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SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAINS

QUARTERLY REPORT NO. 3

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CONTENTS

I. OBJECTIVE

Union Carbide Corporation, Plastics Division, has agreed to provide, on a level of effort basis, between 49 and 55 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 were described in Quarterly Report No. 1.

II. SUMMARY

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

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

DEAB has been used to make several additional polymerization runs. Techniques have been worked out for the hydrolysis of these products, whose complete characterization is still in progress.

Dimethyl α,α'-azobisisobutyrate (DMAB) has been synthesized from readily available materials in a four step synthesis with an overall yield of 58%. This material has been sent to South Charleston for use as an initiator.

III. SCOPE OF PROJECT   *author*

The scope of this work has not changed from the program outlined in the work statement. The major emphasis has been placed on complete characterization of the prepolymers and selecting a suitable initiator for preparation of the required prepolymer.

IV.   INTRODUCTION

In our second quarterly report, we discussed the synthesis and kinetics of DEAB. There we reported the results of the first copolymerizations with this new initiator.

We also discussed the use of organic acid peroxides as initiators, and reported the results of copolymerization studies using them. The COOH terminated products from these studies provided the first clear cut evidence showing the relationships between hydrogen bonding, viscosity, apparent molecular weight and solvent polarity.

This report covers much additional work on characterization of the copolymer samples. We present molecular weight distributions, additional data on VPO molecular weights, and low polymer fractionation by molecular distillation. Some additional copolymers prepared with DEAB are also discussed, as well as the unfinished job of characterizing these products.

The following sections describe our work this quarter and outline our plans for future work.

V.   TECHNICAL DISCUSSION

A.   Molecular Weight Distribution by Gel Permeation Chromatography

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

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

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

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

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

FIGURE 1
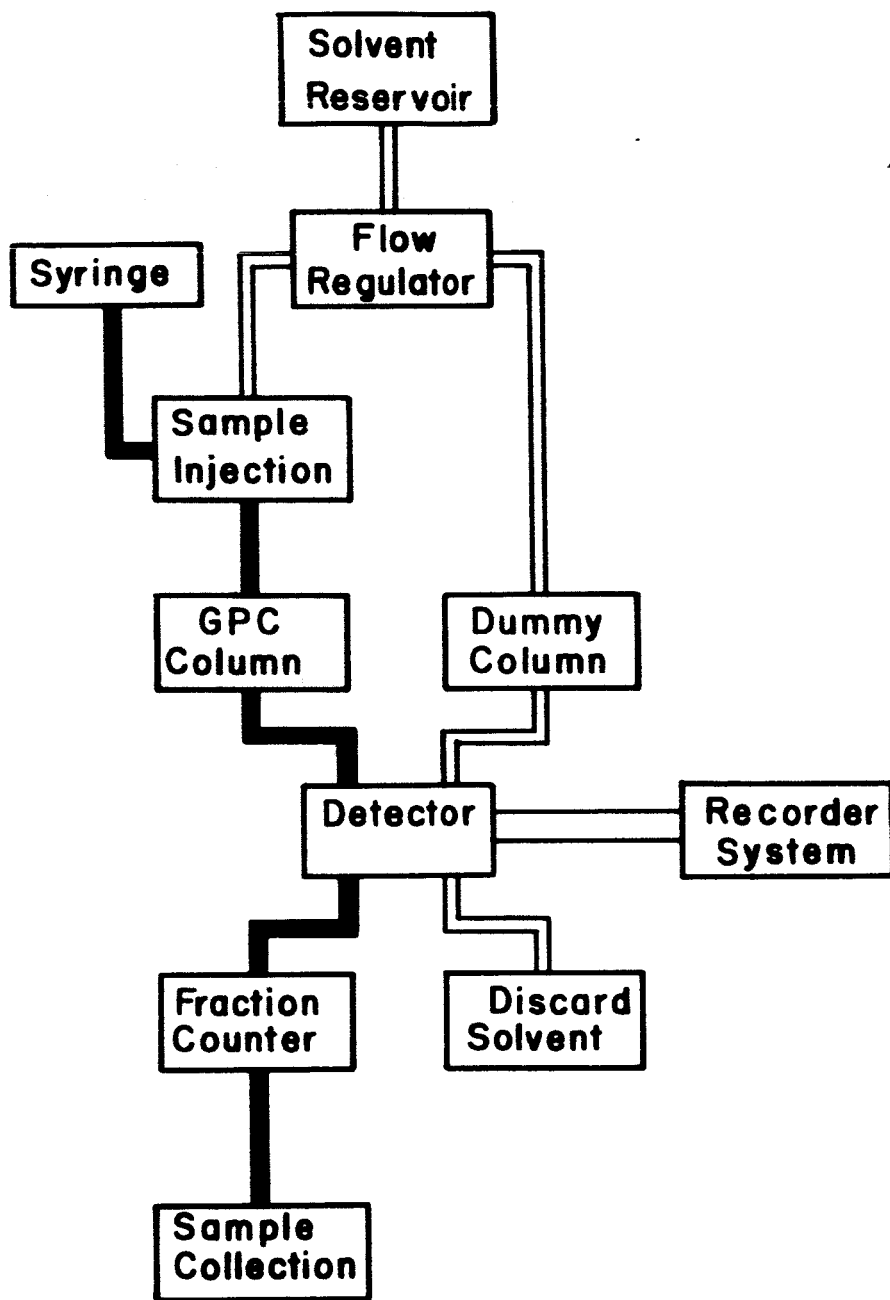
Flow Diagram of GPC Apparatus

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

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

The column configuration was calibrated by chromatographing a series of linear monodisperse polystyrene samples, linear monodisperse polyether samples, and small molecular species, all of which had very accurately determined molecular weights. A plot showing the relationship between A, the extended chain length (calculated from standard bond lengths and angles) of these standards, and RV, the retention volume at which they were eluted from the column is shown in Figure 2.

