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SATURATED HYDROCARBON POLYMERIC BINDER FOR ADVANCED SOLID PROPELLANT

First Annual Addendum to Triennial Report

PERIOD COVERED: October 1, 1968
to
October 1, 1969

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.
J. E. Potts
E. M. Sullivan
E. W. Wise

Publication Date: October 15, 1969

Jet Propulsion Laboratory Contract No. 951210

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

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
Polymer Research and Development
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TECHNICAL CONTENT STATEMENT

This report contains information prepared by Union Carbide Corporation, Chemicals and Plastics Operations Division, under JPL 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, Chemicals and Plastics Operations Division has agreed to assist the Jet Propulsion Laboratory, California Institute of Technology, on a level of effort basis, in the development of a new or improved polymeric binder for advanced solid propellants.

The general objectives are described in Quarterly Report No. 1.

II. SUMMARY

Part 1

The ω-bromoester telomers 27-EMS-71 and 94 prepared from ethylene and propylene using α-bromo-ester telogens in a scale-up effort reported in the triennial report were converted to the carboxyl terminated prepolymers by the methods used successfully on the smaller telomer batches. The prepolymers obtained had carboxyl functionalities lower than expected from the combined bromine and ester functionalities of the starting telomers.

Improved work-up procedures were devised which were intended to recover part or all of the original functionality. These procedures did not give significant improvement in prepolymer functionality.

Reexamination of the telomer samples prepared in the scale-up effort disclosed that the difficulty lay in the original functionality determinations themselves. Repeat elemental analysis of telomer 27-EMS-94 showed only 2/3 the bromine content indicated by the original analysis. The new value was consistent with the best carboxyl functionalities obtained from this telomer, and was also in accord with the telomer composition determined by NMR spectroscopy.

Cyanogen and cyanogen bromide were evaluated as telogens and found to act as powerful retarders of free radical polymerization.

Methyl difluorochloroacetate was prepared and evaluated as a telogen. Its chain transfer activity was too low to be of value for the preparation of telomers.

Two different end group conversion procedures were applied to produce carboxyl terminated prepolymers from ω-bromoester telomers of ethylene with propylene.

In one of the methods, based upon nucleophilic displacement of terminal bromide by the anion of methyl thioglycolate, some measure of success has been obtained, however, the conversion of bromide terminal groups was not quantitative.

The other method using displacement of terminal bromide with cyanide ion followed by hydrolysis to carboxyl has given negative results.

Part 2

Terpolymers of ethylene, propylene and butadiene have been prepared which are difunctional in terminal ester groups. Hydride reduction followed by hydrogenation has given saturated liquid diols from one of these products. A direct correlation between butadiene content and ester functionality was established.

Ethylene/propylene/3-hydroxy-3-methyl butene terpolymers have been prepared by high pressure free radical polymerization. Six samples were prepared having average hydroxyl functionalities over the range 1.2 to 2.0 and with molecular weights ranging from 1100 to 2000. A total of 26 lbs. of liquid terpolymer was prepared.

The source of an initial foaming problem during isocyanate cures of these terpolymers was found to be water or some other substance removable by a drying operation. Dried terpolymer samples cure slowly with toluene diisocyanate without the formation of bubbles at 60°C.

Six samples of ethylene/propylene/vinyl acetate terpolymer were also prepared, a total of 30 lbs. of liquid product. A melt saponification procedure was devised for converting the pendant acetate groups to hydroxyl functionality located randomly along the polymer chain. This resulted in ethylene/propylene/vinyl alcohol liquid terpolymer. These products had secondary hydroxyl average functionalities from 1.24 to 2.67 over a molecular weight range of 1484 to 2646.

III. SCOPE OF PROJECT

The scope of this work remains as outlined in the work statement of our contract and as subsequently revised to include the investigation of other copolymers of ethylene.

IV. INTRODUCTION

In our triennial report issued on October 31 of last year, we discussed the preparation of telomers of ethylene and neohexene with α-bromoester telogens in a continuous high pressure autoclave called the "Unit II" reactor. This reactor system was used to prepare larger quantities of telomer using the most promising telogen, methyl α-bromoisobutyrate, in a scale-up effort. The telomer samples prepared in this effort, 27-EMS-71 and 27-EMS-94, provided a total of 655 grams of raw material from which sufficient carboxyl terminated prepolymer could be prepared to do larger scale curing studies.

The combined ester and bromine functionalities as originally determined were very promising. Both telomer samples contained close to 1.9 functional groups per molecule. In the report to follow, we will discuss the results obtained when these telomers were converted to carboxyl terminated prepolymers.

In previous quarterly reports as well as in our triennial report, we have discussed the preparation of telomers of ethylene with α-olefins other than neohexene. The most promising results were obtained with propylene. In the report to follow, we present the results of some reaction studies on converting the end groups in ethylene/propylene telomers into useful functional groups.

In this report, we also present the results obtained when terpolymerization of ethylene and propylene with a third monomer was used to prepare curable prepolymers.

Prepolymers were obtained having exclusively terminal functional groups, randomly placed functional groups, and also products having functionality of both types.

V. TECHNICAL DISCUSSION - PART 1

BINDER PREPOLYMER SYNTHESIS BY TELOMERIZATION

A. Ethylene/Neohexene Telomers - Scale-Up

In our Triennial Report we discussed the preparation of larger quantities of the methyl α-bromoisobutyrate (MBIB) telomers of ethylene and neohexene.[1] Two different runs were made in the "Unit II" continuous Stirred Autoclave reactor.[2]

A pilot run, 27-EMS-71, yielded 106 grams of telomer, and the scale-up run, 27-EMS-94 yielded 549 grams of telomer.

Preliminary functionality determinations based upon bromine elemental analyses and vapor pressure osmometry indicated that both telomers contained close to one bromine atom per molecule.

We had previously developed an efficient procedure by which the terminal bromide functionality of the ethylene/neohexene telomers could be converted to carboxyl functionality.[3] In this procedure, potassium hydroxide is used to dehydrobrominate the telomer producing terminal double bonds which are subsequently ozonized and oxidatively cleaved to give terminal carboxyl groups. This procedure was applied to the telomer 27-EMS-71 with the following results:

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1. A. C. Ashcraft, J.E. Potts, E.M. Sullivan and E.W. Wise, "Saturated Hydrocarbon Polymeric Binders for Advanced Solid Propellants", Triennial Report, Oct. 31, 1968, Section V-8-G, page 128.

2. Ibid, Section V-8-F, page 124

3. Ibid, Section V-8-H, page 131

Dehydrobromination of 27-EMS-71

67 grams of the telomer was treated with an excess (20% over theoretical) of KOH in the melt at 300 °C for 10 minutes. The acidified product gave a negative Beilstein test showing that no bromine remained, and the infrared spectrum showed that the ester endgroups had been converted to carboxyl groups. The infrared spectrum also showed that double bonds were present in the product as evidenced by the trans C=C absorption at 970 cm^{-1} and the vinylidene absorption at 890 cm^{-1}. From the relative absorptions at these two frequencies we obtain a trans/vinylidene ratio of 2.9.

Ozonolysis and Oxidation

53 grams of the above product was dissolved in a mixture of 200ml heptane and 100ml propionic acid and treated with an excess (16% over theoretical) of ozone/oxygen at 0°C.

The ozonolysis reaction mixture was combined with 225ml. formic acid and treated with 112 ml 30% aqueous hydrogen peroxide. After reacting overnight under reflux, the product was recovered as 50 grams of a slightly cloudy straw colored oil.

The infrared spectrum of this product shows no detectable C=C absorptions and has a very strong carboxyl carbonyl absorption at 1700 cm^{-1}. The product had a neutralization equivalent of 505 and its molecular weight (duplicate determinations by V.P.O. in T.H.F. at 37°C) was 715. This implies a carboxyl functionality of 1.42. Thin layer chromatography confirms this result showing roughly equal proportions of mono and difunctional components. The results of this sequence are summarized in Table I.

In a similar reaction sequence the telomer from the scale-up run, 27-EMS-94, was converted into the carboxyl terminated product, and again the final product had a carboxyl functionality lower than expected based upon the functionality of the starting material. These results are also summarized in Table I.

TABLE I

FUNCTIONALITY CONVERSIONS IN ETHYLENE/NEOHEXENE TELOMERS

Samples 27-EMS	71	94
Original Sample Data		
$\overline{M}n$	800	883
Ester Equiv. Wt[a]	926	1056
Wt % Bromine	9.95	9.54
Ester Functionality	0.87	0.84
Br Functionality	1.00	1.05
Total Functionality	1.87	1.89
Dehydrobrominated Product Data		
Beilstein Test	Negative	Negative
Absorption at 970 cm^{-1} (IR)	Strong	Strong
Absorption at 890 cm^{-1} (IR)	Moderate	Weak
Trans/Vinylidene C=C ratio	2.9	8.4
Final Product Data		
$\overline{M}n$	715	819
Neutralization Equivalent	505	546
COOH Functionality	1.42	1.50
Net Loss in Functionality	0.45	0.49

[a] I.R. Spectrum, Methyl pivalate as reference.

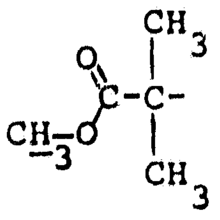
The net loss in functionality of about 0.4 COOH per molecule incurred during the workup of both telomer samples made a closer look at the composition of the starting materials necessary as well as a careful reevaluation of the procedures used during the endgroup conversion reactions.

Analysis of 27-EMS-71 by Nuclear Magnetic Resonance Spectroscopy

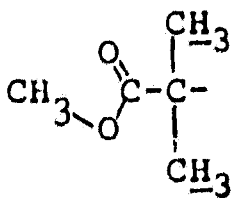
In addition to the major resonances in the N.M.R. spectra of ethylene/neohexene telomers due to the monomer units themselves, there appear weaker resonances which arise from the endgroups. The different endgroup types possible in the ethylene/neohexene telomers are listed in Fig. 1 along with the chemical shift, δ in parts per million, at which the resonance occurs. The protons responsible for the resonance are underlined. The major resonance from the CH_2 units derived from the monomer units occurs at $\delta=1.28$ p.p.m. and the *t*-butyl groups from neohexene give rise to the other major resonance at $\delta=0.87$ p.p.m.

