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SYNTHESIS OF VINYL-TERMINATED FASIL POLYMERS

Midwest Research Institute
Kansas City, Missouri 64110

July 1979

Technical Report AFML-TR-78-165
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.

Harold Rosenberg

H. ROSENBERG
Project Scientist

R. L. VAN DEUSEN, Chief
Polymer Branch

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

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

An investigation of novel vinyl-terminated fluoroalkylarylenesiloxanylene (FASIL) oligomers was undertaken in an effort to provide potential filleting-type aircraft fuel tank sealants to meet long-life and broad-temperature range applications. The monomers, a fluorine-containing silanediol and a diaminodisiloxane, were prepared and polymerized to provide oligomers in a desired molecular weight range. The silanol-terminated oligomers were vinyl-terminated by treatment with vinyldimethylaminodimethylsilane. A chain extender and a crosslinker were also prepared.

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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-5160, "Research on the Synthesis of Vinyl-Terminated 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. 4438-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 fluoroalkylarylenesiloxanylene (FASIL) intermediates, monomers and oligomers, as well as chain extenders and crosslinking agents, to be used in the subsequent development of filleting-type aircraft fuel tank sealants to meet long-life and broad-temperature range applications. The cured elastomeric sealants based on the FASIL polymer system (References 1, 2, 3, and 4) have been selected by the Air Force as candidate materials to provide improved sealants with high thermal stability, reversion resistance, chemical stability, and required low-temperature properties. Channel sealants formulated by the Air Force Materials Laboratory from this AFML-synthesized 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 investigation of the synthesis of FASIL oligomers, their intermediates and monomers, as well as of a FASIL-type chain extender and crosslinker.

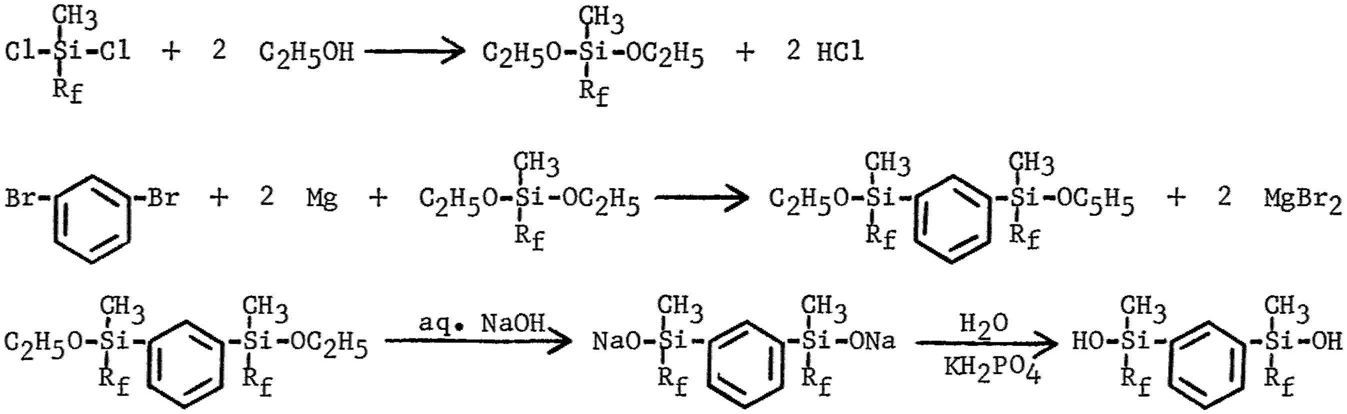
SECTION II

DISCUSSION

The synthesis of monomers, intermediates and oligomers as well as of a chain extender and crosslinker, is discussed in this section.

A. Synthesis of Intermediates and Monomers

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



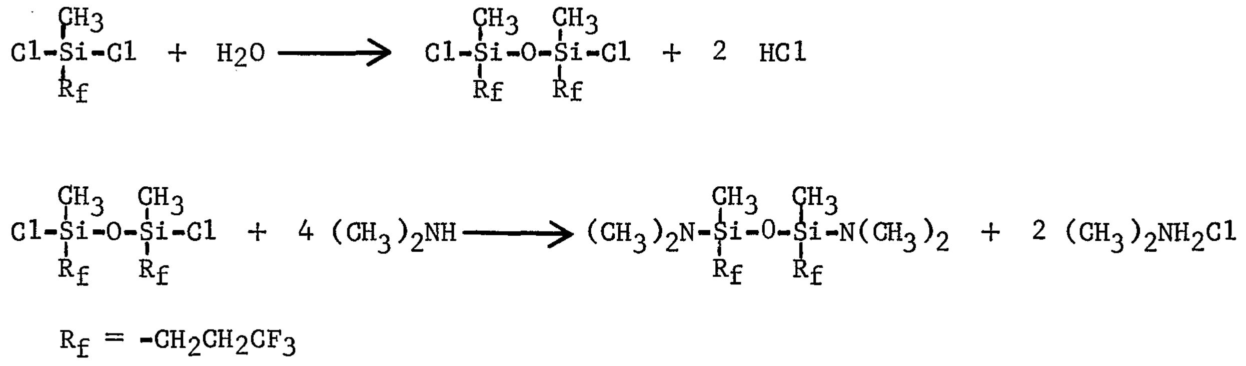
$R_f = -CH_2CH_2CF_3$

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 presence of an impurity, identified as hydroxymethyl(3,3,3-trifluoropropyl)silylbenzene, in the diol was first detected by gel permeation chromatography using Waters Micro Styrogel Columns (10^6, 10^5, 10^4, 10^2, 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 curve in Figure 4. The monoethoxy impurity appears at an elution volume of 73 ml, and although it appears to be a major contaminate, it is actually present in less than 1% concentration (by GLC), but highly absorbed in UV light. Its presence could be detected by TLC on silica gel with methylene chloride elutant as a small spot preceeding 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:



$$Cl-\overset{CH_3}{\underset{R_f}{Si}}-Cl + H_2O \longrightarrow Cl-\overset{CH_3}{\underset{R_f}{Si}}-O-\overset{CH_3}{\underset{R_f}{Si}}-Cl + 2\ HCl$$

$$Cl-\overset{CH_3}{\underset{R_f}{Si}}-O-\overset{CH_3}{\underset{R_f}{Si}}-Cl + 4\ (CH_3)_2NH \longrightarrow (CH_3)_2N-\overset{CH_3}{\underset{R_f}{Si}}-O-\overset{CH_3}{\underset{R_f}{Si}}-N(CH_3)_2 + 2\ (CH_3)_2NH_2Cl$$

$R_f = -CH_2CH_2CF_3$

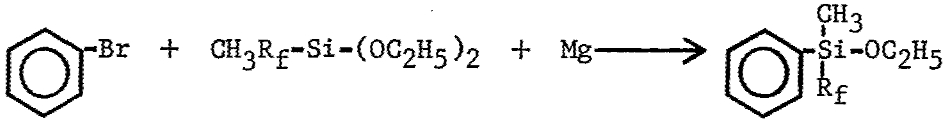
The intermediate compound, 1,3-dichloro-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane, was prepared by the addition of water to an excess of methyl-(3,3,3-trifluoropropyl)dichlorosilane in ether. The best yields were obtained when a 3:1 molar excess of dichlorosilane was employed. About 31% of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

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

Vinyldimethylaminodimethylsilane, the compound used to vinyl-terminate the oligomers, was prepared by treatment of vinyldimethylchlorosilane with excess dimethylamine.

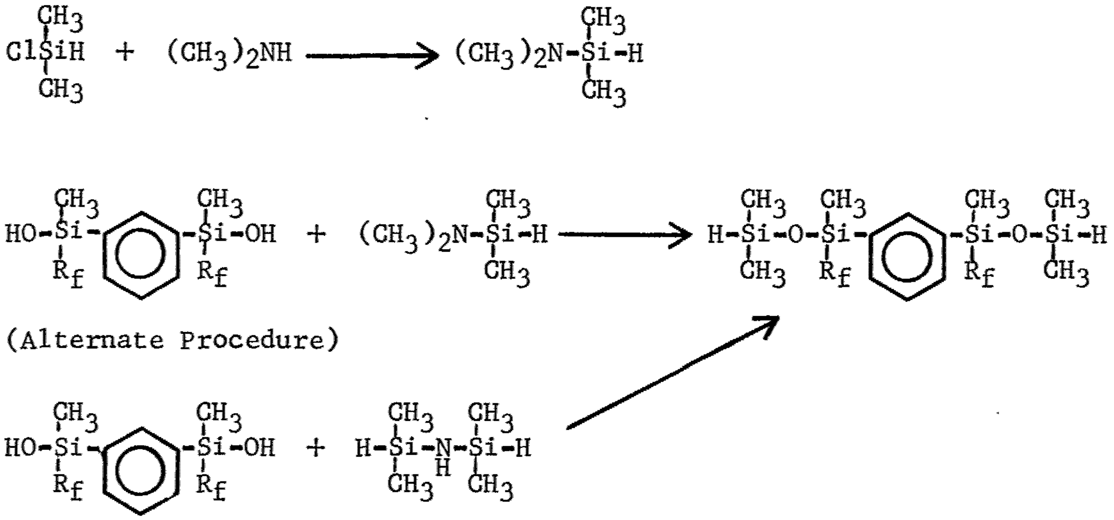
$$CH_2{=}CH(CH_3)_2Si-Cl + (CH_3)_2NH \longrightarrow CH_2{=}CH(CH_3)_2Si-N(CH_3)_2$$

Ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene was prepared by a Grignard reaction to provide proof of structure of the impurity isolated from the diethoxy Grignard preparations.



B. Synthesis of the Chain Extender

The compound, m-phenylenebis-1-[1,3,3-trimethyl-1-(3,3,3-trifluoropropyl)-disiloxane], a chain extender to be utilized with the vinyl-terminated oligomers, was prepared by the following sequence of reactions:

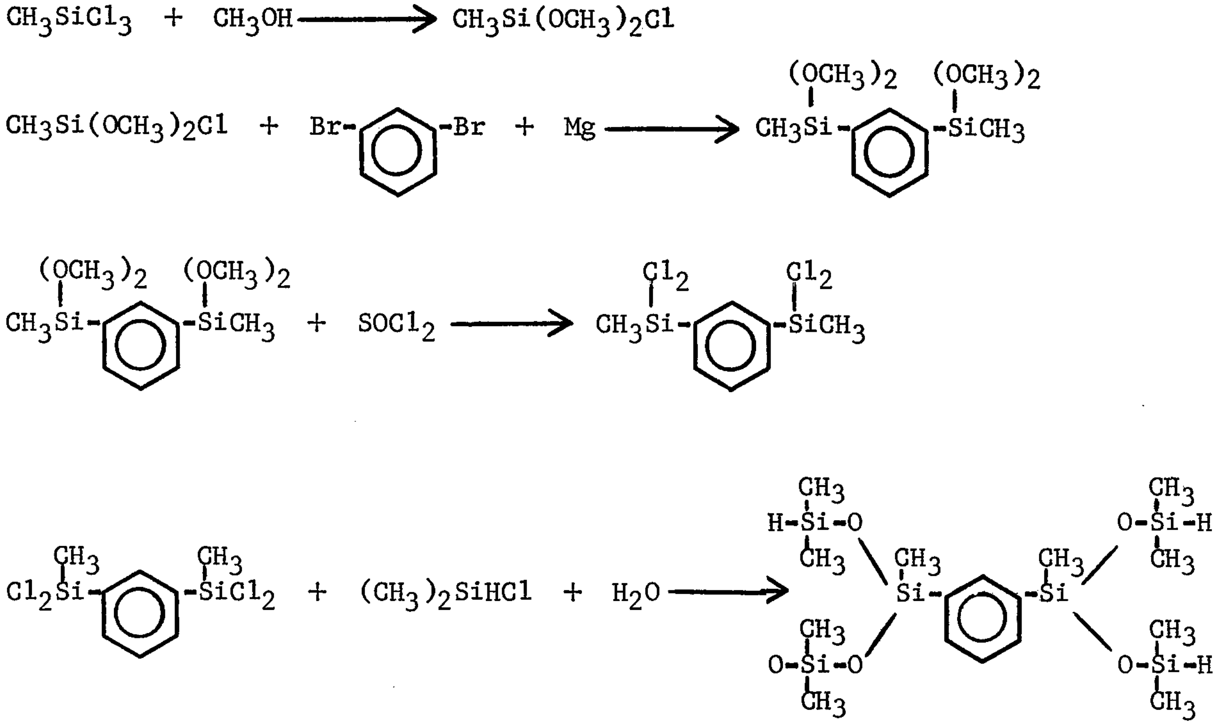


$R_f = -CH_2CH_2CF_3$

The treatment of dimethylchlorosilane with excess dimethylamine gave dimethylaminodimethylsilane which, when reacted with the diol, gave the chain extender. The intermediate compound, dimethylaminodimethylsilane, was difficult to isolate in pure form because of co-distillation with the usual solvents used in the preparation; consequently, it was generally employed as a mixture with the solvent. An alternate procedure, just recently tried, was the reaction of the diol with tetramethyldisilazane. This procedure gave the chain extender in an 82% yield in one step, and the diol was not even purified by distillation.

C. Synthesis of the Crosslinker

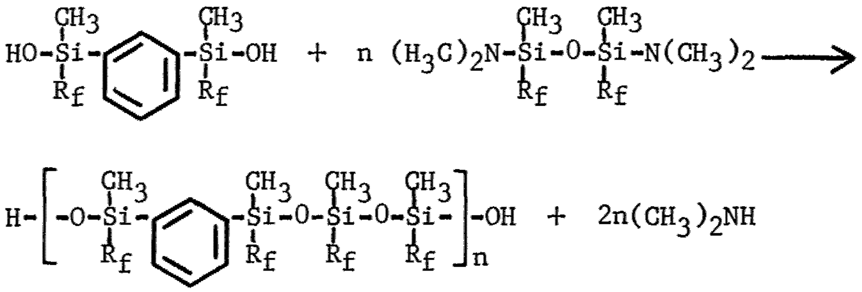
The preparation of m-phenylenebis-3-[(1,1,3,5,5-pentamethyl)trisiloxane], for use as a crosslinking agent in the formulation of a filleting sealant based on room temperature vulcanization of vinyl-terminated oligomers, followed this sequence of reactions:



Chlorodimethoxymethylsilane was prepared by the addition of two equivalents of methanol to one equivalent of methyltrichlorosilane, and its Grignard reaction with m-dibromobenzene gave 1,3-bis(methyldimethoxysilyl)benzene. This tetramethoxy derivative was converted to the tetrachloro compound by treatment with thionyl chloride. A co-hydrolysis reaction with chlorodimethylsilane and high-speed stirring gave the crosslinker in 84% yield.

D. Oligomer Preparation

The oligomer 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.



$R_f = -CH_2CH_2CF_3$

The initial study of oligomer preparation investigated the effect of monomer stoichiometry and the solvent amount. A mixture of the monomers was heated to reflux in toluene. Initially, the dimethylamine evolution was rapid, but ceased after 2 hr. Results were assessed in terms of inherent viscosity determined in tetrahydrofuran at 30° at a concentration of 0.5 g/100 ml. Although there was a wide range of results, a low diamine to diol ratio gave low molecular weight oligomers and higher solvent amounts tended also to give low molecular weight oligomers. These results are summarized in Table 1, page 13.

