SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

QUARTERLY REPORT NO. 7

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TECHNICAL CONTENT STATEMENT

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I. OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics Operations Division has agreed to provide, on a level of effort basis, between 100.8 and 106.8 direct man months of effort to assist the Jet Propulsion Laboratory in the development of a new or improved polymeric binder for advanced solid propellant and hybrid solid grains. The detailed objectives are described in Quarterly Report No. 1.

II. ABSTRACT

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

We have also prepared more examples of ethylene-neohexene telomers using the halogen containing telogens reported last quarter. These telomers have been prepared with high functionalities based upon the terminal groups derived from the telogen used.

Of the three methods which we proposed for converting these terminal groups into carboxyl groups, one has yielded curable prepolymers. This method is based upon elimination of HBr from the telomer end groups, followed by oxidation of the resulting terminal double bond to give a carboxyl group. This route to curable ethylene-neohexene prepolymers is very promising and will be actively pursued in the coming quarter.

III. SCOPE OF PROJECT

The scope of this work has not changed from the program outlined in the work statement.

IV. INTRODUCTION

In our sixth quarterly report we discussed several new telogens and ethylene-neohexene telomers derived from them. Several routes by which the terminal halogen functions could be converted into carboxylic acid functions were described and their feasibility demonstrated using model compounds.

The present report describes additional telomer synthesis and the reduction to practice of one of the routes for placing carboxyl groups on the polymer chain ends.

Because of the relationship between the glass transition temperature of the prepolymer and the low temperature properties of the cured binder it was necessary to develop a rapid and reliable method for measuring glass transition temperature of liquid prepolymers for screening purposes. This work is described in the first part of the technical discussion that follows.

V. TECHNICAL DISCUSSION

A. Glass Transition Temperature Measurement

The liquid copolymers of ethylene with neohexene undergo a well defined transition to a glassy state when cooled to a low temperature. We have measured these transition temperatures by three different methods:

1. Vitrification Point, T_v

This method is fairly rough, however, it gives results which are probably within 10° of the actual glass transition temperature. In this procedure, a sample of the liquid copolymer is cooled in a test tube, using a dry ice/acetone bath. While cooling, the sample is stirred with the bulb of an alcohol filled thermometer. The temperature is noted when a qualitative change from a viscous liquid to a brittle solid is observed. This temperature is called the "Vitrification Point", T_v to distinguish it from a more accurately determined glass transition temperature, T_g.

We have used this method to characterize our copolymers since the beginning of the program and have obtained the largest body of data relating to the glass transition temperature in terms of T_v (See Table I). The data show that the copolymer samples having the lowest molecular weights also tend to have the lowest T_v. This correlation is shown in Figure 1 in which the T_v is plotted against the reciprocal of the number average molecular weight for a large number of copolymer samples. These samples are unhydrolysed ester terminated products (prepared with DEAB or DMAB) or else CCl_4 telomers. A large amount of scatter is present, however, the general trend is evident. A least squares fit to this body of data yields a linear relationship of the form:

$$T_v \approx -17 - \left(\frac{17800}{\overline{Mn}} \right)$$

between T_v and $1/\overline{Mn}$. The above equation corresponds to the solid line shown in Figure 1. Somewhat different fits were obtained when the three sets of copolymers were handled individually.

2. Penetration Temperature, T_p

This measurement depends upon the fact that a very large decrease in shear modulus occurs in the vicinity of the glass transition temperature. Below the T_g, the sample is hard and often brittle, and resists deformation of any kind. Above the T_g, the sample is either soft and rubbery or else

TABLE I

M_n DEPENDENCE OF T_v AND T_p

SAMPLE	TYPE	M_n	T_v	T_p
22-EMS - 99	DEAB	484	-72	-87
108	"	710	-60	
109	"	831	-47	
100	"	2752	-18	-36
126	"	751	-54	
127	"	1018	-42	
136	"	548	-49	
23-EMS - 1	"	552	-50	-66
4	"	837	-40	-54
11	"	869	-41	-50
18	"	1174	-39	-51
20	"	1107	-41	-41
23-EMS - 17	DMAB	1408	-25	-38
34	"	716	-36	
36	"	911	-35	
37	"	891	-39	-50
42	"	706	-40	
39	"	2688	-30	-33
66	"	823	-34	-51
67	"	819	-38	
68	"	815	-36	-58
79	"	566	-50	-73
56	"	1093	-33	-43
57	"	977	-39	-46
58	"	1111	-34	-44
63	"	668	-37	
65	"	373	-65	
90	"	931	-38	-50
91	"	1355	-34	-41

