AD-A097 577   CALIFORNIA STATE UNIV SACRAMENTO DEPT OF CHEMISTRY   F/G 11/9
SYNTHESIS OF HYDROXY-TERMINATED DINITROPROPYL ACRYLATE POLYMERS--ETC(U)
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JANUARY 1981

AIR FORCE ROCKET PROPULSION LABORATORY
Director of Laboratories
Air Force Systems Command
Edwards AFB, Ca 93523

INTERIM REPORT

For the Period
1 January 1979 to 30 September 1980

SYNTHESIS OF HYDROXY-TERMINATED DINITROPROPYL ACRYLATE POLYMERS

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California State University Sacramento
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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
AFRPL-TR-81-11

2. GOVT ACCESSION NO.
AD-A097517

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (*and Subtitle*)
Synthesis of Hydroxy-Terminated Dinitropropyl Acrylate Polymers

5. TYPE OF REPORT & PERIOD COVERED
Interim Report 1 Jan 79 – 30 Sep 80

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
C. S. Kim

8. CONTRACT OR GRANT NUMBER(s)
F04611-79-C-0009

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Chemistry Department
California State University, Sacramento

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Rocket Propulsion Laboratory, MKPA
Edwards AFB CA 93523

12. REPORT DATE
January 1981

13. NUMBER OF PAGES
56

14. MONITORING AGENCY NAME & ADDRESS (*if different from Controlling Office*)

15. SECURITY CLASS. (*of this report*)
Unclassified

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)
Approved for public release, distribution unlimited

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)
N/A

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)
Hydroxy-Terminated Dititropropyl Acrylate Polymers chain transfer agents
Polymerization
Functionality
Initiators
OH-Equivalent Weight

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Studies of free-radical polymerization kinetics using new initiators and chain transfer agents were done with the objective of achieving the synthesis of difunctional Hydroxy-Terminated Dinitropropyl Acrylate polymers. The functionality of the DNPA polymers was increased from 1.6 to 1.8. An infrared method was used to determine OH-equivalent weights. The methods and results are described.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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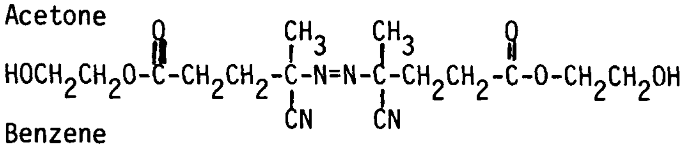
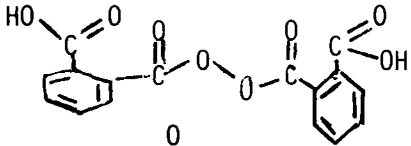
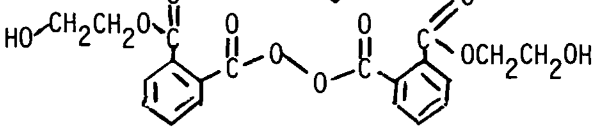
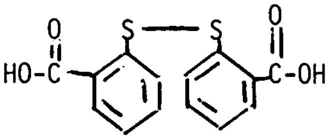
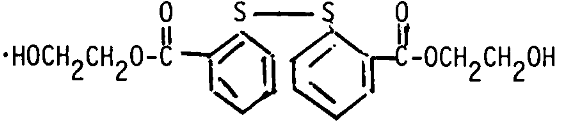
GLOSSARY

ABBREVIATIONS

Ac	Acetone
Azo-OH	 $HOCH_2CH_2O\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}CH_2CH_2\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}O\text{-}CH_2CH_2OH$
B	Benzene
BO	t-Butanol
o-BPO-CO_2H	
o-BPO-OH	
CH	Cyclohexanone
DMF	Dimethyl Formamide
DNPA	Dinitropropyl Acrylate
o-DTB-CO_2H	
o-DTB-OH	
EC	Ethylene Carbonate
GPC	Gel Permeation Chromatograph
HEDS	Hydroxyethyl Disulfide
HPLC	High Pressure Liquid Chromatograph

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C. S. KIM

CALIFORNIA STATE UNIVERSITY, SACRAMENTO

SYNTHESIS OF HYDROXY-TERMINATED DINITROPROPYL ACRYLATE POLYMERS

I. INTRODUCTION

This is an Interim Report submitted in partial fulfillment of the requirements of Contract F 04611-79-C-0009. This report covers the period of January 1, 1979 to September 30, 1980.

Dinitropropyl acrylate (DNPA) polymers were prepared previously via a random free-radical polymerization method. Hydroxyl groups were attached randomly along the main chain of the polymer through the use of hydroxyethyl acrylate. These hydroxyl groups will not only act as chain extenders but also as crosslinkers when reacted with diisocyanates. The binder network will then have a wide distribution of chain lengths between the crosslinkers and many nonload bearing, dangling groups along the main chains. Consequently, the use of this type of prepolymer yields a binder with poor mechanical properties for a solid propellant composite.

The attachments of hydroxyl groups at both ends of the main chain, rather than along the chain, should minimize the above disadvantages, thus improving the mechanical properties of the propellant. This program involved studies of free-radical polymerization kinetics using new initiators and chain transfer agents with the objective of achieving the synthesis of difunctional DNPA polymers.

II. OBJECTIVE

The objective of this program was to develop a technique of synthesizing hydroxy-terminated dinitropropyl acrylate polymers having average molecular weights of 4,000 - 10,000.

III. SUMMARY

The purpose of this project is 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, and the solvent; and the reaction temperature.

The result showed an improvement of the functionality from 1.51 to 1.80. Reproducibility was within 10% of the value of functionality. Further improvement appears less likely, as a short range objective, since there are too many undesirable hydrogen-abstracting side-reactions competing during the free-radical polymerization reaction of DNPA. Not all the side-reactions can be minimized.

Although the functionality value of 1.80 approaches that of some of the commercially available prepolymers, it indicates a 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 chain extension reactions with the primary alcohols would occur prior to the reactions with the secondary alcohols. The resulting binder network should minimize the nonload 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.

A significant portion of this project effort was also spent in developing a new technique for the determination of OH equivalent weight of DNPA polymers. All the current chemical methods require a basic medium, and cannot be used for the DNPA polymers, since the nitro groups undergo reactions with a base. The infrared technique developed in this project shows potential as a general physical method for the determination of OH-equivalent weight of prepolymers.

IV. TECHNICAL BACKGROUND

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

(1) Initiation Step:

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

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

(2) Propagation Step:

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

(3) Termination Step:

(a) By Combination:

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

(b) By Disproportionation

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

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(1,2), succinic acid peroxide(3,4), glutaric acid peroxide(3,4), and 4,4'-Azo-bis-(4-cyanopentanoic acid)(3,4,5) 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(6,7,8,9).

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:

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

(b) chain transfer to monomer:

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

(c) chain transfer to polymer:

$$\mathrm{I{-}M_n^{\cdot}} + \mathrm{PH} \xrightarrow{k_{tr,P}} \mathrm{I{-}M_n{-}H} + \mathrm{P}\cdot$$

(d) chain transfer to solvent:

$$\mathrm{I{-}M_n^{\cdot}} + \mathrm{SH} \xrightarrow{k_{tr,S}} \mathrm{I{-}M_n{-}H} + \mathrm{S}\cdot$$

(e) chain transfer to an additive:

$$\mathrm{I{-}M_n^{\cdot}} + \mathrm{X{-}X} \xrightarrow{k_{tr,X}} \mathrm{I{-}M_n{-}X} + \mathrm{X}\cdot$$

where I-Mn• are the propagating polymer radicals,

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:

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

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

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.

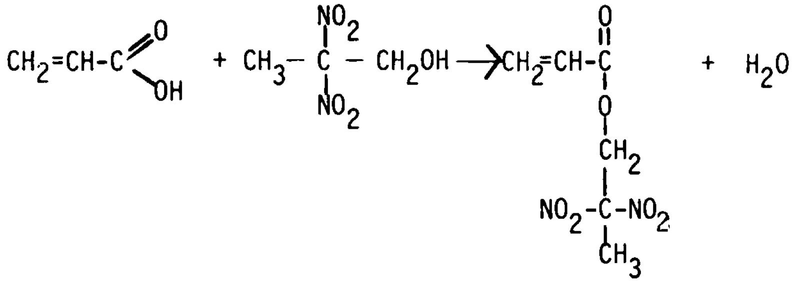
Based on the above discussion, the approach for the successful synthesis of difunctional DNPA polymers should be by (1) modification of polymerization conditions to minimize the side-reaction (a) through (d); and (2) synthesis of effective initiators and chain transfer agents for the polymerization.

V. RESULTS AND DISCUSSION

A. Synthesis of Polymerization Reagents

1. Synthesis of Monomer, Dinitropropyl Acrylate (DNPA)

DNPA was synthesized using dinitroproponal acquired from Cordova Chemical Company of Aerojet Corporation. The reaction involves:



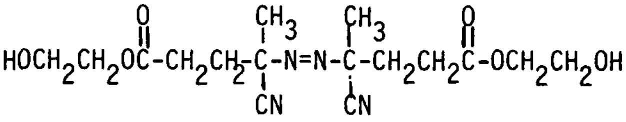
$$CH_2{=}CH{-}C{\overset{O}{\underset{OH}{\lessgtr}}} + CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2OH \rightarrow CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{NO_2}{\underset{CH_3}{C}}{-}NO_2 + H_2O$$

The detailed procedure is described in Experimental Section IV-A. An important consideration is that the DNPA monomers do not undergo an extensive polymerization during the synthesis reaction and later during storage; sufficient amounts of hydroquinone are added to suppress such polymerization. The best method is to prepare "crude" DNPA and store it with 0.1% hydroquinone until needed. The final purification is done prior to its polymerization. The presence of small amounts of reactants, acrylic acid and dinitropropanol, appears to have no significant effect on the free-radical polymerization of DNPA. The impurities which have been identified to cause problems are hydrquinone and DNPA polymers. Hydroquinone, the *polymerization inhibitor*, is necessary during the DNPA synthesis and storage, but has to be removed completely prior to the polymerization. DNPA polymers may form during DNPA synthesis and storage. Since the polymer is nonfunctional, it has to be removed prior to the preparation of difunctional DNPA polymers. Hydroquinone is removed by washing the crude DNPA with a cold, 3% aqueous NaOH solution. This process also eliminates most of the acidic dinitropropanol and acrylic acid. The nonfunctional polymer was removed by a vacuum distillation of DNPA at $90^{o}C/0.6mmHg$. A wiped-film molecular still was used in order to shorten the exposure time of the monomer to a high temperature.

2. Synthesis of Hydroxy-Group Containing Initiators

Common free-radical initiators for vinyl addition polymerizations are azo-compends or peroxides. A main difference between the azo-initiators and the peroxy-initiators is that the peroxides undergo induced decomposition, whereas the azo-initiators do not. This suggests that a peroxide may function not only as an initiator but also as a chain transfer agent for the free-radical polymerization of DNPA. One initiator of each type was selected for synthesis:

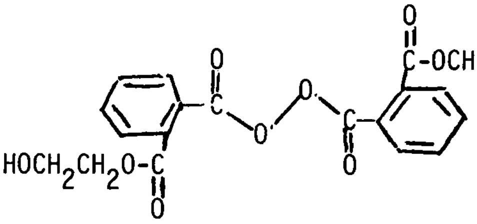
The azo-initiator:



$$HOCH_2CH_2O\overset{O}{\overset{\|}{C}}-CH_2CH_2-\underset{CN}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-N{=}N-\underset{CN}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH$$

(Azo-OH)

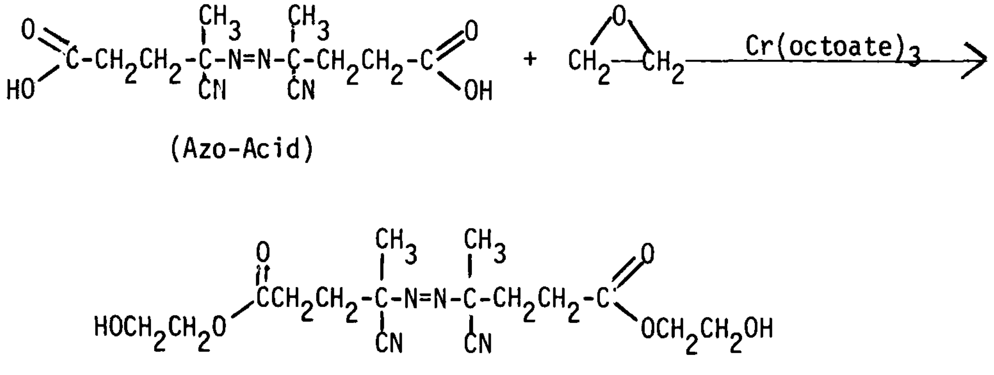
The peroxy-initiator:



(BPO-OH)

a. 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 the concentrations of the reactants and the catalyst increase 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.

