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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)

Several polyformals of novel fluorodiols and fluoronitrodiols provided by Fluorochem, Inc. were prepared. The previously prepared polyformal of tetranitrodioxatridecanediol was obtained with a molecular weight up to 10,000. This soft block has a T_G of $-11^\circ C$. The synthesis of poly(azidoacetals) as potential soft blocks was initiated. The first example successfully synthesized was the polyazidoacetal of 1,6-hexanediol.

New monofunctional, isocyanate-terminated hard blocks with estimated melting points of $50-100^\circ C$ were synthesized, including the 1:1 adduct of docosanol and toluene diisocyanate (TDI).

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heneicosyl isocyanate, and the 1:1 adduct of eicosafluoroundecanol and TDI.   Several energetic (nitro) diisocyanates for use in $(AB)_N$ polymer synthesis were prepared.   Carbonyl chloride terminated nitro- and nitraminediols were prepared by reaction of the diols with triphosgene/pyridine for use as block linking agents.

A large number of segmented polymers containing alternative fluoro- and nitrosubstituted polyformal soft blocks and urethane hard blocks have been synthesized by the block linking approach combining -OH and -NCO terminated blocks.   The properties of these $(AB)_N$ polymers depend strongly on the structure of A and B. Several of these materials were characterized by rheometric measurements (at the University of Massachusetts, Amherst) which show them to be highly viscous liquids at room temperature with quasielastic properties which gradually disappear on hearing.   The polymers exhibit no sharp melting transitions by DSC analysis.   In contrast, a series of ABA polymers synthesized by the same approach ...nd containing a short hydrocarbon (C_{22}) hard (A) block and a nitropolyformal soft (B) block show well-defined melting/ crystallization transitions in the DSC.   Elastomeric properties in the temperature range of $0-45^{\circ}$C were exhibited by these polymers when the $\overline{M}_N$ of the soft block was about 10,000 or higher.   The melt viscosities of the polymers increased with increasing molecular weight of the soft block, especially when TDI was used for chain extension of the soft block before the block linking step.   End-capping of poly(AMMO) $(M \simeq 6200)$ with docosanol/TDI and eicosafluoroundecanol/TDI hard blocks was demonstrated, but the resulting ABA polymers showed no elastomeric properties.

The previously developed method for molecular weight determination, based on gel permeation chromatography/viscometry, was validated using well characterized commercial polymers ranging in molecular weight from 1,000 to 160,000, as well as polymer mixtures.   This method can now be used to accurately determine the M_N of any polymer, copolymer, or polymer blend.

Specific impulse calculations show that the $(AB)_N$ block copolymers prepared in this work have specific impulses near 220.

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ILLUSTRATIONS (Con't)

ILLUSTRATIONS (Con't)

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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), primarily hydroxy terminated fluoro- and nitro-substituted polyformals, which may be useful as binders for cast-curable energetic compositions, and as components for multi-phase segmented (block) copolymers. The major objective is to establish the chemistry for the synthesis of block copolymers from such polydiols and other difunctional energetic polymers, and to provide methods for the characterization of the block copolymers produced. The block copolymers to be synthesized are desired to be elastomers in the temperature range of about -10° to +70°C and liquids at temperatures above about 70-90°C. Low melt-viscosities are desired. It is believed that such properties, if they can be achieved, will permit and facilitate continuous extrusion processing of propellants which use these polymers as binders. The first objective is supported primarily by the Office of the Chief of Naval Research, while research toward the second major objective is supported primarily by the SDI, Office of Innovative Science and Technology. The two efforts are closely related, and funding support overlaps in the area of copolymer synthesis. The results are therefore presented together.

RESULTS AND DISCUSSION

Homopolyformals and -acetals.- Some further efforts were conducted to prepare new polyformals of potential interest as soft or hard blocks for block copolymers, or to improve/scale up the preparation of polymers of demonstrated interest for this use.

The previously investigated[1] and unsuccessful condensation of fluoronitrodiols 1 and 2 with trioxane was revisited and conditions were identified which allowed the preparation of low molecular weight oligoformals

$$HOCH_2C(NO_2)_2CH_2(CF_2)_nCH_2C(NO_2)_2CH_2OH$$
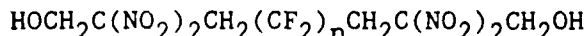
1 : n = 4
2 : n = 6

with the use of sulfolane and BF_3 etherate. The highest $\bar{M}_n$s for 1 were about 1000 (82% yield), and for 2 about 1400 (73% yield). GPCs are shown in Figs. 1 and 2.

Two new, long-chain fluorodiols were obtained from Fluorochem, Inc. It was hoped that these diols (3 and 4) would form higher molecular weight polyformals and copolyformals than the shorter hexane- and heptanediols which we usually work with. This appears to be the case at least for homopolyformal
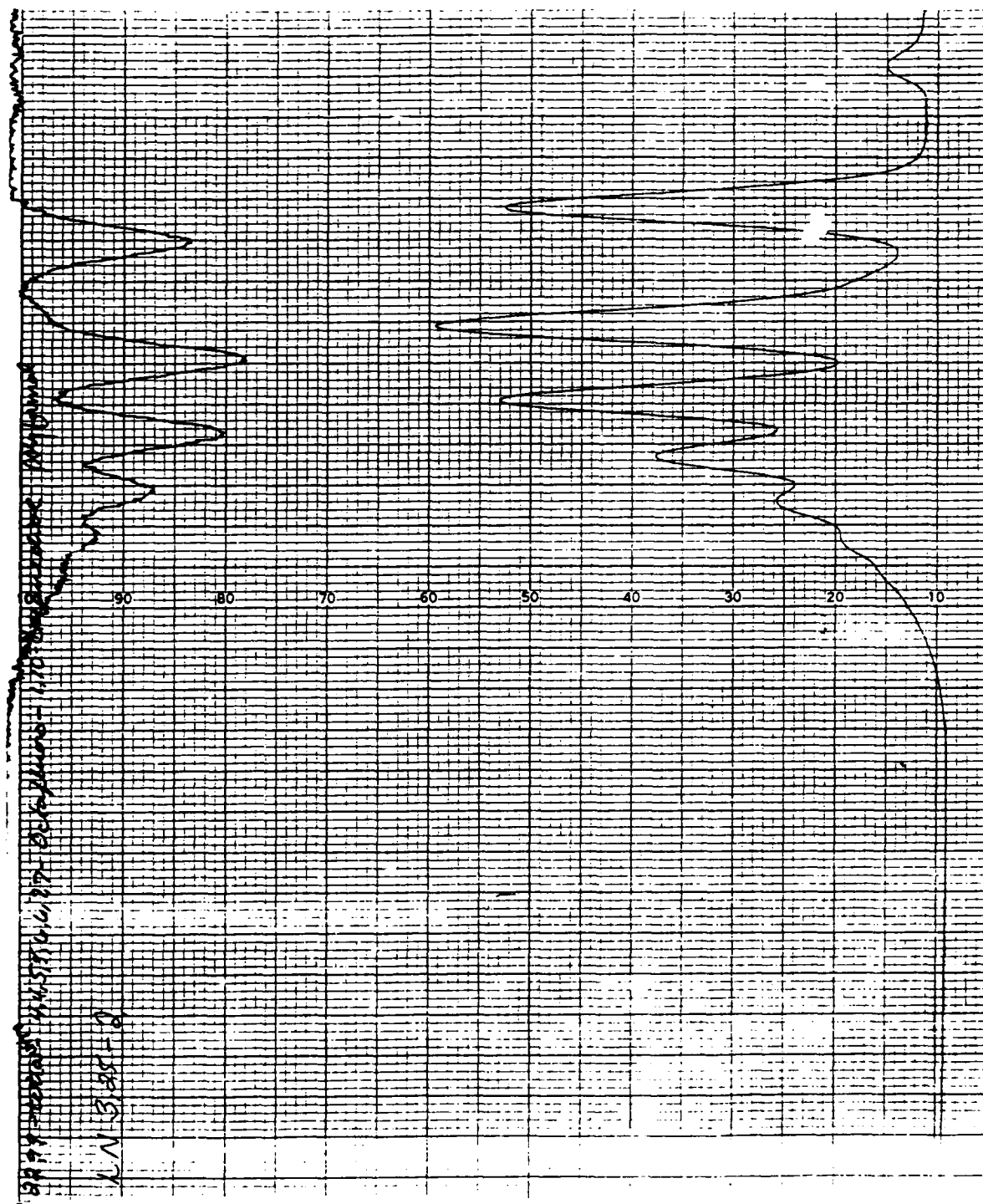
Fig. 1 GP Chromatogram of a Poly[octafluorotetranitrodecane-1,10-diol (1) formal]
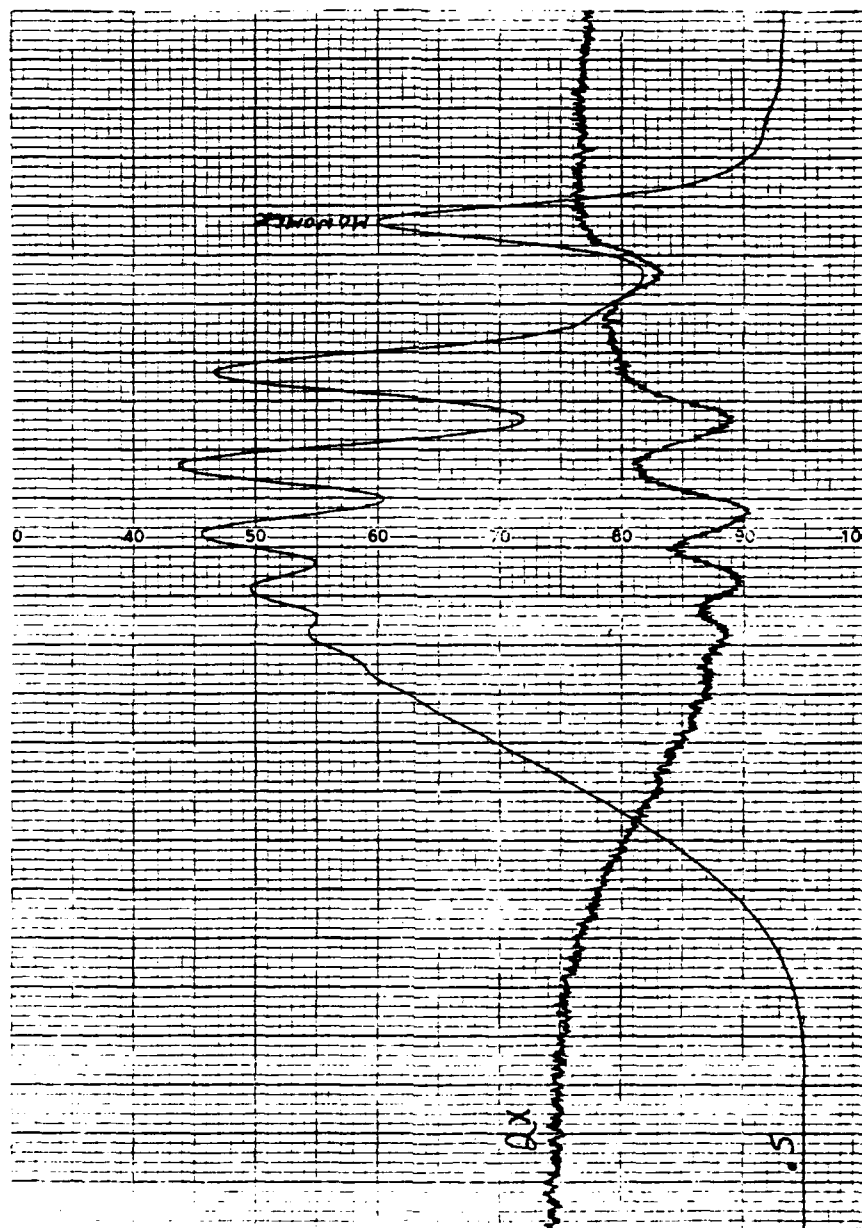
Fig. 2 GP Chromatogram of a Poly[dodecafluorotetranitrododecane-1,12-diol (2) formal]

3

$$HOCH_2CH_2(CF_2)_nCH_2CH_2OH$$
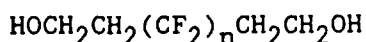
$\underline{3}$: n = 7
$\underline{4}$: n = 13

formation: Diol $\underline{3}$ under the usual conditions with trioxane/sulfolane and BF_3 etherate or $SnCl_4$ gave polyformal resins with $\overline{M}_n$ 8000-9000, while $\underline{4}$ formed partially insoluble materials in at least the same molecular weight range. GPCs are shown in Figs. 3 and 4. It appears that particularly diol $\underline{4}$ may be useful for the preparation of copolyformals with nitrodiols with sufficiently high molecular weight to be useful as soft blocks for ABA polymers.

In collaboration with the NSWC 6.2 Explosives Block, the synthesis of monomers $\underline{5}$ and $\underline{6}$ was scaled up to obtain starting material for the preparation of larger quantities of block copolymers for testing. About 5 lbs of $\underline{5}$ was prepared at Rocketdyne, while $\underline{6}$ is being synthesized (1 lb) in house.

$$HO(CH_2)_3C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)(CH_2)_3OH \qquad \underline{5}$$

$$HO(CH_2)_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)(CH_2)_2OH \qquad \underline{6}$$
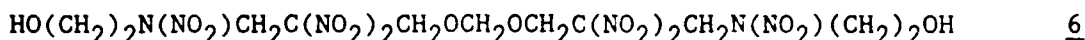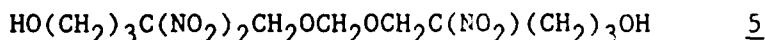
The procedure for the preparation of the high $\overline{M}_n$ polyformal ($\approx 10,000$) of the tetranitrotridecanediol $\underline{5}$ was optimized further to make it reproducible and provide a polymer free of low molecular weight impurities. The improved procedure was scaled up to the 60g level and is ready for production of this polymer on a larger scale. The yield of purified polymer at the 60g level was $\approx 80\%$; the GPC is shown in Fig. 5.

Several attempts were made to increase the $\overline{M}_n$ of the polyformal of $\underline{5}$ beyond the directly attainable 10,000: a) by further reaction of the isolated polymer with $CH_2O/SnCl_4$; these attempts failed, not unexpectedly, because of the reversibility of the formal reaction; b) by chain extension with phosgene (in the form of triphosgene) and base; although this reaction worked with low M_n polymer, it failed with the material of $\overline{M}_n \approx 10,000$. Chain extension with diisocyanates is possible, but alternatives not involving urethane formation are being sought.

To further decrease the glass transition temperature of polyformal soft blocks than has been possible by copolymerization of diols, the synthesis of polyacetals of nitrodiols such as $\underline{5}$ and $\underline{6}$ seemed desirable. To avoid dilution of the energy content, it was decided to attempt the synthesis of azidoacetals. As a model reaction, the polycondensation of $\underline{7}$ and $\underline{8}$ was studied. Polymer formation occurred readily in the presence of BF_3 etherate in vacuo (to remove ethanol); the GP chromatogram is shown in Fig. 6. The

$$N_3CH_2CH(OC_2H_5)_2 \; + \; HO(CH_2)_6OH \longrightarrow HO(CH_2)_6O \left[\overset{\overset{\displaystyle CH_2N_3}{\displaystyle |}}{CH} - O(CH_2)_6O \right]_n H$$

$\underline{7}$ $\qquad\qquad\qquad$ $\underline{8}$
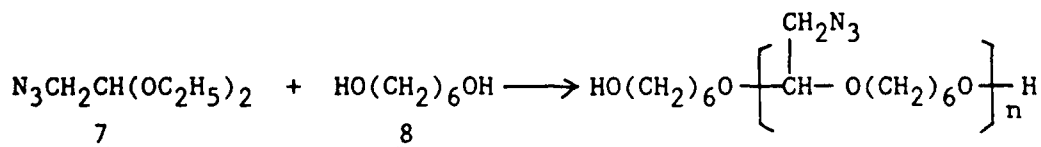
reaction will be studied further and applied to nitrodiols. Since $\underline{7}$ is readily accessible from commercially available bromoacetaldehyde acetal,

4
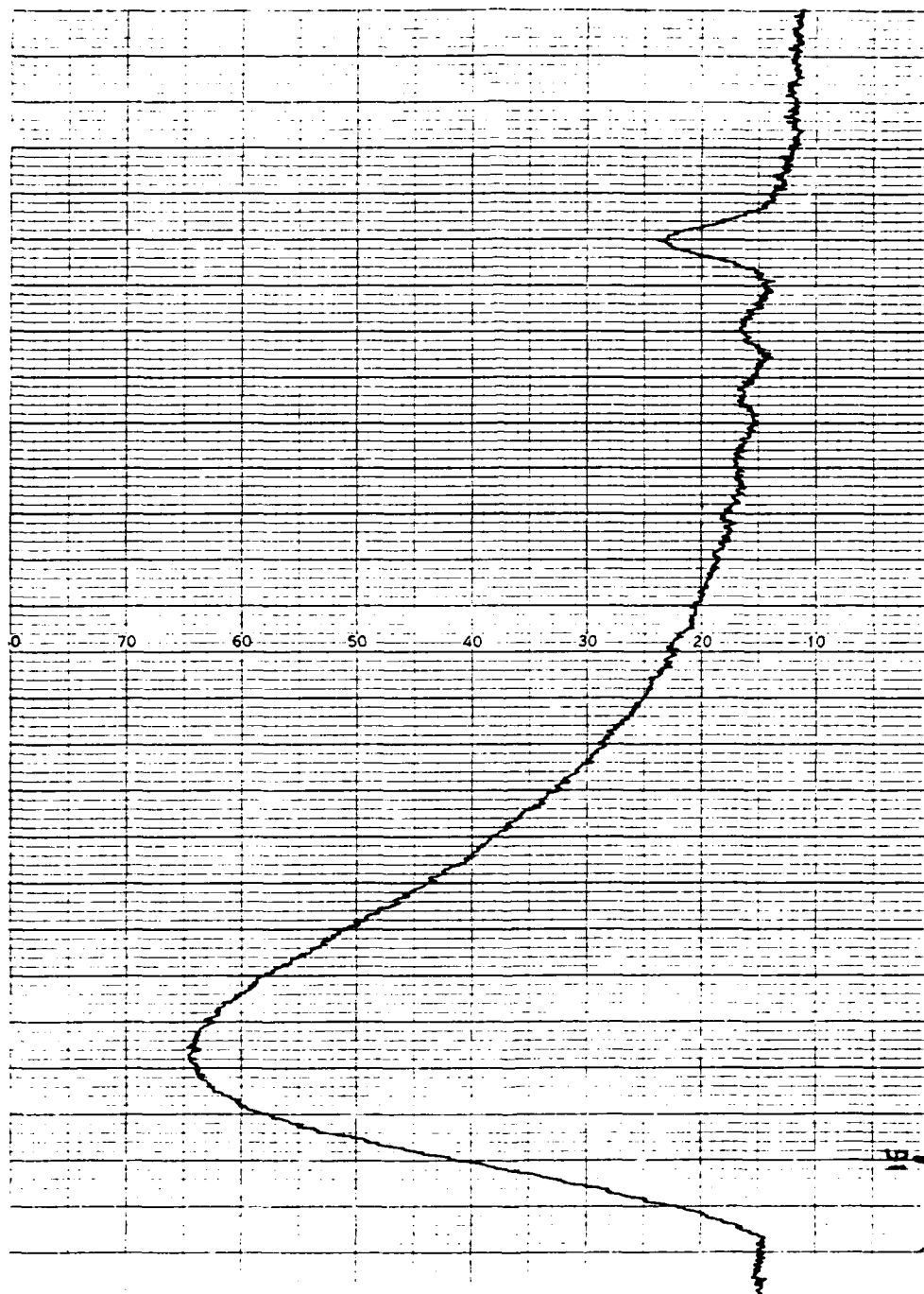
Fig. 3 GP Chromatogram of Poly[tetradecafluoroundecane-1,11-diol (3) formal]

