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October 1980 to
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Synthesis of Hydroxy-Terminated Dinitropropyl Acrylate Polymers and Improved Characterization of Hydroxy-Terminated Prepolymers

March 1983

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A synthesis method for hydroxy-terminated dinitropropyl acrylate polymers via free radical polymerization was developed. A new method to determine hydroxyl equivalent weight was also developed. The synthetic techniques and characterization methods which include determinations for equivalent weight, molecular weight and functionality, are described.

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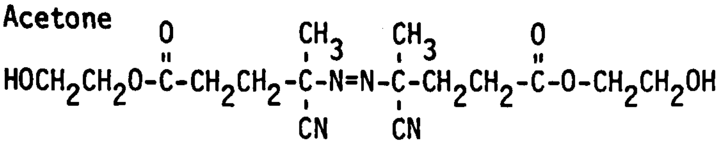
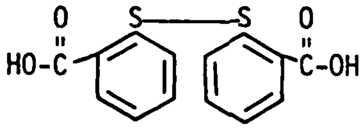
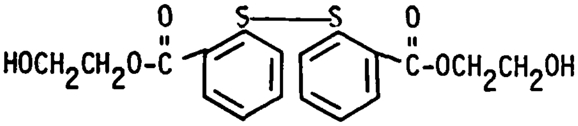
GLOSSARY

ABBREVIATIONS	
AA	Acetic anhydride
Ac	Acetone
Azo-OH	 $HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2OH$
B-2000	Poly-(1,2-butylene)-glycol from DOW Chemical
Carbowax	Polyethylene glycol from Union Carbide
CH	Cyclohexane
DMF	Dimethyl Formamide
DNPA	Dinitropropyl Acrylate
o-DTB-CO_2H	
o-DTB-OH	
EC	Ethylene Carbonate
GPC	Gel Permeation Chromatography
HEDS	Hydroxyethyl Disulfide
HPLC	High Pressure Liquid Chromatography
NMIM	N-methylimidazole
NPGA	Neopentyl azelate polyesterdiol from Wittco
PA	Phthalic anhydride
PCP	Polycaprolactone diol from Union Carbide
PDNPA	Polydinitropropyl acrylate (our experimental)
PEG	Polyethylene glycol
PPG	Polypropylene glycol from Wyandotte
PY	Pyridine
R-45M	Hydroxy-terminated polybutadeine from ARCO
Teracol	Poly-(tetramethylene oxide)- diol from DuPont

1.0 INTRODUCTION

This is the final Technical Report submitted in partial fulfillment of the requirement of Contract F 04611-79-C-0009/P00006. This report covers the period of October 1, 1980 - October 30, 1982.

The initial Contract F 04611-79-C-0009 involved synthesis of hydroxy-terminated dinitropropyl acrylate polymers via a free radical polymerization(1). The contract was extended for two more years for:

A. Continued study of dinitropropyl acrylate polymers; and

B. Development of a more reliable characterization method of prepolymers.

2.0 OBJECTIVE

The initial Contract F04611-79-C-0009 involved synthesis of hydroxy-terminated dinitropropyl acrylate polymers. The objective was expanded to include:

A. Diversification of synthetic procedure for the dinitropropyl acrylate polymers to obtain polymers having hydroxy-functionality ranging from 1.7 to 2.8; and

B. Development of a more reliable characterization method for the determination of equivalent weight, molecular weight, and functionality of prepolymers.

3.0 SUMMARY

3.1 SYNTHESIS OF HYDROXY-TERMINATED DINITROPROPYL ACRYLATE POLYMERS

The purpose of this project was to synthesize dinitropropyl acrylate polymers terminated with hydroxyl groups. If both ends of the polymer chain are terminated by hydroxyl groups, the functionality of the polymer would be 2.0.

A free-radical solution polymerization method was selected for this study. The task involved (a) preparation, purification, and characterization of dinitropropyl acrylate, an OH-containing Azo initiator (Azo-OH), and an OH-containing disulfide (o-DTB-OH); (b) purification and characterization of the polymer; and (c) optimization of polymerization conditions to achieve the desired molecular weight and functionality. Polymerization conditions were examined in terms of types and concentrations of the initiator, the transfer agent, the solvent, and the reaction temperature. These optimization studies were discussed in the previous report(1).

A detailed mechanistic study for this system, through an investigation of the rate of polymerization reaction, fractionation of the resulting DNPA polymers, and analyses of the polymers after various polymerization reaction times, indicates that there are some accompanying side-reactions which place hydroxyl groups along the polymeric chains rather than at the ends of the chains during the polymerization, especially when the reaction period is prolonged. Use of a more effective chain transfer agent, a hydroxyl group-containing aromatic disulfide (ex. o-DTB-OH instead of HEDS), lower reaction temperature (60°C instead of 70°C), and shorter reaction period (4 hours instead of 10 to 20 hours) minimizes the undesireable side-reactions. Under these conditions, OH-functionality of 1.8 may be achieved, and the hydroxyl groups are placed mainly at the ends of the chains.

Although the functionality value of 1.80 approaches that of some of the commercially available prepolymers, it indicates the presence of monofunctional polymers in an amount as high as 20 mole percent. These monofunctional polymers will become non-load bearing chains when a rubber network is formed through the cure reaction with isocyanates, thus resulting in a propellant binder having poor mechanical properties. One of the approaches to remedy this problem is to incorporate a secondary alcohol group along the chain, in addition to the primary alcohol groups at both ends of the chain. This type of polymer would undergo cure reaction with isocyanates such that most of chain extension reactions with the primary alcohols would occur prior to the reactions with the secondary alcohols. The resulting binder network should minimize the non-load bearing chains without sacrificing the elongation capability. Such a polymer was synthesized and the functionality was determined to be 2.80. These DNPA polymers have potential as co-prepolymers or crosslinkers, to be used along with other prepolymers to improve the compatibility of the binder network with the nitro or nitrato-plasticizers.

3.2 IMPROVED CHARACTERIZATION OF HYDROXY-TERMINATED PREPOLYMERS

3.2.1 Determination of OH-Equivalent Weight

The three commonly used chemical methods for the quantitative determination of hydroxyl groups in prepolymers were evaluated. These methods are based on the esterification of the polymer with an excess of acid anhydride followed by hydrolysis and titration of the excess anhydride. The evaluation indicates that a correct determination of the equivalent weight is strongly dependent on the reaction conditions used for esterification of the hydroxyl groups, and the conditions have to be varied depending on the chemical type, size and solubility of the prepolymers. Hence, selection of the right conditions for a given polymer may require a reference value of the equivalent weight of the prepolymer, which has to be obtained independently by another analytical method.

A new physical method for determination of OH-equivalent weight has been developed. This is based on the infrared absorption band of THF/OH complex. Advantages of this method are that the determination is rapid and requires only a semi-micro quantity of the sample. Disadvantages are that proper reference compounds are required for calibration, and that the presence of water interferes with the determination.

3.2.2 Determination of Average Molecular Weight

A combination method of GPC analysis and intrinsic viscosity determination by a capillary viscometry shows promise as a reliable approach for the determination of the molecular weight of prepolymers. Various polystyrene "standards" of proper molecular weight range were analyzed by GPC (V_e) and capillary viscometry $[\eta]$ to obtain the following relationship:

$$\log [\eta] M = 21.0 - 0.59 V_e + 0.0049 V_e^2$$

where $[\eta]$ is the intrinsic viscosity

M is the molecular weight

V_e is the elution volume

The molecular weight of a new experimental sample can then be obtained from the determinations of V_e and $[\eta]$ using the above equation. Evaluation of this method using several polymers of known molecular weight indicates that this is a simple approach and yet gives more reliable and meaningful data than GPC analysis alone.

3.2.3 Determination of Number Average Functionality of Prepolymer of $f_p < 2.0$

The number average functionality of a prepolymer, $\overline{f_p}$, can be determined by Method I, where number average molecular weight ($\overline{M_n}$) and number average equivalent weight (EW) are determined to give $\overline{f_p} = \overline{M_n}/EW$; and by Method II, where a cure study with an isocyanate is used. Error analyses for the prepolymers of $f_p < 2.0$, based on theory and preliminary experimental results, indicate that Method I could give variations in the functionality value as high as 14%, whereas Method II should give the "effective" functionality value with ± 3% accuracy.

4.0 RESULTS AND DISCUSSION

4.1 Synthesis of Dinitropropyl Acrylate Polymers Containing Hydroxyl Groups

In a simple polymerization system, the free-radical polymerization proceeds according to the following steps:

Initiation Step:

$$I_2 \xrightarrow{K_d} 2\ I. \qquad (1)$$

$$I. + M \xrightarrow{K_i} I\text{-}M_1. \qquad (2)$$

Propagation Step:

$$\begin{aligned} I\text{-}M_1. + M &\xrightarrow{K_p} I\text{-}M_2. \\ I\text{-}M_n\cdot + M &\xrightarrow{K_p} I\text{-}M_{n+1}\cdot \end{aligned} \qquad (3)$$

Termination Step:

(a) By Combination:

$$I\text{-}M_n\cdot + I\text{-}M_m\cdot \xrightarrow{K_{tc}} I\text{-}M_n\text{-}M_m\text{-}I \qquad (4)$$

(b) By Disproportionation

$$I\text{-}M_n\cdot + I\text{-}M_m\cdot \xrightarrow{K_{td}} I\text{-}M_n + I\text{-}M_m\text{-}H \qquad (5)$$

If a monomer undergoes polymerization by the mechanism above, and the termination of the propagating radical occurs only by combination and <u>not</u> by disproportionation, a functionally terminated polymer (telechelic polymer) can be synthesized by utilizing initiators containing the desired functional group. For example, monomers such as butadiene and styrene have the above desired chemical properties. Consequently, hydroxy-terminated and carboxy-terminated polybutadienes have been synthesized using hydrogen peroxide(2,3), succinic acid peroxide(4,5), glutaric acid peroxide(4,5), and 4,4'-Azo-bis-(4-cyanopentanoic acid)(4,5,6) as initiators. However, more reactive vinyl monomers such as vinyl acetate, methyl acrylate and methyl methacrylate are known to undergo many bi-molecular hydrogen-abstracting side reactions during chain propagation and also undergo termination substantially by disproportionation(7,8,9,10).

In addition to the undesirable termination by disproportionation, there are other potential side-reactions of the propagating radicals to form dead polymers. In the DNPA polymerization system, these reactions would be:

(a) chain transfer to initiator:

$$I\text{-}M_n\cdot + I\text{-}H \xrightarrow{k_{tr,I}} I\text{-}M_nH + I\cdot$$

(b) chain transfer to monomer:

$$I\text{-}M_n\cdot + M \xrightarrow{k_{tr,m}} I\text{-}M_nH + M\cdot$$

(c) chain transfer to polymer:

$$\text{I-M}_n^{\cdot} + \text{PH} \xrightarrow{k_{tr,P}} \text{I-M}_n\text{-H} + \text{P}\cdot$$

(d) chain transfer to solvent:

$$\text{I-M}_n^{\cdot} + \text{SH} \xrightarrow{k_{tr,S}} \text{I-M}_n\text{-H} + \text{S}\cdot$$

(e) chain transfer to an additive:

$$\text{I-M}_n^{\bullet} + \text{X-X} \xrightarrow{k_{tr,X}} \text{I-M}_n\text{-X} + \text{X}\cdot$$

where I-Mn• are the propagating polymer radicals, and

IH is the initiator,

MH is the monomer,

PH is the polymer,

SH is the solvent, and

XX is the additive.

When one considers all these above reactions for dead polymer formation, the expressions for the average degree of polymerization, $\overline{DP}$, and the average functionality, $\overline{FN}$, of the polymer can be derived as follows:

$$\frac{1}{\overline{DP}} = \frac{(x+1)\sqrt{fk_dk_t}}{k_p}\frac{[I]^{1/2}}{[M]} + \frac{k_{tr,m}}{k_p} + \frac{k_{tr,I}}{k_p}\cdot\frac{[I]}{[M]} + \frac{k_{tr,s}}{k_p}\cdot\frac{[S]}{[M]} + \frac{k_{tr,x}}{k_p}\frac{[X]}{[M]} \qquad (6)$$

$$\overline{FN} = \frac{(x+1)\sqrt{fk_dk_t}[I]^{1/2} + k_{tr,m}[M]_o + k_{tr,I}[I]_o + k_{tr,s}[S]_o + 2k_{tr,x}[X]_o}{\sqrt{fk_dk_t}[I]^{1/2} + k_{tr,m}[M]_o + k_{tr,I}[I]_o + k_{tr,s}[S]_o + k_{tr,x}[X]_o} \qquad (7)$$

$$\text{Where } x = \frac{\text{dead polymers formed by combination}}{\text{dead polymers formed by combination plus disproportionation}}$$

f is the initiator efficiency factor,

k_t is the rate constant for radical termination,

k_d is the rate constant for decomposition of the initiator,

k_p is the rate constant for monomer addition reaction,

$k_{tr,M}$ is the rate constant for radical transfer reaction to monomer,

$k_{tr,I}$ is the rate constant for radical transfer reaction to initiator,

$k_{tr,S}$ is the rate constant for radical transfer reaction to solvent,

$k_{tr,X}$ is the rate constant for radical transfer reaction to the additive,

[M] is the concentration of monomer,

[I] is the concentration of initiator,

[S] is the concentration of solvent, and

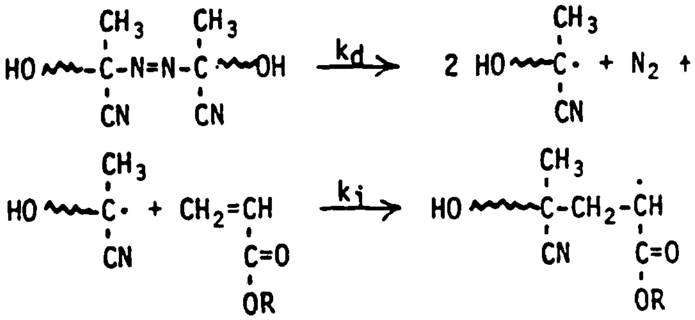
[X] is the concentration of the additive.

The above kinetic analysis indicates that all the reactions leading to dead polymer formation except the chain transfer to polymer (Reaction c), would affect the average molecular weight and the functionality of the polymer. The chain transfer reaction to the polymer (Reaction c) would widen the molecular weight distribution and decrease the average functionality, but would not alter the average molecular weight. Furthermore, additional side-reactions of the propagating radicals with the nitro-groups of DNPA are possible.

Based on the above discussion, the approach for the successful synthesis of difunctional DNPA polymers should be by (1) modification of polymerization conditions to minimize the side-reactions (a) through (d); and (2) synthesis of effective initiators and chain transfer agents for the polymerization.

The desired reaction sequence would be:

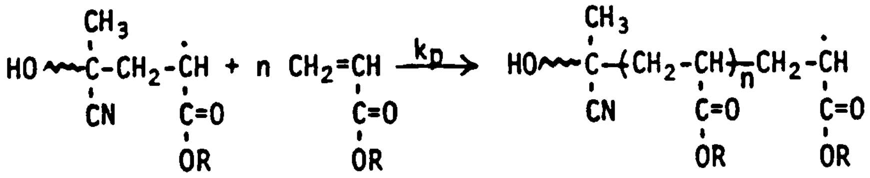
Initiation



$$HO\sim\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}\sim OH \xrightarrow{k_d} 2\ HO\sim\underset{CN}{\overset{CH_3}{C}}\cdot + N_2 +$$

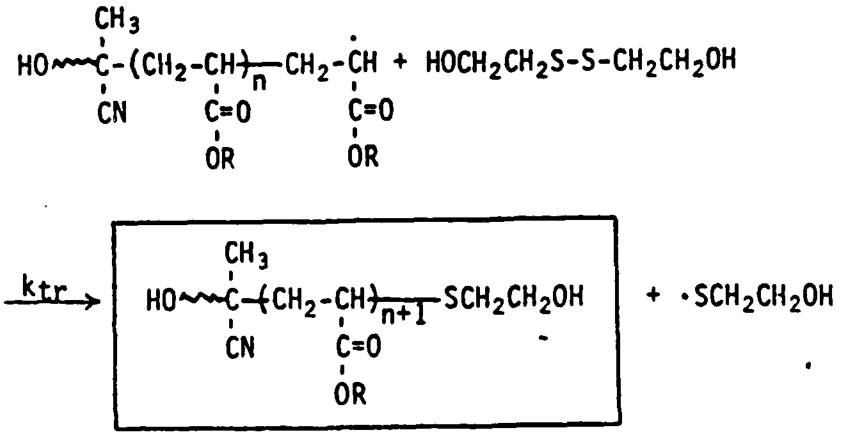
$$HO\sim\underset{CN}{\overset{CH_3}{C}}\cdot + CH_2=\underset{\underset{OR}{C=O}}{CH} \xrightarrow{k_i} HO\sim\underset{CN}{\overset{CH_3}{C}}-CH_2-\underset{\underset{OR}{C=O}}{\dot{C}H}$$

Propagation



$$HO\sim\underset{CN}{\overset{CH_3}{C}}-CH_2-\underset{\underset{OR}{C=O}}{\dot{C}H} + n\ CH_2=\underset{\underset{OR}{C=O}}{CH} \xrightarrow{k_p} HO\sim\underset{CN}{\overset{CH_3}{C}}\left(CH_2-\underset{\underset{OR}{C=O}}{CH}\right)_n CH_2-\underset{\underset{OR}{C=O}}{\dot{C}H}$$

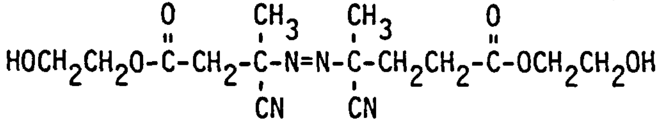
Chain Transfer



$$HO\sim\underset{CN}{\overset{CH_3}{C}}-\left(CH_2-\underset{\underset{OR}{C=O}}{CH}\right)_n CH_2-\underset{\underset{OR}{C=O}}{\dot{C}H} + HOCH_2CH_2S-S-CH_2CH_2OH$$

$$\xrightarrow{k_{tr}} \boxed{HO\sim\underset{CN}{\overset{CH_3}{C}}\left(CH_2-\underset{\underset{OR}{C=O}}{CH}\right)_{n+1}SCH_2CH_2OH} + \cdot SCH_2CH_2OH$$

All other possible side reactions (a) through (d) on pages 7 and 8 should be minimized. Optimization of the polymerization conditions, therefore, should involve selection of suitable (a) solvent, (b) reaction temperature, and (c) concentrations of the reactants.

Our previous report$^{(1)}$ indicated that dinitropropyl acrylate polymers with functionality as high as 1.8, could be synthesized through the above mentioned optimization. This was achieved via polymerization of dinitropropyl acrylate (DNPA) at 65-70°C using  $HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH$ (Azo-OH) as an initiator and $HOCH_2CH_2SSCH_2CH_2OH$ (HEDS) as a chain transfer agent (Table I). It was observed that acetone, cyclohexanone, dimethylformamide and ethylene carbonate were most suitable solvents in terms of their solvating power and their chain transfer activity$^{(1)}$.

4.1.1 Location of Hydroxyl Groups in the Polymer

Additional mechanism studies of the dinitropropyl acrylate free-radical polymerization system were performed in order to evaluate whether or not the 1.8 OH-functionality of PDNPA was due to the presence of hydroxyl groups at the ends of polymer chains rather than along the chains. This was done by (a) fractionation of the polymers, and (b) analysis of the polymers after various polymerization periods.

4.1.1.1 Fractionation of Poly-DNPA

Double batch sizes of the polymer were synthesized using the reaction procedure described in Experimental V-A-(4). The polymer was separated by liquid-liquid extraction into three different fractions by gradually adding poorer solvents as depicted in Table II. GPC scans for one set of unfractionated and fractionated poly-DNPA samples are shown in Figures 1 through 4. GPC retention time, OH-equivalent weight,

TABLE I. POLYMERIZATION OF DNPA SYSTEM[*1]

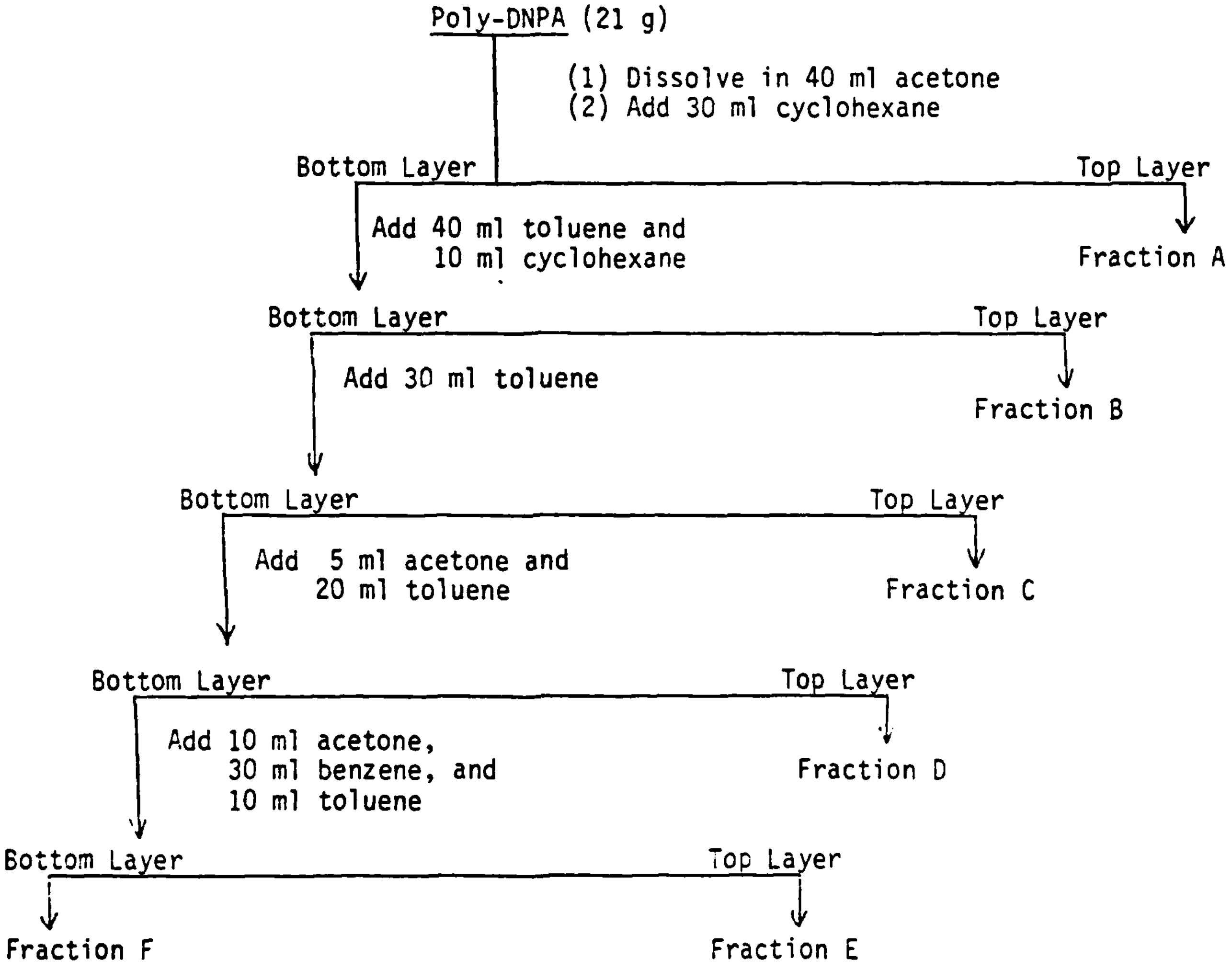
Polyn' System	Reactants[*2]										Rxn Temp (°C)	$\overline{f}_p$[*3]	OH eq. wt.
	DNPA		Azo-OH		HO-CSSC-OH		DMF		⬡=O				
	(g)	(M)	(g)	(M)	(g)	(M)	(g)	(M)	(g)	(M)			
P-4	20.4	1.79	4.29	0.189	20.0	2.32	20.0	4.89	/		65	$1.76<\overline{f}_p<1.80$	2,050
P-5	20.4	1.79	4.29	0.189	20.0	2.32	/		20.0	3.64	65	$1.80<\overline{f}_p<1.82$	2,940
P-6	20.4	1.83	2.50	0.113	20.0	2.38	/		20.0	3.74	65	$1.65<\overline{f}_p<1.71$	2,020
P-7	20.4	1.83	2.50	0.113	20.0	2.38	/		20.0	3.74	55	$1.59<\overline{f}_p<1.65$	2,840
P-8	20.4	1.79	4.29	0.189	5.6	2.32	/		20.0	3.64	65	$1.67<\overline{f}_p<1.71$	2,820
P-9	20.4	2.23	4.29	0.236	20.0	0.812	/		20.0	4.56	65	$1.76<\overline{f}_p<1.80$	2,330

[*1] Reaction time = 10 hours.

[*2] Calculation of molarity based on the following density and molecular weight, respectively. DNPA(1.30, 204.06), Azo-OH(1.20, 406.5), HO-CSSC-OH(1.28,154.2), DMF(0.95,73.09) and cyclohexanone (0.95,98.15)

[*3] Functionality based on cure study

TABLE II. FLOW CHART OF FRACTIONATION



Fraction 1 = Fractions (A + B + C) $\cong$ 7 g

Fraction 2 = Fractions (D + E) $\cong$ 7 g

Fraction 3 = Fraction F $\cong$ 7 g

FIGURE 1. GPC SCAN OF PURIFIED UNFRACTIONATED POLY-DNPA (DP-18)

