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AFML-TR-78-175

ADB037076

SYNTHESIS OF HIGH MOLECULAR WEIGHT FLUOROALKYLARYLENESILOXANYLENE (FASIL) POLYMER

*MIDWEST RESEARCH INSTITUTE
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JANUARY 1979

TECHNICAL REPORT AFML-TR-78-175

Final Report for Period 1 August 1977 to 29 December 1978

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This technical report has been reviewed and is approved for publication.




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Project Scientist



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-78-175	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis of High Molecular Weight Fluoroalkylarylenesiloxanylene (FASIL) Polymer		5. TYPE OF REPORT & PERIOD COVERED Technical Report - Final August 1, 1977-December 29, 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. L. Elliott		8. CONTRACT OR GRANT NUMBER(s) F33615-77-C-5152
9. PERFORMING ORGANIZATION NAME AND ADDRESS Midwest Research Institute 425 Volker Boulevard Kansas City, Missouri 64110		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson AFB, Ohio 45433		12. REPORT DATE January 1979
		13. NUMBER OF PAGES 33
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution limited to U.S. Government agencies only (test and evaluation). Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright- Patterson AFB, Ohio 45433.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Fluoroalkylarylenesiloxanylene (FASIL) polymers and intermediates Channel sealant FASIL monomers		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis of high molecular weight FASIL polymers and the following monomers and intermediates is described: 1. Methyl(3,3,3-trifluoropropyl)diethoxysilane 2. 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene 3. 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene 4. 1,3-Dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane 5. 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane		

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-77-C-5152, "Development of Synthesis of High Molecular Weight Fluoroalkylarylene-siloxanylene (FASIL) Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (MBP) as Project Scientist.

This technical report covers the work conducted from September 1977 to September 1978.

The work at Midwest Research Institute, designated as Project No. 4453-L, was conducted under the supervision of Dr. Cecil C. Chappelow, Jr., Head, Organic and Polymer Technology Section, Environmental and Materials Sciences Division. The work was carried out by Mr. T. J. Byerley, Mr. B. F. Hauber, Mr. R. K. Ruckman, and Mr. R. L. Elliott who served as principal investigator and prepared this report.

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SECTION I

INTRODUCTION

This report covers work carried out in support of the Air Force effort on the synthesis of novel high molecular weight fluoroalkylarylenesiloxanylene (FASIL) polymers (References 1, 2, 3, and 4) to be used in the subsequent development of aircraft integral fuel tank channel sealants to meet long-life and broad-temperature range applications. Channel sealants formulated by AFML from this polymer exhibit improved fuel and oxidation resistance, coupled with better flexibility at low temperatures, when compared with all other candidate materials (Reference 5).

This work encompassed the study of the synthesis of linear high molecular weight FASIL polymers, their intermediates and monomers (Reference 4).

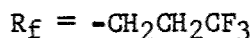
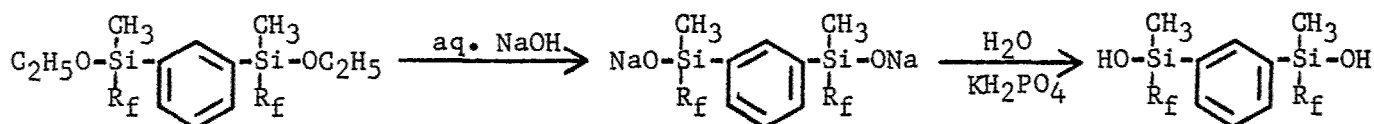
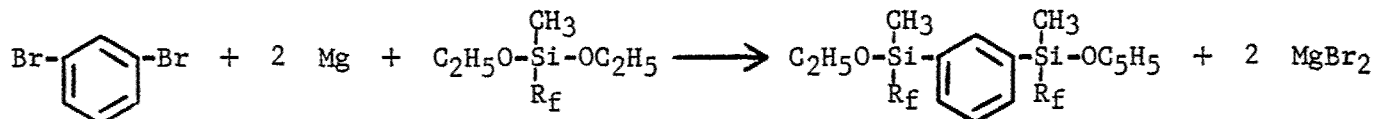
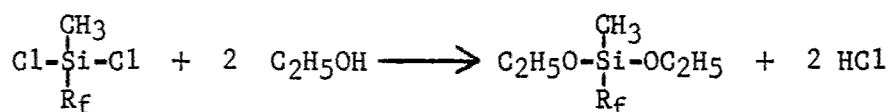
SECTION II

DISCUSSION

The synthesis of monomers, intermediates and high molecular weight FASIL polymers is discussed in this section.

1. Synthesis of Monomers and Intermediates

The following sequence of reactions was followed to synthesize 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene, the diol.



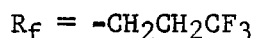
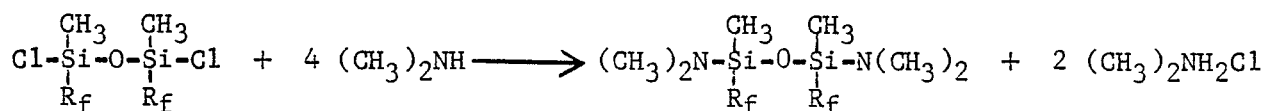
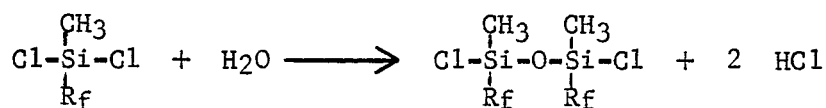
Treatment of methyl(3,3,3-trifluoropropyl)dichlorosilane with excess ethanol gave methyl(3,3,3-trifluoropropyl)diethoxysilane. A Grignard reaction of *m*-dibromobenzene with this compound gave the diethoxy Grignard intermediate, 1,3-[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene, which must be purified carefully to remove ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene, an impurity that probably results from partial reduction of *m*-dibromobenzene during the Grignard reaction. The monoethoxy material is hydrolyzed to the silanol during the synthesis of the diol, and the silanol acts as a chain stopper in the oligomer preparation.

Hydrolysis of the diethoxy Grignard product gave the diol, 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene. The diol could be purified by flash distillation if all traces of base were removed, and using "pure" diethoxy compound gave pure diol. The impurity in the diol which was identified as hydroxymethyl(3,3,3-trifluoropropyl)silylbenzene, was first detected by gel permeation chromatography using Waters Micro Styrogel columns (10^6 , 10^5 , 10^4 , 10^3 , 500, 10^2 , 10^2 Å) with tetrahydrofuran as solvent and a UV

detector. The corresponding monoethoxy derivative was found in the diethoxy Grignard compound before hydrolysis and its presence is shown in the GPC in Figure 4. The monoethoxy impurity appears at an elution volume of 73 ml, and, although it appears to be a major contaminant, it is actually present in less than 1% concentration (by GLC), but highly absorptive in ultra-violet light. Its presence could be detected by TLC on silica gel with methylene chloride elutant as a small spot proceeding the diethoxy Grignard product.

Occasionally the diol would polymerize rather than distill during purification by flash distillation. This polymeric material could be reconstituted to the diol by redissolving it in basic solution and neutralizing it again in the buffered solution.

The other monomer, 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, was prepared by the following sequence of reactions.

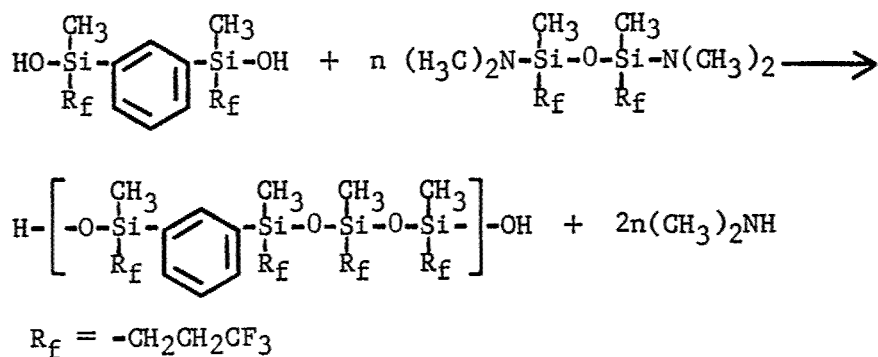


The intermediate compound, 1,3-dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, was prepared by the addition of water to an excess of methyl-(3,3,3-trifluoropropyl)dichlorosilane in ether. The best yields were obtained when a 3:1 molar excess of dichlorosilane was employed. About 31% of the dichlorosilane could be recovered for reuse and the amount of higher boiling oligomers was kept to a minimum.

Treatment of the dichlorodisiloxane with excess dimethylamine gave the dimethylamino monomer.

2. Initial Study of FASIL Polymer

The polymer was prepared by the reaction of the diol, 1,3-bis[hydroxymethyl-(3,3,3-trifluoropropyl)silyl] benzene, and the diamine, 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane.



The initial study of polymer preparation investigated the effect of monomer stoichiometry and, to a lesser extent, the effect of solvent. Melt polymerizations, which gave higher molecular weight polymers, were conducted by heating about 5 g of the diol monomer with the desired amount of the diamine monomer at 150° to 200° for 3 hr. Results were assessed in terms of inherent viscosities, which were determined in tetrahydrofuran at 30° at a concentration of 0.5 g per 100 ml. The polymers were hydrolyzed to remove any amino end groups and washed with methanol to remove any low molecular weight oligomers. The results are summarized in Table 1.

Polymerizations employing a solvent (toluene) gave lower molecular weight polymers, but decreasing the solvent amount gave higher molecular weights. Higher molecular weight polymers were obtained by melt polymerizations using a monomer stoichiometry (the ratio of diamine to diol) between 95 and 100% with lower molecular weight polymers being formed on either side of that range. Since the viscosity increased after a methanol wash for some polymers, some lower molecular weight material was removed during that step. Experiment No. 16 shows the effect of adding the diamine in increments during the polymerization, and the viscosity appeared to peak near 94% of stoichiometry.

3. FASIL Polymer Sample Preparation

At the request of AFML, three 50 g samples of FASIL polymers were prepared. The desired molecular weight ranges were 70,000, 90,000 and 110,000, and the corresponding inherent viscosities (from $K = 1.89 \times 10^{-4}$ and $a = 0.63$ from the Mark-Houwink equation) were calculated to be 0.216, 0.253 and 0.287 dl/g, respectively.