5
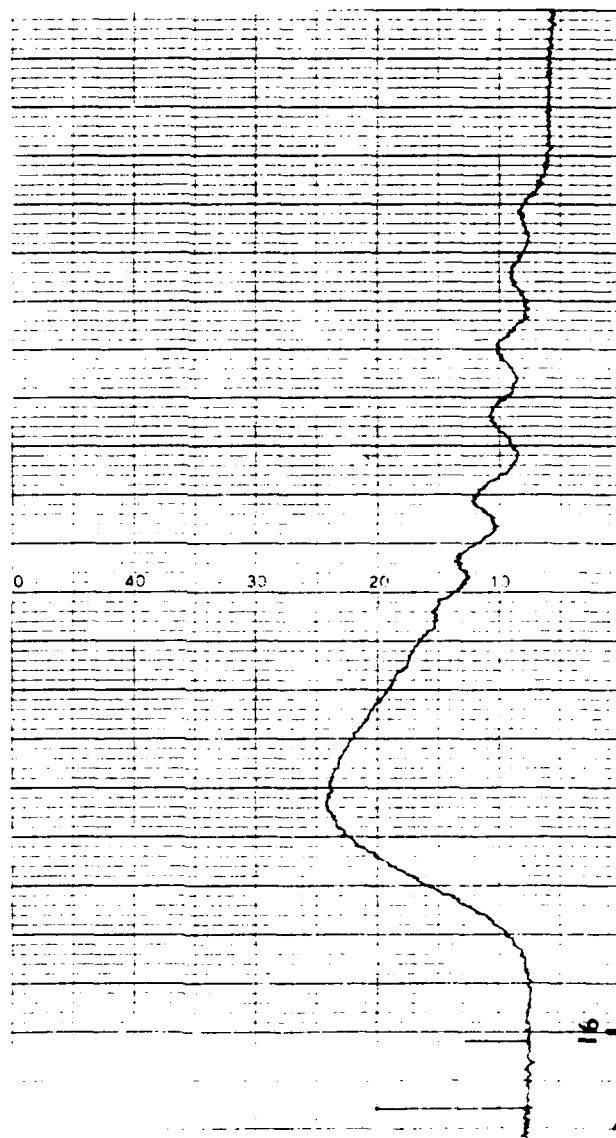
Fig. 4 GP Chromatogram of Poly[hexacosafluoroheptadecane-1,17-diol (4) formal]
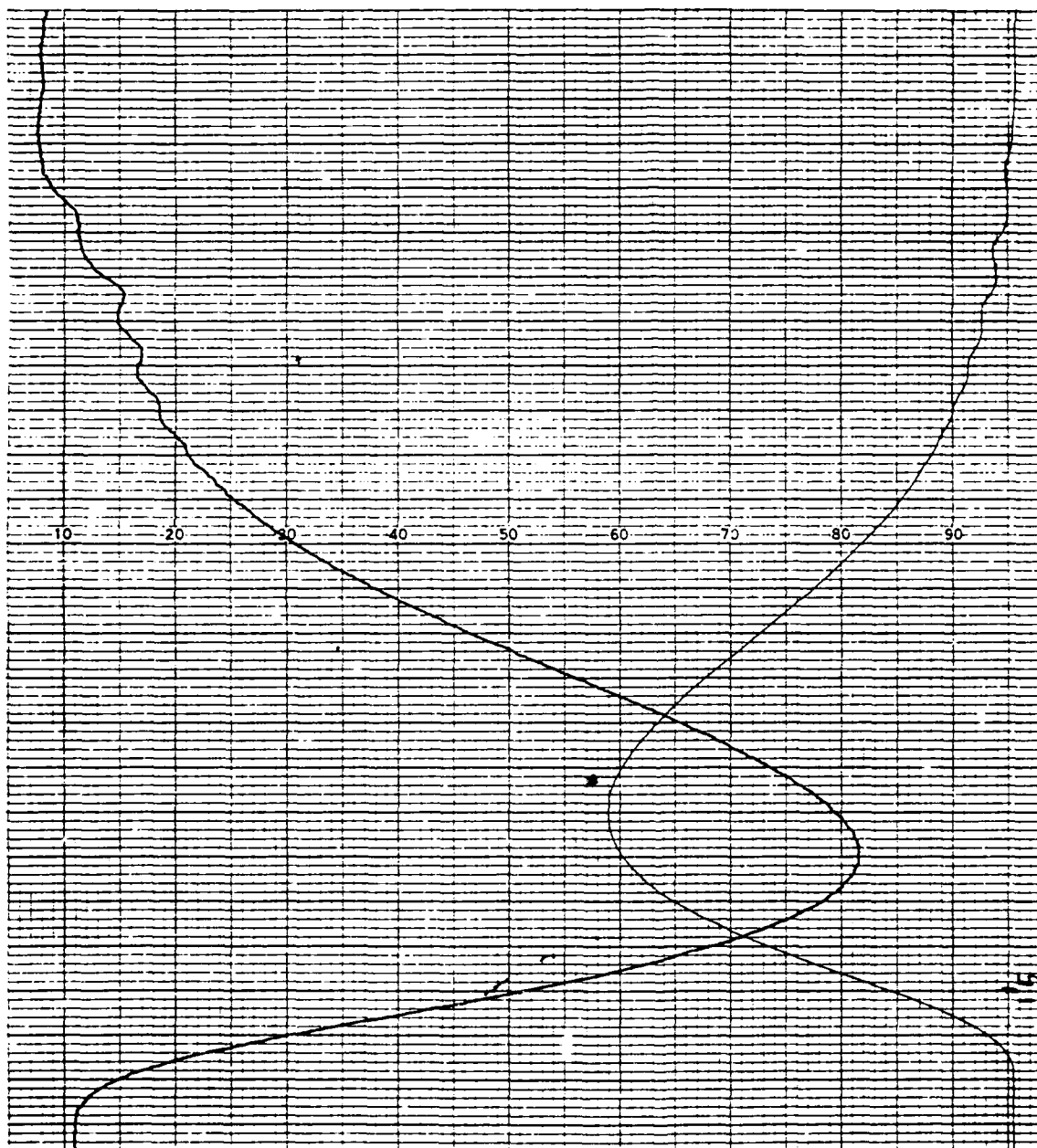
Fig. 5 GP Chromatogram of Poly[tetranitrotridecanediol (5) formal], $\bar{M}_n \simeq 10,000$, 60g Batch

7
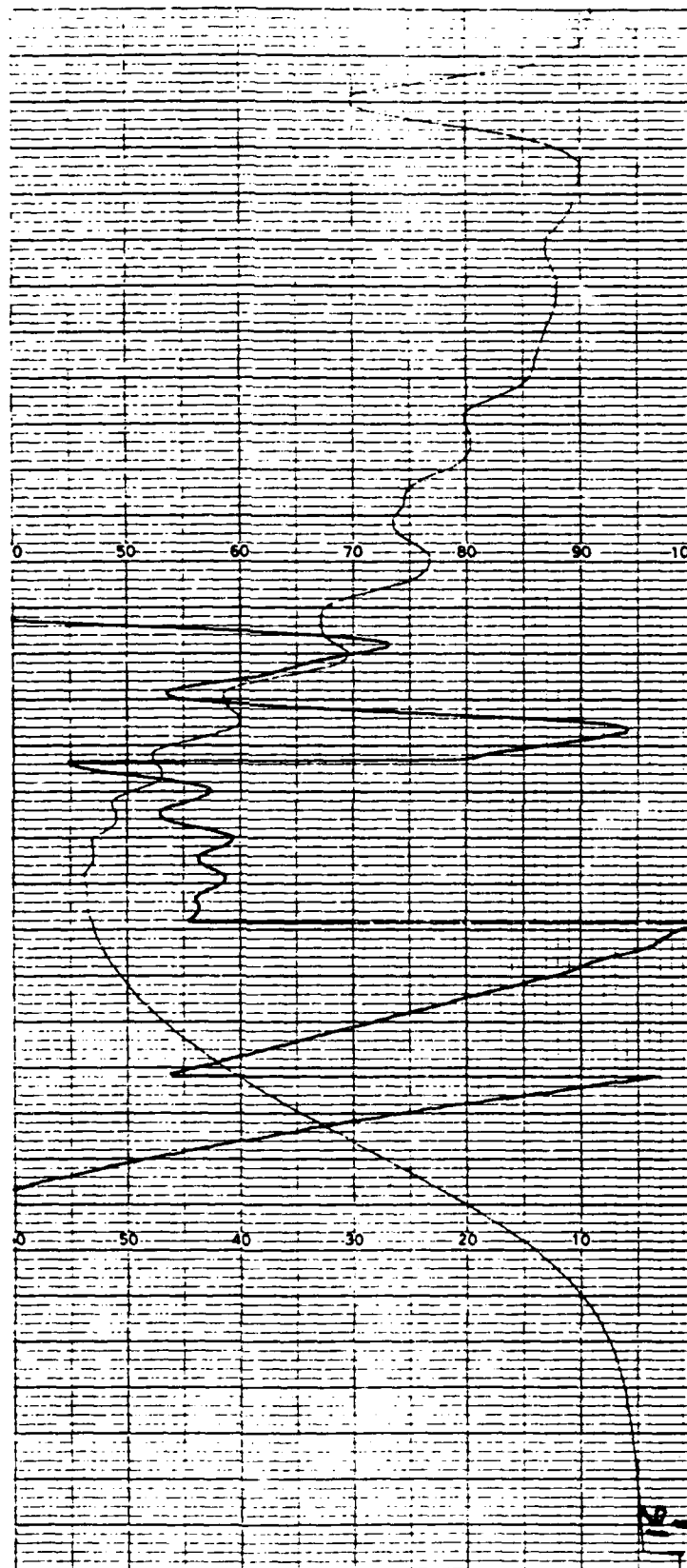
Fig. 6 GP Chromatogram of Poly(hexane-1,6-diol azidoacetal)

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polyazidoacetals should be a practical class of energetic polymers.

Copolyformals.- In an effort to prepare fluorine-free polyformal soft blocks for TPE synthesis, the copolymerization of the hexanitropentadecanediol 6 with hexane-1,6-diol (8) and butane-1,4-diol (9) was pursued. A 70/30 copolyformal of 6 and 8 was readily prepared; M_n was $\approx$ 2400 (GPC, Fig. 7). Similarly, with 9 a 70/30 copolymer was obtained with M_n < 2000. The synthesis of higher molecular weight copolymers is being attempted. In addition, heptane-1,7-diol will be tried as comonomer for this purpose.

Energetic Diisocyanates and Other Difunctional Block Linkers.- The energetic diisocyanate precursor 10 was synthesized. It can be converted in situ by heating to the corresponding diisocyanate which was intended for use in making $(AB)_N$ block copolymers, in which it functions as the hard block.

$$\underset{\text{HOOCCH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\text{COOH}}{} \quad \xrightarrow[\text{2. Me}_3\text{SiN}_3]{\text{1. SOCl}_2}$$

$$N_3\overset{\overset{\displaystyle O}{\|}}{C}\text{CH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\overset{\overset{\displaystyle O}{\|}}{C}N_3$$

10; MP 79-81°C
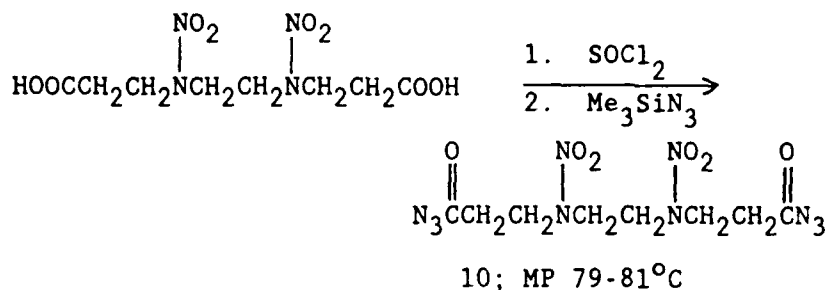
By reaction of the corresponding diols with triphosgene and pyridine, the chlorocarbonate-pyridin complexes 11 and 12 were obtained. Reaction of 11 with hexanediol gave a polyester, indicating that 11 and 12 should also be useful for making $(AB)_N$ block copolymers.

$$\text{HO-R-OH} \; + \; (\text{Cl}_3\text{CO})_2\text{CO} \quad \xrightarrow{\text{pyridine}} \quad \text{Py}^+\text{-N-CO-R-OC-N}^+\text{-Py} \quad 2\,\text{Cl}^-$$

11: R = $CH_2CH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2$

12: R = $CH_2CH_2CH_2\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}CH_2OCH_2OCH_2\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}CH_2CH_2CH_2$

$$\underline{11} + \text{HO(CH}_2)_6\text{OH} \quad \xrightarrow{\text{pyridine}} \quad \text{HO(CH}_2)_6\text{O}\left[\overset{\overset{\displaystyle O}{\|}}{C}\text{OCH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\overset{\overset{\displaystyle NO_2}{|}}{N}\text{CH}_2\text{CH}_2\text{O}\overset{\overset{\displaystyle O}{\|}}{C}\text{O(CH}_2)_6\text{O}\right]_n\!\!-\text{H}$$
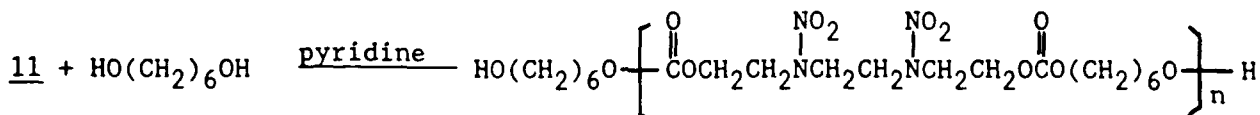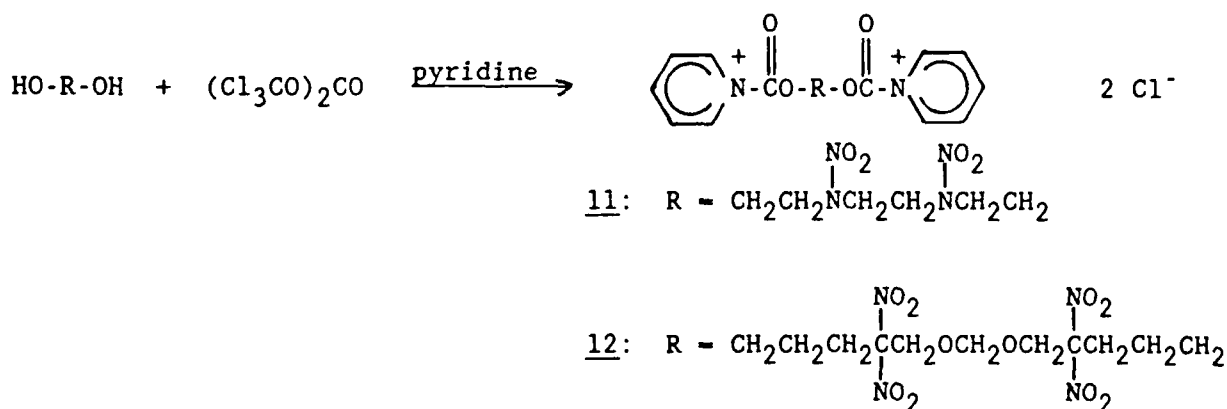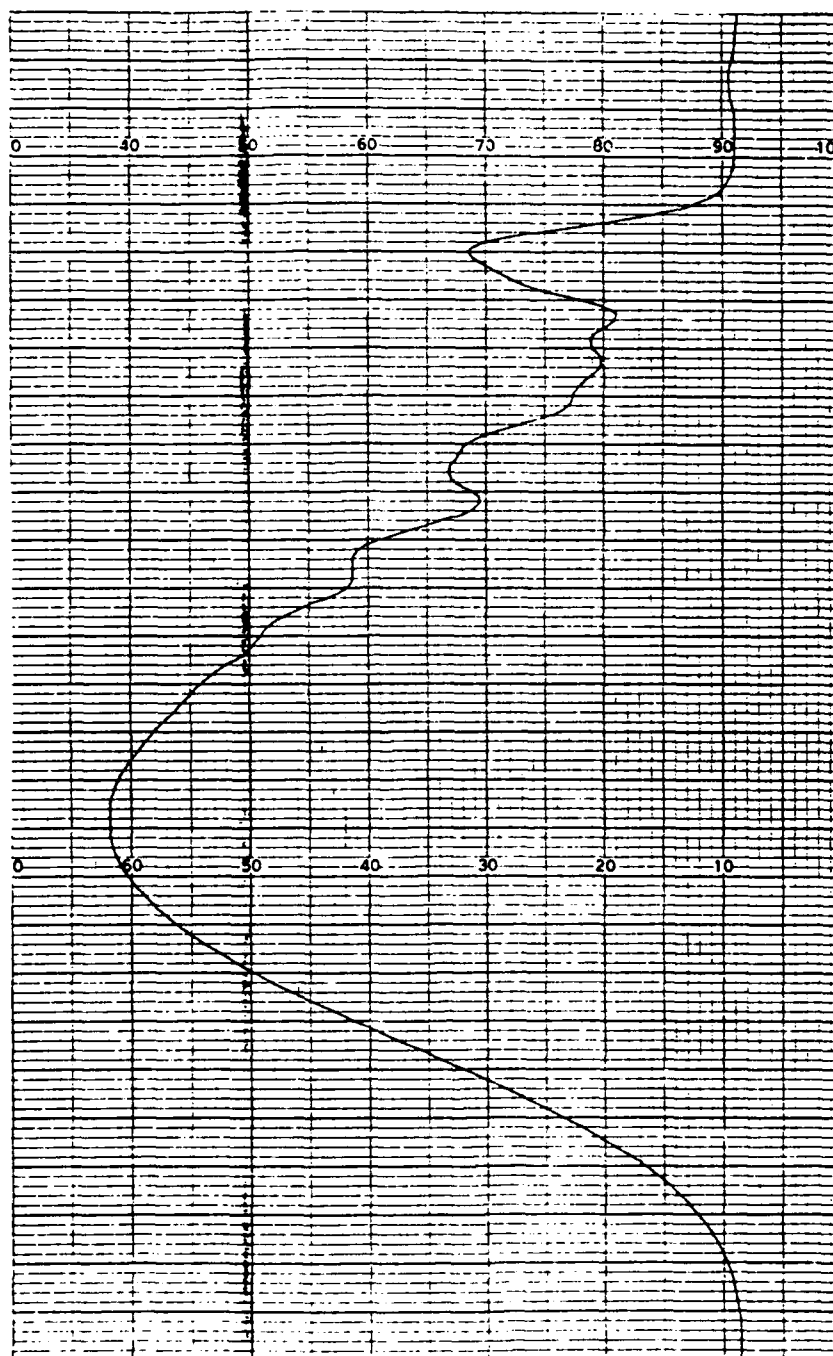
Fig. 7 GP Chromatogram of a Poly[hexanitropentadecanediol (6) formal-co-hexane-1,6-diol formal]

<u>Monofunctional Hard Blocks.</u>- Several isocyanate terminated, mononfunctional "hard blocks" were prepared by reaction of monofunctional alcohols with excess TDI. These non-energetic "blocks" are intended to be used in the synthesis of ABA tri-block polymers with B being an energetic soft block such as the polyformal of $\underline{5}$ or poly(AMMO). Alcohols used initially were docosanol (R - $CH_3(CH_2)_{21}$) which has a melting point of 65-72°C, and eicosofluoroundecanol

$$ROH + OCN\text{-}\langle\bigcirc\rangle\text{-}CH_3 \longrightarrow RO\overset{\overset{O}{\|}}{C}NH\text{-}\langle\bigcirc\rangle\text{-}CH_3$$
NCO   NCO
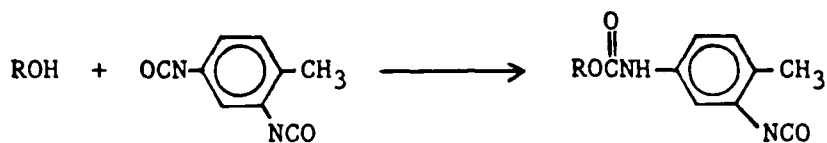
(R - $HCF_2(CF_2)_9$) with a melting point of 95-97°C. The isocyanate $\underline{13}$ was isolated as a white solid, mp 84-5°C, and stored over P_2O_5 without decomposition. $\underline{13}$ was reacted with excess methanol to give the expected urethane $\underline{14}$, mp 94-6°C, whose ^1H NMR spectrum (Fig. 8) integrated correctly

$$CH_3(CH_2)_{21}OH + OCN\text{-}\langle\bigcirc\rangle\text{-}CH_3 \longrightarrow CH_3(CH_2)_{21}O\overset{\overset{O}{\|}}{C}NH\text{-}\langle\bigcirc\rangle\text{-}CH_3$$
NCO   NCO

$\underline{13}$
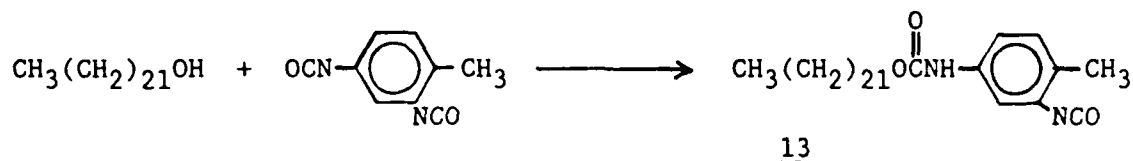
for this structure. $\underline{13}$ was also reacted with $\underline{5}$ (2:1 ratio) to give $\underline{15}$, mp 117-119°C, whose ^1H NMR spectrum (Fig. 9) again integrated correctly for this structure. $\underline{14}$ and $\underline{15}$ showed only one peak in the GPC. Thus, the structure

$$\underline{13} \xrightarrow{CH_3OH} CH_3(CH_2)_{11}O\overset{\overset{O}{\|}}{C}NH\text{-}\langle\bigcirc\rangle\text{-}CH_3 \qquad \underline{14}$$
NHCOCH_3

$$\xrightarrow{\underline{5}} [CH_3(CH_2)_{21}O\overset{\overset{O}{\|}}{C}NH\text{-}\langle\bigcirc\rangle\text{-}CH_3$$
$\underline{15}$ $NHCO(CH_2)_3C(NO_2)_2CH_2O]_2CH_2$
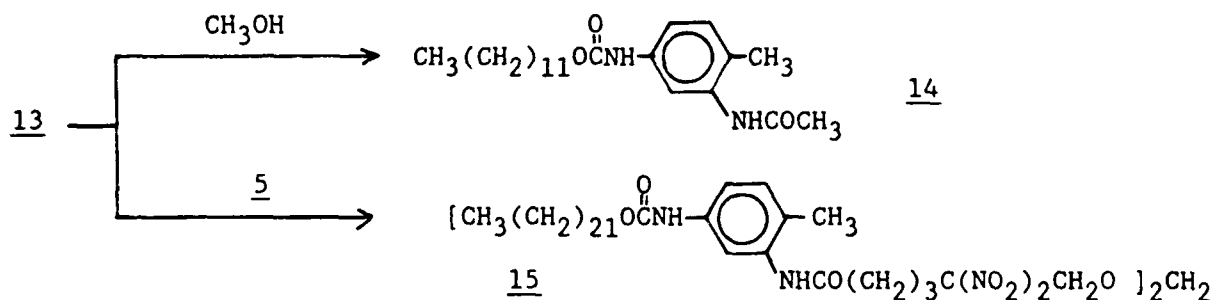
of $\underline{13}$ as a monofunctional, isocyanate terminated "block" seems well established.

