 1,000 ml. n-butyl alcohol.

The mixture was refluxed under a nitrogen atmosphere for three hours. At this point, an aliquot was removed. No trace of the ester carbonyl band remained in the IR spectrum.

The butanol was then removed on a rotary evaporator (using a vacuum pump and an oil bath at 150$^\circ$C) and the residue, a mixture of KOH and the potassium salt of the polymer, taken up in 500 ml water and 500 ml ethyl ether. The two phase mixture was then cooled to 0$^\circ$C and acidified by the slow addition of 250 ml conc. aq. HCl while stirring.

The layers were then separated. The ether layer was then washed 3 x 250 ml water, and 1 x 250 ml sat. aq. NaCl. The combined aqueous layer and washings were then back extracted with an additional 100 ml ether. This ether layer was washed in turn with 3 x 100 ml water and 1 x 100 ml sat. aq. NaCl. The combined ether layers were dried over anh. $MgSO_4$ and evaporated on the rotovac (final evaporation with aid of vacuum pump and oil bath at 150$^\circ$C) to give 83.8 gm., (90% theoretical yield) light tea colored, very viscous syrup.

0.9732 grams required 11.91 ml of 0.0985$\underline{N}$ KOH/Ethanol to reach the phenolpthalein end-point in warm xylene solution:

$$\text{N.E.} = \frac{973.2 \text{ mg.}}{11.91 \text{ ml.} \times .0985 \ \frac{\text{meq.}}{\text{ml.}}}$$

$$= 830 \text{ g/equivalent COOH.}$$

An IR spectrum of the product showed a strong COOH carbonyl band at 1700 cm.$^{-1}$ but no trace of ester carbonyl absorption. A small carbonyl band at 1790 cm.$^{-1}$ could be half of an anhydride doublet, the other half being hidden by the strong COOH peak.

Vapor phase osmometry in THF solution gives a number average molecular weight of 845. Thus there are 1.02 COOH per molecule.

The analytical data for the products from the DEAB runs are given in Table XIV.

## TABLE XIV

## CHARACTERISTICS OF ETHYLENE-NEOHEXENE COPOLYMERS PREPARED WITH DEAB

| | 22-EMS | | | | | 23-EMS | |
|---|---|---|---|---|---|---|---|
| Sample No. | 99 | 108 | 109 | 126 | 127 | 4 | 11 |
| Ester Terminated Precursor Data | | | | | | | |
| Molecular Wt. | | | | | | | |
| 1. Benzene | 482 | 710 | 831 | 751 | 1018 | 837 | 869 |
| 2. THF | 484 | -- | -- | -- | -- | -- | -- |
| Equivalent Wt. | 484 | 534 (av) | 576 (av) | 387 | 584 | 574 | 588 |
| Functionality | 1.0 | 1.34 | 1.44 | 1.94 | 1.75 | 1.46 | 1.47 |
| COOH Terminated Product Data | | | | | | | |
| Molecular Wt. (THF) | 498 | 686 | 791 | 608 | 831 | 779 | 845 |
| Neutralization Equivalent | 401 | 676 | 801 | 605 | 941 | 789 | 830 |
| Functionality | 1.24 | 1.01 | 0.99 | 1.00 | 0.90 | 0.98 | 1.02 |

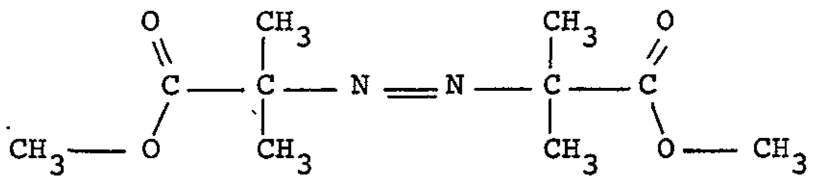
# V. TECHNICAL DISCUSSION, PART 4

## ETHYLENE/NEOHEXENE COPOLYMERS PREPARED WITH DMAB INITIATOR

### Contents

## A. Preparation of DMAB

Dimethyl α, α'-azobisisobutyrate, "DMAB", is of interest to us as an initiator:

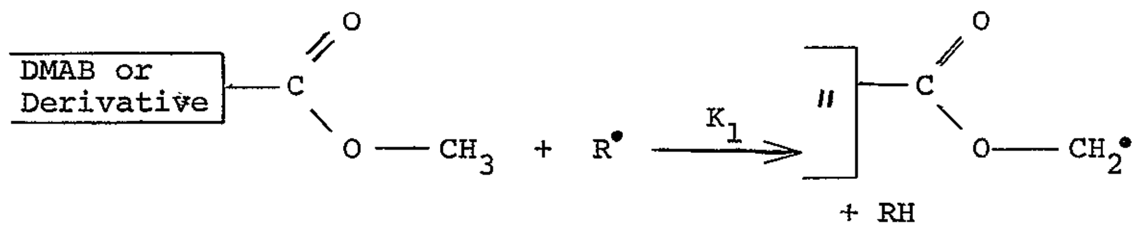


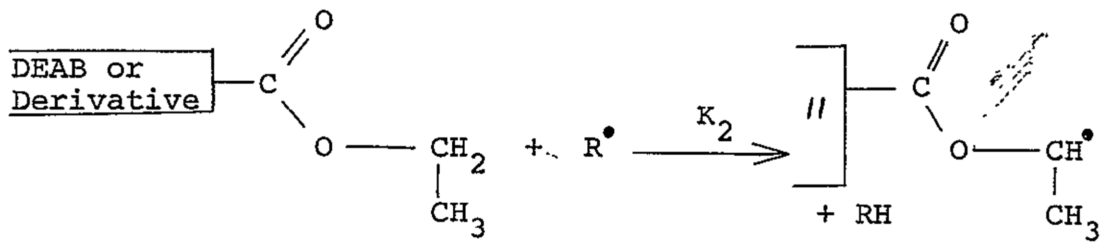
DMAB

Studies on the relative reactivities of aliphatic esters in free radical oxidation reactions, have shown that the methylene hydrogens near the ethereal linkage of ethyl acetate are much more prone to attack than the corresponding methyl hydrogens of methyl acetate[8,9]. The hydrogen upon the tertiary carbon atom of isopropyl acetate is the most reactive of all. This parallels the usual order of C-H bond stability:

primary > secondary > tertiary.

This being the case, the methyl hydrogens adjacent to the ethereal linkage in DMAB should be less prone to undergo hydrogen abstraction reactions with free radicals, than the corresponding methylene hydrogens in DEAB:

1. 

2. 

where $K_1$, the rate of chain transfer of DMAB, is less than $K_2$, the rate of chain transfer of DEAB.

If reaction (2) were significant in our previous DEAB polymerizations, chain transfer would simultaneously produce low functionality and low molecular weight. A simple change to DMAB could solve this problem, assuming, of course, that $K_1$ is really significantly less than $K_2$.

Our route to DMAB is the same as that used by Thiele and Heuser in 1896.[10] Condensation of acetone with hydrazine sulfate in the presence of potassium cyanide at 0°C leads to α, α'-hydrazobisisobutyronitrile, I, in 92-98% yield based on acetone.

The hydrazonitrile is smoothly converted to the protonated hydrazoamide, by standing at room temperature overnight in concentrated hydrochloric acid. Addition of water and refluxing for one hour converts the hydrazoamide to the protonated hydrazoacid. Upon neutralization of the protonated hydrazine with ammonia, the free hydrazoacid is precipitated from solution. After recrystallization from hot water a 75% yield of the hydrazoacid, II, is obtained, m.p. 222-224°C.

When II is dissolved in methanol saturated with anhydrous HCl and refluxed overnight, the protonated hydrazoester is formed. Neutralization of the methanol solution, after addition of an equal volume of water, gave the hydrazoester. It was recovered by $CH_2Cl_2$ extraction, evaporation, and recrystallization from pentane. A 90% yield of crystalline hydrazoester, III, m.p. 51-53°C was obtained.

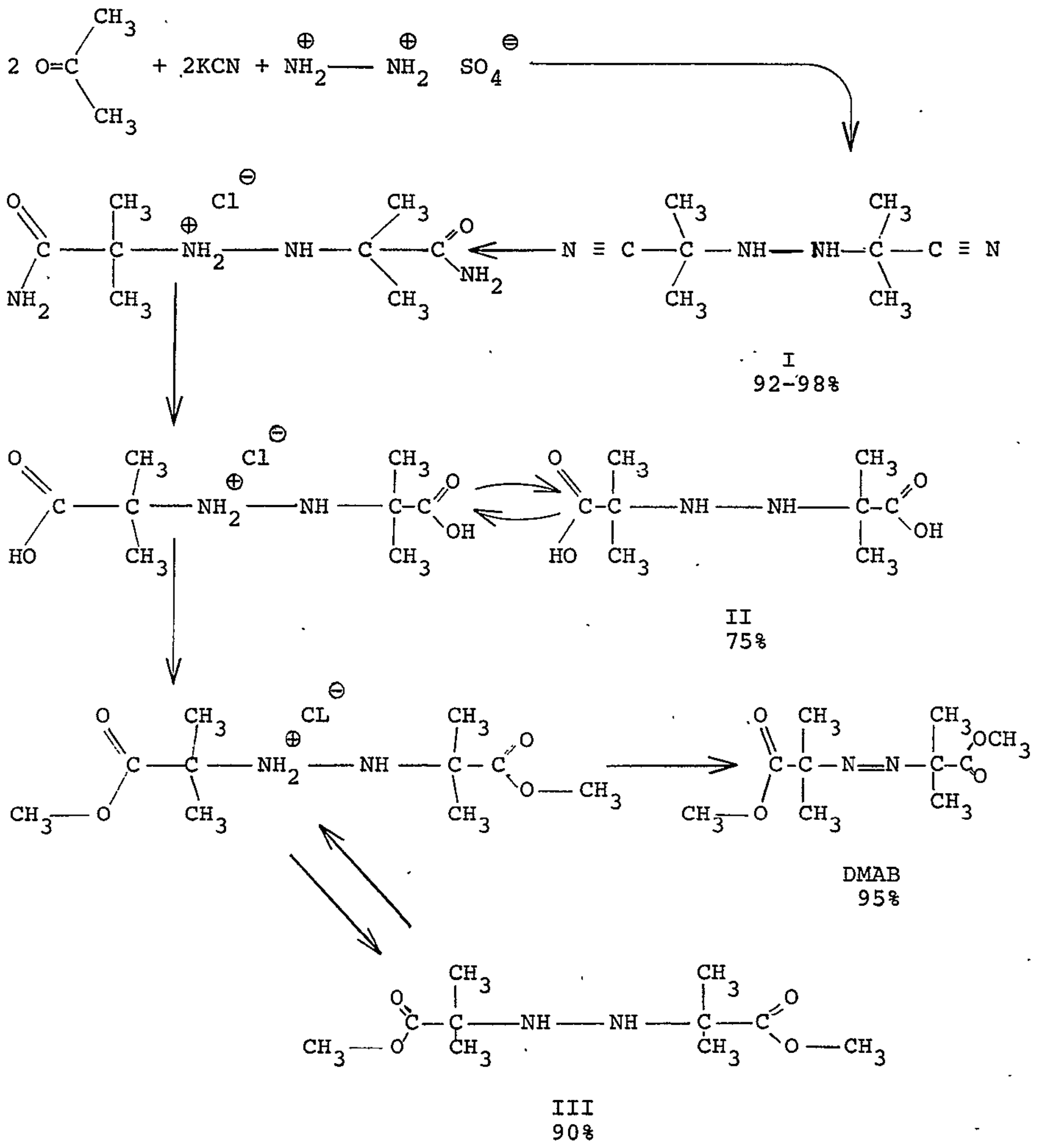
A solution of III in ice cold aqueous acid is then titrated with saturated aqueous bromine water to the slight persistence of a yellowish color of bromine. The azoester is no longer soluble in aqueous acid, so it precipitates out. The product was recovered by extraction, evaporation and low temperature crystallization. Yield: 95% yield, m.p. 27-32°C, a slightly yellow crystalline solid.

The overall yield is 58-62%, based upon acetone. A total of 260 grams of product was prepared and sent to South Charleston. A sample was tested and found to liberate the theoretical volume of nitrogen upon heating.

Mackie and Bywater determined the kinetics of decomposition of DMAB.[11] From their data we calculate the half lives shown in table below:

| T, °C | 70 | 80 | 90 | 100 |
|---|---|---|---|---|
| half life, hrs. | 8.64 | 2.45 | .744 | .228 |

The reactions are outlined below:



## B. Preparation of Ethylene/Neohexene Copolymers With DMAB Initiator

The synthesis of the azo initiator DMAB was described in the preceding section. In order to become familiar with the behavior of DMAB in polymerization, three preliminary runs were made at 80°C at three different pressures. The essential data are tabulated in Table XV. The low pressure runs produced prepolymer in the molecular weight range of interest, while the 20,000 psi run gave a polymer of very high viscosity. The oxygen functionality of these products was low as was the carboxyl functionality after hydrolysis of the terminal esters.

These preliminary results, along with earlier results with DEAB initiated products, led us to suspect that changes in the reaction environment during these batch runs might be responsible for the observed functionalities. In order to check this possibility we carried out a series of polymerization runs at 80°C and at 90°C, in which the reaction time was varied from 15 minutes to several hours. This procedure was in lieu of removing samples periodically from one long run, which is impractical due to the pressure involved.

The results of these runs are summarized in Table XVI. We observed that the oxygen functionality was a decreasing function of reaction time, from which we inferred that changes in the reaction environment during the batch runs were indeed taking place, and that these changes were having an adverse effect on the termination reaction. These ester products were homogeneous, clear, lightly colored oils, whose infra-red spectra were similar to previous DMAB initiated copolymers.

Saponification and recovery using the standard alkaline hydrolysis procedure (discussed in part 3, section C) gave the anticipated carboxyl terminated copolymers. These carboxyl terminated copolymers were analysed for functionality by molecular weight determination (V.P.O. in THF) and by titration with tetrabutylammonium hydroxide to determine their neutralization equivalents. The results of these determinations are summarized in Table XVII. Note that the carboxyl functionalities of the hydrolysed products were fairly uniform, near 1.0 COOH per molecule despite the fact that the oxygen functionalities of their precursors varied between 1.8 and 1.15 depending upon the reaction time and the % conversion obtained during the run. Note also that the products having the highest oxygen functionalities also gave the lowest yield of saponified product. (runs 33 and 44)

These observations lead us to propose that during the initial stages of the polymerization, when the DMAB concentration is the highest, a product of high oxygen functionality is formed which is subsequently lost in the saponification procedure, and that the ester terminated ethylene/neohexene copolymer is essentially monofunctional regardless of the time during the run it is formed.

TABLE XV

PRELIMINARY RUNS WITH DMAB

| Run No. 23 EMS- | 20 | 21 | 22 |
|---|---|---|---|
| Initial Charge | | | |
| Solvent | Benzene | Benzene/ | Benzene |
| Solvent, wt., gms. | 29.6 | 0.00 | 11.1 |
| Neohexene, gms. | 510 | 665 | 605 |
| Initiator, gms. | 1.6 | 2.7 | 3.7 |
| Ethylene, gms. | 192 | 279 | 229 |
| Fed During Run | | | |
| Solvent, gms. | 267 | 293 | 99.6 |
| Initiator, gms. | 14 | -- | 33.2 |
| Reaction Conditions | | | |
| Temperature °C | 80 | 80 | 80 |
| Pressure | 2650 | 20,000 | 4375 |
| Reaction Time, hrs. | 23 | 5.6 | 23 |
| Productivity | | | |
| Yield, gms. | 112 | 71 | 221 |
| % Conversion | 22 | 7.5 | 26.5 |
| Rate, %/hr. | 5 | 1.3 | 1.2 |
| Properties Before Hydrolysis | | | |
| Molecular wt. | 1107 | 3462 | -- |
| Brookfield Viscosity Centipoise | 15,100 | 400,000 | 13,200 |
| Wt. % Oxygen | 3.32 | 0.93 | -- |
| $O_2$ Functionality | 1.15 | 1.01 | -- |
| Properties After Hydrolysis | | | |
| Molecular Weight | 1127 | -- | 1099 |
| Neutralization Equiv. | 1199 | -- | 1131 |
| COOH Functionality | 0.94 | -- | 0.97 |
| Yield Hydrolyzed Product | 86% | | 89% |

## TABLE XVI

## EFFECT OF REACTION TIME ON OXYGEN FUNCTIONALITY OF PREPOLYMER

| Run #23 EMS | 33 | 34 | 31 | 32 | 44 | 41 | 42 | 37 |
|---|---|---|---|---|---|---|---|---|
| Initial Charge | | | | | | | | |
| Benzene, gms. | 30 | → | → | → | 33 | → | → | → |
| Neohexene, gms. | 510 | → | → | → | 501 | → | → | → |
| DMAB, gms. | 1.6 | → | → | → | 1.7 | → | → | → |
| Ethylene, gms. | 188 | → | → | → | 189 | → | → | → |
| Fed During Reaction | | | | | | | | |
| Benzene, gms. | 25.8 | 77.3 | 136.7 | 218.5 | 48.5 | 87.3 | 87.4 | 294 |
| DMAB, gms. | 1.4 | 4.1 | 7.2 | 11.5 | 2.55 | 4.56 | 6.26 | 15.6 |
| Reaction Conditions | | | | | | | | |
| Temperature, °C | 80 | → | → | → | 90 | → | → | → |
| Initial Pressure | 1000psi | → | → | → | 1050psi | → | → | 1000psi |
| Final Pressure | 1000 | 1150 | 1000 | 2000 | 1050 | 1050 | 1225 | 3350psi |
| Time, hrs. | 0.5 | 1.5 | 4.0 | 6.0 | .25 | .50 | 1.0 | 4.5 |
| Productivity | | | | | | | | |
| Yield, gms. | 4 | 12 | 25 | 53 | 5 | 9 | 22 | 87 |
| % Conversion | .57 | 1.7 | 3.56 | 7.56 | .73 | 1.3 | 3.2 | 12.6 |
| Rate, %/hrs. | 1.14 | 1.13 | .89 | 1.26 | 2.9 | 2.6 | 3.2 | 2.8 |
| Properties | | | | | | | | |
| Molecular Wt. | 648 | 716 | 823 | 912 | 553 | 815 | 706 | 891 |
| Wt. % Oxygen | 9.02 | 7.46 | 5.70 | 4.49 | 10.42 | 6.37 | 6.75 | 5.91 |
| $O_2$ Equivalent Weight | 354 | 429 | 562 | 713 | 307 | 503 | 474 | 542 |
| $O_2$/Molecule | 1.83 | 1.66 | 1.48 | 1.28 | 1.8 | 1.62 | 1.49 | 1.65 |

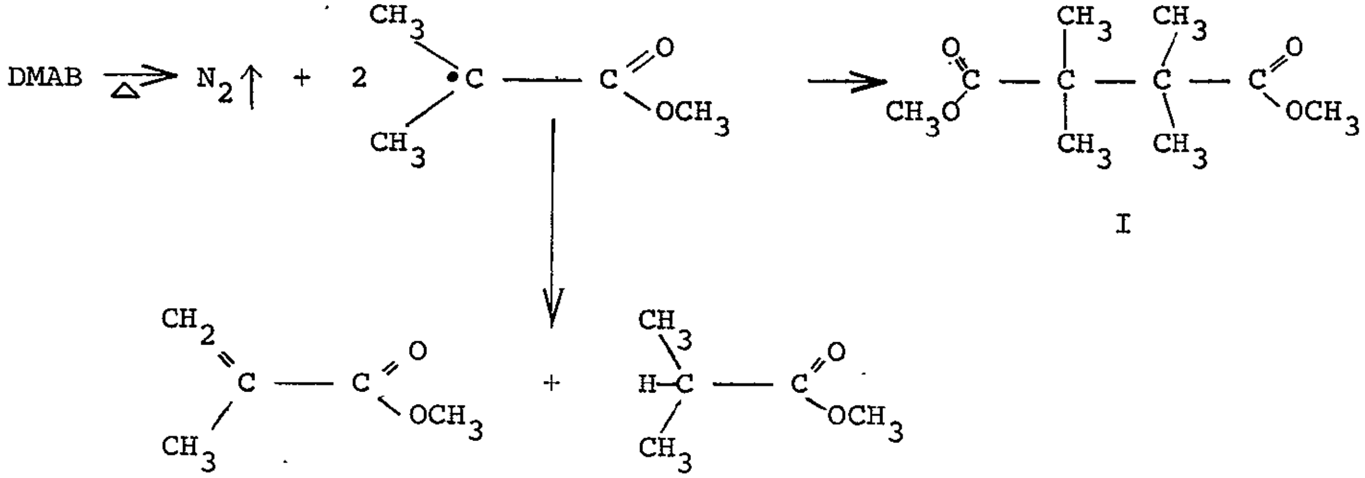
## TABLE XVII

## EFFECT OF REACTION TIME ON COOH FUNCTIONALITY

| Sample | 23 EMS 33 | 34 | 31 | 32 | 44 | 41 | 42 | 37 |
|---|---|---|---|---|---|---|---|---|
| Reaction Time, hrs. | 0.5 | 1.5 | 4.0 | 6.0 | .25 | .50 | 1.0 | 4.5 |
| Neutralization Equiv. | 858 | 792 | 751 | 863 | 556 | 676 | 578 | 745 |
| Mol. Wt. | 907 | 843 | 830 | 943 | 640 | 759 | 617 | 719 |
| Functionality | 1.06 | 1.07 | 1.10 | 1.09 | 1.15 | 1.12 | 1.07 | 0.96 |
| Yield Saponified Product | 79% | --* | 85% | --* | 81% | 86% | 88% | 89% |

* Yield not available, some sample was lost during workup.

Further information upon the processes occurring during polymerizations initiated by DMAB was provided in a study by A. F. Bickel and W. A. Waters[1] of the decomposition of DMAB in refluxing benzene at 80°C. They found that in addition to the coupling product dimethyl tetramethylsuccinate, I, other products were formed which could only arise from the disproportionation of the radicals from DMAB to give methyl methacrylate, II, methyl isobutyrate, III.

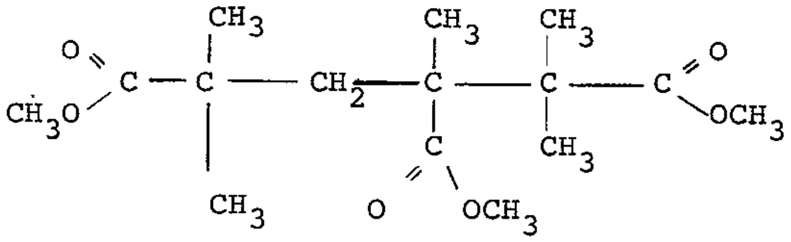


I

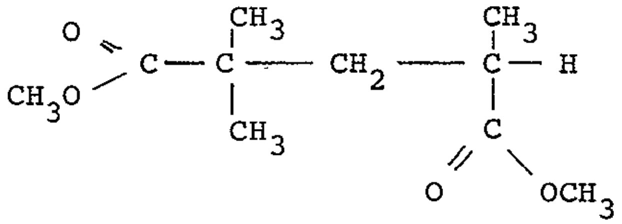
II

III

The other products were low telomers of II with III, compounds IV and V.

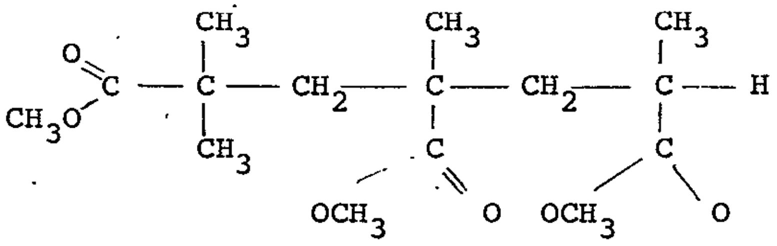


IV



V

Subsequent studies in our laboratories have confirmed this study and shown the presence of the additional telomer VI.



VI

The product distribution found in this study after 5-1/2 hrs. at 76° in 0.1 Molar solution is given below:

| Component | % Total Recovered Product | $O_2$ Functionality |
|---|---|---|
| DMAB | 19 | 2 |
| Dimer I | 35 | 2 |
| Telomer V | 2 | 2 |
| Telomer IV | 19 | 3 |
| Telomer VI | 8 | 3 |
| III | 18 | 1 |
| II | nil | -- |

This study showed that essentially all the methylmethacrylate formed during the disproportionation was used up in forming the telomers, but that a significant quantity of the telogen methyl isobutyrate remained.

These facts provide a convincing rationale for the results we obtained when DMAB was used as an initiator for ethylene/neohexene: The high concentration of DMAB needed for efficient termination of copolymer chains produced a large amount of the cage-recombination and cage-disproportionation products I, II, and III. I was inert and remained in the product until work-up, at which point it was hydrolysed to water soluble tetramethyl succinic acid and lost. In the presence of the radicals from DMAB and the telogen III, II was rapidly converted into methyl methacrylate telomers IV, V, VI and possibly higher forms.* These telomers remained in the product and contributed to the overall oxygen functionality, but were lost upon hydrolysis as water soluble acids. III, which contributed to the formation of telomers V and VI, is also a very active chain transfer agent for ethylene polymerizations, leading to structures as shown on the following page.

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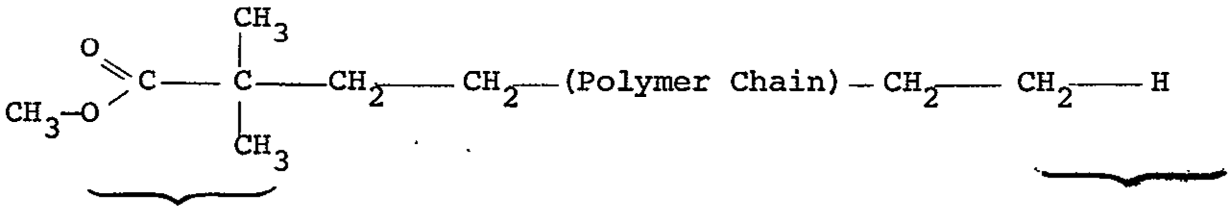
* The reactivity ratios for copolymerization of ethylene with methyl methacrylate are very unfavorable, so little incorporation of methyl methacrylate into the ethylene copolymer is probable under these conditions.



$$\underbrace{CH_3O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}}_{\text{from III}}-CH_2-CH_2-(\text{Polymer Chain})-\underbrace{CH_2-CH_2-H}_{\text{from III}}$$

VII

Structure VII is monofunctional because one end was terminated by a hydrogen atom abstracted from the telogen III in the chain transfer step. Since only structure VII leads to a water insoluble product upon hydrolysis, it is the only significant component in the final isolated product, which should therefore be monofunctional as observed.

## C. Preparation of Ethylene/Neohexene Copolymers in the Continuous Tubular Reactor - DMAB Initiator

In section B we reported the results obtained when dimethyl azobisisobutyrate (DMAB) was used as initiator for batch copolymerizations of ethylene and neohexene in the stirred autoclave reactor. These products had variable oxygen functionalities, depending upon the reaction time, hence upon the degree of conversion, ranging from 1.15 up to 1.38 $O_2$ per molecule.

These ester terminated products, after hydrolysis, yielded materials containing one carboxyl group per molecule. This was explained on the basis of a hydrogen transfer mechanism involving methyl isobutyrate formed from the disproportionation of initiator radicals.

To determine if a product of higher functionality could be prepared under continuous polymerization conditions, we have studied the copolymerization of ethylene and neohexene in a small tubular reactor employing DMAB as initiator.

In this process, comonomers and initiator are fed under pressure into one end of the tubular reactor, which consists of from one to four steel alloy tubes in series (each is 3/16 in. I.D. x 12 ft. long). The reactants are brought up to the required polymerization temperature as they pass through a heated section of the reactor. Polymerization occurs throughout the remainder of the tube and the resulting polymer and unreacted monomers are discharged from the exit end of the reactor to be worked up as required.

Table XVIII summarizes the results obtained in these experiments.

Runs 66, 67, 68, 78, 79 and 80 were all run at constant composition and at a jacket temperature of 151°C; however, the operating pressure was varied. The highest conversions and molecular weights were obtained at 30,000 psi. In runs 85 and 86 less DMAB was used. These runs gave higher molecular weights and lower conversions as we had expected. Runs 81 and 84-B were identical to the first six runs except they were done at the higher jacket temperatures of 171 and 191°C, respectively. Higher conversions and molecular weights were obtained in these runs.

The functionalities reported for the products were calculated from the oxygen content and the number average molecular weight, and are equivalent to the number of $O_2$ units per molecule. With the exception of run 81, the functionalities are similar to the functionalities obtained with DMAB in the stirred autoclave: not much above one per molecule. In Run 81, however, the functionality was over two $O_2$ per molecule. This particular run was made at a jacket temperature of 171°C and at 30,000 psi pressure.

The product from run 81 was then saponified and converted to the -COOH terminated liquid copolymer. The product, obtained in 84% yield was analyzed and found to have a number average molecular weight of 877 (in tetrahydrofuran by vapor phase osmometry) and a neutralization equivalent of 902. One infers from these results that on the average there is 0.97 -COOH group per molecule. The elemental oxygen analysis of 4.18 wt. % gives support to this inference, showing the presence of 1.15 $O_2$ units per molecule.

No further work is planned on the products from the other runs because of their low oxygen functionalities.

This study has shown that the tubular reactor is an effective tool for preparing copolymers of ethylene and neohexene in a continuous process. Good control of molecular weight and product comonomer composition has been achieved. However, using DMAB initiator, we have not attained a significant improvement in the functionality of the copolymers from the tubular reactor as compared with copolymer prepared by the batch process in the stirred autoclave.

## TABLE XVIII

## ETHYLENE/NEOHEXENE COPOLYMERS PREPARED IN THE TUBULAR REACTOR USING DMAB

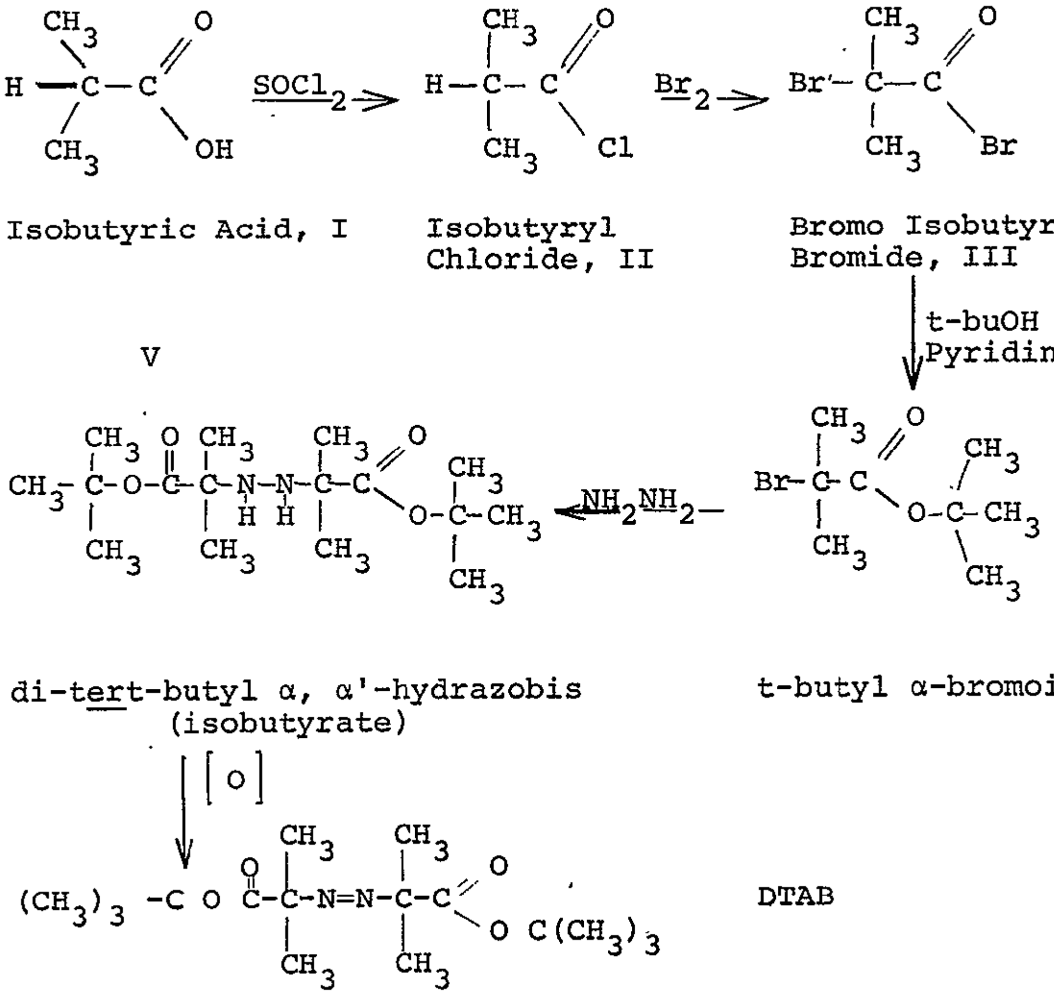
| Run No. | 66 | 67 | 68 | 78 | 79 | 80 | 85 | 86 | 81 | 84-B |
|---|---|---|---|---|---|---|---|---|---|---|
| **FEED COMPOSITION** | | | | | | | | | | |
| *Wt. % Neohexene | 71.5 | 71.5 | 71.5 | 71.5 | 71.5 | 71.5 | 72.3 | 72.6 | 71.5 | 71.5 |
| Wt. % Ethylene | 26.4 | 26.4 | 26.4 | 26.4 | 26.4 | 26.4 | 26.7 | 26.8 | 26.4 | 26.4 |
| Wt. % DMAB | 2.06 | 2.06 | 2.06 | 2.06 | 2.06 | 2.06 | 1.04 | 0.55 | 2.058 | 2.058 |
| Total Feed, wgt. | 701 | 601 | 556 | 679 | 579 | 668 | 612.1 | 734.5 | 623.2 | 566.4 |
| **REACTION CONDITIONS** | | | | | | | | | | |
| Jacket Temperature, °C | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 171 | 191 |
| Pressure, mpsig | | | | | | | | | | |
| Average | 20 | 20 | 20 | 20 | 10 | 30 | 30 | 30 | 30 | 30 |
| Deviation | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 |
| Operating Time, Hrs. | 0.82 | 1.15 | 0.23 | 0.19 | 0.267 | 0.33 | 0.30 | 0.316 | 0.3 | 0.23 |
| Nominal Hold-Up Time, Min. | 2.53 | 4.15 | 0.91 | 0.61 | 1.001 | 1.08 | 1.06 | 0.935 | 1.04 | 0.910 |
| **PRODUCTIVITY** | | | | | | | | | | |
| Yield, Grams | 61 | 53 | 53 | 60 | 35 | 66 | 57 | 57 | 75 | 69 |
| Conversion, % on M's | 8.92 | 9.01 | 9.74 | 9.02 | 6.18 | 10.09 | 9.4 | 7.8 | 12.3 | 12.7 |
| Production Rate, lbs./cu.ft./hr. | 58.2 | 35.9 | 177.1 | 244 | 102 | 154 | 148 | 140 | 194.9 | 230.6 |
| Production Rate, gm. resin/hr. | 74.7 | 46.1 | 227 | 313 | 132 | 198 | 190 | 180 | 250 | 295.7 |
| **PHYSICAL PROPERTIES** | | | | | | | | | | |
| Molecular Weight | 823 | 819 | 815 | 754 | 566 | 823 | 1243 | 1494 | 900 | 946 |
| Brookfield Vis., cps | $4700^{23}$ | $5400^{22}$ | $4500^{22}$ | $3610^{23}$ | $1060^{23}$ | $5200^{23}$ | 28,600 | 49,700 | 7590 | 7350 |
| Sp. Vis., @ 80°C | 0.0303 | 0.0324 | 0.0294 | 0.0297 | 0.0218 | 0.0319 | 0.0503 | 0.0452 | 0.0346 | 0.0273 |
| Wt. % Oxygen | 5.35 | 4.19 | 4.79 | 5.89 | 4.04 | 5.14 | 2.52 | 2.81 | 7.50 | 3.92 |
| Functionality (O) | 1.38 | 1.07 | 1.22 | 1.39 | .72 | 1.32 | 0.98 | 1.31 | 2.11 | 1.16 |
| Description | Sl. Hazy, pale yellow | | | | | | | | | |
| Remarks | | | | | | | | | | |

* Wt. %'s on Total Charge.

## V. TECHNICAL DISCUSSION, PART 5

### ATTEMPTED SYNTHESIS OF DTAB

It is desirable to utilize an initiator having a structure such that chain transfer involving abstraction of a hydrogen atom from the initiator itself is at an absolute minimum. DTAB, ditertiary butyl, α, α'-azobis (isobutyrate) was considered to be such a compound. The following reaction scheme was examined as a possible route to DTAB.



Isobutyric Acid, I

Isobutyryl Chloride, II

Bromo Isobutyryl Bromide, III

t-butyl α-bromoisobutyrate

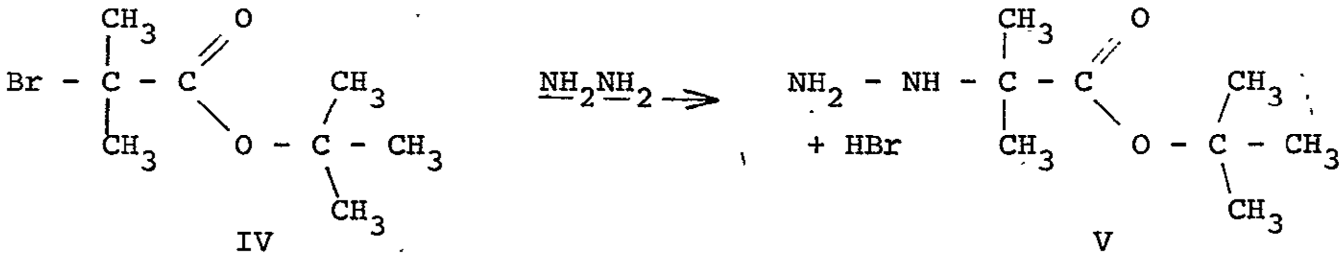
IV

V

di-*tert*-butyl α, α'-hydrazobis (isobutyrate)

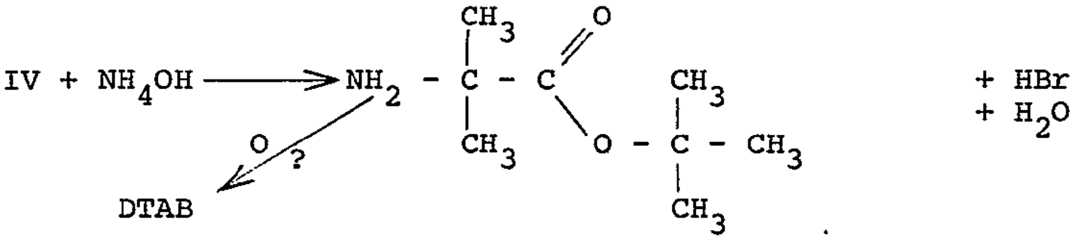
DTAB

All steps in this synthesis were completed without difficulty up to the coupling reaction. Reaction of IV with anhydrous hydrazine gave the monosubstituted hydrazine V as the sole product. No further substitution occurred when V was treated with an excess of IV.



IV V

Bromoester IV failed to react with aqueous ammonia to give the amino ester VI might also have been subsequently



VI

converted to DTAB, via oxidative coupling of the amino groups. No further attempts to synthesize DTAB are planned, in view of the above difficulty, and more importantly, the findings reported in part 4, section B in which the β-hydrogen atoms on the acid portion of the azo ester were found to give rise to a disproportionation reaction yielding methyl isobutyrate, a powerful telogen. Presumably DTAB would yield t-butyl isobutyrate which would undoubtably be a chain transfer agent also.

An intermediate prepared in this attempted synthesis of DTAB, the α-bromoester IV, was subsequently used as a chain transfer agent in the telomerization studies in part 8 of this report.

# V. TECHNICAL DISCUSSION CONT'D, PART 6

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH $CCl_4$ TELOGEN

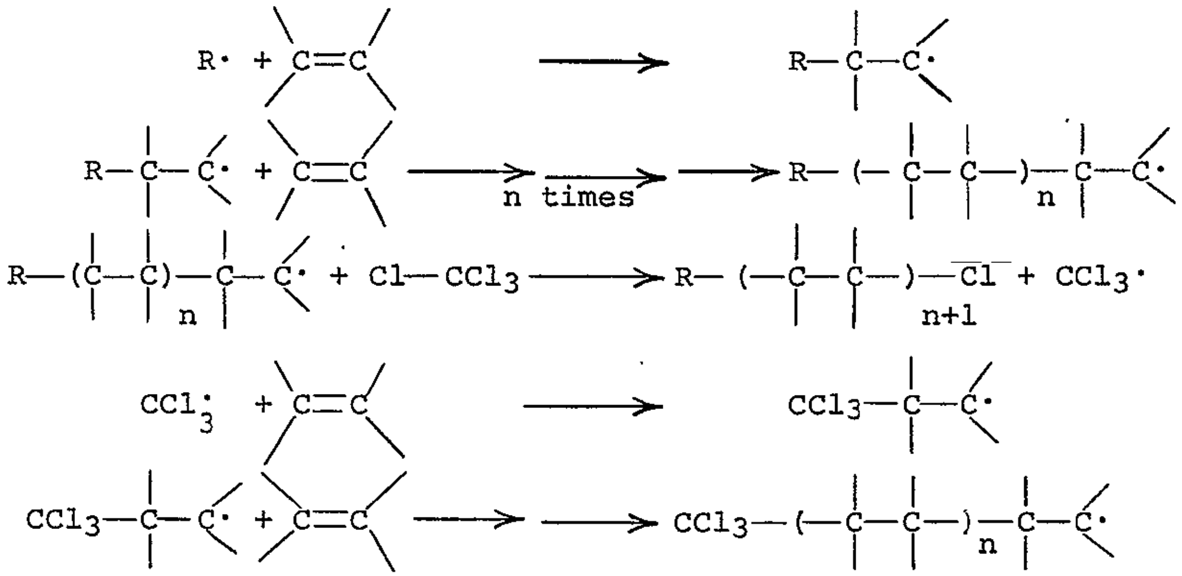
### Contents

# PART 6

# ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH CCl4 TELOGEN

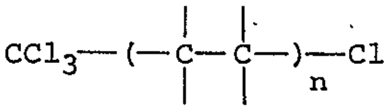
## A. Preparation of Terminally Difunctional Copolymers of Ethylene and Neohexene Using Carbon Tetrachloride as Telogen

The literature contains numerous references[12-16] to the use of carbon tetrachloride as a chain transfer agent, or telogen, in the free radical telomerization of olefins, notably ethylene. When an olefin is treated with carbon tetrachloride in the presence of a source of free radicals, the following chain reaction is set up:



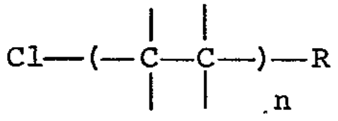
etc.

The next result of this free radical chain reaction is the formation of a large number of molecules containing two functional groups derived from $CCl_4$:



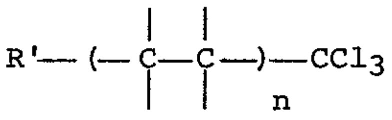
$$CCl_3-(-C-C-)_n-Cl$$

And a small number containing one functional group derived from the initiator:



$$Cl-(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_n-R$$

OR



$$R'-(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_n-CCl_3$$

The average value of n, called $\overline{DP}n$, the number average degree of polymerization, is given by the following simple expression*:

$$\overline{DP}n = \frac{[M]}{C\,[S]}$$

where [M] is the concentration of the monomer, [S] is the concentration of telogen, and C is the "chain transfer coefficient." C is the ratio between the rate constant of the chain transfer reaction and the rate constant of the propagation reaction:

$$C \equiv \frac{K_t}{K_p}$$

In the particularly simple case where $K_t = K_p$ and $C \equiv 1$, the $\overline{DP}n$ is given by the molar ratio of the monomer to telogen, and the relative concentration of the telogen to that of monomer will remain constant.

$$[M] \; / \; [S]$$

will change during the run.

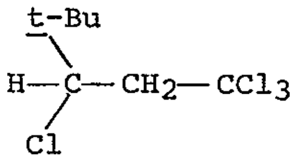
This can be avoided by adding additional material to the reactor to maintain the ratio at some constant value.

---

* See reference 16, Chart 4.

Carbon tetrachloride has been used in the telomerization of ethylene to prepare a variety of low molecular weight $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, and when $\overline{DPn}$ is between 2 and 8, these compounds have been converted into a variety of difunctional chemical intermediates[13,14,15]. The chain transfer coefficient for ethylene telomerization by $CCl_4$ is 3.2 for chain lengths of 3 and higher.[16]

Neohexene has been reacted with $CCl_4$ in the presence of benzoyl peroxide to give a 1:1 adduct. The adduct has the structure[17]:



This shows that the bulky $CCl_3\cdot$ radical prefers to add to the less substituted end of the double bond.

No studies of the co-telomerization of ethylene with neohexene have been reported.

We have completed a series of co-telomerization runs using carbon tetrachloride as the telogen in the presence of a small amount of DMAB initiator. These experiments were carried out in the small stirred autoclave. All the reactants were charged at the beginning of the run. The reaction conditions used and the results obtained from these runs are summarized in Table XVIII. The only parameter which was changed during these four runs is the mole ratio of carbon tetrachloride / Monomers.

As we had expected, the $\overline{Mn}$ of the resulting telomer was strongly dependent upon the mole ratio of carbon tetrachloride used in the run. An approximate degree of polymerization was calculated from the $\overline{Mn}$ for each run, assuming one $CCl_4$ per chain and an average monomer unit weight of 44 (The latter based upon our earlier N.M.R. findings relating the composition of the polymerization mixture to resulting copolymer composition). Plotting $1/\overline{DPn}$ vs. $[S] / [M]$ for each of the four runs, a straight line plot was obtained (See Figure 4) having a slope of 8.9. This is the apparent chain transfer coefficient for this particular comonomer charge composition. The actual curve falls off the straight line at low $[S] / [M]$. Whether this represents experimental uncertainty, or a growing importance of chain transfer to DMAB decomposition products, cannot be determined without further experimentation. The latter hypothesis is certainly more consistent with the lower $Cl_2$ functionalities which resulted in runs 90 and 63.