The preparation of these samples used a scale-up factor of 4 to 5 over the initial polymer study. A small amount of toluene was used as solvent in the first two samples to assist in dispersing the monomers (Table 2). After the diol had dissolved, the solution was heated to reflux. Dimethyl amine

evolution began at about 55°. The desired viscosity range was obtained by adding small increments of diamine. The melt polymerizations were conducted by first mixing the monomers and warming the mixture slowly to assist in dissolving the diol. Usually the polymerization initiated at 50° with an accompanying exotherm to 75° or higher and a rapid evolution of dimethyl amine.

Experiment No. 7 (Table 2) was actually an attempt to prepare a polymer with a viscosity near 0.287 dl/g, or slightly higher than Experiment No. 4. The last incremental addition of diamine raised the viscosity to 0.341 dl/g, and apparently during the hydrolysis to remove amino-end groups, additional polymerization occurred, because the viscosity was increased to 0.541 dl/g ($\bar{M}_v = 300,000$).

SECTION III

EXPERIMENTAL

Temperatures are recorded in degrees Centigrade. IR spectra were measured on a Perkin-Elmer Infracord 137 in the phases noted. NMR spectra were measured on a Varian 360 A. GLC spectra, for quality control, were measured on a Perkin-Elmer Model 154 Fractometer. GPC curves were measured on a Waters 301 UV detector (254 nm). Microanalytical work was performed by Sprang Microanalytical Laboratory. All inherent viscosities were determined at 30° using tetrahydrofuran as solvent and at polymer concentration of 0.5 g/100 ml.

1. Methyl(3,3,3-trifluoropropyl)diethoxysilane

In a 1-l, three-necked flask (flamed-dried under nitrogen) was placed 422 g (2.0 moles) of methyl(3,3,3-trifluoropropyl)dichlorosilane. Absolute ethanol (230 g, 5.0 moles) was added slowly in 1 hr. The reaction initially was endothermic and the temperature was maintained at 15° with an ice bath. The reaction mixture was purged with nitrogen while it was heated to 60° in 2 hr. The excess ethanol was removed by distillation, and distillation of the residue (using an unpacked column) gave 382.8 g (82%) b.p. 92° (90 mm). (infrared spectrum, Figure 1).

2. 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene

Into a 2-l flask (flame-dried under nitrogen) was placed 40.0 g (1.65 g-atom) of oven-dried magnesium turnings, 100 ml of THF, and 2-5 g of the total 188 g (0.80 mole) of 1,3-dibromobenzene, and the reaction was initiated by use of a heating mantle. The remaining 1,3-dibromobenzene in 360 ml of THF was added in about 1 hr. After the mixture was refluxed for 4 hr, 450 ml of THF was added, and the mixture was cooled to ice bath temperature. Methyl(3,3,3-trifluoropropyl)diethoxysilane (386 g, 1.6 moles) was added in 0.5 hr. The mixture was refluxed for 2 hr, then cooled to room temperature and filtered. Solvent was removed from the filtrate on a rotary evaporator. The gummy residue was washed with about 3 liters of petroleum ether in a Waring blender until the salts were a fine, white, free-flowing powder. After the solvent was flashed off, distillation through a 4-plate Oldershaw column gave 230 g (64%) of product, boiling range 100-108° (0.2 mm).

Redistillation through a 10-plate Oldershaw column gave pure material, b.p. 93-94° (0.05 mm), single pot, TLC. An infrared spectrum is shown in Figure 2, and a GPC curve is shown in Figure 3. A GPC curve showing the material before removal of "the impurity component" is shown in Figure 4.

When methyl(3,3,3-trifluoropropyl)diethoxysilane was added to the Grignard reagent at reflux instead of at 0°, the yield of product was 47% (for eight reactions). Concomitant addition, where the diethoxysilane and m-dibromobenzene were added together, gave only a 34% yield. Inverse addition, where the Grignard reagent was added to the diethoxysilane, gave a 43% yield.

An impurity, ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene, b.p. 80° (2 mm), n_D^{25} 1.4451, is present in the early distillation fractions. This material can be hydrolyzed to the silanol, and if it is not removed at this step, it will carry over into the diol preparation and act as a chain stopper in polymerization reactions. An infrared spectrum is shown in Figure 5.

3. 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene

This compound was prepared by a modification of the procedure described by Pike (Reference 6). To a solution of 16.0 g (0.40 mole) of sodium hydroxide in 15 ml of water and 70 ml of methanol was added 44.6 g (0.10 mole) of 1,3-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene in 5 min. A solution of 16 g (0.40 mole) of sodium hydroxide in 80 ml of water was added in 5 min, and the solution was stirred for 0.5 hr. After the solution was poured slowly into a solution of 122.4 g (0.9 mole) of potassium phosphate (monobasic) in 1 liter of water and 500 ml of crushed ice, it was allowed to stand for 0.5 hr. The water layer was decanted from the lower viscous layer and extracted three times with 50 ml of methylene chloride. The lower viscous layer was also extracted with two washes of methylene chloride. The combined methylene chloride layers were washed four times with 100 ml of water, and stripped of solvent. A short-path distillation gave 37.2 g (94%) of diol, b.p. 126-132° (0.03 mm), (infrared spectrum, Figure 6). A GPC curve of the pure diol is shown in Figure 7 and a GPC curve of the diol with "the impurity" is shown in Figure 8.

Sometimes during the course of a distillation of the diol, the material in the distillation pot will undergo self-condensation to dimer and higher material because of the presence of trace amounts of base. Such material may be reconverted to the diol as demonstrated by the following procedure:

The pot residue of an aborted distillation of the diol, weighing 80.9 g (0.207 mole based on the diol), was diluted with a solution of 49.8 g (1.245 moles) of sodium hydroxide in 110 ml of methanol and 125 ml of water. The mixture was stirred for 5 hr and allowed to stand for 90 hr. The clear solution was slowly poured into an ice water solution containing 170 g (1.245 moles) of potassium phosphate (monobasic) and worked up as a regular diol preparation. Distillation gave 68.6 g (85%) of diol boiling at 138-140° (0.08 mm).

4. 1,3-Dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

In a 500-ml flask (flame-dried under nitrogen) were placed 200 ml of ether and 211 g (1.0 mole) of methyl(3,3,3-trifluoropropyl)dichlorosilane. A solution of 6.0 g (0.33 mole) of water dissolved in 44 ml of tetrahydrofuran was added slowly with rapid stirring. Hydrochloric acid evolved during the addition was swept into a water trap with nitrogen. After the addition was completed, the ether was removed by distillation. Distillation of the residue gave 64.6 g (31% recovery) of methyl(3,3,3-trifluoropropyl)dichlorosilane, b.p. 75° (140 mm) and 80.3 g (66%) of the disiloxane, b.p. 110-111° (15 mm).

The best yields were obtained when the molar ratio of dichlorosilane to water was 3:1. Lower ratios of 2.25 and 2.5:1 gave yields of 55 and 58%, respectively, and a higher ratio of 4:1 gave about 53% yields.

5. 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane

About 70 ml of dimethylamine was condensed into a flask cooled to -70° and then diluted with 475 ml of petroleum ether. As the temperature was maintained at -20°, 78.4 g (0.21 mole) of 1,3-dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane was added in 0.5 hr. The reaction mixture was stirred at -20° for 0.5 hr and allowed to warm to room temperature. The salts were removed by filtration and washed with petroleum ether. The combined filtrates were stripped of solvent, and distillation of the residue gave 61.3 g (75%) of product, b.p. 109-110° (9 mm) (infrared spectrum, Figure 9).

6. Initial Study of FASIL Polymer Preparation

The study of the preparation of high molecular weight FASIL polymers from the diol, 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene, and the diamine, 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, dealt largely with the stoichiometry of the monomers, and to a smaller extent, with the effect of solvent amounts. Most of the experiments were carried out without a solvent (melt polymerizations). The initial series of experiments is summarized in Table 1, and the general preparative procedure was as follows:

A flame-dried flask containing 5.003 g (0.0128 mole) of the diol and 4.7038 g (0.0122 mole, 95% of stoichiometry) of diamine was heated to 150° in 1 hr and to 195° in 2 more hours. The polymerization reaction generally initiated at 50° to 55°. A nitrogen sweep was maintained to remove the dimethylamine formed. The polymer was cooled to 110°, dissolved in 10 ml of toluene and 1 ml of water and refluxed for 0.5 hr to hydrolyze any

diamino end groups. The solvent and water were flashed off on a rotary evaporator, and the residue was heated to 200° (0.1 mm) for 2 hr to remove all traces of solvent. The inherent viscosity of the polymer (determined at 0.5 g/100 ml concentration in tetrahydrofuran at 30°) was 0.184 dl/g. The polymer, washed with methanol and dried at 200° (0.1 mm), weighed 8.1 g (97%) and had an inherent viscosity of 0.185 dl/g.

Experiment No. 16 is an example of incremental addition of the diamine to the polymer mix. Starting with 87% of stiochiometry, incremental amounts of diamine were added at 1-hr time intervals, and inherent viscosities were determined at each level. Such a procedure has been described by Patterson (Reference 7) and allows the preparation of a polymer in a desired viscosity range.

TABLE 1
EFFECT OF SOLVENT AMOUNT AND MONOMER STOICHIOMETRY
ON FASIL POLYMER PREPARATION

Experiment No.	Diamine/Diol Ratio (%)	Solvent/Diol Ratio (ml/g)	Inherent Viscosity Initial (dl/g)	Inherent Viscosity Final ^{a/} (dl/g)
1	90	Melt	0.139	0.154
2	91	Melt	0.293	--
3	92.5	Melt	0.161	0.164
4	95	Melt	0.142	0.171
5	95	Melt	0.184	0.185
6	95	Melt	0.248	--
7	97.5	Melt	0.144	0.165
8	100	2:1	0.101	--
9	100	2.5:1	0.162	--
10	100	Melt	0.373	--
11	101	Melt	0.995	0.169
12	102	2:1	0.119	0.157
13	102	1:1	0.160	0.169
14	102	Melt	0.178	--
15	105	2:1	0.095	--
16 ^{b/}	a. 87	Melt	0.133	--
	b. 90		0.136	--
	c. 92		0.164	--
	d. 94		0.188	--
	e. 96		0.179	--
	f. 98		0.173	0.195

^{a/} The polymer was washed with methanol.