FIGURE 1

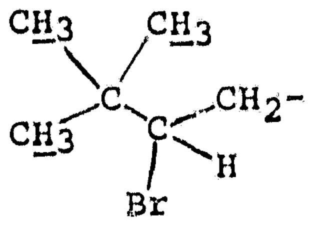
ENDGROUP TYPES IN ETHYLENE/NEOHEXENE TELOMERS PREPARED WITH DMAB AND MBIB



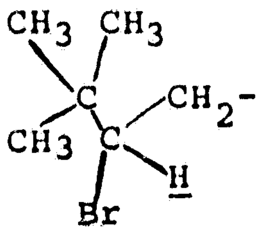
I, δ= 3.62 ppm



II, δ= 1.14 ppm



III, δ= 1.06 ppm



IV, δ= 3.88 ppm

$Br-CH_2-CH_2-$

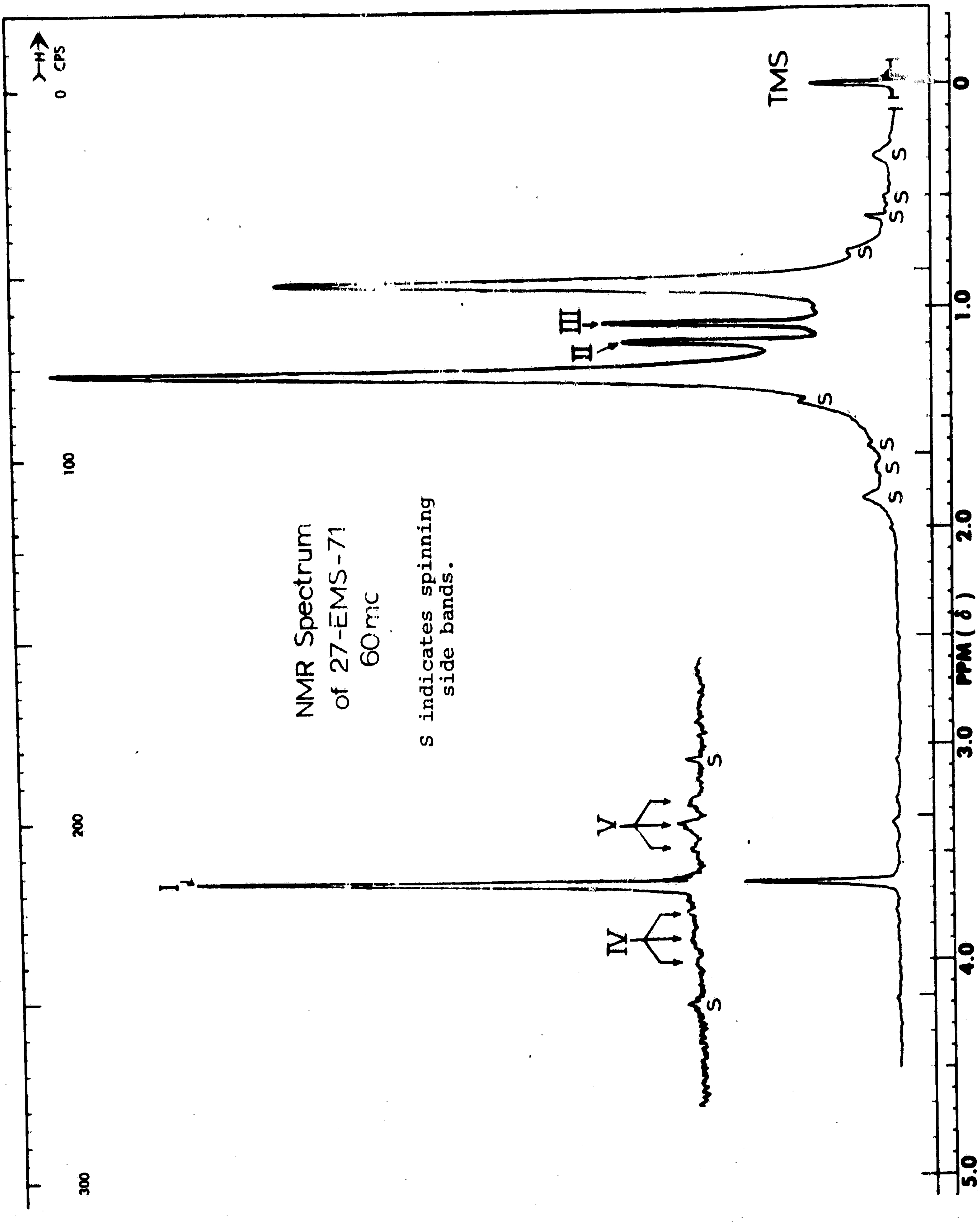
V, δ= 3.34 ppm

N.M.R. analysis of 27-EMS-71 gave an ester equivalent weight of 893 which implies an ester functionality of 0.90. This determination was based upon the relative area of the sharp methoxyl signal at δ= 3,62 ppm. (I) , and is in reasonable agreement with the previous determination based upon the carbonyl absorption in the infrared. See Fig. 2.

The N.M.R. spectrum also gave the molar ratio of ethylene to neohexene in this telomer: 3.1 to 1. (See Part 10-B of our Triennial Report).

The near equality of area of the N.M.R. signals at δ= 1.14 and 1.06 ppm (which represent II, geminal methyl groups derived from DMAB on an ester end group, and III, the t-butyl group from a terminal neohexene residue bearing a bromide) implies that there are not as many terminal bromides on neohexene units as there are ester units per molecule.

FIGURE 2



NMR Spectrum of 27-EMS-71 60mc

S indicates spinning side bands.

If there were, the ratio would be 2:3, not 1:1 as observed. The two weak triplet signals at δ=3.88 and 3.34 ppm lend support to this observation. The former signal is due to the lone hydrogen on the carbon bearing the bromide of the terminal neohexene unit (IV) and the latter is due to the corresponding $-CH_2-$ derived from ethylene (V). Both signals are split into triplets by the adjacent $-CH_2-$ groups. The relative amounts of these groups present cannot be directly determined as yet because of the low signal strength. This may be attempted later using a time averaging computer coupled to the N.M.R. in order to increase the signal-to-noise ratio by summing repetitive scans of the same spectrum. The qualitative results arrived at from this spectrum are significant however:

1) The terminal bromide functionality on neohexene end residues is appreciably lower than the terminal ester functionality, possibly as low as 0.6 per molecule.

2) Some terminal bromide functionality is bound to ethylene end residues.

Attempts to Reclaim the Lost Functionality

We concluded from the N.M.R. results discussed above that under our dehydrobromination conditions the terminal bromide functionality attached to neohexene end residues in telomer sample 27-EMS-71 dehydrobrominated as expected on the basis of our earlier work and gave rise to double bonds which could be converted to COOH groups by the ozonolysis and oxidation steps. The remainder of the bromide functionality, presumably attached to ethylene residues, were also removed during the dehydrobromination procedure but did not give rise to oxidizable double bonds.

A particularly likely possibility was that displacement of the primary Br^- by OH^- occurred to give terminal alcohol functionality. This could have been protected from the subsequent oxidation steps by acetylation with the acetic acid used to acidify the dehydrobromination reaction mixture.

If the above hypothesis were correct, one would expect that saponification of the final product followed by re-oxidation under alkaline conditions (so as to prevent reesterification) would result in recovery of a carboxyl terminated product having the same functionality as the original telomer, namely 1.87.

To test the above hypothesis we treated a 34 g sample of the COOH terminated product derived from 27-EMS-71 with an excess (3.4 times the amount of COOH present) of KOH in the melt at 200°. This was to neutralize the terminal COOH and saponify any terminal acetate or formate units. The infrared spectrum of the resulting melt showed no COOH or ester absorption, strong COO^-K^+ absorption at 1560 cm^{-1} and a moderate OH absorption at 3300 cm^{-1}. Oxygen was then bubbled through the stirred melt at 200°C for a total of 80 minutes. During this time infrared spectroscopy on aliquots showed a decrease in OH absorption and an increase in COO^-K^+ absorption. The product was then acidified with acetic acid and recovered as usual to give an 85% recovery of a slightly cloudy light amber oil.

Thin layer chromatography on SiO_2 in 2% CH_3OH in $CHCl_3$ showed a pronounced increase in the high functionality component at the expense of the monofunctional component as compared with the starting material. The neutralization equivalent was 451, compared to 505 in the starting material. This amounts to a 12% increase in COOH content. If the molecular weight has not been changed by the oxidation procedure the calculated COOH functionality is 1.59, a significant improvement over the 1.42 functionality of the starting material. However a V.P.O. determination of $\overline{M}n$ showed a decrease to 674 which implies a functionality of 1.50.

An improved procedure would result if the dehydrobromination reaction mixture were converted directly into an alkaline aqueous emulsion and directly ozonized without acidification. Under these conditions the unprotected terminal OH groups on ethylene end residues should oxidize as readily as the terminal C=C. Following this procedure all the terminal bromide functionality should yield carboxyl functionality in the final product.

We followed this modified procedure starting with telomer 27-EMS-94. This telomer had a total functionality of 1.89 as determined by V.P.O. molecular weight, bromine elemental analysis and infrared spectroscopy, however, our standard procedure yielded a carboxyl terminated product having a functionality of only 1.50 (See Table I).

Dehydrobromination of 27-EMS-94

50 grams 27-EMS-94 was treated with 26 ml of 5.89 N KOH (.153 eq.OH) and then heated with stirring under a nitrogen atmosphere until the water was all driven off. The reaction mixture was then heated to 300° C and stirred at this temperature for 30 minutes and allowed to cool to below 100°C. 200 ml. H_2O was then added and the resulting mixture homogenized with 250 ml. heptane and another 450 ml. H_2O. A 5ml. aliquot of the emulsified reaction mixture was evaporated to dryness, taken up in $CHCl_3$, filtered and solution cast on a salt plate. The infrared spectrum of this film showed a strong carboxylate salt band, moderate absorption due to the trans-disubstituted c=c and moderate OH absorption.

Ozonolysis

The highly alkaline emulsion was then treated with a 1-liter/minute stream of O_3/O_2 containing 0.65 mmoles O_3/liter for three hours at 20°C. Aliquots were removed at regular intervals and used to prepare films on salt plates as described above. The intensities of the trans - c=c absorption at 970 cm^{-1} and the asymmetric c-c-o stretch of the hydroxyl group at 1030 cm^{-1} relative to the methylene chain skeletal vibration at 719 cm-1 were measured in the I.R. spectrum of each aliquot. These data were used to follow the course of the ozonolysis (See Fig. 3).

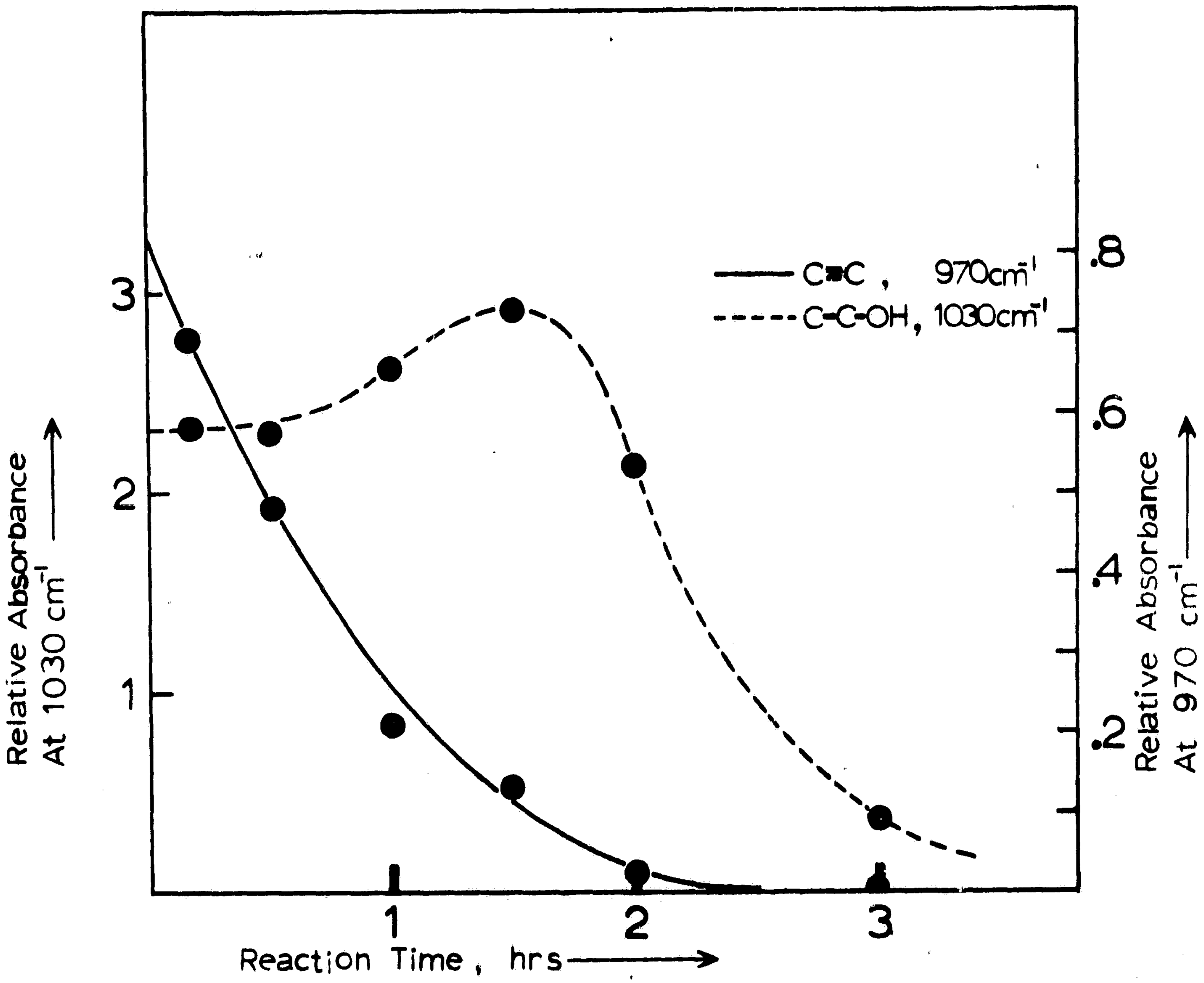
The double bond content decreased rapidly and was virtually gone after 2 hours of ozone treatment. The alcohol content as measured by the c-c-o stretch, however, increased slightly until the double bonds had been largely reacted, and then also decreased to a low value. The initial increase may be due to hydroxyl containing intermediates derived from ozonolysis of the double bonds.

Oxidation

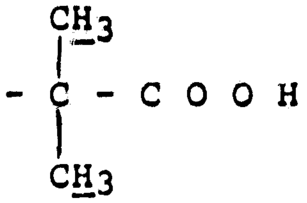
After three hours of ozone treatment the reaction mixture was allowed to remain overnight at 18-20°C and was then slowly heated to reflux and treated with 10 ml. 30% aqueous hydrogen peroxide, added dropwise with stirring. During this phase the reaction mixture was a foaming white emulsion. After 15 min. an aliquot was removed, worked up and examined by infrared spectroscopy. No hydroxyl absorption was noted. To insure the oxidation of any carbonyl functional groups (which could be hidden by the strong COOH carbonyl absorption), 125 ml. formic acid and an additional 20 ml. 30% aqueous hydrogen peroxide were added and reflux continued under these acidic oxidation conditions for 16 hours, cooled and the two phase system worked up by a 5-stage counter current extraction between heptane and water in order to recover all the polymer, yet insure the removal of all water soluble material. After removal of heptane by vacuum stripping, 37 grams of straw colored oil was obtained.