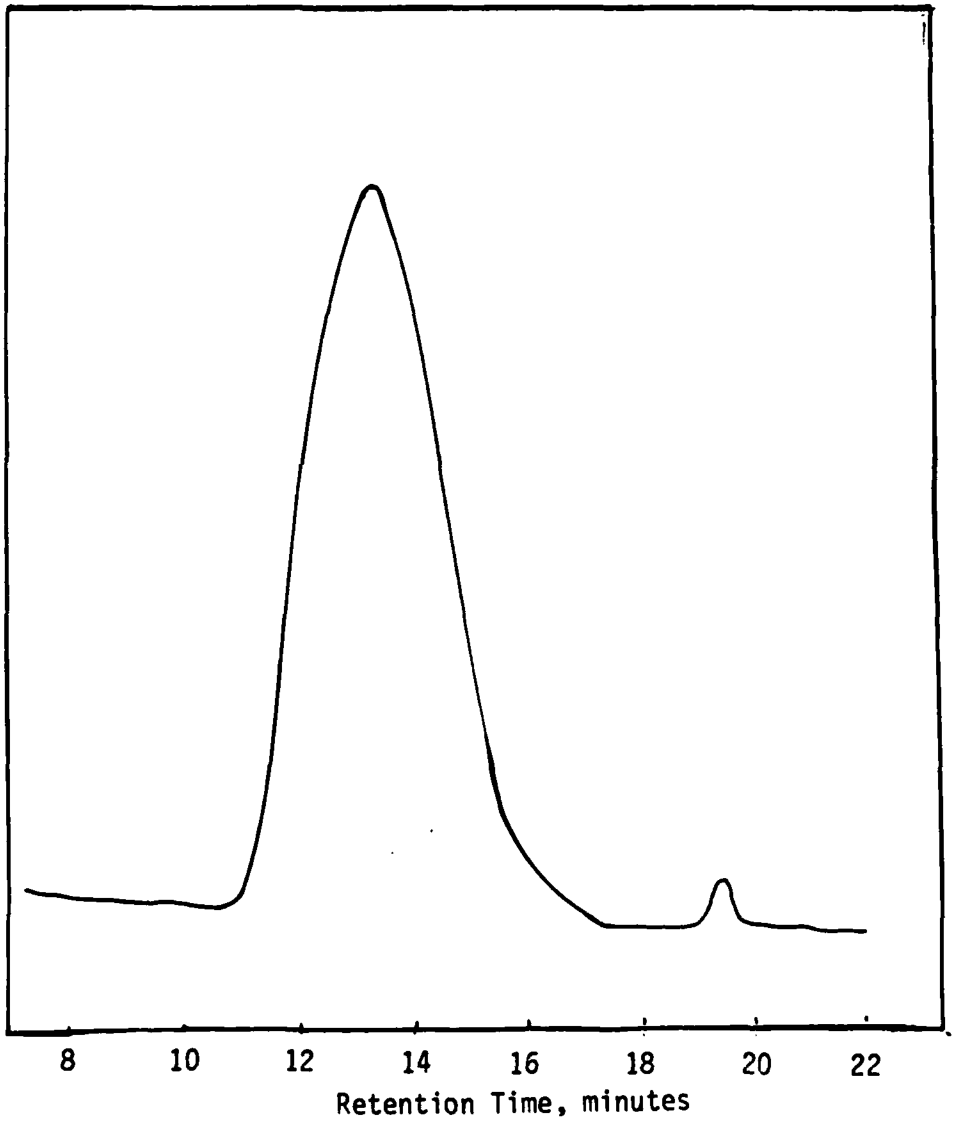


FIGURE 2. GPC SCAN OF DP-18 FRACTION #1

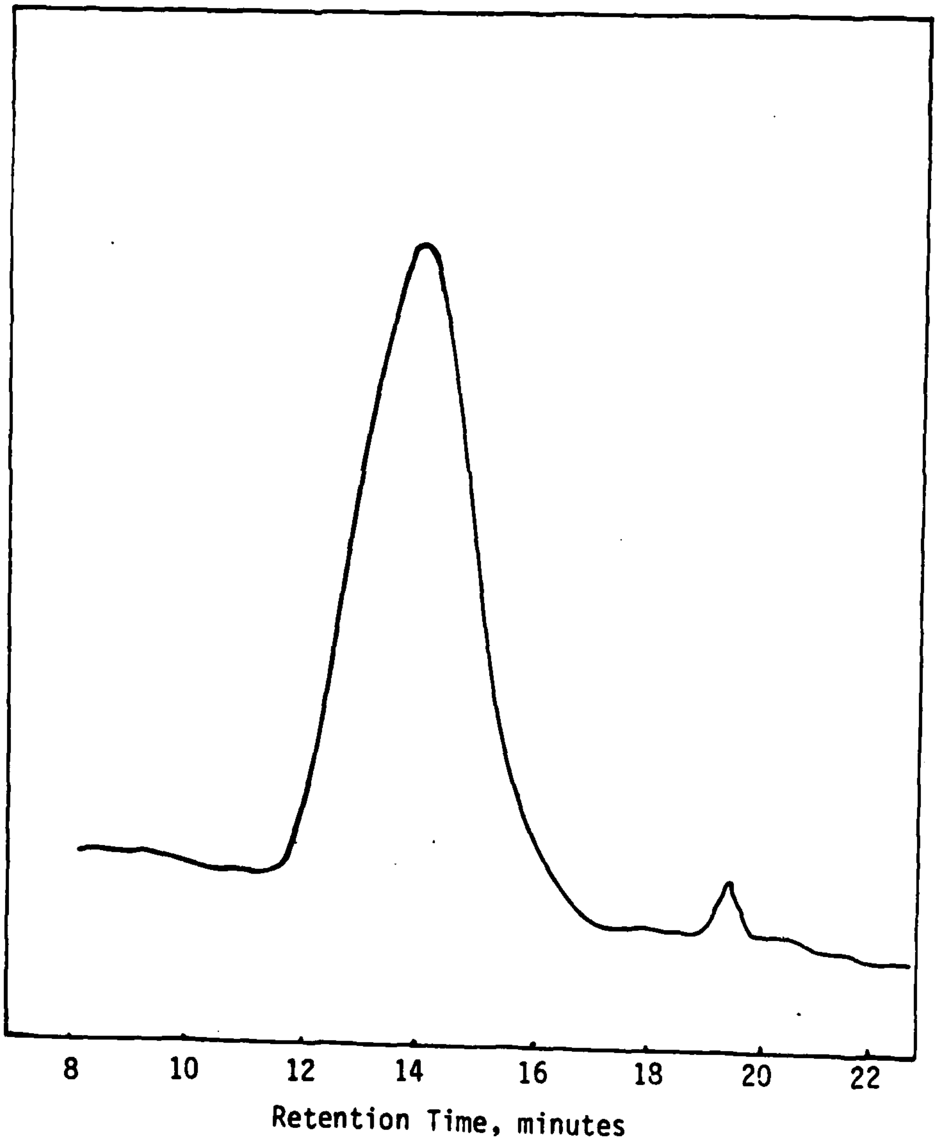


FIGURE 3. GPC SCAN OF DP-18 FRACTION #2

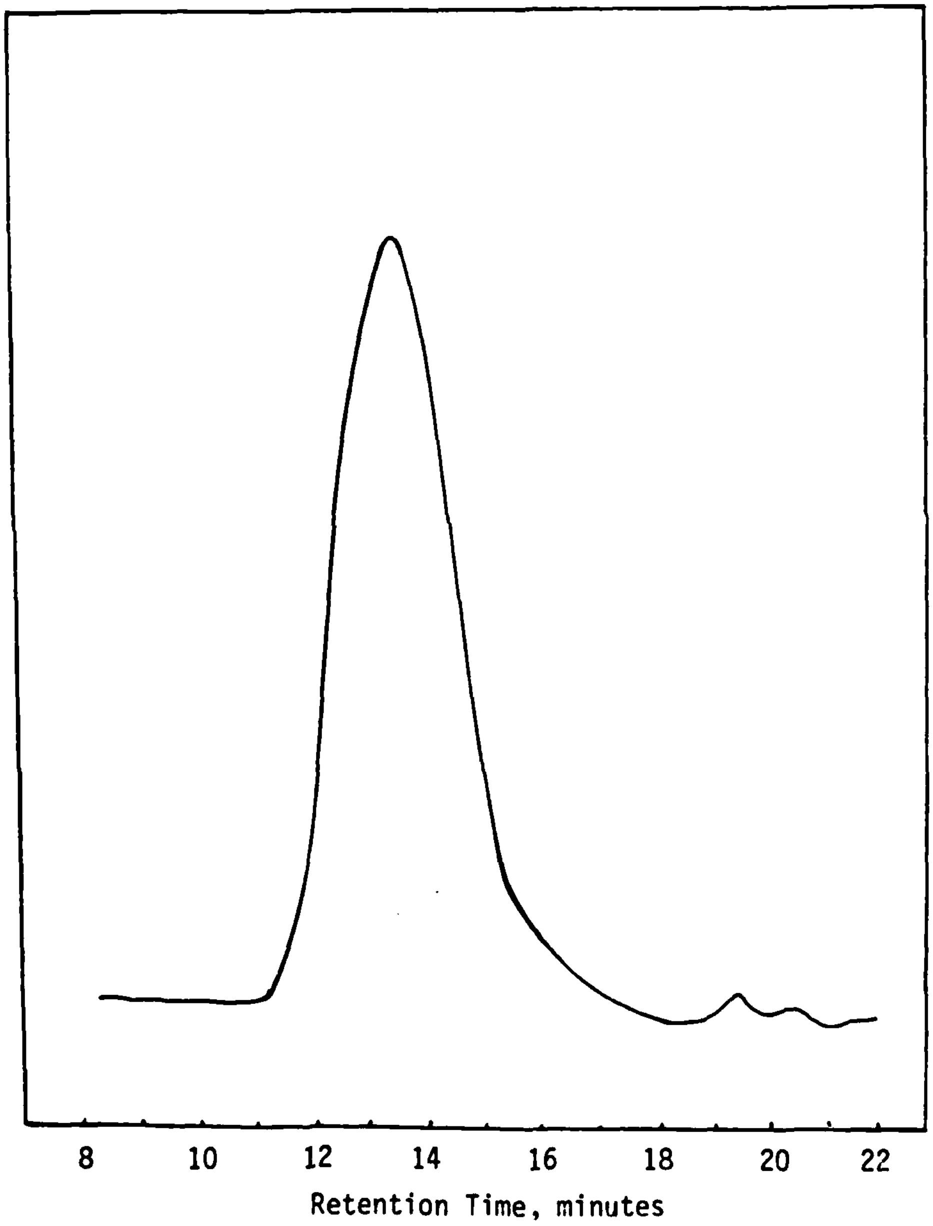
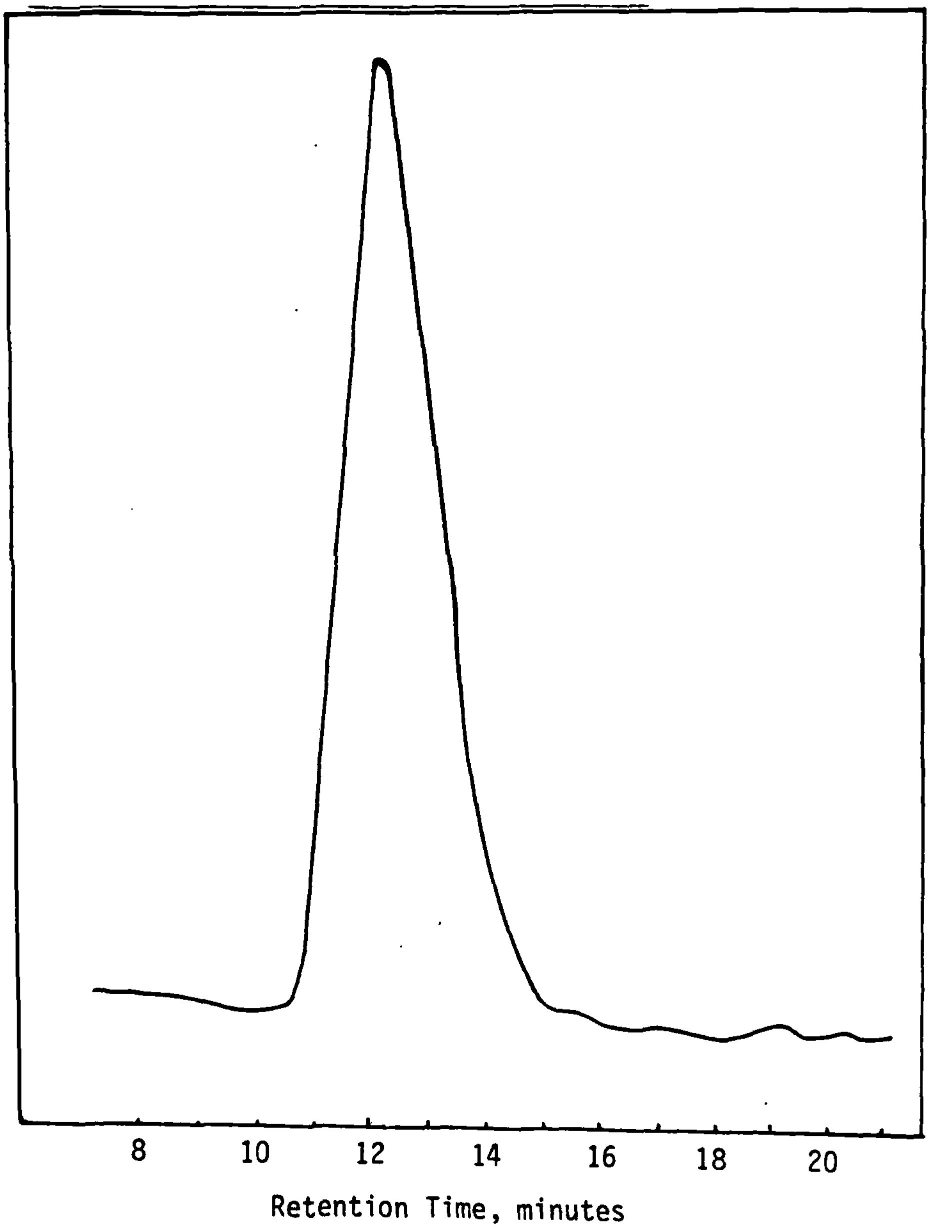


FIGURE 4. GPC SCAN OF DP-18 FRACTION #3



number average molecular weight, and functionality of two sets of fractionated polymer samples were determined and tabulated in Table III. Analysis of these data indicates that the different polymer fractions have different molecular weights (based on GPC and vapor phase osmometry) but have the same functionality. This is in agreement with the derived kinetic expressions (equations 6 and 7 on page 12) that the molecular weight of the polymer varies appreciably with the degree of polymer conversion, whereas the functionality varies little.

4.1.1.2 Effect of Reaction Time on OH-Equivalent Weight and Functionality of Poly-DNPA

A series of free-radical polymerizations was run in acetone solvent, using different reaction times. The results are shown in Table IV. These data indicate that both the molecular weight and functionality of the polymer are dependent on the reaction time. The molecular weight tends to decrease over the early part of the reaction period, but the functionality increases with increasing reaction time. The change in the molecular weight is consistent with the kinetic expression, equation 6, and with the rate of polymerization as shown in Figure 5. The higher monomer concentration at the beginning would result in the higher molecular weight (equation 6). After an hour of reaction, the polymer conversion is about ninety percent (Figure 5), and therefore, one would not expect an appreciable change in the average molecular weight. However, the observed decrease in the OH-equivalent weight and the increase in the functionality with the reaction time is not in agreement with the predicted expression, equation 6. A possible explanation

TABLE III. FRACTIONATION OF POLY-DNPA

Poly-DNPA	GPC Retention Time, minutes	OH-Equivalent Weight[a]	Number Average Molecular Weight	Functionality[d]
DP-7	12.6	3270	4420[b]	1.67
" Fraction 1	13.2	2340	3169[b]	1.67
" Fraction 2	12.7	3275	4360[b]	1.67
" Fraction 3	11.9	6220	8820[b]	1.67
DP-18	12.9	3660	6039[c]	1.65
" Fraction 1	13.7	2520	4133[c]	1.64
" Fraction 2	13.1	3310	5462[c]	1.65
" Fraction 3	12.2	7072	11670[c]	1.65

a. OH eq. wt. was determined by IR method.

b. Number average molecular weights from vapor phase osmometry.

c. Number average molecular weights calculated from OH-equivalent weight and functionality.

d. Functionality was determined by incipient gel point method.

TABLE IV. EFFECT OF REACTION TIME ON THE PROPERTIES OF POLY-DNPA

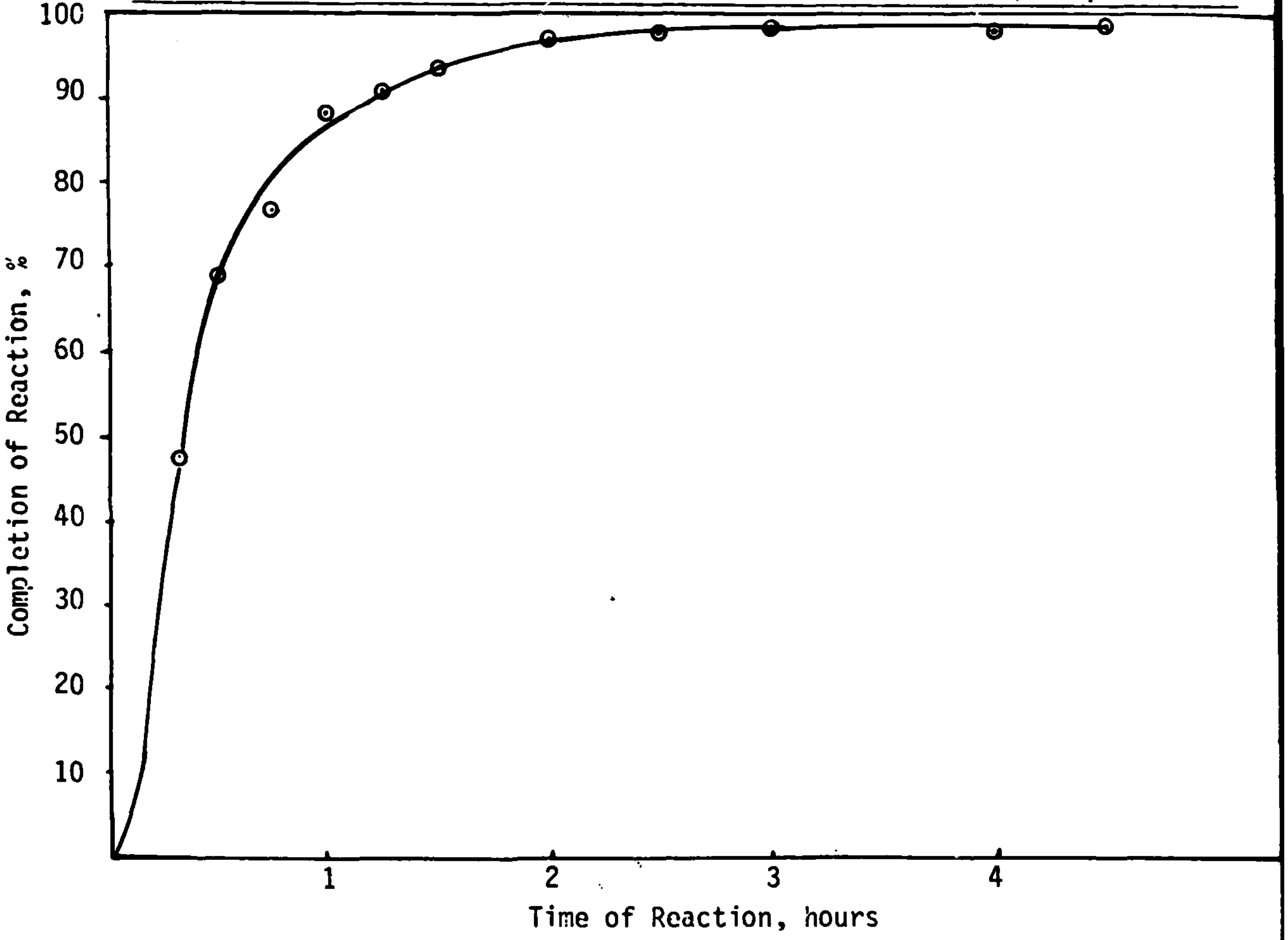
Poly-DNPA	Reaction Time, minutes	OH-equivalent weight[a]	Number Average Molecular Weight[b]	Functionality[c]
DP-15	14	6080	9120	1.51
DP-16	22	5560	8620	1.55
DP-17	41	3780	6090	1.61
DP-7	240	3270	5460	1.67
DP-9	240	3360	5610	1.67
DP-12A	240	3670	6070	1.65
DP-12B	240	3830	6320	1.65
DP-18	240	3660	6039	1.65
DP-20	600	3170	5640	1.78

a. OH eq. wt. was determined by IR method.

b. Number average molecular weights are based on the OH-equivalent weights and the functionalities.

c. Functionality was determined by incipient gel point method.

FIGURE 5. KINETICS OF POLYMERIZATION OF DNPA IN ACETONE (DP-9) AT 70° C



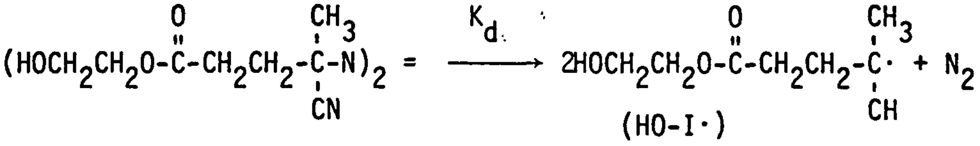
for this discrepency is the presence of side-reactions which incorporate hydroxyl groups into the polymer during and after the polymer formation. Azo-initiators are known to undergo unimolecular decomposition:

$$\frac{-d[I]}{dt} = k_d[I] \qquad (8)$$

$$\text{or} \quad \ln \frac{[I_o]}{[I]} = k_d \cdot t \qquad (9)$$

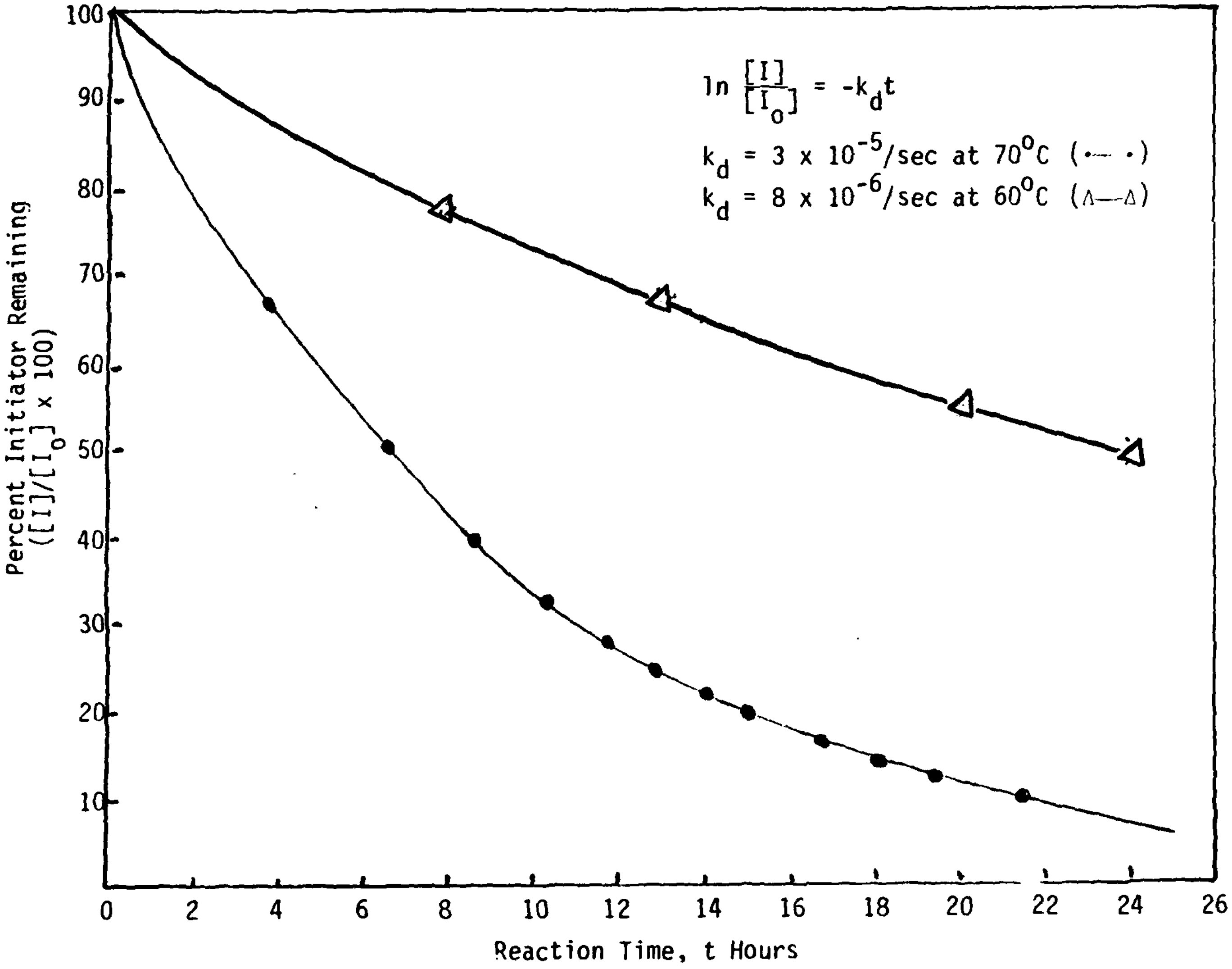
The k_d value of commercially available azoisobutyronitrile (AIBN) is 3×10^{-5}/sec$^{(11)}$. Since AIBN and Azo-OH have similar structures near the azo group, it is reasonable to assume that both compounds have approximately the same rate of decomposition. The decomposition rate is shown in Figure 6. The graph indicates that Azo-OH would create radicals through decomposition, even after the 100% polymer conversion. In fact, practically all the polymer is formed after 3 hours of reaction and only 30% of the initiator is consumed, based on Figure 6. Upon keeping the reaction mixture for a prolonged period at 70°C, the reaction system would be continually creating radicals through decomposition of Azo-OH. Examples of the possible reactions of poly-DNPA, under these conditions, to create a higher functionality would be:

Radical formation by Azo-OH

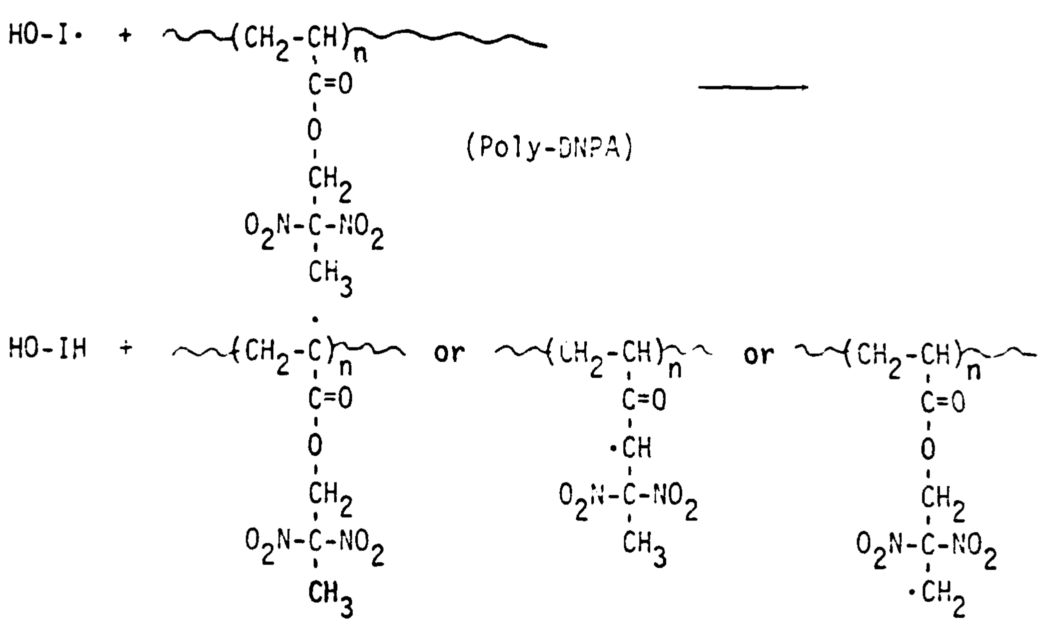


$$(HOCH_2CH_2O\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}CH_2CH_2\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N)_2 = \xrightarrow{K_d} \underset{(HO\text{-}I\cdot)}{2HOCH_2CH_2O\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}CH_2CH_2}\text{-}\underset{CH}{\overset{CH_3}{C}}\cdot + N_2$$

FIGURE 6. DECOMPOSITION RATE OF Azo-OH (Assume $kd_{(AIBN)} = kd_{(Azo\text{-}OH)}$)



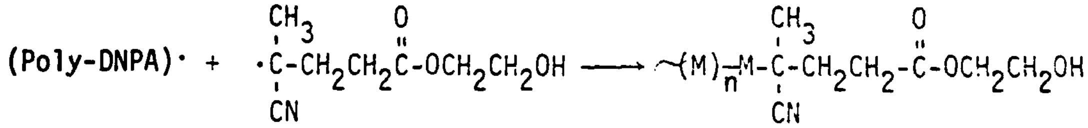
Radical formation in the Polymer



(Poly-DNPA)·

Side-reactions of Polymer

$$(\text{Poly-DNPA})\cdot + HOCH_2CH_2SSCH_2CH_2OH \text{ —— } \sim\!(M)_n\text{-}M\text{-}SCH_2CH_2OH + \cdot SCH_2CH_2OH$$



$$(\text{Poly-DNPA})\cdot + \cdot\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2CH_2\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2OH \longrightarrow \sim\!(M)_n\text{-}M\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_2OH$$

The experimental data in Table IV indicate that the higher functionality of 1.78 for poly-DNPA (DP-20), which was achieved after 10 hours of reaction time at 70°C, is not totally due to simple chain transfer reactions of the poly-DNPA after the polymers have formed. The incorporation of hydroxyl groups on the polymer, by the latter chain transfer reactions of poly-DNPA, would place the hydroxyl groups mainly along the polymeric chain rather than at the ends of the chain. Hence, it is most likely that approximately 85% (=1.51/1.78 x 100) of the OH-groups in DP-20 are located at the ends of the polymeric chain and the remaining 15% along the chains (compare DP-15 and

DP-20 in Table IV). Lower polymerization temperature and shorter reaction time should minimize the above undesirable side-reactions. However, higher functionality can be achieved only if a more efficient chain transfer agent than HEDS is found.

4.1.2 Chain Transfer Activity: HEDS vs o-DTB-OH

The sulfur-sulfur bond strengths of various disulfides reported in the literature are not consistent. Those of alkyl disulfides appear to lie in the range of 60-70 kcal/mole.(12) Recently, Guryanova(13) reported that the S-S bond strength of diphenyl disulfide is as low as 20-26 kcal/mole vs 58-64 kcal/mole for $C_4H_9S\text{-}SC_4H_9$ (Table V). Furthermore, his data in Table V indicate that the substitution of different groups in the para-positions of the phenyl rings of diphenyl disulfide results in higher strengths of the S-S bond. Guryanova's values were based on the sulfur exchange reaction between mercaptans and disulfides in a dry-non-polar solvent, i.e., under conditions which exclude the ionic scission of the S-S bond. The exchange rate was found to be dependent on the structure of disulfide compounds but not on that of mercaptans. The proposed mechanism for the exchange reaction using labeled sulfur atoms is:

$$RS^*\text{-}S^*R \xrightarrow[\Delta]{} RS^*\cdot + \cdot S^*\text{-}R \qquad (10)$$

$$RS^*\cdot + RSH \longrightarrow RS^*H + RS\cdot \qquad (11)$$

$$RS\cdot + RS\cdot \longrightarrow RS\text{-}SR \quad \text{or} \quad RS\overset{*}{\cdot} + RS\cdot \longrightarrow RS\overset{*}{-}SR \qquad (12)$$

The chain transfer activity of disulfides in a free-radical polymerization of DNPA would be enhanced by a lower S-S bond strength. In other

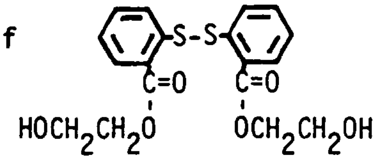
TABLE V.

ENERGY OF S-S BONDS IN DISULFIDES (kcal/mol) OBTAINED BY THE METHOD OF RE-GROUP EXCHANGE

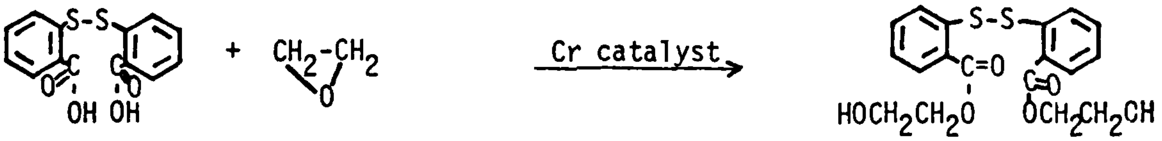
System	Temperature range ($^{\circ}$)	E_{act}	E_{S-S}
$C_4H_9S^*-{}^*SC_4H_9$ C_4H_9S-H	169-231	29	64
$C_8H_{17}S^*-{}^*SC_8H_{17}$ $C_8G_{17}S-H$	176-240	30	66
$C_{14}H_{29}S^*-{}^*SC_{14}H_{29}$ $C_{14}H_{29}S-H$	160-199	29	64
$C_{18}H_{37}S^*-{}^*SC_{18}H_{37}$ $C_{18}H_{37}S-H$	160-204	30	66
$C_6H_5CH_2S^*-{}^*SCH_2C_6H_5$ $C_6H_5CH_2S-H$	180-227	31	68
$C_6H_5S^*-{}^*SC_6H_5$ C_6H_5-H	35-80	10	26
$p\text{-}CH_3C_6H_4S^*-{}^*SC_6H_4CH_3\text{-}p$ $p\text{-}CH_3C_6H_4S-H$	93-142	13	32
$p\text{-}CH_3OC_6H_4S^*-{}^*SC_6H_4OCH_3\text{-}p$ $p\text{-}CH_3OC_6H_4S-H$	101-164	14.4	35
$p\text{-}C_6H_5C_6H_4S^*-{}^*SC_6H_4C_6H_5\text{-}p$ $p\text{-}C_6H_5C_6H_4S-H$	1110-160	14.4	35
$p\text{-}NO_2C_6H_4S^*-{}^*SC_6H_4NO_2\text{-}p$ $p\text{-}NO_2C_6H_4S-H$	104-145	23	52

words, aromatic disulfides would be more effective chain transfer agents than aliphatic disulfides based on the result of Guryanova's work. It would be desirable to synthesize an aromatic disulfide which contains primary hydroxyl groups, and to compare its effectiveness as a chain transfer agent with that of hydroxyethyldisulfide (HEDS).

4.1.2 Synthesis of



The most readily available aromatic disulfide with OH functional groups is orthodithiodibenzoic acid (O-DTB-CO_2H) from Aldrich. O-DTB-CO_2H was converted to the dihydroxyethyldibenzoate (O-DTB-OH) by the following reaction, and the detailed procedure is described in Experimental Section V-A-(2).



(o-DTB-CO_2H) (o-DTB-OH)

4.1.2.2 Kinetic Studies with HEDS and o-DTB-OH

A more desirable aromatic disulfide would be meta- or para-DTB-OH rather than o-DTB-OH, since these isomers would have less steric hindrance for the desired chain transfer reaction. The meta-isomer was also prepared. However, it is insoluble in virtually all the solvents except DMF and DMSO. A good solubility of the compound in the polymer and in the polymerization solvent is crucial if the compound is to act as an effective chain transfer agent. Hence, o-DTB-OH was selected as a model for the study. Table VI gives a summary of various polymerization systems studied. The reactant variations were made such that by using equation 6, page 12, approximate values of the first term (effect of type and concentration of initiator) and the chain transfer constants of HEDS and o-DTB-OH could be estimated. The kinetics were followed by GPC and the reaction mixtures were quenched with hydroquinone after approximately 50% polymerization. The polymers were purified and analyzed for the equivalent weight, the average molecular weights and the functionality. The detailed procedures are described in the Experimental 5.1.6. Although it is more desirable to limit the extent of polymerization to 10-20% for this purpose, the polymerizations were run to approximately 50%, because of the following practical reasons:

(i) Limited amount of available DNPA

(ii) Purification of polymer becomes more difficult with the lower conversion, since all the reactants have to be removed via extraction.

(iii) Kinetic nature of the chain polymerization is such that the rate is not expected to be as reproducible as other systems. For example, different amounts of trace impurities such as oxygen could give different degrees of inhibition and retardation. In order to minimize the variation, same batches of all the reactants and solvent were used.

