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SYNTHESIS OF ENERGETIC MULTI-PHASE POLYMERS

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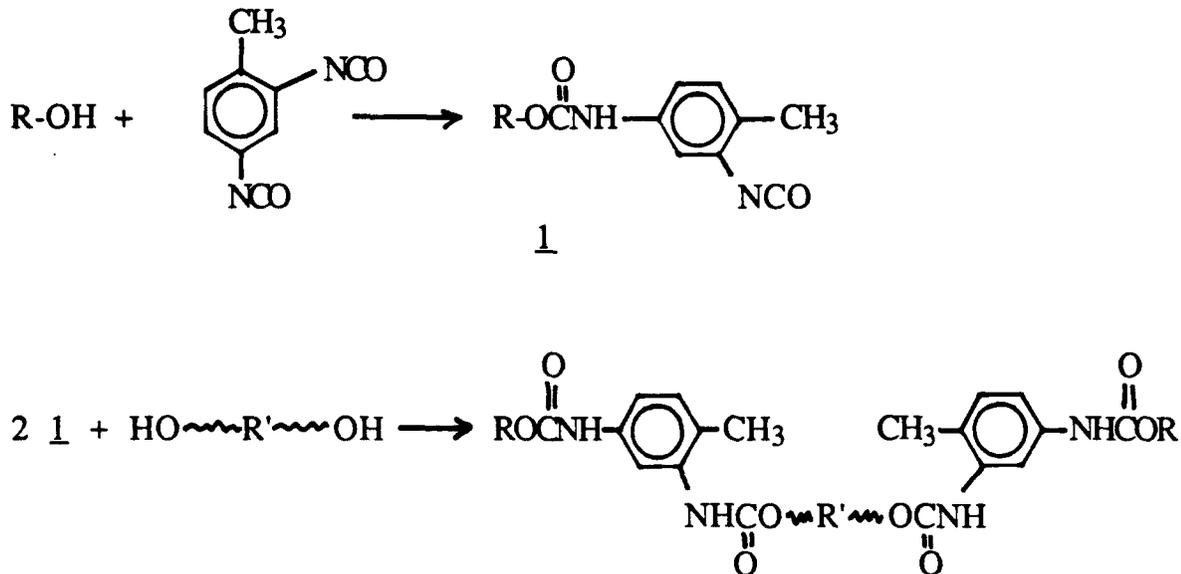
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SYNTHESIS OF ENERGETIC MULTI-PHASE POLYMERS

INTRODUCTION

During the past year the emphasis of this continuing effort on synthesis of energetic thermoplastic elastomers (TPEs) has been the assembly of ABA triblock copolymers from blocks previously synthesized at NSWC and elsewhere using toluene-2,4-diisocyanate (TDI) as the linking agent. The general approach was to end-cap a hydroxy-terminated monofunctional "hard" block with TDI and react the isolated adduct 1 with a hydroxy-terminated, difunctional "soft" block:



This approach introduces a limited number of undesirable urethane linkages into the polymer molecule but is reproducible and less subject to side reactions than the previously investigated use of phosgene as linking agent.¹

Poly(BAMO) of various molecular weights and an alkanol mixture with the nominal composition of $\text{C}_{30}\text{H}_{61}\text{OH}^1$ were used as hard blocks. Nitro- and fluorodiols polyformals, poly(AMMO), poly(NMMO), and GAP were used as soft blocks or soft block components.

All new polymers were characterized by gel permeation chromatography (GPC) and ^1H NMR spectroscopy. Selected polymers were further characterized by DSC, GPC-LALLS (at NAWC China Lake) and FT-IR spectroscopy (at NAWC China Lake).

RESULTS AND DISCUSSION

A. Soft Block Synthesis

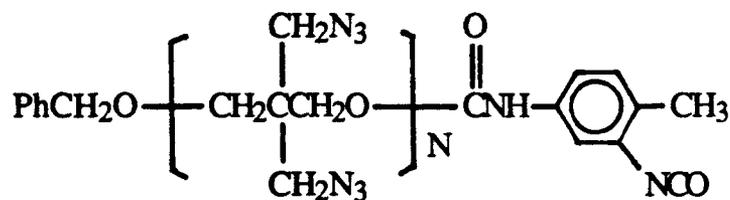
Previously initiated efforts¹ to use commercially available² GAP [poly(glycidyl)azide] as a soft block component were continued. GAP "diol"/GAP "triol" mixtures were chain-extended with TDI to a nominal molecular weight of 20,000. A molar ratio of GAP "diol" to "triol" of 9:1 was found to be adequate to obtain a nearly difunctional soft block while avoiding cross-linking. These soft blocks were not isolated but reacted in situ with the hard block-TDI adducts (see below and experimental section).

B. Hard Block Synthesis/Purification

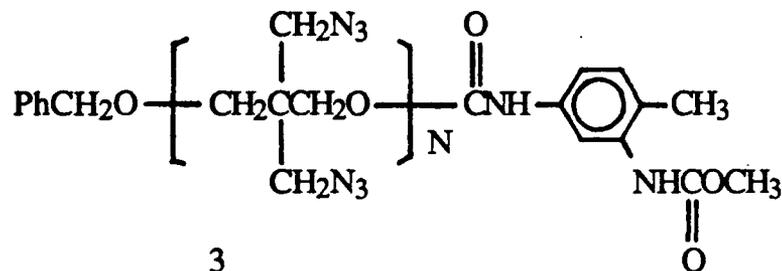
Several lots of monofunctional, hydroxy-terminated poly(BAMO) were received from Thiokol Corp. (R. Wardle). The lots were identified as follows:

Lot 48228, OH equ. wt. 2174
Lot WE8-79, OH equ. wt. 5067 (by NMR)
Lot WE9-69, OH equ. wt. 3469
Lot WE9-71, OH equ. wt. 9524

All lots were purified by column chromatography on Silica Gel to remove or reduce low molecular weight contaminants (in the case of WE9-71, no significant reduction was achieved). The purified poly(BAMO) was then reacted with excess TDI. The resulting adducts 2 were characterized, after reaction with methanol to 3, by GPC and ^1H NMR spectroscopy. Figures 1 and 2 show a typical gel permeation chromatogram and ^1H NMR spectrum, in this case for the urethane from Lot WE8-79. The GPC shows a low molecular weight TDI derivative to be present as an impurity. The ^1H NMR spectrum shows a ratio of aromatic plus NH protons to aliphatic



2



3

protons of 5:98.5 which gives a molecular weight of 4137 for the poly(BAMO). This is in reasonable agreement with the OH equivalent weight found by Thiokol Corp. taking into consideration the presence of a low molecular weight TDI derivative.

C. Synthesis of ABA Triblock Copolymers

Polymers with C₃₀-Alkane¹ Hard Blocks

1. Polymers with poly(AMMO) soft block.- Earlier, two ABA block copolymers with the C₃₀-Alkane/poly(AMMO)/C₃₀-Alkane combination of blocks were made, one with 6250 MW poly(AMMO) and the other with the same poly(AMMO) chain-extended to a MW of 20,000 as soft blocks. The latter polymer (LN3, 81-6) developed good elastomeric properties after storage for several weeks. However, when the synthesis was repeated sometime later with the same lot of poly(AMMO), the properties could not be reproduced.

A new poly(AMMO) sample of higher molecular weight (lot WE8-41) was obtained from Thiokol Corp. The reported \bar{M}_N was 10,262 and the OH equivalent weight was 4762. This lot of poly(AMMO) was also reacted directly with C₃₀OH/TDI adduct to give a somewhat resilient, sticky polymer (15B/28-2). ¹H NMR analysis gave a molecular weight of \approx 16,000 which indicates hard block deficiency. The observed hard block deficiency may be due to a lower functionality than 2 of the poly(AMMO) soft block.

Two additional polymers were made after chain-extension of the poly(AMMO) to nominal molecular weights of 13,000 and 30,000, respectively, with TDI. Both polymers again had less hard block content by ^1H NMR analysis than expected and the properties were not adequate for binder use (modulus too low). The polymers prepared are listed in Table 1.

2. Polymers with poly(NMMO) soft block.- Two approximately difunctional poly(NMMO) soft blocks with different molecular weights were obtained from Thiokol Corp. One sample, lot WE8-29 with OH equivalent weight 4000, was chain-extended with TDI to a nominal MW \approx 16,000 and then end-capped with the $\text{C}_{30}\text{OH}/\text{TDI}$ hard block. The resulting polymer (15B/38) had a MW by ^1H NMR of 25,000, indicating less than the expected amount of hard block to be present. The polymer was essentially a resin with no elastomeric properties. The GPC and ^1H NMR spectrum are shown in Figures 9 and 10.

A second poly(NMMO) sample, lot WE8-88, OH equ. wt. 9434, was end-capped directly with $\text{C}_{30}\text{OH}/\text{TDI}$. The resulting polymers (15B/32 and 15B/36) had ^1H NMR MWs of 22,500 and 25,500, respectively, indicating little hard block deficiency. Both polymers, which resulted from duplicate runs, were somewhat elastomeric but not strong. A small sample of 15B/36 was sent to NAWC for a preliminary characterization. GPC and ^1H NMR spectrum of the latter polymer are shown in Figures 11 and 12.

3. Polymers with GAP soft block.- As stated above, GAP "diol"/"triol" mixtures, initially in a molar ratio of 83:17, later in a ratio of approximately 9:1, were chain-extended with TDI to a nominal molecular weight of 20,000 and were then reacted with C_{30} -alkane/TDI adduct. The polymers obtained are listed in Table 2. ^1H NMR analysis indicates that several of the polymers (15B/24-1, 15B/24-2, 15B/23; see Table 2) have about the expected molecular weight and hard block content. Although a few of the polymers were somewhat resilient, reproducibility was difficult and especially the reactions with diol:triol ratios of 83:17 produced varying amounts of cross-linked elastomer. Because of the unattractive properties of the polymers obtained and the lack of reproducibility of results, no further work with this combination of blocks is recommended.

TABLE 1. ABA TRIBLOCK COPOLYMERS FROM POLY(AMMO) SOFT BLOCKS
AND ALKYLURETHANE HARD BLOCKS

NO.	SOFT BLOCK (OH EQU. WT.)	HARD BLOCK	POLYMER CHARACTERISTICS	REMARKS ((GPC, ¹ H NMR, FIGURES NO.))
LN3, 36-4	LOT 48218 (3215)	C ₂₂ OH-TDI	SLIGHTLY ELASTIC AFTER STORAGE	85% HARD BLOCK (NMR)
LN3, 76-5	LOT 48218 (3215)	C ₃₀ OH-TDI	WAXY	100% HARD BLOCK (NMR)
LN3, 81-6	LOT 48218 (3215) EXTENDED W. TDI TO M _N 20,000	C ₃₀ OH-TDI	INITIALLY RESIN, BECOMING ELASTOMERIC ON STORAGE. WAS NOT REPRODUCIBLE*	T _G = -30°C; T _M = 70-90° (?) M _N (GPC-LALLS) = 16,400
HGA 15B/28-1 BLOCK	LOT WE8-41 (4762) EXTENDED TO M _N 30,000 W. TDI	C ₃₀ OH-TDI	SOMEWHAT RESILIENT; TEARS EASILY	MW (NMR) 40,000 (HARD DEFICIENT); [5, 6]
HGA 15B/28-2 BLOCK	LOT WE8-41 (4762)	C ₃₀ OH-TDI	SOME ELASTICITY; NOT STRONG	MW (NMR) 16,000 (HARD DEFICIENT); [3, 4]
HGA 15B/43 BLOCK	LOT WE8-41 (4762) EXTENDED W. TDI TO M _N 13,000	C ₃₀ OH-TDI	SOMEWHAT RESILIENT; STICKY	MW (NMR) 21,000 (HARD DEFICIENT); [7, 8]

* FIRST SAMPLE OF LOT 48218 DEPLETED. LATER SAMPLE HAD DIFFERENT GPC

TABLE 2. ATTEMPTED SYNTHESIS OF ABA POLYMERS WITH GAP SOFT BLOCKS

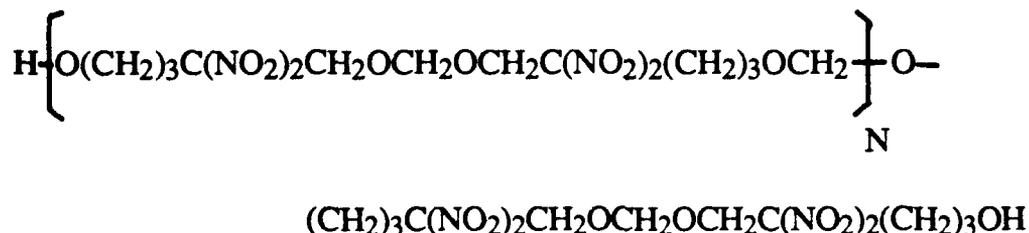
No.	GAP Diol/Triol Mol Ratio	Polymer Characteristics Dichloromethane Fraction (may be cross-linked)	Tetrahydrofuran Fraction	MW by ¹ H NMR	GPCs and ¹ H NMR Spectra, Figures No.
15B/15	83:17	NONE	Slightly Resilient	36,500**	13, 14
15B/18	91:9	NONE	Slightly Resilient	36,000**	15, 16
15B/23	83:17	0.4 g Elastomer	Resin	27,000**	-
15B/24-1	83:17	0.14 g Elastomer	Slightly Resilient	22,500	17, 18
15B/24-2	83:17*	0.7 g Elastomer	Resin, Waxy	20,000	-
15B/30	90:10	NONE	Soft Resin	33,000**	-

*Less TDI used; soft block has lower MW

**MW >> 21,000 indicates hard block deficiency

Polymers with Poly(BAMO) Hard blocks

1. Polymers with TNTDD-pf soft block.- Poly(tetranitrotridecanediol formal), 4 (TNTDD-pf), of an approximate molecular weight of 10,000 was chain-extended with TDI to a MW \approx 20,000 and then reacted with poly(BAMO)/TDI adduct 2.



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Three polymers with different hard block/soft block ratios (molecular weights) were prepared (Table 3). The properties of these polymers are qualitatively similar to those of the polymers with C₃₀-alkane hard blocks and TNTDD-pf soft blocks.

Polymer 15B/44 was sent to NAWC China Lake for characterization (GPC and ¹H NMR spectrum, see Figures 19 and 20). A larger quantity of this polymer is being prepared for plasticization studies and preliminary evaluation.

2. Polymers with GAP soft block.- Also listed in Table 3 are two ABA block copolymers made from GAP diol/triol soft blocks and the poly(BAMO) hard blocks of different molecular weights. Although the polymers were highly opaque, suggestive of strong phase separation, they were not elastomeric but were essentially viscous resins.

3. Polymers with FPF-1 soft block.- Because of the unexpected lack of elastomeric properties of essentially all of the ABA polymers with oxetane and oxirane soft blocks, even those with urethane moieties in the backbone due to chain extension, it was desired to prepare a second ABA polymer with a polyformal soft block.