Elemental chlorine and oxygen analyses combined with the number average molecular weight (benzine, V.P.O.) allows us to calculate $Cl_2$ (average of Cl and $CCl_3$) and $O_2$ functionalities.

The sum of these functionalities is the number of potentially useful groups per molecule available for chemical transformation. These polymers presumably contain an equal number of Cl and $CCl_3$ groups derived from $CCl_4$ as well as some - $CO_2CH_3$ groups and functionless ends. The latter are derived from carbomethoxy isopropyl radicals and their disproportionation products.

Table XIX shows the results obtained from two additional stirred autoclave runs. Runs 126 and 128 were made at a temperature of 160°C using di-tertiary butyl peroxide (DTBP) as the free radical initiator. These runs were pilot studies to determine approximate conditions to use in the tubular reactor. At the higher temperatures required for efficient operation of a tubular reactor, neither DMAB nor AIBN would be suitable initiators. Comparing Run 126 with Run 90 (reported last quarter), which also has a $CCl_4$/Monomer ratio of .003, one notes an increased yield and a decreased viscosity for the product prepared at 160°C. These changes are due to the increased polymerization rate and the greater chain transfer activity of $CCl_4$ at the higher temperature. We cannot evaluate the functionality of the product from Run 126 as yet, however, because of the inconsistencies in the analytical data received on this run (the elemental analyses on C, H, Cl, and O added up to 92%; 1300 molecular weight does not fit the viscosity data at all).

Run 128, in which a larger $CCl_4$/Monomer ratio (.006) was used, gave a product with a lower molecular weight. The analytical data indicate that this telomer contains 1.69 chlorine functional groups (Cl-C- as well as $-CCl_3$) per molecule.

In part 4, Section C, we outlined the procedure used in making ethylene-neohexene copolymers in the tubular reactor using DMAB initiator. Essentially the same procedure was used to prepare the $CCl_4$ telomers with the exception that in some of the runs a "split feed" was used. The split feed allows one to maintain a more nearly uniform level of telogen and initiator throughout the length of the tubular reactor. This is accomplished by injecting fresh initiator and telogen into the polymerization mixture midway along the reactor. In the cases where split feed was used, an inert solvent, iso-octane, was used to convey a dilute solution of DTBP and $CCl_4$ into the reactor's secondary feed. The primary feed mixture was a solution of ethylene, $CCl_4$, and DTBP in neohexene. No added solvent was used in the primary feed.

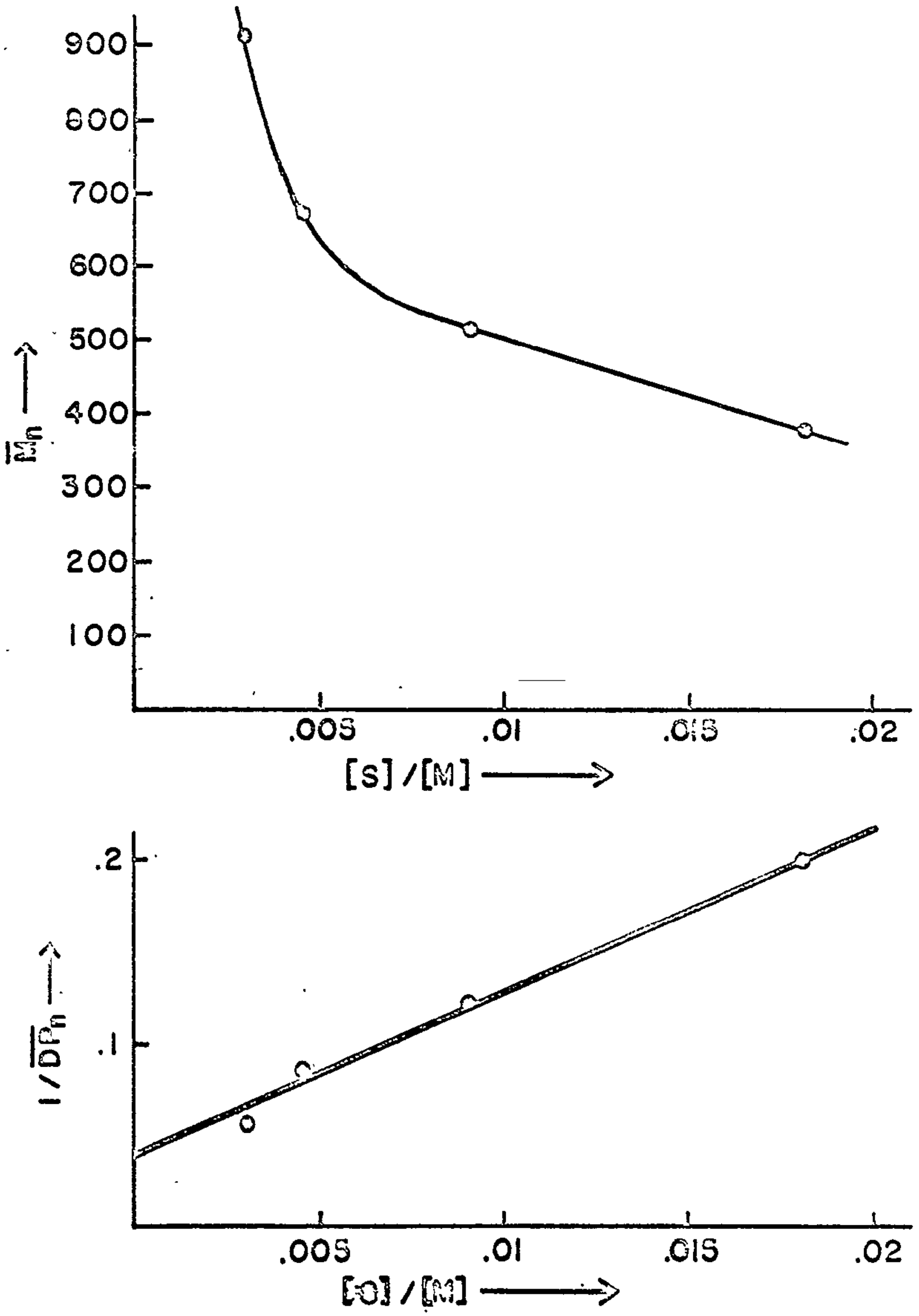
## TABLE XVIII - A

## $CCl_4$ TELOMERS OF NEOHEXENE-ETHYLENE

| Run No. 23EMS | 63 | 64 | 65 | 90 |
|---|---|---|---|---|
| <u>CHARGE</u>: | 222 | 111 | 50 | 333 |
| Mol Ratio $CCl_4$/Monomers, (S)/(M) | 0.0045 | 0.009 | 0.018 | .003 |
| Carbon Tetrachloride, gms. | 12.5 | 24.8 | 49.1 | 8.3 |
| Neohexene, gms. | 718.0 | 714.4 | 707.2 | 718 |
| DMAB, gms. | 0.491 | 0.489 | 0.484 | 0.492 |
| Ethylene, ~ gms. | 265.6 | 264.2 | 261.5 | 265 |
| <u>REACTION CONDITIONS</u> | | | | |
| Temperature, °C | 90 | 90 | 90 | 90 |
| Pressure, psi | | | | |
| Maximum | 15,000 | 15,000 | 15,000 | 15,000 |
| Final | 12,750 | 12,500 | 12,000 | 13,500 |
| Reaction Time, Hours | 3.38 | 4.35 | 4.43 | 4.35 |
| <u>PRODUCTIVITY</u> | | | | |
| Yield, gms. | 62 | 82 | 104 | 58 |
| Conversion, % | | | | |
| On Monomers | 5.03 | 6.1 | ~10.7* | 5.9 |
| On $CCl_4$ | 100 | 90.7 | | |
| Rate, %/Hr. (on M) | 1.49 | 1.4 | 2.7 | 1.4 |
| <u>PHYSICAL PROPERTIES</u> | | | | |
| Molecular Weight | 668 | 512 | 373 | 931 |
| Brookfield Vis., cps | 2810 | 1100 | 184 | 22,100 |
| Specific Vis., 80°C | 0.0294 | 0.0209 | .0140 | 0.034 |
| Wt. % Cl | 18.56 | 25.26 | 34.92 | 12.82 |
| Wt. % O | 0.50 | 1.28 | .55 | .48 |
| Functionality (Cl) | 1.748 | 1.824 | 1.84 | 1.68 |
| (O ) | 0.104 | 0.205 | .06 | .01 |
| TOTAL | 1.852 | 2.029 | 1.90 | 1.69 |
| Distillate, wt. gms. (50°/55 mm to 125°/2 mm) | 9 | 7 | | |
| Description, Copolymer | Pale, yellow oil → | | | white hazy oil |

* Uncorrected for this run.

FIGURE 3


900
800
700
600
500
400
300
200
100
$\overline{M}_n$
.005
.01
.015
.02
[S] / [M]
.2
.1
1 / $\overline{DP}_n$
.005
.01
.015
.02
[S] / [M]

## TABLE XIX

### STIRRED AUTOCLAVE RUNS
### $CCl_4$ TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

| Run No. 23EMS | 126 | 128 |
|---|---|---|
| CHARGE: | | |
| Solvent | -- | -- |
| Solvent Wt. gms. | -- | -- |
| Initiator | DTBP | DTBP |
| Initiator Wt. gms. | .5 | .5 |
| Carbon Tetrachloride, gms. | 8 | 16 |
| Neohexene, gms. | 690 | 686 |
| Ethylene, gms. | 255 | 254 |
| Mol Ratio S/M, $CCl_4$ to Monomers | .003 | .006 |
| REACTION CONDITIONS | | |
| Temperature, °C | 160 | 160 |
| Pressures, psi | | |
| Initial | 15,000 | 15,000 |
| Final | 14,000 | 14,000 |
| Reaction time, hrs. | .17 | 1.0 |
| PRODUCTIVITY | | |
| Yield, gms. | 85 | 68 |
| Conversion, % | 9.0 | 7.2 |
| Rate, % per hr. | 52.9 | 7.2 |
| PHYSICAL PROPERTIES | | |
| Molecular Weight | 1,300* | 587 |
| Brookfield Viscosity, cps | 15,400 | 650 |
| Specific Viscosity, 80°C | .031 | .019 |
| Carbon, Wt. % | 78.79* | 68.47 |
| Hydrogen, Wt. % | 13.46* | 11.37 |
| Oxygen, Wt. % | 0.00* | .17 |
| Chlorine, Wt. % | 0.27* | 20.36 |
| FUNCTIONALITY | | |
| Chlorine ($Cl_2$/mol) | ? | 1.69 |
| Oxygen ($O_2$ /mol) | ? | .06 |
| DESCRIPTION | Colorless, Slightly Hazy Oils | |

* Analytical Results Questioned

All of the $CCl_4$ telomerization products from the tubular reactor were stripped to 155°C at 2 mm, and one drop of stabilizer, dibutyl tin dilaurate, was added prior to stripping to minimize dehydrohalogenation. A distillate fraction, very likely low molecular weight telomers with $CCl_4$, was obtained between 120°C at 300 mm to 155°C at 2 mm. This fraction varied between 9 to 20 weight per cent of the total product. It was not included in conversion calculations.

The results of these tubular reactor runs without split feed are given in Table XX.

With the exception of runs 10 and 12 where t-butyl peroxypivalate (TBPP) was used, di-t-butyl peroxide (DTBP) was used in all of the runs.

In our first run in the tubular reactor the jacket temperature was 220°C. This is the temperature such that 95 per cent of the di-t-butyl peroxide (DTBP) is consumed at a residence time of 60 seconds, providing incoming feed is at 200°C. Two tubes were used, one as a preheater for the first rwo runs. At 220°C, very low Brookfield viscosity product was made with evidence of dehydrochlorination (dark color). Jacket temperature was reduced to 200°C and the color improved with a threefold increase in Brookfield viscosity.

The molecular weight of this product was 667. Dropping the temperature to 180°C, and increasing residence time to three minutes doubled the Brookfield viscosity to 2,200 cps. However, the molecular weight was a bit low (767). From these first five experiments it was obvious that either lower temperatures, lower telogen concentration or both would have to be used to obtain a higher molecular weight.

## TABLE XX

### TUBULAR REACTOR RUNS - NO SPLIT FEED

### $CCl_4$ TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

| Run No. 24EMS | 2 | 4 | 6 | 8 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|
| FEED COMPOSITION | | | | | | | |
| Neohexene, Wt. % | 72.4 | → | → | → | → | 72.6 | 72.8 |
| Ethylene, Wt. % | 26.8 | → | → | → | → | 26.9 | 26.9 |
| $CCl_4$, Wt. % | 0.71 | → | → | → | → | .24 | .28 |
| $CCl_4$, Mole Ratio | .0022 | → | → | → | → | .0007 | .001 |
| Initiator | DTBP | → | → | → | TBPP | TBPP | DTBP |
| Initiator, Wt. % | 0.05 | → | → | → | .079 | .187 | .05 |
| Total Feed, gms. | 7552 | 7630 | 7551 | 6717 | 7419 | 3582 | 7430 |
| REACTION CONDITIONS | | | | | | | |
| Temperature, °C | | | | | | | |
| Jacket | 225 | 203 | 180 | 180 | 160 | 160 | 180 |
| Internal, max. | 222 | 183 | 166 | 166 | 140 | 147 | 165 |
| Pressure, psi | 20 ± 2.5 | 30 ± 2.5 | → | → | → | → | → |
| Operating Time, Hrs. | 3.42 | 3.35 | 3.27 | 2.90 | 3.25 | 1.55 | 3.1 |
| Nominal Hold-up Time, Min. | 0.99 | .96 | 2.83 | 2.83 | 0.95 | 0.94 | 2.73 |
| Number of Tubes | 2 | 2 | 4 | 4 | 2 | 2 | 4 |
| PRODUCTIVITY | | | | | | | |
| Yield, gms. | 242 | 304 | 300 | 277 | 128 | 114 | 203 |
| % Conversion | 3.2 | 4.0 | 4.0 | 4.2 | 1.7 | 3.2 | 2.8 |
| Production Rate, gms./hr. | 70.9 | 90.6 | 91.8 | 95.5 | 39.4 | 73.5 | 65.5 |
| PHYSICAL PROPERTIES | | | | | | | |
| Molecular Wt. | 516 | 667 | 767 | 747 | 649 | 1114 | 1009 |
| Brookfield Visc., cps | 436 | 1212 | 2194 | 2276 | 1350 | 25,100 | 11,000 |
| Specific Visc., @ 80°C | .013 | .016 | .021 | .022 | .018 | .028 | .024 |
| Wt. % Cl | 11.61 | 11.48 | 12.32 | 11.91 | 17.58 | 6.20 | 6.51 |
| Wt. % O | .3 | .27 | 0.0 | 0.0 | .17 | .17 | .19 |
| Description | Dark | Hazy | Straw Oil | → | → | → | → |
| FUNCTIONALITY | | | | | | | |
| $Cl_2$ per molecule | .85 | 1.08 | 1.33 | 1.25 | 1.61 | .97 | .93 |
| $O_2$ per molecule | .09 | .11 | 0.0 | 0.0 | .07 | .12 | .12 |

The next run was made at 160°C using t-butyl peroxypivalate (TBPP), a lower temperature peroxide than DTBP. This resulted in a lower viscosity polymer. Further adjustment of the relative concentrations of $CCl_4$/monomer/initiator resulted in a product of molecular weight 1114 (Run #12). However, this product contained about one $Cl_2$ per molecule.

Returning to 180 C and DTBP, the $CCl_4$/monomer mole ratio was reduced to 0.001 which gave a polymer of 11,000 cps viscosity and 1009 mol. wt. This product also contained only about one $Cl_2$ per molecule.

With some idea of the capability of the system, it was reasonable to go to split feeds such that low concentrations of $CCl_4$ could be used to obtain the high molecular weight, but that the telogen concentrations could be maintained by injection of more $CCl_4$ and catalyst midway in the reactor. When the chain transfer constants are much greater than one, additional telogen should be added to supplant $CCl_4$ already consumed. Such runs are Nos. 16-36, where isooctane solutions of $CCl_4$ and DTBP were injected midway in the reactor. Mole ratios of $CCl_4$ to monomer for the secondary feed were based on 98 per cent of monomers fed; two per cent was considered to be converted to polymer. This procedure, however, did not allow us to obtain products of high chlorine functionality. Copolymers having the desired molecular weight had $Cl_2$ functionalities of slightly less than one. The results are summarized in Table XXI.

We believe that the source of the difficulty is the higher chain transfer coefficient of $CCl_4$ at the temperature required for efficient operation of a tubular reactor.

The effect of temperature on transfer activity of $CCl_4$ may be seen in Figure 5 where the log of the transfer constant* is plotted against the reciprocal of the absolute temperature. Temperatures above 100°C represent maximum internal tube temperatures. At 90°C the transfer constants were taken from stirred autoclave data.

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* The chain transfer coefficients were calculated from the slopes of straight lines fitted to plots of $1/\overline{DP}_n$ against $[S] / [M]$ as discussed in our last quarterly report. We must re-emphasize that this procedure is purely empirical and gives results which only relate to our particular reaction conditions and comonomer compositions.

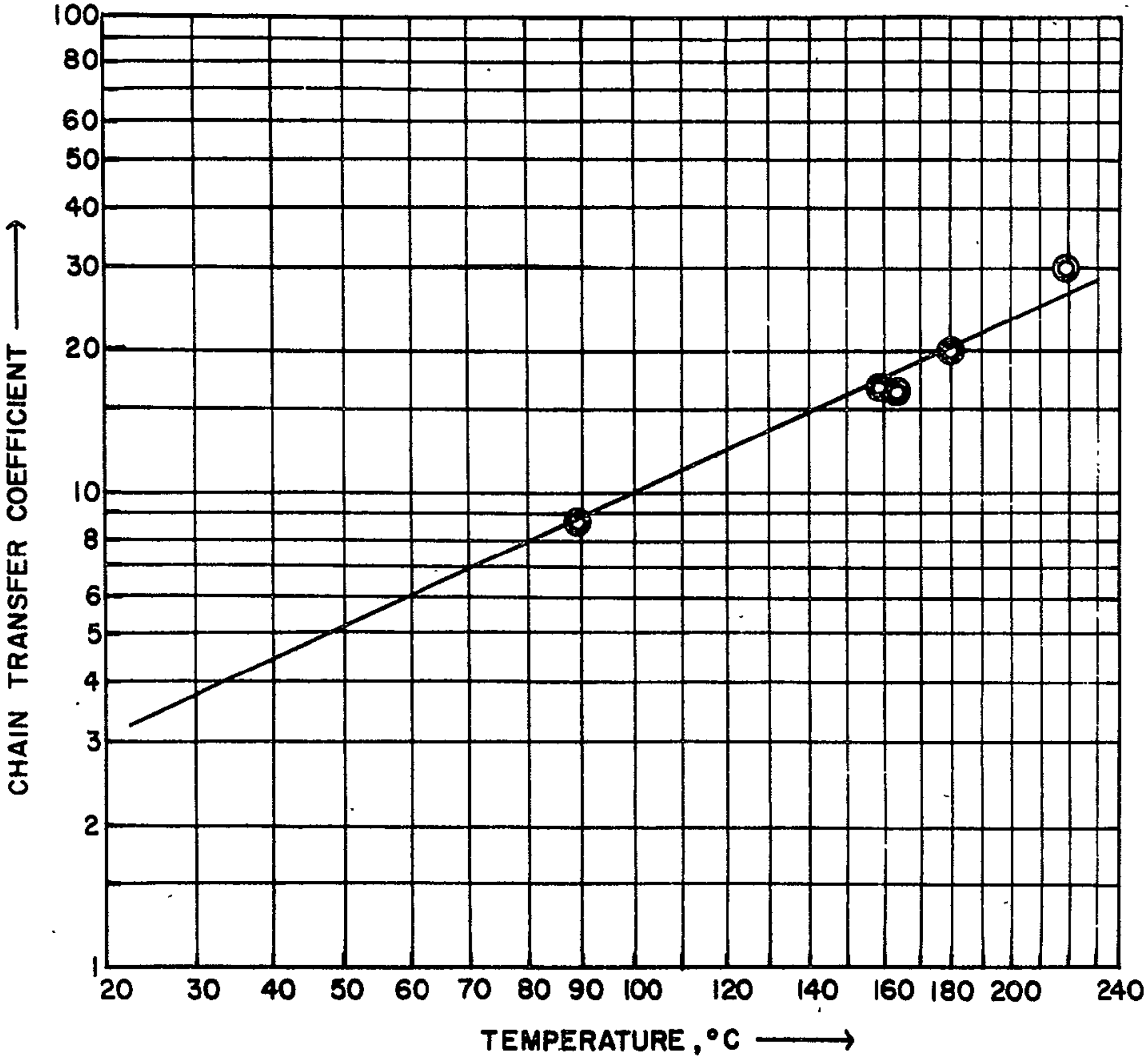
TABLE XXI

TUBULAR REACTOR RUNS - SPLIT FEED

$CCl_4$ TELOMERIZATIONS OF ETHYLENE/NEOHEXENE

| Run No. 24EMS | 16 | 22 | 24 | 28 | 30 | 32 | 36 |
|---|---|---|---|---|---|---|---|
| PRIMARY FEED COMPOSITION | | | | | | | |
| Neohexene, Wt. % | 72.8 | 72.8 | 72.8 | 72.3 | 72.4 | 72.6 | 72.6 |
| Ethylene, Wt. % | 26.9 | 26.9 | 26.9 | 26.8 | 26.8 | 26.9 | 26.9 |
| $CCl_4$, Wt. % | .22 | .253 | .25 | .71 | .71 | .47 | .47 |
| $CCl_4$, Mole Ratio | .0008 | .0009 | .0009 | .0021 | .0021 | .0014 | .0017 |
| Initiator | DTBP | → | → | → | → | → | → |
| Initiator, Wt. % | .075 | .05 | .03 | .20 | .10 | .07 | .07 |
| Total Feed, gms. | 6228 | 7386 | 5651 | 7542 | 7441 | 7731 | 6496 |
| SECONDARY FEED COMPOSITION | | | | | | | |
| Isooctane, Wt. % | 96.5 | 96.8 | 97.0 | 91.7 | 92.5 | 94.9 | 94.9 |
| $CCl_4$, Wt. % | 2.66 | 2.64 | 2.64 | 6.42 | 6.48 | 4.42 | 4.42 |
| $CCl_4$, Mole Ratio | .0013 | .00088 | .0008 | .0019 | .0021 | .0012 | .0012 |
| Initiator, Wt. % | .887 | .559 | .30 | 1.83 | .93 | .64 | .64 |
| Total Feed, gms. | 770 | 666 | 584 | 722 | 780 | 690 | 477 |
| REACTION CONDITIONS | | | | | | | |
| Temperature, °C | | | | | | | |
| Jacket | 180 | 180 | 182 | 180 | 180 | 180 | 170 |
| Internal, max. | 158 | 165 | 160 | 158 | 158 | 158 | 145 |
| Pressure, mpsi | 25 ± 2.5 | 30 ± 2.5 | → | → | → | → | 40 ± 2.5 |
| Operating Time, Hrs. | 3.2 | 3.2 | 2.5 | 3.6 | 3.3 | 3.3 | 3.2 |
| Nominal Hold-up Time, Min. | 3.11 | 2.68 | 2.69 | 2.91 | 2.67 | 2.65 | 3.04 |
| Number of Tubes | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| PRODUCTIVITY | | | | | | | |
| Yield, gms. | 350 | 282 | 88 | 538 | 381 | 278 | 158 |
| % Conversion | 5.64 | 3.83 | 1.2 | 7.2 | 5.2 | 3.6 | 2.4 |
| Production Rate, gms./hr. | 109.4 | 88.1 | 35.4 | 150.8 | 117.3 | 83.8 | 49.9 |
| PHYSICAL PROPERTIES | | | | | | | |
| Molecular Wt. | 976 | 1019 | 841 | 719 | 651 | 726 | 727 |
| Brookfield Visc., cps | 9560 | 8210 | 4680 | 2018 | 1440 | 2100 | 2175 |
| Specific Visc. @ 80°C | .028 | .026 | .024 | .018 | .016 | .018 | .018 |
| Wt. % Cl | 5.67 | 6.67 | 9.23 | 11.76 | 13.86 | 12.13 | 13.41 |
| Wt. % O | .52 | .55 | .37 | .73 | .41 | .26 | .25 |
| Description | Yellowish Tan Oil | Tan Oil | Dk. Tan Oil | Yellowish Tan Oil | → | → | → |
| FUNCTIONALITY | | | | | | | |
| $Cl_2$ Per Molecule | .78 | .96 | 1.10 | 1.19 | 1.28 | 1.24 | 1.38 |
| $O_2$ Per Molecule | .32 | .35 | .09 | .33 | .17 | .12 | .11 |

Figure 4



CHAIN TRANSFER COEFFICIENT OF $CCl_4$ AS A FUNCTION OF TEMPERATURE.

It is significant that the tubular reactor product of highest functionality (Run No. 10, 1.61 $Cl_2$/molecule) was made at very low conversion on both monomers and upon $CCl_4$. To obtain a thousand molecular weight copolymer the mole ratio of $CCl_4$ to monomer must be about 0.003 at 90°C and 0.001 at 160°C. At the latter ratio, assuming 100 per cent efficiency on the $CCl_4$, conversion must be limited to 2.2 per cent on the monomers or non-reactive terminal groups will result. In the higher conversion runs, the $CCl_4$ is depleted before the polymerization is over, even when split feed is used.

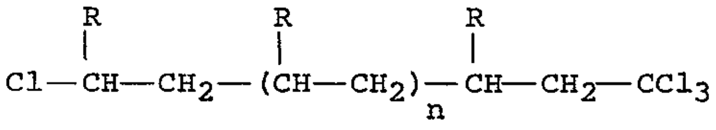
Our results have shown that the continuous tubular reactor is not suitable for preparation of telomers, except in the simple case where the chain transfer coefficient is unity and the telogen/monomer ratio remains constant throughout the tube. A continuous stirred autoclave reactor is not subject to this difficulty since it operates under steady state conditions. In any future continuous telomerizations, we will use the latter approach rather than the tube. For smaller scale operations, the stirred autoclave reactors with continuous feed of telogen (in order to maintain a constant composition) will be the method of choice.

A discussion of experiments which were performed to convert —Cl and —$CCl_3$ groups in these telomers to —COOH groups is given in section B.

B. Reactions of the $CCl_4$ Telomers

Our experiments have shown that one can obtain telomers of ethylene and neohexene having high chlorine functionalities when $CCl_4$ is used as telogen under the proper conditions. The functional groups so introduced, however, must be converted into other functional groups which will be useful for low temperature curing reactions if the telomers are to be used as solid propellant binders.

There are two different kinds of functional groups in these telomers. At one end of each molecule is a chloride function, at the other end is a trichloromethyl group:



$$Cl-\overset{R}{\overset{|}{CH}}-CH_2-(\overset{R}{\overset{|}{CH}}-CH_2)_n-\overset{R}{\overset{|}{CH}}-CH_2-CCl_3$$

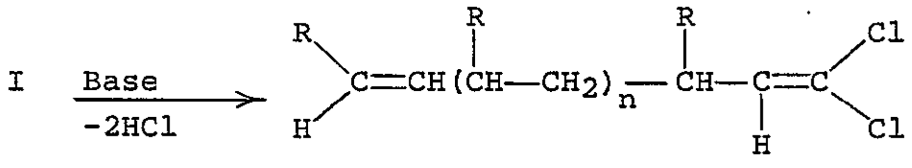
$R = H$ or $\overset{\text{I}}{\underline{t}}$ - butyl

The chemical literature abounds with examples where small molecules containing these functional groups have been converted into carboxylic acids and even di-carboxylic acids.[12,14,15,21-24] Most of these examples have dealt with fairly low molecular weight ethylene telomers containing 1-5 ethylene residues. In these examples, the $CCl_3$ group has been hydrolyzed to COOH under both acidic and basic conditions. The Cl group has been displaced with $CN^-$, $S^-$, $Br^-$ and $I^-$. The products from CN displacement have been hydrolysed to give di-carboxylic acids.

With this background, it appeared that the $CCl_4$ telomers of ethylene and n echexene were very promising intermediates from which curable prepolymers could be produced using standard organic reactions.

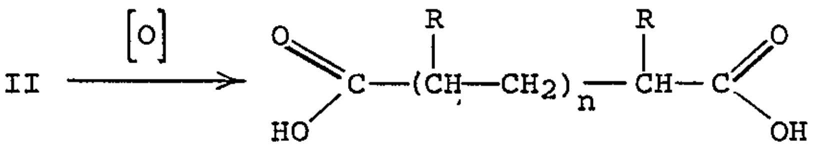
We have tried the following approaches directed toward placing useful functional groups upon the $CCl_4$ telomers:

1. Degradation under strongly alkaline conditions, leading to elimination of HCl:

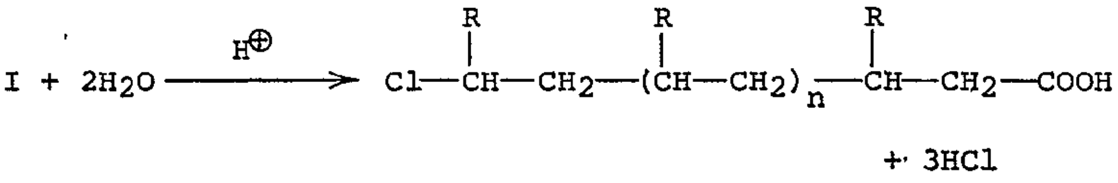


II

This could be followed by oxidation of the unsaturated product to a di-carboxylic acid:

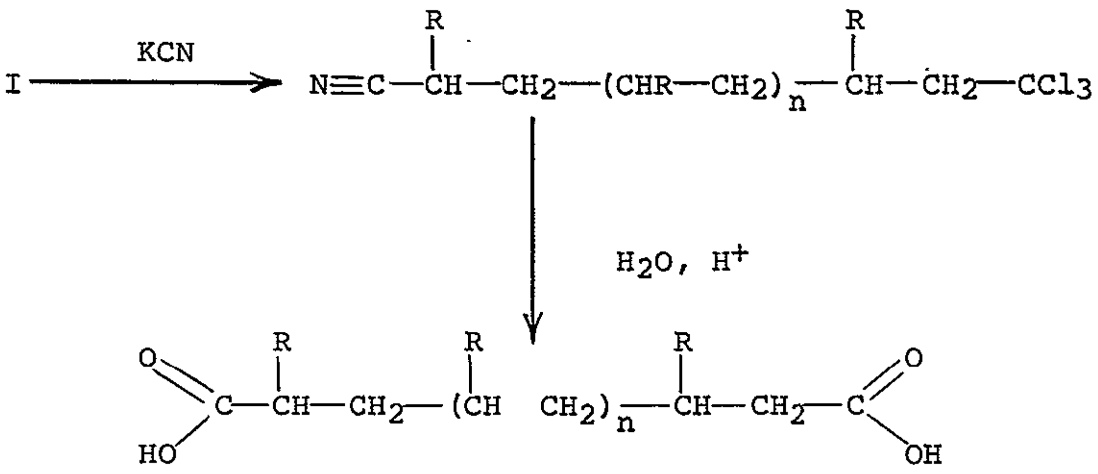


2. Acid hydrolysis of the trichloromethyl group:

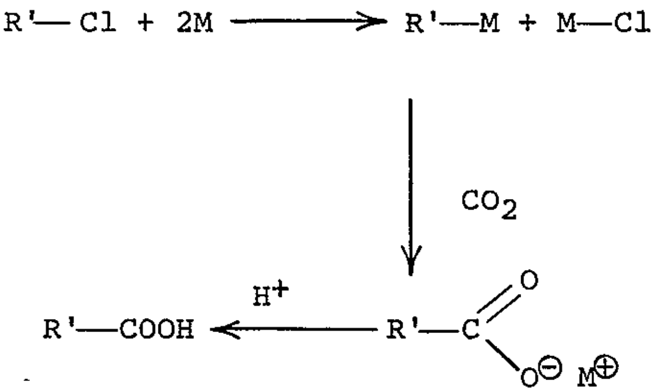


$$I + 2H_2O \xrightarrow{H^{\oplus}} Cl-\overset{R}{\overset{|}{C}H}-CH_2-(\overset{R}{\overset{|}{C}H}-CH_2)_n-\overset{R}{\overset{|}{C}H}-CH_2-COOH + 3HCl$$

3. Nitrile displacement of chloride, followed by hydrolysis to carboxyl:



4. Metalation of the terminal alkyl chloride followed by carbonation of the resultant metal alkyl:



1. Alkaline Degradation

We have used two different sets of conditions under this approach. The first of these is basically similar to the conditions which we had found to be effective in the saponification of C≡N end groups of the AIBN polymers. The $CCl_4$ telomer is dissolved in butanol and treated with potassium hydroxide in a sealed titanium lined bomb at 250°C under autogenous pressure for about 20 hrs. This procedure was tried on $CCl_4$ telomers 23-EMS-63, 64 and 65. The results are shown in Table XXII.

The $—CCl_3$ groups were saponified to $—COO^-$ only to a very minor extent, however a considerable amount of elimination has occurred. This is shown by the presence of unsaturation in the product, as well as by the very low chlorine contents. The strong I.R. bands identified with $CCl_3$ were absent. The presence of over one oxygen per molecule as well as the 1120 $cm^{-1}$ I.R. band suggest that extensive ether formation has occurred as well. These products are certainly not homogenous by any means, however, the presence of $>1$ $C=C$ per molecule encouraged us to continue this approach.

## TABLE XXII

## ALKALINE DEGRADATION OF $CCl_4$ TELOMERS

| Experiment 8433-No. | | 3 | 7-a | 7-b | 7-c |
|---|---|---|---|---|---|
| REACTION CONDITIONS: | | | | | |
| Telomer Used | | 23-EMS-65 | 23-EMS-64 | 23-EMS-63 | 23-EMS-65 |
| Wt. Telomer, gms. | | 1.37 | 20 | 19 | 20 |
| Base Used | | KOH | | | |
| Wt. Base, gms. | | 10 | 17.5 | 20 | |
| Solvent | | Butyl Cellosolve | | Butanol | |
| Vol. Solvent, ml | | 50 | 100 | | |
| Temperature, °C | | 170 | 250 | | |
| Reaction Time, Hrs. | | 20 | 20 | 19 | |
| Yield, gms. | | .68 | 6.38 | 14.6 | 12.71 |
| PRODUCT DATA | | | | | |
| Infrared Analysis | | | | | |
| Frequency | Assignment | | | | |
| 700,780 $cm^{-1}$ | $-CCl_3$ | Absent | Absent | Absent | Absent |
| 1700 $cm^{-1}$ | -COOH | Absent | Weak | Weak | Weak |
| 972 $cm^{-1}$ | -C=C- | Moderate | Moderate | Moderate | Moderate |
| 1120 $cm^{-1}$ | -C-O-C- | Strong | Moderate | Moderate | Moderate |
| Mol. Wt. | | -- | 472 | 610 | 373 |
| Wt. % O | | -- | 5.38 | 2.97 | 5.46 |
| Wt. % Cl | | -- | .82 | 0.0 | .16 |
| Wt. % C=C | | -- | 6.16 | 5.4 | 7.84 |
| Neuralization Equiv. | | -- | 3500 | 3910 | 2710 |
| Beilstein Test | | + | + | + | - |
| FUNCTIONALITY | | | | | |
| COOH/Molecule | | -- | .135 | .156 | .14 |
| O/Molecule | | -- | 1.59 | 1.13 | 1.27 |
| Cl/Molecule | | -- | .11 | 0.0 | 0.0 |
| C=C/Molecule | | -- | 1.2 | 1.4 | 1.23 |

The second procedure we tried under this approach was to treat the telomers with potassium t-butoxide in refluxing tetrahydrofuran. We anticipated these conditions would favor E-1 elimination reactions and lead exclusively to molecules having a double bond at each end. For these experiments we used $CCl_4$ telomers 23-EMS-126, 24 EMS-6 & 10, discussed in part A of this report.

When a $CCl_4$ telomer is added to a refluxing solution of potassium t-butoxide in THF, an immediate exothermic reaction occurs, along with the formation of a white precipitate (presumably KCl since it is water soluble). The reaction is over within one hour. Our preliminary analytical data show that the products isolated from these reactions have no trace of the $-CCl_3$ bonds at 700 and 780 $cm^{-1}$ in their infrared spectra. They all give a strong positive Beilstein test, however, the strong absorption at 970 $cm^{-1}$ (attributed to C=C in the spectra of the KOH/butanol products discussed in the previous section) is not at all evident in the spectra of these products, nor is ether type absorption present either.

2. Acid Hydrolysis

It has been reported that the $-CCl_3$ group is resistant to nucleophilic attack, but is quite susceptible to electrophilic reagents. With this in mind, we have tested the reactivity of the $CCl_4$ telomers with strong mineral acid.

Treatment of telomer 23-EMS-65 with 48% aqueous HBr at 150°C in a sealed pyrex tube for 20 hours gave essentially no reaction at all.

Friedlina and Basileva report[15] that $CCl_4$ telomers of ethylene are readily attacked by fuming nitric acid to give carboxylic acids. The yields are quite good for low telomers, but decrease with higher telomers.

In our experiments, we have found that the $CCl_4$ telomers of ethylene and neohexene are rapidly attacked by warm fuming nitric acid. Brown fumes of $NO_2$ are given off along with HCl gas (the presence of the latter was demonstrated by passing the exit gasses through an $AgNO_3$ solution) from the reaction of the $-CCl_3$ groups.

In a typical experiment, .81g (.0016 moles) of 23-EMS-64 was treated with 10 ml fuming nitric acid and heated for 1 hour in an oil bath at 138°C. When the silver chloride in the trap was collected, dried and weighed, .23g (.0016 moles) was obtained. This corresponds to a 33% conversion of $-CCl_3$ groups.

The product was recovered by diluting with water and extraction with ether. 0.66 gram of a two phase product was recovered after evaporation. 0.48 gram was hexane soluble. This material was a straw colored clear oil. It's I.R. showed about 60% of the original $-CCl_3$ groups remaining. A COOH band of moderate intensity was also present. The hexane insoluble fraction, .14 grams amber oil, contained no $-CCl_3$ functional groups. A very intense -COOH band was present.

The same process was repeated on a larger scale using 18.49g. of 24-EMS-10 and 100 ml fuming nitric acid. The maximum temperature reached was 67°C. Upon work up we obtained 13.23 gms. of a hexane soluble amber oil and 3.17 grams of hexane in-groups. The hexane soluble material had a neutralization equivalent of 988. It's I.R. spectrum showed that about 55% of the $CCl_3$ remained unreacted.

The results of these and other experiments suggest that it will be difficult to obtain a product in which all of the $-CCl_3$ groups have been converted into COOH using this method, and that low yields and considerable by-products are very likely inevitable.

### 3. CN Displacement

The next group of experiments to be discussed are our attempts to effect a displacement of the terminal chloride in structure I with cyanide ion. Table XXIII summarizes the results of these experiments.

No substitution of CN for Cl occurred in any of the experiments. At 100°C no reaction occurred at all. At higher temperatures, particularly in the very polar solvents DMF and sulfolane, decrease in the amount of $-CCl_3$ groups occurred. This was usually accompanied by the appearance of bands at 970 and 800 $cm^{-1}$ in the infrared spectrum. These probably indicate the formation of double bonds.

TABLE XXIII

CN DISPLACEMENT STUDIES ON $CCl_4$ TELOMERS

| Experiment 8433-47 | No. 1 | 2 | 3 | 4-a | 4-b | 5-a | 5-b | 6-a | 6-b | 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| Telomer Used | 23-EMS-64 | 47-1 | 23-EMS-64 | | | | | | | |
| Gms. Telomer | .88 | .85 | .5 | .5 | .5 | .5 | .5 | .5 | .5 | .5 |
| Gms. KCN | 2 | 2 | 1 | -- | 2 | 1 | 1 | 1 | 1 | 1 |
| Gms. KI | -- | .1 | .05 | 2 | .1 | -- | -- | -- | -- | -- |
| Solvent | Butyl Cellosolve | Butanol/$H_2O$ | Butanol | Butanol/$H_2O$ | Butanol/$H_2O$ | Sulfolane | DMF | DMF | Sulfolane | DMF |
| Ml. Solvent | 5 | 10/3 | 2 | 2/.5 | 1/1 | 2 | 2 | 2 | 2 | 2 |
| Temp., C | 160 | 100 | 200 | 200 | 200 | 200 | 100 | 100 | 100 | 150 |
| Reaction Time, Hrs. | 20 | 20 | 5 | 2 | 2 | 4 | 4 | 20 | 20 | 12 |
| Vessel Used | Stirred Flask | Stirred Flask | Sealed Vial, Rocked in Oil Bath → | → | → | → | → | → | → | → |
| Result | No reaction at all. No CN in product. | → | No CN in product. $CCl_3$ bands diminished considerably. C=C bands at 970 and 860 $in^{-1}$ | → | → | No CN or $CCl_3$ in product. C=C bands at 970 and 860 $in^{-1}$ | → | No Reaction | → | $CCl_3$ bands almost gone. No C≡N band. |

### 4. Metalation

The following experiments were done to test the practicality of this route to carboxyl terminated polymers from the $CCl_4$ telomers; $CCl_4$ telomer 23-EMS-128, having $\bar{M}_n$ = 587 containing 3.4 Cl per molecule was used in all cases:

1. The telomer was reacted with a 9 fold excess of potassium metal in refluxing tetrahydrofuran. A dark green reaction mixture resulted which gave a strongly positive Gilman test for the presence of organometallics. Dry $CO_2$ was passed through the reaction mixture until the color was discharged. The mixture was then acidified and worked up to recover the telomer. The product exhibited a strong COOH carbonyl in the infrared, but no trace of the absorption due to the $-CCl_3$ group. The product gave a negative Beilstein test. The neutralization equivalent was 1073.

2. In a similar experiment, $CO_2$ was passed into the reaction mixture from the beginning. The product resulting had an N.E. of 1273, and a small amount of $-CCl_3$ absorption was still present in the I.R. of the product.

Substituting heptane for THF gave a product with a neutralization equivalent of 2074.

3. In another experiment, addition of $CO_2$ was delayed until 3 hours after reaction of the telomer with the potassium. At this point the green color had faded and the Gilman test was negative. No COOH groups resulted when $CO_2$ was added to this reaction mixture. No trace of the $CCl_3$ absorption could be seen in the I.R. spectrum of the product.

When the above experiments were repeated using lithium dispersion in hexane instead of potassium metal, no carbonation was effected however, the $-CCl_3$ groups were no longer present in the products, most of which gave a negative Beilstein test.

We feel that the reason for the failure of the experiments just discussed to introduce carboxyl functionality into the $CCl_4$ telomers is the instability of the metal alkyls at the temperatures used to form them. An alternate approach is to use metal exchange between the telomers and another organometallic such as *t*-butyl lithium. This must be carried out at low temperatures. Under these milder conditions, the telomer organometallic compound may survive long enough to be carbonated.

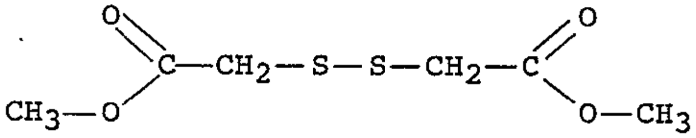
## PART 7

## V. TECHNICAL DISCUSSION, Cont'd

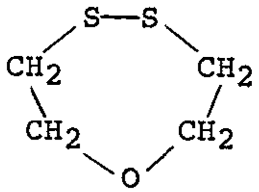
## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH DISULFIDE TELOGENS

### A. Disulfides as Telogens

It has been reported that disulfides can serve as active chain transfer agents in free radical polymerizations. Dinaburg and Vansheidt examined a variety of mercaptans and disulfides as chain transfer agents in the polymerization of styrene at 100°C.[18] Simple dialkyl disulfides had chain transfer coefficients from .005 to .01, whereas, for some disulfides, such as the dimethyl ester of dithioglycolic acid (I), they report values as high as 0.1:



Stockmayer, Howard, and Clarke report that in the polymerization of vinyl acetate, di-n-butyl disulfide has a chain transfer coefficient of 1 and that the diethyl ester of dithioglycolic acid has a coefficient of 1.5. In addition, they reported that the cyclic disulfide 1-oxa-4,5-dithiacycloheptane, II, actually copolymerized with the vinyl acetate.[19]



A polymer which they prepared had a $\overline{DP}n$ of about 90 and had incorporated about 9 disulfide units per molecule. These results were substantiated by Tobolsky and Baysal who were able to copolymerize II with Styrene.[20]

The results indicated that the following chain transfer reactions occur when a disulfide is present in a free radical polymerization:

$$\mathrm{I}\cdot + \mathrm{M} \longrightarrow \mathrm{I{-}M}\cdot$$

$$\mathrm{I{-}M}\cdot + \mathrm{nM} \longrightarrow \longrightarrow \mathrm{I{-}(M)_n{-}M}\cdot$$

$$\mathrm{I{-}(M)_n{-}M}\cdot + \mathrm{R{-}S{-}S{-}R}$$

$$\mathrm{I{-}(M)_{n+1}{-}S{-}R} + \cdot\mathrm{S{-}R}$$

$$\mathrm{R{-}S}\cdot + \mathrm{M} \longrightarrow \mathrm{R{-}S{-}M}\cdot$$

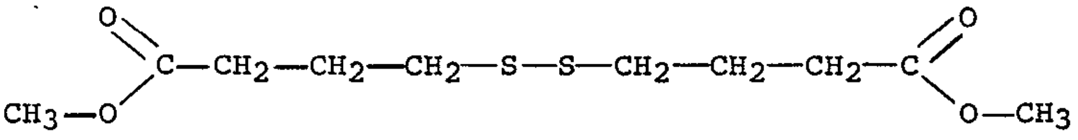
$$\mathrm{R{-}S{-}M}\cdot + \mathrm{nM} \longrightarrow \longrightarrow \mathrm{R{-}S{-}(M)_n{-}M}\cdot$$

$$\mathrm{R{-}S{-}(M)_n{-}M}\cdot + \mathrm{R{-}S{-}S{-}R} \longrightarrow$$

$$\mathrm{R{-}S{-}(M)_{n+1}{-}S{-}R} + \cdot\mathrm{S{-}R}$$

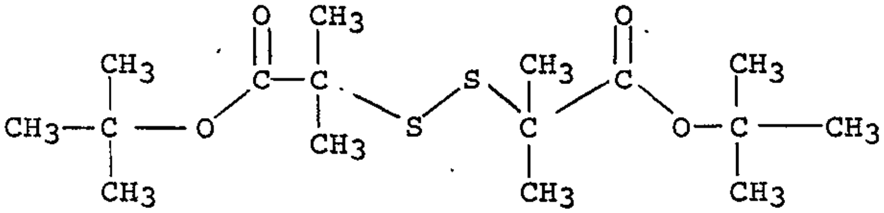
If, as shown above, the disulfide is acyclic, telomers containing two sulfur atoms per molecule result. If the disulfide is cyclic, a high polymer containing two sulfide links for every chain transfer step. In the latter case, the chain transfer reaction is intra-molecular rather than inter-molecular.