^{b/} The diamine was added incrementally.

7. FASIL Polymer Sample Preparation

Three 50-g polymer samples were prepared. The three molecular weight levels desired and their corresponding inherent viscosities (calculated from $K = 1.89 \times 10^{-4}$ and $a = 0.63$) were 70,000 ($\eta_{inh} = 0.216$), 90,000 ($\eta_{inh} = 0.253$), and 110,000 ($\eta_{inh} = 0.287$). These polymer samples were prepared in about 25-g batches using the following procedure.

A solution of 19.9494 g (0.0512 mole) of diol (freshly distilled) and 19.7756 g (0.0515 mole) of the diamine monomer in 10 ml of toluene was refluxed under nitrogen for 2 hr. The inherent viscosity (in tetrahydrofuran at 30°) of the polymer at this stage was 0.142 dl/g. About 2 ml of water and 10 ml of toluene were added and after 1 hr at reflux, the water was removed in a Dean-Stark trap with toluene. To the solution was added 0.01 g of diamine and after 2 hr at reflux the inherent viscosity of a polymer sample was 0.213 dl/g. About 10 ml of toluene was removed by distillation, and after 4 hr at reflux, the inherent viscosity had increased to 0.258 dl/g. After another hydrolysis, solvent was removed on a rotary evaporator and devolatilization at 200° (0.1 mm) for 2 hr gave 33.7 g (90%) of polymer with an inherent viscosity of 0.263 dl/g.

The results of the three polymer preparations are summarized in Table 2. The two samples in each set were combined and the viscosity was re-determined. These three samples were forwarded to the Air Force Materials Laboratory. An infrared spectrum for samples 1, 2, and 3 are shown in Figures 10, 11, and 12, respectively, and the GPC curves are shown in Figures 13, 14, and 15.

The melt polymerization experiments (Nos. 5 and 6) were heated at 175° for a total of 20 hr, during which time additional amounts of diamine were added incrementally.

Experiment No. 7 gave a high molecular weight polymer ($\eta_{inh} = 0.541$ dl/g) that was beyond the desired range. A stoichiometric amount of monomers in a small amount of toluene had been heated for 2 hr at 150°. Since the viscosity (0.284 dl/g) at that time was near the desired level of 0.287 dl/g, the polymer was hydrolyzed to remove any amino-end groups. After hydrolysis, the viscosity had dropped to 0.085 dl/g; consequently, diamine monomer (0.4 g total over a 4 hr period) was added incrementally until an inherent viscosity of 0.341 dl/g was obtained. Hydrolysis treatment and devolatilization of the polymer gave a material with an inherent viscosity of 0.541 dl/g, $\bar{M}_v = 300,000$.

TABLE 2

SYNTHESIS OF HIGH MOLECULAR WEIGHT FASIL POLYMERS

<u>Experiment No.</u>	<u>Diamine/Diol (%)</u>	<u>Solvent/Diol (ml/g)</u>	<u>inh (dl/g)</u>	<u>Weight (g)</u>
Sample No. 1 (η inh desired = 0.216 dl/g)				
1	100	1.5:1	0.210	27.5
2	100	1:1	0.220	25.6
1 + 2	--	--	0.216	53.1
Sample No. 2 (η inh desired = 0.253 dl/g)				
3	100	1:1	0.251	23.1
4	100	0.5:1	0.263	33.7
3 + 4	--	--	0.258	56.8
Sample No. 3 (η inh desired = 0.287 dl/g)				
5	100	Melt	0.285	37.6
6	98	Melt	0.328	29.5
5 + 6	--	--	0.340	67.1
7	100	0.25:1	0.541	24.7

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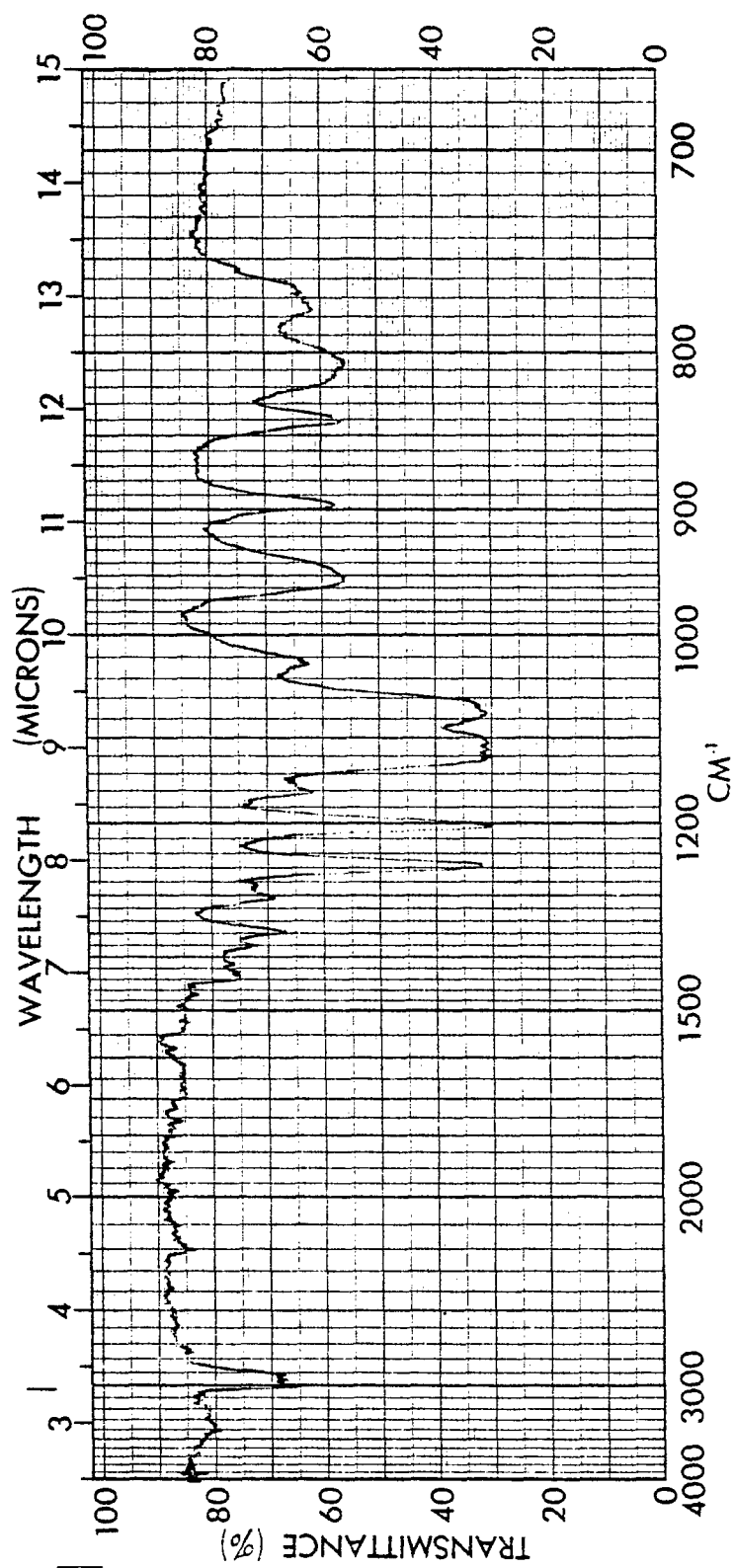


Figure 1 - Infrared Spectrum of Methyl(3,3,3-trifluoropropyl)diethoxysilane (Neat)

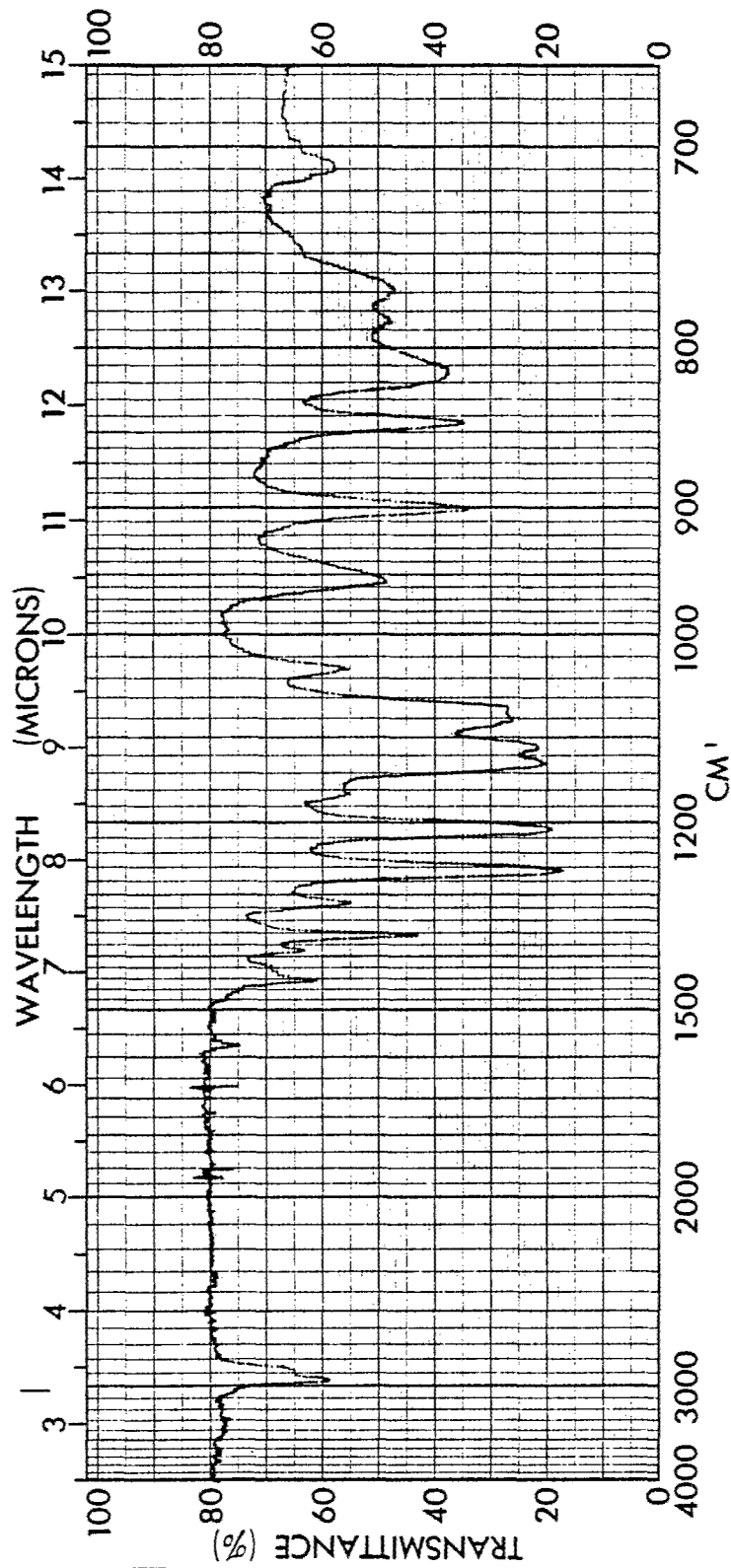


Figure 2 - Infrared Spectrum of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene (Neat)