This polymer was prepared by chain-extending a poly-(hexafluoropentenediol formal), FPF-1, $\overline{M}_N = 5450$, with TDI to a nominal MN of 27,500 and reacting this difunctional soft block with the monofunctional p(BAMO)/TDI adduct of equ. wt. 2350. GP

TABLE 3. ABA TRIBLOCK COPOLYMERS WITH
POLY(BAMO)-TDI HARD BLOCKS

NO.	SOFT BLOCK	HARD BLOCK (OH EQU. WT.)	POLYMER CHARACTERISTICS	REMARKS
HGA 1B/44*	TNTDD-PF 10,000 EXTENDED W. TDI TO MW \approx 20,000	LOT WE8-79 (5076)	RESILIENT, STRONG; LESS SOLUBLE THAN OTHER ABA POLYMERS W. TNTDD-PF	OPAQUE; NMR SHOWS >90% HARD BLOCK
HGA 15B/51*	TNTDD-PF 10,000 EXTENDED W. TDI TO MW \approx 20,000	LOT 48228 (2174)	RESILIENT BUT NOT AS STRONG AS 15B/44	OPAQUE; NMR SHOWS 100%+ HARD BLOCK
HGA 15B/54	TNTDD-PF 10,000	LOT 48228 (2174)	RESILIENT; FAIRLY STRONG	OPAQUE
HGA 15B/52	GAP DIOL/TRIOL 9:1 EXTENDED W. TDI TO MW \approx 20,000	LOT 48228 (2174)	RESIN	OPAQUE
HGA 15B/53	SAME	LOT WE8-79 (5067)	WAXY	OPAQUE

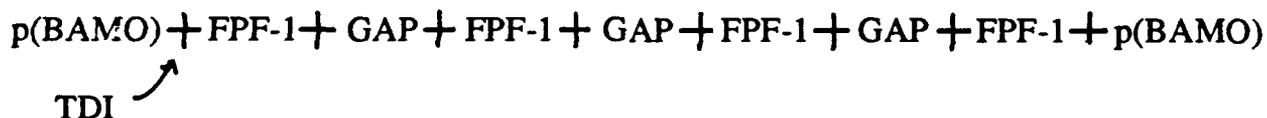
*SENT TO NAWC

chromatogram and ^1H NMR spectrum are shown in Figures 21 and 22. This polymer is an excellent elastomer but does not flow readily at 100°C , apparently due to the presence of many urethane groups.

The synthesis of an analogous polymer is planned in which the FPF-1 soft block contains no urethane groups (FPF-1 with $\bar{M}_N \approx 20,000$ has been prepared in earlier work).

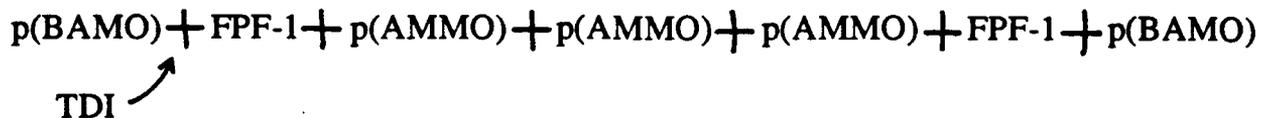
4. Polymers with mixed azidopolyether/FPF-1 soft blocks.- In view of the very different properties of the ABA polymers with polyether and polyformal soft blocks, it was reasoned that a mixture of FPF-1 and GAP or p(AMMO) segments in the soft block should give ABA polymers with properties in between those of the polymers with pure soft blocks. Two such polymers with mixed soft blocks were synthesized:

a. A polymer with mixed FPF-1/GAP soft block having the following nominal structure was made by reacting FPF-1 ($\bar{M}_N = 5450$), GAP diol/triol mixture (9:1), and TDI in a molar ratio 3:2:6, end-capping



this intermediate with FPF-1 followed by reaction with 2 moles of p(BAMO)/TDI adduct (GPC and ^1H NMR spectrum, see Figs. 23 and 24).

b. A polymer with FPF-1/poly(AMMO) soft block with the following nominal structure was prepared by first reacting difunctional poly(AMMO)



(Thiokol lot 48228, OH equ. wt. 3125) with TDI (ratio 3:4), end-capping this intermediate with FPF-1 followed by reaction with p(BAMO)/TDI adduct. GPC and ^1H NMR spectrum are shown in Figs. 25 and 26).

Both polymers show improved elasticity and flow properties relative to the polymers with pure polyether and FPF-1 soft blocks.

Further characterization is needed and additional polymers with FPF-1 spacers will be synthesized.

D. Plasticization Studies

TNTDD-pf Based ABA Polymers

A C₃₀-alkane/TNTDD-pf/C₃₀-Alkane triblock copolymer with a 10,000 molecular weight soft block was mixed in a ratio of 3:1 with various monomeric and oligomeric plasticizers including FEFO, TMETN, GAP azide, GAP, and PGN. The resulting materials were still elastomeric but much softer than the unplasticized polymer. Thus only small amounts of plasticizer (20-25%) can be tolerated by this polymer before loss in mechanical properties becomes significant. Figures 27 and 28 show the DSCs of the polymer plasticized with TMETN and GAP, respectively. The unplasticized polymer has a T_G of approximately 5°C and begins to melt near 70°C. It can be seen that T_M is little affected by either TMETN or GAP, and that T_G is substantially lowered in both cases (to -14 and -21°C, respectively).

When polymer 15B/44 (TNTDD-pf 20,000 soft block, poly[BAMO] 5200 hard block) was similarly plasticized with PGN, GAP, and F+F nitroplasticizer, qualitatively similar changes occurred in mechanical properties. Despite the much higher hard block content, this polymer also cannot be plasticized much beyond the 25% level before properties become unacceptable.

FPF-1 Based Polymer

The poly(BAMO)/FPF-1/poly(BAMO) polymer described above did not dissolve PGN or GAP but can be plasticized with F+F nitroplasticizer to give an elastomer with better flow properties. Incorporation of nitraminediol into the FPF-1 backbone through copolymerization would increase the compatibility with plasticizers such as PGN.

CONCLUSIONS

A series of ABA polymers were synthesized containing polyformal and polyether soft blocks, and very short C₃₀-alkane as well as poly(BAMO) hard blocks. The two very different hard blocks appear to convey similar properties to the polymers containing them, but the

polyether and polyformal soft blocks give polymers with very different properties.

Polymers with pure polyether soft blocks had no significant elastomeric properties and very low moduli, but also low melt viscosities. The polyformal based polymers, in contrast, were either tough and resilient or good elastomers, but have high melt viscosities. Preliminary results suggest that a combination of the two types of soft blocks in the same polymer gives materials with useful TPE properties.

Plasticization studies with monomeric and oligomeric plasticizers indicate that glass transition temperatures and melt viscosities can be lowered significantly. Mechanical properties are, however, adversely affected at plasticizer contents >25% for the polyformal polymers prepared so far.

EXPERIMENTAL SECTION

General.- Melting points are uncorrected. Temperatures are in °C. NMR spectra were obtained on a Varian EM-390 spectrometer; chemical shifts are in ppm relative to TMS internal standard. Silica gel was EM Kieselgel 60, 70-230 mesh.

GPCs were obtained on three Toyo Soda Micropak TSK 3000H size exclusion columns each 30 cm long, with inside diameters of 0.75 cm, preceded by a Toyo Soda Micropak H Series guard column, 7.5 cm long, 0.75 cm diameter. Packing pore size was 1500 Å. A Waters Model 6000A delivery system, Model U6K injector, Model 440 UV detector, and Model R-401 IR detector were used.

Solvents used for polymerization and block linking reactions were of the highest commercially available grade and were stored over a large excess of 4A molecular sieves under a dry nitrogen atmosphere. Reaction vessels were heated with a heat gun while being purged with dry nitrogen. Reagents were added under a dry nitrogen cover.

GAP Soft Block by Chain Extension of GAP "diol"/"triol" Mixture.- A solution of 34.34 g of GAP "diol" and 5.40 g of GAP "triol" in dichloroethane was prepared at a concentration of 0.22 g/mL (0.174 mequiv./mL hydroxyl content) and stored over an excess of 4A molecular sieves.

Typically, the chain-extension was done in situ by reacting 8 mL of the above polymer solution (1.76 g polymer, 1.39 mequiv.) with 0.121 g (0.695 mequiv.) TDI and 3 μ L of dibutyltin dilaurate at 60°C for 24h.

In a separate experiment, 0.5 mL of methanol was added to the reaction mixture after cooling to 40°C, and stirring was continued for another 24h. The product was chromatographed on a short column of Silica gel. Elution with dichloromethane gave 0.4 g of a soluble elastomer (apparently lightly cross-linked?); further elution with a dichloromethane/THF mixture gave the bulk of the polymer as a fluid resin (1.3 g).

Purification of Poly(BAMO): General Procedure.- A solution of 7.5 g of poly(BAMO) in dichloromethane was added to a 12 x 1 inch column of Silica gel. The column was washed with 2 x 200 mL dichloromethane. These washings contained a small amount of low molecular weight material (GPC). The column was next washed with 2 x 100 mL of 5% THF/dichloromethane. Nothing was eluted. The next fractions with 3 x 100 mL of 10% THF/dichloromethane contained the bulk of the poly(BAMO). These fractions were combined to give 7.0 g of polymer which had a much reduced content of low molecular weight components.

End-capping of Poly(BAMO) with TDI: General Procedure.- Fifteen grams of monofunctional poly(BAMO), equiv. wt. 5000, in 43 mL of dichloroethane were reacted with 2.13 mL of TDI (5 fold excess) and 15 μ L of dibutyltin dilaurate by heating to 60°C for 2 days. After cooling to room temperature, hexane, 139 mL, was added in portions with vigorous stirring. The mixture was stirred 24h and filtered through a medium porosity sinter glass funnel under a nitrogen cover, washed with 3 x 50 mL portions of hexane, and dried in vacuo over P₂O₅. Obtained was 14.7 g of a free-flowing powder.

For NMR analysis, 0.25 g was suspended in dichloroethane and heated with 0.25 mL of methanol and 1 μ L of dibutyltin dilaurate to 40°C for 24h. The solvents were removed in vacuo and the solid residue was used directly for analysis.

Synthesis of a C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/28-1); Typical Procedure.- To poly(AMMO) WE8-44, 1.425 g, from a stock solution (0.23 g/mL) in dichloroethane stored over 4A molecular sieves, was added 0.0174 g of TDI (d = 1.225 g/mL, 0.0142 mL) and 3 μ L

dibutyltin dilaurate and the mixture was heated 24h at 60°C. C₃₀-Alkanol/TDI adduct¹, 0.060 g, was added and heating and stirring was continued for 2 days. The temperature was lowered to 40°C, 0.25 mL of methanol was added and stirring continued for 24h.

The mixture was diluted with dichloromethane and poured onto a short column of Silica gel. The column was washed thoroughly with dichloromethane, then the polymer was eluted with 30% THF/dichloromethane. The solvents were removed, finally at 80°/0.1 Torr for 3h.

Synthesis of a C₃₀-Alkane/Poly(NMMO)/C₃₀-Alkane Block Copolymer (15B/36); Typical Procedure.- The procedure was essentially the same as described above for the poly(AMMO) ABA polymer. The poly(NMMO) was chromatographed as described above for poly(BAMO) to reduce the amount of low molecular weight components. Due to its higher molecular weight, the poly(NMMO) was not chain-extended but reacted directly with the C₃₀-alkanol/TDI adduct.

Synthesis of a C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/30); Typical Procedure.- To the solution of the GAP soft block prepared as described above was added 0.108 g of C₃₀-alkanol/TDI adduct and the mixture was stirred at 60°C for 3 days. Addition of methanol and subsequent work-up was done as described above.

Synthesis of a Poly(BAMO)/TNTDD-PF/Poly(BAMO) Block Copolymer (ATR 1/8); Typical Procedure.- A stock solution of TNTDD-pf¹ in dichloromethane which had been dried by percolating through calcium hydride¹ and was stored over 4A molecular sieves (7.83 g polymer, M_N 10,000) was mixed with 0.068 g (0.0557 mL) of TDI and 5 µL of dibutyltin dilaurate. The solution was gradually heated to 60°C while the dichloromethane was distilled off and replaced by dichloroethane. After 24h at 60°C, 4.12 g of poly(BAMO)/TDI adduct (from poly(BAMO) lot WE8-79, OH equiv. wt. 5070) was added and heating and stirring was continued for 3 days. After cooling to 40°C, 2 mL of methanol was added and the solution stirred for 24h. Cooling to room temperature and dilution with dichloromethane was followed by filtration through a Silica gel column. The polymer was eluted with dichloromethane, then 10-20% THF/dichloromethane. All fractions except the last two which contained small quantities of waxy (but high molecular weight) material were combined. Solvents (including sulfolane present in the initial polymer

solution) were removed by heating in vacuo, finally at 100°C/0.1 torr for 3h. Obtained was 10.4 g (86.4%).

Synthesis of a Poly(BAMO)/GAP/Poly(BAMO) Block Copolymer (15B/53): Typical Procedure. Nine milliliters of the GAP diol/triol solution (see above), 0.097 mL of TDI and 5 μ L dibutyltin dilaurate were heated at 60°C for 24h, 1.04 g of poly(BAMO)/TDI adduct (from poly(BAMO) WE8-79) were added, stirring was continued at 60°C for 3d, the temperature was lowered to 40°C, 2 mL of methanol was added and the reaction was completed by stirring another 24h. Isolation of the polymer was by chromatography on Silica gel which gave a fraction (1.03 g) which eluted with dichloromethane and was elastomeric, and a fraction which eluted with THF/dichloromethane and was not. Combination of the two fraction gave, after drying at 80°C/0.1 Torr, a material which was soft and only slightly elastomeric.

Synthesis of a Poly(BAMO)/FPF-1/Poly(BAMO) Block Copolymer (ATR 1/1). FPF-1 ($M_N = 5450$), 1.2 g (0.220 mmol), as a dichloroethane stock solution (0.223 g/mL) was chain-extended with 0.051 g TDI (0.294 mmol) and 3 μ L dibutyltin dilaurate by stirring at 60°C for 24h. The terminal TDI groups were reacted for another 24h with additional FPF-1 (3.59 mL stock solution). Poly(BAMO)/TDI, 0.343 g (0.147 mol), from poly(BAMO) lot 48228 was added and stirring continued for 72h. The mixture was treated with methanol at 40°C for 24h and the polymer isolated by chromatography on Silica gel as usual. All material (1.9 g, 79.3%) was recovered in the THF/dichloromethane fraction.

Synthesis of a Poly(BAMO)/GAP + FPF-1/Poly(BAMO) Block Copolymer (ATR 1/3). FPF-1 ($M_N = 5450$), 0.8 g (0.147 mmol, 3.59 mL of stock solution in dichloroethane), 0.584 g of GAP diol/triol (9:1, see above; 0.22 mmol, 2.65 mL stock solution), 0.077 g of TDI and 3 μ L of dibutyltin dilaurate were reacted at 60°C for 24h, followed by addition of another 0.8 g of FPF-1 and 24h stirring at 60°C. Poly(BAMO)/TDI adduct (Poly(BAMO) lot 48228), 0.345 g (0.147 mmol), was added and the mixture was stirred at 60°C for 3 days. Treatment with methanol and chromatography of the reaction product was by the usual procedure. The dichloromethane and THF/dichloromethane fractions were combined before removal of solvents, finally at 100°C/0.1 Torr for 1h.