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

The following expressions are derived in Appendix A:

$$\bar{A}_n = \frac{\sum H_i}{\sum H_i/A_i} \quad , \quad \bar{A}_w = \frac{\sum H_i A_i}{\sum H_i}$$

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

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

and

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

FIGURE 2
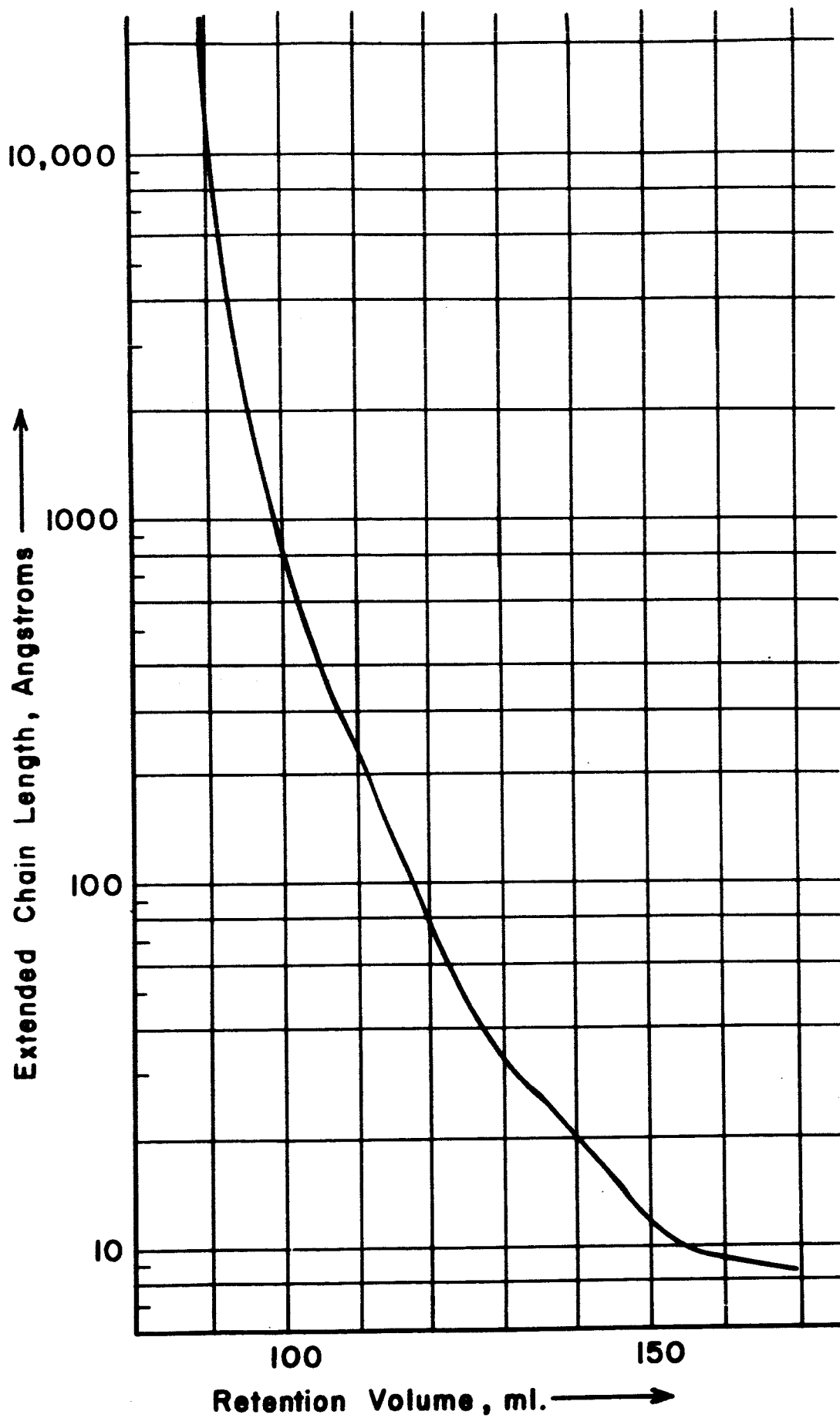
here K is a constant depending upon the polymer being examined, and $\bar{M}_n$ and $\bar{M}_w$ are the number average and weight average molecular weights, respectively.

Figures 3-6 on the page to follow are representative examples of the many GPC curves we have obtained upon ethylene-neohexene copolymers. The data are normalized to the same maximum peak height. Qualitative examination of the curves shows the absence of any significant "high molecular weight tail" on the molecular weight distribution. This would have shown up as a broad leading edge on the peaks, starting near 89 ml retention volume. The absence of a high molecular weight tail is encouraging. If it were present, the molecular weight distribution would be broad and the viscosity-molecular weight relationship would be unfavorable.

22-EMS-52 was the sample having the lowest $\bar{M}_n$ studied. Its GPC curve is shown in Figure 3. Peaks A and B probably represent discrete low molecular weight species which are nearly resolved from the polymer by the GPC column. Hydrolysis of this particular sample gave a COOH terminated product (SK-109-B) whose $\bar{M}_n$ was slightly higher. Peaks A and B were absent from the GPC curve of this hydrolyzed sample, but the curve was otherwise just the same. Presumably the hydrolysis of species A and B led to water soluble or volatile products which were lost upon work up.

Figure 4 shows a very narrow fraction obtained by molecular distillation. See Discussion, Part B for details.

Figure 5 shows the result of blending four samples which were especially prepared to test the reproduceability of the polymerization conditions.

Figure 6 shows the GPC curve on a higher molecular weight material prepared with succinic acid peroxide initiator. This material had the broadest molecular weight distribution of all the ethylene-neohexene copolymers examined.

For each GPC curve obtained, the detector response was measured at each 5 ml interval along the retention volume axis. These data were fed to an IBM 1620 computer in the form of punched cards. The computer assigned a value A_i to each fraction using a tabular form of the function shown in Figure 2. The parameters $\bar{A}_n/\bar{A}_w$, and $\bar{A}_w/\bar{A}_n$ were then calculated according to the equations derived in Appendix A.

The results of these calculations are summarized in Table I, together with other pertinent analytical data.

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

FIGURE 3

Copolymer Sample
22-EMS-52

$\bar{M}_n = 405$
$\bar{A}_n = 36$
$\bar{A}_w = 49$
$\bar{A}_w / \bar{A}_n = 1.36$

Relative Detector Response

Retention Volume, ml.

FIGURE 4

Copolymer Sample
8134-28-3

$\bar{M}_n = 380$ (THF)
$\bar{A}_n = 34$
$\bar{A}_w = 37$
$\bar{A}_w / \bar{A}_n = 1.06$

Relative Detector Response

Retention Volume, ml.

FIGURE 5

Blend of
Copolymer Samples
22-EMS-5,6,7&8

$\bar{M}_n = 1272$
$\bar{A}_n = 108$
$\bar{A}_w = 140$
$\bar{A}_w / \bar{A}_n = 1.29$

Relative Detector Response

Retention Volume, ml.

