

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

QUARTERLY REPORT NO. 2

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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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Ethylene-neohexene prepolymers were prepared using the organic peroxides succinic acid peroxide and glutaric acid peroxide. These initiators result in acid terminated prepolymers which are quite high in viscosity considering their molecular weights. Esterification of the acid end groups results in a drastic decrease in viscosity, which is attributed to elimination of hydrogen bonding association. Functionalities approaching two carboxyl groups per molecular have been obtained based on molecular weight determinations in benzene. Molecular weight determinations in polar solvents such as tetrahydrofuran yield functionalities closer to one.

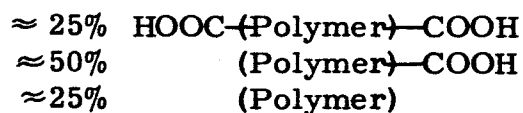
Diethyl α, α' -azobis-isobutyrate has been prepared and its kinetics of thermal decomposition measured at 100°C. This initiator has been used to make three copolymerizations which proceeded very smoothly. The products are being hydrolyzed and characterized.

III. SCOPE OF PROJECT

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

IV. INTRODUCTION

The first quarterly report described the preparation of saturated, amorphous ethylene-neohexene copolymers containing terminal carboxylic acid groups by the free radical high pressure copolymerization of ethylene and neohexene using azobis-isobutyronitrile as initiator followed by hydrolysis of terminal CN groups to COOH groups. These products were liquids at room temperature which cured with a formulation suggested by JPL to yield soft gels. Further examination of these products showed that, contrary to expectation, two types of end groups result from the use of AIBN as initiator and terminator. About 50% of the end groups are CN while the other half are ketene-imine groups. The latter are removed from the polymer by alkaline or acid hydrolysis. The resulting prepolymer is, therefore, made up of a mixture of:



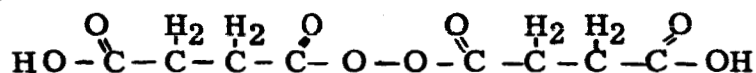
The present report is concerned with the synthesis and analysis of ethylene-neohexene copolymers made with other free radical initiators which are known not to result in ketene-imine groups being placed in the polymers. These fall into two classes, peroxide initiators and azo initiators.

The following sections describe and interpret our experimental results for the period February 1 - April 30, 1966 and outline our plans for future work.

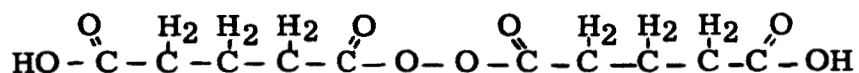
V. TECHNICAL DISCUSSION

A. Preparation of Ethylene-Neohexene Prepolymers Using Organic Peroxide Initiators

These experiments were carried out using succinic acid peroxide and glutaric acid peroxide. The former was obtained from the Lucidol Division of Wallace and Tiernan, Inc. while the latter was synthesized within the Corporation. Their structures are:



Succinic Acid Peroxide (SAP)



Glutaric Acid Peroxide (GAP)

These peroxides decompose at the peroxide linkage, eliminate CO₂ and form primary radicals, which initiate polymerization.

Table I lists data for the preparation of GAP initiated prepolymers with tetrahydrofuran as solvent, and for two SAP runs made using dimethyl formamide and acetone as solvents. These initiators will not dissolve in benzene. Run 43 was made with GAP and DTDBA (dithio dibutyric acid) as a chain terminating agent.

The functionality of products 31, 34 and 38 were all low, regardless of whether the acid number or the oxygen analysis was used to compute the molecular weight equivalent to one carboxylic acid group. The product from run 35 contained nitrogen, indicating that this solvent is an active transfer agent. Run 36 gave only one gram of product.