Synthesis of a Poly(BAMO)/poly(AMMO) + FPF-1/Poly(BAMO) Block Copolymer (ATR 1/4).- Poly(AMMO) lot 48218 (OH equiv. wt. 3125), 1.375 g (7.725 mL of a dichloroethane stock solution), 0.051 g of TDI, and 3 μ L dibutyltin dilaurate were reacted at 60°C for 24h. FPF-1 ($M_N = 5450$), 0.8 g (3.59 mL stock solution) was added and heating was continued for 1 day. Poly(BAMO)/TDI adduct from poly(BAMO) lot 48228, 0.345 g, was added and heating was continued for 3 days. The mixture was treated with methanol and chromatographed as usual. All polymer was recovered in the THF/dichloromethane fraction and was dried in vacuo, finally at 100°C/0.1 Torr for 1h.

REFERENCES

1. H. G. Adolph and L. A. Nock, "Synthesis of Energetic Single Phase and Multi-Phase Polymers", Annual Progress Report for 1990, ONR Work Order N00014-90-WX-24293.
2. GAP "diol" was obtained from Rocketdyne, Canoga Park, CA. It had a reported OH equivalent weight of 1272 and a functionality of 1.95. GAP "triol" was obtained from 3M Company (L-11929). The OH equivalent weight was 1200, with a nominal functionality of 3.

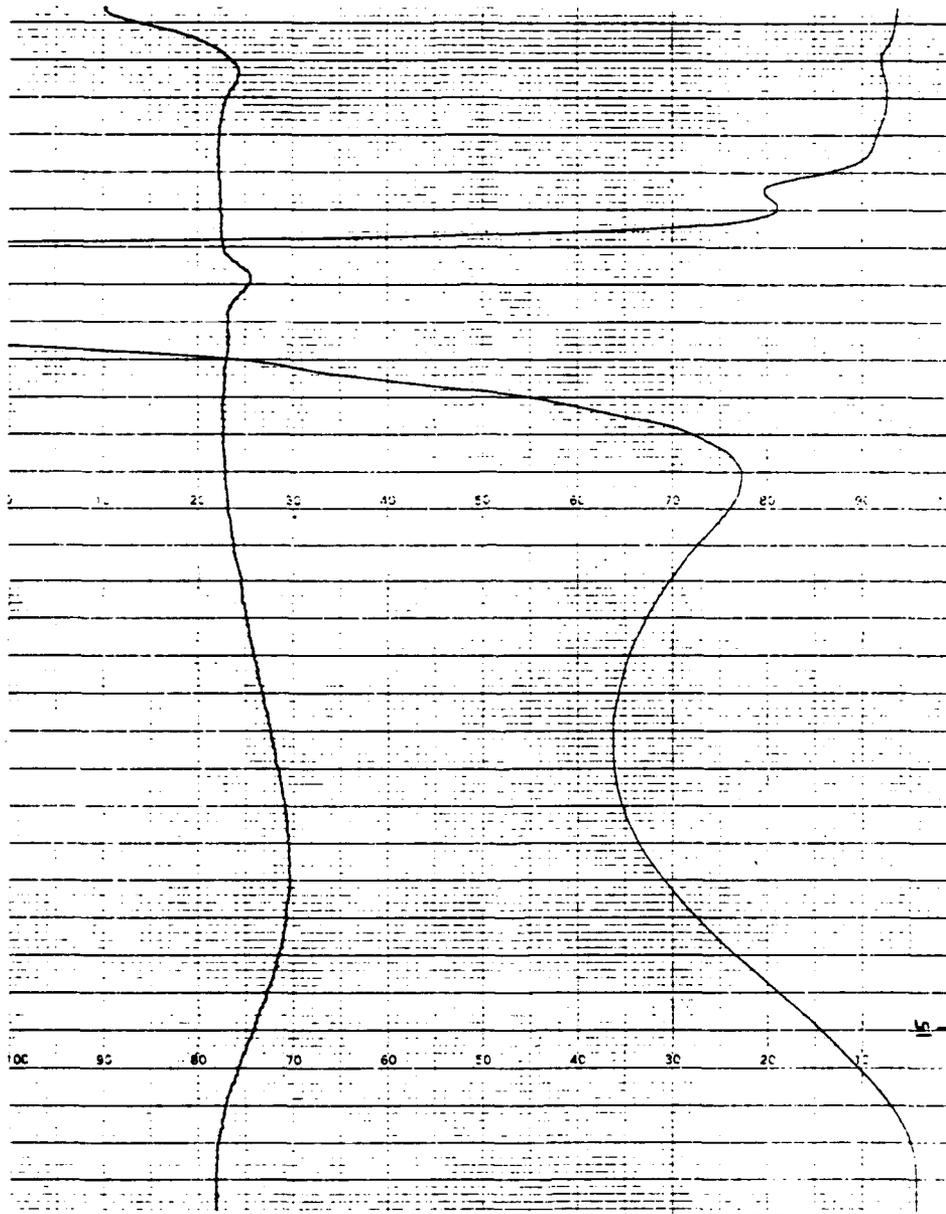


Figure 1. GP Chromatogram of Poly(BAMO)-urethane 2

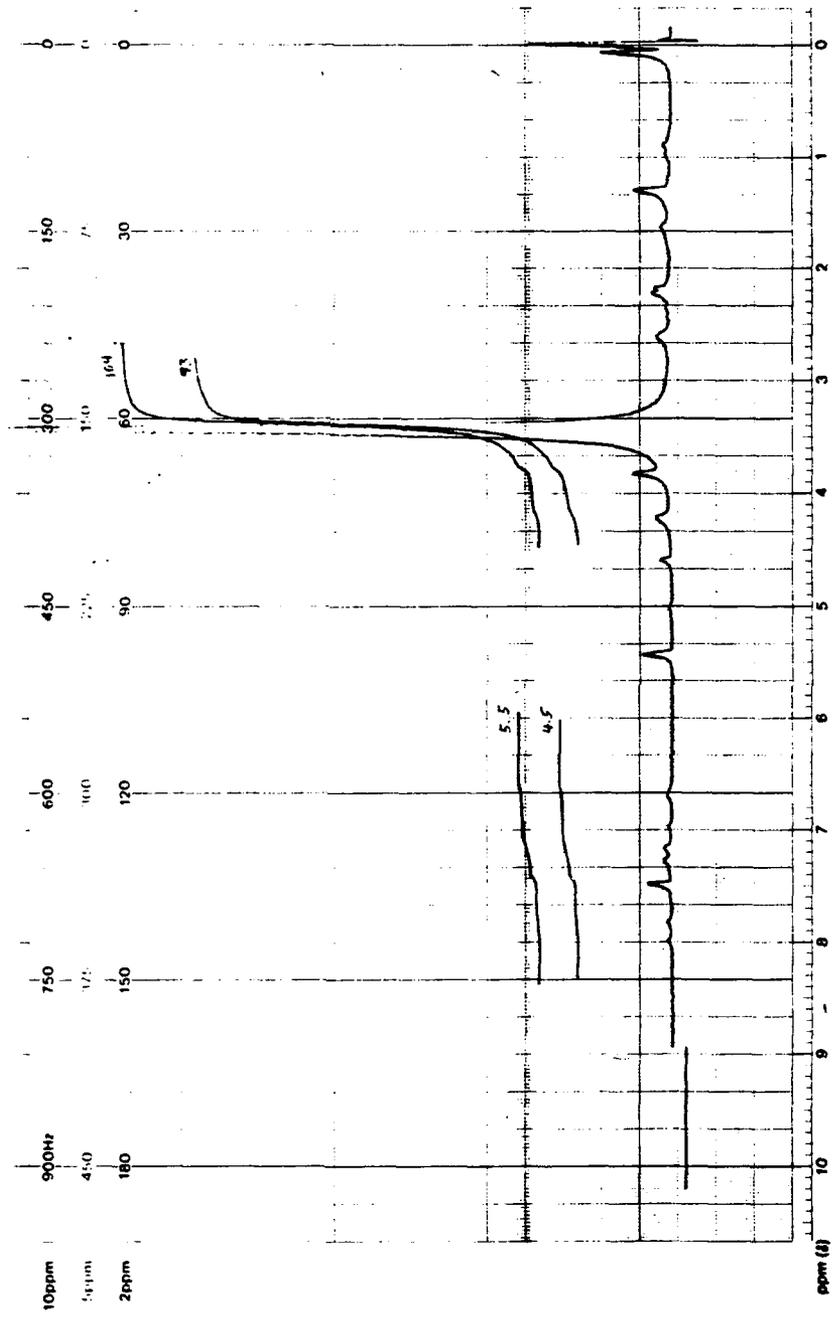


Figure 2. 1H NMR Spectrum of Poly(BAMO)-urethane 3

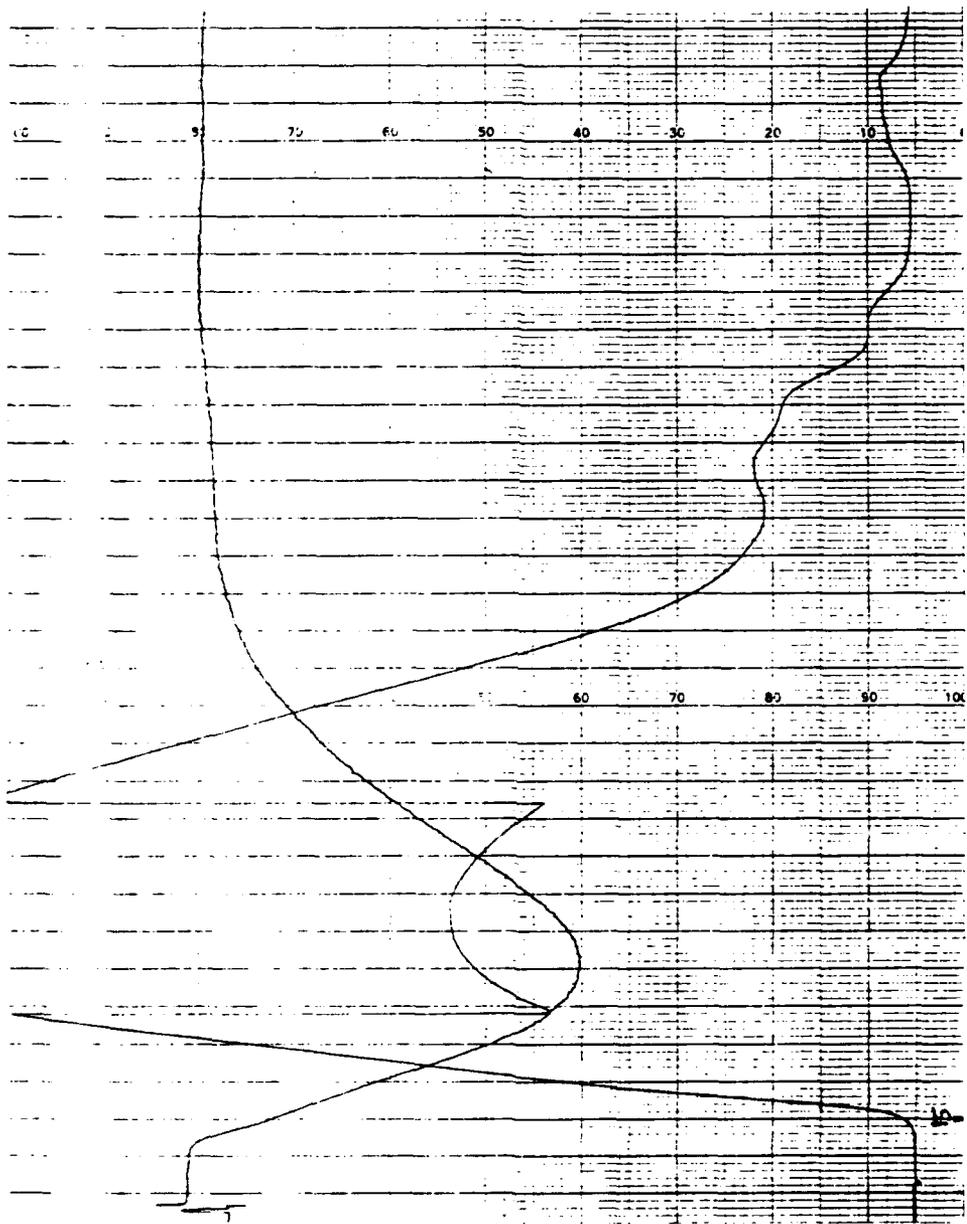


Figure 3. GP Chromatogram of a C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/28-2)

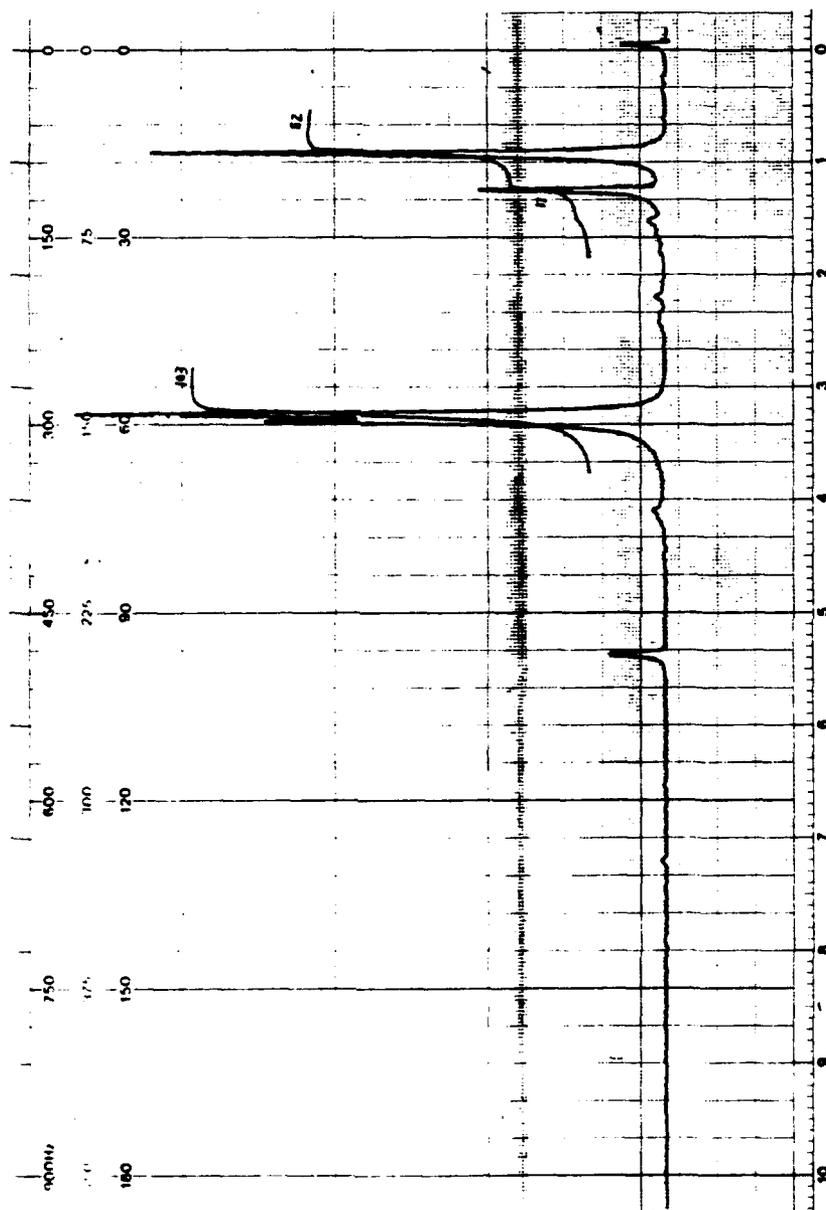


Figure 4. ¹H NMR Spectrum of a C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/28-2)

