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NSWC/WOL TR 78-120
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PREPARATION OF POLY (DINITROPROPYL VINYL ETHER) WITH CROSSLINKING SITES, FOR USE AS A CASTABLE BINDER

BY G. W. LAWRENCE H. G. ADOLPH

RESEARCH AND TECHNOLOGY DEPARTMENT

1 DECEMBER 1978

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

Attempts were made to prepare dinitropropyl vinyl ether (DNPVE) prepolymers of a molecular weight range of 2,000 to 4,000 with hydroxy functionality for use in cast-curable energetic binder systems. Two approaches were pursued. First, part of the dinitropropyl side chains in Poly-DNPVE were reduced to mononitropropyl groups and then hydroxymethylated with aqueous formaldehyde. The desired hydroxy-functional polymer was formed in excellent yield. In a second approach, DNPVE monomer was polymerized using initiator systems capable of introducing functional groups. The system, epichlorohydrin/$SnCl_4$/DNPVE, gave

an incompletely characterized product of the expected elemental composition. However, the structure of the product was not determined.

SUMMARY

This is the final report for the task "Preparation of Poly(dinitropropyl vinyl ether) with Crosslinking Sites, for Use as a Castable Binder," carried out under Air Force sponsorship (AFATL/DLDE, Project Order ATL-7-87). This task was a one-year effort and resulted in the preparation of two polymer systems of potential utility in cast-curable energetic binders.

Julius W. Enig
J. W. ENIG
By direction

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INTRODUCTION AND OBJECTIVE

2,2-Dinitropropyl vinyl ether, DNPVE, was first synthesized in 1970 by the mercuric sulfate catalyzed vinylization of 2,2-dinitropropanol with vinyl acetate.[1] This reaction provides a 50-60% yield of DNPVE of 97-99% purity after two fractional distillations under reduced pressure.

$$CH_3C(NO_2)_2CH_2OH + CH_2{=}CH\text{-}OAc \xrightarrow[0^\circ]{HgSO_4}$$

$$CH_3C(NO_2)_2CH_2O\text{-}CH{=}CH_2$$

DNPVE

In order to obtain a product of sufficient purity for polymerization (see Figure 1), two and sometimes three fractional distillations through a Vigreux column were required, a fact which might be considered a drawback of this synthesis method.

Subsequently, McGuire, Cochoy, and Shackelford discovered an alternate synthesis of DNPVE from 2,2-dinitropropanol and divinylether, using a classified catalyst.[2]

$$CH_3C(NO_2)_2CH_2OH + CH_2{=}CH\text{-}O\text{-}CH{=}CH_2 \longrightarrow$$

$$CH_3C(NO_2)_2CH_2O\text{-}CH{=}CH_2$$

DNPVE

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[1] Adolph, H. G. and Kamlet, M. J., Limited Report Regarding Binder Components, 13 Apr 1971;
Adolph, H. G., "2,2-Dinitroalkyl Vinyl Ethers and Polymers Thereof," U. S. Patent 3,808,182, patented 1974.

[2] McGuire, R. R. and Cochoy, R., "Potential New Binders and Plasticizers for Solid Rocket Propellants," in Proceedings of the AFSC 1973 Science and Engineering Symposium, Kirtland AFB, NM; Shackelford, S. A., McGuire, R. R., and Cochoy, R. E., "One Step Synthesis of Polynitroaliphatic Vinyl Ethers. Monomeric Precursors to Energetic Binder Application," F. J. SLR Technical Report 77-0018, F. J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO, Dec 1977.

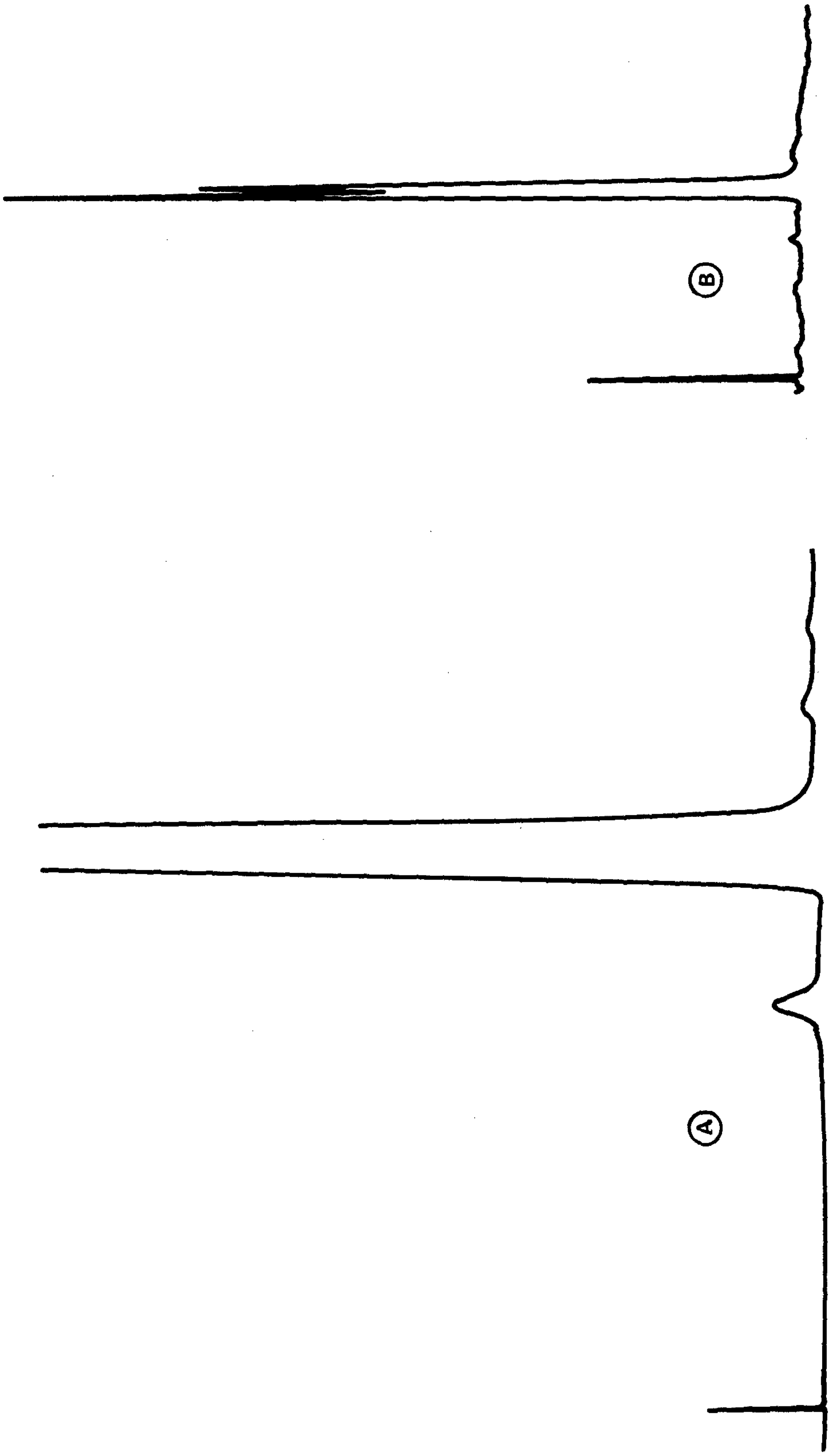

FIGURE 1 GC OF DNPVE SAMPLES USED FOR POLYMERIZATION PREPARED FROM A) DNPOH AND VINYL ACETATE, B) DNPOH AND DIVINYL ETHER

Benziger optimized this synthesis.* It is said to give better yields and a purer product requiring less cumbersome purification than the vinyl acetate method.**

Still another preparation of DNPVE was reported by Coburn who thermolized bis(2,2-dinitropropyl)acetal.[3]

$$[CH_3C(NO_2)_2CH_2O]_2CHCH_3 \longrightarrow CH_3C(NO_2)_2CH_2OH +$$

$$\underset{\text{DNPVE}}{CH_3C(NO_2)_2CH_2O\text{-}CH{=}CH_2}$$

DNPVE can be polymerized cationically in ethylene chloride solution with $SnCl_4$ as catalyst. The product is a polymer of low molecular weight which varies with the monomer concentration.[1] Number average molecular weights obtained with a vapor phase osmometer ranged from 1,000 to 7,000. Gel permeation chromatography of a THF solution gave a $\bar{M}_n$ of 4550 ($\bar{M}_w$ = 8608, both relative to polystyrene) for a sample that had an osmometric molecular weight of ca. 4,000. The molecular size distribution for this sample is shown in Figure 2. Benziger found that the polymerization of DNPVE with an $SnCl_4$/HOAc catalyst under somewhat modified conditions gives a higher molecular weight product (m.w. >15,000).***

The DNPVE polymers prepared so far (m.w. range 1,200-7,000) have softening points between 80 and 130°C. Some significant attributes of these energetic polymers are good thermal and chemical stability.[1] According to the cationic polymerization schemes 1 and 2 shown below, the polymer chain should be terminated by a methyl group at one end, and by one of the following groups at the other: vinyl, hemiacetal, chloroether, acetal, formyl.

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*Benziger, T. M., Los Alamos Scientific Laboratory, Los Alamos, NM; private communication.

**To some extent these advantages are only making up for the fact that divinyl ether is much more costly and less readily available than vinyl acetate.

***Benziger, T. M., Los Alamos Scientific Laboratory, Los Alamos, NM; private communication.

[3] Coburn, M. D., "Synthesis of 2-Nitroalkyl Vinyl Ethers," Synthesis, No. 8, 1977, p. 570.