FIGURE 6

Copolymer Sample
22-EMS-66

$\bar{M}_n = 1465$ (THF)
$\bar{A}_n = 92$
$\bar{A}_w = 146$
$\bar{A}_w / \bar{A}_n = 1.59$

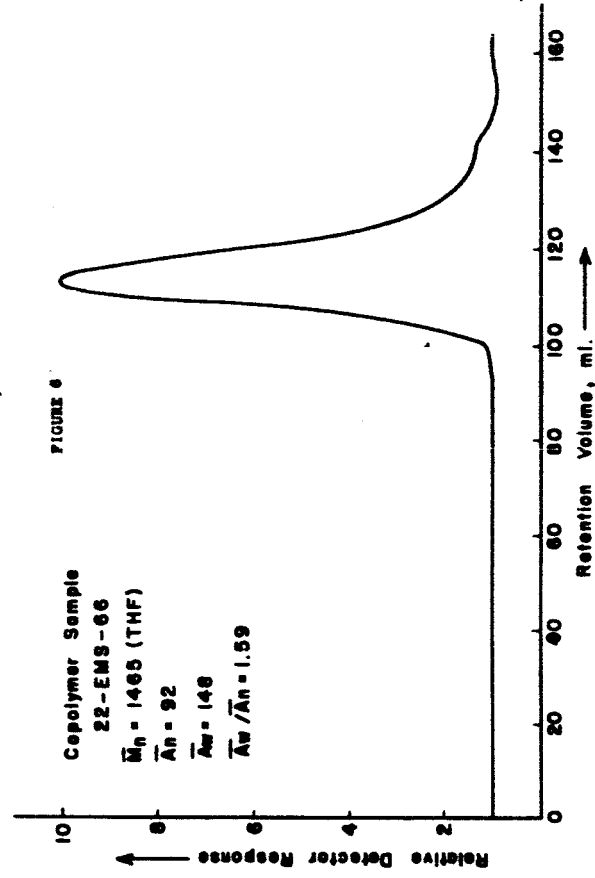Relative Detector Response

Retention Volume, ml.

TABLE I

GPC AND MOLECULAR WEIGHT DATA FOR ETHYLENE-NEOHEXENE COPOLYMERS

Sample Number	End Group	$\bar{M}_n$ Benzene	$\bar{M}_n$ THF	$\bar{M}_n$ Acetone	Retention Volume at Peak Maximum Ml.	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	See Figure
22-EMS-32	CN	459	-	435	123.5	38	55	1.43	-
22-EMS-52	CN	409	-	402	124.0	36	49	1.36	3
22-EMS-66	COOH	2198	1465	-	113.5	92	148	1.59	6
22-EMS-69	COOH	-	818	-	117.5	68	101	1.48	-
22-EMS-70	COOH	1134	791	-	118.0	67	98	1.45	-
22-EMS-71	COOH	2037	-	-	113.5	113	172	1.52	-
22-EMS-109	CO$_2$Et	831	-	-	117.0	71	102	1.43	-
7846-89[a]	CN	1946	1272	-	115.5	108	140	1.29	5
SK-109-B[b]	COOH	685	-	431	124.0	38	51	1.32	-
SK-107-B[b]	COOH	789	-	466	123.5	40	53	1.31	-
8134-28-1[c]	COOH	339	234	-	137.0	22	23	1.07	-
8134-28-2[c]	COOH	511	296	-	132.0	27	29	1.08	-
8134-28-3[c]	COOH	660	380	-	128.5	34	37	1.08	4
8134-28-4[c]	COOH	783	436	-	126.5	39	43	1.08	-
8134-28-5[c]	COOH	880	518	-	125.0	46	49	1.06	-
8134-28-6[c]	COOH	1370	802	-	121.0	68	79	1.16	-

a) A blend of samples 22-EMS-5, 6, 7 and 8.
b) Hydrolyzed 22-EMS-52.
c) Molecular distillation fractions, see Part 2 of Discussion.

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

Figures 7 and 8 show a graphical correlation between $\bar{A}_n$ and the number average molecular weights as determined by VPO in THF and benzene. The $\bar{A}_n$ parameter is a measure of molecular size which is completely independent of the other methods we have used to characterize our polymers. The fact that $\bar{A}_n$ correlates so well with the THF molecular weights greatly increases our confidence in the reliability of the THF molecular weight data.

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

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

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

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

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

Knowing $\bar{A}_n$ as a function of the retention volume, (Figure 2, calibration curve) and having the relationship between $\bar{M}_n$ and $\bar{A}_n$, we can now convert the GPC curves into true molecular weight distribution curves. This was done for sample 7846-89 and the result is shown in Figure 9. Note that most of the sample lies between 400 and 10,000 molecular weight.