The isocyanate $\underline{16}$ was similarly prepared and characterized by ^1H NMR and GPC after reaction with methanol.

$$HCF_2(CF_2)_9CH_2OH + TDI \xrightarrow[70°C]{DCE/DBTDL} HCF_2(CF_2)_9CH_2O\overset{\overset{O}{\|}}{C}NH\text{-}\langle\bigcirc\rangle\text{-}CH_3$$
$\underline{16}$ NCO
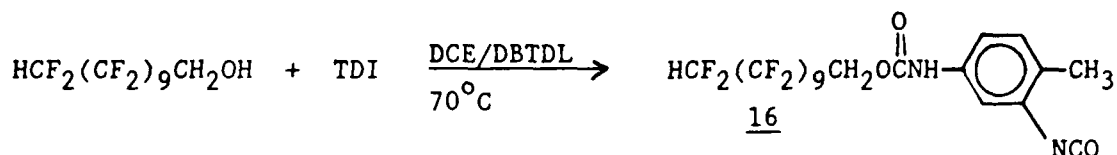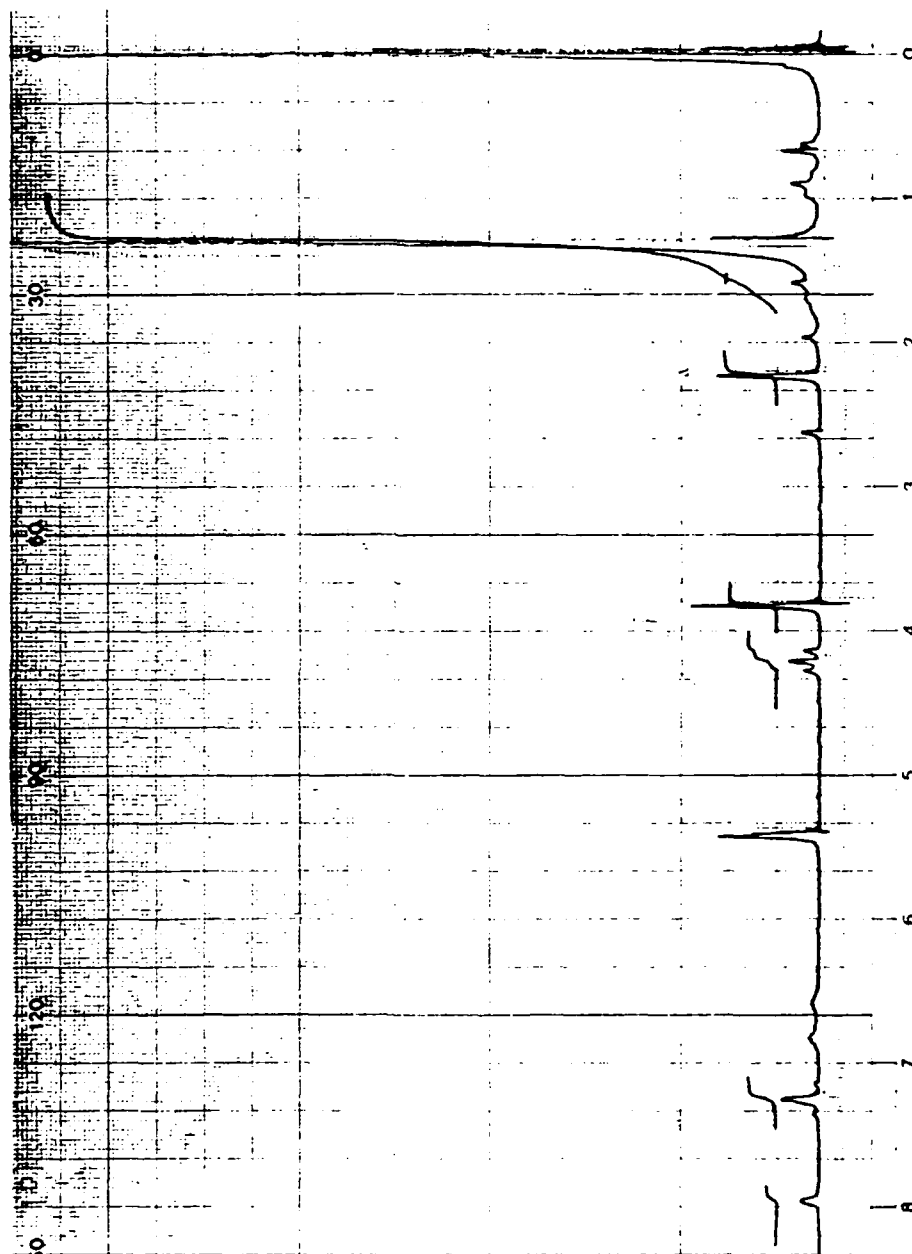
Fig. 8 ^{1}H NMR Spectrum of Urethane 14

12

Fig. 9 ^{1}H NMR Spectrum of Urethane 15

13

$$\underset{\text{DBTDL}}{\overset{\text{MeOH}}{\longrightarrow}} \quad HCF_2(CF_2)_9CH_2O\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}NH-\underset{\underset{\overset{\displaystyle \|}{\displaystyle O}}{NHCOCH_3}}{\overset{}{\bigcirc}}-CH_3 \qquad \underline{17}$$
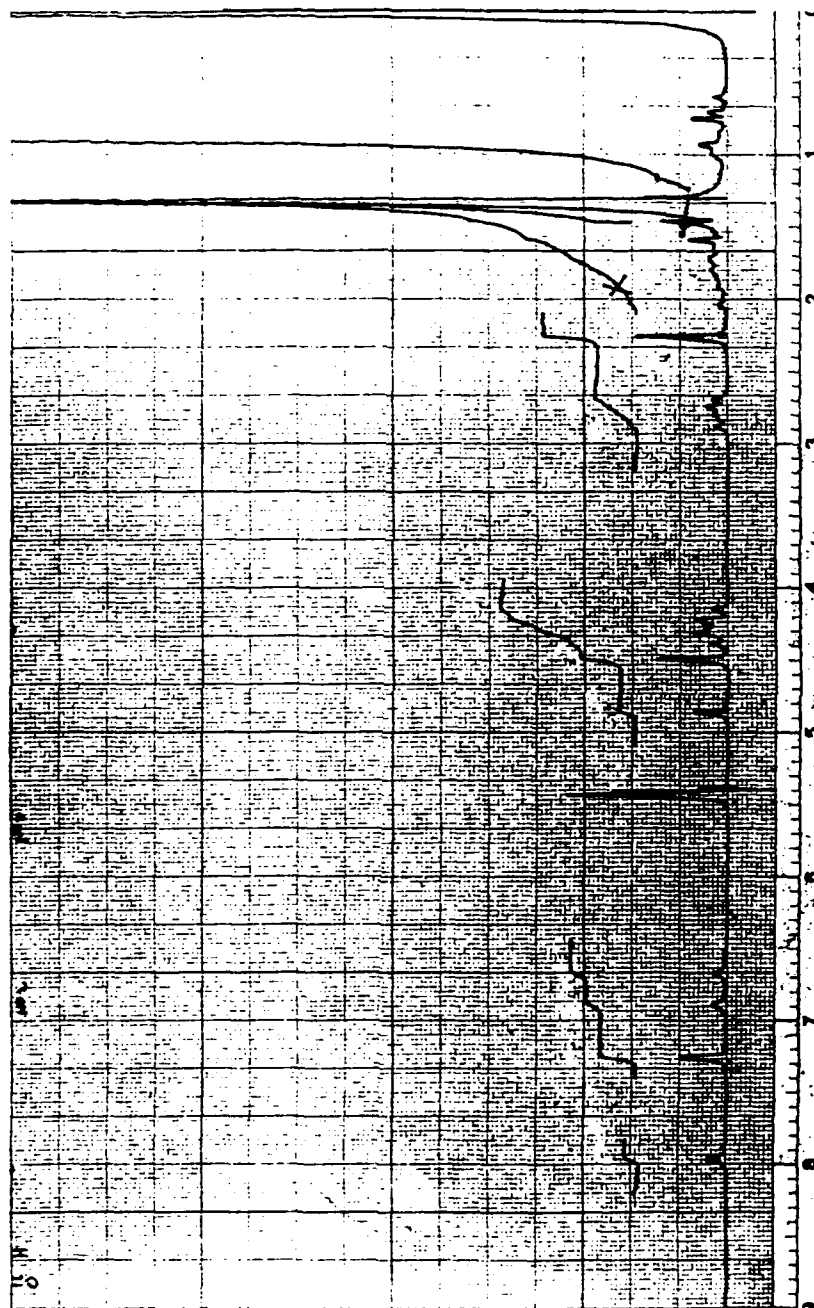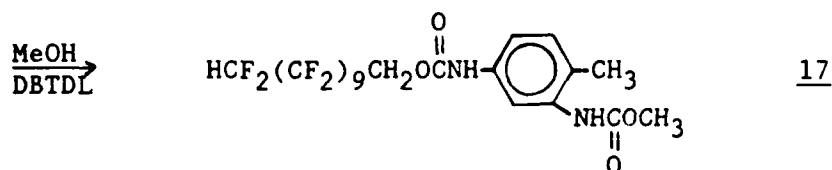
The GPC of $\underline{17}$ (Fig. 10) shows a small peak of higher molecular weight, but the ^{1}H NMR spectrum (Fig. 11) integrates satisfactorily.

The structurally related isocyanate precursor $\underline{18}$ without the additional internal urethane moiety was prepared from docosanoic acid via the acid chloride:

$$CH_3(CH_2)_{20}COOH \xrightarrow{\;SOCl_2\;} CH_3(CH_2)_{20}COCl \xrightarrow{\;(CH_3)_3SiN_3\;} CH_3(CH_2)_{20}CON_3$$
$$\underline{18}$$
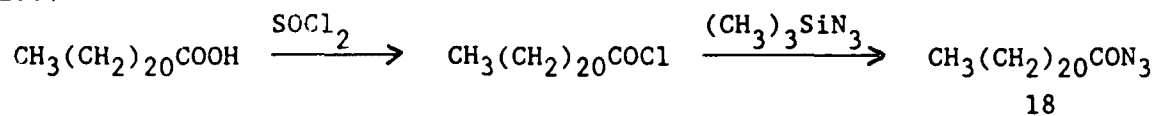
The synthesis of the energetic "hard block" $\underline{19}$ has been initiated. Initial results indicate that the melting point of $\underline{18}$ is too high ($>150^\circ$C), but similar structures with lower melting points can be envisioned.

$$\begin{array}{c}\text{1. } SOCl_2 \\ \text{2. } TMSN_3 \\ \text{3. Heat}\end{array}$$

$$\underline{19}$$
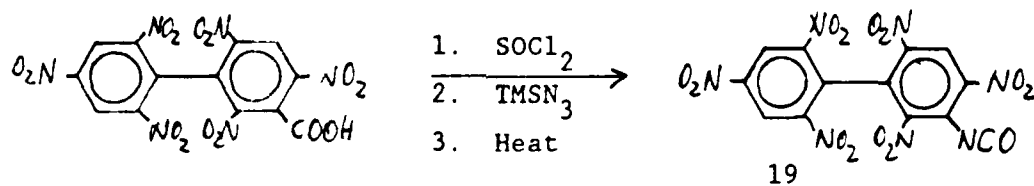
(AB)$_N$ Block Copolymer Synthesis.- In the previous work,[2] we reported the synthesis of (AB)$_N$ block copolymers by chain extension of various polyformal "soft blocks" with diisocyanates. Some of these polymers exhibited quasi TPE

$$HO \sim\sim OH \;+\; OCN-R-NCO \;\longrightarrow\; H\!\left[\!O \sim\sim OCNHRNHC \!\right]_{\!N}\! O\sim\sim OH$$
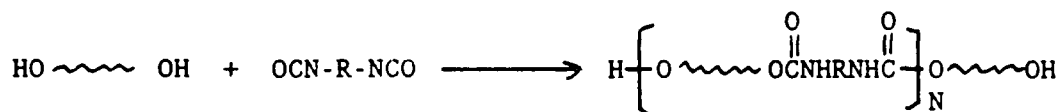
properties. Additional examples were prepared this year, by chain extension of polyformals of $\underline{5}$ with different molecular weights, to complete a study of properties of the resulting "block copolymers" as a function of isocyanate structure. The new polymers prepared are listed in Table 1. Prof. Chien from the University of Massachusetts arranged to have rheological characterization performed on several of these and other (AB)$_N$ polymers prepared by us.
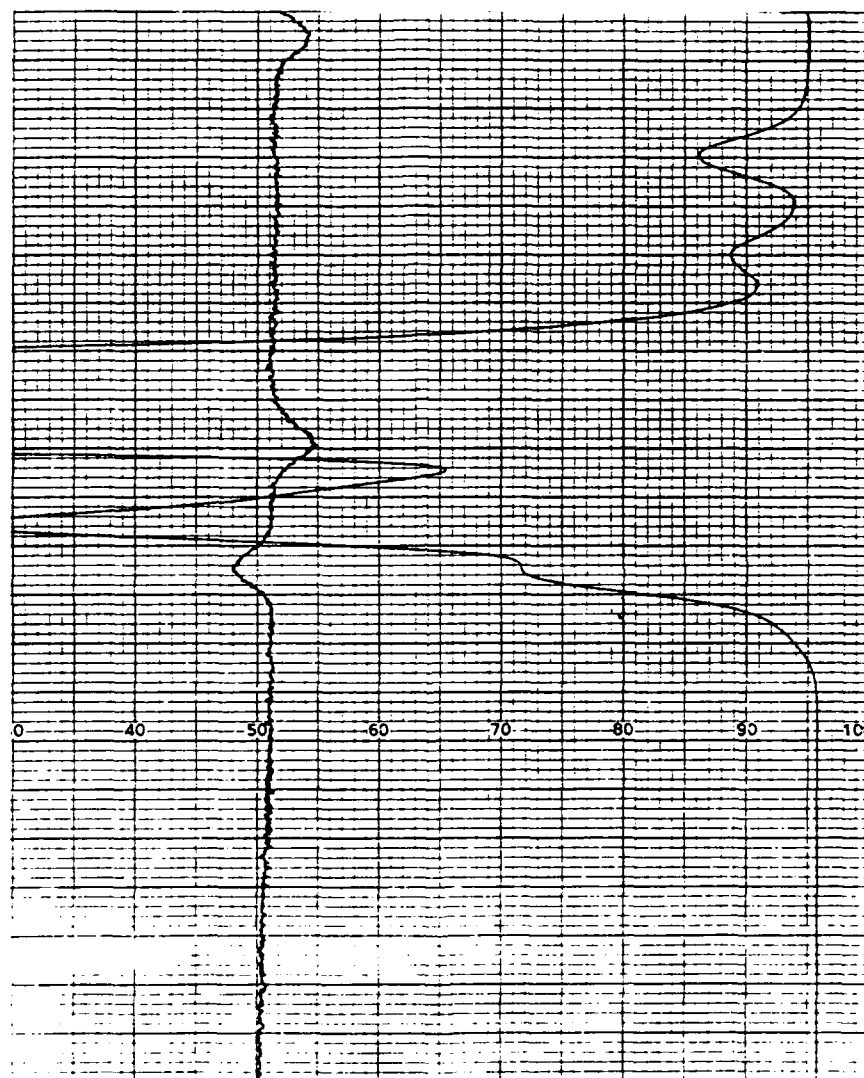
Fig. 10 GP Chromatogram of Urethane 17

15
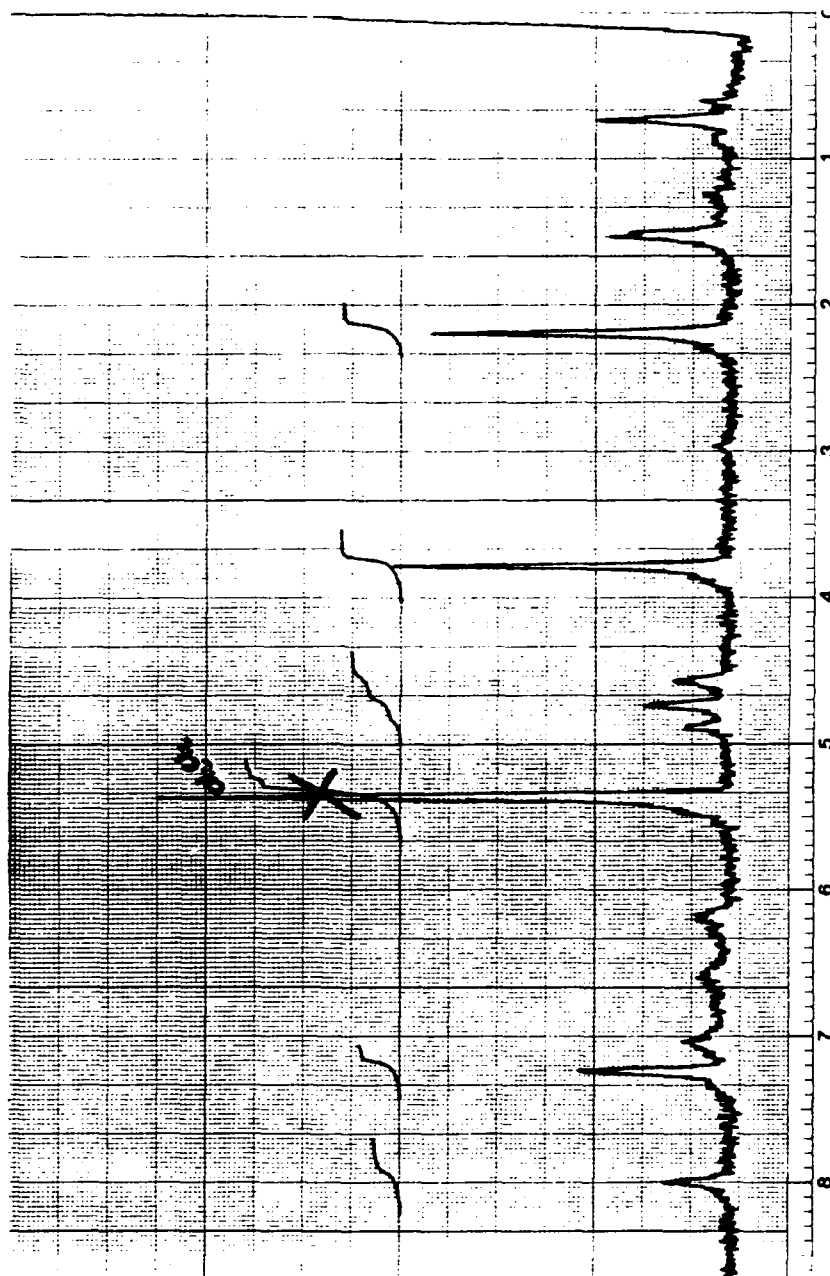
Fig. 11 ^{1}H NMR Spectrum of Urethane 17

Table 1. $(AB)_N$ Polymers Prepared from Polyformals of <u>5</u> by
Chain Extension with OCN-R-NCO

$\bar{M}_n$ of <u>5</u> Polyformal	OCN-R-NCO	$\bar{M}_n$ of Product	Appearance at r.t.
4500		71,000 (GPC)	tough elastomer
7600	OCN⟨ ⟩NCO	123,000 (GPC)	tough elastomer
4500	IPDI	50-60,000 (est'd)	soft elastomer
7600	IPDI	low	soft elastomer
7600	HMDI	$\leq$ 30,000 (est'd)	soft elastomer

Some results of these tests are shown in Figures 12-14. They corroborate previously[2] reported DSC data which show no sharp melting transitions for these polymers. It can be concluded that most, if not all, of the $(AB)_N$ polymers prepared by us are not phase separated. On warming, they gradually soften and lose their elastic properties. Therefore, further work with this type of $(AB)_N$ structure is being deemphasized.

A sample of difunctional poly(AMMO), obtained from R. Wardle (Thiokol Corp.) and having a reported OH equ. wt. of 3125, was also chain-extended with TDI to give a polymer of $\bar{M}_n \approx 25,000 - 30,000$ (GPC, Fig. 15). This material was a resin devoid of elastic properties.