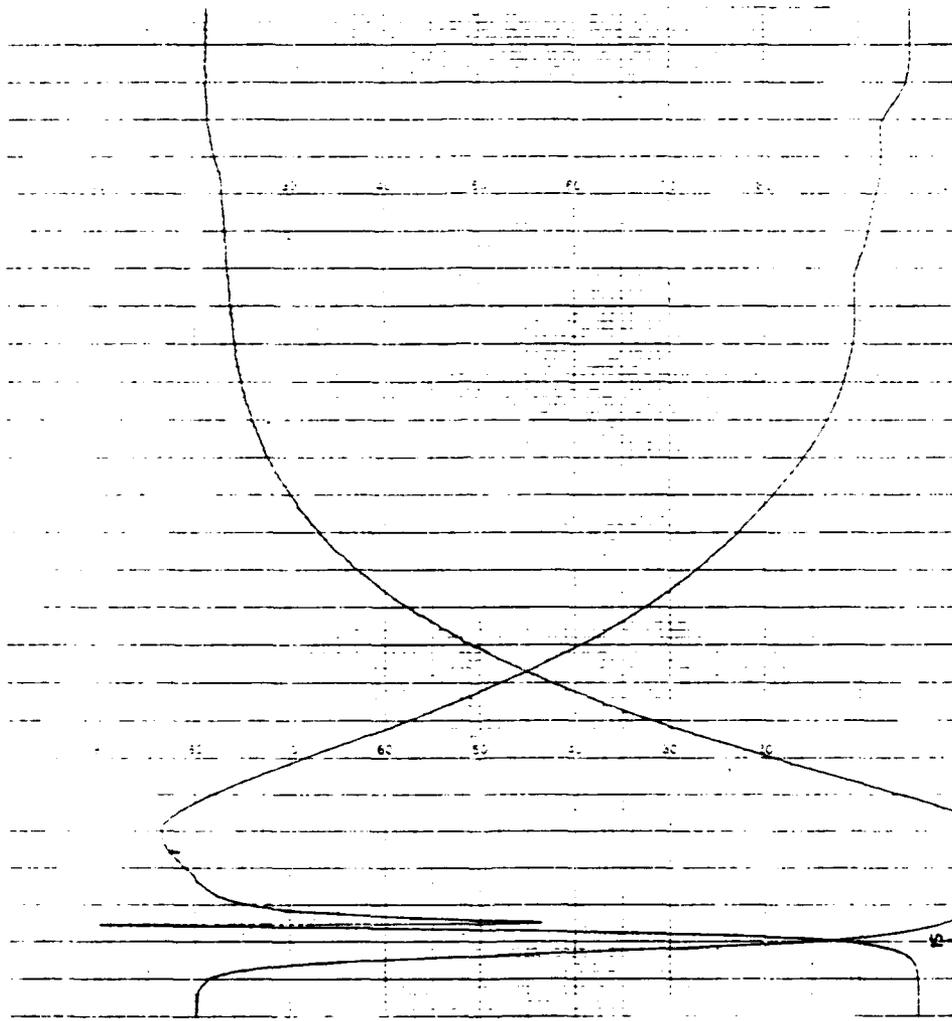


Figure 5. GP Chromatogram of C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/28-1)

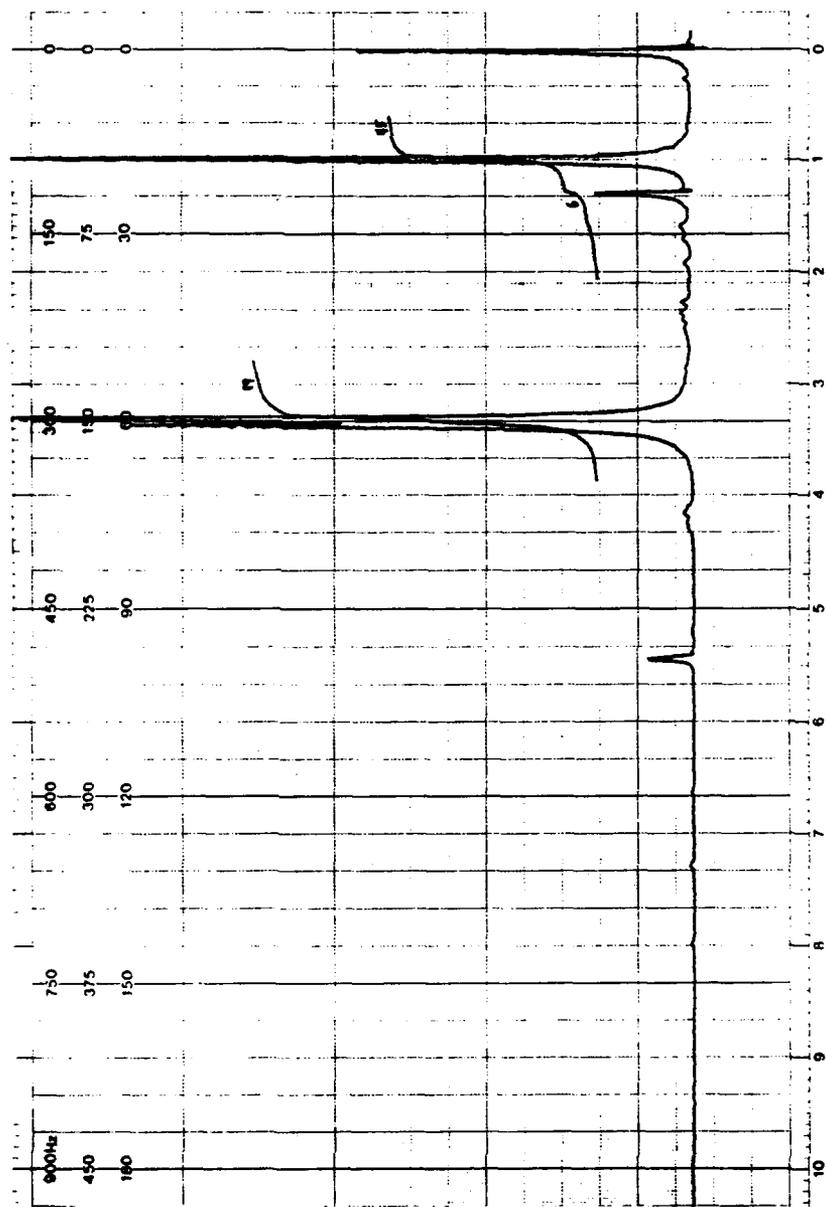


Figure 6. ¹H NMR Spectrum of a C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/28-1)

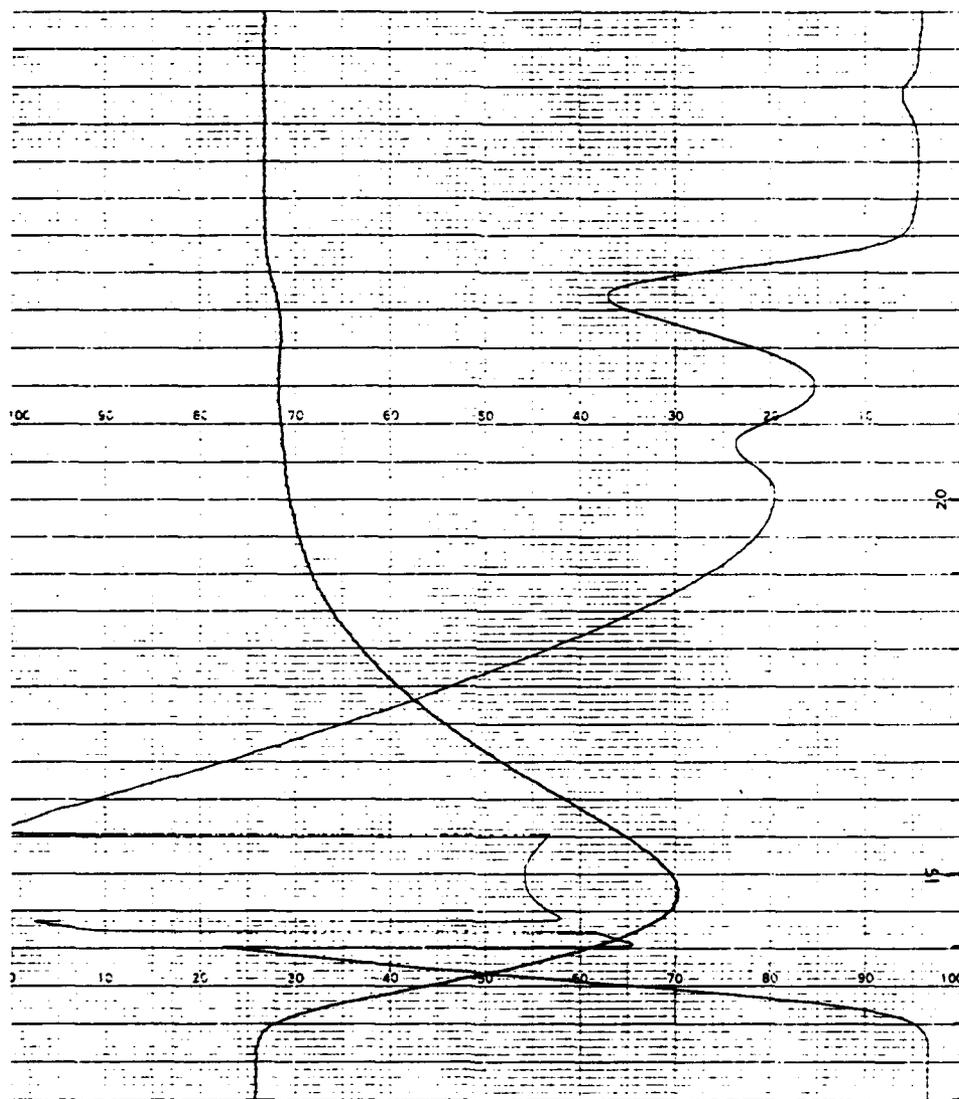


Figure 7. GP Chromatogram of a C₃₀-Alkane/Poly(AMMO)/C₃₀-Alkane Block Copolymer (15B/43)

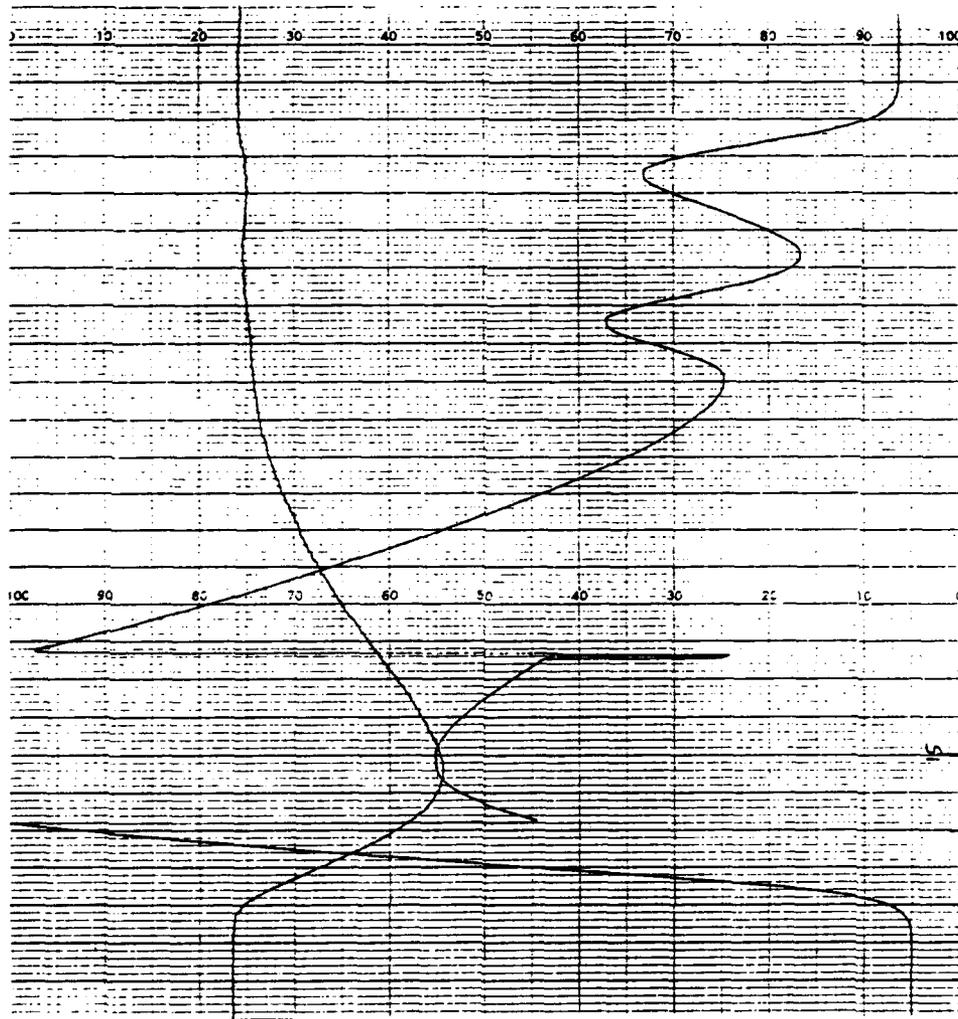


Figure 9. GP Chromatogram of a C₃₀-Alkane/Poly(NMMO)/C₃₀-Alkane Block Copolymer (15B/38)

