SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

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Report Edited By: James E. Potts

Contributors: A. C. Ashcraft, Jr. ⎫
                     J. E. Potts   ⎬   UCC
                     E. M. Sullivan   ⎪
                     E. W. Wise   ⎭

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TECHNICAL CONTENT STATEMENT

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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. This report makes the transition from the exploratory polymer research phase of the work to the product definition or development phase.

II. ABSTRACT

Additional samples of ethylene/neohexene telomers have been prepared by a batch process in the stirred autoclave reactor using bromoacid and bromoester telogens. From our exploratory telomerization studies we have found that the bromoacid CTAC and the bromoester CTAD are the most useful telogens. With them we have achieved the best control of functionality at useful molecular weights.

The product definition and development phase of the work has begun with the start up of operations on the continuous stirred autoclave reactor. Reaction conditions and product goals established in the exploratory research phase are serving as points of reference for telomer synthesis in the continuous reactor.

A total of six runs have been made in the continuous reactor using the bromoacid telogen CTAC. Telogen concentration and reactor residence times were varied and found to give useful and predictable control over the molecular weight without substantially affecting the functionality. Uniform products of high functionality were obtained in these start-up runs.

Conditions for efficiently conducting the dehydrobromination/oxidation reaction sequence have been established using samples prepared in the batch reactor with both CTAC and CTAD telogens. Nearly quantitative conversion of bromide functionality to carboxyl functionality has been achieved along with no loss of the original carboxylic functional groups.

III.   SCOPE OF PROJECT

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

IV.   INTRODUCTION

        In our previous report we introduced several new
halogen containing telogens, or chain transfer agents, and
discussed telomers of ethylene and neohexene prepared with
the aid of these new telogens. The terminal functional
groups on the telomers were derived from the particular
telogen used. The most promising telogens gave telomers
which were either ω-bromoacids or ω-bromoesters. Three
methods were discussed for converting the terminal bromide
into a useful carboxylic acid group. Only one was found to
be effective: dehydrobromination of the ω-bromide to give
a terminal double bond, followed by ozonolysis with oxi-
dative workup to give a carboxyl group. The other methods
(displacement by cyanide followed by hydrolysis, or coupling
via S $^=$) were found to be effective in model compounds, but
failed when applied to the ω-bromo acid telomers.

        In this report we will present the results of
telomer syntheses using a new telogen, two series of batch
telomerizations using our most effective telogens, and we
will compare these results with those we obtained when a
continuous stirred autoclave reactor was used for the telo-
merizations instead of a batch reactor.

        The dehydrobromination/ozonolysis route to carboxyl
end groups was further perfected during this period and used
to convert our ω-bromo acid and ester telomers to carboxyl
terminated products. These results will be reported in detail
in the Technical Discussion to follow.

V. TECHNICAL DISCUSSION

A. Telomer Preparation and Evaluation

The bromoester telogen "CTAF" was evaluated in telo-merizations number 24-EMS-132, 133, 135 and 25-EMS-6. The production data for these runs is summarized in Table I. Run 135 is a repeat of 133, made necessary because a purging opera-tion, which occurred during the preparation for·run 133, caused a loss of some of the neohexene charged to the reactor. For this reason the product from run 133 had a higher ethylene con-tent than planned. This product is a grease, showing evidence of polyethylene crystallinity.

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

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

The nitrogen contents (from AIBN) show that a sub-stantial amount of initiation of polymer chains, $\sim 25\%$, is accomplished by the initiator itself rather than being largely due to the radical derived from the telogen by chain transfer. This, together with the molecular weights obtained, show that CTAF is a sluggish chain transfer agent compared to CTAC and CTAD. Use of a higher concentration of CTAF and a lower con-centration of initiator could alleviate this problem.