Specific impulse calculations for several of the $(AB)_N$ "block copolymers" prepared by chain-extension of polyformal soft blocks were made and are shown in Table 2. The data indicate that the fluorocomonomer used for lowering of T_G has no adverse (or beneficial) effect on performance. Also included are data for GAP azide and GAP nitrate, two potential non-volatile plasticizers for energetic soft blocks in $(AB)_N$ or ABA block copolymers.
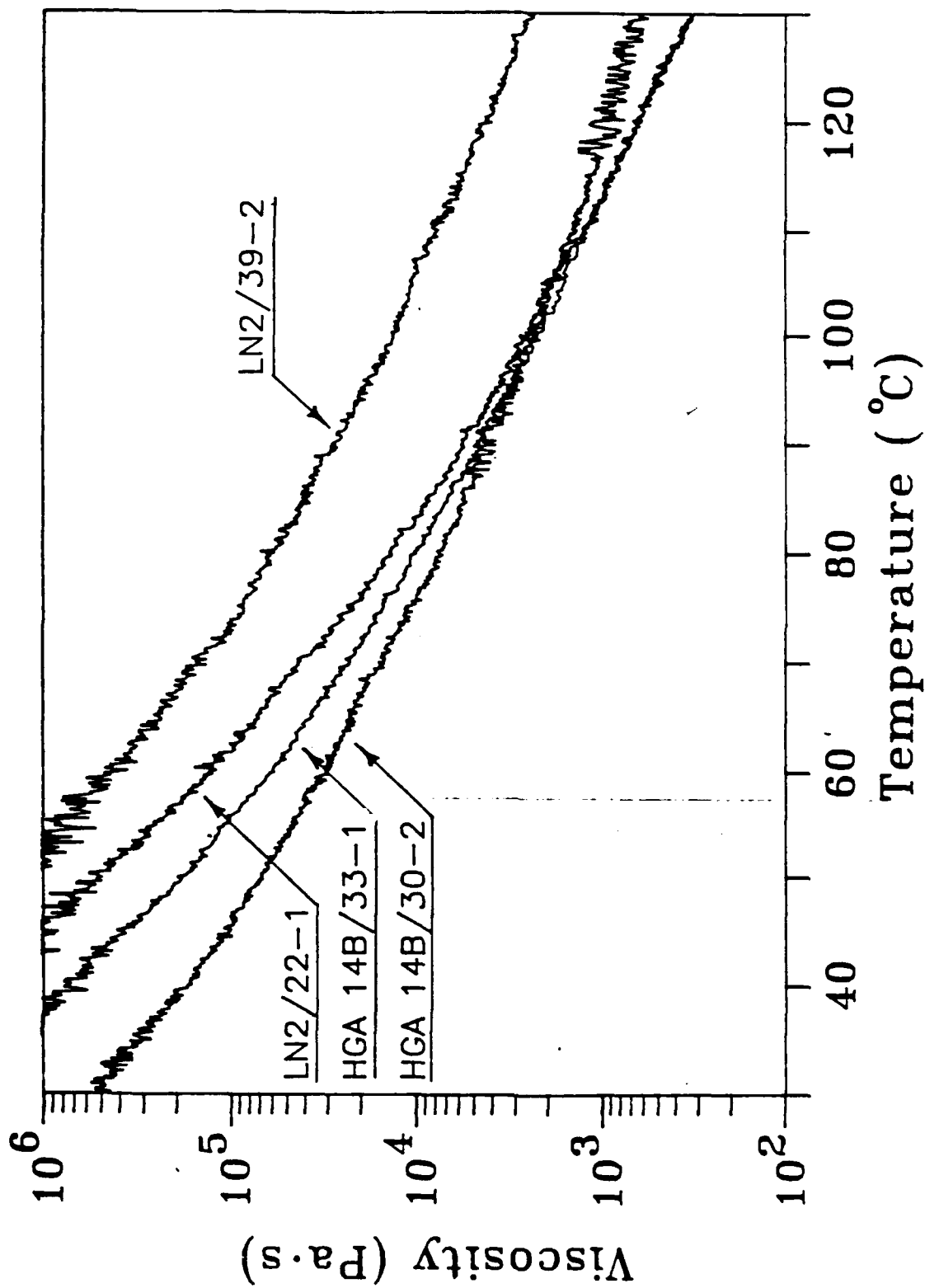
Fig. 12 Viscosity vs. Temperature of Some (AB)$_N$ Block Polymers

18
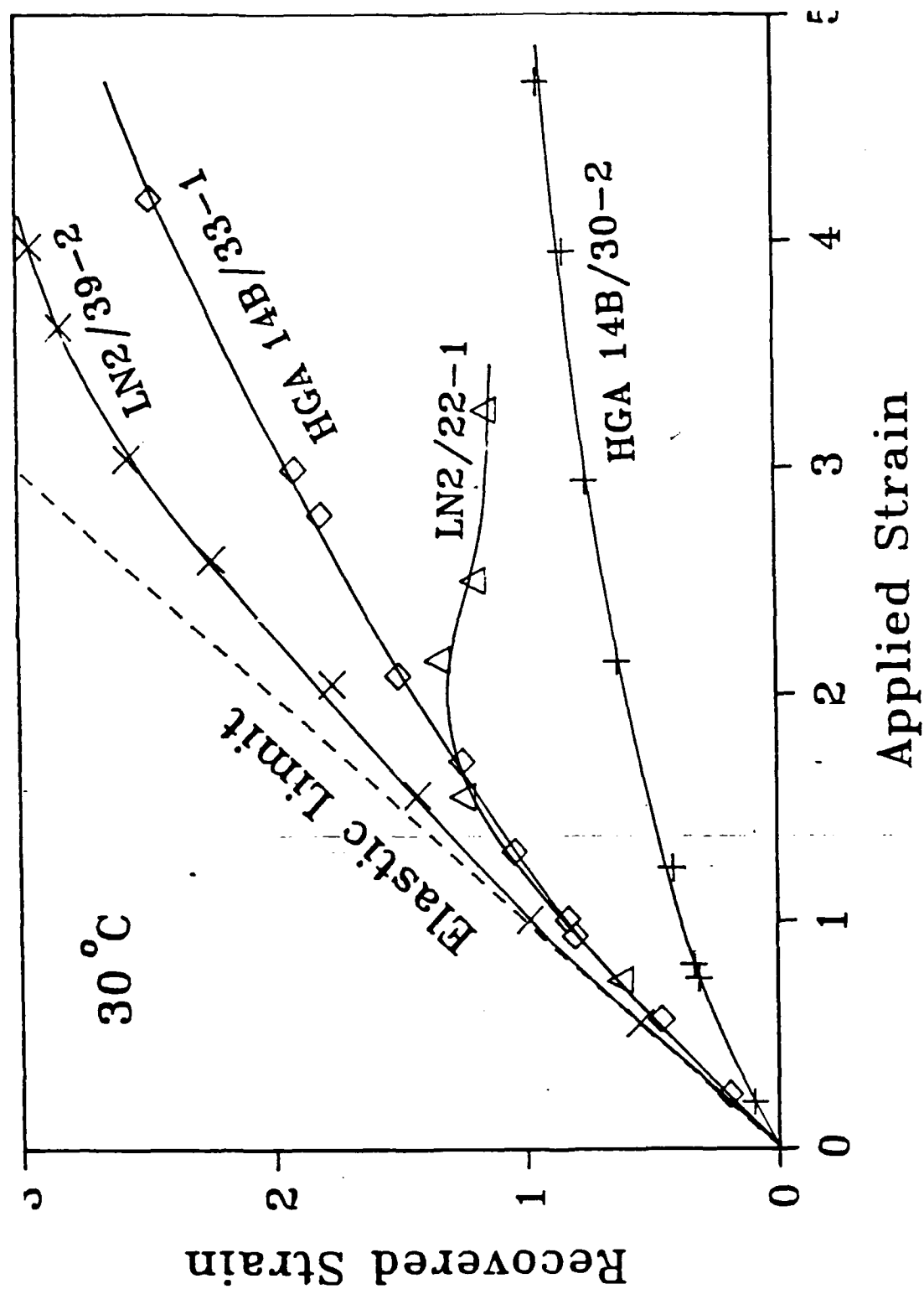
Fig. 13 Recovered vs. Applied Strain at 30°C for Some $(AB)_N$ Block Copolymers

19
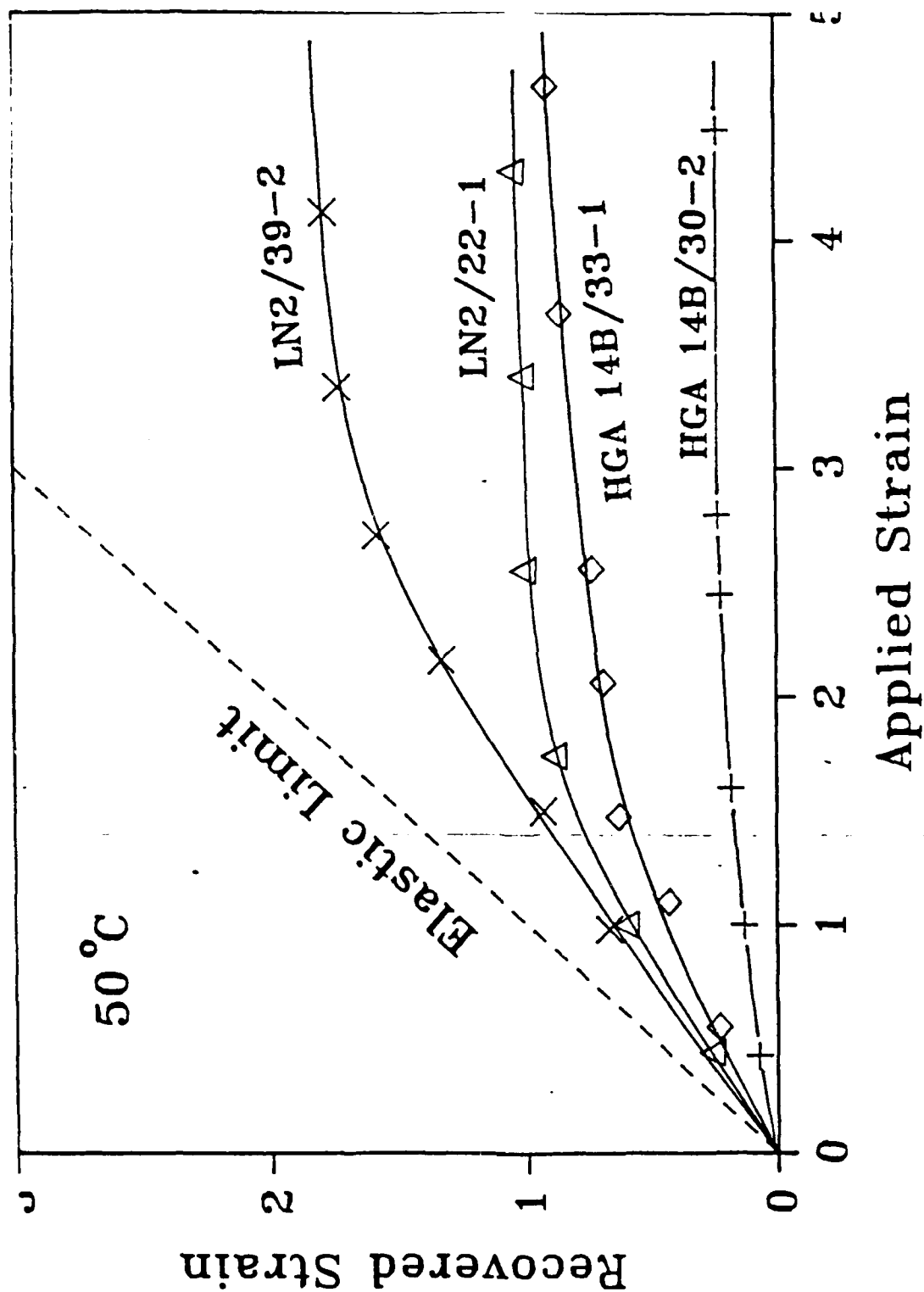
Fig. 14 Recovered vs. Applied Strain at 50°C for Some $(AB)_N$ Block Copolymers
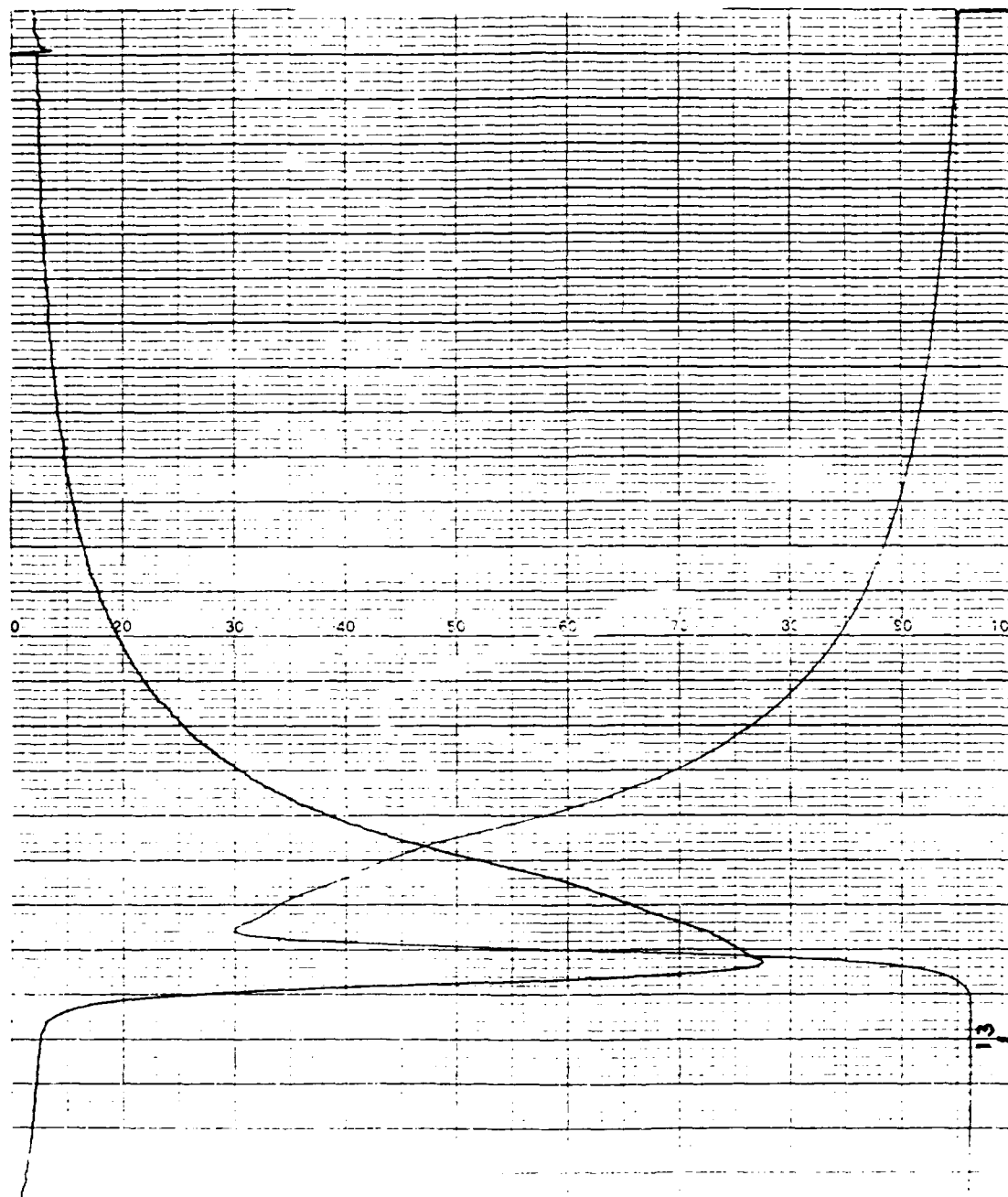
Fig. 15 GP Chromatogram of Poly(AMMO), $\bar{M}_n$ = 3125, Chain Extended with TDI

21

Table 2. Specific Impulse Calculations (PEP Code) for Some
Polyformal/Urethane Block Copolymers

COMPOSITION*	H_F** (cal/g)	D** (g/cm^3)	I_{sp}	$D\text{-}I_{sp}$	P_J Kbar
5 POLYFORMAL/TDI	-196	1.35	222.5	300.3	156
5 POLYFORMAL/DNPDI	-207	1.35	224.2	302.6	157
HNPD DIOL/2 COPOLYFORMAL/TDI	-487	1.30	215.8	280.5	138
HNPD DIOL/2 COPOLYFORMAL/DNPDI	-493	1.30	220.9	287.1	142
HNPD DIOL/OFH DIOL COPOLYFORMAL/TDI	-679	1.52	219.8	334.1	200
HNPD DIOL/OFH DIOL COPOLYFORMAL/DNPDI	-682	1.52	225.2	342.3	206
GAP NITRATE (500)	+182	1.30	219.7	285.6	141
GAP AZIDE (500)	+555	1.25	220.1	275.1	129

*DNPDI = 3,3-Dinitropentane-1,5-diisocyanate
HNPD DIOL = Hexanitrodioxadiazapentadecanediol (6)
OFH DIOL = Octafluoro-1,6-hexanediol

**calculated

ABA Block Copolymer Synthesis.- In an initial reaction scheme for the
synthesis of ABA triblock copolymers, a polyformal of the tetranitrotridecane-
diol 5 ($M_n \approx 9000$) was used as soft block, and was end-capped with excess
TDI. The product was subsequently reacted with (a) methanol, (b) a
monofunctional Poly(dioxolane/trioxane) copolymer (PDT) provided by Dr. Lillya
from the University of Massachusetts, and (c) docosanol.

The product of the reaction with methanol gave a ^{1}H NMR spectrum (Fig.
16) supportive of the expected structure. Docosanol and especially PDT
reacted more slowly and the initial products obtained contain unreacted
starting material, as indicated by GPC and ^{1}H NMR analysis before and after
solvent extraction. Since they exhibit some degree of elasticity, some
triblock formation must have occurred, however.

5 Polyformal + TDI (excess) ⟶

$$CH_3 - \bigcirc - NHCO \sim\sim\sim \underline{5}\ Polyformal \sim\sim\sim OCNH - \bigcirc - CH_3$$
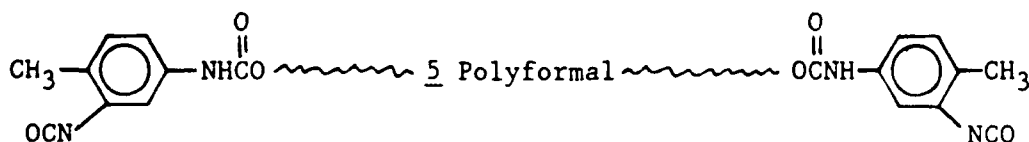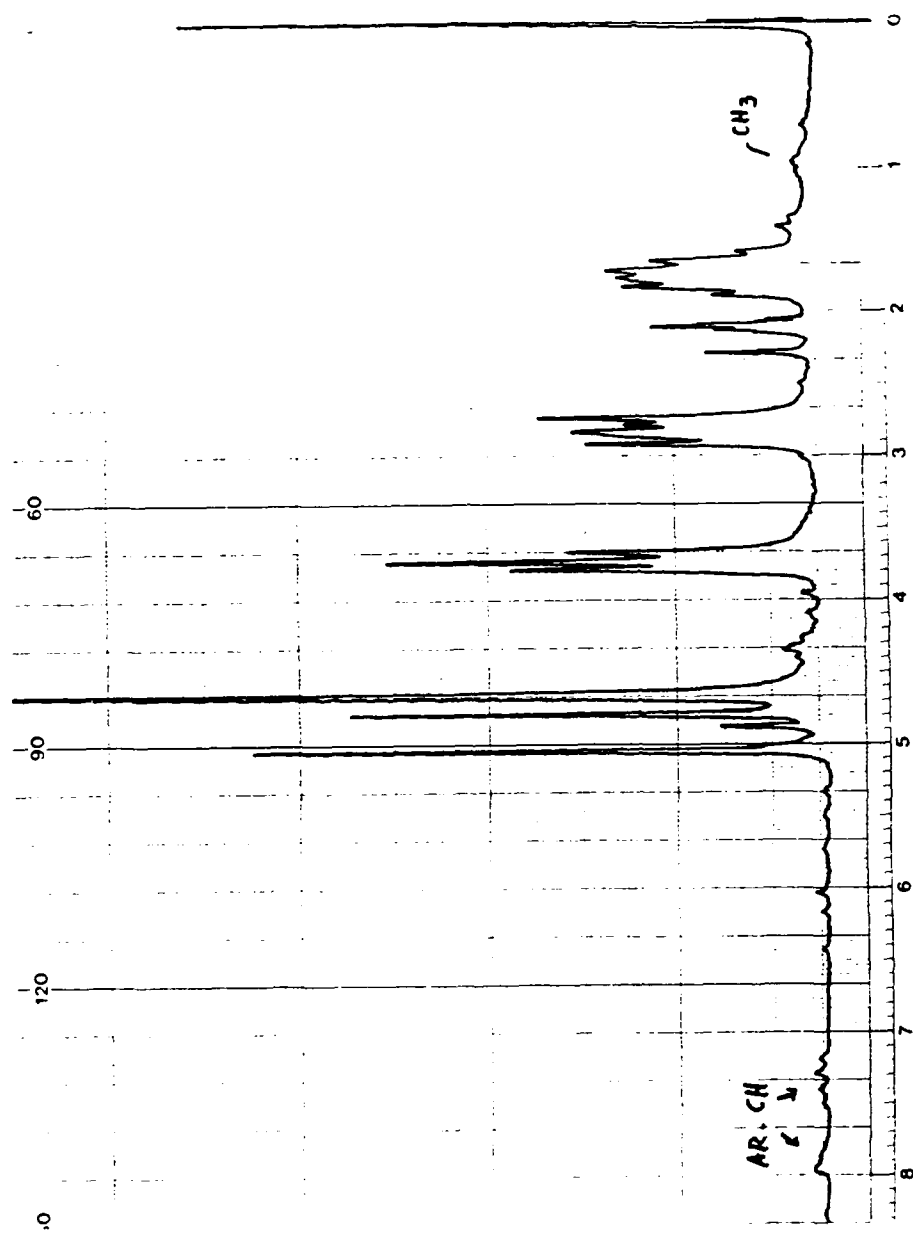
Fig. 16 ^{1}H NMR Spectrum of a Poly($\underline{5}$ formal) after End-capping with TDI and Reaction with Methanol

23

$$\xrightarrow[\text{MeCN; }65\text{-}75^\circ\text{C}]{\text{ROH}}$$

CH$_3$—[benzene ring]—NHCO~~~~ **5** Polyformal~~~~OCNH—[benzene ring]—CH$_3$, with ROCNH substituent (O) on left ring and NHCOR substituent (O) on right ring

R = CH$_3$, PDT, CH$_3$(CH$_2$)$_{21}$

The docosanyl end-capped polymer melted in the range of 70-80°C, the polymer with PDT end blocks at 110-120°C.

Also investigated was the reverse approach, reacting a polyformal of **5** with isocyanate terminated hard blocks such as **13** and **16**.