In order to apply the disulfide chain transfer reaction to our problem, we prepared several disulfides containing ester functions. We reasoned that if disulfides were effective transfer agents for ethylene-neohexene copolymers, the resulting ester terminal groups could be simply and efficiently converted to the desired carboxyl group. We prepared the following disulfides:



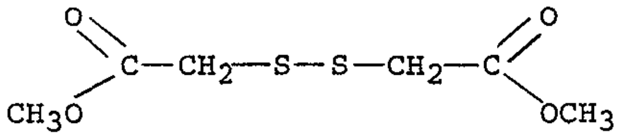
III

Dimethyl γ,γ'-dithiodibutyrate



IV

Di-t-butyl α -dithiobis [isobutyrate]



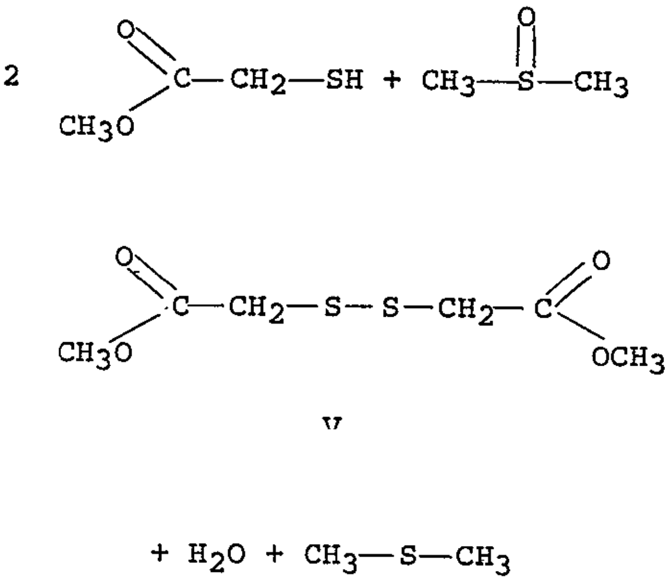
V

Dimethyl Dithioglycolate

III was prepared by esterifying commercially available dithiodibutyric acid with methanolic HCl. The resulting dimethyl ester boiled at 193°C at 2.0mm. It was a pale straw liquid with a faint peppery odor.

IV was prepared by treating tert-butyl α-bromoisobutyrate with an excess of sodium disulfide. The resulting disulfide boiled at 150-155°C at 2-3mm. It was a colorless oil with a faint garlic odor. tert-Butyl α-bromoisobutyrate was on hand as an intermediate in the synthesis of DTAB (See part 5, this report).

V was prepared by esterifying commercially available thioglycolic acid with methanolic HCl and oxidizing the resulting mercapto-ester to the disulfide using dimethyl sulfoxide as oxidant:



V

The product boiled at 119-120°C at 1.4mm. It was a pale straw liquid with a strong garlic odor.

As soon as the disulfide telogens were available we started telomerization studies in the 1.5 l stirred autoclave. The results of these experiments are summarized in Tables XXIV and XXV.

The low polymerization rate for these runs is partly due to the low initiator (DMAB or DTBP) concentration used, but may also reflect a low efficiency of disulfides III and IV as telogens, *i.e.*, they may act as retarders. This would be the case if the reaction between a radical and the disulfide (to product a sulfide terminated chain and a sulfide radical) were rapid, but initiation of a subsequent polymer chain by the resulting sulfide radical were slow.

## TABLE XXIV

### NEOHEXENE/ETHYLENE COPOLYMERS PREPARED IN THE STIRRED AUTOCLAVE

| Run No. 23EMS | 88 | 91 | 92 | 89 | 94 | 101 | 105 | 106 |
|---|---|---|---|---|---|---|---|---|
| **INITIAL CHARGE** | | | | | | | | |
| Disulfide Telogen | III | III | III | IV | IV | IV | III | IV |
| Disulfide Wt., gms. | 5.0 | 5.0 | 9.62 | 5.0 | 12.66 | 12.66 | 10.00 | 10.00 |
| Neohexene, gms. | 720 | 720 | 720 | 720 | 720 | 720 | 687.7 | 687.7 |
| DMAB Cat., gms. | 0.491 | 0.491 | 0.491 | 0.491 | 0.491 | 0.491 | (DTBP).1 | (DTBP).1 |
| Ethylene, gms. | 265 | 265 | 262 | 265 | 262 | 262 | 254.3 | 254.3 |
| Mol Ratio, Telogen/Monomers | 0.001 | 0.001 | 0.002 | 0.0008 | 0.002 | 0.002 | .002 | .0016 |
| **REACTION CONDITIONS** | | | | | | | | |
| Temperature, °C | 90 | 90 | 90 | 90 | 90 | 90 | 160 | 160 |
| Pressure, psig. | | | | | | | | |
| Initial (@ R.T.) | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | -- | -- |
| Maximum | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 |
| Drop | 1000 | 1500 | 3000 | 1250 | 1750 | 1000 | 2900 | 2250 |
| Reaction Time, Hrs. | 4.35 | 4.35 | 4.35 | 4.35 | 4.35 | 2.17 | 3.3 | 3.3 |
| **PRODUCTIVITY** | | | | | | | | |
| Yield, gms. | 30 | 37 | 37 | 35 | 46 | 31 | 60 | 37 |
| Conversion, % | 3.05 | 3.76 | 3.77 | 3.55 | 4.68 | 3.16 | 6.4 | 4.0 |
| Rate, %/Hr. | 0.70 | 0.86 | 0.87 | 0.82 | 1.08 | 1.46 | 2.0 | 1.2 |
| **PRODUCT DESCRIPTION** | Colorless Very Hazy Very Viscous Oil | | Colorless Clear Viscous Oil | | 51. Yellow Clear Oil | | Very Hazy Yellow Oil | Deep Yellow Clear Oil |

DMAB = Dimethyl 2,2'-Azobisisobutyrate
DTBP = Di .*tert*-Butyl Peroxide

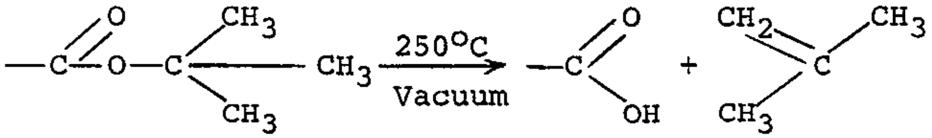
## TABLE XXV

## CHARACTERIZATION OF TELOMERS MADE WITH DISULFIDE TELOGENS

| Run No. 23EMS | 88 | 89 | 91 | 92 | 94 | 101 | 105 | 106 |
|---|---|---|---|---|---|---|---|---|
| Telogen | III | IV | III | III | IV | IV | III | IV |
| Mol. Wt. | 1183 | 1691 | 1355 | 1314 | 2459 | 3235 | 1298 | 2707 |
| Wt. % Sulfur | 2.04 | 2.30 | 2.08 | 4.19 | 1.89 | 0.97 | 2.91 | 1.19 |
| Wt. % Carbon | 80.27 | 81.24 | 81.21 | -- | -- | -- | -- | -- |
| Wt. % Hydrogen | 13.52 | 13.87 | 13.78 | -- | -- | -- | -- | -- |
| Wt. % Oxygen | 4.44 | 2.71 | 2.71 | 3.91 | 1.61 | 0.93 | 3.03 | 1.12 |
| Functionality | | | | | | | | |
| $O_2$ Per Molecule | 1.64 | 1.43 | 1.15 | 1.60 | 1.24 | 0.94 | 1.23 | 0.95 |
| S Per Molecule | .75 | 1.22 | 0.88 | 1.72 | 1.45 | 0.98 | 1.2 | 1.03 |

The product from run 88 was hydrolyzed using KOH/butanol under reflux at atmospheric pressure. The resulting prepolymer contained COOH groups as shown by infrared analysis. The following properties were measured: neutralization equivalent weight, 2214; number average molecular weight in THF, 2027; oxygen content, 1.675%. The carboxyl functionality calculated from Mol. Wt./N.E. was 0.91; calculated from Mol. Wt./$O_2$ Eq. Wt. was 1.06. From the increase in molecular weight it was concluded that product 23 EMS 88 contained some unreacted telogen, which was hydrolyzed and removed during alkaline hydrolysis. Products 91 and 92, made with the same telogen (III), contained unreacted telogen which was verified by comparison with the infrared spectrum of III (dimethyl dithioisobutyrate). It was concluded that III is not active as a transfer agent at 90°C. Run 105 was carried out at 160° which improved the rate of conversion but not the functionality. After alkaline hydrolysis the COOH functionality of 105 was still 1.2.

Runs 89, 94, 101 and 106 were made with telogen IV. Product 89 was chosen for more extensive characterization. Our purpose in using the di-tertiary butyl ester of dithioisobutyric acid as a telogen was to facilitate generation of the COOH end group by mild pyrolysis as shown below:



Pyrolysis of product 89 did not result in formation of COOH as had been expected. Instead, volatile material distilled off which had an infrared spectrum identical with that of telogen IV, with the addition of a weak COOH band. Evidently the telogen was slightly pyrolyzed during distillation. The I.R. Spectrum of the residue from the pyrolysis showed only a trace of acid carbonyl, and the ester carboxyl was weaker than that of the starting material. Subsequent additional pyrolysis did not affect this band intensity. Infrared bands of telogen IV were absent in the spectrum of the residue. Analysis of this pyrolyzed product showed that it had a molecular weight of 3850, and contained 0.42 sulfur atoms per molecule and 0.72 $O_2$ per molecule.

Alkaline hydrolysis of the "pyrolyzed" product gave a material having an N.E. of 11,150, no I.R. ester band and a weak COOH band. If the sulfur functionality previously measured had been on the polymer chain the N.E. after alkaline hydrolysis should have been much smaller. This sulfur must represent residual telogen which was not removed during vacuum pyrolysis, but which was lost during hydrolysis.

These data indicate that sample 89 contained a significant amount of telogen which can be largely removed by vacuum pyrolysis. The ester groups in the product which remained after pyrolysis are not tertiary esters, because of their resistance to pyrolysis. It is concluded that they are derived from the initiator, DMAB.

Samples 94,101 and 106 were not examined in greater detail than described in Table XXV.

Several copolymerization runs were also made with dimethyl dithioglycolate (V) as a transfer agent. The polymerization conditions used are given in Table XXVI and the analytical data are shown in Table XXVII.

The product obtained in run 18 was high in functionality but too low in molecular weight to be of interest as a high energy binder. Some of the molecules were nitrogen terminated from the AIBN initiator used. The products from runs 27, 38 and 68 were higher in molecular weight but were no better than monofunctional. It was concluded that dimethyl dithioglycolate is both a transfer agent and a polymerization retarder. The low functionality indicates that hydrogen transfer is a problem with DMTG. No further work with this telogen is planned.

## TABLE XXVI

### ETHYLENE-NEOHEXENE COPOLYMERIZATIONS WITH DIMETHYL DITHIOGLYCOLATE (DMTG)

| Run No. 24EMS | 18 | 21 | 27 | 38 | 68 |
|---|---|---|---|---|---|
| INITIAL CHARGE | | | | | |
| Solvent | Benzene | | | | Benzene/ t-butanol |
| Gms. Solvent | 14.8 | 14.8 | 14.8 | 14.8 | 16.1 |
| Gms. DMTG | 0.91 | 0.91 | 0.91 | 0.91 | 0.81 |
| Neohexene, gms. | 570 | 570 | 570 | 570 | 568 |
| Ethylene, gms. | 224 | 224 | 210 | 224 | 216 |
| Initiator | AIBN | AIBN | AIBN | AIBN | DTBP |
| Gms., Initiator | 0.1 | 0.1 | 0.2 | 0.4 | 0.2 |
| FED DURING RUN | | | | | |
| Gms., Solvent* | 150 | 150 | 195 | 195 | 145 |
| AIBN, gms. | 0.4 | .4 | 1.8 | 3.6 | 0.5 |
| DMTG, gms. | 8.14 | 8.14 | 8.14 | 8.14 | 9.27 |
| REACTION CONDITIONS | | | | | |
| Temperature, °C | 92 | 60 | 90 | 90 | 140 |
| Pressure, MPSI | | | | | |
| Initial | 2 | 0.4 | 0.3 | 0.1 | 4.2 |
| Final | 15 | 15 | 15 | 15 | 15 |
| Reaction, Time, Hrs. | 3.67 | 5.13 | 3.67 | 3.67 | 2.95 |
| PRODUCTIVITY | | | | | |
| Yield, gms. | 7 | Trace | 12 | 40 | 39 |
| Conv., % | 0.91 | -- | 1.54 | 5.13 | 4.98 |
| Rate, %/Hr. | 0.25 | -- | 0.42 | 1.4 | 1.7 |
| Description | Reddish-Brown Oil | Dis-carded | Clear Oil | Dark Tan Oil | Dark Tan Oil |

* Solvent for feed was 1/1 benzene/t-butanol.

TABLE XXVII

CHARACTERIZATION OF COPOLYMERS MADE WITH DIMETHYLDITHIO-GLYCOLATE

| Run No. 24EMS | 18 | 27 | 38 | 68 |
|---|---|---|---|---|
| Molecular Weight | 514 | 988 | 639 | 939 |
| Wt. % Sulfur | 11.62 | 1.70 | 5.49 | 2.89 |
| Wt. % C | 67.5 | 82.63 | 76.97 | -- |
| Wt. % H | 11.11 | 13.40 | 12.76 | -- |
| Wt. % O | 9.47 | 1.27 | 4.98 | 4.01 |
| Wt. % N | 1.7 | 1.07 | 0.9 | -- |
| Functionality | | | | |
| $O_2$/Molecule | 1.52 | 0.39 | .99 | 1.18 |
| S /Molecule | 1.86 | 0.52 | 1.1 | 0.85 |
| N /Molecule | 0.62 | 0.76 | 0.41 | -- |

# V. TECHNICAL DISCUSSION CONT'D, PART 8

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH BROMINE CONTAINING TELOGENS

### Contents

# PART 8

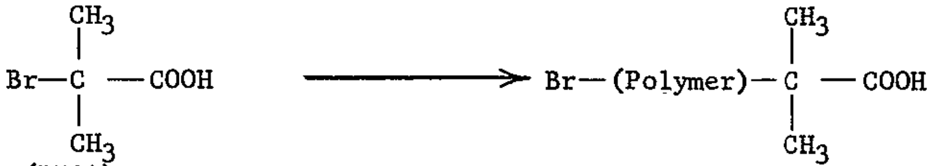
## V. TECHNICAL DISCUSSION, Cont'd

### A. New Telogens and Telomers

In order to circumvent the difficulty we have experienced in converting the terminal groups of the carbon tetrachloride telomer into carboxyl groups, we have conducted a series of experiments using other telogens which lead to more reactive telomer end groups. The telogens tried were: bromotrichloromethane, bromoacetic acid, α-bromoisobutyric acid and tert-butyl α-bromoisobutyrate. Our experiments have shown that all of these telogens are more active than carbon tetrachloride. The bromo-ester was the most active, followed by bromotrichloromethane. Although more active than carbon tetrachloride, the bromo acids were less active than bromotrichloromethane. Based upon our previous experience and published data, we expected the following end groups to result from these telomerizations:

TELOGEN TELOMER

$\mathrm{Br{-}CCl_3} \longrightarrow \mathrm{Br{-}(Polymer){-}CCl_3}$

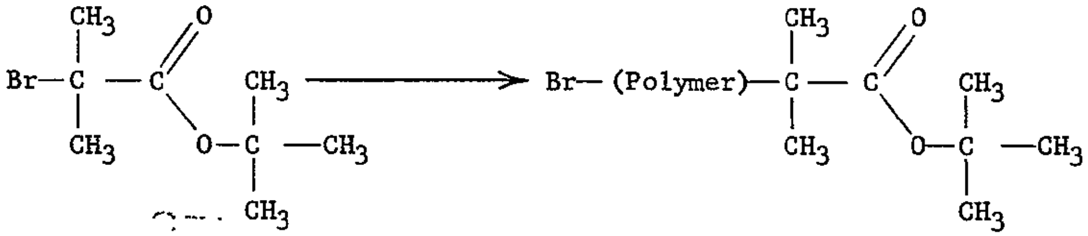


$\mathrm{Br{-}C(CH_3)_2{-}COOH} \longrightarrow \mathrm{Br{-}(Polymer){-}C(CH_3)_2{-}COOH}$

(BIBA)

$\mathrm{Br{-}CH_2{-}COOH} \longrightarrow \mathrm{Br{-}(Polymer){-}CH_2{-}COOH}$

(BAA)

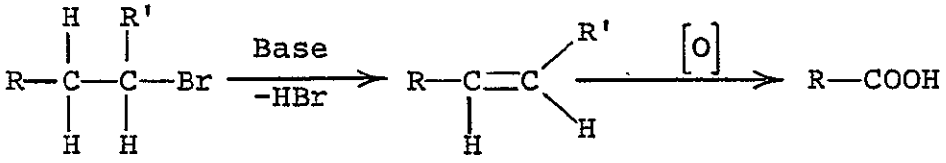


$\mathrm{Br{-}C(CH_3)_2{-}C({=}O){-}O{-}C(CH_3)_3} \longrightarrow \mathrm{Br{-}(Polymer){-}C(CH_3)_2{-}C({=}O){-}O{-}C(CH_3)_3}$

(BBIB)

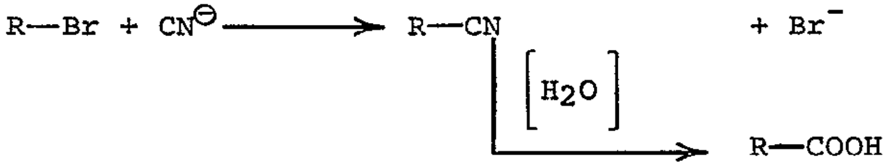
With the probable exception of the telomers from $BrCCl_3$, these products should be easier to convert to the difunctional carboxyl terminated binder materials than any products we have prepared to date. Having one carboxyl per molecule as a starting point, we can now work upon the more reactive bromine group in any of the following ways for example:

1. Elimination, followed by oxidation:



$$R-CH_2-CHR'-Br \xrightarrow[-HBr]{Base} R-CH=CHR' \xrightarrow{[O]} R-COOH$$

2. Displacement with Cyanide, followed by hydrolysis:



$$R-Br + CN^{\ominus} \longrightarrow R-CN + Br^{-}$$

$$R-CN \xrightarrow{[H_2O]} R-COOH$$

3. Displacement with sulfide, leading to coupling:

$$2\,R-Br + S^{\ominus} \qquad R-S-R + 2\,Br^{\ominus}$$

The products from all of the above reactions should contain two carboxyl groups per molecule. Note that reaction 3 leads to a doubling of molecular weight, e.g. a 1000 molecular weight telomer would be converted to a difunctional product, $\overline{M}n$ = 2000.

## B. Preparation of the Telomers

We have made telomerization runs in the stirred autoclave reactor using each of these new telogens and have obtained telomers in all cases. The results of these runs are shown in Table XXVIII. The analytical data are summarized in Table XXIX.

The product from run #62 made with bromoacetic acid telogen has a molecular weight of 934, contains 2.86% oxygen and 4.98% bromine. These data indicate the presence of 0.84 $O_2$ per molecule (the ester end groups) and 0.58 bromine atoms per molecule. A higher percentage of nitrogen (.42%) from the initiator in this product corresponds to about .3 nitrogens per molecule.

The product from run #66 made with t-butyl α-bromoisobutyrate telogen has a molecular weight of 983, contains 3.12% oxygen and 6.86% bromine. These data indicate the presence of 0.95 $O_2$ per molecule (the ester end groups) and 0.84 bromine atoms per molecule.

Especially noteworthy is the functionality obtained to run #24-EMS-72. The product from this run contains 0.96 $O_2$ (ester) groups per molecule and 1.05 bromides per molecule.

Tables XXX and XXXII show the experimental conditions used in fifteen more telomerizations done with the new telogens. The analytical data obtained upon the products from these runs is given in Tables XXXI and XXXIII.

All of these telomerizations were carried out at 90°C in the presence of the same initiator, AIBN.

Methyl α-bromoacetate, MBA, was evaluated as a telogen in telomer runs #24-EMS-132, 133, 135 and 25-EMS-6. The production data for these runs is summarized in Table XXXIV. Run 135 is a repeat of 133, made necessary because a purging operation, which occurred during the preparation for run 133, caused a loss of some of the neohexene charged to the reactor. For this reason the product from run 133 had a higher ethylene content than planned. This product is a grease, showing evidence of polyethylene crystallinity.

Reaction time and telogen/monomer molar ratio were varied in these runs. The average level of initiator (AIBN) was maintained at the same value through all the runs. The effect of reaction time is shown by the increasing yields: 19, 41 and 90 grams for 3.42, 6.25 and 12.25 hours respectively.

Table XXXV summarizes the results obtained upon analysis of these products. As expected, the molecular weights are higher for the runs at lower telogen/monomer ratios, however, the functionalities are rather low.

## TABLE XXVIII

### ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH HALOGEN CONTAINING TELOGENS

| Run No. 24EMS<br>Date 1967 | 48<br>4/3 | 49<br>4/4 | 62<br>4/13 | 66<br>4/18 | 69<br>4/21 | 70<br>4/24 | 71<br>4/25 | 72<br>4/26 | 73<br>4/27 | 74<br>4/28 |
|---|---|---|---|---|---|---|---|---|---|---|
| **INITIAL CHARGE** | | | | | | | | | | |
| Transfer Agent | $CCl_4$ | $BrCCl_3$ | BAA | BIBB | BIBA | $CCl_4$ | $BrCCl_3$ | BBIB | BIBA | BIBA |
| " " , gms. | 0.79 | 0.79 | 0.88 | 1.15 | 0.86 | 1.59 | 2.04 | 2.3 | 1.72 | 0.86 |
| Solvent (Ø=benzene) | Ø | Ø | Ø | Ø | Ø | Ø | Ø/tBuOH | Ø/tBuOH | Ø/tBuOH | Ø/tBuOH |
| " , gms. | 7.2 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.2 | 7.2 | 7.2 | 7.3 |
| Initiator | AIBN | AIBN | AIBN | AIBN | AIBN | AIBN | AIBN | AIBN | AIBN | AIBN |
| " , gms. | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 |
| Neohexene, gms. | 689 | 689 | 689 | 689 | 689 | 689 | 685 | 683 | 683 | 689 |
| Ethylene, gms. | 260 | 262 | 264 | 258 | 263 | 259 | 256 | 259 | 253 | 255 |
| **FED DURING REACTION** | | | | | | | | | | |
| Transfer Agent, gms. | 7.14 | 7.13 | 7.9 | 10.34 | 7.74 | 14.3 | 18.39 | 20.69 | 15.5 | 7.74 |
| Solvent, gms. | 65.4 | 65.4 | 65.4 | 65.4 | 65.4 | 65.4 | 65.9 | 64.9 | 64.9 | 65.4 |
| Catalyst, gms. | 0.66 | 0.66 | 0.66 | 0.60 | 0.60 | 0.60 | 0.59 | 0.59 | 0.59 | 0.60 |
| **REACTION CONDITIONS** | | | | | | | | | | |
| Temperature, °C | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Pressure, mpsi | | | | | | | | | | |
| Initial | 9.0 | 9.0 | 4.5 | 9.8 | 10.25 | 10.0 | 8.2 | 8.5 | 8.0 | 9.5 |
| Final | 13.7 | 15.0 | 17.5 | 14.8 | 16.25 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| Time Hours | 3.67 | 3.72 | 3.04 | 2.58 | 3.57 | 3.60 | 3.58 | 3.67 | 3.58 | 3.58 |
| **PRODUCTIVITY** | | | | | | | | | | |
| Yield, gms. | 47 | 34 | 15 | 31 | 22 | 57 | 40 | 36 | 22 | 18 |
| Conversion, % | 4.96 | 3.57 | 1.58 | 3.30 | 2.6 | 6.0 | 4.25 | 3.82 | 2.35 | 1.91 |
| Rate, %/Hr. | 1.35 | 0.96 | 0.52 | 1.30 | 0.72 | 1.7 | 1.2 | 1.04 | 0.66 | 0.53 |
| **PHYSICAL PROPERTIES** | | | | | | | | | | |
| Brookfield Vis., cps | $14,930^{21}$ | $12,000^{23}$ | -- | $9.710^{22}$ | $7,000^{21}$ | $3,023^{22}$ | $1,350^{22}$ | $1,330^{21}$ | $3,400^{21}$ | -- |
| Sp. Viscosity @ 80°C | 0.023 | 0.028 | 0.028 | 0.024 | 0.028 | 0.019 | 0.013 | 0.010 | 0.015 | 0.020 |
| Freezing Pt., °C | -28 | -35 | -32 | -36 | -32 | -42 | -45 | -48 | -45 | -35 |
| Description | Dk. Tan Oil | Dk. Tan Oil | Dk. Brown Oil | Dk. Tan Oil | Brown Oil | Dk. Brown Oil | Dk. Brown Oil | Dk. Tan Oil | Dk. Brown Oil | Brown Oil |

## TABLE XXIX

### CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| Run No. 24EMS | 48 | 49 | 62 | 66 | 69 | 71 | 72 | 73 | 74 |
|---|---|---|---|---|---|---|---|---|---|
| Telogen . . . . . . . . . . . . . . | $CCl_4$ | $BrCCl_4$ | BAA | BBIB | BIBA | $BrCCl_3$ | BBIB | BIBA | BIBA |
| Mol. Wt. . . . . . . . . . . . . . . | 807 | 995 | 934 | 983 | 357 | 523 | 611 | 485 | 403 |
| Elemental Composition, Wt. % . . . . | | | | | | | | | |
| Oxygen . . . . . . . . . . . . . . | -- | -- | 2.86 | 3.12 | 6.83 | -- | 5.0 | 8.73 | 7.06 |
| Chlorine . . . . . . . . . . . . . | 12.83 | 9.04 | -- | -- | -- | 17.86 | -- | -- | -- |
| Bromine . . . . . . . . . . . . . | -- | 6.10 | 4.98 | 6.86 | 13.41 | 12.53 | 13.70 | 19.09 | 17.00 |
| Nitrogen . . . . . . . . . . . . . | 0 | 0 | 0.42 | 0.0 | 0.25 | 0.29 | 0.26 | 0.41 | 0.4 |
| Neutralization Equivalent. . . . . | -- | -- | -- | | 538 | -- | -- | 386 | 480 |
| Functionality, groups per molecule | | | | | | | | | |
| Oxygen (as $O_2$) . . . . . . . . . | -- | -- | 0.84 | .95 | 0.76 | -- | 0.96 | 1.32 | 0.89 |
| Chlorine (as Cl or $CCl_3$) . . . . | 1.46 | 0.85 | -- | -- | -- | 0.88 | -- | -- | -- |
| Bromine (as Br). . . . . . . . . . | -- | 0.76 | 0.58 | .84 | 0.60 | .82 | 1.05 | 1.16 | 0.86 |
| Nitrogen (as N). . . . . . . . . . | -- | -- | 0.28 | .00 | 0.06 | -- | 0.11 | 0.14 | 0.12 |
| COOH . . . . . . . . . . . . . . . | -- | -- | -- | -- | 0.66 | -- | -- | 1.26 | 0.84 |

The nitrogen contents (from AIBN) show that a substantial amount of initiation of polymer chains, ~25%, is accomplished by the initiator itself rather than being largely due to the radical derived from the telogen by chain transfer. This, together with the molecular weights obtained, show that MBA is a sluggish chain transfer agent compared to BIBA and BBIB. Use of a higher concentration of MBA and a lower concentration of initiator could alleviate this problem.

The lower bromine content of run 135 is due to dehydrobromination occurring during recovery of the telomer. The infrared spectrum of this product shows a strong c = c absorption at 10.35μ). Since COOH is absent, this is most consistent with the presence of α,β-unsaturated ester end groups in this telomer. These could only be derived from an α-bromoester end group resulting from initiation by an α-bromoester radical, presumably formed by hydrogen atom abstraction rather than bromine atom abstraction from MBA. This would indicate that telomers from MBA have little utility as precursors for difunctional carboxy terminated binders. No further telomerizations with MBA are planned, and we plan to do no further reactions upon the products already prepared.

Telomerization run number 25-EMS-22 was made using telogen BBIB. This run is a continuation of the series 24-EMS-90, 93 and 122 reported last quarter. The production data are given in Table XXXVI and the analytical data in Table XXXVII. In addition to this data, the oxygen content was 2.54%. Combined with the molecular weight of 765, this implies an $O_2$ functionality of 0.61.

In order to obtain the best low temperature properties possible with the ethylene/neohexene system, it is advantageous to incorporate the maximum amount of ethylene possible. This is because of the extremely low glass transition temperature (-90°C) of polyethylene. However, if the ethylene content is allowed to become high enough, polyethylene crystallites can form and the product will be a grease or wax rather than a liquid.

Telomerization runs 25-EMS-30, 31 and 32 were made to prepare samples of lower neohexene content. Charges containing 67, 57 and 47% by weight of neohexene, respectively, were used in these runs which are further described in Tables XXXVI and XXXVII.

None of the three products was obtained as a pourable liquid. Two were opaque greases and the third was a mixture of grease and wax. All showed polyethylene crystallinity absorption in the infrared spectrum at 13.7μ.

## TABLE XXX

### ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH HALOGEN CONTAINING TELOGENS

| Run No. 24EMS | 94 | 95 | 116 | 75 | 86 | 87 | 113 | 114 |
|---|---|---|---|---|---|---|---|---|
| <u>INITIAL CHARGE</u> | | | | | | | | |
| Telogen | $CCl_4$ | $BrCCl_3$ | $BrCCl_3$ | BAA | BAA | BAA | BAA | BAA |
| " , gms. | 1.57 | 2.24 | 2.24 | 1.43 | 1.43 | 1.43 | 1.43 | → |
| Solvent, 1:1 | | | | | | | | |
| Benzene: Butanol, gms. | 14.3 | 14.3 | 14.3 | 7.2 | 13.4 | 13.4 | 13.4 | → |
| Initiator, gms. | .13 | .13 | .26 | .066 | .065 | .13 | .13 | .26 |
| Neohexene, gms. | 679 | 680 | → | 684 | 680 | 680 | → | → |
| Ethylene, gms. | 253 | 256 | 254 | 255 | 254 | 255 | 255 | 256 |
| <u>FED. DURING REACTION</u> | | | | | | | | |
| Telogen, gms. | 14.2 | 20.2 | 20.2 | 12.9 | 12.9 | 12.9 | 12.9 | 12.9 |
| Solvent, gms. | 129 | 129 | 137 | 64 | 120 | 120 | 120 | 120 |
| Initiator, gms. | 1.170 | 1.170 | 2.34 | .59 | .587 | 1.170 | 1.17 | 2.34 |
| <u>REACTION CONDITIONS</u> | | | | | | | | |
| Temperature, °C | ← | | | 90 | | | | → |
| Pressure, mpsi | | | | | | | | |
| Initial | 8.30 | 9.00 | 8.00 | 9.00 | 8.40 | 8.25 | 7.75 | 8.10 |
| Final | 15.2 | 16.6 | 15.0 | 15.0 | 17.9 | 16.9 | 13.5 | 15.0 |
| Time, Hrs. | 6.25 | 6.25 | 12.7 | 3.58 | 6.25 | 6.25 | 6.25 | 12.5 |
| <u>PRODUCTIVITY</u> | | | | | | | | |
| Yield, gms. | 87 | 69 | 83 | 22 | 17 | 22 | 38 | 56 |
| Conversion, % | 9.32 | 6.67 | 8.8 | 235 | 1.82 | 2.32 | 3.00 | 5.98 |
| Conv. Rate, %/Hr. | 1.50 | 1.07 | .70 | .66 | .29 | .37 | .48 | .77 |

## TABLE XXXI

### CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| Run No. 24EMS | 94 | 95 | 116 | 75 | 86 | 87 | 113 | 114 |
|---|---|---|---|---|---|---|---|---|
| PHYSICAL PROPERTIES | | | | | | | | |
| Brookfield Visc., cps | 4440 | 3300 | 20,600 | -- | 10,000 | -- | 79,100 | 103,000 |
| Specific Visc., @ 80°C | .018 | .013 | .031 | .023 | .024 | .025 | .032 | .049 |
| Vitrification Temp., °C | 025 | -39 | -31 | -- | -30 | -21 | -20 | -26 |
| $T_G$, °C | -- | -- | -- | -- | -- | -30 | -- | -30 |
| Description | ← Tan Oil → | | | Tan Grease | Tan Heavy Oil → | | Tan Oil → | |
| ANALYTICAL DATA | | | | | | | | |
| Molecular Wt. | 808* | 612* | 1070* | 301* | 853** | 920* | 1090* | 1288** |
| Oxygen, Wt. % | .32 | .47 | -- | 9.34 | 3.92 | 2.21 | 1.61 | 1.35 |
| Chlorine, Wt. % | 12.79 | 14.77 | 6.75 | -- | -- | -- | -- | -- |
| Bromine, Wt. % | -- | 10.2 | 5.11 | 22.6 | 5.0 | 4.84 | 3.67 | 1.76 |
| Nitrogen, Wt. % | .15 | .16 | .25 | .46 | .37 | .47 | .38 | .34 |
| Neutralization Equivalent | -- | -- | -- | 359 | 1500 | 1600 | 1590 | 2170 |
| FUNCTIONALITY | | | | | | | | |
| Oxygen ($O_2$) | .08 | .09 | -- | .90 | 1.05 | .635 | .55 | .54 |
| Chlorine (Cl or $CCl_3$) | 1.46 | .85 | .68 | -- | -- | -- | -- | -- |
| Bromine (Br) | -- | .81 | .69 | .85 | .53 | .56 | .50 | .28 |
| Nitrogen (N) | .09 | .07 | .19 | .07 | .23 | .31 | .30 | .31 |
| Carboxyl (COOH) | -- | -- | -- | .84 | .57 | .58 | .69 | .59 |

* Solvent used was Benzene.
** Solvent used was THF.

## TABLE XXXII

### ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH HALOGEN CONTAINING TELOGENS

| Run No. 24EMS | 92 | 96 | 112 | 115 | 90 | 93 | 122 |
|---|---|---|---|---|---|---|---|
| INITIAL CHARGE | | | | | | | |
| Telogen | BIBA | BIBA | BIBA | BIBA | BBIB | BBIB | BBIB |
| Telogen, gms. | 1.72 | 1.72 | → | → | 2.30 | 2.30 | 2.30 |
| Solvent, 1:1 | | | | | | | |
| Benzene: t-Butanol, gms. | 14.3 | 14.3 | → | → | 13.5 | 13.5 | 13.5 |
| Initiator, gms. | .13 | .13 | .13 | .26 | .13 | .13 | .26 |
| Neohexene, gms. | 680 | 680 | → | → | 679 | 679 | 679 |
| Ethylene, gms. | 254 | 258 | 253 | 254 | 256 | 251 | 256 |
| FED. DURING REACTION | | | | | | | |
| Telogen, gms. | 15.5 | 15.5 | 15.5 | 15.5 | 20.7 | 20.7 | 20.7 |
| Solvent, gms. | 129 | 129 | 129 | 129 | 131 | 131 | 131 |
| Initiator, gms. | 1.170 | 1.170 | 1.17 | 2.34 | .536 | 1.170 | 2.34 |
| REACTION CONDITIONS | | | | | | | |
| Temperature, °C | ← | | | 90 | | | → |
| Pressure, mpsi | | | | | | | |
| Initial | 8.00 | 8.50 | 7.75 | 7.75 | 10.00 | 8.20 | 8.00 |
| Final | 11.4 | 16.9 | 13.5 | 15.4 | 18.6 | 16.0 | 15.0 |
| Time, Hrs. | 6.25 | 6.25 | 6.25 | 12.5 | 6.25 | 6.25 | 12.6 |
| PRODUCTIVITY | | | | | | | |
| Yield, gms. | 37 | 31 | 42 | 62 | 35 | 48 | 98 |
| Conversion, % | 3.96 | 3.30 | 4.50 | 6.64 | 3.75 | 5.17 | 10.5 |
| Conv. Rate, %/Hr. | .63 | .53 | .72 | .53 | .60 | .83 | .84 |

## TABLE XXXIII

## CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| Run No. 24EMS | 92 | 96 | 112 | 115 | 90 | 93 | 122 |
|---|---|---|---|---|---|---|---|
| PHYSICAL PROPERTIES | | | | | | | |
| Brookfield Visc., cps | 4570 | 13,500 | 91,000 | 10,000 | 4000 | 4540 | 29,700 |
| Specific Visc., @ 80°C | .021 | .028 | .04 | .035 | .017 | .022 | .029 |
| Vitrification Temp., °C | -33 | -28 | -23 | -25 | -42 | -38 | -25 |
| $T_g$, °C | -40 | -37.5 | -30 | -- | -47 | -- | -- |
| Description | | | | | Tan Oil | | Dark Brown Heavy Oil |
| ANALYTICAL DATA | | | | | | | |
| Molecular Wt. | 484** | 527** | 1124** | 729** | 709* | 761* | 1539* |
| Oxygen, Wt. % | 5.95 | 5.41 | 2.20 | 3.44 | 3.96 | 3.77 | 1.98 |
| Chlorine, Wt. % | -- | -- | -- | -- | -- | -- | -- |
| Bromine, Wt. % | 12.79 | 13.74 | 4.30 | 7.62 | 9.00 | 8.16 | 3.78 |
| Nitrogen, Wt. % | .26 | .23 | .31 | .32 | .10 | .21 | .20 |
| Neutralization Equivalent | 559 | 620 | 1590 | 923 | -- | -- | -- |
| FUNCTIONALITY | | | | | | | |
| Oxygen ($O_2$) | .90 | .89 | .77 | .78 | .88 | .90 | .95 |
| Chlorine (Cl or $CCl_3$) | -- | -- | -- | -- | -- | -- | -- |
| Bromine (Br) | .68 | .91 | .61 | .70 | .80 | .78 | .72 |
| Nitrogen (N) | .09 | .09 | .25 | .17 | .08 | .11 | .22 |
| Carboxyl (COOH) | .87 | .85 | .71 | .79 | -- | -- | -- |

* Solvent used was Benzene.
** Solvent used was THF.

## TABLE XXXIV

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH MBA

| Run No. 24EMS- | 132 | 133 | 135 | 25-EMS-6 |
|---|---|---|---|---|
| INITIAL CHARGE | | | | |
| Telogen | MBA | MBA | MBA | MBA |
| Telogen, gms. | 1.58 | 1.58 | 1.58 | 1.58 |
| Solvent, 1:1 | | | | |
| Benzene: Butanol/, gms | 14.4 | 14.3 | 14.3 | 14.3 |
| Initiator | AIBN | AIBN | AIBN | AIBN |
| Initiator, gms. | .065 | .13 | .13 | .26 |
| Neohexene, gms. | 679.6 | 679.6 | 679.6 | 679.6 |
| Ethylene, gms. | 251 | 257 | 254 | 254 |
| FED. DURING REACTION | | | | |
| Telogen, gms. | 14.2 | 14.2 | 14.2 | 14.2 |
| Solvent, gms. | 129.8 | 138.0 | 128.0 | 128.5 |
| Initiator, gms. | .59 | 1.17 | 1.17 | 2.34 |
| REACTION CONDITIONS | | | | |
| Temperature, °C | 90 | 90 | 90 | 90 |
| Pressure, mpsi | | | | |
| Initial | 6.00 | 3.25 | 9.00 | 10.50 |
| Final | 15.00 | 8.00 | 14.30 | 17.25 |
| Time, Hrs. | 3.42 | 6.25 | 6.25 | 12.25 |
| PRODUCTIVITY | | | | |
| Yield, gms. | 19.0 | 39 | 41 | 90 |
| Conversion, % | 2.0 | 4.20 | 4.40 | 9.65 |
| Conversion Rate, % per Hr. | .60 | .67 | .70 | .77 |

## TABLE XXXV

### CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| Run No. 24EMS- | 132 | 133 | 135 | 25-EMS-6 |
|---|---|---|---|---|
| <u>PHYSICAL PROPERTIES</u> | | | | |
| Brookfield Visc., cps | -- | -- | 36,200 | 39,800 |
| Specific Visc., @ 80°C | .025 | .035 | .032 | .031 |
| Description | Tan Oil | Tan Grease | Dark Tan Oil | Light Tan Oil |
| <u>ANALYTICAL DATA</u> | | | | |
| Molecular Wt. (Benzene) | 1207 | 1184 | 1373 | 1330 |
| Oxygen, Wt. % | 1.65 | 1.88 | 1.39 | 1.32 |
| Chlorine, Wt. % | -- | -- | -- | -- |
| Bromine, Wt. % | 3.84 | 3.99 | 1.46 | 3.43 |
| Nitrogen, Wt. % | .27 | .34 | .22 | .26 |
| <u>FUNCTIONALITY</u> | | | | |
| Oxygen ($O_2$) | .62 | .68 | .60 | .55 |
| Chlorine (Cl or $CCl_3$) | -- | -- | -- | -- |
| Bromine (Br) | .58 | .59 | .25 | .57 |
| Nitrogen (N) | .23 | .25 | .22 | .25 |

These results imply that the products we have been preparing at 71% by weight of neohexene in the charge are already near the point where crystalline polyethylene can begin to form. Thus no improvement in the low temperature properties can be made by lowering the neohexene content, unless a crystalline fraction is not objectionable.

## C. Telomer Preparation - Composite Batches I and II

Because of the need for larger amounts of ethylene-neohexene telomers, we have run two series of batch telomerizations under similar reaction conditions. A number of samples were needed which could be combined to give a composite batch of uniform properties.

The first telomer series was made using BIBA as telogen. Thirteen runs in all were made: 25-EMS-38 to 49 and 52. The production data for these runs is given in Tables XXXVI and XXXVIII. The main obstacle to obtaining completely reproducible runs is the difficulty of charging exactly the same weight of ethylene to successive runs. This affects the maximum pressure obtained during the run, besides slightly affecting the comonomer composition. The amounts of ethylene charged varied between 282 and 295 grams and the pressure varied between 13,400 and 17,000 psi maximum.

The analytical data for these runs is given in Tables XXXVII and XXXIX. On the basis of similarity of functionality runs 39 and 41 to 49 were selected for blending to give Composite Batch I:

| | | Functionality | | | |
|---|---|---|---|---|---|
| Run 25-EMS | $\overline{M}n$ | Br | COOH | Total | Weight In Blend, gms. |
| 39 | 417 | .90 | .86 | 1.76 | 26.40 |
| 41 | 420 | .91 | .84 | 1.75 | 26.11 |
| 42 | 452 | .94 | .90 | 1.84 | 26.76 |
| 43 | 457 | .91 | .89 | 1.80 | 26.89 |
| 44 | 432 | .90 | .88 | 1.78 | 24.06 |
| 45 | 456 | .92 | .88 | 1.80 | 25.42 |
| 46 | 450 | .89 | .94 | 1.83 | 24.71 |
| 47 | 456 | .90 | .88 | 1.78 | 26.15 |
| 48 | 410 | .94 | .82 | 1.76 | 25.02 |
| 49 | 436 | .88 | .92 | 1.80 | 22.47 |

A total of 254 grams was obtained of a material with an $\overline{M}n$ (calculated) of 438 and a total functionality of 1.8.

The second telomer series was made using BBIB as telogen. Ten runs were made in all: 25EMS69 to 78. The production data are summarized in Table XL. Again, reproducibility of amount of ethylene charged was the main problem encountered.