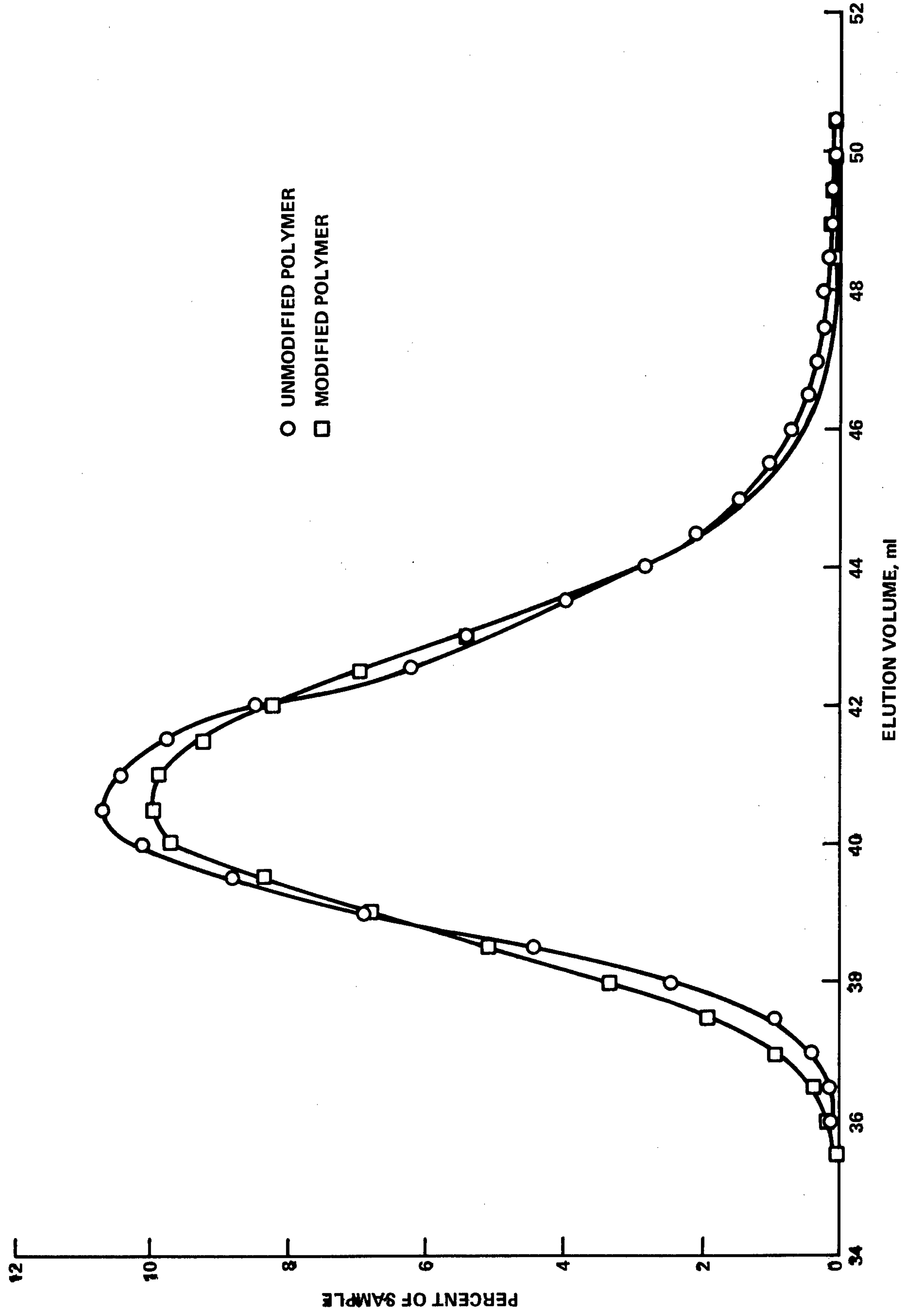


FIGURE 2 GPC OF MODIFIED AND UNMODIFIED POLY-DNPVE

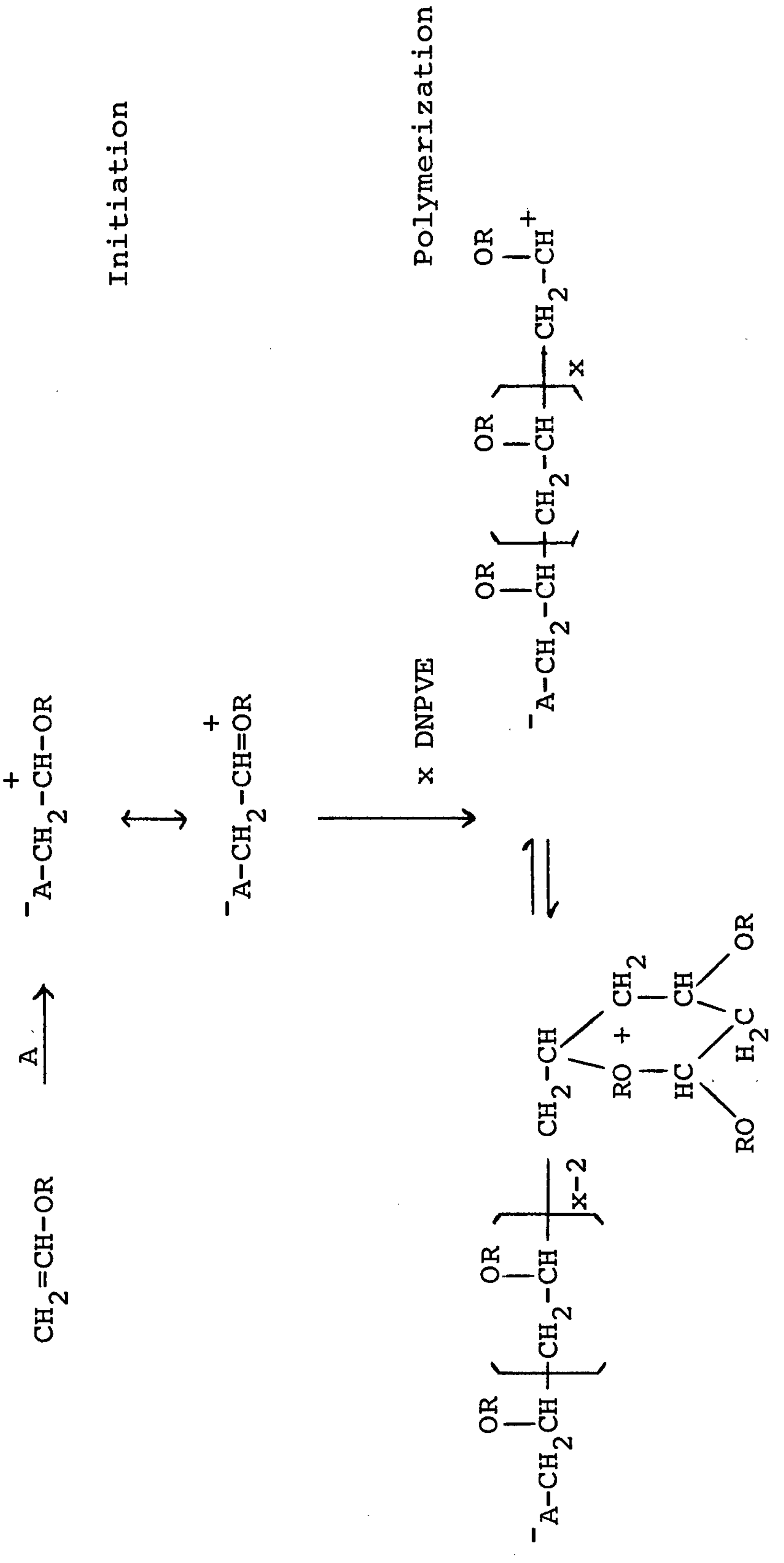
An attempt was made to identify these end groups by nmr analysis at 100 and 220 MHz. A DNPVE sample of molecular weight 4,000 (osmometer) in d_6-acetone showed indeed a doublet at 1.19 ppm which we attribute to a methyl group at one chain end (Figures 3 and 4). However, a second functionality could not be positively identified. Vinyl and aldehyde resonances are absent in both spectra. This leaves the hemiacetal, chloroether, and acetal functions shown in scheme 2. Since the chlorine content of the polymer is essentially zero (see experimental section) and hemiacetals of this type are generally not stable, the acetal group emerges, by way of elimination, as a possible end group. However, then the molecule must contain some other functionality in the chain (Cl, OH, or vinyl) as indicated in scheme 2, which was not found. One possible solution to this puzzle may be that several different end groups are present, in which case the concentration of the individual groups may be too low for detection by the nmr method employed.

In any event, although an occasional hydroxy or vinyl group undetected by the nmr analysis could be present in the polymer, this functionality would be insufficient for crosslinking which would be required if Poly-DNPVE were to be used as a castable binder component. For this purpose a functionality ≥ 2 is needed. Accordingly, it is the objective of this task to develop a method, or methods, which will permit the preparation, from dinitropropyl vinyl ether monomer, of difunctional prepolymers, which, with suitable chain extenders, crosslinking agents, and plasticizers, can be formulated into a cast-curable binder system.

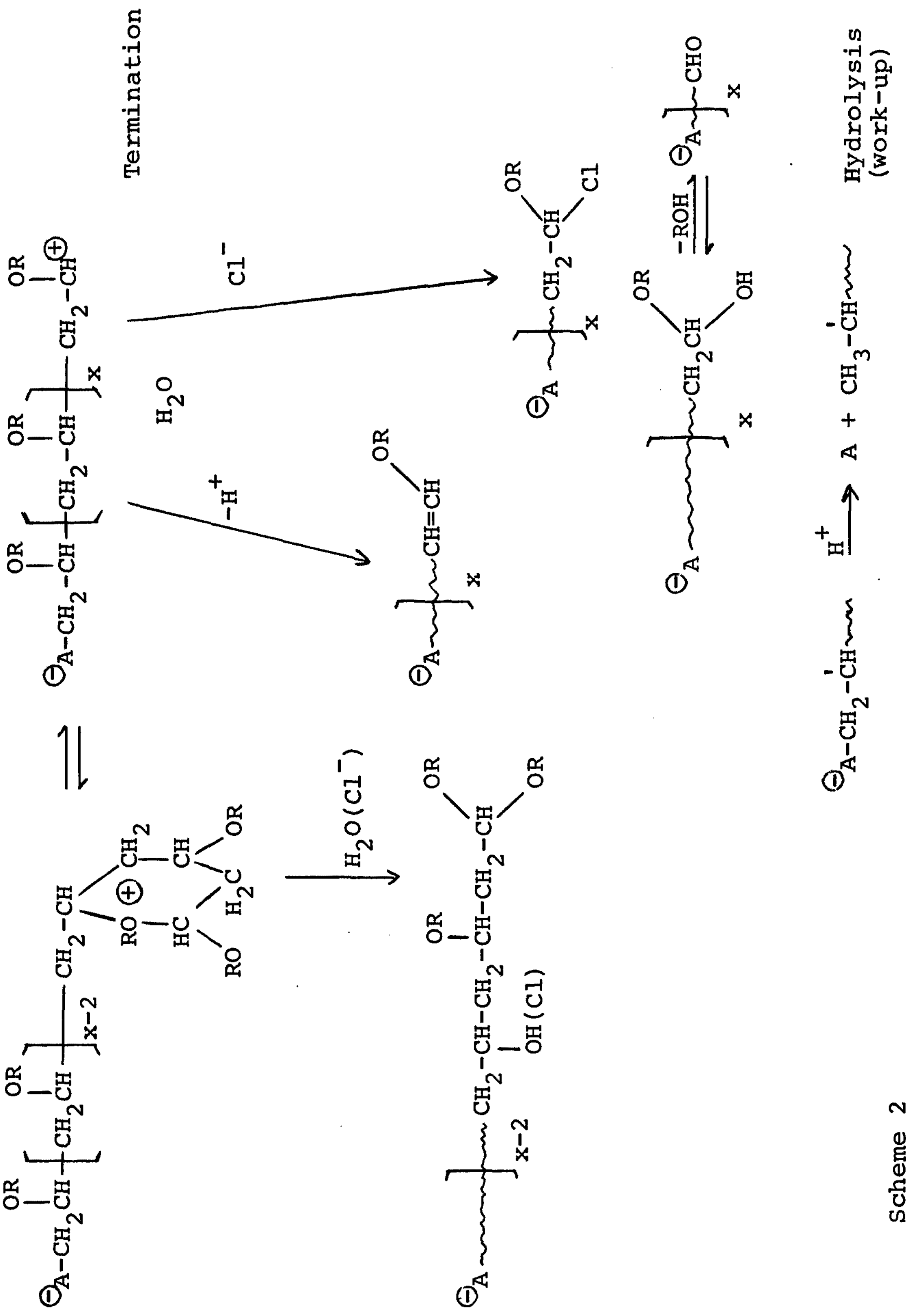
APPROACH

Copolymerization of DNPVE with a monomer having latent functional groups, if successful, would lead to a polymer with a more or less statistical distribution of functional groups over the polymer backbone. Attempts to introduce functional groups into prepolymers by chemical modification of a fraction of the dinitropropyl side-chains would have a similar result. A possible method to produce terminal functional groups would involve the use of special initiation and termination reactions.

In discussions with the sponsor the decision was made that the present effort would concentrate on the approaches involving side-chain modification and tailored initiation and termination reactions. The functional group of primary interest would be the hydroxy group, to permit the use of existing technology for isocyanate curing of the resulting binder. Specifically, DNPVE polymers of low molecular weight (2,000-6,000) would be prepared, and attempts would be made to introduce functional groups by chemical modification of a small percentage of the dinitropropyl side chains; in the second approach, tailored initiation and



Scheme 1



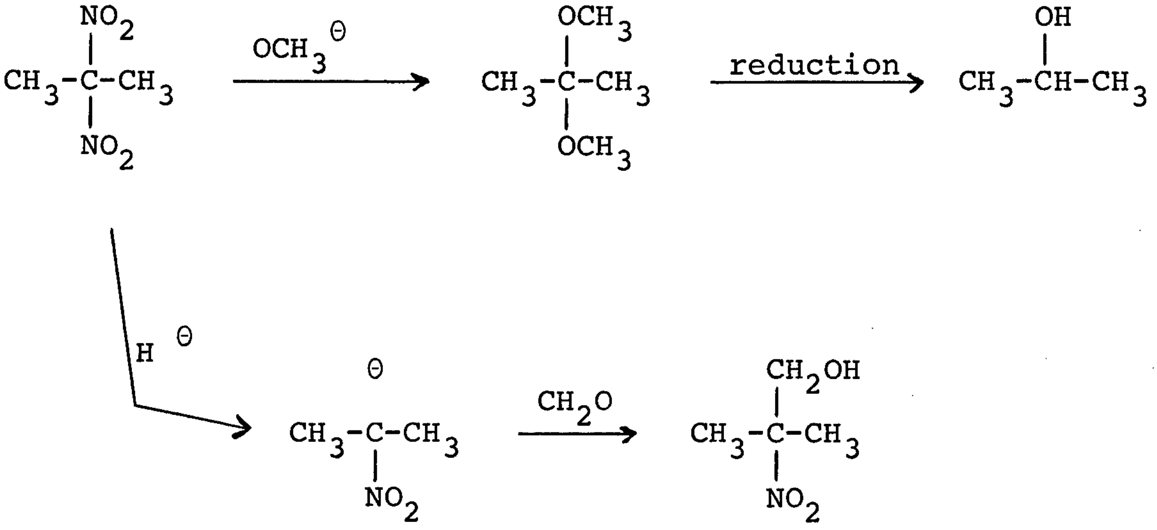
Scheme 2

termination reactions would be investigated which can serve to introduce functional groups at both ends of the prepolymer molecule.