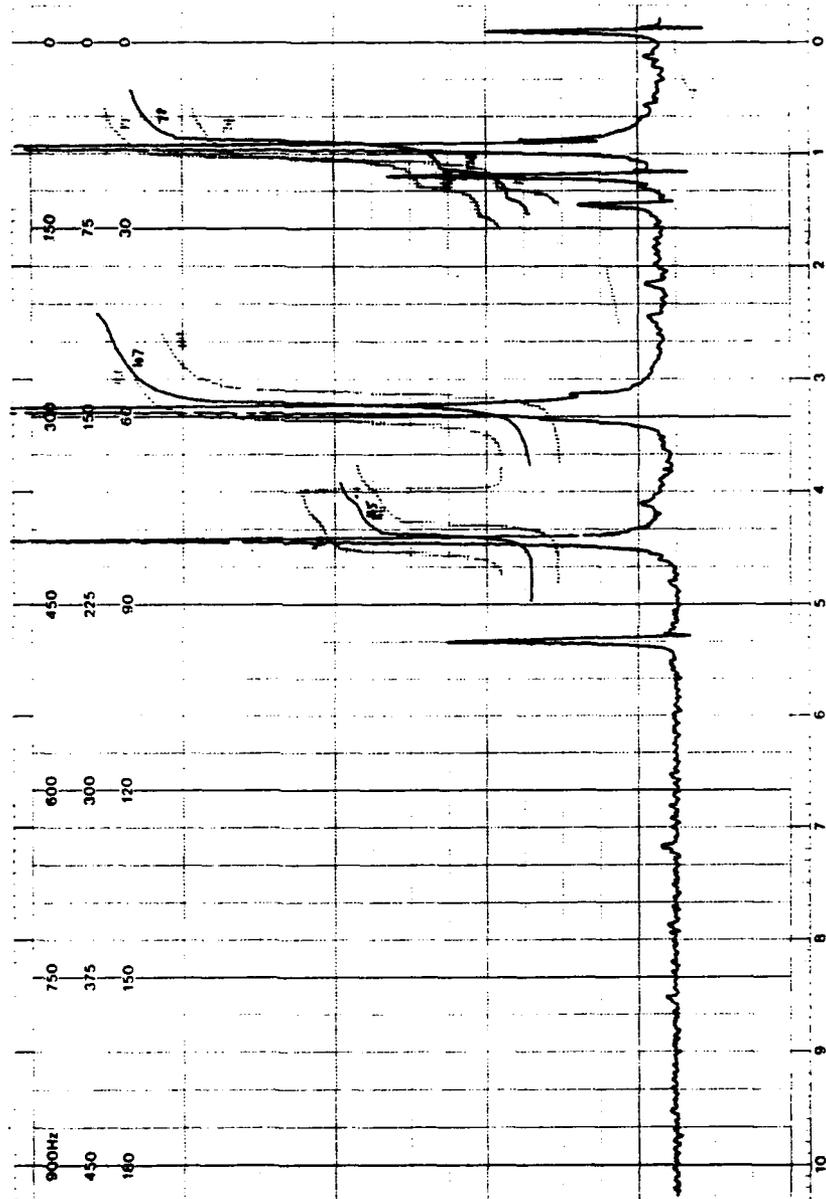


Figure 10. ^1H NMR Spectrum of a C₃₀-Alkane/Poly(NMMO)/C₃₀-Alkane Block Copolymer (15B/38)

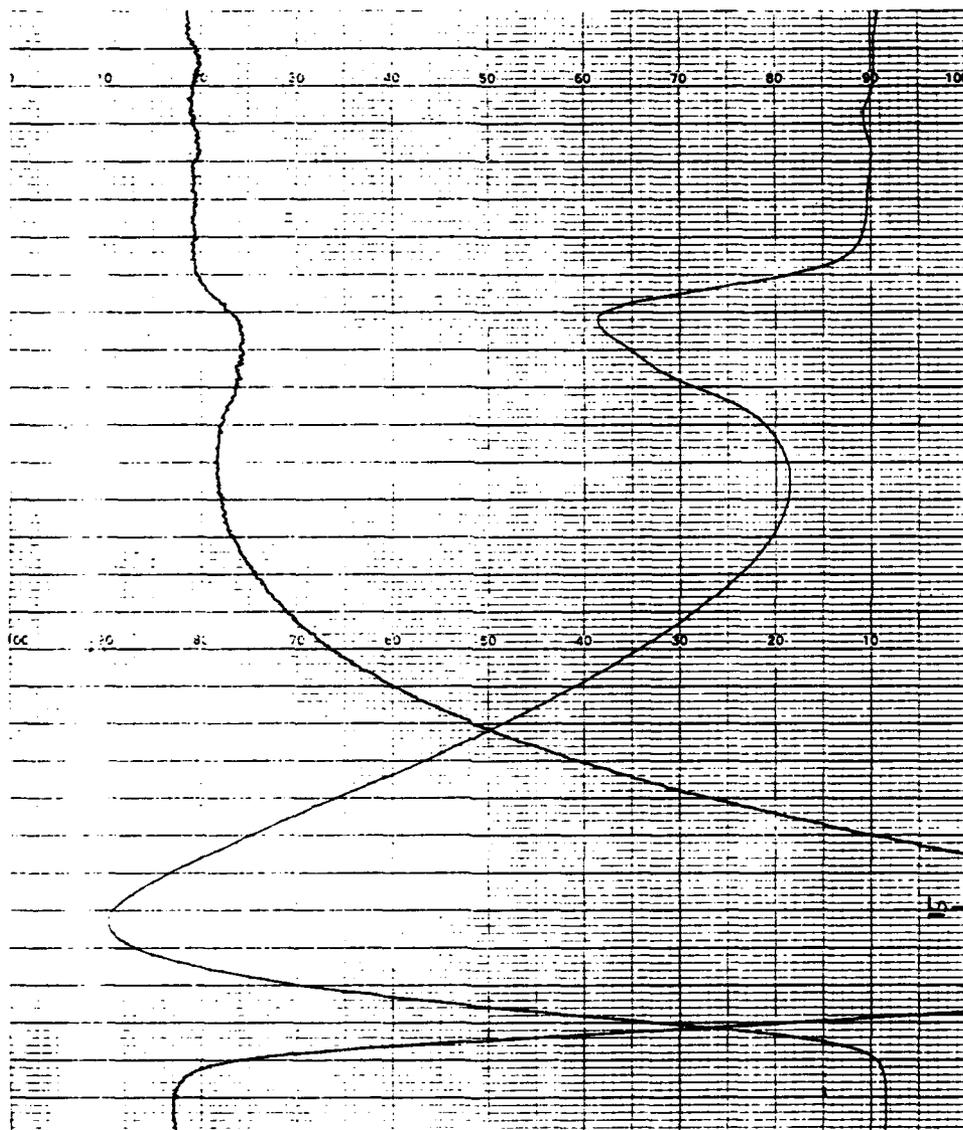


Figure 11. GP Chromatogram of a C₃₀-Alkane/Poly(NMMO)/C₃₀-Alkane Block Copolymer (15B/36)

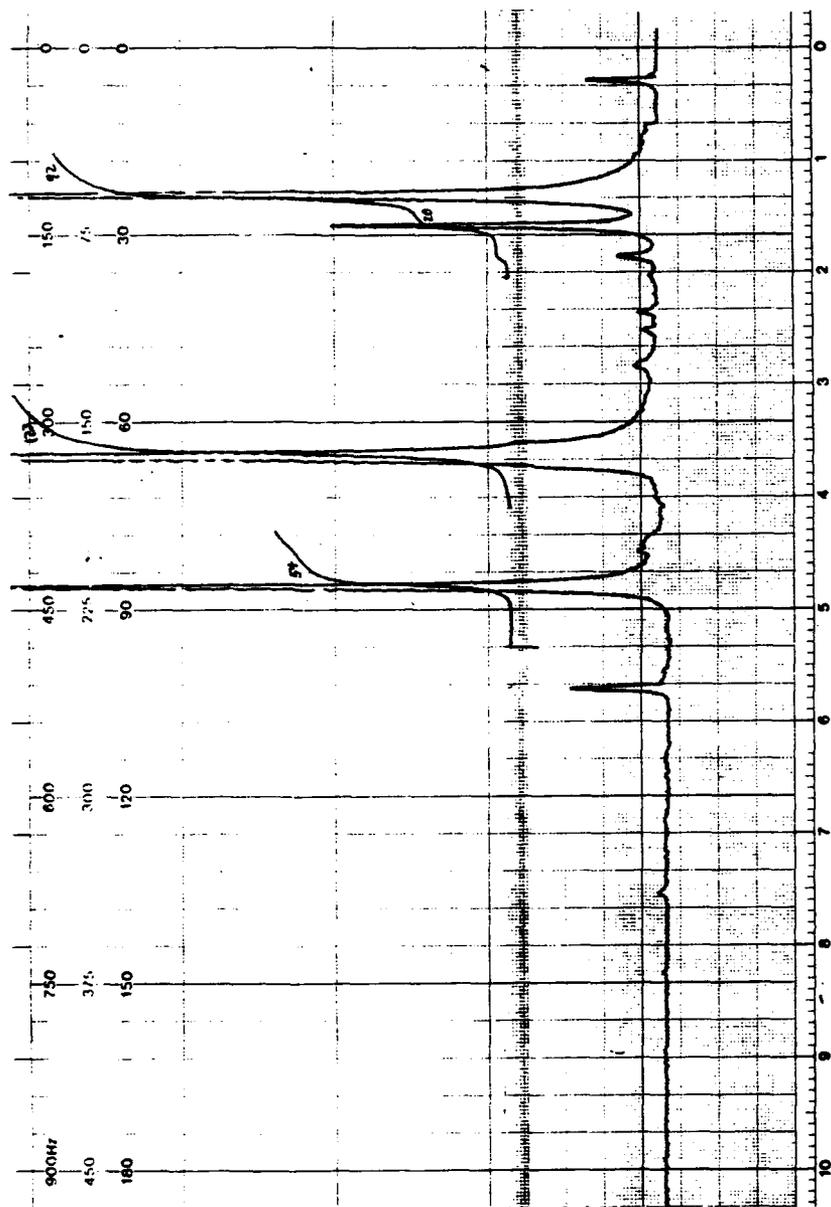


Figure 12. ¹H NMR Spectrum of a C₃₀-Alkane/Poly(NMMO)/C₃₀-Alkane Block Copolymer (15B/36)

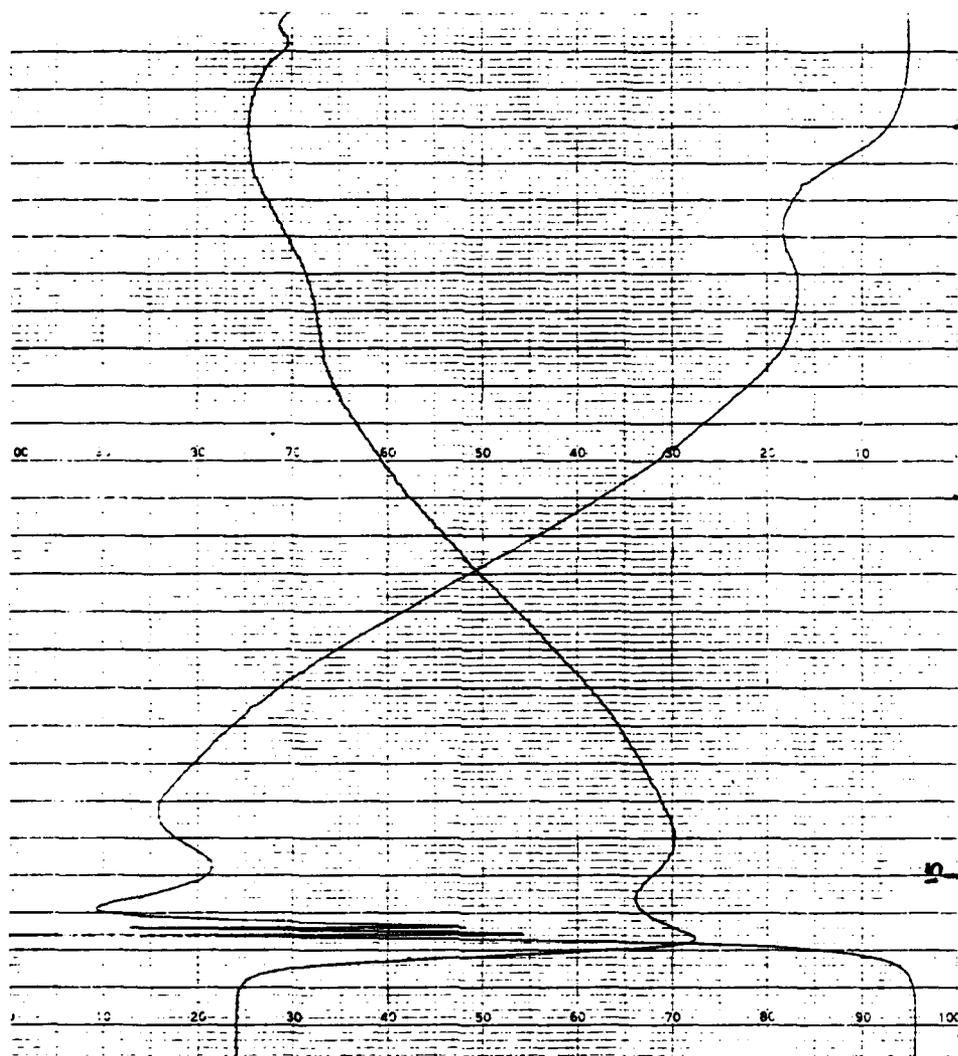


Figure 13. GP Chromatogram of C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/15)

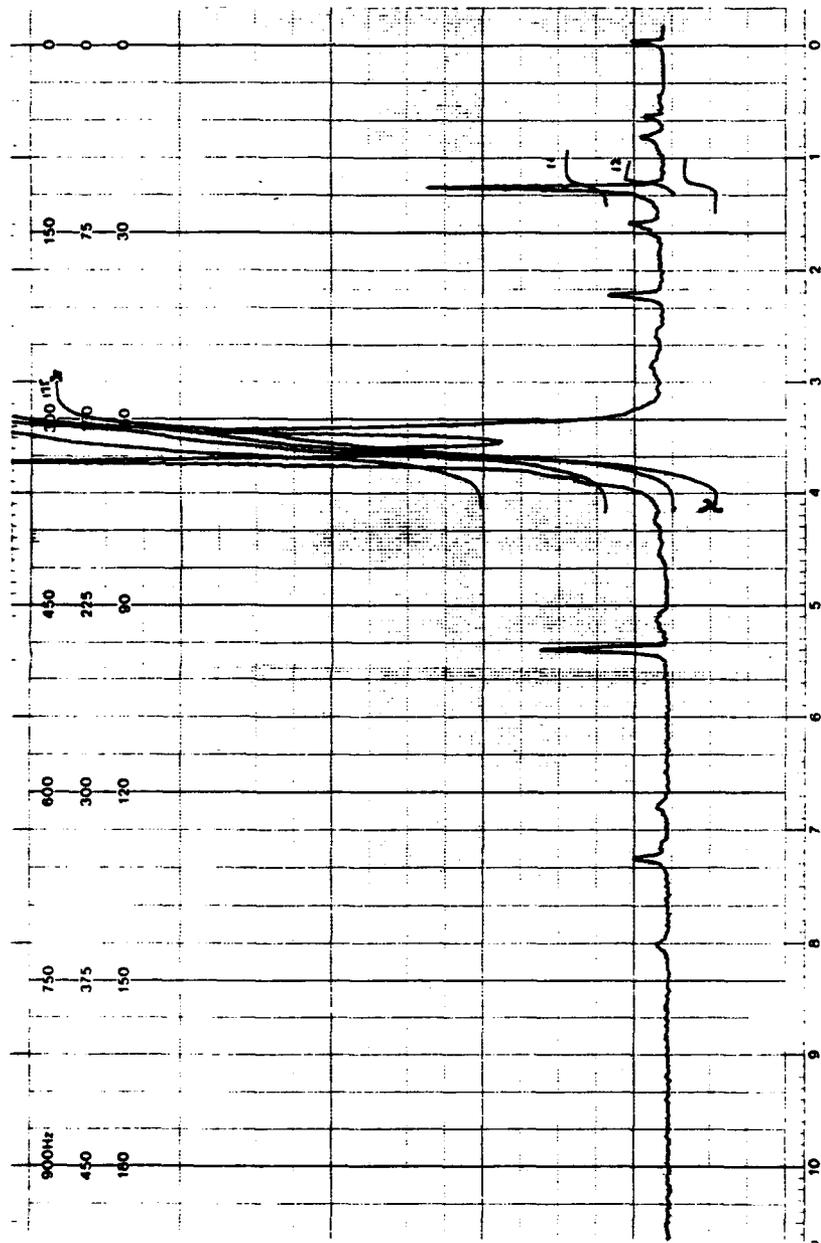


Figure 14. ^1H NMR Spectrum of a C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/15)