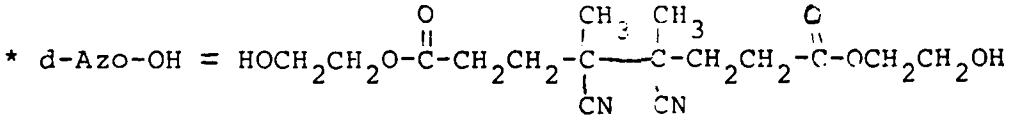
Azo-OH is difficult to purify since it is unstable. Various extraction methods, column chromatography and recrystallization processes failed to remove chromium octoate from the product. The presence of chromium octoate, however, has no detrimental effect on the free-radical polymerization of DNPA and on the subsequent urethane cure reaction. The detailed procedure is described in the Experimental Section. 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 elemental analyses. The infrared method developed for the determination of OH-equivalent weight is discussed in Section V-D-1.

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 I. 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 I. 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:

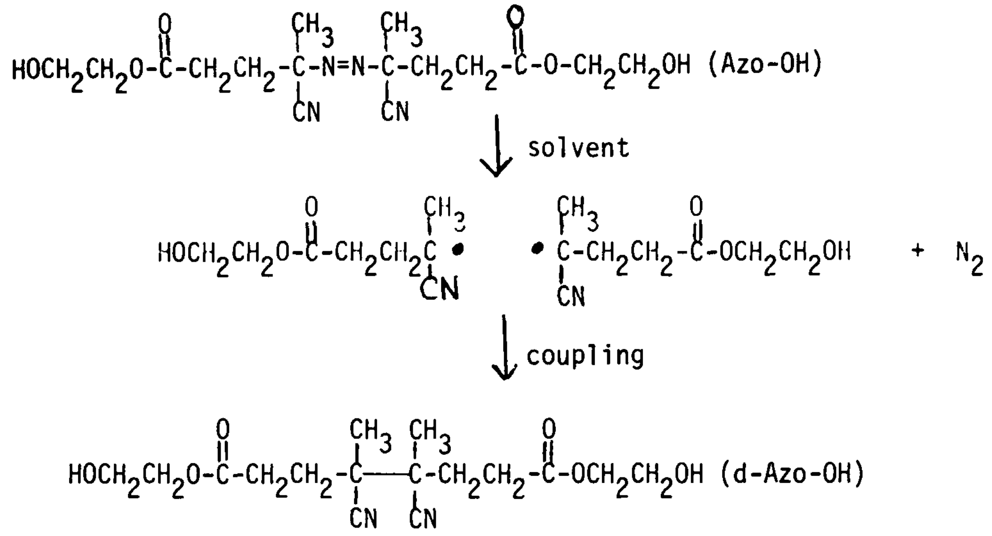
Table I

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



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



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

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

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

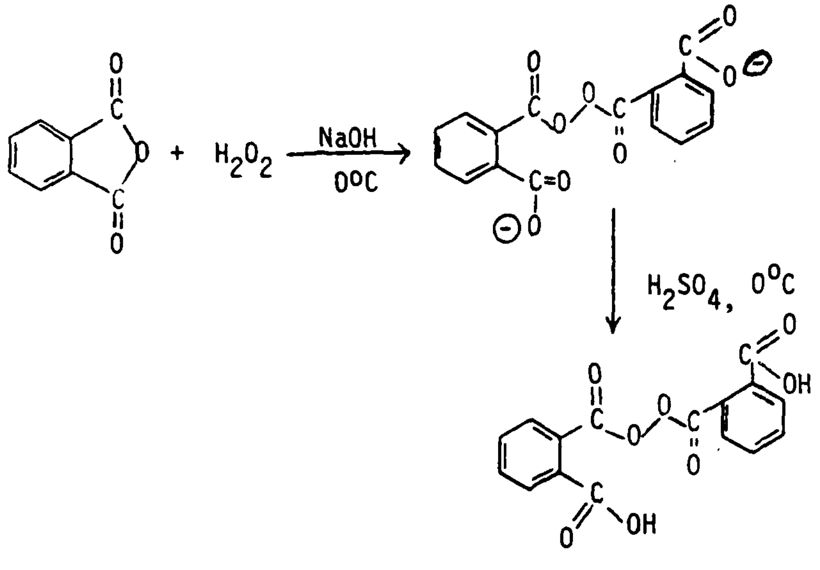
If one assumes that the discrepancy between the calculated value of % N in Row 3 and the experimental value is due to the presence of d-Azo-OH, our Azo-OH sample contains 90.6% Azo-OH, 5.7% d-Azo-OH and 3.7% chromium octoate. The recalculated values based on this composition in Row 4 of Table I show good agreement with the experimental results, with the exception of % H.

b. Attempted Synthesis of BPO-OH

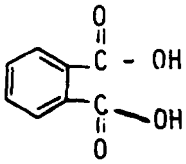
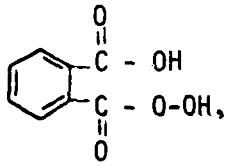
i. Synthesis of Phthaloyl peroxide (BPO-CO_2H)

A benzoyl peroxide was selected over other acyl peroxides because it does not contain active hydrogen atoms. Active hydrogen atoms may cause the formation of undesirable monofunctional polymers through chain transfer reactions.

The precursor of BPO-OH, phthaloyl peroxide (BPO-CO_2H) was synthesized by the following steps based on the method by Baeyer and Villager(10).

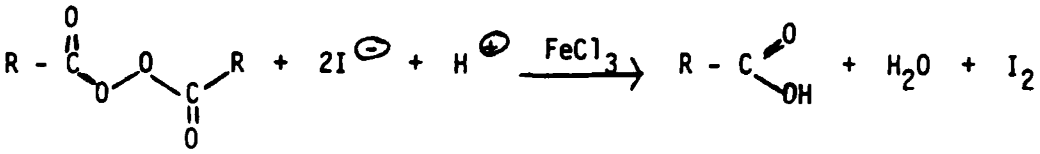


(BPO-CO_2H)

The above reaction was accompanied by many side-reactions to form compounds such as  and , thus yielding only 15% of the desired product, BPO-CO_2H. No attempt was made to improve the yield since the effectiveness of BPO-OH as the initiator and the chain transfer agent was to be evaluated first.

The purified BPO-CO_2H was characterized by quantiative determinations of (a) the peroxy group, (b) the carboxylic acid group, and (c) by elemental analysis.

(a) The peroxy group analysis was made by an iodometric titration in DMF/acetic acid/water using ferric chloride as a catalyst. The iodine liberated by the peroxide was titrated with a 0.1N thiosulfate solution based on the equations below:



$$I_2 + 2\ S_2O_3^{\ominus 2} \longrightarrow S_4O_6^{\ominus 2} + 2I^{\ominus}$$

The thiosulfate solution was standardized using anhydrous potassium dichromate, $K_2Cr_2O_7$, based on the equations below:

$$Cr_2O_7^{\ominus} + 6I^{\ominus} + 14H^{\oplus} \longrightarrow 2Cr^{\oplus 3} + 3I_2 + 7H_2O$$

$$I_2 + 2S_2O_3^{\ominus 2} \longrightarrow S_4O_6^{\ominus 2} + 2I^{\ominus}$$

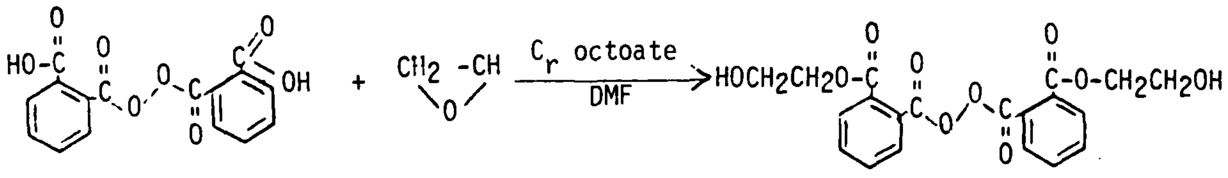
(b) The carboxylic acid group was analyzed by a potentiometric acid-base titration. The titration was carried out in DMF/H_2O with a 0.1N sodium hydroxide solution at 0^{o}C.

(c) Elemental analysis of BPO-CO_2H was made by Galbraith Laboratories, Inc.

The experimental values from the methods (a), (b) and (c) are compared with the calculated values for the compounds which may be present in the reaction mixture. All the observed values agree well with the calculated values of BPO-CO_2H and deviate appreciably from those of the rest of the compounds listed in Table II. It is, therefore, concluded that the purified product is BPO-CO_2H.

ii. Attempted Synthesis of BPO-OH

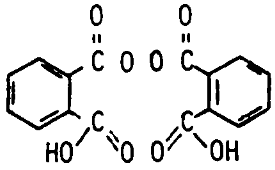
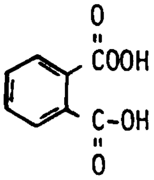
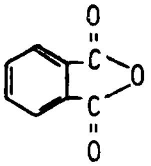
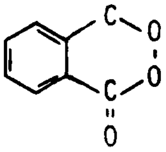
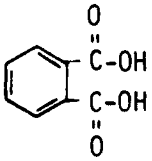
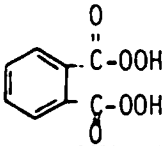
The synthesis of BPO-OH was attempted by reacting BPO-CO_2H with ethylene oxide as follows:



(BPO-CO2H)

(BPO-OH)

TABLE II. Observed Analytical Values of BPO-CO_2H And Calculated Values for the Various Structures

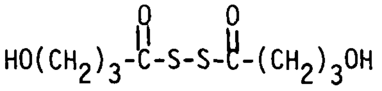
					Molecular Weight	
			% C	% H	Based on Peroxide	Based on CO_2H
Calculated Values Based on the Structures	(1)	 (BPO-CO_2H)	58.18	3.06	330.3	330.3
	(2)		52.75	3.33	182.1	182.1
	(3)		64.87	2.73	-	166.1
	(4)		58.54	2.46	164.1	-
	(5)		57.83	3.65	-	166.1
	(6)		48.49	3.06	198.1	198.1
Observed Values of the Product			58.13	3.08	332.2	342.7

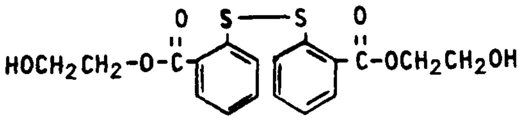
$BPO-CO_2H$ is virtually insoluble in all organic solvents except DMF and DMSO. DMF was selected even though it is not a favorable solvent because of its high boiling point and high solubility in water. The desired product, BPO-OH, undergoes hydrolysis very readily in a basic medium. Even a very dilute sodium carbonate solution appears to cause extensive hydrolysis of BPO-OH; and the basic solution is required to extract the unreacted $BPO-CO_2H$. Various attempts to purify BPO-OH ended up in the hydrolysis of the product. Because of this high instability of BPO-OH, further work was temporarily suspended.