RESULTS AND DISCUSSION

A. Side Chain Modification

Gem-dinitroalkanes, such as 2,2-dinitropropane, have been observed to react with strong bases[4] to form derivatives that can be converted to hydroxy groups according to scheme 3.



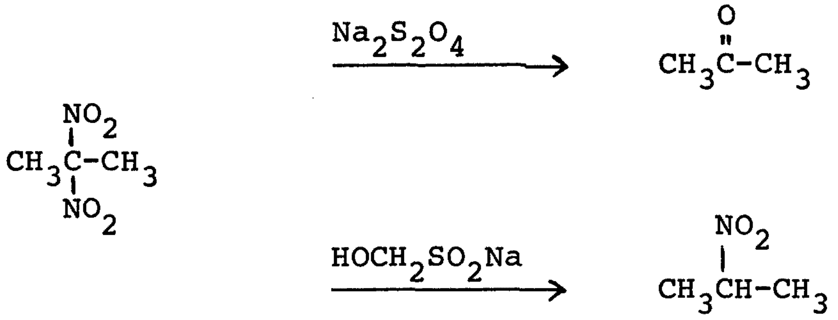
Scheme 3

It appeared to us that either of these sequences might be suitable for functionalizing a portion of the dinitropropyl side chains in Poly-DNPVE. Consequently, using 2,2-dinitropropane as a model compound, we screened a variety of nucleophiles and/or reducing agents as to their reactivity with gem-dinitroalkanes. The solubility properties of Poly-DNPVE required the use of one of the following solvents: dichloromethane, 1,2-dichloroethane, acetone, tetrahydrofuran, acetic acid.

---

[4] Baum, K., Fluorochem, Inc., and Adolph, H., this Center, unpublished results.

In Table 1 are listed the reagents and conditions and results of their reaction with dinitropropane which have been tried in the course of these experiments. It was found that lithium aluminum hydride, sodium formaldehyde sulfoxylate, sodium dithionite, and ammonium sulfide all react reasonably rapidly under conditions suitable for reaction with DNPVE prepolymers. Trimethyl phosphite reacted more slowly; it produced an unidentified product which was neither acetone nor mononitropropane according to a GC analysis of the reaction mixture. In the reaction of DNP with sodium hydrosulfite ($Na_2S_2O_4$), no mononitropropane was detected, but a 50% yield of acetone was isolated as the dinitrophenyl hydrazone. On the other hand, when DNP was reduced with sodium formaldehyde sulfoxylate, no acetone was detected and the GC of the products showed mononitropropane to be present in ca. 50% yield.



$$CH_3\overset{NO_2}{\underset{NO_2}{C}}-CH_3 \xrightarrow{Na_2S_2O_4} CH_3\overset{O}{\overset{\|}{C}}-CH_3$$

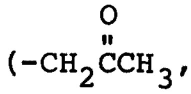
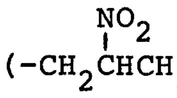
$$CH_3\overset{NO_2}{\underset{NO_2}{C}}-CH_3 \xrightarrow{HOCH_2SO_2Na} CH_3\overset{NO_2}{CH}-CH_3$$

No further attempts were made to identify the products resulting from the successful reductions listed in Table 1, because preliminary experiments indicated that these products would not be indicative of the course of the reaction with DNPVE prepolymers. The polymers behaved differently towards these reducing agents than did DNP (see below). Therefore, we proceeded directly to the study of the reactions of the most promising reducing agents with the prepolymers to be modified; lithium aluminum hydride, sodium formaldehyde sulfoxylate, and sodium hydrosulfite (dithionite).

Lithium Aluminum Hydride Reduction. - Although LAH rapidly reduced DNP in THF solution, the reaction with Poly-DNPVE in THF gave inconclusive results. The reaction appeared much more sluggish and there was little change in the ir and nmr spectra of the recovered polymers. After extended reaction periods, there was a loss of material, pointing to a degradation of the polymer. Although the study of the reaction between Poly-DNPVE and LAH was incomplete, work on this system was terminated in favor of one of the more attractive combinations described below.

Table 1. Reaction of 2,2-Dinitropropane with Various Nucleophiles and Reducing Agents

Reactant/Solvent	Dinitropropane Solvent	Conditions	Results
$NaBH_4$/dil. aqueous base	CH_2Cl_2	1 hr, room temp., phase transfer catalyst	no appreciable reaction
$NaBH_4$ (excess)	THF	20 hr, room temp.	
$LiALH_4$ (excess)	THF	30 min, room temp.	complete reduction
$NaBH_3CN$	THF	16 hr, room temp.	no reaction
KI	acetone	24 hr, reflux	no appreciable reaction
	acetone/water	24 hr, reflux	
$NaHSO_3$/water	CH_2Cl_2	24 hr, room temp., phase transfer catalyst	no appreciable reaction
H_2O_2/dil. aqueous base	CH_2Cl_2	24 hr, room temp., phase transfer catalyst	no appreciable reaction
$(NH_4)_2S$	THF	1 hr, room temp.	no appreciable reaction
	THF/Ethanol	5 hr, room temp.	∿50% reaction
NaOH	CH_2Cl_2	3 hr, room temp., phase transfer catalyst	no appreciable reaction
Sodium formaldehyde sulfoxylate (3 equiv.)/water	CH_2Cl_2	72 hr, room temp., phase transfer catalyst	ca 60% reacted
Sodium formaldehyde sulfoxylate (12 equiv.)/water	CH_2Cl_2	20 hr, room temp., phase transfer catalyst	complete reaction
$Na_2S_2O_4$/dil. aqueous base	CH_2Cl_2	1:2 ratio, 2 hr, room temp., phase transfer catalyst	ca 50% reduction
		same, 1:4 ratio of reactants, 10 minutes	100% reduction
$Na_2S_2O_4$	acetone/dil. aqueous base	24 hr, room temp.	no appreciable reaction
$Na_2S_2O_4$	acetonitrile acetonitrile/water	1 hr, room temp.	no appreciable reaction
Trimethyl phosphite	CH_2Cl_2	5 hr, room temp.	no appreciable reaction
	$ClCH_2CH_2Cl$	6 hr, reflux	complete reaction

Sodium Formaldehyde Sulfoxylate Reduction. - This reaction was carried out with a DNPVE polymer of molecular weight 4,000 (osmometer) dissolved in methylene chloride. Reaction with an aqueous solution of reducing agent was promoted by the use of a phase transfer catalyst (didocyldimethylammonium bromide). Sufficient reducing agent was used to completely reduce the gem-dinitro moieties, and the recovered polymer was characterized by ir and proton nmr. These spectra indicate that both acetonyl groups  $(-CH_2\overset{O}{\overset{\|}{C}}CH_3$, C=O band at 1735 cm^{-1}, CH_3 singlet at $\delta 2.10$ in $CDCl_3/CD_3C(O)CD_3$) and mononitropropyl groups  $(-CH_2\overset{NO_2}{\overset{|}{C}}HCH_3$, nitroband at 1560 cm^{-1}, CH_3 doublet at $\delta 1.49$) are present. Thus the reduction was apparently nonspecific, again in contradistinction to the reaction with 2,2-dinitropropane. No further work was carried out on this system to permit concentration of the effort on the sodium hydrosulfite reduction (see below).

Sodium Hydrosulfite Reduction. - This reagent, in a water-methylene chloride system with phase-transfer catalyst present, was found to reduce poly-DNPVE quite rapidly. The ir and nmr spectra of the completely reacted polymer indicate that reduction of the dinitropropyl groups to mononitropropyl groups is the predominant reaction,

$$CH_3-C(NO_2)_2-CH_2- \longrightarrow CH_3-CHNO_2-CH_2-$$

as no carbonyl absorption is present in the ir spectrum. A more detailed analysis of the spectra of the reduced polymer shows the following: In the nmr, the original CH_2 and CH_3 peaks of the $CH_3C(NO_2)_2CH_2O-$ group have completely disappeared, indicating complete reaction of this group. In the ir, the nitro absorption is weaker and shifted from 1570-80 to 1560 cm^{-1}. These observations indicate that the desired conversion of $C-C(NO_2)_2-C$ to $C-CH(NO_2)-C$ has taken place. At the same time new peaks which can be assigned to $\underline{CH_2}$, $\underline{CH}$, and $\underline{CH_3}$ in the $CH_3CH(NO_2)CH_2O-$ group are observed in the nmr spectrum (see below).

A series of runs carried out with this system to identify suitable conditions for partial reduction of the poly-DNPVE is summarized in Table 2. The following conclusions can be drawn from these experiments: It is possible to achieve partial reduction of the dinitropropyl side-chains in poly-DNPVE by the PTC catalized treatment with SHS in a water-dichloromethane two-phase system. An as yet undetermined fraction of the affected side chains are reduced to the mononitropropyl group; essentially no carbonyl groups are formed; however, the nmr spectra suggest that some other products may be present also, as they contain a

Table 2. Reduction of 0.5g Poly-DNPVE with Sodium Hydrosulfite (SHS) in Dichloromethane-Water at Room Temperature

Run No.	Equivalents SHS	Equivalents Phase Transfer Catalyst	Base Added	Time (hr)	Total Polymer Recovered (g)	Soluble Polymer Recovered (g)	Comments
1	2.6	0.15	no	1	-	0.57	complete reduction; PTC* present in polymer
2	2.6	0.11	yes	2	0.57	0.49	complete reduction; PTC* contaminates polymer
3	2.6	0.055	yes	2	0.44	0.29	incomplete reduction; PTC* present in polymer
4	2.0	0.11	yes (excess)	1.5	0.53	0	completely reduced (ir); completely insoluble
5	2.6	0.026	yes	2	0.44	0.30	partial reduction; some PTC* present in polymer
6	2.6	0.055	no	2	0.45	ca 0.3	same as #3
		none; MeOH Cosolvent					
7	3.2	H_2O: MeOH ∿3:1	no	20	-	"good recovery"	small amount of reduction indicated by nmr
8	16.2	H_2O: MeOH 3:1	no	20	0.34	0	completely reduced; completely insoluble
9	2.6	H_2O: MeOH 1:3	no	20	0.30	0.26	little if any reduction
10	2.6	H_2O: MeOH 3:1**	no	20	0.47	0.43	little if any reduction

* PTC = Phase Transfer Catalyst

** Na_2HPO_4 buffer used

number of unassigned peaks. Several problems with this reaction became apparent. Insoluble (crosslinked?) polymers are formed at the higher pH's which favor rapid reduction, and, more importantly, at lower PTC concentration. PTC contaminates the isolated polymer and its quantitative removal proved to be very difficult. Unfortunately, no reduction occurred in the absence of PTC.

Replacing the PTC by crown ethers or wetting agents was not advantageous, but run #7 (Table 2) indicated that methanol in place of PTC gave slow reduction which was uncomplicated by the above problems. Following up on this observation, a variety of cosolvents for the methylene chloride/water system were tested: ethylene glycol, glyme, DMF, diethylene glycol, butyrolactone, pyridine, acetic acid, and acetonitrile. Of these only one gave a clean reduction which was sufficiently rapid to be feasible: ethylene glycol. Several reduction runs were carried out with SHS in water/ethylene glycol/methylene chloride with very promising results. The spectra of the recovered polymers indicated that no side reactions occurred to any significant extent, and that the degree of reduction could be controlled by the amount of reducing agent used. Little if any insoluble polymer was formed and material recovery was good (for an estimation of yields, see experimental part starting on p. 31).