## TABLE XXXVI

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH BBIB AND BIBA

| RUN # | 22 | 30 | 31 | 32 | 38 | 39 | 40 | 41 |
|---|---|---|---|---|---|---|---|---|
| **INITIAL CHARGE** | | | | | | | | |
| Telogen | BBIB | BIBA → | | | | | | |
| Telogen, gms. | 3.04 | 1.97 | 2.11 | 2.24 | 1.7 | 1.7 | 1.8 | 1.8 |
| Solvent, 1:1 Benzene:Butanol,gms. | | | | | | | | |
| Initiator | AIBN → | | | | | | | |
| Initiator, gms. | .26 | .13 | .12 | .12 | .1 | | | |
| Neohexene, gms. | 679 | 611 | 498 | 393.6 | 628 | 628 | 655 | 655 |
| Ethylene, gms. | 254 | 296 | 376 | 440 | 274 | 269 | 287 | 287 |
| **FED DURING REACTION** | | | | | | | | |
| Telogen, gms. | 27.4 | 17.7 | 19.0 | 20.1 | 15.4 | 15.4 | 16.1 | 16.1 |
| Solvent, gms. | 131 | 126 | 120 | 116 | 100 | | | |
| Initiator, gms. | 2.34 | 1.14 | 1.09 | 1.05 | .9 | | | |
| **REACTION CONDITIONS** | | | | | | | | |
| Temperature, °C | 90 → | | | | | | | |
| Pressure, mpsi | | | | | | | | |
| Initial | 9.65 | 8.00 | 7.80 | 8.30 | 4.90 | 5.75 | 8.75 | 7.40 |
| Final | 17.70 | 15.00 | 15.00 | 15.00 | 15.00 | 11.10 | 14.80 | 13.35 |
| Time, hrs. | 12.5 | 6.50 | 6.58 | 6.53 | 3.42 | 3.08 | 3.08 | 3.08 |
| **PRODUCTIVITY** | | | | Part I, Part II | | | | |
| Yield, gms. | 89 | 38 | 43 | 17 , 57 | 30 | 31 | 30 | 30 |
| Conversion, % | 9.6 | 4.2 | 4.9 | 8.9 | 3.3 | 3.5 | 3.2 | 3.2 |
| Conv. Rate, % per hr. | .77 | .65 | .75 | 1.36 | .97 | 1.12 | 1.04 | 1.04 |

## TABLE XXXVII

## CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| RUN # 25-EMS- | 22 | 30 | 31 | 32-I | 32-II | 38 | 39 | 40 | 41 |
|---|---|---|---|---|---|---|---|---|---|
| **PHYSICAL PROPERTIES** | | | | | | | | | |
| Brookfield Visc., Cps | 2,840 | 21,200 | 29,000 | -- | -- | 13,300 | 3,600 | 8,600 | 8,100 |
| Specific Visc., @ 80°C | .015 | .023 | .025 | .057 | .031 | .018 | .010 | .014 | .017 |
| Description | tan oil | tan oily grease | tan oily grease | lt. tan wax | tan grease | tan oil | → | → | → |
| **ANALYTICAL DATA** | | | | | | | | | |
| Molecular Wt.* | 767 | 526 | 573 | 1,403 | 671 | 415 | 417 | 425 | 420 |
| Bromine, Wt. % | 7.36 | 13.51 | 12.76 | 6.36 | 11.38 | 17.27 | 17.02 | 19.96 | 17.12 |
| Nitrogen, Wt. % | -- | .20 | .17 | .12 | .16 | -- | -- | -- | -- |
| Neutralization Equiv. | -- | 658 | 666 | 1350 | 838 | 514 | 484 | 496 | 497 |
| **FUNCTIONALITY** | | | | | | | | | |
| Bromine (Br) | .71 | .89 | .92 | 1.12 | .96 | .90 | .89 | 1.06 | .90 |
| Nitrogen (N) | -- | .08 | .07 | .12 | .08 | -- | -- | -- | -- |
| Carboxyl (COOH) | -- | .80 | .86 | 1.04 | .80 | .81 | .86 | .86 | .84 |

* Solvent used was Benzene in Run 22, THF in all others.

## TABLE XXXVIII

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH BIBA

| RUN # 25-EMS | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 52 |
|---|---|---|---|---|---|---|---|---|---|
| **INITIAL CHARGE** | | | | | | | | | |
| Telogen | BIBA | → | → | → | → | → | → | → | → |
| Telogen, gms. | 1.8 | → | → | → | → | → | → | → | 1.6 |
| Solvent, 1:1 | | | | | | | | | |
| Benzene:Butanol,gms. | 11.0 | → | → | → | → | → | → | → | 11.8 |
| Initiator | AIBN | → | → | → | → | → | → | → | → |
| Initiator, gms. | .10 | → | → | → | → | → | → | → | 1.6 |
| Neohexene, gms. | 655 | → | → | → | → | → | → | → | 558 |
| Ethylene, gms. | 291 | 282 | 282 | 292 | 290 | 291 | 295 | 293 | 207 |
| **FED DURING REACTION** | | | | | | | | | |
| Telogen, gms. | 16.1 | → | → | → | → | → | → | → | 13.1 |
| Solvent, gms. | 99.9 | → | → | → | → | → | → | → | 106 |
| Initiator, gms. | 0.9 | → | → | → | → | → | → | → | 0.96 |
| **REACTION CONDITIONS** | | | | | | | | | |
| Temperature, °C | 90 | → | → | → | → | → | → | → | → |
| Pressure, mpsi | | | | | | | | | |
| Initial | 9.00 | 7.50 | 8.75 | 8.80 | 9.30 | 9.25 | 9.75 | 8.90 | 1.25 |
| Final | 15.35 | 13.40 | 15.50 | 16.30 | 16.20 | 16.00 | 17.00 | 15.00 | 2.50 |
| Time, hrs. | 3.08 | → | → | → | → | → | → | → | 6.08 |
| **PRODUCTIVITY** | | | | | | | | | |
| Yield, gms. | 32 | 33 | 28 | 30 | 29 | 32 | 30 | 28 | 20 |
| Conversion, % | 3.38 | 3.52 | 2.99 | 3.17 | 3.07 | 3.38 | 3.16 | 2.96 | 2.62 |
| Conv. Rate,% per hr. | 1.10 | 1.14 | .97 | 1.03 | 1.00 | 1.10 | 1.03 | .96 | .85 |

## TABLE XXXIX

## CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| RUN # | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 52 |
|---|---|---|---|---|---|---|---|---|---|
| **PHYSICAL PROPERTIES** | | | | | | | | | |
| Brookfield Visc., Cps | 16,600 | 12,350 | 11,900 | 9,200 | 15,400 | 10,400 | 14,300 | 10,900 | -- |
| Specific Visc., @ 80°C | .015 | .015 | .010 | .011 | .012 | .012 | .008 | .009 | .006 |
| Description | tan oil | light tan oil | tan oil → | | | | | | |
| **ANALYTICAL DATA** | | | | | | | | | |
| Molecular Wt. (THF) | 452 | 457 | 432 | 456 | 450 | 456 | 410 | 436 | 340 |
| Bromine, Wt. % | 16.49 | 15.7 | 16.41 | 15.91 | 15.69 | 15.56 | 18.09 | 15.91 | 19.84 |
| Neutralization Equivalent | 504 | 518 | 493 | 520 | 477 | 517 | 499 | 475 | 350 |
| **FUNCTIONALITY** | | | | | | | | | |
| Bromine (Br) | .93 | .90 | .89 | .91 | .88 | .89 | .94 | .87 | .84 |
| Carboxyl (COOH) | .90 | .89 | .88 | .88 | .94 | .88 | .84 | .92 | .97 |

## TABLE XL

## ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH BBIB

| RUN # | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 |
|---|---|---|---|---|---|---|---|---|---|---|
| **INITIAL CHARGE** | | | | | | | | | | |
| BBIB, gms. | 1.2 | → | → | → | → | → | → | → | → | → |
| Benzene, gms. | 7.3 | → | → | → | → | → | → | → | → | → |
| DMAB, gms. | .093 | → | → | → | → | → | → | → | → | → |
| Neohexene, gms. | 689 | → | → | → | → | → | → | → | → | → |
| Ethylene, gms. | 256 | 259 | 257 | 260 | 258 | 259 | 257 | 255 | 263 | 255 |
| **FED DURING REACTION** | | | | | | | | | | |
| Telogen, gms. | 10.34 | → | → | → | → | → | → | → | → | → |
| Solvent, gms.* | 63.0 | → | → | → | → | → | → | → | → | → |
| Initiator, gms. | .835 | → | → | → | → | → | → | → | → | → |
| **REACTION CONDITIONS** | | | | | | | | | | |
| Temperature, °C | 90 | → | → | → | → | → | → | → | → | → |
| Pressure, mpsi | | | | | | | | | | |
| Initial | 9.00 | 9.50 | 11.75 | 9.00 | 9.75 | 10.0 | 10.0 | 9.10 | 10.90 | 9.90 |
| Maximum | 13.50 | 13.75 | 16.50 | 13.50 | 14.90 | 14.50 | 15.00 | 12.60 | 15.35 | 14.00 |
| Time, hrs. | 3.08 | → | → | → | → | → | → | → | → | → |
| **PRODUCTIVITY** | | | | | | | | | | |
| Yield, gms. | 25 | 33 | 32 | 28 | 30 | 30 | 31 | 26 | 31 | 26 |
| Conversion, % | 2.65 | 3.48 | 3.38 | 2.95 | 3.16 | 3.16 | 3.28 | 2.76 | 3.28 | 2.76 |
| Conv.Rate,% per hr. | .86 | 1.13 | 1.10 | .96 | 1.03 | 1.03 | 1.07 | .90 | 1.07 | .90 |

*1:1 Benzene/t-Butanol

The analytical data are summarized in Table XLI. The samples in this series have a higher molecular weight, but a lower functionality than the samples in the first series made with BIBA. All the samples except #71 were blended to give Composite Batch II:

| | | Functionality | | | |
|---|---|---|---|---|---|
| Run 25-EMS | $\overline{M}n$ | $O_2$ | Br | Total | Weight In Blend, gms. |
| 69 | 885 | 1.34 | .73 | 2.07 | 22.35 |
| 70 | 868 | 1.20 | .58 | 1.78 | 23.49 |
| 72 | 868 | 1.13 | .74 | 1.87 | 23.23 |
| 73 | 748 | 1.30 | .67 | 1.97 | 24.75 |
| 74 | 780 | .65 | .64 | 1.29 | 13.07 |
| 75 | 920 | .93 | .84 | 1.77 | 23.86 |
| 76 | 764 | .67 | .62 | 1.29 | 22.47 |
| 77 | 852 | .71 | .72 | 1.43 | 24.61 |
| 78 | 757 | .51 | .71 | 1.22 | 21.84 |

A total of 200 grams was obtained of a material having an $\overline{M}n$ (calculated) of 825 and a total functionality of 1.65.

### D. Methyl α-Bromoisobutyrate Telogen

Two small batch telomerizations were run to evaluate a new telogen, methyl α-bromoisobutyrate. This new telogen was prepared by simple Fischer esterification of α-bromoisobutyric acid, and is an alternative to the t-butyl ester previously used. The first run was an ethylene/propylene telomerization. The production data are summarized in Table XLII.

The data for these runs clearly demonstrate the effectiveness of methyl α-bromoisobutyrate (MBIB) as a telogen. The functionality of 0.996 Br per molecule is the highest yet obtained for an ω-bromoester telomer of ethylene and neohexene, and similarly .78 Br per molecule was higher than the bromine functionality of any previously prepared telomers of ethylene with propylene.

## TABLE XLI

## CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| RUN # 25-EMS- | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 |
|---|---|---|---|---|---|---|---|---|---|---|
| **PHYSICAL PROPERTIES** | | | | | | | | | | |
| Brookfield Visc., Cps | 4,800 | 10,350 | 9,000 | 4,700 | 3,700 | 4.740 | 4.470 | 2,640 | 5,880 | 2,400 |
| Specific Visc., @ 80°C | .018 | .021 | .015 | .009 | .012 | .014 | .013 | .009 | .018 | .010 |
| Description | light yellow oil | yellow oil → | | | | | | | | |
| **ANALYTICAL DATA** | | | | | | | | | | |
| Molecular Wt. (in benzene) | 885 | 868 | 1,095 | 868 | 748 | 780 | 920 | 764 | 852 | 757 |
| Carbon, wt. % | 76.02 | 77.18 | 77.44 | 76.07 | 75.00 | 77.25 | 76.11 | 77.57 | 78.61 | 77.29 |
| Hydrogen, wt. % | 12.50 | 13.05 | 13.05 | 12.97 | 12.30 | 13.51 | 13.34 | 13.14 | 12.99 | 13.04 |
| Bromine, wt. % | 6 62 | 5.33 | 5.62 | 6.81 | 7.15 | 6.58 | 7.33 | 6.48 | 5.72 | 7.52 |
| Oxygen, wt. % | 4.86 | 4.41 | 3.89 | 4.15 | 5.55 | 2.66 | 3.22 | 2.81 | 2.68 | 2.15 |
| **FUNCTIONALITY** | | | | | | | | | | |
| Oxygen ($O_2$) | 1.34 | 1.20 | 1.33 | 1.13 | 1.30 | .65 | .93 | .67 | .71 | .51 |
| Bromine (Br) | .73 | .58 | .77 | .74 | .67 | .64 | .84 | .62 | .72 | .71 |

## TABLE XLII

## ETHYLENE/NEOHEXENE TELOMERIZATIONS WITH MBIB

| Run No. 27-EMS- | 32 | 33 |
|---|---|---|
| **Initial Charge** | | |
| Benzene, gms. | 7.3 | 10.2 |
| Telogen, gms.[a] | 0.94 | 1.4 |
| DMAB, gms. | 0.093 | .093 |
| Neohexene, gms | 689 | --- |
| Ethylene, gms. | 260 | 417 |
| Propylene, gms. | --- | 366 |
| **Fed During Reaction** | | |
| Telogen, gms. | 8.43 | 12.5 |
| Solvent, gms. | 63 | 92 |
| DMAB, gms. | 0.835 | .835 |
| Mole Ratio, telogen to monomers | 0.00296 | .00326 |
| **Reaction Conditions** | | |
| Temp. °C | 90-91 | 90 |
| Pressure, mpsi | | |
| Initial | 10.3 | 10.75 |
| Maximum | 14.6 | 15.35 |
| Reaction Time, Hrs. | 3.08 | 3.08 |
| **Productivity** | | |
| Yield, gms. | 24 | 18 |
| Conversion, % | 2.53 | 2.32 |
| Rate, %/hr. | 0.82 | .75 |
| **Physical Properties** | | |
| Molecular Wt.[b] | 805 | 803 |
| Brookfield Vis., cps | 2300$^{22}$ | 1000 |
| Specific Vis., @ 80°C | 0.0251 | .0166 |
| Bromine, Wt. % | 9.89 | 7.8 |
| Ester Equivalent Wt.[c] | 886 | 900 |
| **Functionality** | | |
| Bromine | .996 | .78 |
| Ester | .91 | .89 |
| Total | 1.906 | 1.67 |

[a] Methyl α-Bromoisobutyrate

[b] V.P.O. in Benzene

[c] I.R. Spectroscopy with methyl pivalate as standard

## E. Telomer Preparation in the Continuous Stirred Autoclave Reactor

It is often difficult to obtain closely reproducible results in batch type polymerizations; however, it is usually expedient and worthwhile to conduct batch type experiments during the product definition stages of polymer research. When larger quantities of a given product are required, batch methods usually do not give the necessary uniformity of properties. This was amply demonstrated in the preceding section, wherein the only significant variation between batches was in the amount of ethylene charged (±2%), yet the products had molecular weight between 764 and 1095.

Preparing larger quantities of a more uniform product is best done in a continuous type reactor operating under steady-state conditions.

In Part 4, Section C we discussed the use of a continuous tubular reactor for the preparation of ethylene-neohexene copolymers. Because of the fact that a tubular reactor is inherently a progressive reactor, the composition of the reaction mixture is quite different along the length of the tube. This makes a tubular reactor unsuitable for telomerizations using very active telogens such as BIBA and BBIB; broad functionality and molecular weight distributions would be inevitable.

A continuous stirred autoclave reactor differs from the tubular reactor in that the reaction zone is a well mixed pot into which reactants are fed and reaction mixture is withdrawn at a constant rate. After an initial start-up period, a "steady state" condition is achieved. The composition of the reaction mixture is then constant and a very uniform product can be made. The unreacted monomers and the solvent may be recovered from the product mixture and recycled continuously.

We have added to the 1.5 liter stirred autoclave reactor the continuous feed equipment used previously on the tubular reactor and have begun to prepare telomers of ethylene and neohexene. Runs 25-EMS-86, 88, 90, 94, 95 and 96 were made in this reactor, using BIBA telogen and DMAB initiator. The production data are summarized in Table XLIII.

All components of the feed were charged first into a steel cylinder. As the liquid mixture was pumped into the reactor, its composition was kept constant by regulation of the vapor pressure of ethylene in the feed cylinder. Thorough mixing was achieved by three equally spaced six bladed turbines rotating at 1000 RPM inside the reaction vessel. The reaction pressure was controlled by operation of a throttle on the exhaust from the reactor. In these initial runs, the first two changes of reactor volume were discarded and the next three collected as "steady state" product. The material prepared after feed had stopped was also discarded. Higher yields could

## TABLE XLIII

## ETHYLENE/NEOHEXENE TELOMERS PREPARED IN THE CONTINUOUS REACTOR

| RUN # 25-EMS- | 86 | 88 | 90 | 94 | 95 | 96 |
|---|---|---|---|---|---|---|
| **CHARGE (WT. % TOTAL)** | | | | | | |
| Ethylene | 26.35 | 26.57 | 26.68 | → | → | → |
| Neohexene | 61.43 | 61.96 | 62.22 | → | → | → |
| BIBA | 1.68 | .846 | .425 | → | → | → |
| Benzene | 10.40 | 10.45 | 10.53 | → | → | → |
| DMAB | .130 | .132 | .133 | → | → | → |
| Mol. Ratio, Telogen/ Monomers | .006 | .003 | .0015 | → | → | → |
| Total Weight | 3,283 | 3,378 | 3,376 | 3,155 | 4,281 | 3,393 |
| **REACTION CONDITIONS** | | | | | | |
| Temperature, °C | 100 | 100-102 | 91-102 | 80-103.5 | 100-102 | 105-118 |
| Pressure, mpsi | 20 | → | → | → | → | → |
| Holdup time, min. | 27.4 | 27.1 | 26.3 | 14.04 | 41.4 | 3.44 |
| Feed Rate, gms./hr. | 2,189 | 2,252 | 2,251 | 4,207 | 1,427 | 16,965 |
| **PRODUCTIVITY** | | | | | | |
| Yield, gms. | 81 | 73 | 73 | 50 | 101 | 30 |
| Conversion, % | 2.81 | 2.44 | 2.43 | 1.78 | 2.65 | 1.00 |
| Rate, gms./hr. | 54 | 48.7 | 48.7 | 66.7 | 33.7 | 150 |

have easily been obtained merely by continuing to feed reactants for a longer period.

The product data are summarized in Table XLIV. In the series 86, 88 and 90 one sees the effect of telogen content in the feed upon the molecular weight obtain: 1.68, 0.846 and 0.425% giving 394, 490 and 844, respectively. Also note that the rate of product formation and the product functionalities are not changed much by the changes in telogen concentration.

In the series 90, 94, 95 and 96 one can see the effect of hold-up time in the reactor on the product properties. In these runs the feed composition was kept in the same, but the feed rate was changed. Higher rates at the same pressure result in lower residence times in the reactor, higher reaction rates, but lower overall conversions; and because the steady state telogen concentration is higher, high feed rates result in lower molecular weights.

## F. Modification of the Continuous Stirred-Autoclave Reactor

In the preceding section we described the use of a continuous stirred autoclave reactor for the preparation of ethylene neohexene copolymers by telomerization. The reactor itself was of 1.5 liter capacity and could operate at pressures up to 20,000 psi. We used this reactor to prepare telomers at rates between 30 and 150 grams per hour, depending upon the conditions employed. Control of the pressure was obtained by manual adjustment of a throttle valve which controlled rate of removal of product from the reactor.

After this initial work we replaced the original 20,000 psi reactor with another similar reactor rated at 40,000 psi, and have added automatic pressure control features which permit a more uniform operation.

Figure 5 shows a schematic drawing of the modified continuous reactor unit. The legend on the following page identifies the numbered components.

Essentially, the same procedure is followed with the new system as was used in our previous unit. The only differences are the automatic control of pressure and the higher pressure limit. The upper pressure limit is set by the pneumatic pressure rating of 35,000 psi.

We will be conducting most of our telomerizations near this upper limit in order to maximize the rate of propagation. This will improve the productivity, and will allow a higher concentration of telogen to be used.

In subsequent discussion, our original system with the 20,000 psi rated reactor will be designated "Unit I" and the present system with an upper limit of 35,000 psi will be called "Unit II"

## TABLE XLIV

## CHARACTERIZATION OF ETHYLENE/NEOHEXENE TELOMERS

| RUN # 25-EMS- | 86 | 88 | 90 | 94 | 95 | 96 |
|---|---|---|---|---|---|---|
| **PHYSICAL PROPERTIES** | | | | | | |
| Brookfield Visc., cps | 3,590 | 7,090 | 24,600 | 18,400 | 52,400 | 8,300 |
| Specific Visc,@80°C | .0083 | .0125 | .0226 | .0236 | .0292 | .0137 |
| Description | Black Oil | Tan Oil | → | → | → | Dark Brown Oil |
| **ANALYTICAL DATA** | | | | | | |
| Molecular Wt. (THF) | 394 | 490 | 844 | 705 | 1,123 | 564 |
| Bromine, Wt. % | 15.41 | 13.32 | 6.95 | 8.84 | -- | 11.2 |
| Carbon, Wt. % | 65-73 | 69.00 | 76.2 | 73.99 | 80.3 | 71.04 |
| Hydrogen, Wt. % | 10.77 | 11.13 | 12.6 | 12.31 | 13.9 | 12.18 |
| Oxygen, Wt. % | 8.09 | 6.55 | 4.25 | 4.86 | -- | 5.58 |
| Neutralization Equivalent | 408 | 551 | 848 | 750 | 1,174 | 678 |
| **FUNCTIONALITY** | | | | | | |
| Bromide (Br) | .76 | .82 | .73 | .78 | -- | .79 |
| Oxygen ($O_2$) | 1.00 | 1.00 | | 1.07 | -- | .98 |
| Carboxyl (COOH) | .97 | .89 | 1.00 | .94 | .96 | .83 |

## LEGEND FOR FIGURE 6

1. Ethylene cylinder with regulator for maintaining constant feed pressure.
2. Mixed feed cylinder with eductor tube.
3. Scales, capacity 90 Kg. ± 10 gms.
4. Regrigerated bath, to -35°C.
5. Pneumatic feed flow control via regulated rheostat for DC motor giving variable pump rpm.
6. Triplex pumps, 60 mpsi max., 7/16" dia., pistons x 5/8" stroke.
7. Emergency vent valve.
8. Pneumatic pressure transmitter, to 35 mpsi.
9. Pressure controller for emergency vent.
10. Magnedrive autoclave, 1.5 liter capacity, 316 s.s. lined, 40 mpsi max., at 350°C, 3 each 6-bladed turbines equally spaced on agitator shaft, jacketed for heating by circulating heat transfer fluid.
11. Air driven motor, up to 200 rpm.
12. Pressure controller for motor valve 14.
13. Temperature recorder, 0-500°C, IC TC, circular chart.
14. Motor valve, to 50 mpsi at 100°F.
15. Diverter valve*.

16.\
17.} Product receivers, stainless steel, 6 gal., capacity, to 300 psi.

18. Diverter valve*, for vent gas.

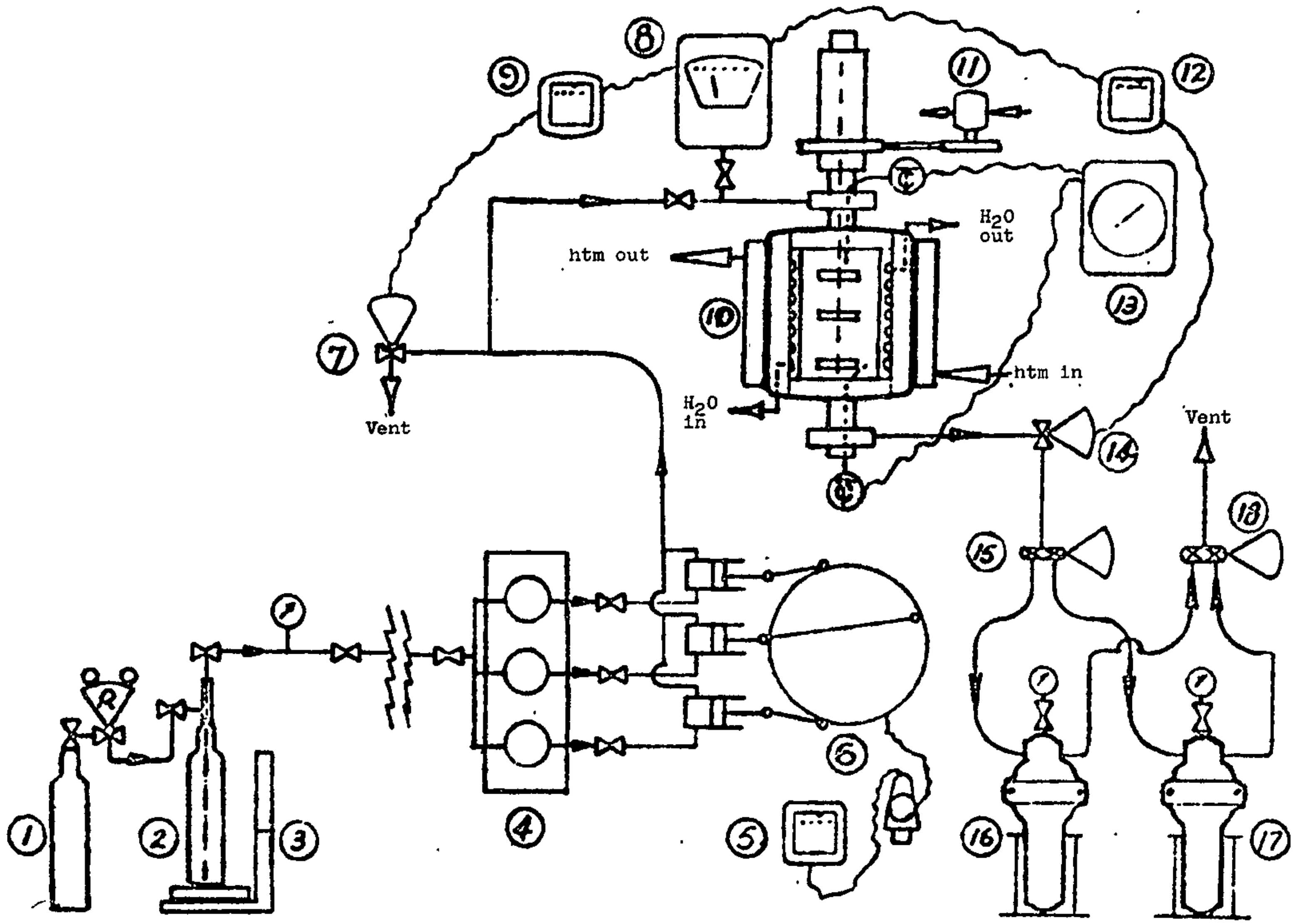
Not Shown: Heat transfer system, 22.5 KW electrical heat for 25 gal. heat transfer medium (htm). Temperature controller-recorder for heat transfer system.

---

* Diverter valves operated by electrical switch in control room.

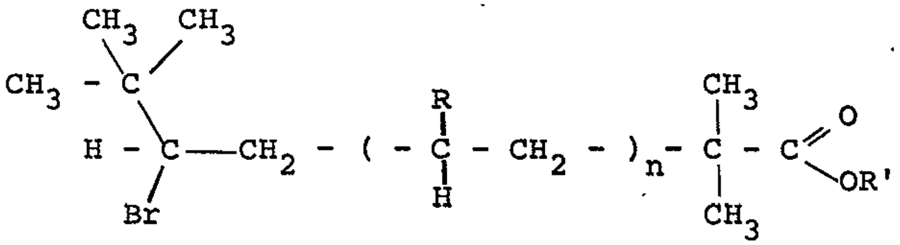
# FIGURE 6

## CONTINUOUS STIRRED AUTOCLAVE REACTOR, UNIT II



## G. Ethylene/Neohexene Telomerization Scale-Up

In previous reports we have shown that the ω-bromoester telomer of ethylene/neohexene having the structure shown below,



R = H or t-Bu, R' = H, $CH_3$ or t-Bu

can be converted to carboxyl terminated binder precursors by the sequence of dehydrobromination followed by ozonolysis. High efficiencies were obtained in converting the terminal halogen functional groups into carboxyl groups. However, the telomer samples themselves were not high enough in functionality to be converted into difunctional binder material.

In the batch run 27-EMS-32 discussed in Part 8, Section D of this report, it was found that the methyl ester telogen was effective in giving a telomer containing essentially one bromide and one ester group per molecule at a useful molecular weight.

Having demonstrated (1) an efficient chemical modification sequence leading to carboxyl terminated molecules and (2) an effective synthesis of a difunctional telomer, the next goal was to combine these achievements in a larger batch of ethylene/neohexene telomer. Before the large scale continuous telomerizations could be attempted, however, a pilot run using the conditions expected to be effective was necessary to avoid waste of effort and material. It was also necessary to incorporate a larger quantity of neohexene into the telomer to avoid haze in the final product: The ethylene/neohexene telomers prepared at the higher reactor pressures now available have tended to be hazy. It was suspected that this was due to a higher relative polymerization rate of ethylene at the higher pressures now in use. Run 27-EMS-71 was planned to investigate this latter problem, and if successful, to serve as the pilot run for the longer continuous runs planned.

Table XLV summarizes the results from this continuous run at 35,000 psi reactor pressure.

The results from this run showed that the haze was indeed eliminated by the incorporation of more neohexene and demonstrated that the high bromine functionality obtained in the small batch runs could be duplicated in the continuous unit. Having established this, run 27-EMS-94 was made to provide one pound of high functionality telomer.

The conditions were kept as close as possible to those used in the preceding run, except that a higher concentration of telogen was used to give a product of higher molecular weight. 549 grams of telomer was obtained having a molecular weight of 883 and containing 1.05 Br per molecule. The conditions used and product data are summarized in Table XLV.

## TABLE XLV

## NEOHEXENE/ETHYLENE COPOLYMERS, SCALE-UP

| Run No. 27-EMS- | 71 | 94 |
|---|---|---|
| Charge, Wt. % on Total | | |
| Ethylene | 23.95 | 23.75 |
| Neohexene | 64.67 | 64.67 |
| Telogen[a] | 0.866 | 0.779 |
| Benzene | 10.41 | 10.41 |
| DMAB | 0.088 | 0.088 |
| Mole Ratio, Telogen/Monomers | 0.0029 | 0.0031 |
| 25°C Vapor Pressure, psig | 365 | 350 |
| Wt. Feed Used, gms. | 4076 | 29,933 |
| Reaction Conditions | | |
| Internal Temp., °C | 110-111 | 109-110 |
| Pressure, mpsi | $35 \begin{smallmatrix} +0.4 \\ -0.2 \end{smallmatrix}$ | 35 |
| Nominal Hold-up Time, min. | 29.3 | 28.3 |
| Ave. Feed Rate, gm./hr. | 2145 | 2173 |
| Productivity | | |
| Yield, gms. | 106 | 549 |
| Conversion, % | 2.93 | 2.07 |
| Rate, gm./hr. | 55.8 | 40.7 |
| Rate, lbs./cu.ft./hr. | 2.34 | 1.71 |
| Physical Properties | | |
| Brookfield Vis., cps. | $2600^{23}$ | $2750^{24}$ |
| Sp. Vis., @ 80°C | 0.0131 | 0.022 |
| Description | Light Tan Clear Oil | Light Tan Oil |
| Analytical Data | | |
| Molecular Wt.[b] | 800 | 883 |
| Wt., % Br | 9.95 | 9.54 |
| Ester Equivalent Wt.[c] | 926 | 1056 |
| Functionality | | |
| Bromine | .996 | 1.054 |
| Ester | .87 | .84 |
| Total | 1.87 | 1.89 |

[a] Methyl α-Bromoisobutyrate

[b] V.P.O. in Benzene

[c] I.R. Spectrum, Methyl Pivalate as Reference

## H. Reactions of Telomers

We have proposed three routes by which the bromide terminated telomers may be converted to carboxyl terminated prepolymers. These are:

1. Elimination of HBr followed by oxidation.
2. Displacement by $-CN^-$ followed by hydrolysis.
3. Displacement by $S^=$ leading to coupling.

We have conducted some experiments using 11-bromohendecanoic acid as a model for the bromine terminated telomers discussed earlier:

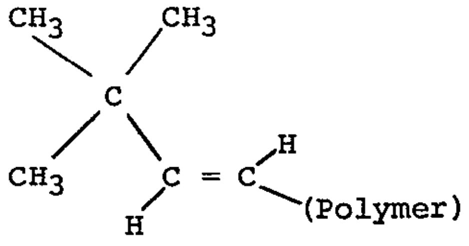
$$Br - (CH_2)_{10} - COOH$$

We have found that it dehydrobrominates readily under the action of potassium t-butoxide and is converted to 11-hendecenoic acid.

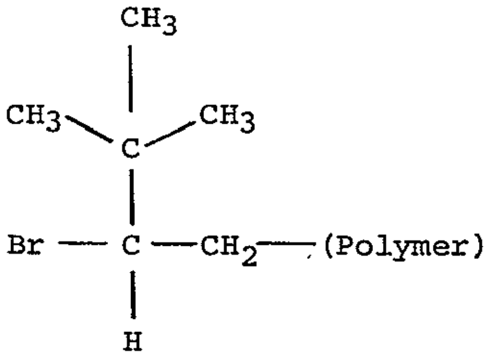
The bromo acid also reacts rapidly with sodium sulfide to give a new crystalline carboxylic acid in high yield. The new acid contains no halogen and its NMR spectrum is consistent with the structure of the $C_{22}$ sulfide coupling product, $HOOC - (CH_2)_{10} - S - (CH_2)_{10} - COOH$.

We have also found that $CN^-$ displacement works on model compounds, and that a dimercaptide is as effective as sulfide in route (3) for giving coupled products. However, when these reactions were applied to the bromide terminated telomers, routes (2) and (3) led to HBr elimination, not Br displacement, under forcing reaction conditions. Milder conditions gave no reaction at all. We found that only route (1) gave useful results.

When one treats a sample of a bromide terminated telomer with potassium hydroxide in refluxing n-butanol, complete elimination of HBr from the end groups can be obtained. This is supported by both spectral and elemental analysis data. The products exhibit a strong absorption at 970 $cm^{-1}$ in the infrared spectrum due to the grouping:



which is present in the spectrum of the caustic treated material but not in that of the original sample. No detectable amount of vinyl absorption (890 $cm^{-1}$) was present in the dehydrobrominated material. This is indirect evidence that the original terminal bromides were part of the structure shown below:



and not Br—$CH_2$—$CH_2$—(Polymer)

Further support for HBr elimination is given by the negative Beilstein test and the low bromine contents (shown by elemental analysis of the products).

Treatment of the above unsaturated products with ozone in chloroform at -4 to -5°C led to an intermediate ozonide product which showed no trace of the 970 $cm^{-1}$ band in its infrared spectrum. This ozonide was worked up by oxidation with aqueous peracetic acid.

We have applied this reaction sequence to three different telomers: 24-EMS-90, 92 and 93. The results are summarized in Table XLVI.

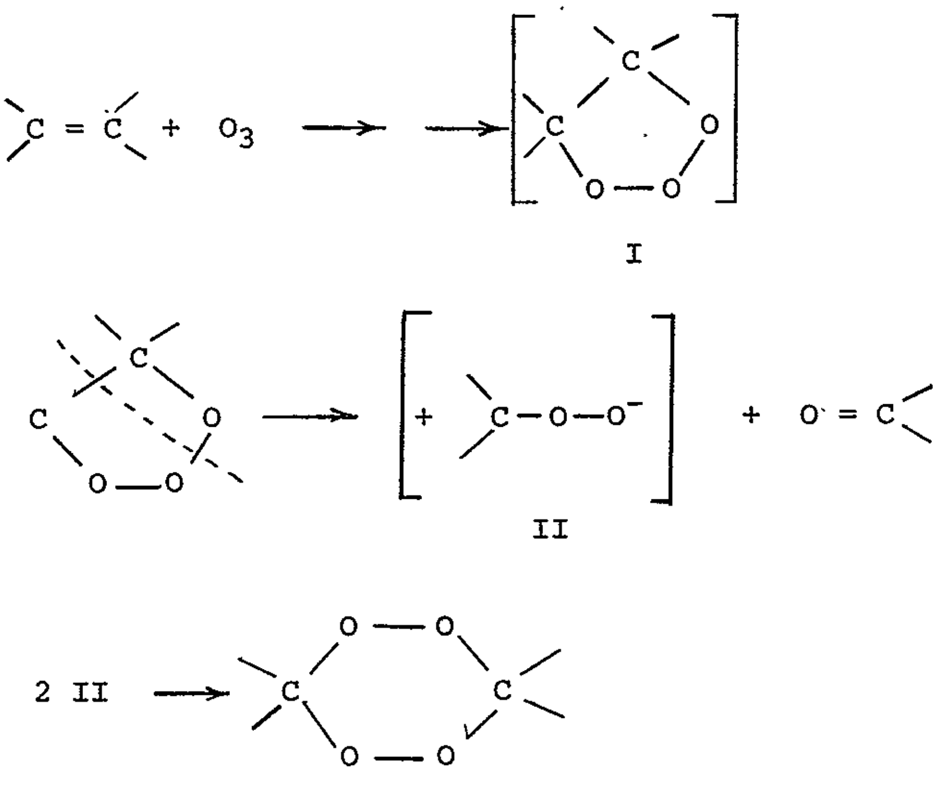
The molecular weights shown for the dehydrobrominated products are in rough agreement with the expected values resulting from loss of HBr and the ester end group. The weak positive Beilstein and 2% bromine content in the product from 93 shows that the dehydrobromination was incomplete in this case, and that a longer reaction time may be called for.

The carboxyl functionalities shown for the final products are lower than expected and not in agreement with the $O_2$ functionalities calculated from the oxygen contents. At present we have not established which functionality is correct. Both could be correct if the final work up of the ozonide was incomplete. This would result in non-COOH oxygen in the final product and account for the discrepancy between the two functionalities. This position, however, is not completely reasonable in view of the fact that curing experiments using the product from 24-EMS-93 have given positive results.

The diepoxide EP-221 and MAPO were used in these experiments. In the epoxide cures, 10% of the total COOH equivalents were supplied by tricarballylic acid. Iron octoate was also added as an epoxide curing catalyst. In both the epoxide and aziridine cures, a stoichiometric ratio of COOH to curing agent was used.

Curing was done at 80°C for 16 hours. Soft rubbery cures were obtained both with MAPO and EP-221.

From the results of these experiments we concluded that the COOH functionality in the dehydrobrominated and ozonized final product was not as high as one would expect based upon the original telomer functionality. In an attempt to achieve a higher conversion of functionality, an improved ozonolysis procedure and oxidative workup was devised based upon ozonolysis in a reactive solvent medium. This was to avoid formation of peroxidic dimer structure (III) from the decomposition of the terminal double bond ozonide (I):



III

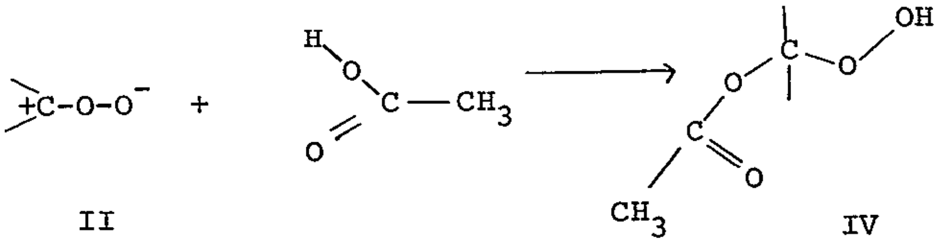
The peroxidic dimer structure III is resistant to hydrolysis and could be a major source of difficulty in attaining high conversion of terminal double bonds to carboxyl groups.

TABLE XLVI

FUNCTIONALITY CONVERSIONS IN ETHYLENE/NEOHEXENE TELOMERS

| Samples 24-EMS # | 90 | 92 | 93 |
|---|---|---|---|
| Original Sample Data | | | |
| $\bar{M}_n$ | 709 | 484 | 761 |
| Wt. % Oxygen | 3.96 | 5.95 | 3.77 |
| Wt. % Bromine | 9.00 | 12.79 | 8.16 |
| $O_2$ Functionality | .88 | .90 | .90 |
| Br Functionality | .80 | .68 | .78 |
| Dehydrobrominated Product Data | | | |
| $\bar{M}_n$ | 565 | 367 | 517 |
| Wt. % Br | 0.65 | 1.18 | 2.03 |
| Neutralization Equivalent | 579 | 393 | 592 |
| COOH Functionality | .93 | 1.03 | .87 |
| Br Functionality | .03 | .08 | .13 |
| Absorption at 970 $cm^{-1}$ | Strong | Strong | Strong |
| Beilstein Test | Negative | Negative | Negative |
| Ozonized and Worked Up Product Data | | | |
| $\bar{M}_n$ | 594 | 506 | 563 |
| Wt. % Oxygen | 9.96 | 12.93 | 10.94 |
| Neutralization Equivalent | 495 | 424 | 499 |
| $O_2$ Functionality | 1.85 | 2.04 | 1.92 |
| COOH Functionality | 1.20 | 1.20 | 1.13 |

In order to avoid this, we conducted the ozonolysis in a medium containing acetic acid, which should add to the zwitterionic structure II and prevent dimerization.



Hydrolysis of the adduct IV was expected to be quite facile. The results of these experiments are now presented.

### 1. Studies on 24-EMS-122

Ethylene/neohexene telomer sample 24-EMS-122 was discussed in Part 8, Section B of this report. This telomer has a molecular weight of 1539, has 0.95 $O_2$ per molecule in the form of a t-butyl ester end group and contains 0.75 Br per molecule.

50.9 grams (33 mmoles ) of 24-EMS-122 was dehydrobrominated by heating and stirring under reflux in an inert atmosphere with 100 grams (1.784 moles) KOH pellets and 500 ml n-butanol which had been purified by distillation from KOH under a nitrogen atmosphere. Reflux was continued for 64 hours, at which point the mixture was steam distilled to remove the butanol, then cooled. The semisolid polymer mass was then removed and taken up in hexane, dried over anh. $MgSO_4$ and evaporated to give 44.63 grams slightly cloudy straw colored syrup. The Beilstein test for halogen was completely negative. The infrared spectrum of the product showed a trans disubstituted double bond absorption at 970 $cm^{-1}$, no trace of the t-butyl ester absorption, and a strong broad carboxylate salt absorption at 1565 $cm^{-1}$.

These findings are completely consistent with complete dehydrobromination and concurrent saponification of the t-butyl ester end groups.

44.15 grams of the dehydrobrominated product was dissolved in $CCl_4$ and diluted to 250 ml to give a stock solution containing 8.83g (~6.14 mmoles) of polymer per 50 ml.

50 ml of this solution was diluted with 50 ml $CCl_4$ and 50 ml of acetic acid and cooled to 0°C. A stream of ozone/oxygen was passed through the solution at a rate of .2 liters per minute for 38-1/2 minutes. A total of 0.25 cu. ft. of a 27.53 mmoles/cu. ft. ozone mixture were passed through the solution. A KI trap in series with the sample chamber was back titrated with sodium thiosulfate after acidification, .08 mmoles ozone had been consumed in the KI trap. These results show that 6.3mmoles (6.14 mmoles theory) ozone was consumed by the sample.

The ozonized solution, ∿150 ml volume, of 24-EMS-122 was kept at 0°C while the following workup methods were tried upon aliquots removed by pipette:

a) 25 ml. ozonized solution, 10 ml formic acid and 5 ml 30% $H_2O_2/H_2O$ were combined and heated to reflux with stirring overnight.

b) 25 ml. of the ozonized solution was heated under reflux with 100 ml. rapidly stirred conc. HCl overnight.

c) 25 ml. of the solution was shaken vigorously with 70% aq. $HNO_3$ and the mixture allowed to stand overnight at room temperature.

The lower $CCl_4$ layer was separated after each of the above treatments, washed with distilled water and dried over anhydrous $MgSO_4$, then evaporated to give 1 to 1.2 grams of liquid product:

a) This product was a slightly cloudly, nearly colorless oil, the infrared spectrum of which shows no C = C absorption at 970 $cm^{-1}$. A clean sharp carboxyl absorption at 1703 $cm^{-1}$ is the only absorption present in the carboxyl region. Its relative intensity is 1.66 times the relative intensity of the carboxyl absorption of the acidified starting material.

b) This product was a slightly cloudy straw colored oil. Again, the I.R. shows no C = C absorption, however, in the carbonyl region, the carboxyl peak is only slightly more intense than in the starting material, and there is a new absorption at 1724 $cm^{-1}$. This is probably due to incomplete oxidation of the aldehydic fragments of ozonide hydrolysis.

c) This product was a light greenish yellow oil showing a complex carboxyl region in the I.R. In addition to the main COOH peak, there were weaker absorptions at 1800, 1724, 1630, 1580 and 1550 $cm^{-1}$. The increase in relative intensity of the carboxyl peak amounted to only 1.3 times that of the acidified starting material.

We concluded from the above experiments that procedure a) was the best way to work up the bulk of the solution from the ozonolysis; accordingly, this procedure was scaled up 3 times to process the remaining 75 ml. of ozonolysis mixture. 3.64 grams of nearly colorless cloudy oil resulted. A similar enhancement of the carboxyl absorption resulted, and the product had a neutralization equivalent of 900. This should be compared with the theoretical value of 830 which would have been obtained if 100% of the original functional groups had either remained as or been converted to carboxyl groups. Since the original molecular weight was 1536, the final product, after conversion of the available functional groups to COOH, should have a molecular weight of 1408. With an N.E. of 900 this implies a functionality of 1.57 COOH per molecule out of a possible 1.69.

## 2. Studies on 25-EMS-22

Ethylene/Neohexene telomers sample 25-EMS-22 is described in Part 8, Section B of this report. It has a molecular weight of 767, has about 0.61 $O_2$ per molecule as *t*-butyl ester groups and contains 0.71 Br per molecule.

Following the same procedure used on 24-EMS-122, 50.11 grams (.065 moles) was dehydrobrominated by treating it with 100 grams KOH in 500 ml. *n*-butanol. After working up as described before, 45.2 grams of a very viscous syrup, light amber in color, was obtained. The product gave a negative Beilstein test. Infrared spectroscopy shows the expected *trans* internal -CH=CH- at 970 $cm^{-1}$, no ester carbonyl, and a strong broad carboxylate salt band at 1565 $cm^{-1}$.