3. Synthesis of OH-Group Containing Chain Transfer Agent

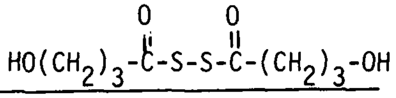
Hydroxyl-group containing disulfide compounds below were considered for use as the chain transfer agent in the DNPA polymerization system:

(a) $HOCH_2CH_2-SS-CH_2CH_2OH$ (HEDS)

(b)

$HO(CH_2)_3-\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}-(CH_2)_3OH$

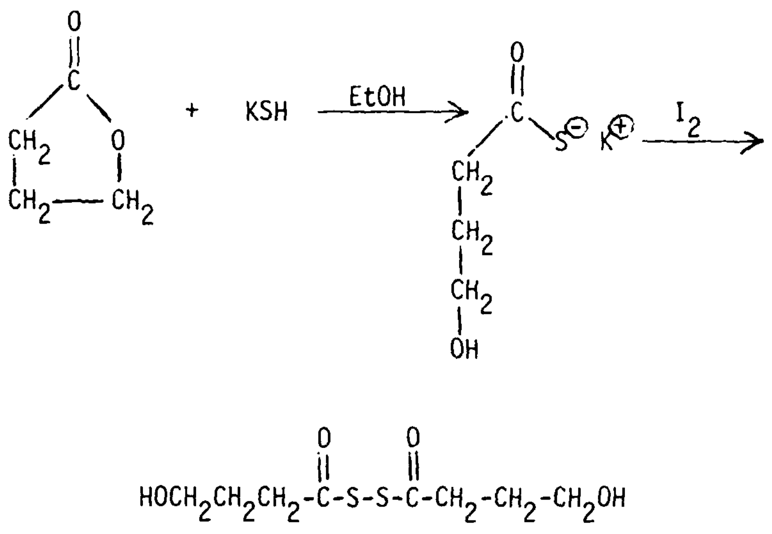
(c)


(a) HEDS was purchased from Aldrich and used as is. Its purity is 98% or better, and the main impurity is H_2O. The precurser, $HOCH_2CH_2SH$, which should be absent in the DNPA polymerization, was not detected as an impurity.



(b) Attempted Synthesis of $HO(CH_2)_3-\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}-(CH_2)_3-OH$

The synthesis of the acyl disulfide was attempted as follows:

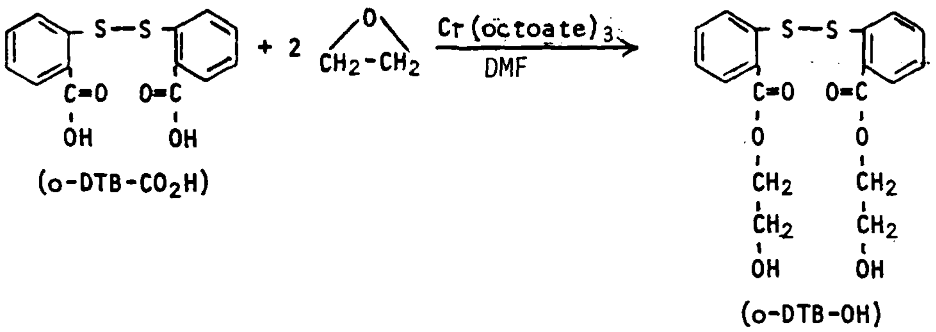


$$HOCH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2OH$$

An infrared scan of the reaction products showed that the above reaction steps produce the desired acyl disulfide along with other sulfur compounds. Unfortunately, various attempts at purification resulted in decomposition of the desired product. There appear to be disproportionation reactions occuring to form hydrogen disulfide and sulfur among others. A literature search on the aliphatic disulfides indicates that the impure acyl disulfides are extremely unstable and undergo decomposition to form sulfur and hydrogen sulfide; only a pure acetyl disulfide showed some stability when stored in a sealed ampoule. Because of the unusual instability of the acyl disulfide, the attempted purification of the desired product was discontinued.

(c) 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 Aerojet Corporation. Since o-DTB-CO_2H showed limited solubility in tetrahydrofuran, the reaction was run in dimethylformamide at 45°C under nitrogen atmosphere. The product was purified by removing the acid with cold $NaHCO_3$ solution washes and removing chromium octoate with benzene. The detailed procedure is described in the Experimental Section. The dried amorphous powder showed the following characteristics:

Melting Point: 103 - 112°C
OH-Eq. Wt. by IR Method: 201 (Theoretical: 197)
GPC Attached (Fig. 1)

Although the synthetic procedure may need modifications, all the analyses are consistent with the structure of o-DTB-OH. A small shoulder on the UV peak in the GPC scan (Fig. 1) may be due to the presence of para and/or meta isomers of DTB-OH. A GPC scan of the precurser, o-DTB-CO_2H, shows a similar shoulder (Fig. 2). Further study can be made by IR and HPLC using a reverse phase column.

Figure 1. GPC Scan of o-DTB-OH

Solvent: THF

Columns: 100 Å, 500 Å, 1,000 Å

Sample Size: 1.5 μl of 5% solution

Flow Rate: 1.7 ml/min

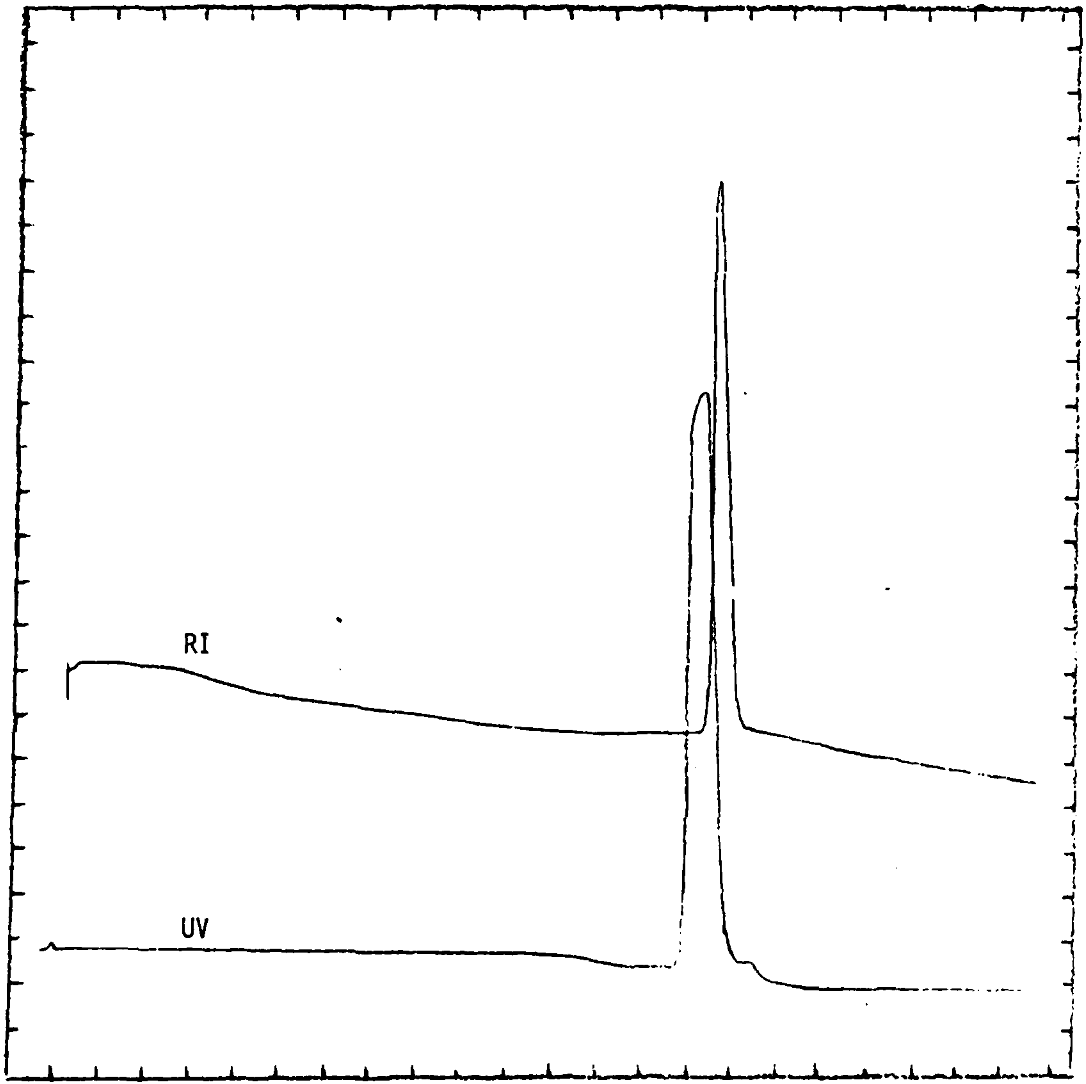


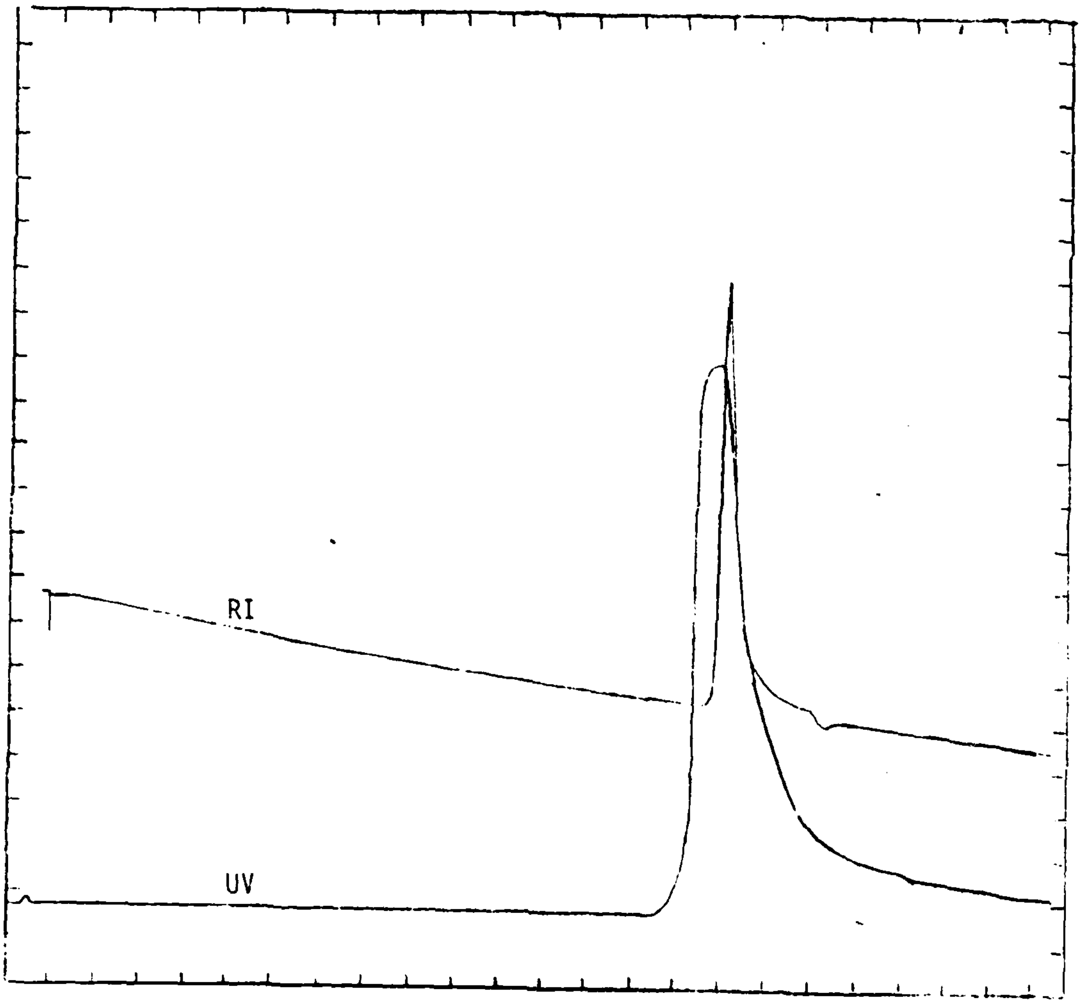
Figure 2. GPC Scan of o-DTB-CO_2H

Solvent: THF

Columns: 100 Å, 500 Å, 1,000 Å μ-Styragels

Sample Size: 1.5 μl of 5% solution

Flow Rate: 1.7 ml/min



B. Synthesis of OH-Terminated DNPA Polymers

(1) Purification of reactants and polymer product

Factors influencing the functionality of the polymers may be evaluated only if the purified polymers give reproducible results. The data in Table III show appreciable batch-to-batch variations in the values of the equivalent weight and the functionality. Causes of the variations found to this date are: (a) certain impurities present in the polymerization mixture, and (b) variations in purification procedure of the resulting polymers.