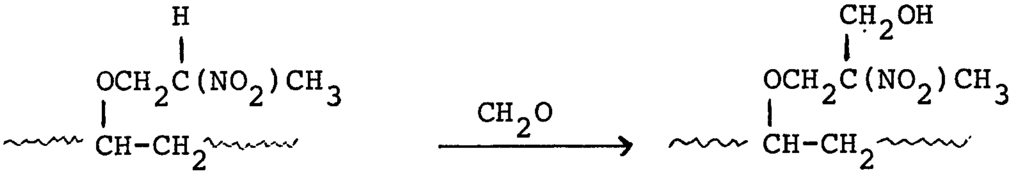
Figures 3 and 5 are proton nmr spectra of unreduced and partially reduced polymer. The differences in the spectra are those expected on the basis of partial reaction according to scheme 4:

$$\sim\overset{\displaystyle \mathrm{OCH_2C(NO_2)_2CH_3}}{\mathrm{CH}}\mathrm{-CH_2}\sim \longrightarrow \sim\overset{\displaystyle \mathrm{OCH_2\overset{H}{C}(NO_2)CH_3}}{\mathrm{CH}}\mathrm{-CH_2}\sim$$

Scheme 4

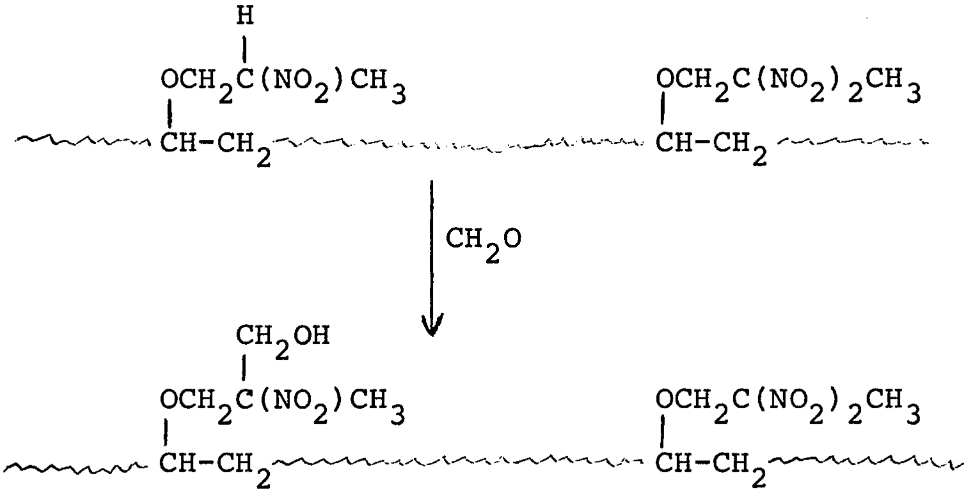
Peak E is assigned to the methyl group in the mononitropropyl group; it is split by the neighboring hydrogen (Peak F); the CH_2 of the mononitropropyl group overlaps with the original Peak C. Thus, the nmr spectra are in full support of the postulated reaction.

The degree of reduction was not established at this point - although a crude estimate can be obtained from the nmr spectrum - because it was felt that this might be more readily accomplished after reaction of the nitropropyl groups with formaldehyde to give primary alcohol functions (scheme 5). A discussion of functionality determinations will be given in the section entitled "Characterization of Modified Poly-DNPVE."



Scheme 5

Hydroxymethylation of Reduced Poly-DNPVE. - Initial attempts to react partially reduced polymer, dissolved in methylene chloride, with aqueous formaldehyde and base according to scheme 6, gave little or no reaction other than self-condensation of the formaldehyde.



Scheme 6

A number of solvent systems were then tried that dissolved the polymer and also the formaldehyde solution or at least the base catalyst for the addition reaction. The treated polymer was isolated and analyzed by nmr for disappearance of the acidic hydrogen (F, Figure 5) and the methyl doublet (E, Figure 5). Three systems were found that appear to achieve hydroxy methylation as judged by the nmr criteria described above: dioxane/aq. formalin/triethylamine (requires heating); acetone/aq. formalin/triethylamine; methylene chloride/ethylene glycol/aq. formalin/triethylamine. The nmr spectra of the polymers obtained from these three systems were essentially identical and provide strong (but not conclusive) evidence for successful hydroxymethylation (Figure 6): The peak for the acidic proton in Figure 5 at δ 4.85 is absent in Figure 6, and the doublet E in Figure 5 has reverted to a methyl singlet in Figure 6. However, no distinct

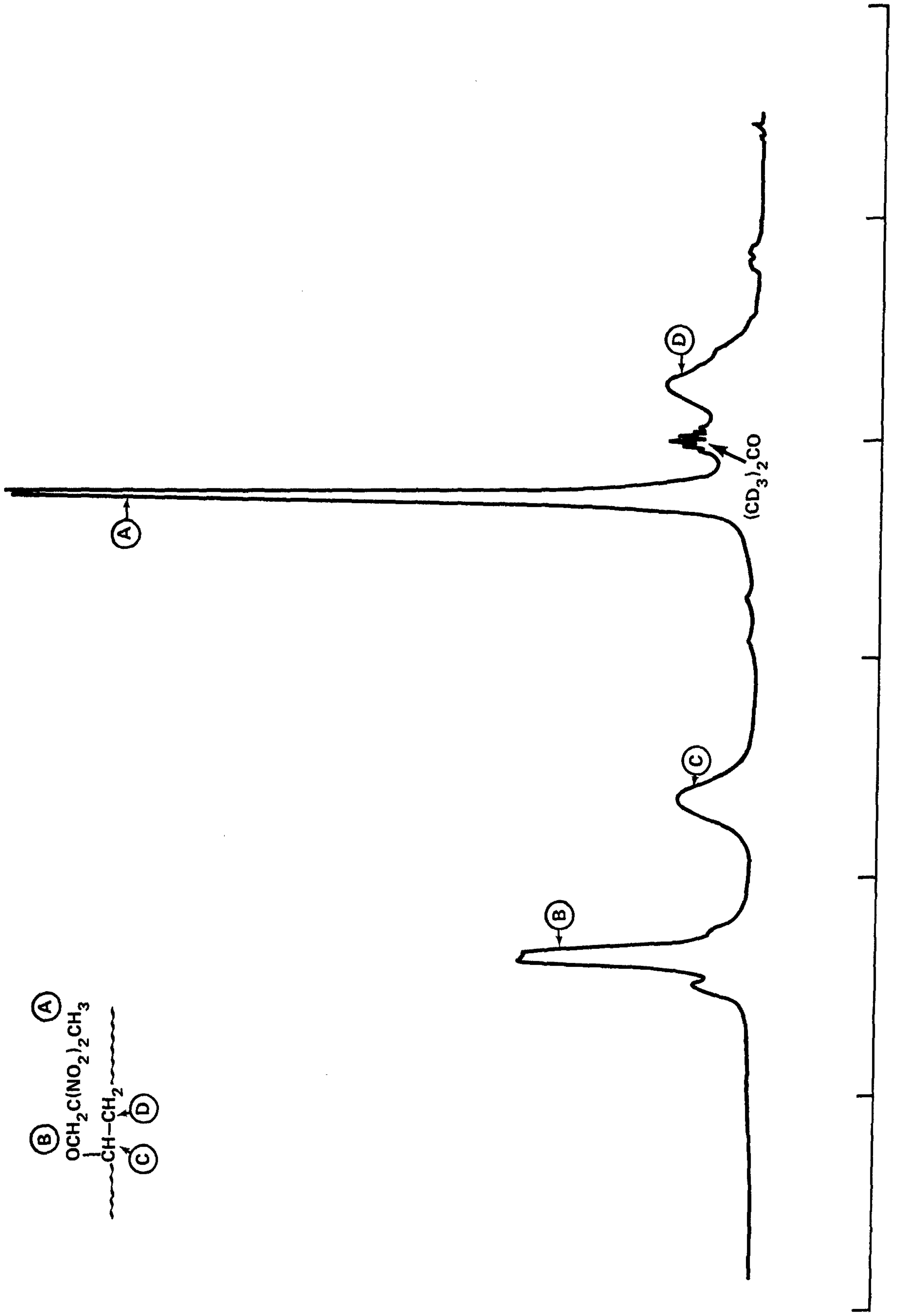


FIGURE 3 100 MHz NMR SPECTRUM OF POLY-DNPVE (M.W. 4,000)