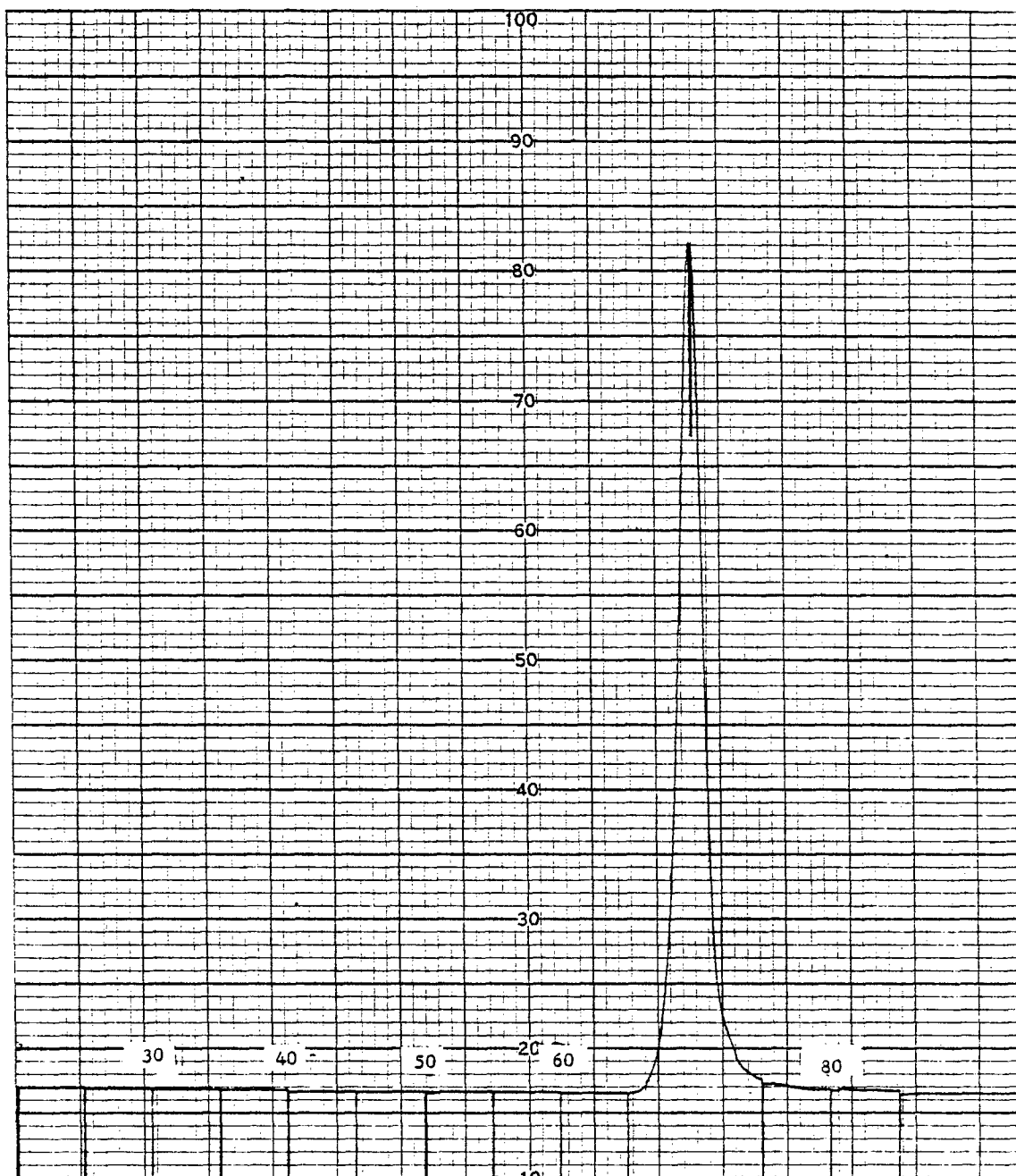


Figure 3 - GPC Curve of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene

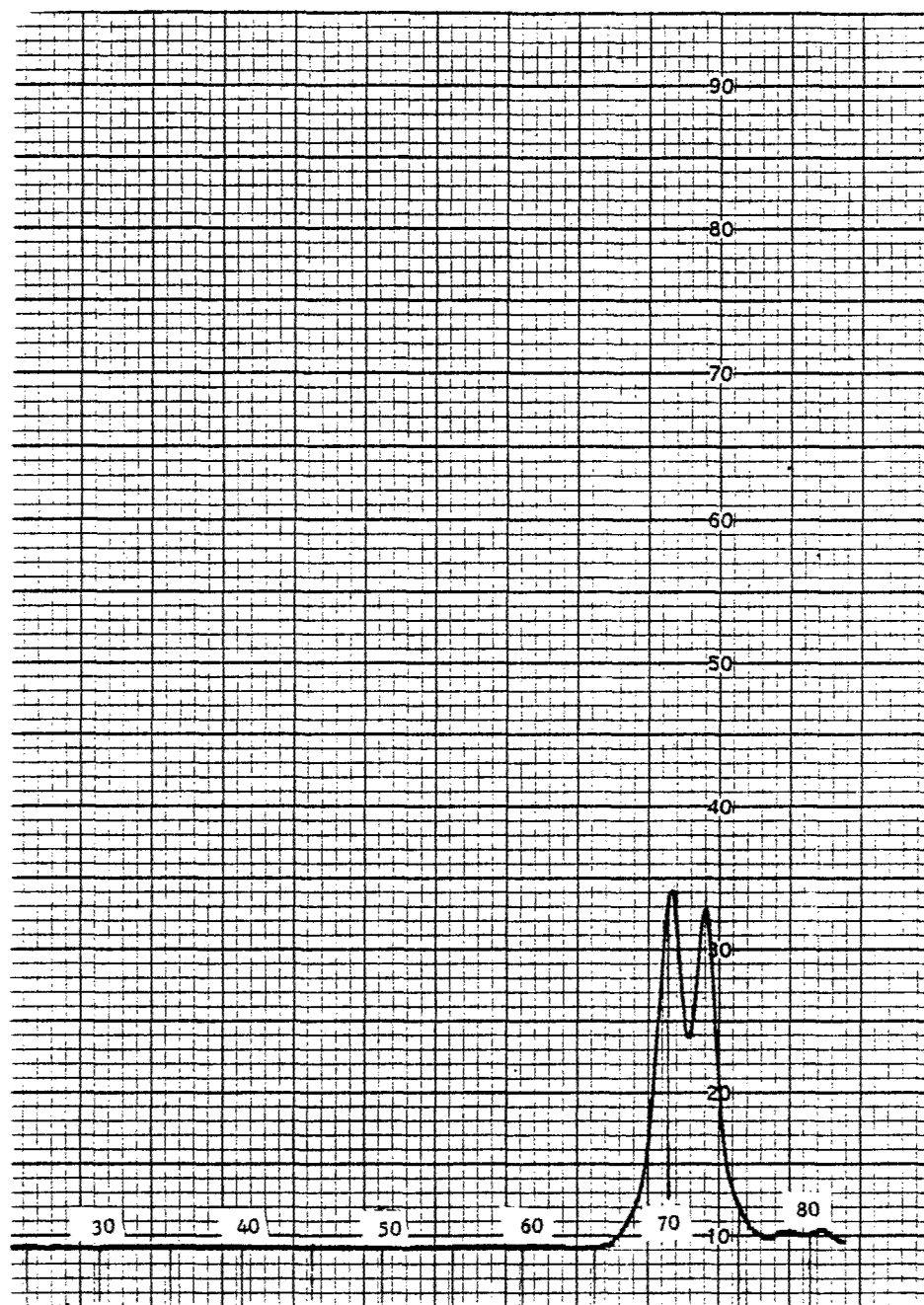


Figure 4 - GPC Curve of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene Containing an Impurity