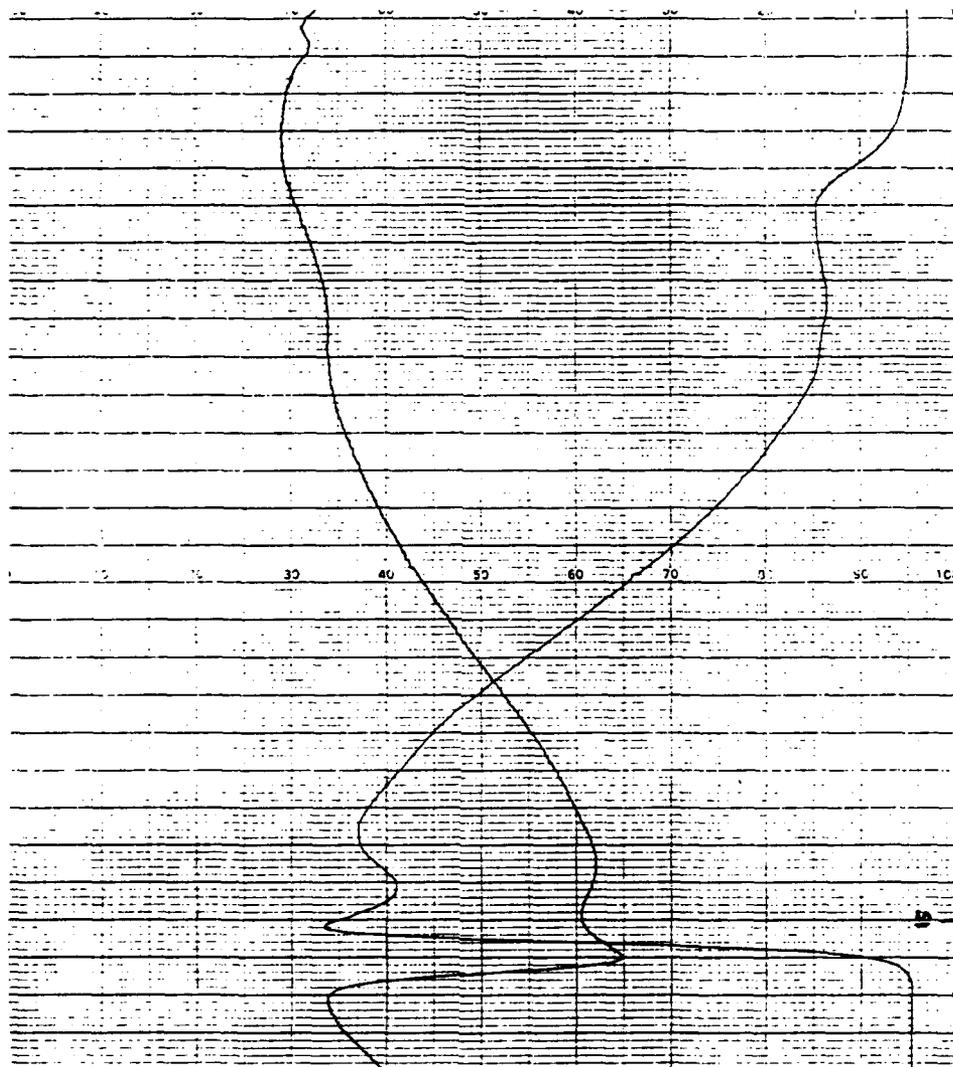


Figure 15. GP Chromatogram of a C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/18)

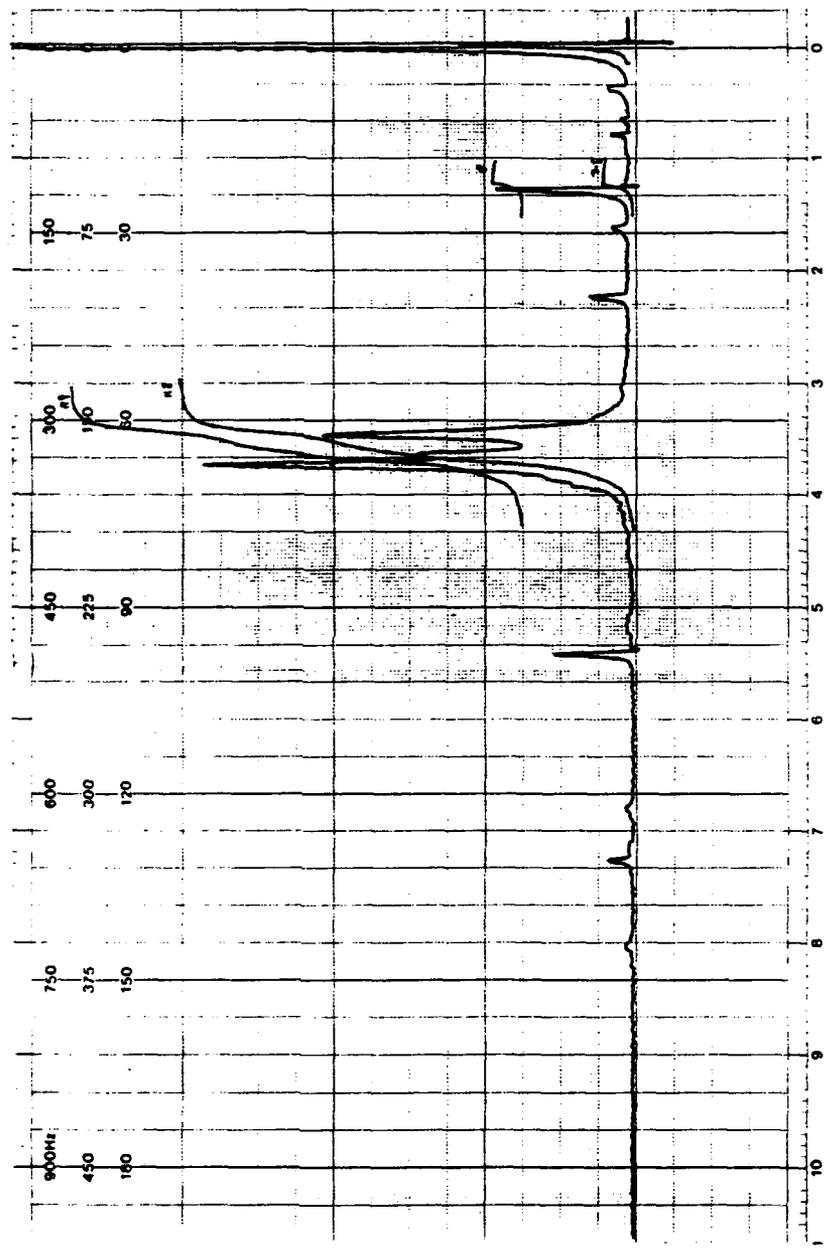


Figure 16. ^1H NMR Spectrum of a C_{30} -Alkane/GAP/ C_{30} -Alkane Block Copolymer (15B/18)

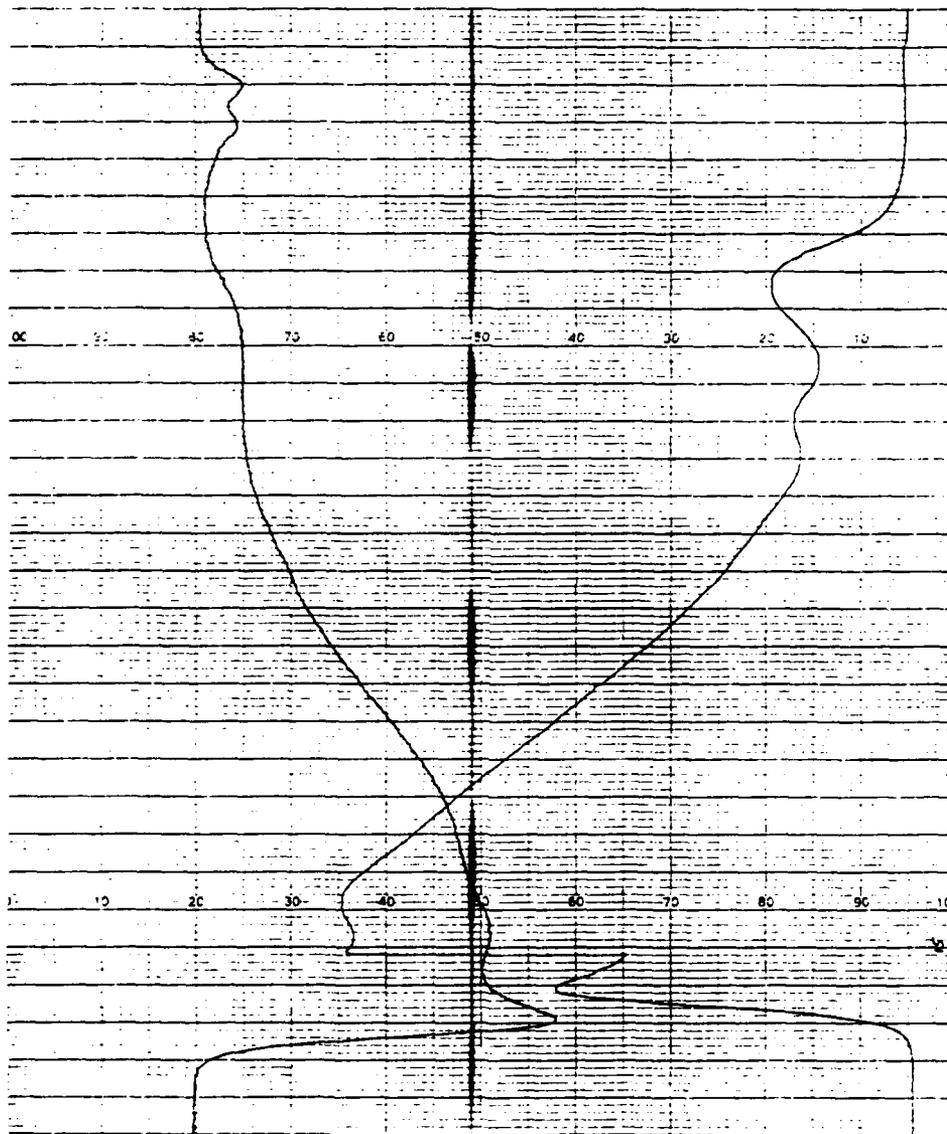


Figure 17. GP Chromatogram of a C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/24-1)

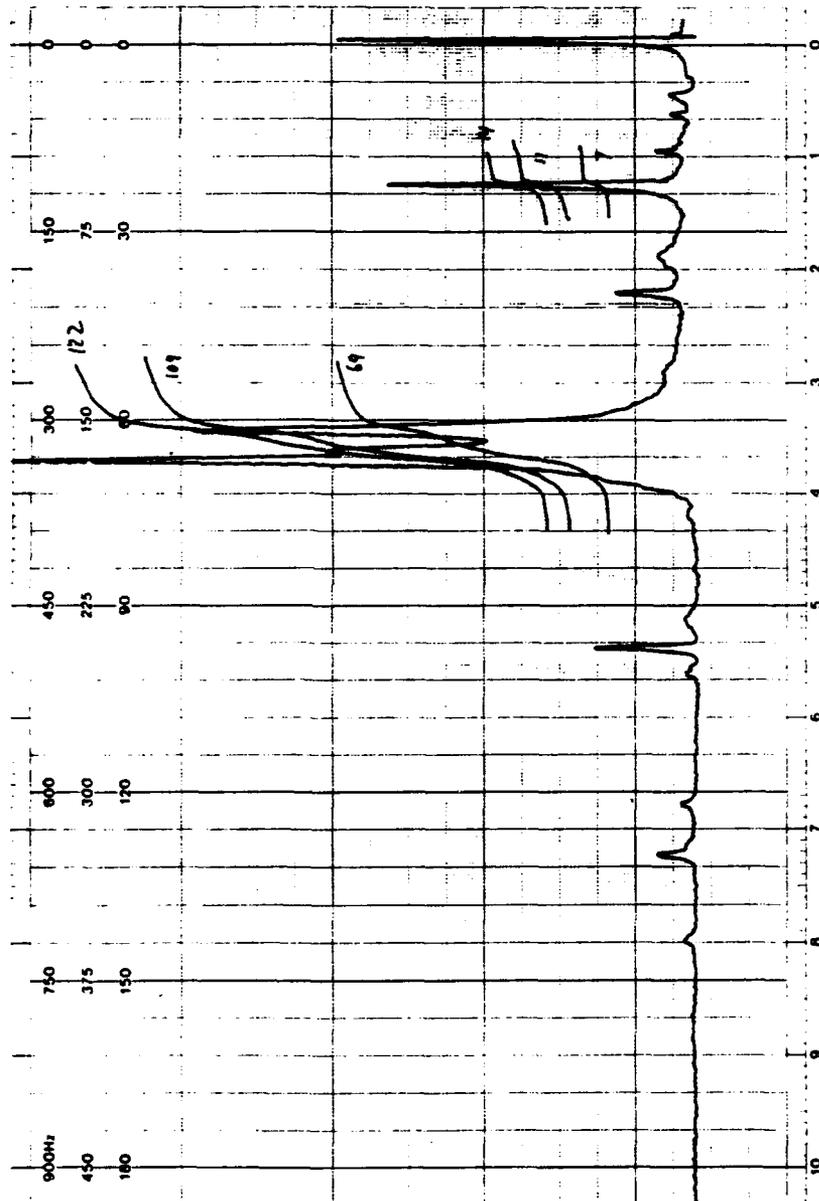


Figure 18. ¹H NMR Spectrum of a C₃₀-Alkane/GAP/C₃₀-Alkane Block Copolymer (15B/24-1)

