SATURATED HYDROCARBON POLYMERIC BINDER FOR ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

PERIOD COVERED: October 1, 1968
December 31, 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.
J. E. Potts
E. M. Sullivan
E. W. Wise

Publication Date: July 1, 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 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, 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 propellant and hybrid propellant grains. The general objectives are described in Quarterly Report No. 1.

II. ABSTRACT

The ω-bromoester telomers of ethylene with neohexene which were prepared in a scale-up effort 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 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 telomers themselves disclosed that the difficulty lay in the original functionality determinations. Repeat elemental analysis showed only 2/3 the bromine content indicated by the original analysis. The new value was consistent with the best carboxyl functionality obtained and was also in accord with the telomer composition determined by N.M.R. 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.

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 previous quarterly report as well as in the triennial report 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 & 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 & 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.

V. TECHNICAL DISCUSSION

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 phase 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:

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 evidinced 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 theortical) 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 reflex, 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 neutratization 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 func-

tionality 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

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

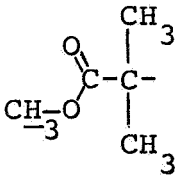
$\overline{M}n$	715	819
Neutratization Equivatent	505	546
COOH Functionality	1.42	1.50
Net Loss in Functionality	0.45	0.49

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.

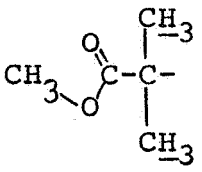
[a]I.R. Spectrum, Methyl pivalate as reference.

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

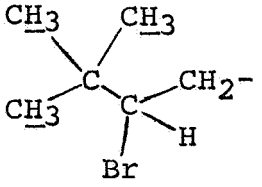
In addition to the major resonances in the N.M.R. spectra of ethylene/neohexene telomers due to the monomer units themselves, there appear weaker resonances which arise from the endgroups. The different endgroup types possible in the ethylene/neohexene telomers are listed in Fig. 1 along with the chemical 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 δ=1.28 p.p.m. and the t-butyl groups from neohexene give rise to the other major resonance at δ=0.87 p.p.m.



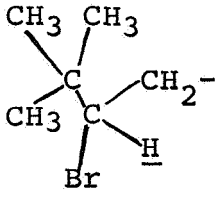
I, δ= 3.62 ppm



II, δ= 1.14 ppm



III, δ= 1.06 ppm



IV, δ= 3.88 ppm

V, δ= 3.34 ppm

Fig. 1 Endgroup types in Ethylene/Neohexene Telomers prepared with DMAB and MBIB.

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.