TABLE I

Neohexene/Ethylene Copolymers

Acid Peroxide Catalyzed Runs

Run No	22 EMS-	31	34	38	43	35	36
<u>Initial Charge</u>							
Solvent		THF	THF	THF	THF	DMF	Acetone
Solvent Wt., gms.		50	74	43	38	62	98
Neohexene, gms.		635	255	426	426	364	125
Neohexene Wt. % Monomers		75	70	73	73	70	70
Catalyst,		GAP	GAP	GAP	GAP	SAP	SAP
Wt. gms.		3.8	7.4	9.3	4	6	2
Ethylene, gms.		211	109	158	158	156	53.4

Fed During Reaction

Solvent, gms.	268	670	329	721	571	882
Catalyst, gms.	51	66	84	36	56	18
DTDBA, gms.	--	--	--	34	--	--

Reaction Conditions

Temperature, °C	95	90	95	95	90	60
Pressure,						
Initial, psi	4100	500	700	750	500	400
Final, psi	5300	2200	900	20,000	4300	6750
Reaction Time, hrs.	6.5	6.5	6.5	3.0	4.5	6.0

Productivity

Yield, gms.	155	120	168	105	35	1.0
Conversion, %	18.3	32.9	28.8	18.0	6.7	0.5
Rate, % per hr.	2.8	5.1	4.4	6.0	1.5	0.1

- NOTES: 1. GAP = glutaric acid peroxide
 2. SAP = succinic acid peroxide
 3. THF = tetrahydrofuran
 4. DMF = dimethyl formamide

5. Per cent conversion is yield in grams divided by total weight of monomers charged times 100.

TABLE I - cont'd

Neohexene/Ethylene Copolymers

Acid Peroxide Catalyzed Runs

	31	34	38	43	35	36
<u>Physical Properties</u>						
Mol. Wt.	943	415	526	459	467	
Brookfield Vis., Centipoise, 25°C	22,610	555	3105	816	--	D i s c a r d e d
Sp. Vis. at 80°C	0.022	0.017	0.017	0.015	0.016	
Acid Number	54	103	53	96	--	
Nitrogen, Wt. %	--	--	--	--	3.41	
Carbon, Wt. %	81.80	77.89	79.12	75.3	--	
Hydrogen, Wt. %	13.71	13.16	13.45	13.15	--	
Oxygen, Wt. %	4.94	8.49	7.86	8.09	7.71	
Sulfur, Wt. %	--	--	--	3.26	--	
<u>Functionality</u>						
By Acid No.	0.91	0.76	0.5	0.79	--	--
By O ₂ Analysis	1.46	1.10	1.29	1.16	0.56	--
<u>Description</u>	Lt. Yellow Heavy Oil	Yellow Oil	Yellow Oil	Yellow Oil	Dark Tan Oil	Tan Grease

- NOTES:
- Specific Viscosity determined with 0.4% polymer in methyl cyclohexane at 80°C.
 - Acid Number defined as milligrams KOH per gram of polymer.
 - COOH functionality Run 43 derived from sulfur analysis 0.47. DTDBA used as chain stopper.
 - O₂ functionality results from both ester and carboxyl groups from peroxide initiators.

TABLE II

Ethylene-Neohexene Copolymers - Succinic Acid Peroxide Runs

In Benzene-Tertiary Butanol Mixed Solvent

Run No.	22 EMS	62	64	66	70
<u>Initial Charge</u>					
Solvent		<u>50/50 Benzene/t-BuOH</u>			
Wt. gms	410	402	99	99	
Neohexene, gms.	315	315	494	484	
Initiator	SAP	SAP	SAP	SAP	
Wt. gms.	21.6	30.2	5	5	
Ethylene, gms.	116	116	1000 psi	161	
			at RT		
<u>Fed During Reaction</u>					
Solvent, gms.	222	222	480	495	
Initiator, gms.	--	--	51	45.5	
DTDBA, gms.	22	22	--	--	
<u>Reaction Conditions</u>					
Temperature, °C	95	95	100	110	
Pressure, psig					
Initial	100	800	2225	850	
Final	Gage	7700	15,000	16,000	
	Plugged				
Reaction Time	3.5	1.5	4.25	2.0	
<u>Productivity</u>					
Yield, gms	7.0	22	104	84	
Conversion, %	1.6	5.1	15.4	13	
Rate, %/hr.	0.5	1.02	4.4	6.5	