Using the reaction conditions established for the preparation of **15**, **13** was reacted with several polyformals of **5** in a ratio of 2:1 in an attempt to prepare ABA polymers of the general structure **20**. In several attempts, the **5**

CH$_3$(CH$_2$)$_{21}$OCNH—[benzene ring]—CH$_3$

NHCO[(CH$_2$)$_3$C(NO$_2$)$_2$CH$_2$OCH$_2$OCH$_2$C(NO$_2$)$_2$(CH$_2$)$_3$O-CH$_2$]$_N$O(CH$_2$)$_3$C(NO$_2$)$_2$

CH$_3$—[benzene ring]—NHCO(CH$_2$)$_{21}$CH$_3$

-CH$_2$OCH$_2$OCH$_2$C(NO$_2$)$_2$(CH$_2$)$_3$OCNH

polyformal was extended with TDI prior to reaction with **13**. This leads to polymers of higher molecular weight, but also to the incorporation of additional urethane moieties. The polymers prepared are listed in Table 3.

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Table 3. ABA Polymers by Reaction of <u>13</u> with Polyformals of <u>5</u>; Ratio 2:1

Polymer Number	Polyformal of <u>5</u> $(\bar{M}_n)^*$	Wt% of <u>13</u> in final product	$\bar{M}_n^{**}$	$T_G^{\ddagger}$ (°C)	$T_M^{\ddagger\ddagger}$	Character- istics (at room temp.)	GPC/DSC Fig. No.
1	9000 (11,500)	8.3	13,000	4	-50	elastic; not tough	17,18
2	7600 (7800)	11.7	(8,600)			elastic; tough	19
3	7600 extended w. TDI	8.5	16,500	-2	-50	elastic; tough	20,21
4	4460	18.0	(5500)	-	-	plastic; tough	22
5	4460 extended w. TDI	10.0	(10,000)	-	-	elastic; tough	23
6	4460 extended w. TDI	8.5	(11,500)	-	-	elastic; tough	24
7	4460 extended w. TDI	5.4	(18,500)	-	-	elastic; not tough	25

*Estimated from the GP chromatogram; values in parentheses determined by GPC/ viscosimeter method

**No. 1 and 3 determined by GPC/viscosimeter method, others estimated from the GP chromatogram

$\ddagger$by DSC

 Visual inspection indicated that all polymers in Table 3 melted in the range 60-70°C, while the DSCs for polymers 1 and 3 (Figs. 18 and 21) show endothermic transitions over a wider and lower temperature range. Polymers 1, 2, and 4, which have soft blocks without additional urethane moieties, have low melt viscosities and flow readily when molten. The others are more viscous and resemble more the $(AB)_N$ polymers prepared earlier by chain- extension of soft blocks with diisocyanates. Thus, it appears that the presence of many urethane groups in the polymer may be undesirable from viscosity considerations. The polymers prepared are being characterized more fully.
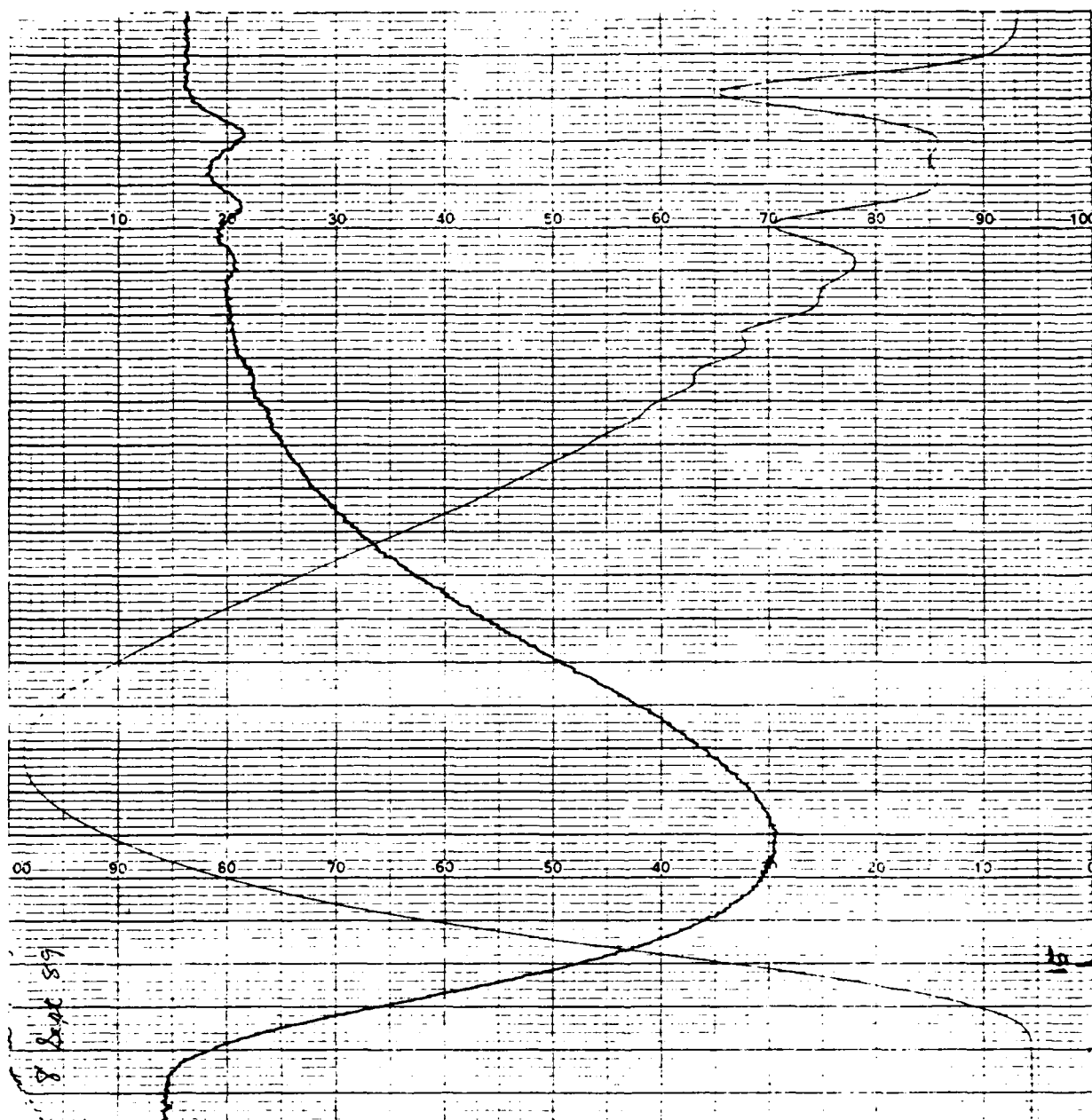
Fig. 17 GP Chromatogram of ABA Block Polymer from Poly($\underline{5}$ formal), $\overline{M}_n \sim 9000$, and Isocyanate $\underline{13}$

26
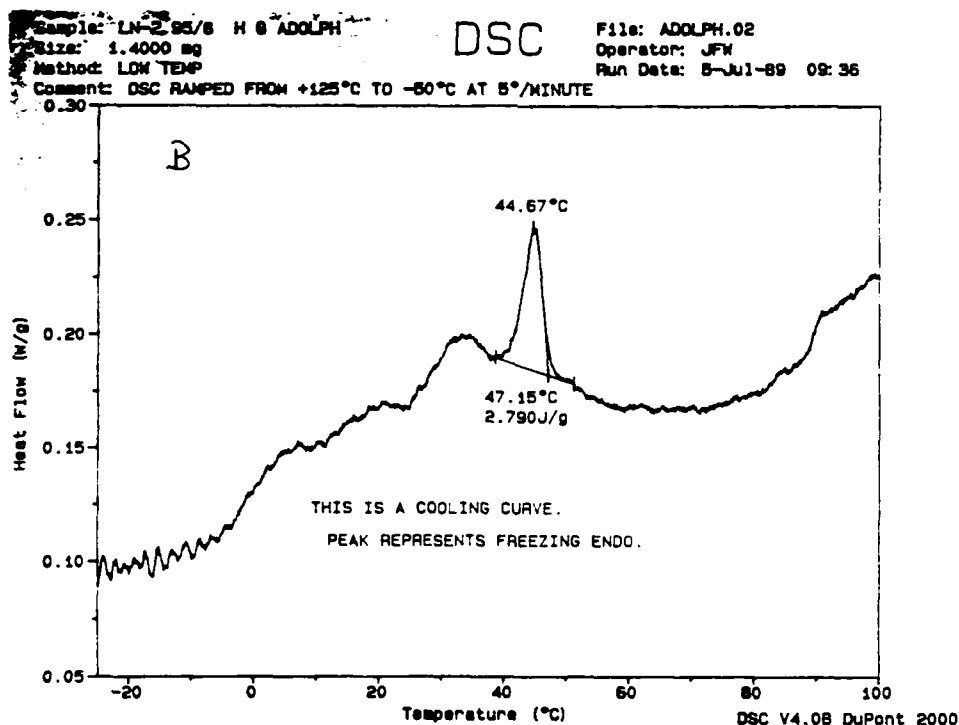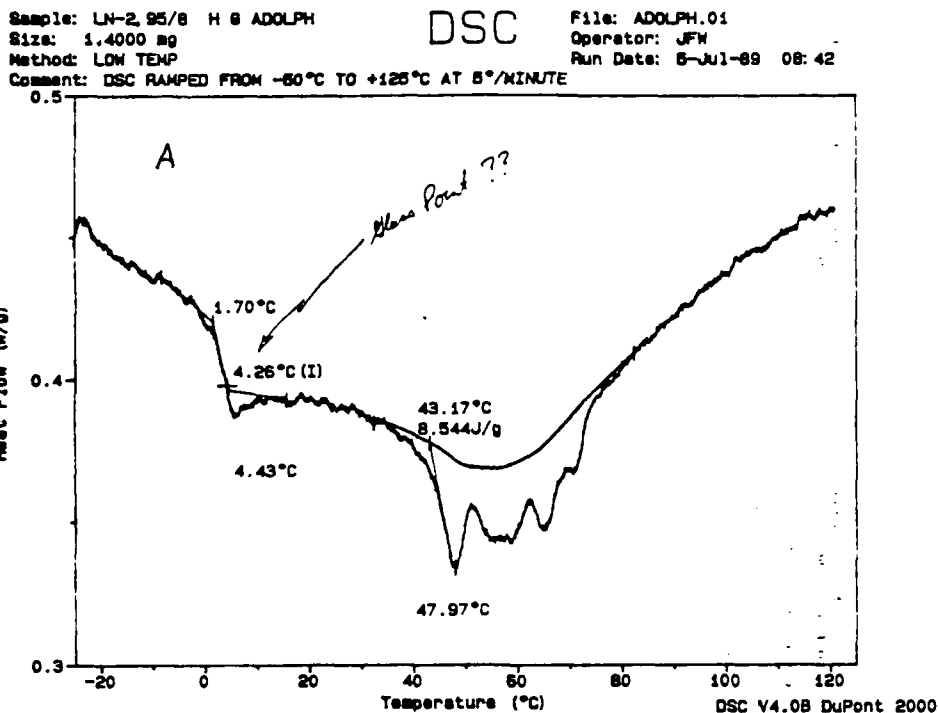
Fig. 18 DSC Traces for ABA Block Polymer from Poly($\underline{5}$ formal),
$\overline{M}_n$ 9000, and Isocyanate $\underline{13}$; (A) heating, (B) cooling
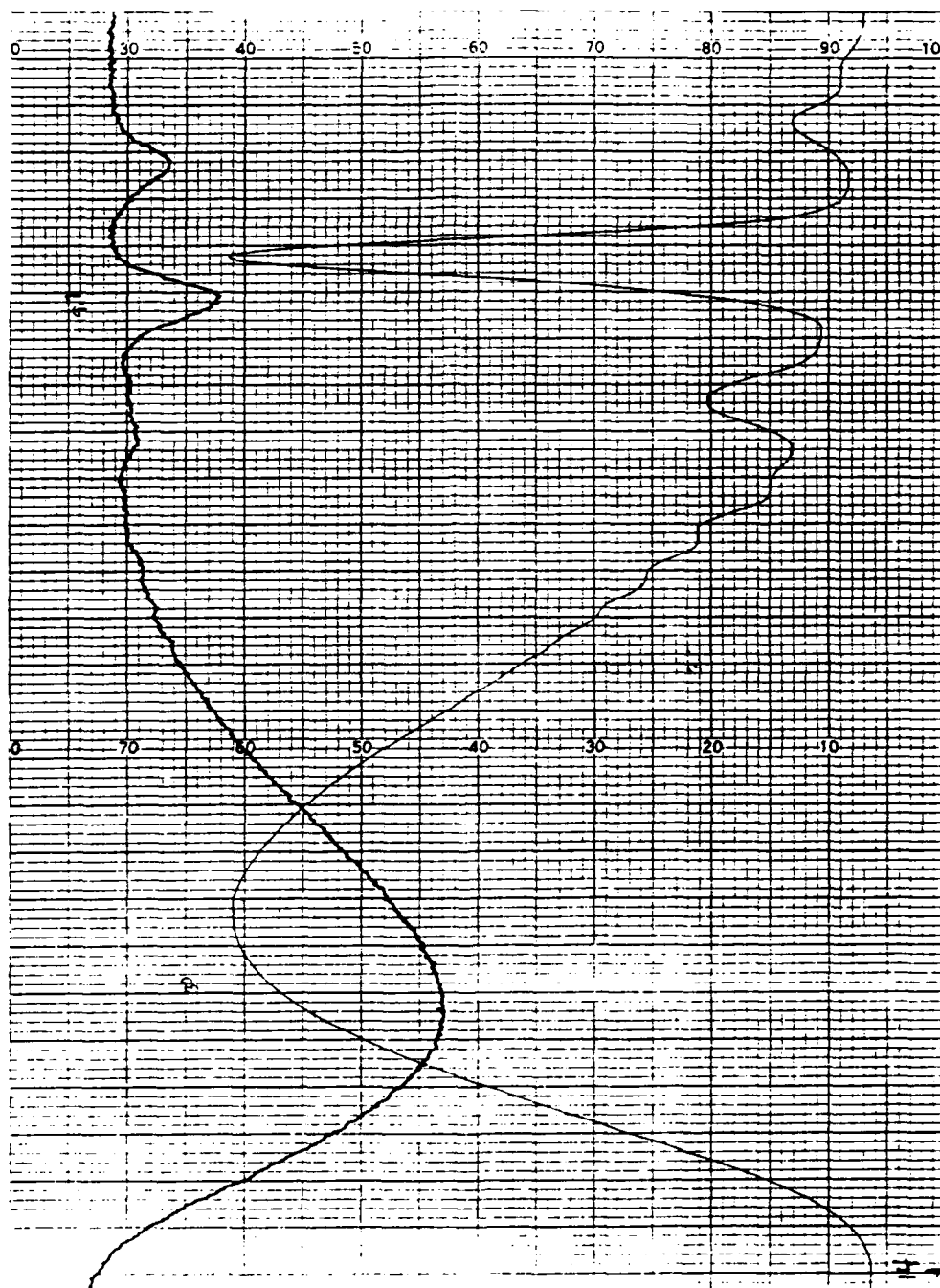
Fig. 19 GP Chromatogram of ABA Block Polymer from Poly(5 formal), $\bar{M}_n \simeq 7600$, and Isocyanate 13
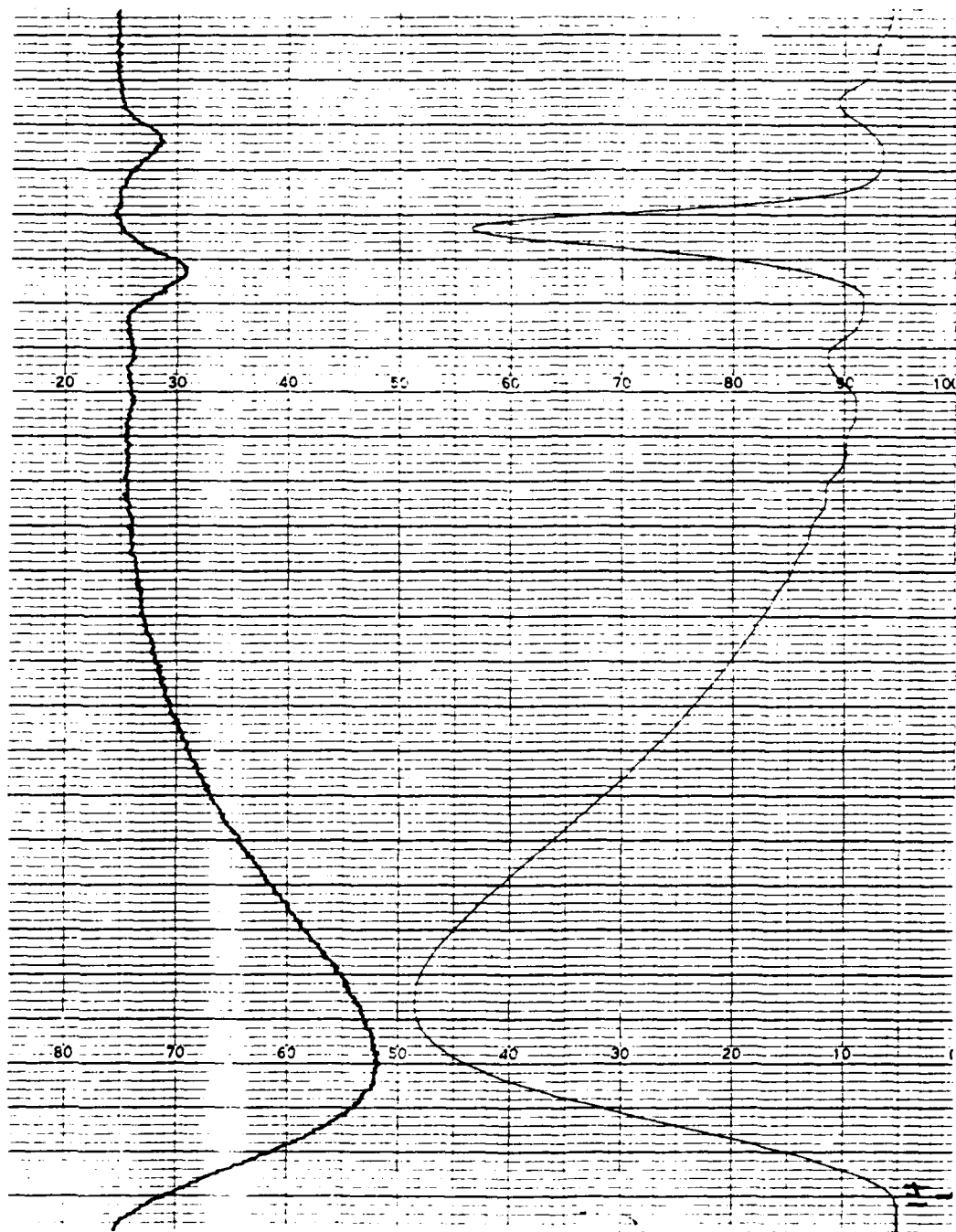
28

Fig. 20 GP Chromatogram of ABA Block Polymer from Poly($\underline{5}$ formal), $\bar{M}_n$ 7600, TDI, and Isocyanate $\underline{13}$

29

A

-5.89°C

45.34°C
8.408J/g

-2.26°C (I)

2.41°C

51.14°C

Temperature (°C)
DSC V4.08 DuPont 200(

COOLING CURVE   PEAK AT 44.05   IS FREEZING EXOTHERM

B

44.05°C

46.30°C
6.796J/g

5.80°C

3.27°C (I)