The lower bromine content of run 135 is due to de-hydrobromination occurring during recovery of the telomer. The infrared spectrum of this product shows a strong $c = c$ absorbtion at 10.35μ, corresponding to a trans-internal double bond. This is not present in the spectra of the other pro-ducts. In addition to this, a second carbonyl band at 5.86μ is observed (main band at 5.75μ). Since COOH is absent, this is most consistent with the presence of α,β-unsaturated ester end groups in this telomer. These could only be derived from an α-bromoester end group resulting from initiation by an α-bromoester radical, presumably formed by hydrogen atom abstrac-tion rather than bromine atom abstraction from CTAF. This

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TABLE I

NEOHEXENE/ETHYLENE TELOMERS

RUN # 24-EMS-	132	133	135	25-EMS-6
INITIAL CHARGE				
Telogen	CTAF	CTAF	CTAF	CTAF
Telogen, gms.	1.58	1.58	1.58	1.58
Solvent, 1:1 Benzene:Butanol/,gms.	14.4	14.3	14.3	14.3
Initiator	AIBN	AIBN	AIBN	AIBN
Initiator, gms.	.065	.13	.13	.26
Neohexene, gms.	679.6	679.6	679.6	679.6
Ethylene, gms.	251	257	254	254
FED DURING REACTION				
Telogen, gms.	14.2	14.2	14.2	14.2
Solvent, gms.	129.8	138.0	128.0	128.5
Initiator, gms.	.59	1.17	1.17	2.34
REACTION CONDITIONS				
Temperature, ^{o}C	90	90	90	90
Pressure, mpsi				
Initial	6.00	3.25	9.00	10.50
Final	15.00	8.00	14.30	17.25
Time, hrs.	3.42	6.25	6.25	12.25
PRODUCTIVITY				
Yield, gms.	19.0	39	41	90
Conversion, %	2.0	4.20	4.40	9.65
Conversion Rate, % per hr.	.60	.67	.70	.77

TABLE II

NEOHEXENE/ETHYLENE TELOMERS

RUN # 24-EMS-	132	133	135	25-EMS-6
PHYSICAL PROPERTIES				
Brookfield Visc., Cps	--	--	36,200	39,800
Specific Visc., @ 80°C	.025	.035	.032	.031
Description	tan oil	tan grease	dark tan oil	light tan oil
ANALYTICAL DATA				
Molecular Wt. (benzene)	1207	1184	1373	1330
Oxygen, Wt. %	1.65	1.88	1.39	1.32
Chlorine, Wt. %	--	--	--	--
Bromine, Wt. %	3.84	3.99	1.46	3.43
Nitrogen, Wt. %	.27	.34	.22	.26
FUNCTIONALITY				
Oxygen (O_2)	.62	.68	.60	.55
Chlorine $(Cl$ or $CCl_3)$	--	--	--	--
Bromine (Br)	.58	.59	.25	.57
Nitrogen (N)	.23	.25	.22	.25

would indicate that telomers from CTAF have little utility as precursors for difunctional carboxy terminated binders. No further telomerizations with CTAF are planned, and we plan to do no further reactions upon the products already prepared.

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

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

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

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

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

B. Telomer Preparation - Composite Batches I and II

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

TABLE III

NEOHEXENE/ETHYLENE TELOMERS

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

TABLE IV

NEOHEXENE/ETHYLENE TELOMERS

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

A - Solvent used was Benzene

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

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

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

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

The second telomer series was made using CTAD as telogen. Ten runs were made in all: 25-EMS-69 to 78. The production data are summarized in Table VII. Again, reproducibility of amount of ethylene charged was the main problem encountered.