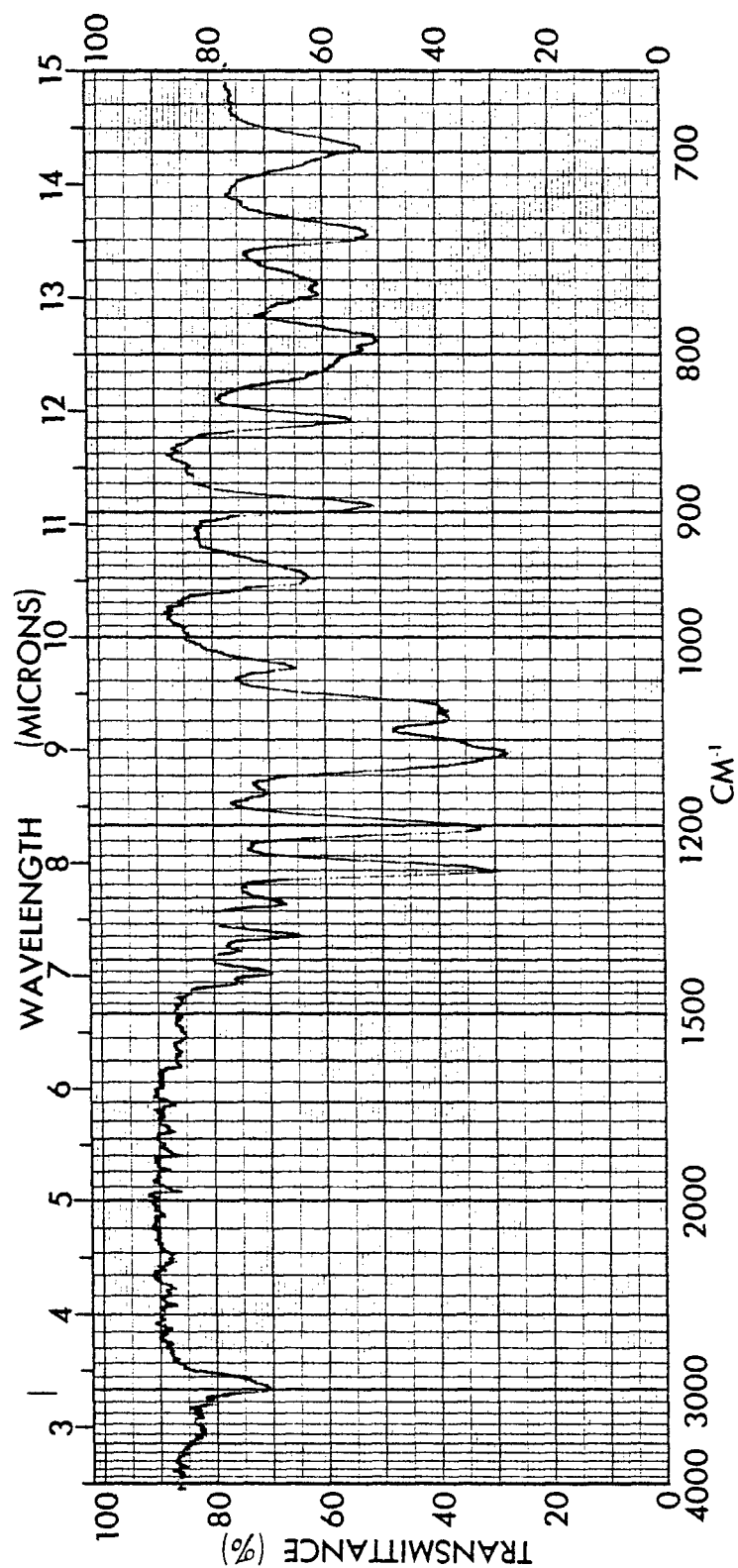


Figure 5 - Infrared Spectrum of Ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene (Neat)

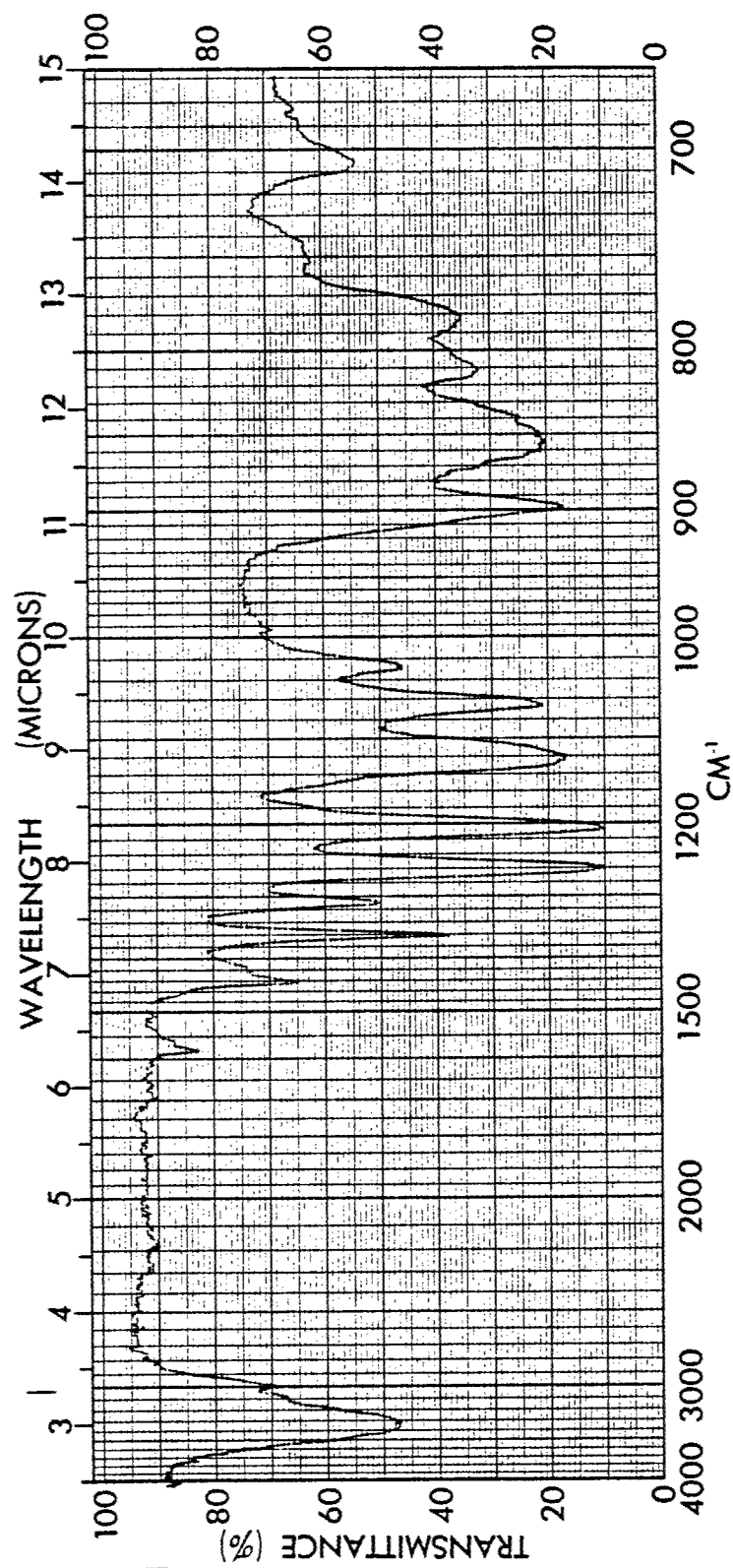


Figure 6 - Infrared Spectrum of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene (Neat)

