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SYNTHESIS OF ENERGETIC SINGLE PHASE AND MULTI-PHASE POLYMERS

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Investigation of the synthesis of polyformals from fluoro- and nitrodiols was continued at a low level The synthesis of 3,5,5,11,11,13-hexanitro-3,13-diaza-7,9 dioxapentadecane-1,15-diol polyformal, a high energy nitro polymer for use in cast-curable binders, was completed. A new fluoropolyformal was prepared from 3M fluoropolyether diol L-9939. One pound of 2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol polyformal was prepared for evaluation in pyrotechnic formulations.

A series of copolyformals was prepared from nitrodiols and fluorodiols with th objective to obtain energetic prepolymers with low T_G useful as cast-curable binder and as energetic soft blocks for thermoplastic-elastomeric (TPE) block copolymers. Several of the new polymers appear to meet this goal, based on qualitative observation of their properties. A copolymer of 2,2,3,3,4,4,5,5-octafluorohexane-

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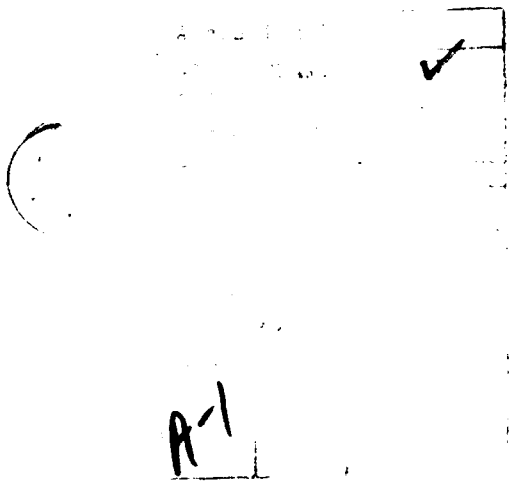
19. Abstract (Cont'd)

1,6-diol and 3-nitrazapentane-1,5-diol may be useful as a replacement for hexafluoropentanediol polyformal (FPF-1) in cast-curable binder applications. A second copolymer of bis(hydroxyethyl)orthocarborane, with octafluorohexanediol, was prepared.

The synthesis of a series of acid chloride-terminated polyesters from fluoro- and nitrodiols and 4,4-dinitropimeloyl chloride and malonyl chloride, respectively, and their reaction with monomeric and polymeric diols to form $(AB)_N$ block copolymer was investigated. Polyesters based on dinitropimeloyl chloride were too unreactive for block linking or significant chain extension. With malonyl chloride, indicatio of block copolymer formation was obtained in some cases, but reproducibility was difficult. Further work is needed in this area.

$(AB)_N$ block copolymers were obtained readily by end-capping hydroxy-terminated FPF-1 with diisocyanates and linking these "soft blocks" with nitrodiols, and with nitrodiol polyformals. Several of these polymers have TPE characteristics. Simple chain-extension of hydroxy-terminated FPF-1 with diisocyanates such as TDI, 3,3-dinitropentane diisocyanate, 3-nitrazapentane diisocyanate in some cases also gave polymers with TPE properties. A diacid diazide was prepared and used successfully as diisocyanate precursor for this block copolymer synthesis. The model reaction o a nitro-substituted α,ω-diazidoalkane with fluorodinitroacetonitrile was studied an found to be too slow for block copolymer synthesis.



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SYNTHESIS OF ENERGETIC SINGLE PHASE AND MULTI-PHASE POLYMERS

INTRODUCTION

The work described in this report has several objectives. One is to synthesize and characterize energetic single phase polymers (homo- and copolymers), specifically hydroxy-terminated fluoro- and nitro-substituted polyformals and polyesters, which are useful as binders for cast-curable energetic compositions, and as components for segmented multi-phase (block) copolymers. A second set of objectives is to establish the chemistry for the synthesis of block copolymers from such polydiols and other difunctional polymers, and to provide methods for characterization of the block copolymers produced. The block copolymers to be synthesized are desired to be elastomers in the temperature range of about -50°C to +80°C and plastic at temperatures above about 80-100°C. Low melt-viscosities are desired as well. It is believed that these properties will permit and facilitate continuous extrusion processing of propellants which use such polymers as binders. The first objective is supported primarily by the Office of the Chief of Naval Research, while research toward the second objective is supported primarily by the SDIO Office of Innovative Science and Technology. The two efforts are closely related, and funding support overlaps in the area of copolymer synthesis. The results of both programs are therefore presented together.

RESULTS AND DISCUSSION

Homopolyformals.- Only isolated efforts were conducted in this area since the work on the synthesis of homopolyformals from fluoro- and nitrodiols has substantially been completed.[1]

Work was continued on the synthesis and purification of the polyformal of the hexanitropentadecanediol 1 in order to obtain a reproducible synthesis procedure amenable to scale-up. A procedure for removal of the reaction

$$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$$

1

solvent sulfolane by trituration with dichloromethane/water has been worked out. Precipitation of the polymer from a THF solution with methanol removed low molecular weight cyclic and linear formals present in the crude polymer (see Figs. 1 and 2). Evaluation of this polymer as a cast-curable binder component is planned with support from the 6.2 Explosives Block.

Attempts were made to prepare polyformals from the two diols 2 and 3 which were received from Fluorochem, Inc.

$$HOCH_2C(NO_2)_2CH_2(CF_2)_nCH_2C(NO_2)_2CH_2OH$$

2: n = 4
3: n = 6

These attempts have not been successful, probably mostly because of the poor solubility of the diols in sulfuric acid as well as in sulfolane. In both cases, there was essentially no reaction with CH_2O/H_2SO_4 or with trioxane/BF_3 etherate/sulfolane.

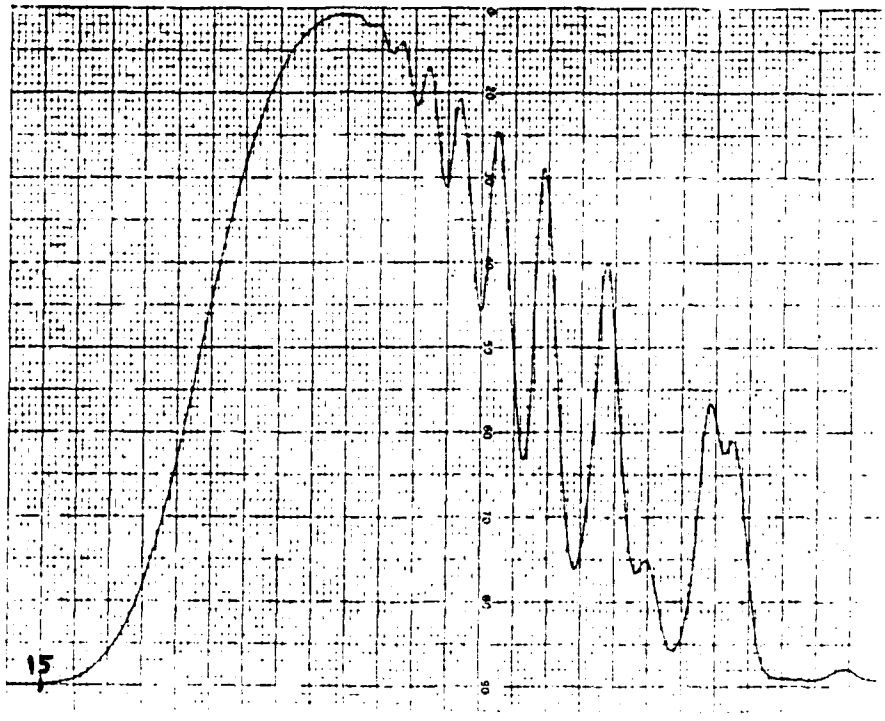


Fig. 1. GP Chromatogram of Crude $HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ Polyformal

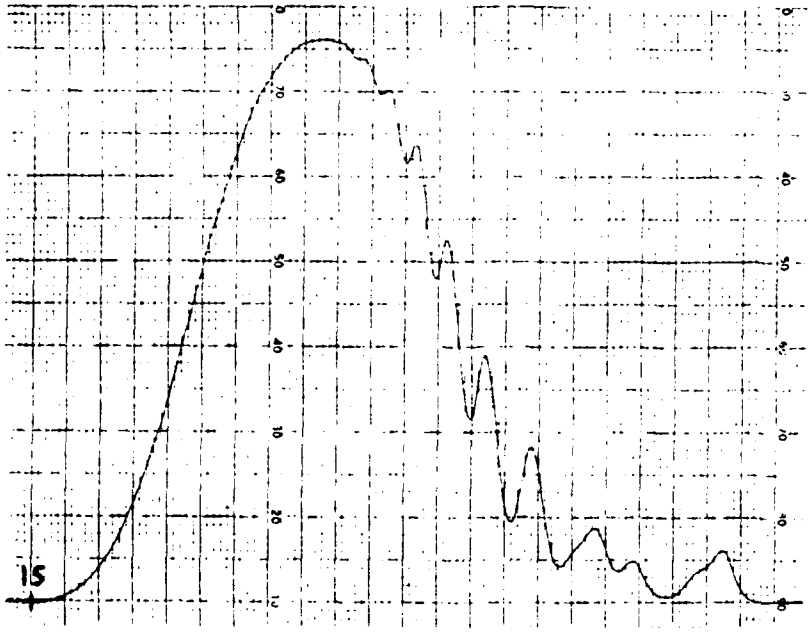


Fig. 2. GP Chromatogram of Purified $HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ Polyformal

A new fluorohomopolymer was prepared from a perfluoroether diol having the approximate structure 4 which was obtained from 3M (L-9939). This liquid polymer had $M_n \approx 2600$ and was obtained in >90% yield. The GP chromatogram and ^{1}H-NMR spectrum are shown in Figs. 3 and 4. The new polymer has a higher

$$HOCH_2\overset{CF_3}{\overset{|}{C}}FO(CF_2)_3O(CF_2)_4O(CF_2)_3O\overset{CF_3}{\overset{|}{C}}FCH_2OH$$

4

fluorine content than previously prepared fluoropolyformals. It is expected to have a lower viscosity and T_G and should be of interest for use in cast-curable binders and as a soft block for fluorinated block copolymers.

Also during the past year, approximately one pound of 2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol polyformal was prepared and sent to NSWC Crane (R. Shortridge) for evaluation. This polymer had $M_n = 2445$, $M_w = 4826$, $D_p = 1.97$.

Formal Copolymers.- It was shown in the previous work[1] that copolyformals could be formed of various combinations of fluorodiols and nitrodiols. ^{1}H-NMR analysis indicated that the copolymers obtained were somewhat segmented: the less acidic diol predominated in the center of the polymer chains, the more acidic (less reactive) diol was concentrated at the ends. This ratio could be changed towards more complete randomization by gradual addition of the more reactive monomer to the mixture of formaldehyde/acid/less reactive monomer. The current effort was directed more specifically towards the synthesis of copolymers useful as energetic soft blocks. It was expected that the combination of a fluorodiol and a nitrodiol would best meet this objective. The formation of copolyformals from the fluorodiols 5 and 6 and the nitrodiols 7 - 11 was therefore studied. Although 5 readily forms homopolymers with

$HOCH_2(CF_2)_4CH_2OH$ 5

$HOCH_2(CF_2)_3O\overset{CF_3}{\overset{|}{C}}FCH_2OH$ 6

$HOCH_2CH_2N(NO_2)CH_2CH_2OH$ 7

$HOCH_2CH_2N(NO_2)CH_2CH_2N(NO_2)CH_2CH_2OH$ 8

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ 9

$HOCH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2OH$ 10

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ 11

molecular weights > 5000 in the reaction with formaldehyde and sulfuric acid, copolymerization with as little as 20 mol % of 7 was not successful. This amount of 7 inhibited polymer formation almost completely, probably due to the relatively high basicity of the nitramine moiety in 7. Copolymers can be obtained with trioxane/BF_3 etherate in sulfolane, but only with a very low content of 7 (1-2 mol %).

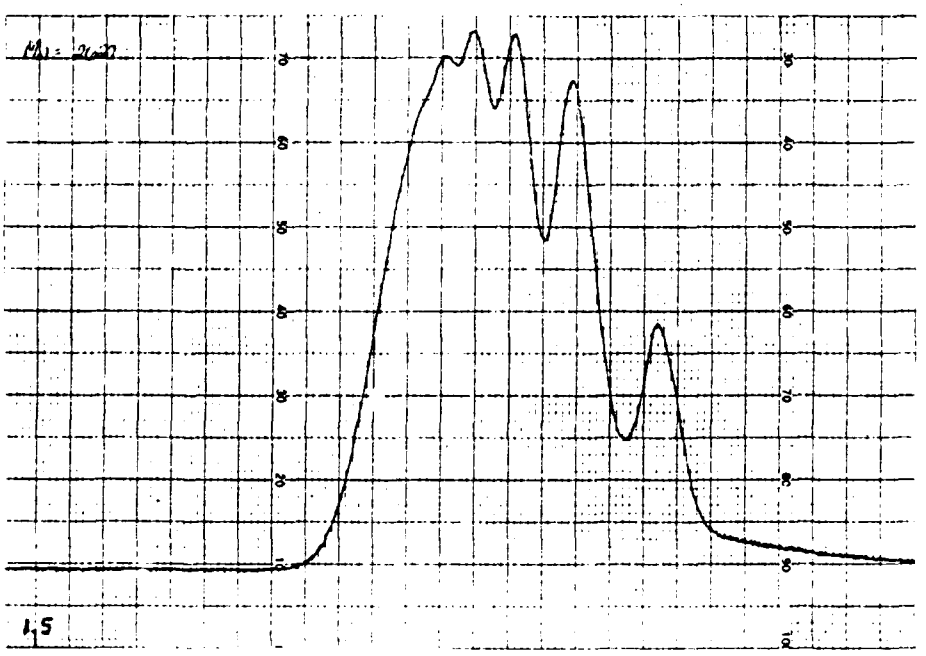


Fig. 3. GP Chromatogram of a Polyformal of 3M Perfluoropolyether Diol L-9939

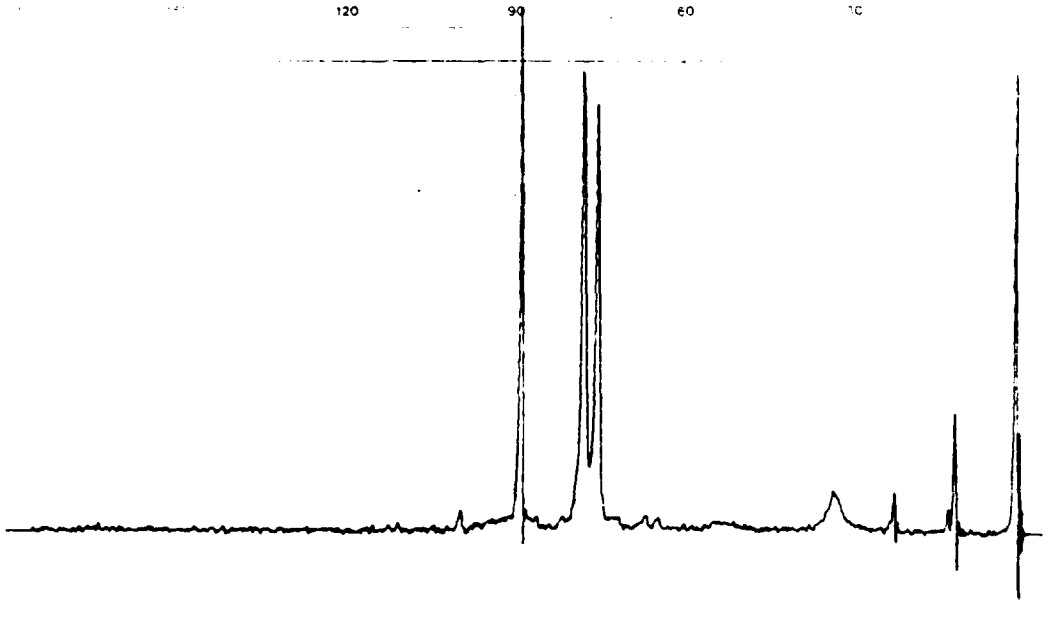


Fig. 4. ^{1}H-NMR Spectrum of a Polyformal of 3M Perfluoropolyether Diol L-9939

These copolymers are not of interest as energetic soft blocks; they are, however, of interest as cast-curable binders because the small amount of 7 makes the fluoropolymer miscible with energetic plasticizers. Because 5 is substantially cheapter than hexafluoropentanediol, the 5/7 copolyformal is a potential replacement for hexafluoropentanediol polyformal in cast-curable energetic binders. A GP chromatogram and ^{1}H-NMR spectrum of a representative 5/7 copolyformal (feed ratio 97.5:2.5 mol%) of M_n = 2089 are shown in Fig. 5 and 6. The copolymerization of 6 and 7 has not been studied but should be of interest for the same reasons.

Copolymerization of 5 and 10 with trioxane/BF_3 etherate in sulfolane was more successful but was accompanied by significant cleavage of the central O-CH_2-O group of 10 and formation of 5,5-dinitro-1,3-dioxane. This is in contrast to the earlier copolymerization of 10 with the more reactive 4,4-dinitroheptanediol which occurred with very little cleavage of 10. The copolymers of 5 and 10 were obtained in ratios of 90/10, 80/20, and 60/40 in yields of > 80%. Only the 60/40 composition would be of interest as an energetic soft block, if the by-product dinitro-1,3-dioxane can be removed. A GP chromatogram of a crude 60/40 copolymer is shown in Fig. 7.

The copolymerization of 5 and 8 occurred readily with trioxane/BF_3 etherate (but not with CH_2O/H_2SO_4) in molar ratios from 1:10 to 10:1. An initial side reaction was the formation of polymer chains with formaldehyde dimer and trimer units, i.e., ~~OCH_2OCH_2O~~ instead of ~~OCH_2O~~, but this could be minimized by increasing the BF_3 etherate concentration. Four 20g samples with 5/8 feed ratios of 15/85, 30/70, 50/50, and 70/30 were prepared. These copolymers are viscous resins at room temperature; they have been characterized by GPC and by ^{1}H- and ^{19}F-NMR spectroscopy. Table 1 lists OH equivalent weights, experimental monomer ratios and intrinsic viscosities. Figures 8-19 show GPCs of the four 20g samples as well ^{1}H- and ^{19}F-NMR spectra. Further characterization (thermomechanical, thermogravimetric, and DSC analysis, viscosity determination, and molecular weight characterization) and evaluation as block copolymer components is underway. Copolymerization studies with 6 and 8 are also planned

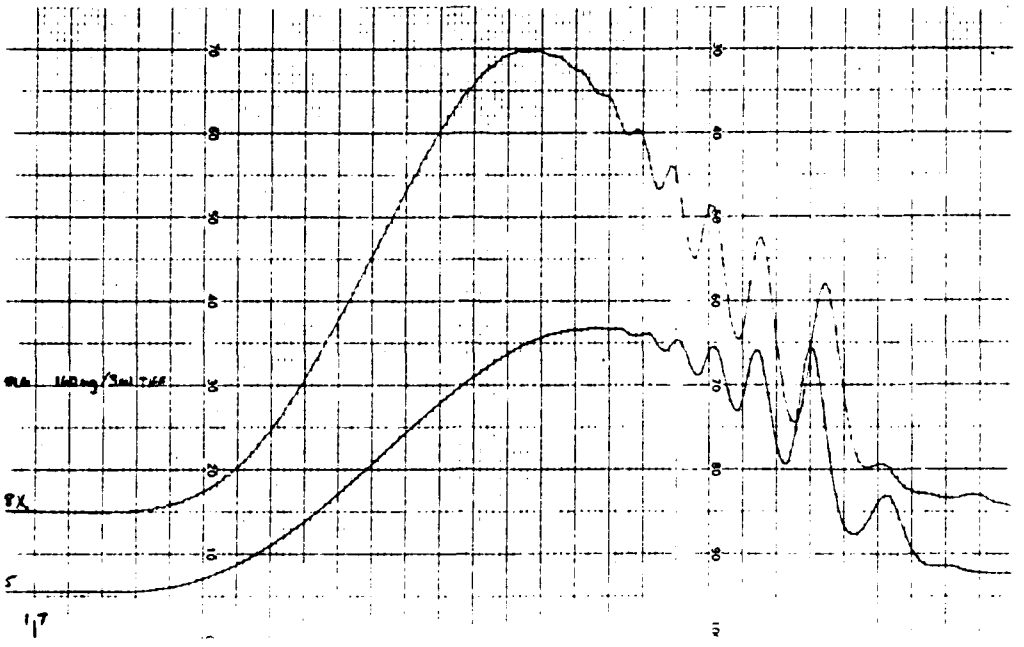


Fig. 5. GP Chromatogram of a Copolyformal of 5 and 7 (97.5:2.5)

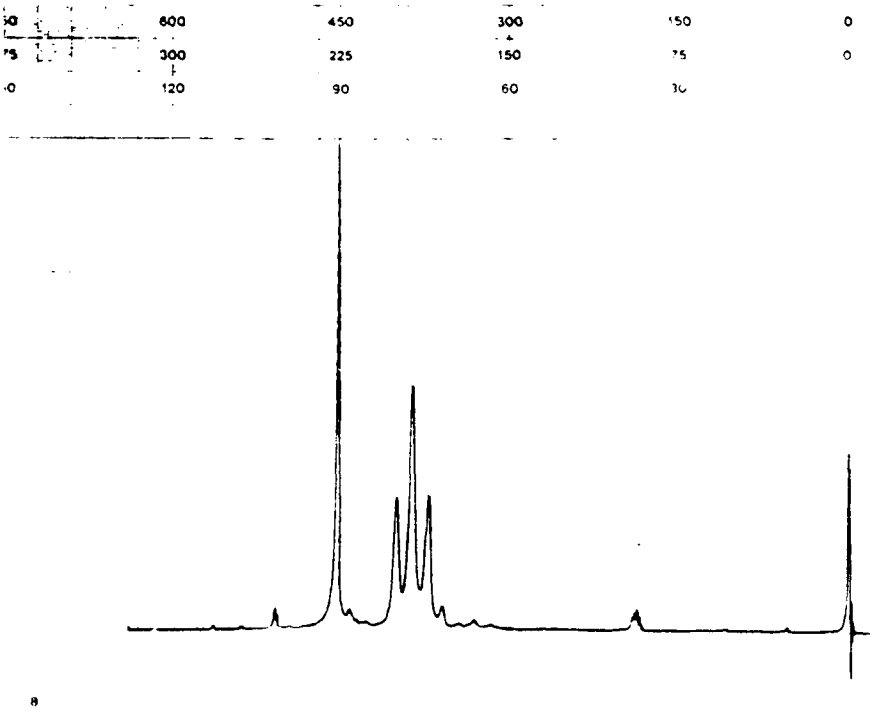


Fig 6. ^{1}H-NMR Spectrum of a Copolyformal of 5 and 7 (97.5:2.5)