TABLE V

NEOHEXENE/ETHYLENE TELOMERS

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

TABLE VI

NEOHEXENE/ETHYLENE TELOMERS

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

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

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

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

C. Telomer Preparation in the Continuous Stirred Autoclave Reactor

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

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

TABLE VII

NEOHEXENE/ETHYLENE TELOMERS

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

*1:1 Benzene/t-Butanol

TABLE VIII

NEOHEXENE/ETHYLENE TELOMERS

RUN # 25-EMS-	69	70	71	72	73	74	75	76	77	78
PHYSICAL PROPERTIES										
Brookfield Visc., Cps	4,800	10,350	9,000	4,700	3,700	4.740	4.470	2,640	5,880	2,400
Specific Visc., @ 80°C	.018	.021	.015	.009	.012	.014	.013	.009	.018	.010
Description	light yellow oil	yellow oil							→	
ANALYTICAL DATA										
Molecular Wt. (in benzene)	885	868	1,095	868	748	780	920	764	852	757
Carbon, wt. %	76.02	77.18	77.44	76.07	75.00	77.25	76.11	77.57	78.61	77.29
Hydrogen, wt. %	12.50	13.05	13.05	12.97	12.30	13.51	13.34	13.14	12.99	13.04
Bromine, wt. %	6 62	5.33	5.62	6.81	7.15	6.58	7.33	6.48	5.72	7.52
Oxygen, wt. %	4.86	4.41	3.89	4.15	5.55	2.66	3.22	2.81	2.68	2.15
FUNCTIONALITY										
Oxygen (O₂)	1.34	1.20	1.33	1.13	1.30	.65	.93	.67	.71	.51
Bromine (Br)	.73	.58	.77	.74	.67	.64	.84	.62	.72	.71

In our Quarterly Report No. 5 we discussed the use of a continuous tubular reactor for the preparation of ethylene-neohexene copolymers. Because of the fact that a tubular reactor is inherently a progressive reactor, the composition of the reaction mixture is quite different along the length of the tube. This makes a tubular reactor unsuitable for telomerizations using very active telogens such as CTAC and CTAD: broad functionality and molecular weight distributions would in inevitable.

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

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

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

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

TABLE IX

NEOHEXENE/ETHYLENE TELOMERS

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

TABLE X

NEOHEXENE/ETHYLENE TELOMERS

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

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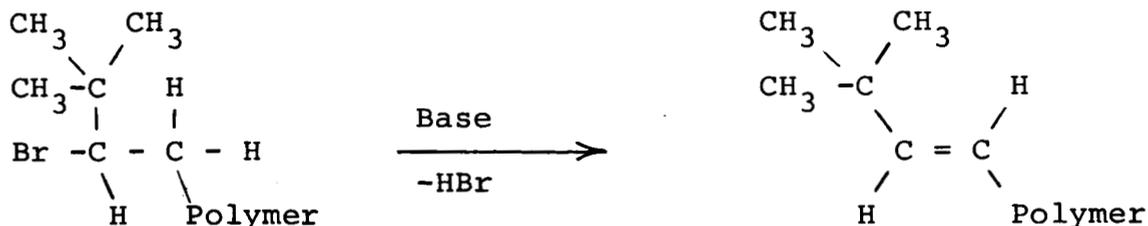feed rates result in lower molecular weights.

D. <u>Telomer Reactions - Dehydrobromination and Ozonolysis</u>

In our last quarterly report we discussed the results
of several methods attempted for converting the terminal
bromine atom of the ethylene-neohexene telomers (such as
those prepared with CTAC or CTAD telogen) into a reactive
carboxyl group. Because of the unreactivity of the terminal
bromine toward displacement by CN$^-$ and S$^=$, as well as the
formation of a <u>trans</u> disubstituted carbon-carbon double bond
upon dehydrobromination, we concluded that the bromine was
present as a secondary bromide in a neopentyl environment.
This could only arise if neohexene is the final monomer unit
just prior to bromide abstraction from the. telogen, as shown
below:

```
CH3    CH3
  \   /
   \ /
    C
   / \
CH3  ·C - CH2 - Polymer  +  TBr  ───────────>
     /
    H
```

```
  CH3    CH3
    \   /
     \ /
CH3 - C
      |
Br  - C - CH2 - Polymer  +  T·
     /
    H
```
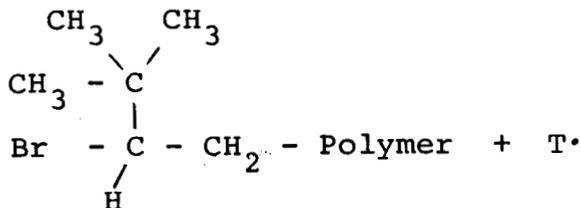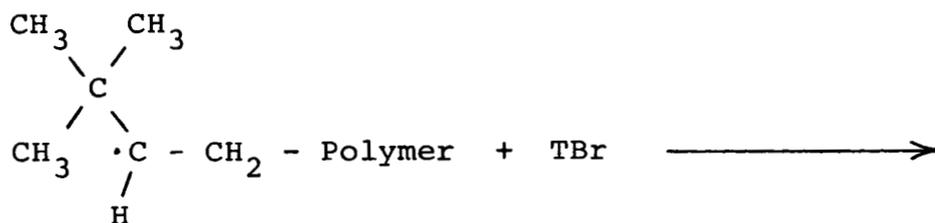
TBr is the Telogen, CTAC or CTAD.