The kinetic curves in Figure 7 indicate that the extent of polymerization varied from 43% (M-1) to 59% (M-4). Some of this variation is due to

TABLE VI. KINETIC STUDY OF DNPA POLYMERIZATION

Total rxn. vol. = 60ml; Extent of poly'n = 50%;

Sample No.	Reagents						Rexn. time (hr.)	% yield after purification	GPC*2		OH-Eq. Wt.*3 (IR)	$\bar{f}$*4
	DNPA		Initiator		Chain Trans. Ag. [X]	Acetone [S]			$10^3\bar{M}n$	Mw/Mn		
	$[M]_0$*1	[M]	$[I]_0$	[I]								
			Azo-OH									
M-1	0.1	0.075	0.005	0.005	HEDS 0.084	0.53	1.00	30	12.4	1.75	8,100	1.43
M-10	0.1	0.075	0.005	0.005	HEDS 0.12	0.47	1.00	24	11.4	1.79	7,600	1.45
M-4	0.1	0.075	0.01	0.01	HEDS 0.084	0.50	1.00	45	10.5	1.85	6,300	1.51
M-7	0.1	0.075	0.01	0.008	DBT-OH 0.020	0.56	4.00	34	10.5	1.70	5,500	1.60
M-3	0.1	0.075	0.01	0.008	DTB-OH 0.033	0.54	4.00	15	12.3	1.63	8,100	1.52
			AIBN									
M-5	0.1	0.075	0.01	0.01	0	0.65	0.67	20	25.4	1.83	-	-
M-8	0.1	0.075	0.01	0.01	HEDS 0.084	0.49	1.00	36	12.7	1.80	8,200	1.45
M-9	0.1	0.075	0.01	0.008	DTB-OH 0.033	0.53	4.00	31	9.9	1.70	6,500	1.52

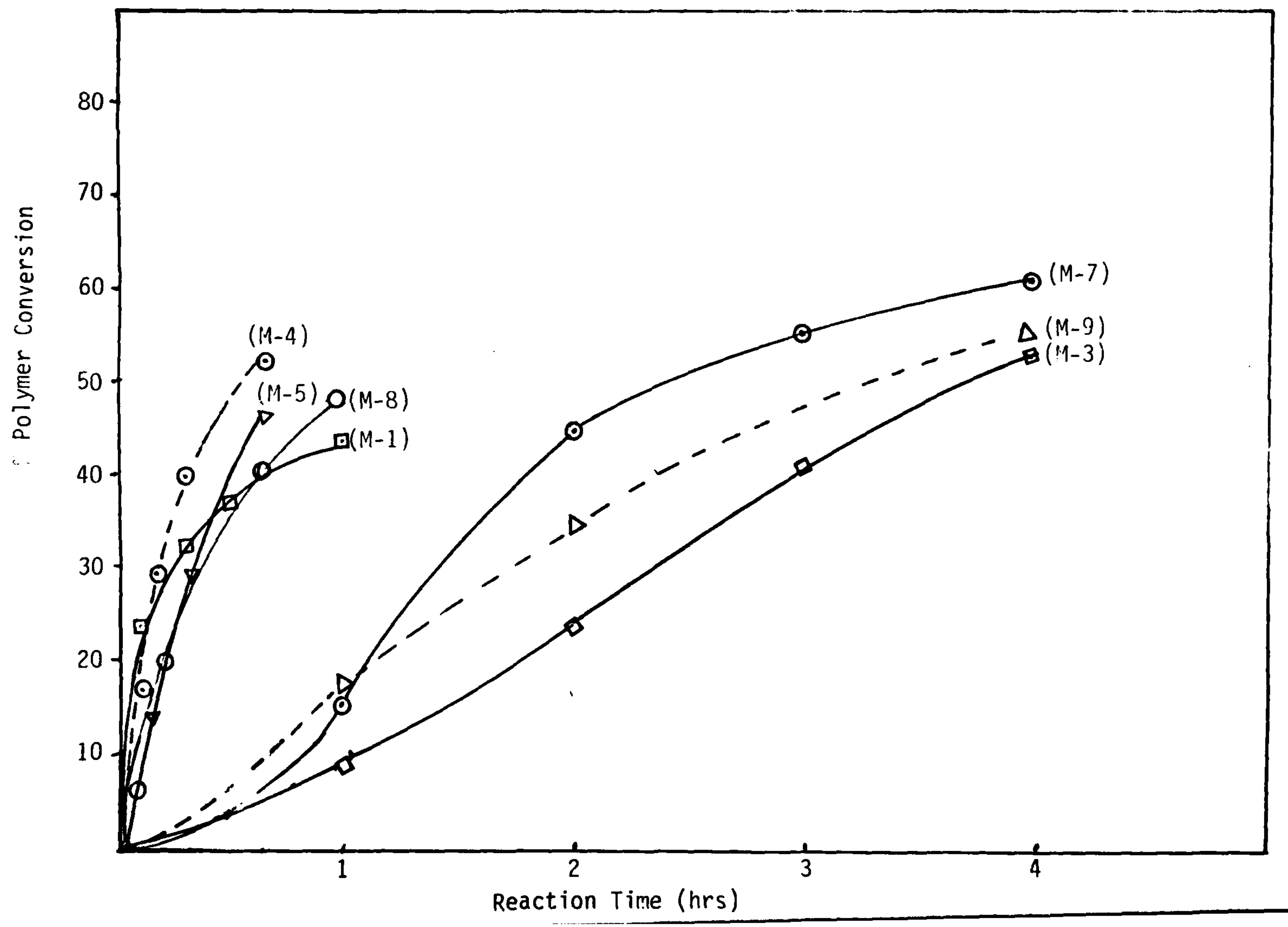
*1 $[\ ]_0$ = number of moles present initially (t=0)
$[\ ]$ = number of moles present at $t_{ave} = (t_{final} - t_0)/2$

*2 GPC values based on PS standards in THF at 26-27°C.

*3 OH equivalent weight based on THF/OH complex as measured by IR.

*4 Effective functionality based on incipient gel-point determination (uncorrected).

FIGURE 7. KINETIC OF DNPA POLYMERIZATION



different initiator concentration, since the rate of polymerization, R_p, is equal to ($k_p \sqrt{\frac{k_i}{k_t}} \cdot [M][I]^{1/2}$). The kinetic curves in Figure 7 also indicate that HEDS acts as a chain modifier only, whereas o-DTB-OH acts as a mild retarder and inhibitor. The initial inhibition may be due to the presence of impurities in o-DTB-OH, and the retardation may be by o-DTB-OH and/or the impurities.

Experimental data of Table VI are evaluated by using equation 6, page 12.

$$\frac{1}{DP} = \frac{(x+1)\sqrt{fk_d \cdot k_t}}{k_p} \frac{[I]^{1/2}}{[M]} + \frac{k_{tr,m}}{k_p} + \frac{k_{tr,I}}{k_p} \frac{[I]}{[M]} + \frac{k_{tr,s}[S]}{k_p[M]} + \frac{k_{tr,x}[X]}{k_p[M]}$$

The equation can be rewritten if it is assumed that the variations [I]/[M] and [S]/[M] are negligible. This is a reasonable approximation, since these terms are expected to be smaller than the rest of the terms on the right side of equation.

For the DNPA system: $\frac{1}{DP} = \frac{204}{M_n}$

where 204 = MW of DNPA monomer

M_n = no. ave. MW of polymer

Hence, $$\frac{204}{M_n} = A + B \frac{[I]^{1/2}}{[M]} + C_x \frac{[X]}{[M]} \qquad (13)$$

where A = constant, $B = \frac{(x+1)\sqrt{fk_d k_t}}{k_p}$, C_x = chain transfer constant = $\frac{k_{tr,x}}{k_p}$.

Equation (13) is used with an additional assumption that the average monomer concentration of all the polymerization systems is 0.075 m/60 ml. Since total volume for all the systems is the same, 60 ml, the number of moles of the reactants were used without converting to molarity.

(a) $\underline{C_{HEDS} \text{ from (M-10)-(M-1) and (M-8)-(M-5)}}$

(M-1): $16.5 \times 10^{-3} = A + B \frac{\sqrt{0.005}}{0.075} + C_{HEDS} \frac{0.084}{0.075}$

(M-10): $18.0 \times 10^{-3} = A + B \frac{\sqrt{0.005}}{0.075} + C_{HEDS} \frac{0.12}{0.075}$

(M-10)-(M-1): $1.5 \times 10^{-3} = C_{HEDS}(1.6-1.1) = 0.5\ C_{HEDS}$

$$\underline{C_{HEDS} = 3.0 \times 10^{-3}}$$

(M-5): $8.02 \times 10^{-3} = A + B' \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \frac{0.00}{0.075}$

(M-8): $16.0 \times 10^{-3} = A + B' \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \frac{0.084}{0.075}$

(M-8)-(M-5): $8.0 \times 10^{-3} = C_{HEDS}(1.12-0)$

$$\underline{C_{HEDS} = 7.1 \times 10^{-3}}$$

On average, $\boxed{C_{HEDS} = (5.1 \pm 2.0) \times 10^{-3}}$

(b) $\underline{C_{DTB\text{-}OH} \text{ from (M-4)-(M-7) and (M-9)-(M-5)}}$

(M-4): $19.5 \times 10^{-3} = A + B \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \frac{0.084}{0.075}$

(M-7): $19.5 \times 10^{-3} = A + B \frac{\sqrt{0.008}}{0.075} + C_{DTB\text{-}OH} \frac{0.020}{0.075}$

Since $B \frac{\sqrt{0.01}}{0.079} \cong B \frac{\sqrt{0.008}}{0.075}$, then $C_{HEDS} \frac{0.084}{0.079} \cong C_{DTB\text{-}OH} \frac{0.020}{0.079}$

Thus $C_{DTB\text{-}OH}/C_{HEDS} \cong \frac{0.084}{0.020} = 4.2$

$$\underline{C_{DTB\text{-}OH} = 4.2 \times 5.1 \times 10^{-3} = 21 \times 10^{-3}}$$

(M-5): $8.02 \times 10^{-3} = A + B' \frac{\sqrt{0.01}}{0.075} + 0$

$$(M\text{-}9):\quad 20.6 \times 10^{-3} = A + B' \frac{\sqrt{0.008}}{0.075} + C_{DTB\text{-}OH} \cdot \frac{0.033}{0.075}$$

$$(M\text{-}9)\text{-}(M\text{-}5):\quad 12.6 \times 10^{-3} \cong 0.44\, C_{DTB\text{-}OH}$$

$$\underline{C_{DTB\text{-}OH} = 29 \times 10^{-3}}$$

On average, $\boxed{C_{DTB\text{-}OH} = (25 \pm 4) \times 10^{-3}}$

(c) <u>$(x+1)\sqrt{fkdkt}/kp$ for Azo-OH from (M-4)-(M-1)</u>

$$(M\text{-}1):\quad 16.5 \times 10^{-3} = A + B \frac{\sqrt{0.005}}{0.075} + C_{HEDS} \cdot \frac{0.084}{0.075}$$

$$(M\text{-}4):\quad 19.5 \times 10^{-3} = A + B \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \frac{0.084}{0.075}$$

$$(M\text{-}4)\text{-}(M\text{-}1):\quad 3.0 \times 10^{-3} = (1.33-0.94)B$$

$$B = \left(\frac{(x+1)\sqrt{fkdkt}}{kp}\right)_{Azo\text{-}OH} = \underline{7.7 \times 10^{-3}}$$

(d) <u>$(x+1)\sqrt{fkdkt}/kp$ for AIBN from (M-4)-(M-8)</u>

$$(M\text{-}4):\quad 19.5 \times 10^{-3} = A + B \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \cdot \frac{0.084}{0.075}$$

$$(M\text{-}8):\quad 16.0 \times 10^{-3} = A + B' \frac{\sqrt{0.01}}{0.075} + C_{HEDS} \cdot \frac{0.084}{0.075}$$

$$(M\text{-}4)\text{-}(M\text{-}8):\quad 3.5 \times 10^{-3} = 1.33\,(B-B')$$

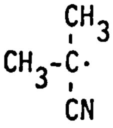
$$B-B' = 2.6 \times 10^{-3}$$

$$B' = \left(\frac{(x+1)\sqrt{fkdkt}}{kp}\right)_{AIBN} = (7.7-2.6) \times 10^{-3} = \underline{5.1 \times 10^{-3}}$$

If we assume that $\sqrt{fkd}$ for AIBN and Azo-OH is the same, the average value of the first term is:

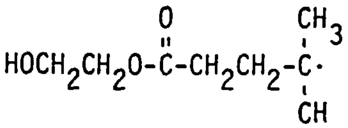
$$\underline{\frac{(x+1)\sqrt{fkdkt}}{kp} = (6.4 \pm 1.3) \times 10^{-3}}$$

The above assumption is reasonable, since the radicals formed,



$CH_3\text{-}\overset{CH_3}{\underset{CN}{C}}\cdot$

and



$HOCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2\text{-}\overset{CH_3}{\underset{CH}{C}}\cdot$

, should have about the same stability.

When all of the above values are substituted into equation (6), the kinetic expressions for the DNPA polymerization systems with HEDS and with o-DTB-OH are:

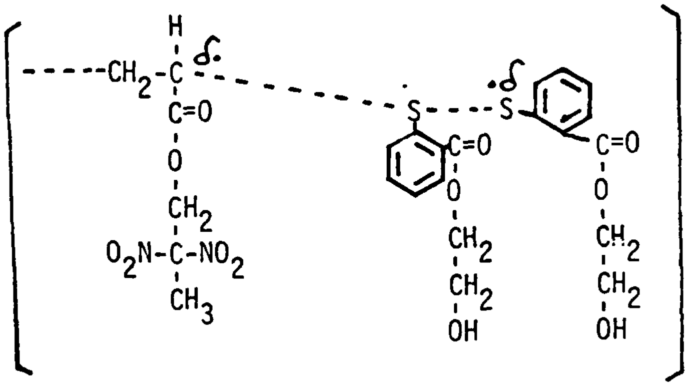
<u>For HEDS</u>: $$\frac{204}{Mn} = 6.4 \times 10^{-3} \frac{[I]^{1/2}}{[M]} + \frac{k_{tr,m}}{kp} + \frac{k_{tr,I}}{kp}\frac{[I]}{[M]} + \frac{k_{tr,s}}{kp}\frac{[S]}{[M]} + 5.0 \times 10^{-3} \frac{[HEDS]}{[M]}$$

<u>For o-DTB-OH</u>: $$\frac{204}{Mn} = 6.4 \times 10^{-3} \frac{[I]^{1/2}}{[M]} + \frac{k_{tr,m}}{kp} + \frac{k_{tr,I}}{kp}\frac{[I]}{[M]} + \frac{k_{tr,s}}{kp}\frac{[S]}{[M]} + 25 \times 10^{-3} \frac{[o\text{-}DTB\text{-}OH]}{[M]}$$

The above analysis indicates that the first term has an appreciable degree of influence on the molecular weight. In order to achieve a greater functionality, the last term should be significantly greater than the sum of the rest. Obviously, this was not achieved based on the values of equivalent weight and functionality of the polymers in Table VI. In spite of the fact that S-S bond energies are approximately 64 and 15-23 kcal/mole for HEDS and o-DTB-OH, respectively, (Table V), the low values of chain transfer constants, 5×10^{-3} and 25×10^{-3}, are rather discouraging. These low values may be due to two unfavorable factors at the transition state of the bimolecular chain transfer reaction$^{(1)}$. They are:

(i) significant steric hindrance for the bimolecular orientation, and

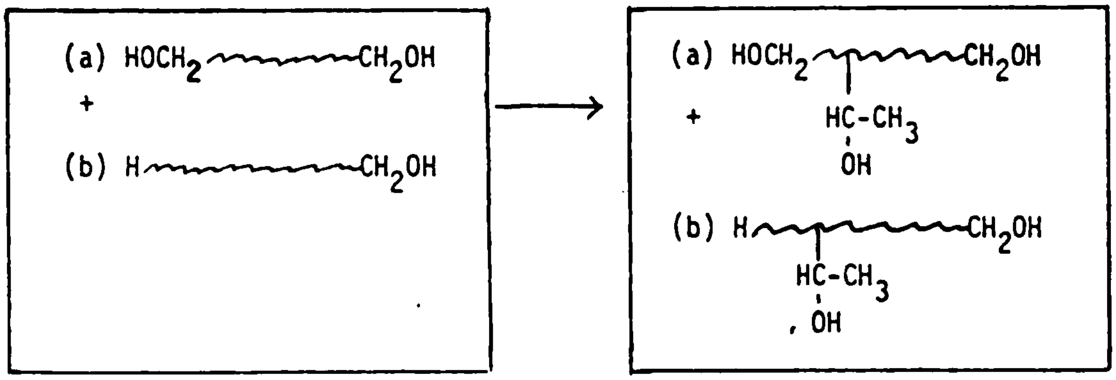
(ii) unfavorable polar effect since both reactants are electron acceptors



Nevertheless, the functionality of the polymer may be improved upon incremental addition of the initiator and the monomer, thus making the last term substantially larger than the first. The higher functionality, however, can be achieved only if the term, $\frac{k_{tr,s}}{k_p} \cdot \frac{[S]}{[M]}$, remains small.

4.1.3 Synthesis of Poly-DNPA with the OH- Functionality Greater than 2.0

As discussed previously, free-radical vinyl polymerizations of DNPA are accompanied by several hydrogen-abstracting side reactions. By minimizing these undesirable side-reactions through modification of polymerization conditions and incremental addition of monomer and initiator, and by using an aromatic disulfide as the chain transfer agent, one may produce the polymer with an OH-functionality of approximately 1.8. This value still means that about 20 mole % of the polymers are monofunctional. These monofunctional polymers will become non-load bearing chains when a rubber network is formed through the cure reaction with isocyanates, thus resulting in a propellant binder having poor mechanical properties. One of the methods to remedy this problem would be to incorporate an additional hydroxyl group along the chain with a secondary alcohol group, i.e. Convert Mixture A to Mixture B as below.



[A] [B]

Advantages of the polymers in Mixture B over A are expected to be as follows:

(1) Part of the B -(b) polymeric chain will be load-bearing after the cure reaction, whereas all the A -(b) polymeric chain would be non-load bearing.

(2) Incorporation of a correct amount of the secondary alcohol group in the polymer and/or using a suitable OH/NCO ratio should provide a proper degree of cross-linking sites for the rubber network formation, thus eliminating the need for an additional cross-linker.

(3) The secondary alcohols along the chains are less reactive toward an isocyanate than the primary alcohols at the end of the polymeric chains. This molecular design should allow most of the chain extension to occur prior to cross-linking during the cure reaction. Furthermore, if the cure reaction

is not complete (i.e., does not reach 100%), all the necessary chain extension is still assured through the primary alcohols, and only the cross-linking through the secondary alcohols would be incomplete. A complete cure reaction usually does not occur if the plasticizer content is high. Elongation capability of the propellant is significantly affected by the degree of chain extension. The molecular design of Mixture B will still allow the propellant to retain the mechanical properties of a completely cured rubber network, even though the cure reaction does not reach 100%.

An example is shown in Table VII, where an incorporation of a small amount of 2-hydroxylpropyl acrylate as a comonomer in the DNPA radical addition polymerization system allows the functionality to increase, such that Mixture B can be attained. Amounts of the secondary alcohol groups along the polymeric chains can be readily varied to a suitable concentration to optimize the mechanical properties. These polymers may be used as comonomers as well as cross-linkers with other difunctional prepolymers such as polycaprolactone and polyethylene glycol. Mark(14) recently prepared bimodal networks by tetrafunctionally end-linking mixtures of various proportions of relatively long and short chains of polydimethylsiloxane, and demonstrated that the ultimate properties were improved for the bimodal systems. Although his experiment was performed under the equilibrium conditions, the concept should be tested in the propellant binder systems.

TABLE VII. INCORPORATION OF CROSS-LINKER WITHIN THE POLYMER

Polymerization Conditions:

	DNPA	HPA	Azo-OH	Disulfide	Acetone	EW	fexp	$\overline{Mn}$ by
M-7 (Polymer [A])	0.1m	0.0m	0.01m	(o-DTBOH) 0.02m	0.56m	5500	1.6	10,500
M-11 (Polymer [B])	0.1m	0.005m	0.01m	(HEDS) 0.12m	0.44m	2750	2.5	8,000
M-13 (Polymer [B])	0.1m	0.005m	0.1m	(o-DTBOH) 0.016m	0.46m	3100	2.6	13,000

4.2 IMPROVED CHARACTERIZATION OF HYDROXY-TERMINATED PREPOLYMERS

Characterization of hydroxy-terminated prepolymers involves the determination of the number average molecular weight ($\overline{M}_n$), OH-equivalent weight (EW), and functionality (f), among other parameters. An accurate knowledge of the equivalent weight is important for calculating the quantity of isocyanate required for cure, and is also the basis for the determination of functionality. The functionality is important because it allows one to estimate the amount of crosslinker required, and also indicates the quality of the prepolymer. Functionalities lower than 2.0 indicate the presence of monofunctional species which result in many non-load bearing, dangling chains in the urethane rubber network; thus, causing poor mechanical properties.

Some of the problems chemists encounter in characterization of the prepolymers include:

(1) variation in results by different analytical methods,
(2) poor reproducibility with some methods,
(3) large sample size, and
(4) difficulty in applying standard analytical methods to certain prepolymers, because of the differences in chemical structure.

There appears to be a need for an evaluation of the currently available analytical methods, and for development of a more reliable characterization procedure for the prepolymers.

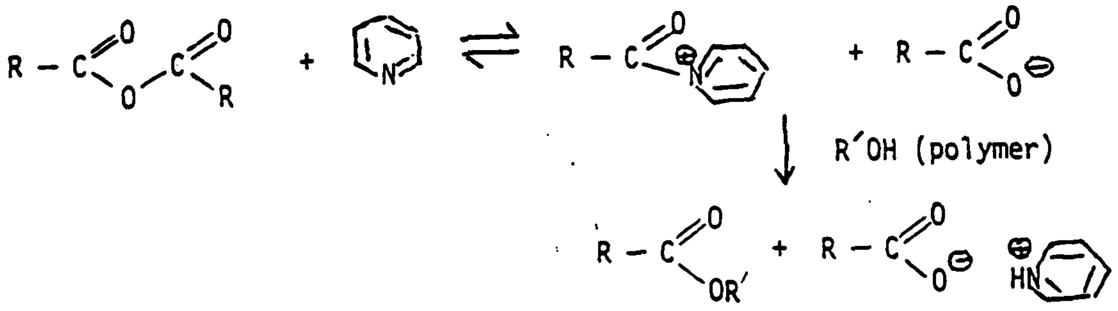
4.2.1 Determination of OH-Equivalent Weight

4.2.1.1 Evaluation of Various Chemical Methods Utilized for Determination of OH-Equivalent Weight

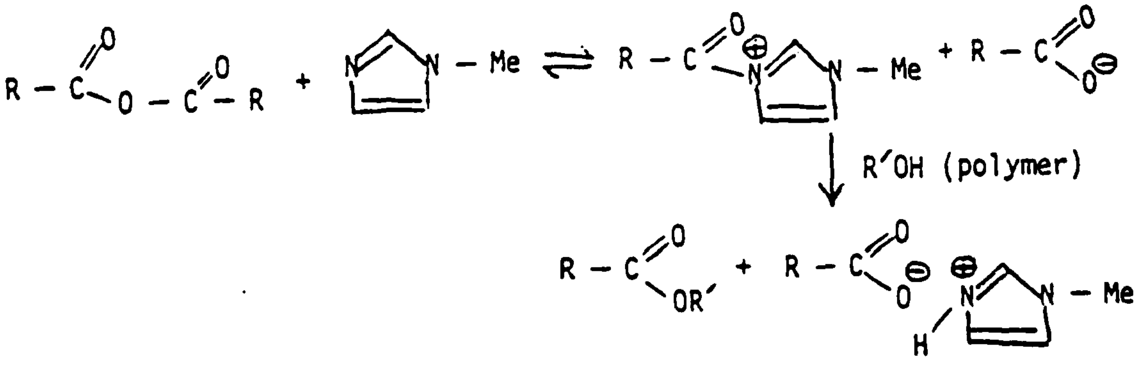
The three commonly used chemical methods for the quantitative determination of hydroxyl groups in prepolymers have been selected for study. All of the methods involve (1) reaction with an excess amount of acid anhydride in the presence of a base catalyst; (2) hydrolysis of the excess acid anhydride after completion of esterifications; and (3) titration of the carboxylic acid groups with a dilute KOH solution using an indicator and/or by a potentiometric method.

The reactions are:

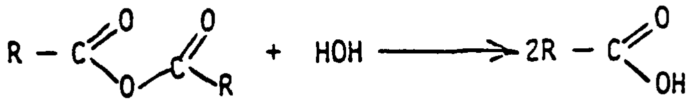
(1) Esterification of polymer



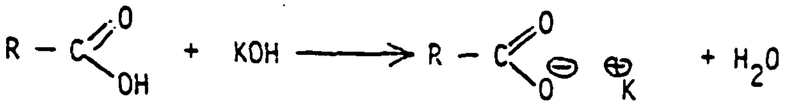
or



(2) Hydrolysis of excess acid anhydride



(3) Titration



Reaction conditions for the esterifications are tabulated in Table VIII. They are based on reactions of prepolymer with (a) acetic anhydride (AA) in the presence of N-methylimidazole (NMIM) reported by Conners(15), and (b) phthalic anhydride (PA) in the presence of pyridine (PY) reported by Cohen(16). Procedures with slight variations of the methods by Conners and Cohen have been reported by Dee(17) and Aerojet(18), and they are also included for our study.

Seven commercially available prepolymers and our experimental DNPA polymer were analyzed by the methods outlined in Table VIII. Several observations are made based on the experimental results in Table IX.

(1) A more basic catalyst such as NMIM, in place of pyridine, allows one to reduce the esterification time and temperature appreciably. Conners and Pandit(15) have shown that the catalytic activity of NMIM is approximately 100 times greater than that of pyridine when simple alcohols are esterified.

TABLE VIII. ESTERIFICATION CONDITIONS FOR ANALYSIS OF HYDROXY-TERMINATED POLYMERS

Method	Ref.	Anhydride/Catalyst	Molar Ratio, Anhydride/Polymer	Polymer Sample Size	Rexn. Time (Hrs.)	Rexn. Temp (°C)
(A)-1	(15)	AA/NMIM	2/1	4 meq.	0.25	45
(A)-2	-	AA/NMIM	2/1	4 meq.	0.50	45
(A)-3	(17)	AA/NMIM	2/1	4 meq.	0.25	steam bath
(B)-1	(16)	PA/PY	10/1	3 meq.	1.00	115 (reflux)
(B)-2	-	PA/PY	10/1	3 meq.	2.00	115 (reflux)
(B)-3	(18)	PA/PY	2/1	3-10 meq.	2.00	98

TABLE IX. OH-EQUIVALENT WEIGHT OF POLYMERS BY VARIOUS METHODS

		AA/NMIM Methods*			PA/PY Methods*		
Polymers	Vendors	(A)-1	(A)-2	(A)-3	(B)-1	(B)-2	(B)-3
PCP-0240	981	998, 1000	-	-	973, 970	-	-
NPGA	1007	1040, 1050	-	-	1230, 1220	-6970	990, 979
Carbowax	1650	1710, 1760	-	-	-	-3320, -2830	1680, 1690
PPG	918	1130, 1160	-	-	-	-6060	928, 923
B-2000	1000	1540, 1550	1060	-	1030, 1090	-	1020, 1040
Teracol	500	850, 850	420	-	6720, 5920	-6940	500, 500
R-45M	1300	1430, 1430	-	1150	-	-	1350, 1350
PDNPA	2910**	2970	decomp'n	-	decomp'n	-	decomp'n

---

* Refer to Table VIII for the reaction conditions.

** Based on IR-Method

(2) Necessary reaction time and temperature for the complete esterification of the polymers vary with the type of polymers. (Compare methods (A)-1 and (A)-2 for B-2000 and Teracol.)

(3) Longer reaction time and the higher temperature may cause side-reactions, which may even give negative values for EW. (Compare methods (A)-1 and (A)-3 for R-45M, and (B)-1 and (B)-3 for NPGA and Teracol.)

(4) Nitrogroup-containing polymers tend to undergo decomposition by the basic catalysts.

(5) The procedure from Aerojet(18) (Method (B)-3 in Table VIII), which is a modification of Cohen's method(16), appears to give the best results for the common prepolymers, although one expects difficulty with R-45M by this method. (See Experimental 5.2.1.

A preliminary conclusion based on the data in Table IX is that one can determine a correct equivalent weight of prepolymer by selecting proper esterification conditions, if the other functional groups present in the polymer are chemically inert to the reagents. Selection of the reaction conditions for the esterification may require a reference value of the equivalent weight of the prepolymer obtained independently by another analytical method.

4.2.1.2 Determination of OH-Equivalent Weight from the Infrared Absorption Band of THF/OH Complex

A new physical method for determination of OH-equivalent weight has been developed and published(19). A copy is attached as the Appendix. Technical background as well as advantages and disadvantages of the method are described in the article.

Other physical methods, such as an NMR method(20), have been cited; however, these are only specific for certain polymers. It is believed that the most reliable approach for the OH-equivalent weight determination of a new experimental prepolymer would be initially to use both the infrared and one of the chemical methods for comparison. The subsequent routine analysis would be done with the infrared method, since it requires only a semi-micro quantity of sample and much less time, but gives more reproducible results (especially if a FTIR is available).

4.2.2 Determination of Number Average Molecular Weight and Polydispersity

Polymers, in their purest form, are mixtures of molecules of different molecular weight. Hence, both the average molecular weight and the distribution of different molecular weights within a polymer are required in order to fully characterize it. The most important average molecular weights which are determined are:

(i) The number average molecular weight, $\overline{M_n}$, is determined by the measurement of colligative properties and is defined as:

$$\overline{M_n} = \frac{\Sigma n_i M_i}{\Sigma n_i} \qquad (1)$$

(ii) The weight-average molecular weight, $\overline{M_w}$, is obtained from light-scattering measurements and is defined as:

$$\overline{M_w} = \frac{\Sigma n_i M_i^{\,2}}{\Sigma n_i M_i} \qquad (2)$$

(iii) The viscosity-average molecular weight, $\overline{M_v}$, is obtained from viscosity measurements defined by:

$$\overline{M_v} = \left(\frac{\Sigma n_i M_i^{\,a+1}}{\Sigma n_i M_i} \right)^{1/a} \text{, where a is a constant} \qquad (3)$$

For a polydisperse polymer, the average values decrease in the order, $\overline{M_w} > \overline{M_v} > \overline{M_n}$ as shown in Fig. 8.

The main interest of propellant chemists in this area is the number average molecular weight and the polydispersity, which is defined as $\overline{M_w}/\overline{M_n}$. The discussion is, therefore, confined to these two.

Two commonly used methods for determination of number average molecular weight for prepolymers are:

(a) vapor phase osmometry (VPO), and

(b) gel permeation chromatography (GPC).