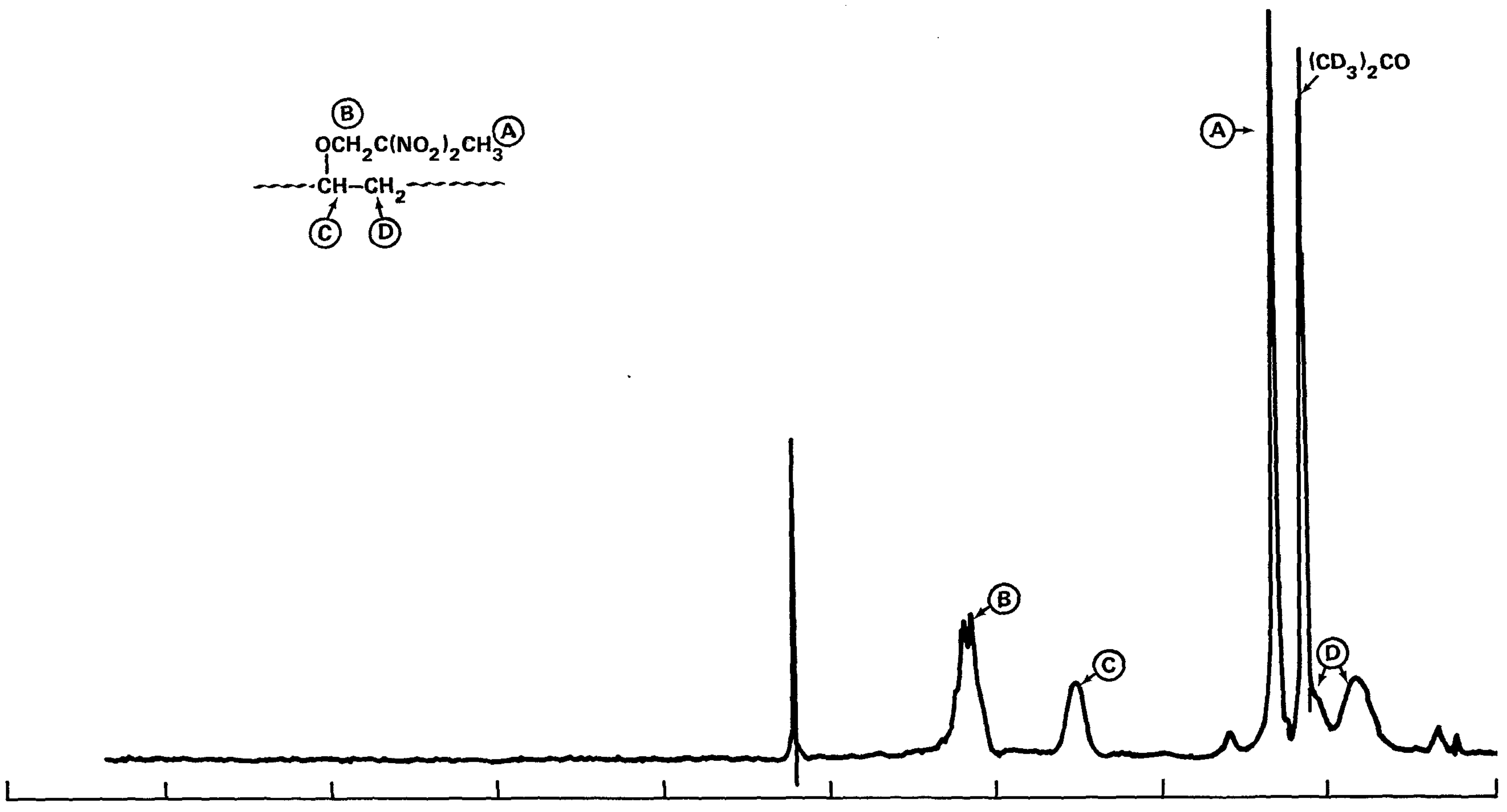


FIGURE 4 220 MHz NMR SPECTRUM OF POLY-DNPVE IN d_6-ACETONE/DCℓ/D_2O

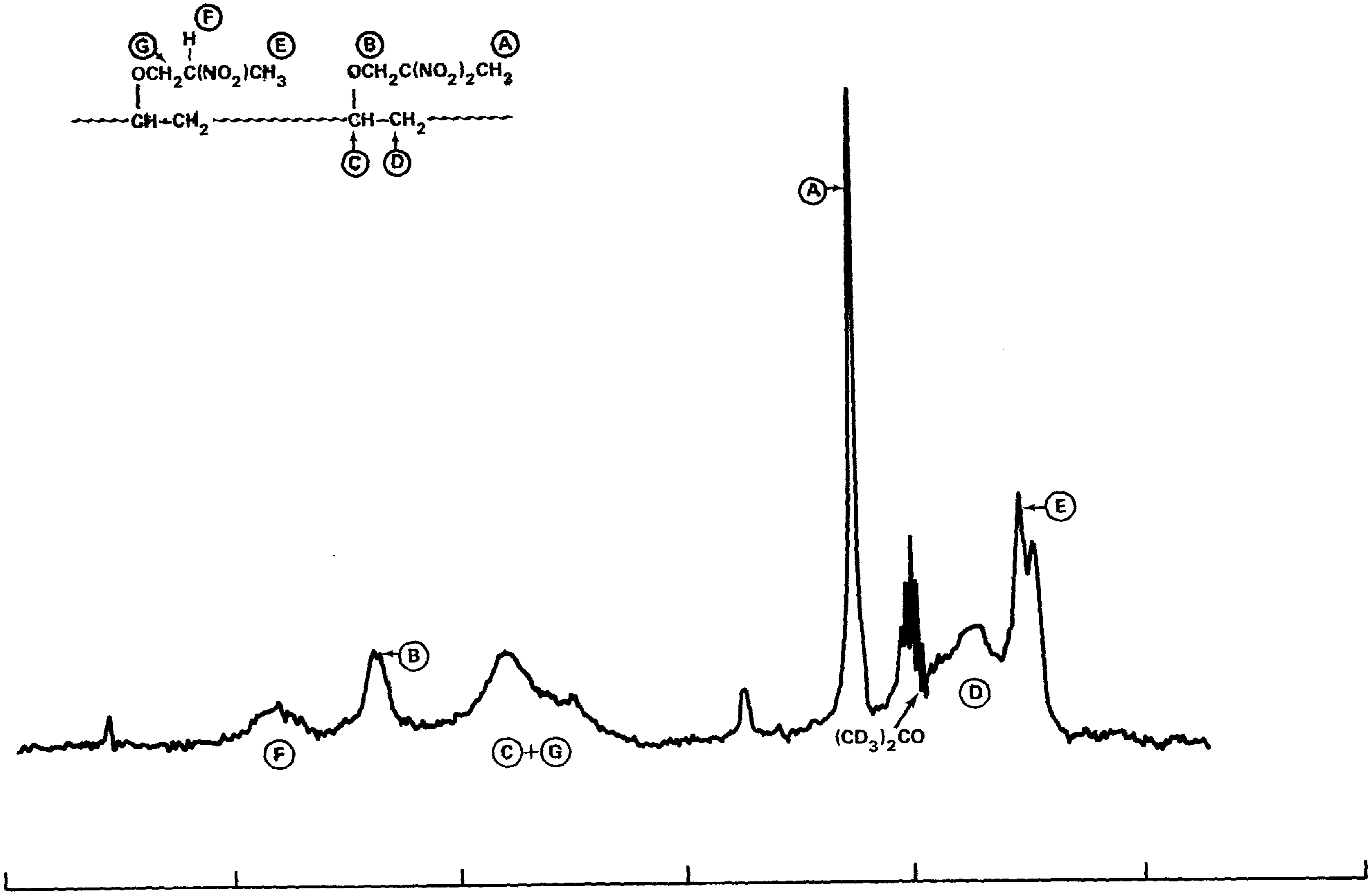


FIGURE 5 100 MHz NMR SPECTRUM OF POLY-DNPVE (M.W. 4,000), PARTIALLY REDUCED

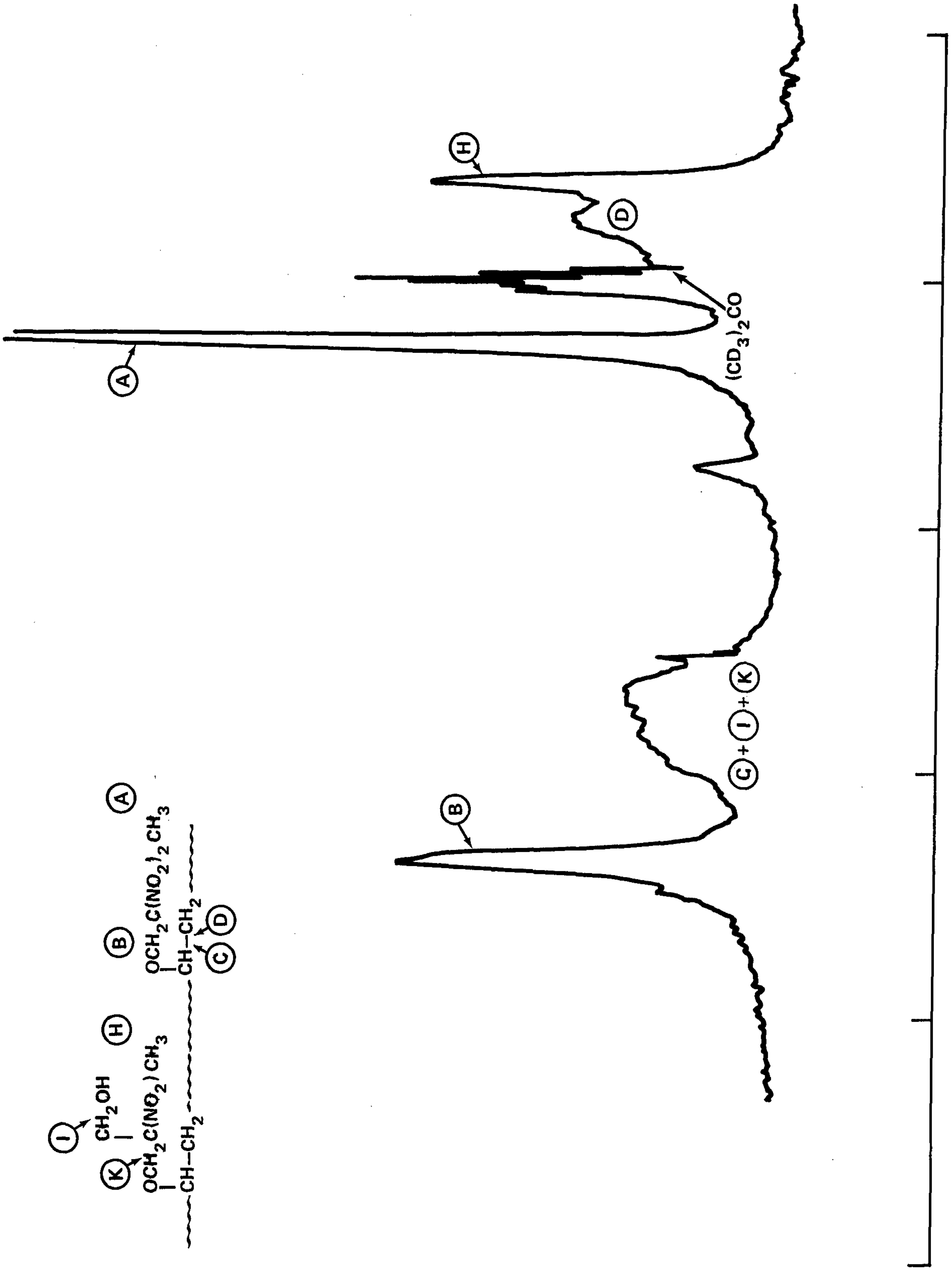


FIGURE 6 100 MHz NMR SPECTRUM OF POLY-DNPVE (M.W. 4,000), PARTIALLY REDUCED AND HYDROXYMETHYLATED peaks for the new methylene group I or the hydroxy group are evident. Closer inspection of the spectrum in Figure 6 reveals that the broad absorption between δ 3.5 and 4.0 has increased in width as well as in intensity (compared to Figure 5) and it can be assumed that the peak for the CH_2 group I is included here. The absorption of the OH group was not identified.

To obtain further confirmation for the presence of hydroxy groups in the polymer, an attempt was made to cure the solution in BDNPF/A, of a polymer corresponding to Figure 6, with a diisocyanate.

It was noted that while the starting and the partially reduced polymers were readily and completely soluble in the formal/acetal plasticizer, the hydroxymethylated material was only partially soluble. This is not too surprising as we estimate that 30-40% of the original dinitropropyl groups had been modified in this particular product, and such a high content of hydroxy groups could well cause the observed insolubility. This gum stock, despite the inhomogeneity, cured readily to a rubbery solid when mixed with the appropriate amounts of dibutyl tin dilaurate and HMDI, and heated overnight at 70°C. There can be little doubt, therefore, that the attempted hydroxymethylation had been successful. It has thus been demonstrated that the first proposed approach for making crosslinkable Poly-DNPVE is a workable approach.

Characterization of "Modified" Poly-DNPVE. - More quantitative attempts were made to characterize the hydroxymethylated Poly-DNPVE with respect to molecular weight and hydroxy content. For this purpose, a sample with a lower degree of side chain modification than that of Figure 6 was prepared (sample 66-3a, see experimental part). The gel permeation chromatogram of this material, together with that of the starting Poly-DNPVE, is given in Figure 2. M_n was found to be 5,092 (M_w=9298; dispersity, 1.83), relative to polystyrene. Figure 2 indicates that no significant change in molecular weight or molecular weight distribution occurred during side chain modification.

This polymer had better solubility in BDNPF/A than the earlier sample and cured to a somewhat softer rubber under the same conditions as were described above.

Several standard methods for hydroxy group determination were tried on the same polymer sample. These methods and the results obtained were as follows (Table 3). It is evident that there is poor agreement between the results obtained; the problem of identifying a reliable method for hydroxy determination in the DNPVE polymer was not completely solved.

Table 3. Hydroxy Determination for "Modified" Poly-DNPVE, (Sample 66-3a)

Method	Hydroxy Content	
	milliequivalents/g	functionality[a]
Acetic Anhydride/ Pyridine	1.18[b]	4.7
	1.46[c]	5.9
	2.55[d]	10.2
Tosyl Isocyanate	2.40[e]	9.6
Nmr Analysis	1.40[f]	5.6
	1.39[g]	5.6

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a. based on an osmometric molecular weight of 4,000.

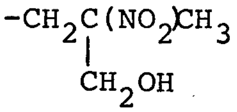
b. Atlantic Research Corp., Gainesville, VA.

c. Clark, Means, and Perkins Microanalytical Laboratory, Urbana, IL.

d. Herron Testing Laboratories, Inc., Crobaugh Division, Cleveland, OH.

e. Atlantic Research Corp., Gainesville, VA.

f. undisclosed nmr method, Andrulis Research Corp., Bethesda, MD.

g. based on comparison of methyl peaks (height x half width) for $-CH_2C(NO_2)_2CH_3$ and  $-CH_2\underset{\displaystyle CH_2OH}{\underset{|}{C}}(NO_2)CH_3$ in the nmr spectrum of the modified polymer.

A less direct approach to determine the functionality of the modified polymer involved elemental analysis of the reduced polymer. Comparison with the values of the starting polymer allows one to calculate the degree of reduction. If the assumption is made that hydroxymethylation is quantitative, then the functionality of the modified polymer can be obtained. In Table 4 are given the results of such an analysis for another sample of modified Poly-DNPVE with a lower degree of reduction than that analyzed above (see experimental part).

Table 4. Degree of Reduction of Poly-DNPVE by Elemental Analysis (Sample 3200)

Element	Starting Polymer		Reduced		
	Calc'd	Found	Calc'd for 100% Red.	Found	Calc'd for 27% Reduction
C	34.09	34.49	45.79	36.66	36.62
H	4.58	4.53	6.92	5.24	5.12
N	15.91	15.69	10.68	14.44	14.78
O	45.42	45.00	36.60	43.56	43.52

This degree of reduction would correspond to 1.65 meq of hydroxyl per g of modified polymer 3200. Nmr analysis of the reduced intermediate (comparison of height x half widths of methyl peaks for $CH_3CH(NO_2)CH_2$- and $CH_3C(NO_2)_2CH_2$) gave 25% conversion in good agreement with the elemental analysis. However, nmr analysis after hydroxymethylation indicated only 16% conversion. Whether this can be attributed to incomplete hydroxymethylation is not clear. This modified polymer cured readily to a rubbery material under the previously described conditions, which might not be expected for such a low degree of conversion.

It is clear from these examples that in the event of a follow-on effort, immediate attention must be given to the development of a suitable method for hydroxy determination in modified Poly-DNPVE.

B. Tailored Initiation Reactions

Although the mechanism of polymerization of alkyl vinyl ethers is not straight forward[5] and nothing is known about the

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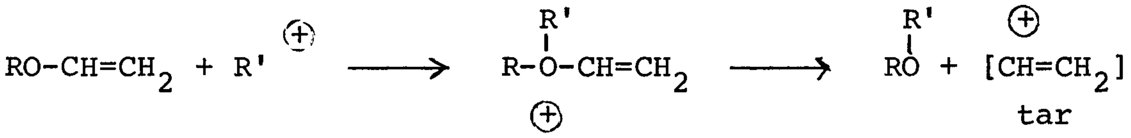
[5] Plesch, P. H., ed., The Chemistry of Cationic Polymerization (New York: Pergamon Press, 1963, p. 375)

mechanism of the DNPVE polymerization, it may be assumed that the growing polymer chain carries a positive charge, and that directly or indirectly, a proton has become attached to the initiation site of the polymer molecule (this is substantiated by the nmr spectrum; see p. 8). An obvious question is, can DNPVE polymerization be initiated by other cationic groups which would also serve, directly or after chemical modification, as a functional group for cross-linking. This approach to prepare functional DNPVE polymers has the advantage that it leads to terminal functional groups which give cross-linked polymers with better physical properties than statistically distributed functional groups.