The resulting bromide is naturally quite resistant to displacement reactions, however, it is easily eliminated in the presence of bases to give a terminal double bond:

```
 CH3   CH3                                      CH3   CH3
   \   /                                          \   /
 CH3-C   H                                      CH3 -C       H
    |   |            Base                            \      /
 Br -C - C - H      ──────────>                      C = C
    \   \           -HBr                            /     \
     H   Polymer                                   H       Polymer
```

We next attempted the ozonolysis of the resulting double bonds, with apparent success: the infrared band at 970 cm^{-1} due to the transinternal C = C was completely absent in the ozonized product. Upon working up the product, however, the COOH functionality obtained was not as high as expected. Evidentally, some other oxygen containing functional groups were present. More recently we have developed an improved oxidative workup procedure which gives carboxyl terminated products of higher functionality. The results of these experiments are now presented:

1. Studies on 24-EMS-122

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

50.9 grams (0.33 moles) of 24-EMS-122 was dehydrobrominated by heating and stirring under reflux in an inert atmosphere with 100 grams (1.784 moles) KOH pellets and 500 ml n-butanol which had been purified by distillation from KOH under a nitrogen atmosphere. Reflux was continued for 64 hours, at which point the mixture was steam distilled to remove the butanol, then cooled. The semisolid polymer mass was then removed and taken up in hexane, dried over anh. $MgSO_4$ and evaporated to give 44.63 grams slightly cloudy straw colored syrup. The Beilstein test for halogen was completely negative. The infrared spectrum of the product showed a trans disubstituted double bond absorption at 970 cm^{-1}, no trace of the t-butyl ester absorption, and a strong broad carboxylate salt absorption at 1565 cm^{-1}.

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

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

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

The ozonized solution, ~150 ml volume, of 24-EMS-122 was kept at $0^{\circ}C$ while the following workup methods were tried upon aliquots removed by pippette:

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

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

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

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

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

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

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

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

The sample was submitted for molecular weight determination by vapor phase osmometry in T.H.F. A value of 1247 was obtained. If this determination is correct, either chain degradation or selective loss of high molecular weight material has occurred during some step of the process. The sample has been re-submitted for further testing.