FIGURE 3

INFRARED ABSORBANCE DUE TO DOUBLE BONDS AND HYDROXYL GROUPS IN ALIQUOTS FROM OZONOLYSIS



The neutralization equivalent was 619 and the molecular weight (V.P.O. in T.H.F. at 37°C) was 959, implying a carboxyl functionality of 1.55. This product gave a negative Beilstein test, showed no hydroxyl or unsaturation in its infrared spectrum, and its N.M.R. spectrum showed no evidence of unreacted endgroups from the original telomer. The N.M.R. spectrum did show the presence of two different types of COOH endgroups. I (derived from the original ester endgroup) gives a resonance at $\delta= 1.17$ ppm due to the geminal methyl groups near COOH, and II (derived from either $-CH_2-CH_2-OH$ oxidation or $-CH_2-CH{=}CH-\underline{t}-$Butyl ozonolysis) gives a resonance at $\delta=2.31$ ppm due to the $-C\underline{H}_2-$ adjacent to COOH.



$$-\overset{\displaystyle C\underline{H}_3}{\underset{\displaystyle C\underline{H}_3}{C}}-COOH$$

I, $\delta=1.17$ ppm

$$-CH_2-C\underline{H}_2-COOH$$

II, $\delta=2.31$ ppm

Thin layer chromatography confirms the functionality determination by showing approximately equal amounts of mono and difunctional polymer components in the final product.

Re-Examination of the Telomer 27-EMS-94

The lower than expected COOH functionality resulting from the rather exhaustive recovery procedures used, prompted a re-examination of the bromine and ester functionality of the starting material, telomer 27-EMS-94.

A sample was submitted to a different analytical laboratory for bromine and oxygen elemental analysis. The results obtained are listed below for comparison with the original data.

	Original Data	New Data
Molecular Wt.	883	878
Wt % Bromine	9.74	5.74
Wt % Oxygen	——	3.48
Ester Eq. Wt.	1056	——
Functionality		
Bromine	1.05	0.63
Oxygen	——	0.96
Ester	0.84	——
Total	1.89	1.59

The total functionality of 1.59 (ester O_2 plus Br) calculated from the new analytical data is in rather good agreement with the best COOH functionalities obtained in the products derived from 27-EMS-94. Our original procedure gave a product having a functionality of 1.50, and the more exhaustive procedure just reported, which was designed to recover all of the bromide functionality, gave 1.55. As yet unexplained is the great discrepancy between original bromine analysis and the new determination.

The new data however were confirmed by a careful N.M.R. analysis of the telomer 27-EMS-94 using the C.A.T. computer coupled with the N.M.R. spectrometer. This allowed summing of many repetative scans of the N.M.R. spectrum and resulted in a great enhancement of the signal to-noise ratio, which permitted analysis of the weak signals from the bromine bearing endgroups for the first time. Figure 4 shows a small section of the enhanced N.M.R. spectrum showing the region of interest. The remainder of the spectrum is similar to that shown in figure 2 for telomer 27-EMS-71. Note that the weak resonance IV at δ= 3.88 ppm in Fig. 2 (due to the single methinyl proton on a neohexene endgroup) was not properly located due to the high noise level. The CAT-enhanced spectrum shown in Figure 4 shows that the correct chemical shift for this proton is δ= 3.76 ppm.

The combined area of resonances I and IV, and the areas of resonances V, II, and III were measured and used to calculate the values for the two different types of bromine functionality relative to the ester functionality. The results are shown below:

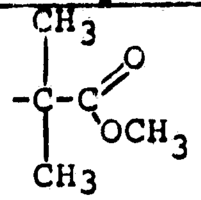
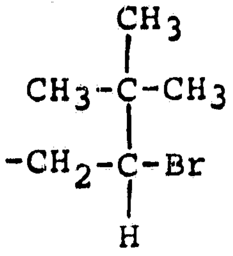
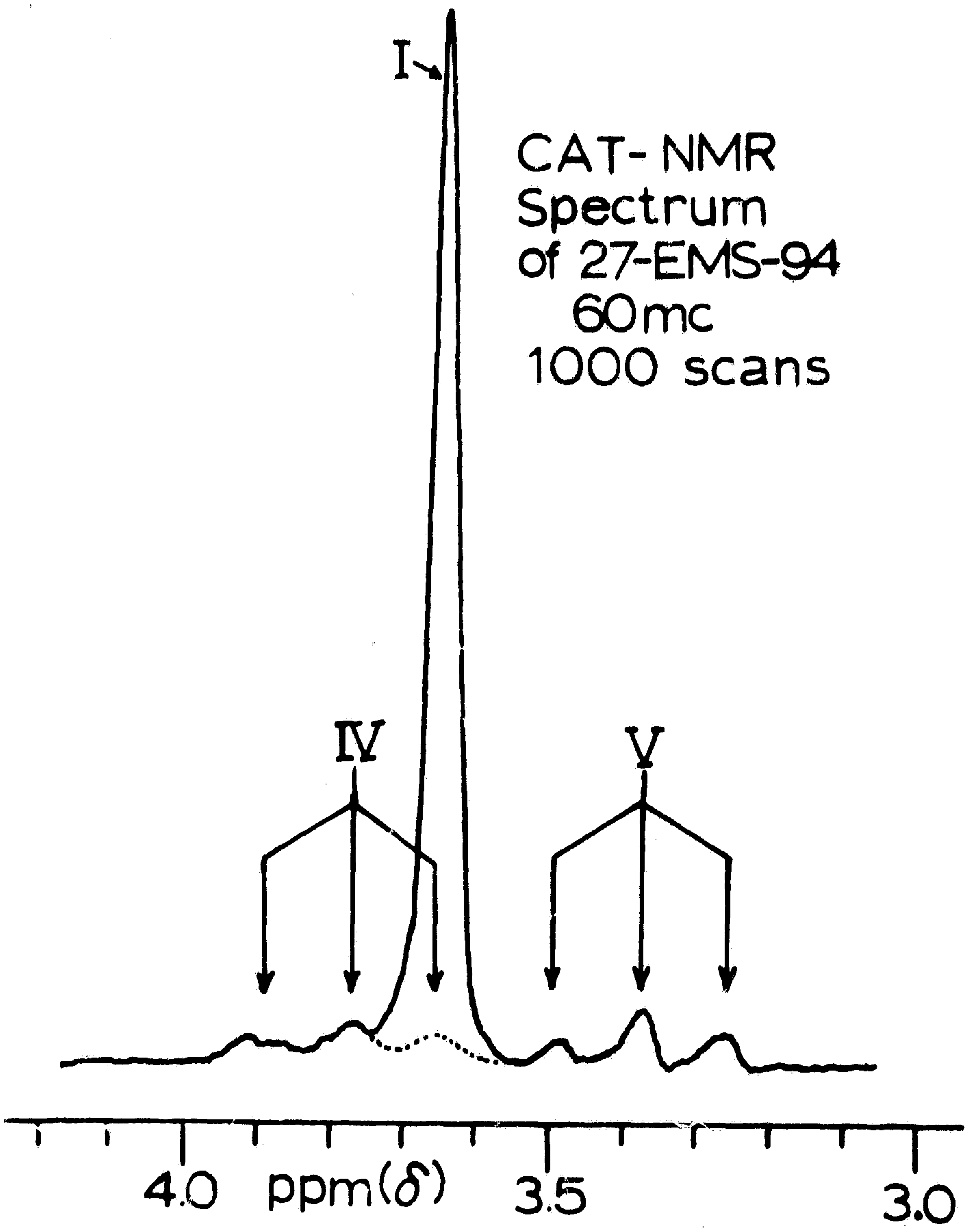
Group	Relative Functionality
	1.00
$-CH_2-CH_2-Br$	0.20
	0.56
All bromides	0.76
Total Functionality Relative to Ester	1.76

FIGURE 4


I
CAT-NMR
Spectrum
of 27-EMS-94
60mc
1000 scans
IV
V
4.0
ppm(δ)
3.5
3.0

We thus arrive at the result that the total functionality of 27-EMS-94 is 1.76 times the ester functionality, or about 1.6 . This again is in good agreement with the value 1.59 as determined by elemental analysis and VPO, and the value 1.55 which was the best COOH functionality obtained in a prepolymer prepared from 27-EMS-94.

Conclusions

The above results lead us to the conclusion that the lower than expected COOH functionalities in products derived from the scaled-up telomers 27-EMS-71 and 27-EMS-94 are not entirely due to incomplete conversion of the telomer endgroups, but rather must result from functionality deficiencies in the telomers themselves. At present we have no explanation for this deficiency.

It may be possible to enrich the carboxyl terminated prepolymers derived from 27-EMS-71 and 94 using the techniques of counter current distribution as described in our Triennial Report.

B. Cyanogen and Cyanogen Bromide as Telogens

If cyanogen, I, or cyanogen bromide, II, were effective as chain transfer agents in free radical polymerization, telomers of the type shown below might be prepared using them as telogens:

$$\underset{\text{I}}{N\equiv C-C\equiv N} \xrightarrow[\text{radical initiator}]{CH_2=CHR} N\equiv C-(CH_2-CHR)_n-C\equiv N$$

$$\underset{\text{II}}{Br-C\equiv N} \xrightarrow[\text{radical initiator}]{CH_2=CHR} N\equiv C-(CH_2-CHR)_n-Br$$

These telomers could then be converted to carboxyl terminated prepolymers by standard organic reactions if their original functionalities were high enough. To test this possibility we conducted some small scale exploratory batch telomerizations in the presence of I and II. The results are summarized in Table II.

Both I and II acted as powerful retarders and resulted in very low conversion rates in all three of the runs. The products from runs 106 and 107 were both black greases, and had infrared spectra showing no chain-methylene absorption at 13.9 μ at all. No nitrile absorption was present either, however strong NH and amide absorption were present as well as a moderate absorption at 4.65 μ , a region in which absorptions of functional groups containing "cumulene" structures typically appear (ie, ketenes, allenes, ketene-imines etc). These observations, together with the high nitrogen content, are most consistent with the interpretation that cyanogen itself was acting as a conjugated monomer rather than as a chain transfer agent.

The product from run 115 was a tan oil. Its infrared spectrum showed the characteristic features of DMAB initiated liquid ethylene copolymers. No nitrile absorption was present. This fact, together with the low bromine functionality, shows that cyanogen bromide is not an effective telogen. However, like cyanogen, it acts as a powerful retarder for the copolymerization giving a conversion rate of only 0.17% per hour.

No further telomerization studies with either cyanogen or cyanogen bromide are planned.

TABLE II

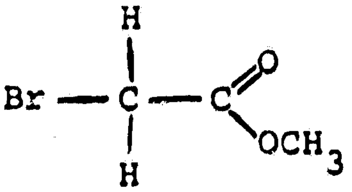
TELOMERIZATION WITH CYANOGEN AND CYANOGEN BROMIDE

Run #27-EMS Telogen Used	106 Cyanogen	107 Cyanogen	115 Cyanogen Bromide
Initial Charge, gms			
1:1 Benzene/t-Butanol	10.2	10.2	10.2
Telogen	5.0	4.0	0.82
DMAB Initiator	0.093	0.279	0.093
Ethylene	415	423	423
Propylene	350	365	363
Fed During Reaction			
1:1 Benzene/t-Butanol	79.6	79.0	98.0
DMAB Initiator	0.835	2.51	0.835
Telogen	—	—	7.36
Reaction Conditions			
Temperature °C	90	90	90
Pressure, psi			
Initial	11,500	11,500	8450
Final	17,000	16,250	14200
Time, hrs.	3.08	3.08	3.08
Productivity			
Yield, gms	2.0	2.0	4.0
Conversions %	0.26	0.25	0.51
Rate, %/m	0.09	0.08	0.17
Properties			
Molecular Wt. (VPO)	—	—	741
Specific Viscosity	0.055	0.032	.024
Wt % N	12.22	6.15	0.37
Wt % Br	—	—	3.39
Functionality			
Nitrogen	—	—	0.20
Bromine	—	—	0.31

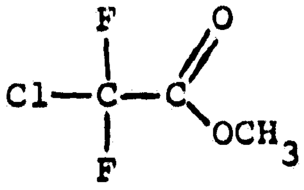
C. Chlorodifluoroacetic Acid Esters as Telogens

We have evaluated methyl bromoacetate, I, as a chain transfer agent for the preparation of ethylene/neohexene telomers. It was unsatisfactory because hydrogen abstraction effectively competed with bromine abstraction in reactions with polymer radicals. This resulted in low functionalities.[4]

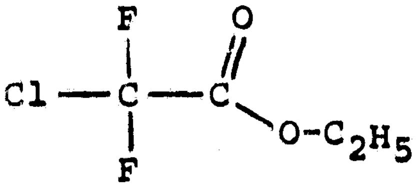
Having no α-hydrogen atoms to interfere in this manner, esters of chloro or bromodifluoroacetic acid might prove to be more effective telogens. To test this possibility we prepared the methyl and ethyl esters of chlorodifluoroacetic acid, II and III.