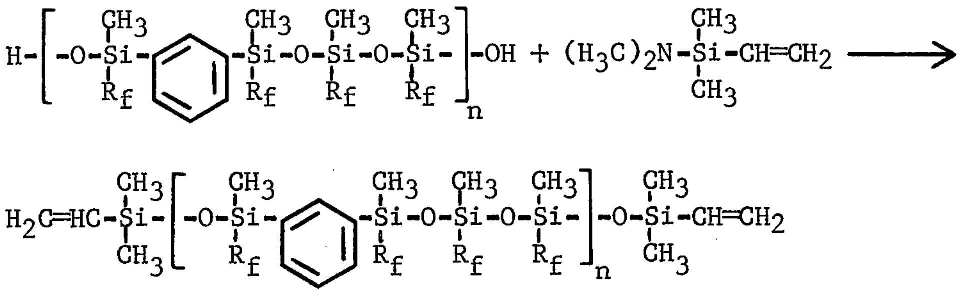
E. Inherent Viscosity - Molecular Weight Relationship

Six of the oligomers reported in Table 1, page 13, were selected for number-average molecular weight determinations by membrane osmometry. From the inherent viscosities and apparent number average molecular weights obtained, the constants in the Mark-Houwink equation, $\eta = KM^a$, were determined to be $K = 1.89 \times 10^{-4}$ and $a = 0.63$.

F. Oligomer Sample Preparation

Using the knowledge and experience obtained in the preliminary oligomer study, three 250-g samples of oligomers within the range of 0.03, 0.04, and 0.05 inherent viscosities were prepared. Out of 15 oligomer preparations, only one went awry, that is, one came out with a molecular weight that was too high. These oligomer data are summarized in Table 3, page 16. The weight of the sample with an inherent viscosity of 0.052 was raised to 250 g by incorporating 32 g of oligomers in the desired molecular weight range that had been prepared previously. Infrared and NMR spectra and GPC curves were obtained on these vinyl-terminated oligomers. These samples were forwarded to the Air Force Materials Laboratory.

Vinyl termination was accomplished by reacting the silanol-terminated oligomers with vinyldimethylaminodimethylsilane.



$R_f = -CH_2CH_2CF_3$

SECTION III

EXPERIMENTAL

Temperatures were recorded in degrees Centigrade. Infrared 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.

A. 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).

B. 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 evaporated, 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.

C. 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).

D. 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.

E. 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 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).

F. Vinyldimethylaminodimethylsilane

To an excess of dimethylamine in petroleum ether cooled to -20° was added 24.2 g (0.20 mole) of vinyldimethylchlorosilane. After the addition was completed, the mixture was stirred as it was allowed to warm to 25°. The salts were removed by filtration, and distillation of the filtrate gave 12.5 g (48%) of product boiling at 102° [Lit. b.p. 105-106° (Reference 7)].

G. Ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene

Distillation of combined low-boiling fractions from the preparation of 1,3-bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene gave material boiling at 93° (5 mm), n_D^{26} 1.4452, single peak GLC. This material was identical to ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene prepared by the reaction of methyl(3,3,3-trifluoropropyl)diethoxysilane, bromobenzene, and magnesium, b.p. 80° (2 mm), n_D^{26} 1.4451. The NMR, GLC, and IR spectra were identical.

H. Preparation of Extender - m-Phenylenebis-1-[1,3,3-trimethyl-1-(3,3,3-trifluoropropyl)disiloxane]

1. Dimethylaminodimethylsilane: To a solution of 50 ml (40.5 g, 0.9 mole) of dimethylamine in 200 ml of heptane at -20° was added dropwise 28.3 g (0.3 mole) of chlorodimethylsilane while the temperature was maintained at -20 to -10° with a Dry Ice bath. After the chlorosilane was added, the mixture was maintained at -10° for 0.5 hr, and allowed to warm to ambient temperature. The mixture was filtered and the salts were washed immediately with heptane. The combined filtrates was distilled, and the product was collected as a mixture with heptane. A fraction weighing 73 g contained 18 g (58%) of dimethylaminodimethylsilane (by GLC), boiling at 65-90°.

2. m-Phenylenebis-1-[1,3,3-trimethyl-1-(3,3,3-trifluoropropyl)disiloxane]: To 18 g (0.17 mole) of dimethylaminodimethylsilane contained in a 73-g mixture with heptane was added 30 g (0.08 mole) of 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene dissolved in 50 ml of ether. The mixture was heated to reflux for 0.5 hr, and then cooled and stripped of solvent on a rotary evaporator. Distillation gave 36.3 g (93%) of slightly impure product. Redistillation gave 26.5 g (68%) of product, b.p. 94-95° (0.06 mm), single peak (GLC), n_D^{26} 1.4281 (infrared spectrum, Figure 10).

Anal. Calcd. for $C_{18}H_{32}F_6Si_4O_2$: C, 42.66; H, 6.37; F, 22.49; Si, 22.17. Found: C, 42.74; H, 6.26; F, 22.60; Si, 22.04.

In an alternate synthesis, 30.3 g (0.078 mole) of diol which had been prepared by the hydrolysis of the diethoxy compound by the usual procedure, but not purified by distillation, was dissolved in 35 ml of ether and added to a solution of 12.4 g (0.093 mole) of tetramethyldisilaxane in 100 ml of hexane at 55°. After 2 hr of reflux, distillation gave 32.3 g (82%) of the extender boiling at 104° (0.1 mm), single peak GLC.

I. Preparation of Crosslinker - m-Phenylenebis-3-[(1,1,3,5,5-pentamethyl)trisiloxane]

1. Chlorodimethoxymethylsilane: To 149.5 g (1.0 mole) of methyltrichlorosilane was added 64.0 g (2.0 moles) of anhydrous methanol dropwise under a nitrogen atmosphere. The reaction was endothermic. After the addition was completed, the reaction mixture was purged with nitrogen and heated to expel hydrochloric acid. Distillation gave 129.7 g (89%) of chlorodimethoxymethylsilane, b.p. 93-95°C.

2. 1,3-Bis(methyldimethoxysilyl)benzene: The procedure followed was similar to that of Breed (Reference 8) for the preparation of the 1,4-derivative. A flask (flame-dried under nitrogen) containing 10.7 g (0.44 g-atom)

of magnesium turnings, 3.4 g (0.014 mole) of m-dibromobenzene and 20 ml of tetrahydrofuran was warmed to initiate reaction. Then a mixture containing 43.8 g (0.186 mole) of m-dibromobenzene, 61.8 g (0.44 mole) of chlorodimethoxymethylsilane and 90 ml of tetrahydrofuran was added dropwise so as to maintain reflux. The mixture was refluxed 2 hr after the addition was completed and cooled to 26°. The reaction mixture was diluted with hexane to precipitate the salts, filtered, and the salts were washed with more hexane. The combined filtrates were stripped of solvent and distillation gave 29.7 g (52%) of product boiling at 105-108° (0.3 mm).

3. 1,3-Bis(dichloromethylsilyl)benzene: The procedure followed was similar to that described by Roberts (Reference 9). To 125.9 g (0.44 mole) of 1,3-bis(methyldimethoxysilyl)benzene was added 235.7 g (1.98 moles) of thionyl chloride in 2 hr. The mixture was heated to 85° (reflux) for 5 hr, and excess thionyl chloride was removed by distillation. Vacuum distillation of the residue gave 98.8 (74%) of 1,3-bis(dichloromethylsilyl)benzene, b.p. 92-93° (0.15 mm).

4. m-Phenylenebis-3-[(1,1,3,5,5-pentamethyl)trisiloxane]: To a 2-l flask containing 700 ml of water was added dropwise a mixture of 57.6 g (0.189 mole) of 1,3-bis(dichloromethylsilyl)benzene and 142.9 g (1.51 moles) of chlorodimethylsilane in 100 ml of toluene in 0.5 hr, similar to the procedure described by Kim (Reference 10), while being stirred at high speed. After the mixture was stirred an additional 0.5 hr, the toluene layer was separated, washed with water and dried over sodium sulfate. Distillation gave 73.4 g (84%) of product, b.p. 106° (0.06 mm), n_D^{26} 1.4383, single peak (GLC) (infrared spectrum, Figure 11).

Anal. Calcd. for $C_{16}H_{38}Si_6O_4$: C, 41.50; H, 8.27; Si, 36.40. Found: C, 41.57; H, 8.33; Si, 36.88, 37.00.

J. Initial Study of Oligomer Preparation

In order to define the parameters for the preparation of FASIL oligomers in a desired molecular weight range, the effects of the solvent amounts and the stoichiometry of the monomers, 1,3-bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene (the diol) and 1,3-bis(dimethylamino)-1,3-dimethyl-1,3-bis(3,3,3-trifluoropropyl)disiloxane (the diamine), were investigated. Such a series of experiments is listed in Table 1, and the general polymerization procedure was as follows:

A solution of 5.0219 g (0.0129 mole) of diol and 4.7983 g (0.0125 mole, 96.9% of stoichiometry) in 10 ml of toluene (a 2:1 ml of solvent to grams of diol ratio) was heated to reflux for 2 hr while a slow flow of nitrogen was passed through the system. The evolution of dimethylamine had ceased by this time. The toluene was removed on a rotary evaporator, and the residue

TABLE 1

EFFECT OF SOLVENT AMOUNT AND MONOMER STOICHIOMETRY ON FASIL OLIGOMER PREPARATION

Run No.	Diamine/Diol Ratio (%)	Solvent/Diol Ratio (ml/g)	Inherent Viscosity (dl/g)
1	81	5:1	0.041
2	83	5:1	0.042
3	85	5:1	0.031
4	85	5:1	0.046
5	86	2:1	0.044
6	87	5:1	0.058
7	88	2:1	0.052
8	90	2:1	0.064
9	90	2:1	0.094
10	90	2:1	0.063
11	90	5:1	0.059
12	90	2.5:1	0.065
13	90	7.5:1	0.060
14	90	5:1	0.066
15	92	2:1	0.093
16	94	2:1	0.103
17	94	2:1	0.040
18	94	2:1	0.042
19	95	2:1	0.063
20	95	2:1	0.089
21	95	5:1	0.087
22	95	2.5:1	0.085
23	95	7.5:1	0.097
24	95	5:1	0.082
25	96	2:1	0.067
26	96[a]	2:1	0.039
27	96	2:1	0.070
28	96	2:1	0.046
29	97	2:1	0.050
30	97	2:1	0.050
31	97	2:1	0.060
32	97	2:1	0.054
33	97[b]	2:1	0.075
34	97	2:1	0.075[c]
35	98	2:1	0.062
36	100	2:1	0.054
37	100[a]	2:1	0.026
38	100	2:1	0.101
39	100	5:1	0.107
40	100	7.5:1	0.097
41	105	2:1	0.037

---

[a] The solvent was tetrahydrofuran.

[b] The diol was redistilled.

[c] After end-capping, the viscosity was 0.071.

was devolatilized at 200 (0.1 mm) for 2 hr. There was obtained 8.3 g (93%) of oligomer with an inherent viscosity of 0.050.

With the exceptions noted in the table, all experiments followed this procedure. The inherent viscosities were determined at a concentration of 0.5 g of oligomer per 100 ml of tetrahydrofuran at 30° since the oligomers were not completely soluble in toluene.

K. Inherent Viscosity-Molecular Weight Relationship

Six FASIL oligomers, representing a range of molecular weights, were selected for number-average molecular weight determination by membrane osmometry. These samples were washed with methanol and devolatilized so as to obtain a single peak by gel permeation chromatography (GPC).

Osmometry determination of number-average molecular weight averages were determined at 4-5 concentrations each in tetrahydrofuran, and the limiting values of reduced osmotic pressures at zero concentration were obtained by extrapolation to infinite dilution. The molecular weight averages, $\overline{M}_n$, were calculated from the latter. These were graphically plotted against the inherent viscosity values and a straight line plot was obtained by least squares. This curve was used to project the experimental points to the curve, which allowed the assignment of "apparent $\overline{M}_n$" values. The results are shown in Table 2. GPC curves are shown in Figures 12-17.

TABLE 2

MOLECULAR WEIGHT DETERMINATION

Sample No. (Table 1)	Initial Viscosity (dl/g)	Final Viscosity (dl/g)	$\overline{M}$ ($\pm$ 10%)	Apparent $\overline{M}_n$
41	0.037	0.050	7,200	6,800
7	0.052	0.057	10,000	9,500
35	0.062	0.085	12,000	13,200
27	0.070	0.091	21,000	20,300
15	0.093	0.113	23,000	23,600
16	0.103	0.125	30,000	29,700

The inherent viscosities for these polymers were plotted against their apparent molecular weights and a straight sine was obtained on log-log paper. The slope of the curve (a) was 0.63 and the Y intercept (K) was 1.89 x 10^{-4}. The viscosity $\overline{M}_v$ was obtained with these (a) and (K) values with the Mark-Houwink equation, $\eta = KM^a$.

Light-scattering determinations were unsuccessful because the refractive index of the solvent, tetrahydrofuran, was so close to that of the polymer solution that the light-scattering increments were not well distinguished above baseline scatter.

L. Oligomer Preparation

In a typical oligomer preparation, a flask containing 29.9998 g (0.077 mole) of freshly-prepared diol and 130 ml of dry toluene was heated to 55° and 23.6316 g (0.0615 mole, 80.0% of stoichiometry) was added dropwise over a 0.5-hr period as the temperature was raised to reflux. After 2 hr, a sample had an inherent viscosity of 0.041 dl/g. To insure silanol termination, 5 ml of water was added and after 0.5 hr of reflux, the water was removed with a Dean-Stark trap. Some toluene was distilled out to insure that all water was out of the system, and the oligomer was end-capped by the addition of excess vinyldimethylaminodimethylsilane as the solution was refluxed for 2 hr. Solvent was removed on a rotary evaporator, and the residue was heated to 200° (0.1 mm) for 2 hr. The oligomer, weighing 48.2 g, had an inherent viscosity of 0.040 dl/g (in tetrahydrofuran at 30°).

In general, the molecular weight of the oligomer could be controlled by the stoichiometry of the monomers (the diamine to diol ratio) and by the solvent to diol ratio (ml/g). An example is shown in Table 3, where the syntheses of three 250 g-samples of oligomers, vinyl-terminated, are listed. The three inherent viscosities desired were 0.03, 0.04, and 0.05 dl/g. These three samples were forwarded to the Air Force Materials Laboratory. The infrared spectra for samples Nos. 1, 3, and 3 are shown in Figures 18, 19, and 20, respectively; the GPC curves in Figures 21, 22, and 23, respectively; and the NMR spectra in Figures 24, 25, and 26, respectively.