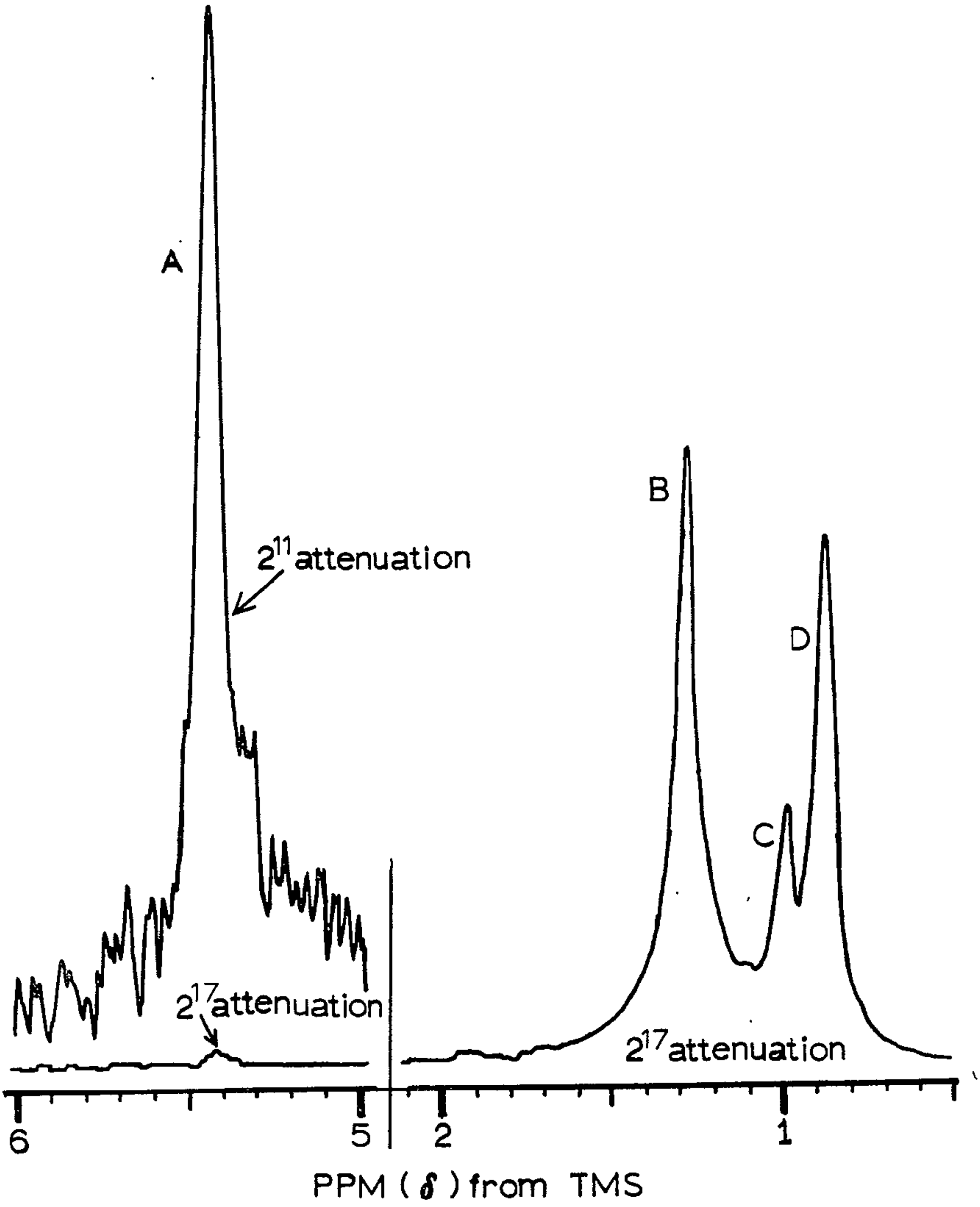
44.05 grams of this material was dissolved in $CCl_4$ and diluted to 250 ml. Some of this solution was submitted for nuclear magnetic resonance (N.M.R.) analysis using a time average computer coupled with the N.M.R. machine. Summing of 100 scans of the spectrum sufficed to give a useful signal-to-noise ratio (about 10:1) in the olefinic proton region, and allowed us to determine the -CH=CH- content of the dehydrobrominated telomers. Figure 6 shows the final output of the computer after 100 scans.

Peak A, the olefinic proton signal is shown twice, once at an attenuation of $2^{11}$, and again at $2^{17}$. The intensity factor is thus $2^6$ or 64x. The rest of the spectrum is shown at an attenuation of $2^{17}$. No peaks were present between 5 and 2 ppm downfield from tetramethyl silane (TMS). Peak B is the signal from the $-CH_2-$ groups derived from both ethylene and neohexene, peak C is probably the signal from the geminal methyl groups adjacent to the carboxylate, and D is due to the t-butyl groups on neohexene. Relative areas of A and B+C+D were determined by weighing cutouts of the spectrum. According to the areas, there is 1 CH=CH group for every 70 "$CH_2$" groups ("$CH_2$" is a lumping together of all the aliphatic signals, including CH and $CH_3$). This corresponds to a C=C equivalent weight of 1016.

After loss of HBr and saponification of the ester end group, the original $\overline{M}_n$ of 767 should change to 676, thus the product contains 0.66 -HC=CH- out of a possible 0.71.

240 ml. of the $CCl_4$ solution (containing 42g dehydrobrominated 25-EMS-22) and 120 ml. of acetic acid was cooled to 0°C and then treated with a stream of 23.7 mmoles per cu. ft. ozone/oxygen mixture for 58 minutes. 2.00 cu. ft. were passed through during this time: 47.4 mmoles of ozone. A KI trap in series with the reaction mixture required 2.35 ml. of .1011 N thiosulfate to titrate the iodine liberated upon acidification of the resulting iodate solution.

FIGURE 6


A
$2^{11}$attenuation
$2^{17}$attenuation
B
D
C
$2^{17}$attenuation
6
5
2
1
PPM (δ) from TMS

This represents only 0.1 mmole of ozone, thus 47.3 mmoles were consumed by the sample. Theory, based on the C=C content determined by NMR, requires 41.4 mmoles for addition to the C=C present.

The colorless, somewhat cloudy solution resulting from ozonolysis was combined with 150 ml. formic acid and 75 ml. 30% aqueous $H_2O_2$ and heated under reflux for ∿20 hours, then cooled. The reaction mixture was worked up using several water washes to remove the acetic and formic acid and other water soluble impurities. Each water wash was back extracted with $CCl_4$ to avoid material losses from the polymer solution. The final extracts were dried over anh. $MgSO_4$, filtered and neutralized equivalent = 516.

The molecular weight at this stage should be 645, implying a functionality of 1.25. This is to be compared with the starting material which contained 0.61 $O_2$ and 0.71 Br per molecule = a potential functionality of 1.32. The acid functionality of the final product represents a 95% conversion of all functional groups present in the original telomer.

### 3. Studies on Composite Batch I

Composite batch I (hereinafter called I) is described in Part 8, Section C of this report. The molecular weight and elemental analyses of this composite were calculated as a weighted average of the values obtained for the individual batches. The calculated functionalities for the composite are: 0.91 Br per molecule, 0.89 COOH per molecule and 1.80 total.

254 grams (.53 eq. Br, .51 eq. COOH) of I was treated with 465 grams (8 fold excess) of KOH in 2500 ml *n*-butanol solution. The mixture was heated and stirred under reflux in a nitrogen atmosphere for 42 hrs., then steam distilled to remove the butanol. After cooling, the aqueous phase was decanted and the "fudge-like" mass of polymer potassium salt taken up in 2-liters of hexane and separated from most of the water which was held within the salt. A true solution did not result because of the high polarity of this low molecular weight salt. The hexane and the remaining water were removed by evaporation *in vacuo* leaving behind 266 grams of a very viscous amber syrup.

This was taken up in 2-liters of $CCl_4$ and acidified by the addition of 35 cc. (.612 moles, an 11.5% excess) acetic acid. This caused the polymer (now in the free COOH form) to dissolve and sodium acetate to precipitate out. This mixture was then dried over anh. $MgSO_4$ and filtered. Then the solvent was removed by vacuum evaporation to give 210 grams light amber syrup (212 grams theoretical yield), containing no halogen detectable by the Beilstein test.

The N.M.R. spectrum of the product indicated a lower than normal neohexene content and showed olefinic protons corresponding to about .66 CH=CH per molecule. In the infrared spectrum of this product was a strong absorption at 970 $cm^{-1}$ due to trans disubstituted double bonds. A very intense carboxylic acid absorption and a broad band at 1550 $cm^{-1}$ due to carboxylate salt are also present.

200 grams of dehydrobrominated I was dissolved in 1200 ml. $CCl_4$ and diluted to 2000 ml. with acetic acid. After cooling to 0°C, the solution was treated with a stream of 27.5 mmoles per cu. ft. ozone/oxygen mixture for 2-1/4 hrs. A total of 12.11 cu. ft. passed through during this time; 0.333 moles of ozone. Titration of the acidified KI trap showed an excess of 3.4 mmoles, therefore, .33 moles were consumed by the sample. An infrared spectrum of a small aliquot from the ozonolysis mixture showed no C=C absorption at 970 $cm^{-1}$.

The ozonolysis mixture was then heated with 1000 ml. formic acid to reflux, and 500 ml. 30% aqueous $H_2O_2$ was added cautiously, dropwise with stirring. After all the $H_2O_2$ had been added and the exotherm had subsided, the reaction mixture was heated overnight with stirring for a total reaction time of 20 hours, then worked up as previously described. 163 grams of a cloudly straw colored syrup was obtained (neutralization equivalent = 303).

The infrared spectrum of this product showed a shoulder at 1730 $cm^{-1}$ on the COOH peak at 1703 $cm^{-1}$, appropriate for the presence of a small amount of carboxylic ester in the sample. In accordance with this hypothesis, the sample had a saponification equivalent different from its neutralization equivalent: 264. Thus, there are 1/303 or. 3.3 meq. COOH/gram, and 1/264 or 3.79 meq. (COOH + COOR)/gram, and therefore, .49 meq. COOR/gram. This corresponds to an ester equivalent weight of 2040.

Molecular weight determination by V.P.O. in THF solvent gave the value 383. From these data we conclude that the sample contains 1.27 COOH per molecule and an additional .19 ester groups per molecule for a total of 1.46 carboxylic groups.

Saponification of 5 grams of the above product with 50% aqueous NaOH, followed by acidification and work-up gave 4.75 grams of a product with an N.E. of 286.

The final product obtained from the five gram saponification contained 1.34 COOH per molecule. This value represents an increase of 0.45 COOH per molecule over the original 0.89.

If all of the terminal bromide originally present had undergone β-elimination to give double bonds, one would expect the equivalent weight (based on C=C) to be near 400. By measuring the olefinic proton content using N.M.R. spectroscopy, we found an equivalent weight of 550. This corresponds to 0.66 CH=CH per molecule.

Thus, 0.66 of the bromine atoms were eliminated as HBr rather than nearly all of the .91. We expected the latter to occur based upon our experience with the higher molecular weight products 24-EMS-122 and 25-EMS-22.

The negative Beilstein test upon the dehydrobrominated product from the composite batch I showed that all of the bromide had reacted. We infer from this that the remaining 0.25 Br per molecule has participated in a different reaction. The most reasonable possibility is that some nucleophilic displacement of $Br^-$ by $OH^-$ or $C_4H_9O^-$ has occurred concurrently with the β-elimination reaction. No OH (other than COOH) absorption could be seen in the infrared spectrum of the product; however, a moderate absorption at 1120 $cm^{-1}$ could be due to a butyl ether end group.

If these observations do indicate that up to 25% of the bromide end groups of the original molecule have participated in displacement reactions, we must conclude that in this particular sample primary bromides are present. These could only be derived from chain transfer occurring when the growing copolymer radical has an ethylene residue as an end group:

$$\text{Polymer} - CH_2 - CH_2\cdot \quad + \quad T{-}Br \longrightarrow$$

$$\text{Polymer} - CH_2 - CH_2 - Br + T\cdot$$

(TBr is the telogen BIBA)

We had previously ruled out this type of chain transfer on the basis of the low chemical reactivity of the halogen end groups of the other telomers thus far examined. Even under forcing conditions, we had never obtained any observable amount of $CN^-$ or $S^=$ displacement of halogen; elimination to give - CH = CH had previously been the only reaction found.

In contrast to this behavior, telomer samples which we have prepared from ethylene alone using BIBA telogen only give rise to displacement reactions; no vinyl groups are produced at all:

$$T\text{-}(CH_2\text{-}CH_2)_n\text{-}Br + OH^- \longrightarrow T\text{-}(CH_2\text{-}CH_2)_n\text{-}OH + Br^-$$

$$T\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}CH_2CH_2\text{-}Br \not\xrightarrow{\cancel{-HBr}} T\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}CH{=}CH_2$$

It thus seems most reasonable to conclude that the telomerizations which provided the samples for composite batch I were atypical in some respect which led to incorporation of a much larger fraction of ethylene than normal, and thus to a greater probability of having terminal ethylene units. This is confirmed by the N.M.R. spectra which show an ethylene to neohexene molar ratio of about 8:1. At the very low molecular weights attained in this series of telomerizations, this amounts to only slightly more than one neohexene residue per telomer chain. On a purely statistical basis one would expect a distribution of molecular types, some having only one and some having more than one neohexene residue.

In a more typical telomer of ethylene and neohexene, the ethylene to neohexene ratio is near 3:1. At a molecular weight of 1000, this means that the average molecule contains about 6 neohexene residues. From our experience with attempted displacement reactions upon such products, and the high conversion of functional groups obtained in the workup of 24-EMS-122 ($M_n$= 1539) and 25-EMS-22 ($\bar{M}_n$ = 767), it is highly probable that these more typical telomers contain one of the neohexene residues at the bromide terminated end of the chain.

### 4. Summary of Reaction Studies

Ethylene/Neohexene telomers prepared with the telogens BIBA and BBIB can be dehydrobrominated essentially quantitatively in boiling concentrated KOH/n-Butanol. This process gives rise to *trans*-internal double bond functionality, as long as the neohexene content of the telomer is high enough.

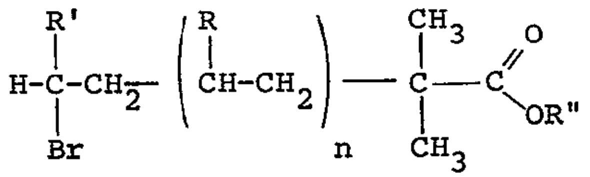
Ozonolysis of the dehydrobrominated telomers is also quantitative, and if a reactive solvent medium such as $CCl_4$/Acetic acid is used to carry out the ozone addition, subsequent problems of decomposing inert polymeric peroxides do not arise. Under these conditions, performic acid workup gives a high conversion of ozonide to carboxylic acids.

Part of the problem of obtaining a functionality as high as the particular sample will allow, is traceable to the *n*-butanol used for the dehydrobrominations. Incomplete removal of *n*-butanol, during the steam distillation used in the workup, allows subsequent esterification of some of the carboxyl groups after acidification. This gives a low COOH content, although an additional saponification step was shown to recover most of the COOH groups in a usable form.

We have recently conducted "melt" dehydrobrominations in which no solvent at all is used. In these reactions, aqueous NaOH or KOH is added to the well stirred liquid telomer at 250°C. The water flashes off and is swept away by a nitrogen purge, leaving the caustic in a highly divided solid state. Under these conditions, dehydrobromination reactions and saponification reactions are rapid and complete. Thirty minutes normally suffices to dehydrobominate a telomer sample to the point that a negative Beilstein test is obtained on the recovered product. Recovery is also greatly simplified and much more easily applied to a large scale process. We will report details of this method in subsequent reports as it is applied to the newer telomer samples.

## I. Ethylene/Neohexene Telomer Reaction Studies: Dehydrobromination

All of the following results were obtained for ethylene/neohexene telomers where the telogens used were α-bromoisobutyric acid and its *t*-butyl ester. The structure of these telomers is given by the formula on the following page:



$$H-\underset{Br}{\overset{R'}{C}}-CH_2-\left(\overset{R}{C}H-CH_2\right)_n-\underset{CH_3}{\overset{CH_3}{C}}-C\overset{O}{\underset{OR''}{\diagdown}}$$

where R is H or t-butyl
R' is predominantly t-butyl
R" is H, t-butyl, or methyl

Our first dehydrobromination procedure consisted of refluxing the telomer in a concentrated solution of KOH in n-butanol (100 g. per 500 ml. of solvent). The butanol was then removed by steam distillation and the product recovered by acidification with acetic acid and extraction into hexane or heptane, followed by evaporation to give the dehydrobrominated copolymer. This procedure satisfactorily eliminated all of the terminal halogen and gave a product with terminal double bonds. The terminal ester groups from the telogen or initiator were also saponified and converted to COOH.

This procedure, however, had a few drawbacks:

1) An inert atmosphere was necessary to avoid dark colored products, presumably arising from butanol oxidation.

2) Removal of all traces of butanol solvent was required prior to acidification and workup. This was to avoid re-esterfication of the terminal COOH groups introduced by the telogen or initiator.

3) Small amounts of vinylidene type double bonds resulted from the dehydrobromination.

Since problems 1) and 2) resulted directly from the butanol used as the solvent and problem 3) might have been indirectly related to the solvent used, we conducted a series of experiments in which no butanol was used in most of the trials. The conditions used are summarized below:

a) Base used: potassium acetate
Solvent used: molten potassium acetate
Temperature: 300°C

In this procedure the telomer is added to a flask containing molten potassium acetate at 300°C. For 3 g. of telomer, 50 g. of KOAc was used. The resulting solution was stirred under an inert atmosphere for 10 minutes and then allowed to cool. The solid reaction mixture was then taken up in water, made acidic with acetic acid and the telomer recovered by extraction with heptane.

b) Base used: potassium hydroxide
Solvent used: n-butanol
Temperature: 117°C, reflux

This is the old procedure, previously discussed, with steam distillation used to completely remove the butanol upon workup.

c) Base used: sodium hydroxide
Solvent used: none
Temperature: 250°C

In this procedure the telomer is heated to between 150 and 200°C under a stream of nitrogen, and an aqueous solution of a 2 to 3-fold amount (based upon total $Br^-$ and -COOR equivalents in the telomer sample) of sodium hydroxide is added dropwise with stirring. After the addition is complete and all water has been driven off, the temperature is raised to 250°C and kept there for 10 minutes. Workup as in (a).

d) Base used: potassium hydroxide
Solvent used: none
Temperature: 300°C

The same sequence of operations as in (c).

e) Base used: potassium *t*-butoxide
Solvent used: toluene
Temperature: 110°C, reflux

In this procedure the telomer is refluxed for 65 hours under an inert atmosphere in a toluene solution containing a 2-fold amount (based upon total equivalents) $Br^{\ominus}$

and -COOH present in the telomer) of potassium t-butoxide, and the resulting aqueous suspension of the copolymer is acidified with acetic acid and the product is recovered by heptane extraction.

The products were recovered from all of these procedures in essentially quantitative yield as slightly cloudy light amber oils, giving a negative Beilstein test. Double bond formation was shown by the appearance of olefinic proton signals in the N.M.R. Specta as well as the characteristic hydrogen-carbon bond deformation bands in fingerprint region of the infrared spectra. Strong absorption near 970 $cm^{-1}$ showed the presence of CH=CH (trans), and a much weaker absorption near 890 $cm^{-1}$ showed the presence of $C=CH_2$ (vinylidene). The latter absorption was much more apparent in the spectra of products prepared with method "a" or "b".

Considering only the yield (nearly quantitative) and the residual halogen content (negative Beilstein test) of the final product, all four procedures gave equivalent results. However, the distribution of double bond types produced was different in each of the procedures evaluated. We observed an interesting correlation between the type of C=C functionality introduced and the polarity of the reaction medium. Table XLVII shows the results we obtained when the products from the various dehydrobromination procedures were analyzed for double bond content by infrared spectroscopy.*

The vinyl content in all the examples shown can only arise from the loss of HBr by β-elimination from an ethylene end residue:

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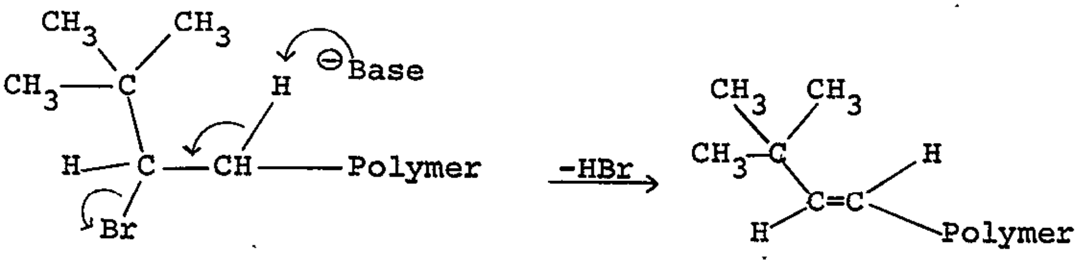
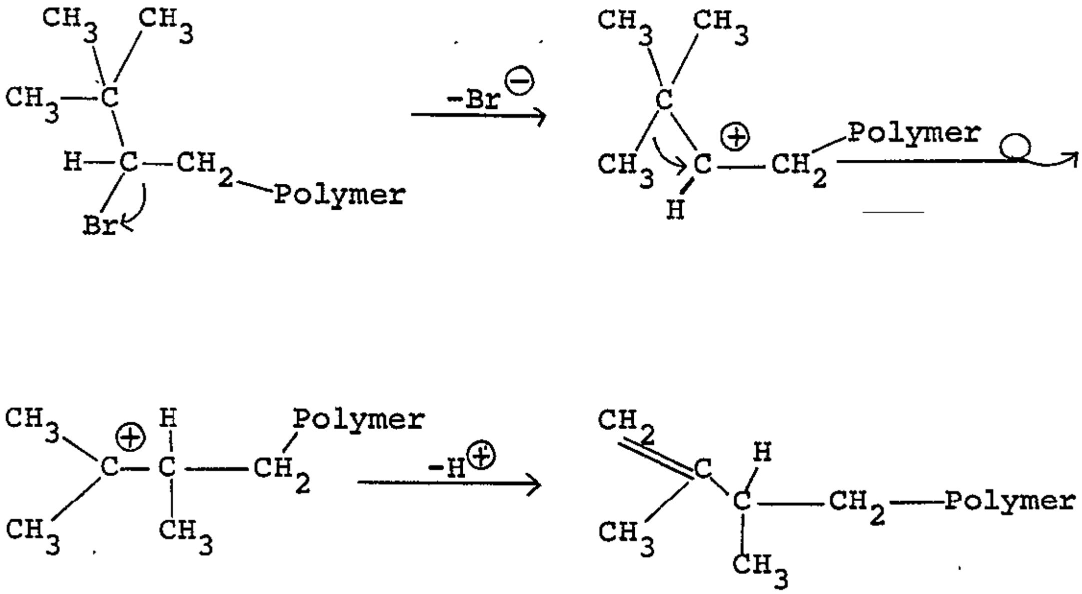
* See Part 10, Section G for the method which was used in this analysis.

whereas, the vinylidene and the trans-internal double bonds can only arise from elimination of HBr from a neohexene residue. The trans-internal result from the β-elimination reaction which we have discussed in previous reports:



The vinylidene double bonds probably result from a unimolecular dissociation, followed by a carbonium ion rearrangement:



The carbonium ion formation is favored in highly polar reaction media which can support charge separation. Once formed, the neopentyl carbonium ion undergoes a facile 1, 2 methyl migration leading to the more stable tertiary carbonium ion, which in turn loses a proton to give the vinylidene functional group.

Our experiments are in accord with this generalization in that the greatest amount of vinylidene is formed in the highly polar molten potassium acetate medium of method "a". In methods "c", "d" and "e" the reaction media are non-polar and much less vinylidene is formed. Method "b" is intermediate in this respect.

Since vinylidene endgroups lead to methyl ketone functional groups upon ozonolysis, a subsequent oxidation step (using, for example, sodium hypobromite) is required following procedures "a" and "b" to obtain the highest possible COOH functionality. Because of this we favor the latter two methods. Method "d" is especially attractive since no solvent is required, and since a complete reaction is obtained in very short reaction times.

## TABLE XLVII

## INFRARED ANALYSIS FOR DOUBLE BOND TYPE

| Telomer Sample | Dehydrobromination Procedure Used | Percent of Total Double Bonds |  |  | Trans/Vinylidene |
|---|---|---|---|---|---|
|  |  | Vinyl | Vinylidene | *Trans*-internal |  |
| 25-EMS-88 | a) Molten KOAc | 3 | 28 | 69 | 2.5 |
| 25-EMS-22 | b) KOH/Butanol | 4 | 23 | 73 | 3.2 |
| 25-EMS-40 | c) NaOH/250°C No Solvent | 4 | 13 | 83 | 6.4 |
| 8725-35-1 | d) KOH/300°C No Solvent | 0 | 11 | 89 | 8.1 |
| 25-EMS-88 | e) K*t*BuO/Toluene | 10 | 1 | 89 | 89 |

# V. TECHNICAL DISCUSSION CONT'D, PART 9

## ETHYLENE COPOLYMERS WITH OTHER α-OLEFINS

### Contents

Page

A. Ethylene/Propylene Telomers as Saturated Amorphous Binder Precursors

# PART 9

# ETHYLENE COPOLYMERS WITH OTHER α-OLEFINS

## A. Ethylene/Propylene Telomers as Saturated Amorphous Binder Precursors

### 1. Preparation

At the beginning of this program, the scope of our research effort was restricted to the synthesis and evaluation of copolymers of ethylene with neohexene as saturated hydrocarbon binder precursors. An olefinic comonomer is necessary to prevent crystallization of the ethylene units in the polymer backbone, which leads to solid waxes, useless as propellant binders. Neohexene was the most attractive choice of the possible α-olefin comonomers because it contains no allylic hydrogen atoms. Other α-olefins, such as propylene or butene-1 were not seriously considered at the beginning of this program.

At that point we depended upon recombination of growing polymer radicals with initiator radicals (present in much higher than normal "catalytic" amounts) to provide functional groups upon the chain ends. The deleterious effect of chain transfer to comonomer upon the functionality of the product was to be avoided if at all possible.

More recently however, we have been using extremely reactive chain transfer agents (telogens) to place the functional groups upon the chain ends. These telogens have an active halogen atom which is much more readily abstracted than an allylic hydrogen atom. In this environment, productive chain transfer, i.e., chain transfer leading to usable functional groups, may be expected to compete with chain transfer to monomer to such an extent that a product of useful functionality can be obtained.

To test out this hypothesis we tried a few small batch telomerizations of ethylene with propylene in which bromo-trichloromethane was used as the telogen.*

Telomerization runs 24-EMS-134 and 136 were made using ethylene/propylene comonomers with $BrCCl_3$ telogen and dimethyl α,α'-azobisisobutyrate (DMAB) as initiator. The production and analytical data are summarized in Tables XLVIII and IL. Functionality was determined from the halogen analyses and the molecular weight.

Our choice of telogen concentration was too high in these initial runs and telomers of very low molecular weight resulted. The total halogen functionalities were high however, 2.31 and 1.84 groups per molecule, and the penetration temperatures were far lower than any previously encountered in this program, -100 and -95°C.

These results encouraged us to try a series of continuous telomerizations at lower effective concentration of telogen. We also substituted the more useful telogen α-bromoisobutyric acid or its t-butyl ester in place of the $BrCCl_3$. The production and analytical data are given in Tables L and LI.

The first three runs, 25-EMS-103, 104 and 105, were made in the Unit I reactor using α-bromoisobutyric acid telogen. These runs were made at 20,000 psi pressure, the upper limit of this reactor. Holdup time was varied by using different feed rates at the same pressure. In these runs we found that slightly higher production rates are obtained at the expence of lower overall conversion if high feed rates are used. This is illustrated by run 25-EMS-103 in which a production rate of 201

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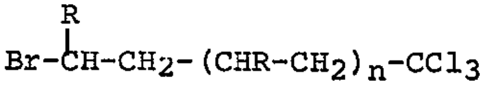
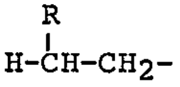
* When $BrCCl_3$ is the telogen, the growing polymer radical abstracts a bromine to give a bromide terminated chain and a trichloromethyl radical which can initiate another polymer chain. The telomer which results has the structure:

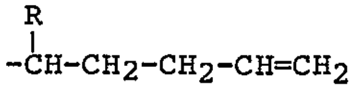


$$Br-\overset{R}{\overset{|}{C}}H-CH_2-(CHR-CH_2)_n-CCl_3$$

To the extent that chain transfer to propylene can also occur, the following telomer end groups are also possible:



and



$$H-\overset{R}{\overset{|}{C}}H-CH_2- \quad \text{and} \quad -\overset{R}{\overset{|}{C}}H-CH_2-CH_2-CH=CH_2$$

The first of these is of no value as a functional group, however the vinyl end group is a potential precursor to a COOH group.

grams of telomer per hour was obtained at 2.26% conversion of monomers. At this rate, over 3 kilos of telomer can be produced in a single run of three eight hour shifts (allowing ample time for start-up and shut-down operations).

The next two runs, 25-EMS-106 and 27-EMS-19, were also made in the Unit I reactor at 20,000 psi, but using the t-butyl ester telogen. The conditions used were very similar to those chosen for run #25-EMS-104, and the productivity obtained was nearly identical. In this respect, the two telogens are interchangeable. The α-bromo ester telogen is less active as a chain transfer agent, however, and as a result the products from run 25-EMS-106 and 27-EMS-19 have higher molecular weights than 25-EMS-104, even though the molar ratio of telogen to monomers was the same, .0015.

The last ethylene/propylene telomerization run, 27-EMS-34, was made in the recently set up Unit II reactor, operating at 35,000 psi. A lower molar ratio of telogen to monomers was used in this run to compensate for the higher propagation rate at the higher pressure so as to obtain the same target molecular weight, near 1000 g/mole. The higher pressure also had a beneficial effect upon the productivity. 4.56% conversion was obtained at a rate of 122 g. telomer per hour, the highest of the whole series.

## 2. Physical Properties

The telomers produced with α-bromoisobutyric acid telogen were amber colored, pourable oils (the color is a peculiarity of this particular telogen, and may be due to HBr loss from the telogen itself - addition of a trace of alkali causes the color to disappear). When the t-butyl ester of α-bromoisobutyric acid was used instead the telomers obtaind had a light straw color.

Two important conclusions can be drawn from the physical property data given in Table LI:

a) The Brookfield viscosity of the carboxyl terminated ethylene/propylene telomers is significantly lower than that of other saturated carboxyl terminated binders at comparable molecular weights.

b) The very low penetration temperatures suggest that cured binders prepared from ethylene/propylene carboxyl terminated liquids will have excellent low temperature properties.

## TABLE XLVIII

### ETHYLENE/PROPYLENE TELOMERS

| Batch Run # | 24-EMS-134 | 24-EMS-136 |
|---|---|---|
| Initial Charge | | |
| $BrCCl_3$, gms. | 2.72 | 3.42 |
| Solvent, gms. | 11.4 | 14.0 |
| AlBN, gms. | 0.1 | 0.13 |
| Ethylene, gms. | 330 | 384 |
| Propylene, gms. | 420 | 528 |
| Fed During Reaction | | |
| $BrCCl_3$, gms. | 41.1 | 30.8 |
| Solvent, gms. | 172.2 | 129.5 |
| AlBN, gms. | 1.91 | 1.14 |
| Reaction Conditions | | |
| Temp., °C | 90 | 90 |
| Pressure, mpsi | | |
| Initial | 4.20 | 10.40 |
| Maximum | 9.25 | 15.00 |
| Time, hrs. | 4.25 | 6.42 |
| Productivity | | |
| Yield, gms. | 35 | 49 |
| Conversion, % | 4.85 | 5.48 |
| Rate, %/M. | 1.14 | .85 |

TABLE IL

ETHYLENE/PROPYLENE TELOMERS

| Run # | 24-EMS-134 | 24-EMS-136 |
|---|---|---|
| Physical Properties | | |
| Brookfield Viscosity, cps | - | 163 |
| Specific Viscosity, 80°C | .009 | .011 |
| Vitrification Temperature | below -80°C | below -80°C |
| Penetration Temperature | -100°C | -95°C |
| Analytical Data | | |
| Molecular Weight* | 343 | 421 |
| Bromine, Wt. %† | 27.07 | 17.94 |
| Chlorine, Wt. %† | 35.76 | 22.58 |
| Functionality | | |
| Bromine (Br) | 1.16 | 0.95 |
| Chlorine ($CCl_3$) | 1.15 | 0.89 |

* By vapor phase osmometry in benzene.

† By Paar bomb combustion followed by potentiometric titration with silver nitrate.

## TABLE L

## ETHYLENE/PROPYLENE TELOMERS

| Continuous Run # 25-EMS-<br>Continuous Unit # | 103<br>I | 104<br>I | 105<br>I | 106<br>I | 27-EMS-19(d)<br>I | 34<br>II |
|---|---|---|---|---|---|---|
| **Charge, Wt. % on Total** | | | | | | |
| Benzene | 10.53 | → | → | 11.49 | → | 10.89 |
| Ethylene | 47.87 | → | → | 44.83 | → | 46.29 |
| Propylene | 40.80 | → | → | 42.56(c) | 42.56(d) | 40.84 |
| Telogen | .66(d) | → | → | .96(b) | → | 1.82 |
| DMAB | .14 | → | → | .15 | → | .14 |
| Mole Ratio, Telogen/Monomers | .0015 | → | → | → | → | .0031 |
| Vapor Pressure of Feed, 25°C, psi | 480 | 540 | 575 | 540 | 510 | 540 |
| Wt. Feed Used, gms. | 5345 | 5502 | 2185 | 7056 | 6539 | 7080 |
| **Reaction Conditions** | | | | | | |
| Temp., °C | 123 | 110 | 100 | 110 | 110 | 105-107 |
| Pressure, mpsi | 20 | → | → | → | → | 35 |
| Nominal Holdup Time, min. | 5.1 | 13.2 | 29.4 | 13.9 | 15.9 | 18.8 |
| Avg. Feed Rate, gms/hr. | 12,070 | 3377 | 1689 | 3377 | 3269 | 3078 |
| **Productivity** | | | | | | |
| Yield, gms. | 107 | 136 | 73 | 175 | 172 | 281 |
| Conversion, % | 2.26 | 2.79 | 2.63 | 2.80 | 2.97 | 4.56 |
| Rate, g/hr. | 201 | 97.1 | 41.8 | 93.1 | 86.0 | 122 |

(a) α-bromoisobutyric acid

(b) t-butyl -bromoisobutyrate

(c) Propylene used contained ~25% impurities, mostly propane.

(d) Repeat of 106. Pure propylene used.

## TABLE LI

## ETHYLENE/PROPYLENE TELOMERS

| Continuous Run # 25-EMS- | 103 | 104 | 105 | 106 | 27-EMS-19 | 34 |
|---|---|---|---|---|---|---|
| **Physical Properties** | | | | | | |
| Brookfield Viscosity, cps | 2805 | 2912 | 3156 | 6830 | 5620 | 5000 |
| Specific Viscosity, 80°C | - | - | - | - | .031 | .033 |
| Penetration Temperature, °C | -74 | -69 | -73 | -66 | - | - |
| **Analytical Data** | | | | | | |
| Molecular Weight | 744(a) | 775(a) | 684(a) | 1189(b) | 1190(b) | 1074(b) |
| Bromine, Wt. % | 7.50 | 6.53 | 7.73 | 3.84 | 3.96 | 5.49 |
| Neutralization Equiv. | 1137 | 1156 | 960 | - | - | - |
| **Functionality** | | | | | | |
| Bromine (Br) | .70 | .63 | .66 | .57 | .59 | .74 |
| Carboxyl (COOH) | .65 | .67 | .71 | - | - | - |

(a) By V.P.O. in THF

(b) By V.P.O. in Benzene

Figure 7 shows the room temperature Brookfield viscosities of saturated carboxyl terminated liquid binders plotted as a function of their molecular weights (a log-log plot was used for convenience and to more nearly linearize the data). The data for carboxyl terminated ethylene/neohexene telomers is that which we reported in our previous Quarterly Report for telomers prepared in the Unit I continuous stirred autoclave reactor at 20,000 psi using α-bromoisobutyric acid telogen (CTAC).

The data for hydrogenated carboxyl terminated polybutadiene was taken from Figure 1, page 22, of the final report (February 1966) by D. E. Johnson and A. J. DeMilo on Contract AF04(611)-10386 for the Air Force Rocket Propulsion Laboratory at Edwards, California. These saturated binders contained ethyl branches resulting from the 1,2-vinyl content (around 30% of the total unsaturation) of the original polybutadiene.

The data for ethylene/propylene telomers is taken from Tables IL and LI of the present report. Three of the samples have COOH end groups and may be compared with the other carboxyl terminated saturated binders.

The lower viscosity of the ethylene/propylene telomers is probably due to the decreased bulk of the methyl branches in the new telomers as compared with the ethyl branches in hydrogenated carboxyl terminated polybutadienes, or the t-butyl branches in ethylene/neohexene copolymers. This lower viscosity should facilitate propellant formulation and casting of grains at lower temperatures than are conventionally required.

Figure 8 shows the results obtained when the penetration temperatures of the ethylene/propylene telomers were plotted as a function of the reciprocal of the molecular weight. A reasonably good linear fit was obtained, which when extrapolated to $1/\overline{M}_n=0$, gave a penetration temperature near -50°C at infinite molecular weight. At $\overline{M}_n=1000$, $T_p$ is -67°C.

### 3. Functionality

The high functionalities which were achieved in the low molecular weight telomers of $BrCCl_3$ (see Table IL) have not yet been obtained in the higher molecular weight telomers of α-bromoisobutyric acid or its t-butyl ester (see Table LI). The lower telogen concentration employed in the more recent runs was selected in order to attain a higher molecular weight. Under these conditions, chain transfer to propylene becomes more probable as the telogen concentration is reduced.

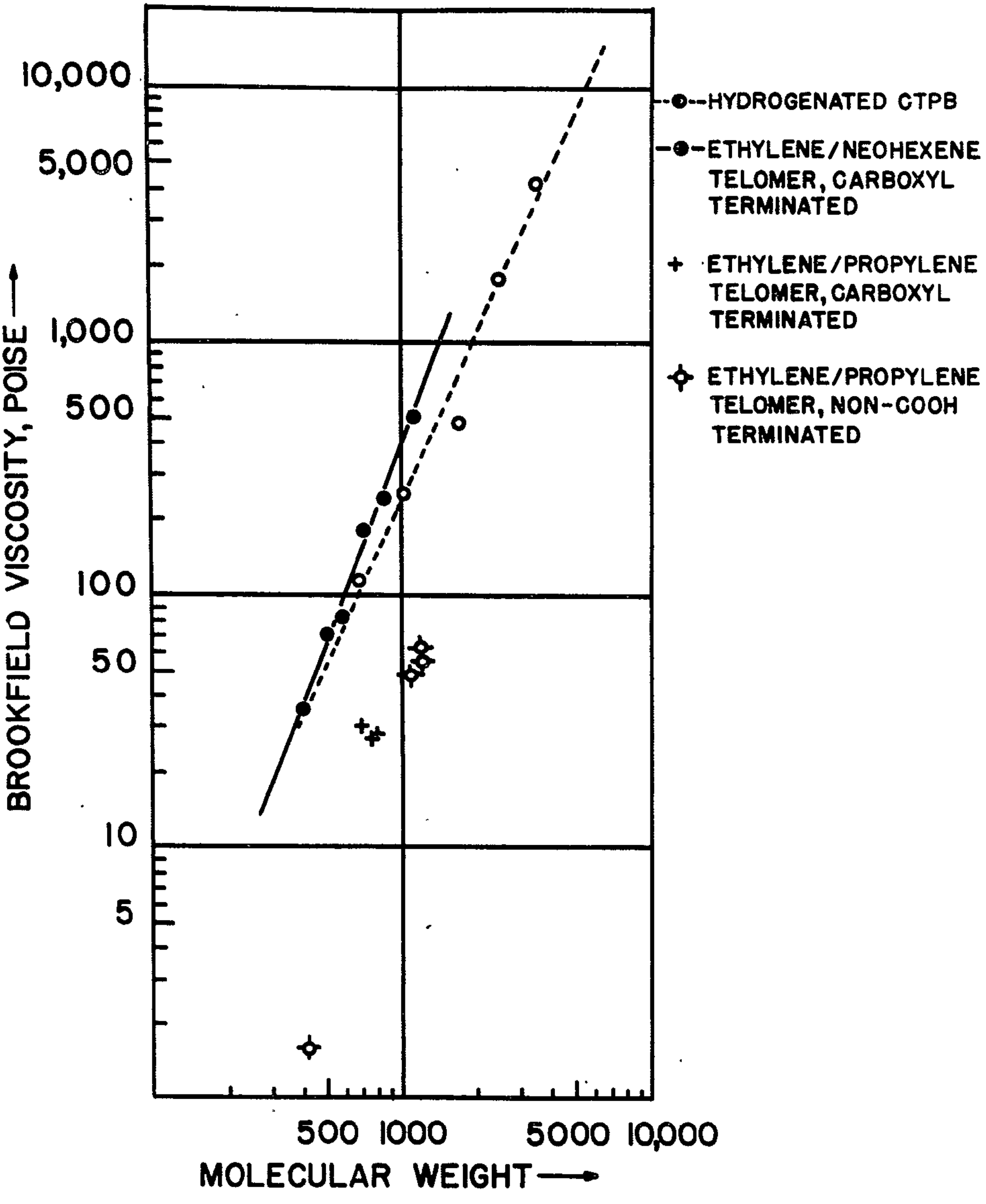


FIGURE 7. BROOKFIELD VISCOSITY—MOLECULAR WEIGHT RELATIONSHIPS

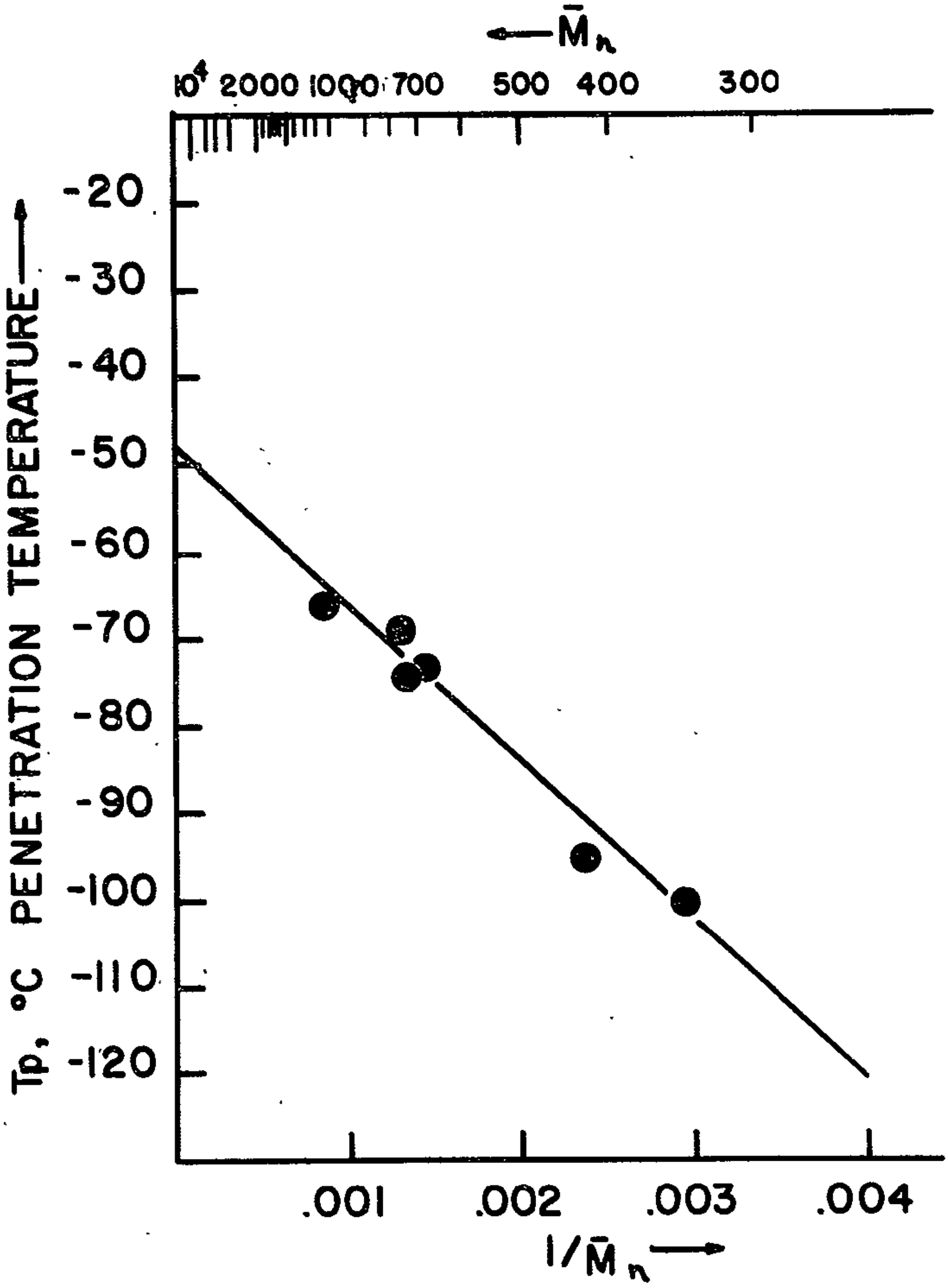


FIGURE 8. MOLECULAR WEIGHT DEPENDENCE OF THE PENETRATION TEMPERATURE OF ETHYLENE/PROPYLENE TELOMERS

An exception to this trend is found in run 27-EMS-34. This is the first continuous run in the Unit II reactor. t-Butyl α-bromoisobutyrate was used as the telogen and the reactor internal pressure was 35,000 psi. The telomer produced in this run had the highest functionality in the whole series of continuous runs: 0.74 bromine per molecule.

This higher functionality may be directly attributed to the higher reactor pressure. This leads to a higher propagation rate and thus requires that the telogen to monomer molar ratio be increased from .0015 to .0031 in order to control the molecular weight. At this higher telogen concentration, relatively less chain transfer to propylene monomer could occur, hence the higher functionality.

Telomerization at very high reactor pressures is undoubtedly the best means available to us to obtain higher functionality and productivity in the preparation of ethylene/propylene copolymers.

### 4. Chemical Modification - Br to COOH

Since the new ethylene/propylene telomers have only recently been prepared and characterized, chemical modification studies directed toward conversion of the bromine functionality into carboxyl functionality are just beginning. However, some experiments have been completed which point out the greater reactivity toward displacement reactions of the terminal bromide in the ethylene/propylene telomers.

Dehydrobromination of telomer samples 25-EMS-103, 104 and 105 using NaOH in the polymer melt at 250°C led to products containing no bromine (negative Beilstein test) after short reaction periods (15 minutes). However, judging from the infrared spectra of the products, less than the theoretical double bond content was produced.