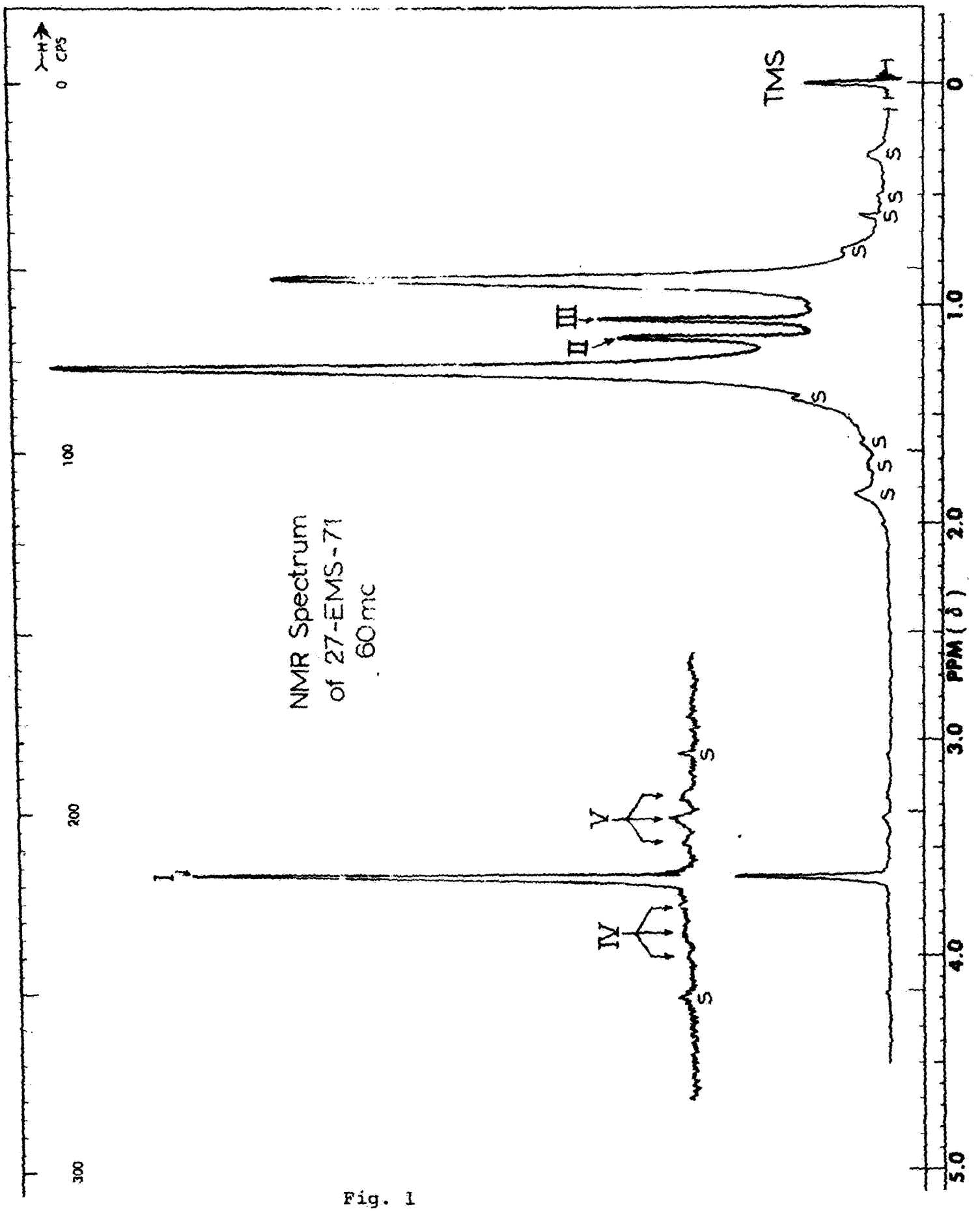

NMR Spectrum
of 27-EMS-71
60 mc
TMS
I
II
III
IV
V
S
0 CPS
100
200
300
0
1.0
2.0
3.0
4.0
5.0
PPM (δ)