SAMPLE	TYPE	M_n	T_v	T_p
24-EMS - 2	$CC1_4$	516	-57	-70
4	"	667	-43	-56
6	"	767	-40	-71
8	"	747	-44	-57
10	"	649	-39	
12	"	1114	-30	-45
14	"	1009	-30	-47
16	"	976	-31	-49
22	"	1019	-30	
24	"	841	-32	-52
28	"	719	-37	-56
30	"	651	-41	-60
32	"	726	-37	-55
36	"	727	-35	-55
48	"	807	-28	-48

POLYMERS PREPARED WITH:

DMAB ⊙ ------
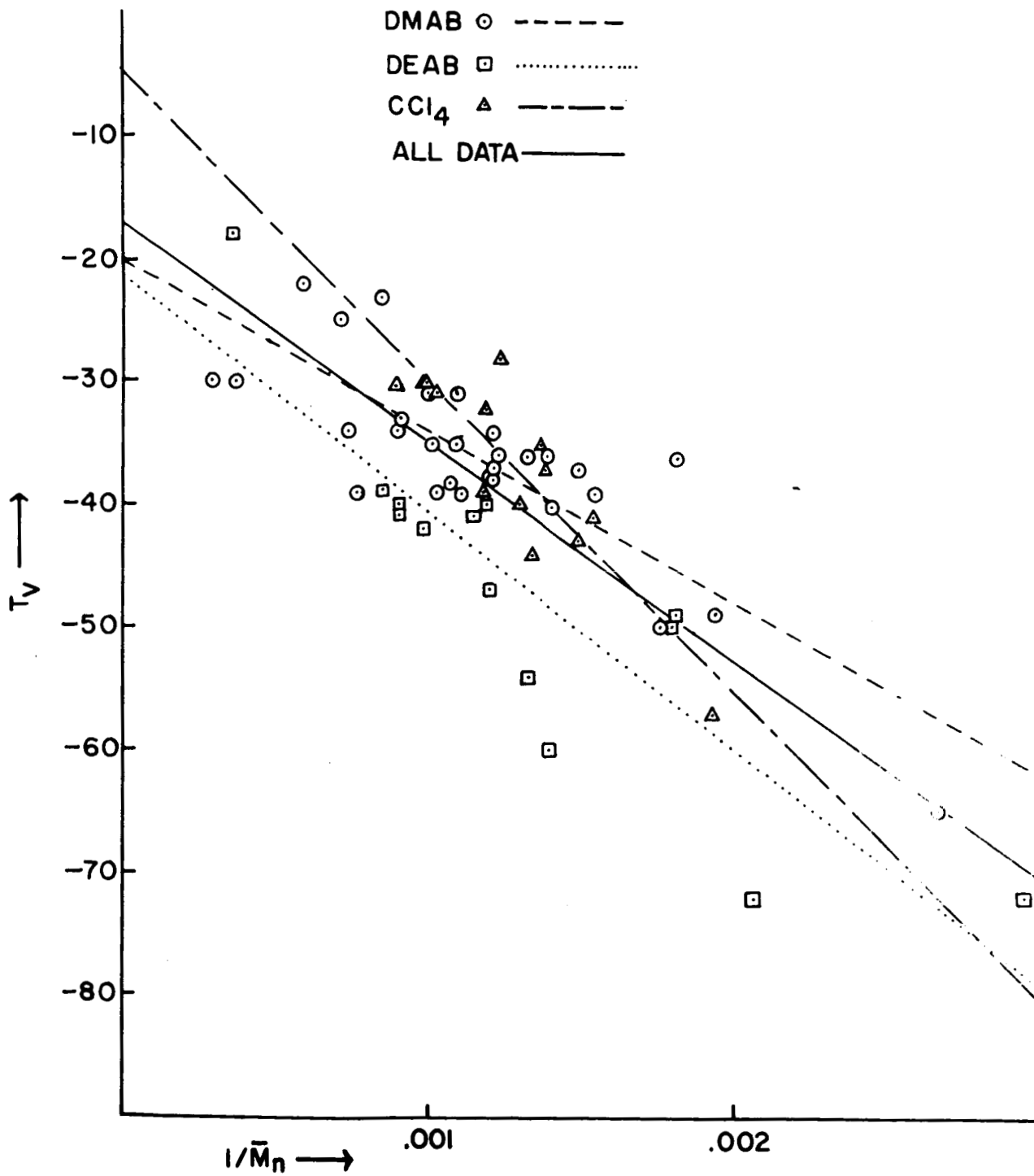DEAB ▣ ············
CCl₄ △ —·—·—
ALL DATA ——————