(a) Potent Impurities in the Polymerization Mixture:

The impurities which have been identified to cause the variations are hydroquinone and DNPA polymer initially present in the monomer. The very small amounts of DNPOH and/or acrylic acid present in DNPA appear to be harmless. DNPA monomer was stored with 0.1% hydroquinone, and the monomer was distilled prior to use. The vacuum distillation apparently did not remove hydroquinone completely. The monomer was found to be contaminated by its own polymer when it was exposed to a high temperature during the distillation or when stored for a prolonged period without a stabilizer. Hydroquinone acts as a polymerization inhibitor, and thus causes variations in the molecular weight and functionality of the resulting polymer depending on the amount present. Contamination of the monomer by its own polymer prior to actual polymerization to produce a functionally terminated polymer would give DNPA polymers having lower average functionality, since the polymer formed during the storage or distillation of the monomer would have the functionality of zero. A proper approach to remedy these problems is to wash the monomer with a cold, 3% sodium hydroxide solution to remove hydroquinone and vacuum distill immediately before its use. The wiped-film

Table III

Batch-To-Batch Variations in DNPA Polymer Synthesis
(Polymerization for 23 hours at 65^oC)

Sample No.	Polymerization Ingredients				% Yield	E. W.	$f_{exp.}$
	DNPA	Azo-OH	HEDS	CH-one			
16'	0.1 m	0.011 m	0.13 m	0.20 m	76	2940	1.80
24	0.1 m	0.011 m	0.13 m	0.20 m	77	2830	1.76
41	0.1 m	0.011 m	0.13 m	0.20 m	70	3610	1.69
17	0.1 m	0.011 m	0.036 m	0.20 m	89	2830	1.68
25	0.1 m	0.011 m	0.036 m	0.20 m	81	3300	1.73
35	0.1 m	0.007 m	0.093 m	0.20 m	80	3070	1.59
38	0.1 m	0.007 m	0.093 m	0.20 m	77	2910	1.64

molecular still will be used in order to shorten the exposure time of the monomer to a high temperature.

The impurities present in the rest of the reactants were not evaluated carefully other than as indicated in Section V-A, Synthesis of Polymerization Reagents. However, these reactants were used from the same batches to minimize the batch-to-batch variation. When the final selection of all the polymerization reactants and the solvent is made, the effects of impurities will be better evaluated.

(b) Effect of Purification Procedure (Fractionation)

When DNPA undergoes polymerization by a free-radical chain reaction, the resulting reaction mixture contains undecomposed initiator, side-products from the decomposition of initiator, unreacted DNPA, solvent, chain transfer agent, and the polymer product having a wide distribution of molecular weight. Elimination of all the undesired components from the DNPA polymer, i.e., purification, is mainly based on relative solubility. Hence, some of the low molecular weight polymers will be fractionated (eliminated) depending on type and amount of the solvent used during the purification procedure. If the functionality of each polymer molecule varies with the size of the molecule, average functionality of the DNPA polymer product is expected to vary depending on the purification method, i.e., depending on the degree of elimination of the lower molecular weight fraction. A preliminary study indicates that elimination of the lower molecular weight fraction by an additional soaking of the polymer with methanol lowers the functionality (see Table IV).

Table IV

EFFECT OF ADDITIONAL METHANOL WASH OF DNPA POLYMERS ON THE FUNCTIONALITY

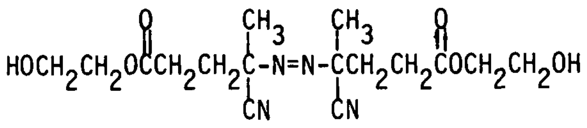
Sample No.	Eq.Wt.	f_{exp}		Eq.Wt.	f_{exp}
P-24	1,230	1.83	Additional Soaking in MeOH Overnight →	2,830	1.76
P-25	2,320	1.79		3,300	1,73

The result shown in Table IV may be mainly due to the elimination of residual $HOCH_2CH_2SSCH_2CH_2OH$ rather than the loss of the lower molecular weight polymer fraction. Further fractionation study has to be performed before the result can be explained. Meanwhile, a more rigorous purification procedure, i.e., soaking the polymer in methanol overnight, has been adopted in order to insure the elimination of undesirable impurities. Detailed purification procedure is described in the experimental section.

(2) Optimization of Polymerization Conditions Using Azo-OH as the Initiator and HEDS as the Chain Transfer Agent

Based on the kinetic mechanism study of the free-radical polymerization of DNPA in Section IV, Technical Background, the following initiator and chain transfer agent were selected initially to optimize the polymerization conditions:

Initiator:



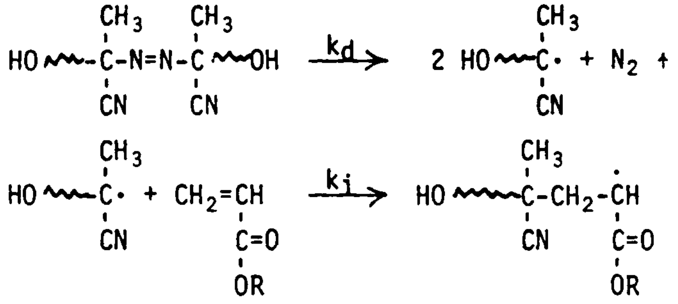
$$HOCH_2CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2OH$$

(Azo-OH)

Chain Transfer Agent: $HOCH_2CH_2S-SCH_2CH_2OH$ (HEDS)

The desired reaction for the difunctional polymer would be:

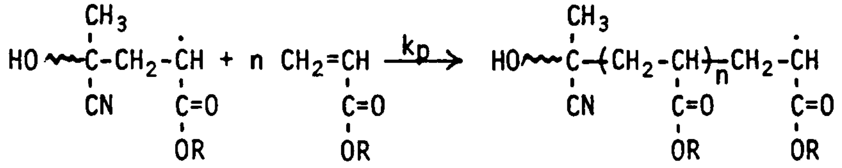
Initiation



$$HO\sim C(CH_3)(CN)-N=N-C(CH_3)(CN)\sim OH \xrightarrow{k_d} 2\ HO\sim \dot{C}(CH_3)(CN) + N_2\uparrow$$

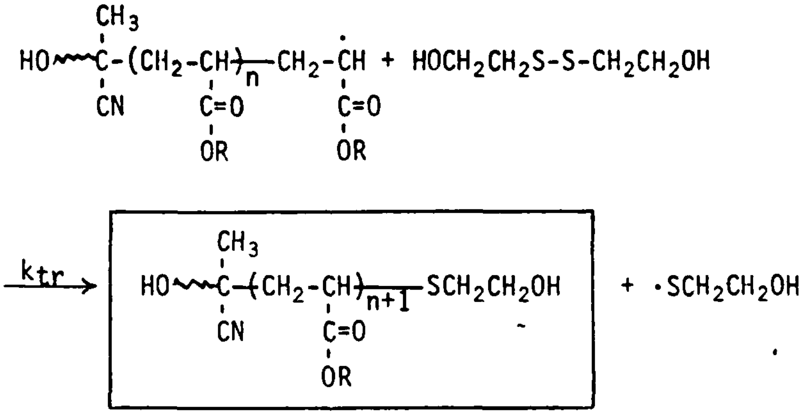
$$HO\sim \dot{C}(CH_3)(CN) + CH_2=CH(C=O)OR \xrightarrow{k_i} HO\sim C(CH_3)(CN)-CH_2-\dot{C}H(C=O)OR$$

Propagation



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

Chain Transfer



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

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

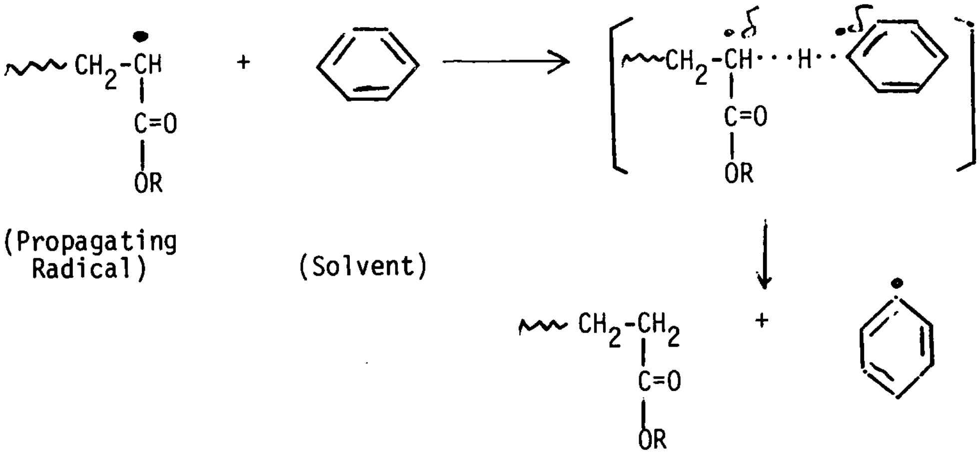
All other possible side-reactions (a) through (e) on Pages 4 and 5 in Section IV, Technical Background, should be minimized. Optimization of the polymerization conditions, therefore, should involve selections of suitable (a) solvent, (b) reaction temperature, and (c) concentrations of the reactants.

(a) Selection of Solvent

A desirable solvent for synthesis of hydroxy-terminated DNPA polymer should be one which undergoes the least degree of chain transfer reaction with the propagating polymeric radicals. The factors considered were (i) enthalpy at the transition state, (ii) donor-acceptor combination, and (iii) steric factor.

(i) Enthalpy factor at the transition state

The solvent should be such that a stable radical does not form via a chain transfer reaction with the propagating radical:



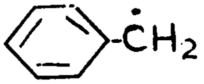
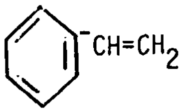
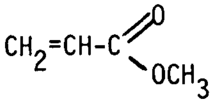
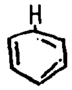
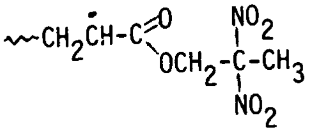
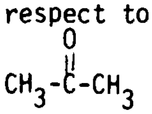
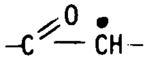
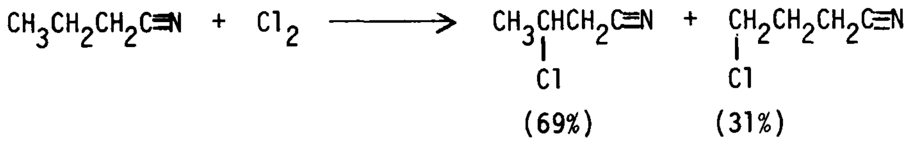
The above chain transfer reaction occurs more readily if the solvent can form a more stable radical. For example,  is much more stable than ; hence, the above reaction would occur far more readily with toluene than with benzene. Based in this consideration, the following solbecause the transition state is better stabilized by the extra electron delocalization. The examples in Table V clearly demonstrate this effect:

Table V

EXPERIMENTAL CHAIN TRANSFER CONSTANT, $({}^{k+r}/{}_{kp})\times 10^4$, AT 60^oC

	 (Donor)	 $CH_2=CH-C(=O)OCH_3$ (Acceptor)
 (donor)	0.02	0.6
n-BuS-H(acceptor)	210,000	17,000

The chain transfer activity of n-BuSH is far greater than that of  with the propagating radicals of both monomers in Table V, mainly because of the enthalpy factor discussed in (i). Furthermore, the data demonstrates the favorable effect of a donor-acceptor combination: methyl acrylate, an electron acceptor, has a higher activity with benzene, an electron donor, than does styrene, an electron donor. Methyl acrylate has a lower activity with n-BuSH, an electron acceptor, than does styrene. Since the propagating radical of DNPA,  $\sim CH_2\dot{C}H-C(=O)OCH_2-C(NO_2)_2-CH_3$, is a strong electron acceptor, the solvent should also be an electron acceptor in order to minimize the chain transfer reaction. Unfortunately, all the solvents considered in (i) are electron donors. A search for a solvent which would be favorable with respect to both enthapy factor and polar effect, was not successful. However,  $CH_3-C(=O)-CH_3$ and  were selected for evaluation. These ketones form more stable radicals ( $-C(=O)-\dot{C}H-$) than the ones selected in (i), but they are electron acceptors, and the polar effect may outweigh the enthalpy factor. This hypothesis is based on the previous work on radical chlorinations of alkanes substituted with electron withdrawing groups.(12, 13, 14) For example, the major product on radical chlorination of cyanopropane was found to be the β-chlorinated, and very little α-chlorinated product was observed:

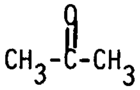
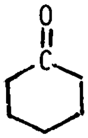
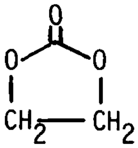
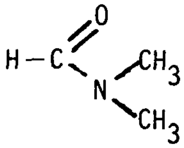
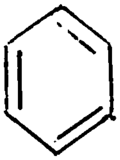
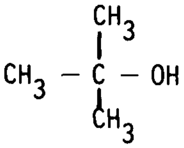


$$CH_3CH_2CH_2C\equiv N + Cl_2 \longrightarrow \underset{\underset{(69\%)}{Cl}}{CH_3CH}CH_2C\equiv N + \underset{\underset{(31\%)}{Cl}}{CH_2}CH_2CH_2C\equiv N$$

The enthalpy consideration alone would predict the major product to be the α-chlorinated, $CH_3CH_2\underset{Cl}{C}HC\equiv N$, since the radical intermediate, $CH_3CH_2\dot{C}HC\equiv N$, is more stable than the radicals on the β or γ carbon. The most likely explanation for the absence of the α-chloro-product would be the polar effect; chlorine atom is strongly electrophilic (acceptor), and the relatively electron-deficient carbon atom to the cyano-group will not give a favorable acceptor-donor combination. If the polar effect does outweigh the enthalpy factor, $CH_3\overset{O}{\overset{\|}{C}}-CH_3$ would be most favorable. Since the chain transfer reactions mainly involve bimolecular H-abstracting reactions; the number of gram hydrogen atoms per 100ml of the selected solvents are tabulated in Table IV. Ethylene carbonate and benzene have the least number of hydrogen atoms available for the chain transfer per volume.