Fig. 1

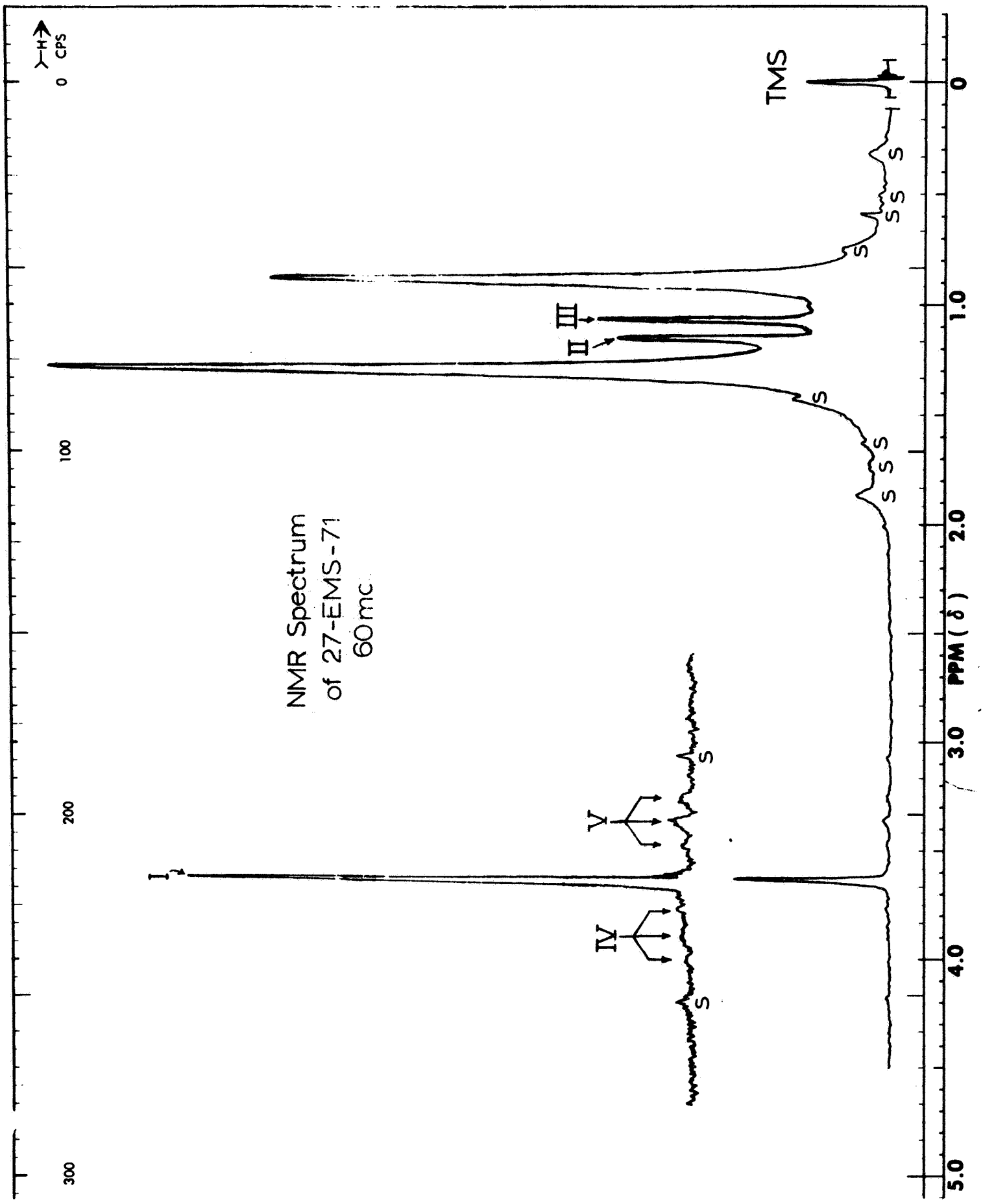

NMR Spectrum
of 27-EMS-71
60mc
TMS
I
II
III
IV
V
S
0
100
200
300
1.0
2.0
3.0
4.0
5.0
PPM (δ)
H
CPS

Fig. 2

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 is that displacemnt 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 Mn showed a decrease to 674 which implies a functionality of 1.50. This molecular weight result is being checked.

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 $CHCI_3$, 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 m moles 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 assymetric c-c-o stretch of the hydroxyl group at 1030 cm^{-1}

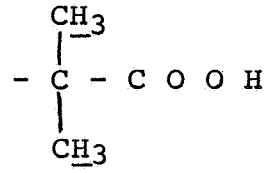
relative to the methylene chain skeletal vibration at 719 cm were measured in the I.R. spectrum of each aliquot. This date was used to follow the course of the ozonolysis (See Fig. 3).

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.

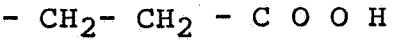
Oxidation

After three hours of ozone treatment the reaction mixture was allowed to remain overnight at 18-20°C and was then slowly heated to reflex 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.

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 endgroup. I (derived from the original ester endgroup) gives a resonance at δ= 1.17 ppm due to the germinal methyl groups near COOH, and II (derived from either $-CH_2-CH_2-OH$ oxidation or $-CH_2-CH=CH-t$-Butyl ozonolysis) gives a resonance at δ=2.31 ppm due to the $-\underline{CH_2}-$ adjacent to COOH.



I, δ=1.17 ppm



II, δ=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.