-3.34°C

Temperature (°C)
DSC V4.08 DuPont 200(
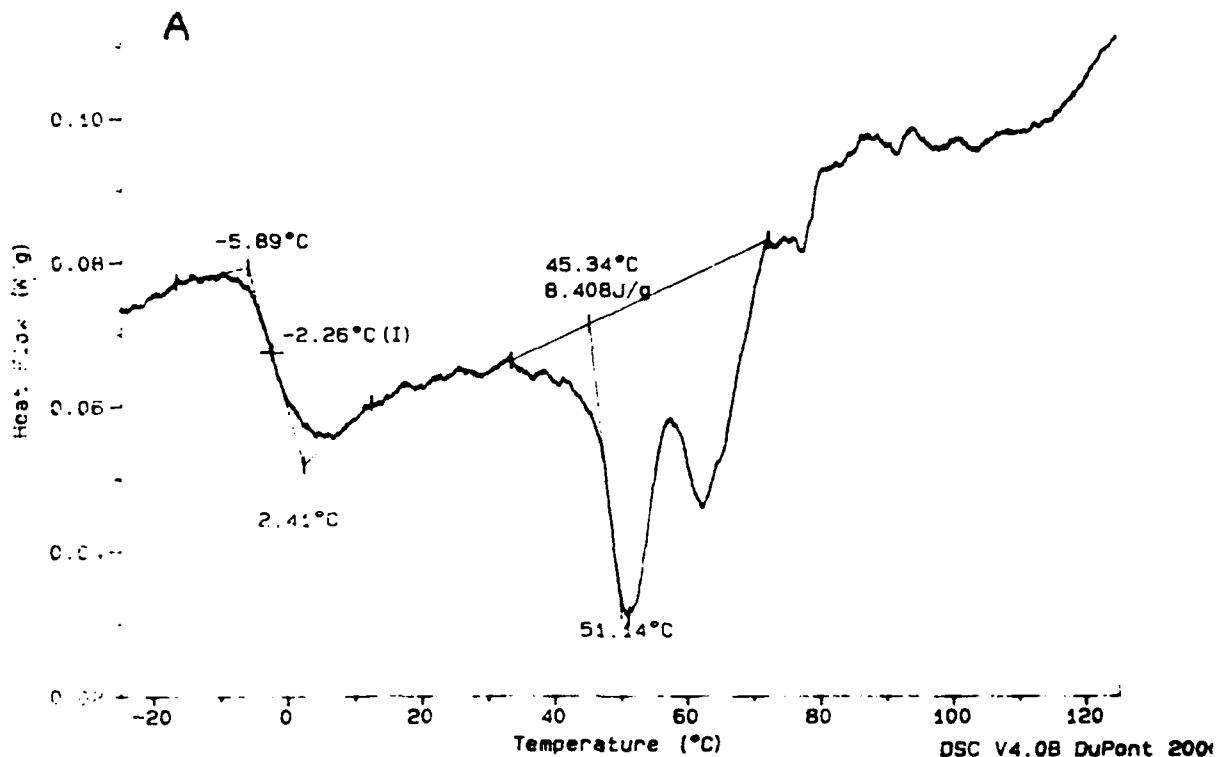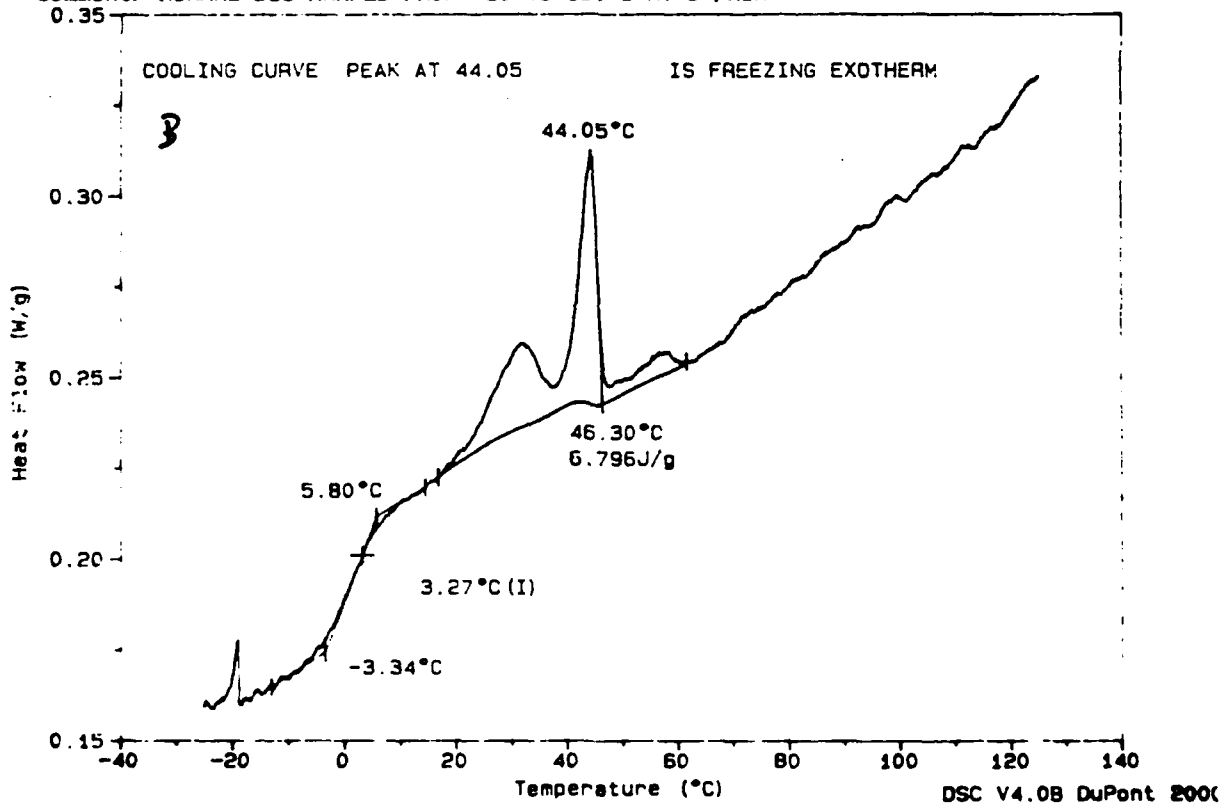
Fig. 21 DSC Traces for ABA Block Polymer from Poly(5 formal),
$\bar{M}_n$ 7600, TDI, and Isocyanate 13; (A) heating, (B) cooling
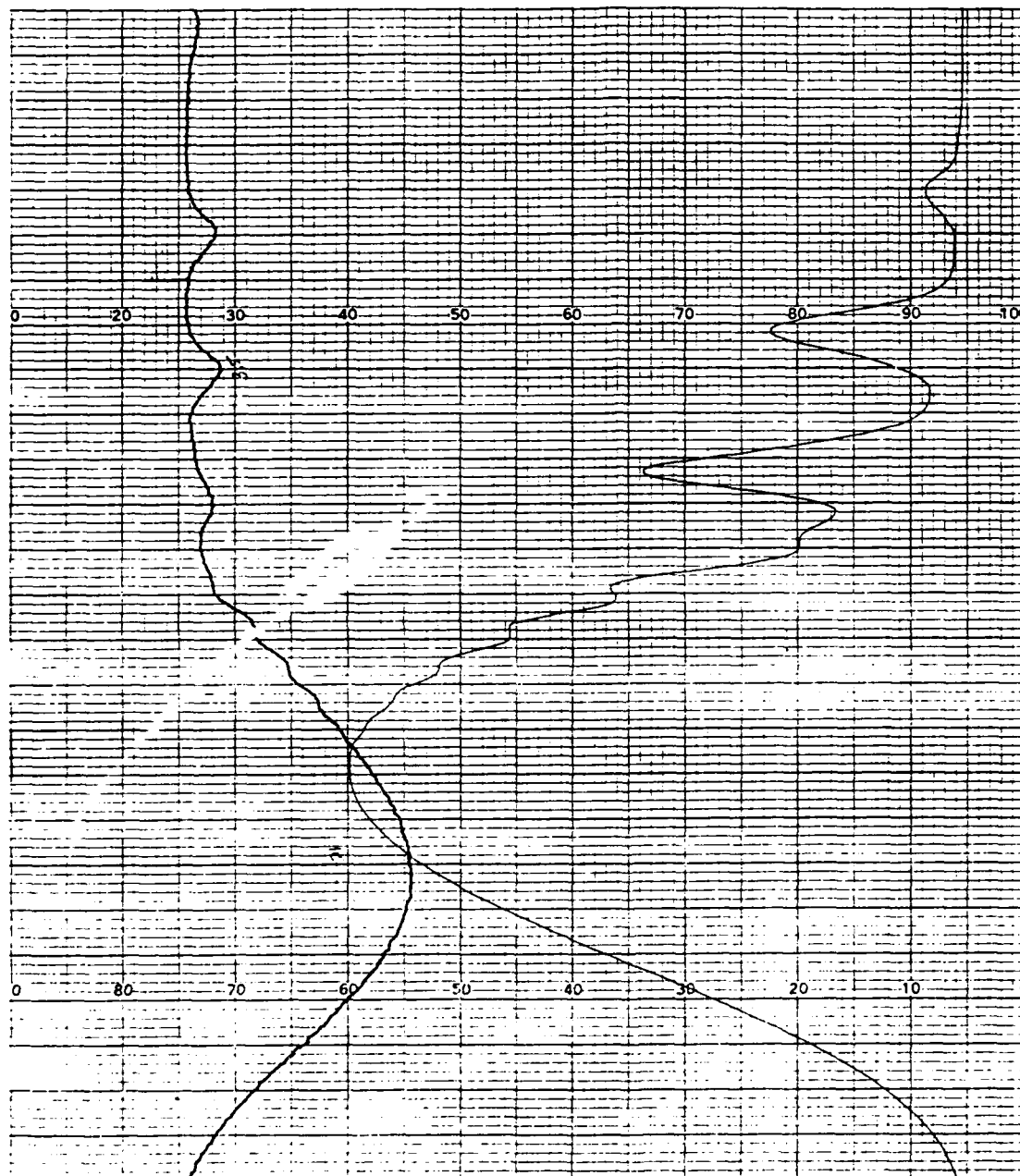
Fig. 22 GP Chromatogram of ABA Block Polymer from Poly(5 formal), $\overline{M}_n \simeq 4460$, and Isocyanate 13

31
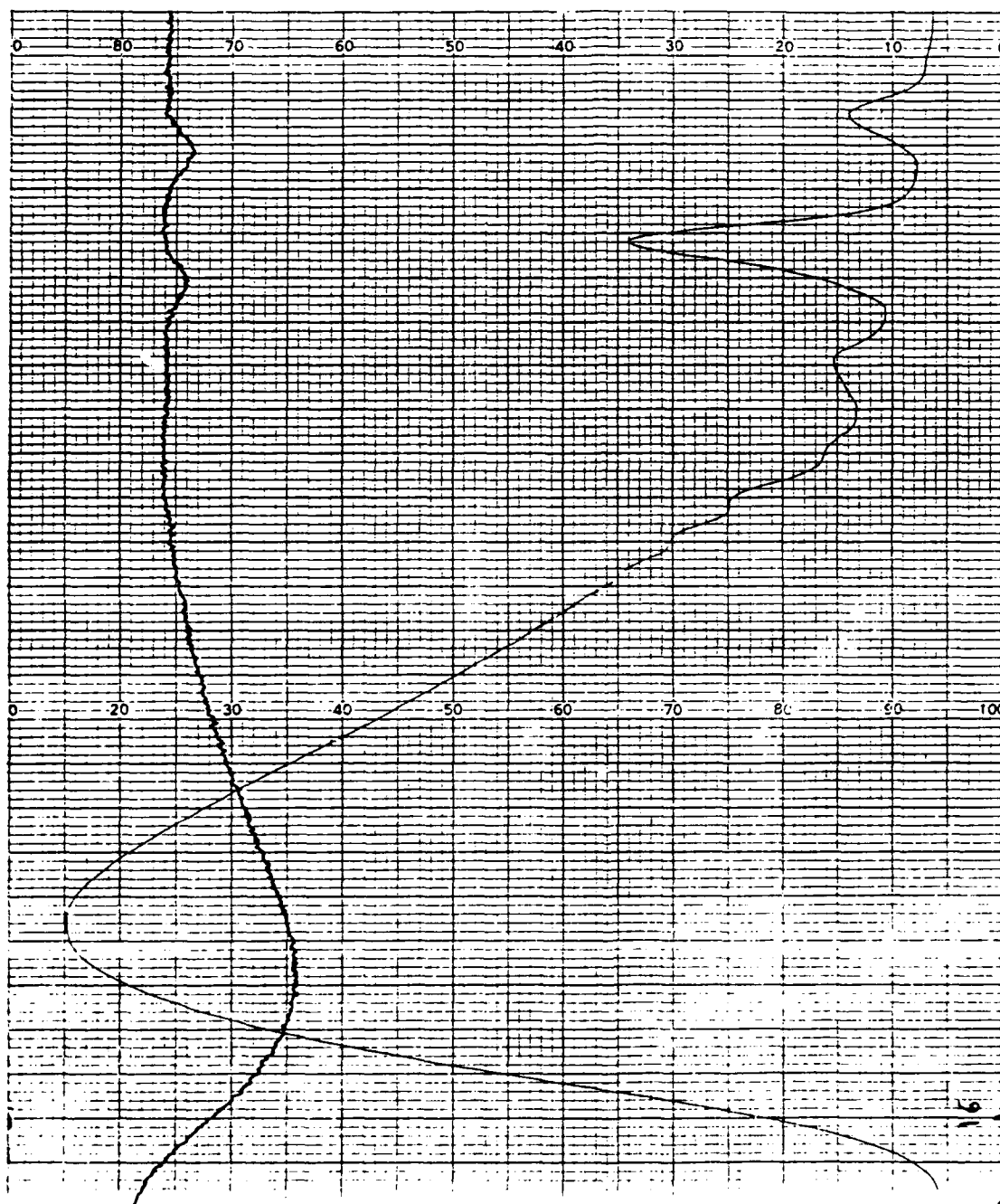
Fig. 23 GP Chromatogram of an ABA Block Polymer from Poly($\underline{5}$ formal), $\overline{M}_n \simeq 4460$, TDI, and Isocyanate $\underline{13}$ (10% $\underline{13}$)
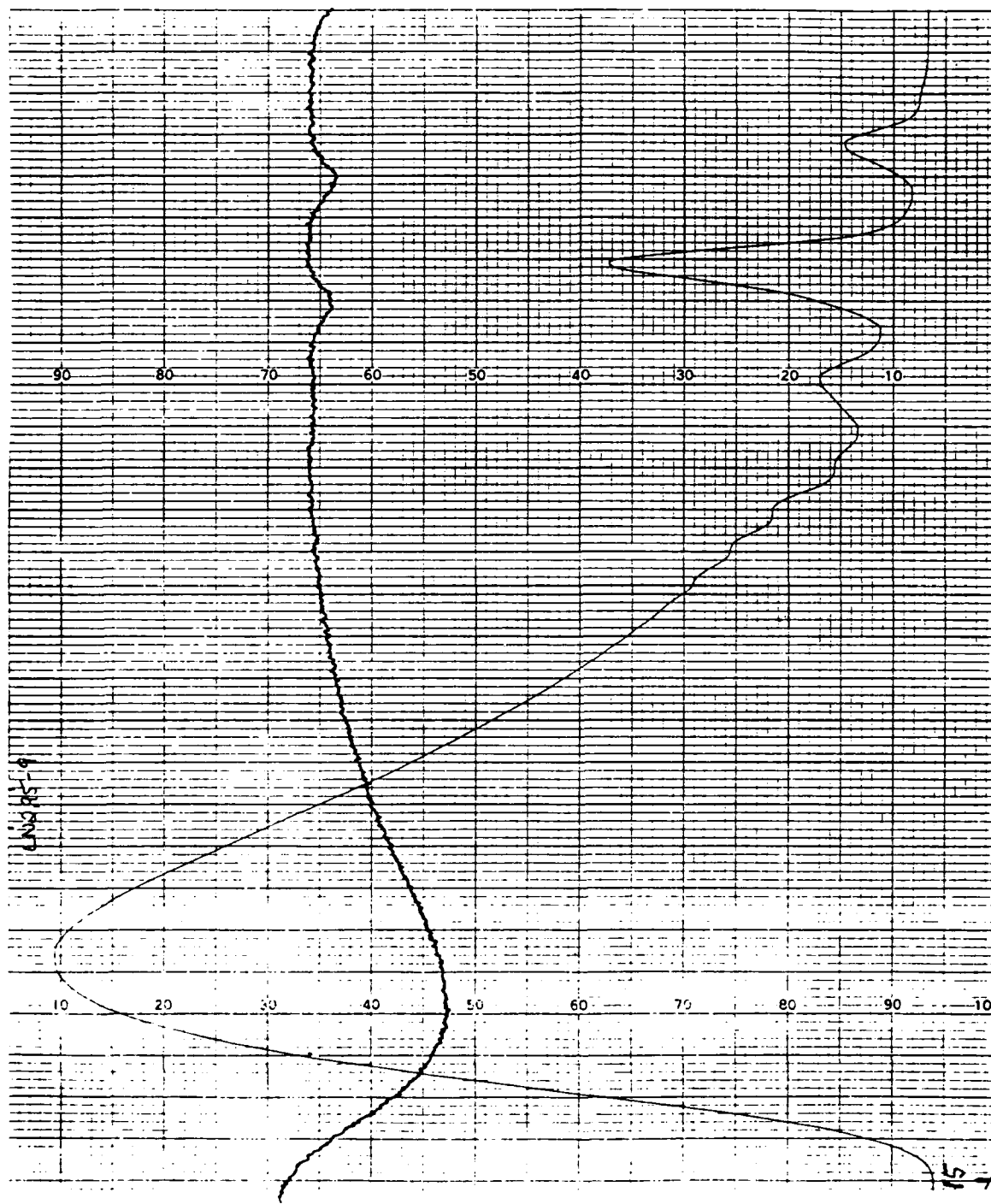
Fig. 24 GP Chromatogram of an ABA Block Polymer from Poly($\underline{5}$ formal), $\overline{M}_n \simeq 4460$, TDI, and Isocyanate 13 (8.5% $\underline{13}$)
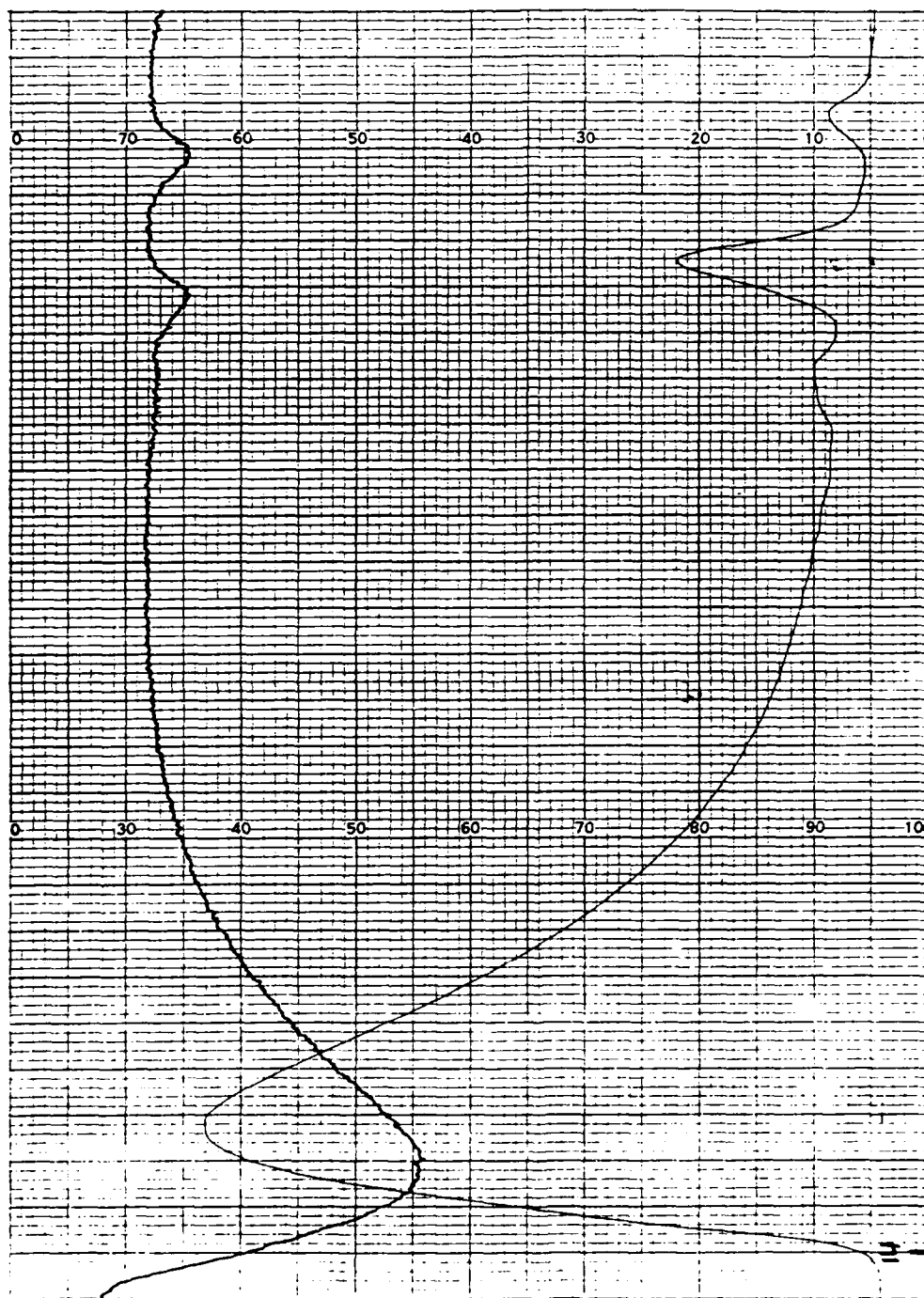
Fig. 25 GP Chromatogram of an ABA Block Polymer from Poly($\underline{5}$ formal), $\overline{M}_n \simeq 4460$, TDI, and Isocyanate $\underline{13}$ (5.4% $\underline{13}$)

Using analogous reaction conditions, 16 was reacted with the polyformal of 5 of M_n = 9000 (ratio 2:1) to give a soft resin which contained unreacted 16 by GPC. Further characterization is in progress.

In a similar fashion, PDT was reacted with TDI to the isocyanate 21. It was in turn reacted with the polyformal of 5 at 70° in sulfolane. The product, a soft, slightly elastomeric material which does not melt below 120°C, is currently being characterized.

$$PDT\text{-}O\overset{\overset{\displaystyle O}{\|}}{C}NH-\langle\bigcirc\rangle-CH_3$$

21   NCO
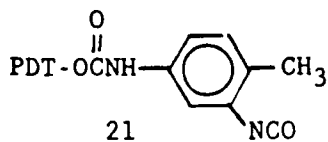
In order to assess possible effects of changes in the hard block structure on the ABA polymer properties, 5 polyformal ($M_n \simeq 7600$) was reacted with octadecyl isocyanate to the ABA polymer. This polymer (GPC, Fig. 26) was a resin with no elastomeric properties. Also, docosanoic azide (18) was heated in the presence of 5 polyformal to generate the isocyanate and the corresponding ABA polymer (22) (GPC, Fig. 27). This polymer was less elastomeric and softer than the corresponding polymer made with the docosanol/TDI adduct 13 as hard block. This indicates that the additional urethane groups in the polymer containing TDI contribute to its properties.

$$CH_3(CH_2)_{20}N H\overset{\overset{\displaystyle O}{\|}}{C}O\sim\sim\sim\sim 5\ Polyformal \sim\sim\sim\sim O\overset{\overset{\displaystyle O}{\|}}{C}NH(CH_2)_{20}CH_3$$

22
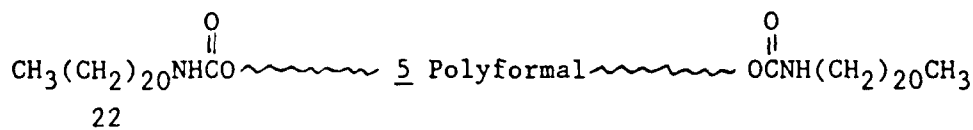
The hard blocks 13 and 16 were also reacted with the difunctional poly(AMMO) sample of OH equ. wt. 3125 obtained from Thiokol Corp. With 13, the product (GPC, Fig. 28) was initially waxy but on storage became somewhat elastomeric. The ^{1}H NMR spectrum (Fig. 29) indicates the presence of about 80% of the expected amount of docosyl groups in the polymer. With 16, reaction occurred also to give a polymer resin with no elastic properties. Characterization of this material is incomplete.