TABLE 3

SYNTHESIS OF OLIGOMERS - VINYL-TERMINATED

No.	Diamine/Diol (%)	Solvent/Diol (ml/g)	Inherent Viscosity (dl/g)	Final[a] Inherent Viscosity (dl/g)	Weight (g)
0.03 (Sample No. 1) (Composite viscosity 0.034)					
1	80.0	6:1	0.032	0.023	48.9
2	80.0	5:1	0.030	0.033	49.0
3	80.0	7.5:1	0.026	0.028	59.5
4	80.0	5:1	0.032	0.030	53.4
5	80.0	4:1	0.035	0.029	53.4
0.04 (Sample No. 2) (Composite viscosity 0.040)					
6	80.0	4:1	0.042	0.040	48.2
7	80.0	5:1	0.037	0.040	51.3
8	82.5	4:1	0.044	0.043	54.3
9	82.5	4:1	0.044	0.042	57.1
10	82.5	4:1	0.044	0.041	59.9
0.05 (Sample No. 3) (Composite viscosity 0.052)					
11	85.0	4:1	0.049	0.048	53.3
12	87.5	4:1	0.051	0.049	59.7
13	90.0	4:1	0.063	0.051	54.8
14	90.0	4:1	0.051	0.047	57.2
Misc.	-	-	-	0.052	32.1

---

[a] After end-capping.

REFERENCES

1. Choe, E. W. and Rosenberg, H., "Arylenesiloxane Polymers for Use as High-Temperature Aircraft Integral Fuel Tank Sealants", AFML-TR-75-182, Part I, December 1976; ibid., Part II, December 1977.

2. Rosenberg, H. and Choe, E. W., Coatings and Plastics Preprints, 37(1), 166 (1977); ibid., in Organometallic Polymers (C. E. Carraher, J. E. Scheats and C. U. Pittman, Jr. Eds.), Academic Press, New York 1978.

3. Goldfarb, I. J., Choe, E. W. and Rosenberg, H., Coatings and Plastics Preprints, 37(1), 1972 (1977); ibid., in Organometallic Polymers (C. E. Carraher, J. E. Sheats and C. U. Pittman, Jr. Eds.), Academic Press, New York, 1978.

4. Rosenberg, H. and Choe, E. W., Abstracts of Papers, 172nd Nat. Meeting, Amer. Chem. Soc., San Francisco, CA., August 1976, FLUO 41.

5. Rosenberg, H. and Choe, E. W., Coatings and Plastics Preprints, 40(1), 793 (1979).

6. Pike, R. M., J. Polym. Sci., 50,151 (1961).

7. Patterson, W. J., and Bilow, N., J. Polym. Sci. A-1, 7, 1089 (1969).

8. Breed, L. W., Haggerty, Jr., W. J., and Baiocchi, F., J. Org. Chem., 25, 1163 (1960).

9. Roberts, J. D., and Mazur, R. H., J. Am. Chem. Soc., 73, 2059 (1951).

10. Kim, Y. K., Riley, M. O., Cappo, G. R., and Carter, P. L., AFML-TR-70-278, Part V, p. 29, May 1975.

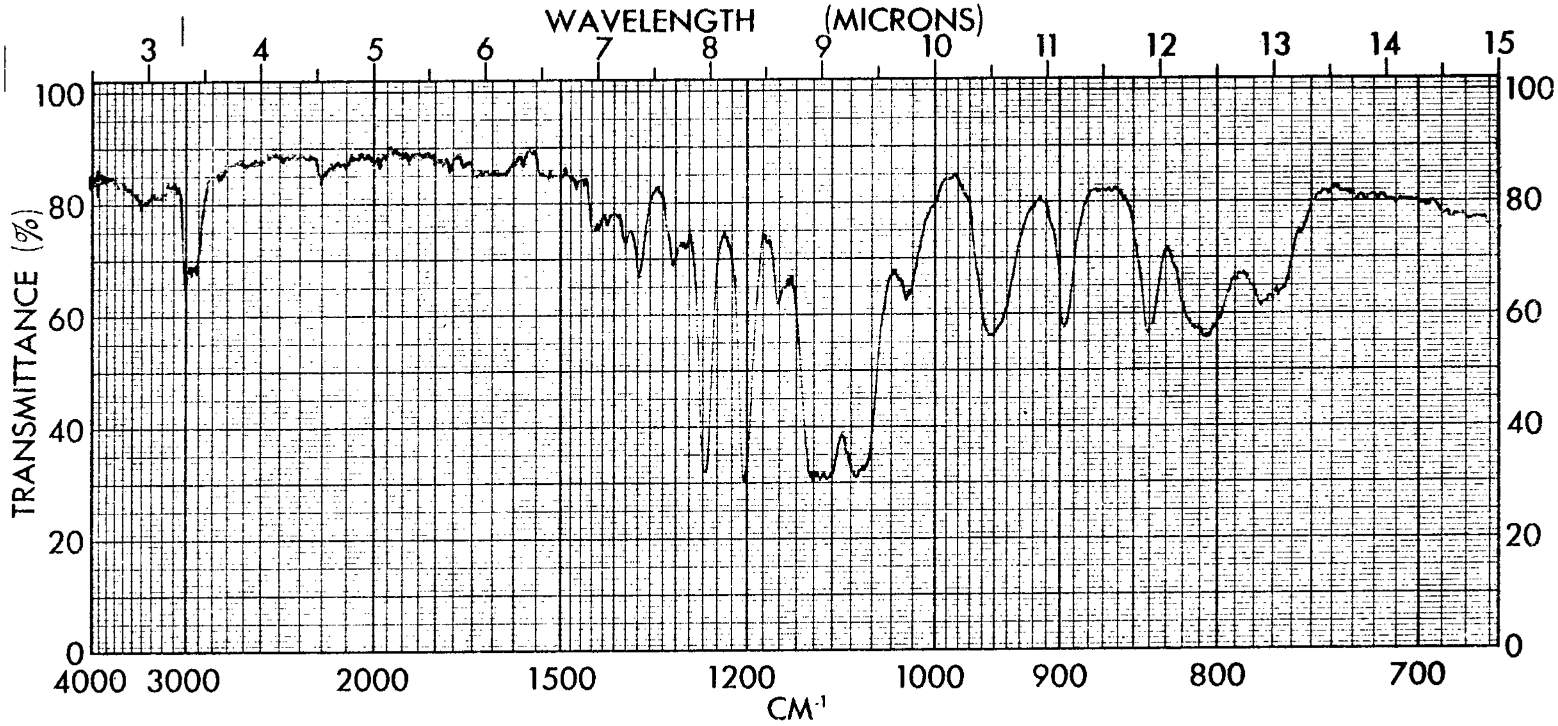


Figure 1 - Infrared Spectrum of Methyl(3,3,3-trifluoropropyl)diethoxysilane (Neat)

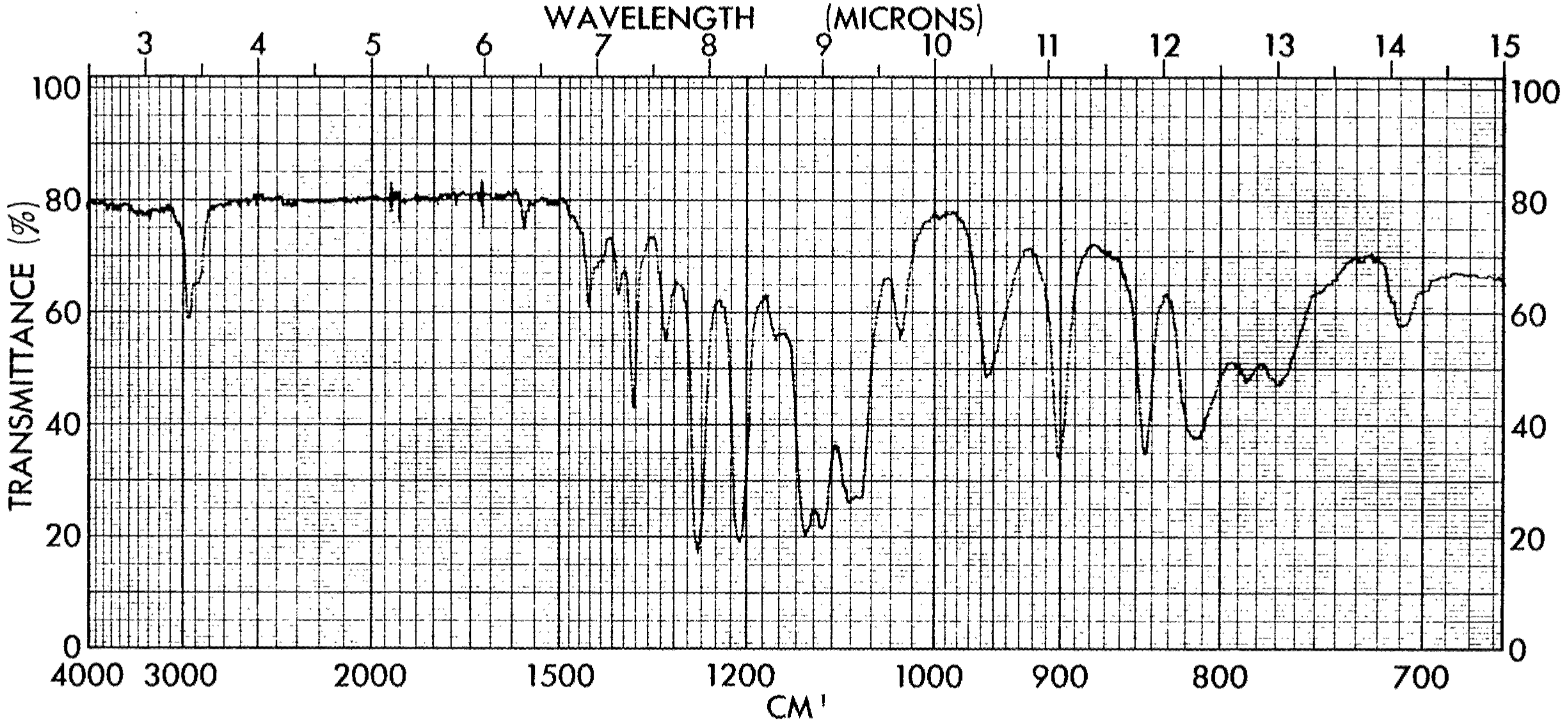


Figure 2 - Infrared Spectrum of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene (Neat)