FIGURE 8

$\overline{M}_n$ (in benzene) ⟵

(Angstroms) $\overline{A}_n$ ⟶

FIGURE 7

$\overline{M}_n$ (in tetrahydrofuran) ⟵

(Angstroms) $\overline{A}_n$ ⟶

FIGURE 9

Blend of
Copolymer Samples
22-EMS-5,6,7&8

$\overline{M}n = 1272$
$\overline{M}w = 1645$

Molecular Weight ⟶

Relative Detector Response

10

8

6

4

2

400

1000

4000

10,000
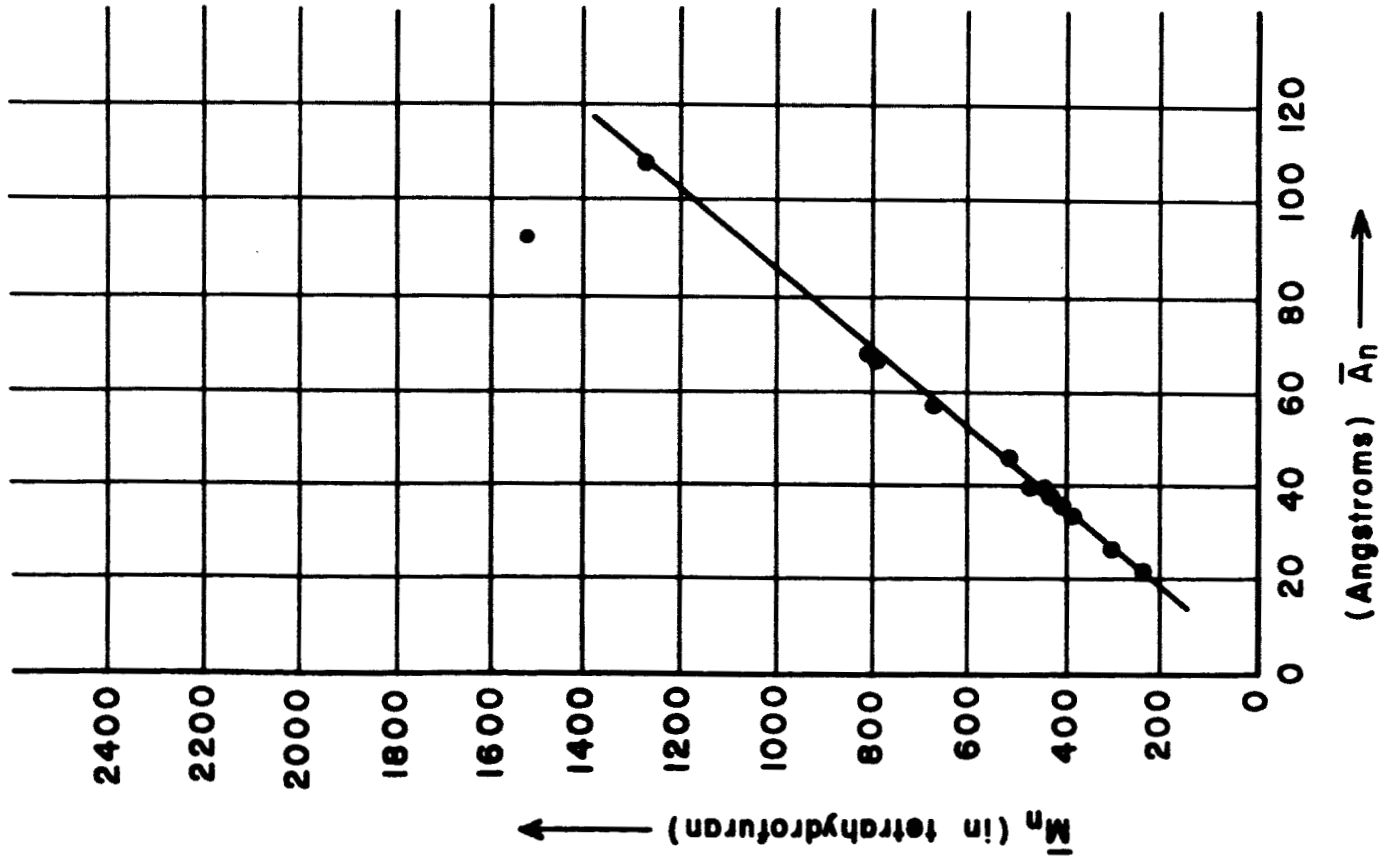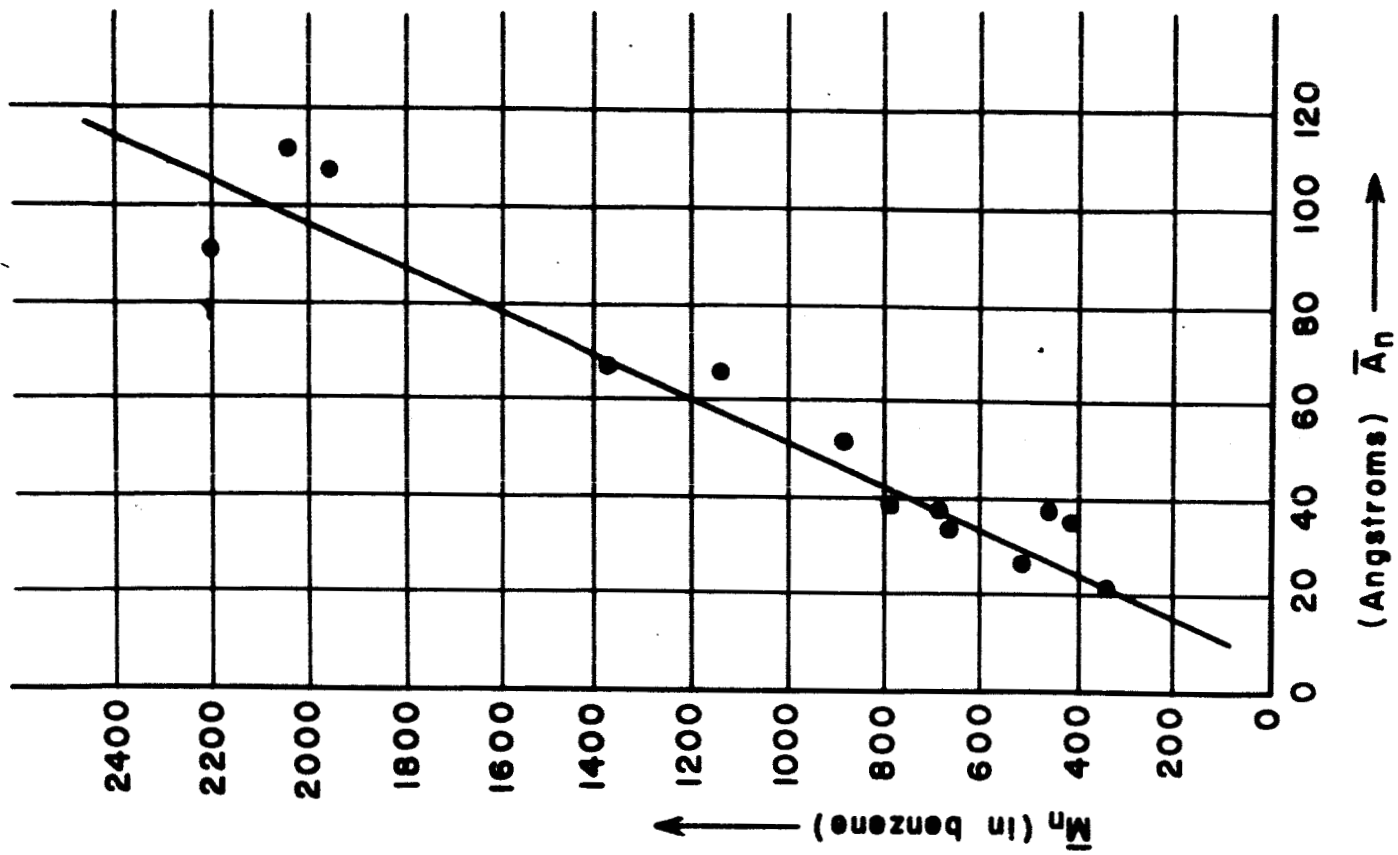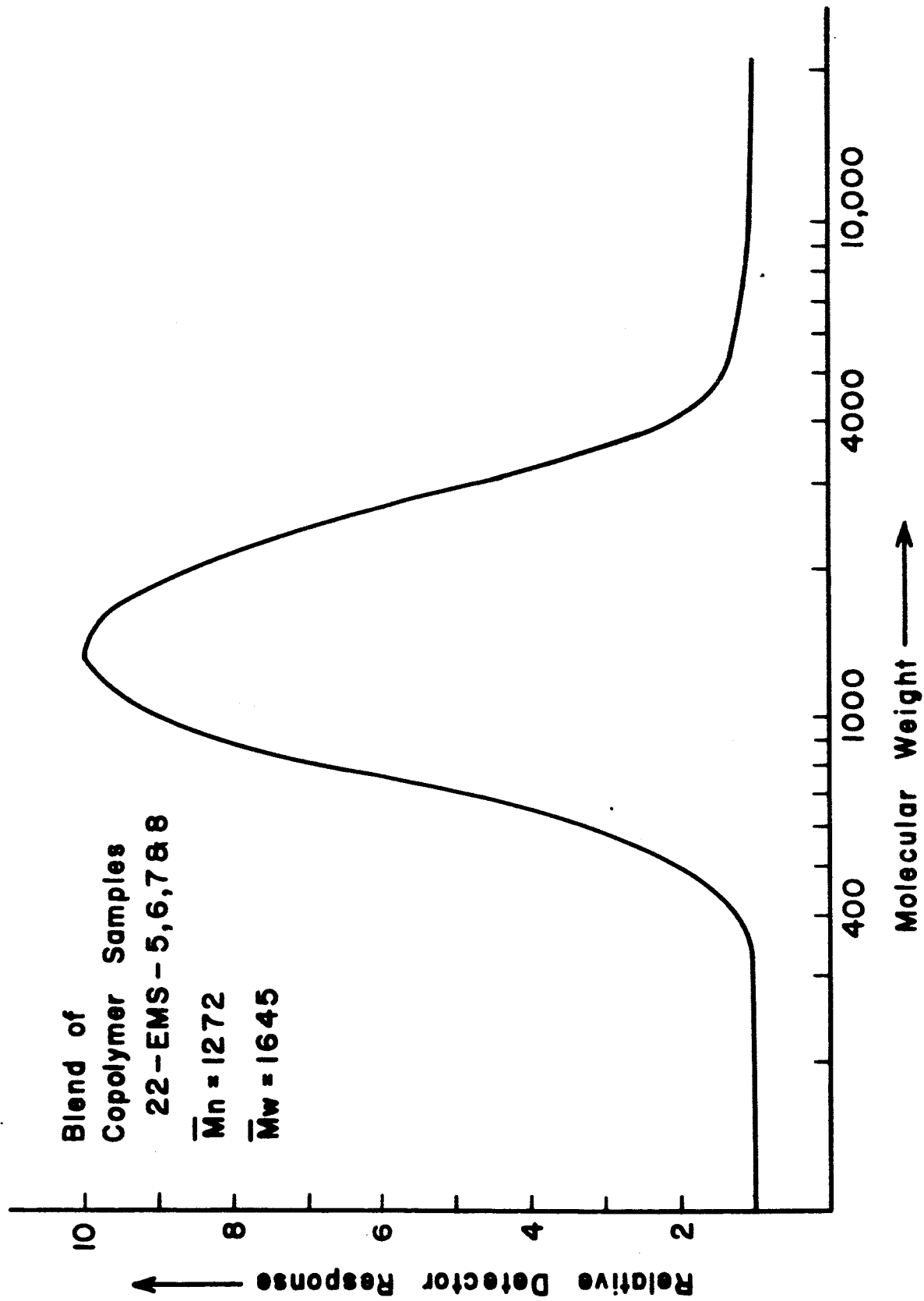
B. Fractionation of an Ethylene-Neohexene Copolymer by Molecular Distillation