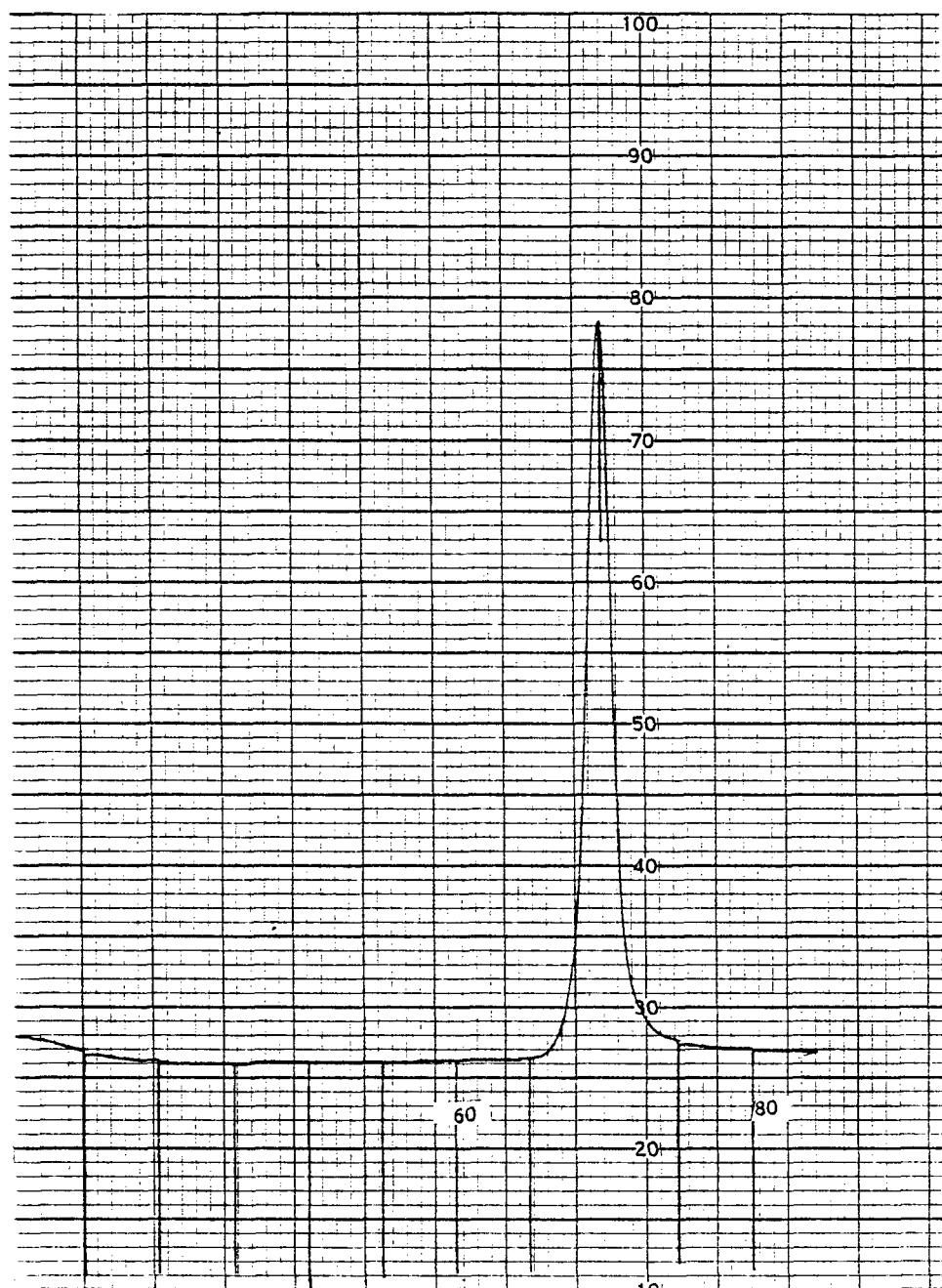


Figure 7 - GPC Curve of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene

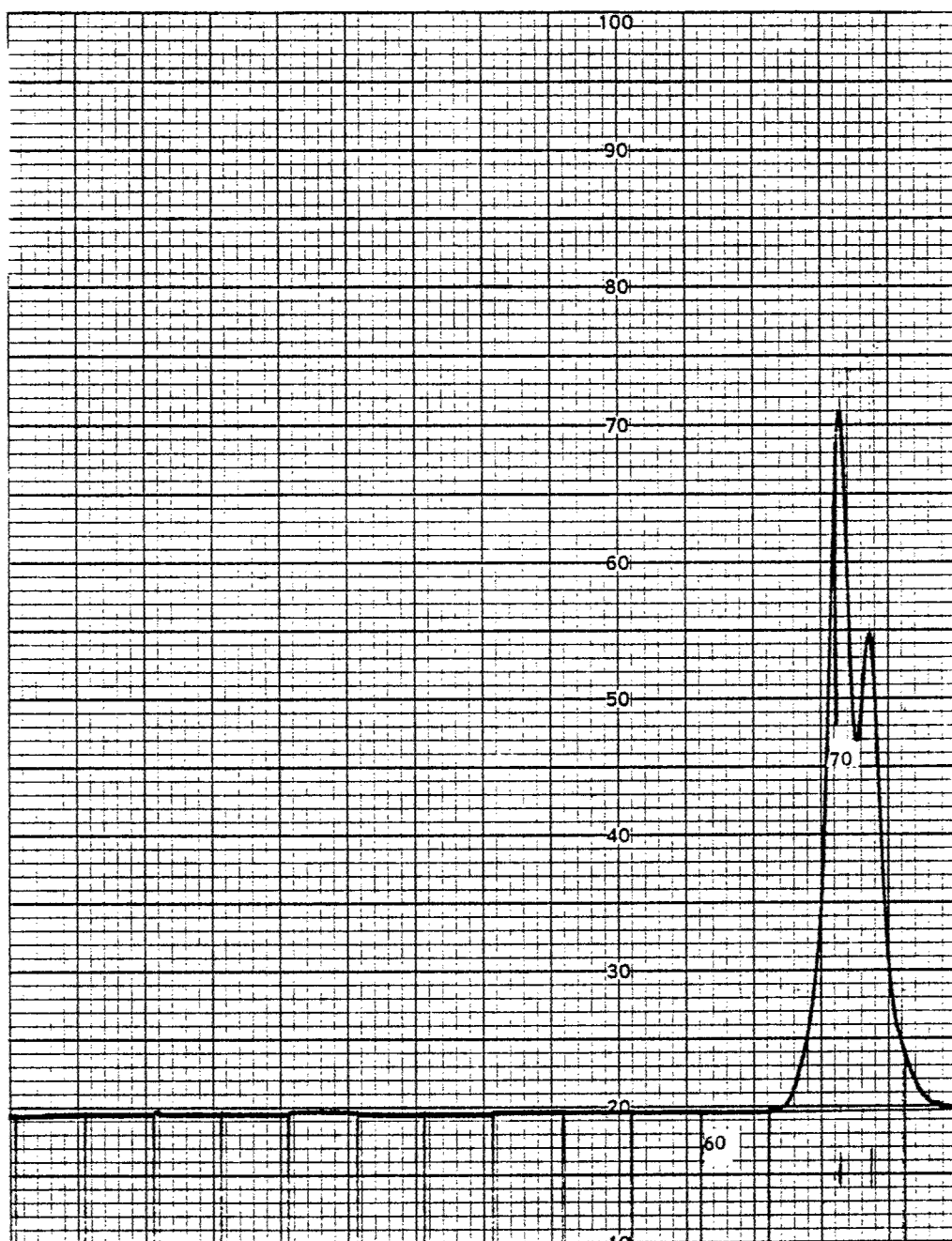


Figure 8 - GPC Curve of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene with Impurity

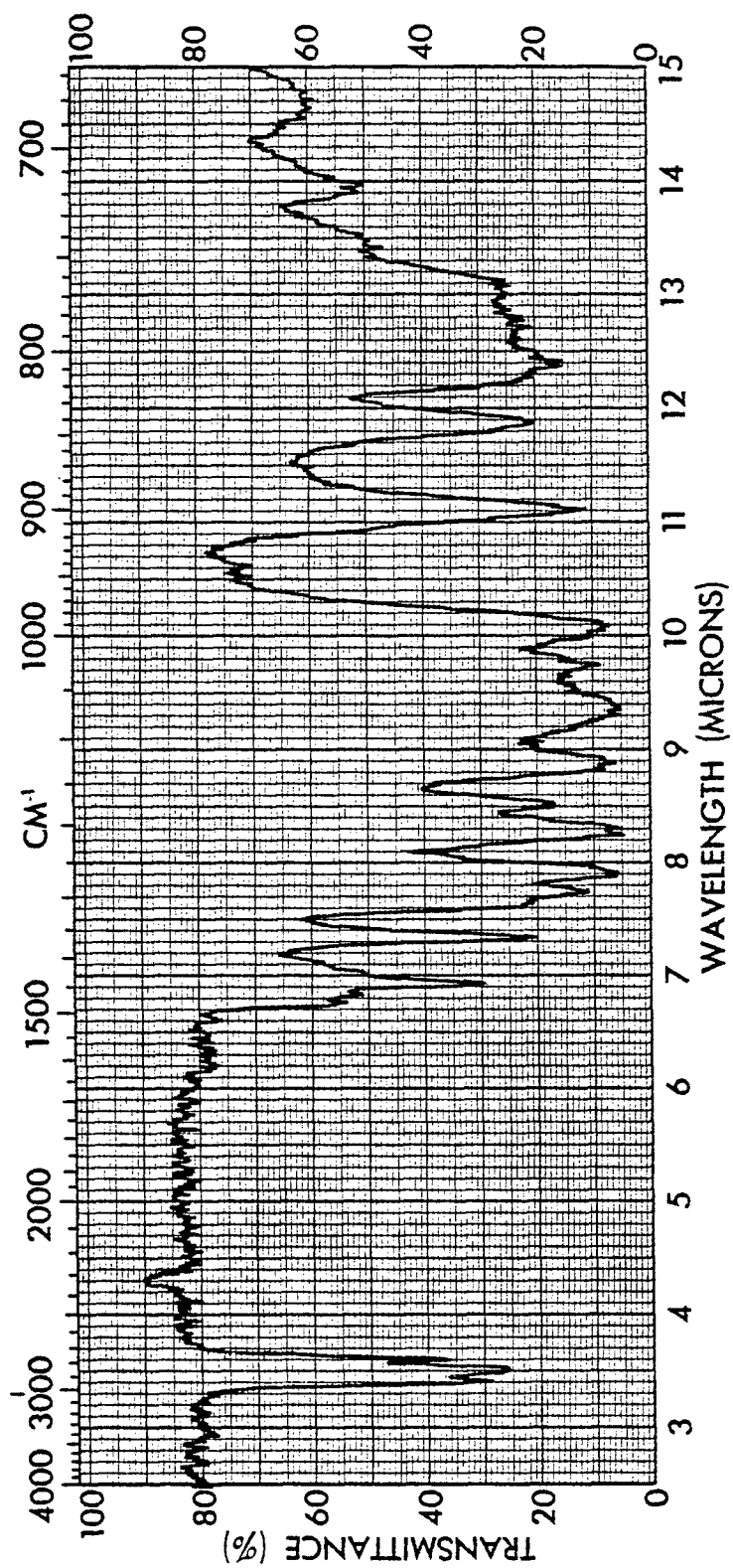


Figure 9 - Infrared Spectrum of 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxane (Neat)

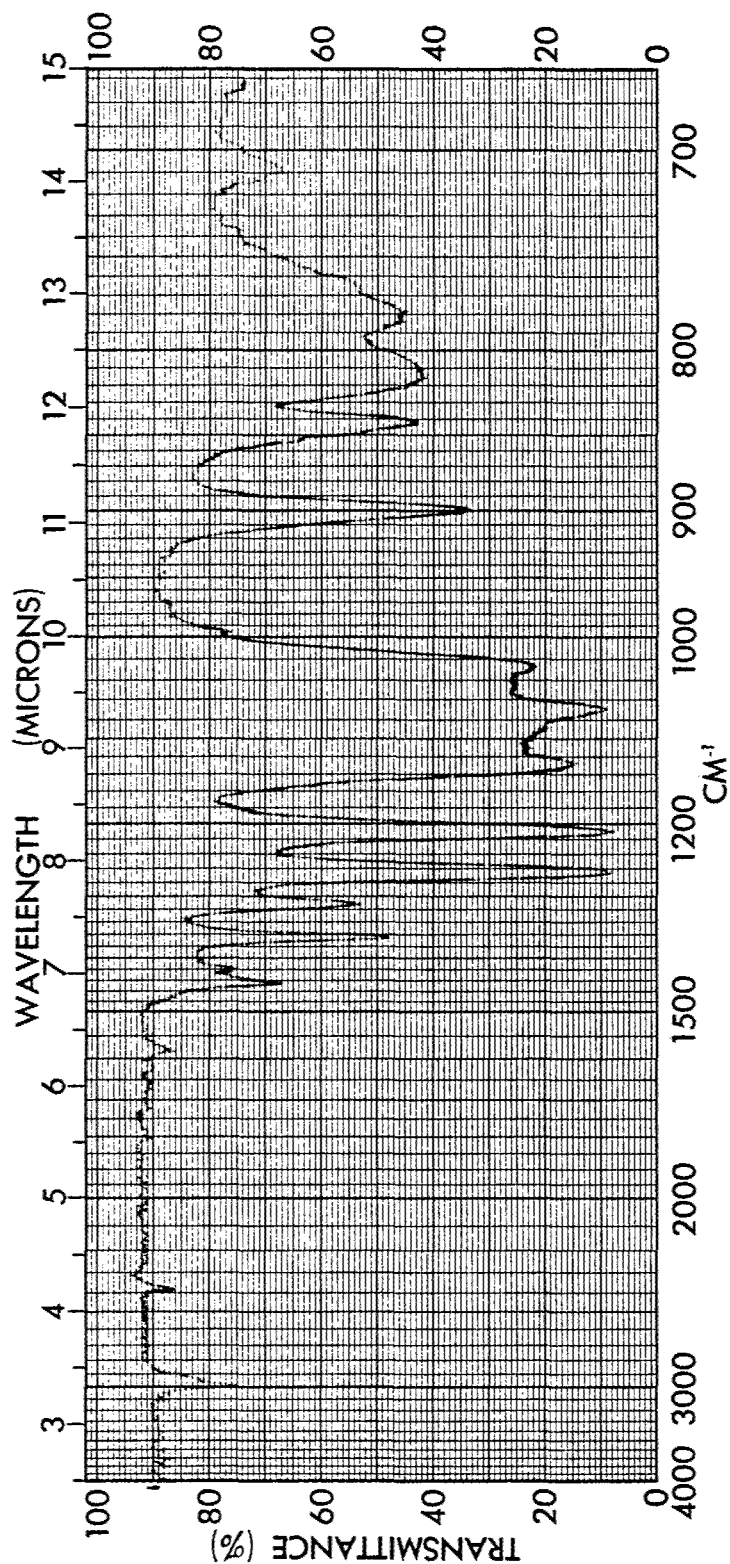


Figure 10 - Infrared Spectrum of FASIL Polymer Sample No. 1 (Neat)