The low functionality in these runs was attributed to solvent chain transfer effects primarily, although the possibility that these catalysts might possess transfer activity was not ignored. It was decided to search for a solvent which would dissolve both the acid catalyst and the polymer and not be an active transfer agent. A 50/50 mixture of benzene and tertiary butanol was found to dissolve DTDBA whereas benzene would not. However, no good solvent for SAP which was low in transfer activity was found.

Table II lists those runs made with SAP initiator where the mixed benzene/t-BuOH solvent was used. Run 62 was made with all SAP charged initially and a solution of DTDBA charged during the reaction. A low yield indicated that the DTDBA acted as a retarder; 68% of the DTDBA was recovered unchanged. Run 64 was a repeat of 62 using one third more catalyst. This tripled the yield compared to Run 62.

Run 66 utilized a slurry technique for feeding SAP. A 50/50 mixture of benzene/t-BuOH was used to slurry the SAP which was kept in suspension by cycling past the suction check of a high pressure injection pump using a Viking gear pump. The rupture disk on the pump blew which terminated the run. This was caused by a plugged feed line. However, this run gave 100 grams of product, which reflected the absence of DTDBA and the continual replenishment of initiator during the run.

Run 70 was a SAP slurry run similar to 66 except that the temperature was increased 10° to 110° and the catalyst feed rate was doubled which halved the reaction time. The yield was 84 grams. In order to scale up this run safely it would be necessary to place the recycling slurry behind an explosion proof barricade and install remote control equipment. Scale up to a 2 gallon autoclave would necessitate recycling 2/3 of a pound of peroxide in slurry. The danger arises in injecting the peroxide slurry with a high pressure piston pump. Crystals of peroxide might be detonated by friction if caught between the piston and cylinder walls.

Run 64 gave a gross product of molecular weight (benzene) 769 and Brookfield viscosity 27,000 cps at room temperature. The acid number was 170.4. This results in an apparent functionality of 2.34 acid groups per molecule. From a sulfur content of 12.69% (assuming one S atom per COOH group) the functionality was 3.05 COOH groups per molecule. This product later separated into two phases and was not further investigated.

The following characterization data were obtained for the product from Run 66.

Brookfield Viscosity	238,000 cps
Molecular Weight in Chloroform	1432
Molecular Weight in THF	1465
Molecular Weight in Benzene	2198
Neutralization Equivalent	1630

The functionality calculated from these data are:

$$\begin{aligned} F (\text{Benzene}) &= \frac{2198}{1630} = 1.34 \text{ COOH groups/molecule} \\ F (\text{CHCl}_3) &= \frac{1432}{1630} = 0.88 \text{ COOH groups/molecule} \\ F (\text{THF}) &= \frac{1465}{1630} = 0.90 \text{ COOH groups/molecule} \end{aligned}$$

This product was reacted with thionyl chloride to convert the COOH groups to COCl groups. This lowered the viscosity from 238,000 to 90,000 cps as a result of elimination of hydrogen bonding. The acid chloride was converted into the ester which reduced the viscosity to 12,000 cps. The drop from 238,000 cps to 12,000 cps illustrates the effect on viscosity of eliminating hydrogen bonding.

The following characterization data were obtained for the product from Run 70.