Table VI

NUMBER OF GRAM H ATOMS PER 100 ml SOLVENT

Solvent	Density(20^{0}C)	Mol.Wt.	Moles/100ml	g H atoms/100 ml
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	0.790	58.1	1.36	8.16
	0.948	98.2	0.966	9.65 α 3.86 β 3.86 γ 1.93
	1.32	88.1	1.50	6.00
	0.949	73.1	1.30	9.09 $\overset{O}{\overset{\|}{C}}-H$ 1.30 CH_3 7.79
	0.879	78.1	1.13	6.75
 $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{\|}{\underset{\|}{C}}}}-OH$	0.789	74.1	1.07	9.58 OH 1.07 CH_3 8.51

All the solvents listed in Table VI were tested. The DNPA polymer formed became insoluble in t-butanol and only partially soluble in benzene. Preliminary experiemental results (Table VII) on the rest of the solvents, dimethylformamide, ethylene carbonate, cyclohexanone, and acetone, indicate that they do not cause the variation in the functionality of polymer, within the experimental error. The batch-to-batch variations of the syntheses have been 10-20% in equivalent weight and 4-10% in the average functionality (Table III). The reason for small difference among the above solvents may be that these solvents do not have high enough chain transfer activity in comparison with other ingredients in the polymerization system (see Equation (7) in Section IV, Technical Background), and/or the hydrogens on these solvents have similar reactivity toward the propagating radical. The most logical solvent to select, if their chain transfer activity is similar, would be acetone, since it is less expensive and also easier to remove after the polymerization.

(b) Selection of Polymerization Temperature

DNPA polymers were synthesized at 55°C, 65°C, 75°C, and at 90°C in order to examine the effect of reaction temperature on the polymer functionality. The results in Table VIII indicate that 65°C is more favorable than 55°C. The difference between 65°C and 75°C is not obvious, and it is possible that counteracting factors influence the functionality. For example, rates of the unfavorable disproportionate reaction in the radical termination step and of the desired chain transfer reaction increase more substantially than those of other reactions when the reaction temperature is raised 75°C from 65°C. A higher functionality was observed at 90°C but a temperature as high as 90°C may be unsuitable, since other undesirable side-reactions, such as with the nitro-groups, may increase. The reaction temp-

Table VII

EFFECT OF SOLVENT TYPE ON DNPA POLYMERS
(Polymerization Temperature: 65°C for 10-23 Hours)

	Polymerization Ingredients					
Sample No.	DNPA	Azo-OH	$(HOCH_2CH_2S)_2$	Solvent	Eq.Wt.	f_{exp}
4	0.1m	0.004m	0.073m	B 0.12m (12g)	8,120	1.51
PJ-8	0.1m	0.005m	0.073m	BO 0.35m (26g)	---*	--*
PJ-27	0.1m	0.004m	0.073m	DMF 0.22m (16g)	4,360	1.68
PJ-11	0.1m	0.005m	0.13m	DMF 0.27m (20g)	1,040	1.76
PJ-24	0.1m	0.005m	0.13m	EC 0.23m (20g)	2,380	1.73
15	0.1m	0.011m	0.13m	DMF 0.27m (20g)	2,500	1.78
16	0.1m	0.011m	0.13m	CH 0.20m (20g)	2,940	1.78
31	0.1m	0.011	0.13m	Ac 0.29m (17g)	3,830	1.74

* Polymer with M.W. over 10,000: Eq.Wt. and fexp were not determined.

Table VIII

EFFECT ON REACTION TEMPERATURE ON POLYMER FUNCTIONALITY
(Reaction Time = 23 Hours)

	Polymerization Ingredients						
Sample No.	DNPA	Azo-OH	$(HOCH_2CH_2S)_2$	CH	Rexn Temp	Eq.Wt.	f_{exp}
20	0.1m	0.011m	0.13m	0.20m	65°C	2,330	1.78
21	0.1m	0.0062m	0.13m	0.20m	65°C	2,020	1.68
22	0.1m	0.011m	0.13m	0.20m	55°C	2,800	1.71
23	0.1m	0.0062m	0.13m	0.20m	55°C	2,840	1.65

erature will be restricted to 65°C - 75°C for the optimization study.

(c) Variation of the Concentration of Reactants

Two initiator concentrations were selected and the effect of difference in the concentration on the polymer functionality was examined using DMF and cyclohexanone. The results in Table IX indicate that the higher initiator concentration gives higher functionality. This means that the first terms in Equations (6) and (7) in Section IV, Technical Background, still play an important role in influencing the degree of polymerization and the functionality. If there is substantial disproportionation reaction in the termination step, chemical reaction (5), this may not be minimized, since the ratio of disproportionation to combination in the termination step is inherent to the monomer structure.

Table IX

EFFECT OF INITIATOR CONCENTRATION ON FUNCTIONALITY
(Polymerization Conditions: 65°C for 23 Hours)

	Polymerization Ingredients					
Sample No.	DNPA	Azo-OH	$(HOCH_2CH_2S)_2$	Solvent	Eq.Wt.	f_{exp}
12	0.1m	0.0062m	0.13m	DMF 0.27m	2,520	1.73
15	0.1m	0.011m	0.13m	DMF 0.27m	2,500	1.78
21	0.1m	0.0062m	0.13m	CH 0.20m	2,020	1.68
20	0.1m	0.011m	0.13m	CH 0.20m	2,330	1.78

It is obvious that the concentration of HEDS should be increased over that of solvent, and the data in Table X support the theory. Unfortunately, the polymer formed is insoluble in HEDS, and the maximum allowable concentration of HEDS is limited by the solubility. If there is an OH-group containing disulfide which is a good solvent for DNPA polymer, its use as the solvent as well as the chain transfer agent, would improve the polymer functionality.

Table X

EFFECT OF CONCENTRATION OF HEDS ON FUNCTIONALITY

Sample No.	DNPA	Azo-OH	HEDS		RenT	Eq.Wt.	f_{exp}
16	0.10m	0.011m	0.13m	0.20m	65°C	2940	1.80
17	0.10m	0.011m	0.036m	0.20m	65°C	2830	1.68

(3) Polymerization Using Azo-OH as the Initiator and o-DTB-OH as the Chain Transfer Agent

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.(15) Recently, Guryanova(16) reported that the S-S bond strength of diphenyl disulfide is as low as 20-26 kcal/mole vs 58-64 kcal/mole for $C_4H_9S-SC_4H_9$ (Table XI). Furthermore, his data in Table XI 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 labelled sulfur atoms is:

$$(1) \quad RS^{*}-S^{*}R \xrightarrow[\Delta]{} RS^{*}\cdot + \cdot S^{*}R$$

$$(2) \quad RS^{*}\cdot + RSH \longrightarrow RS^{*}H + RS\cdot$$

$$(3) \quad RS\cdot + RS\cdot \longrightarrow RS-SR \quad \text{or} \quad RS\overset{*}{\cdot} + RS\cdot \longrightarrow RS\overset{*}{-}SR$$

Table XI

Energy of S-S Bonds in Disulfides (kcal/mol)

Obtained by the Method of RS-Group Exchange

System	Temperature range (°)	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-$CH_3C_6H_4S^*-{}^*SC_6H_4CH_3$-$p$ p-$CH_3C_6H_4S-H$	93-142	13	32
p-$CH_3OC_6H_4S^*-{}^*SC_6H_4OCH_3$-$p$ p-$CH_3OC_6H_4S-H$	101-164	14,4	35
p-$C_6H_5C_6H_4S^*-{}^*SC_6H_4C_6H_5$-$p$ p-$C_6H_5C_6H_4S-H$	1110-160	14,4	35
p-$NO_2C_6H_4S^*-{}^*SC_6H_4NO_2$-$p$ p-$NO_2C_6H_4S-H$	104-145	23	52

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 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), which was discussed above in Section V-B-2.

DNPA polymers were synthesized using the same numbers of moles of polymerization ingredients, except for the use of two different chain transfer agents (Table XII).

o-DTB-OH definitely has a higher chain transfer activity than HEDS on a molar basis, and is consistent with the finding of Guryanova. However, the actual amount of o-DTB-OH used on a weight basis (14.3 g) was 2.6 times greater than that of HEDS (5.6 g). The comparison on a weight basis would be more practical for our purpose, and this will be examined.

Table XII

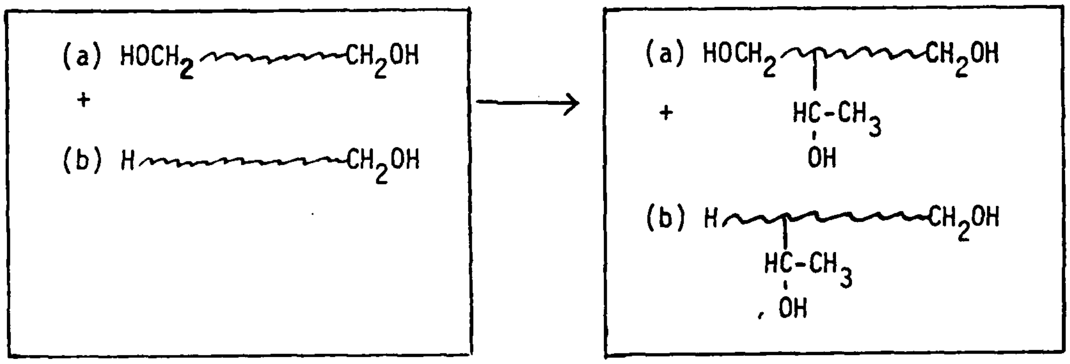
COMPARISON OF HEDS VS o-DTB-OH AS CHAIN TRANSFER AGENT

(0.010m DNPA, 0.011m Azo-OH, 0.20m0 at 65^{o}C, 23 hours)

Sample No.	HO-R-S-S-R-OH	OH-E.W.	f_{exp}
18	o-DTB-OH 0.036m(14.3g)	4860	1.76
26	o-DTB-OH 0.036m(14.3g)	5280	1.73
17	HEDS 0.036m(5.6g)	2830	1.68
25	HEDS 0.036m(5.6g)	3300	1.65

C. Synthesis of OH-Terminated DNPA Polymers Having Functionality Greater Than 2.0

Free-radical vinyl polymerization systems are usually accompanied by many hydrogen-abstracting side reactions, thus creating appreciable amounts of polymers having functionality of 1.0. Not all the side reactions can be minimized and this is why the functionality of 2.0 cannot be obtained by this method. We have achieved functionality as high as 1.80 through various modifications of the polymerization conditions. This value, however, indicates that about 20 mole % of the polymers are still 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) A 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 XIII, where an incorporation of a small amount of 2-hydroxypropyl acrylate as a comonomer in the DNPA radical additional 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.