The above results indicate that a useful approach to prepare ABA block copolymers consisting of the linking of preformed hard and soft blocks has been identified. However, the properties of the polymers produced are not yet what is desired in terms of melt behavior, viscosity, and elasticity. It is believed that higher molecular weight hard and soft blocks are required to achieve acceptable properties. This will be the goal of our future research.

Polymer Characterization.- To further validate the new GPC method[2] to determine absolute number average molecular weight (M_n) and intrinsic viscosity using the differential viscometer, the M_n of several additional standard samples of varying chemical structure and molecular weights ranging from 10,000 to 200,000 were determined. The results which are presented below compare favorably with the expected values.

35
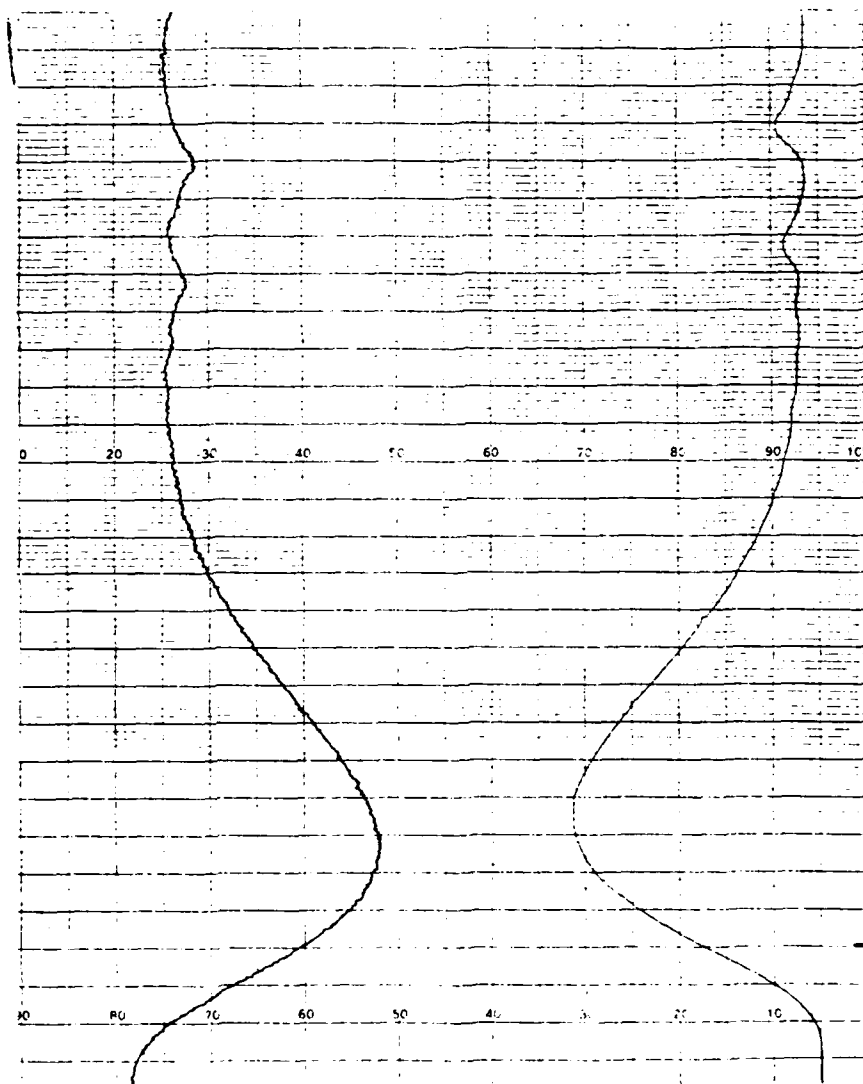
Fig. 26 GP Chromatogram of ABA Block Polymer from Poly($\underline{5}$ formal), $\bar{M}_n \cong 7600$, and Octadecyl Isocyanate

36
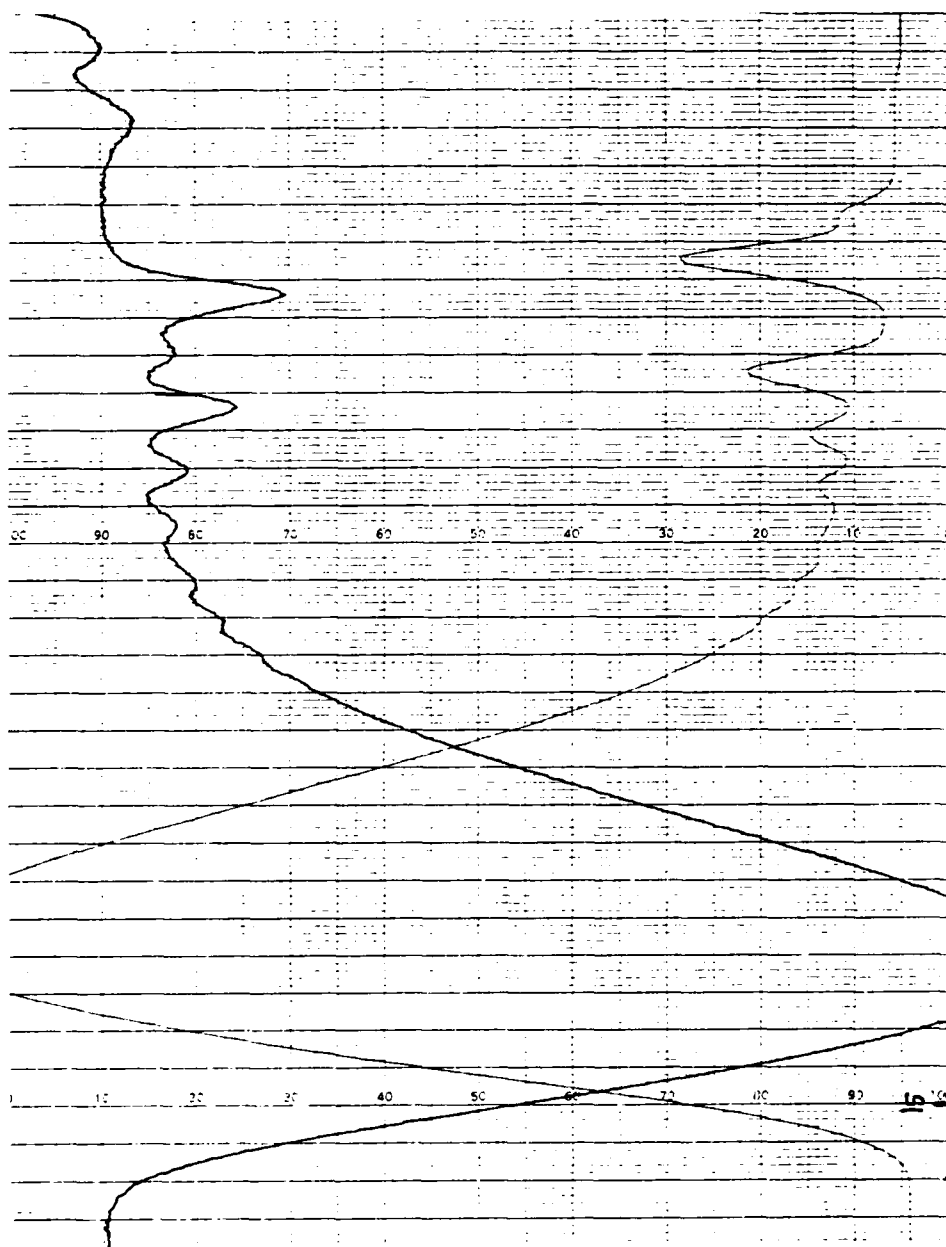
Fig. 27 GP Chromatogram of ABA Block Polymer from Poly($\underline{5}$ formal), $\overline{M}_n \simeq 7600$, and Heneicosyl Isocyanate

37
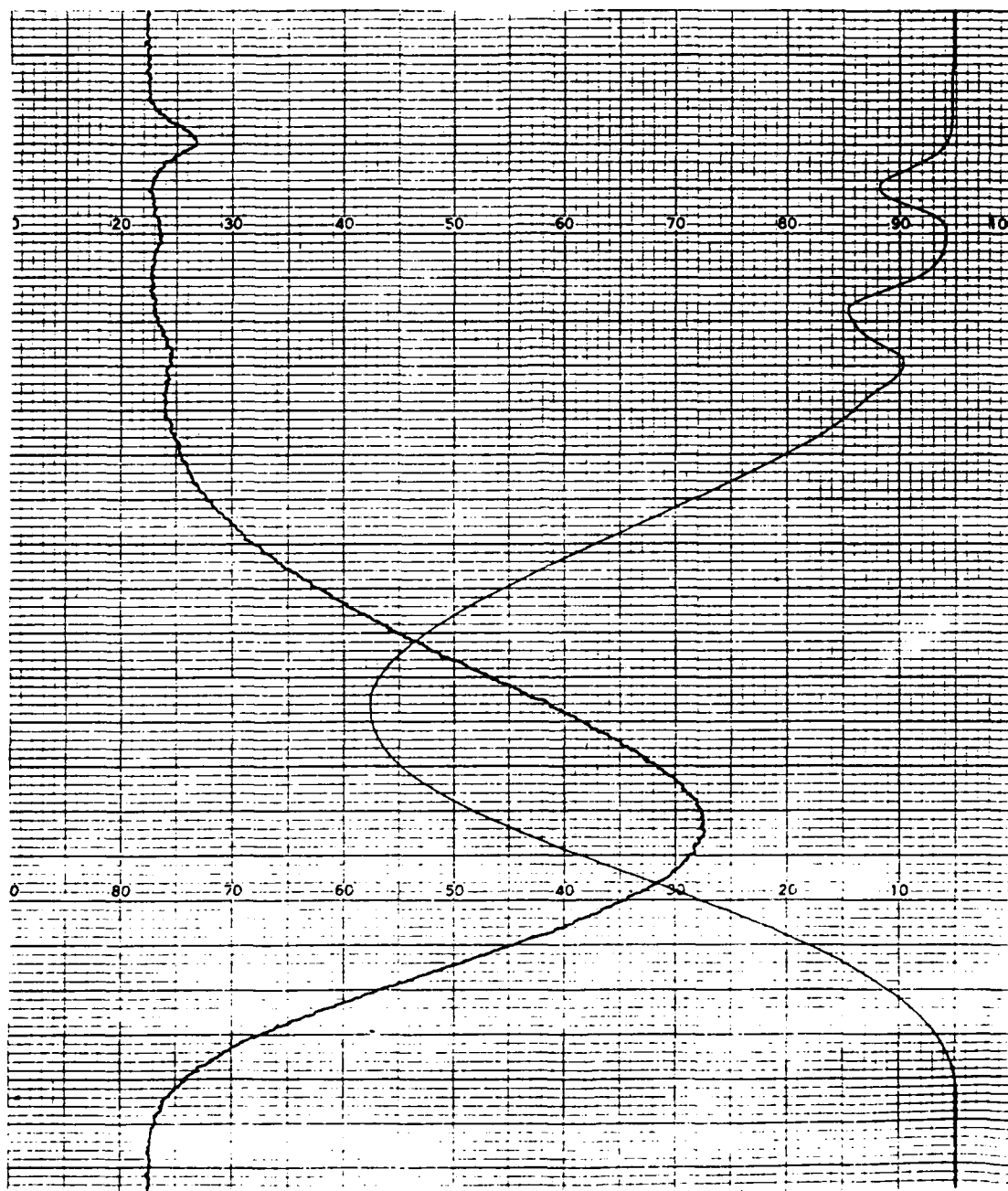
Fig. 28 GP Chromatogram of Product from Poly(AMMO) and 13
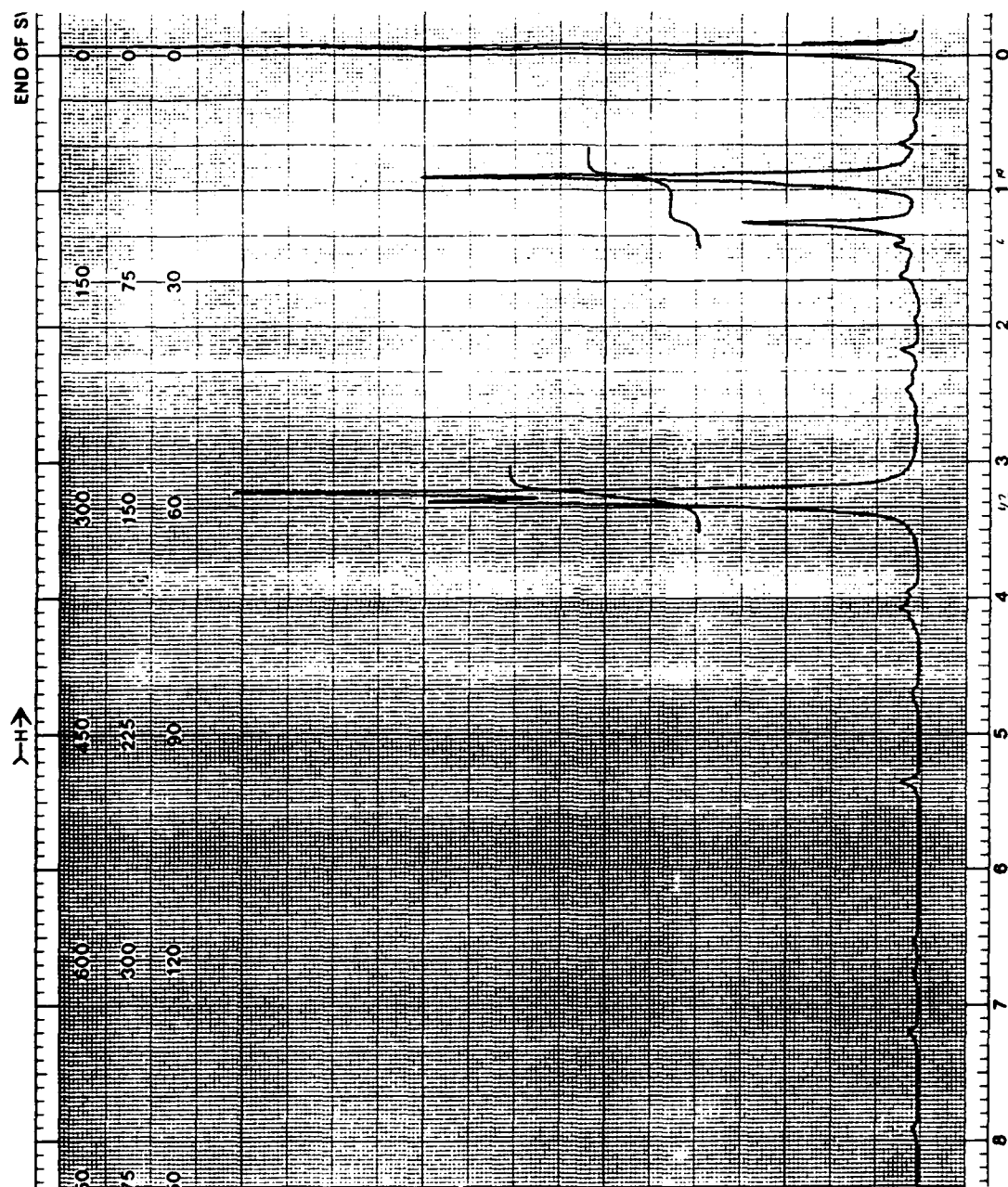
Fig. 29 ^{1}H NMR Spectrum of Product from Poly(AMMO) and 13

39

Table 4. Comparison of Reported and Measured Molecular Weights for Some Standard Polymer Samples

Polymer	Sample	$\overline{M}_n$ reported	$\overline{M}_n$ measured	$[\eta]$ (mL/g)
polystyrene	PS-ALD	119,500	123,000	83.0
	PS-NBS	136,500	133,000	86.0
PMMA	PMMA-ALD	46,400	52,700	31.5
	PMMA-PSc1	63,000	66,897	44.3
	PMMA-PSc2	166,500	167,933	90.6
poly(butadiene)	PBD-PSc	139,500	138,428	219.0

In addition, the $\overline{M}_n$s of several mixtures of polystyrene, PMMA, poly(vinyl acetate), and poly(butadiene) were measured and compared with expected values. The results are presented in Table 5.

Table 5. Comparison of Calculated and Measured Molecular Weights for Some Polymer Mixtures[*]

Polymer	Ratios	$\overline{M}_n$ expected	$\overline{M}_n$ measured	$[\eta]$ (mL/g) expected	$[\eta]$ (mL/g) measured
PS	homopolymer	137,000		86.0	
PMMA	homopolymer	46,400		31.5	
PVAC	homopolymer	89,900		68.5	
PBD	homopolymer	139,500		225.0	
PS:PMMA	70:30	85,400	86,500	72.3	68.1
	30:70	57,100	59,700	48.0	49.0
PS:PVAC	50:50	108,000	112,000	79.1	78.7
PMMA:PVAC	50:50	61,300	62,800	49.6	48.4
PS:PBD	50:50	137,000	144,000	157.0	148.0

[*]PS is polystyrene, PMMA is poly(methyl methacrylate), PVAC is poly(vinyl acetate), and PBD is poly(butadiene). $\overline{M}_n$s of the homopolymer samples were supplied by the vendor.

The demonstrated ability to accurately measure the $\overline{M}_n$s and the intrinsic viscosities of polymer mixtures with differing chemical compositions, ratios, and molecular weight distributions confirms the universal application of the method. As a result, it is now possible to accurately determine the absolute $\overline{M}_n$ and intrinsic viscosity of any polymer, copolymer, polymer blend or mixture. Mark-Houwink constants, chemical structure, chemical composition, and dn/dc values are not needed.

40

EXPERIMENTAL SECTION

Melting points are uncorrected. Temperatures are in $^\circ$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 in ppm relative to TMS internal standard. Silica gel was EM Kieselgel 60, 70-230 mesh, throughout.

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.

Some GPC experiments, and measurements of intrinsic viscosities using the newly developed methods, were carried out using a Waters model 6000A solvent delivery system connected to a Molytek Thermalpulse II flowmeter, and a Waters U6K manual injector. The detector used was a Viscotek model 100 Differential viscometer. The eluant was unstabilized tetrahydrofuran. The flow rate was nominally 1 mL/min. Intrinsic viscosities were determined both with GPC columns connected and without columns connected. GPCs were carried out using Toyo Soda, TSK, H series columns which were 30 cm in length. For polymers whose M_n were below 5000, three columns, each with packing pore size of 1500 A (TSK-3000H) were used. For polymers whose M_n were above 5000, four columns with packing pore sizes of 1500 A (TSK-3000H), 10^4 A (TSK-4000H), 10^5 A (TSK-5000H), and 10^6 A (TSK-6000H), respectively, were used.

Data were collected using an IBM PC/AT microcomputer equipped with a Data Translation DT-22805 data acquisition board, and an 80287 math coprocessor chip. The data collection and data reduction software was written in-house using the ASYST version 2.10 scientific programming language. Number average molecular weights were determined using the new algorithm described earlier.[2]

Poly(2,2,9,9-tetranitro-4,4,5,5,6,6,7,7-octafluorodecane-1,10-diol formal).- Under a N_2 atmosphere, .890 g of diol 1 (1.79 mmol) was stirred with 2.8 mL of dry sulfolane (4A sieves) and .46 mL of BF_3 etherate until homogeneous. A solution of .054g of trioxane (1.8 mmol) in .5 mL of dry CH_2Cl_2 (4A sieves) was added and the mixture was stirred at 22°C for -20 hrs. The reaction was quenched with 20 mL of water and stirred, after addition of 20 ml of ether, for 1 hr. The organic phase was separated and evaporated at 30°C/20 Torr.

The crude polymer was triturated with water at $40^{\circ}C$, adding a few mL of CH_2Cl_2 when necessary for stirring, until no sulfolane could be detected in the ^1H NMR spectrum. The polymer was dissolved in ether, the solution was stirred overnight with -.25 g of silica gel, filtered, and stripped at $40^{\circ}C/20$ Torr. The polymer had a M_n - 1000 with a yield of 82%.

Poly(2,2,11,11-tetranitro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-1,12-diol formal).- Under a N_2 atmosphere, .98 g of diol 2 (1.6 mmol) was stirred with 2.0 mL of dry sulfolane (4A sieves) and .39 mL of BF_3 etherate until homogeneous. A solution of .05 g of trioxane (1.6 mmol) in .5 mL of dry CH_2Cl_2 (4A sieves) was added and the mixture was stirred at $22^{\circ}C$ for -20 hrs. The reaction mixture was quenched with 20 mL of water and 20 mL of CH_2Cl_2 and was stirred for 1 hr. The organic phase was separated and evaporated at $60^{\circ}C/20$ Torr. The crude polymer was triturated with water at $40^{\circ}C$, adding a few mL of CH_2Cl_2 when necessary for stirring, until no sulfolane could be detected in the ^1H NMR spectrum. The polymer was redissolved in CH_2Cl_2, the solution was stirred overnight with -.25 g of silica gel, filtered, and stripped ($60^{\circ}C/20$ Torr). The polymer had a M_n - 1500 with a yield of 73%.