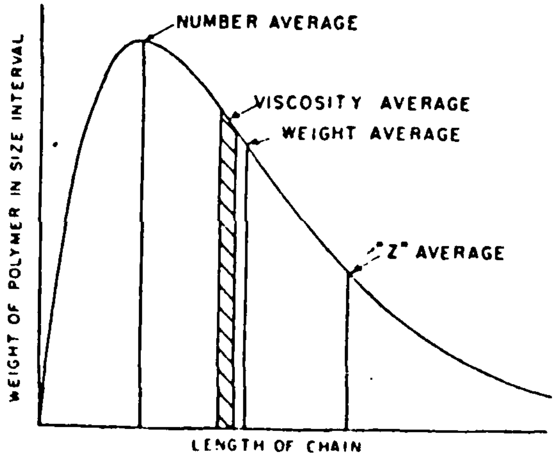
FIGURE 8. EXPRESSIONS OF VARIOUS AVERAGES OF POLYMER MOLECULAR WEIGHT

$$\overline{M}n = \frac{\sum_{i=1}^{\infty} n_i M_i}{\sum_{i=1}^{\infty} n_i}$$

$$\overline{M}v = \left[\frac{\sum_{i=1}^{\infty} n_i M_i^{1+\alpha}}{\sum_{i=1}^{\infty} n_i M_i}\right]^{1/a}$$

$$\overline{M}w = \frac{\sum_{i=1}^{\infty} n_i M_i^{2}}{\sum_{i=1}^{\infty} n_i M_i}$$

$$\overline{M}z = \frac{\sum_{i=1}^{\infty} n_i M_i^{3}}{\sum_{i=1}^{\infty} n_i M_i^{2}}$$



4.2.2.1 Vapor Phase Osmometry (VPO)$^{(21)}$

This method is based on a well-established concept that the addition of a nonvolatile solute to a solvent results in the lowering of the vapor pressure of the solution, and that the amount of lowering is dependent on the concentration. The change in vapor pressure is linear with respect to concentration, in dilute solution, and follows Raoult's Law.

$$\text{Raoult's Law:} \quad \frac{P^o - P}{P^o} = \frac{n_2}{n_1 + n_2} \cong \frac{n_2}{n_1} = \frac{w_2 M_1}{w_1 M_2} \qquad (4)$$

where P^o and P are the vapor pressure of the pure solvent and the solution, respectively, n_1 and n_2 are the number of moles of solvent and solute, respectively, w_1 and w_2 are the weights of solvent and solute, and M_1 and M_2 are the molecular weights of the solvent and solute. The expression $(P^o - P)$ is often expressed as ΔP. If the concentration of a solute, c, is the mass of solute per kilogram, then

$$\Delta P = P^o \frac{cM_1}{M_2} \qquad (5)$$

Since it is difficult to measure the vapor pressure of the solution with the degree of accuracy required, the measurement of the temperature difference between the solution and the pure solvent at the same vapor pressure is used. This relationship is derived from the differential form of the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = \frac{H_v P^o}{R T_b^{\,2}} \qquad (6)$$

where H_v = the molar heat of vaporization of the solvent

T_b = the boiling point of the solvent

R = the gas constant

By combining equations (5) and (6) and combining all the constants into one, the following equation can be derived:

$$\frac{\Delta T}{c} = \frac{k}{\overline{M_n}} \quad (7)$$

where M_2 is replaced by $\overline{M_n}$.

Because the instrument used gives a difference of resistance, ΔR, between a pair of thermisters in the sample chamber, rather than a direct readout of the temperature difference, the above equation is changed to:

$$\frac{\Delta R}{c} = \frac{k}{\overline{M_n}} \quad (8)$$

where k = the instrument constant for a given solvent.

Number average molecular weights of some commercial prepolymers and our experimental DNPA polymers were determined using a Perkin-Elmer Model 115 Molecular Weight Apparatus. The instrument constant, K, was obtained by using pure 2,2-dinitropropylacrylate (DNPA) and 5,5'-dithio-bis-(2-nitro)-benzoic acid (DTNBA) in methylethylketone (MEK) at 40°C (Fig. 9). Molecular weights of the prepolymers were determined in MEK at 40°C by extrapolating the ΔR/C values to zero concentration based on the following equation (Figs. 10 and 11):

$$\lim_{c \to o} \frac{\Delta R}{c} = \frac{K}{\overline{M_n}}$$

FIGURE 9.

CALIBRATION CURVE FOR DETERMINATION OF INSTRUMENT CONSTANT K BY VPO

Solvent=MEK; T=40.1°C

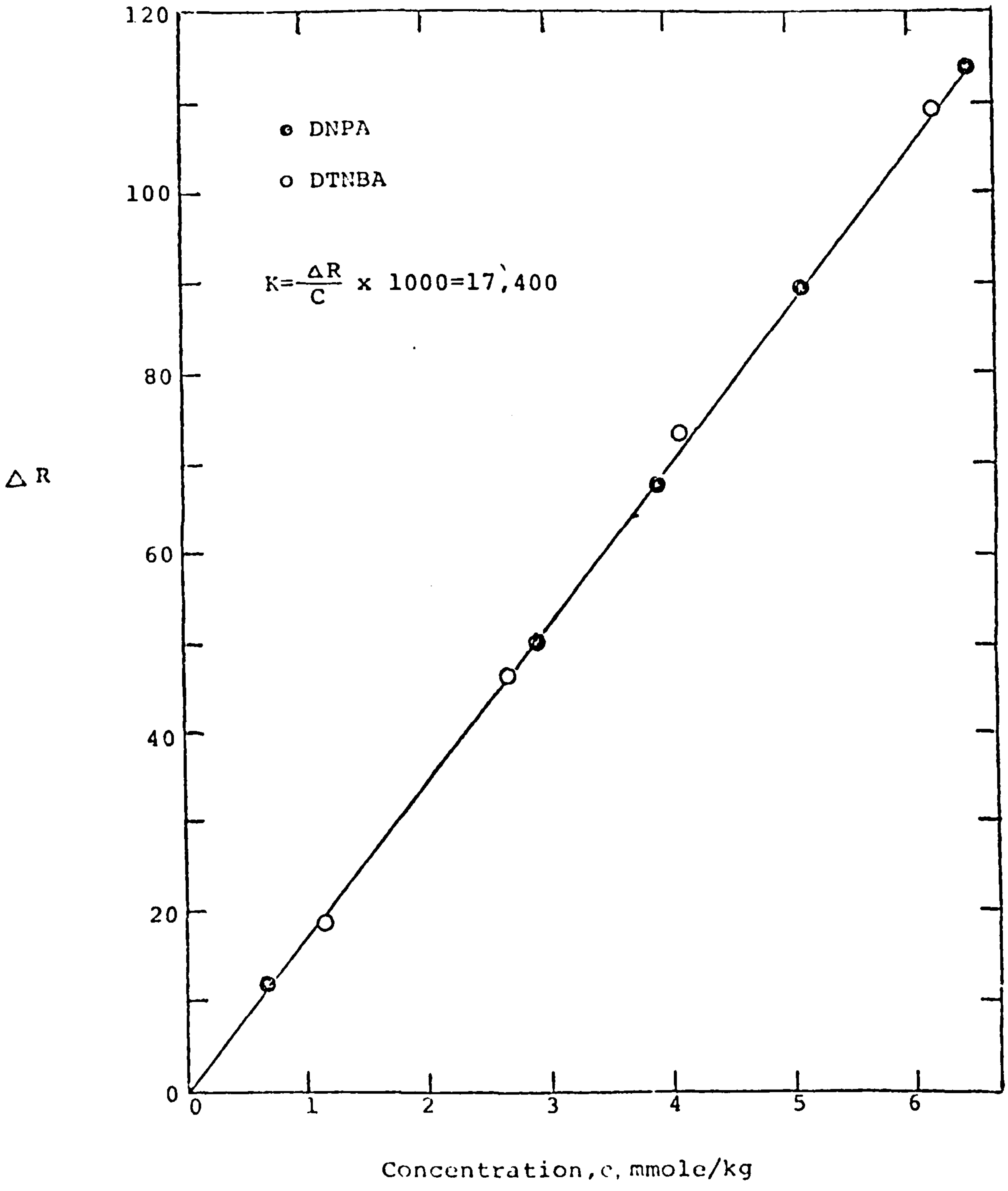


FIGURE 10. VAPOR PHASE OSMOMETRY PLOTS OF COMMERCIAL POLYMERS

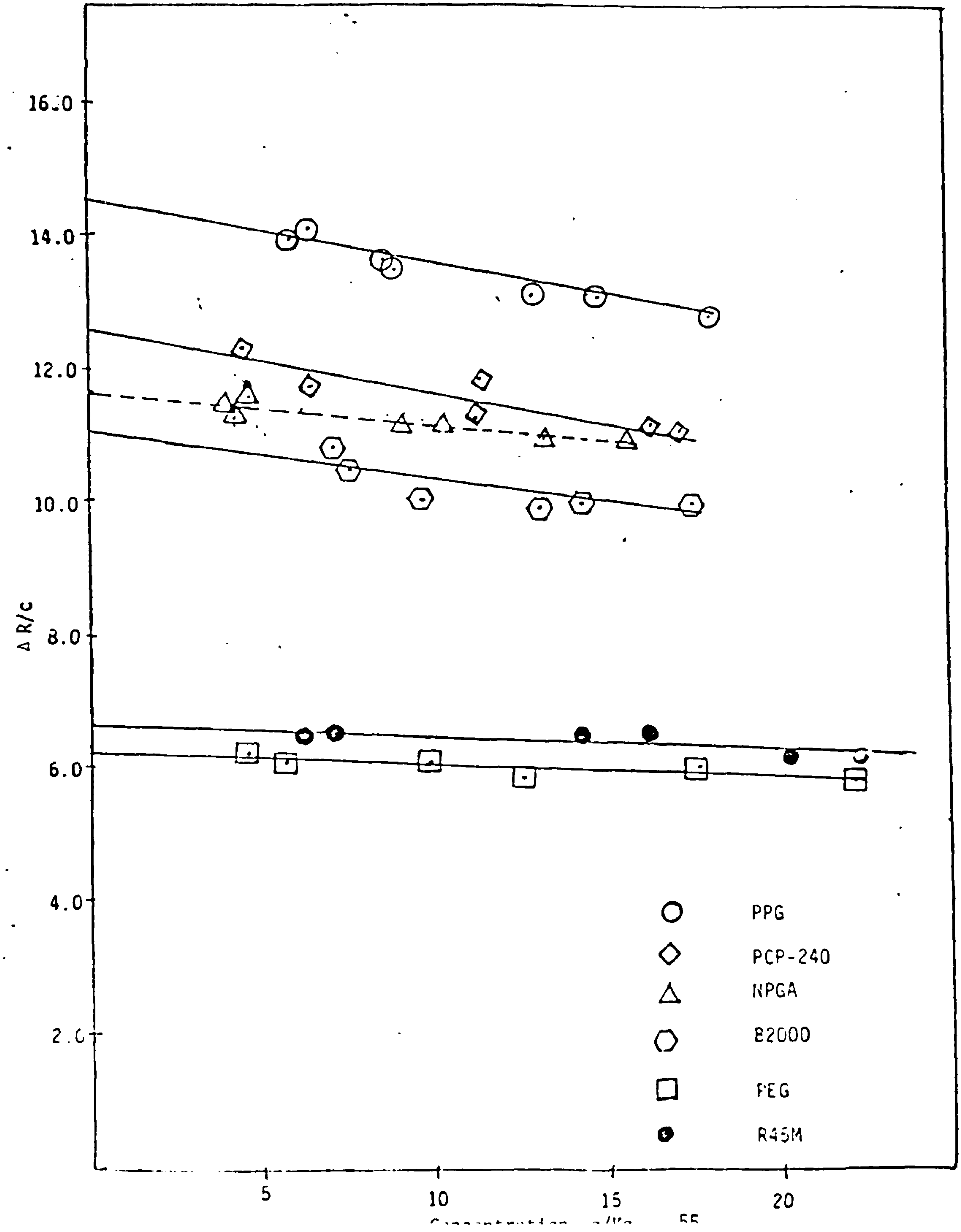
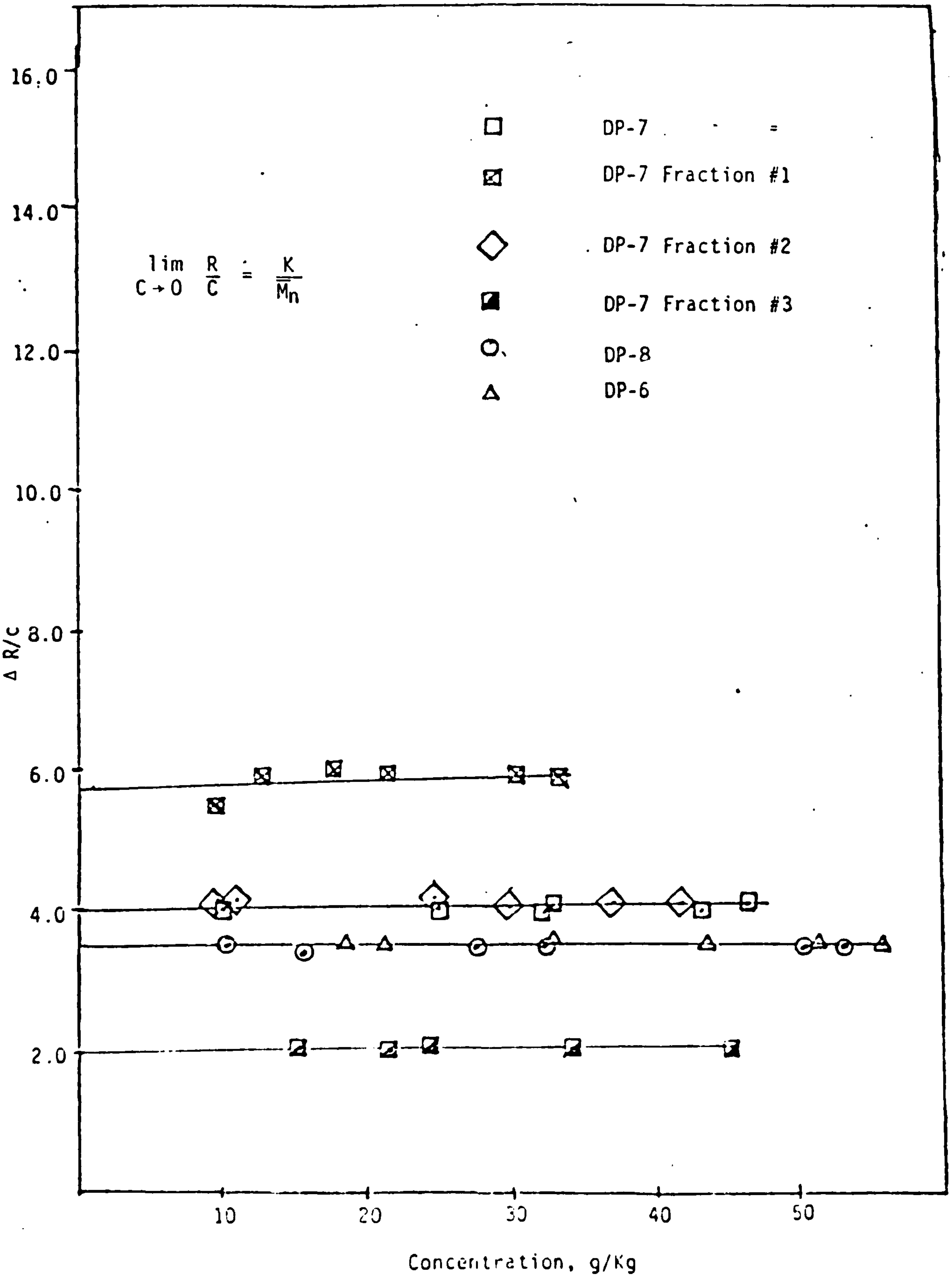


FIGURE 11. VAPOR PHASE OSMOMETRY PLOTS OF POLY-DNPA



The experimental values by VPO are consistently lower than the $\overline{M_n}$ values supplied by the vendors (Table X). The primary reason appears to be the presence of trace amounts of small molecules such as monomer and/or solvent in the prepolymers. For example, it is extremely difficult to eliminate the monomer completely from the DNPA polymer sample as shown in the GPC scan of "purified" DNPA polymer (Fig. 12).

This difficulty in eliminating small molecules appears to be a common problem. "Polystyrene standards" purchased for calibration have narrow molecular weight distributions. Average molecular weights of standards are determined by the suppliers as shown in Table XI. Suppliers determine number average molecular weight ($\overline{M_n}$) by vapor phase osmometry, weight average molecular weight ($\overline{M_w}$) by light scattering, and viscosity average molecular weight ($\overline{M_v}$) by capillary viscometry. These averages are defined as shown in Fig. 8, and therefore, the relative values should always be in the order; $\overline{M_w} > \overline{M_v} > \overline{M_n}$. Dispersity of molecular weights of "polystyrene standards" as indicated by $\overline{M_w}/\overline{M_n}$ is usually less than 1.1. One can use this ratio to estimate the value of $\overline{M_w}$ from $\overline{M_n}$, and vice versa. The values in parentheses in Table XI are estimated average molecular weights. For example, the calculated $\overline{M_w}$ value of (2720)* from the experimental $\overline{M_n}$ value of 2570 and $\overline{M_w}/\overline{M_n} = 1.06$, is much smaller than the $\overline{M_v}$ value of 3600, whereas $\overline{M_w}$ should be greater than $\overline{M_v}$. This indicates that the experimental $\overline{M_n}$ value by VPO is erroneous, i.e. much lower than the actual $\overline{M_n}$. Other examples of this type can be cited from Table XI. It can be concluded from the above discussions that the determination of number average molecular weight by vapor phase osmometry is reliable <u>only if</u> the polymer sample is <u>not</u> contaminated by small molecules such as monomers and solvents.

TABLE X. THE NUMBER AVERAGE MOLECULAR WEIGHTS ($\overline{M}n$) OF COMMERICAL PREPOLYMERS BY VAPOR PHASE OSOMETRY

Polymer	Vendor's $\overline{M}n$	Concentration g/kg	ΔR	$\overline{M}n$ by VPO	% Deviation*
PPG	1580	14.57	192.2	1240	22
		12.83	169.3		
		8.67	117.1		
		8.50	116.1		
		6.19	87.2		
		5.80	81.0		
B 2000	1800		172.0	1610	11
		14.28	143.3		
		12.99	129.6		
		9.72	98.6		
		7.43	78.1		
NPGA	1800	15.67	171.0	1540	14
		12.15	133.2		
		11.24	102.2		
		10.10	114.4		
		4.64	54.0		
		4.23	47.9		
PCP 240	1960	11.26	188.9	1410	28
		16.38	180.6		
		11.44	135.4		
		6.44	75.3		
		4.60	56.9		
Carbowax	3050	22.16	129.3	2850	7
		17.72	108.0		
		12.55	74.0		
		9.92	60.7		
		5.67	34.6		
		4.43	27.8		
R45M	3380	37.64	229.9	2760	18
		34.16	205.9		
		23.84	153.4		
		22.04	142.6		
		12.11	76.4		
		10.78	68.4		

$$* \quad \% \text{ Deviation} = \frac{\text{Vendor's } \overline{M}n - \overline{M}n \text{ by VPO}}{\text{Vendor's } \overline{M}n} \times 100$$

FIGURE 12. GPC SCAN OF PURFIED POLY-DNPA (DP-18)

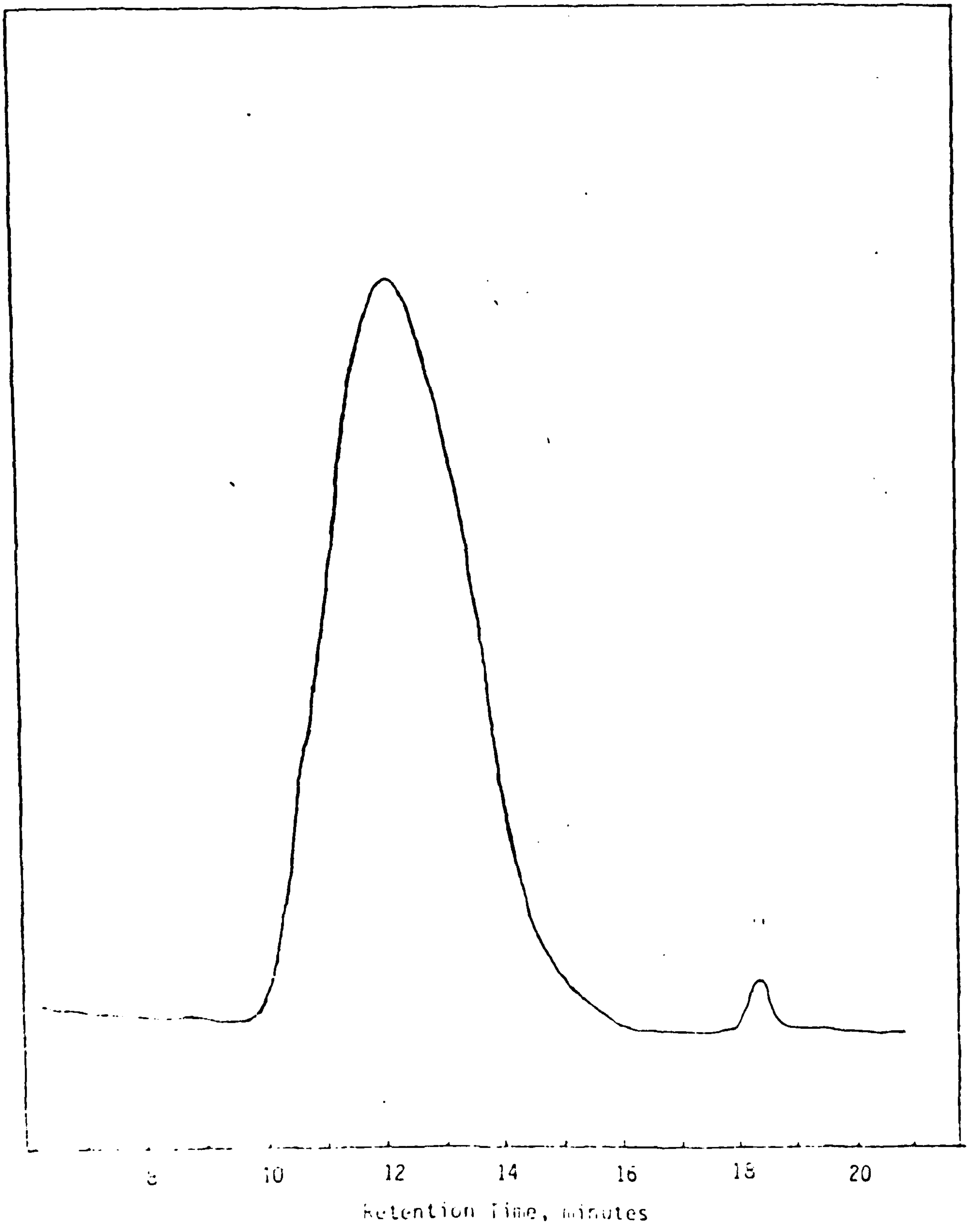


TABLE XI.

POLYSTYRENES FOR CALIBRATION

M_w	M_v	M_n	M_w/M_n**
(1050)*	1024	811	1.30
(1900)*	2100	1790	1.06
(2720)*	3600	2570	1.06
(9600)*	9100	9050	1.06
20,400	17,400	15,100 (19,200)*	1.06
53,700	47,400	51,150 (50,660)*	1.06

* (   ) calculated values from M_w/M_n

** determined by GPC analysis.

4.2.2.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) is a technique which can be used to characterize the polydispersity of polymeric materials, and also to determine various types of average molecular weights, such as number average, viscosity average, weight average and "Z"-average molecular weight if proper reference polymers are available. The conventional calibration method for determining the molecular weight by GPC is to use "standard" or "reference" polymers of low dispersity and known molecular weights. Several kinds of "standard" polymers are commercially available. Plots of the logarithm of molecular weight (M) vs elution volume (V_e) follow the relationship below for the same type polymers:

$$\log M = a + bV_e + cV_e^2 \tag{9}$$

If an experimental sample has the same chemical structure and configuration (linear, branched, etc.) as the "standard" polymer, the molecular weight can be determined from the calibration curve by simply determining the elution volume under the same conditions. However, a change in the chemical structure and/or in the configuration of the macromolecule could cause a change in the dimension for the same molecular weight. Nevertheless, the values of average molecular weights for the prepolymers, determined by GPC using equation (9), are commonly reported without any qualifying references. When chemists accept these results at face value and calculate the functionality (f) of the prepolymers from the relationship, $f = \overline{M_n}/EW$, the result is quite often erroneous. This is why there is much confusion as to the validity of these values. This problem of confusion is understandable, since not many well-characterized "standard" polymers are available for calibration. Newly synthesized, experimental polymer samples will most likely have unknown molecular configurations and unknown degrees of polymer-solvent interactions. Reference samples having similar configuration and polymer-solvent interactions are usually not available. Although the low angle laser light scattering photometer, which has recently become available, may be utilized as a detector for GPC to determine the absolute molecular weight, this instrument is expensive to maintain. Furthermore, the accurate determination of low molecular weight polymers (prepolymers) is difficult by the light scattering method because of the reduced sensitivity.

Since GPC is based mainly on the difference of the molecular size, more meaningful calibration should be based on the plots of logarithm of hydrodynamic volume (V_h) vs elution volume (V_e), and then relating V_h to M. The hydrodynamic volume, V_h, is defined as the volume of swollen polymer molecule in a given solvent. This approach is discussed below.

4.2.2.3 Molecular Weight Determination from GPC and Intrinsic Viscosity

Polymer solution viscosities are commonly measured by capillary viscometers, such as Ubbelohde or Ostwald-Fenske type viscometers(22). The nomenclature involved is shown below.

NOMENCLATURE OF SOLUTION VISCOSITY

Common Name	Precise Name	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_0 = t/t_o$
Specific viscosity	- - - -	$\eta_{sp} = \eta_r - 1 = (\eta-\eta_0)/\eta_0 = (t-t_o)$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/C$
Inherent viscosity	Logarithmic Viscosity number	$\eta_{inh} = (\ln\eta_r)/C$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/C) = [(\ln\eta_r)/C]_{C\to 0}$

where C = conc. in g/ml.

The Einstein equation for the viscosity (η) of suspended, spherical, rigid particles states that

$$\eta = \eta_0(1 + 2.5\phi) \tag{10}$$

where η_0 is the viscosity of the solvent, and ϕ is the volume fraction of suspended particles.

The Einstein equation can be modified to include asymmetric species

$$\eta = \eta_0(1 + k\phi) \tag{11}$$

where k is a parameter which depends upon the shape of the suspended particles.

For a polymer solution having concentration, c g/ml,

$$\phi = \frac{N_o c}{M} \cdot V_h \tag{12}$$

where N_o is Avogadro's number, M is the molecular weight of polymer particles, and V_h is the volume of dissolved polymer particle (hydrodynamic volume).

Substitution of equation (12) and (11) and rearrangement of the resulting equation gives:

$$\eta = \eta_0(1 + \frac{kN_o c}{M} \cdot V_h)$$

$$\frac{\eta}{\eta_0} - 1 = \frac{kN_o c}{M} \cdot V_h \tag{13}$$

By definition,

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \tag{14}$$

Substitution of equation (14) into (13) allows:

$$\frac{\eta_{sp}}{c} = \frac{kN_o \cdot V_h}{M}$$

At infinite dilution (i.e. approximate dilution in GPC)

$$[\eta_{sp}/c]_{c\to o} = [\eta] = \frac{kN_o V_h}{M} \quad \text{or}$$

$$V_h = kN_o[\eta] \cdot M \tag{15}$$

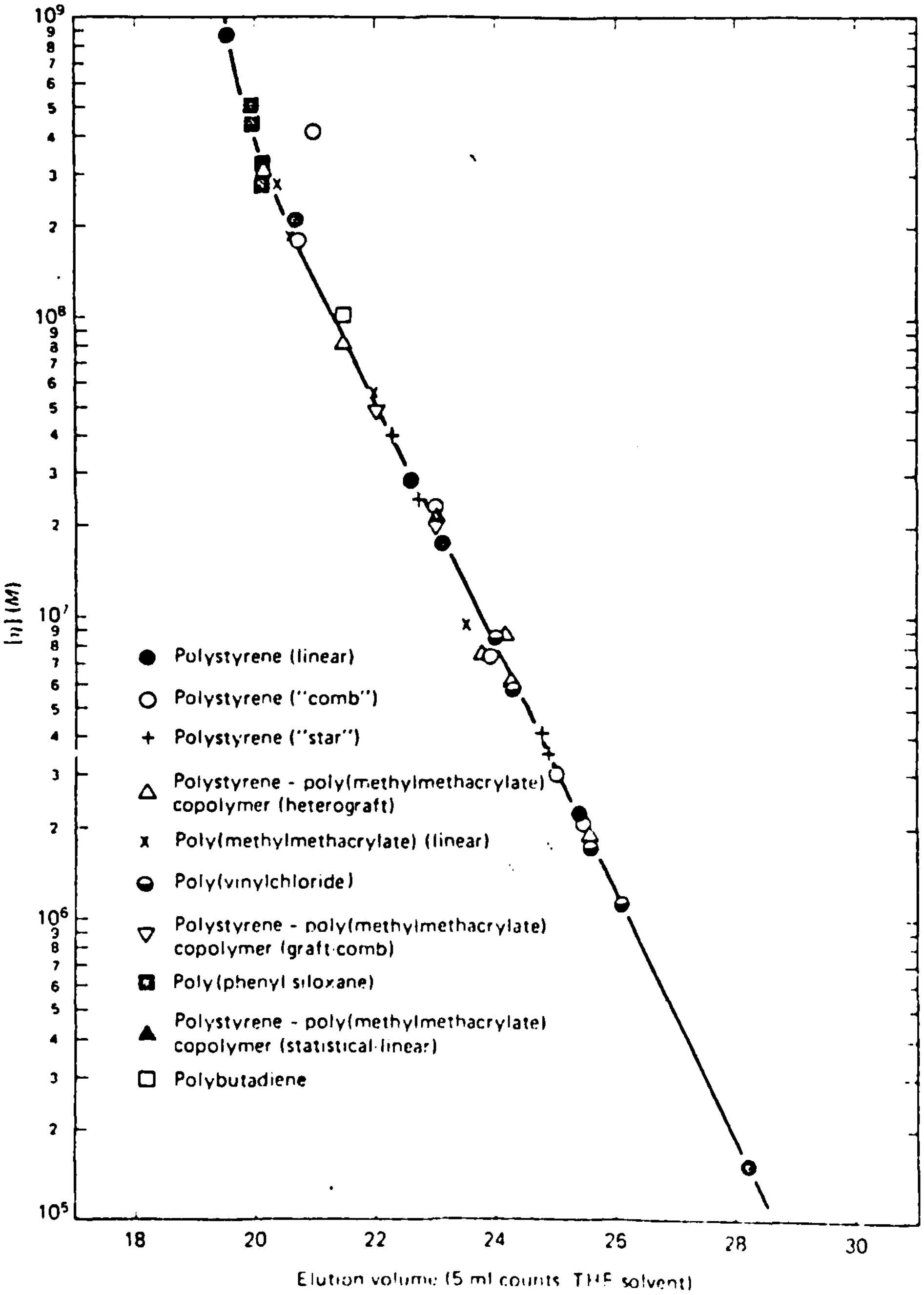
If it is assumed that the shapes of all the amorphous polymer particles at infinite dilution are swollen, random coils, which are approximately spherical, then k in equation (15) would be constant and approximately 2.5 for all polymers. Hence, if the GPC plots of log V_h vs elution volume V_e, of all polymers having different chemical structures and/or configurations follow the relationship log $V_h = a + bVe + cVe^2$, then log $([n]\cdot M)$ vs elution volume should follow a similar relationship. One could then determine the molecular weight from the determinations of intrinsic viscosity and elution volume of the polymer using the same solvent, where no special reference (standard) polymers are required. A universal calibration curve based on this concept, equation (16), has been substantiated for many polymers of molecular weight range, 20,000 - 500,000 (Fig. 13)(23).

$$\log [n][M] = a' + b'V_3 + c'V_e^2 \qquad (16)$$

where V_e = elution volume

Applications of equation (16) to molecular weight determinations of prepolymers, which have much lower molecular weight (500 - 10,000) may be feasible, if accurate values of intrinsic viscosities of prepolymers can be determined. The values of intrinsic viscosities are dependent on the difference in the viscosities of the dilute polymer solutions and the solvent as shown in equation (14). The difference in the values becomes smaller as the molecular weight of polymer decreases, and this may be the primary reason that the viscosity molecular weight determination method is recommended only for polymers of molecular range 15,000-10^6.(24) Accuracy of the determination of intrinsic viscosity of these low molecular weight prepolymers, therefore, was investigated using viscometers of different capillary sizes.