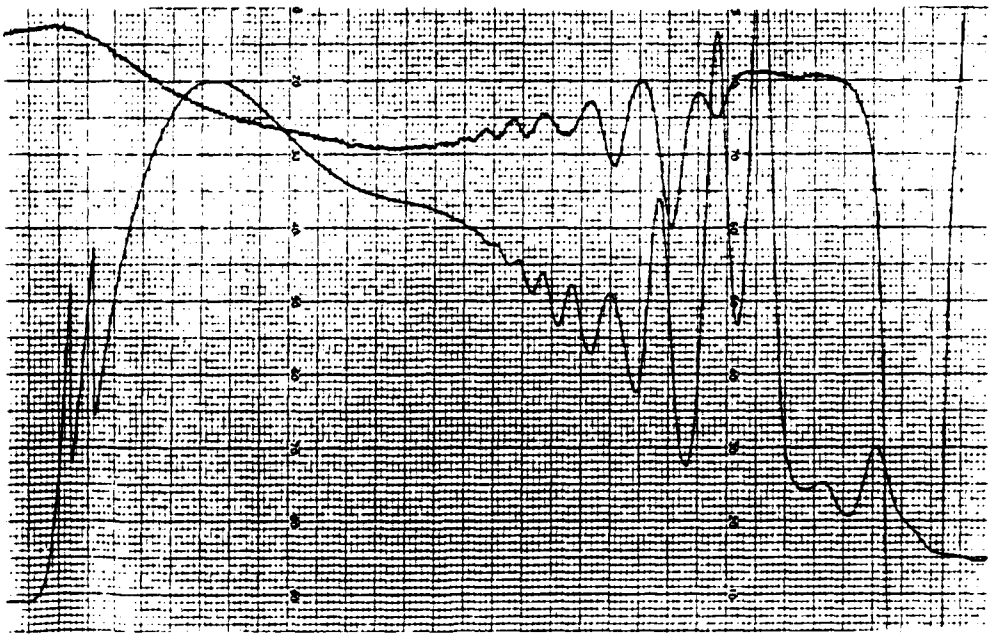


Fig. 7. GP Chromatogram of a Copolyformal of 5 and 10 (60:40)

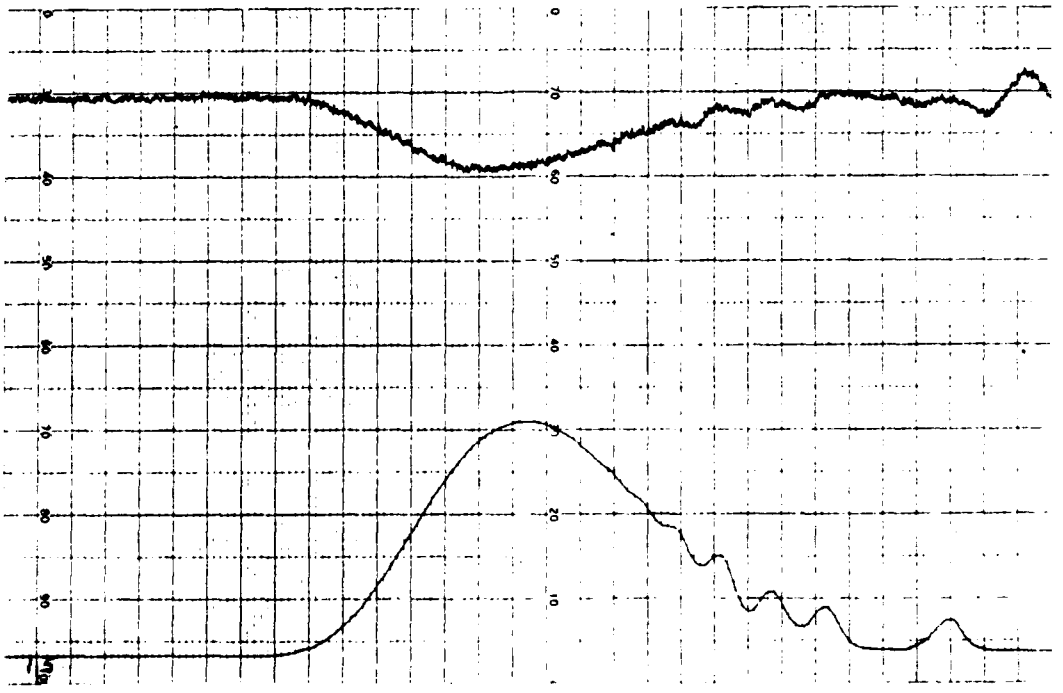


Fig. 8. GP Chromatogram of a Copolyformal of 5 and 8 (15:85, 20g Sample)

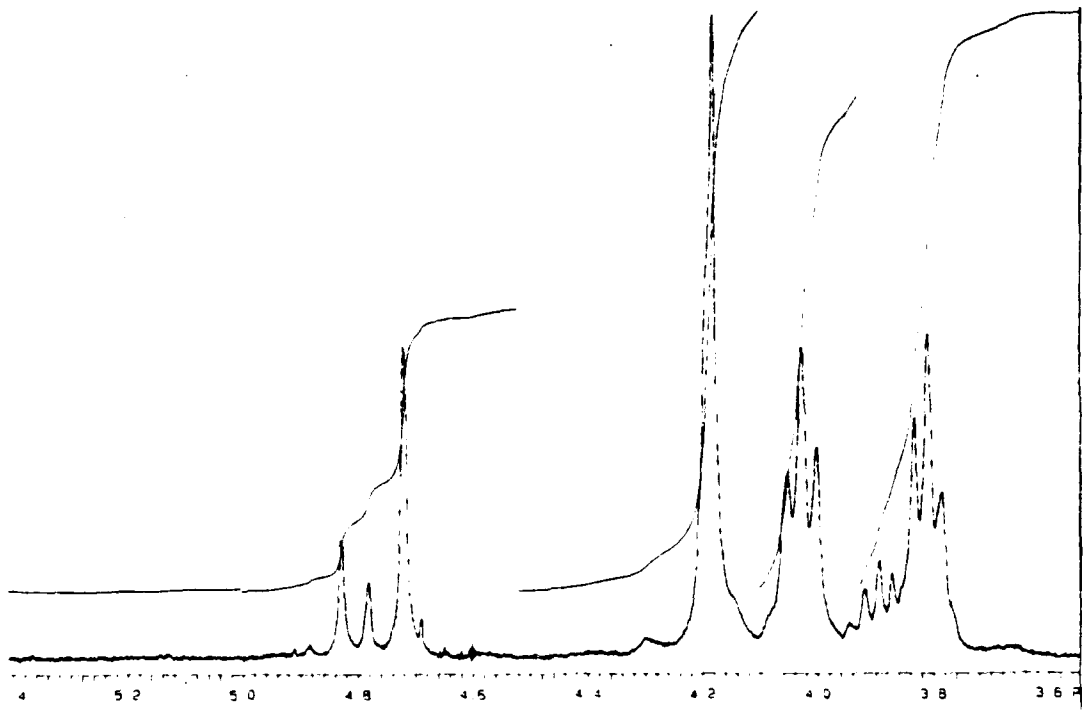


Fig. 9. ^{1}H-NMR Spectrum of a Copolyformal of 5 and 8 (15:85, 20g Sample)

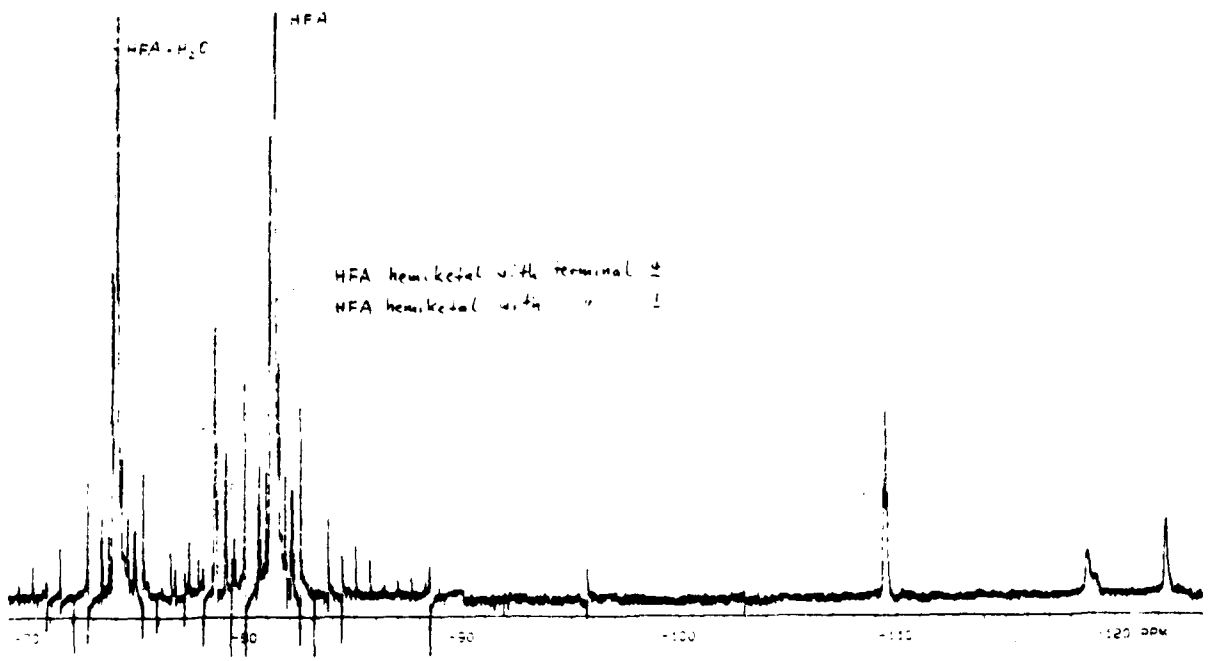


Fig. 10. ^{19}F-NMR Spectrum of a Copolyformal of 5 and 8 (15:85, 20g Sample) after addition of hexafluoroacetone.

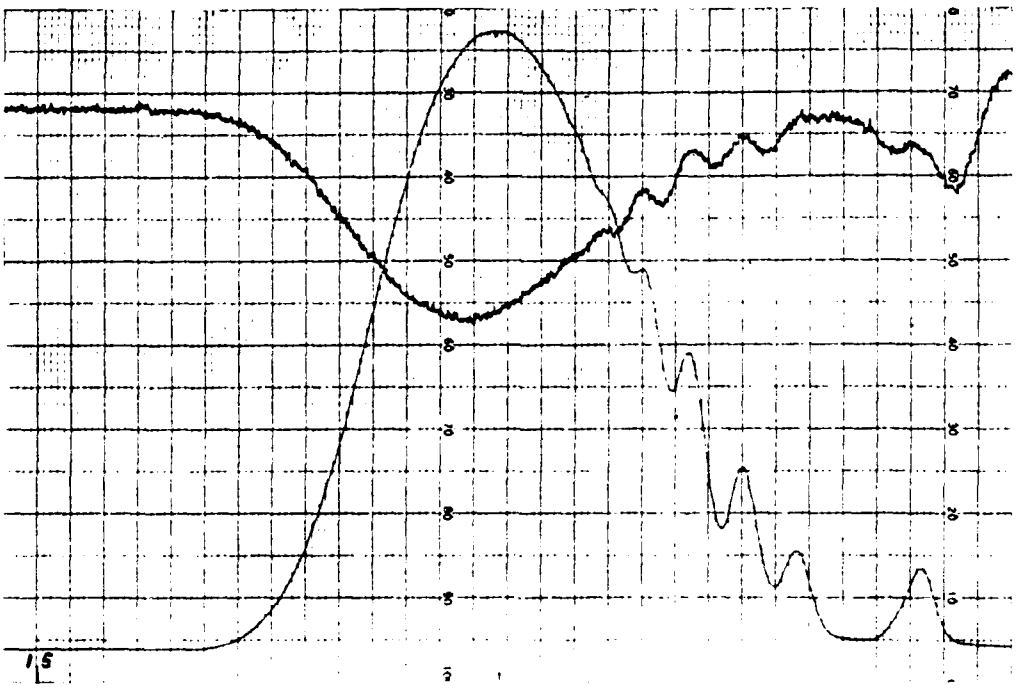


Fig. 11. GP Chromatogram of a Copolyformal of 5 and 8 (30:70, 20g Sample)

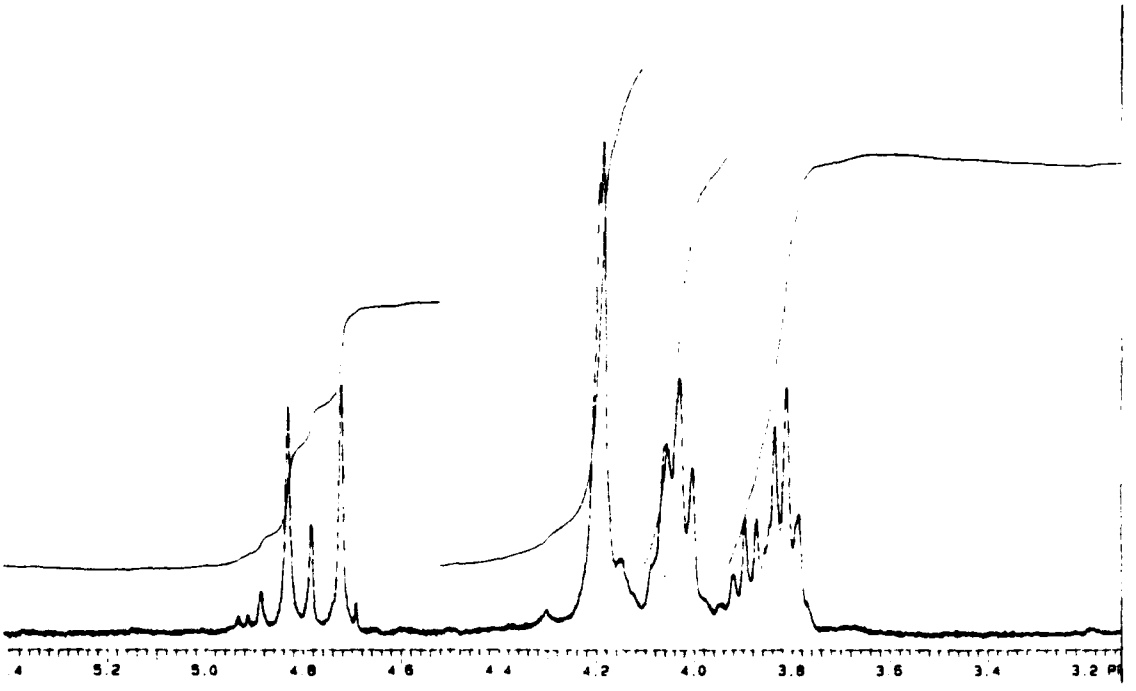


Fig. 12. ^{1}H-NMR Spectrum of a Copolyformal of 5 and 8 (30:70, 20g Sample)

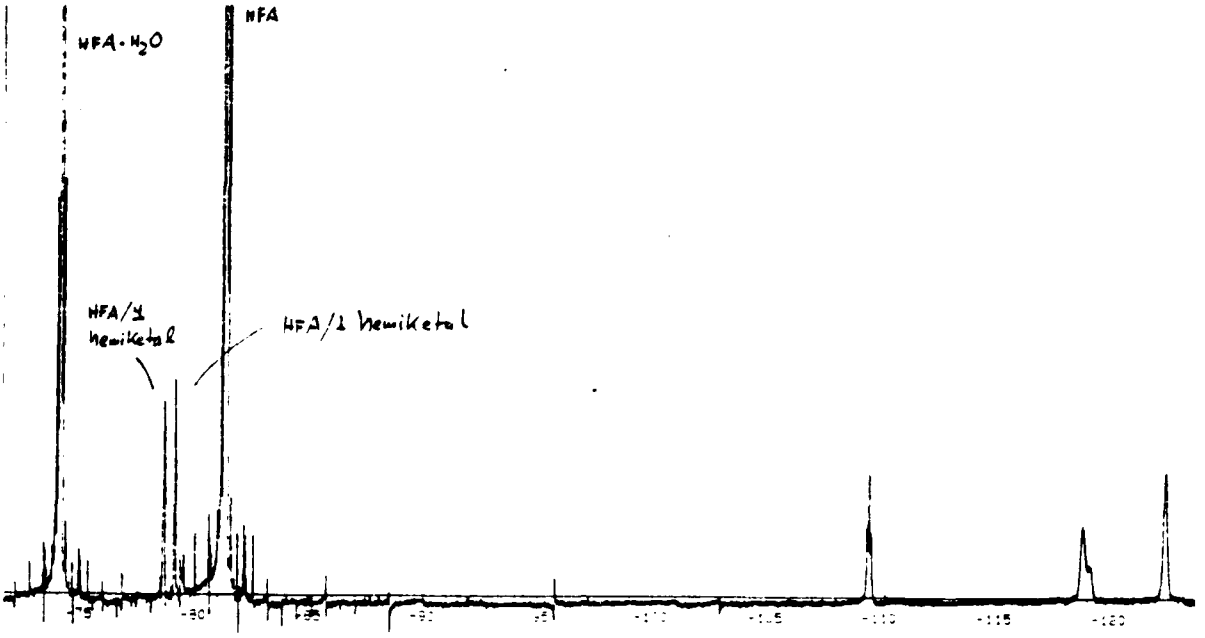


Fig. 13. ^{19}F-NMR Spectrum of a Copolyformal of 5 and 8 (30:70, 20g Sample) after addition of hexafluoroacetone.

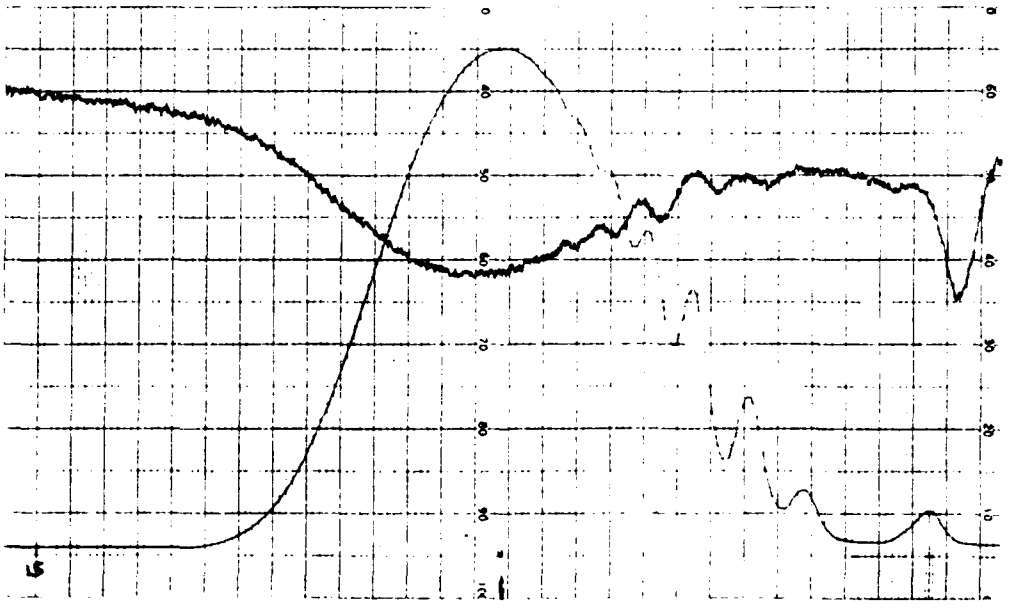


Fig. 14. GP Chromatogram of a Copolyformal of 5 and 8 (50:50, 20g Sample)

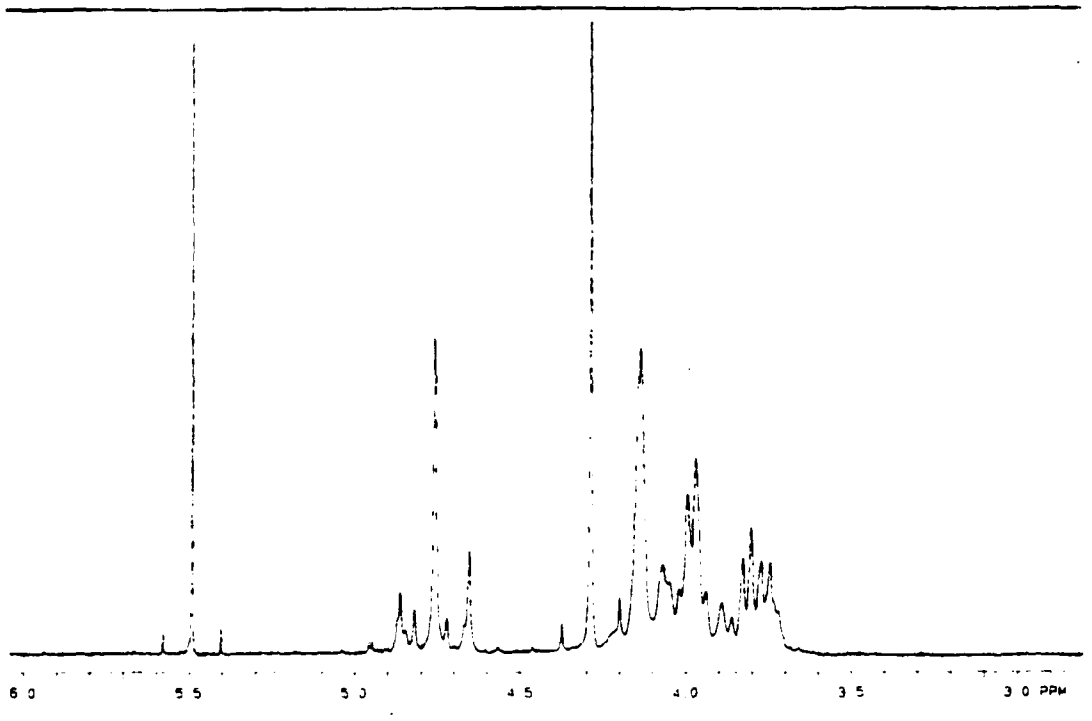


Fig. 15. ^{1}H-NMR Spectrum of a Copolyformal of 5 and 8 (50:50, 20g Sample)

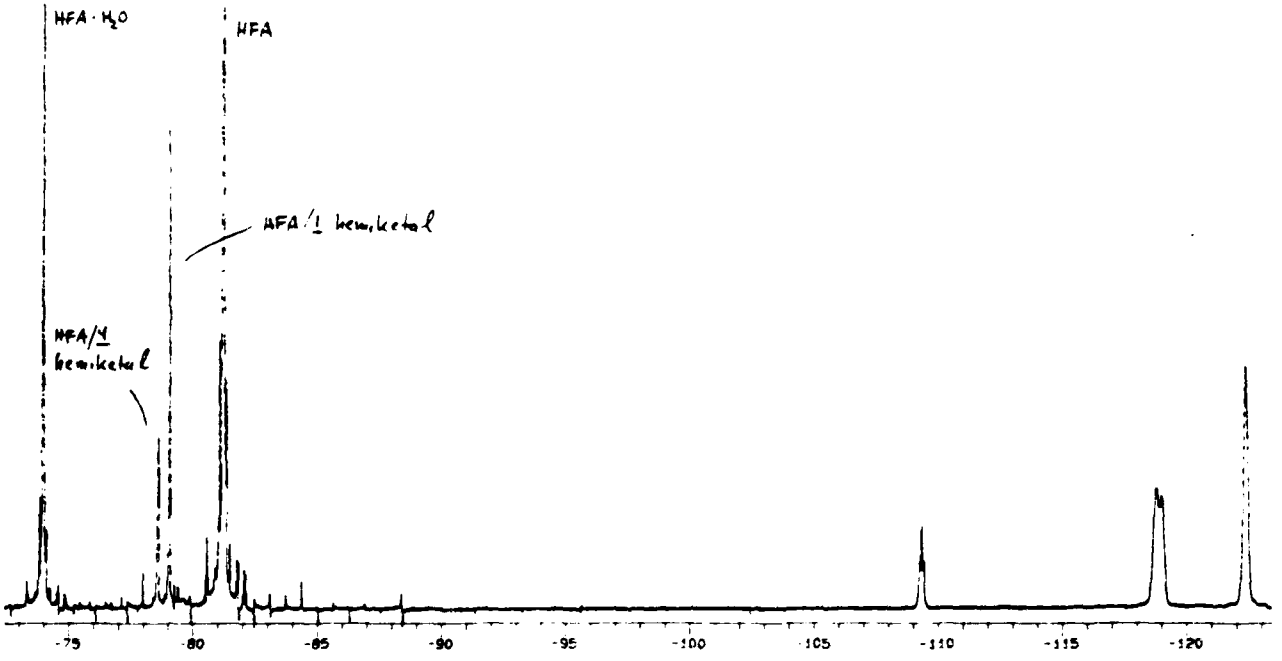


Fig. 16. ^{19}F-NMR Spectrum of a Copolyformal of 5 and 8 (50:50, 20g Sample) after addition of hexafluoroacetone.