FIGURE 1

Dependence of T_V Upon Molecular Weight

a viscous liquid, and can be easily deformed. In the case of our liquid copolymer samples, we have found that a weighted needle does not penetrate the polymer glass below the T_g, but easily and rapidly sinks into the sample above the T_g. The exact temperature at which the needle begins to penetrate the sample we have called the "penetration temperature", T_p, to distinguish it from T_v and T_g measured by other procedures.

Our procedure allows us to perform rapid and reproducible measurements of T_p, and is well suited for routine examination of a large number of samples. The apparatus which we use to measure T_p is built around a standard type of penetrometer (Precision Scientific Co.) fitted with a sharply pointed needle. The needle is weighted with 150 gm weights which bear against a short lever arm that is coupled to the shaft of a potentiometer. A dry cell is connected to the potentiometer which delivers a variable voltage output depending upon the position of the weight (and hence the point of the needle). The electrical position readout is recorded on a strip chart recorder simultaneously with the sample temperature (measured by a thermocouple mounted adjacent to the point of the penetrometer needle).

A few drops of the polymer sample are placed in an aluminum foil cup which is then rapidly cooled in liquid nitrogen to give a small button of glassy polymer. The sample is then immersed in a methanol bath, pre-chilled below the glass transition temperature expected for the sample. After placing the penetrometer needle and the thermocouple junction upon the polymer button, the bath is allowed to warm up while continuously recording the temperature and position readouts.

We have measured the T_p of a large number of our liquid copolymer samples. Table I and Figure 2 show the effect which molecular weight has upon T_p for ethylene-neohexene copolymers with non-associating end-groups. These copolymers were taken from three different sets of samples: 1) samples prepared with DEAB initiation, 2) samples prepared with DMAB initiator, and 3) samples prepared in the presence of CCl_4 as chain transfer agent.

Note that acceptable values for T_p can be obtained only if the molecular weight is low enough. The functional dependence observed for this family of polymers is:

$$T_p \approx -20.4 - \left(\frac{26800}{M_n} \right)$$

When samples with carboxyl end groups were examined, we found that a given carboxyl terminated product always showed a higher T_p than the ester terminated product from which it had been prepared. There is too much scatter in the data to permit derivation of a useful equation relating T_p with $1/M_n$. However, individual values tend to be 20 to 30° higher than the T_p for ester terminated materials of comparable molecular weight. The difference becomes smaller at higher molecular weights.
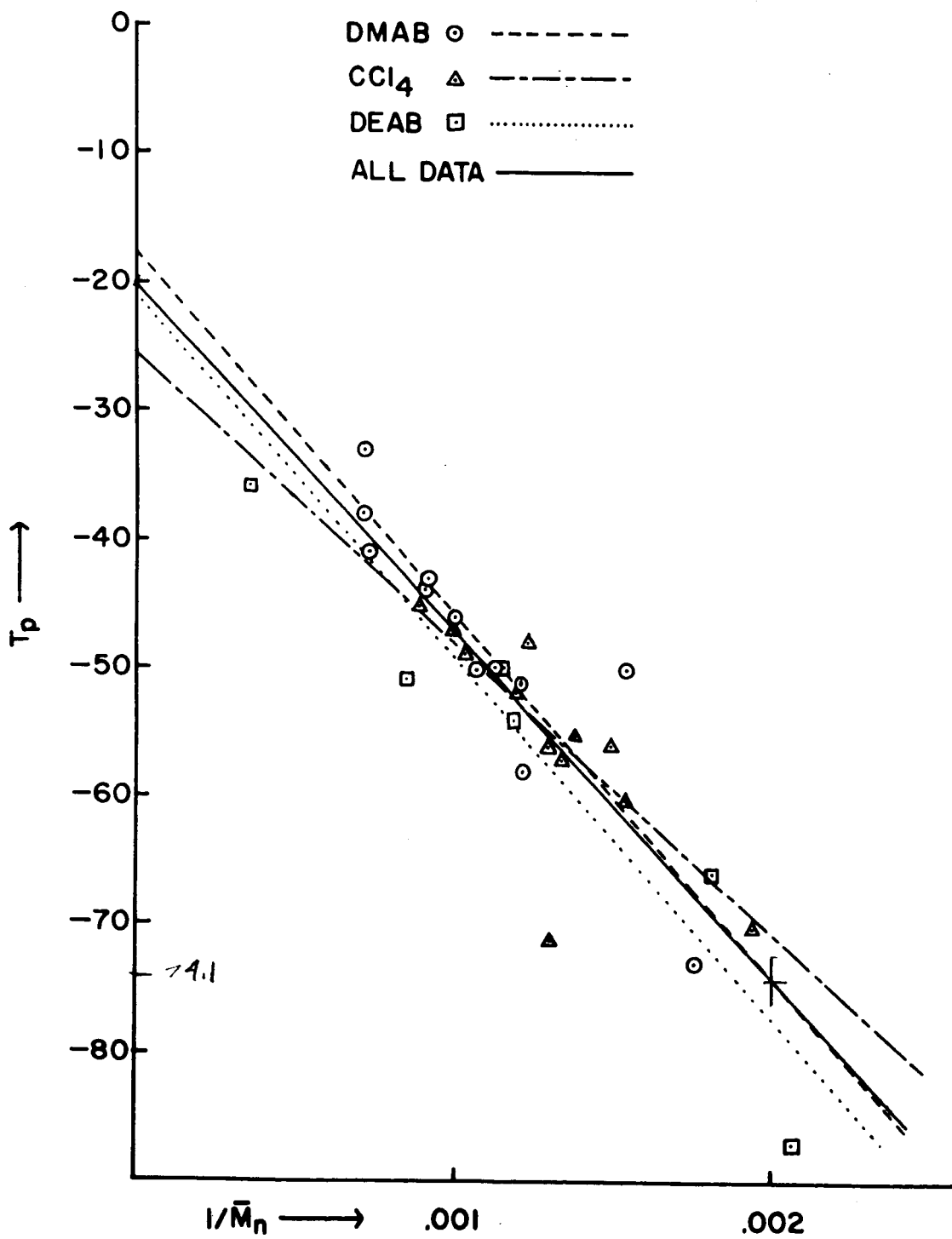
POLYMERS PREPARED WITH:

DMAB ⊙ ------

CCl_4 △ -·-·-·

DEAB ▣ ············

ALL DATA ————

FIGURE 2

Dependence of T_p Upon Molecular Weight

In view of the influence of carboxyl groups on glass transition temperature and the fact that we are primarily interested in the low temperature properties of the cured binder, which contains no free carboxyl groups, it would appear that T_g screening data obtained on ester terminated prepolymers would be more meaningful than measurements made on acid terminated prepolymers.

3. Torsion Pendulum Measurements

Use of the torsion pendulum has been widely accepted[*] as a valid method for measuring the glass transition in polymers. In this method, the sample, a cellulose blotter saturated with the glassy polymer, is coupled to a torsion pendulum. Measurement of the damping characteristics of the pendulum, as the sample temperature is changed, allows one to observe changes in the physical properties of the polymer/blotter system. Below the glass transition temperature, these properties are largely determined by the rigid polymer glass.

The outstanding advantage of this method is that secondary transitions, occurring below the glass transition, can be detected, as well as crystalline transitions. The main disadvantage to this method is that it is time consuming and not well suited for the routine evaluation of a large number of samples. The results are also somewhat dependent upon the frequency of oscillation of the torsion pendulum, higher T_g's being found at higher frequencies.

Three parameters are determined by the torsion pendulum: shear modulus, G'; loss modulus, G''; and dissipation factor, G''/G'. In the vicinity of the T_g, a rapid decrease of G' and an increase in G'' occurs as well as an increase in the ratio G''/G'. Changes in all three of these parameters have been used to indicate the position of the glass transition temperature.

We have made comparatively few torsion pendulum T_g measurements, however, a good correlation was found to exist between T_p, as discussed in part 2), and the break in the plot of G' versus T. These measurements are probably equivalent and within experimental error of each other. The maximum point in the G''/G' versus T curve also correlates with T_p, but is systematically shifted to a slightly higher temperature.