I



II



III

II and III were easily prepared from the acid by esterification using the corresponding alcohol and sulfuric acid.

Three batch telomerizations were run to evaluate methyl chlorodifluoroacetate as a telogen. Two of these runs were ethylene/propylene telomerizations carried out at 90°C and having telogen/monomer ratios of 0.003 and 0.0045 respectively. DMAB initiator and the telogen were fed in during the run to simulate steady state conditions. In both runs only traces of halogen were found in the products, implying very low values for the chain transfer coefficient.

The other run was an ethylene/neohexene telomerization carried out under similar conditions with a telogen/monomer ratio of 0.0045. The resulting product contained no detectable halogen. This confirms the results from the ethylene/propylene telomerizations. Methyl chlorodifluoroacetate is not active as a chain transfer agent in ethylene copolymerizations. The results of these runs are summarized in Table III.

The use of bromine or iodine in place of the chlorine is probably required in order for the carbon-halogen bond to be weak enough for free radical displacement reactions to occur at the halogen atom to give the difluoroacetate radical.

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[4] Ibid, Section V-8-B, page 102

TABLE III

METHYL CHLORODIFLUOROACETATE AS A TELOGEN

Run #28-EMS	15	17	19
Initial Charge, gms			
Propylene	393	393	—
Neohexene	—	—	678
Ethylene	395	397	265
Solvent	10.4	10.4	10.4
DMAB Initiator	0.094	0.094	0.13
Telogen	0.78	1.16	0.85
Mole Ratio of Telogen to Monomers	.003	.0045	.0045
Fed During Reaction			
Solvent	92.7	92.7	92.7
Telogen	6.98	9.48	7.67
Initiator	0.844	0.844	1.17
Reaction Conditions			
Temp. °C	90	90	90
Pressure, mpsi	12.7	10.0-16.0	10.0-15.4
Time, hrs	3.08	3.08	3.08
Productivity			
Yield, gms	11	13	48
Conversion, 70	1.4	1.46	5.09
Rate, %/m	0.46	0.47	1.66
Properties			
Molecular Wt.	1562	1956	3095
Specific Viscosity	.045	.047	.057
Wt % Chlorine	0.11	Trace	0
Wt % Fluorine	Trace	Trace	0
Saponification Equivalent	1212	1984	1449
Penetration Temperature, °C	-75	-75	-45

D. Ethylene/Propylene Telomers - Chemical Modification of Terminal Groups

We have previously reported that attempts to convert the terminal bromide of the ethylene/propylene telomers to a carboxyl group failed when we used the methods which were successful for the ethylene/neohexene telomers. The reason we proposed for this was that the less sterically hindered terminal bromides in the ethylene/propylene telomers were more subject to displacement than those in the ethylene/neohexene telomers. This resulted in a large amount of terminal OH or acetate when KOH or KOAc were used, respectively, for melt dehydrobromination reactions. Since terminal unsaturation was essential for the subsequent ozonolysis and oxidation steps, the final COOH functionality was less than calculated based on the starting material's ester and bromide functionality.

It was proposed at that time that several reactions based upon displacement of terminal bromide might be feasible and lead to higher carboxyl functionalities:

1. Displacement of $\mathrm{Br}^{\ominus}$ by thioglycolate ion.

2. Sulfide coupling of two molecules resulting in displacement of two $\mathrm{Br}^{\ominus}$.

3. $\mathrm{CN}^{\ominus}$ displacement of $\mathrm{Br}^{\ominus}$ followed by hydrolysis.

Reaction (1) was tried on 22 grams of ethylene/propylene telomer 27-EMS-40 (Mol. wt. = 819, 0.81 Br per molecule). An equimolar quantity of potassium *t*-butoxide and a twofold molar excess of methylthioglycolate (I) was added to the polymer dissolved in 50 ml. dry diglyme solvent.

$$\underset{\text{(I)}}{CH_3\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}SH} \xrightarrow[\Delta]{\text{K OtBu}} CH_3\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}S^{\ominus}\ K^{\oplus} + tBuOH\uparrow$$

When the reaction mixture was heated at 150°C, 1.6 g. of a distillate (probably *t*-butanol) was obtained, bp 75-90°C, and a white solid (later shown to be KBr) precipitated. An aliquot of the organic layer was worked up and the recovered product analyzed. A positive (but very weak) Beilstein test for halogen was obtained and the infrared spectrum showed an increase in the ester absorption, but no significant changes in the C=C region.

The reaction mixture was then refluxed with an excess of aqueous KOH to saponify all ester end groups and the methyl thioglycolate. After acidification and workup as usual, 20 grams of product were obtained. Mol. Wt. = 960, neutralization equivalent = 1230. T.L.C. shows a large nonfunctional fraction. However, the infrared spectrum shows ester absorption as well as COOH absorption, which indicates that the saponification step did not proceed to completion.

The product from the above experiment was then further treated by melt saponification using an excess of finely divided KOH at 150°C for 20 minutes. The product was recovered by acidification with acetic acid, taking up the polymer in heptane and water washing prior to drying and vacuum stripping to give the liquid product, neutralization equivalent = 1052.

The infrared spectrum showed an increase in the carboxyl content of about twofold, with no ester remaining at all.

Thin layer chromatography (in 2% methanol in $CHCl_3$) showed a decrease in the nonfunctional fraction as compared with the starting material as well as an increase in both the mono- and difunctional components, presumably due to saponification of the ester groups which behave like nonfunctional ends in this T.L.C. system.

As yet we have not attempted to utilize reaction (2) proposed above.

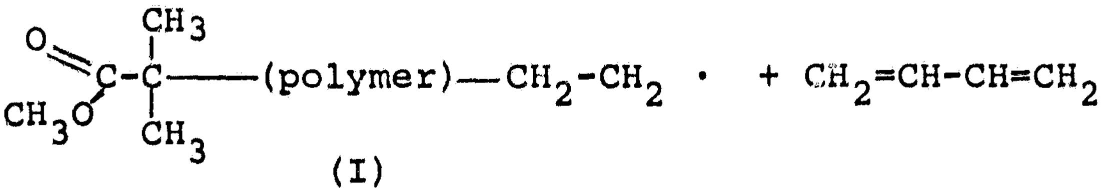
To test reaction (3) 20 grams of another ethylene/propylene sample 27-EMS-34-1 (mol. wt. = 1050, .72 Br per molecule) was treated with a large excess of KCN in DMSO solvent. The reaction mixture was heated briefly to 100°C with stirring under nitrogen and then kept at 60°C overnight. The product was taken up in heptane and washed with water to remove excess KCN and the DMSO. After evaporation, 18 grams of product were obtained having a strong positive Beilstein Test and showing weak CN absorption in the infrared, corresponding to about .11 CN per molecule or about 14% reaction. A possible reason for the failure of this reaction to go to completion may lie in the inhomogenous nature of the reaction mixture: the telomer is nearly insoluble in the KCN/DMSO layer.

V. TECHNICAL DISCUSSION - PART 2

BINDER PREPOLYMER SYNTHESIS BY TERPOLYMERIZATION

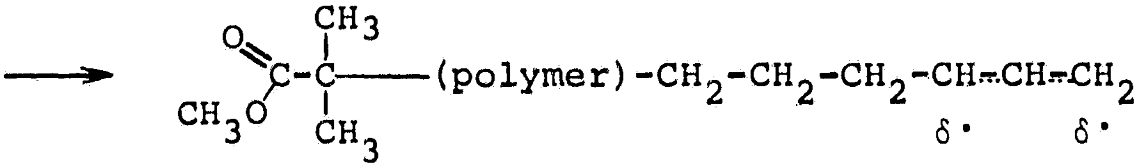
A. Ethylene/Propylene Butadiene Terpolymers

Incorporation of a small quantity of butadiene into an ethylene/propylene copolymerization offered the possibility that rather stable polymer radicals would result when butadiene reacted with a growing ethylene/propylene copolymer chain I:



$CH_3O(O{=})C{-}C(CH_3)_2{-}(polymer){-}CH_2{-}CH_2\cdot + CH_2{=}CH{-}CH{=}CH_2$

(I)



$\longrightarrow CH_3O(O{=})C{-}C(CH_3)_2{-}(polymer){-}CH_2{-}CH_2{-}CH_2{-}\overset{}{\underset{\delta\cdot}{CH}}{\approx}CH{\approx}\underset{\delta\cdot}{CH_2}$

II

The resonance stabilized radical II could then persist long enough to become terminated by recombination with other radical species (such as another radical like itself or a radical derived from the initiator). The experiment described below was performed to see if this terpolymerization approach would lead to interesting prepolymers.

Run 27-EMS-132 was performed in the Unit II continuous stirred autoclave reactor. The charge to the reactor contained 42.49% ethylene, 41.20% propylene, 4.30% butadiene and 2.00% DMAB and 10% benzene. After steady state had been reached, the reactor was operated at 106-109°C, 35,000 psi and at a feed rate of 4710 gms./hr. In 35 minutes of steady state operation, 30 gms. of copolymer was obtained--a tan colored oil of 180 cps viscosity at 21°C.

Infrared spectroscopy showed the presence of both vinyl and _trans_-disubstituted double bonds as well as the ester end groups derived from DMAB.

Vapor pressure osmometry in benzene solution gave a value of 550 for the number average molecular weight. Combining this result with the elemental oxygen content of 12.91 wt. %, we calculate an O_2 functionality of 2.2.

We have also examined the above product by nuclear magnetic resonance (NMR) spectroscopy and have found that in spite of the low butadiene content in the feed to the reactor, the product (obtained at a fairly low conversion) contained a significantly high proportion of butadiene. The analysis indicated 42 wt. % butadiene, 7 wt. % propylene, 12 wt. % ethylene and 39 wt. % end groups derived from DMAB initiator. From these values we obtain an equivalent weight of 260 based on the ester functionality present. When combined with the VPO number average molecular weight of 550, this gives an average functionality of 2.1 ester groups per molecule, in reasonable agreement with the value determined by the oxygen elemental analysis and reported above.

When 20 grams of this terpolymer was reduced with lithium aluminum hydride in ether, 17 grams of liquid product resulted which exhibited only a trace of ester carbonyl absorption in the infrared, but a very intense hydroxyl band at 3400 cm^{-1}. The unsaturation still remained at this point.

Hydrogenation of 16 grams of the hydroxyl terminated product using Raney nickel catalyst gave 13 grams of a yellow oil which showed none of the original unsaturation bands in the infrared. Hydroxyl content was determined by the phthalic anhydride/pyridine method and found to be 4.12 meq/g, corresponding to an equivalent wt. of 243. The V.P.O. molecular weight was 546 indicating an overall hydroxyl functionality of 2.2 per molecule.

Since the 1,4 polymerized butadiene residues give two ethylene units upon hydrogenation and the 1,2 polymerized residues yield butene-1 units, the final product is essentially a difunctional hydroxy terminated liquid ethylene/propylene copolymer containing ethyl branches derived from the original 1,2-polymerized butadiene residues.

Several variations in this basic copolymer synthesis are possible which may lead to useful rocket binder materials:

1. The method as actually completed involving hydride reduction/hydrogenation leading to saturated liquid diols.

2. Hydrolysis of the initial product followed by hydrogenation leading to saturated liquid diacids.

3. Hydrolysis or hydride reduction followed by adduction of the vinyl groups leading to trifunctional binder components.

4. Use of AIBN as the initiator followed by hydride reduction/hydrogenation leading to saturated liquid diamines.

To further explore the scope of this terpolymerization, we made additional runs at different butadiene contents. In these runs our goal was to prepare terpolymers of lower butadiene content, and still retain the desirable difunctionality apparently conferred by butadiene to the product.