Molecular Weight in Benzene	1453
Brookfield Viscosity	87,500 cps
Oxygen Concentration	6.65%
Acid Number	76.8
Neutralization Equivalent	731

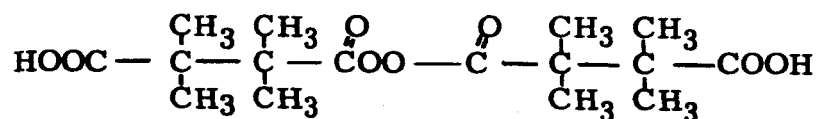
$$\text{Functionality} = \frac{1453}{731} = 1.98 \text{ COOH/molecule}$$

This product was further purified and resubmitted for molecular weight and acid number with the following results:

Molecular Weight in Benzene	1134
Molecular Weight in THF	791
Neutralization Equivalent	793
Functionality (Benzene) =	$\frac{1134}{793} = 1.43$
Functionality (THF) =	$\frac{791}{793} = 0.999$

The Brookfield Viscosity of this product was 87,500 cps, which is quite high for a material with a number average molecular weight of 791. To test the possibility that this anomaly is due to hydrogen bonding association the acid terminated product was esterified. Conventional Fischer esterification, with ethanol and p-toluene sulfonic acid did not proceed to completion; however, the partially esterified product had a viscosity of 8,000 cps. By thionyl chloride treatment followed by reacting the acid chloride with ethanol in the presence of pyridine the residual COOH groups were converted to COOC₂H₅. The viscosity of the esterified product was only 230 cps, which confirms the hypothesis that COOH association caused the high viscosity of the acid product. The number average molecular weight of the esterified product was 880, showing that no degradation of the product occurred.

The low functionality of the SAP initiated product made in mixed benzene/ t-butanol suggests that SAP itself is a chain transfer agent. A desirable alternate catalyst is tetramethyl succinic acid peroxide.

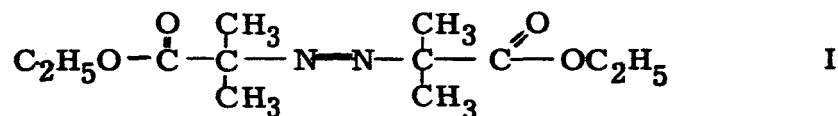


This catalyst contains no hydrogen atoms alpha to a carboxyl group and is not likely to undergo chain transfer reactions. The precursor of this catalyst, tetramethyl succinic acid is available.

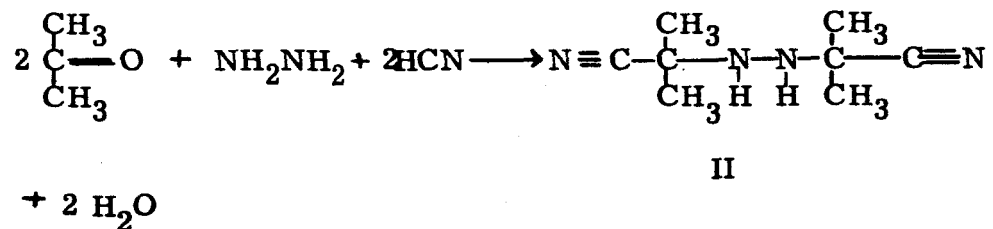
B. Preparation of Diethyl- α,α' -Azobis-isobutyrate Initiator and Measurement of Rate of Decomposition

1. Preparation

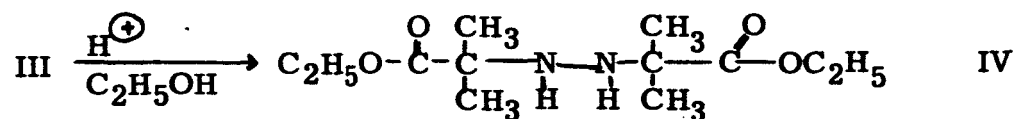
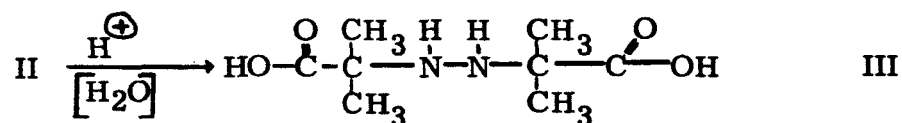
Diethyl- α,α' -azobis-isobutyrate (I) DEAB can be prepared by two routes at present.