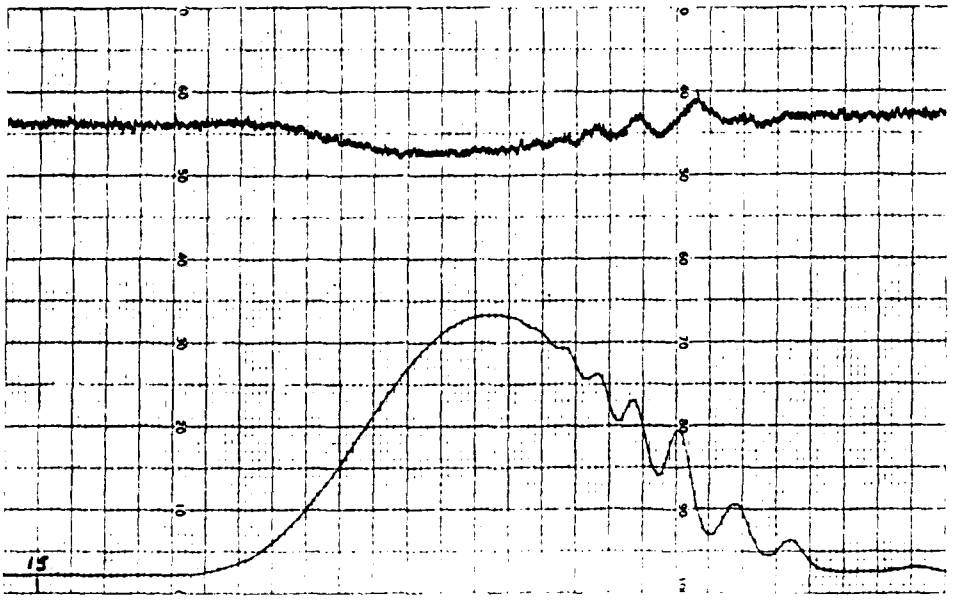


Fig. 17. GP Chromatogram of a Copolyformal of 5 and 8 (70:30, 20g Sample)

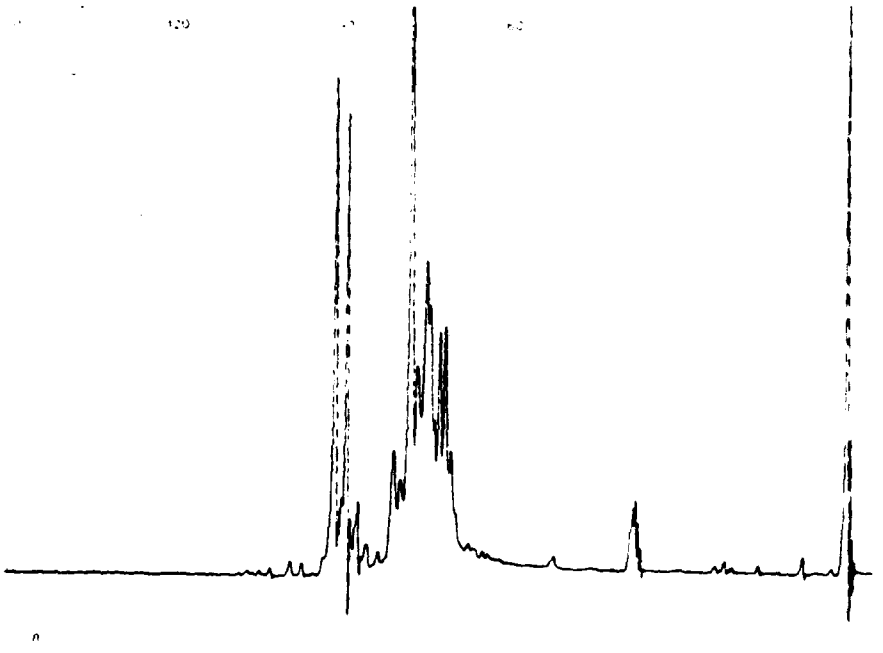


Fig. 18. ^{1}H-NMR Spectrum of a Copolyformal of 5 and 8 (70.30, 20g Sample)

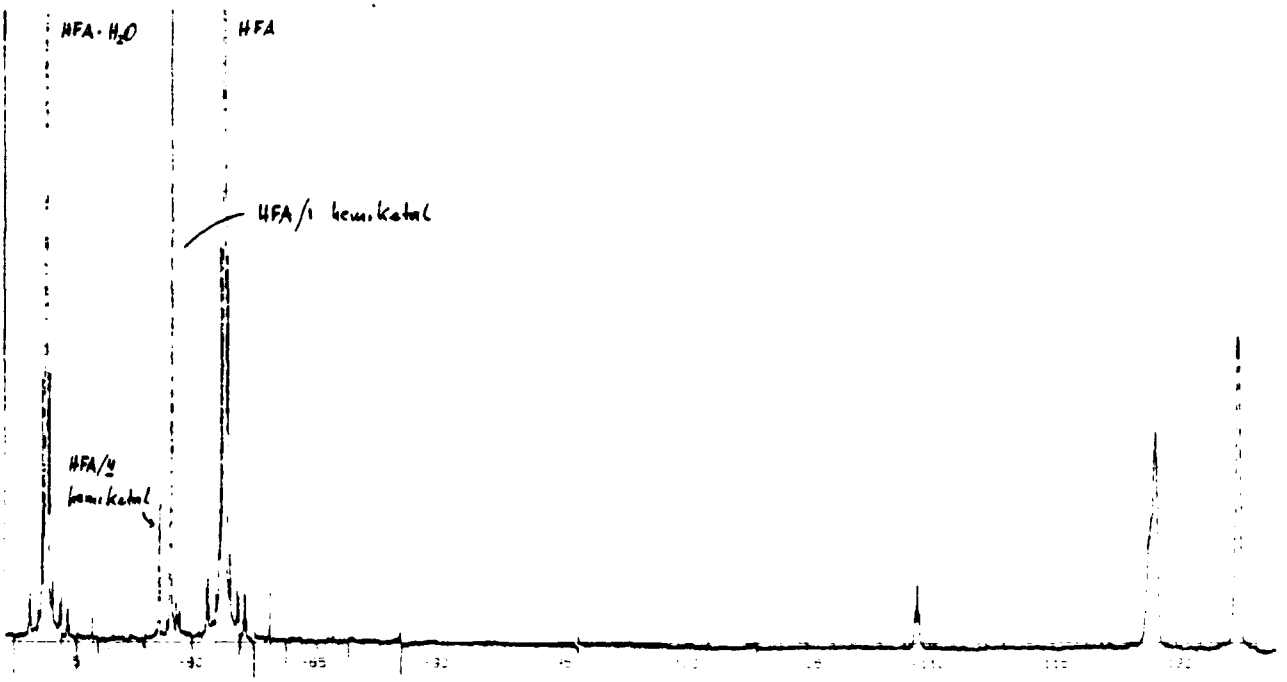


Fig. 19. ^{19}F-NMR Spectrum of a Copolyformal of 5 and 8 (70:30, 20g Sample) after addition of hexafluoroacetone.

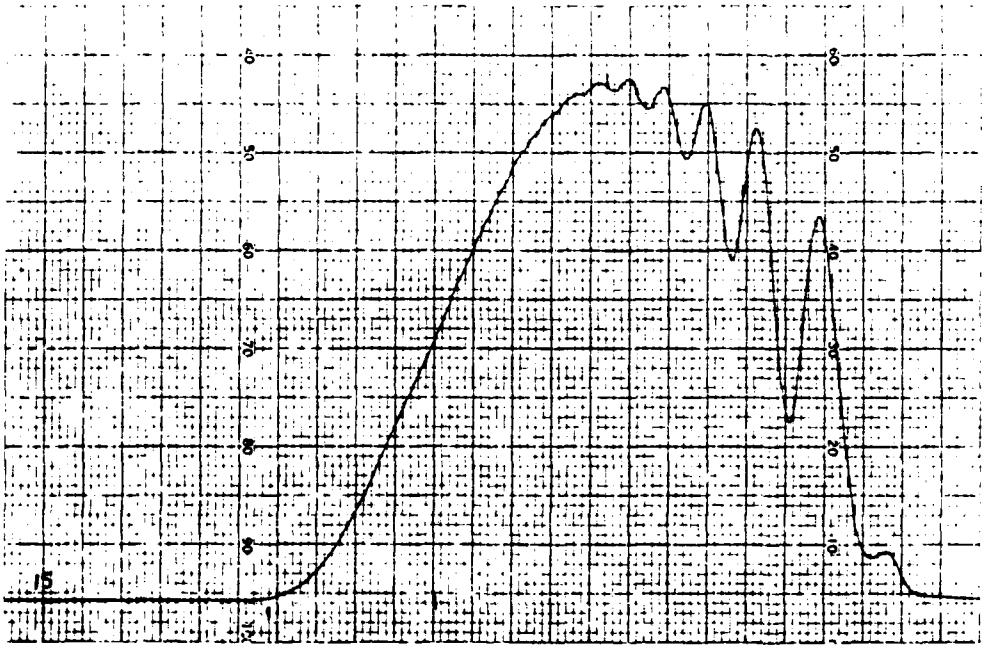


Fig. 20. GP Chromatogram of $HOCH_2(CF_2)_4CH_2OH$ - CO - $HOCH_2CH_2$-$C_2B_{10}H_{10}$-CH_2CH_2OH Polyformal (Mass Detector)

Table 1. Properties of 20g Samples of Random Copolymers of 5 and 8

Feed Ratio	Yield [%]	OH equ. wt*	Monomer Ratio** overall	end units	Intrinsic viscosity [mL/g]
70/30	85	1025 (1028)	65/36	85/15	4.605
50/50	85	1113 (1070)	52/48	73/27	4 543
30/70	85	1192	27.5/72.5	52/48	4.462
15/85	73	1182 (?)	17/83	30/70	4.272

*Determined by ^{19}F-NMR, numbers in parenthesis by the p-toluenesulfonyl isocyanate method; the value for 15/85 is questionable because of solubility problems

**Determined by ^{19}F-NMR

Copolymers of 5 and 9 and 6 and 9 have also been prepared in ratios from 10/90 to 90/10, using the trioxane/BF_3 etherate/sulfolane method. Up to the 20/80 ratio, the polymers were solids while higher contents of 5 or 6 gave resins which may be useful as energetic soft blocks. The polymers prepared so far are listed in Table 2. More complete characterization is in progress. The 5/9 and 6/9 copolymer pairs are the highest energy copolymers with "soft block potential" which we have prepared so far.

Table 2. Copolyformals of 5 and 9 and 6 and 9

Feed Ratio	Yield [%]	Appearance	$\bar{M}_n$ (est'd from GPC)
5/9			
10/90	>70	solid	2157
20/80	>70	solid	
50/50	85-90	viscous resin	
80/20	85-90	resin	
90/10	85-90	resin	2600
6/9			
10/90	>70	solid	2358
50/50	85-90	viscous resin	
80/20	75-80	resin	
90/10	80-85	resin	2254

Previously we reported the formation of a copolyformal from the nitrodiol 11 and the bis(hydroxyethyl)orthocarborane 12. A second formal copolymer of

$$HOCH_2CH_2\text{-}C_2B_{10}H_{10}\text{-}CH_2CH_2OH$$

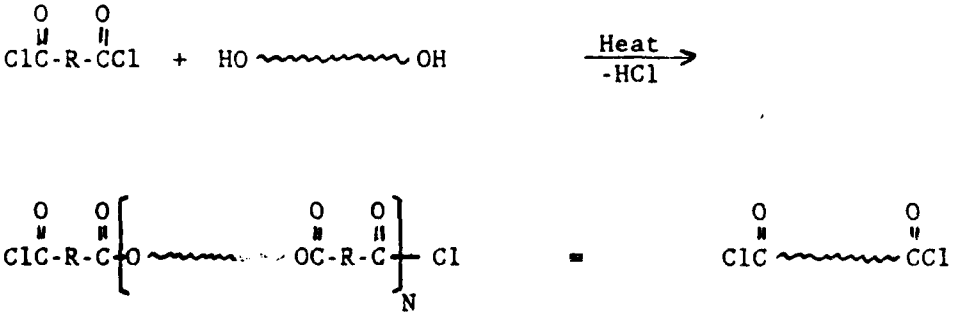
12

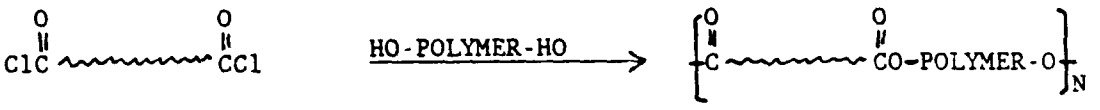
12 was prepared, using 5 as comonomer (monomer ratio 20:80), by reaction of the monomer mixture with BF_3 etherate/trioxane in sulfolane. The polymer is a resin and has a relatively low molecular weight (see the GP chromatogram, Fig. 20), as was the case with the previously prepared copolymer of 12. A mass detector was used for the GP chromatographic characterization of the copolymer because both monomer units are UV inactive, and offset each other in the RI detector. Figure 21 shows the ^{1}H-NMR spectrum of the copolymer which provides evidence for copolymer formation: A "mixed" formal CH_2 signal is present at 4.82 ppm, and the carborane C-CH_2-C signal is shifted upfield as was the case with the previously prepared copolymer from 11 and 12.

Block Copolymer Synthesis.- Our first approach to the synthesis of thermoplastic elastomers is to prepare $(AB)_N$ type block copolymers composed of alternating soft and hard blocks A and B which are immiscible, at least at ambient temperature, and therefore give rise to phase separation in the block copolymer. A number of such blocks are available from the previous work funded by the SDIO/IST office, ONR, and from the NSWC IR program, but further refinement of their properties will be needed as part of this effort. The major problem at hand is to develop methods for linking up such blocks in an alternating fashion, the structural characterization of the resulting block copolymers, and the tailoring of their structure to achieve the desired thermal and mechanical characteristics.

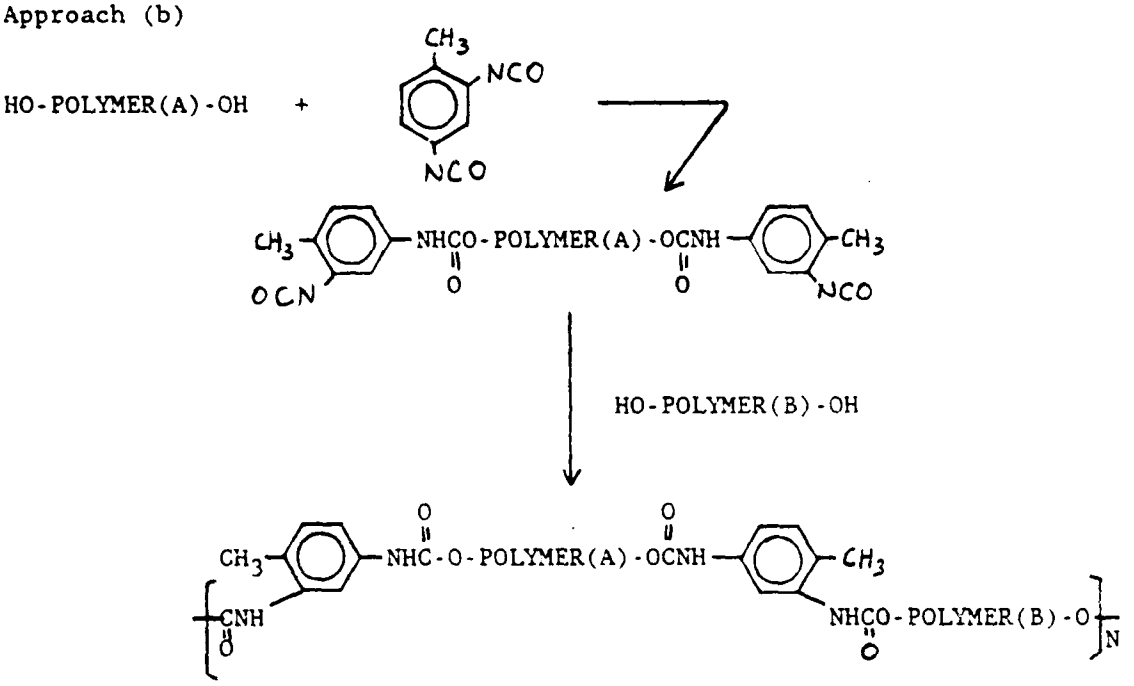
During the past year, several approaches toward $(AB)_N$ block copolymer synthesis have been initiated: (a) the synthesis and reaction of acid chloride-terminated polyesters with a hydroxy-terminated polyester or polyformal; (b) end-capping hydroxy-terminated blocks with a free or semi-blocked diisocyanate, followed by reaction with a second hydroxy-terminated block; (c) reaction of two hydroxy-terminated blocks with formaldehyde/acid (planned); (d) reaction of a nitrile-terminated block with an azide-terminated block.

Approach (a)

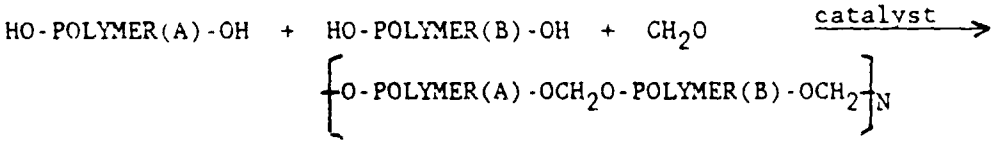




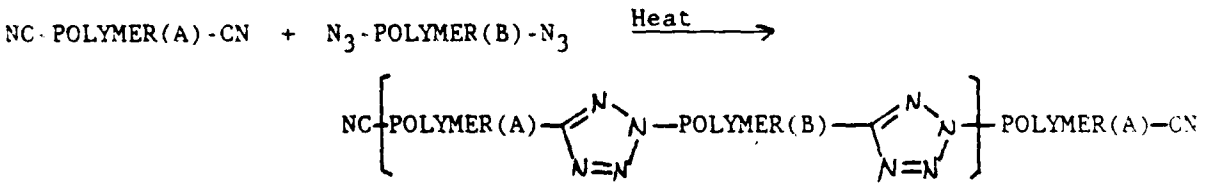
Approach (b)



Approach (c)



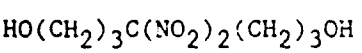
Approach (d)



Approach (a): Investigation of approach (a) was started with 4,4-dinitropimeloyl chloride (13) as the acid chloride Diols used were hexafluoropentanediol (14), 4,4-dinitroheptanediol (15), 3,6-dinitro-3,6-diazaoctanediol (8), and DINOL (10)

13

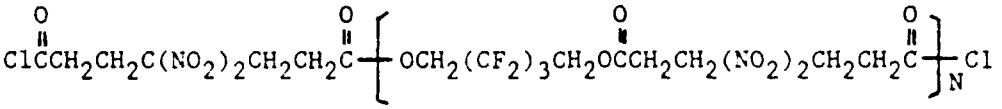
14



15

14 was reacted with 13 (mol ratio 4:5) under heptane at 95-100°C overnight to produce an acid chloride-terminated polymer (GP chromatogram, Fig. 22). As a

13 + 14 ⟶



model reaction for block copolymer formation, the reaction of this polymer with a number of diols was studied. The polymer was reacted with an excess of (a) 15 in dichloroethane (80°/3 days), (b) 8 in dichloroethane (reflux, 2 days). GP chromatographic analysis indicated that no further reaction had occurred. With 8 under refluxing heptane overnight, however, reaction occurred and according to the GP chromatogram (Figs. 23a and 23b) a polymer terminated with 8 was produced. This can be concluded from the relative intensities of the RI, UV and mass detector traces before and after treatment with 8. They show that a strongly UV absorbing species was added, in constant increments, to the polymer chains present, which leads to a disproportionate increase in the UV absorptivity of the lower oligomers.

Analogous experiments were conducted with 13 and 8 as polymer-forming units and 14 and 15 as end-capping agents. In this case, no clear-cut evidence for formation of acid chloride-terminated polymer or end-capping was obtained. Another diol/diacid chloride pair investigated briefly was DINCL (10)/13 which were reacted under heptane at 95-100°C until HCl evolution was complete. End-capping was attempted with 15 in dichloroethane. No evidence was found for end-capping, the molecular weight actually decreased. However, when reactions with 14 and 15 were carried out neat, an increase in molecular weight was observed.