Table XIII

Incorporation of Cross-Linker Within the Polymer

	Polymerization Conditions						
	DNPA	HPA	Azo-OH	HEPS	DMF	EW	F_{exp}
Polymer[A]	0.1m	0m	0.005m	0.08m	0.22m	4300	1.76
Polymer[B]	0.1m	0.005m	0.005m	0.08m	0.22m	1550	2.80

D. Characterization of Dinitropropyl Acrylate Polymers

1. Determination of OH-Equivalent Weight

A common method used in the determination of OH-equivalent weight of prepolymer involves the reaction of a prepolymer with an acid anhydride in the presence of a base. This method cannot be utilized for polymers containing nitro groups, because they undergo reaction with base.

Our approach was to use an IR method using the associated OH peak in the region of 3500 cm^{-1}. The best solvent selected for this system is tetrahydrofuran (THF). THF is an excellent solvent for polydinitropropyl acrylates (PDNPA) and also gives a single, sharp associated OH-peak at 3435 cm^{-1} in the concentration region of 10-60 meq/l. Other solvents, such as ethyl acetate and methyl ethyl ketone, are undesirable since they have a carbonyl overtone band near 3500 cm^{-1} and also tend to give more than one hydroxyl peak (Fig. 3-a).

The primary difficulty encountered with this method was due to the presence of overtone bands of ester groups of PDNPA in the same region. DNPA, and α,β-unsaturated ester, gives an overtone peak at 3475 cm^{-1}, and PDNPA, a saturated ester, at 3490 cm^{-1}, as shown in Fig. 4. Since the analysis requires a quantitative determination of OH-groups at a concentration level as low as 10 milli-equivalents, the ester overtone of PDNPA interferes with the analysis. There are many more ester groups than OH groups present in a molecule of PDNPA. It was observed that the best approach to negate the effect of the overtone band is to use a 15% PDNPA solution in THF as a reference. The DNPA polymer used for the reference should not contain OH-groups; hence, it was synthesized using azoisobutyronitrile (AIBN) as an initiator and t-dodecylmercaptan as the chain transfer agent:

Fig. 3

Hydroxyl Bands of $HOCH_2CH_2SSCH_2CH_2OH$ (45 meq/l)
In Various Solvents; 1.0 mm KBr cells

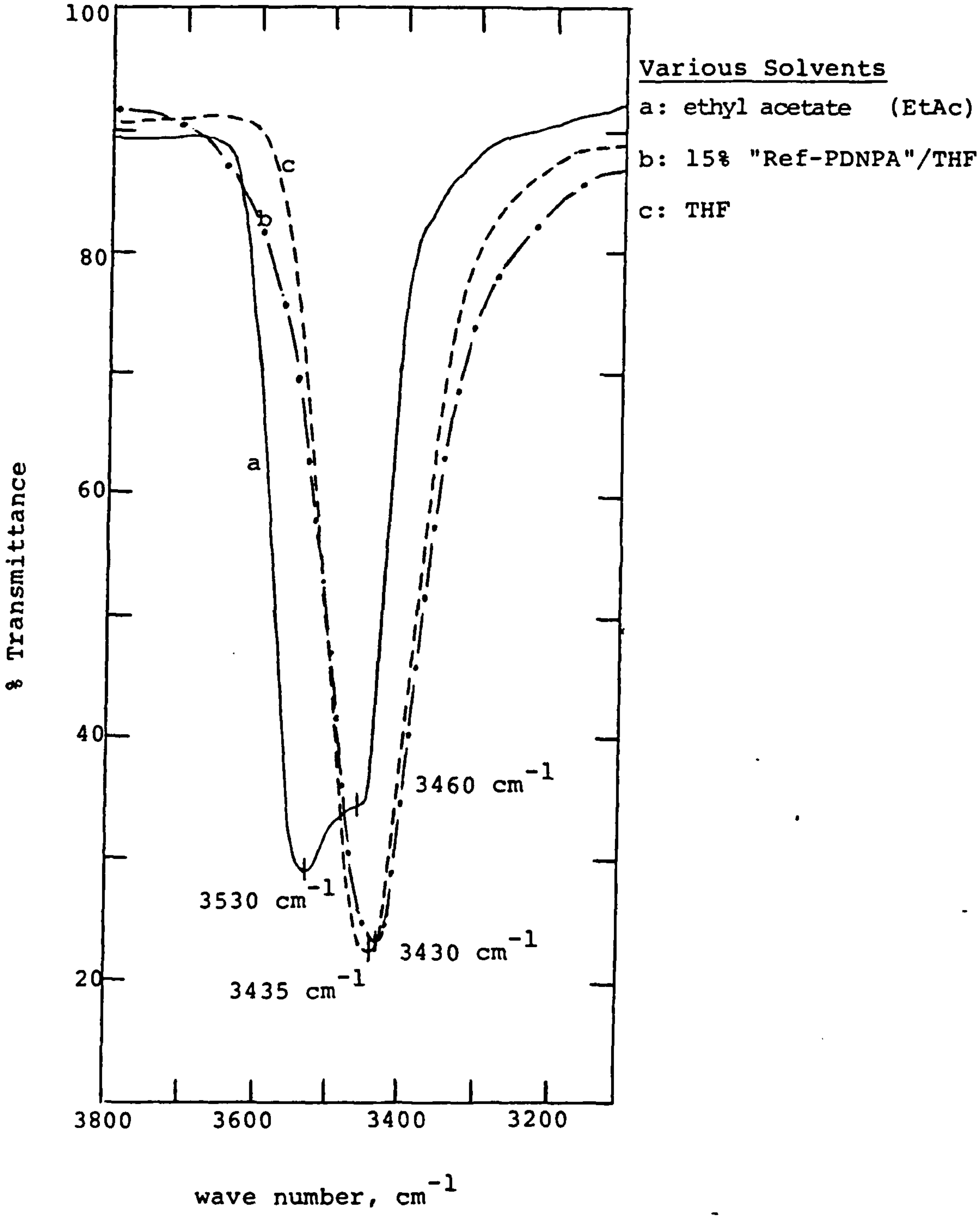
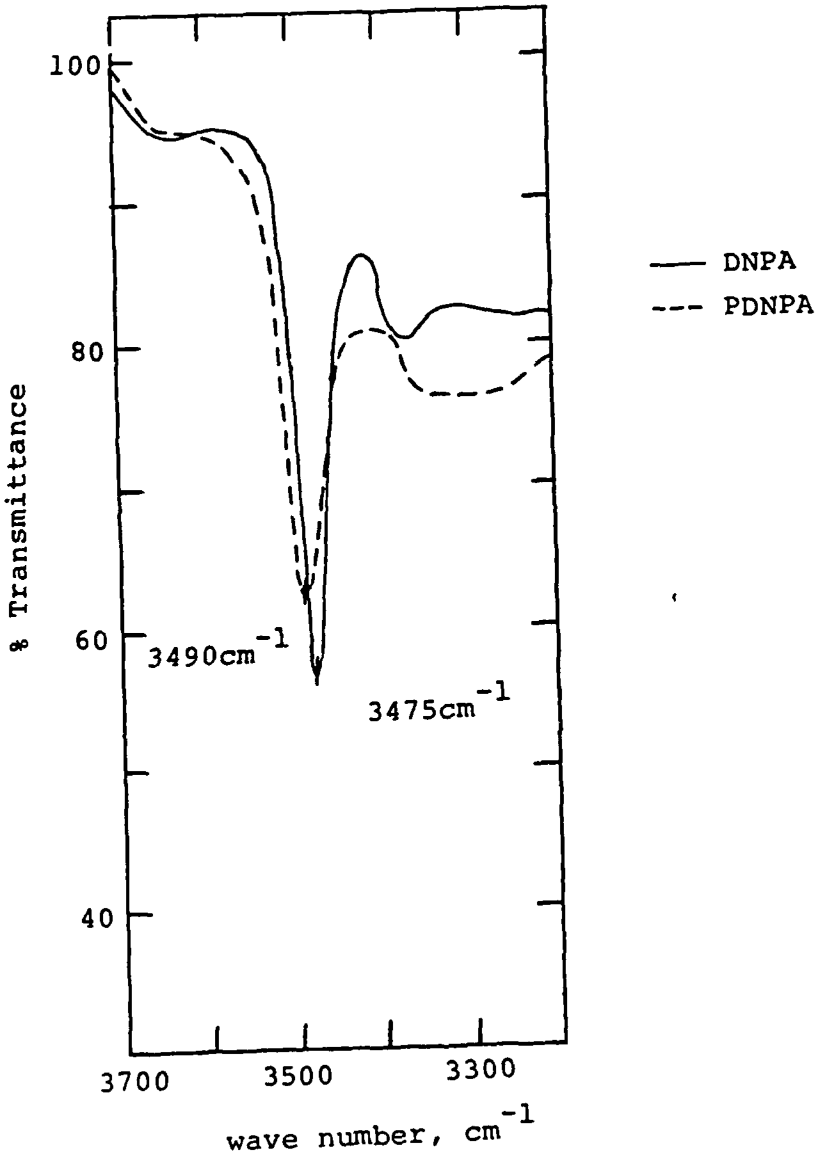
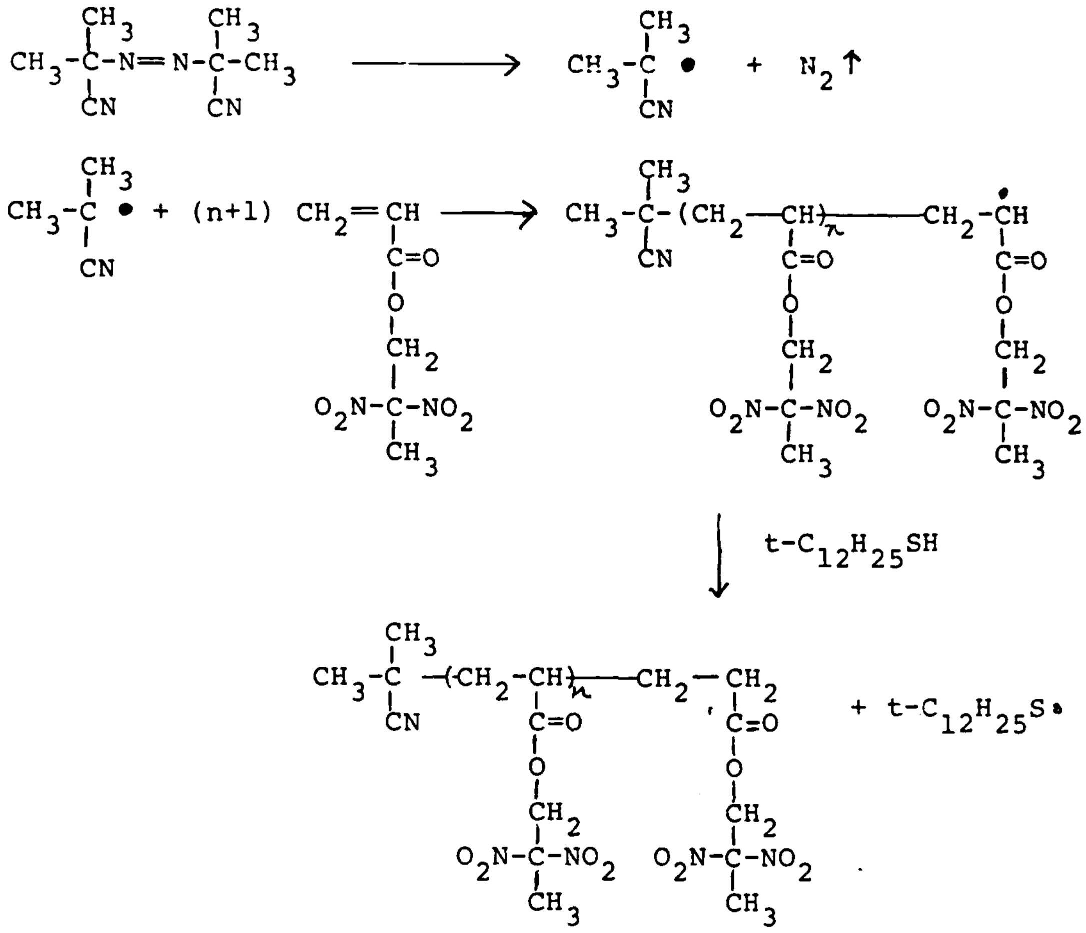


Fig. 4

Ester Overtone Bands of DNPA and PDNPA:
15 Weight % Solution in THF
1 mm KBr cells





(Ref-PDNPA = PDNPA With No OH-Groups)

When a 15% by weight THF solution of a PDNPA samples containing OH-groups analyzed against the reference containing 15 wt. % "Ref-PDNPA" in THF, the peak observed 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 Fig. 5: The OH peak of $HOCH_2CH_2SSCH_2CH_2OH$ (HEDS) at a concentration of 45 meq/l, using 15% "Ref-PDNPA" in THF as a solvent (Fig. 5-b), and that using THF only as a solvent (Fig. 5-c) give the same absorbance. The slight shift in the wave length from 3535 cm^{-1} to 3530 cm^{-1}, due to the presence of 15% PDNPA, is within the experimental error. Different primary alcohols, i.e., $HOCH_2CH_2SSCH_2CH_2OH$ (HEDS) and $HOCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$ (HEA), give the absorption peaks at the same wave length having the same intensity (Fig. 5). 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 becomes large as in the case with the OH-terminated PDNPA.