The terpolymerizations were run in the continuous stirred autoclave reactor at 110-114^{o}C with pressures up to 35,000 psi. The butadiene content in the reactor charge was varied between 0.25 and 4.35 wt. % in the different runs of this series. 1.00 Wt. % DMAB initiator was used in each of the runs. The results of these runs are shown in the table below:

Run #28-EMS-	27	44	45	66	67
Wt. % Butadiene in Charge	4.35	2.23	1.13	0.50	0.25
% Conversion	2.00	1.92	2.24	4.21	7.53
Wt. % Butadiene in Product	48.3	39.0	30.2	11.6	4.6
Molecular Weight	615	458	554	781	1022
Ester Functionality	1.88	1.57	1.46	1.58	1.18

The above data show that as the butadiene content of the terpolymer is reduced by decreasing the butadiene content in the charge, the functionality also decreases from nearly two ester groups per molecule to values below 1.5. The molecular weight of the product, as well as the yield, increase with decreasing butadiene content.

In the light of these findings, we conclude that the incorporation of low levels of butadiene into a DMAB initiated ethylene/propylene copolymer does not allow the production of a difunctional terpolymer. Over 4 wt. % butadiene in the charge is needed in order for the functionality to approach 2; and in this range the butadiene incorporation into the terpolymers is near 50% by weight.

B. Ethylene/Propylene/HMB Liquid Terpolymers as Binder Prepolymers

1. Preparation

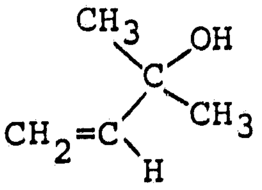
3-Hydroxy-3-methyl butene, HMB, is an interesting monomer for providing hydroxyl functionality in ethylene copolymers for several reasons:

a. It will copolymerize readily with ethylene.

b. It is not an active chain transfer agent.

c. No reactions subsequent to the polymerization step are required.

d. The tertiary hydroxyl groups introduced have a lower rate of reaction with isocyanates than the primary and secondary hydroxyl groups in other hydroxylic prepolymers currently available.



HMB

3-Hydroxy-3-Methyl Butene

With these facts in mind, we prepared a terpolymer of ethylene with propylene and HMB during a UCC sponsored program of exploratory ethylene copolymerizations. This first sample was prepared in the continuous stirred autoclave Unit II reactor at 117-122°C and 25,000 psi pressure using AIBN as the free radical initiator. A 16.3% conversion to terpolymer was obtained giving 533 grams of liquid resin having the following characteristics:

Sample Designation	28-EMS-9
Brookfield Viscosity, Poise	218
Molecular Weight	1122
Hydroxyl Equivalent Wt.	647
Hydroxyl Functionality	1.72
Penetration Temperature	-62°C

This sample was submitted to JPL where it was evaluated as a binder using toluene diisocyanate as cross-linking agent. This evaluation showed that significant advantages in propellant mix pot life and viscosity could be obtained using the 3-hydroxy-3-methyl butene terpolymer. Some foaming was noted, however, in the cures done at 190°F and 220°F (88°C and 105°C, respectively). This suggested the presence of water or other impurities interfering with the isocyanate-hydroxyl curing reaction and leading to CO_2 evolution.

Further Terpolymer Synthesis

Having established some definite advantages to be gained through the use of HMB terpolymers in solid propellant binders, we conducted a series of terpolymerizations to provide more material for evaluation as well as to provide information in the following areas:

1. Relationship between termonomer charged and hydroxyl content of resulting terpolymer.

2. The source of the foaming encountered in the initial cures at JPL.

3. Variation of cured gumstock mechanical properties with prepolymer average functionality and molecular weight.

The production data and the results of our analyses are summarized in Table IV.

TABLE IV

ETHYLENE/PROPYLENE/3-HYDROXY-3-METHYL BUTENE TERPOLYMERS

Run No. 28-EMS	96	100	102	104	106	113
Charge Composition						
Ethylene, wt. %	39.51	43.27	43.47	37.26	42.71	42.00
Propylene, wt. %	33.36	36.86	37.03	34.38	39.43	38.77
HMB[a], wt. %	13.18	9.54	9.37	13.76	17.35	18.68
Benzene, wt. %	13.18	9.54	9.37	13.76	0.00	0.00
Initiation Used	AIBN[b]	→	→	→	DTBP[c]	→
Initiator, wt. %	0.77	0.80	0.73	0.83	0.506	0.55
Reaction Conditions						
Temperature, °C	98-143	114-131	90-140	119-126	163-240	150-240
Pressure, mpsi	24-26	22-33	22-30	25-29	24-27	24-26
Hold-Up Time, min.	14.2	12.24	12.37	13.52	12.38	12.70
Avg Feed Rate, gms/hr	4356	4880	4806	4550	3998	3894
Total Wt. in Feed, gms	15,813	14,655	10,093	16,061	13,234	11,340
Productivity						
Yield, gms	1775	1914	1067	2035	4474	3358
Conversion, %	13.04	14.6	11.76	14.83	33.98	29.8
Production Rate, gms/hr	489	637	508	576	1352	1153
Physical & Chemical Properties						
Brookfield Viscosity, poise	290	319	388	247	467	276
Reduced Viscosity	.115	.092	.114	.111	.120	.051
Mol. Wt(VPO in ØCl @37.5°C)	1375	1706	1990	1625	1479	1528
OH Equiv. Wt.(IR Spectroscopy)	938	1575	1438	1088	764	801
OH Functionality	1.47	1.08	1.38	1.49	1.94	1.97

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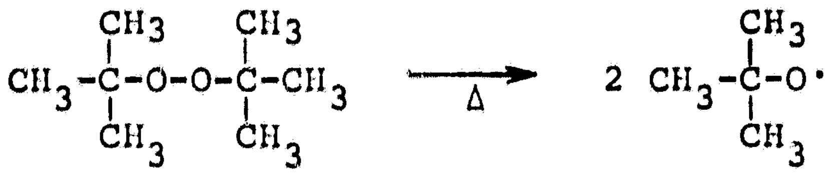
a. 3-Hydroxy-3-Methyl-Butene
b. Azobisisobutyronitrile
c. Di-*tertiary*-butyl-peroxide

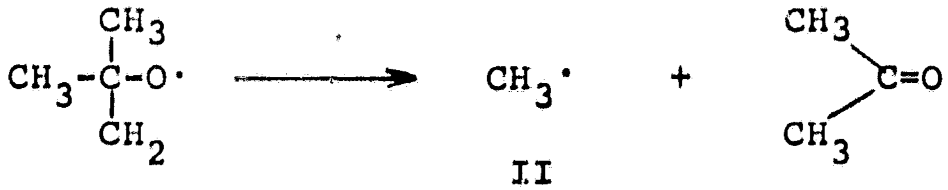
Azobisisobutyronitrile (AIBN) was used as the initiator in runs 96 to 104, while di-tert-butyl peroxide (DTBP) was used in runs 106 and 113. The use of DTBP necessitates a higher polymerization temperature because of its greater thermal stability. The higher chain transfer activity of propylene at these temperatures is compensated for by a higher rate of polymerization which leads to higher conversions and greater overall productivity.

DTBP yields the following products upon decomposition and is expected to yield endgroups which do not interfere with subsequent curing reactions:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{} 2\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot$$

DTBP I



$$CH_3-\overset{CH_3}{\underset{CH_2}{C}}-O\cdot \longrightarrow CH_3\cdot + (CH_3)_2C=O$$

II

Radicals I and II are both active initiators and will lead to tert-butoxy and methyl end groups, respectively.

The AIBN initiated terpolymerizations yielded light amber colored oils in 11 to 15% conversion, while the two terpolymerizations initiated with DTBP yielded nearly colorless products at roughly doubled rates and conversions. Over 14 kg of terpolymer was obtained from these runs.

The molecular weights of the terpolymers were measured by vapor pressure osmometry in chlorobenzene solvent. A four point extrapolative procedure was employed as described in the appendix.

The hydroxyl equivalent weight of the terpolymers was measured by infrared spectroscopy in CCl_4 containing

25 vol. % ethylacetate following the procedure of Hudson and Muenker[5]. These measurements were combined with the V.P.O. molecular weights to give the functionalities listed in Table IV. Figure 5 shows the approximately linear relationship between the amount of termonomer charged to the reactor and the hydroxyl content of the resulting terpolymers.

2. Investigation of the Foaming Problem

As our first objective in evaluating the HMB terpolymers in urethane cures it was necessary to determine the source of the foaming encountered in the cures done with the initial sample 28-EMS-9. Three possible explanations for this foaming required consideration:

a. The terpolymer was contaminated with water.

b. The terpolymer contained some COOH groups.

c. The tertiary urethane linkage is thermally unstable at the propellant processing, curing or subsequent use temperatures.

If either of the first two conditions actually were the cause of the foaming encountered, the problem could be circumvented with little or no difficulty, however, the third might place serious temperature limitations upon the utility of ethylene/propylene/HMB terpolymers as rocket propellant binders.

The following experiments were designed to determine whether any of the three possible conditions were actually the cause of the observed foaming. Terpolymer sample 28-EMS-106 as obtained from the reactor and routine solvent stripping procedure was used in these experiments.

A cure formulation was prepared from 33.358 grams (43.6 meq OH) terpolymer 28-EMS-106, 3.826 grams (43.9 meq NCO) toluene diisocyanate and .014 grams of NIAX-D22 catalyst*. The

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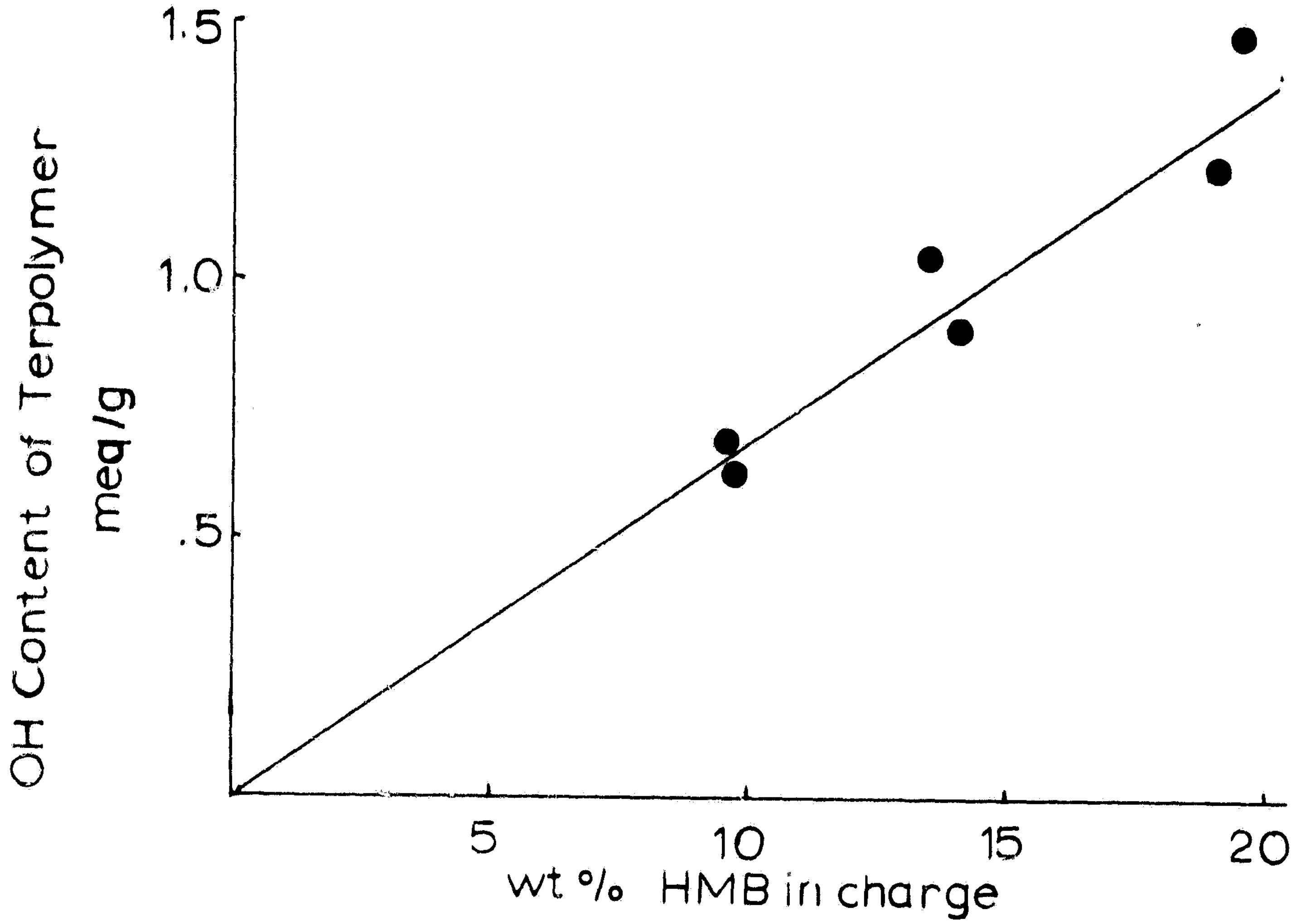
[5] See "Functionality Determination of Binder Prepolymers", Quarterly Progress Report #1, Oc. 1 - Dec. 31, 1966, by B. E. Hudson and A. H. Muenker of ESSO Research and Engineering Co. of Linden, N. J. for Air Force Contract No. FO4611-67-C-0012.