FIGURE 13. UNIVERSAL CALIBRATION IN GEL-PERMEATION CHROMATOGRAPHY FOR A VARIETY OF POLYMERS IN TETRAHYDROFURAN



4.2.2.3.1 Capillary Viscometry of Prepolymers

The rate of flow of liquid through a capillary of radius r and length l is given by Poiseville's equation:

$$\frac{dV}{dt} = \frac{\pi P r^4}{8\eta l} \qquad (17)$$

where η is the viscosity of the liquid,

P is the pressure head causing the flow,

$\frac{dV}{dt}$ is the volume of liquid flowing through the capillary in unit time.

If a constant volume of liquid V and an average pressure $\overline{P}$ are used, equation (17) can be expressed as:

$$V/t = \pi\overline{P}r^4/8\eta l \text{ for solution,}$$

$$\text{and } V/t_o = \pi\overline{P}_o r^4/8\eta l \text{ for solvent}$$

The average pressure producing flow is given by

$$\overline{P} = \rho g\overline{h} \qquad (18)$$

where ρ is the density of the liquid,

$\overline{h}$ is the average head of liquid, and

g is the acceleration due to gravity

Hence, the viscosity ratio of the solution to solvent becomes:

$$\eta/\eta_o = t\ /t_o\rho_o \qquad (19)$$

$$\text{or} \quad \eta_{sp} = (\eta/\eta_o - 1 \cong (t-t_o)/t_o \qquad (20)$$

For an infinitely dilute solution, it can be assumed that $\rho \cong \rho_o$, and the following equation results:

$$[\eta] = \lim_{c \to o} \eta_{sp}/c = \lim_{c \to o} \frac{(\eta-\eta_o)/\eta_o}{c} = \lim_{c \to o} \frac{(t-t_o)}{t_o} \qquad (21)$$

where $[\eta]$ is defined as the limiting viscosity number or intrinsic viscosity,

t is the efflux time of the solution,

t_o is the efflux time of the solvent, and

c is the concentration in g/ml

$[\eta]$, therefore, describes the ability of the polymer molecules to increase the viscosity of the solvent in the absence of any intermolecular interactions. Measurements of (η_{sp}/c) are usually made for a series of dilute solutions of different concentrations by determining flow times, and plots of η_{sp}/c vs concentration are used to determine the intrinsic viscosity, $[\eta]$, as the Y-intercept of the plots via extrapolation. However, the extrapolation for our low molecular weight polymers created more deviation than using the average value. Furthermore, virtually all the prepolymers having molecular weight less than 10,000 gave a slope close to zero at the concentration level of 0.6 - 1.1 g/dl. Hence, measurements on polymer solutions with polymer molecular weight less than 10,000 were made at concentration levels of 0.5 - 1.1 g/dl, and the average value was used as that of $[\eta]$.

Cannon-Ubbelohde dilution viscometers with solution charge capacity of 8-40 ml were used. Two capillary sizes with calibration constants of 0.008 (C_l) and 0.004 (C_s) were selected for evaluation, where the calibration constant is defined as $\frac{\text{viscosity in centistokes}}{\text{efflux time in sec.}}$. Efflux time was measured using the Wescan Model 221 viscosity timer. Capillary sizes mentioned above gave THF efflux time of 140 seconds for (C_s) and 61 seconds for (C_l). Tetrahydrofuran (THF) was selected as the solvent, since it was found to be a universal solvent for prepolymers having different chemical structures ranging from non-polar polymers such as polybutadiene, to highly polar polymers, such as polydinitropropylacrylate, and also is a good solvent to be used with μ-styragel columns.

Although THF has the above advantages, it has the disadvantages of high vapor pressure, low surface tension, and being hygroscropic. Hence, more careful experimental procedure is needed to obtain an accurate result. The effect of the hygroscopic nature of THF on the determination of intrinsic viscosity of the solution was examined as shown in Table XII. Variations in the values determined in "dry" THF and in THF containing 0.05 and 0.15% H_2O were not significant within the experimental error. ("Dry" THF is kept over molecular sieve 4Å, and may not be completely anhydrous.) However, there was a variation in the actual efflux time for THF at different moisture levels. In order to minimize the effect of moisture, "dry" THF was used and the efflux time was measured after equilibration for 10 minutes in a 20°C water bath, exposed to ambient atmosphere. (This data will be used in conjunction with GPC data, and GPC columns trap any moisture in the solvent; hence the use of anhydrous THF for viscometry.) The detailed procedure is described in Experimental V-B-(2).

In general, it is advantageous to use a viscometer with a smaller capillary size such that the efflux time is greater than 100 sec. This way, $(t-t_0)$ will have more significant figures. Unfortunately, the smaller capillary seems to give more scattered values of efflux time than the large capillary for most operators. This is probably due to its higher sensitivity to any foreign particles in the capillary, and other

TABLE XII. EFFECT OF THE PRESENCE OF MOISTURE IN THF ON THE VALUES OF INTRINSIC VISCOSITY

PPG, MW 2020 at 26°C

Wt% H_2O in THF	Conc'n PPG, g/ml	nsp/c, ml/g
(1) "Anhydrous"	11.06×10^{-3}	6.22
(t_o = 139.45 sec)	12.62×10^{-3}	6.17
	17.82×10^{-3}	6.07
	Ave.	6.15 ± 0.06
(2) 0.05	10.91×10^{-3}	6.12
(t_o = 139.79 sec)	13.08×10^{-3}	6.21
	14.02×10^{-3}	6.24
	Ave.	6.19 ± 0.05
(3) 0.15	9.92×10^{-3}	6.04
(t_o = 140.72 sec)	15.68×10	6.19
	21.14×10^{-3}	6.12
	Ave.	6.12 ± 0.05

factors such as vibration of the set-up, vertical position of the capillary, etc. Data obtained by a trained operator, using the large and small capillaries shown that there is no significant difference in the accuracy (Table XIII). The best compromise appears to be to use the capillary size which gives t_o of $\sim$ 100 sec.

The above study indicates that reasonably reproducible values of intrinsic viscosity can be obtained for polymers having molecular weight less than 10,000, but there is room for further improvements in accuracy.

(ii) Gel Permeation Chromatography (GPC): Effect of Polymer Concentration, Flow Rate, Pressure and Temperature on the Elution Volume

GPC apparatus consists essentially of columns packed with rigid porous beads with a continuous stream of solvent flowing through the columns. The beads used here are made of a highly cross-linked polystyrene with a distribution of pore sizes. As a polymer solution flows through a series of μ-styragel columns (made by Waters), the smaller molecules will diffuse into the appropriate pores of the beads and thus their flow rate through the columns is retarded. On the other hand, larger molecules will be unable to enter the smaller pores and will remain in the solvent going around the beads. In this way, the larger molecules will pass through the columns relatively quickly whereas the smaller molecules will take longer. The following relationship for a given polymer-solvent system can be obtained as previously described:

$$\log M = a + bV_e + cV_e^2 \tag{9}$$

TABLE XIII. EFFECT OF DIFFERENT CAPILLARY SIZE ON INTRINSIC VISCOSITY

PEG 4820 at 26.0°C

A. Small Capillary

	Conc'n, g/ml	Efflux time, sec	η_{sp}/c, ml/g
Run #1*	0.00	139.79 ± 0.43	-
	5.82×10^{-3}	148.23 ± 0.09	10.4
	8.20×10^{-3}	152.63 ± 0.10	11.2
	10.1×10^{-3}	155.68 ± 0.26	11.2
	12.2×10^{-3}	158.38 ± 0.07	10.9
Run #2*	0.00	140.41 ± 0.14	-
	6.89×10^{-3}	150.54 ± 0.26	10.5
	7.25×10^{-3}	151.33 ± 0.08	10.7
	8.40×10^{-3}	152.70 ± 0.08	10.4
	11.68×10^{-3}	158.31 ± 0.04	10.9

$$[\eta]_{ave} = \underline{10.8 \pm 0.3}\ \text{ml/g}$$

B. Large Capillary

Conc'n, g/ml	Efflux time, sec	η_{sp}/c, ml/g
0.00	61.37 ± 0.03	-
5.78×10^{-3}	65.27 ± 0.03	11.0
7.74×10^{-3}	66.45 ± 0.03	10.7
9.87×10^{-3}	67.27 ± 0.20	9.74
10.01×10^{-3}	67.90 ± 0.10	10.5

$$[\eta]_{ave} = \underline{10.5 \pm 0.3}\ \text{ml/g}$$

---

* Runs #1 and #2 were made by different operators on different days

Commercial "standard" polymer samples listed in Table XIV were used for study. These polymers should have $\overline{M_w}/\overline{M_n}$ of less than 1.1 according to Vendor's GPC data, although the ratios, $\overline{M_v}/\overline{M_n}$, of PS-2, PS-3 and PS-6 do not agree. These discrepancies are most likely due to the scatter in their values of various molecular weight determinations. Reproducibility of the values of elution volume of these polymers was examined under two sets of conditions; (a) at a flow rate of 1.0 ml/min. using 0.25 wt% polymer solution, and (b) at 1.5 ml/min. using 1.0 wt%. The pressure and the temperature for condition (a) were 600-650 psi and 23.8-26.3°C, and for condition(b) were 950-1100 psi and 24.7-28.7°C. Average deviations in the elution volumes of these samples were ± 0.17 ml under condition (a) and ± 0.08 ml under condition (b) (Table XV). The result, therefore, implies that at the lower flow rate of 1.0ml/min., the elution volume may be more sensitive to variation of the conditions such as pressure and the temperature. This observation seems to coincide with our previous finding that $[\eta]$ values scatter more with the small capillary than the larger one.

4.2.2.3.3 GPC-Capillary Viscometry Combination Method for Molecular Weight Determination of Prepolymers

The GPC condition (b) (Table XV) was used to evaluate the determination of molecular weight by the combination method, GPC-Capillary viscometry. When one evaluates equations (9) and (16) for all the polymers in Table XV, they become:

TABLE XIV. COMMERCIAL "STANDARD" POLYMER SAMPLES WITH NARROW MOLECULAR WEIGHT DISTRIBUTION

"Standard" Polymers	Vendor	Vendor's Molecular Weights			
		$\overline{M}_w$*3	$\overline{M}_v$*4	$\overline{M}_n$*5	$\overline{M}_w/\overline{M}_n$*6
PS-1	PC*1	-	1,024	811	1.30
PS-2	PC	-	2,111	1,790	1.06
PS-3	PC	-	3,600	2,570	1.06
PS-4	PC	-	9,100	9,050	1.06
PS-5	PC	20,900	17,440	15,100	1.06
PS-6	PC	53,700	47,400	51,150	1.06
PBD-1	PC	-	-	395	1.17
PBD-2	PC	-	-	960	1.07
PBD-3	PC	-	-	2,350	1.13
			$\overline{M}$*7		
PEG-1	PL*2		1,000		-
PEG-2	PL		1,580		-
PEG-3	PL		4,820		-
PEG-4	PL		9,230		-
PPG-1	PL		980		-
PPG-2	PL		2,020		-

---

*1 Pressure Chemicals Co., Pittsburg, PA 15201

*2 Polymer Laboratories, Inc., Stow, Ohio 44224

*3 By light scattering method

*4 By capillary viscometry

*5 By vapor phase osmometry

*6 By GPC

*7 Method not given

TABLE XV. GPC ELUTION VOLUME OF VARIOUS "STANDARD" POLYMERS AT THE FLOW RATES OF 1.0 ml/min AND 1.5 ml/min

μ Styragel Columns: 10Å, 2 x 500Å, 2 x 10^3Å, 10^4Å

M.W. of Polymer "Standards"	[η] at 27°C ml/g	Elution Volume, ml	
		Condition A[*4]	Condition B[*5]
PS 1020[*1]	3.48	51.35 ± 0.20	49.94 ± 0.02
PS 2110	3.66	47.25 ± 0.20	46.17 ± 0.05
PS 3600	5.74	44.66 ± 0.51	43.95 ± 0.00
PS 9100	7.23	42.37 ± 0.17	41.44 ± 0.03
PS 17440	14.0	39.51 + 0.19	38.59 ± 0.10
PS 47400	27.2	36.25 ± 0.11	35.34 ± 0.10
PBD 460	3.14	52.72 ± 0.03	50.80 ± 0.01
PBD 1030	5.24	48.77 ± 0.21	47.40 ± 0.01
PBD 2660	9.33	44.58 ± 0.18	43.41 ± 0.11
PEG 1000	4.30	49.88 ± 0.02	48.50 ± 0.18
PEG 1580	5.03	48.22 ± 0.00	46.50 ± 0.10
PEG 4820	10.8	43.71 ± 0.05	42.52 ± 0.16
PEG 9230	12.4	41.22 ± 0.28	40.13 ± 0.21
PPG 980	3.58	49.12 ± 0.31	48.19 ± 0.06
PPG 2020	6.15	45.97 ± 0.09	45.15 ± 0.11
	Average deviation	± 0.17	± 0.08

---

*1 $\bar{M}_v$ by vendor

*2 $\bar{M}_w$ calculated from vendor's values of $\bar{M}_n$ and $\overline{M_w}/M_n$

*3 $\bar{M}$ by vendor, but the method not indicated

*4 Condition A: Flow rate = 1.0 ml/min; C = 0.25 wt% polymer solution; T = 23.8 - 26.3°C; P = 600 - 650 psi

*5 Condition B: Flow rate = 1.5 ml/min; C = 1.0 wt% polymer solution; T = 24.7 - 28.7°C; P = 950 - 1100 psi

Equation (9):

$$\log M = a + bV_e + cV_e^2$$

$a = 12.9 \pm 2.2$ (17% deviation)

$b = -0.31 \pm 0.11$ (35% deviation)

$c = 0.0021 \pm 0.0010$ (47% deviation)

Equation (16):

$$\log [n] \cdot M = a' + b'V_e + c'V_e$$

$a' = 18.7 \pm 1.9$ (10% deviation)

$b' = -0.47 \pm 0.08$ (17% deviation)

$c' = 0.0034 \pm 0.0010$ (29% deviation)

The result is extremely encouraging: the deviations for a' and b' for the combination method are far superior to those based on GPC only. It is believed that more careful experiments would improve the accuracy further. This means that one can determine the molecular weight of an unknown experimental prepolymer if one has a set of "standard" polystyrene calibration kits. If all the chemists in the solid propellant industry use the same polystyrene calibration kit by Pressure Chemicals, and then determine the elution volume by GPC and [n] by capillary viscometry, the molecular weight values reported would be far more reliable and meaningful. This approach is demonstrated below:

Let us assume that the polybutadienes, polyethylene glycols and polypropylene glycols in Table XV are polymers with unknown molecular weight.

"Standard" polystyrene from Pressure Chemicals with molecular weight range, 1000 to 47,000 are used as references. Equations (9) and (16) based on the polystyrene "standards" become:

Equation (9):

$$\log M = 11.4 - 0.24 V + 0.0015 V^2 \text{ for polystyrene}$$

Equation (16):

$$\log [\eta] \cdot M = 21.0 - 0.59 V_e + 0.0049 V_e^2 \text{ for polystyrene}$$

When the above equations are used to determine the molecular weights of the other prepolymers, the results in Table XVI are obtained. The values obtained from equation (16) are far closer to those of the vendors than the ones from equation (9). In fact, the ratios of the values of molecular weight from equation (16) to those from equation (19) should indicate the ratio of the hydrodynamic volume of polystyrene to that of the unkown polymer for the same molecular weight.

An attempt has been made also to apply this concept to some of the prepolymers used for propellant binders. Unfortunately, most of these prepolymers have much higher polydispersity than $\overline{M_w}/\overline{M_n} \cong 1.1$. Hence, these polymers would have required fractionation to obtain a fraction with dispersity of less than 1.1. Because of limited time, the polymers in Table XVII were evaluated without fractionation. The polydispersity values, $\overline{M_w}/\overline{M_n}$, are also listed in Table XVII. Retention volumes which correspond to the GPC peaks were used for this purpose. Again, the ratios of hydrodynamic

TABLE XVI. MOLECULAR WEIGHT DETERMINATION BASED ON PS STANDARDS BY GPC ONLY (EQN 9) AND BY GPC/CAPILLARY VISCOMETRY (EQN 16)

Polymers of $M_w/M_n \leq 1.1$

Polymer	V_e (min)*1	Vendor's MW	M from Eqn (9)*2	[n] (ml/g)	M from Eqn (16)*2	M (Eqn 16) / M (Eqn 9)
PBD	50.80	460	790	3.14	840	1.1
PBD	47.40	1030	1690	5.24	1250	0.74
PBD	43.41	2660	4590	9.33	2860	0.62
PEG	48.50	1000	1310	4.30	1100	0.84
PEG	46.50	1580	2100	5.03	1730	0.82
PEG	42.52	4820	5820	10.8	4650	0.80
PEG	40.13	9230	11,300	12.4	8910	0.79
PPG	48.19	980	1410	3.58	1450	1.0
PPG	45.15	2020	2930	6.15	2250	0.76

---

*1 Retention volume correspondint to the GPC peak
1.0% solution, flow rate 1.5 ml/min, T = 24.7 - 27.7°C, P = 950-1100 psi

*2 Eqn (9): $\log M = a + bV_e + cV_e^2$
Eqn (16): $\log [n] \cdot M = a' + b'V_e + c'V_e^2$

TABLE XVII. MOLECULAR WEIGHT DETERMINATION BASED ON PS STANDARDS BY GPC ONLY (EQN 9) AND BY GPC/VISCOMETRY (EQN 16)

PREPOLYMERS FOR PROPELLANT BINDERS

	GPC					
Polymer	$\overline{M}_w/\overline{M}_n$	V_r *1 (min)	M from Eqn (9) *2	[n] (ml/g)	M from Eqn (16) *2	$\frac{M\ (\text{Eqn }16)}{M\ (\text{Eqn }9)}$
BAMO-1	3.4	43.05	6220	9.5	3250	0.52
BAMO-3	2.7	42.45	7320	10.4	3800	0.52
GAP	1.3	45.53	2550	3.9	3110	1.2
PCP-0240	2.0	43.97	4560	10.1	2120	0.46
PCP-0260	1.8	42.51	7240	13.9	2770	0.38
PDNPA-4	1.8	39.35	16,500	9.4	17,100	1.04
PDNPA-6	1.7	40.05	13,200	8.3	13,800	1.04
PEG-1000	1.4	48.47	1200	5.1	940	0.78

---

*1 Retention volume corresponding to the GPC peak

*2 Eqn. 9 : $\log M = a + bV_e + cV_e^2$

Eqn. 16: $\log [n] \cdot M = a' + b'V_e + c'V_e^2$

values of polystyrene to those of the polymers indicate that the swollen particles of BAMO, PCP and PEG are larger and those of GAP are smaller than those of polystyrene. Hydrodynamic volumes of PDNPA are about the same as those of polystyrene for the same molecular weight. Once the ratio of the hydrodynamic volume of the experimental sample having a low dispersity, $\overline{M_w}/\overline{M_n} \leq 1.1$, to that of "standard" polystyrene is determined, this ratio could be utilized as a correction factor to determine all the average molecular weight values, $\overline{M_n}$, $\overline{M_v}$ and $\overline{M_w}$ in that range. Since the ratio for PDNPA to polystyrene is approximately one, the average molecular weight values of PDNPA from GPC, using polystyrene as the calibration standard, can be used without the viscosity determination for this range of molecular weight.

4.2.3 Determination of Number Average Functionality of Prepolymers of $\overline{f}p < 2.0$

Number average hydroxyl functionality of prepolymers can be determined by at least two methods:

Method I:

Number average molecular weight, $\overline{M_n}$, and hydroxy equivalent weight, EW, are determined independently. From these results the functionality, $\overline{f}p$, can be calculated as follows:

$$\overline{f}p = \frac{\overline{M_n}}{EW} \qquad (22)$$

Method II:

The average functionality of alcohol-containing prepolymers can be determined utilizing a cure study with an isocyanate. It is based on the theory that diols react with diisocyanates to form infinitely long chains, defined as a "gel", if stoichiometric amounts of the reactants are used$^{(25)}$:

$$\sum_{i=1}^{n} \frac{(f_i - 2)e_i}{f_i} = 0 \qquad (23)$$

where f_i = the functionality of individual polymer molecule,

e_i = equivalents/g of the polymer.

Hexamethylene diisocyanate (HDI) has functionality of 2.0 and is commercially available with purity of 99.3%. An infinitely long chain can be obtained by reacting HDI and hydroxy-terminated prepolymer, if the prepolymer has number average functionality of 2.0. For polymers having functionality less than 2.0, an additional crosslinker, i.e., a polyol having a functionality greater than 2.0, has to be incorporated to achieve a "gel". Hence the general equation (23) can be written as equation (24):

$$\frac{(\bar{f}_x - 2)e_x}{\bar{f}_x} + \frac{(\bar{f}_p - 2)e_p}{\bar{f}_p} = 0 \qquad (24)$$

where $\bar{f}_x$ = number average functionality of polyol, $\bar{f}_x > 2.0$

$\bar{f}_p$ = number average functionality of polymer, $\bar{f}_p < 2.0$

e_x = equivalents/g of polyol

e_p = equivalents/g of polymer

Average functionality of the prepolymer can be calculated from equation (24), if a polyol ($f > 2.0$) with known equivalent weight and functionality is available.

It would be most desirable to utilize both methods in order to check the correlation of the resulting values. However, each method has limitations; some of the limitations are discussed below:

4.2.3.2 Evaluation of Method I: $f_p = \frac{\overline{M_n}}{EW}$

An accurate determination of number average functionality depends on accurate values for both the equivalent weight and number average molecular weight. It is believed that the accuracy of equivalent weight determination is within 5%. Three well-developed methods have been discussed previously:

(1) Chemical methods using acid anhydrides,

(2) Infrared method using THF-associated OH-bands, and

(3) NMR method after silation of the OH-groups (only applicable to certain polymers).

The method of choice is dependent on the type of polymer; it is advisable to use at least two methods, especially when the polymer is a new, experimental sample.

An accurate determination of number average molecular weight of prepolymers is more difficult. Two possible methods are:

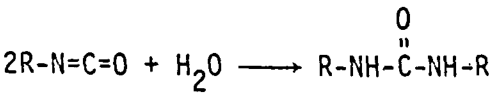
(1) Vapor phase osmometry, and

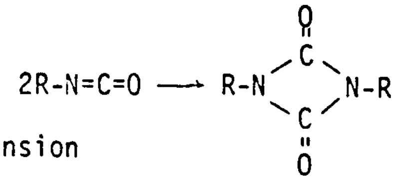
(2) Gel permeation chromatography - capillary viscometry method.

As discussed earlier, the determination of number average molecular weight by vapor phase osmometry is reliable, only if the polymer sample is not contaminated by small molecules such as monomers and solvents. The accuracy of GPC-capillary viscometry is yet to be evaluated. However, the reproducibility is not expected to be better than 10%. If the probable errors in $\overline{M_n}$ and $\overline{EW}$ are each 10%, then the probable error in fp is 14%.

4.2.3.2 Evaluation of Method II: Effective Functionality from Incipient "Gel" Formation

The effective functionality determination is based on a cure study, with an assumption that the reaction is 100% complete and without any side reactions. There is virtually no step-wise polymerization reaction whose conversion is 100% and is void of side-reactions. In spite of the fact that the reaction of alcohols with isocyanates is a clean, rapid reaction, there are three important side-reactions. In addition, the extent of the cure reaction must be analyzed. These four problem areas are discussed below.

(1) 
$2R\text{-}N{=}C{=}O + H_2O \longrightarrow R\text{-}NH\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}NH\text{-}R$

(2) Homopolymerization of isocyanate 

(3) Cyclization rather than chain extension

(4) Extent of reaction

The presence of water or any other active hydrogen will consume the isocyanate reagent. Homopolymerization of isocyanate can be catalyzed by an acid or a base, but more so by nucleophiles. For example, even mild nucleophiles, such as ethers, appear to catalyze isocyanate homopolymerization. Cyclization and the extent of cure reaction are expected to be dependent on the concentrations of isocyanates and alcohols, and therefore, the plasticizer or solvent content will affect these reactions. The effect of dilution has been experimentally demonstrated by Oberth and earlier workers(25). Furthermore, the consumption of isocyanate reagent by side reactions causes imbalance in stoichiometry, and thus lowers the extent of polymerization.

$$\overline{DP} = \frac{(1+r)}{(1+r-2rp)} \tag{25}$$

where $\overline{DP}$ = the degree of polymerization defined by:

$$\frac{\text{number of molecules present initially}}{\text{number of molecules remaining after time } t}$$

p = the extent of reaction defined by:

$$\frac{\text{number of groups that reacted}}{\text{number of groups present initially}}$$

r = molar ratio of the reactants defined such that it is less than equal or equal to 1.0:

$$\frac{\text{number of moles of isocyanate}}{\text{number of moles of alcohol}}$$

For example, if 5 mole % of isocyanate is consumed via side-reactions and the extent of the isocyanate reacted, p, is 0.99, equation (17) gives a value of

$$\overline{DP} = \frac{(1 + 0.95)}{1 + 0.95 - (2 \times 0.99 \times 0.95)} = 28$$

Therefore the degree of cure reaction is 28, rather than the infinitely connected long chains as assumed.

Based on equations (24) and (25), one can analyze possible errors in the determination of number average functionality of prepolymers of $fp \leq 2.0$. Table XVIII shows the effects of (i) loss of isocyanate due to side-reactions; (ii) the equivalent weight determination, which may be higher or lower than the actual value. The analysis, as summarized in Table XVIII, shows that:

(i) Loss of isocyanate causes a significant decrease in the apparent functionality value; i.e. an error of approximately -7% in f_p if the isocyanate loss is 5 mole %.

(ii) Higher apparent equivalent weight values cause a decrease in the apparent functionality, by approximately the same degree; i.e. deviation of +10% in $(EW)_{app.}$ causes error of -9% in f_p. Lower apparent equivalent weight does not affect the functionality value appreciably; however, it does lower the degree of polymerization, and therefore may cause branching rather than gel formation.

The above analysis indicates that a more accurate functionality determination can be made (1) if the molar ratio of isocyanate to alcohol (n_{NCO}/n_{OH}) is one or slightly higher, and (2) if the deviation in the equivalent weight determination is such that the apparent value is the same or slightly lower, but not higher. Since atmospheric moisture is impossible to avoid, unless one uses a dry box, the use of a slight excess of isocyanate may be a prudent approach.

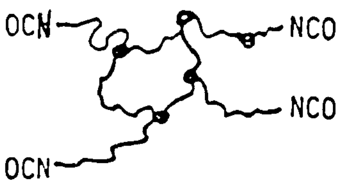
TABLE XVIII. % ERROR IN FUNCTIONALITY VALUE DUE TO IMBALANCE IN STOICHIOMETRY AS CALCULATED FROM EQUATIONS (24) & (25) (FOR $\bar{f}_p < 2.0$)

	True $\overline{E.W.}$	True $\bar{f}_p$	Deviation in exp. $\overline{E.W.}$ value	Loss of NCO, (mole %)	$\bar{f}_{app}$	Error in $\bar{f}_p$
I.	500	1.80	0	5%	1.69	- 6.3%
			0	10%	1.56	-13.3%
			+10%	0	1.64	- 8.8%
			-10%	0	1.82(24)*	+ 1.1%
II.	1000	1.99	0	5%	1.88	- 5.6%
			0	10%	1.75	-12.1%
			+10%	0	1.81	- 9.0%
			-10%	0	1.991(19)*	0%
	1000	1.80	0	5%	1.69	- 6.1%
			0	10%	1.56	-13.3%
			+10%	0	1.64	- 8.9%
			-10	0	1.82(24)*	+ 1.1%
	1000	1.65	0	5%	1.54	- 6.6%
			0	10%	1.41	-14.5%
			+10%	0	1.50	- 9.1%
			-10%	0	1.68(29)*	+ 1.8%
III.	2000	1.80	0	5%	1.69	- 6.1%
			0	10%	1.41	-14.5%
			+10%	0	1.64	- 8.9%
			-10%	0	1.82(24)*	+ 1.0%
		1.65	0	5%	1.54	- 6.7%
			0	10%	1.41	-14.5%
			+10%	0	1.50	- 9.1%
			-10%	0	1.68(29)*	+ 1.8%

---

* ( ): Degree of polymerization

However, one of the problems of excess isocyanate in the cure system, is chain terminations due to imbalance in stoichiometry as shown below.



An ideal elastomeric network is based on an infinite network formation, i.e. $\overline{DP} = \infty$. The polymeric network with $\overline{DP} = 20$ may act as a branched polymer rather than an elastomer. It is difficult to predict what should be the practical limiting value for $\overline{DP}$, in order for the binder to behave like an elastomer. This has to be evaluated by experiments such as swelling in suitable solvents and modulus variations. A preferable method of detecting the "gel" point would be to utilize a "dynamic mechanical analyzer" which measures the resonance frequency curves against temperature of the cured samples. If the polymer undergoes crosslinking, the modulus remains the same or increases with increasing temperature, whereas the modulus of non-crosslinked polymer, i.e. linear or branched polymer, will decrease with increasing temperature (Fig.14).(26)

Percent errors in the functionality determination in calculated Table XVIII were evaluated experimentally using polycaprolactone, PCP-0240, and polyethylene glycol, PEG 4000. A semi-micro approach was used, where about 1.0g of polymer samples were required for a duplicate determination (Experimental V-B-(3)). Effects of (i) imbalance in NCO/OH stoichiometry, (ii) higher or lower apparent equivalent weight determination due to an experimental error were examined (Tables XIX and XX).

FIGURE 14. LOG E (10) VERSUS TEMPERATURE FOR CRYSTALLINE ISOTACTIC POLYSTYRENE, FOR POLYSTYRENE SAMPLES A AND C, AND FOR LIGHTLY CROSS-LINKED ATACTIC POLYSTYRENE.