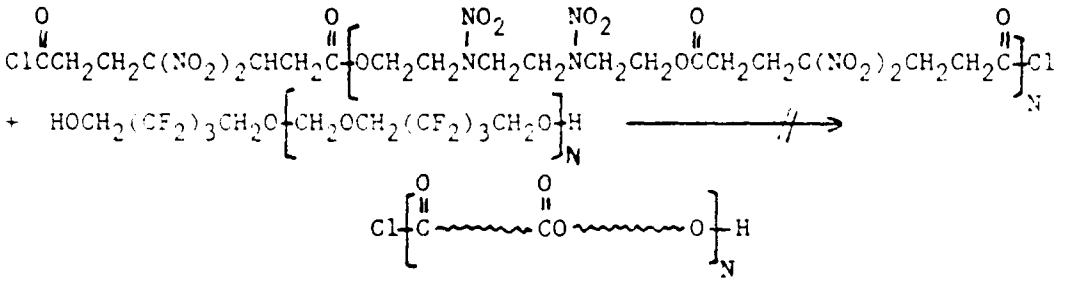
The above screening results indicated some promise, but also a need for a more detailed study. This was carried out in the system 15/13.

When 15 was reacted with 13 (ratio 5:6) in sulfolane, a polymer was formed as expected, but subsequent reaction with 8 failed to occur. The same reactions under heptane or in acetonitrile and nitroethane gave polymer formation as well as end-capping; the GP chromatograms shown in Figures 24 and 25 clearly indicate the disproportionally large increase in UV absorptivity of the lower oligomers due to end-capping.

Next, the acid chloride-terminated polymer 15/13, prepared in MeCN or in dichloroethane/MeCN, was reacted at 85°C and 65°C, respectively, with FPF-1 (polyformal of 14); no reaction occurred and no block-copolymer was

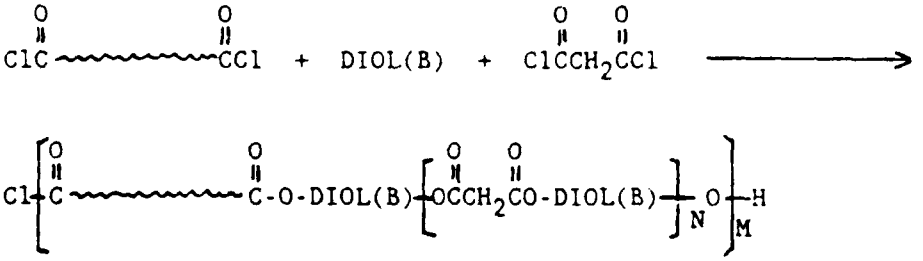
produced. Similarly, when the same acid chloride-terminated polymer was reacted with an OH-terminated one made from 8 and 13, in MeCN at 75-85°C, there was no evidence of reaction such as had been observed with 18 monomer. Thus, it appears that the hydroxy-terminated polymer reacts much slower than the monomer with the acid chloride end groups of the 15/13 polymer. Since the reaction temperature cannot be increased much further due to limited thermal stability of the reactants, the ~~~C(=O)Cl HO~~~ linking reaction is probably not feasible for the system investigated here, unless it can be catalyzed.

This conclusion is supported by the results of another set of experiments in which a mixture of FPF-1, 8, and 13 (ratio 1:4:5) were heated with the intent to form an acid chloride-terminated polymer from 8 and 13 in situ, and react it with FPF-1. Polymer formation occurred readily but the subsequent coupling step was found to be extremely slow, even at 100°C in sulfolane solvent. Only when the reaction was conducted neat at 150°C was there evidence in the GP chromatogram (Fig. 26) of formation of a high molecular



weight material containing nitramine groups (UV detector trace). However, even under these conditions, the reaction was incomplete, and partial decomposition had occurred already.

To obtain a polyester with more reactive acid chloride end groups, malonyl chloride was chosen as the acid component in place of 13. Two acid chloride-terminated polyesters were prepared by reaction of hexafluoropentanediol, 14, and of 4,4-dinitroheptanediol, 15, with malonyl chloride. The polymers were characterized by GPC (Figs. 27 and 28) and were reacted further with a mixture of a second diol and malonyl chloride in a ratio needed for in situ formation of a hydroxy-terminated polyester. This variant of approach (a) has been used extensively to prepare commercial



thermoplastic elastomers, using esters instead of acid chlorides.

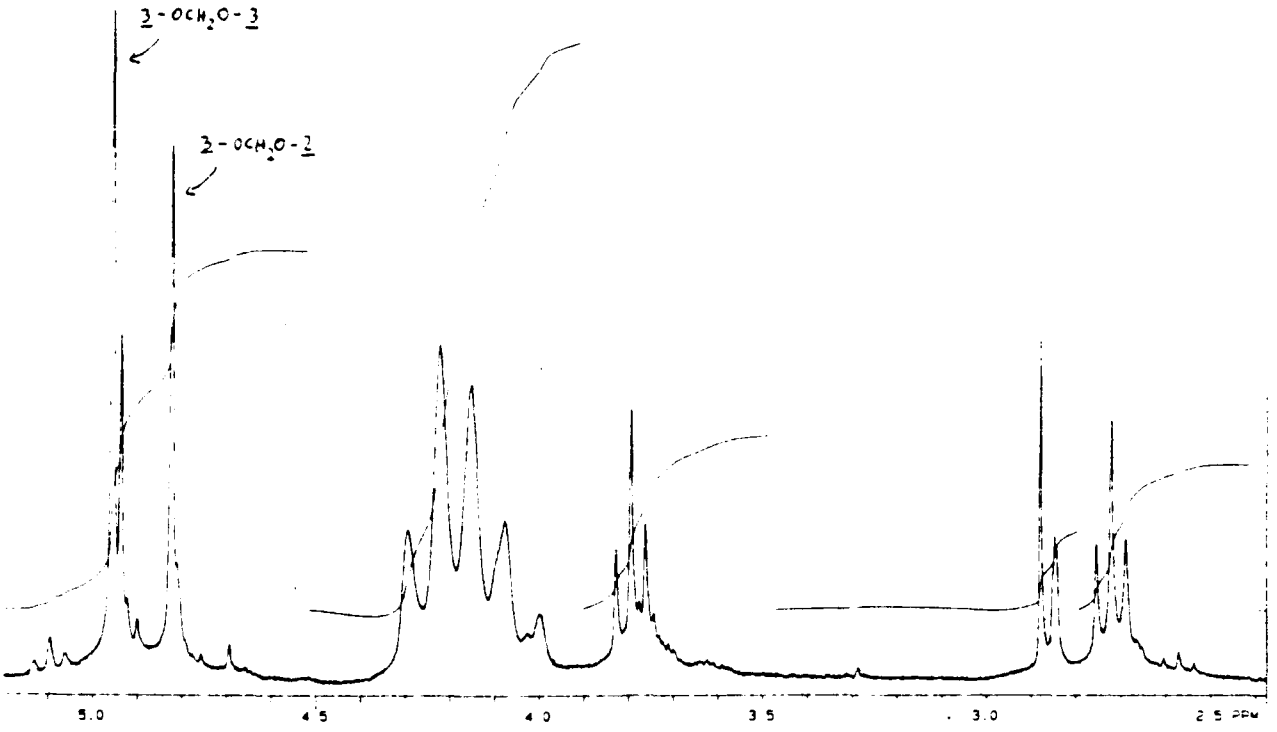


Fig. 21. ^{1}H-NMR Spectrum of $HOCH_2(CF_2)_4CH_2OH$ - CO - $HOCH_2CH_2$-$C_2B_{10}H_{10}$-CH_2CH_2OH Polyformal

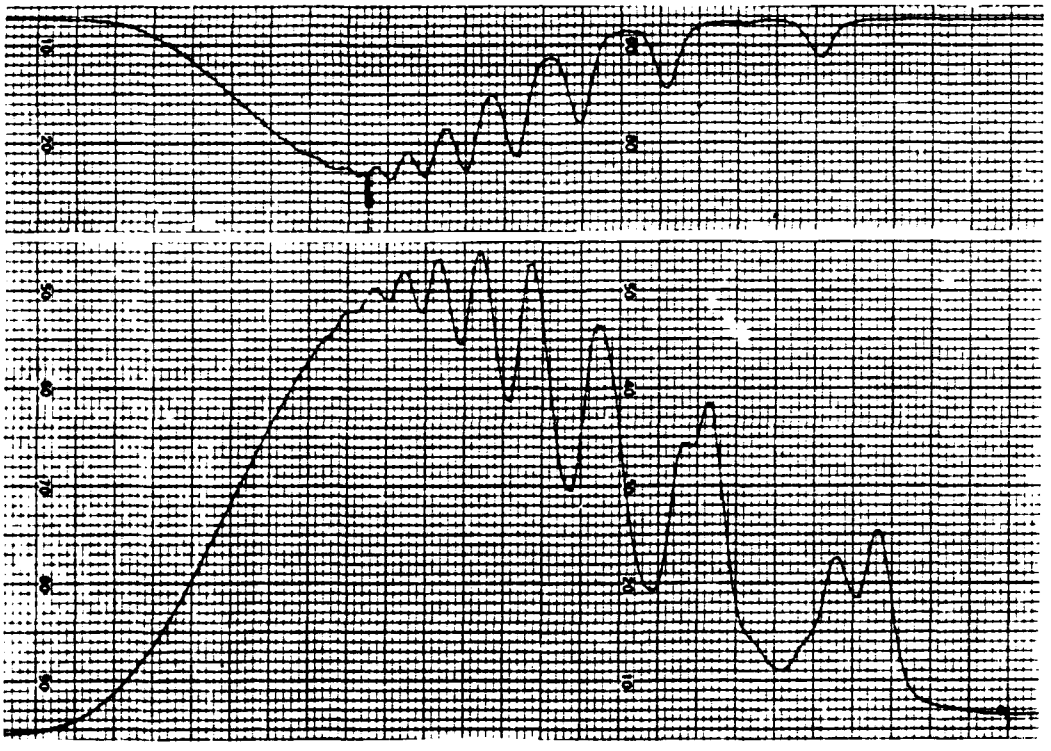


Fig 22. GP Chromatogram of a Polyester from Hexafluoropentane-1,5-diol and 4,4-Dinitropimeloyl Chloride (mol ratio 4:5)

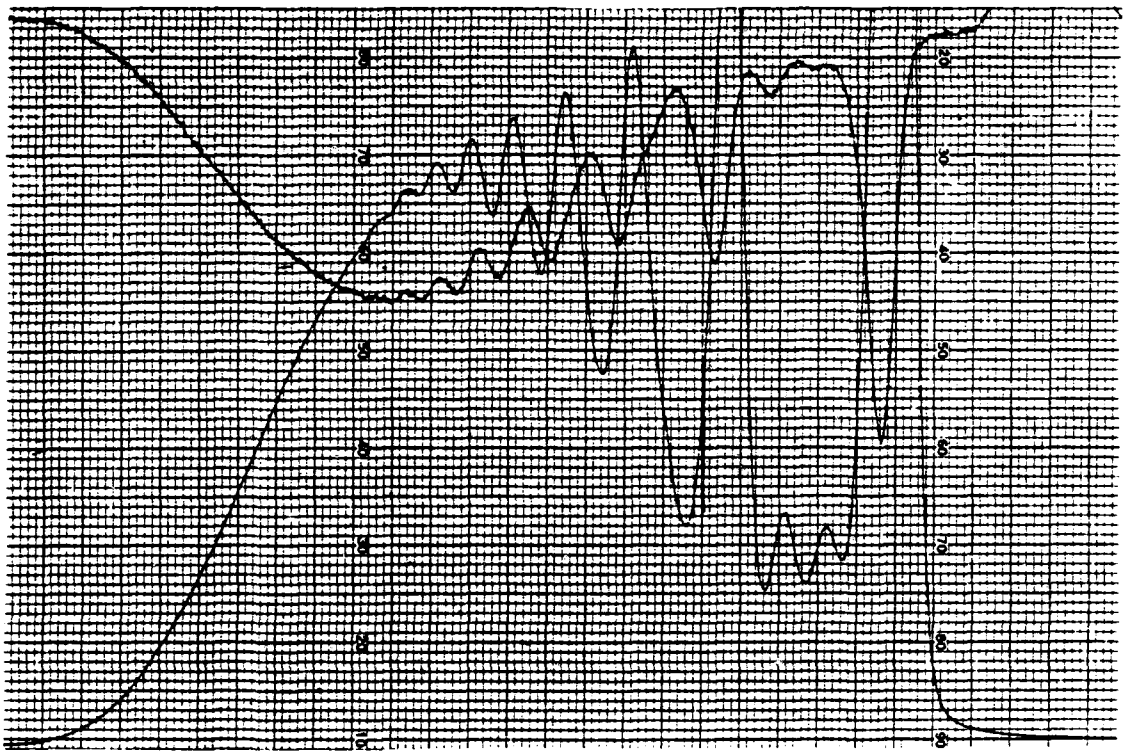


Fig. 23a. GP Chromatogram of a Polyester from Hexafluoropentane-1,5-diol and 5,5-Dinitropineloyl Chloride (mol ratio 4:5) after Reaction with Excess 3,6-Dinitro-3,6-diazaoctane-1,8-diol (RI/UV Detectors)

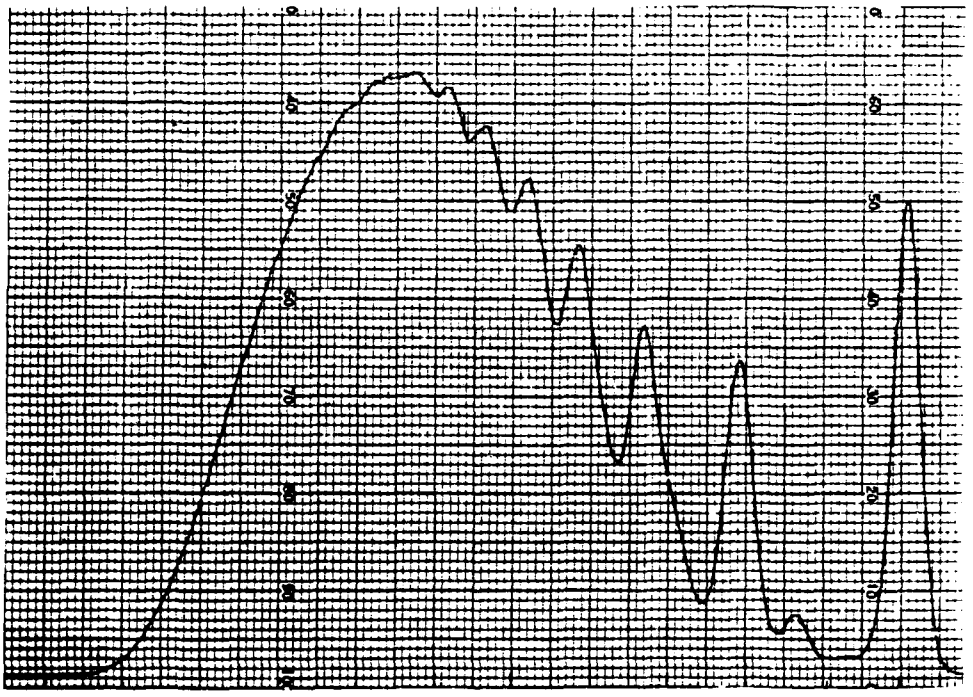


Fig. 23b. GP Chromatogram of the same Polyester as in Fig. 23a, But Mass Detector Trace

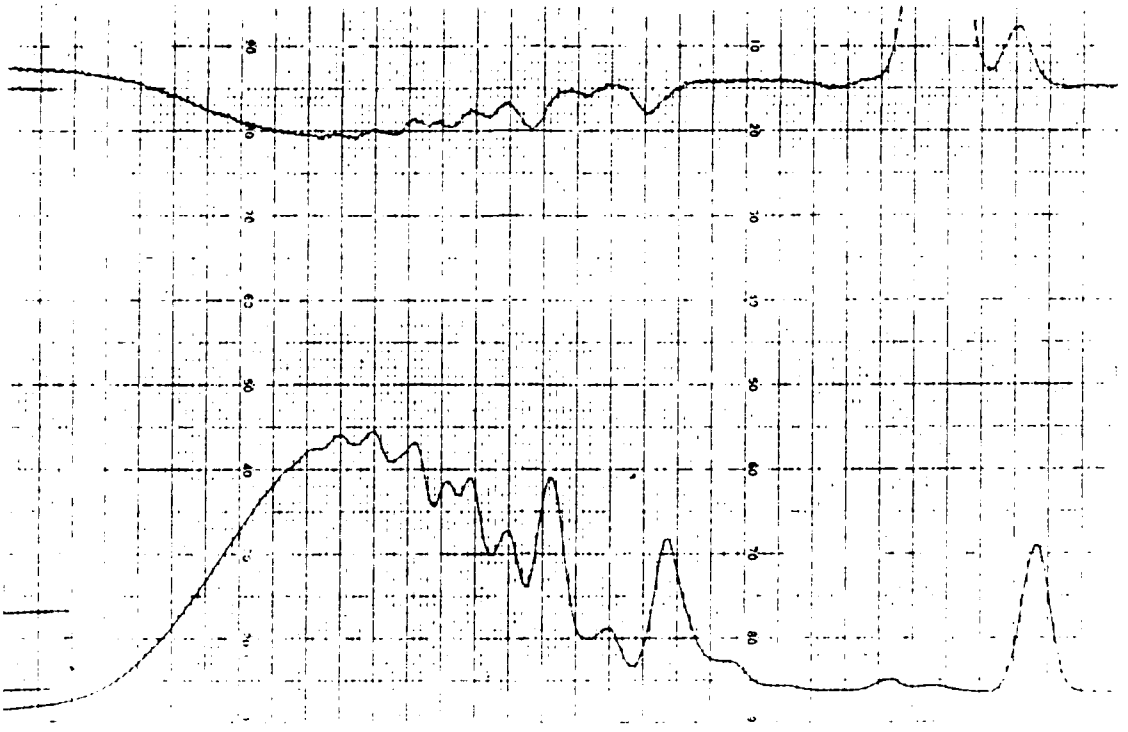


Fig. 24. GP Chromatogram of a Polyester from 4,4-dinitroheptane-1,7-diol and 4,4-Dinitropimeloyl Chloride (mol ratio 5:6)

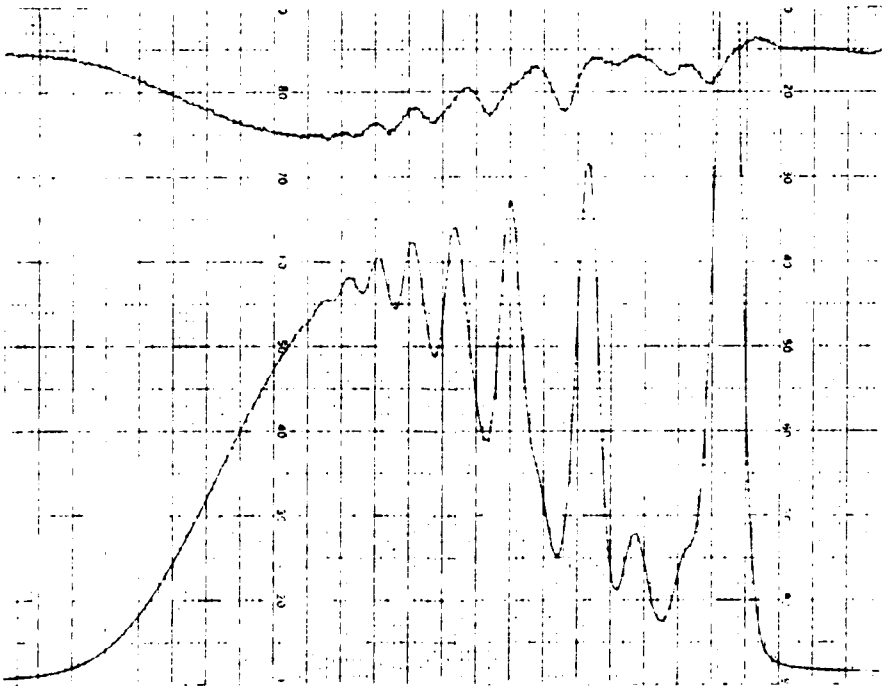


Fig. 25. GP Chromatogram of a Polyester from 4,4-dinitroheptane-1,7-diol and 4,4-Dinitropimeloyl Chloride After Reaction with Excess 3,6-Dinitro-3,6-diazaoctane-1,8-diol

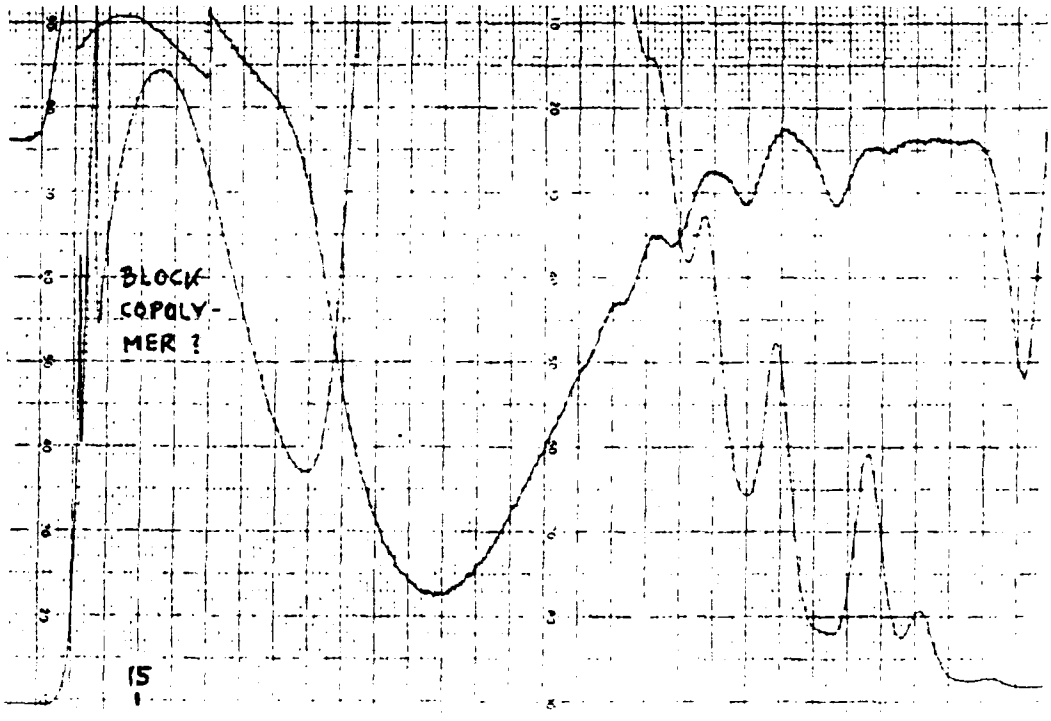


Fig. 26. GP Chromatogram of a Reaction Product of Hexafluoropentanediol Polyformal ($\bar{M}_n$ = 5450) + 3,6-Dinitro-3,6-diazaoctanediol + 4,4-Dinitropimeloyl Chloride (mol ratio 1:4:5)

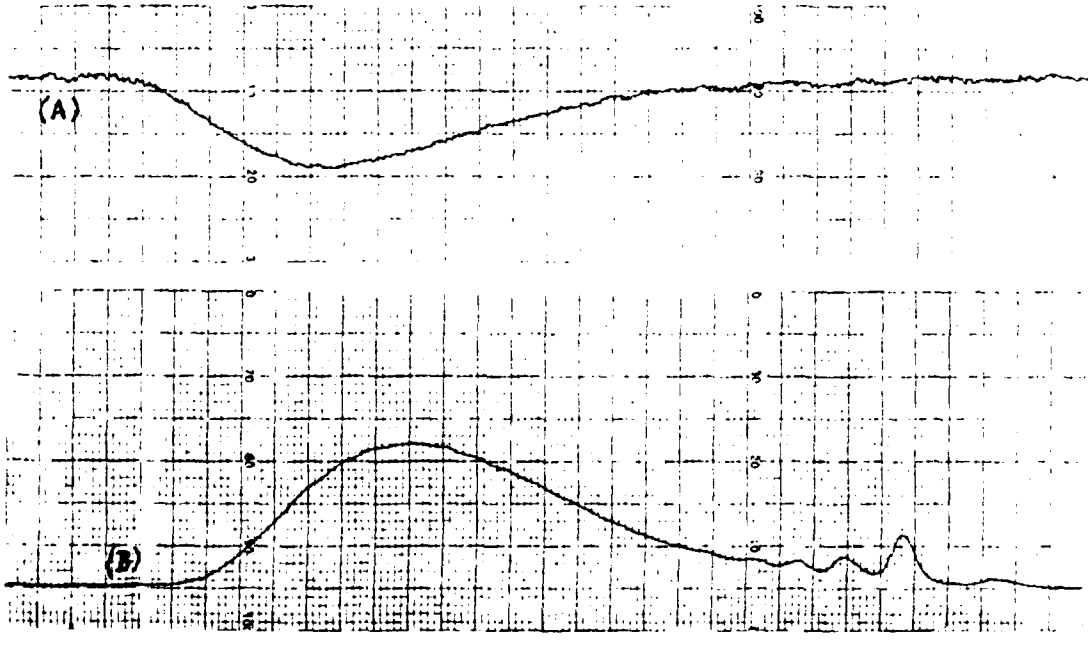


Fig. 27. GP Chromatogram of a Polyester from Malonyl Chloride and Hexafluoropentanediol (ratio 6:5); (A) UV Detector; (B) Mass Detector

In the first example studied, the acid chloride terminated polyester prepared from 15 and malonyl chloride (ratio 5:6) was reacted with a 6:5 ratio of 14 and malonyl chloride (the overall ratio of the two polymers is 1:1) at 60°C in dichloroethane for 5 days. The GPC (Fig. 29) shows qualitatively that a polymer of higher molecular weight than that of the starting polymer was formed. Since the reaction between diol and acid chloride monomers is considerably faster than any reaction involving a polymer chain, this can be taken as evidence of block copolymer formation. However, the isolated polymer was a gum and had no elastomeric properties.