* Union Carbide's brand of dibutyltindilaurate urethane catalyst.

FIGURE 5

OH CONTENT OF TERPOLYMER AS A FUNCTION OF TERMONOMER IN CHARGE



NCO to OH equivalent ratio is 1.01. Upon mixing the above components at room temperature a clear solution was initially obtained, however, very soon after addition of the catalyst, the formulation began to foam. The very fluid frothy formulation was poured into a mold composed of glass plates (14 x 9 cm, 3mm deep cavity) and allowed to cure at room temperature for eight days. At this time, the upper surface was found to be a partially cured tacky foam, and after stripping from the mold, the lower surface was found to be clear and only slightly tacky, having a Shore-A hardness of 5%. Upon storage at room temperature, the hardness gradually increased to 20% after 30 days. Because of the non-uniform foamed character of the cured formulation, no attempt to determine additional physical properties was made.

350 Grams of 28-EMS-106 was dissolved in 2500 ml heptane and treated with 100 grams of anhydrous magnesium sulfate, the solution filtered and evaporated to recover the dried terpolymer.

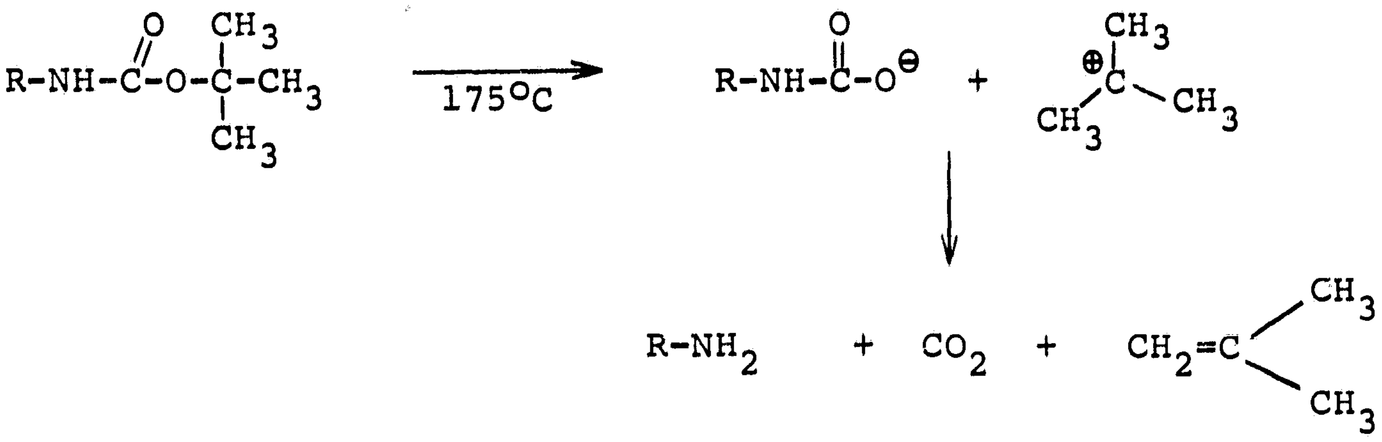
When a cure formulation employing the same proportion of ingredients used previously was tried on the "dried" 28-EMS-106, a perfectly clear mix was obtained showing no signs of foaming at room temperature. This is consistent with the hypothesis that the terpolymer was "wet" as prepared and that the water + isocyanate reaction led to CO_2 evolution and the observed foaming. However, it does not prove that water itself was the actual foam generating impurity removed by the "drying" step. The clear fluid mixture was then poured into a mold and cured at 60°C for 60 hrs. at which time it was removed and found to be a clear tack-free rubber having a Shore-A hardness of 30%.

The above results suggest that condition (a) is responsible for the foaming in the aforementioned terpolymers, i.e. the terpolymers contain water which reacts with the isocyanate to give the unstable carbamic acid, which then decomposes with the liberation of CO_2. Note that terpolymer 28-EMS-106 prepared with DTBP initiator has no terminal functional groups which can provide carboxyl groups to satisfy condition (b).

With regard to possible condition (c) that the foaming was caused by decomposition of the tertiary carbamate linkages themselves, we have found that carbamates of primary, secondary and tertiary alcohols exhibit a threshold temperature above which appreciable decomposition of the carbamate linkage occurs.

This information came from a kinetic study done several years ago in these laboratories. This study showed that in the case of primary and secondary alcohol carbamates, appreciable decomposition begins to occur between 225 and 235°C. Above this temperature fission of the carbon-oxygen single bond occurs to regenerate the alcohol and the isocyanate, which itself is unstable at this temperature leading to CO_2 evolution and carbodiimide formation.

In the case of tertiary alcohol carbamates, however, appreciable decomposition begins to occur above 175°C, and by a different mechanism. In this case, fission of the oxygen-tertiary carbon bond occurs to give a tertiary carbonium ion and the anion of the carbamic acid. In all cases studied, the tertiary alcohols had β-hydrogen atoms, and subsequent degradation involved loss of the β-hydrogen from the tertiary carbonium ion to give olefin, CO_2 and an amine as the ultimate decomposition products:



We estimate from the kinetic data in the above study that the half-life for the decomposition of the t-butanol carbamate of toluene diisocyanate (TDI) is about 580 days at 80°C, too long to account for the foaming observed at JPL. At 120°C, however, the half-life is only 4.5 days and may account for some of the bubbles we observed. However, at 60°C the reaction is completely insignificant since the half-life is almost ten years.

The same kinetic studies also revealed that the tertiary alcohol carbamates of hexamethylene diisocyanate (HDI) are far more stable than those of TDI having half-lives of 90,000, 220 and 40 days at the temperatures of 80, 120 and 135°C, respectively. This greater stability as well as the lower reactivity of HDI should be very useful in propellant formulations requiring superior thermal stability. Other aliphatic diisocyanates can be devised which have the above advantage of HDI, but which have a lower volatility and present less of a toxicity hazard.

We conclude from these studies that contamination with water or some other impurity removable with drying agents is the cause of the foaming previously observed with isocyanate cures of the ethylene/propylene/HMB terpolymers. Thermal instability of tertiary carbamates will become significant at temperatures above 175°C but not under the conditions which were used for the cure studies.

3. Curing Experiments

Having established that the foaming problem encountered in the isocyanate curing of the 3-hydroxy-3-methyl butene terpolymers was either due to adventitious water or some other contaminant removed by a "drying" step, larger quantities of dried terpolymer were prepared for curing studies using the following procedure:

The terpolymer was dissolved in 6 parts of heptane and the solution stirred over granules of drierite (anhydrous $CaSO_4$) amounting to 1/3 the weight of terpolymer being dried. The dried solution was then filtered and the terpolymer recovered by evaporation of the heptane on a rotary vacuum evaporator. Terpolymer samples 28-EMS-96, 104, and 106 were subjected to this treatment. The OH equivalent weights and number average molecular weights were then redetermined for these products since both quantities are subject to change upon removal of any fraction from the original terpolymer. The revised results are listed below:

Dried terpolymer from	28-EMS-96	-104	-106
Molecular Weight	1674	1544	1510
OH Equivalent Weight	950	1018	981
OH Avg. Functionality	1.75	1.52	1.54

Using the above information, the cure formulations listed below were prepared:

Formulation	A	B
Terpolymer used, 28-EMS-	96	104
Gms Terpolymer	10.000	10.000
Meq. OH	10.53	9.82
Gms. TDI	1.063	0.983
Meq. NCO	12.22	11.29
NCO:OH ratio	1.15	1.15
Mg. NIAX D-22	11	11

The formulations were mixed under vacuum and poured into the teflon lined mold shown in Figure 6 and cured at 90°C for 19 hrs. and then at 75°C for an additional 100 hrs., cooled to room temperature and stripped from the molds, leaving the steel end-tabs attached. The formulations were found to have cured to soft rubbery solids having some bubbles near the mold edges, evidently due to trapped air from between the teflon strips. The centers of the 3/8" square bars were solid and quite clear showing no voids of any kind.

The following properties were measured on the cured samples:

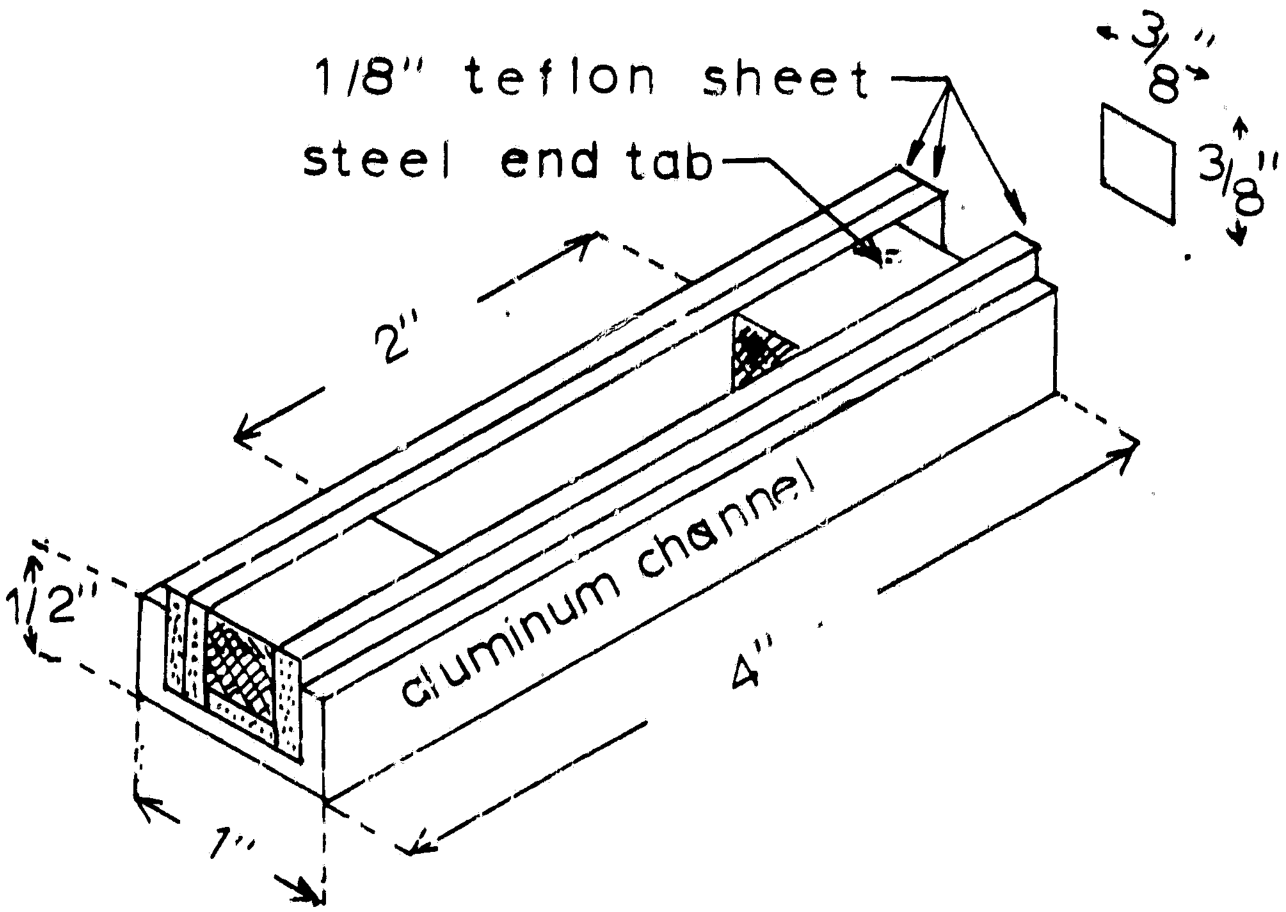
Formulation	A	B
Shore-A Hardness, %	37	30
Tensile Modulus,psi	164	109
Tensile Strength, psi	44	31
Elongation at Break, %	35	30

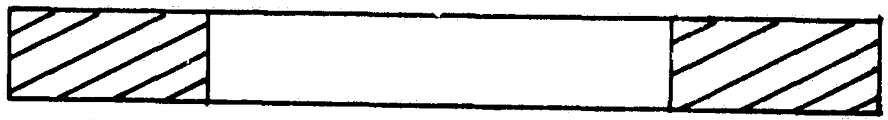
In both cases, the break was in the rubber itself rather than at the bond to the steel end-tabs. This indicates an adhesive bond strength to steel which is at least as large as the indicated tensile strength.