The OH-peaks of HEA and HEDS, dissolved in a 15% "Ref-PDNPA"/THF show <u>no</u> shift in wave length over the OH-concentration range of 10-60 meq/l (Fig. 6 and 7). Furthermore, a plot of absorbance versus concentration gives a linear relationship (Fig. 8). An optimum concentration of the OH-concentration for the accurate determination using 1 mm solution cells, appears to be 30-50 meq/l. In order to prepare a solution having the above OH-concentration range; the weight % polymer in THF must vary from 5 weight % to 15 weight %, depending on the equivalent weight of the polymer. The effect of varying the equivalent weight percentage of polymers was studied and the result is summarized in Table XIV. The deviation due to the change in weight % polymer concentration in THF is negligible within the experimental error. Hence, the procedure for the OH-equivalent weight determination includes the adjustment of the polymer solution from 5 to 15 weight % so that the OH-concentration becomes approximately 30 meq/l.

Fig. 5

Hydroxyl Bands of Primary Alcohols in THF and in 15 wt % "Ref-PDNPA"/THF; 1.0 mm KBR cells

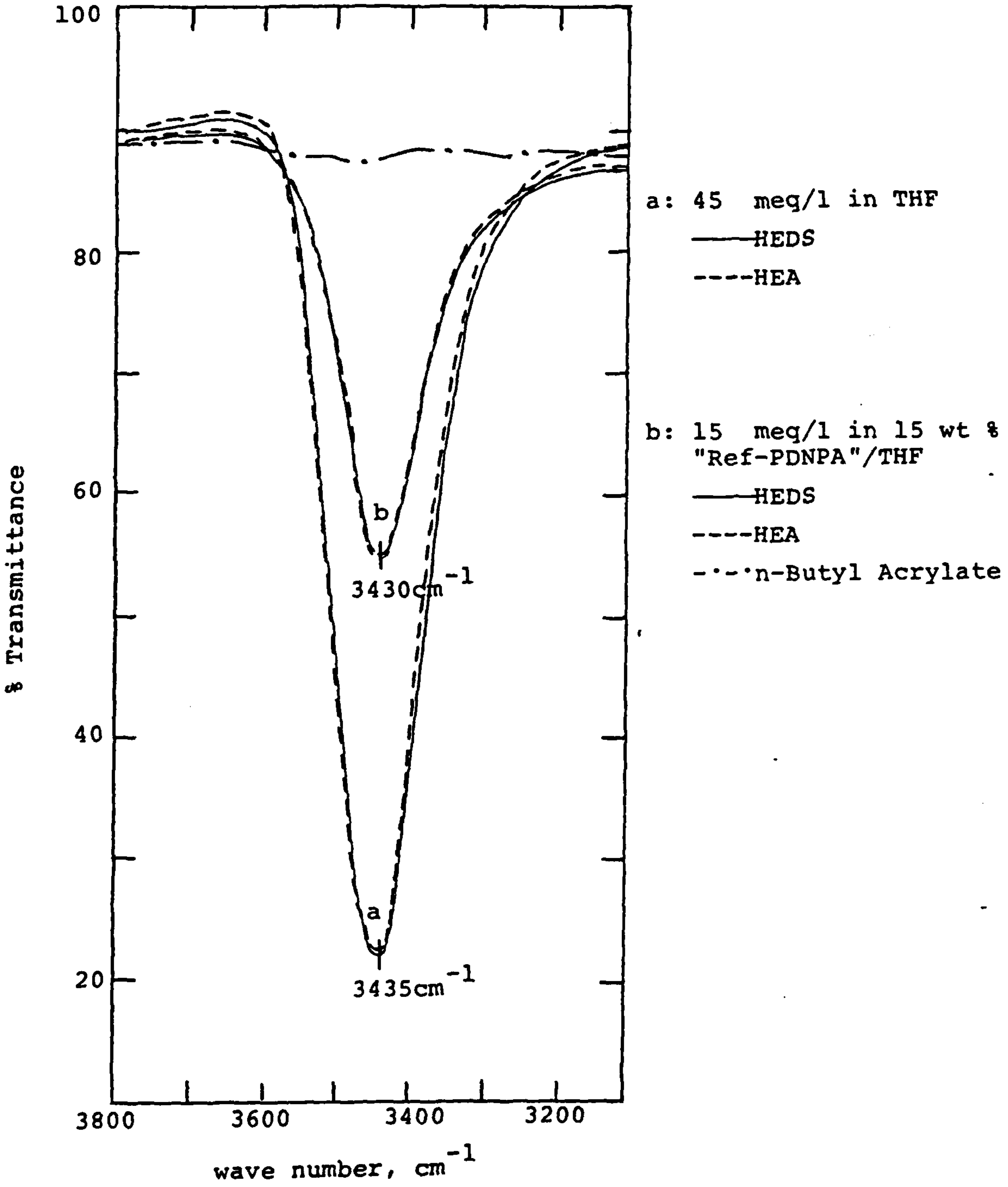


Fig. 6

Hydroxyl Bands of $HOCH_2CH_2SSCH_2CH_2OH$ in 15 wt. %
"Ref-PDNPA"/THF at Various Concentration Levels
1 mm KBr cells

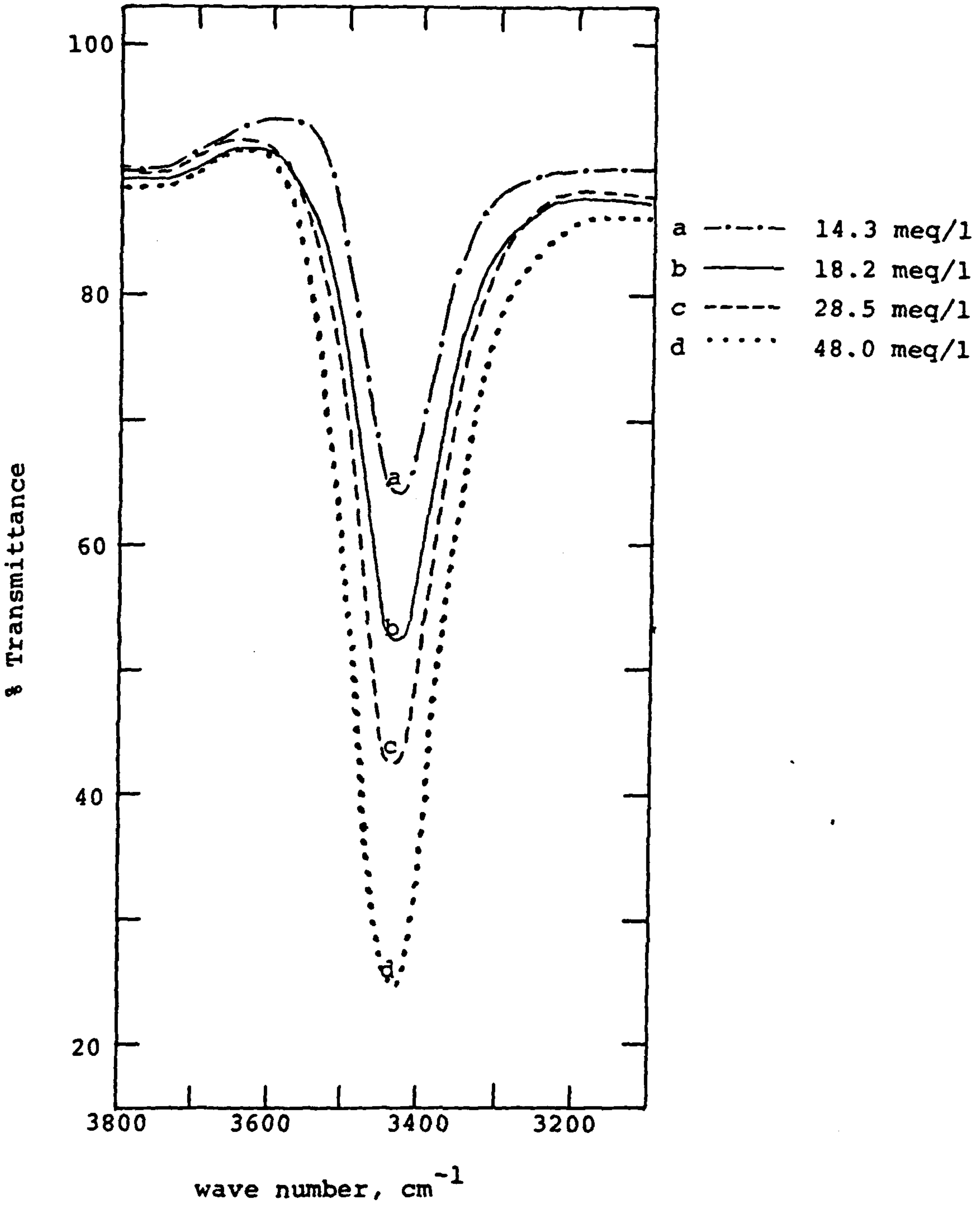


Fig. 7

Hydroxyl Bands of $HOCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$ in 15 wt. % "Ref-PDNPA"/THF at Various Concentration Levels

1 mm KBr cells

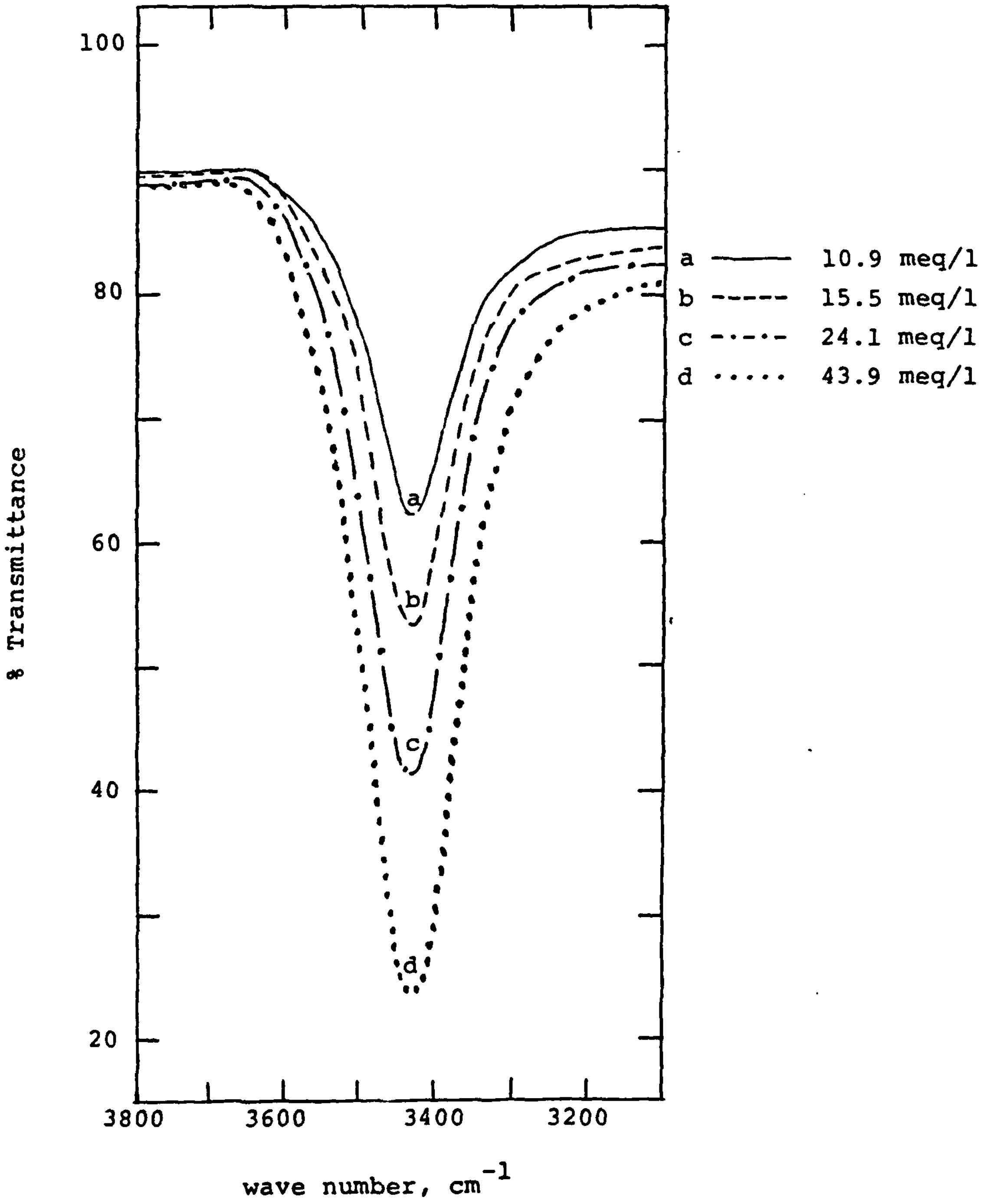


Fig. 8

Absorbance of Hydroxyl Bands vs Concentration
Solvent: 15 wt % "Ref-PDNPA" in THF
1 mm KBr cells