In a second example, an acid chloride-terminated polymer from 15 was reacted with a hexafluoropentanediol polyformal ($\bar{M}_n$ = 5450) in dichloroethane at 60°C. The result is shown in Figure 30 (compare with Fig. 28). Again, the formation of a higher molecular weight polymer is evident in Fig. 30. When $SnCL_4$ was added to the mixture, an insoluble material was formed which could not be analyzed by GPC.

In a similar fashion, an acid chloride-terminated polyester was prepared from 14 and malonyl chloride (ratio 5:6) in DCE at 60°C and was then reacted with 8 and malonyl chloride (ratios 3.4:2.7 and 6:4) in DCE at 60°C. Again substantial increases in molecular weight are shown by GPC analysis (Figs. 31 and 32), especially in the second case where a higher molecular weight would be expected (mol ratio of blocks = 1:1).

We conclude from these experiments that the synthesis of block copolymers from malonyl chloride-terminated polyesters should be possible; however, the reaction needs to be studied in more detail to allow higher molecular weight polymers to be obtained.

In order to increase the energy of the polyesters from malonyl chloride, 10 was used as the diol component Several polymers in the molecular weight range 3000-4000 were made by condensation of 10 with malonyl chloride. A representative GP chromatogram is shown in Fig 33. They were end-capped with methanol, trifluoroethanol, and t-butanol for endgroup analysis by NMR, and attempts were made to couple them with 8 and with 14. With methanol, a decrease of molecular weight was observed which indicates cleavage of the polymer by trans-esterification. With trifluoroethanol, this was not the case.

When the polymer was reacted with FPF-1 in DCE at 55°C, only a slow interaction with attendant gradual increase in molecular weight was observed. More vigorous conditions will be required to achieve block copolymer formation.

With 8, reaction was more facile and a high molecular weight polymer was formed in one case; however, in a subsequent reaction, this could not be duplicated.

Further characterization of the malonyl chloride/10 polymers, including end-group analysis, is underway to aid in understanding their reactivity.

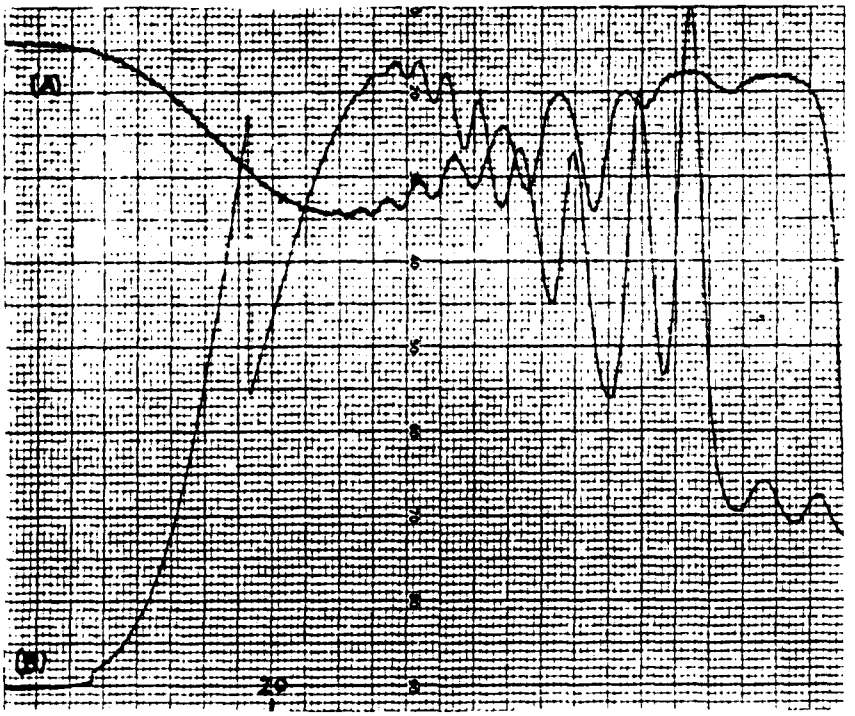


Fig. 28. GP Chromatogram of a Polyester from Malonyl Chloride and 4,4-Dinitroheptanediol (ratio 6:5); (A) RI Detector; (B) UV Detector

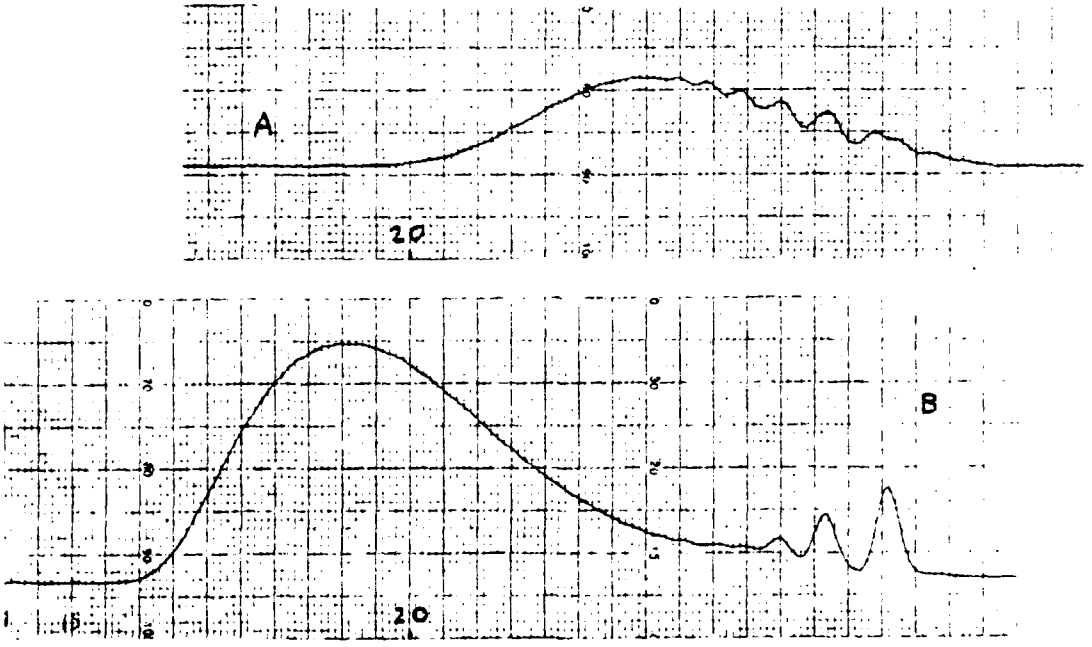


Fig. 29. GP Chromatogram of (A) a Polyester from Dinitroheptanediol and Malonyl Chloride, and (B) after Reaction with Hexafluoropentanediol and Additional Malonyl Chloride; Mass Detector

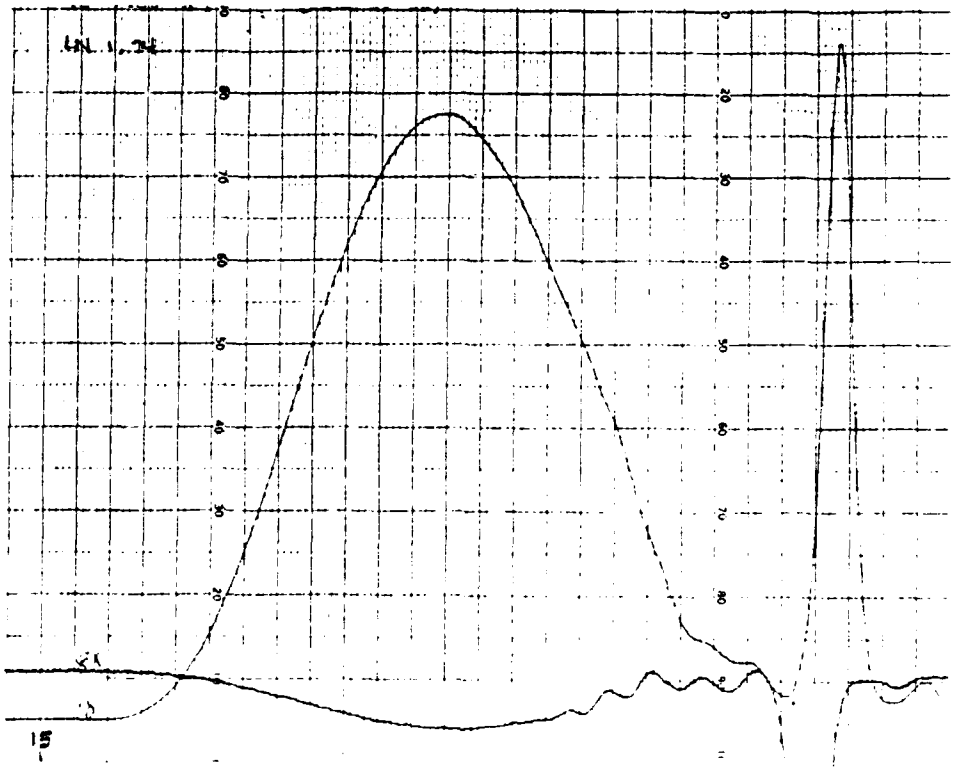


Fig. 30. GP Chromatogram of the Polyester of Fig. 28 after Reaction with Hexafluoropentanediol Polyformal

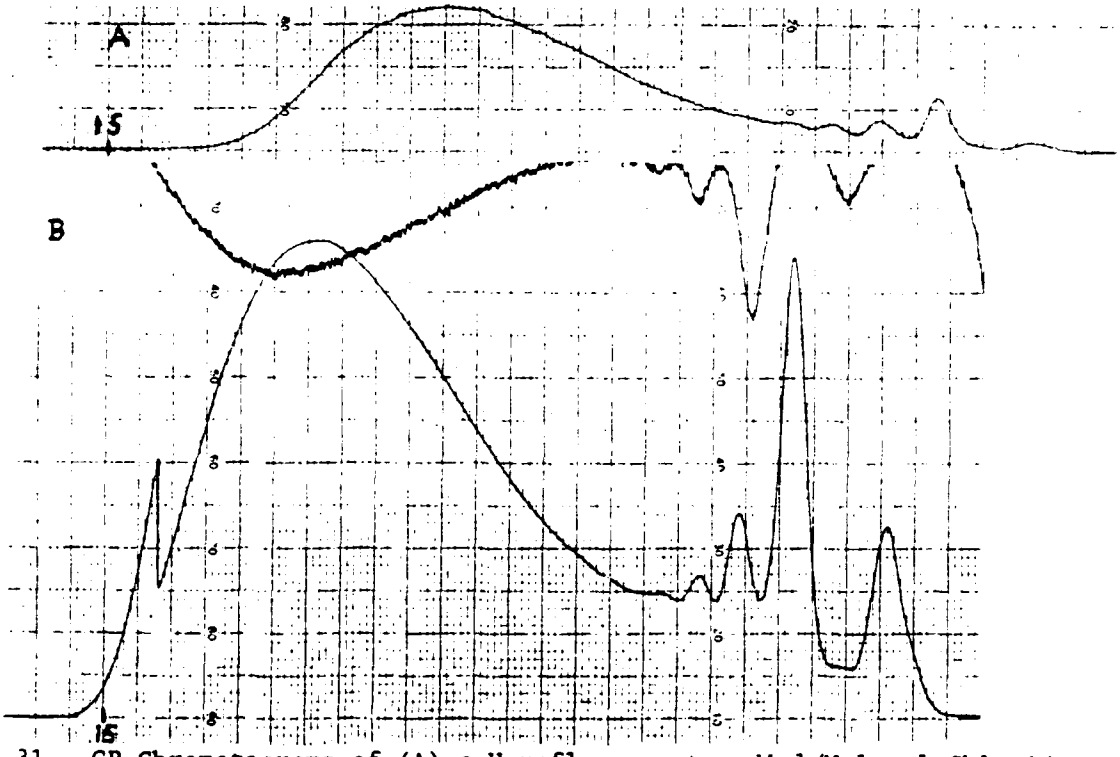


Fig. 31. GP Chromatograms of (A) a Hexafluoropentanediol/Malonyl Chloride Polyester, and (B) after Reaction with 8 and Additional Malonyl Chloride

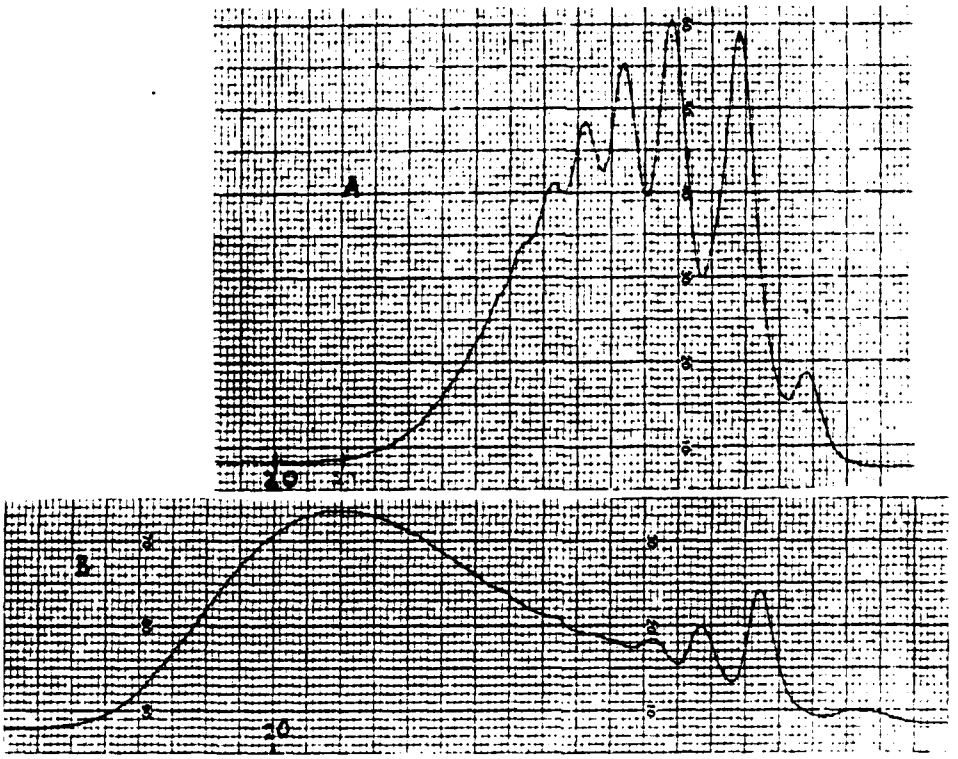


Fig. 32. GP Chromatograms of (A) a Hexafluoropentanediol/Malonyl Chloride Polyester, and (B) after Reaction with 8 and Additional Malonyl Chloride

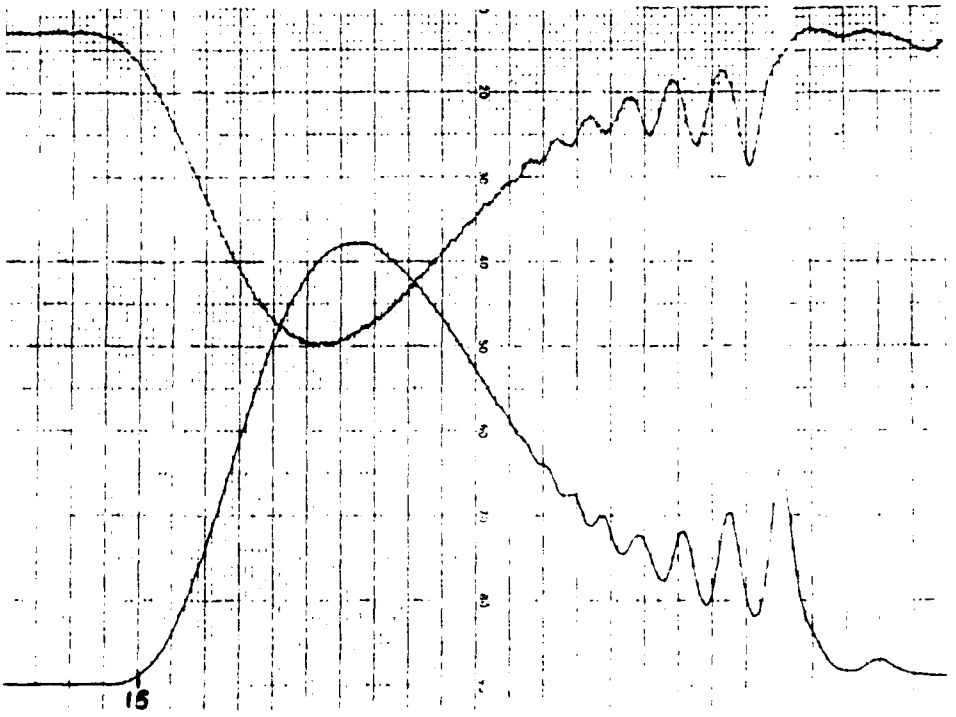


Fig. 33. GP Chromatogram of a Polyester from $HOCH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2OH$ and $ClC(=O)CH_2C(=O)Cl$ (mol ratio 9:10)

Approach (b): This approach to block copolymer synthesis, coupling of isocyanate- and hydroxy-terminated blocks, was also studied extensively during the past year. Initially, attempts were made to end-cap diols such as 11 and 9 with 2,4-toluenediisocyanate (TDI) in the hope that the difference in

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$

11

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$

9

reactivity of the two isocyanate groups in TDI would prevent chain extension. However, this was not the case, and statistical product distribution was observed in the presence and absence of a catalyst. Next, an excess of TDI was reacted with a hexafluoropentanediol polyformal (FPF-1), the excess of unreacted TDI was removed by solvent extraction, and the resulting end-capped polymer was reacted with methanol. GPC and ^{1}H-NMR analysis of the product showed that (a) no detectable increase in molecular weight had occurred and (b) the original polymer had been completely end-capped with TDI, leaving one free isocyanate group at each end. This can be concluded from the following observations: the peak maxima in the GPC (Fig. 34) are shifted only slightly (the end-capped polymer is at a higher retention time; some shift is to be expected because the properties of the polymer change with end-capping). The integrals of the OCH_3 and CH_3 peaks in the ^{1}H-NMR (Fig. 35) are approximately equal; since ony a little tolylene bis(methylurethane) is present in the GPC, this is proof that no or few internal toluene diurethane units are present in the end-capped polymer, and that one free isocyanate group per TDI unit was present before reaction with methanol.

After the structure of isocyanate-terminated fluoropolyformal had been established, it was reacted with a nitrodiol to demonstrate chain extension and "block" copolymer formation. This reaction proceeded smoothly in a number of examples. After quenching of the reaction with methanol, the polymers were isolated by solvent removal and analyzed by GPC. All polymers were elastomeric to varying degrees and eluted near or at the exclusion limit of the GPC columns used which indicates molecular weights $\geq$ 10,000. These are qualitative indications that the desired reaction had occurred, and that TPE properties can be obtained with this approach using very short "hard blocks".

A second diisocyanate, 3-nitro-3-azapentane-1,5-diisocyanate (13-diisocyanate) was also tested in this coupling scheme. It was much less reactive than TDI, and no block copolymer was formed under comparable reaction conditions (room temperature). At higher temperatures, a block copolymer was obtained but it was cross-linked and insoluble in organic solvents.

An attempt was also made to carry out the block copolymer formation from FPF-1, TDI, and nitrodiol in one step, i.e., without first end-capping the FPF-1. This attempt was not successful. A mixture of low molecular weight polymers was obtained.

The polymers prepared to date by chain-extension of isocyanate-end-capped FPF-1 and some preperties are listed in Table 3, the GP chromatograms in Figs.

36-40. It is seen that polymers 8-1 and 15-1 have significantly lower melting ranges than the others. However, all melts are very viscous. We plan to characterize these block copolymers in more detail (DSC, viscosity measurements), and to study the effect of molecular weight variation on properties.