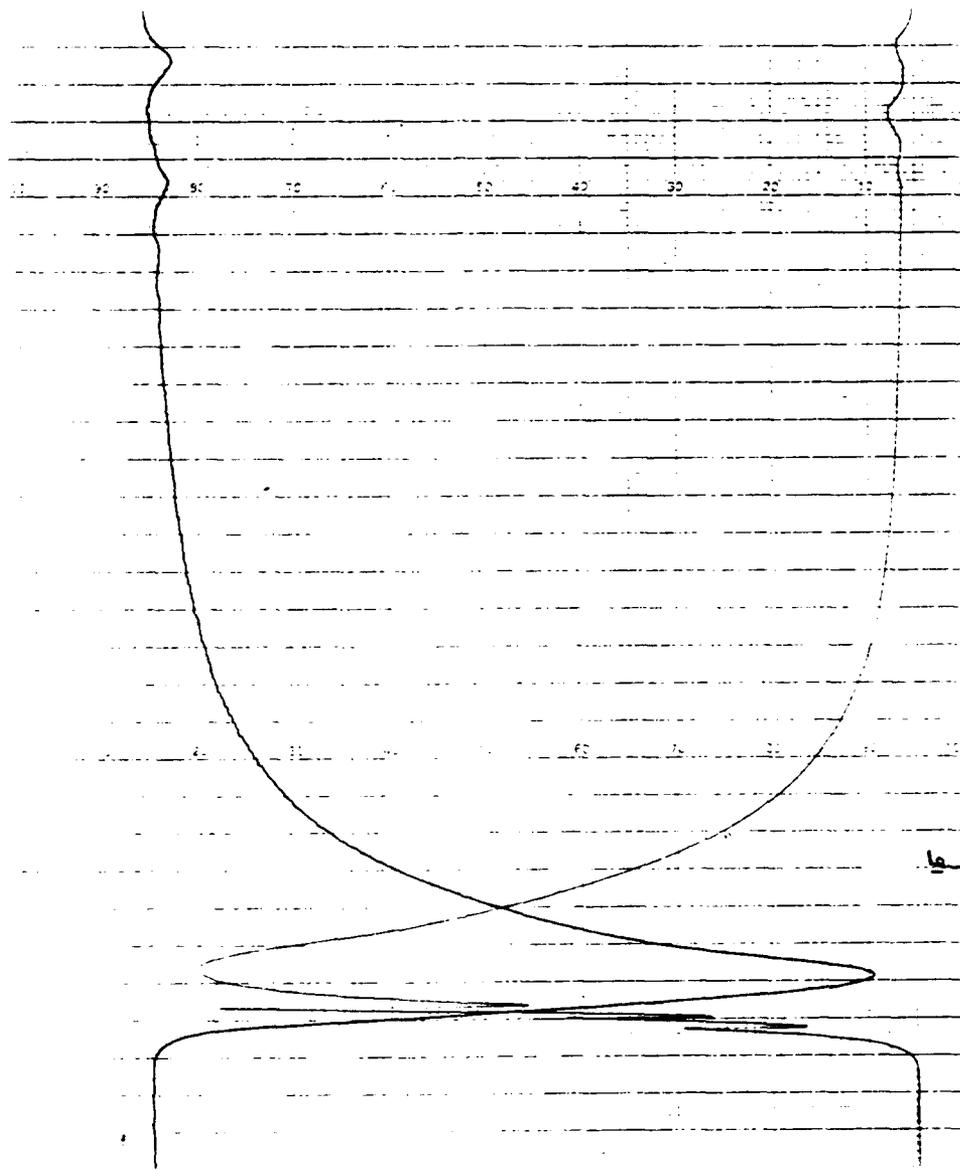


Figure 19. GP Chromatogram of a Poly(BAMO)/TNTDD-PF/Poly(BAMO) ABA Triblock Polymer (15B/44)

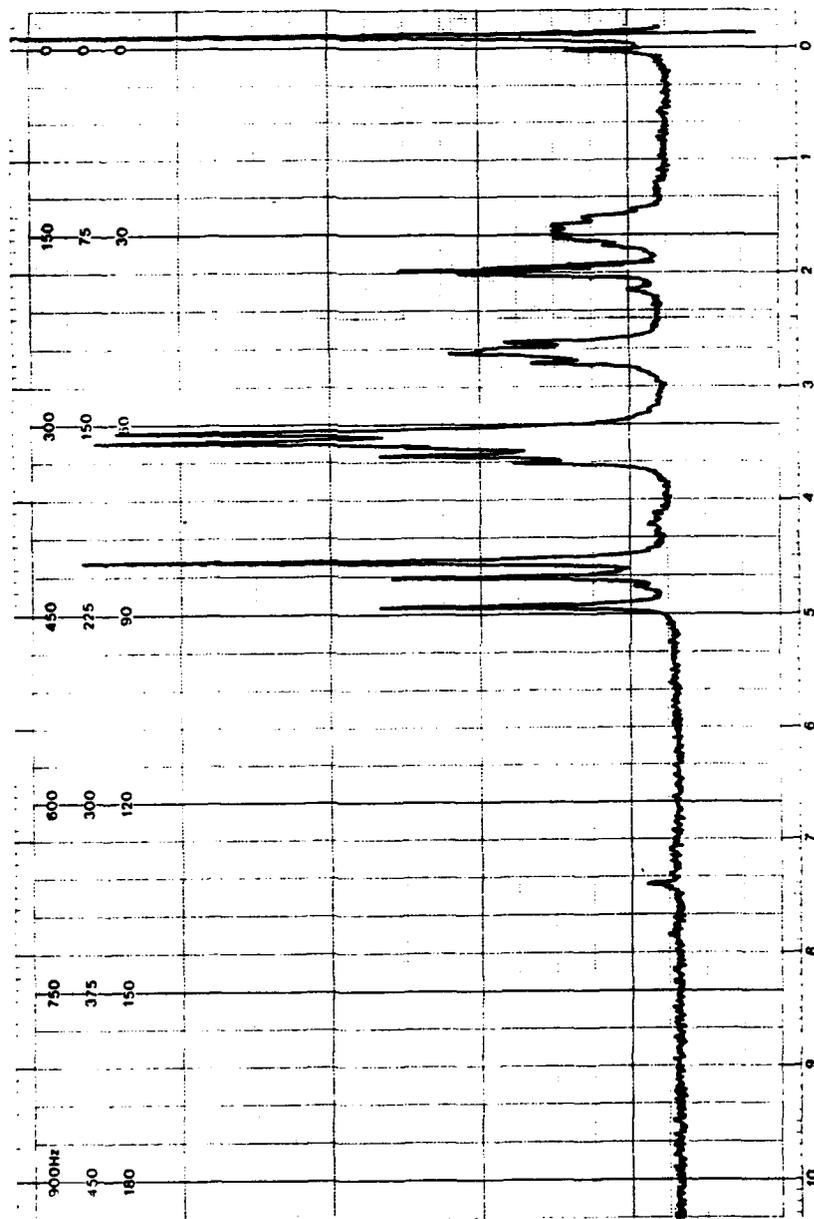


Figure 20. ¹H NMR Spectrum of a Poly(BAMO)/TNTDD-PF/Poly(BAMO) ABA Triblock Polymer (15B/44)

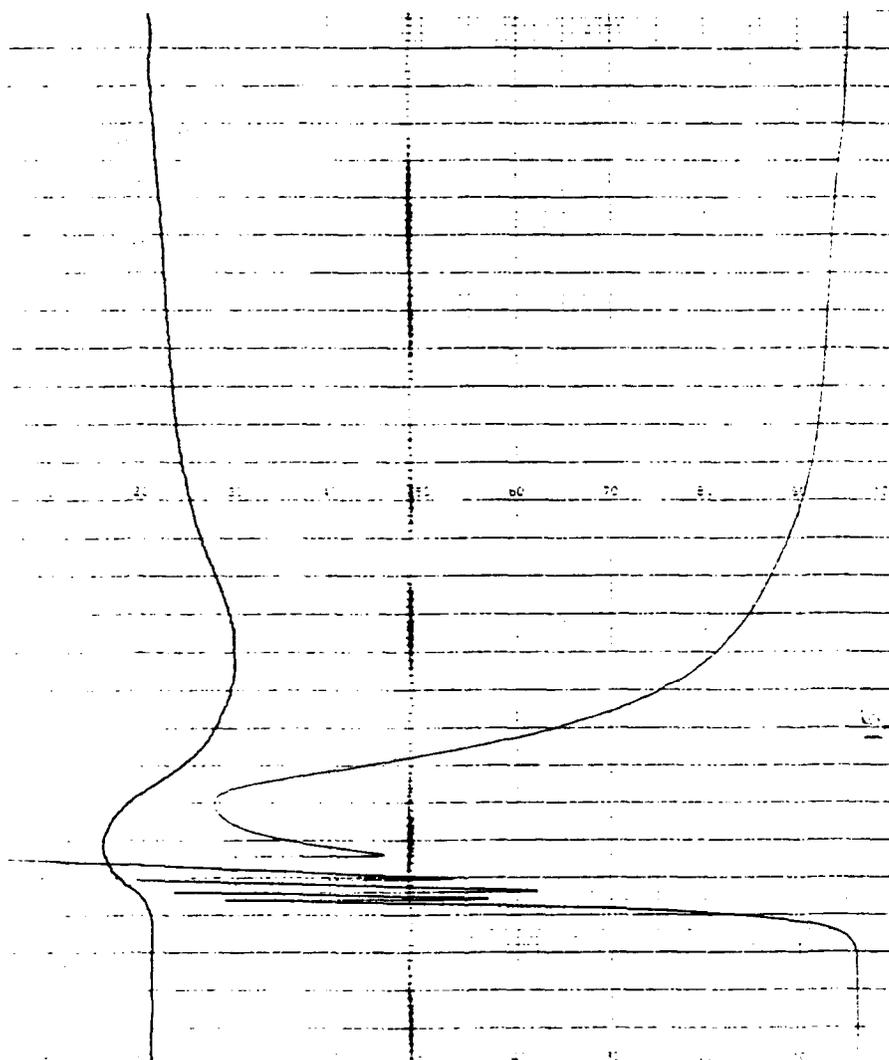


Figure 21. GP Chromatogram of a Poly(BAMO)/FPF-1/Poly(BAMO) Block Copolymer

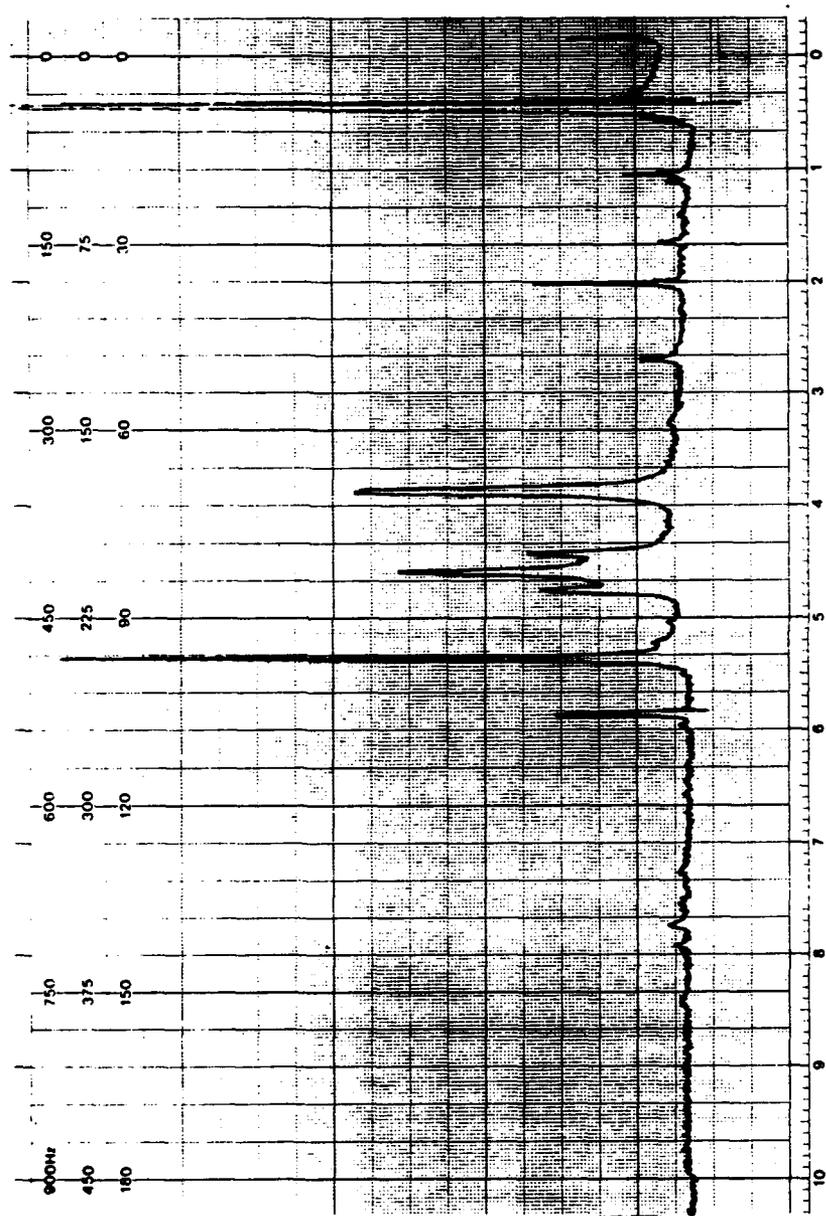


Figure 22. ^1H NMR Spectrum of a Poly(BAMO)/FPF-1/Poly(BAMO) Block Copolymer .

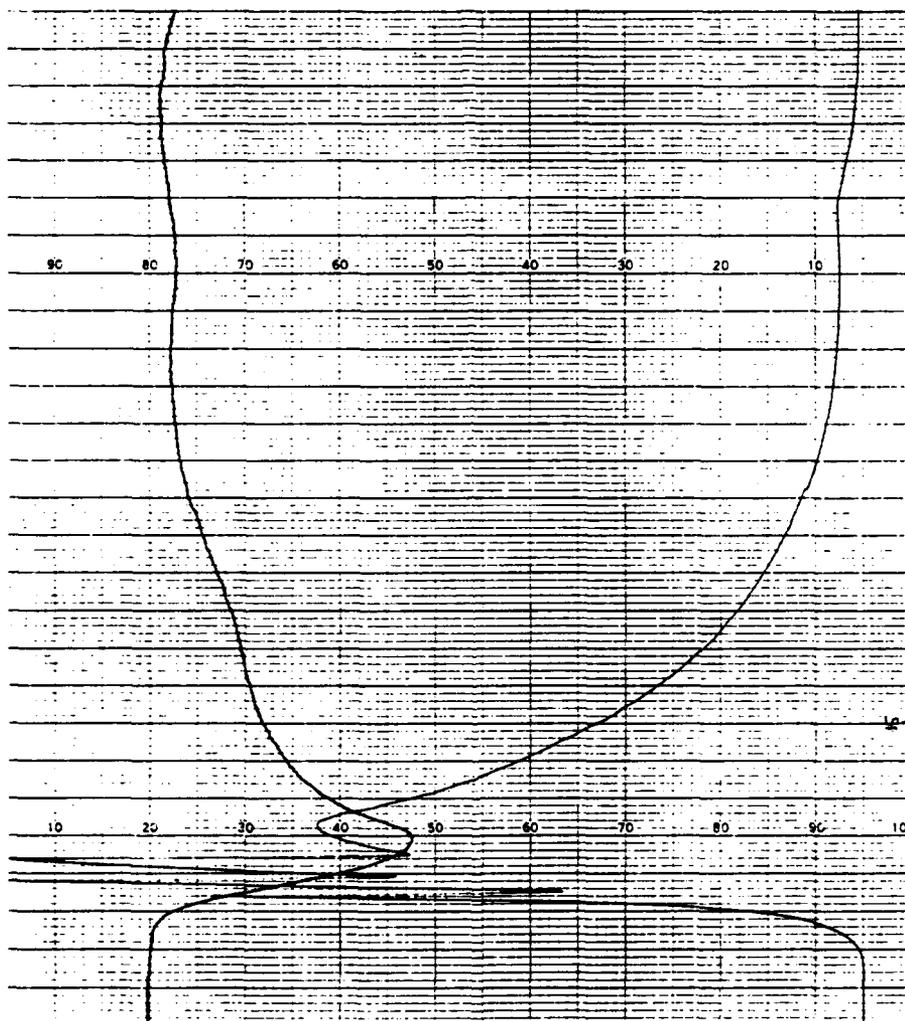


Figure 23. GP Chromatogram of a Poly(BAMO)/FPF-1 + GAP/Poly(BAMO) Block Copolymer