Polyformal of Diol 3 (Fluorochem C_7F_{14} Diol).- To a solution of 5.00 g of diol 3 (11.4 mmol) and .341 g of trioxane (11.4 mmol) in 6.60 mL of dry sulfolane (4A sieves), under a N_2 atmosphere, was added .706 mL of $SnCl_4$. The reaction mixture was stirred for 2-3 min. until gelation occured; then the reaction was stored at room temperature for 24 hrs. The gel was broken up with a spatula, dissolved in 75 mL of ether, and stirred with 75 mL of water for 1 hr. The organic phase was separated and evaporated at $35^{\circ}C/20$ Torr. The crude polymer was dissolved in THF and the solution dripped into 250 mL of vigorously stirred water at -50°C. The polymer precipitaced, while the THF was evaporated by means of an air stream. The water was decanted and the precipitated polymer was rinsed with fresh water. The sulfolane-free polymer was redissolved in 50 mL of ether and stirred with 50 mL of .1N H_2SO_2 and 3 mL of 30% H_2O_2 for 3 hrs. The organic phase was separated, stirred with 50 mL of 1% KOH and 1.5 mL of 30% H_2O_2 for 3 hrs, separated, and washed with brine. The ether layer was then stirred with 15 mL of $MgSO_4$ for -3 hrs, filtered, and stirred overnight with 10 mL of silica gel. The silica gel was filtered off and the solvent was removed by heating at $20-65^{\circ}C/20$ Torr. The polymer had an estimated M_n of 8-9000 with a yield of 88%.

Polyformal of Diol 4 (Fluorochem $C_{13}F_{26}$ Diol).- To a solution of 1.00 g of diol 4 (1.35 mmol) and .040 g of trioxane (1.33 mmol) in 1.5 mL of dry sulfolane (4A sieves) under a N_2 atmosphere was added .32 mL of BF_3 etherate. The mixture was stirred at $22^{\circ}C$ for 24 hrs. The polymer precipitated out of solution and was deposited on the sides of the flask. The liquid was decanted and the flask was rinsed with water. The polymer was dissolved in THF and dripped into 100 mL of vigorously stirred water at $60^{\circ}C$. The THF was evaporated in an air stream. The water was decanted and the remaining polymer was dried under vacuum (1 Torr) at $50^{\circ}C$ over P_2O_5. The polymer had an estimated M_n of 8000.

Scale up (60g batch) of Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal).- Under a N_2 atmosphere, 57.60 g of diol 5 (.144 mol) and 4.40 g of

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trioxane (.147 mol) was dissolved in 48 mL of dry sulfolane (4A sieves) and 4.5 mL of dry CH_2Cl_2 (4A sieves). To the solution , cooled to 18-20°C, was added 8.48 mL of $SnCl_4$. The mixture was stirred at 20-22°C for 20-24 hrs, then quenched with 600 mL of water and 520 mL of CH_2Cl_2 and stirred for 1 hr. The organic phase was separated and stirred with 600 mL of .1N H_2SO_4 and 28 mL of 30% H_2O_2 for 3 hrs, separated, then stirred with 600 mL of 1% KOH and 15 mL of 30% H_2O_2 for 3 hrs. The organic phase was separated and washed with 600 mL of brine, stirred with 45 mL $MgSO_4$ for .5 hr, filtered, and evaporated at 45°C/20 Torr. The remaining liquid was triturated with 350 mL portions of water to remove most of the sulfolane. The crude polymer was dissolved in a minimum amount of CH_2Cl_2 and loaded onto a silica gel column. The residual sulfolane, cyclic materials, and some low molecular weight materials were eluted with CH_2Cl_2. Lastly, the polymer was eluted with 30/70 THF/CH_2Cl_2. The polymer solution was stirred with 30 mL of silica gel for 48 hrs, filtered, and stripped (60°C/1 Torr). The polymer yield was ~70% with an estimated $\underline{M}_n$ of 8000.

Poly(hexane-1,6-diol azidoacetal).- A mixture of 1.59 g (10 mmol) of diethylazidoacetal, 1.18 g of hexane-1,6-diol (10 mmol), and 3 drops of BF_3 etherate was stirred at room temperature for 24 hr, then heated to 60°C for 24 hr with intermittent application of aspirator vacuum to remove ethanol formed. The mixture was cooled in ice water, and 0.1 mL of BF_3 etherate was added dropwise. Then, heating at 60°C and intermittent application of vacuum was continued for 2 days. The polymer was cooled, diluted with dichloromethane, the solution washed with water, and dried ($MgSO_4$). The solvent was removed under vacuum. The product was a resin at room temperature.

Poly(3,5,5,11,11,13-hexanitro-3,13-diaza-7,9-dioxapentadecane-1,15-diol formal-co-hexane-1,6-diol formal), Monomer Ratio 7:3.- Under a N_2 atmosphere, 2.128 g of diol $\underline{6}$ (4.092 mmol), .207 g of diol $\underline{8}$ (1.75 mmol), and .175 g of trioxane (5.83 mmol) were dissolved in 2.0 mL of dry sulfolane (4A sieves) and 1.0 mL of dry CH_2Cl_2 (4A sieves) with slight warming. The mixture was cooled to 18-20°C and .35 mL of $SnCl_4$ was added. The mixture was stirred overnight at 22°C for 20-24 hrs, then was quenched with 20 mL of water and 15 mL of CH_2Cl_2 and was stirred for 2 hrs. The organic phase was separated, stripped (60°C/20 Torr), and triturated with water until no sulfolane could be detected in the ^{1}H NMR spectrum. The copolymer was redissolved in CH_2Cl_2 and stirred with 5 mL of silica gel overnight, filtered, and stripped at 55°C/20 Torr. The copolymer had an estimated $\underline{M}_n$ of 2400.

Poly(3,5,5,11,11,13-hexanitro-3,13-diaza-7,9-dioxapentadecane-1,15-diol formal-co-butane-1,4-diol formal), Monomer Ratio 7:30.- Under a N_2 atmosphere, 2.128 g of diol $\underline{6}$ (4.092 mmol), .169 g of diol $\underline{9}$ (1.89 mmol), and .176 g of trioxane (5.87 mmol) were dissolved in 3.0 mL of dry sulfolane (4A sieves). The mixture was cooled in an ice bath and .6 mL of BF_3 etherate was added. After stirring for 20-24 hrs at 20°C, the reaction was quenched with 30 mL of water and 25 mL of CH_2Cl_2 and was stirred for 1 hr. The organic phase was separated and washed with 25 mL of brine. The solvents were evaporated (50°C/20 Torr) and the remaining liquid was triturated with water until no sulfolane could be detected in the ^{1}H NMR spectrum. The sulfolane-

free copolymer was redissolved in CH_2Cl_2, the solution stirred overnight with 5 mL of silica gel, filtered, and stripped (55°C/20 Torr). The resulting copolymer had an estimated M_n of 1500.

4,7-Dinitro-4,7-diazadecanedioyl azide.- CAUTION: Acyl azides are sensitive explosives and must be handled with appropriate care. A mixture of 10 g of 4,7-dinitro-4,7-diazadecanedioc acid (34.0 mmol) and 60 mL of thionyl chloride was slowly heated to 60°C and stirred for 24 hrs. The reaction was cooled to room temperature. The pale yellow solution was further cooled in a dry ice/acetone bath and hexanes were added to precipitate the acid chloride. The solid was collected by suction filtration and washed with hexanes. The crude material was recrystallized from dry CH_2Cl_2 (4A sieves), dried under vacuum, and stored over P_2O_5. 2.0 g of the acid chloride was again recrystallized in CH_2Cl_2 under a N_2 atmosphere, dried under vacuum, and then, under a N_2 atmosphere, dissolved in -30 mL of dry CH_3CN (4A sieves). The solution was cooled in an ice bath, 2.0 mL of trimethylsilyl azide was added, the cooling was removed, and the mixture was stirred overnight at 20°C. The CH_3CN was evaporated without heating at 20 Torr to leave an oil which began to crystallize on standing or when seeded. (Seed crystals were obtained by evaporating a small aliquot of the CH_3CN solution and inducing the residual oil to crystallization by scratching) CCl_4 was slowly added and crystallization continued overnight at 0°C. The white solid was collected by suction filtration and washed with a small amount of cold isopropyl ether. The acyl azide was dried under vacuum over P_2O_5 and stored at 5°C. The melting point was 79-81°C

3,6-Dinitro-3,6-diazaoctane-1,8-diol bis(chlorocarbonate), pyridine adduct (11).- Under a N_2 atmosphere, 5.1 g of triphosgene (17.3 mmol) were dissolved in 19 mL of dry CH_2Cl_2 (4A sieves). Added were 4.5 g of 3,6-dinitro-3,6-diazaoctane-1,8-diol followed by an additional 10 mL of dry CH_2Cl_2 (4A sieves). The mixture was stirred for 10 min., but the diol remained mostly undissolved. The mixture was cooled in an ice bath to -5°C and a solution of 4.2 mL of pyridine (52.0 mmol) in 20 mL of dry CH_2Cl_2 (4A sieves) was slowly dripped in over a 45 min. period. When 70-80% of the pyridine solution had been added, the diol was dissolved; then a new precipitate began forming. The reaction was allowed to warm to room temperature and 15 mL of anhydrous hexane was added. The solid was filtered, washed with four 30 mL portions of 50/50 CH_2Cl_2/hexane, and dried under vacuum over P_2O_5. The melting point was 77°C.

1:1 Adduct of Docosanol and Toluene-2,4-diisocyanate (13).- Under a N_2 atmosphere, 5.00 g of docosanol (15.3 mmol) were dissolved in -25 mL of dry dichloroethane (4A sieves) at 65°C. After the addition of 6.55 mL of TDI (46.1 mmol) and -50 μL of dibutyltin dilaurate, the mixture was stirred for 48 hrs. The reaction was cooled to room temperature and then further cooled in an ice bath. The solid was collected by suction under a blanket of N_2 and was washed several times with dry, chilled dichloroethane. The product was dried under vacuum over P_2O_5. MP - 84-85°C.

Reaction of Docosanol/TDI adduct 13 with methanol and with 4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol.- 1. A small amount of 13 was dissolved in a few mL of dry CH_2Cl_2 (4A sieves) under a N_2 atmosphere. After

the addition of ~1 mL of methanol and 2-3 μL of dibutyltin dilaurate, the mixture was warmed to 30°C and stirred overnight. The solvents were evaporated to yield a white solid (14) with a mp of 94-96°C.

2. Under a N_2 atmosphere, .40 g of isocyanate 13 (.80 mmol) and .16 g of diol 5 (.40 mmol) were dissolved in 3 mL of dry dichloroethane (4A sieves) at 50°C. Added were ~5 μl of dibutyltin dilaurate and the mixture was stirred for 24 hrs. The temperature was decreased to 35°C, 1 mL of methanol was added, and stirring was continued for 3-4 hrs. The reaction was cooled in an ice bath and the solid was collected by suction filtration and washed with cold dichloroethane. Obtained was a white solid (15) with a melting point of 117-119°C.

1:1 Adduct of 1H,11H,11H-eicosafluoroundecanol and Toluene-2,4-diisocyanate, (16).- 2.0g of alcohol (3.77 mmol) were dissolved in 10 mL of dry dichloroethane (4A sieves) at 65-70°C under a N_2 atmosphere. After addition of 1.60 mL of TDI (11.2 mmol) and ~15 μL of dibutyltin dilaurate, the reaction mixture was stirred for 24 hrs. The heating was removed and the reaction was allowed to cool to room temperature. The reaction mixture was further cooled in an ice bath and the white solid was collected by suction filtration under a N_2 blanket. The solid was washed several times with chilled dichloroethane, then dried under vacuum (1 Torr) over P_2O_5. The product (16) had a melting point of 94°C.

The functionality of the adduct was determined by ^{1}H NMR after reacting the isocyanate with methanol. A small amount of the isocyanate was dissolved in dry dichloroethane (4A sieves) at 35-40°C. After the addition of ~.5 mL of methanol and 1-2 μL of dibutyltin dilaurate, the mixture was stirred overnight, then stripped (65°C/20 Torr). Obtained was a white solid (17) with a melting point of 115°C.

Heneicosoyl azide (18).- Thionyl chloride (5 mL) was added to 0.75 g (2.202 mmol) of dosocanoic acid and the mixture was heated to reflux for 3.75 hr. The mixture was allowed to cool and excess thionyl chloride was removed under vacuum. Dichloromethane (5 mL) was added, the mixture was warmed to 35 mL to facilitate dissolution of the acid chloride, and was then returned to room temperature. Trimethylsilyl azide (0.279 g, 2.422 mmol) was added and the mixture stirred at 30° for 66 hr. Evaporation of volatiles at $\leq$25°C gave 0.862 g of a cream colored powder, whose [1]H NMR spectrum indicated the presence of some unreacted acid chloride. Filtration of a dichloromethane solution through a column of silica gel (Kieselgel 60, EM) gave a fraction of 0.126 g of pure 18. [1]H NMR ($CDCl_3$): δ 0.90 (s, 3), 1.37 (m, 40), 3.35 (t, 2) ppm.

Chain Extension of Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal) with Diisocyanates.- A mixture of 2.24g of the poly(5 formal), M_n = 4460, (0.502 mmol) and .09g of cubanediisocyanate (0.5 mmol) were dissolved in 6 mL of dry dichloroethane (4A sieves) under a N_2 atmosphere. 1-2 μL of dibutyltin dilaurate was added and the mixture was heated to 35°C and stirred 20-24 hrs. After the addition of 1 mL of methanol, the stirring was continued for ~16 hrs. The solvents were evaporated at 60°C/20 Torr.

The following (AB)N block copolymers listed in Table 1 were prepared by the same procedure:

poly($\underline{5}$ formal) ($\bar{M}_n$ — 7600)/cubanediisocyanate
poly($\underline{5}$ formal) ($\bar{M}_n$ — 4500)/IPDI
poly($\underline{5}$ formal) ($\bar{M}_n$ — 7600)/IPDI
poly($\underline{5}$ formal) ($\bar{M}_n$ — 7600)/HMDI

<u>Chain Extension of Poly(AMMO) with Toluene-2,4-diisocyanate.</u>- A solution of 1.030 g of poly(AMMO), M_n — 6250, (0.1648 mmol) in 3.5 mL of dry dichloroethane (4A sieves) under a N_2 blanket was heated to $35^\circ C$. TDI (.027 mL, 0.19 mmol) and 3 μL of dibutyltin dilaurate were added and the mixture was stirred for 24 hrs. After the addition of 1 mL of methanol, stirring was continued overnight. The solvents were evaporated at $60^\circ C$/20 Torr.

<u>Endcapping of Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal) with Toluene-2,4-diisocyanate.</u>- Under a N_2 atmosphere, 1.530 g of poly($\underline{5}$ formal), M_n — 6250, (0.245 mmol) were dissolved in 4.0 mL of dry dichloroethane (4A sieves). After the addition of .104 mL of TDI (0.731 mmol) and 2 μL of dibutyltin dilaurate, the mixture was heated to $35^\circ C$ and stirred overnight. The reaction mixture was cooled to room temperature and triturated with 10 mL of anhydrous hexane, keeping a N_2 blanket over the material at all times. To remove any residual unreacted TDI, the viscous resin was triturated 4 times with 8 mL portions of anhydrous hexane, adding 1-2 mL of dry dichloroethane (4A sieves) when necessary for stirring. The isocyanate endcapped resin was stored under N_2.

The functionality of the above product was determined by ^{1}H NMR after reacting it with methanol: to a mixture of 3 mL of dry CH_3CN (4A sieves), .1 mL of methanol, and ~2 μL of dibutyltin dilaurate at $35^\circ C$, was added a small amount of the TDI endcapped polymer. The mixture was stirred overnight 20-24 hrs, then stripped at $60^\circ C$/20 Torr.

<u>ABA Block Copolymer by Reaction of TDI-endcapped Poly(5 formal) with 1-Docosanol.</u>- A solution of .515 g of TDI-endcapped poly($\underline{5}$ formal) (0.078 mmol) in 5 mL of dry CH_3CN (4A sieves) was prepared under a N_2 atmosphere as described above. The solution was heated to $65-70^\circ C$ and .056 g of 1-dosocanol (0.17 mmol) and 1-2 μL of dibutyltin dilaurate were added. The mixture was stirred for 3-4 days, then cooled to $35^\circ C$. Approximately 1 mL of methanol was added and stirring was continued overnight. The solvents were evaporated at $65^\circ C$/20 Torr.

<u>ABA Block Copolymer by Reaction of Poly(5 formal) and Isocyanate 13.</u>- Under a N_2 atmosphere, 1.007 g of poly($\underline{5}$ formal), M_n ~9000, (0.11 mmol) were dissolved in 4 mL of dry dichloroethane at $50^\circ C$. Added were .091 g of $\underline{13}$ (0.188 mmol) and ~5 μL of dibutyltin dilaurate, and the mixture was stirred for 48 hrs. The temperature was decreased to $35^\circ C$, and 1 mL of methanol was added. Stirring was continued overnight, then the solvents were stripped at $65^\circ C$/20 Torr.

Two other polymers in Table 3 were prepared using the same procedure:

poly($\underline{5}$ formal), $\overline{M}_n$ - 7600/Docosanol-TDI adduct ($\underline{13}$)
poly($\underline{5}$ formal), $\overline{M}_n$ - 4460/docosanol-TDI adduct ($\underline{13}$)

ABA Block Copolymer by Reaction of Chain extended Poly(5 formal) with Isocyanate 13.- A solution of 1.5 g of poly($\underline{5}$ formal), M_n - 7600, (0.197 mmol) in 5 mL of dry dichloroethane (4A sieves) was prepared at 35°C under a N_2 atmosphere. .008 mL of TDI (0.0562 mmol) and -5 μL of dibutyltin dilaurate were added, and the mixture was stirred overnight. The temperature was increased to 50°C and .140 g of isocyanate $\underline{13}$ (0.28 mmol) were added. The stirring was continued for 2-3 days. The temperature was decreased to 35°C, 1 mL of methanol was added, the mixture was stirred for 3-4 hrs, and was then stripped at 65°C/20 Torr.

The following ABA block copolymers from Table 3 were prepared using the same procedure, except the prepolymers were extended with different amounts of TDI:

poly($\underline{5}$ formal), $\overline{M}_n$ - $\underline{4460}$ extended with 0.016 mL TDI/g polymer to
$\overline{M}_n$ -9000/Docosanol-TDI adduct ($\underline{13}$)
poly($\underline{5}$ formal), $\overline{M}_n$ - $\underline{4460}$ extended with 0.018 mL TDI/g polymer to
$\overline{M}_n$ -10,500/Docosanol-TDI adduct ($\underline{13}$)
poly($\underline{5}$ formal), $\overline{M}_n$ - $\underline{4460}$ extended with 0.024 mL TDI/g polymer to
$\overline{M}_n$ -17,500/Docosanol-TDI adduct ($\underline{13}$)

ABA Block Copolymer by Reaction of Poly(5 formal) with Isocyanate 16.- A dry solution of .970 g of poly($\underline{5}$ formal), M_n -8000, (0.121 mmol) in 5 mL of dichloroethane (from a stock solution dried over 4A sieves) was heated to 55-60°C under a N_2 atmosphere. Added were .172 g of isocyanate $\underline{16}$ (0.244 mmol) and 2-3 μL of dibutyltin dilaurate. The solution was stirred for 24 hrs. The reaction temperature was decreased to 35°C, 10 drops of methanol were added, and stirring was continued for 3 hrs. The reaction was allowed to cool to room temperature, and the reaction mixture was dripped into -75 mL of methanol. The methanol was decanted from the precipitated polymer and the residual solvents were removed at 60°C/20 Torr.

ABA Block Copolymer by Reaction of Poly(5 formal) with Octadecyl Isocyanate.- Poly($\underline{5}$ formal)(M_n ≈ 7600, 1.38 g, 0.1816 mmol), 5 mL of dry dichloroethane (4A sieves), octadecyl isocyanate (0.1073 g, 0.364 mmol) and 1 drop of dibutyltin dichloride were heated to 50°C for 3 days. Methanol (0.25 mL) was added and heating was continued for 24 hr. Removal of solvents under vacuum gave the crude polymer.

ABA Block Copolymer by Reaction of Poly(5 formal) with Heneicosoyl azide.- Poly($\underline{5}$ formal) (M_n ≈ 7600, 2.32 g, 0.305 mmol), dichloroethane (5 mL, dried over 4A sieves), heneicosoyl azide (0.234 g, 0.64 mmol) and 1 drop of dibutyltin dichloride were heated at 60-65°C for 5 days, 0.25 mL of methanol was added and reaction was continued at 40°C for 2 days. The polymer, obtained by removal of solvents in vacuo, was more elastomeric than the polymer of the preceding procedure.

Reaction of Poly(AMMO) with Isocyanate 13.- A dry solution of .915 g of poly(AMMO), M_n = 6250, (0.1464 mmol) in 5 mL of dichloroethane (from a stock solution dried over 4A sieves) was heated to 55°C and .160 g of 13 (0.32 mmol) and 3 μL of dibutyltin dilaurate were added. This mixture was stirred for 20-24 hrs, then the temperature was decreased to 35°C, 10 drops of methanol were added, and stirring was continued for 3 hrs. The heating was removed and the reaction mixture was dripped into ~75 mL of methanol to precipitate the polymer. The methanol was decanted and the polymer was heated to 60°C/20 Torr to remove any residual solvents.

Reaction of Poly(AMMO) with Isocyanate 16.- A dry solution of .915 g of poly(AMMO), M_n = 6250, (0.1464 mmol) in 5 mL of dichloroethane (from a stock solution dried over 4A sieves) was heated to 55°C under a N_2 atmosphere. .233 g of 16 and 3 μL of dibutyltin dilaurate were added and the mixture was stirred for 20-24 hrs. The temperature was decreased to 35°C, 1 mL of methanol was added, and stirring was continued for ~3 hrs. After cooling to room temperature, the reaction mixture was dripped into ~75 mL of methanol to precipitate the polymer. The resulting polymer was heated to 65°C/20 Torr to remove any residual solvents.

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