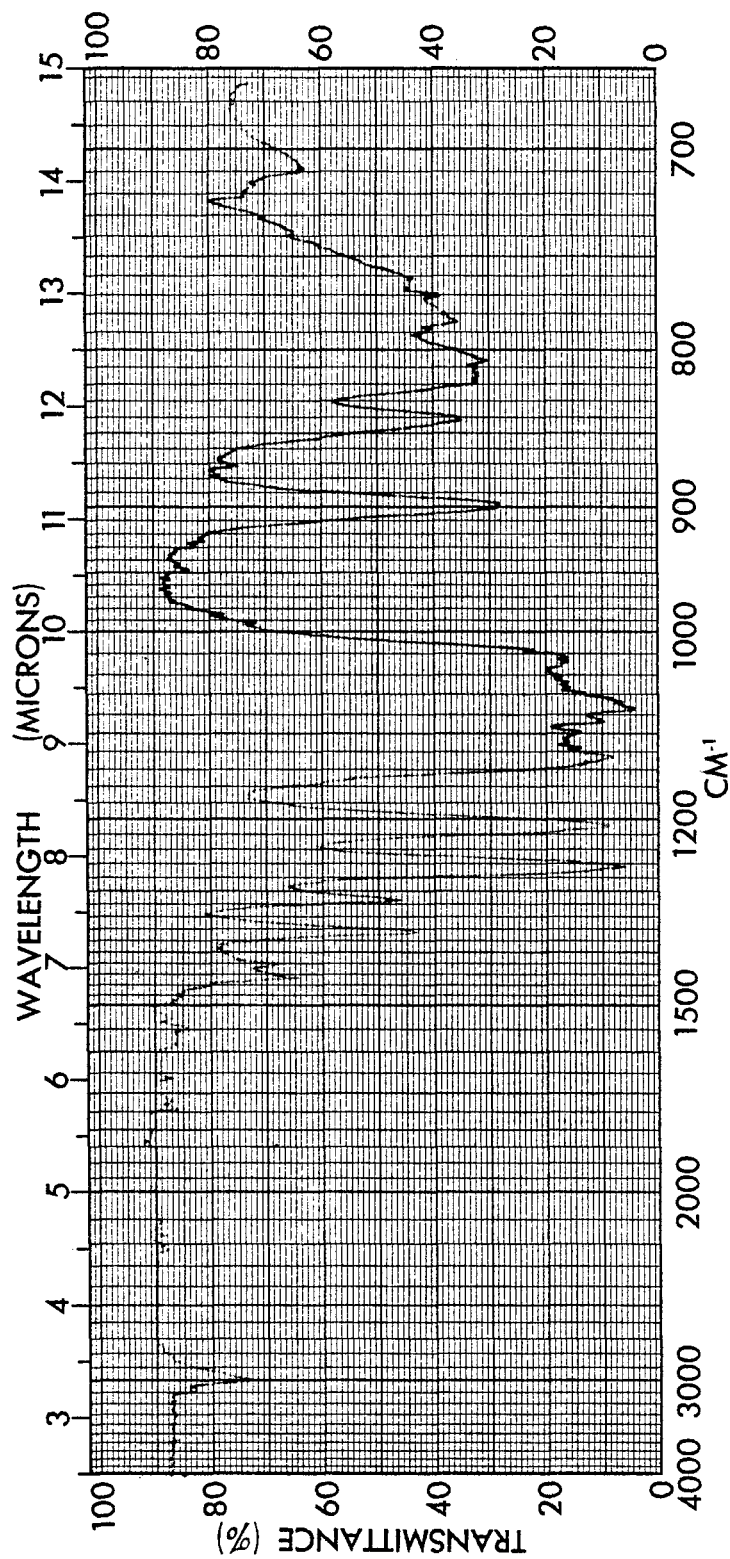


Figure 11 - Infrared Spectrum of FASIL Polymer Sample No. 2 (Neat)

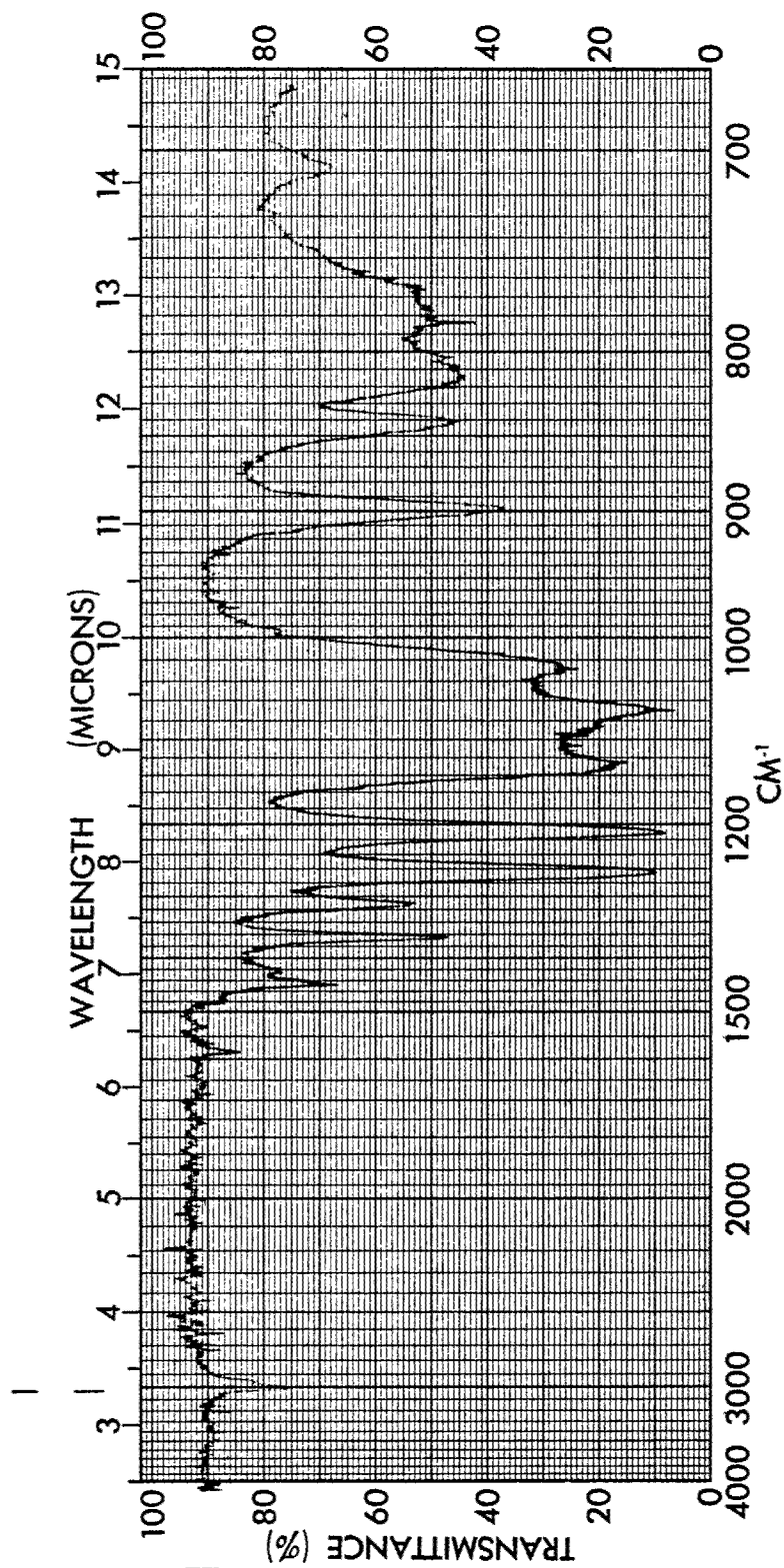


Figure 12 - Infrared Spectrum of FASIL Polymer Sample No. 3 (Neat)