A number of cationic and latent cationic species which could meet the above requirements are listed in Table 5. The interaction of several of these potential initiators with DNPVE was studied in some detail, although no reports could be found in the literature of vinyl ether polymerizations by these reagents. It should be noted that many of the initial adducts (Table 5) contain active C-H groups which could transfer a proton to unreacted monomer and thus produce nonfunctional polymers.

Preliminary experiments with reagents #2-#6 were not encouraging. With #4 and #6, extensive cleavage of the DNPVE molecule with formation of DNPOH derivatives was taking place.



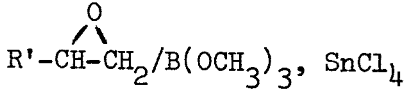
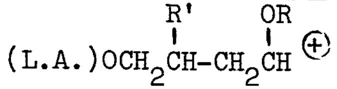
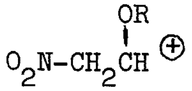
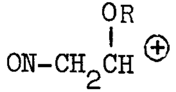
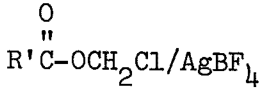
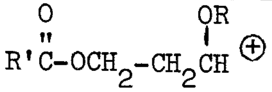
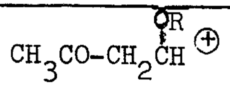
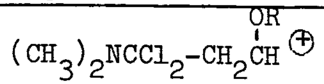
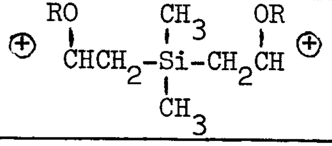
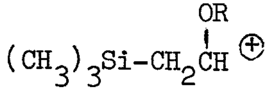
$$RO\text{-}CH{=}CH_2 + R'^{\oplus} \longrightarrow R\text{-}\underset{\oplus}{\overset{R'}{O}}\text{-}CH{=}CH_2 \longrightarrow \overset{R'}{RO} + \underset{\text{tar}}{\overset{\oplus}{[CH{=}CH_2]}}$$

Polymers resulting from the reactions with #4 were fractionated by column chromatography and gave fractions which apparently contained carbonyl groups as part of the polymer chain as indicated by the ir and nmr spectra. However, the yield of these polymer fractions was quite low. It was concluded from this work that the chloromethyl pivalate/silver tetrafluoroborate system may hold promise as an initiating system which can introduce a hydroxyl function at the beginning of the chain. However, a more detailed study is required to optimize the reaction for better yields.

With reagents #2 and #5 polymers were obtained which contained no additional functionality. The reagents were not further investigated although rigorous exclusion of moisture during the reaction might produce a different result.

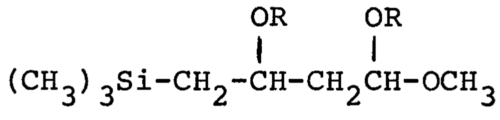
In order to simplify the structure elucidation of the reaction products, the dichlorosilane-$AgBF_4$ reaction (#7) was modelled with the monofunctional trimethyl silyl chloride. No reaction occurred between these reagents and DNPVE, even when

Table 5. Reaction of DNPVE with Cationic Reagents [OR = $OCH_2C(NO_2)_2CH_3$]

#	Cation	Initial Adduct	Reaction Conditions and Results
1	 $R'\text{-}\overset{O}{CH\text{-}CH_2}/B(OCH_3)_3,\ SnCl_4$	 $(L.A.)OCH_2\overset{R'}{CH}\text{-}CH_2\overset{OR}{CH}^{\oplus}$	a. $B(OCH_3)_3$, no reaction b. R'=CH_3; $SnCl_4$: CH_2Cl_2, 0°C, 18 hrs; chromatography → solid (31%) and liquid (50%) fractions of polymer; nmr inconclusive (see text). c. R'=$ClCH_2$; $SnCl_4$: CH_2Cl_2, 0°C, 18 hrs; yellow solid (100%); fractional precipitation and chromatography → 47% fraction with 2.79% Cl.
2	$NO_2^+\ BF_4^-$	 $O_2N\text{-}CH_2\overset{OR}{CH}^{\oplus}$	MeCN; -40 to 0°C, 20 hrs; oil (95%), low m.w. polymer by ir and nmr; nmr indicates CH_3 at beginning of chain, not O_2NCH_2-.
3	$NO^+\ BF_4^-$	 $ON\text{-}CH_2\overset{OR}{CH}^{\oplus}$	not attempted.
4	 $R'\overset{O}{\overset{\parallel}{C}}\text{-}OCH_2Cl/AgBF_4$	 $R'\overset{O}{\overset{\parallel}{C}}\text{-}OCH_2\text{-}CH_2\overset{OR}{CH}^{\oplus}$	CH_2Cl_2, -78 to 0°C, 18 hrs; oil (80%); chromatography → 41% liquid containing low m.w. dinitropropyl and pivaloyl compounds; 24% low m.w. polymer with weak carbonyl group.
5	$CH_3CO^+\ SbCl_6^-$	 $CH_3CO\text{-}CH_2\overset{OR}{CH}^{\oplus}$	CH_2Cl_2, -78 to 0°C, 2 hrs; → 60% oil; probably low m.w. polymer; no CO in ir.
6	$(CH_3)_2N{=}CCl_2{}^+Cl^-/AgBF_4$	 $(CH_3)_2NCCl_2\text{-}CH_2\overset{OR}{CH}^{\oplus}$	a. 1,2-dichloroethane, r.t., 1 hr; 32% dinitropropyl-N,N-dimethyl carbamate isolated. b. 1,2-dichloroethane, -30°C, 1 hr; chromatography → 21% BDNPA, 65% low m.w. polymer; no dimethylamino groups.
7	$(CH_3)_2SiCl_2/AgBF_4$	 ${}^{\oplus}\overset{RO}{CH}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2\overset{OR}{CH}^{\oplus}$	not attempted.
8	$(CH_3)_3SiCl/AgBF_4$	 $(CH_3)_3Si\text{-}CH_2\overset{OR}{CH}^{\oplus}$	a. CH_2Cl_2, r.t.; high yield of DNPOH (G.C.). b. for other conditions, see Table 6.

triethylamine was present. However, when $AgBF_4$ was added to solutions of silyl chloride and DNPVE a rapid reaction occurred.

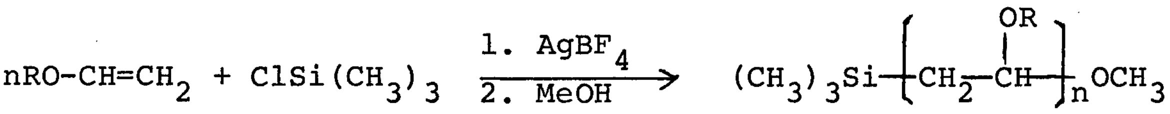
In dichloromethane DNPVE and trimethylsilyl chloride (1:1) gave, again, mostly dinitropropanol. In acetonitrile, DNPVE and TMSCl (2:1 ratio), after several hours reaction and quenching with methanol, gave an oil whose nmr spectrum reveals the presence of trimethylsilyl groups and shows other peaks that can be attributed to the expected structure



$$(CH_3)_3Si-CH_2-\overset{OR}{\overset{|}{C}}H-CH_2\overset{OR}{\overset{|}{C}}H-OCH_3$$

$R = CH_3C(NO_2)_2CH_2-$

A number of trials were carried out using polar and relatively non-polar solvents and ratios of DNPVE: ClTMS from 1:1 to 10:1, in an effort to obtain the 1:1 adduct as well as trimethylsilyl initiated oligomers:



$$nRO-CH=CH_2 + ClSi(CH_3)_3 \xrightarrow[\text{2. MeOH}]{\text{1. }AgBF_4} (CH_3)_3Si\left[CH_2-\overset{OR}{\overset{|}{C}}H\right]_n OCH_3$$

$R = CH_3C(NO_2)_2CH_2$

These reactions are summarized in Table 6.

Although some trials (#3, 8, 10) gave indications that the trimethysilyl group was present in an isolated low molecular weight polymer, these reactions were difficult to reproduce, possibly because of interference by traces of moisture. A report in the literature which claims a trimethylsilyl cation initiated polymerization of styrene[6] (giving a polymer containing TMS groups) is not well substantiated and is in apparent conflict with other reports which question the - even transient - existence of the trimethylsilyl cation in solution.[7]

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[6] Minoura, Y. and Toshima, H., "Polymerization of Vinyl Monomers with Chlorosilane Compounds and Metal Halides," J. Polymer Science, (A-1), Vol. 11, 1972, p. 1109.

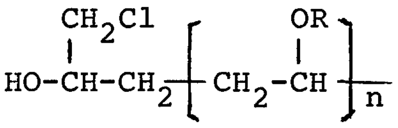
[7] Murphy, M. K. and Beauchamp, J. L., "Positive Ion Chemistry of Fluoromethylsilanes," J. Am. Chem. Soc., Vol. 98, No. 19, 1976, p. 5781.

Table 6. Reactions of DNPVE with Chlorotrimethylsilane (TMSCl) and Silver Tetrafluoroborate (SB)

#	Molar Ratio, DNPVE: TMSCl:SB	Solvent	Conditions	Product	Remarks
1	2:1:1	MeCN	Add TMSCl at -30°C; then 1 hr at 0°C	DNPVE (80%)	Little or no reaction
2	2:1:1	"	Same, but 60 hr at 0°C	Viscous oil; no starting material	nmr shows no TMS groups present
3	2:1:1	"	React TMSCl + SB at room temp., add DNPVE at -40°C, then 18 hr r.t.	Viscous oil (50% yield); no starting material	nmr shows strong TMS peak; not removed by alumina treatment
4	2:1:1	"	Same (repeat reaction)	Viscous oil (>90% yield); no DNPVE	nmr indicates low m.w. polymer. No TMS groups present
5	4:1:1	"	Mix reagents at -30°C, then 2 hr r.t.	Resin (80%); no starting material	Same as #4
6	4:1:1	$MeNO_2$	Add SB at -30°C, then 15 min at r.t.	Oil (85%); no DNPVE left	Rapid reaction in this solvent; no TMS groups in nmr
7	1:1:1	CH_2Cl_2	Addition and 45 min reaction at r.t.	Semisolid material identified as DNPOH	--
8	10:1:1	"	Mixed at 0°C, then 2 hr r.t.	Oil and solid; no DNPVE left (>90% yield)	Oil shows small TMS peak in nmr, solid none
9	2:1:1	$ClCH_2CH_2Cl$	Reactants mixed neat at -30°C; solvent added, then 1 hr r.t.	Oil (80%); no DNPVE left	nmr indicates polymer without TMS
10	1:1:0 ($SnCl_4$ catalyst)	"	96 hr 0°C, and 12 hr r.t.	Semisolid (60-70%)	Polymeric material; small TMS peak in nmr

It was concluded at this point that the TMSCl/$AgBF_4$ reagent does not reliably initiate the DNPVE polymerization. Because the observed problems would be compounded with the difuntional reagent, dichlorodimethylsilane, needed to prepare a difunctional Poly-DNPVE, the work was terminated in favor of screening other cationic initiators.