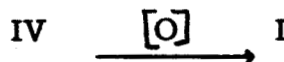
The first starts with the condensation of acetone with hydrazine in the presence of HCN to give α,α' -hydrazobis-isobutyronitrile, II.



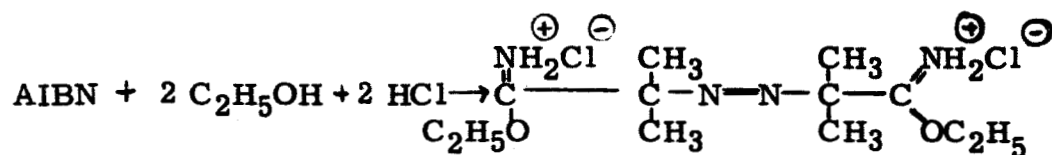
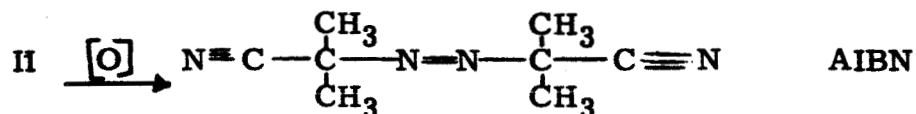
This material can be hydrolyzed to the dicarboxylic acid III and then esterified with ethanol to give the diethyl- α,α' -hydrazobis-isobutyrate, IV.



The hydrazoester IV can be oxidized to I by a variety of methods:

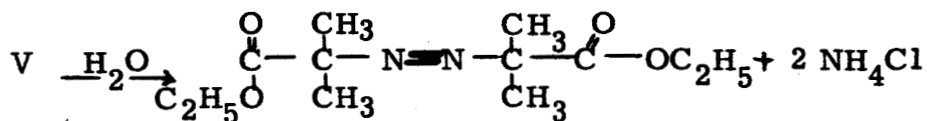


An alternate procedure is to oxidize II to give α, α' -azobis-isobutyronitrile (AIBN) and then react AIBN with HCl in anhydrous ethanol to give the iminoether hydrochloride V.



V

Mild hydrolysis of V gives I directly.

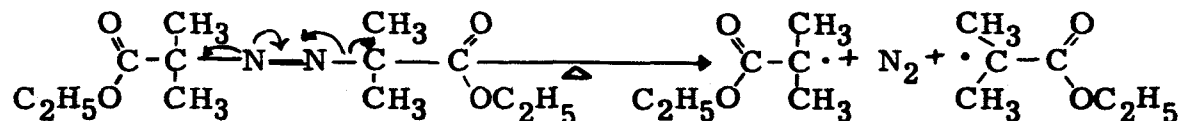


I

The procedure adopted was the latter, using commercially available AIBN. This provided I in two steps which are easily carried out in the laboratory. The former route is more economical for production purposes.

2. Rate of Decomposition of DEAB

Diethyl- α, α' -azobis-isobutyrate (DEAB) decomposes smoothly when heated to yield nitrogen gas and free radicals:



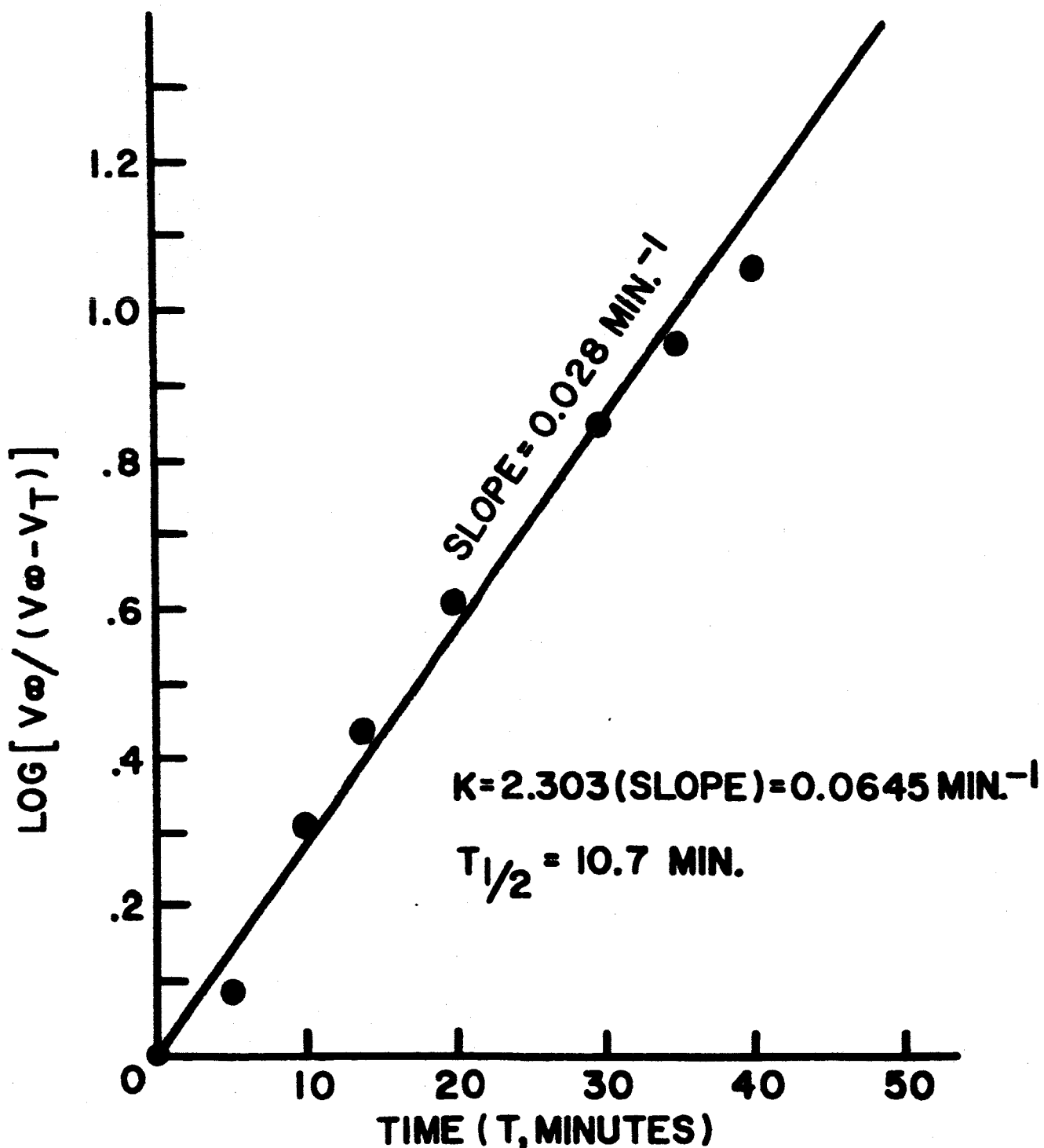
I

The carboethoxy group in the radical derived from structure I stabilizes the radical in much the same way as the CN group stabilizes the cyanoisopropyl radical derived from AIBN.