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

TABLE II

Sample, 22-EMS#	41	42	50	55-B	Composite
Wt. used	360.64	350.81	237.52	326.92	1275.89
M_n of Sample ($\emptyset$H)	407	309	354	517	384
Moles used	.886	1.136	0.672	0.631	3.325
CN. Eq. Wt. (IR)	350	315	371	501	373
Eq. CN	1.03	1.11	.64	.65	3.43
Nitrogen Analysis	6.85%	6.63%	6.19%	5.10%	6.28%
N. Eq. Wt.	205	212	227	274	225
Eq. Nitrogen	1.79	1.69	1.05	1.19	5.72
Functionality:					
N/molecule	1.97	1.46	1.56	1.42	1.70
CN/molecule	1.16	0.98	.96	1.03	1.03

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

$$M_n \text{ (THF)} = 385 \quad 6.75\% \text{ Nitrogen} \quad (207 \text{ eq. wt.})$$
$$M_n \text{ ($\emptyset$H)} = 393 \quad .88\% \text{ Oxygen} \quad (1820 \text{ eq. wt.})$$

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

Functionality, calculated from elemental+IR analysis:

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

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* Peak absorbance per mil of sample thickness

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

$$9 \quad \text{——} \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \text{—} C \equiv N \quad \Big\}$$

$$\text{from} \quad \bullet \overset{\overset{\displaystyle CH_3}{\diagdown}}{\underset{\underset{\displaystyle CH_3}{\diagup}}{C}} \text{—} C \equiv N$$

$$7 \text{—} N {=} C {=} \overset{\overset{\displaystyle CH_3}{\diagup}}{\underset{\underset{\displaystyle CH_3}{\diagdown}}{C}} \quad \Big\}$$

$$2 \text{—} N \text{—} \overset{\overset{\displaystyle O}{\|}}{C} \text{—} \overset{\overset{\displaystyle CH_3}{\diagup}}{\underset{\underset{\displaystyle CH_3}{\diagdown}}{C}} \text{——} H \quad \Big\}$$

$$\text{from} \quad \bullet N = C = \overset{\overset{\displaystyle CH_3}{\diagup}}{\underset{\underset{\displaystyle CH_3}{\diagdown}}{C}}$$

$$2 \text{——} H \quad \text{(non-functional)} \quad \Big\} \quad \text{chain transfer or disproportionation?}$$

__
20 end groups
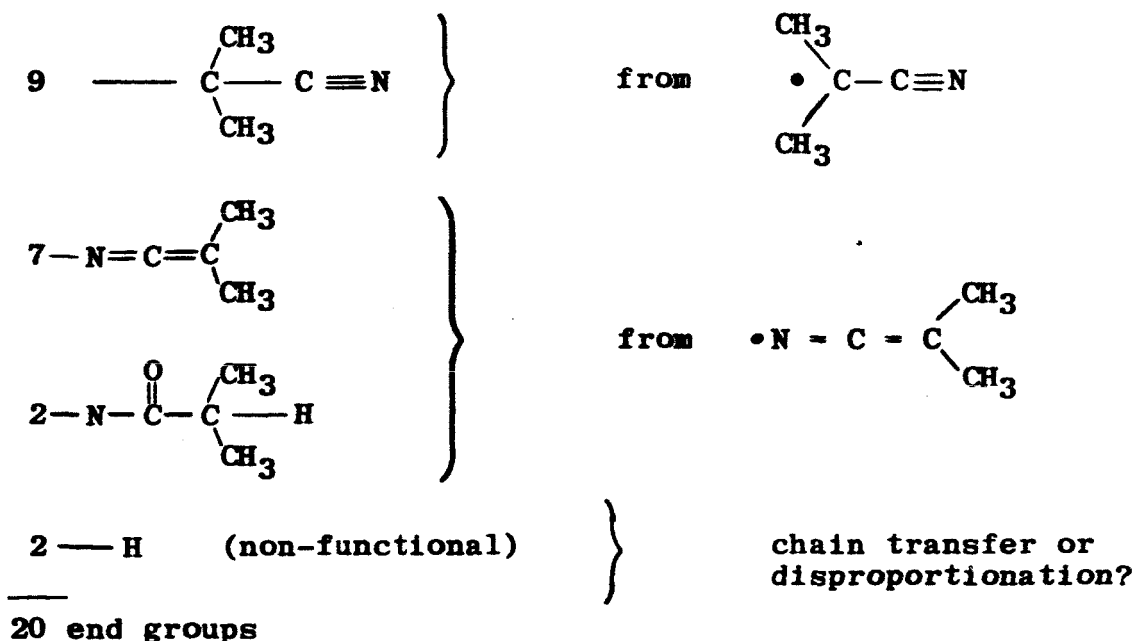
The amide end groups can be derived from the ketene imine end groups by hydrolysis under very mild conditions.