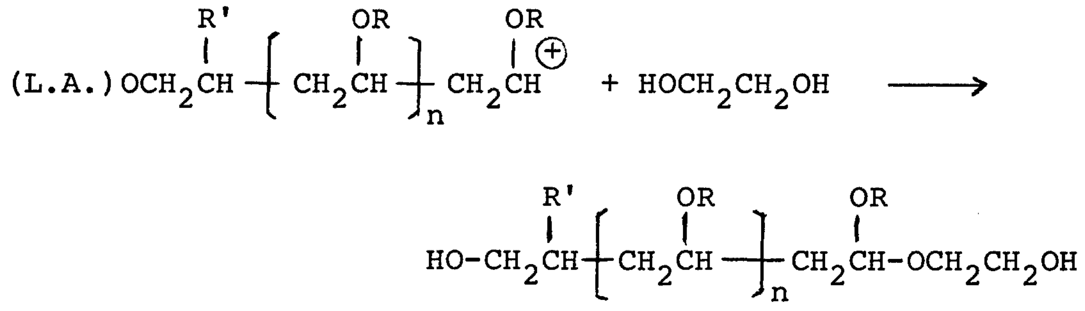
Initiation of DNPVE polymerization with epoxide/Lewis acid catalyst systems (Table 5, #1) was also investigated in somewhat greater detail. With propylene oxide/$SnCl_4$ several different polymers were obtained and purified by column chromatography. IR and nmr spectra of these polymers were compared to Poly-DNPVE and poly(propylene oxide). Unfortunately, it was not possible to establish on the basis of these spectra whether the expoxide was incorporated in the DNPVE polymer. No further characterization of these polymerswas attempted during this effort. In addition to the propylene oxide/$SnCl_4$ system, epichlorohydrin/$SnCl_4$ was found to initiate DNPVE polymerization as well. The reaction was carried out using 5:1 ratio of DNPVE and epichlorohydrin. The resulting polymers were fractionated by fractional precipitation from acetone/methanol and by column chromatography to separate out epichlorohydrin homopolymers. The nmr spectra of methanol soluble and insoluble fractions seemed to indicate that much of the epichlorohydrin homopolymerized; however, the chlorine analysis of the methanol insoluble fraction (ca. 60% of the total polymer) showed chlorine content of 3.1% (3.9% is theory for 5:1 DNPVE: epichlorohydrin mixture). The material was reprecipitated from dichloromethane/methanol and chromatographed to attempt further fractionation, but it appeared to be homogeneous and the chlorine content changed little (2.7% after chromatography). Since it has been established that Poly-DNPVE does not incorporate chlorine from $SnCl_4$ during homopolymerization, it appears that a copolymer of DNPVE and epichlorohydrin may have been formed. However, its structure has not been established. An epichlorohydrin unit may be present at the head of the chain as desired,



$$HO{-}\underset{}{\overset{\displaystyle CH_2Cl}{\overset{|}{CH}}}{-}CH_2{-}\left[CH_2{-}\overset{\displaystyle OR}{\overset{|}{CH}}\right]_n{-}$$

or, such units may be distributed randomly throughout the polymer.

Further characterization of this interesting material could not be carried out within the time frame and the budget of this task. Similarly, the original plans to study termination reactions that would introduce a hydroxy function in the termination step, for example, by reaction with ethylene glycol according to scheme 7, could not be carried out.



$$(\mathrm{L.A.})\mathrm{OCH_2}\overset{\mathrm{R'}}{\mathrm{CH}}\left[\mathrm{CH_2}\overset{\mathrm{OR}}{\mathrm{CH}}\right]_n\mathrm{CH_2}\overset{\mathrm{OR}}{\mathrm{CH}}{}^{\oplus} + \mathrm{HOCH_2CH_2OH} \longrightarrow \mathrm{HO{-}CH_2}\overset{\mathrm{R'}}{\mathrm{CH}}\left[\mathrm{CH_2}\overset{\mathrm{OR}}{\mathrm{CH}}\right]_n\mathrm{CH_2}\overset{\mathrm{OR}}{\mathrm{CH}}\mathrm{{-}OCH_2CH_2OH}$$

Scheme 7

CONCLUSIONS AND RECOMMENDATIONS

This work has shown that crosslinkable prepolymers can be prepared from low molecular weight Poly-DNPVE by partial reduction of the dinitropropyl to mononitropropyl groups followed by hydroxymethylation by aqueous formaldehyde.

The resulting polymers are solids which must be mixed with plasticizers to produce a castable binder. Their characterization with regard to functionality of the prepolymer and physical and mechanical properties of the cured binder matrix is incomplete.

The initiation of DNPVE polymerization with a variety of cationic reagents was studied which could introduce a functional group at the initiation site. This work has met with only limited success. Epichlorohydrin/$SnCl_4$ and DNPVE in a ratio of 1:5 produced a low molecular weight Poly-DNPVE apparently containing epichlorohydrin units. A thorough characterization of this product could not be completed.

The new polymers resulting from this work have potential utility in energetic binders for composite explosives and propellants. A follow-on effort involving characterization and further development of these materials and their evaluation as energetic binder components is recommended.

EXPERIMENTAL

General. Melting points and boiling points are uncorrected. Elemental analyses and molecular weights were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee; gas chromatographic analyses were done with a HP 5750 gas chromatograph on a 6-ft, 1/8-inch column with 10% silicon gum rubber UC-W982 on AW-DMCS chromosorb W, 80-100 mesh, using a thermal conductivity detector and helium carrier gas. NMR spectra were obtained on a HA-100 spectrometer; chemical shifts are in ppm relative to TMS ($\delta 0.00$) as internal standard. Infrared spectra were taken on a Beckman IR-4. Neat liquids were taken between salt plates; solids were pressed into KBr discs.

All reagents except DNPVE are commercially available. Tin (IV) chloride was distilled under nitrogen and stored in a dry box.

Reduction of 2,2-Dinitropropane (DNP). The preliminary screening of reducing agents was carried out by mixing the reagents listed in Table 1 and monitoring the decrease in DNP with time by GC.

The retention times and molar response factors for isothermal analysis of DNP and 2-nitropropane were determined by injecting a known volume of a standard (10%) solution of sample onto the column and integrating the area of the peak using width at half height times height. The response of 2-nitropropane at 28° was 2.7×10^{-9} mole/mm^2 and for DNP at 70° was 9.1×10^{-10} mole/mm^2.

Commercial sodium hydrosulfite was determined to be 76% active by titration.[8] An aqueous solution of sodium hydrosulfite which was stirred for 2.5 hrs retained only 34% activity.

Sodium hydrosulfite (1.5 eq) added to a stirred 2-phase mixture of 2N sodium hydroxide (6 eq), DNP in CH_2Cl_2, and phase transfer catalyst, reduced the DNP concentration to 13% in 10 min at room temperature. Addition of another 0.25 eq of sodium hydrosulfite reduced [DNP] to 7.5%. GC analysis of the organic phase showed that no 2-nitropropane was present. Acetone was determined by acidifying the aqueous phase to pH$\sim$6, adding potassium permanganate until the reaction mixture barely remained pink, and adding the separated aqueous phase to 2,4-DNPH in 2N HCl at 50°. After 30 min the hydrazone derivative was filtered and weighed. A 50% yield of acetone was found.

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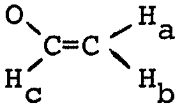
[8] Kolthoff, I. M. and Belcher, R., Volumetric Analysis, Vol. 3 (New York: Interscience, Inc., 1957), pp. 297-298.

Aqueous sodium formaldehyde sulfoxylate (12 eq) completely reduced DNP in methylene chloride during 20 hr stirring at room temperature, when phase transfer catalyst was present. The organic phase of this mixture was found by GC analysis to contain a 50% yield of 2-nitropropane, but no acetone.

Preparation of 2,2-Dinitropropyl Vinyl Ether (DNPVE). 2,2-Dinitropropanol (248 g of 30% solution in 1,2-dichloroethane, 74.4 g of DNPOH (0.496 moles), dried over activated molecular sieves 5A) and divinyl ether (Marshallton, containing 5-6% ethanol by nmr, 52.0 g (0.74 moles)) were cooled for 20 minutes in an ice-water bath with stirring under a Drierite drying tube. Pyridine (1 ml (0.0124 moles)) was added, followed by 12 ml of 1 M catalyst solution.* The solution was heated at 35°C for three hours, then cooled in an ice-water bath. Sodium borohydride (5.0 g (0.132 moles)) in 200 ml of water was added in portions with vigorous stirring. After the gas evolution ceased, the organic phase was separated. The aqueous phase was extracted three times with dichloromethane (50 ml each). The extracts combined with the organic phase were dried with magnesium sulfate, filtered and concentrated on the rotary evaporator. The obtained oil was distilled through a 20-cm Vigreaux column wrapped with aluminum foil and glass wool. At 0.12-0.15 mm Hg fraction 1 (43°C, 5.9 g of DNPVE with ∿6% impurity) and fraction 2 (43-41°C, 55.8 g of DNPVE with <1% impurity by GC) were taken. The theoretical yield is 88.0 g.

After five months standing at room temperature in a brown bottle, the DNPVE was not polymerizable by the tin (IV) chloride method. Crude DNPVE (10.0 g) dissolved in carbon tetrachloride (20 ml) was chromatographed on neutral alumina with 300 ml of carbon tetrachloride. Upon removal of the solvent under vacuum DNPVE suitable for polymerization was obtained in 86% yield.

Nmr ($CDCl_3$): δ6.39 (m, 1; H_c; J_{ac} = 12 Hz, J_{bc} = 6 Hz



); 4.47 (s, $C\underline{H_2}C(NO_2)_2$); ca. 4.43 (m, H_a or H_b; $J_{ab} \simeq 3\ H_2$); 4.18 (unsymm. m, H_a or H_b); 2.21 (s, 3; $C(NO_2)_2C\underline{H}_3$).

GC analyses (Figure 1) were done with temperature programming from 80°-160° at 6°/min at a flow meter setting of 2.5.

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*The composition of the catalyst solution is given in reference 2, Shackelford, et al; F. J. SLR Technical Report 77-0018.

Preparation of Polymer Sample 3200. In a 50 ml 3-neck flask flushed with dry nitrogen was placed DNPVE purified by alumina filtration (8.1 g (4.6x10^{-2} moles)), 14 crushed pellets of "Linde" type 5A molecular sieves, and 1,2-dichlorethane (18 ml). The mixture was cooled to 0°C in an ice bath with mechanical stirring for 30 minutes. Tin (IV) chloride (0.15 ml (1.3x10^{-3})) was syringed through a septum into the solution. Stirring was continued for 18 hrs at 0°C under a positive pressure of nitrogen. The mixture was diluted with 1,2-dichloroethane (40 ml), filtered to remove the molecular sieves, and triturated efficiently with 100 ml of 2N H_2SO_4 at ambient temperature for 1.5 hrs. The phases were separated; the organic phase was washed with water (50 ml) and dried ($MgSO_4$). This solution was extracted with 0.1N sodium hydroxide (2x50 ml), dried again ($MgSO_4$) and filtered. The filtrate was rotary evaporated to give a white solid, polymer 3200 (7.7 g, 95%), molecular weight 3200 (osmometer, acetonitrile).

Anal. Calcd for $C_5H_8N_2O_5$: C, 34.09; H, 4.58; N, 15.91; O, 45.42. Found: C, 34.49; H, 4.53; N, 15.69; O, 45.10.

Preparation of Polymer Blend "M". Several samples of poly-DNPVE with a nominal molecular weight of 4000* (osmometer, acetonitrile) were thoroughly mixed in a mortar and pestle. A redetermination of the molecular weight (osmometer, acetonitrile) gave 3400.

Anal. Calcd for $C_5H_8N_2O_5$: C, 34.09; H, 4.58; N, 15.91; O, 45.42; Cl, 0.0. Found: C, 34.04; H, 4.80; N, 15.65; O, 45.42; Cl, 0.15.

This material was used for most of the exploratory work on side-chain modification and also for determination of nmr spectra (Figures 3 and 4) and molecular size distribution (Figure 2).

Gel Permeation Chromatography of Modified and Unmodified DNPVE Polymers. The solutions of polymer, modified and unmodified, were examined by gel permeation chromatography on a Waters Model 202 instrument. Five microstyragel columns, 10^6, 10^5, 10^4, 10^3, and 10^2 Å nominal porosity, were used. The solvent was tetrahydrofuran stabilized with BHT, the flow rate was 1 ml/min., and the differential refractive index (Rl) detector was set at an attenuation of 2X. Both samples were strongly UV absorbing. Figure 2 shows the normalized Rl curves for the two samples. It can be seen that they are similar. The columns were calibrated with polystyrene samples of known molecular weight and size.

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*Prepared according to the procedure given in: Adolph, H. G. and Kamlet, M. J., "Synthesis of Advanced Binder and Plasticizer Components," NOLTR 71-40, 13 Apr 1971.

Sodium Formaldehyde Sulfoxylate Reduction of Poly-DNPVE. Poly-DNPVE (0.2 g, 1.14 mmole), sodium formaldehyde sulfoxylate (1.22 g, 7.95 mmole), PTC (0.03 g), dichloromethane (2 ml), and water (2 ml) were stirred at room temperature for 2.5 days. Then the organic phase was separated, dried ($MgSO_4$), filtered, and evaporated in vacuo to give a viscous oil as the main product. Spectral data are described on p. 14.