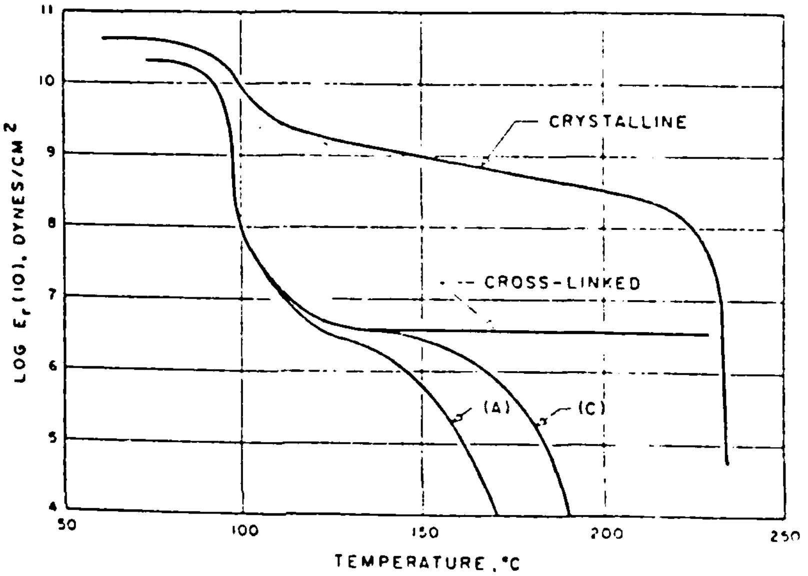


TABLE XIX. FUNCTIONALITY DETERMINATION OF PCP-0240 BY GEL FORMATION

PEG 4000 (1690) IN 50% CYCLOHEXANONE

(EW)app	+10% (1800)	0% (1690)				-10% (1520)	
f(app) xs. HDI*	0%	-5%	0%	+3%	+5%	0%	+4%
1.87 (+1.1%)	-	-	no	-	no	-	-
1.85 (0%)	-	-	yes(12) yes(12)	yes(12) yes(12)	yes(11) yes(11)	-	-
1.83 (-1.1%)	-	-	yes(8) yes(8)	yes(7) yes(7)	yes(6) yes(6)	no	-
1.82 (-1.6%)	no no	no	-	yes(5)	yes(4)	no	-
1.81 (-2.2%)	no no	no	yes(5)	-	yes(6) yes(6)	yes(5)	yes(4)
1.79 (-3.2%)	yes(8) yes(8)	no	yes(6) yes(5)	-	yes(5) yes(5)	yes(5)	yes(5)
1.73 (-6.5%)	yes(5)	no	-	-	-	-	-
1.71 (-7.6%)	yes(6)	yes(7)	-	-	-	-	-

yes = gelled; no = did not gel

( ) = app. swelling ratio, Vs/Vo

* hexamethylenediisocyanate

TABLE XX. FUNCTIONALITY DETERMINATION OF PEG 4000 BY GEL FORMATION

PCP-0240 (980) IN 50% CYCLOHEXANONE

$(EW)_{app}$	+10% (1080)	0% (980)			-10% (880)
f_{app} \ xs. HDI*	0%	-5%	0%	+5%	0%
1.96 (+4.6%)	-	-	no no	no no	no no
1.92 (+2.4%)	no	-	no	yes(9) no no	no yes(14)
1.90 (+1.4%)	no	-	no	no yes(8) no	yes(8) yes(8)
1.87 (0%)	yes(10) yes(10)	no no	yes(8) yes(8) yes(8)	yes(8) yes(8)	yes(8) yes(8)
1.83 (-2.1%)	yes(8)	no	yes(8) yes(9) yes(8)	yes(8) yes(8)	-
1.81 (-3.3%)	-	no	yes(8)	-	-
1.77 (-5.6%)	-	yes(68) no no	-	-	-
1.71 (-10%)	yes(8)	yes(41)	-	-	-

yes = gelled; no = did not gel

( ) = app. swelling ratio, V_s/V_o

* Hexamethylenediisocyanate

4.2.3.2.1 Effect of imbalance in stoichiometry

(i) PCP-0240: If one assumes the true functionality of PCP-0240 to be 1.87 (Table XIX), the molar NCO/OH = 1.05, i.e. the use of 5 mole % excess isocyanate, gives an apparent functionality value of 1.92, a deviation of +2.4%. The molar NCO/OH = 0.95, i.e. the use of 5 mole % less isocyanate gives the value, 1.77, a deviation of -5.6%.

(ii) PEG 4000: If one assumes the true functionality of PEG 4000 to be 1.85 (Table XX), the use of 5 mole % excess isocyanate would cause a deviation of less than 1.1%. Using 5 mole % less isocyanate causes a deviation of -7.6%. The experimental results for both PEG and PCP, therefore, are consistent with the predicted % errors based on theory (Table XVIII).

4.2.3.2.2 Effect of experimental errors in equivalent weight determination

It is assumed that true equivalent weights of PCP-0240 and PEG 4000 are 980 and 1690, respectively, and true functionalities 1.87 and 1.85 respectively.

If $(EW)_{app}$ is 10% less than $(EW)_{true}$, the deviation in the functionality value caused by the experimental error in the equivalent weight determination is +2.4% for PCP (Table XIX) and +2.2% for PEG 4000. If $(EW)_{app}$ is 10% greater than $(EW)_{true}$, the deviations are 0% for PCP and -3.2% for PEG 4000. The experimental errors are, in general, less than those predicted in Table XVIII, and lie within ±3%.

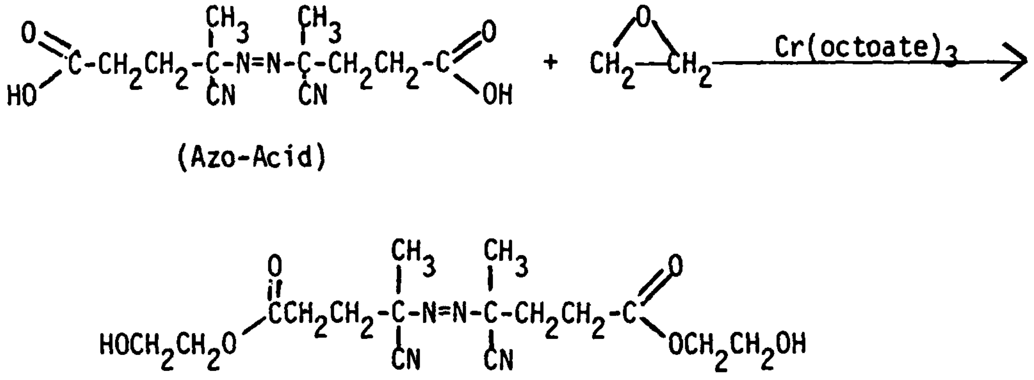
The error analyses based on theory (Table XVIII) and experimental data (Tables XIX and XX) for the determination of "effective" functionality by incipient "gel" formation, as discussed above, indicate that this is a more reliable and practical method than Method I, i.e. by $\overline{M_n}$/EW. The highest percent error would be expected if the NCO/OH ratio is less than 1.0. Conversely, a higher NCO/OH ratio (e.g., 1.05) does not cause a significant deviation in the functionality determination. Hence, if one uses a molar NCO/OH ratio of 1.05 one should be able to obtain functionality values within ±3% of the true value, assuming that experimental errors in the equivalent weight determination are within ±10%. The use of 5 mole % excess isocyanate, therefore, is recommended, since some isocyanate may be lost via side-reactions with water, homopolymerization, etc.

5.0 EXPERIMENTAL

5.1 SYNTHESIS OF HYDROXY-TERMINATED DINITROPROPYL ACRYLATE POLYMERS

5.1.1 Synthesis and Characterization of Azo-OH

The hydroxy group containing azo-initiator was synthesized by esterification of 4,4'-azobis-(4-cyanovaleric acid):



(Azo-Acid)

(Azo-OH)

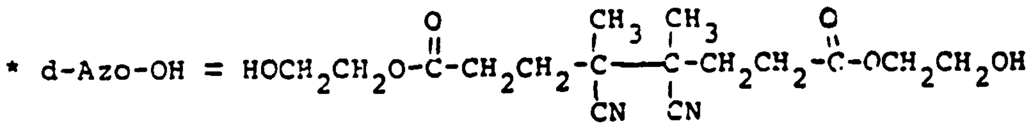
Azo-acid, 65% in water, was purchased from Aldrich Chemicals, and chromium octoate, 76% in octanoic acid, was acquired from Cordova Chemical Company of the Aerojet Corporation. It was determined that increasing the concentrations of the reactants and the catalyst increases the reaction rate. The reaction temperature was kept at 45°C in order to avoid appreciable decomposition of the azo-compound. The concentration of chromium octoate was kept at the lowest possible level, since a method for its complete removal from the product has not been found.

Azo-OH is difficult to purify since it is unstable. Various extraction methods, column chromatography and recrystallization processes failed

TABLE XXI.

EQUIVALENT WEIGHT AND ELEMENTAL ANALYSIS OF Azo-OH

Row		OH eq wt	% C	% H	% N	% Cr
1.	Cal'd assuming 100% Azo-OH	184.2	52.17	6.57	15.21	0.00
2.	Experimental values of Azo-OH sample	189	52.89	6.90	13.72	0.40
3.	Cal'd values assuming that sample consists of 96.3% Azo-OH and 3.7% Cr(octoate)$_3$	191.3	52.45	6.68	14.65	0.40
4.	Cal'd values assuming sample consists of 90.6% Azo-OH, 5.7% d-Azo-OH,* 3.7% Cr-octoate	190.4	52.69	6.70	13.72	0.40
5.	% dev. based on the cal'd values in Row 4.	0.74	-0.38	-3.0	0	0



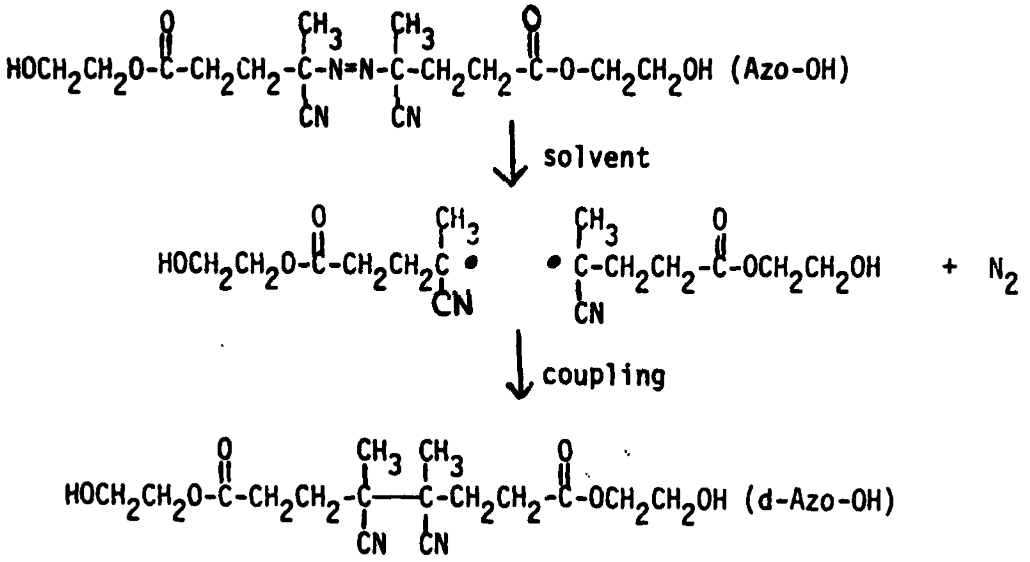
* d-Azo-OH = $HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\overset{CH_3}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH$

to remove chromium octoate from the product. The presence of chromium octoate, however, has no detrimental effect on the free-radical polymerization of DNPA and on the subsequent urethane cure reaction. The detailed procedure is as follows:

To a solution of 20.2g Azo-acid (65% purity in H_2O), and 1.0g chromium octoate (76% purity in octanoic acid) in 80 ml THF, 15 ml of liquid ethylene oxide was added through a condenser cooled with circulating ice water. The reaction mixture was stirred for nine (9) hours at 45°C and then allowed to stand overnight at room temperature.

The reaction mixture was concentrated using a rota-vac at 40°C with an aspirator vacuum until most of the THF had been removed. The residue was dissolved in 50 ml CH_2Cl_2 and washed with 2 x 50 ml of a 10% aqueous $NaHCO_3$ solution followed by a water wash. The organic solution was dried over 13X Molecular Sieves. The solvent was removed via a rota-vac at 30°C, initially with an aspirator vacuum and finally with an oil pump vacuum. The green amorphous product weighing 16.8g (close to 100% yield) was obtained. Several attempts at further purification to remove chromium octoate were not successful. Purification techniques used were (1) extraction methods using various solvents, (2) column chromatography using various absorbents, and (3) recrystallization using various solvents.

In order to minimize the batch-to-batch variation, six batches of Azo-OH were synthesized and combined. The combined product was characterized by an infrared method and by elemental analyses. The calculated analytical data for 100% pure Azo-OH and the experimental values for the combined Azo-OH sample are shown in Rows 1 and 2 of Table XXII. If we assume that the chromium is present in the form of chromium octoate, the Azo-OH sample is contaminated by 3.71% of chromium octoate. The recalculated values for the Azo-OH sample accounting for the presence of 3.71% chromium octoate, are shown in Row 3 of Table XXII. There is still an appreciable discrepancy between the calculated and experimental values of % N. This may be because of the decomposition of Azo-OH during its synthesis and purification. Azo-compounds are known to undergo decomposition and the resulting "caged radicals" mainly undergo a coupling reaction as shown below:



$$HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2OH \text{ (Azo-OH)}$$

$$\downarrow \text{solvent}$$

$$HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2CH_2\underset{CN}{\overset{CH_3}{C}}\bullet \quad \bullet\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH \quad + \quad N_2$$

$$\downarrow \text{coupling}$$

$$HOCH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\overset{CH_3}{C}}-\underset{CN}{\overset{CH_3}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH \text{ (d-Azo-OH)}$$

If one assumes that the discrepancy between the calculated value of % N in Row 3 and the experimental value is due to the presence of d-Azo-OH, our Azo-OH sample contains 90.6% Azo-OH, 5.7% d-Azo-OH and 3.7%

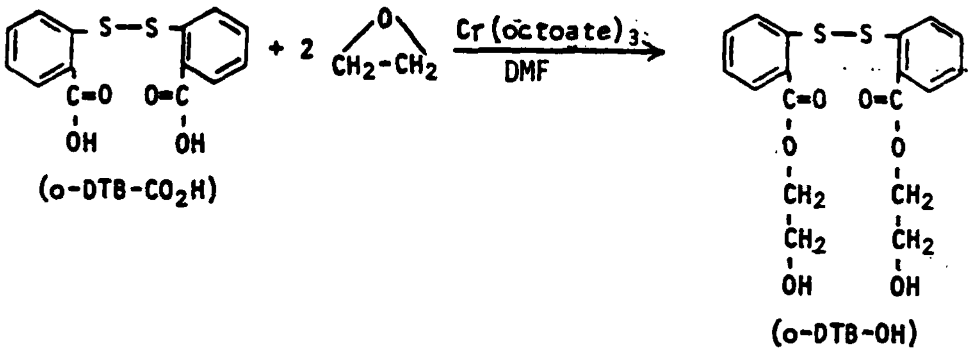
TABLE XXII. VARIATIONS DUE TO THE DIFFERENCE IN THE END-POINT DETERMINATION

Polymers	Methods	Equivalent Weight End-Point Determination By Indicator	Equivalent Weight End-Point Determination By Electrode
PCP-0240	AA/NMIM	967, 990	998, 1000
	PA/PY	967, 980	970, 973
NPGA	AA/NMIM	968, 1030	1040, 1050
	PA/PY	-4090	-6970
Carbowax	AA/NMIM	1730, 1610	1760, 1710
	PA/PY	-2700	-3320
PPG	AA/NMIM	1110, 990	1130, 1160
	PA/PY	-3525	-6060
B2000	AA/NMIM	1000	1060
	PA/PY	1170, 1260	1030, 1090
Teracol	AA/NMIM	408	420
	PA/PY	-5204	-6940
R-45M	AA/NMIM	1150	1190
	PA/PY	1390, 1350	1240 (?)

chromium octoate. The recalculated values based on this composition in Row 4 of Table XXI show good agreement with the experimental results, with the exception of % H.

5.1.2 Synthesis and Characterization of o-DTB-OH

o-DTB-OH was synthesized by the following reaction using chromium octoate as a catalyst and DMF as a solvent:



o-DTB-CO_2H was purchased from Aldrich Chemicals and chromium octoate, 76% in octanoic acid, was acquired from Cordova Chemical Company of the Aerojet Corporation.

o-DTB-CO_2H, 30.6g (0.1 mole) and chromium octoate (76% purity in octanoic acid), 0.6 g. were dissolved in 84 ml of dimethylformamide in a 200 ml 3-neck flask equipped with a stirrer, thermometer, and a condenser cooled with circulating ice-water. Nitrogen was bubbled into the solution for 15 minutes at room temperature and the reaction flask was heated to 45°C with nitrogen still bubbling. The nitrogen inlet was disconnected and 30 ml

(0.6 mole) of liquid ethylene oxide was added quickly through the ice-cooled condenser, followed by sealing the reaction system with a balloon. The reaction mixture was stirred for seven hours at 43-45°C (the reflux temperature), and then allowed to stand overnight at room temperature.

Ethylene oxide was removed using a rota-vac at 40°C with an aspirator vacuum, and the residue was poured into 800 ml of ice-cold 5% $NaHCO_3$ solution with stirring. The precipitated crude product was suction filtered and redissolved in a mixture of 50 ml DMF and 250 ml CH_2Cl_2. (A small amount of DMF appears to aid the solubility of the crude product in CH_2Cl_2). The organic solution was washed twice with 175 ml of cold 10% $NaHCO_3$ solution and then twice with 300 ml of ice-water. The dried organic layer was subjected to rota-vac under vacuum at 30-35°C to remove CH_2Cl_2, and the resulting residue was washed with benzene to remove chromium octoate. The almost colorless, amorphous solid was dried over P_2O_5 in vacuo overnight. The product, o-DTB-OH, weighing 19.6 g (50% yield) showed the following characteristics:

Melting Point: 105-112°C
OH-Equivalent Weight by IR Method: 201 (theoretical: 197)

5.1.3 Synthesis of Dinitropropyl Acrylate (DNPA)

Into a 2-liter, 3-neck round bottom flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser were added 2.2 moles (158.8 g) acrylic acid, 2.0 moles (500 g) of a 60% dinitropropanol in ethylene dichloride (833 g of the solution) and 3.4 g hydroquinone. The reaction mixture was heated to approximately 40°C, and the rapid addition of polyphosphoric acid (400 g) was begun. The exothermicity of the reaction raised the reaction temperature to about 60°C at the end of the addition. The reaction mixture was stirred for six more hours at 60-65°C.

After stirring overnight at room temperature, the reaction mixture was poured slowly with stirring into an ice-solution containing 280 g NaOH and 800 g H_2O. The black precipitate was filtered off and the crude reaction mixture was extracted with 4 x 300 ml of CH_2Cl_2. The combined CH_2Cl_2 solution was washed with 400 ml of a cold 3% aqueous NaOH solution (pH = 10) and then with 2 x 500 ml of 10% NaCl solution. The final water wash had a pH of 5. The methylene chloride solution was dried over anhydrous $MgSO_4$, and the solvent removed on a rota-vac at 40°C with an aspirator vacuum. The resulting liquid weighed 300 g (crude yield = 81%). The crude product is stored in a refrigerator with 0.1% hydroquinone, and is purified immediately prior to its use. Hydroquinone is removed by washing the 1/1-crude DNPA/CH_2Cl_2 with a cold, 3% aqueous NaOH solution followed by a 5% NaCl solution wash. The methylene chloride solution is dried over anhydrous $MgSO_4$ solution and methylene chloride is removed via a rota-vac at 30°C with an aspirator vacuum. The residue is distilled at 90°C/0.6 mmHg using a wiped-film molecular still. A detailed analysis of product composition was presented in the previous report.(1)

5.1.4 An Example of Solution Polymerization of DNPA

All the DNPA polymers in this study were prepared as follows: DNPA, 20.40 grams, Azo-OH, 2.49 grams and HEDS, 20.00 grams, were placed into a 100 ml three-neck round bottom flask, equipped with an overhead stirrer, and a reflux condenser. The third neck of the flask was covered with a rubber sleeve septum and nitrogen gas was passed through the system for 20 minutes. During this time the solvent was also degassed by passing nitrogen through 35 ml of solvent in a 50 ml flask, which was also sealed with a rubber sleeve septum, with a syringe needle as an outlet. Upon completion of this degassing, 25.0 ml of the solvent was removed from the flask with a syringe and injected into the three neck reaction vessel. The system was made air tight, and a slight nitrogen pressure was maintained through the condenser.

The reaction mixture was heated rapidly, over a 3-5 minute period to the reaction temperature of 60°C, with constant stirring. The reaction mixture was held at this temperature, ±2°C, for the duration of the reaction. After the desired reaction time, the mixture was cooled with an ice-bath and simultaneously quenched with 10 ml of methanol containing 1% hydroquinone.

5.1.5 Purification of Poly-DNPA

Approximately 50% of the acetone was removed from the reaction mixture with a rotary evaporator at 35-40°C. The resulting dispersion was poured slowly into 300 ml of ice cold methanol, with vigorous stirring. The resulting fine precipitate of poly-DNPA was allowed to settle while cooling in an ice bath. The methanol was decanted and the polymer was washed with another 150 ml of cold methanol. The polymer was then dissolved in a minimum amount of methylethyl ketone, and centrifuged to remove any solid material which may have been present. This solution was then poured slowly into 800 ml of ice cold water, with constant vigorous stirring. The resulting polymer was washed three times with 400 ml portions of cold water. This washing was followed with a soaking in 300 ml of methanol for thirty minutes. The polymer was dried under vacuum, overnight, and then ground into a fine powder. This powder was soaked again in 150 ml of methanol overnight. The resulting polymer was dried under vacuum over phosphorous pentoxide, to constant weight.

5.1.6 Kinetic Study of Polymerization

Kinetics of the polymerization reaction described above was followed by measuring the ratio of DNPA to poly-DNPA in the reaction mixture. A Waters model 6000A HPLC was used with six microstragel GPC columns of 100, 2 x 500, 2 x 1000, and 10,000 Å. A calibration curve was created by preparing 2% solutions of DNPA, poly-DNPA and HEDS or o-DTB-OH in tetrahydrofuran (THF) containing 0.1% hydroquinone (HQ) at various DNPA/poly-DNPA ratios. HEDS or o-DTB-OH had to be included in the calibration samples because HEDS, o-DTB-OH and DNPA had overlapping GPC peaks. Since HEDS or o-DTB-OH was used as a chain transfer agent, it was assumed that its concentration remained the same throughout the polymerization. Samples for analysis of polymerization kinetics were obtained by removing 1 ml of samples through the septum at various times during the reaction and quenching with approximately 9 ml of ice-cold THF containing 0.1% HQ. Typical GPC scans of the calibration samples and of the kinetic samples are shown in Figs. 15, 16 and 17.

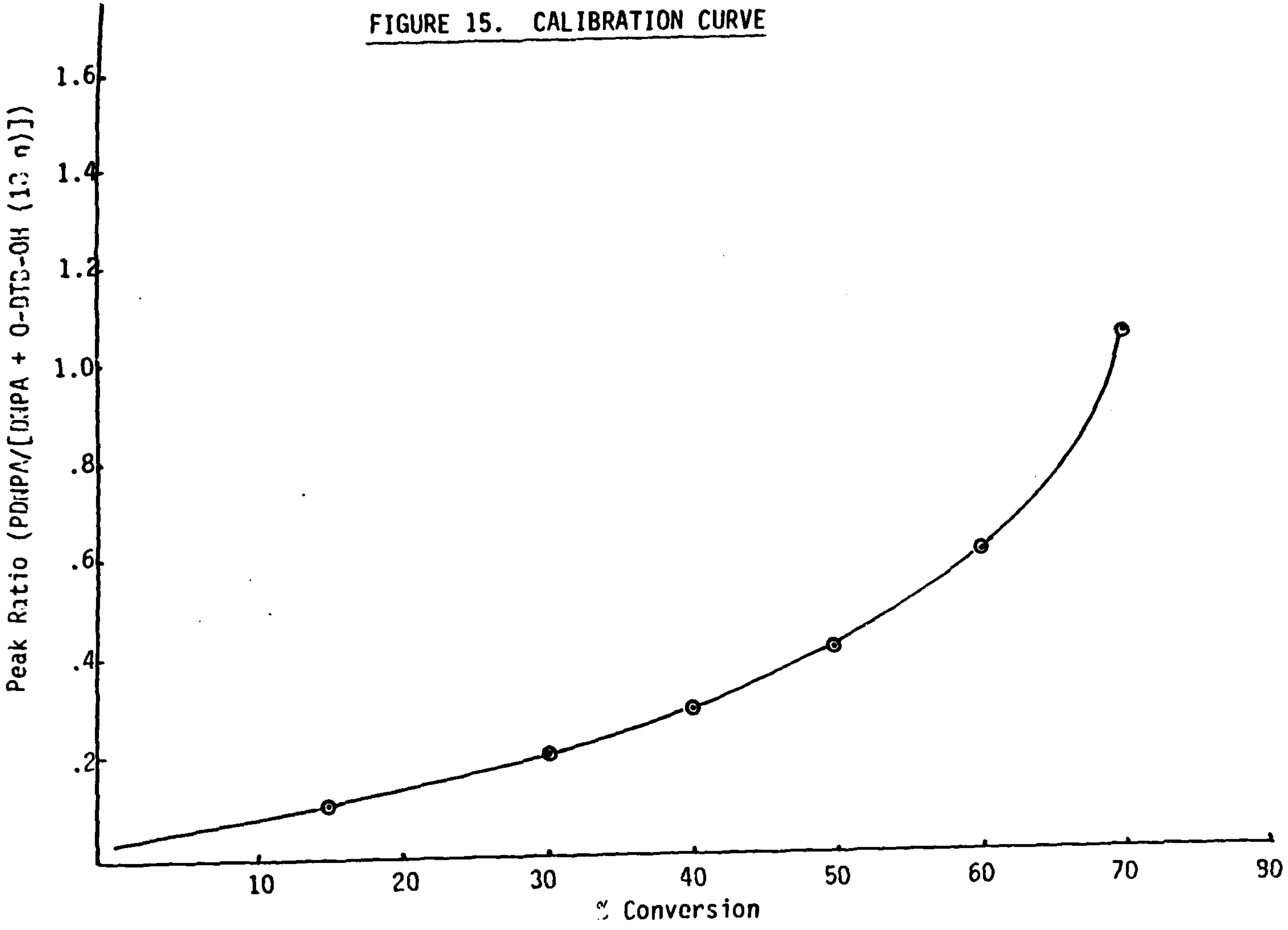


FIGURE 15. CALIBRATION CURVE

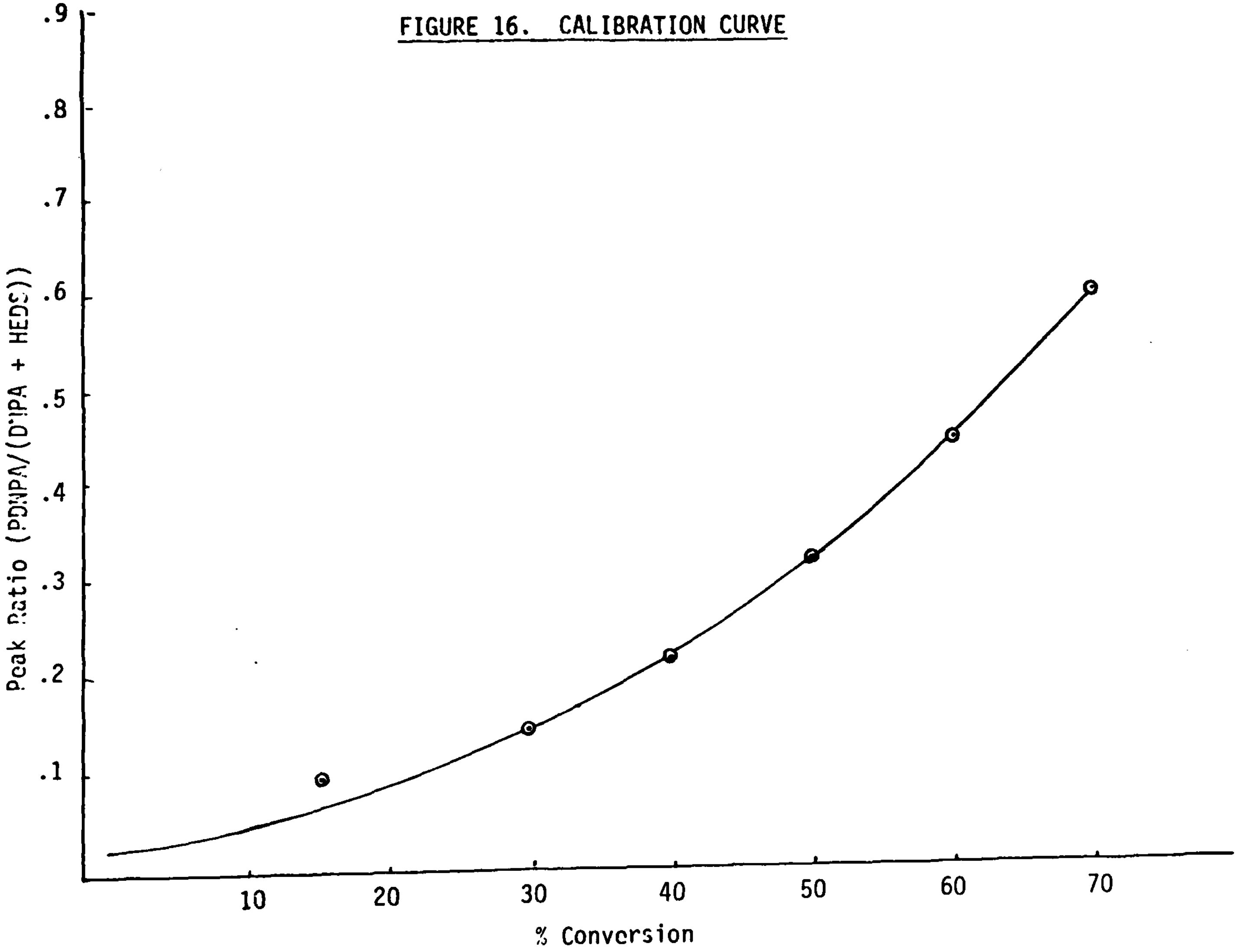
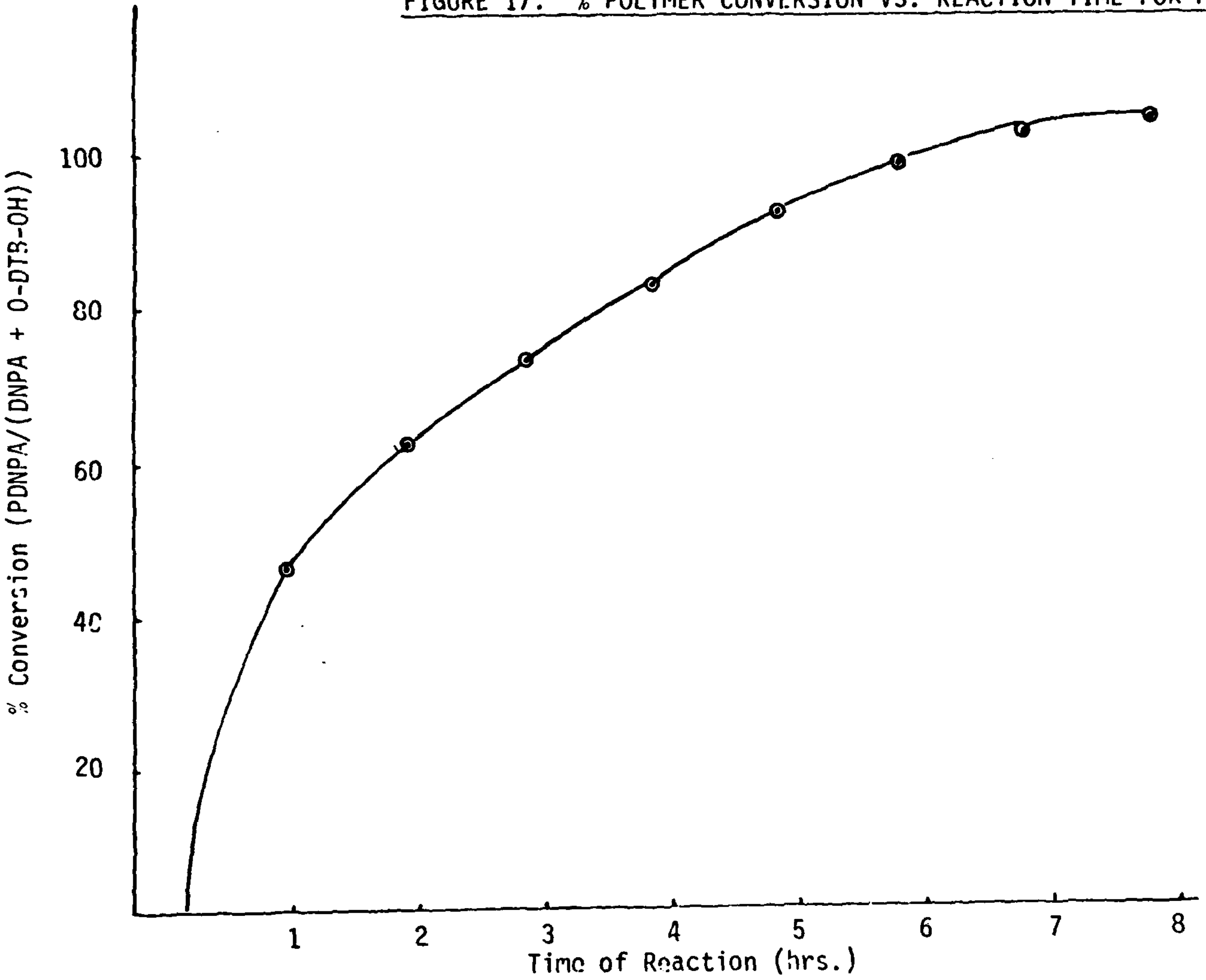


FIGURE 16. CALIBRATION CURVE

FIGURE 17. % POLYMER CONVERSION VS. REACTION TIME FOR M-13



5.2 IMPROVED CHARACTERIZATION OF HYDROXY-TERMINATED PREPOLYMERS

5.2.1 Evaluation of Chemical Methods Utilized for Determination of OH-Equivalent Weight

5.2.1.1 AA/NMIM Methods

Method (A)-1(15): A three meq. sample of dried polymer was weighed into a 250 ml Ehrlenmeyer flask containing 20 ml of anhydrous dichloromethane. Exactly 4.00 ml (6 meq) of AA/dichloromethane reagent and 4 ml of NMIM were added, and the mixture was purged with gaseous nitrogen, sealed, and placed in a thermostated bath at 45°C (with mechanical agitator) for 15 min. The excess AA was hydrolyzed with 3 ml of water, and the reaction flask was heated an additional 5 min. The molar ratio of anhydride to alcohol was about 2:1. After cooling, 200 ml of chloroform and 35 ml of methanol were added, and the reaction mixture was titrated with a 0.5 N KOH solution. A pH meter was used, and the end point was approximated graphically. It was noted that the glass electrode must be well within the aqueous phase for accurate readings. Thymol blue indicator was used, but its end point determination was difficult.