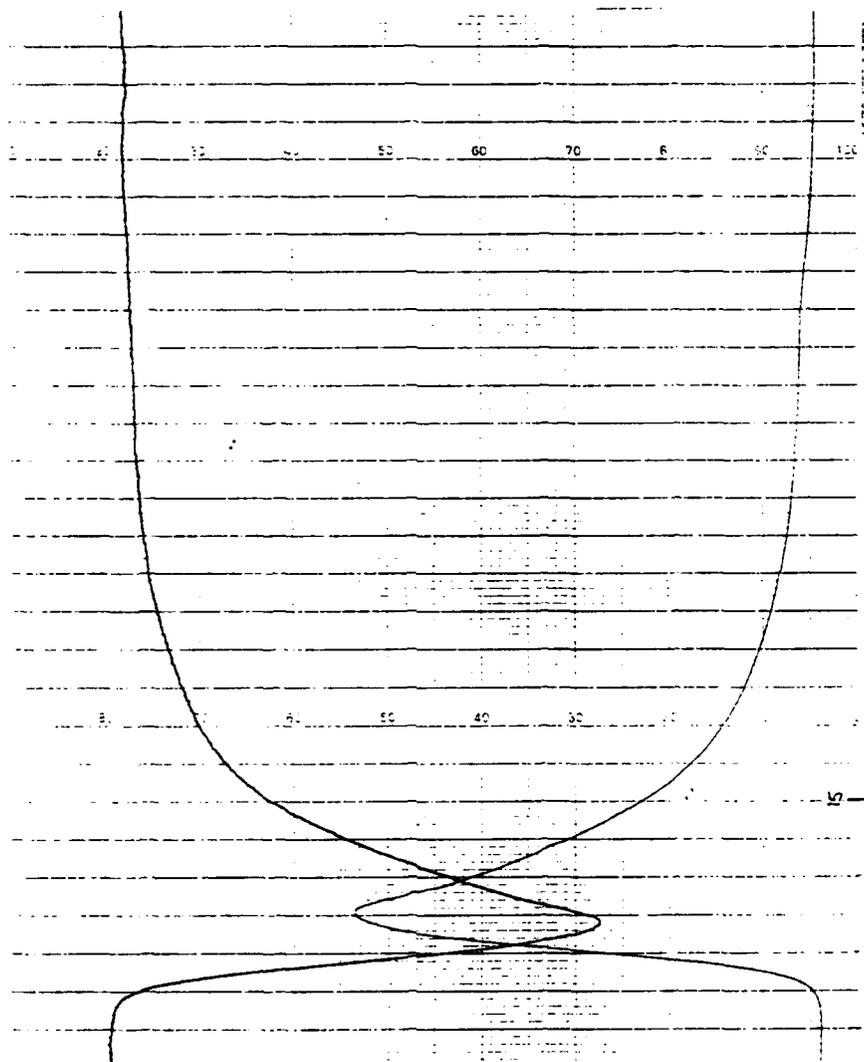


Figure 25. GP Chromatogram of a Poly(BAMO)/FPF-1 + Poly(AMMO)/Poly(BAMO) Block Copolymer

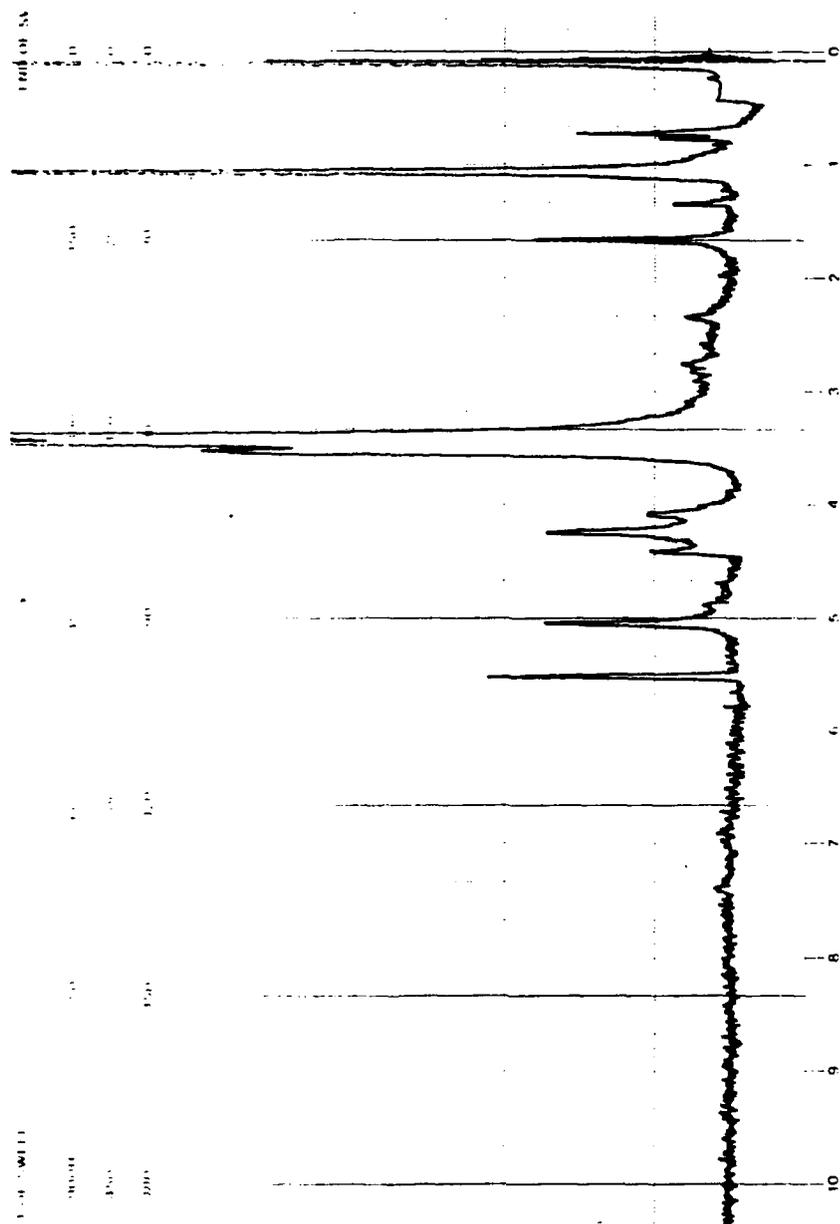


Figure 26. ¹H NMR Spectrum of a Poly(BAMO)/FPF-1 + Poly(AMMO)/Poly(BAMO) Block Copolymer

Sample: HGA 15B/1-1 + TMETN
Size: 6.5710 mg
Method: DSC 5/MIN WARMING
Comment: 5°C/MIN UNDER NITROGEN -50 TO +150

DSC

File: 091191HG.07
Operator: JFK
Run Date: 11-Sep-91 13:00

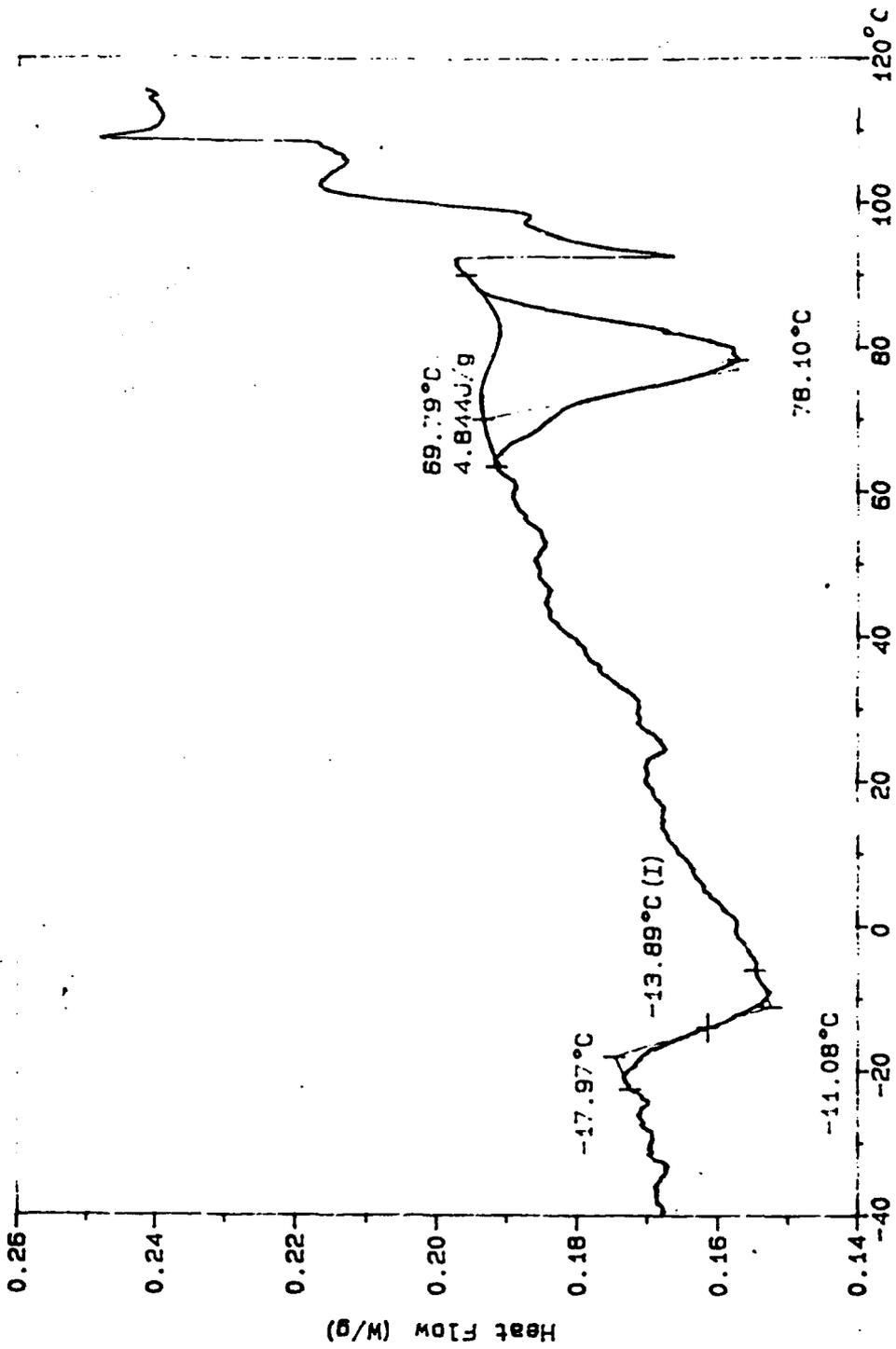


Figure 27. DSC of C₃₀-Alkane/TNTDD-PF ABA Triblock Polymer Plasticized with TMETN

Size: 7.9650 mg
 Method: DSC 5/MIN WARMING
 Comment: 5°C/MIN UNDER NITROGEN -50 TO +150
 Operator: JFW
 Run Date: 11-Sep-91 11:53

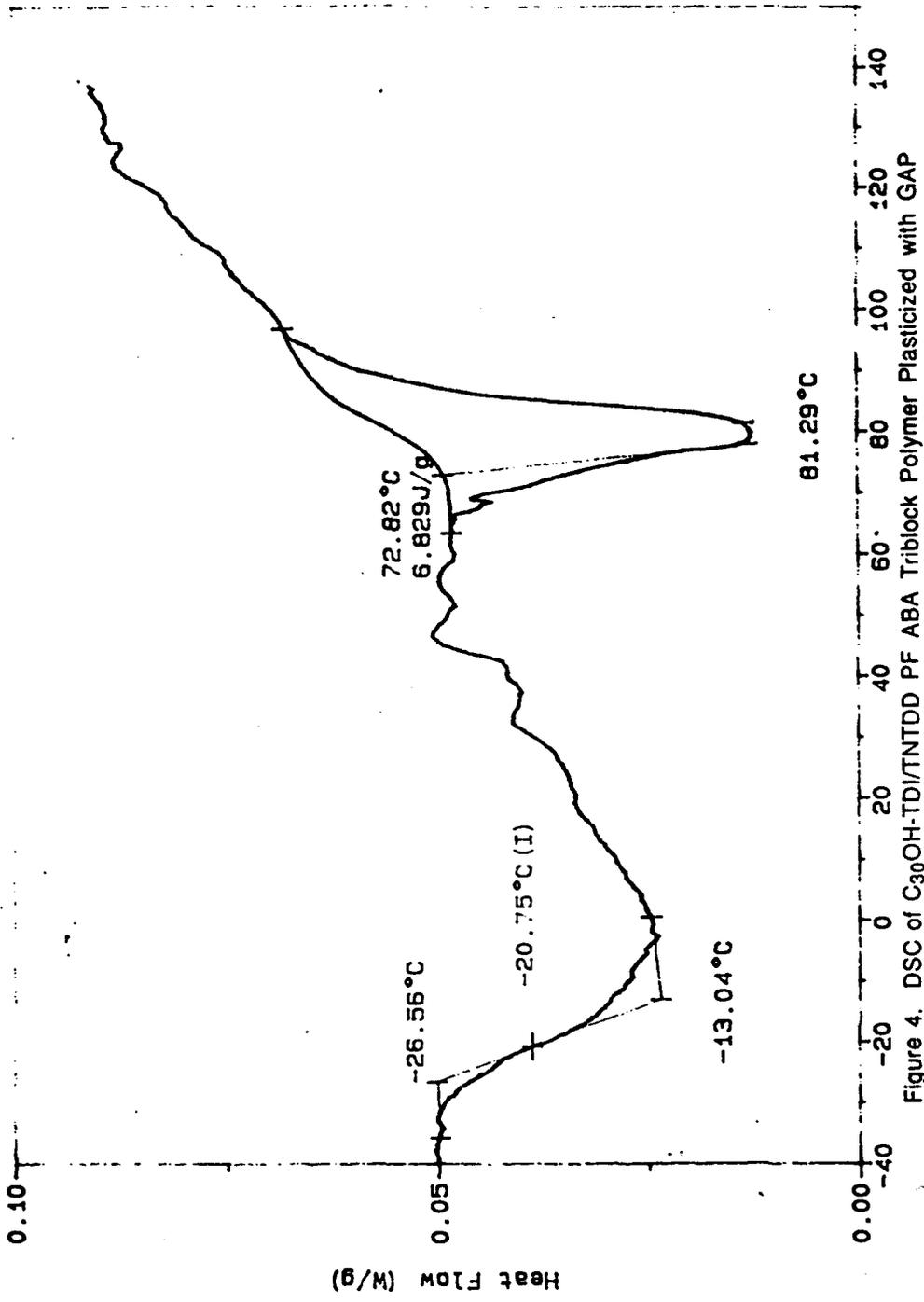


Figure 4. DSC of C₃₀OH-TDI/TNTDD PF ABA Triblock Polymer Plasticized with GAP

Figure 28. DSC of C₃₀-Alkane/TNTDD-PF ABA Triblock Polymer Plasticized with GAP

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