Table 3. $(AB)_N$ Block Copolymers from Isocyanate-end-capped FPF-1, and Some of Their Properties

#	Synthesis	Characteristics	Approximate Melting Range
14B/8-1	FPF-1 (1900) end-capped with TDI then coupled with 9	Tough, only slightly rubbery	90-100°
14B/8-3	same except FPF-1 (5450)	strong elastomer	120-125°
14B/8-4	FPF-1 (5450) TDI end-capped, coupled with 9 polyformal	tough elastomer	>120°
14B/11-2	FPF-1 (5450) TDI end-capped, coupled wtih 11	strong elastomer	>130°
14B/15-1	FPF-1 (5450) TDI end-capped, coupled with 8	strong rubber	95-110°
14B/15-5	FPF-1 (5450) end-capped with nitrazapentane diisocyanate, then coupled with 8	very tough, cross-linked	>130°

We have also considered the use of a partially blocked diisocyanate for the end-capping reaction. This would have the advantage that the end-capped polymer can be isolated and purified without encountering the problem of possible hydrolysis of the free isocyanate groups. In the second step, the blocked isocyanate group would be de-blocked in situ to give the free isocyanate. To test the concept, the partially blocked TDI was prepared as shown and reacted with heptafluorobutanol at room temperature in a model end-capping reaction:

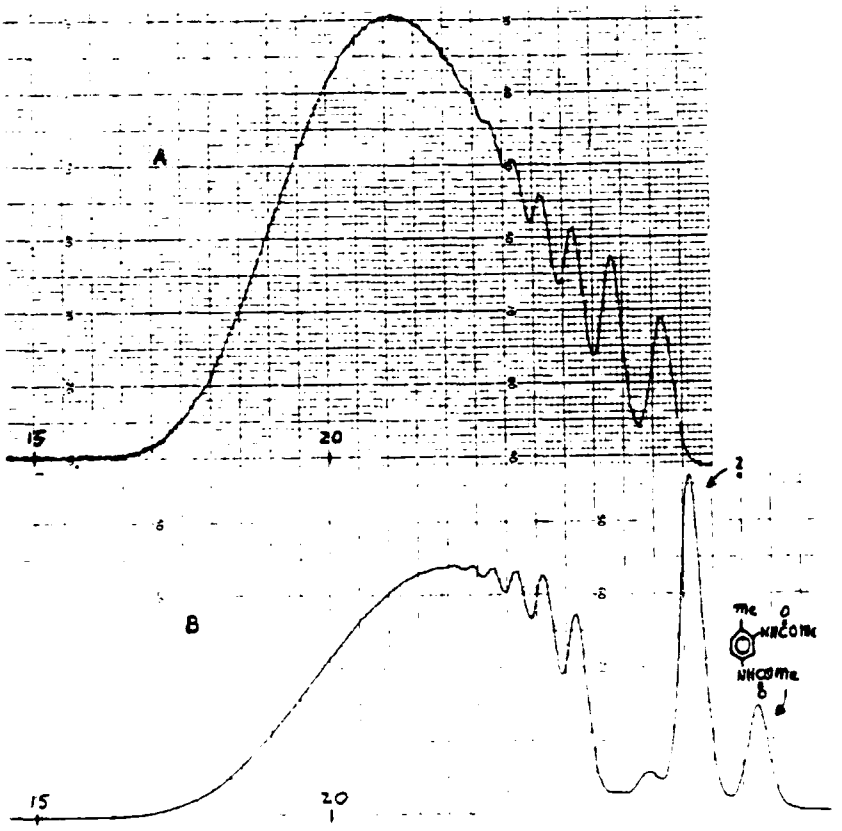


Fig. 34. GP Chromatograms of (A) FPF-1 with $\bar{M}_n$ = 1910 (RI Detector), (B) the same Polymer after End-capping with TDI and Methanol (UV Detector)

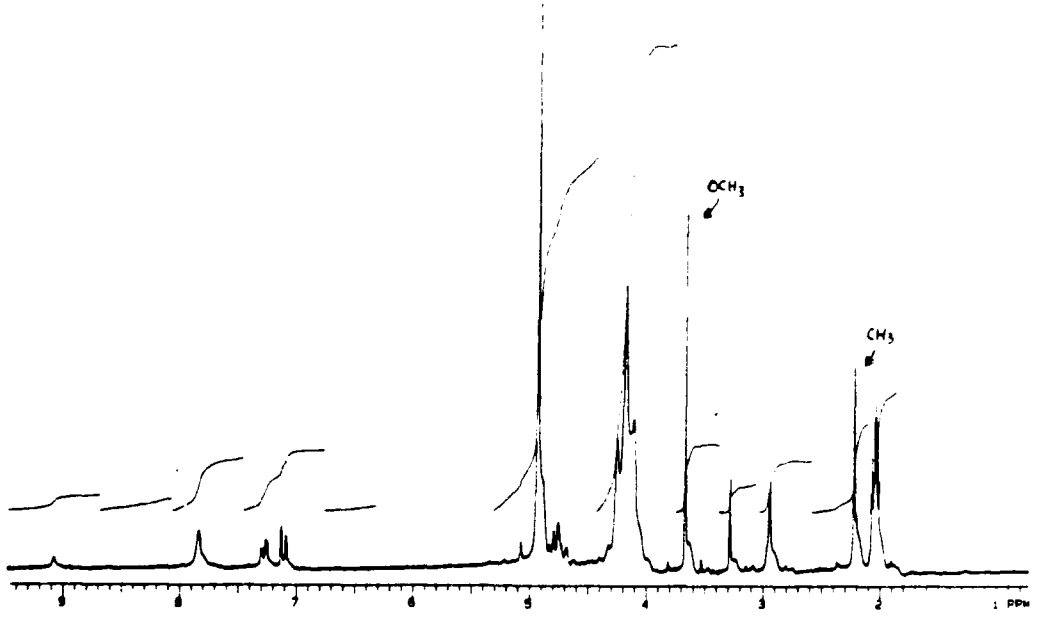


Fig. 35. ^{1}H-NMR Spectrum of FPF-1 After End-capping with TDI and Methanol

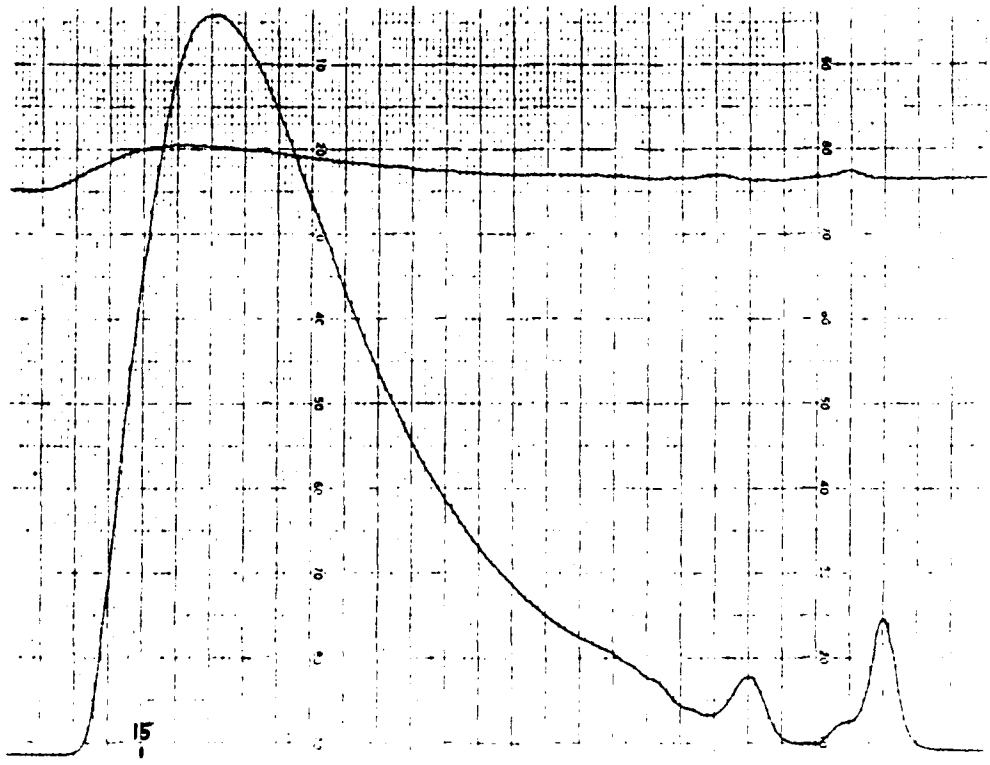


Fig. 36. GP Chromatogram of a Block Copolymer of TDI-End-capped FPF-1 ($\bar{M}_n$ = 1910) and Diol 9 (UV-Detector)

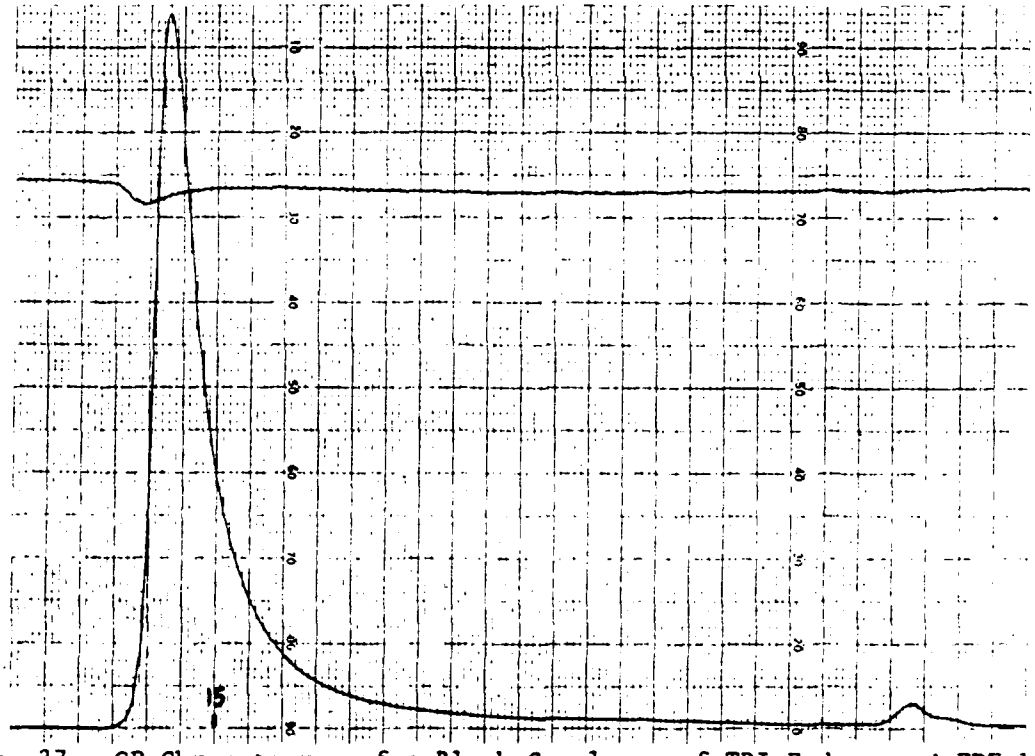


Fig. 37. GP Chromatogram of a Block Copolymer of TDI-End-capped FPF-1 ($\bar{M}_n$ = 5400) and Diol 9 (UV Detector)

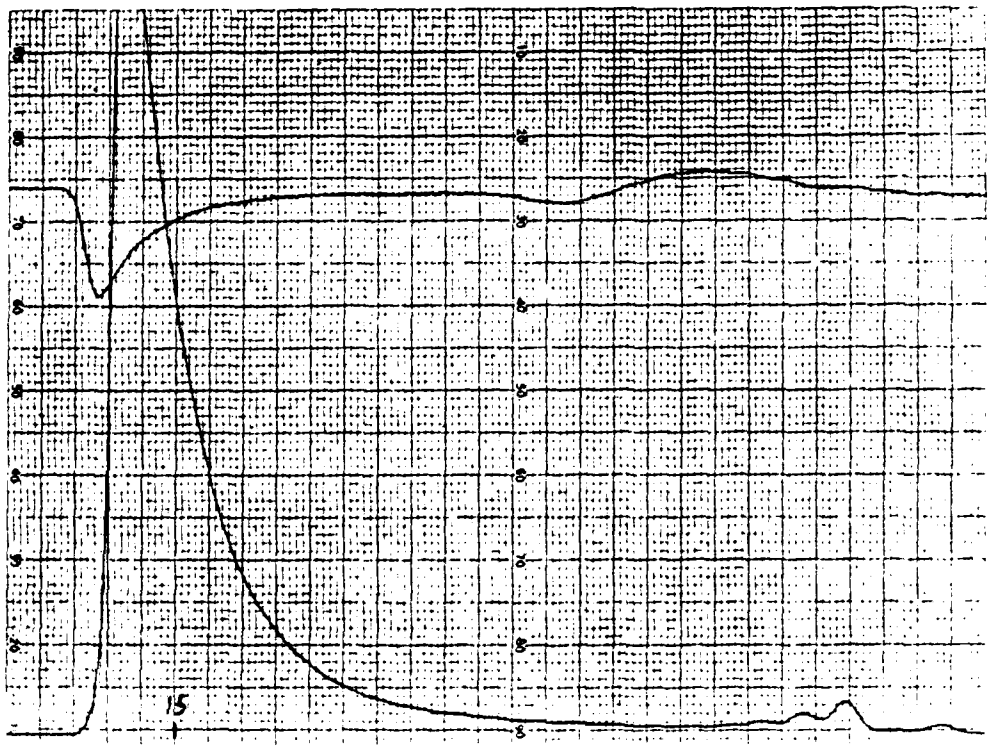


Fig. 38. GP Chromatogram of a Block Copolymer of TDI-End-capped FPF-1 (M_n = 5450) and a Polyformal of Diol 9 ($M_n \simeq 2000$) (UV Detector)

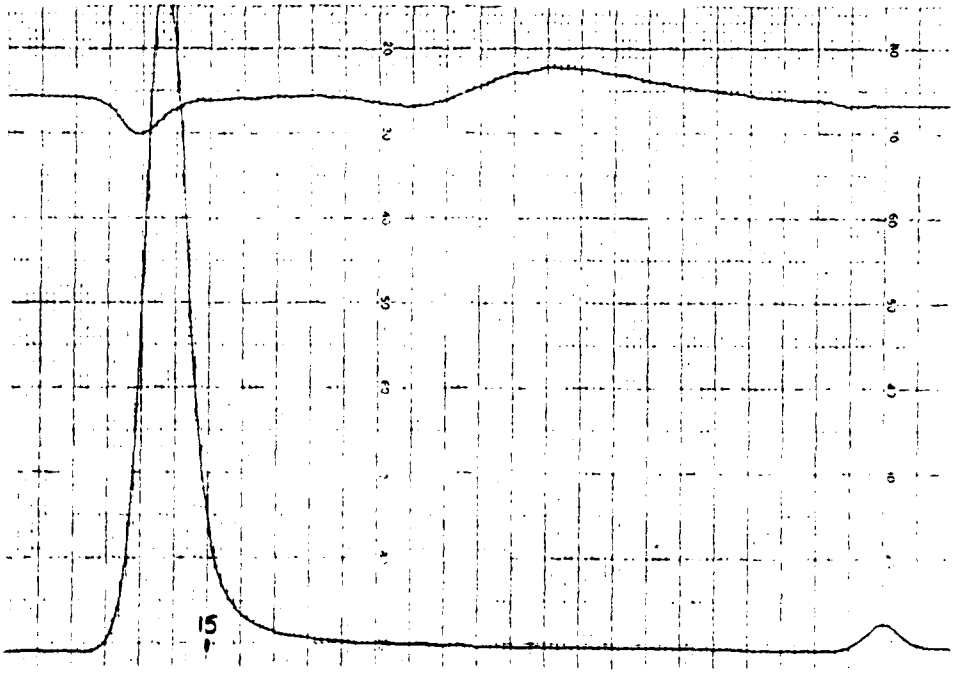


Fig. 40. GP Chromatogram of a Block Copolymer of TDI-End-capped FPF-1 (M_n = 5450) and Diol 11 (UV Detector)

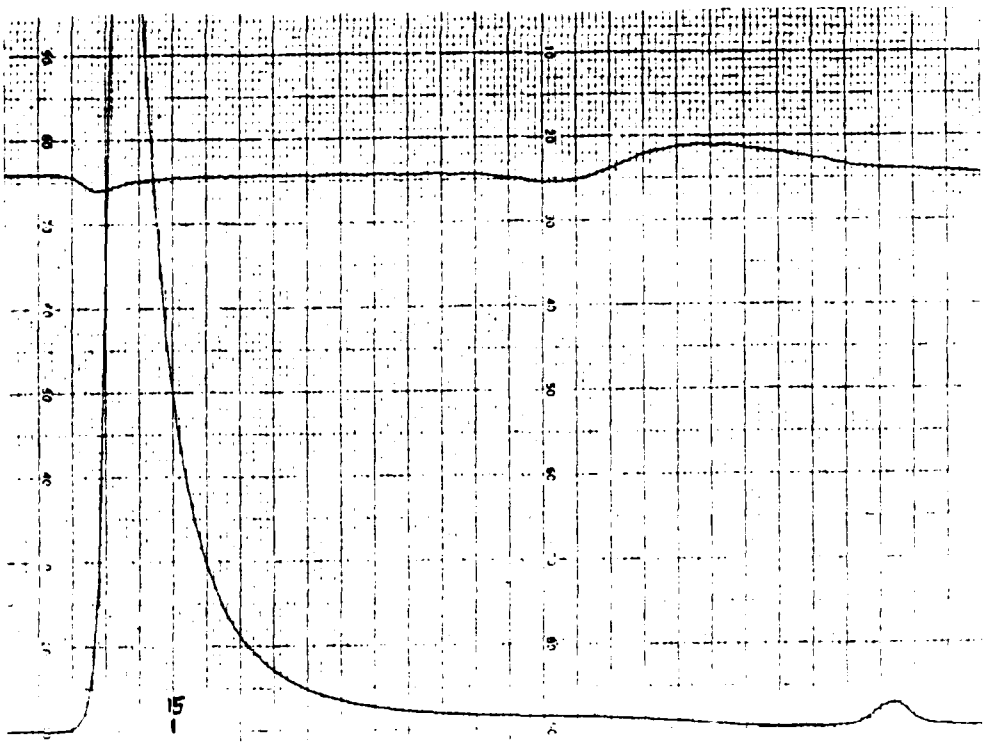


Fig. 41. GP Chromatogram of a Block Copolymer of TDI-End-capped FPF-1 (M_n = 5450) and Diol 8 (UV Detector)

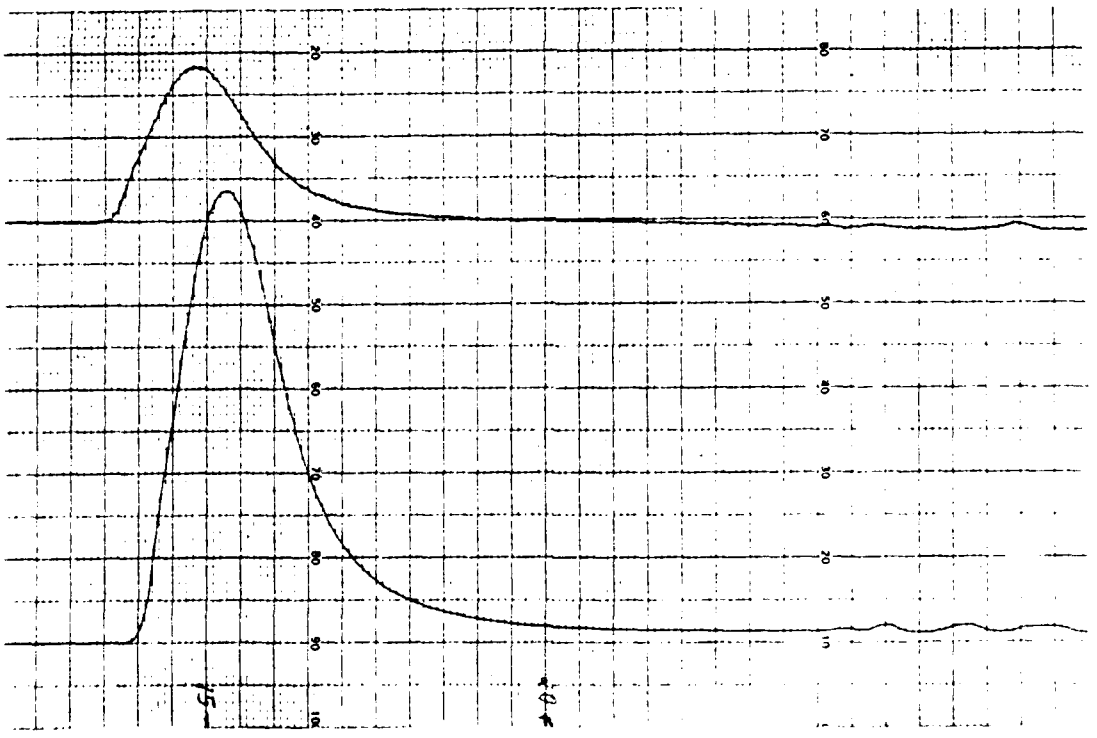
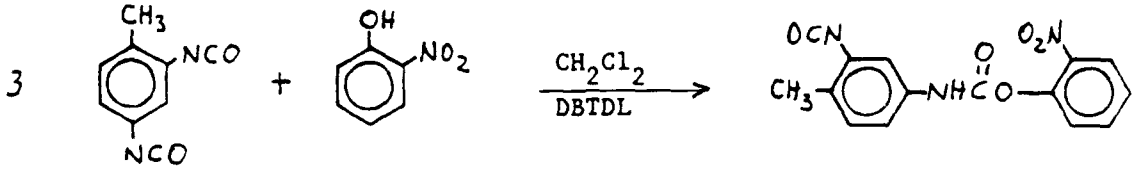
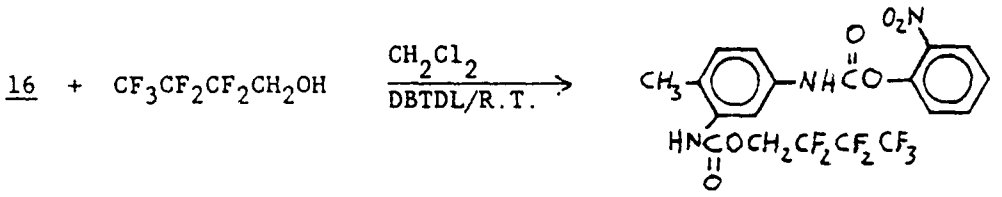


Fig. 42. GP Chromatogram of FPF-1 ($\bar{M}_n$ = 2100) Chain-extended with 3,3-Dinitropentane Diisocyanate

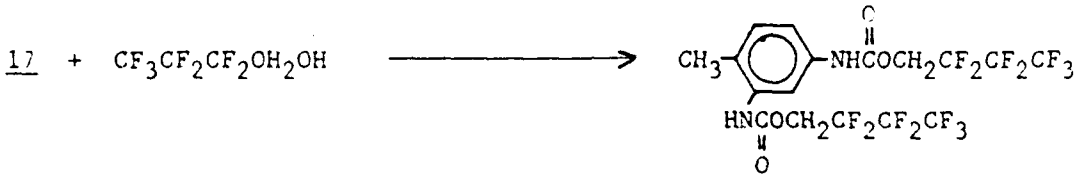


16; 93%



17; 77%

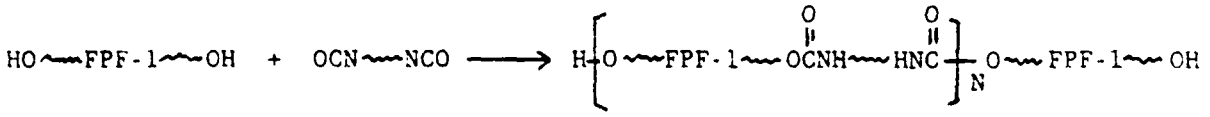
17 was reacted with a second molecule of heptafluorobutanol at elevated temperature as a model for the block copolymer formation. Reaction conditions and results are shown in the table below.