Method (A)-2: The same as (A)-1 except the reaction time was 0.50 hours.

Method (A)-3: The same as (A)-1 except the reaction flask was heated over steam bath.

5.2.1.2 PA/PY Methods

Method (B)-1(16): A three meq sample of dried polymer was weighed into a 100 ml round bottom flask and 50 ml of phthalic anhydride stock solution (0.6 N) in anhydrous pyridine was added. This mixture was refluxed at 115°C in a dry system for one hour, and then cooled to room temperature. Thirty ml of water was then added to hydrolyze the excess anhydride. The molar ratio of anhydride to alcohol was approximately 10:1. After hydrolysis of the excess anhydride and cooling to room temperature, the reaction mixture was titrated to a phenophthalein end point with standard NaOH solution (0.5 N). The end point was approximated graphically by use of a pH meter.

Method (B)-2: The same as (B)-1 except the reaction time was 2.0 hours.

Method (B)-3(18): Carefully pipet 25 ml of phthalic anhydride (PA)-pyridine (PY) solution (112 g PA/800 ml PY) into a 200 ml pressure bottle. Purge the bottle for 2 minutes with nitrogen and weigh in the polymer sample so that the molar ratio of alcohol (polymer) to PA is approximately 1:2. Stopper the pressure bottle and heat the bottle for two hours at 98 ± 2°C.

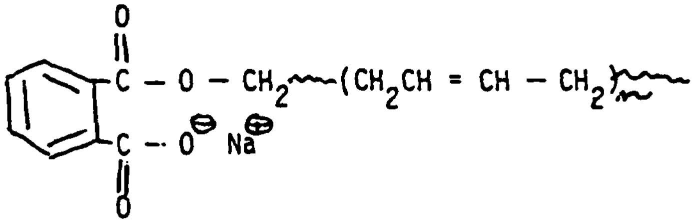
Allow the bottle to cool to room temperature before opening, and then titrate the contents as in (B)-1.

5.2.1.3 Titration of Carboxylic Acids

Variations in the values of equivalent weight of the prepolymers due to the difference in the end-point determinations are shown in Table XXII.

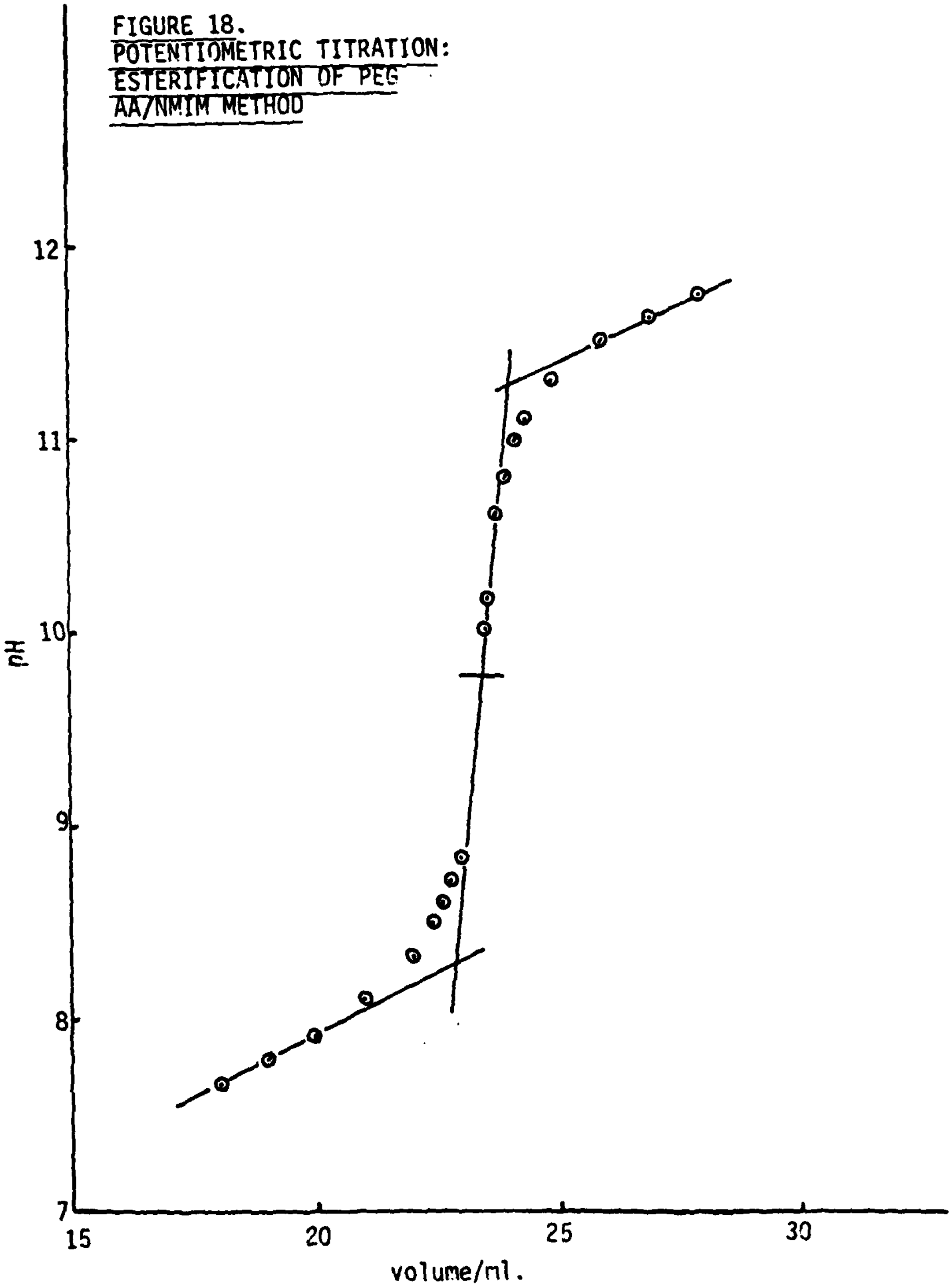
Potentiometric titration appears to be more reproducible than the end-point determination using phenolphthalein as an indicator, if the polymer-attached sodium carboxylates are partially soluble in water, or if AA was used (Figs. 18 and 19).

A difficulty arises when a completely water-insoluble polymer such as R-45 is used with PA. The half-ester (the structure below) still is insoluble in water, and consequently, the titration using a pH meter becomes difficult (Fig. 20).



If AA was used in place of PA, the half-ester is no longer present, and all the acetic acid can be readily titrated in the aqueous phase (Fig. 21).

FIGURE 18.
POTENTIOMETRIC TITRATION:
ESTERIFICATION OF PEG
AA/NMIM METHOD



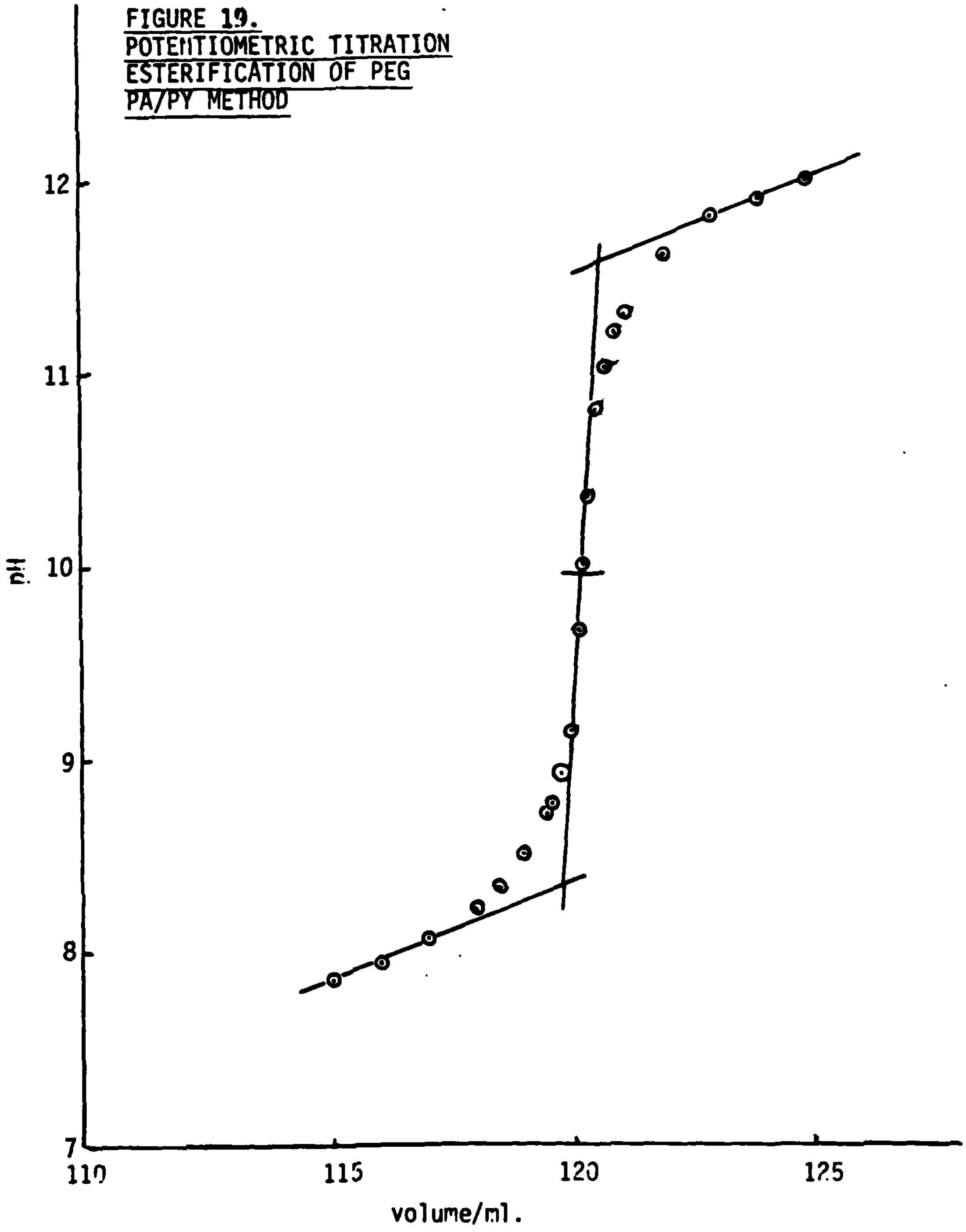


FIGURE 19.
POTENTIOMETRIC TITRATION
ESTERIFICATION OF PEG
PA/PY METHOD

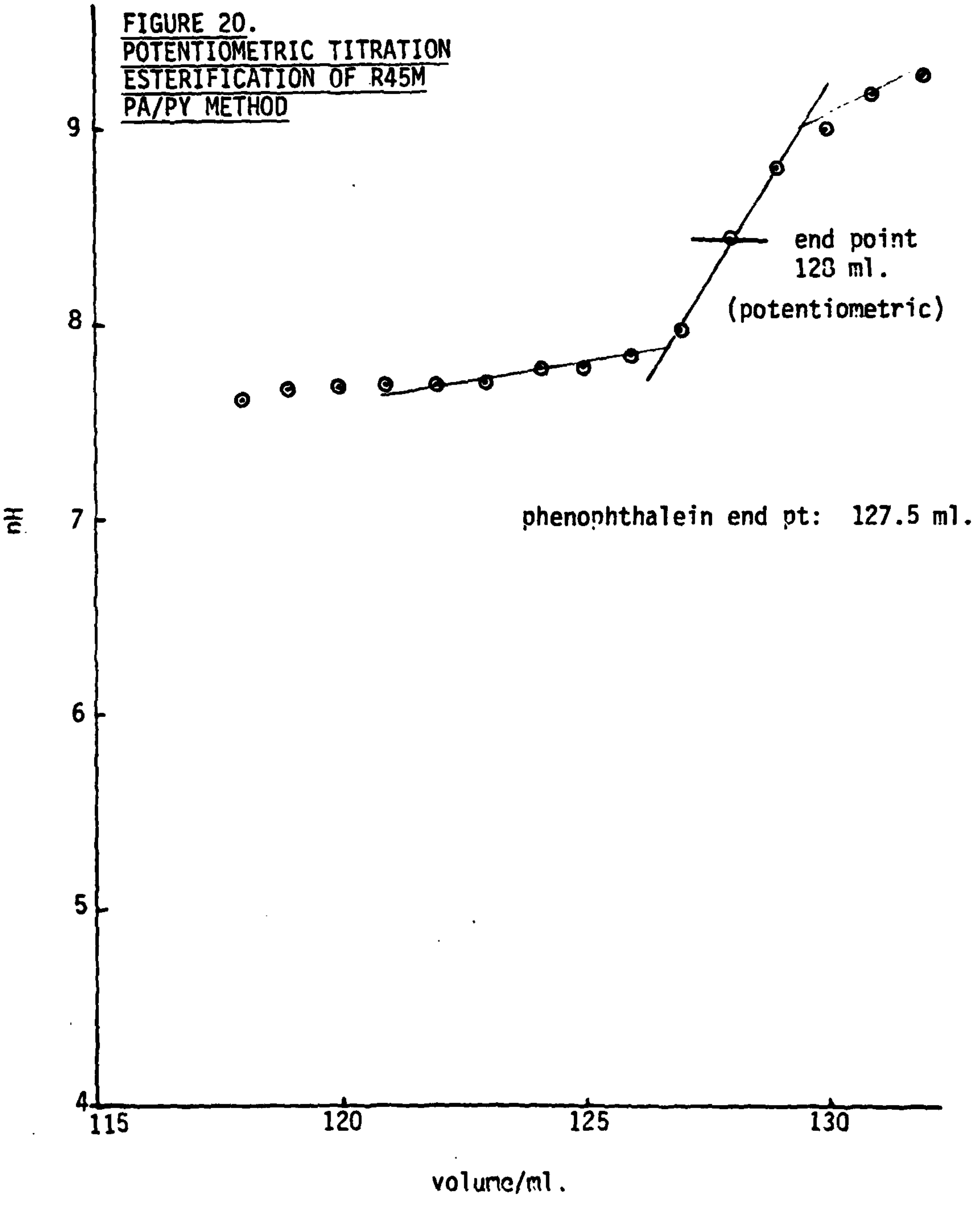
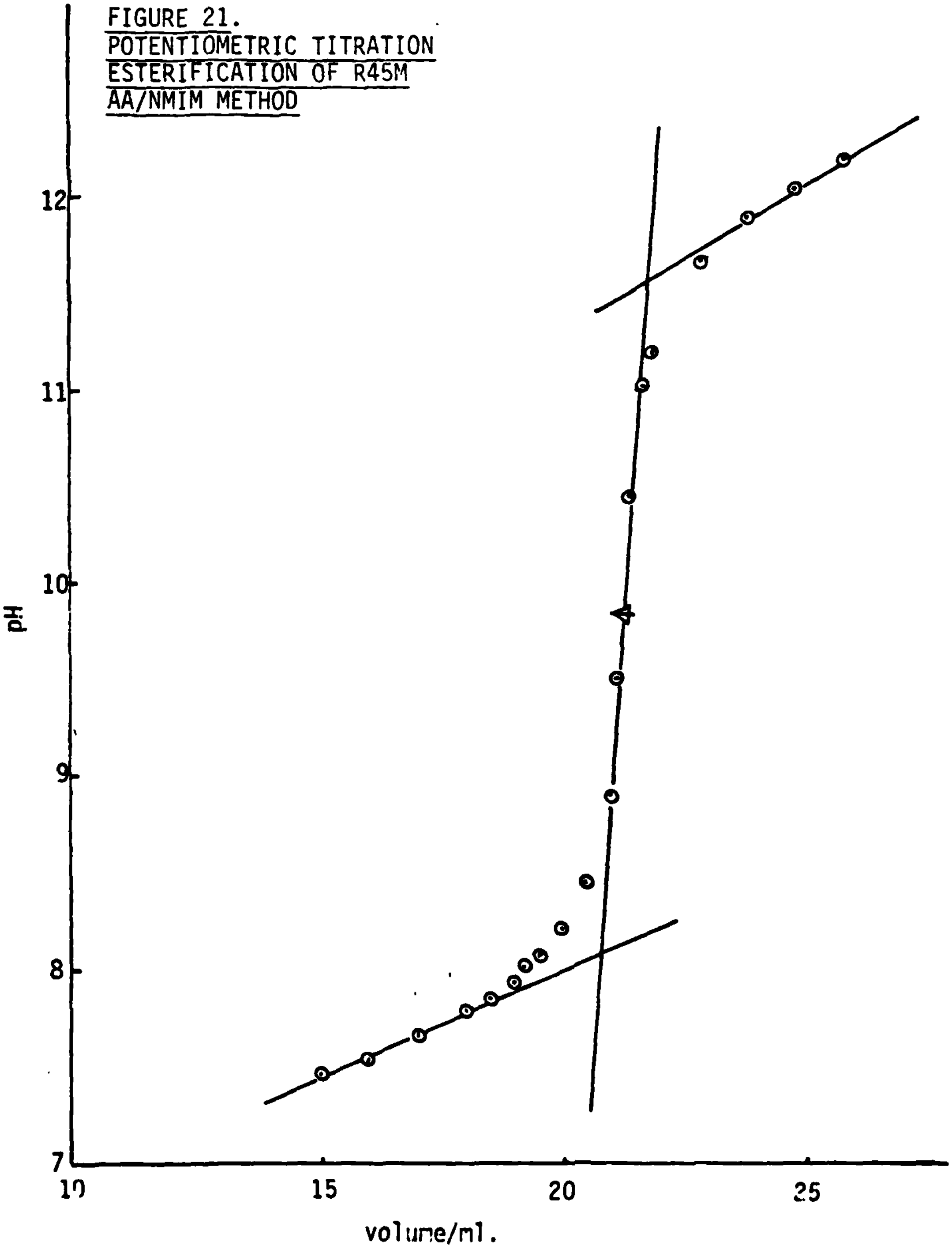


FIGURE 20.
POTENTIOMETRIC TITRATION
ESTERIFICATION OF R45M
PA/PY METHOD

FIGURE 21.
POTENTIOMETRIC TITRATION
ESTERIFICATION OF R45M
AA/NMIM METHOD



5.2.2 Procedure for Determination of Intrinsic Viscosities of Prepolymer Solution in Tetrahydrofuran

1. Glassware Calibration

   1.1 Clean a 10 ml volumetric flask and dry at 105°C for 1 hour. Cool in a dry box and equilibrate to room temperature.

   1.2 Determine the tare weight of the flask.

   1.3 Fill the flask to the mark with water at 26°C.

   1.4 Determine the apparent weight of the water at 26°C.

   1.5 Calculations:

$$\text{Volume @ } 26^{\circ}\text{C} = \text{wt.(g)} \times \frac{1}{\text{density(g/ml)}} \text{ at } 26^{\circ}\text{C}$$

2. Determination of Intrinsic Viscosity

   (Note: All glassware must be clean, dry, and calibrated prior to use.)

   2.1 Determine the tare weight of a clean, dry, 10 ml volumetric flask that has equilibrated to room temperature in a dry box.

   2.2 Weigh accurately 50 mg of the prepolymer into the flask. The final concentration will be 0.5 g/dl.

   2.3 Prepare a minimum of four (4) concentrations in the range of 0.5 g/dl to 1.2 g/dl.

   2.4 Dissolve the polymer in "dry" THF,* but do not bring the flask to the mark. Allow a minimum of 2 hrs for the polymer to become completely solvated.

   2.5 Prior to viscometry determinations, equilibrate the solutions to 26.0°C in a water bath and bring to volume with THF also at 26.0°C.

   2.6 Fill a clean, dry viscometer with "dry" THF and equilibrate to 26.0°C for 10 minutes. Adjust the position of the viscometer in the water bath such that the capillary is vertical. Determine the efflux time of the solvent (t_o). Repeat the determination at least three times.

   2.7 Remove the solvent and dry the viscometer with N_2(g).

   2.8 With the use of the filter apparatus and syringe, deliver the prepolymer solution into the viscometer. Equilibrate to 26.0°C for 10 minutes. Secure the capillary in the vertical position as determined by the bubble leveler. Determine the efflux time of the solution(t_1). Repeat the determination at least three times.

   2.9 Remove the solution from the viscometer and rinse repeatedly with THF to insure that no polymer is remaining in the capillary. Dry the viscometer with N_2(g).

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* "Dry" THF = HPLC grade THF kept over MS4Å.

2.10 Repeat steps 2.8 and 2.9 for the remaining solutions.

2.11 From the efflux times of the solvent (t_0) and the prepolymer solutions at four (4) concentrations (t_1 through t_4), calculate the specific viscosity η_{sp}, and η_{sp}/c. The intrinsic viscosity, $[\eta]$, is determined from the y-intercept of the plot. For the polymers with molecular weight less than 20,000, use the average weight for $[\eta]$.

3. Calculations

3.1 Specific Viscosity η_{sp}:

$$\eta_{sp} = (t - t_0)/t_0$$

5.2.3 Determination of Number Average Functionality of Prepolymers of fp < 2.0

The functionality of DNPA polymers was determined using the technique developed by Oberth (25) based on a cure study with an isocyanate. For polymers having functionality less than 2.0, an additional cross-linker, i.e., a polyol having a functionality greater than 2.0, has to be incorporated to achieve a "gel". Hence the general equation (1) can be rewritten as equation (2),

$$\sum_{i=1}^{n} \frac{(f_i-2)e_i}{f_i} = 0 \qquad (1)$$

$$\frac{(f_x-2)e_x}{f_x} + \frac{(f_p-2)e_p}{f_p} = 0 \qquad (2)$$

where f_x = functionality of polyol, $f_x > 2.0$

f_p = functionality of polymer, $f_p < 2.0$

e_x = equivalents/g of polyol

e_p = equivalents/g of polymer

or

$$f_p = 2/\left(1 + \frac{(f_x-2) \cdot e_x}{f_x \cdot e_p}\right) \qquad (3)$$

f_p was determined from equation (3) using polycaprolactone (PCP0310: eq wt = 294, f_x = 3.30) as the polyol and the stoichometric amount of HDI as the curing agent. Cyclohexanone was used as the solvent.

Typical cure formulations of PDNPA (P-12) having an equivalent weight of

2520 are:

(a) for $f_p = 1.71$:

0.277 meq. polymer (50% solution) : 0.9780 g
0.086 meq. PCP (50% solution) : 0.0491 g
0.278 meq. HDI : 0.0234 g
2 drops of 10% FeAA in dimethyl phthalate

(b) for $f_p = 1.76$:

0.215 meq polymer (50% solution) : 1.0803 g
0.075 meq PCP (50% solution) : 0.0443 g
0.290 meq HDI : 0.0244 g
2 drops of 10% FeAA in dimethyl phthalate

After curing overnight at 50°C, formulation (a) gave a gel, whereas (b) was still fluid. Hence the effective functionality of the polymer is between 1.71 and 1.76.

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7.0 APPENDIX

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Determination of Hydroxyl Concentrations in Prepolymers from the Infrared Absorption Band of Tetrahydrofuran-Associated Hydroxyl Groups

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The commonly used chemical methods for the quantitative determination of hydroxyl groups in prepolymers involve reactions with excess acid anhydride in the presence of base. These chemical methods require large sample sizes and frequently different chemical methods give different results depending on the type of prepolymers. Our recently developed physical method utilizes the strong infrared absorption band of tetrahydrofuran (THF)-associated hydroxyl groups at 3450 cm^{-1}. The hydroxyl concentration level of approximately 30 mequiv/L is low enough that the O–H groups are completely associated with the solvent (THF), and there are no apparent free or self-associated OH peaks. Variables such as temperature, concentration, bulk dielectric properties, and the structure of the alcohols have been studied to determine their effects on the characteristics of the THF-associated OH absorption peak. These studies show that the IR method has a general applicability. The OH equivalent weight values by this method compare well with those supplied by the vendors on a variety of commercial prepolymers. The molecules having OH equivalent weight as high as 3000 were analyzed using 1.0-mm solution cells. Those having the higher values could be analyzed if cells having longer pathlengths were used. Contrary to the chemical methods, the IR method requires (1) a very dry sample since small amounts of water interfere and (2) the sample to be completely soluble in THF.

Various prepolymers terminated with hydroxyl groups are commercially available for the production of urethane rubbers and plastics. Some of these prepolymers are also used in solid rocket propellant formulations for the formation of an elastomeric binder network through cure reaction with isocyanates. An accurate and reliable value of the hydroxyl content of the prepolymer is important, since the functionality determination of the polymer and the amount of the isocyanate needed for the cure reaction to form a favorable elastomeric network are based on the hydroxy equivalent weight of the prepolymer.

The most commonly used methods for the quantitative determination of hydroxyl groups in these prepolymers involve reaction with an excess amount of accid anhydride in the presence of a base catalyst (*1–4*). The excess anhydride is hydrolyzed after completion of the above reaction, and the carboxylic acid groups are titrated with a dilute KOH solution. These chemical methods have the following disadvantages in various degrees: (1) Duplicate analysis of the prepolymers requires 6–12 g of sample, depending on the OH equivalent weight; this amount is sometimes too large for experimental research samples. (2) Certain polymers require prolonged reaction time for complete reaction. (3) Different chemical methods (i.e., changes in acid anhydride, base catalyst, reaction time, and temperature) may give different values of the equivalent weight depending on the type of polymers. (4) Certain prepolymers are so insoluble in water that titration with a KOH solution becomes difficult even in the presence of an organic cosolvent (e.g., hydroxy-terminated polybutadiene polymers). (5) Prepolymers containing functional groups which undergo reaction with base cannot be analyzed by this chemical method.

Other chemical methods are also known. For example, the hydroxyl compound is allowed to react with an excess of butyl or phenyl isocyanate, ususally in the presence of a catalyst such as ferric acetylacetonate. After completion of the reaction, the excess isocyanate is converted to a derivative by urea by excess dibutylamine; the excess secondary amine is back-titrated with hydrochloric acid. This method also has the advantages listed above.

There appears to be a need for a physical method which is rapid and requires only a semimicroquantity of sample. This method could also be used to evaluate the chemical methods or vice versa. In this paper, an infrared study of hydroxyl groups based on the tetrahydrofuran-associated OH peaks is described and its application to the analysis of prepolymers is evaluated.

EXPERIMENTAL SECTION

The infrared work was performed with a Perkin-Elmer Model 621 double beam spectrometer. Absorbance measurements were made by using sets of calibrated 0.5-mm and 1.0-mm KBr and BaF_2 cells. The spectrometer was operated at a scan time of 32 min for full frequency range. The attenuator speed was set at 1100, the gain at 4.0–5.0, and the suppression at *zero*. The slit program was set at 1000, which gives 2.6–2.7 cm^{-1} spectral slit width in the 3400–3500-cm^{-1} range. The samples were scanned between 3800 and 3400 cm^{-1}, and the absorbance was determined by measuring I_0 and I at the ν_{max} of the tetrahydrofuran associated OH bands.

Tetrahydrofuran was refluxed for a few hours over $LiAlH_4$ and distilled. All the alcohol samples had purity greater than 98% based on GLC and were dried over 4A molecular sieves if liquid or dried in vacuo over P_2O_5 if solid.

RESULTS AND DISCUSSION

An alcohol solution may give several OH stretching vibrational bands in the infrared spectrum: (a) free (unassociated), (b) self-associated (dimers, trimers, etc), (c) solvent associated (1/1-, 1/2-, 1/3-complexes, etc.), and (d) other associated OH bands if the solution contains other functional groups which are proton acceptors (electron donors).

A general trend of the effect of hydrogen bonding on the infrared spectrum is to shift and broaden the O–H stretching absorption. The integrated intensity also increases markedly. A completely satisfactory explanation for these phenomena is yet to be proposed and evaluated. Some of the observations reported in the literature are described below, although a close examination of the experimental data in the literature reveals that there are many exceptions. (1) The greatly broadened absorption often consists of several overlapping bands corresponding to equilibrium concentrations of several hydrogen bonded species, such as dimers, trimers, etc. The relative amounts of these different species in solution depends on (a) the solute concentration, (b) the type of solvent, and (c) the

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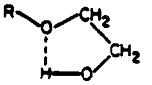
temperature. (2) Steric hindrance of bulky groups surrounding a proton donor site tends to inhibit hydrogen bond formation. (3) The absorption frequency shift from the unassociated (free) to the associated species has been correlated with the X–Y distance in the X–H⋯Y unit. The relationship is such that the shifts are greater the closer the approach of X to Y (*5–7*). (4) The frequency shift of a given proton donor to a variety of proton acceptors can be related to the heat of formation of the H bonds. The half-bandwidth and integrated intensities also correlate with enthalpy, at least for certain compounds (*8*). Enthalpy of hydrogen bond formation is usually 2–10 kcal/mol. (5) Integrated intensities of associated peaks vary significantly with temperature (*8*). This may be due to the changes in H-bonded distance or configuration.

Because of the strong dependence of OH bands on external factors as described above, OH absorptions are not considered suitable for quantitative analysis. Nevertheless, one of several OH peaks has been selected for quantitative determinations by several references (*9, 10*). Obviously, such an empirical method requires a careful calibration curve at a constant temperature and a relatively constant composition and the results should be carefully evaluated.