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

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

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

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

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

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

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

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

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

TABLE III

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

	CN Starting Material	Distillation Fractions					
Sample		1	2	3	4	5	6
B.p., °C		150	160-165	175-185	185-190	185-190	Residue
Pressure, microns Hg		50-100	40-60	5-10	5-10	2-5	-
Yield, gms	1209	289	147	157	103	39	336
Color	Straw	Lt. Amber	Amber	Reddish Amber	Tea Color	Tea Color	Black
Brookfield Viscosity, cps. at 22°C	-	1,660	91,600	136,000	1,460,800	-	1,900,00
Acid Number	-	137	156	157	130	99	87
Wt. % Nitrogen	6.75	1.61	1.65	1.68	1.42	1.34	.86
Wt. % Oxygen	.88	12.57	12.14	11.00	9.97	8.73	6.28
Neutralization Equivalent	-	410	360	358	431	567	645
Nitrogen Equivalent Wt.	207	872	850	835	988	1048	1630
Oxygen Equivalent Wt.	1820	127	132	145	160	133	255
$\bar{M}_n$ (v.p.o. in benzene)	393	339	511	660	783	880	1370
$\bar{M}_n$ (v.p.o. in THF)	385	234	296	380	436	518	802
$\bar{M}_w/\bar{M}_n$ (by gel-permeation chromatography in THF)	~1.4	1.07	1.08	1.08	1.08	1.06	1.16
Functionality:							
1.COOH per chain (benzene $\bar{M}_n$)	.89 (CN/Chain)	.83	1.42	1.84	1.82	1.55	2.13
2.COOH per chain (THF $\bar{M}_n$)		.57	.82	1.06	1.01	.92	1.24
3.Nitrogen per chain (THF)	1.86	.27	.35	.45	.44	.50	.49
4.Oxygen per chain (THF)	.211	1.84	2.24	2.62	2.73	2.84	3.14

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C. **Preparation of Ethylene-Neohexene Prepolymers using DEAB Initiator**

The synthesis and rate of decomposition of DEAB were reported in our last quarterly report (No. 2 covering Feb. 1, 1966 to April 30, 1966), in which we also reported preliminary data for three copolymerizations using this new initiator. Additional runs have been completed since then. The results of these later runs are shown in Table IV. Figure 10 shows the viscosity-$\bar{M}_n$ relationship.

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

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

The ester end groups are very easily hydrolysed provided that care is taken upon work-up to avoid re-esterification. For solubility reasons, n-butanol is the preferred solvent. Both the copolymers and KOH will dissolve to a large extent in refluxing butanol.

The procedure used in the hydrolysis of 23-EMS-11 is typical and is described in detail in Appendix B. The key to the procedure is to completely remove all traces of butanol before the potassium salt of the polymer and the excess KOH are neutralized with HCl. Otherwise, extensive re-esterification will occur. Since the butyl ester is nearly indistinguishable from the ethyl ester at this molecular weight, re-esterification upon work-up has the same symptoms as incomplete hydrolysis during the reaction.

The analytical data for the products from the DEAB runs (including those reported last quarter) are given in Table V.

The equivalent weight-functionality data shown in Table V are to be regarded as provisional, pending further confirmation. There is some evidence that our infrared procedure for determining equivalent weight of the ester terminated products may be in error. The calibration curve for the ester carbonyl band will be rechecked with freshly prepared pure diethyl tetramethyl succinate.

The COOH titration will also be rechecked using potentiometric methods.