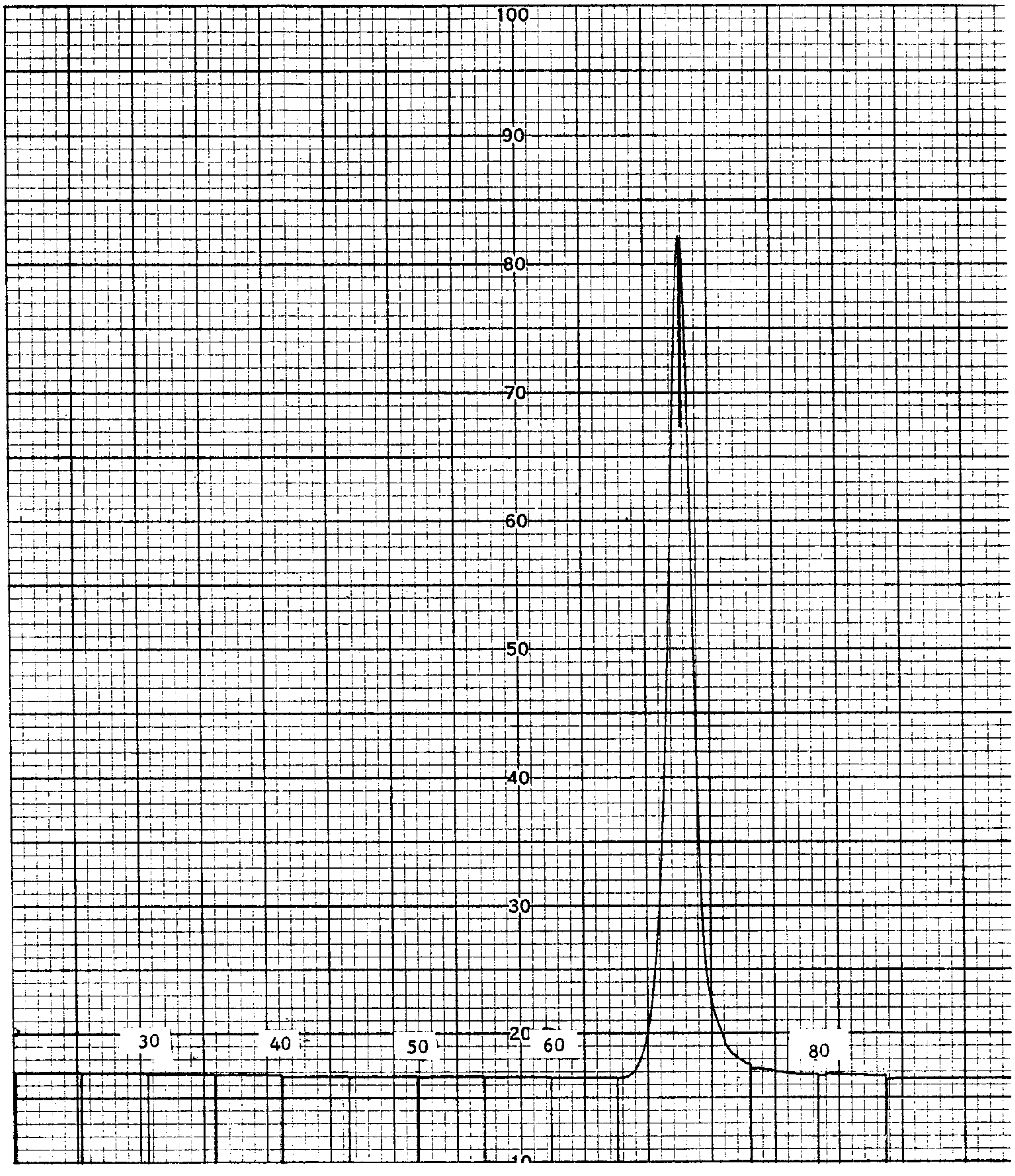


Figure 3 - GPC Curve of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene

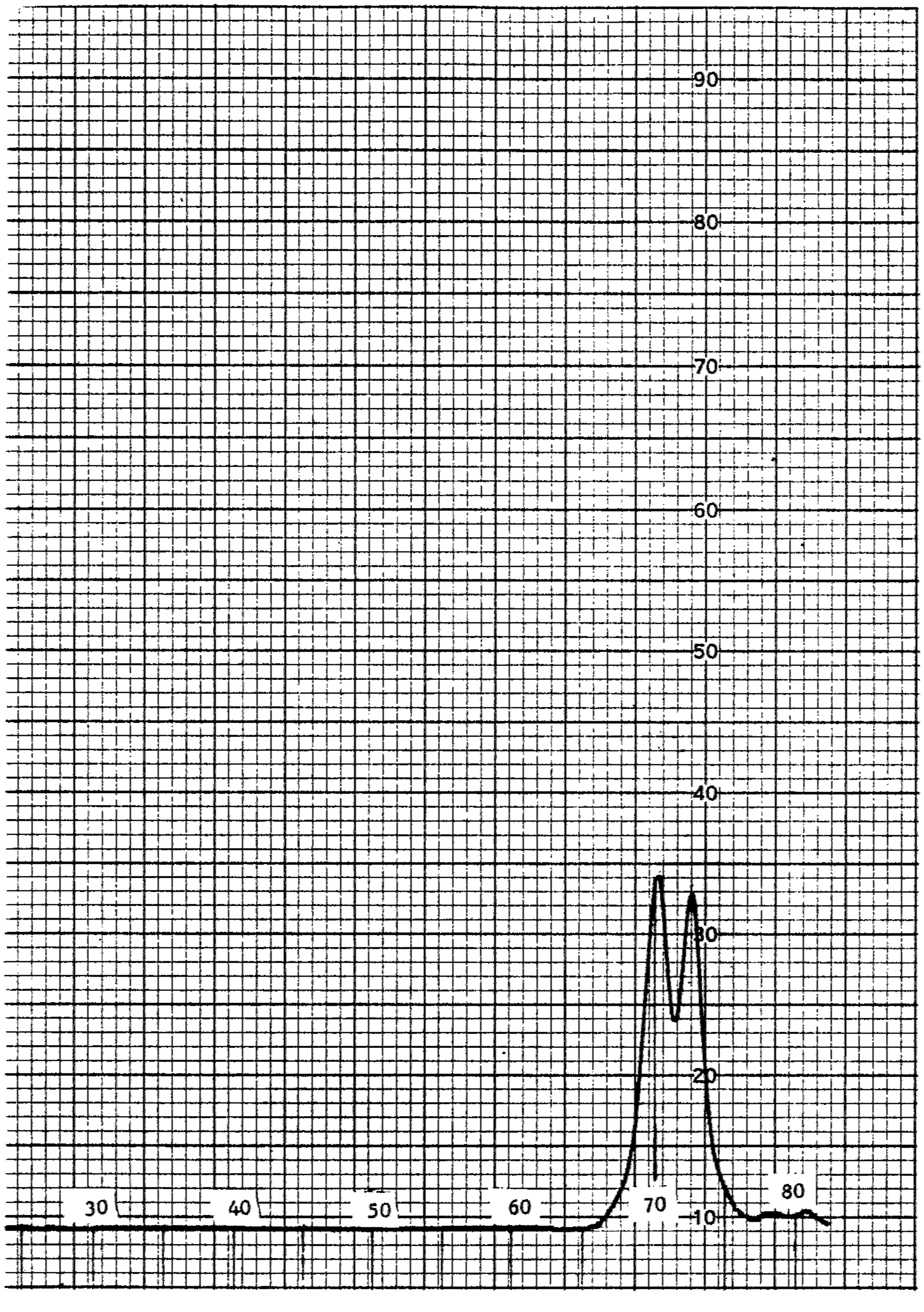


Figure 4 - GPC Curve of 1,3-Bis[ethoxymethyl(3,3,3-trifluoropropyl)silyl]benzene Containing an Impurity

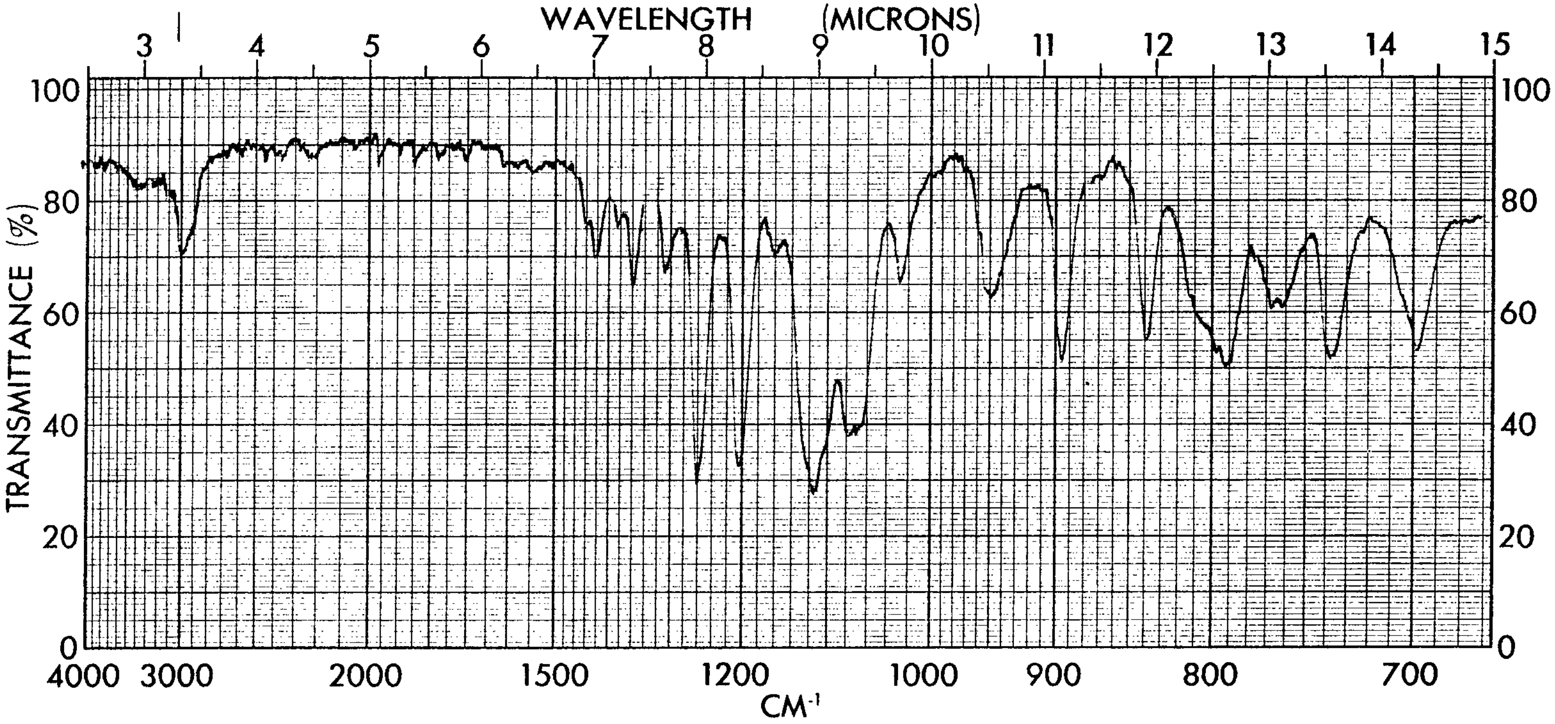


Figure 5 - Infrared Spectrum of Ethoxymethyl(3,3,3-trifluoropropyl)silylbenzene (Neat)

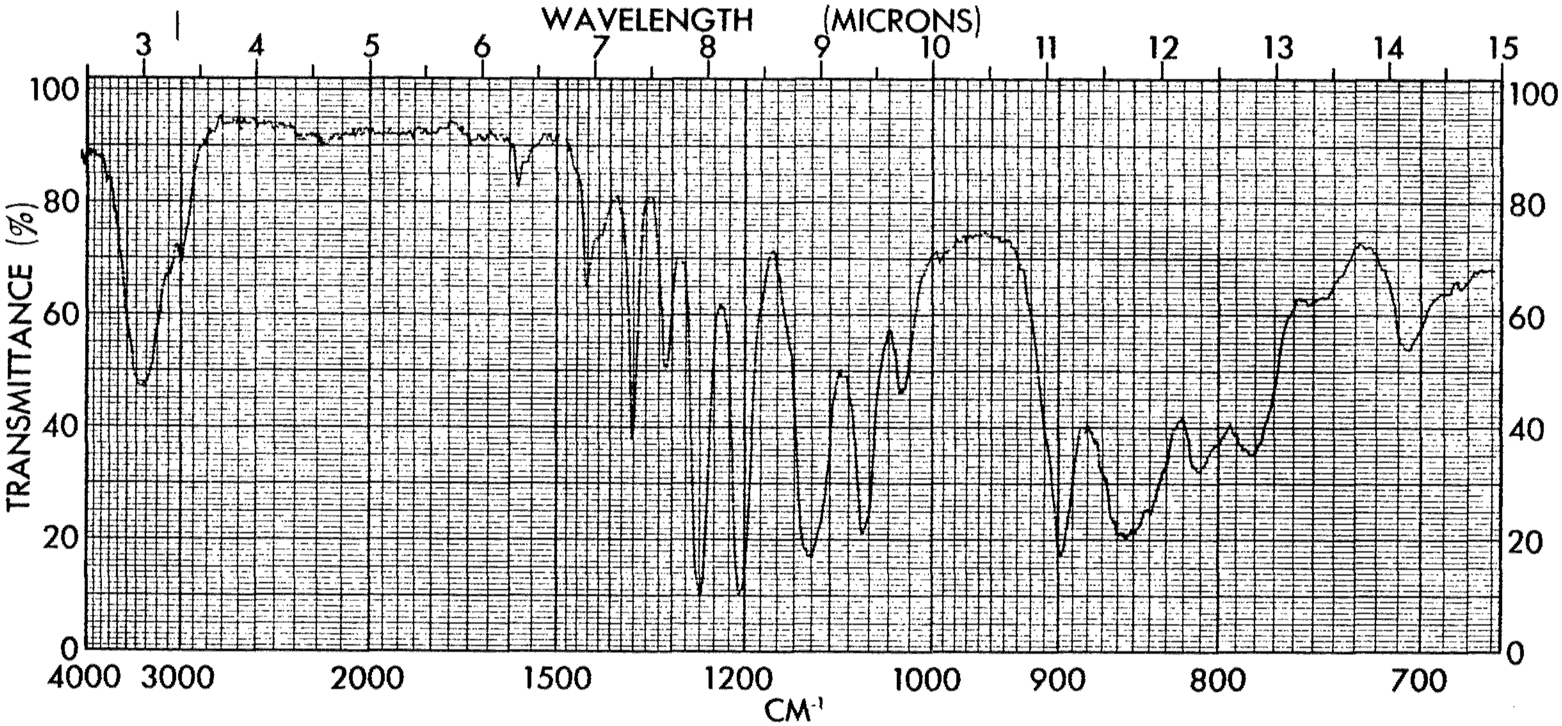


Figure 6 - Infrared Spectrum of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene (Neat)

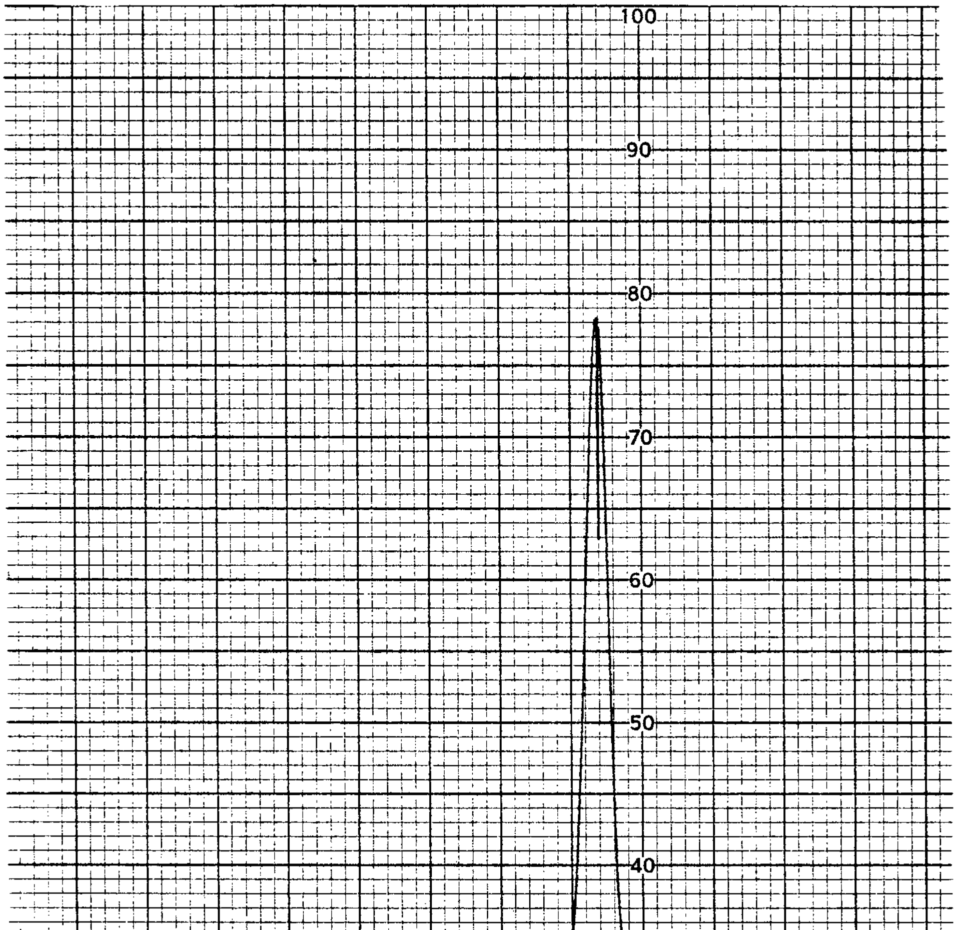


Figure 7 - GPC Curve of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene

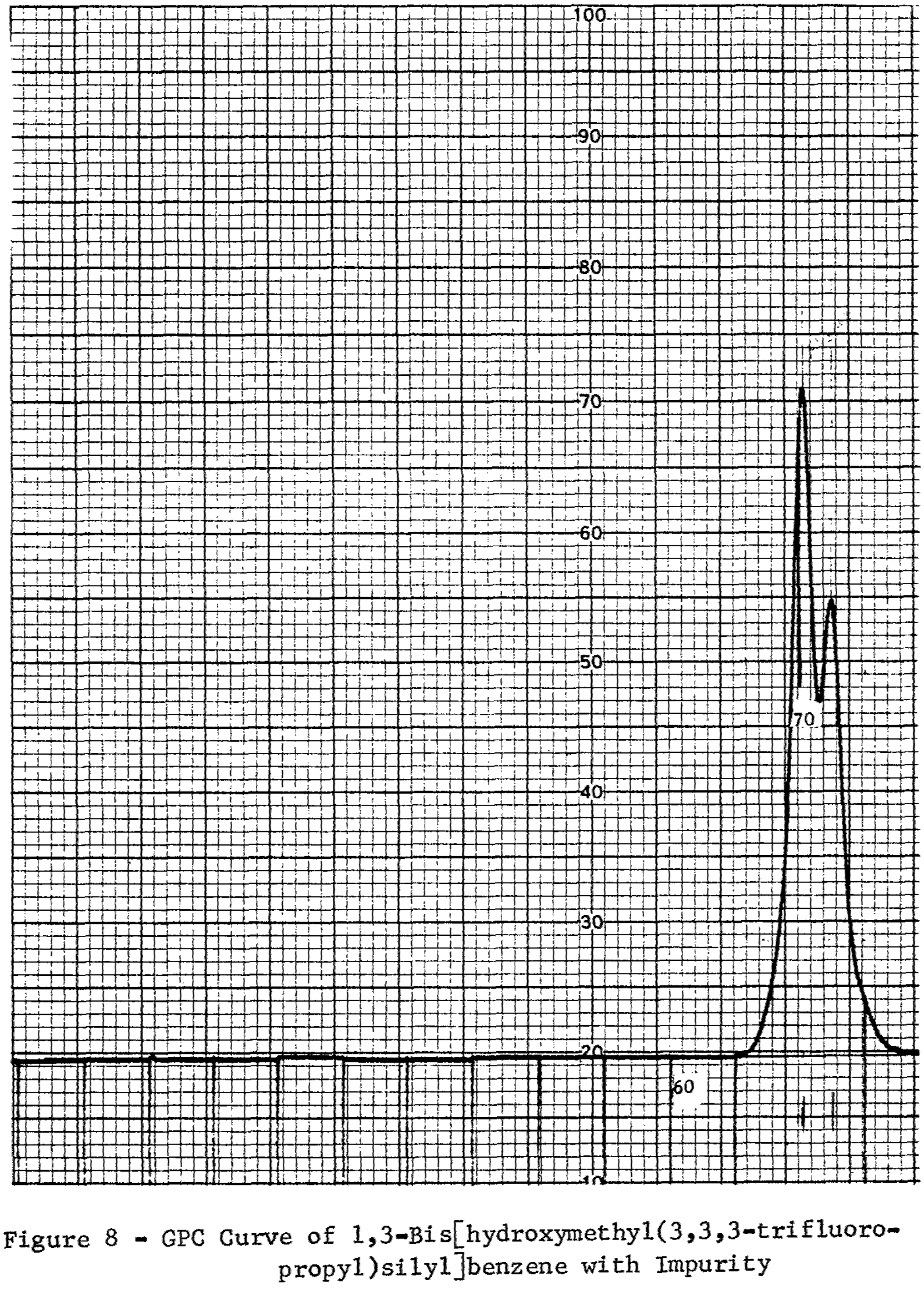


Figure 8 - GPC Curve of 1,3-Bis[hydroxymethyl(3,3,3-trifluoropropyl)silyl]benzene with Impurity