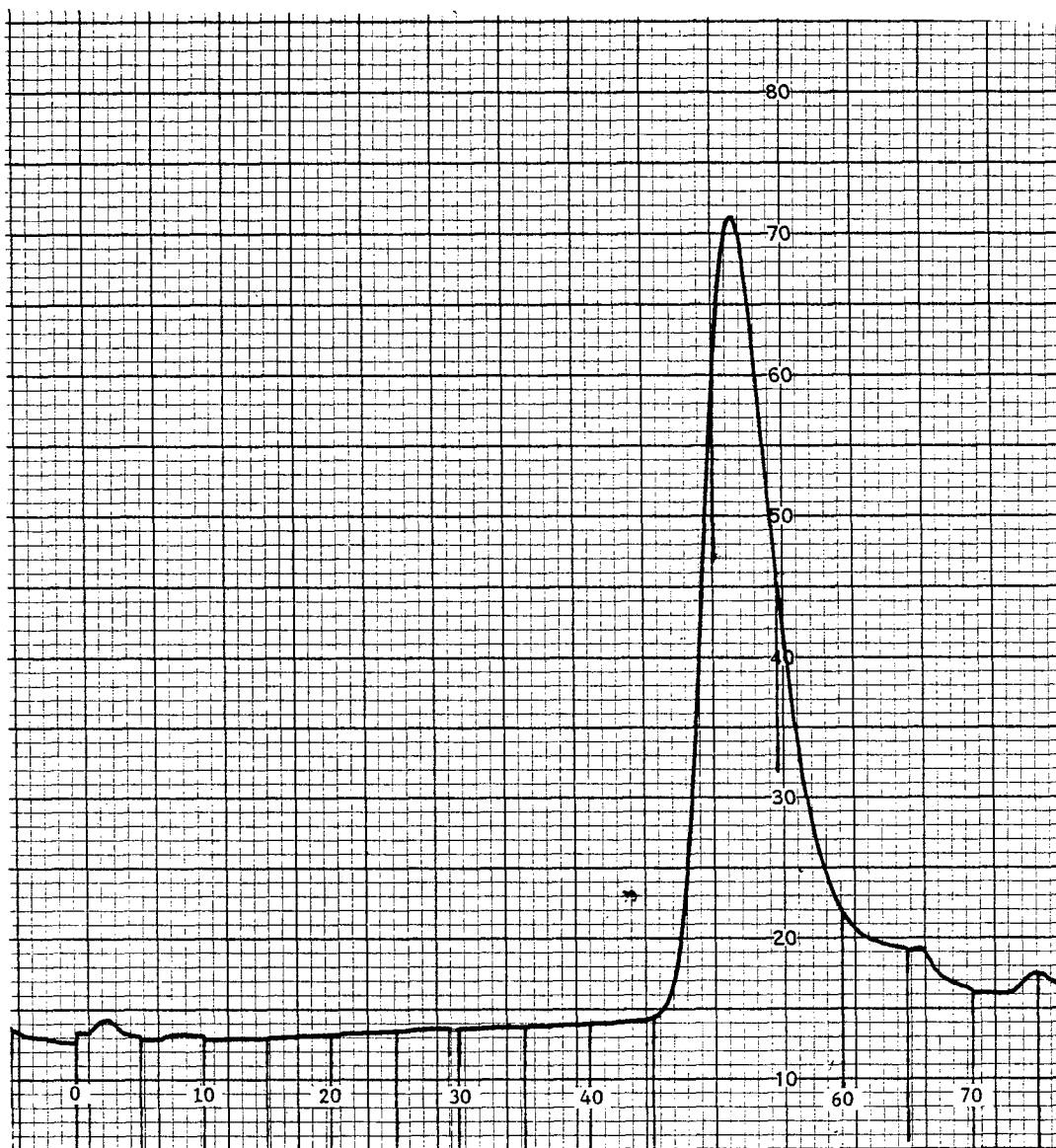


Figure 13 - GPC Curve of FASIL Polymer Sample No. 1 ($\eta_{inh} = 0.216$)

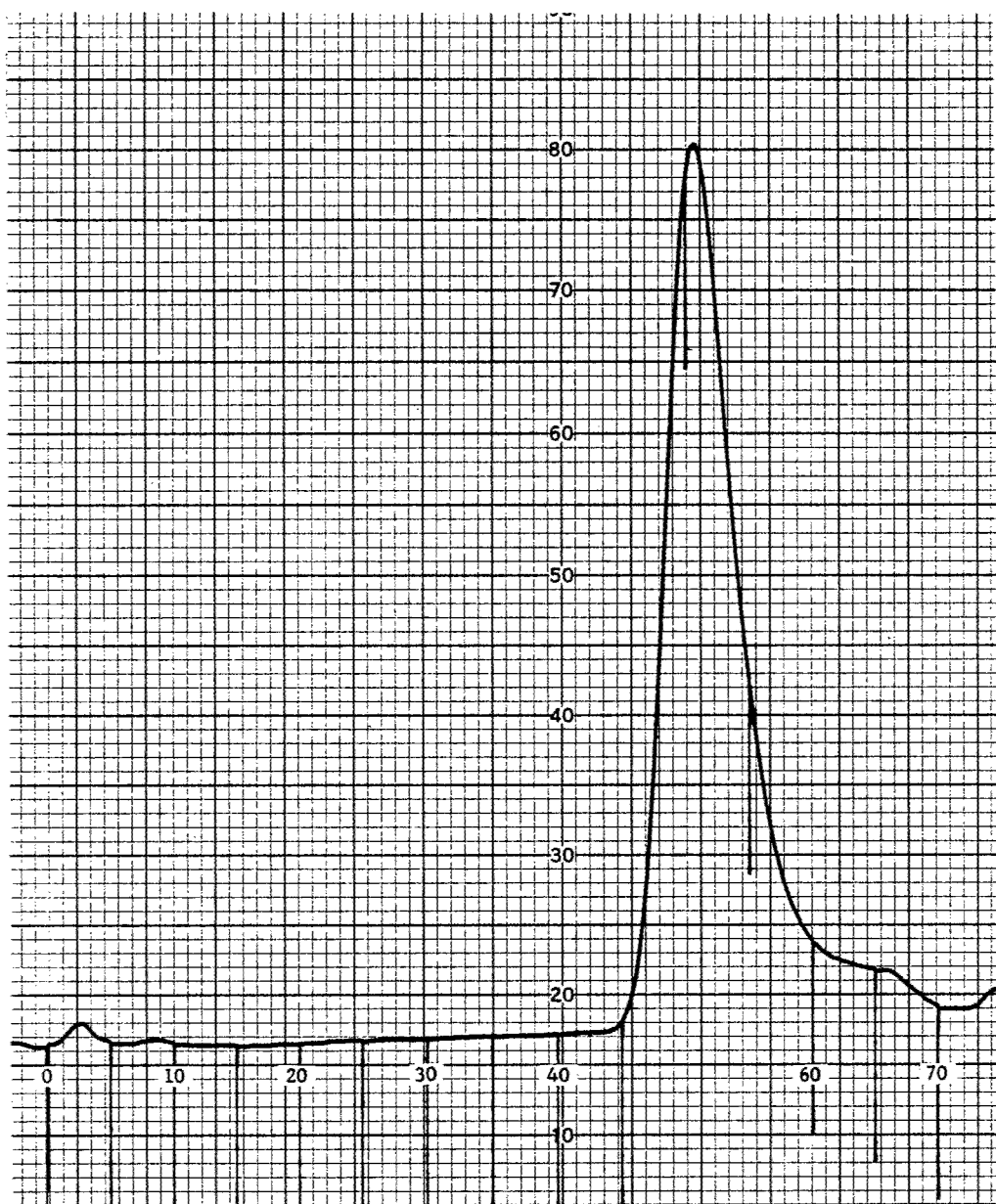


Figure 14 - GPC Curve of FASIL Polymer Sample No. 2 ($\eta_{inh} = 0.258$)

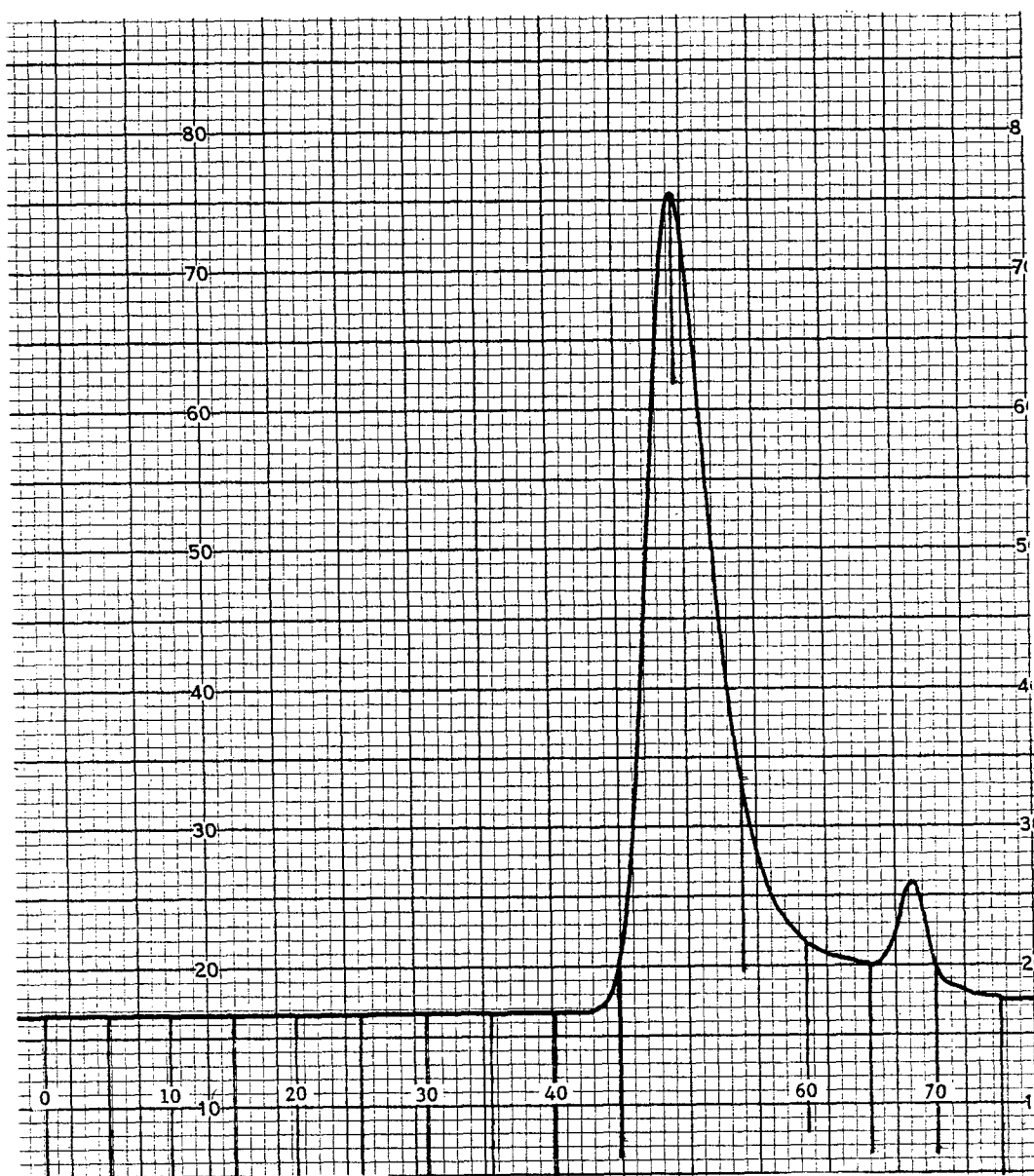


Figure 15 - GPC Curve of FASIL Polymer Sample No. 3 ($\eta_{inh} = 0.340$)