Ozonolysis of the dehydrobrominated telomers in acetic acid/carbon tetrachloride solution at 0°C, followed by oxidative workup using peracetic/performic acid mixtures gave products containing no residual unsaturation and having enhanced COOH contents.

To illustrate these findings with a specific example, telomer sample 25-EMS-104 originally had 0.63 Br per molecule and .67 COOH per molecule. Oxygen analysis indicates 0.83 $O_2$ per molecule, the difference being the ester groups derived from the initiator. The total functionality is thus 1.46. After dehydrobromination, ozonolysis, and oxidation a product was obtained having a molecular weight of 740 and a neutralization equivalent of 588 and hence containing 1.26 COOH per molecule. This represents a net gain of .43 COOH group per molecule, about 2/3 the expected amount.

The infrared spectrum of the product exhibited both carboxylic acid and ester carbonyl bands. However, after saponification, no significant increase in COOH content was observed as determined by titration. This suggests that the ester groups seen in the infrared spectrum were acetate or formate groups derived from terminal hydroxyl groups. These, in turn, were most probably the result of a direct displacement of bromide by hydroxyl during the dehydrobromination step. This reaction was not significant in the dehydrobromination of ethylene/neohexene telomers due to the highly hindered nature of the secondary neopentyl bromide end groups.

When molten potassium acetate was used, both as the solvent and the base, for the dehydrobromination reaction (method a in Part B of this report) more evidence was provided which pointed out the greater reactivity of the terminal halogen toward displacement. Strong acetate absorptions and weak c=c absorptions were present in the infrared spectrum of the (Beilstein negative) product resulting from molten potassium acetate treatment of 25-EMS-104. These show that nucleophilic displacement of bromide can readily occur in this system.

In view of the above results, several reactions, which failed when they were applied to ethylene/neohexene telomers due to the very hindered nature of the terminal halogen may become feasible for the ethylene/propylene telomers:

1) $\mathrm{RO_2C{-}CH_2^{\ominus}}$ displacement of $\mathrm{Br^{\ominus}}$
2) $\mathrm{S}^{\textcircled{=}}$ coupling, displacing 2 $\mathrm{Br^{\ominus}}$
3) $\mathrm{CN^{\ominus}}$ displacement of $\mathrm{Br^{\ominus}}$, followed by hydrolysis to COOH.

The greater reactivity of the halogen end groups in the new telomers may make the above reactions useful for changing $\mathrm{Br^{\ominus}}$ to COOH in the ethylene/propylene telomers.

## B. Ethylene/Propylene Telomerizations in the Continuous Reactor

The Unit II continuous stirred autoclave reactor rated at 35,000 psi pressure was used to prepare two more ethylene/propylene telomers, 27-EMS-40 and -56. The production and analytic data for these runs are summarized in Tables LII and LIII along with the run 27-EMS-34 previously reported.

In run 40 the methyl ester telogen was used, giving .80 bromines per molecule, the highest yet attained for a telomer containing propylene. In run 56, a higher concentration of propylene was used in the feed in an attempt to incorporate more propylene into the telomer. The resulting product had somewhat less haze than the earlier runs, however the functionality was lower. This may be an indication that more chain transfer to propylene monomer occurred at the higher propylene concentration used in this run.

## TABLE LII

## ETHYLENE/PROPYLENE TELOMERS

| Continuous Run # 27-EMS- | 34 | 40 | 56 |
|---|---|---|---|
| Charge, Wt. % on Total | | | |
| $C_2H_4$ | 46.29 | 46.94 | 44.20 |
| $C_3H_6$ | 40.84 | 40.63 | 42.90 |
| Telogen | 1.82[a] | 1.47[b] | 1.82[a] |
| DMAB | 0.14 | .14 | 0.14 |
| Benzene | 10.89 | 10.82 | 10.90 |
| Mole Ratio, Telogen/Monomers | 0.0031 | 0.0031 | 0.00315 |
| R.T. Vapor Pressure, psig | 540 | 600 | 507 |
| Wt. Feed Used, gms. | 7080 | 6711 | 6788 |
| Reaction Conditions | | | |
| Internal Temp. °C | 105-107 | 108-114 | 109-119 |
| Pressure, mpsi | 35 ± 1 | 35 ± 1 | 35 ± 0.4 |
| Nominal Holdup, Min. | 18.8 | 14.65 | 8.28 |
| Ave. Feed Rate, gms./hr. | 3078 | 3948 | 7022 |
| Productivity | | | |
| Yield, gms. | 281 | 264 | 145 |
| Conversion, % | 4.56 | 4.52 | 2.45 |
| Rate, gm/hr. | 122 | 155.3 | 149.9 |
| Rate, #/cu.ft./hr. | 5.1 | 6.5 | 6.3 |

[a] *t*-Butyl α-Bromoisobutyrate

[b] Methyl α-Bromoisobutyrate

TABLE LIII

CHARACTERIZATION OF ETHYLENE/PROPYLENE TELOMERS

| Continuous Run # 27-EMS- | 34 | 40 | 56 |
|---|---|---|---|
| Physical Properties | | | |
| Brookfield Viscosity, cps | $5000^{24^\circ C}$ | $11,600^{22^\circ C}$ | $4030^{23}$ |
| Specific Viscosity, 80°C | .0326 | .0243 | 0.023 |
| Penetration Temperature, °C | -68 | -66 | -66 |
| Analytical Data | | | |
| Molecular Weight[a] | 1074 | 819 | 862 |
| Bromine, Wt. % | 5.49 | 7.81 | 5.68 |
| Ester Equivalent Wt.[b] | 1292 | 1145 | 1378 |
| Functionality | | | |
| Bromine | .74 | .80 | .61 |
| Ester | .83 | .72 | .63 |
| Total | 1.57 | 1.52 | 1.24 |

[a] By V.P.O. in Benzene

[b] By I.R. spectroscopy, with methyl pivalate as standard

## C. Other α-Olefin Comonomers

In the last quarterly report were discussed the lower values for the glass-transition temperature obtained in our liquid copolymers when propylene was incorporated into the copolymers in place of neohexene. Because of the lower glass transition temperature in homopolymers of the higher α-olefins (see table below), ethylene copolymers containing these olefins in place of propylene should in principle, have even lower values for Tg than those obtained with propylene.

| Olefin | Tg of Homopolymers* |
|---|---|
| Ethylene | -125°C |
| Propylene | - 20°C |
| Butene-1 | - 25°C |
| Pentene-1 | - 40°C |
| Hexene-1 | - 50°C |

* From "Polymer Handbook", Ed. by J. Brandrup and E. M. Immergut, Interscience, N. Y. (1966).

To test this possibility, three small batch runs were made in which butene-1, pentene-1 and hexene-1 were substituted for propylene as the comonomer. Production data is given in Table LIX. Comparing the Tp values of -85, -79 and -81 with the values for Tp obtained on the ethylene/neohexene and the ethylene/propylene runs done so far, we find that the three values are roughly ten degrees lower than the ethylene propylene telomer of comparable molecular weight and twenty to thirty degrees lower than the comparable ethylene/neohexene telomers. Figure 9 illustrates this comparison.

These runs show that a significant advantage in low temperature properties can be realized using the other α-olefin comonomers, however the lower functionalities obtained in these trial runs are discouraging. As is probably the case with propylene, the limiting factor controlling the functionality with these α-olefin comonomers is chain transfer to monomer.

Further work in this area will be done if there is sufficient interest in the lower penetration temperatures obtainable with these comonomers.

## TABLE LIX

## ETHYLENE TELOMERS WITH OTHER α-OLEFINS

| Run # 27-EMS | 39 | 43 | 44 |
|---|---|---|---|
| Initial Charge | | | |
| Solvent, gms. | 14.3 | 13.2 | 13.3 |
| Telogen, gms.[a] | 1.4 | 1.3 | 1.2 |
| DMAB, gms. | .12 | .12 | .13 |
| α-Olefin | Butene-1 | Pentene-1 | Hexene-1 |
| α-Olefin, gms. | 436 | 499 | 570 |
| Ethylene, gms. | 383 | 348 | 340 |
| Fed During Run | | | |
| Telogen, gms. | 12.5 | 11.7 | 11.2 |
| Solvent, gms. | 237.0 | 136.9 | 126.7 |
| DMAB, gms. | 1.01 | 1.07 | 1.14 |
| Reaction Conditions | | | |
| Temp. °C | 90 | 90-91 | 90 |
| Pressure, mpsi | | | |
| Initial | 11.0 | 10.95 | 8.25 |
| Maximum | 17.3 | 19.0 | 16.75 |
| | 3.08 | 3.08 | 3.08 |
| Productivity | | | |
| Yield gms. | 5.0 | 20.0 | 15.0 |
| Conversion, % | 0.61 | 2.36 | 1.65 |
| Rate, % per hr. | 0.20 | 0.77 | 0.54 |
| Physical Properties | | | |
| Specific Viscosity, 80°C | .0131 | .0172 | .0152 |
| Tp, °C[b] | -85 | -79 | -81 |
| Analytical Data | | | |
| Molecular Weight[c] | 613 | 844 | 775 |
| Bromine, Wt. % | 4.72 | 5.98 | 7.69 |
| Functionality | | | |
| Bromine | .36 | .63 | .75 |

[a] t-Butyl α-Bromoisobutyrate

[b] By method discussed under "New Technology in last quarter's report.

[c] By V.P.O. in benzene.

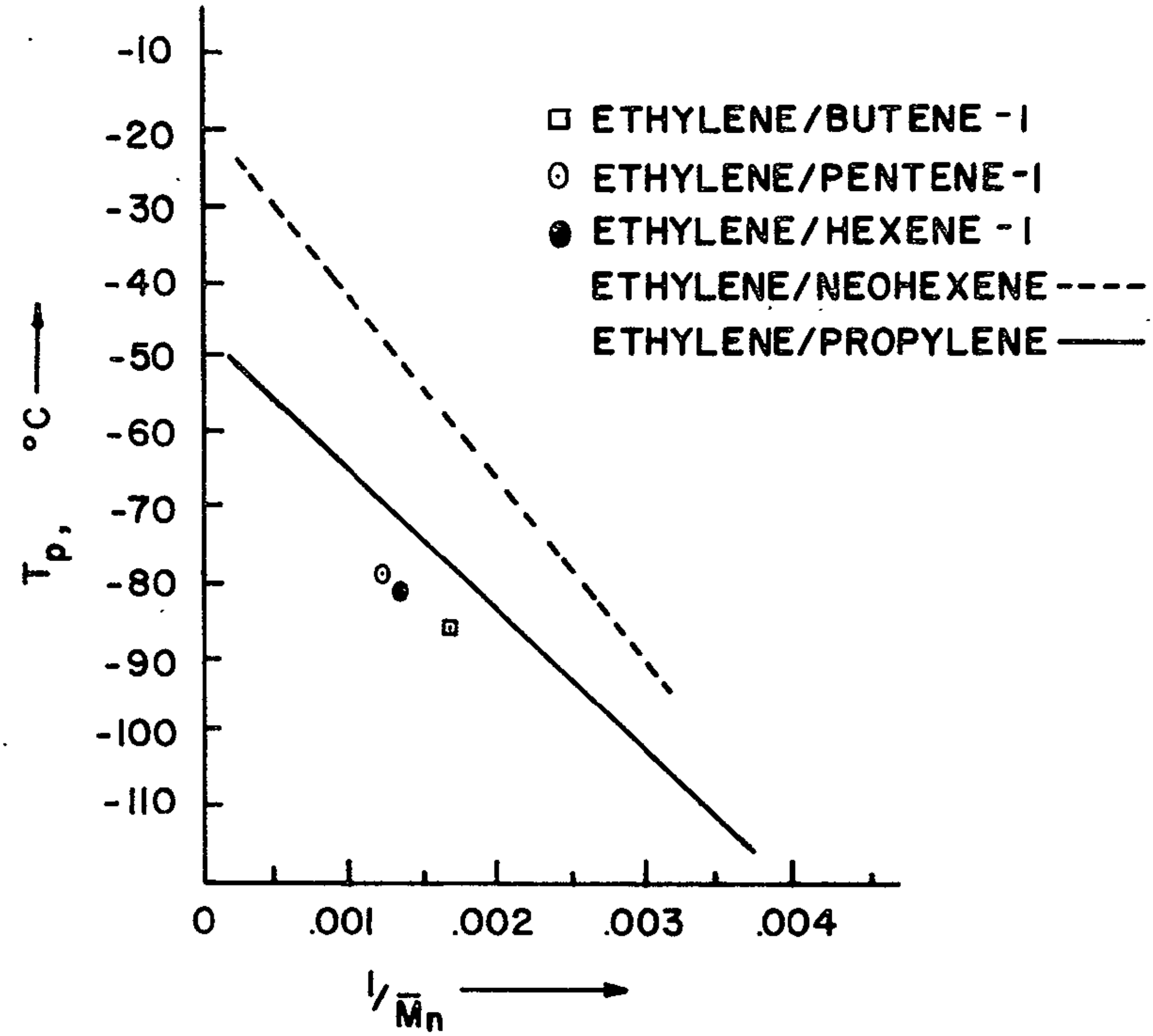


FIGURE 9

PENETRATION TEMPERATURES

OF ETHYLENE/OLEFIN TELOMERS

## V. TECHNICAL DISCUSSION CONT'D, PART 10

## ANALYTICAL METHODS

### Contents

Page

# PART 10

# ANALYTICAL METHODS

## A. Gas Chromatographic Analysis of Neohexene Monomer

Although we were given positive assurance by the vendor that the polymerization grade neohexene we have been using is very pure, it seemed prudent to verify this fact ourselves. The presence of certain impurities could result in chain transfer and lead to low carboxyl functionality in the prepolymer. Neohexene is one of thirteen isomers of hexene, (not counting cis-trans isomers) and is the only one which does not have allylic hydrogen atoms. The presence of any of these isomers would lead to chain transfer reactions which would have an adverse affect on functionality. Because of the possibility that one or more of these isomers might be formed from neohexene by isomerization during its manufacture, it was decided to examine neohexene using a high resolution gas chromatograph.

The thirteen isomers of hexene are listed in Table LX with their boiling points and their structural formulas. Neohexene is much lower in boiling point than the other isomers. Samples of five of these isomers were purchased covering the whole range of boiling points.

A Perkin-Elmer Model 226 gas chromatograph was used to analyze our neohexene as well as each of the five isomeric hexenes. Then a synthetic mixture of neohexene and the other five isomers was prepared and analyzed under the same conditions. The gas chromatograph was equipped with a 300 ft. long column of 0.01 inch I. D. stainless steel capillary tubing internally coated with Dow-Corning 550 silicone grease. The column was operated at 40°C under an inlet pressure of 15 psi of carrier gas. The column achieves a separation efficiency of 300,000 theoretical plates.

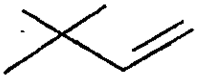
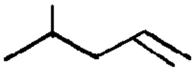
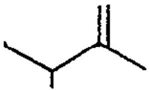
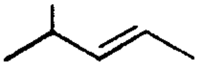
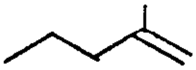
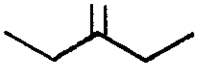
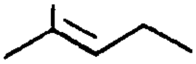
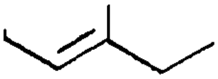
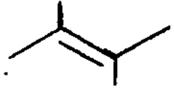
A chromatogram showing the purity of our polymerization grade neohexene is shown in top graph of Figure 10, (Appendix). The lower chromatogram is the result obtained when the synthetic mixture of six isomers was analyzed. Note the excellent resolution of the different isomers which are eluted from the column in order of their respective boiling points, neohexene first and 2,3 dimethyl butene-2 last.

Immediately following the elution of the neohexene peak in the upper chromatogram, the sensitivity of the detection system was increased by a factor of 500. Even at this great sensitivity, no other components other than neohexene were detectable. A peak of the order of two times the size of the random noise in the signal from the detector would represent only 70 parts per million of the injected sample.

From these studies we have concluded that the neohexene we are using is not contributing any impurities of any consequence to the polymerization system.

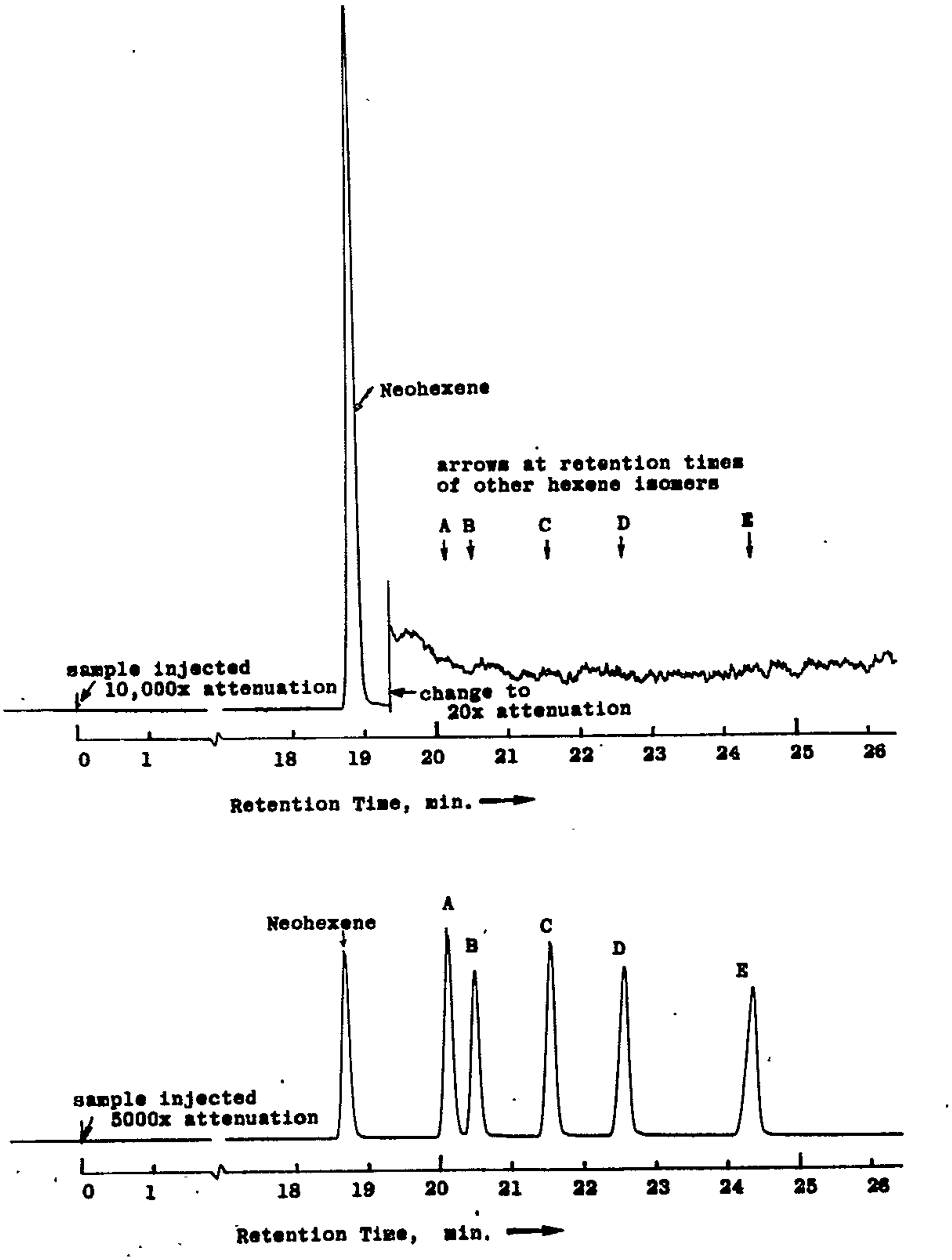
## TABLE LX

## BOILING POINTS AND STRUCTURAL FORMULAE OF HEXENE ISOMERS

| Name | °C Boiling Point | Structural Formula |
|---|---|---|
| 3,3-Dimethylbutene-1<br>(Neohexene) | 41.2 |  |
| 4-Methylpentene-1 | 53.6 |  |
| 3-Methylpentene-1 | 53.6 |  (Sample A) |
| 2,3-Dimethylbutene-1 | 56.0 |  |
| 4-Methylpentene-2 | 57.7 |  (Sample B) |
| 2-Methylpentene-1 | 61.5 |  |
| Hexene-1 | 63.5 |  (Sample C) |
| 2-Ethylbutene-1 | 66.2 |  |
| 2-Methylpentene-2 | 67.2 |  (Sample D) |
| Hexene-3 | 67.5 |  |
| 3-Methylpentene-2 | 67.6 |  |
| Hexene-2 | 67.9 |  |
| 2,3-Dimethylbutene-2 | 73.0 |  (Sample E) |

## FIGURE 10

## GAS CHROMATOGRAPHIC ANALYSIS OF NEOHEXENE MONOMER

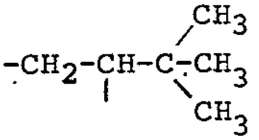


## B. NMR Measurement of Neohexene Level in Copolymer

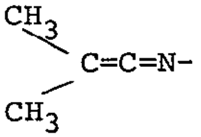
A method for analysis of comonomer ratio in ethylene/neohexene copolymers was needed to compare with the comonomer ratio in the charge to the reactor. This cannot be done by elemental analysis nor is infrared analysis suitable because of its need for reference standards. Nuclear magnetic resonance (NMR) spectroscopy offers a convenient solution to this problem. It is non-destructive, requires only a small sample and gives results independent of any external calibration since it literally counts protons. The requirements are that the sample be a liquid (or soluble in a convenient solvent) and that the protons on the species to be analysed be chemically different.

There are only four different groups which can be present in the ethylene-neohexene copolymers prepared with azobisisobutryonitrile. These are:

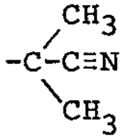
$-CH_2-CH_2-$ (from ethylene),



(from neohexene)

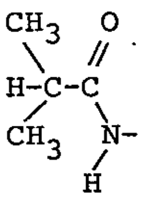


and

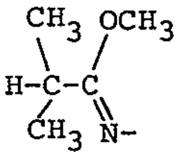


(both from initiator).

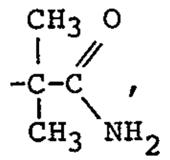
If any hydrolysis of end groups has occurred, additional groups such as:



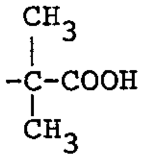
,



,



, or



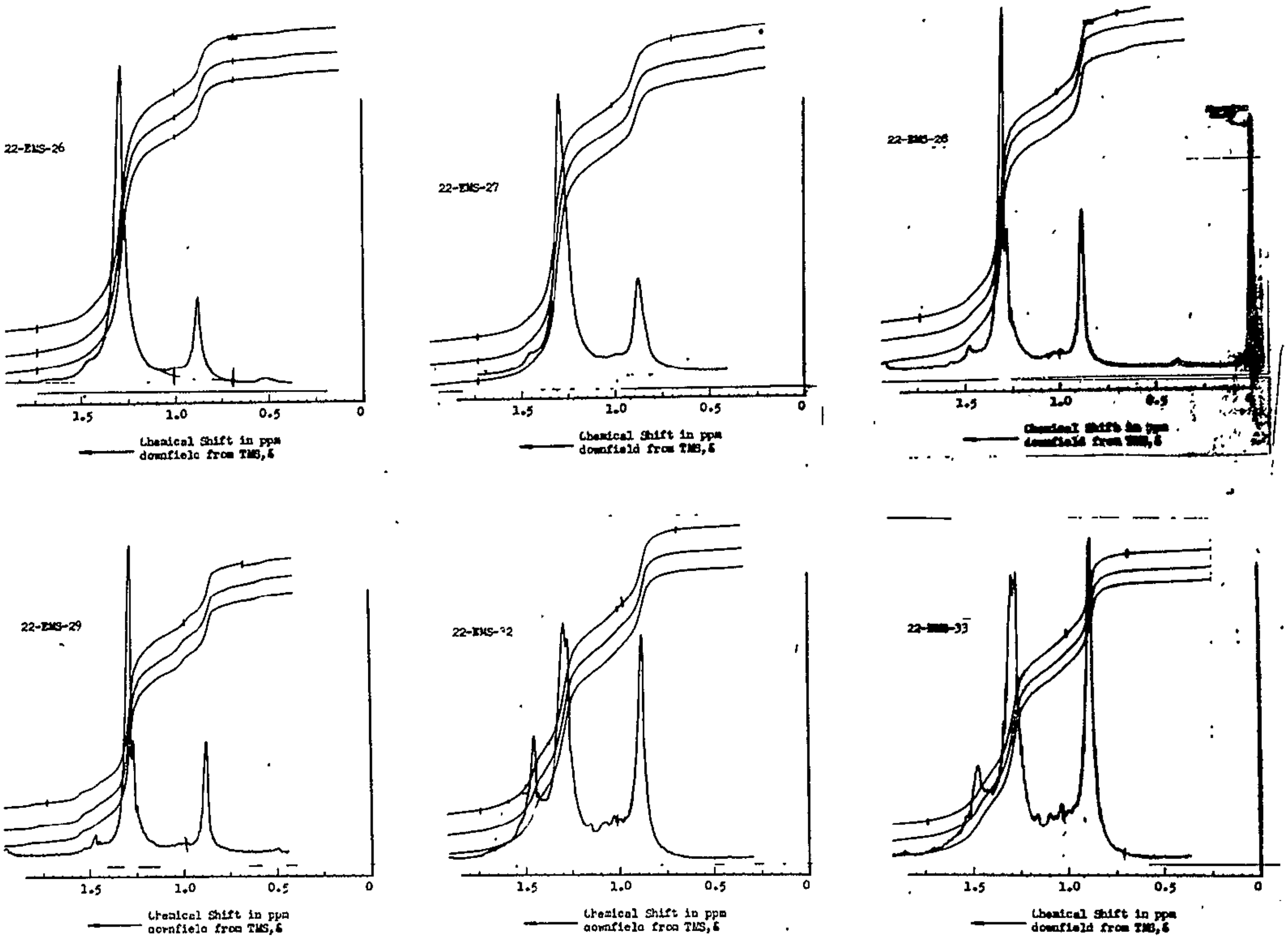
$-\overset{CH_3}{\underset{CH_3}{C}}-COOH$

could be present, but they should not be found in freshly prepared copolymer, and will be ignored for the present discussion.

The NMR spectra in Figure 11 were taken with a Varian A-60 spectrometer operating at a frequency of 60 megacycles per second, employing a sweep width of 250 cps. The samples used were those discussed in Part I, Section A, prepared to define the optimum Neohexene level required.

# FIGURE 11

# NMR SPECTRA OF ETHYLENE/NEOHEXENE COPOLYMERS



A broader region of the spectrum was scanned initially, but no low field protons (such as vinyl or aromatic) were found. The samples were dissolved in tetrachloroethylene and tetramethyl silane (TMS) was used as the internal standard. Field increases from left to right, and $\delta$, the chemical shift in parts per million downfield from TMS, is measured from right to left. Spectrum integrals are superimposed upon the spectra.

The high field peak at $\delta = 0.88$ ppm is immediately recognized as the resonance of the well shielded protons on the tert-butyl groups attached to the neohexene residues. The methylene protons from both ethylene and neohexene residues give rise to the broad peak centered at $\delta = 1.28$ ppm. The signal due to the methine protons of the neohexene residues is also hidden in this peak. The protons on the methyl groups of the initiator residues on the chain ends are deshielded by the presence of the electron withdrawing groups C=C=N and C≡N, and give rise to partially resolved peaks in the same region. In the spectra of the more fluid samples, a peak at 1.26 ppm is probably due to these groups. Tetramethylsuccinodinitrile, a initiator recombination product, gives rise to the peak at 1.44 ppm.

It is apparent that the only peak which is resolved from the rest of the spectrum enough to be separately integrated, is the one assigned to the tert-butyl protons of the neohexene residues. The fraction of the total spectrum area taken up by this peak is equal to the fraction of the total number of protons in the sample which are contributed by the tert-butyl groups. Let total area of the spectrum be "T" and the area of the 0.88 ppm peak be "A". Then 4A/3T is the fraction (the factor 4/3 arises because of the twelve protons in each neohexene residue; we have only "counted" the nine on the tert-butyl group) of all the protons in the sample which are attached to neohexene.

Because of the poor resolution of the low field peaks, additional information is needed to calculate the fraction of the protons on ethylene residues. This additional information comes from the nitrogen elemental analysis. Since all groups derived from the initiator have the formula ($C_4H_6N$), one can multiply the wt. % nitrogen in the sample by the gravimetric factor 4.85 and directly obtain the weight percent of initiator residues in the sample, both end groups and recombination products (these groups are the sole source of nitrogen in the sample):

Wt. % initiator residues = 4.85 wt. % nitrogen
Wt. % comonomer residues = 100 - 4.85 x wt. % nitrogen

These comonomer residues have the empirical formula $(CH_2)_n$. Therefore, every 14.03 grams of comonomer residues contains two moles of protons, or 0.142 moles H per gram of comonomers. Similarly, every 68.10 grams of initiator residue contains six moles of protons, i.e., 0.882 moles H per gram of initiator residue. Let $H_{co}$ represent the moles of protons on comonomer residues in 100 grams of sample and $H_{cat}$ represent the moles of protons on initiator residues in 100 grams of sample.

$$H_{co} = 0.142 \; \frac{\text{moles H}}{\text{gm. comonomer}} \; \text{x} \; (100-4.85 \; \text{x wt. \% N})$$

$$\frac{\text{gm. comonomer}}{\text{100 gm. sample}}$$

$$H_{init.} = 0.882 \; \frac{\text{moles H}}{\text{gm. initiator}} \; \text{x} \; (4.85 \; \text{x wt. \% N})$$

$$\frac{\text{gm. initiator}}{\text{100 gm. sample}}$$

"P", the fraction of all protons contributed to the total by the comonomer residues alone, is thus: $P = H_{co}/H_{co} + H_{init.})$.

Having corrected for the presence of the end groups, the fraction of all the protons in the sample which are on ethylene residues is simply, $P - 4A/3T$, and, taking into consideration the fact that ethylene has only four protons, while neohexene has twelve, the ethylene to neohexene comonomer ratio, R, is given by:

$$R = \frac{(P - 4A/3T)}{4} \div \frac{(4A/3T)}{12}$$

The results are summarized in Table LXI.

## TABLE LXI

## NMR ANALYSIS OF ETHYLENE - NEOHEXENE COPOLYMERS

| Sample | 4A/3T | % N | P | P-4A/3T | R, Ethylene To Neohexene Ratio |
|---|---|---|---|---|---|
| 22-EMS-26 | 0.257 | 1.93 | 0.940 | 0.683 | 8.0 |
| 22-EMS-27 | 0.296 | 2.28 | 0.930 | 0.634 | 6.4 |
| 22-EMS-28 | 0.332 | 2.64 | 0.915 | 0.583 | 5.3 |
| 22-EMS-29 | 0.344 | 2.84 | 0.908 | 0.564 | 4.9 |
| 22-EMS-32 | 0.362 | 6.79 | 0.767 | 0.405 | 3.4 |
| 22-EMS-33 | 0.403 | 7.06 | 0.756 | 0.353 | 2.6 |

## C. Molecular Weight Distribution by Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) is a very effective tool for fractionating mixtures of materials having different molecular sizes. It is especially useful as an analytic device for quantitatively determining molecular weight distributions in polymeric materials, but may also be used as a preparative device for obtaining small fractions having very narrow molecular weight distributions.

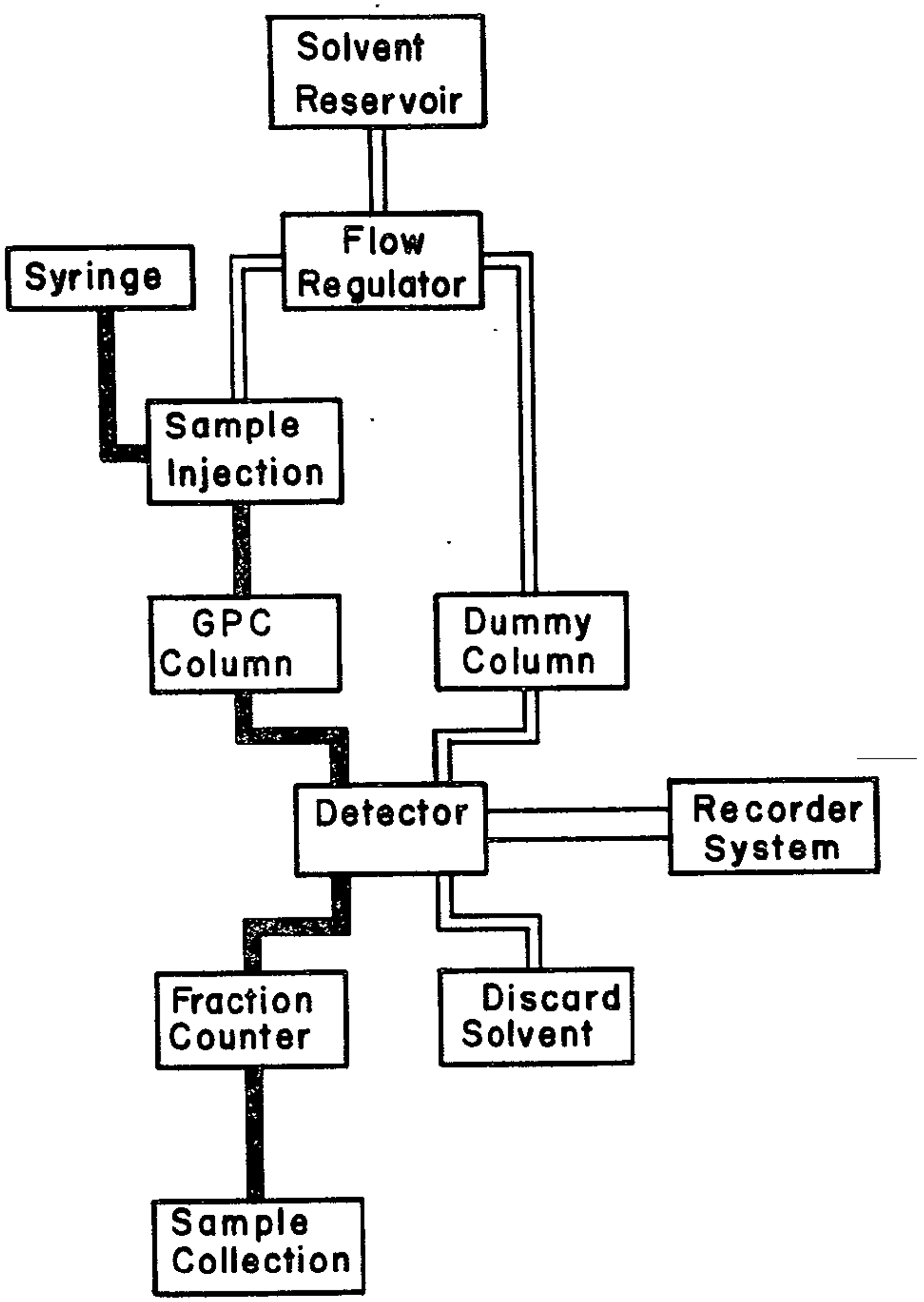
We have used GPC to determine the molecular weight distributions of a variety of samples of our ethylene-neohexene copolymers. In addition to this information, GPC also provided us with an independent check on the validity of molecular weights as determined by Vapor Phase Osmometry (VPO) in different solvents. Before discussing the results, however, a brief description of the GPC technique will be given.

Our instrument is a modified Waters Associates Series 200 GPC unit. A flow diagram showing the basic features of this unit is given in Figure 12. The solvent, in this case tetrahydrofuran, passes from a reservoir into a flow regulating system where it is split into two streams. One stream passes through a sample injection device at a rate of 1 ml. per minute. In this device the solvent stream may be diverted through a loop containing a fixed volume of a solution of the material to be analyzed. The sample is then carried through the GPC column and through the detector, after which it may be collected as individual fractions or discarded. The other solvent stream from the flow regulating system, passes through a dummy GPC column and then through the blank side of the detector.

The detector is a device for making a very sensitive comparison of the refractive index of the solvent, emerging from the dummy column, with the refractive index of the solution, emerging from the GPC column. Using an attenuation of one eighth maximum sensitivity, a fraction containing a concentration of only .04% material gives rise to an average signal strength of 40 millivolts. This is a 40% scale deflection on our particular recording system.

The GPC column configuration used in this work consists of a series of four 4 ft. x 3/8 in. stainless steel tubes having an inside diameter of .305 in. These tubes are packed with particles of highly crosslinked polystyrene, swollen with tetrahydrofuran. The gel particles in the first column have pores in the gel network with an apparent size of 10,000 Å, the second 900 Å, the third 100 Å and the fourth only 45 Å. These apparent pore sizes are determined by the extended chain length of the

FIGURE 12



Flow Diagram of GPC Apparatus

smallest molecule excluded from the interior of the gel network, and free to flow unimpeded through the interstitial voids and be eluted. Thus, molecules with an apparent chain length longer than 10,000 Å would pass through all four columns and emerge at a retention volume equal to the interstitial volume of the column. Molecules smaller than 10,000 Å but larger than 900 Å would be retarded by the first column, depending upon how easily the molecules are able to diffuse into the gel network, but would pass unhindered through the second, third and fourth column; and so forth for smaller molecules.

The effect, of this selective retardation of the flow of the smaller molecules, is to fractionate the sample on the basis of the apparent chain length of the molecules in solution. For many practical purposes, this is equivalent to fractionation on a molecular weight basis.

The column configuration was calibrated by chromatographing a series of linear monodisperse polystyrene samples, linear monodisperse polyether samples, and small molecular species, all of which had very accurately determined molecular weights. A plot showing the relationship between A, the extended chain length (calculated from standard bond lengths and angles) of these standards, and RV, the retention volume at which they were eluted from the column is shown in Figure 13.

Note that as one goes to longer and longer apparent chain lengths, the curve assymptotically approaches a retention volume of about 89 ml. This is the interstitial void volume of the column. Molecules too large to fit into any pores in the gel network are eluted at this volume.

The following expressions are derived at the end of this section.

$$A_n = \frac{\Sigma\, H_i}{\Sigma\, H_i\, A_i} \quad , \quad \bar{A}_w = \frac{\Sigma\, H_i\, A_i}{\Sigma\, H_i}$$

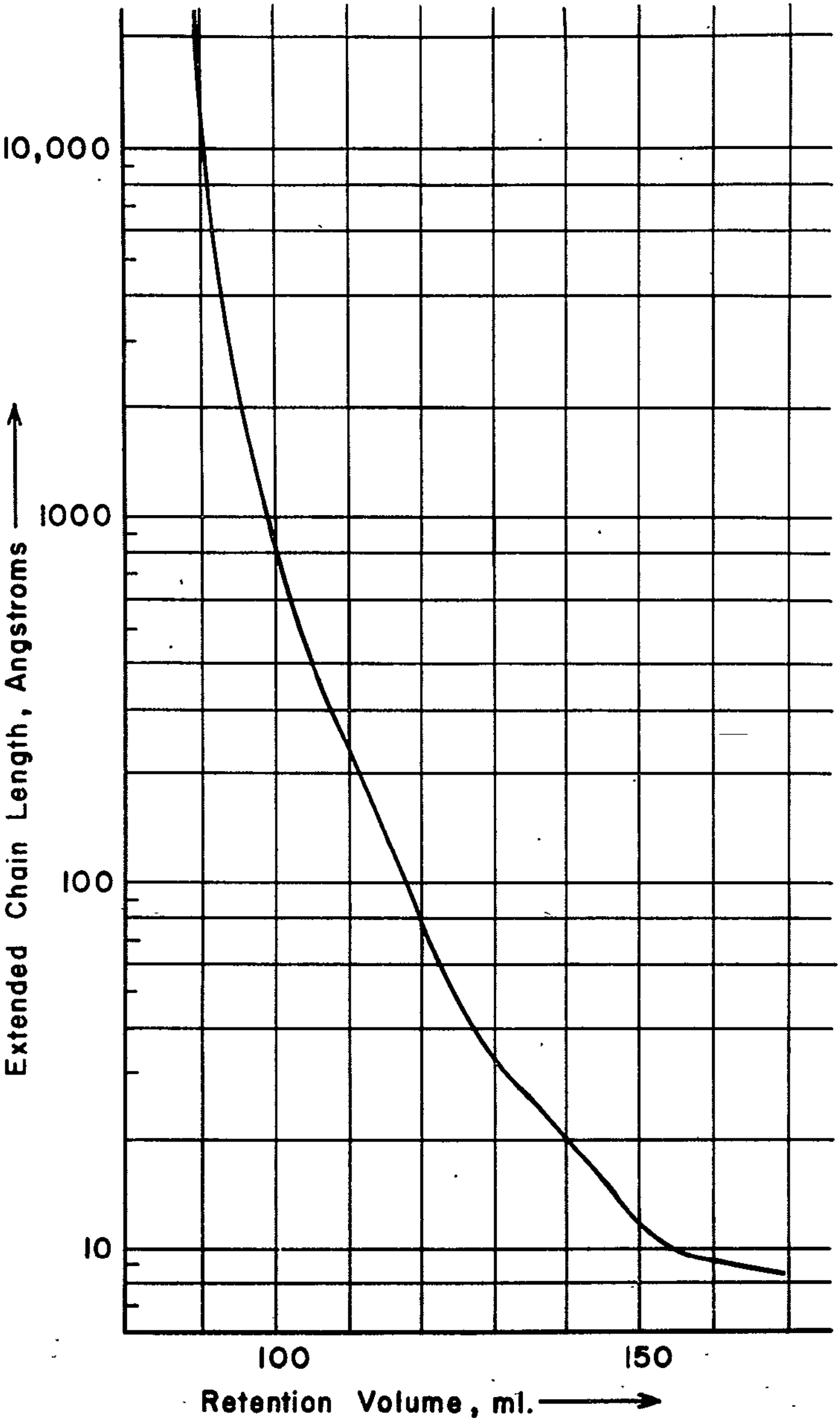
$\bar{A}_n$ and $\bar{A}_w$ are the number average and weight average apparent chain lengths of a given polymer sample. $H_i$ is the average detector response during the elution of fraction i. $A_i$ is the extended chain length in Angstroms of the calibration standard having the same retention volume as fraction i. Also:

$$\bar{M}_n = K \cdot \bar{A}_n \quad , \quad \bar{M}_w = K \cdot \bar{A}_w$$

and

$$\bar{M}_w/\bar{M}_n \equiv \bar{A}_w/\bar{A}_n \quad ,$$

FIGURE 13


10,000
1000
100
10
Extended Chain Length, Angstroms
100
150
Retention Volume, ml.

here K is a constant depending upon the polymer being examined, and $\overline{M}_n$ and $\overline{M}_w$ are the number average and weight average molecular weights, respectively.

Figures 14-17, on the pages to follow, are representative examples of the many GPC curves we have obtained upon ethylene-neohexene copolymers. The data are normalized to the same maximum peak height. Qualitative examination of the curves shows the absence of any significant "high molecular weight tail" on the molecular weight distribution. This would have shown up as a broad leading edge on the peaks, starting near 89 ml. retention volume. The absence of a high molecular weight tail is encouraging. If it were present, the molecular weight distribution would be broad and the viscosity-molecular weight relationship would be unfavorable.

22-EMS-52 was the sample having the lowest $\overline{M}_n$ studied. Its GPC curve is shown in Figure 14. Peaks A and B probably represent discrete low molecular weight species which are nearly resolved from the polymer by the GPC column. Hydrolysis of this particular sample gave a COOH terminated product (SK-109-B) whose $\overline{M}_n$ was slightly higher. Peaks A and B were absent from the GPC curve of this hydrolyzed sample, but the curve was otherwise just the same. Presumably the hydrolysis of species A and B led to water soluble or volatile products which were lost upon work up.

Figure 15 shows a very narrow fraction obtained by molecular distillation. See Part I, Section G for details.

Figure 16 shows the result of blending four samples which were especially prepared to test the reproduceability of the polymerization conditions.

Figure 17 shows the GPC curve on a higher molecular weight material prepared with succinic acid peroxide initiator. This material had the broadest molecular weight distribution of all the ethylene-neohexene copolymers examined.

For each GPC curve obtained, the detector response was measured at each 5 ml. interval along the retention volumn axis. These data were fed to an IBM 1620 computer in the form of punched cards. The computer assigned a value $A_i$ to each fraction using a tabular form of the function shown in Figure 13. The parameters $\overline{A}_n/\overline{A}_w$, and $\overline{A}_w/\overline{A}_n$ were then calculated according to the equations derived at the end of this section.