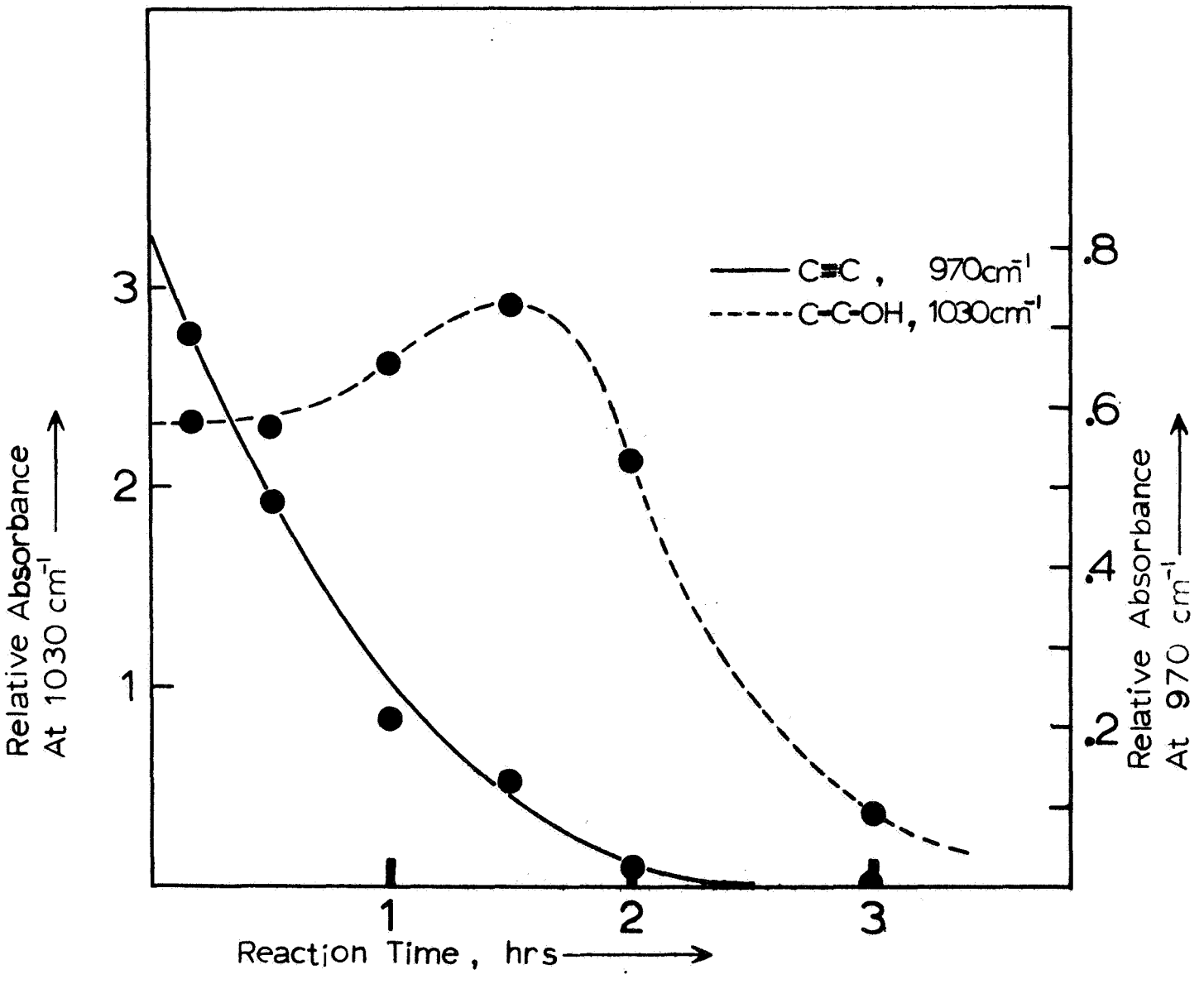


Figure 3. Infrared Absorbance due to Double Bonds and Hydroxyl Groups in Aliquots from Ozonolysis

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 0_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 ratio. 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 on the following page:

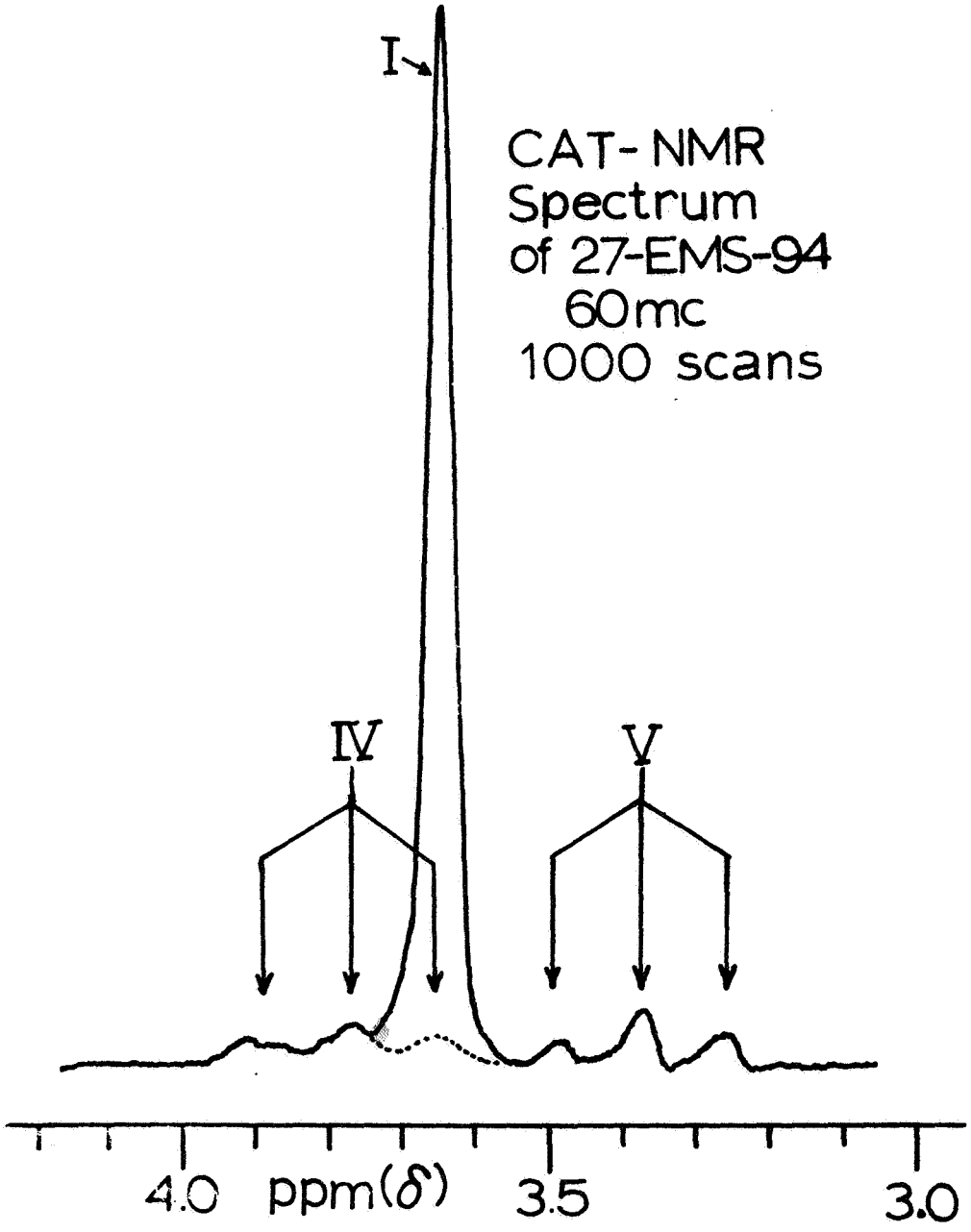
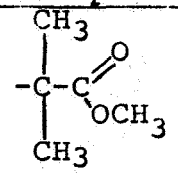
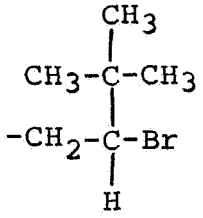

I
CAT-NMR
Spectrum
of 27-EMS-94
60mc
1000 scans
IV
V
4.0
ppm(δ)
3.5
3.0

Fig. 4

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

We thus arrive at the result that the total functionality of 27-EMS-94 is somewhere between 1.5 and 1.7, depending upon the actual ester functionality. 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.

V. TECHNICAL DISCUSSION

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:

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

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

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

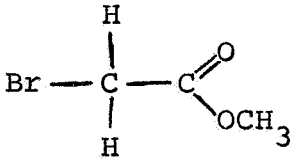
Run #27-EMS Telogen Used	106 Cyanogen	107 Cyanogen	115 Cyanogen Bromide
Initial Charge, gms			
1:1 Benzene/t-Butanol	10.2	10.2	10.2
Telogen	5.0	4.0	0.82
DMAB Initiator	0.093	0.279	0.093
Ethylene	415	423	423
Propylene	350	365	363
Fed During Reaction			
1:1 Benzene/t-Butanol	79.6	79.0	98.0
DMAB Initiator	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

V. TECHNICAL DISCUSSION

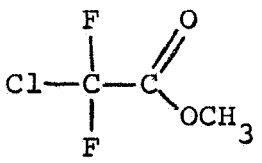
C. Chlorodifluoroacetic Acid Esters as Telogens

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]

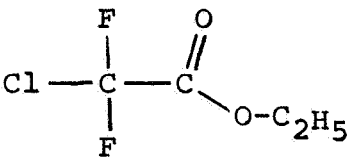
Having no α-hydrogen atoms to interfere in this manner, esters of chloro or bromodifluoroacetic acid might prove to be more effective telogens. To test this possibility we prepared the methyl and ethyl esters of chlorodifluoroacetic acid, II and III.



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 carbonhalogen bond to be weak enough for free radical displacement reactions to occur at the halogen atom to give the difluoroacetate radical.

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, %	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

VI. PLANS FOR FUTURE WORK

In the quarter to come we plan to study methods for converting the endgroups of the ethylene/propylene telomers into functional groups useful in prepolymers. A brief survey of other types of binders using our T.L.C. method is also planned in order to better define the scope of this method for analysis of functionality distribution in prepolymers.

VII. BIBLIOGRAPHY

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

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

4. Ibid, Section V-8-B, page 102