A sample of the dried terpolymer sample 28-EMS-106 was submitted to JPL for evaluation in propellant formulations.

FIGURE 6

TEFLON LINED MOLD AND END BONDED TEST SPECIMEN USED IN CURE STUDIES





TEST SPECIMEN, ACTUAL SIZE

C. Ethylene/Propylene/Vinyl Alcohol Liquid Terpolymers as Binder Prepolymers

1. Preparation of Vinyl Acetate Containing Terpolymers

Ethylene and vinyl acetate are known to undergo free radical copolymerization in a very nearly ideal fashion, i.e., propagating copolymer radicals with an ethylene terminal unit show the same preference for one of the monomers over the other as do propagating copolymer radicals with a vinyl acetate terminal unit. In the terms of the theory of copolymerization[6], the reactivity ratio product, r_1r_2, is unity. In this special case, the copolymer composition is equal to the composition of the comonomer mixture and a perfectly random distribution of monomer units along the copolymer chain results. Because of this most useful situation and the fact that vinyl acetate copolymers can be readily converted to vinyl alcohol copolymers by hydrolysis, we considered the possibility that terpolymers useful in solid propellants might be prepared from ethylene, propylene and vinyl acetate.

Terpolymerizations With Vinyl Acetate

We prepared such a terpolymer in the Unit II continuous reactor during the same program which produced the sample 28-EMS-9 discussed in the preceding section. The vinyl acetate terpolymer, sample 28-EMS-5, was prepared at 124-132°C under a pressure of 25,000 psi with AIBN as the initiator. The feed to the reactor consisted of 5.74% vinyl acetate, 33.0% ethylene, 28.8% propylene and 1.14% AIBN, the remainder being benzene added to insure solution of the initiator. During a 15 minute period of steady state polymerization, 177 grams of liquid terpolymer were obtained. This corresponds to a 24% conversion. The product had the following characteristics:

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[6] P. J. Flory, "Principles of Polymer Chemistry", Chapter V, 1953, Cornell University Press.

Sample Designation	28-EMS-5
Brookfield Viscosity, poise	159
Molecular Weight	1639
O_2 Equivalent Weight	719
O_2 Functionality	2.28
Penetration Temperature	-66°C

50 Grams of the above terpolymer was heated to 160°C and treated with 40 ml (.24 eq. OH ∿3 fold excess) of 5.9 N aq. KOH added dropwise with stirring under a stream of nitrogen. After the water had been boiled off, the reaction mixture was heated at 160°C for 1 hr. 10 min., cooled, dissolved in heptane, filtered and the hydrolyzed polymer recovered by evaporation of the solvent to give 47 grams clear liquid product. Infrared spectroscopy showed that the acetate groups had been completely removed. The hydroxyl equivalent weight was found to be 515 using the infrared method.

Treatment of 5 grams of the above product with a stoichiometric amount of toluene diisocyanate resulted in a rubbery gumstock having a Shore-A hardness of 75 after curing at room temperature overnight.

These results encouraged us to conduct a more extensive series of terpolymerizations employing vinyl acetate as the third monomer. The results of this effort are shown in Table V. The Unit II continuous stirred autoclave was used in all these runs.

The higher temperature necessitated by the use of DTBP initiator was helpful in that much faster reaction rates and greater productivity resulted, however, irregularities in feed rate, which were of no consequence in the lower temperature runs with AIBN, produced temperature surges giving rise to the wide temperature ranges shown. Because of these ranges, which were different for each run, the other variables, i.e. feed composition, do not correlate as well with product properties such as molecular weight or acetate content as they would under more uniform conditions. The products actually obtained, however, cover a range of molecular weights (1430 to 2565) and functionalities (1.6 to 3.0) which permit an assessment of the effect these parameters have upon the properties of isocyanate cured gumstocks prepared from the terpolymers.

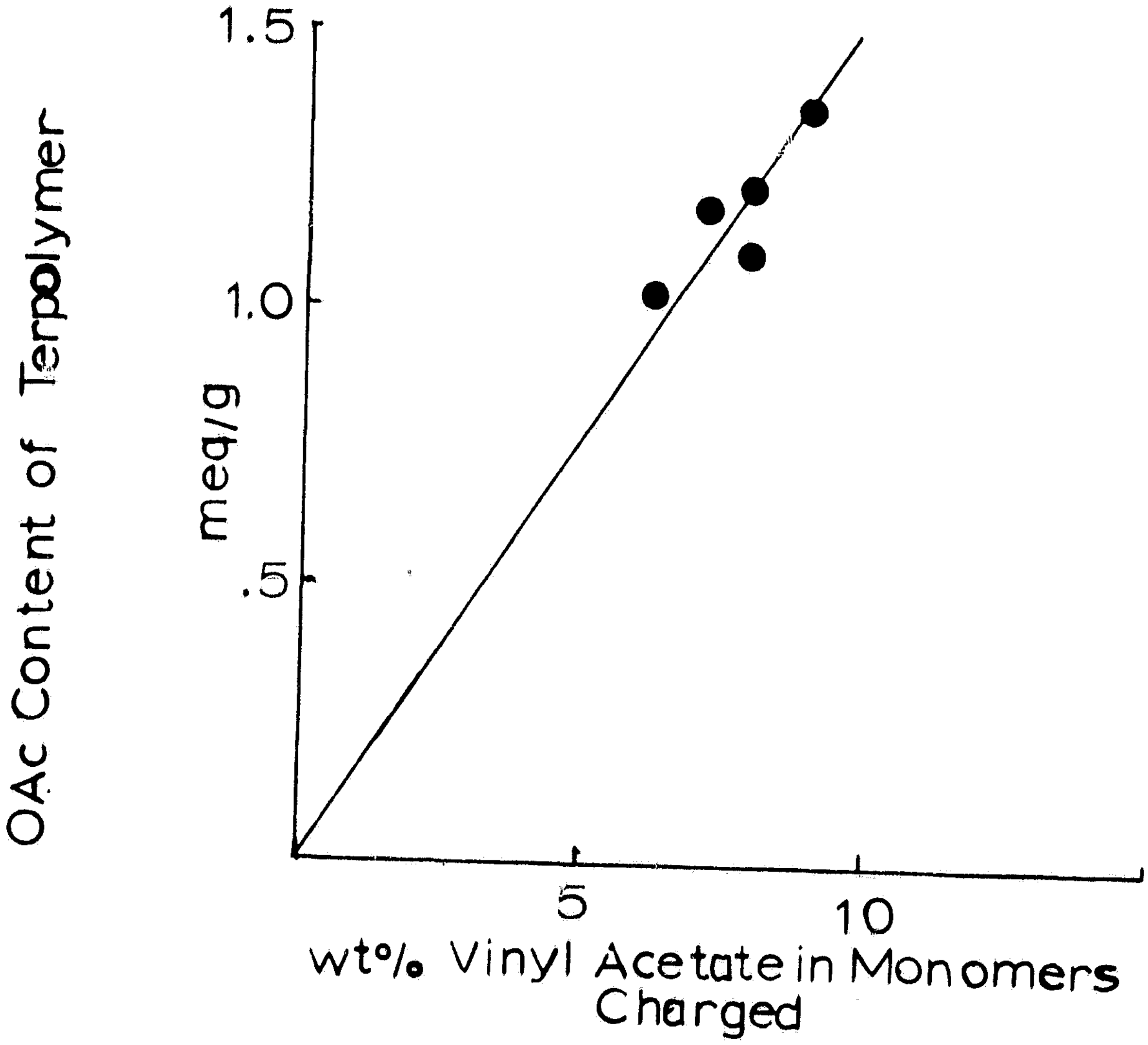
TABLE V

ETHYLENE/PROPYLENE/VINYL ACETATE TERPOLYMERS

Run No. 28-EMS-	94	108	115	118	121	122
Charge Composition						
Ethylene, wt. %	36.8	34.0	47.7	47.8	46.0	46.9
Propylene, wt. %	29.8	30.2	44.1	44.1	46.0	46.9
Vinyl Acetate, wt. %	5.11	6.22	7.82	7.83	7.84	6.25
Benzene, wt. %	27.4	28.9	-	-	-	-
Initiator Used	AIBN	→	DTBP	→	→	→
Initiator, wt. %	.90	.72	.41	.21	.11	.05
Reaction Conditions						
Temperature, °C	114-140	121-136	147-245	234-260	160-218	191-210
Pressure, mpsi	35	25	→	→	→	→
Hold Up Time, min.	14.8	13.7	13.1	5.6	4.3	4.5
Avg. Feed Rate, gms/hr.	4074	4296	4270	10,030	11,520	11,010
Total Wt. in Feed, gms	16,120	11,857	9907	11,966	8637	9727
Productivity						
Yield, gms	3032	1857	4202	5681	1209	1351
Conversion, %	26.2	20.5	42.0	47.6	14.0	13.9
Production Rate, g/hr.	768	673	1811	4767	1471	1410
Physical & Chemical Properties						
Brookfield Viscosity, poise	473	254	106	55	92	74
Reduced Viscosity	.167	.138	.090	.090	.110	.117
Mol. Wt. (V.P.O. in ØCl)	2565	2086	1522	1430	1718	1849
OAc Equivalent Wt.	845	737	910	910	822	966
OAc Functionality	3.04	2.83	1.67	1.57	2.09	1.91

FIGURE 7

ACETATE CONTENT OF TERPOLYMER AS A FUNCTION OF VINYL ACETATE IN CHARGE



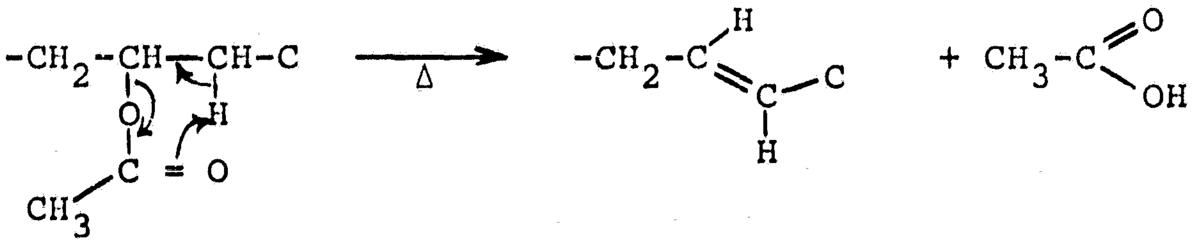
2. Hydrolysis of Vinyl Acetate Terpolymers

The general procedure used for hydrolysis of the acetate functionality in the terpolymers is as follows: 500 grams of the terpolymer is placed in a 1-ℓ. resin kettle equipped with mechanical stirrer, addition funnel, provision for sweeping with nitrogen and a thermocouple well. The kettle and contents are heated with an external heating mantle until the thermocouple immersed in the sample indicates a temperature >100°C.

At this point, a concentrated aqueous solution of potassium hydroxide, (or NaOH in later experiments) amounting to a 20% excess of OH^- over the OAc content, is added dropwise with stirring, continued heating and sweeping with a nitrogen stream. After the addition is complete and all the water has been driven off, the polymer melt is heated to the reaction temperature, usually 160°C, and stirred under a nitrogen atmosphere until the infrared spectrum of aliquots show no more acetate units remain.

The reaction mixture is then allowed to cool to ∿100°C and taken up in 500 ml heptane and allowed to cool to room temperature, filtered under pressure through a fine porosity filter paper to remove the finely divided potassium acetate precipitate and then the solvent removed on a rotary evaporator. The hydrolyzed terpolymer is finally passed through a wiped film molecular distillation apparatus at 200°C/0.3mm pressure to insure removal of volatile material.

The typical yield from 500 grams terpolymer is 425 grams of devolatilized ethylene/propylene/vinyl alcohol prepolymer. A summary of the results of the hydrolysis experiments is given in Table VI. Note that the hydroxyl functionality of the hydrolyzed products are lower than the acetate functionalities of the terpolymers from which they were derived. This results from an ester pyrolysis reaction which occurs to a limited extent at the temperatures used for the hydrolysis:



That the above reaction has indeed occurred is demonstrated by the weak absorption observed in the infrared spectra of the hydrolyzed products at 970cm^{-1} indicative of a <u>trans</u>-disubstituted double bond.

This side reaction may be avoided by conducting the hydrolysis at lower temperatures. Since this involves long reaction times, a preferable alternative procedure, should higher functionalities be required, is lithium aluminum hydride reduction of the acetate functionality to hydroxyl.