Table II shows the actual data obtained. $T_{G'}$ represents the break point in the G' versus T curve, i.e., the point where the high modulus, characteristic of the glassy polymer, begins to fall off rapidly with increasing T:

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* L. E. Nielsen, Rev. Scientific Instruments , 22, 690 (1951)
  J. A. Faucher and J. V. Koleske, Phys. and Chem. of Glasses, 7, 202 (1966)

TABLE II

SAMPLE	END GROUP	T_v	T_p	$T_{G'}$
23-EMS- 4	Ester	-40	-54	-52
23-EMS-11	"	-41	-50	-50
24-EMS-90	"	-47	-61	-58
" 87	Acid	-21	-37	-40
" 92	"	-33	-46	-50
" 96	"	-28	-45	-47
" 112	"	-23	-37	-38
" 114	"	-26	-36	-38

In some of the torsion pendulum experiments, we carried out measurements from -170° up to +20°C. These measurements showed a secondary transition in the copolymers which occurs near -120°C.

Because of the comparative ease with which T_p can be obtained, and the near-equivalence of the results with $T_{G'}$ obtained with the torsion pendulum, we will continue to measure T_p and use it for routine characterization of polymer low temperature properties.

B. Telomer Preparation

In our last quarterly report, we discussed the pre-
liminary results obtained when ethylene and neohexene were
cotelomerized in the presence of several new bromine containing
telogens. Telogen CTAC is typical of these telogens and par-
ticipates in the following sequence of events: A propagating
polymer radical abstracts a bromine from the telogen yielding
a bromide terminated polymer chain and an acid radical. This
reinitiates another polymer chain which terminates in the same
manner as did the first chain. In the presence of a small amount
of a free radical initiator to start the whole process going,
the resulting polymer molecules will have the fragments from the
telogen at either end of the molecule.

In Table VI of our last report, we gave the experimental
conditions for ten such telomerizations in which CTAA, CTAB,
CTAE, CTAC, and CTAD were used as telogens. Analytical data
were presented for the products of two of these runs. The re-
mainder of the data is presented in Table III. Especially
noteworthy is the functionality obtained in run #24-EMS-72
which contains 0.96 O_2 (ester) groups per molecule and 1.05
bromides per molecule.

Tables IV and VI show the experimental conditions
used in fifteen more telomerizations done in the last quarter.
The analytical data obtained upon the products from these runs
is given in Tables V and VII.

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

TABLE III

RUN #24-EMS	48	49	71	69	74	73	72
Telogen	CTAA	CTAB	CTAB	CTAC	CTAC	CTAC	CTAD
Mol. Wt.	807	995	523	357	403	485	611
Elemental Composition, Wt. %							
Oxygen	--	--	--	6.83	7.06	8.73	5.0
Chlorine	12.83	9.04	17.86	--	--	--	--
Bromine	--	6.10	12.53	13.41	17.00	19.09	13.70
Nitrogen	0	0	0.29	0.25	0.4	0.41	0.26
Neutralization Equivalent	--	--	--	538	480	386	--
Functionality, groups per molecule							
Oxygen (as O_2)	--	--	--	0.76	0.89	1.32	0.96
Chlorine (as Cl or CCl_3)	1.46	0.85	0.88	--	--	--	--
Bromine (as Br)	--	0.76	.82	0.60	0.86	1.16	1.05
Nitrogen (as N)	--	--	--	0.06	0.12	0.14	1.05
COOH	--	--	--	0.66	0.84	1.26	--

TABLE IV

RUN #24-EMS	94	95	116	75	86	87	113	114
Initial Charge								
Telogen	CTAA	CTAB	CTAB	CTAE	CTAE	CTAE	CTAE	CTAE
" , gms.	1.57	2.24	2.24	1.43	1.43	1.43	1.43	↑
Solvent; 1:1								
Benzene: Butanol, gms.	14.3	14.3	14.3	7.2	13.4	13.4	13.4	↑
Initiator, gms.	.13	.13	.26	.066	.065	.13	.13	.26
Neohexene, gms.	679	680		684	680	680		
Ethylene, gms.	253	256	254	255	254	255	255	256
Fed. During Reaction								
Telogen, gms.	14.2	20.2	20.2	12.9	12.9	12.9	12.9	12.9
Solvent, gms.	129	129	137	64	120	120	120	120
Initiator, gms.	1.170	1.170	2.34	.59	.587	1.170	1.17	2.34
Reaction Conditions								
Temperature, °C				90				
Pressure, mpsi								
Initial	8.30	9.00	8.00	9.00	8.40	8.25	7.75	8.10
Final	15.2	16.6	15.0	15.0	17.9	16.9	13.5	15.0
Time, hrs.	6.25	6.25	12.7	3.58	6.25	6.25	6.25	12.5
Productivity								
Yield, gms.	87	69	83	22	17	22	38	56
Conversion, %	9.32	6.67	8.8	235	1.82	2.32	3.00	5.98
Conv. Rate, %/hr.	1.50	1.07	.70	.66	.29	.37	.48	.77