TABLE IV

ETHYLENE-NEOHEXENE COPOLYMERS PREPARED WITH DEAB

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

FIGURE 10

FIGURE 10

Brookfield Viscosity (25°C), cps vs. No. Avg. Molecular Weight
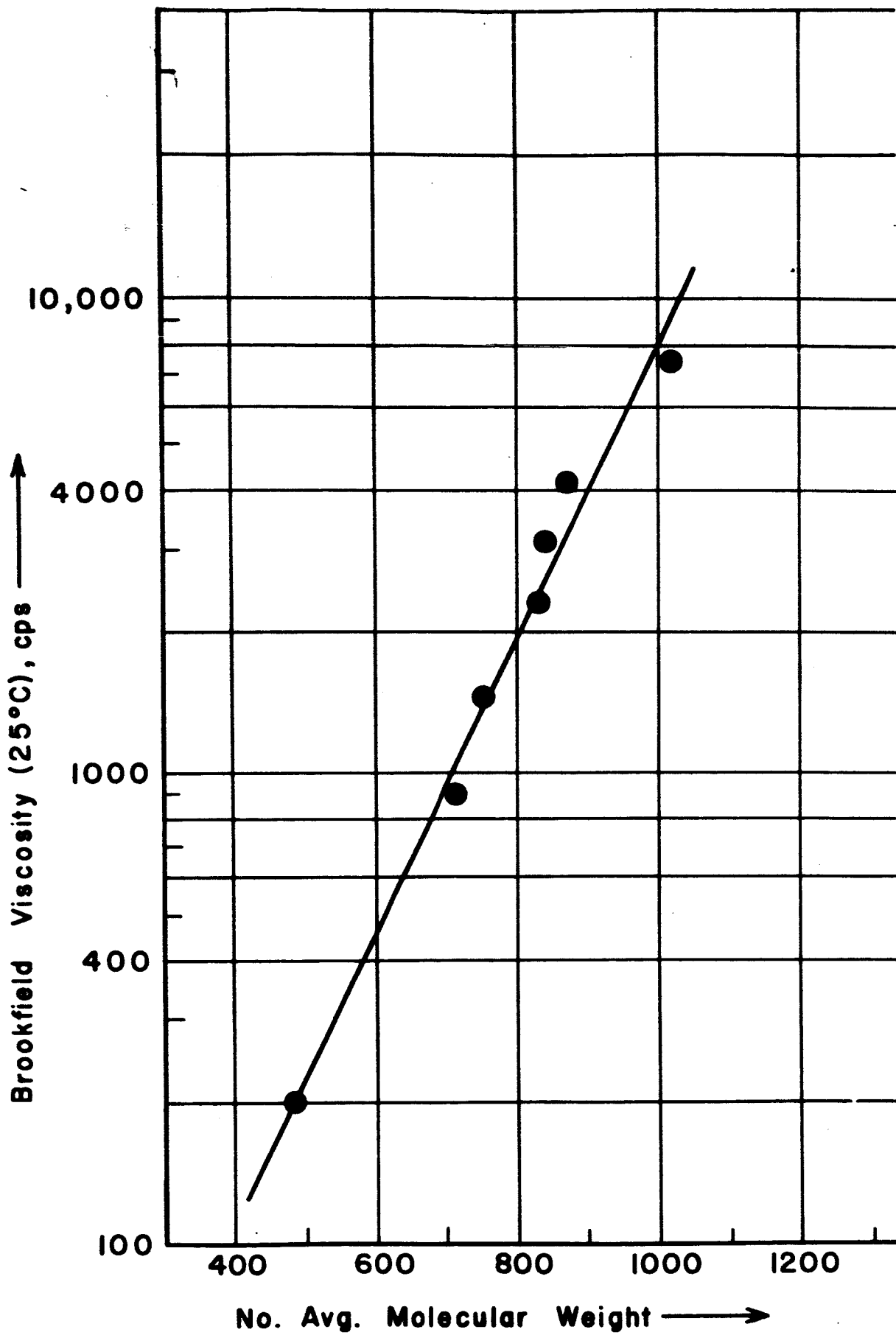
TABLE V

CHARACTERISTICS OF ETHYLENE-NEOHEXENE COPOLYMERS PREPARED WITH DEAB

|	22-EMS					23-EMS	
Sample #	99	108	109	126	127	4	11
Ester Terminated Precursor Data							
Molecular Wt.							
1. Benzene	482	710	831	751	1018	837	869
2. THF	484	-	-	-	-	-	-
Equivalent Wt.	484	534(av)	576(av)	387	584	574	588
Functionality	1.0	1.34	1.44	1.94	1.75	1.46	1.47
COOH Terminated Product Data							
Molecular Wt. (THF)	498	686	791	608	831	779	845
Neutralization Equivalent	401	676	801	605	941	789	830
Functionality	1.24	1.01	0.99	1.00	0.90	0.98	1.02

D. Preparation of DMAB

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

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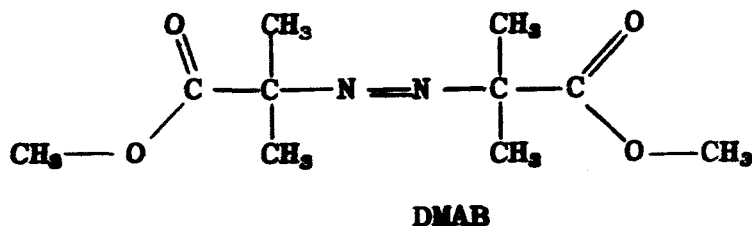
Studies on the relative reactivities of aliphatic esters in free radical oxidation reactions, have shown* that the methylene hydrogens near the ethereal linkage of ethyl acetate are much more prone to attack than the corresponding methyl hydrogens of methyl acetate. The hydrogen upon the tertiary carbon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

primary > secondary > tertiary.

This being the case, the methyl hydrogens adjacent to the ethereal linkage in DMAB should be less prone to undergo hydrogen abstraction reactions with free radicals, than the corresponding methylene hydrogens in DEAB:
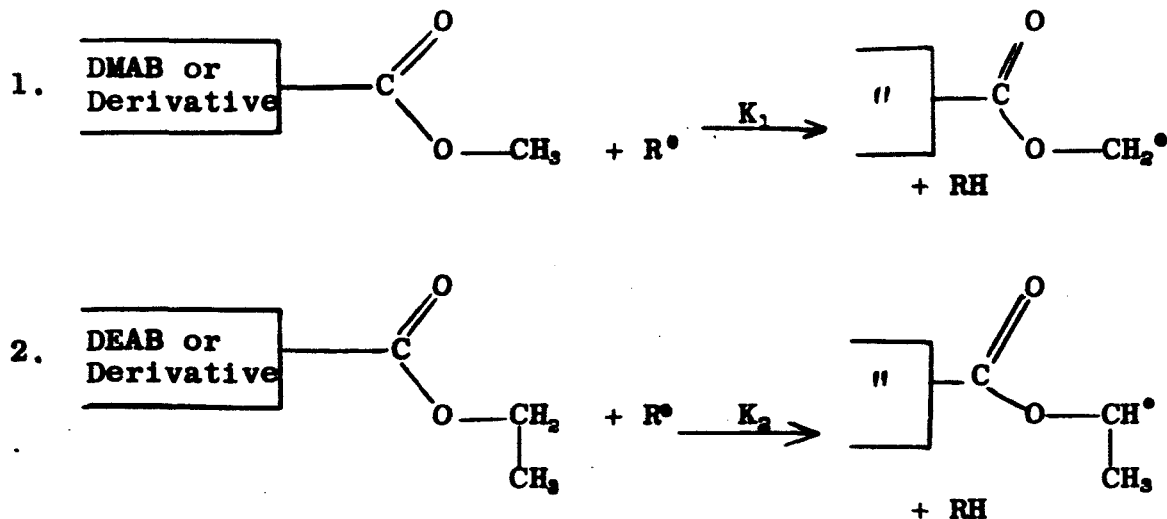
where K_1, the rate of chain transfer of DMAB, is less than K_2, the rate of chain transfer of DEAB.

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*A. Fish and A. Waris, J.C.S., 4513 (1962).
    "   "   J.C.S., 820 (1963).