TABLE VI

HYDROLYSIS OF ETHYLENE/PROPYLENE/VINYL ACETATE TERPOLYMER

Notebook Ref., 9170	65-1	73-3-B	78-1-D	84-16
Terpolymer Used, 28-EMS-	94	121	122	118
Terpolymer Molecular Weight	2565	1718	1849	1430
Terpolymer Functionality	3.04	2.09	1.91	1.57
Terpolymer Used, gms	500	1006	1189	2011
Yield Hydrolyzed Product, gms	450	677*	1010	1617*
Properties of Hydrolyzed Prepolymers				
$\overline{M}_n$ (VPO in ØCl)	2646	1647	1880	1484
OH Equiv. Wt.	992	1058	1096	1200
OH Functionality	2.67	1.56	1.72	1.24
Brookfield Viscosity				
25°C, poise	2200	520	330	260
80°C, poise	26	-	6.2	4.3

* Losses occured during workup.

VI. PLANS FOR FUTURE WORK

Three samples of ethylene/propylene prepolymers containing tertiary alcohol functionality and one sample containing secondary alcohol functionality have been submitted to Jet Propulsion Laboratory for evaluation in actual propellant formulations. Further terpolymer synthesis will be attempted in which some terminal functionality is introduced by the initiator.

Urethane systems will be examined in which the random functionality terpolymers and the terpolymers with partial terminal functionality are used as the source of crosslinking in diol/diisocyanate formulations.

Prepolymer synthetic work will again be directed toward the preparation of telechelic difunctional prepolymers.

VII. APPENDIX

A. Procedure for Determination of the Number Average Molecular Weight by Vapor Pressure Osmometry (V.P.O.)*

The technique of vapor pressure osmometry is based upon the fact that a solution exhibits a lower vapor pressure at a given temperature than the pure solvent. Because of this fact, solvent vapor will condense onto a droplet of a solution placed into a chamber saturated with solvent vapor, until the heat of vaporization liberated by the condensing solvent vapor raises the temperature of the droplet of solution to the point that the solution's vapor pressure just balances the vapor pressure of the pure solvent. The temperature difference which develops between a solution droplet and a solvent droplet adjacent to one another in a chamber saturated wtih solvent vapor is thus a colligative property of the solution related directly to its molar concentration.

This temperature difference is normally quite small, but can be measured with sufficient precision by placing the droplets of solution and solvent upon the beads of matched thermistors which are connected to a bridge circuit designed

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* For this work we used a model 302 Hewlett Packard Vapor Pressure Osmometer.

between the two thermistors. The relationship between ΔR and the molar concentration is given by:[6]

$$1.\quad \Delta R = a_1 C_m + a_2 C_m^2$$

or alternatively:

$$2.\quad \frac{\Delta R}{C_m} = a_1 + a_2 C_m$$

The parameter a_1 is independent of the solute and depends only upon the thermodynamic properties of the solvent and the thermistor characteristics. The parameter however varies with the solute properties and the interactions between the solvent and solute as well. Thus, given a particular solvent and instrument, the parameter a_1 is a constant and can be determined by measurement of ΔR as a function of the concentration of a pure chemical substance of known molecular weight.

A very convenient procedure generally used for determining a_1 from these data is to prepare a plot of $\Delta R/C_m$ versus C_m. Extrapolation of the linear plot usually obtained to $C_m = 0$ gives a_1 directly as the value of the intercept on the $\Delta R/C_m$ axis. The slope of the linear plot gives a_2.

For an unknown solute of molecular weight M, the following relationship holds between ΔR, M, and the concentration of the solute expressed in terms of grams/liter:

$$1')\quad \Delta R = a_1 \frac{C_g}{M} + a_2 \frac{C_g^2}{M^2}$$

and

$$2')\quad \frac{\Delta R}{C_g} = \frac{a_1}{M} + \frac{a_2}{M^2} C_g$$

---

[6] F. W. Billmeyer, Jr., and V. Kokle, J. Am. Chem. Soc., 86, 3544 (1969).

A plot of $\Delta R/C_g$ versus C_g extrapolated to $C_g = 0$ gives a_1/M as the intercept and a_2/M^2 as the slope. Having previously determined a_1, M is given by:

$$M = \frac{a_1}{\left(\frac{\Delta R}{C_g}\right)_{C_g \to 0}}$$

Unfortunately, this simple and traditional V.P.O. procedure has a major shortcoming: fitting of a linear equation to plots of $\Delta R/C$ vs. C in order to determine the parameters a_1 and a_2 in the original equations 1 and 1' is justifiable only when the errors inherent in the measurement of ΔR and C have a correlation factor of 1.0 between them[7]. This is not the case. C being determined by weight and dilution, is rather precisely known, while ΔR is subject to random fluctuations which become a serious fraction of the measured value at low concentrations. This leads to excessive scatter of data points at low concentrations, and frequently a net upward curvature of the plot as $C \to 0$. This makes accurate manual extrapolation to $C = 0$ difficult, and least squares fitting of the data to a linear equation statistically unsound since too much weight is given to the less precisely known values of ΔR obtained at low values of C.

To avoid this problem, it is preferrable to fit the data directly to the quadratic equations 1 and 1' rather than use the simpler linear equations. This cannot be accomplished by a convenient graphical procedure, however. To facilitate handling all the data resulting from routine V.P.O. measurements, a short Fortram program was written for the IBM 1130. This program uses a least squares subrontine fitting the data to a quadratic equation passing through the origin to give instrument calibration constants from ΔR vs. C_m measurements on known standards and $\overline{M}_n$ and a_2 parameter values from measurements of ΔR vs. C_g on unknowns.

We have calibrated our instrument in chlorobenzene solvent at 37°C using cholesterol and sucrose octaacetate as primary standards. The resulting a_1 value was found to be 146.7 ohms x liters/mole.

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[7] A. Adicoff and W. J. Murbach, Anal. Chem., 39, 302 (1967).

Unknown polymer samples are accurately weighed and dissolved in the same chlorobenzene solvent used to saturate the V.P.O. vapor space. Four different concentrations are generally used: 100, 75, 50, and 25 g/l. The data points are usually plotted as $\Delta R/C_g$ vs. C_g as they are obtained. This permits a quick check upon the consistency of the data and allows an early estimate of the molecular weight if a good linear fit is obtained. Subsequently, the data from a series of molecular weight determinations are transferred to punched cards and read into the computer along with standardization data. After the data has been processed, a printout of the final results is obtained.

The Fortran program "VPO2" used for the data reduction is given in Figure 8 and a sample of the printout resulting from it is given in Figure 9.

B. Application of Thin Layer Chromatography for the Analysis of Binder Prepolymers

We have applied our Thin Layer Chromatography (T.L.C.) methods for qualitative analysis of binder prepolymer functionality distribution to other prepolymers and binder ingredients. Some interesting and useful results were obtained. These were reported at the ICRPG meeting in Huntsville on March 12. The results presented demonstrated the following:

1. COOH terminated prepolymers can be characterized by T.L.C.

   a. Use of a fairly polar eluting solvent such as 2% methanol in chloroform with silica gel plates results in separation of several types of COOH terminated prepolymers into well resolved components.

   b. Correlation of the T.L.C. results with the known average functionalities of prepolymer fractions obtained by Column chromatography has allowed identification of the above components with the non-, mono- and difunctional prepolymer fractions. As expected, the nonfunctional components are more easily eluted than the monofunctional components, which in turn, are eluted more rapidly than the difunctional components.

FIGURE 8

FORTRAN PROGRAM VPO2 FOR VPO DATA REDUCTION

```
C       VAPOR PHASE OSMOMETRY DATA REDUCTION
C
        REAL K,KCAL,MN
        DIMENSION RC(25)
        COMMON C(25),R(25)
      4 READ(2,10)J
        L=J-3
        IF(L)6,5,6
      6 READ(2,12)
        WRITE(3,12)
        WRITE(3,16)
     16 FORMAT(1H ,' DELTA R      CONC.       R/C')
     12 FORMAT(50H                                                  )
        READ(2,10)II
     10 FORMAT(I2)
        DO 3 I=1,II
        READ(2,11)R(I),C(I)
     11 FORMAT(2F10.5)
        RC(I)=R(I)/C(I)
      3 WRITE(3,17)R(I),C(I),RC(I)
     17 FORMAT(F8.4,2X,F8.4,2X,F8.4)
        CALL MLSQQ(II,K,S)
        WRITE(3,14)K,S
     14 FORMAT(1H ,'A1=',E12.4,'  A2=',E12.4)
        GO TO(1,2,3),J
      1 KCAL=K
        GO TO 4
      2 MN=KCAL/K+.5
        WRITE(3,15)MN
     15 FORMAT(30H THE NUMBER AVERAGE MOL WT IS ,F6.0)
        GO TO 4
      5 CALL EXIT
        END
        SUBROUTINE MLSQQ(N,A1,A2)
C        LEAST SQUARES FIT OF BIVARIATE DATA, QUADRATIC THRU ORIGIN
        COMMON X(25),Y(25)
        SY=0.
        SXY=0.
        SX=0.
        SXQ=0.
        SXK=0.
        DO 1 I=1,N
        SY=SY+Y(I)
        SXY=SXY+X(I)*Y(I)
        SX=SX+X(I)
        SXK=SXK+X(I)**3
      1 SXQ=SXQ+X(I)**2
        T1=SY*SXK-SXQ*SXY
        T2=SX*SXY-SY*SXQ
        B=SX*SXK-SXQ**2
        A1=T1/B
        A2=T2/B
        RETURN
        END
```

FIGURE 9

SAMPLE OF PRINTOUT FROM VPO2

```
CHOLESTEROL IN CHLOROBENZENE
 DELTA R      CONC.       R/C
 1.9100     0.0133   143.3934
 3.9400     0.0271   145.3338
 7.3500     0.0523   140.3743
11.4500     0.0821   139.4131
 9.4400     0.0654   144.3425
14.3200     0.1041   137.5600
18.2000     0.1349   134.9147
21.5400     0.1615   133.3746
A1=  0.1467E 03  A2= -0.8479E 02
28-EYS-96-2
 DELTA R      CONC.        R/C
 3.7100    35.5200      0.1044
 6.3100    56.9100      0.1108
 9.7000    81.3400      0.1192
13.2400   101.0700      0.1309
A1=  0.8768E-01  A2=  0.4154E-03
THE NUMBER AVERAGE MOL WT IS  1674.

28-EYS-106-D
 DELTA R      CONC.        R/C
 3.5000    33.4000      0.1047
 5.3100    47.3500      0.1121
 5.6000    50.7300      0.1103
 8.8100    75.0500      0.1173
 9.4200    78.3000      0.1203
11.9100   101.8900      0.1168
15.5800   117.0000      0.1331
A1=  0.9671E-01  A2=  0.2732E-03
THE NUMBER AVERAGE MOL WT IS  1518.
170-65-1
 DELTA R      CONC.        R/C
 2.0700    28.8100      0.0718
 3.9500    52.8600      0.0747
 5.8900    71.9300      0.0818
10.0200   102.1900      0.0980
A1=  0.5518E-01  A2=  0.4061E-03
THE NUMBER AVERAGE MOL WT IS  2660.

9170-96-7
 DELTA R      CONC.        R/C
 2.3800    33.1100      0.0718
 5.2600    65.4800      0.0803
 7.4700    86.7600      0.0860
 9.3500   103.6900      0.0901
A1=  0.6337E-01  A2=  0.2596E-03
THE NUMBER AVERAGE MOL WT IS  2316.
```

c. Because of (a) and (b) a qualitative evaluation of prepolymer functionality distribution is possible in comparatively short times, 45 minutes to an hour in most cases.

d. The same T.L.C. method used for analysis of the COOH terminated prepolymers works well when applied to other binder ingredients such as Dimer and Trimer Acid.

2. OH terminated prepolymers can also be characterized by T.L.C.

a. Use of a less polar eluting solvent than described in 1-a is necessary for OH terminated prepolymers. 40% $CHCl_3$ in heptane has worked well for us and gives well resolved separations of such prepolymers as Telagen-S into three or more components.

b. Correlation of our T.L.C. results with column chromatographic studies by Muenker at ESSO allows identification of the above components as the non-, mono-, di- and possibly higher functional fractions Telagen-S.

c. Having identified the components, a rapid qualitative evaluation of hydroxyl terminated prepolymer functionality distribution by T.L.C. is also possible.

3. Quantitative analyses of functionality distributions in prepolymers can also be accomplished by T.L.C. In our work a manually operated reflectance densitometer was used to obtain plots showing the variation of reflectance along the path of the eluted components on a T.L.C. plate. Resolved components show up as individual peaks on such a plot. The area under a given peak is proportional to the amount of that component present in the original mixture. For accurate work of this type, a determination of the proportionality constant between the "blackness" of the spot and the amount of the component present should be made for each component.

pgf