2. Studies on 25-EMS-22

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

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

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

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

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

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

FIGURE 1
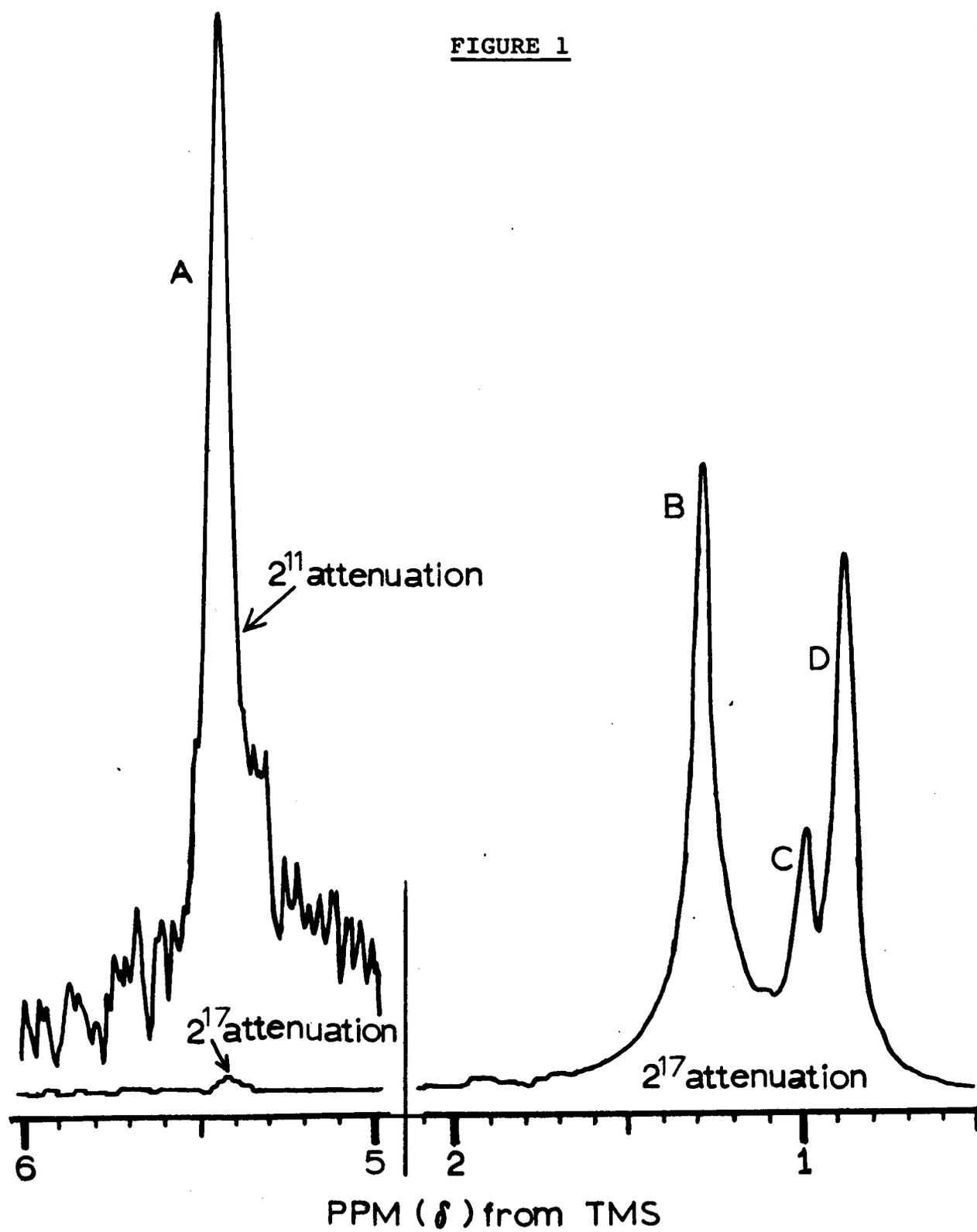
This represents only 0.1 mmole of ozone, thus 47.3 mmoles were consumed by the sample. Theory, based on the C=C content determined by NMR, requires 41.4 mmoles for addition to the C=C present.

The colorless, somewhat cloudy solution resulting from ozonolysis was combined with 150 ml. formic acid and 75 ml. 30% aqueous H_2O_2 and heated under reflux for ~20 hours, then cooled. The reaction mixture was worked up using several water washes to remove the acetic and formic acid and other water soluble impurities. Each water wash was back extracted with CCl_4 to avoid material losses from the polymer solution. The final extracts were dried over anh. $MgSO_4$, filtered and evaporated to give 38.76g pale straw colored cloudy syrup, neutralization equivalent = 516.