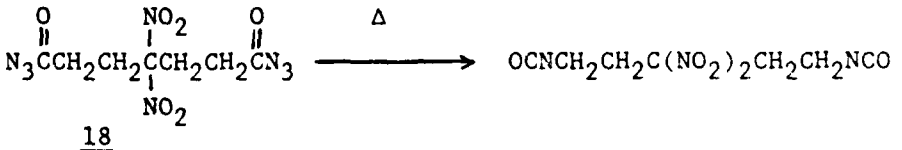
Solvent	Temperature [°C]	Molarity	Catalyst	Reaction Time (min)	Yield (%)
toluene	110	0.2	DBTDL	30	83
acetonitrile	82	0.2	DBTDL	75	80
acetonitrile	55	0.2	DBTDL	480	≈50

These results show that the use of partially blocked isocyanates may be feasible as an alternative approach to block copolymer formation with urethane linking groups. It is probably desirable to replace o-nitrophenol with a more acidic phenol to facilitate de-blocking.

Since very good thermoplastic-elastomeric (TPE) properties were obtained with only monomeric diols serving as "hard blocks", the properties of "block copolymers" with just the diurethane moiety as "hard block" were investigated. FPF-1 was chain-extended with a number of different isocyanates.



As can be seen in Table 4, some of the polymers obtained show TPE properties; all melt lower than those with longer hard blocks. Therfore, this approach has some merit but will require the testing and probably the synthesis of additional isocyanates. The isocyanates can be added as such or in the form of an isocyanate precursor such as the acid diazide which can be thermolyzed to the diisocyanate in situ:



18

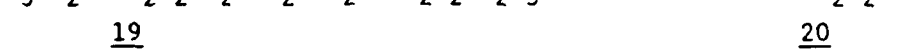
18 is stable at room temperature. Thermolysis (dichloroethane, 60°C) in the presence of trifluoroethanol and dibutyl tin dilaurate gave the expected diurethane in high yield.

GP chromatograms of the urethane "block copolymers" are shown in Figures 42-47.

Table 4. Polymers Prepared by Chain-extension of FPF-1 with Diisocyanates

#	Synthesis	Characteristics	Approximate Melting Range
14B/30-2	FPF-1 (2100) + 3,3-dinitro-pentane diisocyanate (in situ)	rubbery but soft	70-80°
14B/27-4	FPF-1 (2100) + nitraza-pentane diisocyanate	soft, slightly rubbery	75-85°
14B/27-3	FPF-1 (2100) + TDI	resin	-
14B/30-1	FPF-1 (5450) + 3,3-dinitropentane diisocyanate (in situ)	soft, slightly rubbery	<80°
14B/27-1	FPF-1 (5450) + TDI	soft, slightly rubbery	<80°
14B/27-2	FPF-1 (5450) + nitraza-pentane diisocyanate	rubbery but soft	>100°

Approach (d): This approach was investigated briefly with a model reaction using diazide 19 and fluorodinitroacetonitrile, 20. It was found that this reaction is quite slow at 60°C in DCE and is probably not useful as a linking



19

20

reaction where high yields would be required.

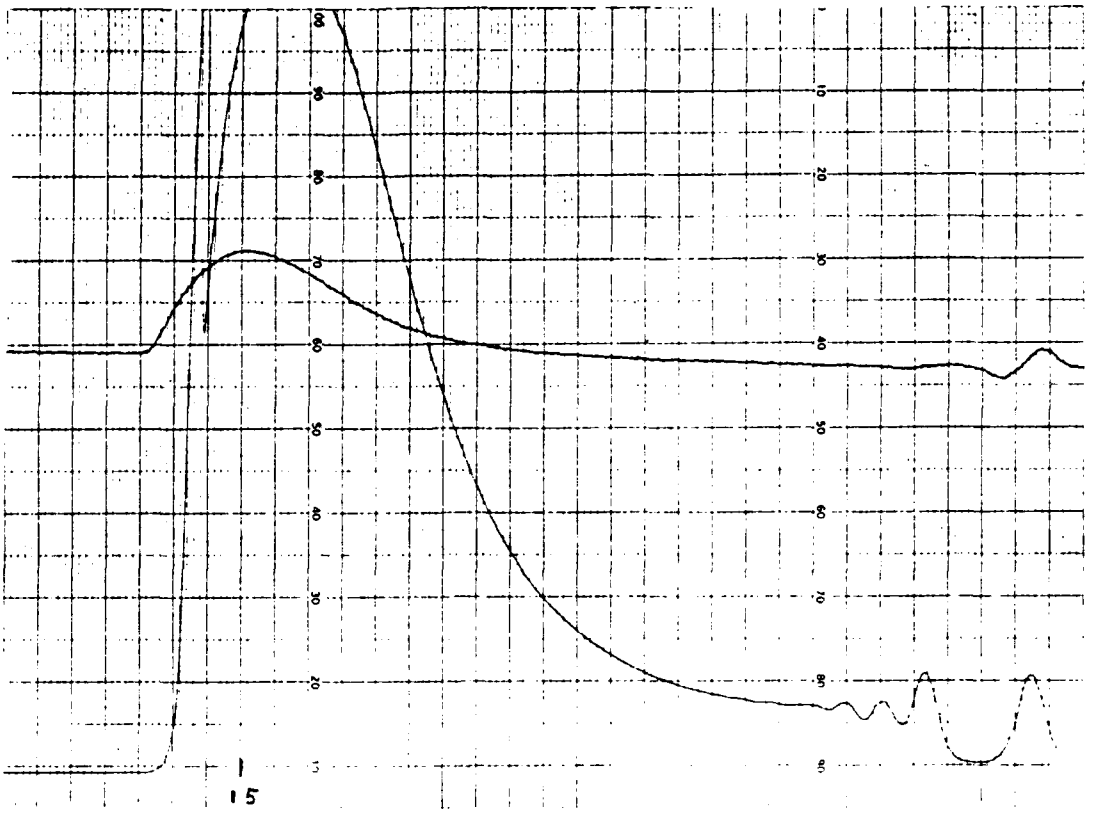


Fig. 43. GP Chromatogram of FPF-1 ($\bar{M}_n$ = 2100) Chain-extended with 3-Nitrazapentane Diisocyanate

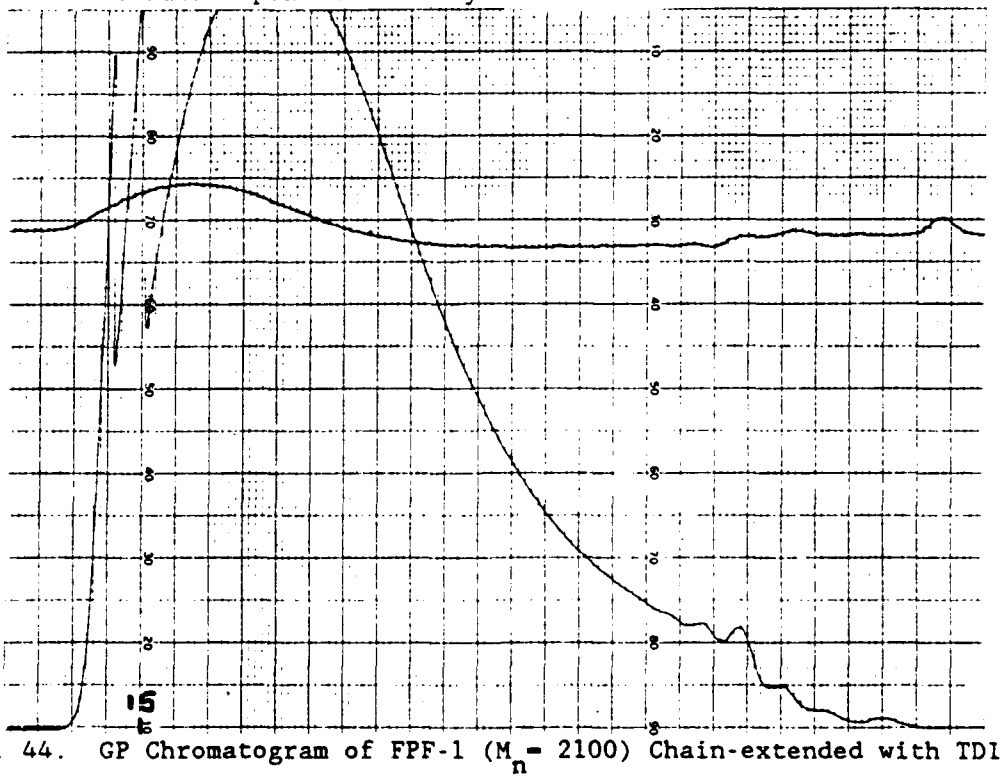


Fig. 44. GP Chromatogram of FPF-1 (M_n = 2100) Chain-extended with TDI

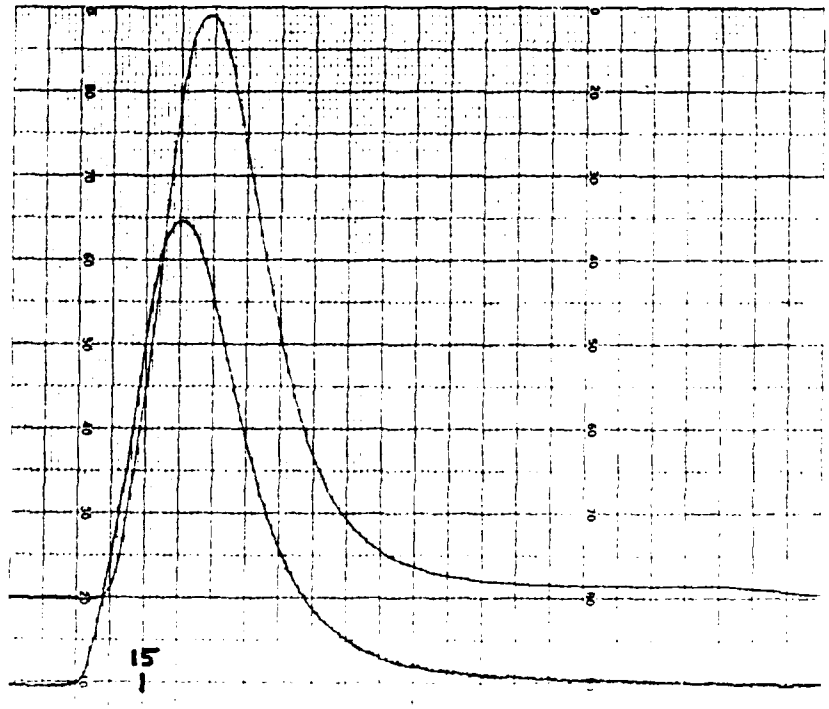


Fig. 45. GP Chromatogram of FPF-1 ($\bar{M}_n$ = 5450) Chain-extended with 3,3-Dinitropentane Diisocyanate

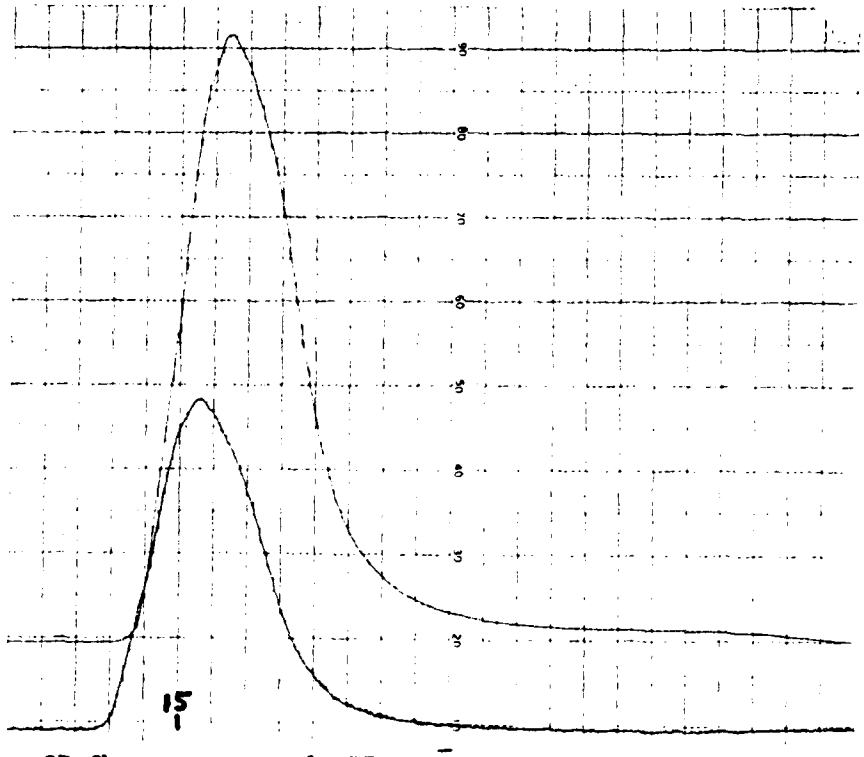


Fig. 46. GP Chromatogram of FPF-1 ($\bar{M}_n$ = 5450) Chain-extended with TDI

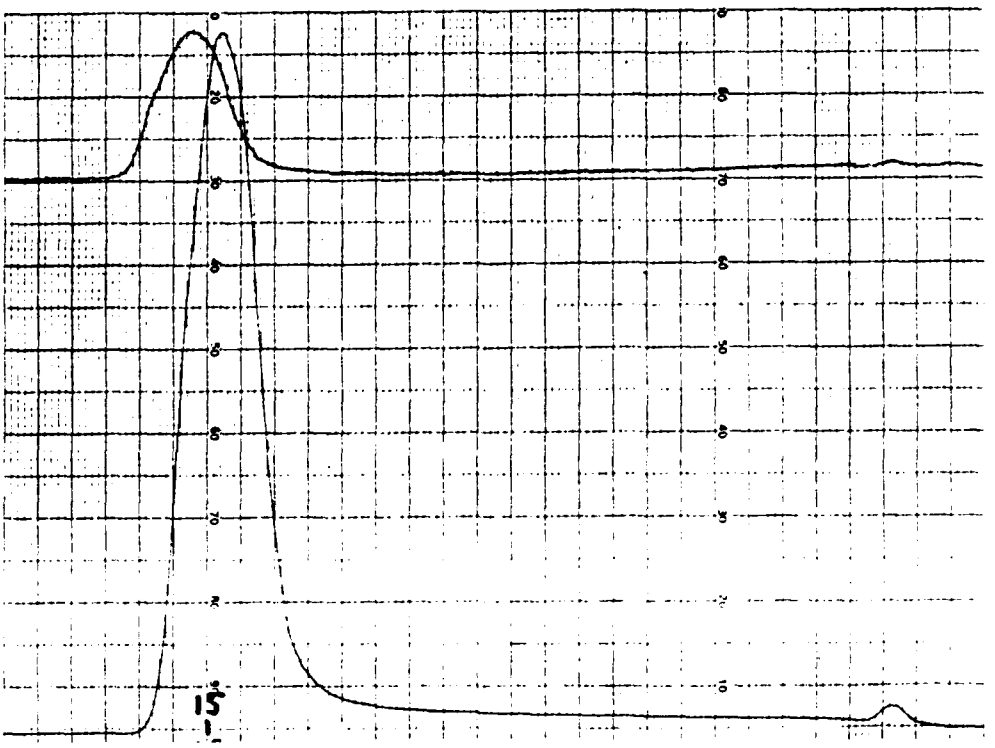


Fig. 47. GP Chromatogram of FPF-1 ($\bar{M}_n$ = 5450) Chain-extended with 3-Nitrazapentane Diisocyanate

Polymer Characterization.- In order to achieve reliable characterization of block and random copolymers and polymer blends by means of the quantitative measurement of their molecular weight distribution parameters (MWDP), a new GPC system has been built, tested, and is operational. The new system consists of a Waters 6000A solvent delivery system, a Waters U6K manual injector, a Molytek Thermalpulse II flowmeter, a Gilson Model 116 variable wavelength uv detector, a Viscotek Model 100 differential viscometer, and an ACS evaporative mass detector.

The utility of GPC rests not only upon the fractionation of the sample material by molecular size but also (i) the determination of concentration of the eluting species and (ii) the conversion of molecular size into corresponding molecular weights. Conventional GPC detectors such as uv or refractive index respond not only to concentration but also to chemical composition. As a result, it is difficult to accurately measure true concentration or weight fraction of the eluting polymer when multicomponent samples are involved. Similarly, conversion of molecular size to molecular weight has traditionally been done through the use of Mark-Houwink constants. These constants must be determined for each polymer individually by using standard samples of known and narrow molecular weight distributions. Generally, the Mark-Houwink constants are either not known or impossible to determine for multicomponent samples.

The new GPC system circumvents many of these complexities. The mass detector responds only to the amount of sample eluting and not to chemical composition. As a result, it can be used to determine the concentration or weight fraction of eluting species directly. The molecular size of a polymer is related to molecular weight through intrinsic viscosity, which is available from the differential viscosity detector. This permits the determination of the molecular weight of the eluting species in conjunction with the universal calibration curve directly, thus obviating the need for Mark-Houwink constants.

The GPC injector and detectors have been connected to an IBM PC/AT personal computer via a Data Translation DT2805 A/D conversion system so that automatic data collection and data reduction to yield the MWDP could be achieved. A menu driven/user friendly software package was written in ASYST programming language to control data collection, data storage and retrieval, and GPC peak presentation and editing. (The calibration and data reduction segments of the package are not yet menu driven.)

An automated system was developed for the rapid off-line determination of intrinsic viscosities. Advantages over the conventional Ubbelhode determination are that only 10-100mg of sample are required vs 1-10g conventionally and that determinations can be made within 5 minutes vs several hours conventionally. Reproducibility of results is well within ±2% and good agreement has been achieved with reported results for polystyrene. This system is also computer operated and menu driven.

A method for the determination of the absolute number average molecular weight of any polymer or copolymer by GPC using only the differential viscometer detector and the universal calibration curve has been developed. The following equation, whose derivation is not shown here, is the basis for this method:

$$\bar{M}_n = \frac{3\Phi\, c_I V_I}{4\pi\, V_s} \sum \frac{Vh_i}{n_{sp_i}}$$

where $\bar{M}_n$ is the number average molecular weight, Φ is Flory's constant (adjusted to reflect hydrodynamic radius), c_I is the volume of the injection concentration, V_I is the injection volume, V_m is the slice volume of the chromatogram, Vh_i is the hydrodynamic volume of each eluting species (obtained from the elution volume and the universal calibration curve), and n_{sp_i} is the specific viscosity of each eluting species (obtained from the differential viscosity detector output).

The method is being tested by computer simulation and experimentally in order to validate it and to determine the extent of its practical application. This method for determining $\bar{M}_n$ is independent of that employed using the new GPC system as described above. As such, it may be used (upon validation) as a complement, to verify results, and improve the precision of the new system.

A variation of our technique for OH endgroup analysis by NMR has been tested. Previously, terminal $HOCH_2$~~~~ groups were determined by ^{1}H-NMR after reaction of the hydroxyl group with either hexafluoroacetone or trifluoroacetic anhydride. In some cases, this is not possible because of the overlap of the terminal CH_2 signal with other peaks in the spectrum. Determining the CF_3 of the bound hexafluoroacetone by ^{19}F-NMR has proved a useful alternative in such cases.

EXPERIMENTAL SECTION

Melting points are uncorrected. Temperatures are in ^{o}C. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained in part on a Varian EM-390 spectrometer, in part on a Varian XL-200 NMR spectrometer. Chemical shifts are im ppm relative to TMS internal standard.

Gel Permeation Chromatography, General Procedure. Analyses of homopolymers and copolymers were performed using a Waters Model 6000A solvent delivery system, Model U6K injector, Model 440 ultraviolet (UV) absorbance detector, and Model R-401 refractive index detector. A Toyo Soda Micropak H-series guard column, 7.5 cm in length and 0.75 cm in diameter and three Toyo Soda Micropak TSK 3000H size exclusion columns, each 30 cm in length, with inside diameters of 0.75 cm, and packing pore sizes of 1500 A were used. The eluant was deaerated Burdick & Jackson tetrahydrofuran with water content less than 0.01% in order to maximize peak resolution. Solvent flow was nominally 1.0 mL/min. Chart speed was 1.0 cm/min. Data were collected by a DIGITAL MINC microcomputer using a Chromatix CMX-10 dual channel interface module. Data reduction was performed with the Chromatix GPC2 software package. The sample (25-50 mg) was dissolved in 5 ml of deaerated tetrahydrofuran, and approximately 100 μL aliquot was filtered through a Millipore 0.5μ FH type filter and injected into the instrument. Calibration curves were constructed, whenever possible, using the peak positions and molecular weights of the

resolved oligomers of each sample.

Analyses of some copolymers were performed using a Waters Model 6000A solvent delivery system, Waters U6K injector, Molytek Thermalpulse II flowmeter, Gilson Model 116 variable wavelength uv detector, Viscotek Model 100 differential viscometer, and ACS Model 750/14 mass detector. The size exclusion columns, eluant, solvent flow rate, and chart speeds were the same as those described above. Data were collected by an IBM PC/AT using a Data Translation DT-2805 A/D board. Data reduction was carried out using a software package developed in-house in ASYST programming language. Sample preparation was as described above with the exception that the injection volume was 20-25 μL. Calibration curves were constructed as described above.

Intrinsic Viscosity Determinations, General Procedure. Intrinsic viscosity measurements were carried out using a Waters Model 6000A solvent delivery system, Waters U6K injector, Molytek Thermalpulse II flowmeter, and Viscotek Model 100 differential viscometer. Data were collected as described in the preceeding paragraph. The solvent was deaerated Burdick and Jackson tetrahydrofuran. Solvent flow rate was approximately 0.8 mL/min and precisely determined. Samples were prepared by dissolving a measured amount of approximately 50-100 mg of sample polymer into exactly 5.0 mL of solution. The injection volume was exactly 15 μL. Data reduction was carried out using a software package developed in-house in ASYST.