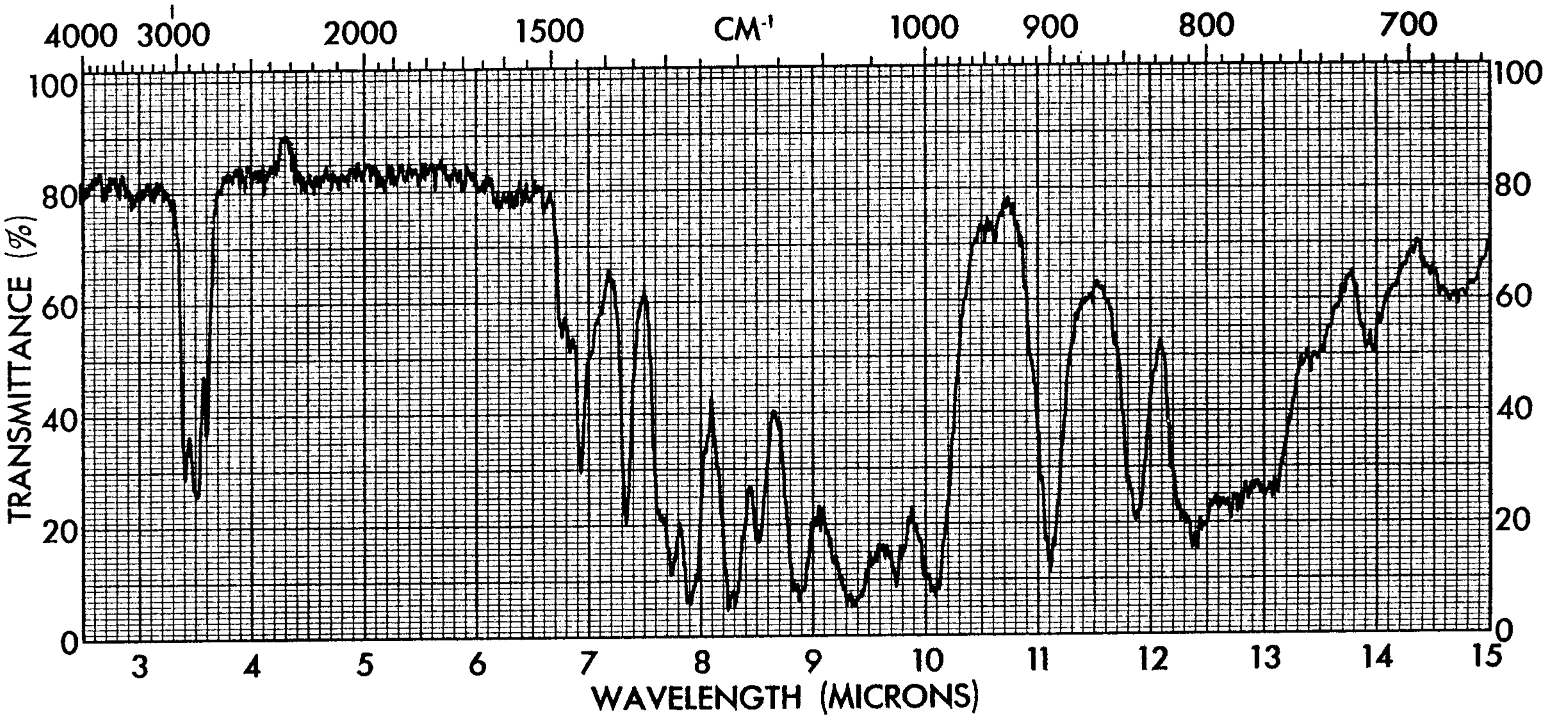


Figure 9 - Infrared Spectrum of 1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-bis-(3,3,3-trifluoropropyl)disiloxane (Neat)

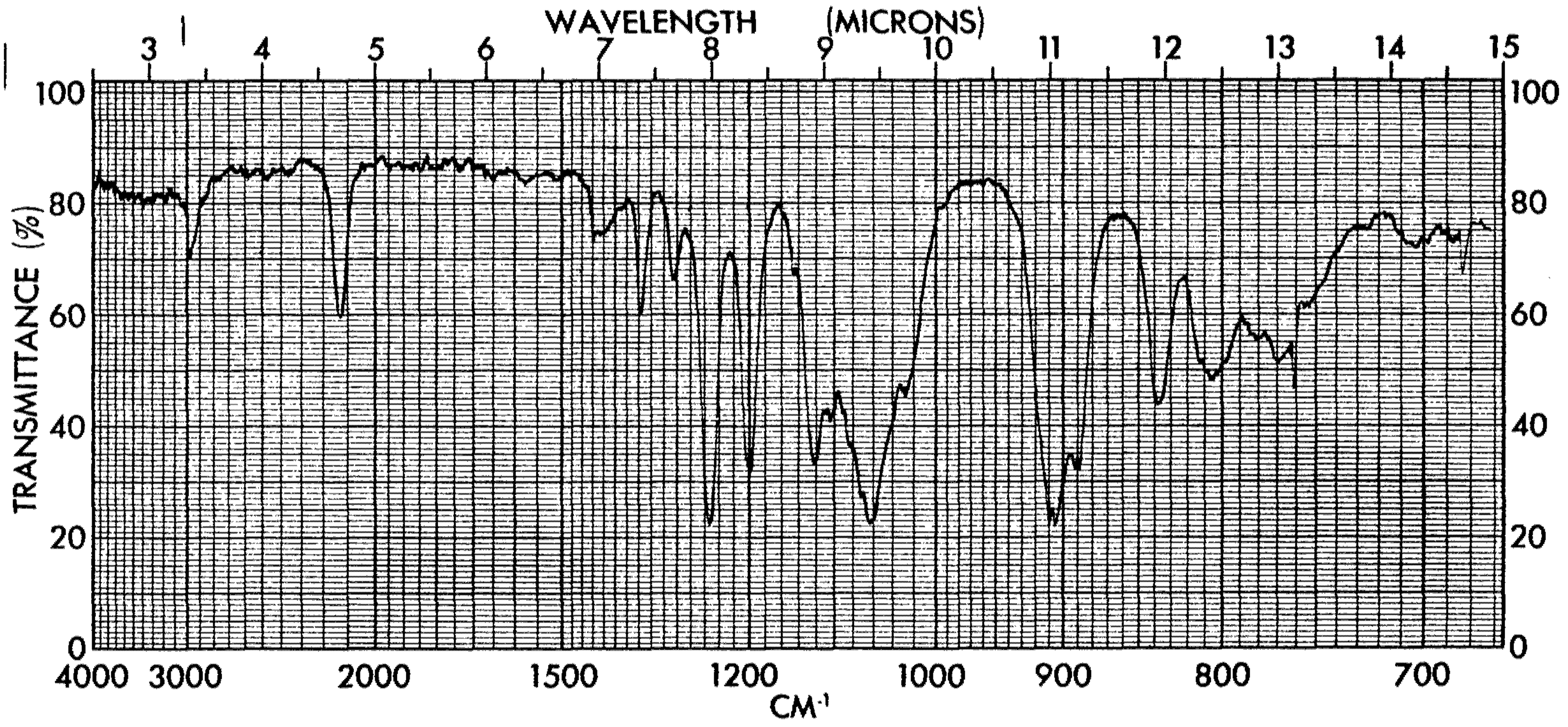


Figure 10 - Infrared Spectrum of m-Phenylenebis-1-[1,3,3-trimethyl-1-(3,3,3-trifluoropropyl)disiloxane] (Neat)

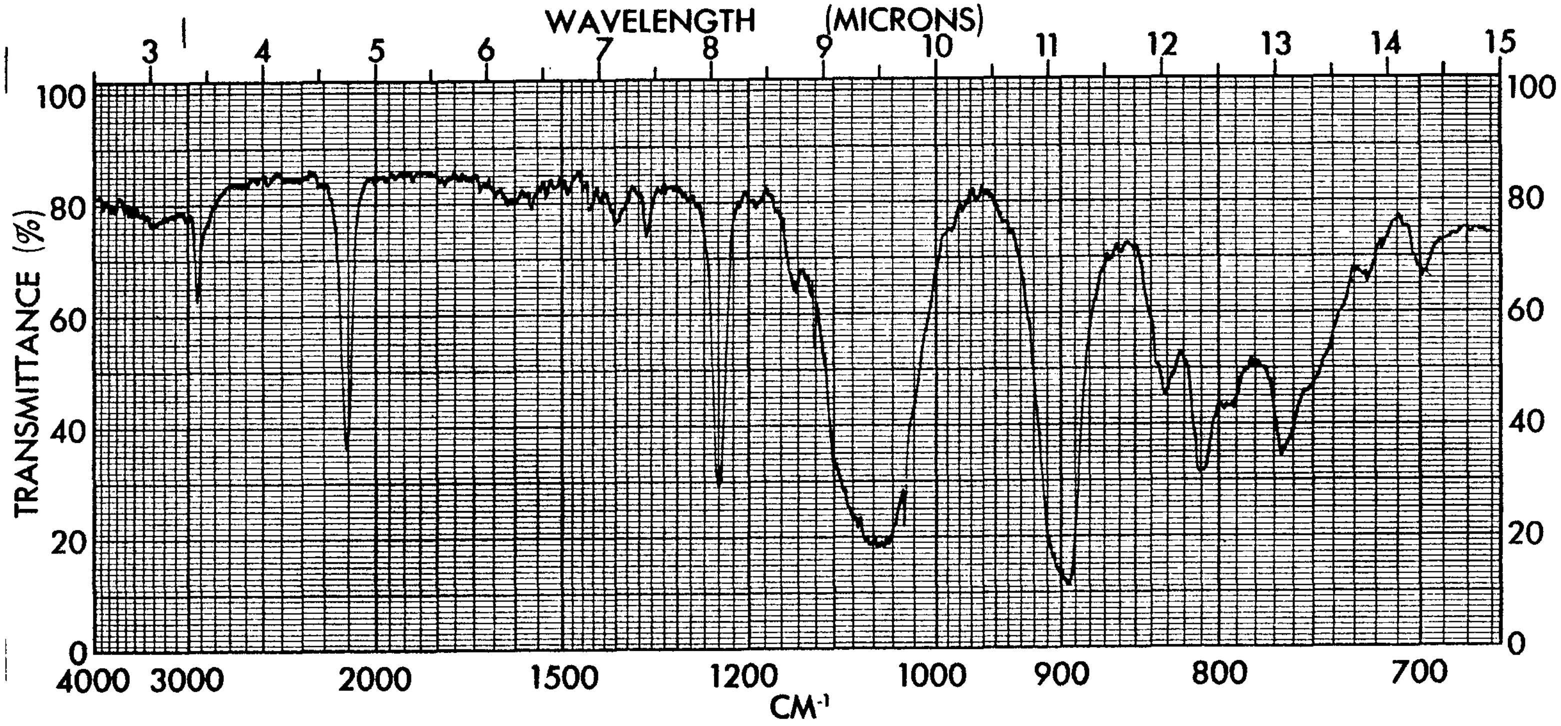
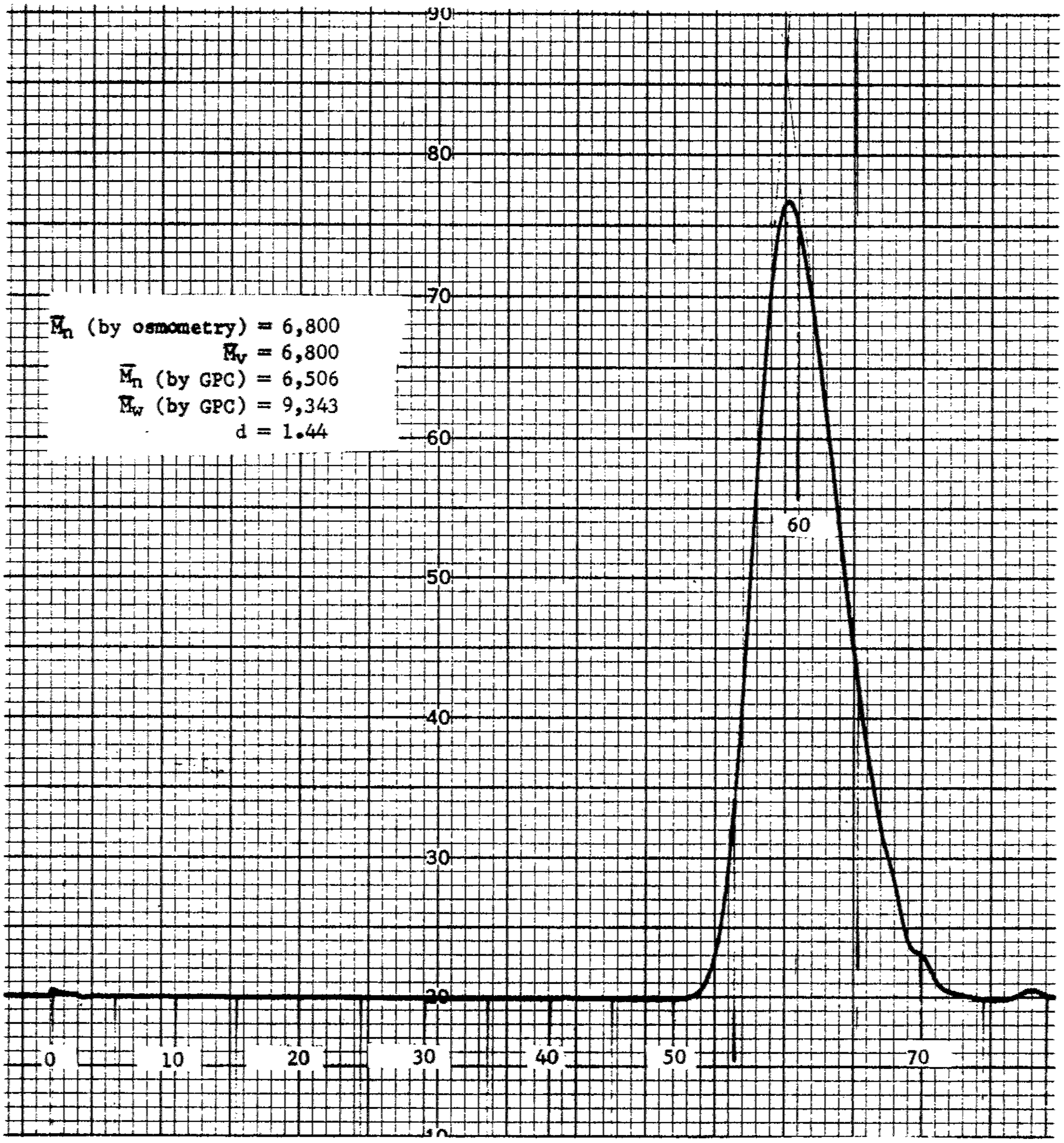