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

3. Studies on Composite Batch I

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

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

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

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

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

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

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

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

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

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

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

Thus 0.66 of the bromine atoms were eliminated as HBr rather than nearly all of the .91. We expected the latter to occur based upon our experience with the higher molecular weight products 24-EMS-122 and 25-EMS-22.
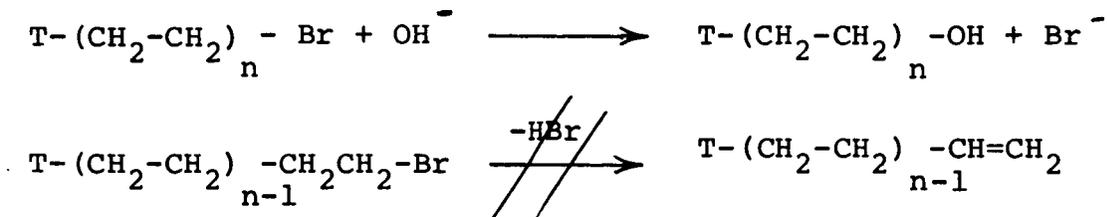
The negative Beilstein test upon the dehydrobrominated product from the composite batch I showed that all of the bromide had reacted. We infer from this that the remaining 0.25 Br per molecule has participated in a different reaction. The most reasonable possibility is that some nucleophilic displacement of Br^- by OH^- or $C_4H_9O^-$ has occurred concurrently with the β-elimination reaction. No OH (other than COOH) absorption could be seen in the infrared spectrum of the product, however, a moderate absorption at 1120 cm^{-1} could be due to a butyl ether end group.

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

Polymer - CH_2 - $CH_2\cdot$ + T Br $\longrightarrow$

Polymer - CH_2 - CH_2 - Br + T $\cdot$

(TBr is the telogen CTAC)
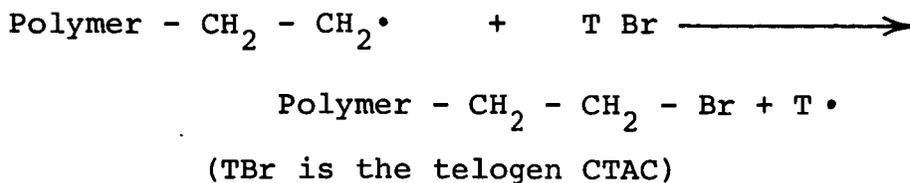
We had previously ruled out this type of chain transfer on the basis of the low chemical reactivity of the halogen end groups of the other telomers thus far examined. Even under forcing conditions, we had never obtained any observable amount of CN^- or $S^=$ displacement of halogen; elimination to give - CH = CH has always been the only reaction found. This was in accord with the equation for chain transfer given on page 18 which results in secondary bromides in a hindered neopentyl environment.

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

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

$$T\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}CH_2CH_2\text{-Br} \xrightarrow{\quad -HBr \quad}\!\!\!\!/\!\!/\!\!\!\! \quad T\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}CH=CH_2$$

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

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

4. Summary of Reaction Studies

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

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

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

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

VI. PLANS FOR FUTURE WORK

In the preceding report period we have developed efficient techniques for converting the terminal halogen of our ω-bromo carboxylic telomers into an additional carboxyl group. In the quarter to follow we will apply these techniques to the telomers of greatly improved functionality which are now being prepared under steady state conditions in the continuous stirred autoclave reactor. We will also conduct the continuous telomerizations for longer time periods in order to provide large quantities of uniform telomers. The availability of standard products of optimized properties will make possible a more thorough and conclusive evaluation of our prepolymers as solid propellant binders.

We also plan to conduct telomerizations using other olefins in place of neohexene in the continuous stirred autoclave reactor.

VII. <u>NEW TECHNOLOGY</u>

In response to a request from M. F. Mott, Assistant Patent Counsel to the National Aeronautics and Space Administration, we are preparing a full and complete disclosure of of our technique for rapidly determining glass transition temperatures. This technique is based upon the use of a weighted penetrometer needle resting on the surface of a material cooled below its glass transition temperature.

A brief description of the method was presented in our seventh quarterly report. The full report on this useful technique will be included in our next quarterly report.

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