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

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

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

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

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

The overall yield is 58-62%, based upon acetone. A total of 260 grams of product was prepared and sent to South Charleston. A sample was tested and found to liberate the theoretical volume of nitrogen upon heating.
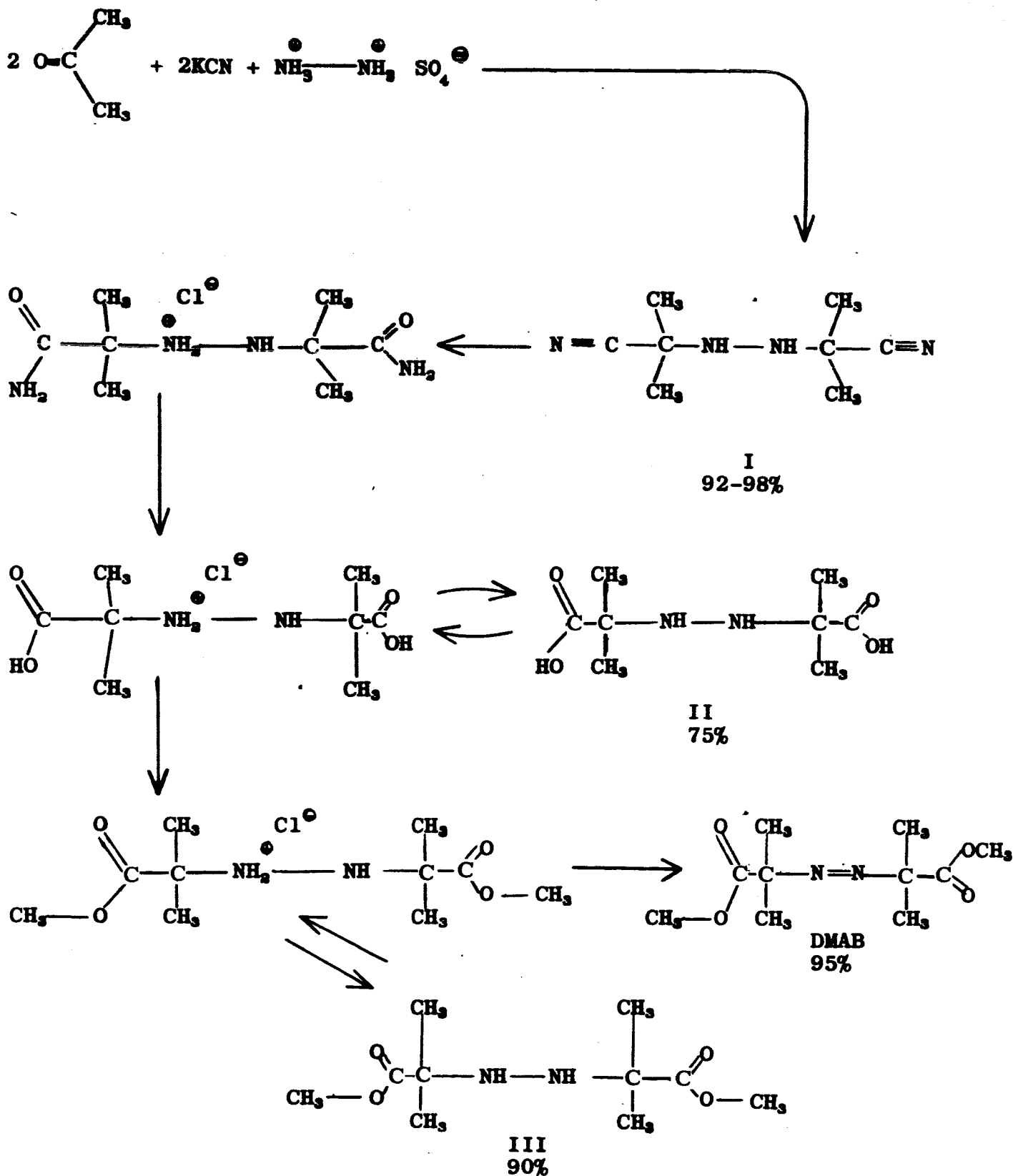
Mackie and Bywater**determined the kinetics of decomposition of DMAB. From their data we calculate the half lives shown in the table below:

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

*Thiele and Heuser, Ann, Vol. 290, pg. 1, (1896)
**J. S. Mackie and S. Bywater, Can. J. Chem., 35, 570 (1957)

The reactions are outlined below:

$$2\ O=C(CH_3)_2 + 2KCN + NH_3\text{---}NH_3\ SO_4^{\ominus} \longrightarrow$$

I
92-98%

II
75%

DMAB
95%

III
90%

A few polymerizations have been carried out using DMAB, however, the characterization of the products is far from complete.

-23-

VI. PLANS FOR FUTURE WORK

During the next quarter we plan to finish our evaluation of the prepolymers made with DEAB.

Prepolymers will be made using DMAB and those products characterized.

We plan to conduct a critical study of the possible sources of contamination of our polymerization system. We will examine our monomers, solvents and initiators for chain transfer agents.

Analytical techniques, particularly the COOH assay, will be re-examined. We plan to use potentiometric techniques to verify visual indicator titrations.

Our initiator synthesis will continue, with di-t-butyl α,α'-azobisisobutyrate (DBAB) as a goal.

VII. APPENDIX

A. Derivation of Equations for GPC

Having the relationship between A and RV for our linear monodisperse standards, we assume a linear correspondence between the molecular weight of a given type of polymer molecule and the chain length of the standard having the same retention volume:*
$$M = KA$$
where K is a constant depending upon the polymer being chromatographed.

We assume the following relationship:
$$H_i = Lc_i **$$
where H_i is the average detector response during the elution of fraction i, L is a constant, and c_i is the concentration in g/ml of the polymer in fraction i.

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* This assumption is not always valid. For example, in a "poor" solvent in which the polymeric solute is in a tightly coiled conformation, there would be a much higher order dependence of M upon A. The limiting case would be, $M = K/6 \pi A^3$, in which the molecules of interest are coiled into close packed spherical conformations, but the calibration standards are completely extended.
The assumption is valid when both the polymer of interest and the linear monodisperse standard have similar degrees of coiling in the solvent system employed.

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

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

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

And the total weight in all the fractions is:

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

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

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

where M_i is the molecular weight in fraction i. This can be expressed in terms of A_i, the extended chain length of the calibration standard having the same retention volume as fraction i.

$$M_i = KA_i$$

Therefore:

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

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

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

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

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

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

and:

$$\bar{M}_w/\bar{M}_n = \bar{A}_w/\bar{A}_n.$$

B. Hydrolysis of 23-EMS-11

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

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

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

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

0.9732 grams required 11.91 ml of 0.0985N KOH/Ethanol to reach the phenolpthalein end—point in warm xylene solution.:

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

= 830 g/equivalent COOH.

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

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

C. Glossary of Acronyms

AIBN   α,α'—Azobisisobutyronitrile
DBAB   Di-t-butyl α,α'—Azobisisobutyrate
DEAB   Diethyl α,α'—Azobisisobutyrate
DMAB   Dimethyl α,α'—Azobisisobutyrate
GPC   Gel Permeation Chromatography