The kinetics of decomposition of I in xylene solution at 100°C was studied. The evolved nitrogen was collected in a gas burette and the volume, V_t , measured as a function of time. After the reaction had gone to completion the total volume of evolved nitrogen, V_∞ , was measured. At any time, t , the quantity $V_\infty - V_t$ represents the amount of nitrogen yet to be evolved and hence is proportional to the amount of I remaining in the reaction mixture. V_∞ is proportional to the original amount of I, therefore the ratio, $[V_\infty - V_t] \div V_\infty$, represents the fraction of I remaining in the reaction mixture at time t . According to the usual kinetic procedure for first order reactions, a graph of the logarithm of the fraction of I remaining in the reaction mixture plotted versus time gives a straight line passing through the origin, with a slope of $-K/2.303$, where K is the first order rate constant.

Since $-\log [(V_\infty - V_t) \div V_\infty] = +\log [V_\infty \div (V_\infty - V_t)]$, we plotted the latter quantity versus time as shown in Figure I. At 100°C the rate constant was 0.0645 reciprocal minutes and the half life was 10.7 minutes (compared with 7 minutes for AIBN).

FIGURE I



KINETICS OF DECOMPOSITION OF
DIETHYL- α, α' , AZOBIS-ISOBUTYRATE (DEAB)
IN XYLENE AT 100° C

C. Ethylene-Neohexene Copolymers Prepared with DEAB

Table III lists the reaction conditions used in preparing the first series of copolymers with the new catalyst. These were carried out in benzene at 90°C, a solvent in which all the components in the reaction are soluble, including DEAB. In order to traverse the molecular weight range of interest in this work, the catalyst concentration was varied as was the pressure.

As expected, the samples varied in viscosity and molecular weight from 200 cps to 2300 cps. In appearance they were pale yellow liquids. The end groups are esters which are being hydrolyzed to the acid.

The molecular weight of sample 99 was determined in two polar and one non-polar solvent with remarkable agreement. Hydrogen bonding is not a problem in the ester terminated products, which accounts for the agreement between molecular weight data in benzene and THF and also the observed low viscosities.

It will be recalled that DEAB was thought to be preferable to AIBN because of the latter's tendency to place ketene-imine groups on the end of polymer chains. No evidence for the presence of ketene-acetal formation in the DEAB polymer has been found, which is a very encouraging fact.

These products are being characterized as to functionality and will be reported on more fully in subsequent reports.

TABLE III

Ethylene-Neohexene Copolymers Prepared With DEAB

	<u>Run No.</u>		
<u>Initial Charge</u>	99	108	109
Benzene, wt. gms.	30	65	12
Neohexene, gms.	472	527	591
DEAB, gms.	10	7.2	4.0
Ethylene, gms.	175	195	218
<u>Fed During Reaction</u>			
Benzene, gms.	270	195	145.6
DEAB, gms.	90	65	36.4
<u>Reaction Conditions</u>			
Temperature, °C	90	90	90
Initial Pressure, psig	990	1400	2800
Final Pressure, psig	2400	2675	3625
Reaction Time, hrs.	4.5	4.5	4.5
<u>Productivity</u>			
Yield, gms.	176	180	164
% Conversion	27.2	22.7	20.3
Rate, % per hr.	6.1	5.1	4.5
<u>Physical Properties</u>			
Brookfield Viscosity, 25°, cps.	203	898	2323
No. Avg. Mol. Wt. in			
Benzene	482	710	830
CHCl ₃	478		
THF	484		

VI. PLANS FOR FUTURE WORK

During the next quarter it is planned to examine more completely the prepolymers which have been made with the initiator DEAB. Additional product will be made using the most promising reaction conditions.

Dimethyl α, α' -azobis-isobutyrate, DMAB, and dineopentyl α, α' -azobis-isobutyrate, DNAB, will be synthesized using the synthetic route described for DEAB. These initiators will be used to prepare prepolymers which will be compared to the DEAB initiated products.

The molecular still will be used to fractionate selected prepolymer samples to determine functionality distribution as a function of polymer molecular weight. The molecular weight distribution and weight to number average molecular weight ratio will be determined for the gross sample and fractions obtained by molecular distillation. The Waters Gel Phase Chromatography apparatus will be used in these studies.