Figure 11 - Infrared Spectrum of m-Phenylenebis-3-[(1,1,3,5,5-pentamethyl)trisiloxane] (Neat)



$\overline{M}_n$ (by osmometry) = 6,800

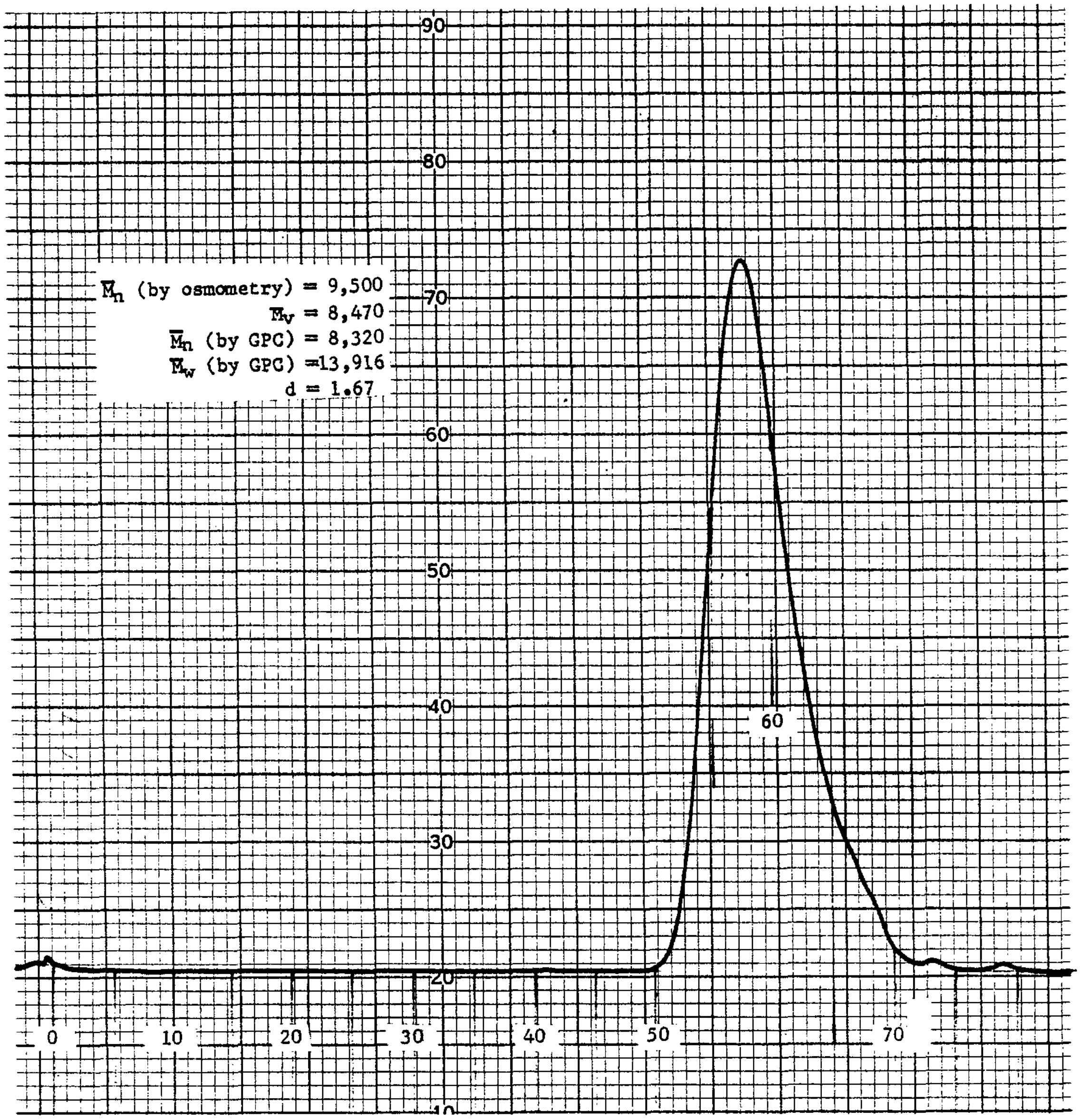
$\overline{M}_v$ = 6,800

$\overline{M}_n$ (by GPC) = 6,506

$\overline{M}_w$ (by GPC) = 9,343

d = 1.44

Figure 12 - GPC Curve of Oligomer No. 41 (Table 1)



$\overline{M}_n$ (by osmometry) = 9,500

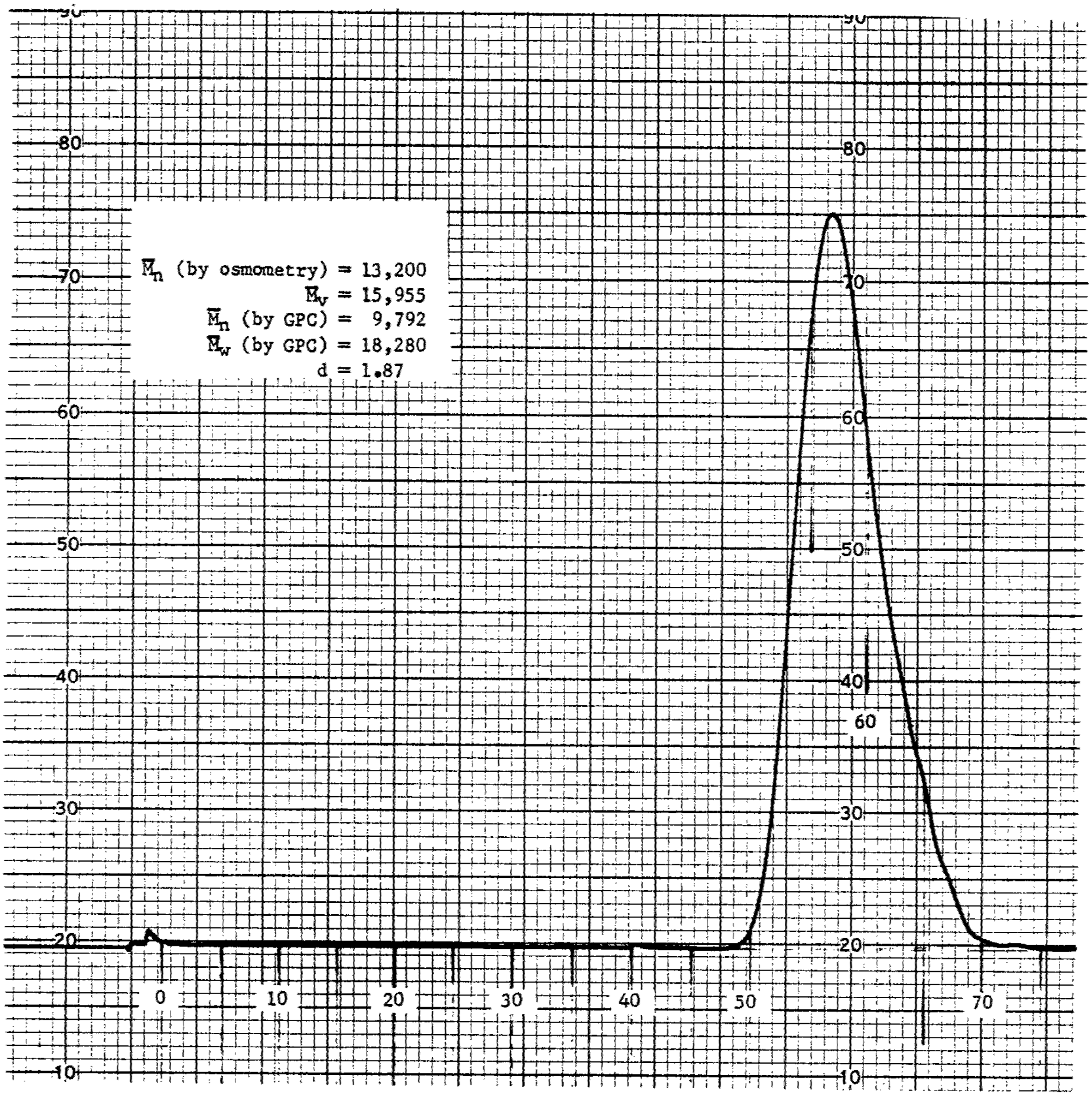
$\overline{M}_v$ = 8,470

$\overline{M}_n$ (by GPC) = 8,320

$\overline{M}_w$ (by GPC) =13,916

d = 1.67

Figure 13 - GPC Curve of Oligomer No. 7 (Table 1)



$\overline{M}_n$ (by osmometry) = 13,200

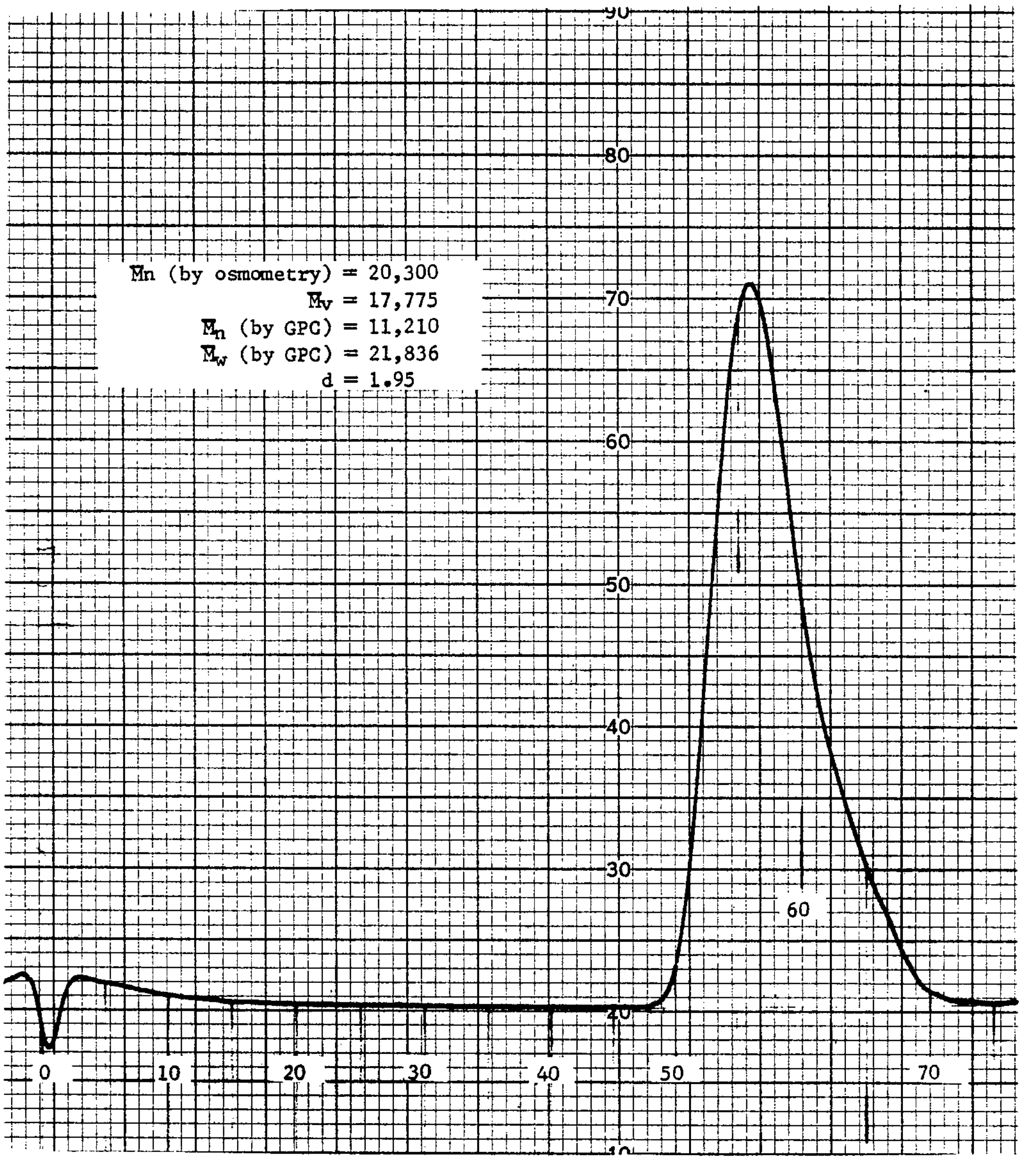
$\overline{M}_v$ = 15,955

$\overline{M}_n$ (by GPC) = 9,792

$\overline{M}_w$ (by GPC) = 18,280

d = 1.87

Figure 14 - GPC Curve of Oligomer No. 35 (Table 1)



$\bar{M}n$ (by osmometry) = 20,300
$\bar{M}_v$ = 17,775
$\bar{M}_n$ (by GPC) = 11,210
$\bar{M}_w$ (by GPC) = 21,836
d = 1.95

Figure 15 - GPC Curve of Oligomer No. 27 (Table 1)