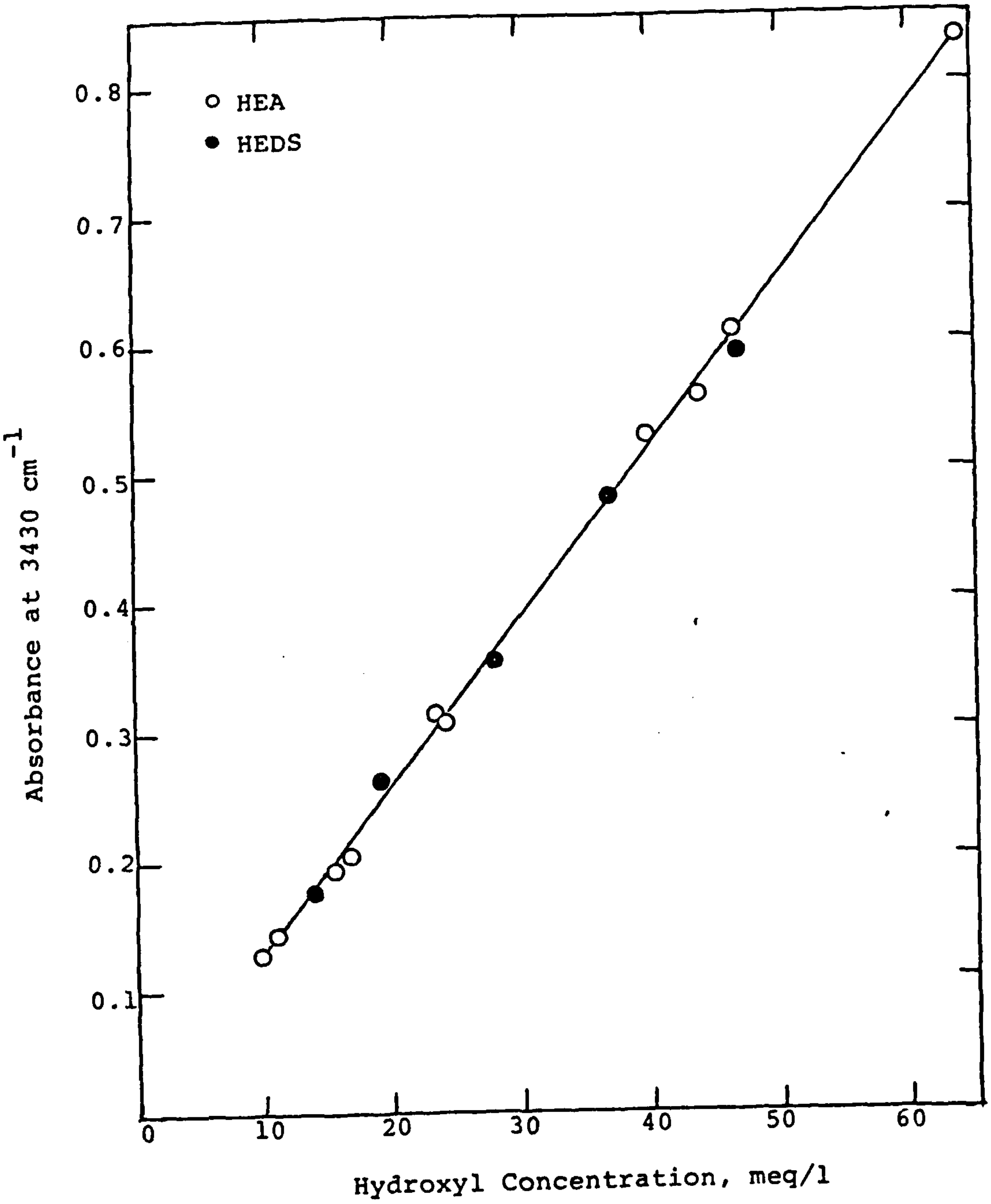


Table XIV

EFFECT OF VARIATION OF WT. % POLYMER ON DETERMINATION OF OH-EQUIVALENT WEIGHT

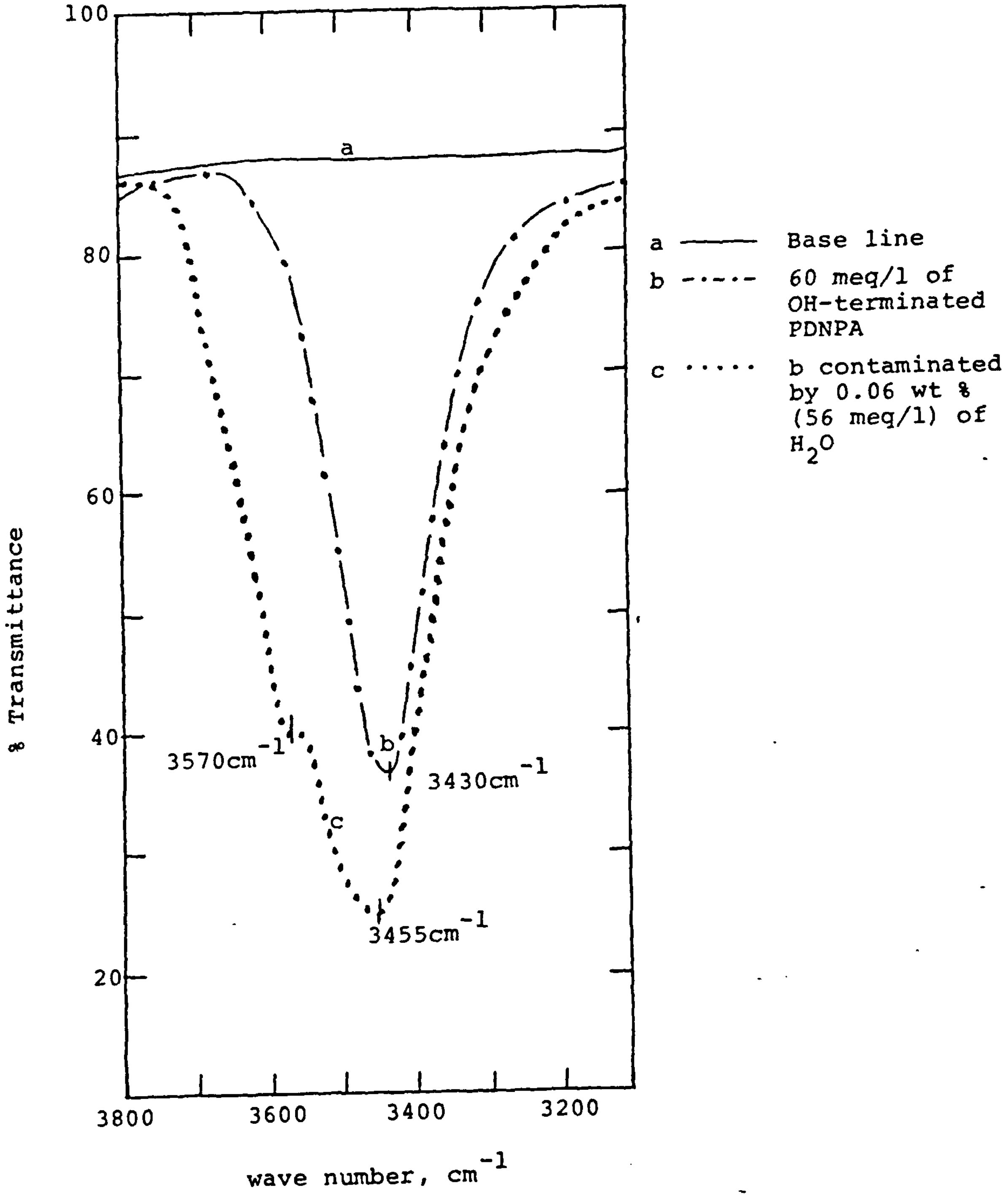
Sample No.		Wt. % DNPA Polymer in THF	Eq. Wt.	Average Eq. Wt.	% Deviation
P-24	(a)	5.0%	1170,1190	1180	0.8%
	(b)	7.5%	1170,1230	1200	2.5%
	(c)	Average of (a) & (b)		1190	0.8%
P-25	(a)	7.5%	2220,2230	2225	0.2%
	(b)	15.0%	2270,2270	2270	0.0%
	(c)	Average of (a) & (b)		2248	1.0%
P-26	(a)	5.0%	1160,1180	1170	0.9%
	(b)	15.0%	1120,1130	1125	0.4%
	(c)	Average of (a) & (b)		1148	0.9%

Based on the above discussion, Fig. 8 may be used to determine the OH-equivalent weight of some alcohols. The equivalent weights of Azo-OH and PDNPA samples were determined using Fig. 8.

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 Fig. 9. The primary reason for this is due to the low molecular weight of water in comparison with that of the polymer. However, 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

Fig. 9

Effect of the Presence of Water on the Hydroxyl Bands
Solvent: 15 wt % "Ref-PDNPA" in THF 0.5 mm KBr cells



wave number. Hence, all the samples must be dried over P_2O_5 in vacuo and the THF distilled from $LiAlH_4$ for this analysis.

2. Determination of Number Average Functionality

The functionality of DNPA polymers was determined using the technique developed by Oberth(17) based on a cure study with an isocyanate. It is based on the theory that a diol (f_p=2.0) reacts with a diisocyanate (f_i=2.0) to form infinitely long chains, defined as a "gel." This occurs only if there are no side-reactions and no cyclization reactions. Since it is impossible to avoid all the side-reactions, this method gives an "effective functionality" which is most likely less than the theoretical value.

For the 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),

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

or

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

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

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

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) <u>for f_p=1.71:</u>

0.583 meq. polymer (50% solution) : 2.934g

0.250 meq. PCP (20% solution) : 0.368g

0.833 meq. HDI (30% solution) : 0.234g

4 drops of 10% FeAA in dimethyl phthalate

(b) <u>for f_p=1.76:</u>

0.644 meq polymer (50% solution) : 3.241g

0.226 meq PCP (20% solution) : 0.332g

0.870 meq HDI (30% solution) : 0.244g

4 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.

IV. EXPERIMENTAL SECTION

A. 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 allowed to stir 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.

B. Synthesis of Azo-OH

To a solution of 20.2 g Azo-acid (65% purity in H_2O), and 1.0 g 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 16.8 g (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 adsorbents, and (3) recystallization using various solvents.

C. Synthesis of o-DTB-OH

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-DTBA, 30.6 g (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 subject 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)

D. An Example of Solution Polymerization of DNPA

Into a 100 ml round bottom flask were added 0.10 mole (20.4 g) DNPA, 0.01 mole (4.29 g) Azo-OH, 0.2 mole (20.0 g) cyclohexanone and 0.127 mole (5.59 g) HEDS (98% Aldrich Chemical Co.). After the solution mixture had been vigorously degassed with nitrogen for 15 minutes, the mouth of the flask was sealed with a sleeve type rubber septum. The entire solution was degassed with N_2 for another 10 minutes, using needles as inlet and outlet. The reaction mixture was agitated in a 65°C water bath under a N_2 atmosphere for twenty hours.

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