Special procedures to circumvent the above problems have been reported. The most common one is the use of a very dilute solution in an inert solvent, where the concentration of associated species is negligible. The concentration usually has to be less than 10 mequiv/L, and therefore a long path-length in a highly transparent solvent such as CCl_4 has to be used. Another case reported utilized hydroxyl groups which are intramolecularly associated to the β-oxygen to form a five-membered ring



This type of association is sterically favorable and thus gives a relatively sharp peak with molar absorptivity relatively independent of concentration. Unfortunately, this method is limited to alcohols having a specific structure. Hydroxyl concentrations of polypropylene glycols were determined by this method. The absorbance of the neat polymers was measured at 3520 cm^{-1} (*11*).

The method for OH determination of the polymers in this study was to utilize the solvent-associated peak under conditions such that practically all the OH groups are completely associated to the solvent, and the presence of free or self-associated OH peaks is negligible. It was theorized that the OH-associated band will not be influenced strongly by the external factors described above if (1) the molecular structure of the solvent is such that it is a most favorable base (electron donor) for H bonding in terms of steric and electronic configurations, and (2) a large number of the solvent molecules are always available around the hydroxyl groups. Under these conditions, the conformation of the alcohol/solvent complex would remain relatively constant with small changes in the alcohol concentration and temperature. The solvent selected for this purpose is tetrahydrofuran (THF). All the alcohols listed in Table I show a single and relatively sharp THF-associated OH peak in the 3500-cm^{-1} region in the concentration range of 10–70 mequiv/L. Other polar solvents, such as ethyl acetate and cyclohexanone, give more than one hydroxyl peak under the same conditions (Figure 1). Additional advantages of using the THF-associated OH peaks are that (1) THF is an excellent solvent for most polar and nonpolar prepolymers, (2) THF is transparent in the region of 3500 cm^{-1}, and (3) the associated peak has a significantly higher intensity than the free peak.

I. Evaluation of the THF-Associated OH Bands. The characteristics of the THF-associated OH absorption bands were examined with respect to the various factors which may influence the quantitative analysis.

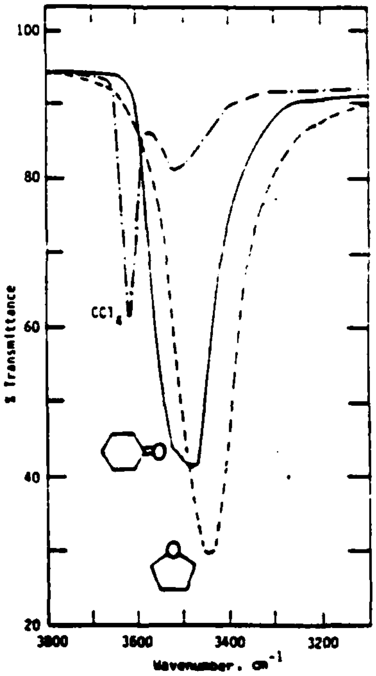


Figure 1. Hydroxyl bands of $CH_2{=}CHC(O)OCH_2CH(OH)CH_3$ in various solvents: c = 36 mequiv/L; 1 mm BaF_2 cells.

A. Effect of Change in the Hydroxyl Concentration. In order to obtain a single THF-associated OH peak without the presence of other OH bands, one must use a very dilute solution. Optimum concentrations for an accurate determination using 1.0-mm solution cells appear to be 25–55 mequiv/L, where the percent transmittance is approximately 20–50. In this transmittance region, total percent error in absorbance resulting from cumulative errors in measurements of I_0 and I, and from stray light and cell inequalities, is minimized (*12*). The OH peaks of hydroxyethyl disulfide (HEDS) dissolved in THF (Figure 2), and in a mixed solvent containing THF and 15 wt % of dinitropropyl acrylate (DNPA) polymer (Figure 3), show *no* shift in frequency over the OH concentration range of 10–70 mequiv/L. Furthermore, the plot of absorbance vs. concentration for all the alcohol/THF complexes of HEDS, hydroxyethyl acrylate (HEA), and 2-hydroxypropyl acrylate (HPA) is linear, with a correlation coefficient of 0.999 (Figure 4).

B. Effect of Temperature. When the sample cell is placed in the cell compartment of the Perkin-Elmer 621, the sample solution heats up rapidly from room temperature to approximately 55 °C. The change in this temperature range does not appear to disturb the OH/THF complex of the sample solutions significantly, as demonstrated in Figure 5. The wavenumber of the peak, the half-bandwidth, and the peak intensity show no appreciable change for an hour after the sample is placed in the cell compartment, whereas the temperature of the sample varies from 26 to 55 °C. The variations, if any, are within experimental error. Obviously, a thermostated cell compartment is not necessary for the absorbance measurement. This is contrary to the report by Becker, who observed that frequency shift and molar absorptivity of the 1/1 OH/base complex changed as much as 40% when the temperature increased from −10 to +60 °C, although the half-bandwidth did not show much variation (*8*).

C. Effects of Change in the Solution Bulk Properties and the Presence of Other Electron Donors. The OH/THF complex of HEDS at a concentration of 45 mequiv/L in pure THF as a solvent (Figure 6a) and in a solvent con-

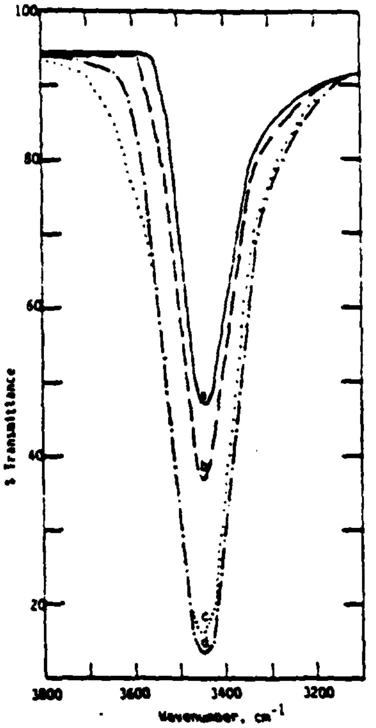


Figure 2. Hydroxyl bands of $(HOCH_2CH_2)_2S_2$ in THF at various concentrations, 1-mm BaF_2 cells: a = 21.5 mequiv/L; b = 28.1 mequiv/L; c = 55.2 mequiv/L; d = 63.6 mequiv/L.

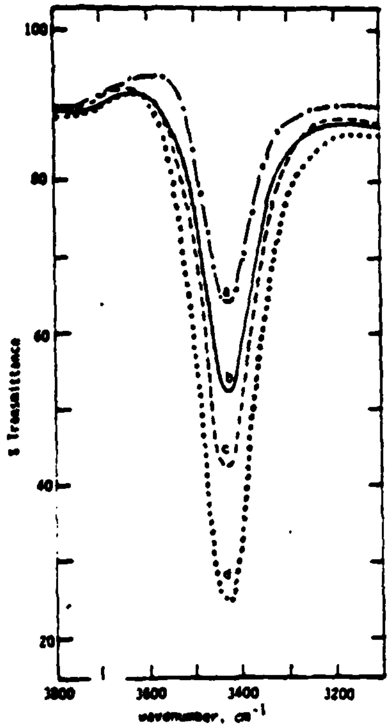


Figure 3. Hydroxyl bands of $(HOCH_2CH_2)_2S_2$ in 15 wt % "Ref-PDNPA"/THF, 1-mm KBr cells: a = 14.3 mequiv/L; b = 18.2 mequiv/L; c = 28.5 mequiv/L; d = 48.0 mequiv/L.

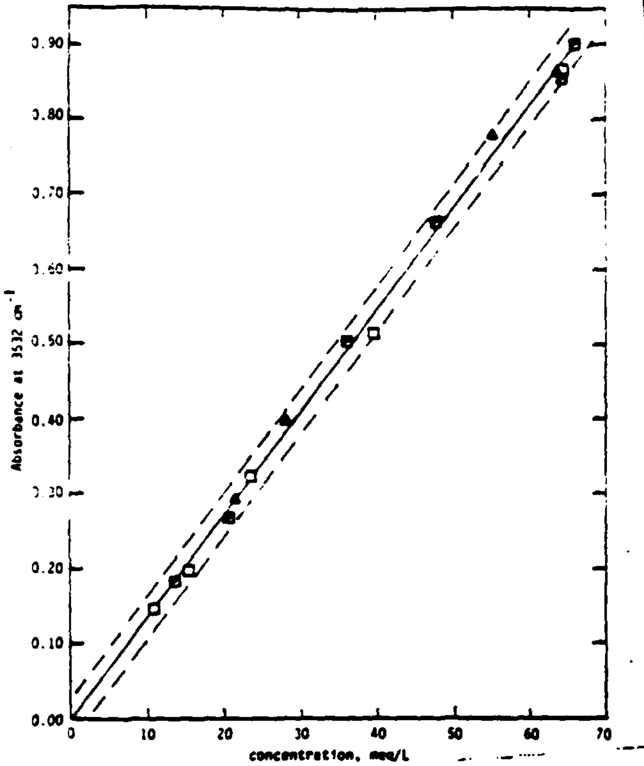


Figure 4. Absorbance vs. concentration in THF, 1-mm BaF_2 cells: (◇) hydroxyethyl disulfide (HEDS); (□) 2-hydroxypropyl acrylate (HPA) (▲) hydroxyethyl acrylate (HEA); regression line, slope = 0.0136, intercept = −0.0002, correlation coefficient = 0.999, 2σ = 0.03.

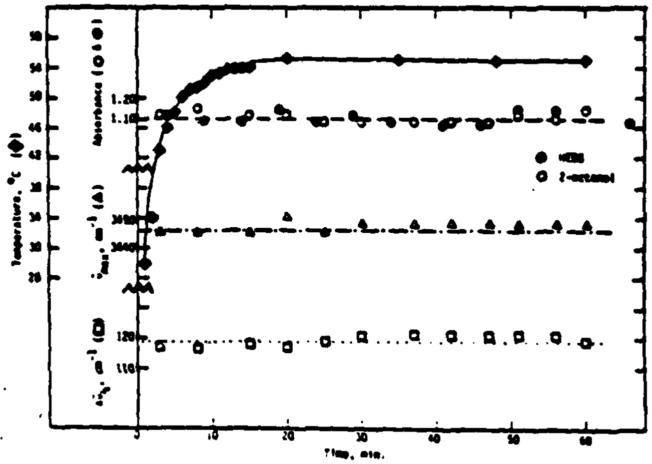
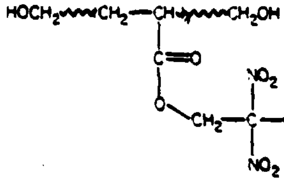


Figure 5. Absorbance, $\bar{\nu}_{max}$, and $\Delta\bar{\nu}_{1/2}$ of alcohols in THF at various temperatures: 77.8 mequiv/L; 1.0-mm BaF_2 cells.

taining as much as 15 wt % DNPA polymer (Figure 6b) gives the same absorbance, although there may be a slight shift in frequency from 3532 to 3530 cm⁻¹ between the two samples. In another experiment, hydroxyl equivalent weights of hydroxy-terminated DNPA polymer samples were determined by varying the weight percent polymer present in THF from 5 to 15. The deviation in values of the equivalent weight due to change in the weight percent of the polymer in THF was negligible within experimental error (Table II). The structure of DNPA polymer is



The above experiments indicate that (1) the change in the solvent bulk dielectric properties and (2) the presence of other electron donors such as nitro and ester groups in these limited concentrations do not appreciably affect the absorbance of the OH/THF complex at 3530 cm⁻¹.

D. Effect of Alcohol Structure. 1. Primary, Secondary, and Tertiary Alcohols. The bulky groups sur-

Table I. THF Associated OH Bands of Various Alcohols at 40 mequiv/L

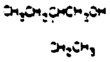
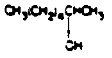
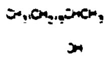
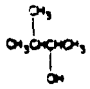
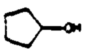
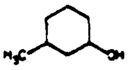
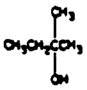
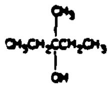
compounds	CCl_4 solution: (a) free OH ν_{max}, cm^{-1}	CCl_4 solution: (b) self-assoc OH ν_{max}, cm^{-1}	THF solution (c) THF-assoc OH ν_{max}, cm^{-1}	freq shift a − c $\Delta\nu_{max}$, cm^{-1}
(A) Primary Alcohols				
(1) $CH_3(CH_2)_{\text{[illegible]}}CH_2OH$	3644	3506	3482	162
(2) $CH_3(CH_2)_{\text{[illegible]}}CH_2OH$	3644	3503	3484	160
(3) $CH_3(CH_2)_{\text{[illegible]}}CH_2OH$	3643	3530	3484	159
(4)  $CH_3CH_2\underset{CH_2CH_3}{CH}CH_2OH$	3646	3516	3482	164
(B) Secondary Alcohols				
(1)  $CH_3(CH_2)_6\underset{OH}{CH}CH_3$	3635	3498	3478	157
(2)  $CH_3(CH_2)_6\underset{OH}{CH}CH_3$	3634	3496	3478	156
(3)  $CH_3\overset{CH_3}{CH}\underset{OH}{CH}CH_3$	3637	3498	3480	157
(4) 	3631	3500	3475	156
(5) 	3627	3488	3475	152
(C) Tertiary Alcohols				
(1)  $CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_3$	3622	3500	3477	145
(2)  $CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$	3622	3500	3476	146
(D) Special Alcohols (β-Alkoxyethanol)				
(1) $CH_3CH_2OCH_2CH_2OH$	3612	3477	3460	152
(2) $CH_3(CH_2)_3OCH_2CH_2OH$	3612	3492	3456	156
(3) $CH_3CH_2(OCH_2CH_2)_2OH$	3609	3474	3456	153
(E) Special Alcohols				
(1)  $CH_2{=}CH\overset{O}{C}OCH_2CH_2OH$	3623	3515, 3460	3432	191
(2)  $CH_2{=}CH\overset{O}{C}OCH_2\overset{OH}{CH}CH_3$	3629	3522, 3460	3432	197
(3) $HOCH_2CH_2SSCH_2CH_2OH$	3635	3582	3432	203

Table II. Effect of Variation of Weight Percent Polymer on Determination of OH Equivalent Weight

sample no.	wt % DNPA polymer in THF	equiv wt	av equiv wt	% variation
P-24 (a)	5.0	1170, 1190	1180	1.7
(b)	7.5	1170, 1200	1185	2.5
(c)	av of (a) and (b)		1183	0.4
P-25 (a)	7.5	2220, 2230	2225	0.4
(b)	15.0	2270, 2270	2270	0.0
(c)	av of (a) and (b)		2248	2.0
P-26 (a)	5.0	1160, 1180	1170	1.7
(b)	15.0	1130, 1150	1140	1.8
(c)	av of (a) and (b)		1155	2.5

rounding the OH groups show a definite influence on the frequency shift of the band, $\Delta\nu_{max}$, and the absorbance of the OH/THF complex. Both the $\Delta\nu_{max}$ and absorbance increase as the alcohols are changed from tertiary alcohols to primary alcohols (Table I and Figure 7). All the plots of absorbance vs. concentration of primary, secondary, and tertiary alcohols give good linear relationships with intercept close to zero. The slopes increase from tertiary alcohols to primary alcohols although the difference between those of primary and secondary alcohols are insignificant at the 95% confidence level. It is believed that some of the scatter of the absorbance for primary and secondary alcohols in Figure 7 are due to an impurity in the alcohols, although they were dried over 4A molecular sieves and were shown by GLC to have greater than 98% purity.

2. Alkoxy Substitution on β-Carbon. Alcohols substituted with alkoxy groups on the β-carbon are expected to give at least two OH bands regardless of the ratio of OH groups to THF, since intramolecular H bonding to form a five-membered ring is sterically favorable (*13*) and not affected significantly by the concentration. Although β-alkoxyethanols give a single peak at 3460 cm^{-1} this peak may consist of

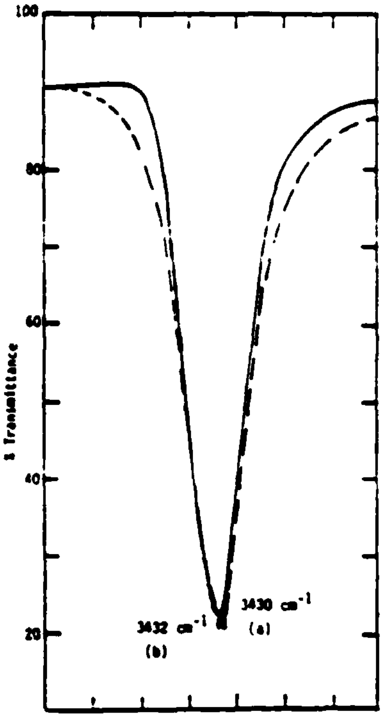


Figure 6. Hydroxyl bands of $(HOCH_2CH_2)_2S_2$ (HEDS) in various solvents: a = THF; b = 15 wt % "Ref-PDNPA"/THF; 45 mequiv/L; 1.0-mm KBr cells.

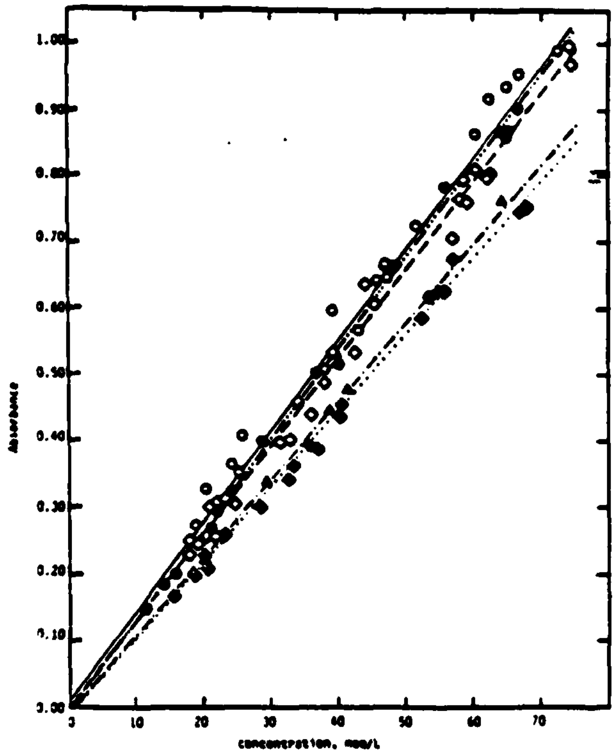


Figure 7. Absorbance vs. concentration of various alcohols in THF, 1.0-mm BaF_2 cells: (○) primary alcohols, $2\sigma = 0.06$; (◇) secondary alcohols, $2\sigma = 0.05$; (●) hydroxyethyl disulfide, hydroxyethyl acrylate, 2-hydroxypropyl acrylate, $2\sigma = 0.03$; (△) tertiary alcohols; (◆) β-alkoxyethanols, $2\sigma = 0.03$.

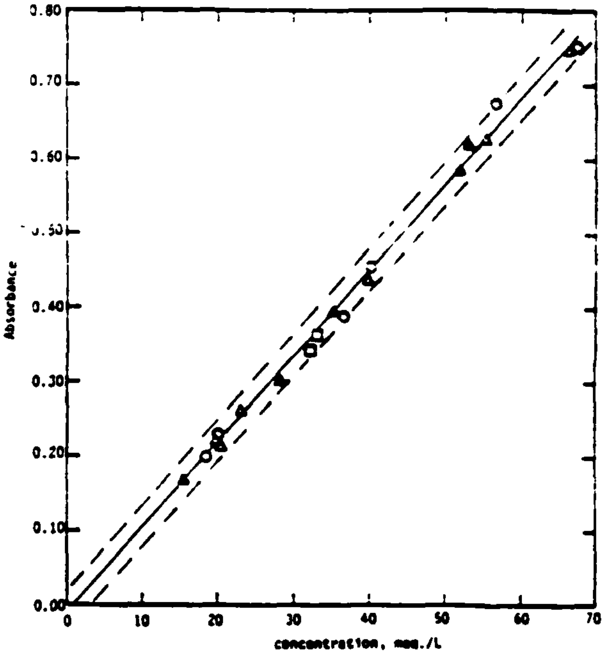


Figure 8. Absorbance vs. concentration for β-alkoxy alcohols in THF, 1.0-mm BaF_2 cells: (▲) $CH_3CH_2OCH_2CH_2OH$; (△) $CH_3CH_2(OCH_2CH_2)_2OH$; (○) $CH_3CH_2CH_2CH_2OCH_2CH_2OH$; regression line, slope = 0.0115, intercept = −0.012, correlation coefficient = 0.999, 2σ = 0.03.

overlapping bands of at least two major hydroxyl complexes, i.e., intramolecular H-bonded and the OH/THF complex. The ratio of these two bands would remain constant with a small change in the concentration. The values of $\Delta\nu_{max}$ and absorbance of all the β-alkoxyethanols tested give a good linear relationship when plotted against the concentration (Table IA vs. ID; Figure 8).

3. Substitution of Ester and Disulfide Groups on β-Carbons. Although oxygen and sulfur atoms are situated on the β-carbons in these alcohols, the intramolecular H bonding is expected to be negligible in the presence of a large number of stronger proton acceptors such as THF. The $\Delta\nu_{max}$ values of these alcohols differ from those of primary alcohols (195 cm⁻¹ vs. 160 cm⁻¹ in Table I), and yet the absorbances are the same. In fact, plots of absorbance vs. concentration for HEDS, HEA, and HPA give a linear relationship with correlation coefficient of 0.999 and coincide with the plots for primary and secondary alcohols combined (Figures 4 and 7).

4. Size of Alcohol Molecules. Although the THF-associated OH bands appear to be affected by the substituents surrounding the alcohols (microscopic effect) as discussed above, molecular weight of the alcohols appears to cause no significant change. For example, primary and secondary butanols give the same frequency shifts and absorbances as the corresponding octanols. Furthermore, $CH_3CH_2OCH_2CH_2OH$ gives the same values as $CH_3CH_2OCH_2CH_2OCH_2CH_2OH$. This observation and that discussed in section C above indicate that the increase of molecular weight of the alcohols, or specifically the change from monomer to polymer, has no significant effect on the absorbance of THF-associated OH bands, as long as the other parts of the alcohol molecules do not interfere with the OH/THF complex microscopically. This finding is consistent with the proposals made by others that the bulk dielectric effects have relatively little importance, and the frequency shifts, if any, may be in the order of 5 cm⁻¹ (*14*).

In summary, the above analysis indicates that THF-associated alcohols in the concentration range of 10–70 mequiv/L give relatively sharp, single bands in the 3450-cm⁻¹ region. The absorbances of the solutions give linear Beer–Lambert relationships with high correlation coefficients and are not significantly affected by the change in temperature from 25 to 55 °C or by the molecular size. The change of bulk dielectric

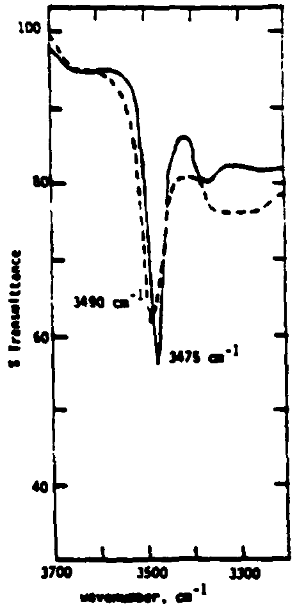


Figure 9. Ester overtone bands of DNPA and PDNPA, 15 wt % in THF, 1-mm KBr cells: (—) DNPA; (---) PDNPA.

properties by the addition of as much as 15 wt % foreign polymers or incorporation of relatively small amounts of other electron donors such as esters and nitro groups do not appear to affect the absorbance of the OH/THF complex. Structural changes of alcohols surrounding the OH groups *do* cause variation in the frequency shift and absorbance. However, the absorbance in general appears to be less sensitive to structural change than is the frequency shift. For practical purposes, primary and secondary alcohols including β-hydroxy esters and disulfides give the same absorbances in the 10–70 mequiv/L concentration range.

II. Quantitative Analysis of OH Groups in Prepolymers. Application of the infrared study described in section I to the hydroxyl equivalent weight determination of our experimental DNPA polymers will be described in detail first and then the values obtained for some commercially available prepolymers by this method will be compared with values obtained by other methods.

A. Determination of OH Equivalent Weight of DNPA Polymers. The primary difficulty encountered with this method was due to the presence of overtone bands of ester groups of DNPA polymers which overlap the OH band used for analysis. DNPA (an α,β-unsaturated ester) gives an overtone peak at 3475 cm^{-1}, and DNPA polymer (a saturated ester) has a peak at 3490 cm^{-1}, as shown in Figure 9. Since the analysis requires a quantitative determination of OH groups at a concentration level as low as 10 mequiv/L, the ester overtone of DNPA polymer interferes with the analysis. There are many more ester groups than OH groups present in a molecule of DNPA polymer. It was observed that the best approach to negate the effect of the overtone band is to use a DNPA polymer solution in THF as a reference, with concentration ranging from 5 to 15% polymer, depending on the equivalent weight. The deviation due to the change in the weight percent polymer concentration in THF is negligible, as discussed previously (Table II). The DNPA polymer used for the reference does not contain OH groups and will be called "Ref-PDNPA".

When a 15 wt % THF solution of DNPA polymer containing OH groups is analyzed against the reference containing 15 wt % "Ref-PDNPA" in THF, the absorbance measured in the region of 3500 cm^{-1} should be that of the associated OH peak only, since the ester overtone peak is compensated. This is demonstrated in Figure 6: The OH peak of HEDS at a concentration of 45 mequiv/L, using 15% "Ref-PDNPA" in THF as a solvent (Figure 6b), and that using THF only as a solvent (Figure 6a) give the same absorbance. Different primary alcohols, i.e., HEDS and HEA, give absorption peaks at the same frequency and intensity (Figure 10). The ester groups of HEA and n-butyl acrylate (nBA) show no appreciable overtone peaks at this concentration. In other words, the ester overtone peak is negligible when the molar ratio of OH group to ester group is one. The overtone peak becomes a problem only when the molar ratio of the ester to the hydroxyl groups become large, as in the case with the OH-terminated DNPA polymer.

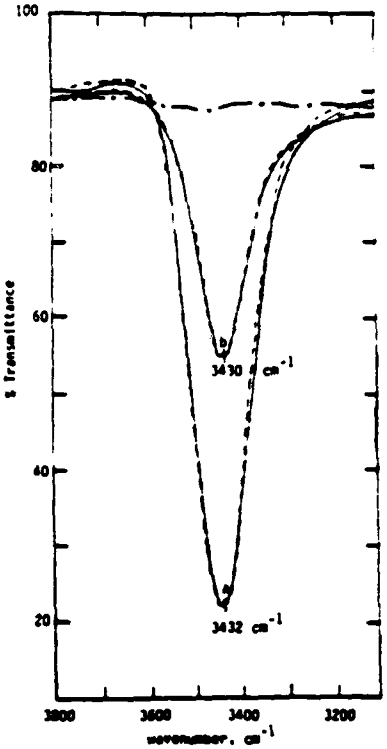


Figure 10. Hydroxyl bands of primary alcohols in THF and in 15 wt % "Ref-PDNPA"/THF, 1.0-mm KBr cells: (—) HEDS, (---) HEA, (-·-) n-butyl acrylate: a = 45 mequiv/L in THF, b = 15 mequiv/L in 15 wt % "Ref-PDNPA"/THF.

The OH peaks of HEA and HEDS dissolved in 15 wt % "Ref-PDNPA"/THF show *no* shift in frequency over the OH concentration range of 10–60 mequiv/L (Figure 3). Furthermore, a plot of absorbance vs. concentration of HEA, HPA, and HEDS gives a linear relationship with correlation coefficient of 0.999 and is identical with that in THF only (Figure 4).

Since the experimental polymers containing OH groups are similar in structure to HEA, HPA, and HEDS, the calibration curve of Figure 4 can be used for the OH equivalent weight determination. The polymer solutions range from 5 to 15 wt % so that the OH concentration becomes approximately 30 mequiv/L.

B. Comparison of the Infrared Method with Other Methods. The OH equivalent weight of hydroxy-terminated polymers, R45M (polybutadiene), HTPBN (butadiene–acrylonitrile copolymer), PCP-0240 (polycaprolactone), and Teracol (polytetrahydrofuran) were determined by using the calibration curve of Figure 4. These have the same absorbance–concentration relationship as that of all the primary and secondary alcohols which have been tested (Figure 7). The equivalent weight of PEG (polyethylene glycol) was determined by using the calibration curve based on β-alkoxyethanols (Figure 8). All the values by the IR method correspond well with those supplied by the vendors and those by

Table III. OH Equivalent Weights of Prepolymers: Comparison of IR Method with Other Methods

prepolymers	vendor's eq wt	IR method	chemical methods PA/PY (*1*)	AA/NMDM (*2*, *3*)
R45M	1300	1280	1350	1440
HTPBN	1820	1770		
PCP-0240	980	970	970	1000
PEG	1660	1630[a]	1670	1740
Teracol	500	480	500	850

[a] Alkoxyethanols used for calibration.

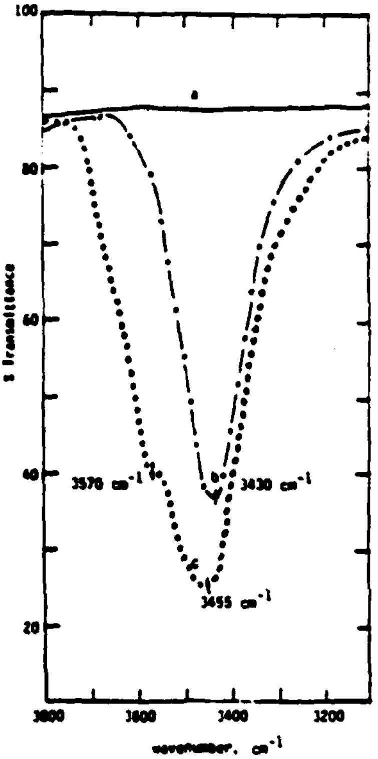


Figure 11. Effect of the presence of H_2O on the hydroxyl bands, 15 wt % "Ref-PDNPA" in THF, 0.5-mm KBr cells: a = base line, b = 60 mequiv/L of OH terminated PDNPA, c = b contaminated by 0.06 wt % H_2O.

some of the chemically known methods (Table III).

It should be emphasized that this method requires great care to avoid contamination by water or other alcohols. The presence of less than a drop of water in the 10 mL solution, i.e., 0.06 wt % H_2O, could cause considerable error in the determination as shown in Figure 11. This is not the case with the common chemical methods. The primary reason for this is due to the low molecular weight of water in comparison with that of the polymer. Fortunately, the presence of water can be detected by the presence of another peak at 3570 cm^{-1} and the shift of the hydroxyl peak to a higher frequency. All the samples must be dried over P_2O_5 in vacuo and the THF distilled from $LiAlH_4$ for this analysis. The precision, therefore, depends mainly on the technique of sample preparation, although the sensitivity of the instrument is also a factor. Reproducibility of the analyses using the Perkin-Elmer Model 621 double beam spectrometer is within 2.5%. Furthermore, a careful analysis is needed to differentiate the absorbance of the OH/THF complex, if other functional groups in the sample also absorb in the region of 3400–3500 cm^{-1}. An example with the overtone band of the ester groups in DNPA polymers is described in section IIA. Functional groups which may give fundamental bands are alcohols, phenols, water, amides, amines, imines, and sulfonic acids; the overtone bands of carboxylic acids, acid anhydrides, aldehydes, and ketones may also appear.

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