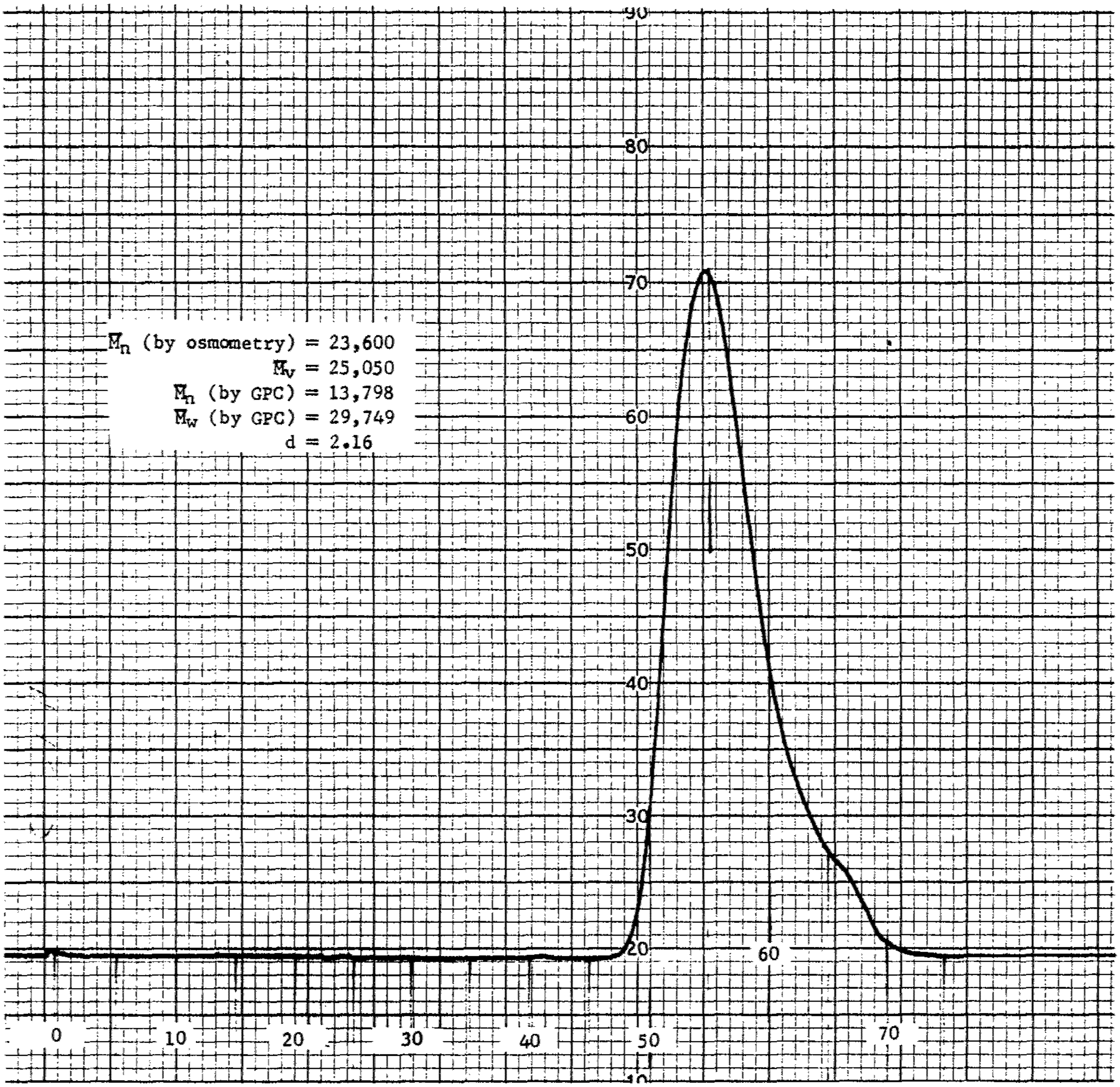
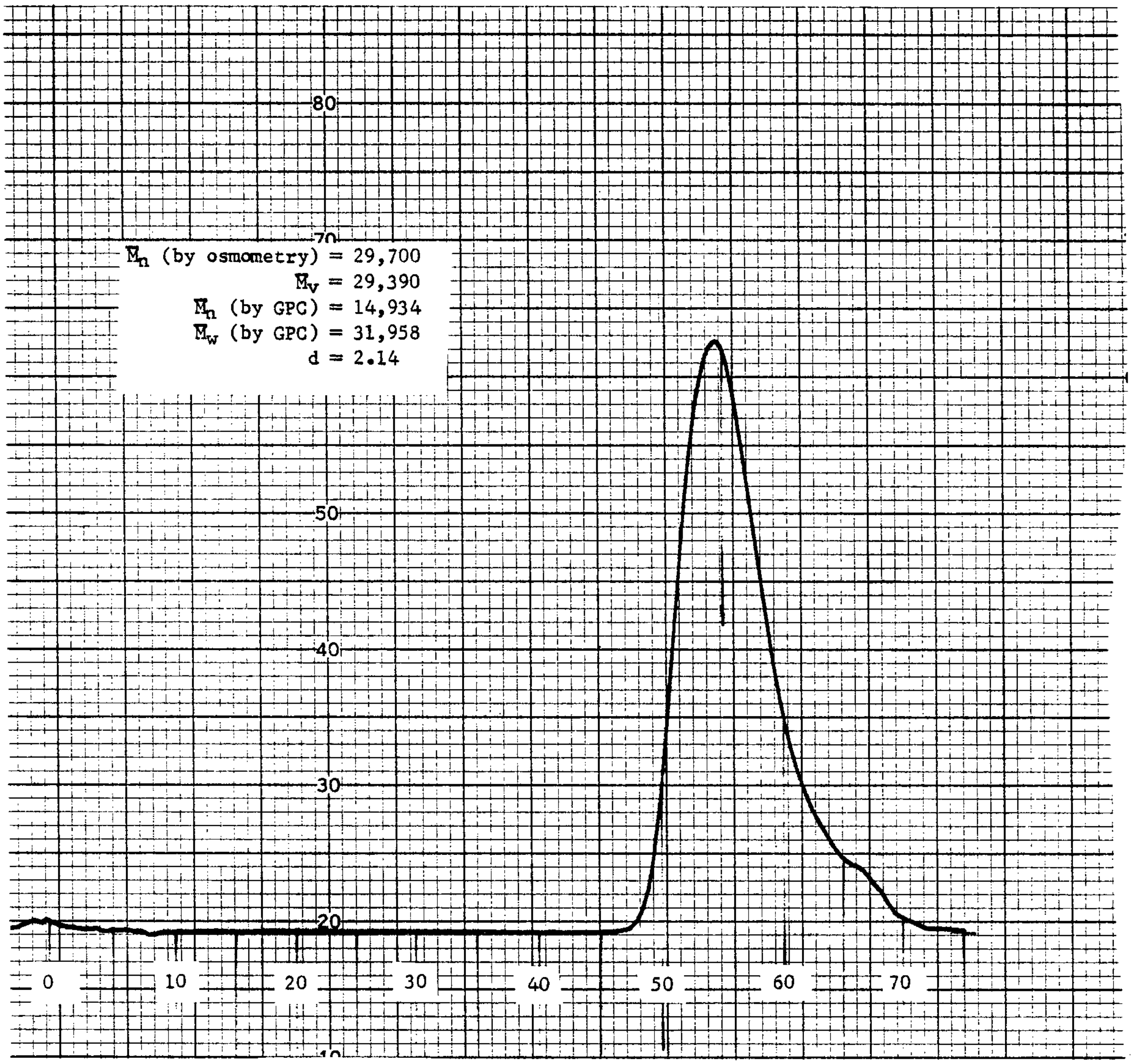


Figure 16 - GPC Curve of Oligomer No. 15 (Table 1)



$\overline{M}_n$ (by osmometry) = 29,700
$\overline{M}_v$ = 29,390
$\overline{M}_n$ (by GPC) = 14,934
$\overline{M}_w$ (by GPC) = 31,958
d = 2.14

Figure 17 - GPC Curve of Oligomer No. 16 (Table 1)

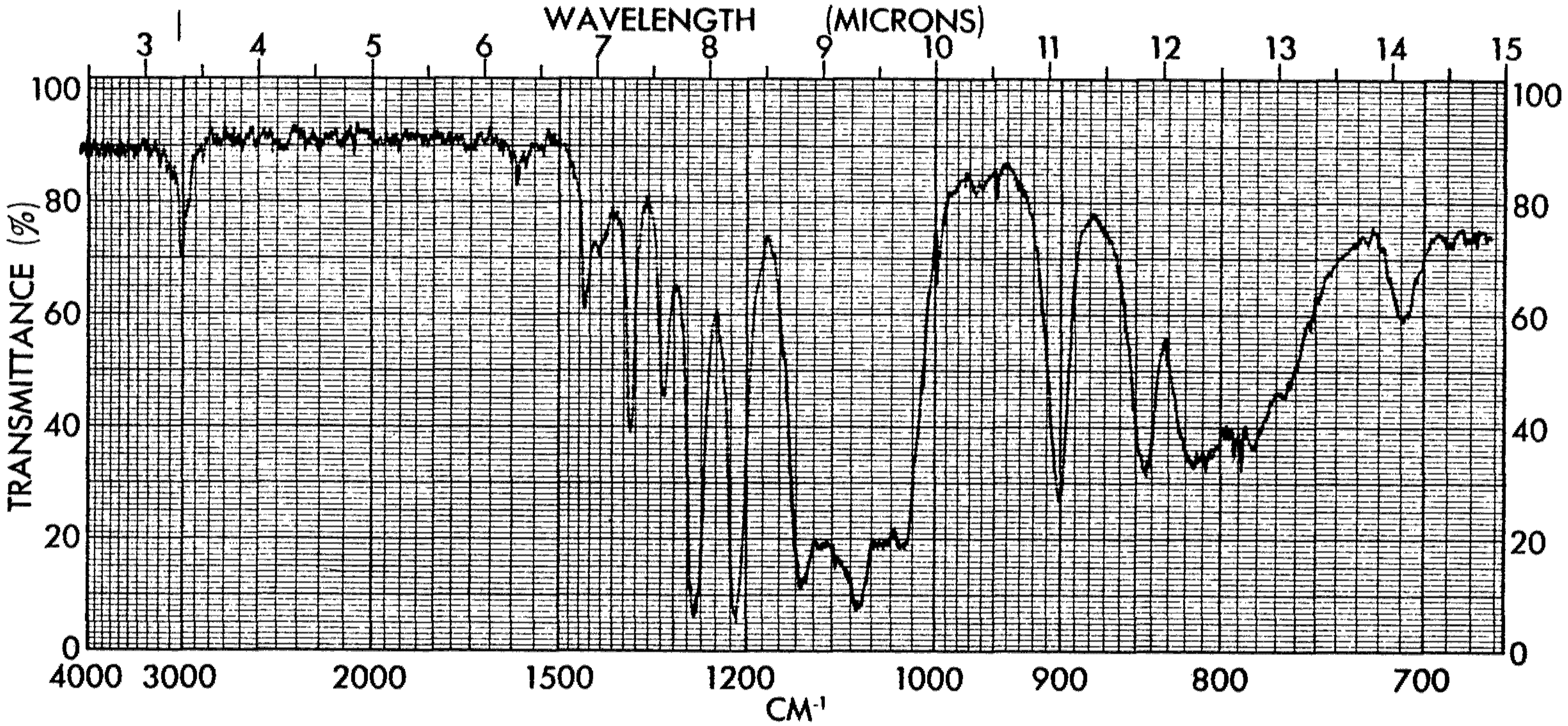


Figure 18 - Infrared Spectrum of Oligomer Sample No. 1 (250 g) (Neat)

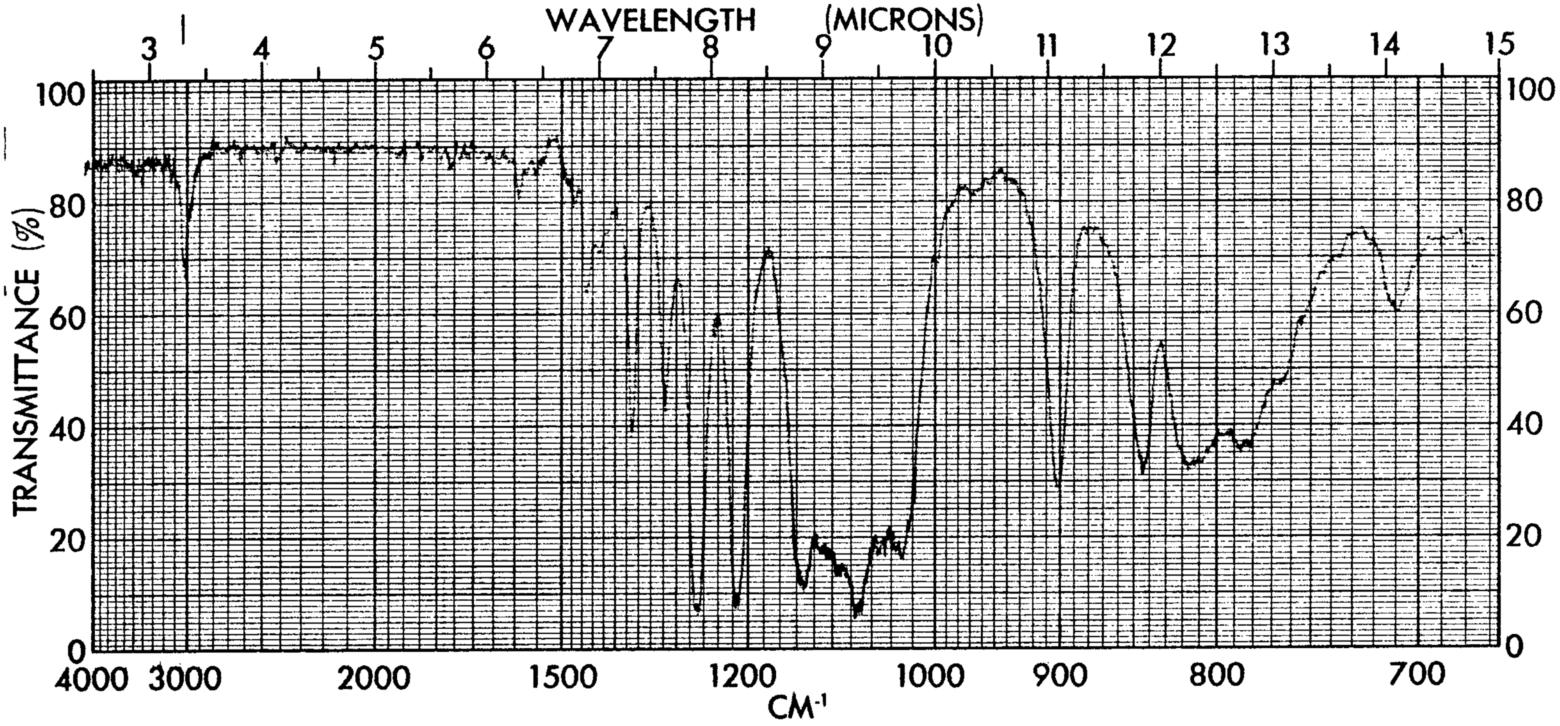


Figure 19 - Infrared Spectrum of Oligomer Sample No. 2 (250 g) (Neat)