TABLE V

RUN #24-EMS	94	95	116	75	86	87	113	114
Physical Properties								
Brookfield Visc., cps	4440	3300	20,600	--	10,000		79,100	103,000
Specific Visc., @ 80°C	.018	.013	.031	.023	.024	.025	.032	.049
Vitrification Temp., °C	-25	-39	-31	--	-30	-21	-20	-26
T_G, °C	--	--	--	--	--	-30	--	-30
Description	←—— tan oil ——→		←——	tan grease	tan heavy oil	——→	←—— tan oil ——→	
Analytical Data								
Molecular Wt.	808[a]	612[a]	1070[a]	301[b]	853[b]	920[a]	1090[a]	1288[b]
Oxygen, Wt. %	.32	.47	--	9.34	3.92	2.21	1.61	1.35
Chlorine, Wt. %	12.79	14.77	6.75	--	--	--	--	--
Bromine, Wt. %	--	10.2	5.11	22.6	5.0	4.84	3.67	1.76
Nitrogen, Wt. %	.15	.16	.25	.46	.37	.47	.38	.34
Neutralization Equivalent	--	--	--	359	1500	1600	1590	2170
Functionality								
Oxygen (O_z)	.08	.09	--	.90	1.05	.635	.55	.54
Chlorine (Cl or CCl_3)	1.46	.85	.68	--	--	--	--	--
Bromine (Br)	--	.81	.69	.85	.53	.56	.50	.28
Nitrogen (N)	.09	.07	.19	.07	.23	.31	.30	.31
Carboxyl (COOH)	--	--	--	.84	.57	.58	.69	.59

a – Solvent used was Benzene
b – solvent used was THF

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TABLE VI

RUN #24-EMS	92	96	112	115	90	93	122
Initial Charge							
Telogen	CTAC	CTAC	CTAC	CTAC	CTAD	CTAD	CTAD
Telogen, gms.	1.72	1.72	↑	↑	2.30	2.30	2.30
Solvent, 1:1							
Benzene: t Butanol, gms.	14.3	14.3	↑	↑	13.5	13.5	13.5
Initiator, gms.	.13	.13	.13	.26	.13	.13	.26
Neohexene, gms.	680	680	↑	↑	679	679	679
Ethylene, gms.	254	258	253	254	256	251	256
Fed. During Reaction							
Telogen, gms.	15.5	15.5	15.5	15.5	20.7	20.7	20.7
Solvent, gms.	129	129	129	129	131	131	131
Initiator, gms.	1.170	1.170	1.17	2.34	.586	1.170	2.34
Reaction Conditions							
Temperature, °C	↕ 90 →						↑
Pressure, mpsi							
Initial	8.00	8.50	7.75	7.75	10.00	8.20	8.00
Final	11.4	16.9	13.5	15.4	18.6	16.0	15.0
Time, hrs.	6.25	6.25	6.25	12.5	6.25	6.25	12.6
Productivity							
Yield, gms.	37	31	42	62	35	48	98
Conversion, %	3.96	3.30	4.50	6.64	3.75	5.17	10.5
Conv. Rate, %/hr.	.63	.53	.72	.53	.60	.83	.84