The weight average to number average molecular weight ratios for the copolymers are in the range 1.2 to 1.5. This is to be considered quite small for polymers prepared by free radical polymerization and is indicative of a narrow molecular weight

FIGURE 14

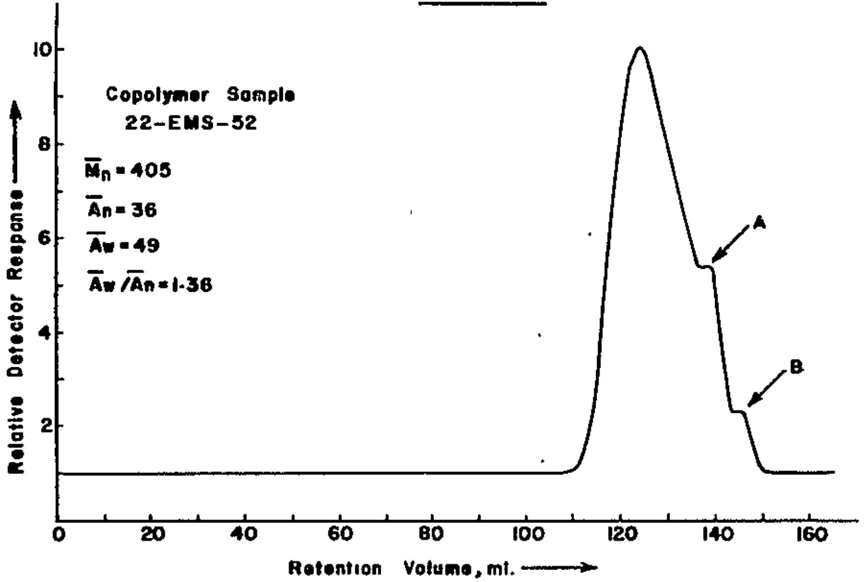


FIGURE 15

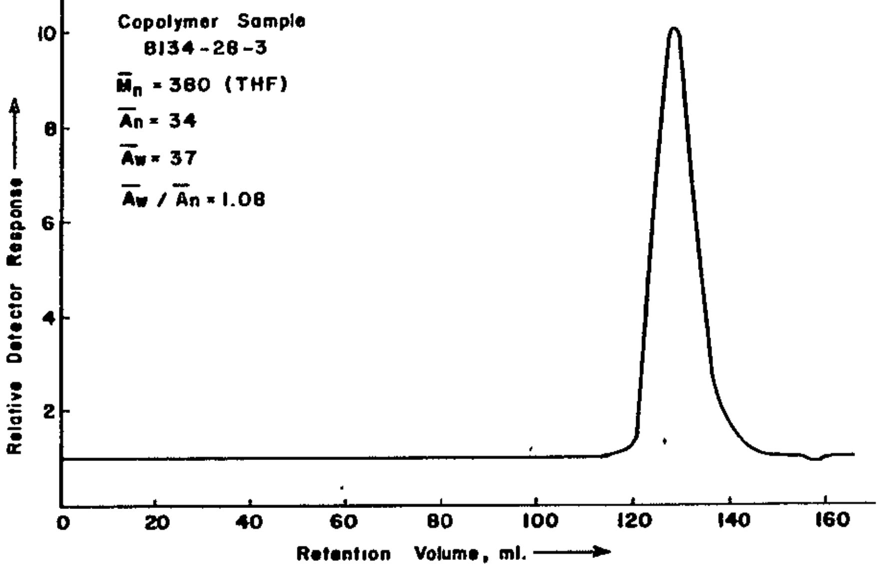


FIGURE 16

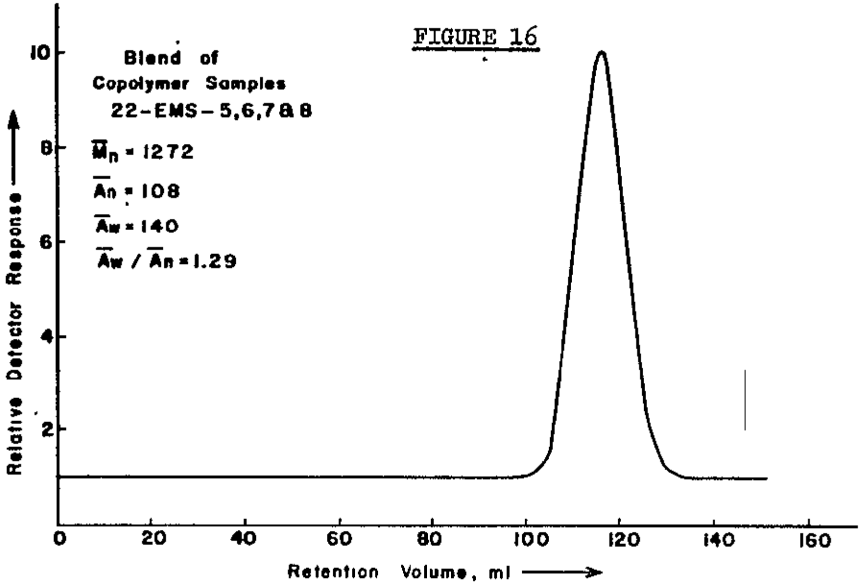
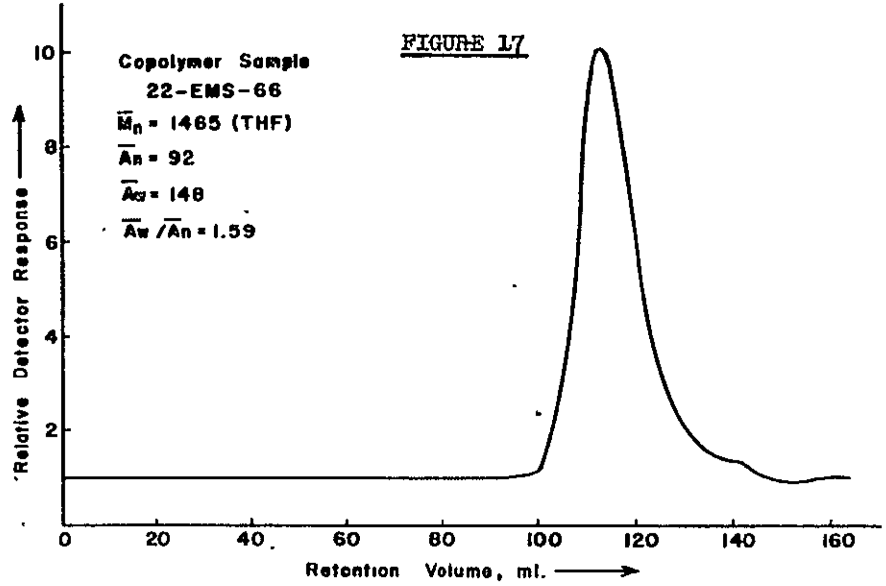


FIGURE 17



## TABLE LXII

## GPC AND MOLECULAR WEIGHT DATA FOR ETHYLENE-NEOHEXENE COPOLYMERS

| Sample Number | End Group | Benzene | THF | Acetone | Retention Volume At Peak Maximum Ml. | $\bar{A}_n$ | $\bar{A}_w$ | $\bar{A}_w/\bar{A}_n$ | See Figure |
|---|---|---|---|---|---|---|---|---|---|
| 22-EMS-32 | CN | 459 | - | 435 | 123.5 | 38 | 55 | 1.43 | - |
| 22-EMS-52 | CN | 409 | - | 402 | 124.0 | 36 | 49 | 1.36 | 14 |
| 22-EMS-66 | COOH | 2198 | 1465 | - | 113.5 | 92 | 148 | 1.59 | 17 |
| 22-EMS-69 | COOH | - | 818 | - | 117.5 | 68 | 101 | 1.48 | - |
| 22-EMS-70 | COOH | 1134 | 791 | - | 118.0 | 67 | 98 | 1.45 | - |
| 22-EMS-71 | COOH | 2037 | - | - | 113.5 | 113 | 172 | 1.52 | - |
| 22-EMS-109 | $CO_2Et$ | 831 | - | - | 117.0 | 71 | 102 | 1.43 | - |
| 7846-89[a] | CN | 1946 | 1272 | - | 115.5 | 108 | 140 | 1.29 | 16 |
| SK-109-B[b] | COOH | 685 | - | 431 | 124.0 | 38 | 51 | 1.32 | - |
| SK-107-B[b] | COOH | 789 | - | 466 | 123.5 | 40 | 53 | 1.31 | - |
| 8134-28-1[c] | COOH | 339 | 234 | - | 137.0 | 22 | 23 | 1.07 | - |
| 8134-28-2[c] | COOH | 511 | 296 | - | 132.0 | 27 | 29 | 1.08 | - |
| 8134-28-3[c] | COOH | 660 | 380 | - | 128.5 | 34 | 37 | 1.08 | 15 |
| 8134-28-4[c] | COOH | 783 | 436 | - | 126.5 | 39 | 43 | 1.08 | - |
| 8134-28-5[c] | COOH | 880 | 518 | - | 125.0 | 46 | 49 | 1.06 | - |
| 8134-28-6[c] | COOH | 1370 | 802 | - | 121.0 | 68 | 79 | 1.16 | - |

[a] A blend of samples 22-EMS-5, 6, 7 and 8.
[b] Hydrolyzed 22-EMS-52.
[c] Molecular distillation fractions, see Part I, Section G.

distribution. (Typical values of this ratio are: 1 for a monodisperse system such as a living polymer, 2 for the "most probable distribution" in condensation polymers, and 10-20 for polyethylene).

Figures 18 and 19 show a graphical correlation between $\bar{A}_n$ and the number average molecular weights as determined by VPO in THF and benzene. The $\bar{A}_n$ parameter is a measure of molecular size which is completely independent of the other methods we have used to characterize our polymers. The fact that $\bar{A}_n$ correlates so well with the THF molecular weights greatly increases our confidence in the reliability of the THF molecular weight data.

On the other hand, the poor correlation, with the benzene molecular wieght data implies that our earlier interpretation was correct: The use of nonpolar solvents for molecular weight determinations allows hydrogen bonded dimers to form. These lead to higher values for the apparent molecular weight depending upon the degree of association. This in turn is dependent upon the amounts of polar impurities (such as a trace of butanol or water from the hydrolysis procedure) present in the polymer.

Comparing the results for 22-EMS-52 and SK-109-B we see that the values $\bar{M}_n$ (acetone) and $\bar{A}_n$ are not affected much by the change from $C \equiv N$ end groups to COOH. The $\bar{M}_n$ (benzene) value is increased by a factor of 1.6. This is additional evidence that $\bar{M}_n$ (polar) is a more reliable measure of average molecular size than $\bar{M}_n$ (non-polar).

The relationship between $\bar{A}_n$ and $\bar{M}_n$ (polar) is given by:

$$\bar{M}_n = 11.43 \ \bar{A}_n$$

where 11.43 is the slope of the straight line in Figure 7. The only sample which does not follow this rule is 22-EMS-66, which also is abnormal in that it has the broadest molecular weight distribution of all of the samples so far examined.

Knowing $\bar{A}_n$ as a function of the retention volume, (Figure 13, calibration curve) and having the relationship between $\bar{M}_n$ and $\bar{A}_n$, we can now convert the GPC curves into true molecular weight distribution curves. This was done for sample 7846-89 and the result is shown in Figure 20. Note that most of the sample lies between 400 and 10,000 molecular weight.

FIGURE 18

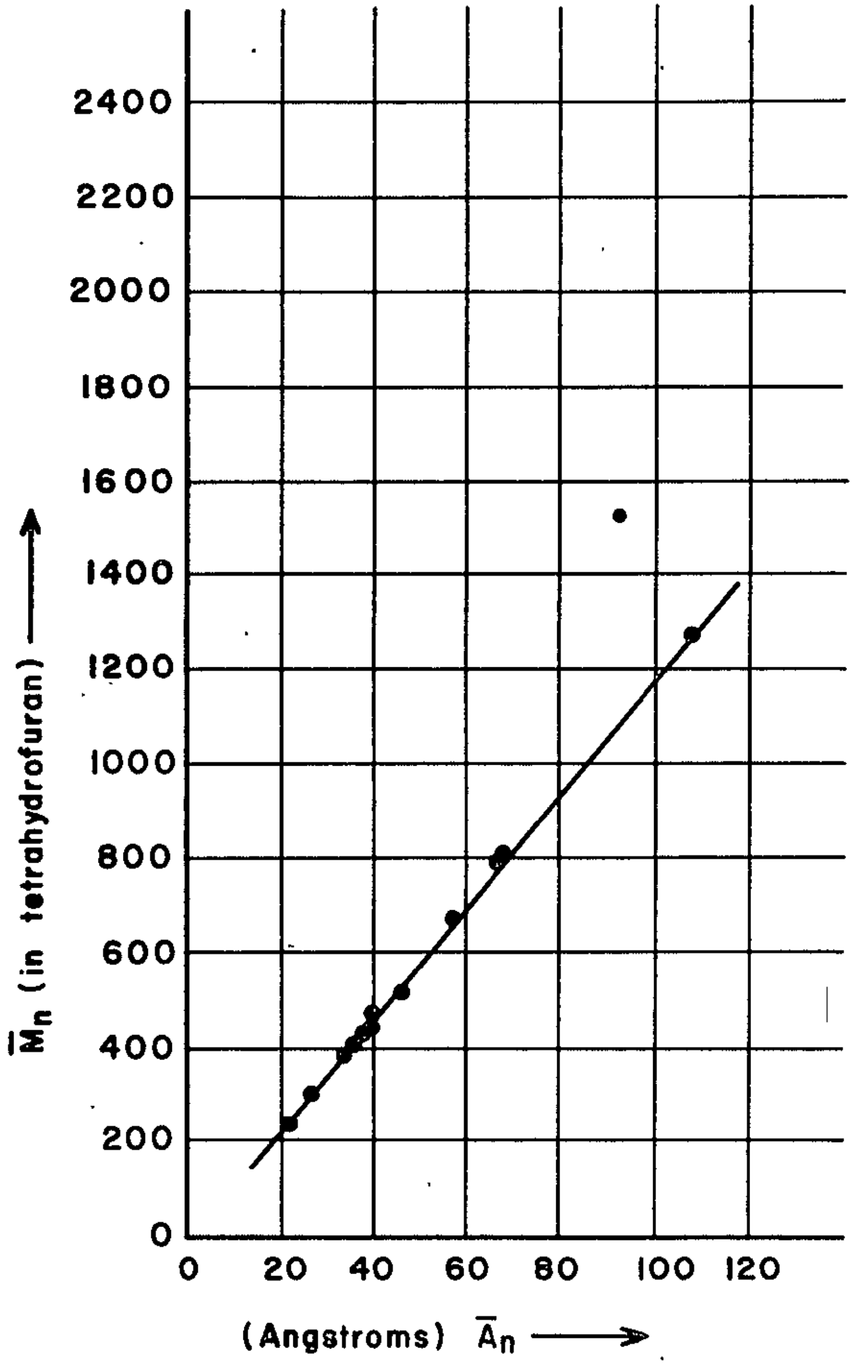


FIGURE 19

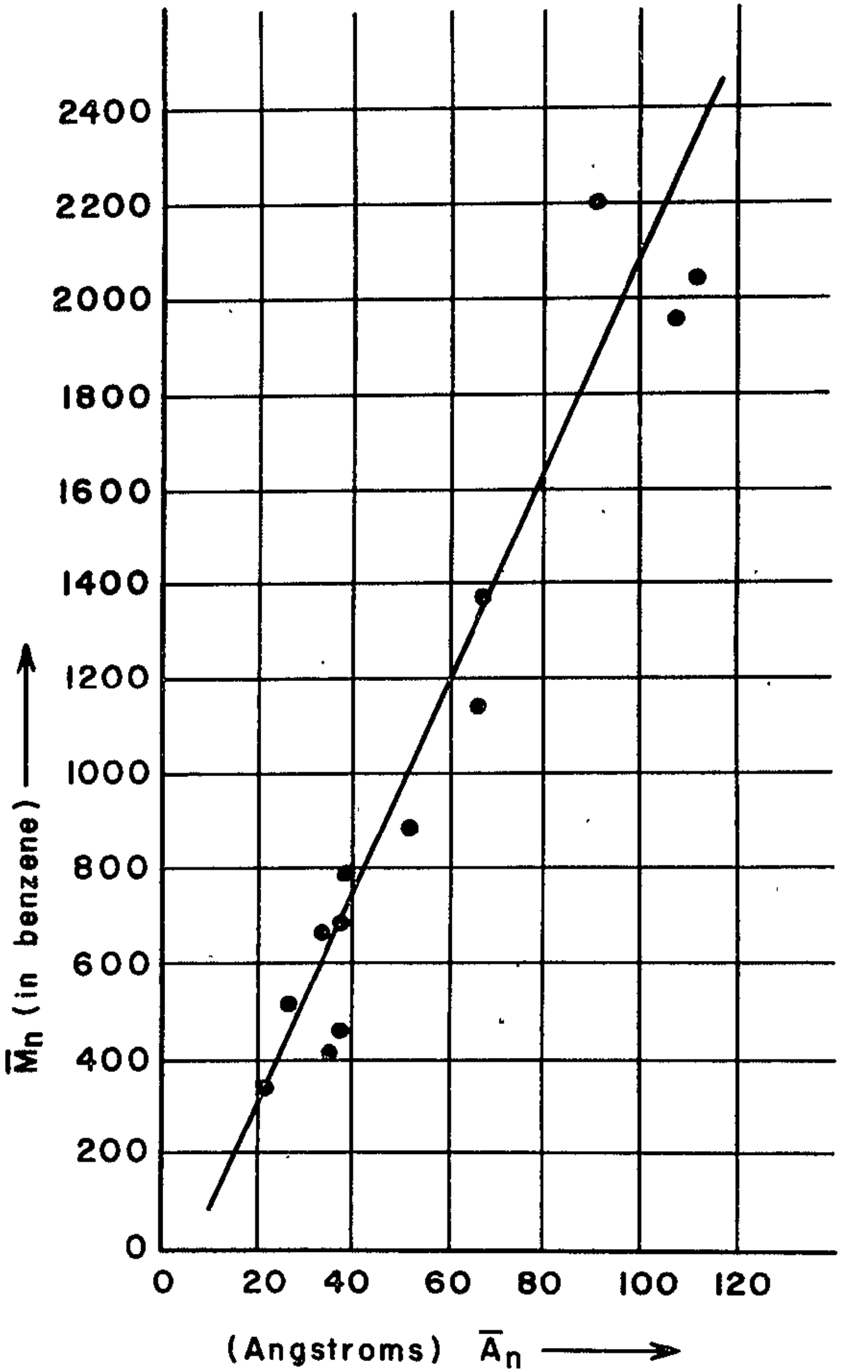
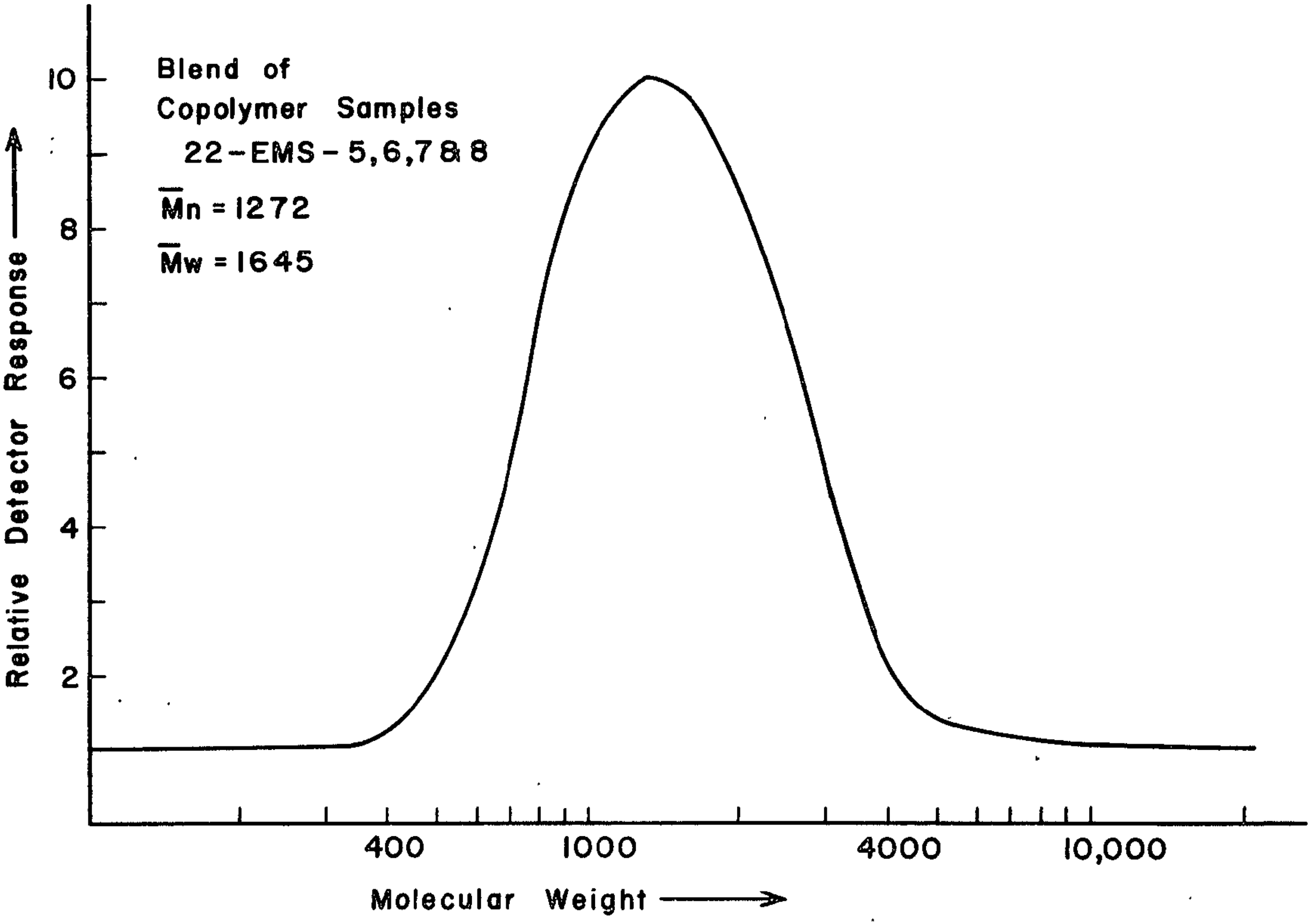


FIGURE 20


Blend of
Copolymer Samples
22-EMS-5,6,7 & 8
$\overline{M}n = 1272$
$\overline{M}w = 1645$
Relative Detector Response
10
8
6
4
2
400
1000
4000
10,000
Molecular Weight

## Derivation of Equations for GPC

Having the relationship between A and RV (retention volume) for the linear monodisperse standards, we assume a linear correspondence between the molecular weight of a given type of polymer molecule and the chain length of the standard having the same retention volume:*

$$M = KA$$

where K is a constant depending upon the polymer being chromatographed.

We assume the following relationship:

$$H_i = Lc_i^{**}$$

where $H_i$ is the average detector response during the elution of fraction i, L is a constant, and $c_i$ is the concentration in g/ml. of the polymer in fraction i.

The weight, $W_i$, of polymer in fraction i having a volume $V_i$ is therefore given by:

$$W_i = \frac{V_i}{L} H_i$$

And the total weight in all the fractions is:

$$W_{total} = \Sigma W_i$$

$\bar{M}_n$, the number average molecular weight is given by:

$$\bar{M}_n = \frac{\Sigma W_i}{\Sigma W_i/M_i}$$

where $M_i$ is the molecular weight in fraction i. This can be expressed in terms of $A_i$, the extended chain length of the

---

* This assumption is not always valid. For example, in a "poor" solvent in which the polymeric solute is in a tightly coiled conformation, there would be a much higher order dependence of M upon A. The limiting case would be, $M = \frac{K}{6} \Pi A^3$

in which the molecules of interest are coiled into close packed spherical conformations, but the calibration standards are completely extended.

The assumption is valid when both the polymer of interest and the linear monodisperse standard have similar degrees of coiling in the solvent system employed.

** This assumption is not valid for very low molecular weight fractions where the end groups make an important contribution to the refractive index.

calibration standard having the same retention volume as fraction i.

$$M_i = KA_i$$

Therefore:

$$\overline{M}_n = \frac{\Sigma \frac{V_i}{L} H_i}{\Sigma \frac{V_i}{L} \frac{H_i}{KA_i}} = K\left(\frac{\Sigma H_i}{\Sigma H_i/A_i}\right) = K\overline{A}_n$$

The quantity in parenthesis is in the number average apparent chain length, $\overline{A}_n$.

$\overline{M}_w$ the weight average molecular weight is given by:

$$\overline{M}_w = \frac{\Sigma W_i M_i}{\Sigma W_i}$$

By the same derivation used for $\overline{M}_n$ we have:

$$\overline{M}_w = K\left(\frac{\Sigma H_i A_i}{\Sigma H_i}\right) = K\overline{A}_w,$$

and:

$$\overline{M}_w/\overline{M}_n \equiv \overline{A}_w/\overline{A}_n.$$

## D. Examination of Our Method For Determining the Neutralization Equivalent

If functionality (F) is defined as:

$$\text{Functionality (F)} = \frac{\text{No. Avg. Mol. Wt. } (\overline{M}_n)}{\text{Neutralization Equivalent (N.E.)}}$$

it is apparent that a low functionality will be observed if $\overline{M}_n$ is erroneously low or N.E. is erroneously high. The drastic effect of using a non-polar solvent in the determination of $\overline{M}_n$ has already been discussed in the preceding section.

Our standard procedure was to titrate a xylene solution of the prepolymer with a solution of KOH in ethanol to the phenolphthalein end point. This method was found to have several deficiencies:

1. Ethanolic KOH titrant is not stable, discolors on standing and must be frequently restandardized.

2. The color change of phenolphthalein does not occur exactly at the time equivalence point.

3. The potentiometric end point is not sharp.

4. KOH is not basic enough to quantitatively titrate all of the acidic groups present.

Fortunately, deficiencies (1) and (2) tend to cancel one another.

After considerable investigation we have adopted a new procedure in which the polymer is dissolved in methyl ethyl ketone and titrated with 0.1 normal tetrabutyl ammonium hydroxide in isopropanol. The end point can be determined either potentiometrically or visually. Using glass versus standard calomel electrodes a very sharp end point is observed at -550 millivolts. Thymol blue undergoes its color change exactly on the vertical portion of the potentiometric titration curve and can be used successfully except when the polymer solution is highly colored.

Using this revised procedure it has been found that neutralization equivalents are somewhat lower than the results from the older method, which, in effect, increases the concentration of COOH present. An example of how this affects N.E. and functionality is given on the following page.

| Sample No. | Neutralization Equivalent Old Method | New Method | $\overline{M}_n$ | Functionality Old | New |
|---|---|---|---|---|---|
| 23-EMS-4 | 789 | 779 | 779 | 0.99 | 1.00 |

It is seen that the error in the old data was small, at least in this instance. Because of the ease of obtaining reproducible results with the new procedure, it will be used as the standard method.

## Polymeric Anhydride Formation

Another possible cause of error in functionality determinations is the formation of intermolecular anhydride groups during work-up procedures. Our suspicions were aroused by unexplainable increases in viscosity of certain samples of prepolymer during work-up and the occurence of infrared absorptions similar to the anhydride doublets in the 5 micron region. Obviously, anhydrides which might not hydrolyze rapidly during N.E. determinations would raise the N.E. of the sample and also raise the observed molecular weight.

Anhydrides are known to react quantitatively and rapidly with morpholine to give morpholides and the corresponding carboxylic acid. Morpholine may be titrated with strong acid in the presence of carboxylic acids. A published method for the analysis of anhydrides in the presence of the corresponding acids is based on these facts.[26] Using this procedure we found no measurable amount of anhydride in a copolymer sample (hydrolyzed 23-EMS-11) which exhibited the infrared absorptions "characteristic" of anhydrides.

To further strengthen the evidence that anhydrides are not a problem, we subjected a sample of a known difunctional polymer (EMPOL-1010 dimer acid) to a more severe thermal cycle than ever used in work-up of our samples: 6 hours at 150°C under vacuum in a rotary evaporator. There was no change in neutralization equivalent as a result of this treatment. If anhydrides formed they were completely hydrolyzed during the titration procedure.

## E. Functionality Distribution Studies

In addition to the average functionality, the functionality distribution* is of fundamental importance in determining the manner in which a given carboxyl terminated binder sample will cure and the physical properties of the resultant product. For example, a material containing 50% difunctional molecules and 50% nonfunctional molecules would be expected to cure with a trifunctional aziridine or epoxide to give an insoluble gel plasticized with the nonfunctional component, whereas a material having the same average functionality of one COOH per molecule but composed entirely of monofunctional molecules would not be expected to cure at all. Because of the importance of the functionality distribution, we have explored several functionality fractionation procedures, both from an analytical and a preparative viewpoint. For these experiments extensive use has been made of the carboxyl terminated ethylene/neohexene liquid copolymer obtained from "Composite Batch I"**. This material has an average functionality of 1.34 COOH per molecule and a $\bar{M}_n$ of 383.

### 1. Column Chromatography

Adsorption Chromatography on silica gel has been successfully applied to the analysis of hydroxyl terminated liquid binder samples[27,28]. The procedure to be described below for the carboxyl terminated ethylene/neohexene copolymer sample is similar to that used by Quacchia and DiMilo[2] except that a more polar solvent sequence was required in order to elute the more strongly adsorbed carboxyl terminated polymer.

Four grams of ethylene/neohexene copolymer sample 8725-6-7 (1.34 COOH per molecule) was dissolved in 20 ml. $CCl_4$ and introduced into a 4.6 cm. diameter column containing 400 grams of 100-200 mesh silica gel (Matheson Coleman and Bell, SX144-6, used as supplied) packed wet in $CCl_4$. The column was then eluted with $CCl_4$ (2160 ml.), $CCl_4/CHCl_3$ mixtures (1080 ml.), $CHCl_3$ (8640 ml.) and $CHCl_3$/ethanol mixtures (5760 ml.) to give 49 fractions of 360 ml. each. The solvents were evaporated and the elution profile shown in Figure 21 was constructed from the weights of the individual fractions. The fractions were combined as shown in Figure 21 and Table LXIII to give eight composite fractions. Fractions

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* The term "functionality distribution: will be used to indicate the relative proportions of non-, mono-, di- and higher functionality fractions present in a given sample.

** Part B, Section C of this report.

IV and VI contained the bulk of the material, 68% and 17% respectively, with small intermediate fractions comprising the remainder.

TABLE LXIII
COLUMN CHROMATOGRAPHY FRACTIONS

| Fraction | Wt. Mg. | N.E. | $\overline{M}_n$ | Functionality |
|---|---|---|---|---|
| I | 43.7 | - | - | - |
| II | 51.8 | - | - | - |
| III | 322.8 | - | - | - |
| IV | 2858.2 | 345 | 492 | 1.4 |
| V | 164.3 | - | - | - |
| VI | 708.2 | 138 | 294 | 2.1 |
| VII | 51.8 | - | - | - |
| VIII | 21.3 | - | - | - |

The two major fractions IV and VI were analyzed by vapor phase osmometry in THF to determine their molecular weights and titrated to determine their neutralization equivalents. From these results, average functionalities were calculated. Fraction VI was thus found to be of lower average molecular weight than the starting material and difunctional whereas Fraction IV was higher in average molecular weight than the starting material, and contained both monofunctional and difunctional components. The column's failure to separate these components of Fraction IV is not understood at this point. A chromatographic procedure using smaller columns with lower loading may be required to fully resolve this fraction.

### 2. Thin Layer Chromatography

Thin layer chromatography (TLC) is an analytical tool giving separations of mixtures of compounds comparable to those obtained with paper chromatography. It is also faster and more convenient, typical separations taking only 15 to 30 minutes.

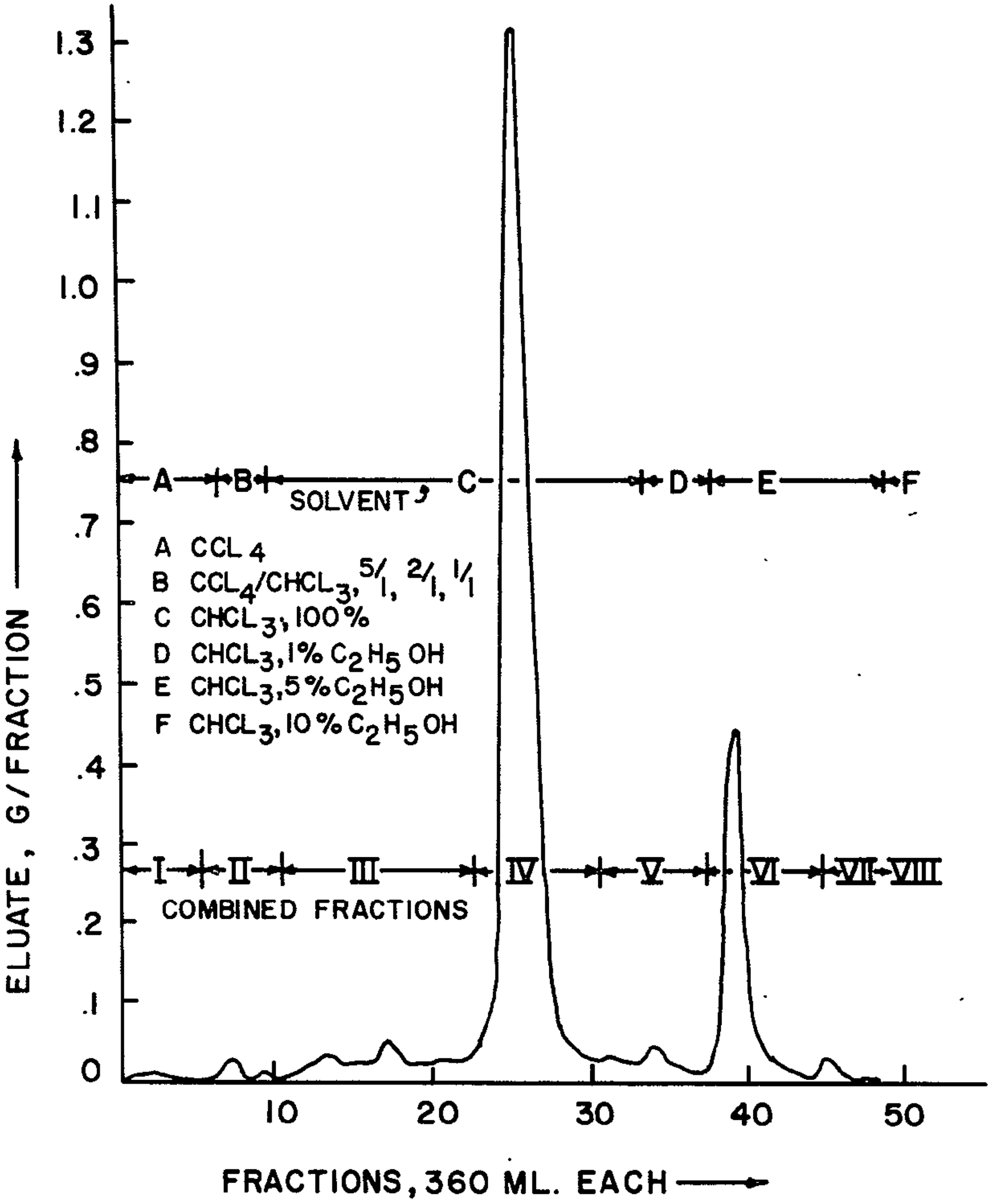
The TLC medium used in this work was commercially available silica gel coated glass plates*. The material to be analyzed is applied in the form of a small spot near one end of the plate (typical spot contains 1 µl of a 5% solution or about 50 µg of material). The plate is then placed, spot end down, into a developing tank containing a shallow layer of the solvent to be used to develop the chromatogram. The solvent rises on the plate by capillary action, passes the

---

* Supplied by Brinkman Instrument Co. in a variety of sizes.

FIGURE 21

SILICA GEL COLUMN CHROMATOGRAM OF 4 GRAMS OF 1.34 FUNCTIONALITY ETHYLENE/NEOHEXENE COPOLYMER



"spot" and begins elution of the different components. After the solvent front has risen high enough (usually about 10 cm. in our chromatograms), its position is marked and the plate removed from the developing chamber, dried, and sprayed with a suitable reagent to make the eluted spots visible. Both aqueous potassium permanganate and 5% nitric acid in concentrated sulfuric acid have been effective for this purpose.

Just as in paper chromatography, compounds are characterized by an $R_f$ value which is the fractional distance travelled by a given spot compared with the solvent front, both distances being measured from the point of application of the original spot.

In order to obtain conditions of separation similar to those of the column chromatography discussed previously, chloroform/ethanol mixtures were used as the developing solvent. Five percent ethanol in chloroform was found to give a convenient spread of spots on the finished chromatogram. Five percent $CCl_4$ solutions of the copolymers and fractions thereof to be analyzed were prepared and 1 or 2 µl were applied to the TLC plate to give the original spot. Figure 22 shows the results of TLC analysis of the 1.34 functionality material used in Section I and the Fractions I through VIII obtained from it by column chromatography.

The chromatogram labelled "O" is the starting material. Two major components are evident. On the basis of the reasonable assumption that the material of highest functionality has the lowest $R_f$, the streak between 0 and .4 $R_f$ is probably the difunctional fraction, and the streak between .5 and .8 is the monofunctional fraction. The chromatograms of the other fractions in the series bear out these conclusions. Fraction VI of functionality 2.1 gives a single streak between 0 and .3 $R_f$ and Fraction IV of functionality 1.4 shows two streaks from .1 to .4 and from .6 to .8, similar in general appearance to the starting material.

Fractions I and II contain a trace component concentrated by the column chromatography. This material has an $R_f$ greater than .9 and probably represents a small amount of nonfunctional material. Fraction III contains both mono- and nonfunctional material. Fraction V is largely difunctional with traces of mono- and nonfunctional components.

Fractions VII and VIII (which were stripped from the column using 5% and 10% ethanol in $CHCl_3$, respectively) contain some highly polar material having a very low $R_f$ (0 to .2). However, these fractions also contain some material behaving as if it were nonfunctional, with an $R_f$ greater than .9. We believe the latter material to be esterified carboxyl terminated material formed during elution of a tightly bound fraction of high functionality.

These thin layer chromatograms illustrate the utility of TLC as a qualitative analytical tool for the characterization of carboxyl terminated binder samples. We are at present refining these techniques and plan to routinely use TLC to analyze the products from our reactions on binder precursors.

### 3. Countercurrent Distribution

The chromatographic methods described in the preceding sections are very useful for analytical separations to characterize binder samples, however they are impractical for preparing quantities of known difunctional material larger than a few grams. Countercurrent distribution between immiscible solvent pairs is another separation technique which can achieve separations comparable to those obtained by chromatographic methods, however it is much more amenable to scale-up than column chromatography.

We have found that useful separations on the basis of functionality can be achieved using the immiscible solvent system, dimethyl formamide/pentane.

The first countercurrent distribution experiment was performed using the molecular distillation residue fraction 8134-28-2. This particular liquid copolymer of ethylene and neohexene was an appropriate candidate for this study because of its functionality of 1.24 COOH per molecule. The $\bar{M}_n$ was determined by vapor phase osmometry in THF to be 802.

Using manual extraction methods, twenty grams of this material was separated into 10 fractions by distribution between the two solvents. Fractions 1 and 2 contained the bulk of the low functionality components: 10.12 grams liquid copolymer, $\bar{M}_n = 1010$, NE = 1060, having .95 COOH per molecule. Fractions 8, 9 and 10 contained the high functionality material: 4.68 grams liquid copolymer, $\bar{M}_n$ - 745, NE = 377, with 2.00 COOH per molecule. Fractions 3 - 7 represent the remainder, 5.20 grams, of intermediate functionality material.

This procedure was then applied to separate copolymer sample 8725-6-7 (functionality 1.34)*. 82.3 grams of this material was separated into 10 fractions using the 10 stage countercurrent scheme illustrated in Figure 23. One liter separatory funnels with manual shaking and transfer of lower phases were employed for this purpose.

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* See Part 1 for column chromatography on this material.

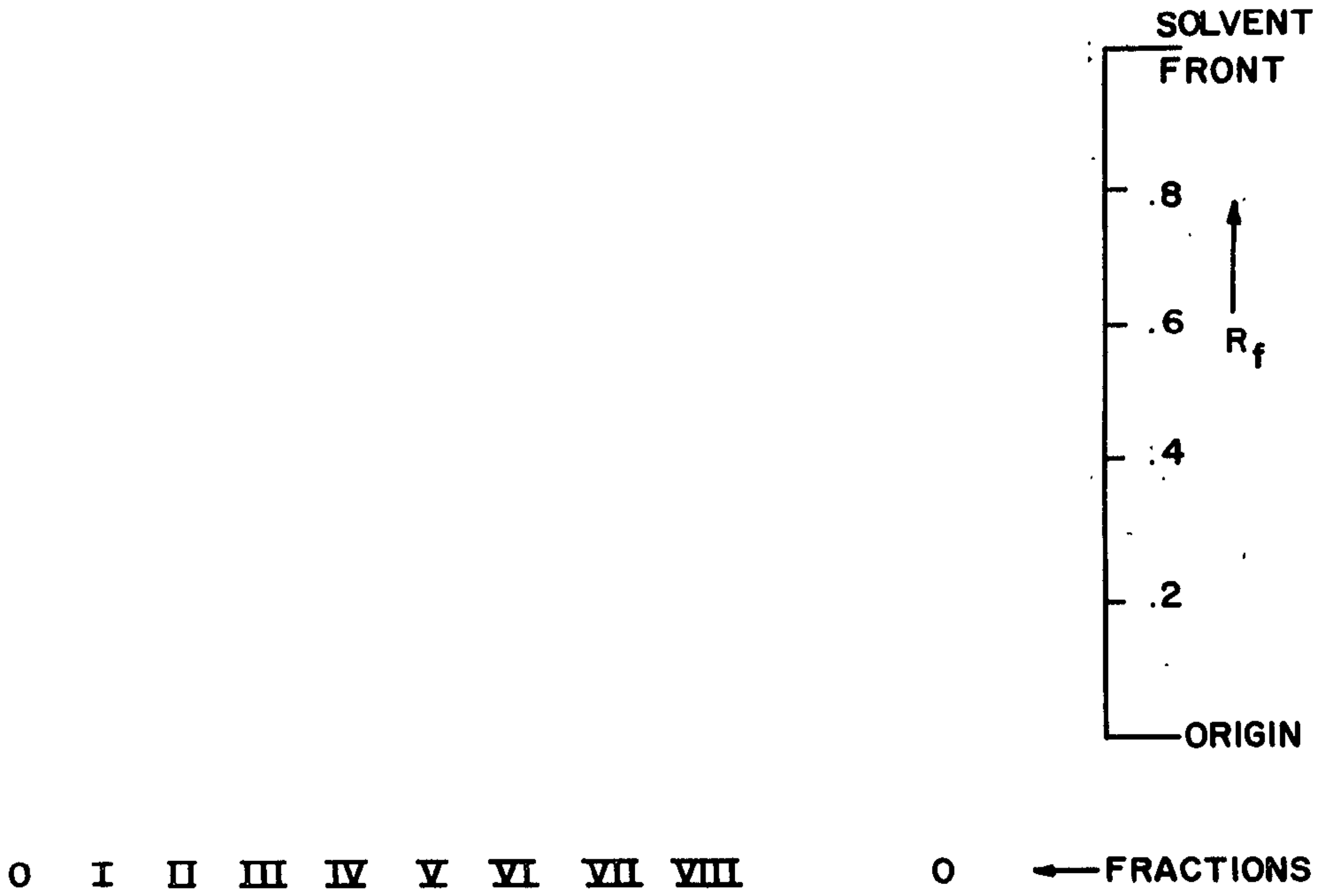

FIGURE 22

THIN LAYER CHROMATOGRAMS OF COLUMN CHROMATOGRAPHY FRACTIONS

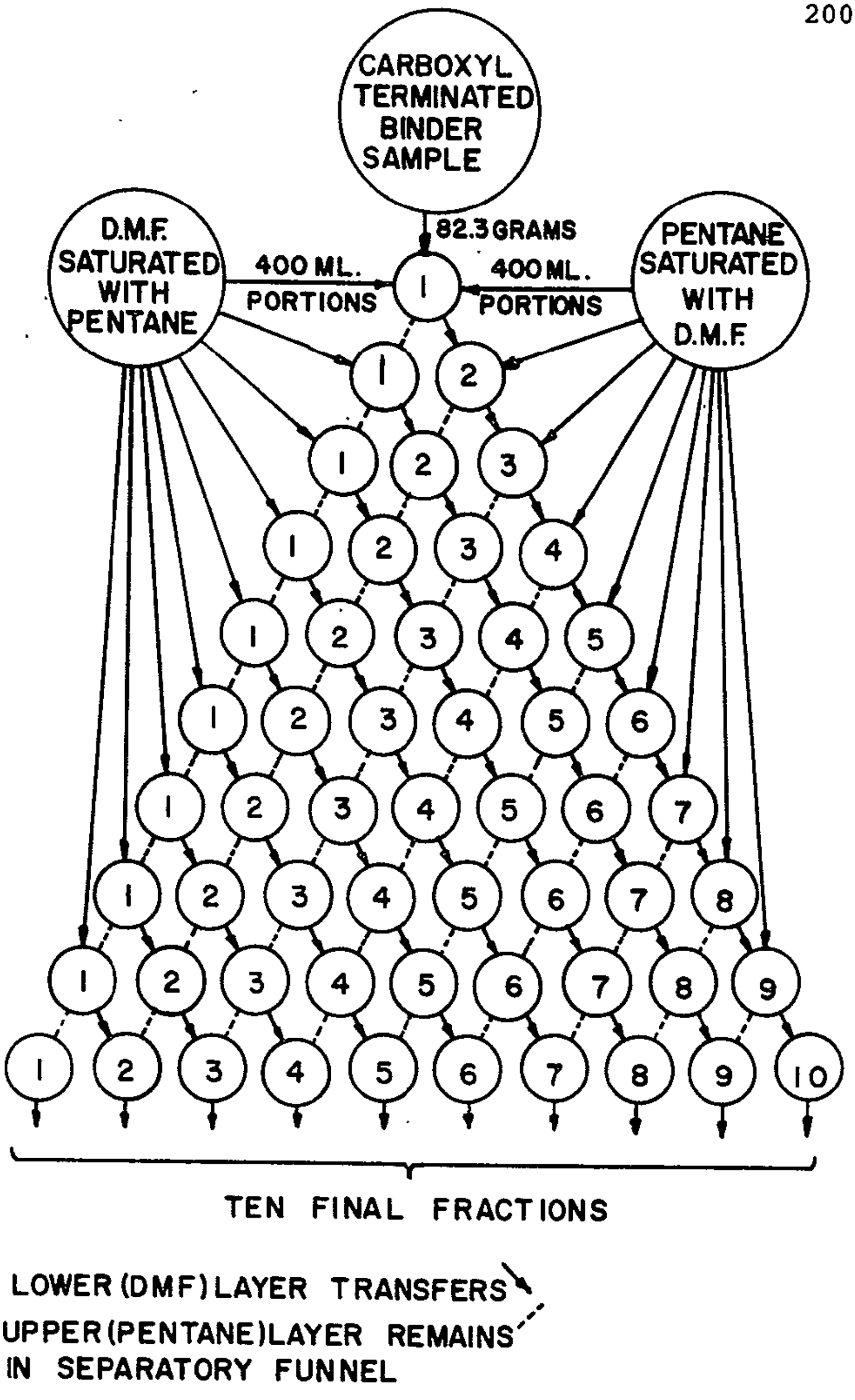

FIGURE 23

10 STAGE COUNTERCURRENT SEPARATION SCHEME

The ten fractions resulting from this procedure were recovered by solvent evaporation followed by water washing to remove the D.M.F. The fractions were then dried <u>in vacuo</u> prior to analysis. Table LXIV gives the weights and analytical data obtained on these fractions. The weight distribution among the ten fractions is shown plotted in Figure 24 and the acid content distribution in Figure 25.