Polyformal of 3,5,5,11,11,13-Hexanitro-3,13-diaza-7,9-dioxapentadecane-1,15-diol (11). - In a 25 mL 3-neck flask with mechanical stirrer, under a blanket of nitrogen, 3.04g of 7, 2 mL of sulfolane, and 0.158g of trioxane are stirred until homogeneous. The solution is cooled in an ice-bath and 0.6 mL of BF_3 etherate is added dropwise from a syringe. The cooling is removed and stirring is continued at ≈20°C overnight. Then 10 mL of dichloromethane is added with continued stirring. After the mixture is homogeneous, 10 mL of water and 0.5 mL of 30% hydrogen peroxide are added, and the mixture is stirred vigorously for 1h. Another 10 mL of water is added, and the mixture is stirred, with nitrogen passing through the system, until the dichloromethane has evaporated. The aqueous phase is decanted. A few mL of dichloromethane and 15 mL of water are added and the mixture is stirred at 45-50°C in a stream of nitrogen until the dichloromethane is evaporated; this process is repeated 2-3 more times. The polymer is then cooled with ice, broken up under water, and stirred with water in an ice-bath until it has turned into a powder which can be collected readily in a cold Buchner funnel, washed with ice-water, and dried. The polymer softens on warming to room temperature. In the ^{1}H-NMR spectrum no sulfolane is detected, but a small amount of dichloromethane is still present. Heating at 50°C/0.1 mm removes the dichloromethane and turns the polymer into a hard glass. The yield is 2.7g.

The crude polymer is dissolved in 5-10 mL of tetrahydrofuran and the solution poured into 50 mL methanol with stirring. Decanting the solvents gives the material of Fig. 1 as a gum. Retained solvent can be removed by heating to 50°in an N_2 stream under reduced pressure.

Polyformal of Fluorodiol 3M L-9939.- To a stirred homogeneous solution of 5.00g of L-9939, 1.93 mL of 80% H_2SO_4, and 1.33 mL of 90% H_2SO_4 under a N_2 atmosphere was added a solution of 0.126g of trioxane in 0.87 mL of

dichloromethane. The mixture was stirred overnight at room temperature, then poured into and stirred with a mixture of 30 mL of ice-water, 1.25 mL of 30% H_2O_2, and 30 mL of ether. The ether layer was stirred for 30 min with 30 mL of 5% aqueous KOH, then washed with brine, stirred with silica gel (1.5g, Kieselgel 60) overnight, filtered and evaporated in vacuo. The residual resin was heated at 115-120°/0.1 Torr for several hours. Obtained was 4.6g (>90%) of polyformal with $\bar{M}_n$ = 1640, $\bar{M}_w$ = 2780 (GPC), OH equ. wt. = 1350 (isocyanate method). A second run with 0.152g of trioxane gave $\bar{M}_n$ = 2100, $\bar{M}_w$ = 3375 (GPC).

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol-Co-3-nitro-3-azapentanediol Polyformal (97.5:2.5).- 27.0 mL of BF_3 etherate was added dropwise with stirring to an ice-cooled solution of 29.28g (0.118 mol) of 5, 0.45g (0.0030 mol) of 7, and 3.44g of trioxane in 30 mL of dry sulfolane (4A sieves) under a N_2 blanket. The mixture was then stirred 20h at room temperature, diluted with 150 mL of dichloromethane, and stirred with 200 mL of water for 0.5h. The organic phase was washed with 150 mL of brine, freed of solvent at 60°/20 Torr, and triturated with 3-4 portions of water to remove residual sulfolane (none detected by ^{1}H-NMR, Varian 390). The polymer was dissolved in 150 mL of dichloromethane, stirred with silica gel (2g Kieselgel 60) overnight, and filtered. Removal of solvents at 60°/20 Torr gave 28.95g (93%) of viscous liquid, $\bar{M}_n$ = 1950, $\bar{M}_w$ = 3840 (GPC).

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol-Co-3,6-Dinitrazaoctane-1,8-diol Polyformal, General Procedure, described for 50:50 Composition.- BF_3 etherate, 6.3 mL, was added dropwise under a N_2 blanket to a stirred solution (prepared by 3-4h mixing) of 6.01g (0.0229 mol) of 5, 5.46g (0.0229 mol) of 8, and 1.38g of trioxane in 12 mL of dry (4A sieves) sulfolane. The mixture was stirred overnight at room temperature, diluted wtih 80 mL of dichloromethane, and stirred with 100 mL of water for 0.5h. The organic layer was washed with 60 mL of brine, evaporated at 60°C/20 Torr, and the remaining liquid was digested at 70°C with 65 mL portions of water until no sulfolane could be detected in the ^{1}H-NMR spectrum (Varian 390). The copolymer was dissolved in 100 mL of dichloromethane, stirred overnight with 1.5g Kieselgel 60, filtered, and evaporated to give 10.77g (89%) of a yellow/orange resin. $\bar{M}_n$ = 2080, $\bar{M}_w$ = 3300 (GPC); OH equ. wt. = 1113 (^{19}F-NMR), 1070 (isocyanate method).

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol-Co-2,8-Dinitro-4,6-dioxanonane-1,9-diol Polyformal (60:40).- To a stirred solution of 3.600g (0.0137 mol) of 5, 2.317g (0.0092 mol) of 10, and 0.588g of trioxane in 3ml of dry (4A sieves) sulfolane under a N_2 blanket was added dropwise 5.4 mL of BF_3 etherate. The solution was stirred overnight at room temperature, diluted with 45 mL of dichloromethane and stirred with 50 mL of water fo 0.5h. The organic layer was washed with 45 mL of brine, evaporated at 60°/20 Torr, and the remaining liquid was digested with three 30 mL portions of water and with 30 mL 50/50 MeOH/H_2O, with heating up to 70°C. The resulting copolymer was dissolved in 50 mL dichloromethane, stirred with 0.8g of silica gel overnight, filtered, and evaporated at 60°/20 Torr. Obtained was 5.51g (89%) of a viscous resin.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol-Co-3,5,5,7-Tetranitro-3,7-diazanonane-1,9-diol Polyformal, General Procedure, Described for 50:50 Composition.- BF_3 etherate, 1.4 mL, was added dropwise, under a N_2 blanket, to a solution of 1.007g (0.0038 mol) of 5, 1.300g (0.0038 mol) of 9, and 0.230g of trioxane in 2 mL of dry (4A sieves) sulfolane. The solution was

stirred overnight at room temperature, diluted with 15 mL of dichloromethane, and stirred with 20 mL of water for 0.5h. The organic layer was washed with 15 mL of brine, evaporated at 60°/20 Torr, and the remaining liquid was triturated at 80°C with 25 mL portions of water until no sulfolane could be detected by ^{1}H-NMR (Varian 390). The resulting copolymer was dissolved in 30 mL of dichloromethane, the solution was stirred with 0.5g of Kieselgel 60 overnight, filtered, and freed of solvent in vacuo (20-0.1 Torr) at 90°C for 8h. Obtained was 2.2g (≈90%) of a resin, $\bar{M}_n$ = 2410, $\bar{M}_w$ = 5120 (GPC), OH equ. wt. 2000 (by ^{1}H-NMR), 1258 (by isocyanate method).

Other compositions were prepared similarly with the following modifications: 80:20 and 90:10, 1.8 mL of BF_3 etherate was used. 20:80, 0.079g of 5, 0.898g of 9, 0.080g of trioxane, 0.3 mL of BF_3 etherate; after stirring overnight, 10 mL of dichloromethane was added and the mixture poured into 30 mL of water containing 0.4g $NaHCO_3$ and 0.4 mL of 30% H_2O_2. The reaction flask was rinsed with 10 mL of 1:1 dichloromethane/methyl acetate which was added to the above. The mixture was stirred vigorously for 3h until the organic solvents had evaporated, the residue was triturated with ice-water and small amounts of dichloromethane. The resulting white solid was isolated by filtration.

2,4,4,5,5,6,6-Heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol-Co-3,5,5,7-tetranitro-3,7-diazanonane-1,9-diol Polyformal, General Procedure, Described for 50:50 Composition.- To a stirred solution of 1.258g (0.0038 mol) of 6, 1.308g (0.0038 mol) of 9, and 0.230g of trioxane in 2 mL of dry (4A sieves) sulfolane under a N_2 blanket was added dropwise 1.4 mL of BF_3 etherate and the solution was then stirred overnight at room temperature. The reaction mixture was diluted with 15 mL of dichloromethane and stirred with 20 mL of water for 0.5h. The organic layer was washed with 15 mL of brine. The solvent was evaporated and the remaining liquid was digested at 80°C with 25 mL portions of water until no sulfolane could be detected in the ^{1}H-NMR spectrum (Varian 390). The resulting copolymer was dissolved in 30 mL of dichloromethane and the solution was stirred with 0.5g of Kieselgel 60 overnight, filtered, and freed of solvent at 90°/20 Torr for 8h. Obtained was 2.4g (≈90%) of polymer, $\bar{M}_n$ = 2470, $\bar{M}_w$ = 5310 (GPC); OH equ. wt. = 1600 (^{19}F-NMR), 1335 (isocyanate method).

Other compositions were prepared similarly with the following modifications: 80:20 and 90:10, 1.8 mL of BF_3 etherate were used; 10:90, use 0.898g of 9, 0.096 of 6, 0.082g of trioxane, 0.3 mL of BF_3 etherate, and follow the modification described above for the 20:80 composition of 5 and 9.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol-Co-bis(hydroxyethyl)o-Carborane Polyformal; Monomer Ratio 4:1.- In a 3-neck flask under a N_2 blanket, 1.2254g of fluorodiol 5, 0.2712g of 12, and 1.5 mL of sulfolane were warmed with stirring until homogeneous. After cooling to room temperature, 0.158g of trioxane were dissolved in the mixture. 0.6 mL of BF_3 etherate were added with ice-cooling, and stirring was continued at room temperature for 24h. The mixture is diluted with 10 mL of dichloromethane and immediately quenched with 10 mL of water. The dichloromethane is removed with a stream of nitrogen and the water is decanted. The residue is digested with water several times at 45-50° until no sulfolane is detected in the ^{1}H-NMR spectrum (Varian 390).

Reaction of 4,4-Dinitropimeloyl Chloride with Diols, General Procedure.- The following two examples describe typical procedures which were used to conduct this condensation reaction. Reactions with other diols such as 8 and 10 were run under similar conditions. For the reactions with 10 adaptions of the procedure given in reference 2 were also used.

4,4-Dinitroheptane-1,7-diol/4,4-Dinitropimeloyl Chloride Polyester (5:6).- 0.55g (0.0025 mol) of dry 15 and 0.86g (0.0030 mol) of freshly recrystallized 13 were weighed into a 3-neck round bottom flask under a dry N_2 atmosphere. With continued protection from moisture, 10 mL of dry heptane was added and the mixture was heated at 65-70° under a slow stream of nitrogen for 0.5h, then at 85-95° overnight. Completeness of reaction at this point was established by GPC analysis in a blank experiment. The crude polymer was used for further reaction without purification or transfer to avoid hydrolysis of the acid chloride end groups. In one case, 0.24g (0.001 mol) of 8 was added to the mixture which was then heated at 95° for 2 days and analyzed by GPC.

2,2,3,3,4,4-Hexafluoropentanediol/4,4-Dinitropimeloyl Chloride Polyester (4:5).- 0.718g (0.0025 mol) of 13, and 10 mL of heptane was prepared with exclusion of moisture as above and was heated under a slow stream of N_2 at 40-50° for 0.5h, then at 95-100° overnight. Completeness of reaction under these conditions had been established by GPC in a blank experiment. The crude polymer was used directly for end-capping experiments and chain extension. For example, 0.27g (0.001 mol) of 8 was added and the mixture was refluxed overnight and analyzed by GPC.

Condensation of FPF-1, Dinitropimeloyl Chloride (13) and 3,6-dinitrazaoctanediol (9).- 3.1g of FPF-1 (M_n = 5450), 0.817g of 13, and 0.541g of 8 were heated under a slow stream of N_2 and with stirring, for 72h at 100-110°, then for 24h at 150°. HCl evolution was still incomplete at this time. The GP chromatogram of this material, which was a dark brown gum, is shown in Fig 26.

Reaction of Malonyl Chloride with Diols, and Follow-on Reactions of Acid Chloride-Terminated Polyesters, General.- Because of the high reactivity of malonyl chloride, all operations were performed with thorough exclusion of moisture. The malonyl chloride was distilled before use, and the diols were dried over P_2O_5. All solvents were dried over 4A molecular sieves.

Attempted Coupling of 2,2,3,3,4,4-Hexafluoropentane-1,5-diol/Malonyl Chloride (6:5) and 3,7-Dinitro-3,7-diazaoctane-1,8-diol/Malonyl Chloride (5:6) Polyesters.- To 0.509g (0.0024 mol) of 14 was added 5 mL of dichloroethane. The mixture was heated to 60° to dissolve the diol, after which 0.20 mL (0.0020 mol) of malonyl chloride was added. The mixture was then heated at 65° for about 6h. 0.476g (0.0020 mol) of 8 and 0.23 mL (0.0024 mol) of malonyl chloride were then added and the mixture was heated at 60-70° for 5 days. The solvent was removed in vacuo and the product was analyzed by GPC (it was not completely soluble in tetrahydrofuran).

Attempted Coupling of 2,2,3,3,4,4-Hexafluoropentane-1,5-diol/Malonyl Chloride (5:6) and 4,4-Dinitroheptane-1,7-diol/Malonyl Chloride (6:5) Polyesters.- To 0.424g (0.002 mol) of 14 was added 5 mL of dichloroethane and 0.338g (0.23 mL, 0.0024 mol) of malonyl chloride. The mixture was heated at 70° overnight, then was added a reaction mixture consisting of 0.8g (0.0036

mol) of 15, 5 mL of dichloroethane, and 0.42g (0.29 mL, 0.003 mol) of malonyl chloride that had been heated at 60-65° overnight. The combined reaction mixtures were heated at 55-60° for 3 days. Dichloromethane was added, the mixture was washed with water and the water was extracted with dichloromethane. After drying the combined solutions, the solvent was removed in vacuo at 55°, finally at 0.1 Torr.

Reaction of a 2,2,8,8-Tetranitro-4,6-dioxanonane-1,9-diol/Malonyl Chloride (9:10) Polyester with 3,6-Dinitro-3,6-diazaoctanediol.- To 1.55g (0.0045 mol) of 10 in 5 mL of dichloroethane heated at 55° was added 0.49 mL (0.005 mol) of malonyl chloride. After about 4h, 0.119g (0.0005 mol) of 8 was added. The mixture was heated at 55° for 2 days. Then 0.007 mL of trifluoroethanol was added and heated at 55° for the weekend to react residual acid chloride groups. The solvent was then removed in vacuo (55°, 20-0.1 Torr).

End-capping of FPF-1 with Diisocyanates.- 2.10g of FPF-1 (M_n = 1900), 4 mL of dry (4A sieves) dichloroethane, 0.93 mL of toluene-2,4-diisocyanate and 1 μL of dibutyl tin dilaurate were stirred at room temperature under a dry nitrogen atmosphere for 24h. 5 mL of dry hexane were added, the mixture was stirred for several hrs and the solvent was decanted. The residue was triturated 3 times with 5 mL of dry hexane at 40-50°, and was dissolved in 5 mL of dry (4A sieves) acetonitrile. 0.5 mL of methanol and 1 μL of DBTDL were added, the mixture was stirred 24h at room temperature, and the polymer was isolated by removal of the solvents in vacuo.

When 3-nitro-3-azapentane diisocyanate was used, the reaction mixture was initially heated at 65° for 36h. Quenching with methanol was at 65° for 24h.

Chain-extension of Diisocyanate-end-capped FPF-1 with Diols, General Procedure.- FPF-1 was end-capped as described above but not quenched with methanol. Instead, the appropriate amount of diol, generally 1 equivalent, was added together with 1 μL of DBTDL, and the mixture was stirred 3-4 days at room temperature. Then 0.5 mL of methanol was added and stirring was continued 24h. The mixture was diluted with dichloromethane, filtered, and the solvent was removed in vacuo.

When 3-nitrazapentanediisocyanate was used the reaction and the methanol quench were done at 60°.

2-Nitrophenyl-3-Isocyano-4-methylphenyl Carbamate (16).- A solution of toluene-2,4-diisocyanate (10.82g, 0.0622 mol), 2-nitrophenol (2.78g, 0.020 mol), and dibutyltin dilaurate (2 drops) in dichloromethane (50 mL) was stirred at room temperature for 1.5h, followed by the addition of 5 drops more of DBTDL catalyst. After about 3h, a solid began to precipitate. After 4h the solvent was removed under vacuum and the solid residue was triturated with dry toluene (30 mL) and filtered to yield the product (3.70g, 59%) as a white solid: M.P. 118-120°; ^{1}H-NMR ($(CD_3)_2CO$): δ 9.60 (br s, 1, NH), 7.10-8.30 (m, 7, phenyl CHs), 2.30 (s, 3, CH_3).

The toluene filtrate was evaporated under vacuum and the residue was triturated with isopropyl ether and filtered to give a white solid (2.10g): M.P. 116-135°. The ^{1}H-NMR spectrum of this product indicated that it was a mixture of the above carbamate and approximately 20-30% of the biscarbamate

from reaction at both isocyanate groups: in addition to the methyl singlet at δ 2.30, another methyl singlet appeared at δ 2.22, which could be attributed to the biscarbamate.

Reaction of Isocyanate 16 with Heptafluorobutanol to give 17.- A solution of 16 (4.61g, 0.0147 mol), 1H,1H-heptafluorobutanol-1 (3.31g, 0.0180 mol) and dibutyltin dilaurate (0.2 mL) in dry dichloromethane (150 mL) was stirred at room temperature for 3 days. The solvent was then evaporated under reduced pressure and the solid residue was triturated with isopropyl ether (40 mL) and filtered to yield the crude product 17 (6.51g, 86.2%) as a white solid: M.P. 138-142°. Two recrystallizations from 1,2-dichloroethane gave 17 as a microcrystalline solid (M.P. 174-176°C) containing only traces of impurities as determined by thin layer chromatography (silica gel, 5% CH_3CN-benzene); ^{1}H-NMR ($(CD_3)_2CO$): δ 9.40 (br s, 1, NH), 8.39 (br s, 1, HN), 7.10-8.12 (m, 7, phenyl CHs), 4.95 (t, 2, CH_2), 2.32 (s, 3, CH_3).

Reaction of 17 with Additional Heptafluorobutanol.- A solution of 17 (1.03g, 0.002 mol), 1H,1H-heptafluorobutanol-1 (0.405g, 0.0022 mol) and dibutyltin dilaurate (2 drops) in toluene (10 mL) was heated under reflux for 1h. Thin layer chromatography (silica gel, 5% CH_3CN-benzene) indicated that the reaction was complete after 30 min. The toluene was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (25 mL) and washed with 5% aqueous sodium carbonate until the wash liquid was colorless. The organic phase was finally washed with water, saturated aqueous salt solution, dried ($MgSO_4$) and evaporated to a colorless oil. The oil was dissolved in isopropyl ether (25 mL), filtered to remove some insoluble matter and evaporated to give the product (0.95g, 82.7%) as a white solid. Recrystallization from isopropyl ether-hexane gave colorless crystals: M.P. 117-118°; ^{1}H-NMR ($(CD_3)_2CO$): δ 9.23 (br s, 1, HN), 8.54 (br s, 1, NH), 7.90 (d, 1, phenyl CH) 7.21-7.58 (m, 2, phenyl CH s), 4.90 (t, 4, 2 CH_2), 2.30 (s, 3, CH_3).

When this reaction was conducted under the same conditions in refluxing CH_3CN, it required 75 min for completion, to give approximately the same yield of product.

4,4-Dinitropimeloyl azide.- A mixture of 1.148g (4.0 mol) of freshly recrystallized 4,4-dinitropimeloyl chloride, 1.01g (8.8 mol) of trimethyl silyl azide, and 6 mL of acetonitrile was stirred at room temperature for 3h. After addition of 40 mL of ethyl acetate, the solution was washed with 5% aqueous $NaHCO_3$ and with brine, dried over $MgSO_4$ and filtered. The solvents were removed at room temperature under vacuum to give 1.22g of a pale yellow oil. After trituration with a mixture of 5 mL of isopropyl ether and 5 mL of ether and cooling in ice, 0.95g (79%) of the crystalline diazide was filtered off; M.P. 66-8° (dec). ^{1}H-NMR (d_6-acetone): δ 2.70 (unsymm. t), 3.07 (unsymm. t).

Chain-extension of FPF-1 with Diisocyanates; General Procedure.- A mixture of 3.85g of FPF-1 (M_n = 2100), 0.32g (0.26 mL) of 2,4-TDI, 1 μL of DBTDL, and 8 mL of dichloroethane was stirred 4 days at room temperature, 1 mL of methanol was added and stirring was continued for 1-2 days, the mixture was diluted with dichloromethane, filtered, and freed of solvent in vacuo. With 3-nitrazapentanediisocyanate the reaction and quench temperature was 60°, with 3,3-dinitropentane diisocyanate it was 60-65°.

2,2,8,8-Tetranitro-4,6-dioxanonane-1,9-diol (DINOL) Ditriflate.- To a stirred mixture of 30.5g of DINOL and 200 mL of dichloromethane was added, with ice-cooling, 50g of triflic anhydride, followed by a solution of 14g of pyridine in 25 mL of dichloromethane. The mixture was stirred at room temperature for 65h, ice-water was added and the mixture stirred 2h. The separated organic phas was evaporated to dryness, taken up in dichloromethane/hexane (60:40) and chromatographed on silica gel (Kieselgel 60) to remove the by-product, 5,5-dinitro-1,3-dioxane. Final purification was by crystallization from 1:1 dichloromethane/hexane. The product was identified by its ^{1}H-NMR spectrum ($CDCl_3$): δ 4.58 (s, 4), 4.92 (s, 2), 5.40 (s, 4).

1,9-Diazido-2,2,8,8-tetranitro-4,6-dioxanonane (19).- A mixture of 2.10g of the above ditriflate, 5 mL of dry acetonitrile, and 0.4g of lithium azide was allowed to react at room temperature for 2 days, then refluxed overnight. A mixture of 2 products was formed from which the desired diazide was isolated by chromatography on silica gel (Kieselgel 60) with 1:1 dichloromethane/hexane. ^{1}H-NMR ($CDCl_3$): δ 4.50-4.54 (several overlapping singlets, 8), 4.87 (s, 2).

Reaction of Diazidononane 19 with Fluorodinitroacetonitrile.- A mixture of 0.23g of 19, 0.19g of fluorodinitroacetonitrile (20), and 3 mL of dichloroethane was heated at 60° for 3 days. NMR and TLC analysis showed the formation of 2 new compounds (mono- and di-adducts?) and the presence of much 19. Further heating at reflux for 2 days produced no change in the ^{1}H-NMR spectrum. Apparently, the unreacted fluorodinitroacetonitrile had decomposed.

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