TABLE VII

RUN #24-EMS	92	96	112	115	90	93	122
Physical Properties							
Brookfield Visc., Cps @ 80°C	4570	13,500	91,000	10,000	4000	4540	29,700
Specific Visc.,	.021	.028	.04	.035	.017	.022	.029
Vitrification Temp., °C	-33	-28	-23	-25	-42	-38	-25
T_g, °C	-40	-37.5	-30	-	-47	-	-
Description					tan oil		dark brown heavy oil
Analytical Data							
Molecular Wt.	484[b]	527[b]	1124[b]	729[b]	709[a]	761[a]	1539[a]
Oxygen, Wt. %	5.95	5.41	2.20	3.44	3.96	3.77	1.98
Chlorine, Wt. %	-	-	-	-	-	-	-
Bromine, Wt. %	12.79	13.74	4.30	7.62	9.00	8.16	3.78
Nitrogen, Wt. %	.26	.23	.31	.32	.10	.21	.20
Neutralization Equivalent	559	620	1590	923	-	-	-
Functionality							
Oxygen (O_2)	.90	.89	.77	.78	.88	.90	.95
Chlorine (Cl or CCl_3)	-	-	-	-	-	-	-
Bromine (Br)	.68	.91	.61	.70	.80	.78	.72
Nitrogen (N)	.09	.09	.25	.17	.08	.11	.22
Carboxyl (COOH)	.87	.85	.71	.79	-	-	-

a – Solvent used was Benzene
b – Solvent used was THF

C. Reactions of Telomers

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

1. Elimination of HBr followed by oxidation.

2. Displacement by $-CN^-$ followed by hydrolysis.

3. Displacement by $S^=$ leading to coupling.

We reported examples where (1) and (3) were applied to a model compound to give the expected products.

We have since found that CN^- displacement also works on model compounds, and that a dimercaptide is as effective as sulfide in route (3) for giving coupled products. However when these reactions were applied to the bromide terminated telomers, routes (2) and (3) led to HBr elimination, not Br displacement, under forcing reaction conditions. Milder conditions gave no reaction at all. We found that only route (1) gave useful results. This sequence of reactions was outlined in our letter report of July 13, 1967.

When one treats a sample of a bromide terminated telomer with potassium hydroxide in refluxing n-butanol, complete elimination of HBr from the end groups can be obtained. This is supported by both spectral and elemental analysis data. The products exhibit a strong absorbtion at 970 cm^{-1} in the infrared spectrum due to the trans grouping:
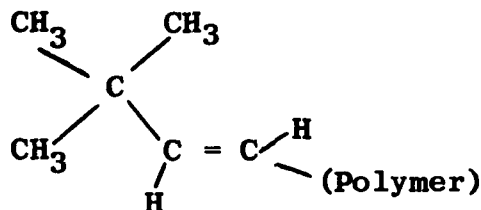
which is present in the spectrum of the caustic treated material but not in that of the original sample. No detectable amount of vinyl or vinylidene absorbtion was present in the dehydrobrominated material. This is indirect evidence that the original terminal bromides were part of the structure

$$CH_3$$

$$CH_3 \diagdown \underset{\displaystyle C}{} \diagup CH_3$$

$$Br \text{---} C \text{---} CH_2 \text{---} \text{(Polymer)}$$

$$H$$
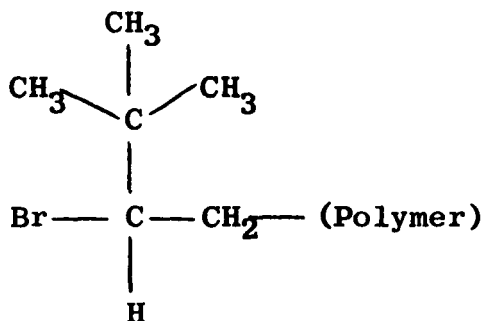
and not $Br \text{---} CH_2 \text{---} CH_2 \text{---}$ (Polymer).

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

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

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

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

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

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

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

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

In the coming quarter we will concentrate our efforts upon this route of elimination followed by oxidation in order to obtain larger amounts of materials for a more systematic curing study. The functionality question will also be examined in great detail to determine whether the final step in the reaction sequence is indeed converting all of the ozonide to COOH end groups.

VI. PLANS FOR FUTURE WORK

During the next quarter the emphasis will be on making larger amounts of high functionality prepolymer for use in curing studies. The glass transition temperature measurment technique developed recently will be used for screening prepolymer samples. Polymerizations will be carried out using lesser amounts of neohexene in the charge, in order to determine the minimum concentration of neohexene which can be present in the prepolymer without obtaining a grease.

VII. NEW TECHNOLOGY

Data are being obtained to support a patent application covering the use of certain new telomerizing agents in making prepolymers.