Sodium Hydrosulfite Reduction of Poly-DNPVE (Preparation of Sample 66-3a). Polymer blend M (3.2 g), CH_2Cl_2 (128 ml), ethylene glycol (80 ml), water (96 ml), and sodium hydrosulfite (1.5 eq, 4.8 g) were vigorously stirred by a mechanical stirrer for six hours at room temperature. After standing 15 hrs the phases were separated. The aqueous phase was extracted three times with 50 ml each of CH_2Cl_2. The combined organic phase was added to 100 ml water and the dichloromethane was evaporated from the vigorously stirred mixture.

The white precipitate (2.9 g) was filtered, washed with water, and dried. This polymer was soluble in dichloromethane. On the basis of the recovered weight and assuming a 100% yield, the degree of reduction of this polymer is estimated to be 40%. Integration of the nmr peaks at δ2.28 and 1.51 ppm using the height times width at half height method indicated the conversion of dinitro- to mononitropropyl to be 35% (see, however, Table 3 and the discussion on p. 22).

Hydroxymethylation of Reduced Polymer. Three procedures using different solvents were developed, but insufficient data exists to select a preferred procedure.

Procedure A: 0.3 g of a reduced polymer sample was stirred with a mixture of dichloromethane (4 ml), ethylene glycol (2.5 ml), and 37% formalin-triethylamine (1 ml, 5:1 v/v) at room temperature for three days. The mixture was acidified to pH∿2 with conc. HCl, then diluted with water (25 ml). The aqueous phase was saturated with sodium chloride, and the dichloromethane was evaporated from the mixture. The white precipitate (0.3 g) was filtered and dried under vacuum over $KOH-P_2O_5$. This material was triturated with acetone (10 ml). The acetone insoluble material was removed by centrifuging. The acetone solution was diluted with water. The acetone was evaporated from the mixture. The white solid (0.23 g) was filtered and dried. The nmr peak at $\delta = 4.80$ ppm for $-C\underline{H}(NO_2)-$ was absent, therefore the reaction was largely complete. This material formed a soft rubber under the crosslinking conditions for polymer sample 66-3a (see below).

Procedure B: A reduced polymer sample (0.3 g) was stirred in dioxane (4 ml) and 37% formalin-triethylamine (5/1 v/v, 1 ml). The solution was heated to 60°C over 10 min., held at temperature for five min., and allowed to cool for 30 min. The solution was diluted with water (50 ml), saturated with salt, stirred 20 min., and filtered to give a white solid (0.29 g) which was washed with water and dried. From the disappearance of the nmr peak at $\delta = 4.80$ ppm, the reaction was determined to be essentially complete.

Procedure C (Preparation of Sample 66-3a, Continued): The reduced polymer (2.9 g, see procedure above) was stirred with 37% formalin-triethylamine (15 ml; 4:1 v/v) in acetone (40 ml) for three hours at room temperature; the solution was acidified to pH$\sim$6 with conc. HCl, then diluted with water (100 ml) to give a white solid (2.85 g) which was dried under vacuum over KOH-P_2O_5 overnight. Since the peak at $\delta = 4.80$ ppm for $-\underline{H}C(NO_2)-$ was still present, the reaction was repeated for 20 hours with 37% formalin and triethylamine (12 ml, 5:1 v/v). After the same workup a white solid (2.5 g) was obtained. The nmr peak at $\delta = 4.80$ ppm was no longer present.

Nmr (acetone-d_6): δ 4.39 (s,$C\underline{H}_2C(NO_2)_2$); 3.71 (very broad s, $C\underline{H}CH_2$); 2.29 (s, $C(NO_2)_2C\underline{H}_3$); 1.74 (very broad s, $CHC\underline{H}_2$); and 1.63 (s, $C(NO_2)(CH_2OH)C\underline{H}_3$).

Crosslinking of Polymer 66-3a. Hydroxymethylated polymer 66-3a (0.15 g, see above) was dissolved in BDNPF/A plasticizer (50/50) with the aid of acetone (0.5 ml). The acetone was evaporated. The resulting viscous oil was heated at 55° under vacuum overnight. Then hexamethylene diisocyanate (HMDI, 2.2% in dichloromethane) and dibutyltindilaurate in dichloromethane (0.3%, 1 ml) were added, consecutively. Dry acetonitrile (0.5 ml) was added to facilitate solution. The solvents were evaporated at room temperature under vacuum for 15 min., and the resulting viscous oil was heated at 70°C for 20 to 48 hrs under a Drierite tube. A rubbery solid was obtained in each run.

Run	Plasticizer/Polymer ratio (w/w)	HMDI [mg]*	Cure Time (hr)
1	2.3	9.5	20
2	3.0	14.5	48
3	4.0	9.5	20

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*based on assumed functionalities of 3 in runs 1 and 3, and of 4.5 in run 2.

Initiation Reactions (Table 5), General Description. All runs were assembled in a dry box kept at low humidity with an open dish of phosphorous pentoxide. Solvents were distilled from phosphorous pentoxide under nitrogen and stored in the dry box over freshly activated molecular sieves. The reagents (see Table 5) were generally weighed into a three-necked reaction flask in the dry box. Usually one of the liquid reagents was weighed in a syringe in the dry box. The reaction flask was removed from the dry box and used while being kept under a positive pressure of nitrogen. Then the liquid reagent contained in the syringe was introduced into the flask through a septum. The progress of the reaction was generally followed by monitoring the decrease of DNPVE by GC. The reactions were quenched with methanol, filtered, and generally extracted with 0.05 N aqueous sodium hydroxide. The organic phase was evaporated to give the product which was analyzed by GC and/or spectroscopically (ir, nmr), or was subjected to column chromatography followed by the analysis of individual fractions (see Table 5).

Chromatography was performed with a column (25 mm x 250 mm) prepared from a slurry of Brinkmann silica gel (7734) in the least polar solvent to be used. The column was eluted successively with increasingly polar solvents or solvent combinations until a material balance was obtained or methanol had been used as the solvent.

Reaction of DNPVE with Trimethylsilylchloride/$AgBF_4$. Procedure A: DNPVE (1.0 g, 5.68 mmol) and silver tetrafluoroborate (2.82 mmol) dissolved in acetonitrile (5 ml) were cooled to -30°C with stirring. Trimethylsilylchloride (0.35 ml, 2.82 mmol) was syringed in through a septum under a positive pressure of nitrogen. A white precipitate formed immediately. After 2.5 days at 0-4°C methanol (1 ml) was added. The mixture was filtered. The filtrate diluted with dichloromethane (20 ml) was extracted with 0.1 N sodium carbonate. The organic phase was separated, dried ($MgSO_4$), filtered, and the solvent removed under vacuum to give a light brown oil (0.9 g). An nmr spectrum was obtained in $CDCl_3$ with benzene as internal lock; no peak near $\delta = 0$ indicative of a trimethylsilyl group was present.

Procedure B: Silver tetrafluoroborate (0.55 g, 0.5 eq) was dissolved in acetonitrile (10 ml) at room temperature. On addition of trimethylsilyl chloride (0.31 g, 0.5 eq) a voluminous white precipitate formed. The mixture was immediately cooled to -40°C. DNPVE (1.0 g) was added to the stirred mixture. After 15 min. the reaction was allowed to warm to room temperature and was then stirred overnight. The mixture was filtered. Methanol (2 ml), followed by triethylamine (0.3 ml), was added to the filtrate. The volatile materials were removed on a rotary evaporator. The residue dissolved in dichloromethane (20 ml) was extracted with 10 ml of HCl(0.2 N), then with water (10 ml), and dried ($MgSO_4$). By filtration, followed by evaporation in vacuo, a viscous brown oil (0.5 g) was obtained. A peak in the nmr ($CDCl_3$, benzene lock) at $\delta = 0.10$ was observed. The oil dissolved in dichloromethane (20 ml) was percolated through alumina (5.0 g). A light brown oil (0.4 g) was obtained on removal of the solvent in vacuo; nmr ($CDCl_3$, benzene and TMS lock) δ 0.10 (s, $SiC\underline{H}_3$); 1.1 (d), 1.26 (m); 1.6 (broad s); 2.14 (s, $C(NO_2)_2C\underline{H}_3$); 3.24 (s); 3.26 (s); 4.22 (broad m); and 4.42 (broad m). On the basis of the peak at $\delta = 0.10$, the material contains trimethylsilyl groups; however, repetition of this procedure gave an oil (1.0 g), whose nmr spectrum differed substantially from that reported above and had no peak for the trimethylsilyl group.

DNPVE Initiation with Propylene Oxide - Tin Chloride. Propylene oxide (0.055 g, 0.1 eq) dried over 3A molecular sieves and dissolved in dichloromethane (1.0 ml) was added to a mixture of DNPVE (2.0 g), dichloromethane (2.3 ml), four crushed pellets of molecular sieves 5A, and tin (IV) chloride (0.246 g, 0.1 eq) at 0° in 0.1 ml increments every 10 minutes. After 18 hrs at 0°, the reaction mixture was diluted with dichloromethane and filtered. The filtrate was stirred with 2 N H_2SO_4 (18 ml) for 1.5 hrs. The acid phase was separated. The organic phase was extracted (2 x) with NaOH (0.075 N, 18 ml), dried ($MgSO_4$), filtered, stripped and freed from solvent under vacuum to give a light fluffy solid (1.9 g). This solid was chromatographed on a silica gel column prepared with dichloromethane. By elution with dichloromethane and up to 2% methanol-dichloromethane, 15 oily fractions were obtained. Combined, these fractions accounted for 50% of the material but were too small individually to merit further investigation. Elution with 3% methanol-dichloromethane gave a solid fraction (32% of the material). Elution with 3 to 100% methanol in dichloromethane gave eight more solid fractions (10% of the material). The nmr spectrum (acetone-d_6) of the largest solid fraction (32% of the material) resembled that of a low molecular weight Poly-DNPVE: δ 4.36 (s, $C\underline{H}_2C(NO_2)$); 3.65 (broad s, $CHCH_2$); 2.75 (m, small); 2.26 (s, $C(NO_2)_2C\underline{H}_3$); 1.77 (broad s, $CHC\underline{H}_2$); and 1.17 (broad s, $CHC\underline{H}_3$). Although the nmr spectrum had no new features, no conclusion can be reached from it about the incorporation of propylene oxide into the polymer, as it is uncertain whether the 1-hydroxy-2-propyl group would have peaks that would not overlap with the rest of the spectrum.

Epichlorohydrin - Tin Chloride Initiation of DNPVE. Epichlorohydrin (0.103 g, 0.2 eq) dried over 3A molecular sieves and dissolved in dichloromethane (1 ml) was added to a mixture of DNPVE (1.0 g) and tin (IV) chloride (0.289 g, 0.2 eq) in dichloromethane (1 ml) at 0° in 0.01 ml increments every minute. After 18 hours at 0° the reaction solution was diluted with dichloromethane and stirred with H_2SO_4 (2 N, 18 ml) for 1.5 hours. The acid phase was separated. The organic phase was extracted (2 x) with

NaOH (0.05 N, 10 ml), dried ($MgSO_4$), filtered, and stripped *in vacuo* to give a straw yellow solid (1.0 g). This solid was stirred with methanol (10 ml) to give an insoluble (0.68 g) and a soluble fraction (0.32 g). The insoluble material was stirred with another 10 ml of methanol to give an insoluble product (0.63 g) which had a chlorine content of 3.16%. This material was taken up in dichloromethane (0.6 ml) and was reprecipitated with methanol (20 ml) to give, after four hours stirring, a solid (0.50 g, 2.47% Cl). A portion of this solid (0.15 g) was chromatographed on a silica gel column (12 x 170 mm) prepared with dichloromethane. Elution with dichloromethane (30 ml) and 3% methanol-dichloromethane (32 ml) gave only trace amounts of material. Elution with 11 ml more of 3% methanol-dichloromethane gave a solid fraction of 0.14 g; chlorine content 2.68% Cl. Further elution with 3% methanol-dichloromethane (17 ml) gave the remainder of the material (0.01 g). The nmr spectrum of the main chlorine containing product again gave no clear indication of the presence of additional structural features over those present in Poly-DNPVE.

GLOSSARY

BDNPF/A	Bis(2,2-dinitropropyl)formal/acetal mixture (1:1)
BHT	Butylated Hydroxytoluene
DMF	Dimethylformamide
DNP	2,2-dinitropropane
2,4-DNPH	2,4-dinitrophenylhydrazine
DNPOH	2,2-dinitropropanol
DNPVE	2,2-dinitropropyl vinyl ether
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HMDI	Hexamethylene Diisocyanate
LAH	Lithium Aluminum Hydride
NMR	Nuclear Magnetic Resonance Spectroscopy
PTC	Phase Transfer Catalyst
SHS	Sodium Hydrosulfite
THF	Tetrahydrofuran
TMSCl	Trimethylsilyl chloride

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