Vapor phase osmometry with tetrahydrofuran solvent was used to determine the number average molecular weights of Fractions 1, 2, 9 and 10. Because of the difficulty of completely removing all traces of D.M.F. however, the measured values should be considered as lower limits on the true molecular weights*.

TABLE LXIV

COUNTERCURRENT DISTRIBUTION FRACTIONS

| Fraction | Weight, g. | N.E. | Mn | Functionality |
|---|---|---|---|---|
| 1 | 12.01 | 1142 | 1018 | .9 |
| 2 | 4.88 | 700 | 734 | 1.1 |
| 3 | 3.92 | 557 | - | - |
| 4 | 3.16 | 500 | - | - |
| 5 | 3.30 | 438 | - | - |
| 6 | 3.96 | 384 | - | - |
| 7 | 5.15 | 340 | - | - |
| 8 | 8.26 | 291 | - | - |
| 9 | 12.67 | 243 | 407 | 1.4 |
| 10 | 25.90 | 180 | 327 | 1.8 |

Because of the uncertainty in the molecular weight, thin layer chromatography was used to check the functionality of the various fractions. Following the procedure outlined in Part A-2, 1 µl of 10% $CCl_4$ solutions from each of the fractions was applied to a silica gel TLC plate which was developed in 5% ethanol in chloroform and subsequently treated with 5% $HNO_3$ in $H_2SO_4$ and heated to visualize the streaks. The chromatogram obtained is shown in Figure 26. The first and last spots applied to the plate were the starting material of 1.34 functionality.

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* The values originally obtained for Fractions 9 and 10 were 336 and 309 respectively. After heating small samples overnight <u>in vacuo</u> at 110°C and resubmitting them for $\bar{M}n$ determination the values in Table LXIV were obtained.

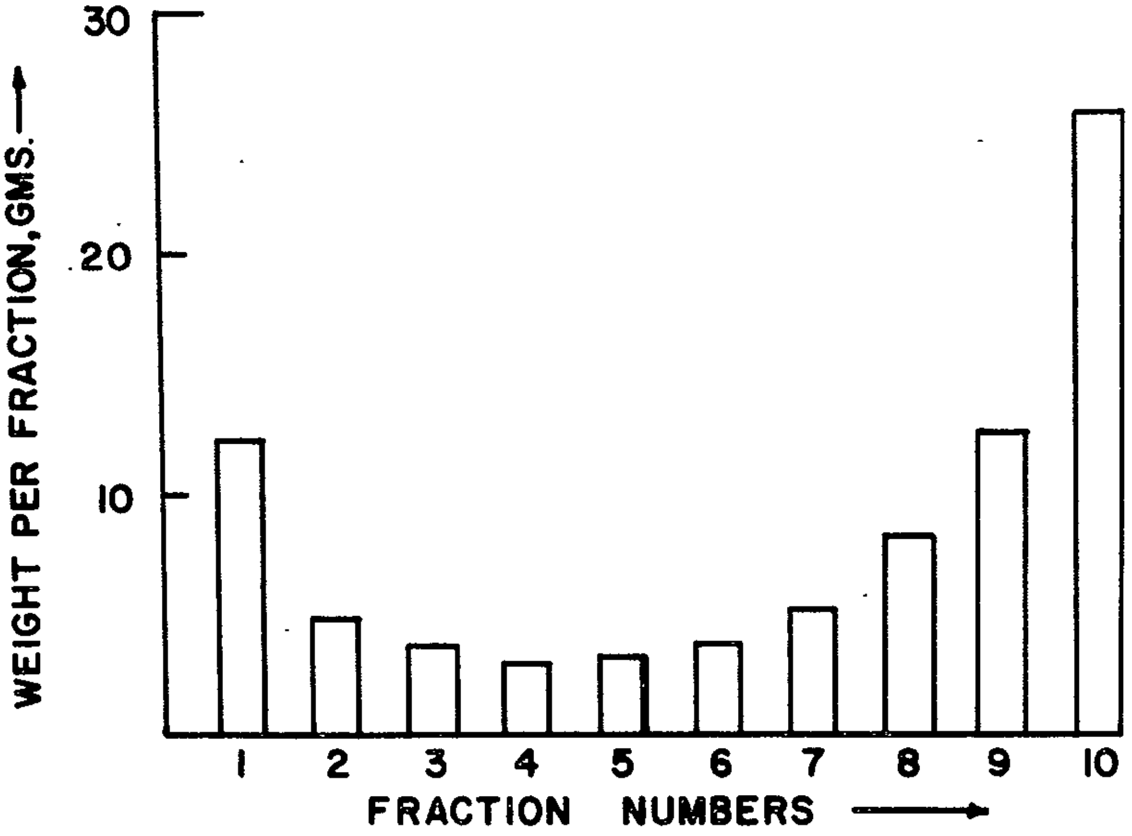


FIGURE 24

WEIGHT DISTRIBUTION

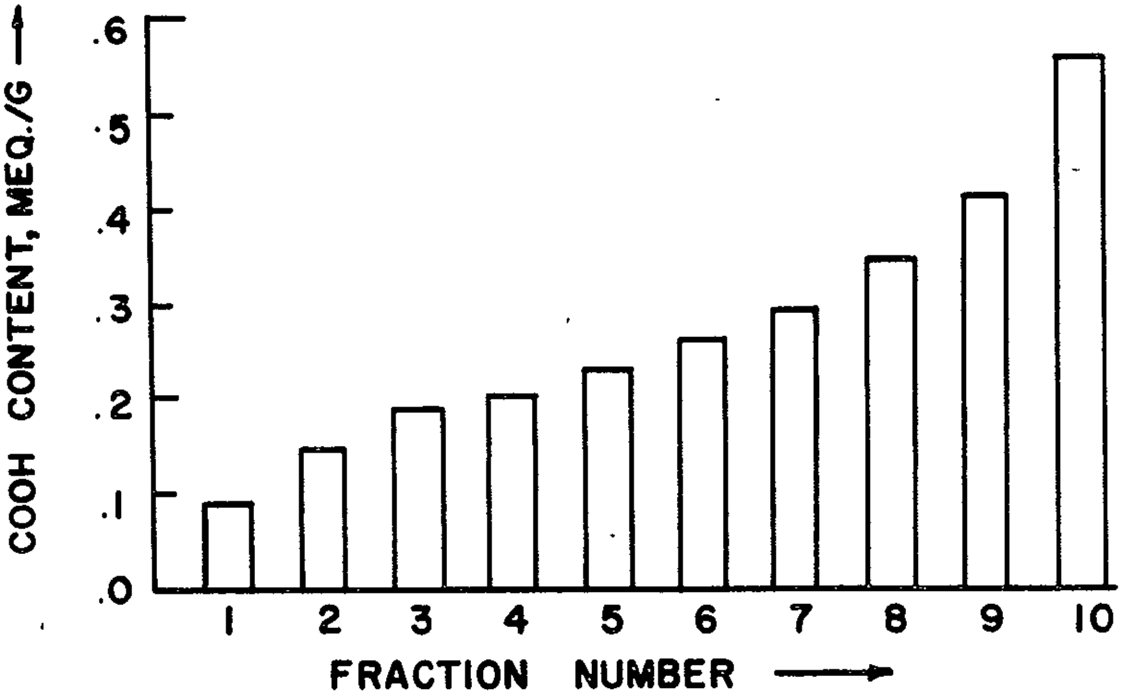


FIGURE 25

ACID CONTENT DISTRIBUTION

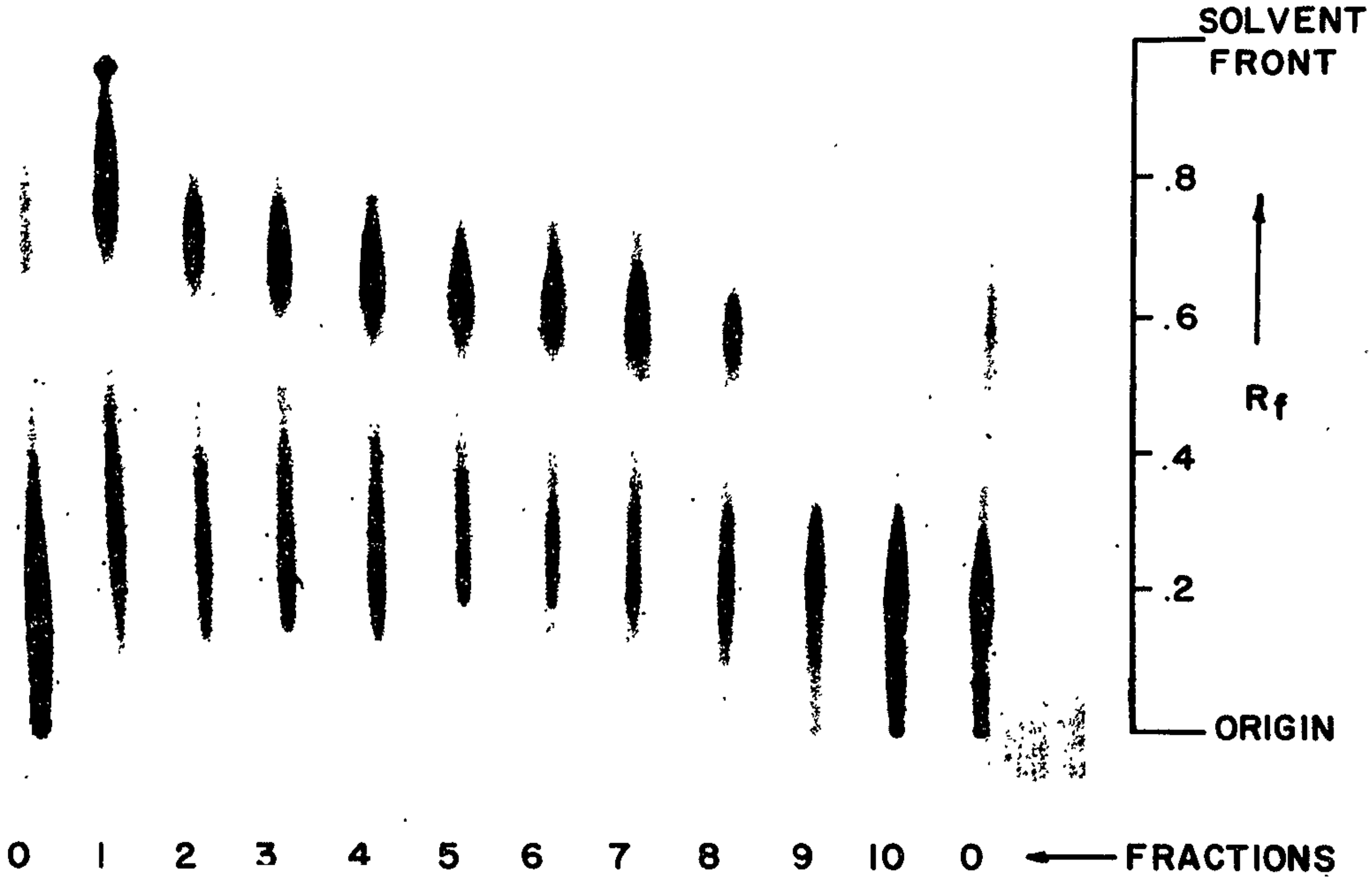
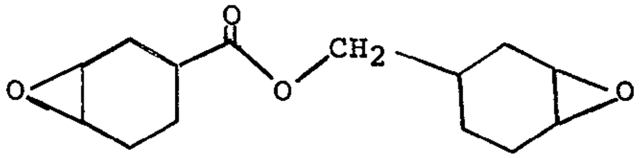


FIGURE 26

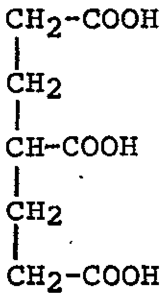
THIN LAYER CHROMATOGRAMS OF THE COUNTERCURRENT DISTRIBUTION FRACTIONS

It is evident from the chromatogram that Fraction 10 is mostly difunctional and contains only a trace of monofunctional material whereas the remainder of the fractions contain large amounts of both components. Fractions 1 and 2 both contain a significant amount of nonfunctional material.

To verify these conclusions, Fraction 1 and Fraction 10 were evaluated for ability to cure using the formulations shown in Table LXV. EP-221 is a diepoxide and octric acid (1, 3, 5-tricarboxypentane) is a trifunctional acid added to provide crosslinks. Stannous octoate was the cure catalyst.



EP 221



$$\begin{array}{l} CH_2\text{-}COOH \\ | \\ CH_2 \\ | \\ CH\text{-}COOH \\ | \\ CH_2 \\ | \\ CH_2\text{-}COOH \end{array}$$

Octric Acid

TABLE LXV

CURE FORMULATIONS FOR COUNTERCURRENT FRACTIONS

| Formulation | A | B |
|---|---|---|
| Fraction Used | 1 | 10 |
| Equivalents COOH | | |
| From binder Fraction | .0018 | .009 |
| From Octric Acid | .0002 | .001 |
| Total | .0020 | .010 |
| Equivalent Epoxide | .0020 | .010 |
| Grams Catalyst | .008 | .040 |
| Temperature | 110°C | 110°C |
| Time | 45 hrs. | 16 hrs. |
| Cure | Incomplete | Complete |

In agreement with our expectations, formulation A did not cure even after 45 hrs. at 110°C. Only an increase in viscosity was observed. Formulation B, on the other hand, did cure completely to give a crosslinked resin, insoluble in hot toluene.

From this experiment we conclude that countercurrent distribution between D.M.F. and pentane is effective in recovering a substantial portion of the difunctional material from an otherwise unuseable binder material of low functionality. It is expected however that the main utility of this method will be in upgrading binder materials which already have high functionalities, for example, to remove the 20% of monofunctional molecules which may be present in a binder of 1.8 overall functionality.

## F. Glass Transition Temperature Measurement

The liquid copolymers of ethylene with neohexene undergo a well defined transition to a glassy state when cooled to a low temperature. We have measured these transition temperatures by three different methods:

### 1. Vitrification Point, $T_V$

This method is fairly rough, however, it gives results which are probably within $10^o$ of the actual glass transition temperature. In this procedure, a sample of the liquid copolymer is cooled in a test tube, using a dry ice/acetone bath. While cooling, the sample is stirred with the bulb of an alcohol filled thermometer. The temperature is noted when a qualitative change from a viscous liquid to a brittle solid is observed. This temperature is called the "Vitrification Point", $T_V$ to distinguish it from a more accurately determined glass transition temperature, Tg.

We have used this method to characterize our copolymers since the beginning of the program and have obtained the largest body of data relating to the glass transition temperature in terms of $T_V$ (See Table LXVI). The data show that the copolymer samples having the lowest molecular weights also tend to have the lowest $T_V$. This correlation is shown in Figure 27 in which the $T_V$ is plotted against the reciprocal of the number average molecular weight for a large number of copolymer samples. These samples are unhydrolysed ester terminated products (prepared with DEAB or DMAB) or else $CCl_4$ telomers. A large amount of scatter is present, however, the general trend is evident. A least squares fit to this body of data yields a linear relationship of the form:

$$T_V = -17-\left(\frac{17800}{\overline{M}n}\right)$$

between $T_V$ and $1/\overline{M}n$. The above equation corresponds to the solid line shown in Figure 27. Somewhat different fits were obtained when the three sets of copolymers were handled individually.

### 2. Penetration Temperature, $T_P$

This measurement depends upon the fact that a very large decrease in shear modulus occurs in the vicinity of the glass transition temperature. Below the $T_g$, the sample is hard and often brittle, and resists deformation of any kind. Above the $T_g$, the sample is either soft and rubbery or else

## TABLE LXVI

## $M_n$ DEPENDENCE OF $T_v$ AND $T_p$

| Sample | Type | $M_n$ | $T_v$ | $T_p$ | Sample | Type | $M_n$ | $T_v$ | $T_p$ |
|---|---|---|---|---|---|---|---|---|---|
| 22-EMS- 99 | DEAB | 484 | -72 | -87 | 24-EMS- 2 | $CCl_4$ | 516 | -57 | -70 |
| 108 | " | 710 | -60 | | 4 | " | 667 | -43 | -56 |
| 109 | " | 831 | -47 | | 6 | " | 767 | -40 | -71 |
| 100 | " | 2752 | -18 | -36 | 8 | " | 747 | -44 | -57 |
| 126 | " | 751 | -54 | | 10 | " | 649 | -39 | |
| 127 | " | 1018 | -42 | | 12 | " | 1114 | -30 | -45 |
| 136 | " | 548 | -49 | | 14 | " | 1009 | -30 | -47 |
| 23-EMS- 1 | " | 552 | -50 | -66 | 16 | " | 976 | -31 | -49 |
| 4 | " | 837 | -40 | -54 | 22 | " | 1019 | -30 | |
| 11 | " | 869 | -41 | -50 | 24 | " | 841 | -32 | -52 |
| 18 | " | 1174 | -39 | -51 | 28 | " | 719 | -37 | -56 |
| 20 | " | 1107 | -41 | -41 | 30 | " | 651 | -41 | -60 |
| 23-EMS- 17 | DMAB | 1408 | -25 | -38 | 32 | " | 726 | -37 | -55 |
| 34 | " | 716 | -36 | | 36 | " | 727 | -35 | -55 |
| 36 | " | 911 | -35 | | 48 | " | 807 | -28 | -48 |
| 37 | " | 891 | -39 | -50 | | | | | |
| 42 | " | 706 | -40 | | | | | | |
| 39 | " | 2688 | -30 | -33 | | | | | |
| 66 | " | 823 | -34 | -51 | | | | | |
| 67 | " | 819 | -38 | | | | | | |
| 68 | " | 815 | -36 | -58 | | | | | |
| 79 | " | 566 | -50 | -73 | | | | | |
| 56 | " | 1093 | -33 | -43 | | | | | |
| 57 | " | 977 | -39 | -46 | | | | | |
| 58 | " | 1111 | -34 | -44 | | | | | |
| 63 | " | 668 | -37 | | | | | | |
| 65 | " | 373 | -65 | | | | | | |
| 90 | " | 931 | -38 | -50 | | | | | |
| 91 | " | 1355 | -34 | -41 | | | | | |

a viscous liquid, and can be easily deformed. In the case of our liquid copolymer samples, we have found that a weighted needle does not penetrate the polymer glass below the $T_g$, but easily and rapidly sinks into the sample above the $T_g$. The exact temperature at which the needle begins to penetrate the sample we have called the "penetration temperature", $T_p$, to distinguish it from $T_v$ and $T_g$ measured by other procedures.

Figure 28 shows the essential working components of the apparatus which we use for measuring Tp. The key element is the penetrometer needle, A. We used a penetrometer needle of the type specified by ASTM method D-5, weight 2.5 grams. The needle is attached to a freely moving vertical conforming to ASTM method D-5. The shaft has a weight of 47 1/2 grams. Weights, C, of 50,100 or 150 grams may be loaded on the top of the shaft C. For our purposes 150 grams worked well. A fixed collar on shaft B bears upon an arm connected to a freely moving verticle rack, D, which engages pinion, E, which drives a pointer, F, providing visual read-out of the position of needle A. Scale divisions correspond to 1/10 mm. movement of A, therefore estimates of position can readily be made to the nearest 1/50 mm.

To provide for greater ease in determining the penetration temperature we have added a tangent arm, G, which contacts the lower side of the flange supporting weights C. This tangent arm drives the shaft of a 1000Ω one turn step-less potentiometer which, in conjunction with rheostat L, serves as a voltage divider for a 1.5 volt dry cell. The rheostat is adjusted so as to give an output voltage between 2 and 6 millivolts over the normal range of needle movement corresponding to about 5 mm. This voltage is connected to one of the six channels of a Leeds and Northrop Speedomax recorder giving a 10 inch strip chart record of 0 to 8 millivolts. This system gives a nearly linear readout of the penetrometer needle position.

A few drops of the polymer sample are placed in an aluminum foil cup J, which is then rapidly cooled in liquid nitrogen to give a small button of glassy polymer. The sample is then immersed in a methanol bath K, pre-chilled below the glass transition temperature expected for the sample. After placing the penetrometer needle and the thermocouple junction upon the polymer button, the bath is allowed to warm up while continuously recording the temperature and position readouts.

Below Tp, needle A rests on the top of the sample and a straight line is recorded on one channel of the recorder corresponding to this position. Another channel is meanwhile recording the rising sample temperature. When Tp is reached,

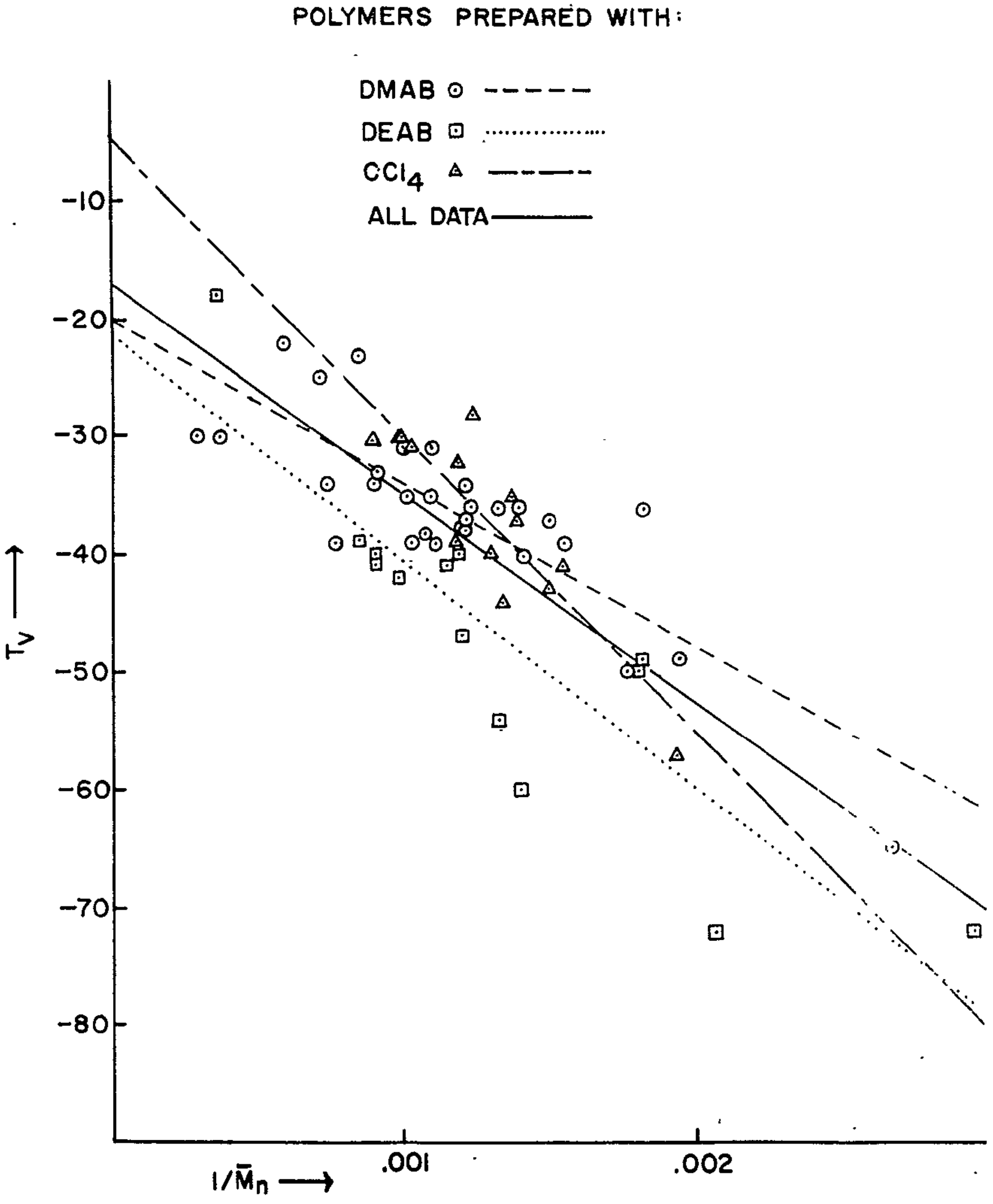
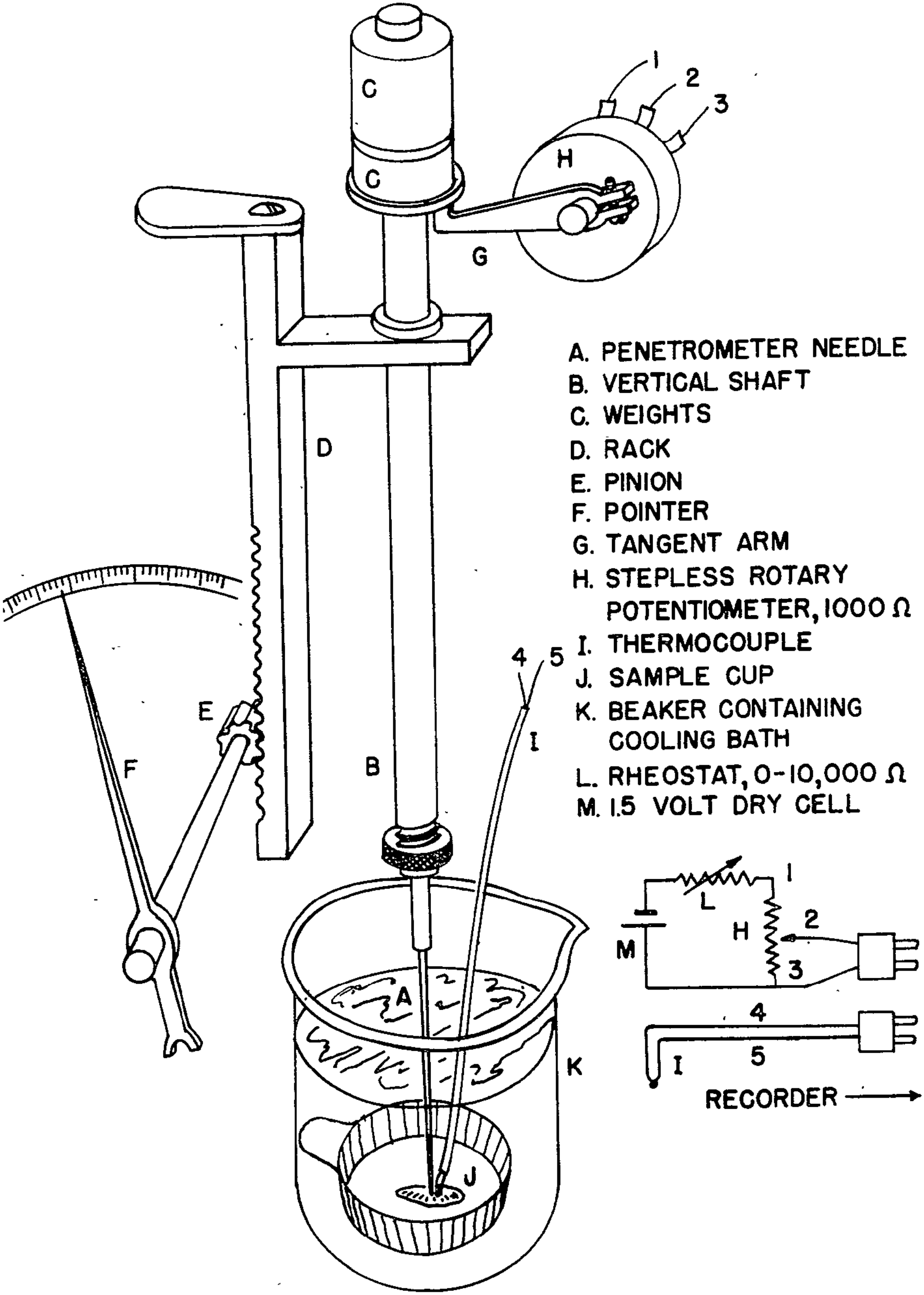


FIGURE 27

Dependence of $T_v$ Upon Molecular Weight

FIGURE 28

PENETRATION TEMPERATURE APPARATUS



A. PENETROMETER NEEDLE
B. VERTICAL SHAFT
C. WEIGHTS
D. RACK
E. PINION
F. POINTER
G. TANGENT ARM
H. STEPLESS ROTARY POTENTIOMETER, 1000 Ω
I. THERMOCOUPLE
J. SAMPLE CUP
K. BEAKER CONTAINING COOLING BATH
L. RHEOSTAT, 0-10,000 Ω
M. 1.5 VOLT DRY CELL

the needle suddenly begins to penetrate the sample. This is recorded as an abrupt end point on the strip chart and may be compared with the corresponding temperature later on. When the needle reaches the bottom of the sample and strikes the cup J, another straight line is produced. Figure 29 shows a typical result for an ethylene propylene telomer.

We have measured the $T_p$ of a large number of our liquid copolymer samples. Table LXVI and Figure 30 show the effect which molecular weight has upon $T_p$ for ethylene-neohexene copolymers with non-associating end-groups. These copolymers were taken from three different sets of samples: 1) samples prepared with DEAB initiation, 2) samples prepared with DMAB initiator, and 3) samples prepared in the presence of $CCl_4$ as chain transfer agent.

Note that acceptable values for $T_p$ can be obtained only if the molecular weight is low enough. The functional dependence observed for this family of polymers is:

$$T_p = -20.4 - \left(\frac{26800}{M_n}\right)$$

When samples with carboxyl end groups were examined, we found that a given carboxyl terminated product always showed a higher $T_p$ than the ester terminated product from which it had been prepared. There is too much scatter in the data to permit derivation of a useful equation relating $T_p$ with $1/M_n$. However, individual values tend to be 20 to 30° higher than the $T_p$ for ester terminated materials of comparable molecular weight. The difference becomes smaller at higher molecular weights.

In view of the influence of carboxyl groups on glass transition temperature and the fact that we are primarily interested in the low temperature properties of the cured binder, which contains no free carboxyl groups, it would appear that $T_g$ screening data obtained on ester terminated prepolymers would be more meaningful than measurements made on acid terminated prepolymers.

### 3. Torsion Pendulum Measurements

Use of the torsion pendulum has been widely accepted* as a valid method for measuring the glass transition in polymers.

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* L. E. Nielsen, Rev. Scientific Instruction, 22, 690 (1951)
J. A. Faucher and J. V. Koleske, Phys. and Chem. of Glasses, 7, 202 (1966).

FIGURE 29

RECORDER OUTPUT FOR $T_p$ DETERMINATION

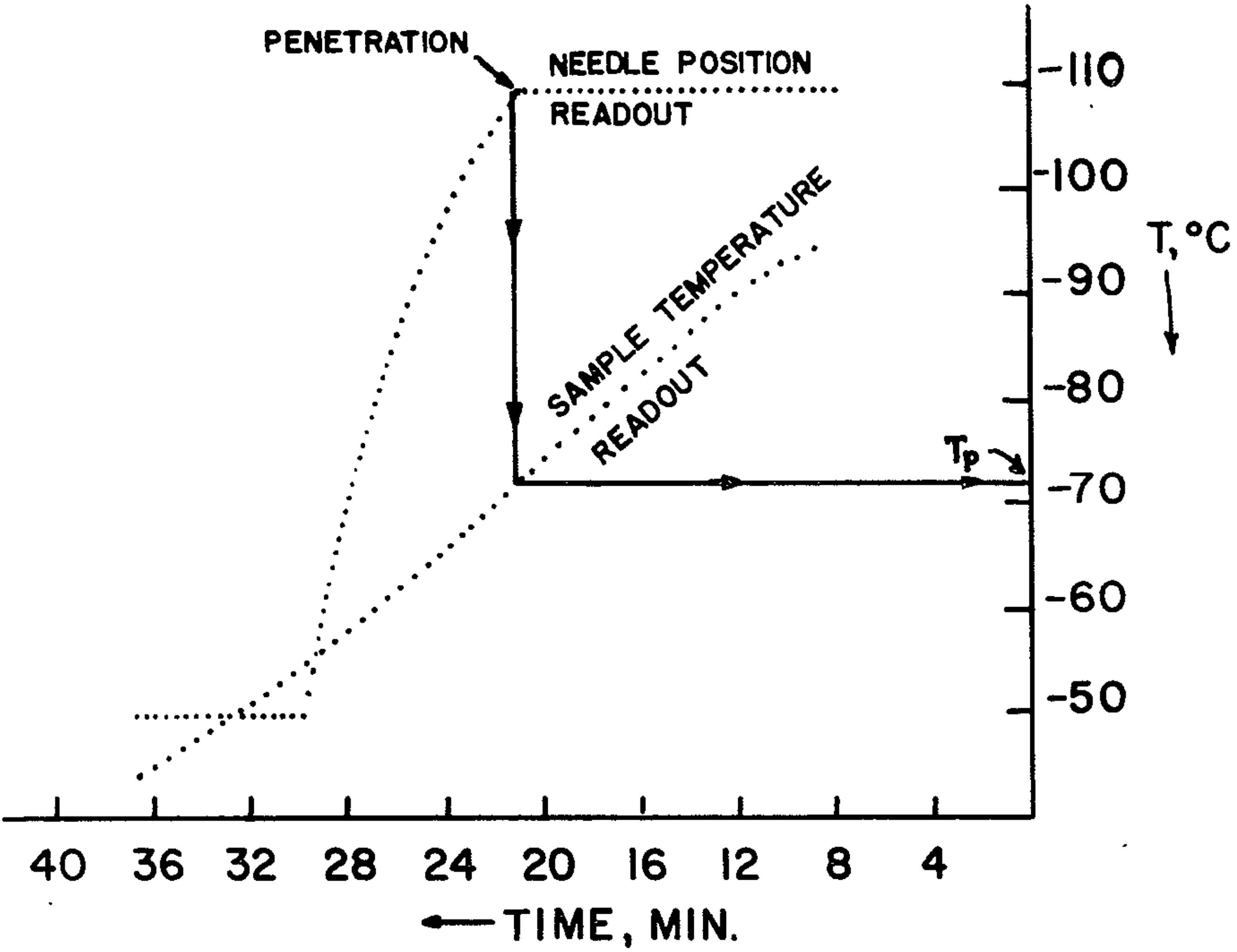
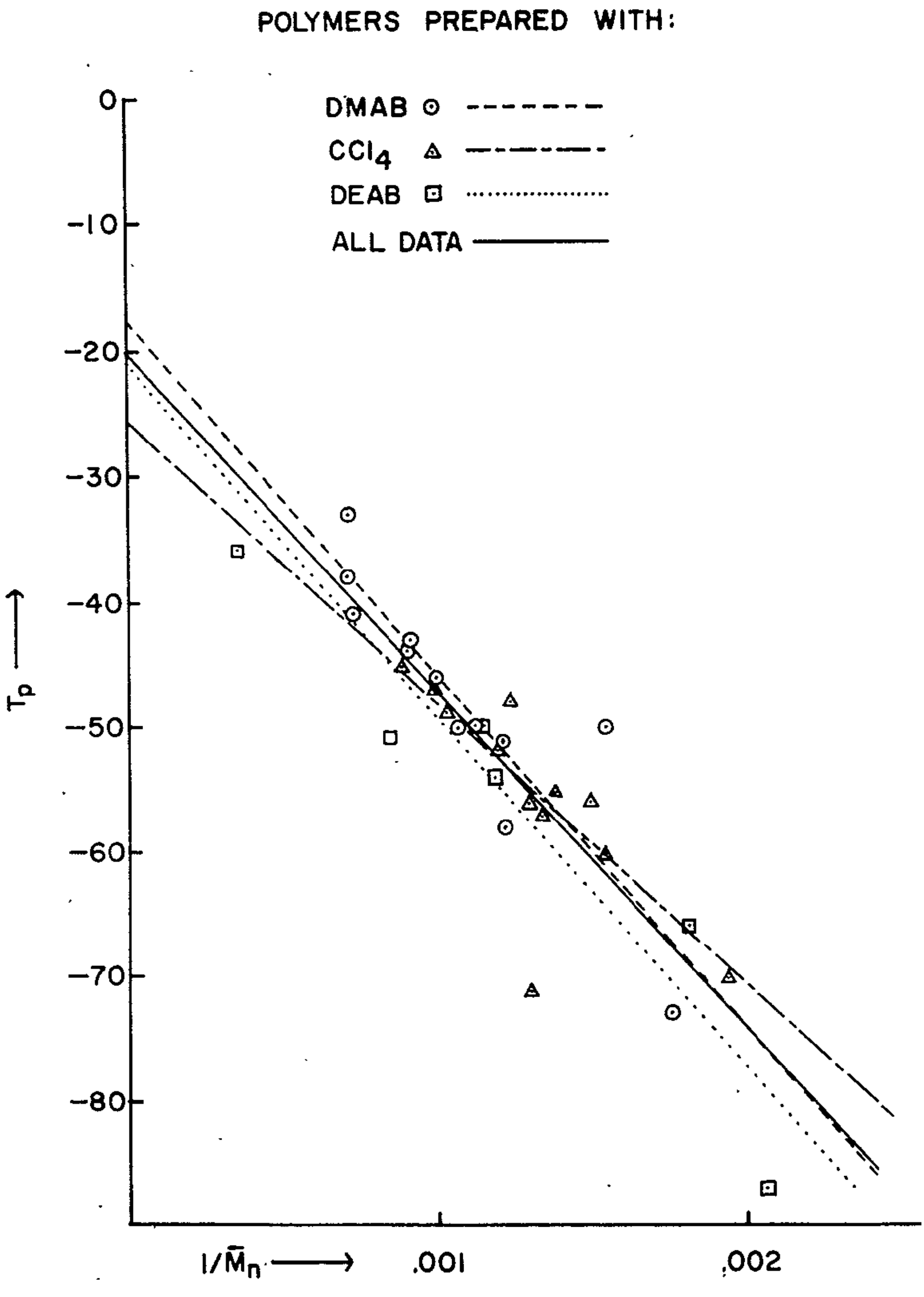


FIGURE 30

DEPENDENCE OF $T_p$ UPON MOLECULAR WEIGHT



In this method, the sample, a cellulose blotter saturated with the glassy polymer, is coupled to a torsion pendulum. Measurement of the damping characteristics of the pendulum, as the sample temperature is changed, allows one to observe changes in the physical properties of the polymer/blotter system. Below the glass transition temperature, these properties are largely determined by the rigid polymer glass.

The outstanding advantage of this method is that secondary transitions, occurring below the glass transition, can be detected, as well as crystalline transitions. The main disadvantage to this method is that it is time consuming and not well suited for the routine evaluation of a large number of samples. The results are also somewhat dependent upon the frequency of oscillation of the torsion pendulum, higher $t_g$'s being found at higher frequencies.

Three parameters are determined by the torsion pendulum: shear modulus, G'; loss modulus, G"; and dissipation factor, G"/G'. In the vicinity of the $T_g$, a rapid decrease of G' and an increase in G" occurs as well as an increase in the ratio G"/G'. Changes in all three of these parameters have been used to indicate the position of the glass transition temperature.

We have made comparatively few torsion pendulum $T_g$ measurements, however, a good correlation was found to exist between $T_p$, as discussed in Part 2), and the break in the plot of G' versus T. These measurements are probably equivalent and within experimental error of each other. The maximum point in the G"/G' versus T curve also correlates with $T_p$, but is systematically shifted to a slightly higher temperature.

Table LXVII shows the actual data obtained. $T_{G'}$ represents the break point in the G' versus T curve, i.e., the point where the high modulus, characteristic of the glassy polymer, begins to fall off rapidly with increasing T.

## TABLE LXVII

## COMPARISON OF $T_v$ $T_p$ AND $T_g$ VALUES

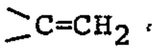
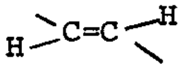
| Sample | End Group | $T_v$ | $T_p$ | $T_{G'}$ |
|---|---|---|---|---|
| 23-EMS- 4 | Ester | -40 | -54 | -52 |
| 23-EMS-11 | " | -41 | -50 | -50 |
| 24-EMS-90 | " | -47 | -61 | -58 |
| 24-EMS-87 | Acid | -21 | -37 | -40 |
| 24-EMS-92 | " | -33 | -46 | -50 |
| 24-EMS-96 | " | -28 | -45 | -47 |
| 24-EMS-112 | " | -23 | -37 | -38 |
| 24-EMS-114 | " | -26 | -36 | -38 |

In some of the torsion pendulum experiments, we carried out measurements from -170° up to +20°C. These measurements showed a secondary transition in the copolymers which occurs near -120°C.

Because of the comparative ease with which $T_p$ can be obtained, and the near-equivalence of the results with $T_{G'}$ obtained with the torsion pendulum, we will continue to measure $T_p$ and use it for routine characterization of polymer low temperature properties.

## G. Infrared Analysis for Double Bonds

Our method for determining the type of unsaturation present is based upon the C-H out of plane wagging vibrations in the infrared spectrum in the vicinity of 900 cm$^{-1}$. Anderson and Seyfried (Anal. Chem., 20, 998) give a table summarizing the absorption coefficients for various functional groups, including several types of double bonds. The pertinent values are summarized below:

| Functional Group | Structure | Absorption @ Maximum µ | cm$^{-1}$ | Absorption Coefficient |
|---|---|---|---|---|
| Vinyl | $-CH=CH_2$ | 10.98 | 909 | 50.3 |
| Vinylidene |  $>C=CH_2$ | 11.24 | 889 | 43.1 |
| Trans-internal |  | 10.36 | 965 | 35.6 |

From the infrared absorption at the peak maximum, and the absorption coefficients given above, the weight fraction (W.F.) of a given functional group can be calculated from:

$$W.F. = A/(10 \times b \times c \times p \times K)$$

where A = absorption at peak maximum
b = cell thickness in mm
c = volume fraction of sample (1 for neat samples)
p = density of sample
K = absorption coefficient from table above.

However, the cell thickness is difficult to determine accurately in the demountable gasket-spaced-cells which we have found to be most useful for liquid polymers, and the density of a given sample is seldom known with enough accuracy. Accordingly, for the present work, we have only determined the relative values of the weight fractions of the different double bond types in a given sample as measured from a single scan of a nominally 1 mil (.0254 mm.) thick preparation of the neat liquid polymer. Each relative value is proportional to the ratio A/K for the functional group in question, since in a single scan, b, c, and p remain constant. Therefore, if

$R_1$ = A vinyl/50.3

$R_2$ = A vinylidene/43.1

$R_3$ = A trans/35.6

$R_T = R_1 + R_2 + R_3$

Then the percent of total double bonds which are vinyl is $100R_1/R_T$, the percent vinylidene is $100R_2/R_T$ and the percent trans-internal is $100R_3/R_T$.

## VI. PLANS FOR FUTURE WORK

We plan to complete the conversion of the ethylene/neohexene telomers produced in the scale-up runs to the carboxyl terminated products.

Studies on the ethylene/propylene telomer end group conversion will also continue. Separation methods such as countercurrent extraction will also be applied to the products from these telomers.

We plan to synthesize the fluorinated analog of DMAB for use as an initiator.

Copolymerization and telomerization studies will also be conducted to prepare liquid ethylene copolymers containing functional groups other than carboxyl.

## VII. NEW TECHNOLOGY

### ITEM 1.

U. S. Patent Application #481,907
Applicants: James E. Potts
Arnold C. Ashcraft, Jr.
Edgar W. Wise

Title: Propellant Compositions

Date Revealed to NASA: October 26, 1965

Progress Reports: See Quarterly Reports #1 and #2, Contract #951210

Union Carbide Corporation, on October 10, 1966, granted the National Aeronautics and Space Administration, an agency of the United States of America, an irrevocable, non-exclusive, non-transferable, royalty-free license for the practice of each invention disclosed in the above patent application.

### ITEM 2.

Data are being obtained to support a patent application covering the use of certain new telomerizing agents in making prepolymers.

### ITEM 3.

A technique for rapidly determining the glass transition temperature of liquid polymeric binders was developed. This technique is based upon the use of a weighted penetrometer needle to detect the glass transition of a cooled binder sample which is allowed to warm up through its glass transition temperature. The method is described in detail in section 10-F-2 of this report.

### ITEM 4.

A thin layer chromatography technique for the analysis of liquid rocket binder samples has been developed. This technique allows a rapid qualitative determination of the functionality distribution present in binder samples. The method is described in technical discussion section 10-E-2 of this report.

## ITEM 5.

Countercurrent distribution between dimethylformamide and pentane has been shown to be an effective tool for the separation of the difunctional component of a low functionality ethylene/neohexene carboxyl terminated liquid binder. The method is described in technical discussion Section A-3 of this report.

cmd/lvm/jb

# VIII. GLOSSARY

| | | |
|---|---|---|
| Telogen | - | a chain transfer agent. |
| BAA | - | bromoacetic acid. |
| BIBA | - | α-bromoacetic acid. |
| BBIB | - | <u>tert</u>.-butyl α-bromoisobutyrate. |
| Telomer | - | a low molecular weight polymer prepared with the aid of a telogen. |
| Functionality | - | average number of functional groups per molecule. |
| N.E. | - | neutralization equivalent, the number of grams of a substance which is neutralized by one equivalent of base. |
| DMAB | - | dimethyl α,α'-azobis isobutyrate. |
| AIBN | - | α,α'-azobis isobutyronitrile. |
| DMTG | - | dimethyl dithioglycolate. |
| DTBP | - | di-<u>tert</u>.-butyl peroxide. |
| TBPP | - | <u>tert</u>.-butyl peroxypivalate. |
| Beilstein Test | - | a flame test for halogen. |
| Gilman Test | - | a color test for organometallics. |
| Sulfolane | - | tetramethylene sulfone. |
| THF | - | tetrahydrofuran. |
| DMF | - | dimethyl-formamide. |
| NMR | - | nuclear magnetic resonance. |
| I.R. | - | infrared. |
| DTAB | - | di-t-butyl α,α'-azobisisobutyrate. |
| DEAB | - | diethyl α,α'-azobisisobutyrate. |
| SAP | - | succinic Acid peroxide. |
| GAP | - | glutaric Acid peroxide. |
| MBIB | - | methyl α-bromoisobutyrate |

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