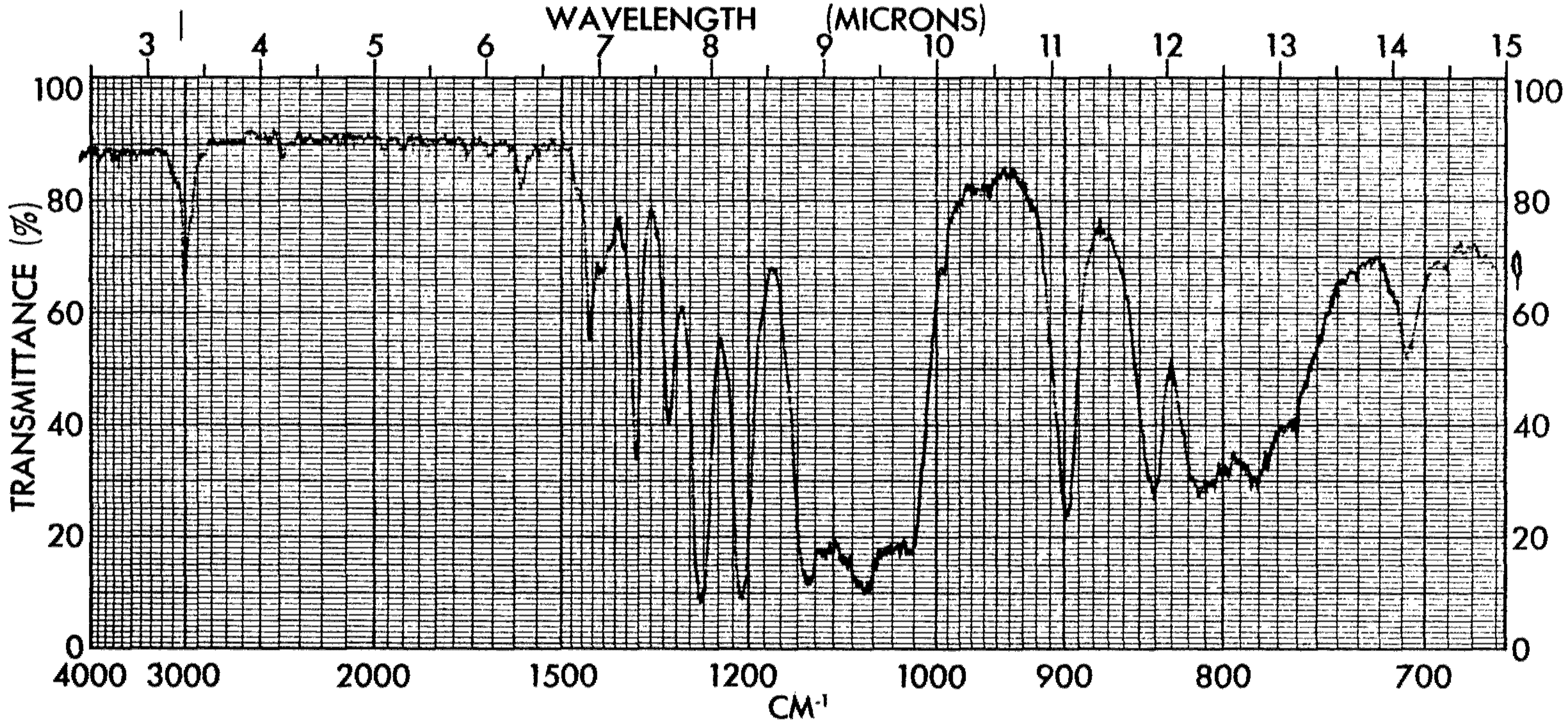


Figure 20 - Infrared Spectrum of Oligomer Sample No. 3 (250 g) (Neat)

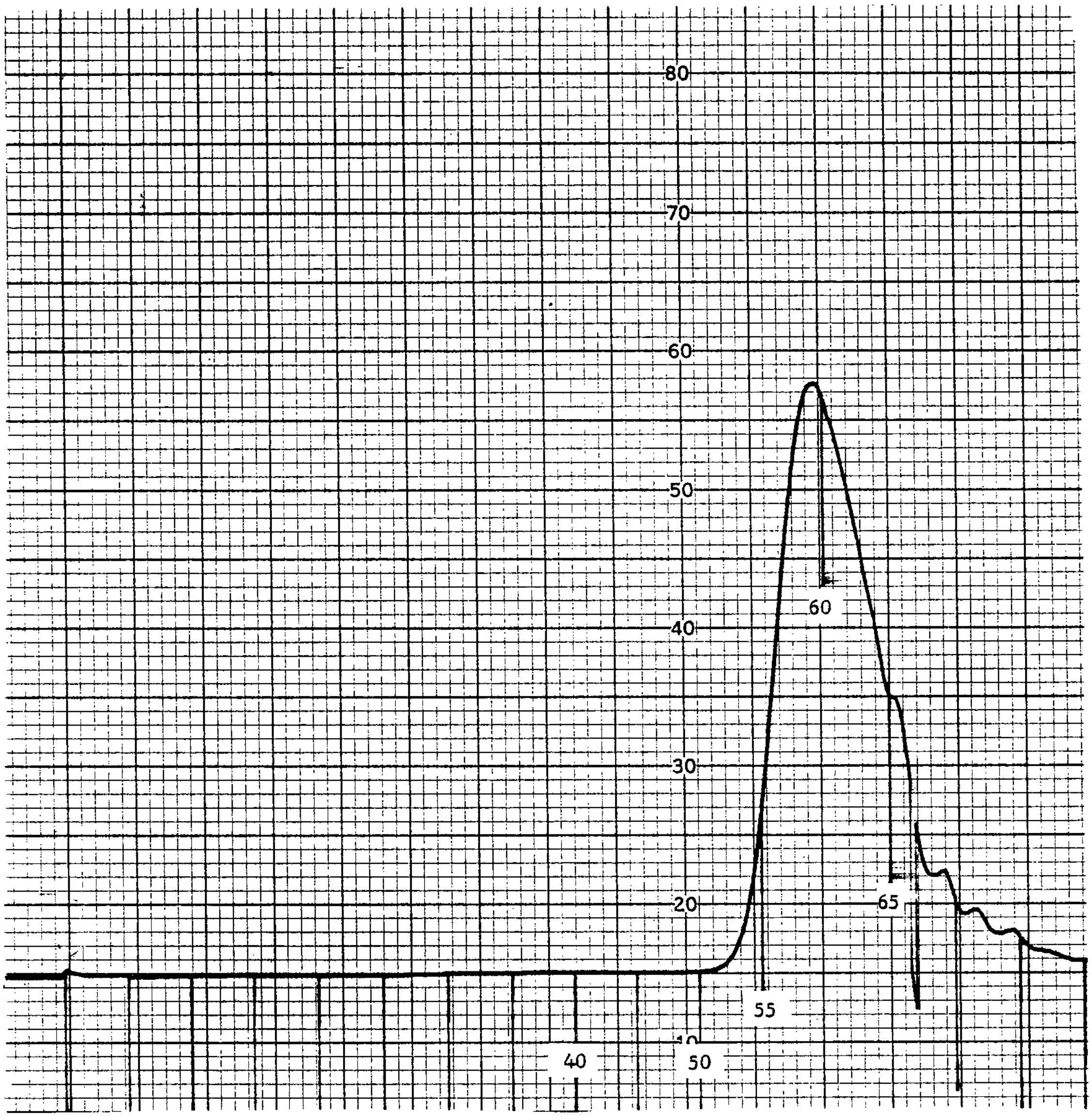


Figure 21 - GPC Curve of Oligomer Sample No. 1 (250 g)

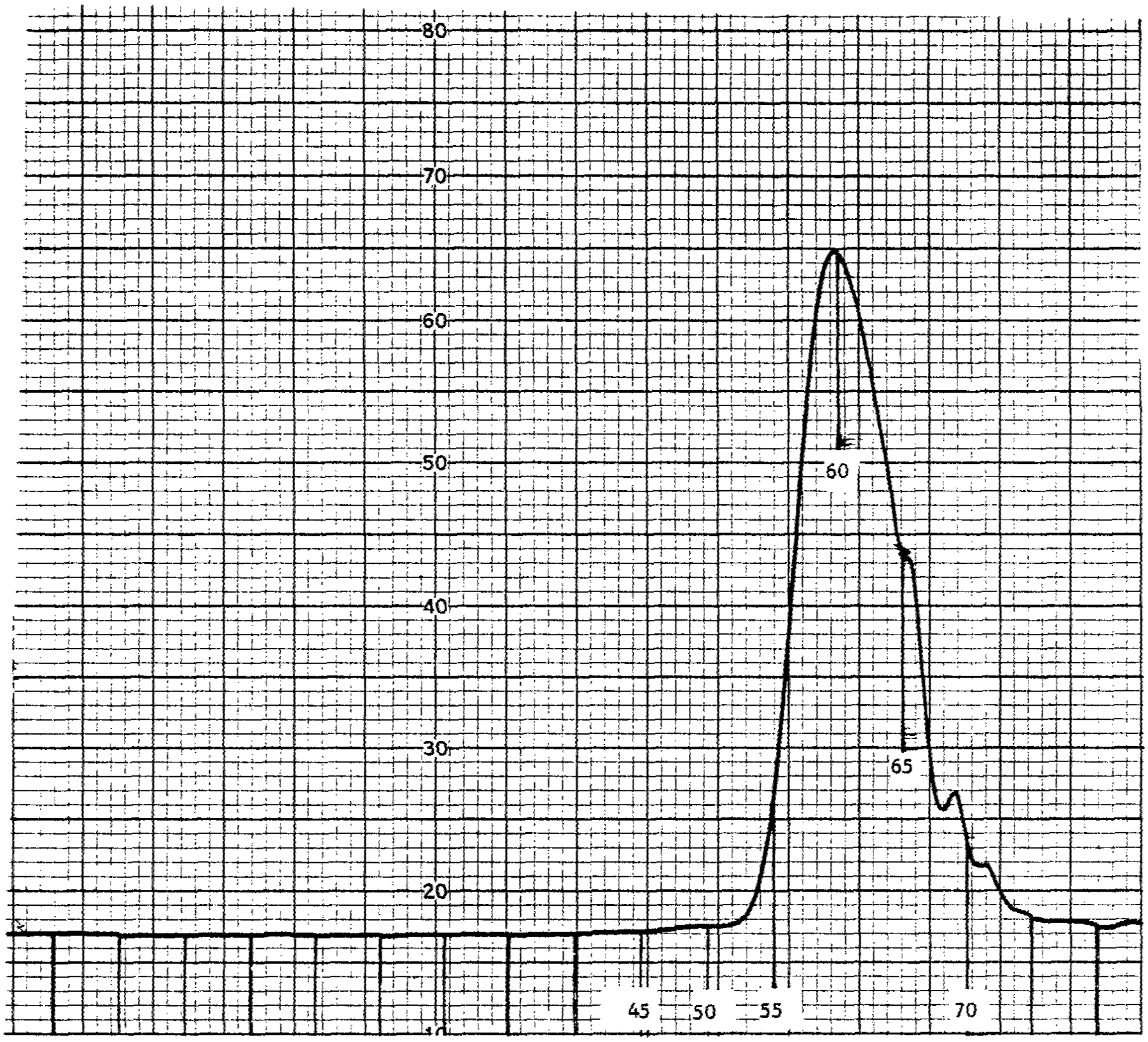


Figure 22 - GPC Curve of Oligomer Sample No. 2 (250 g)

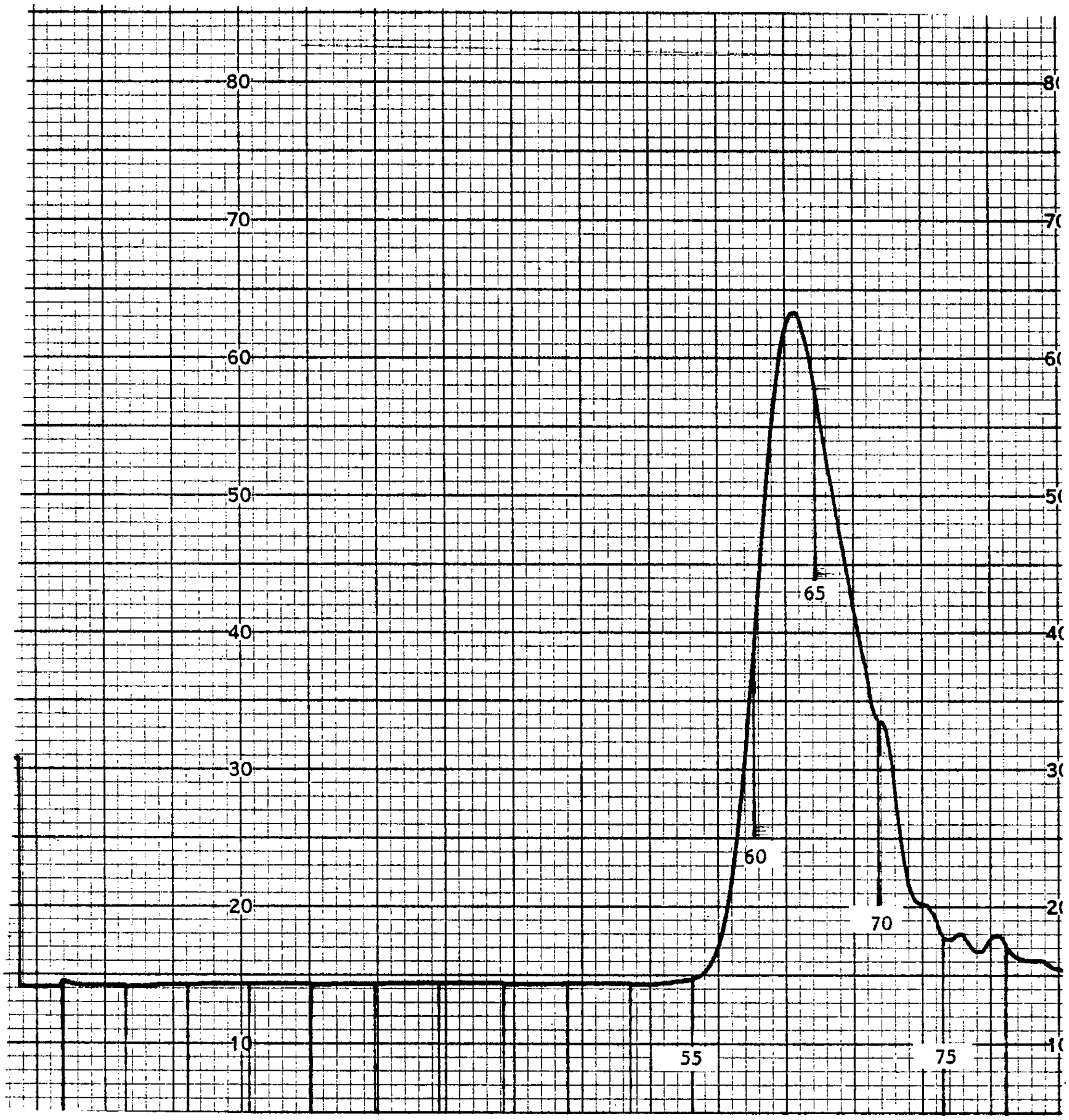
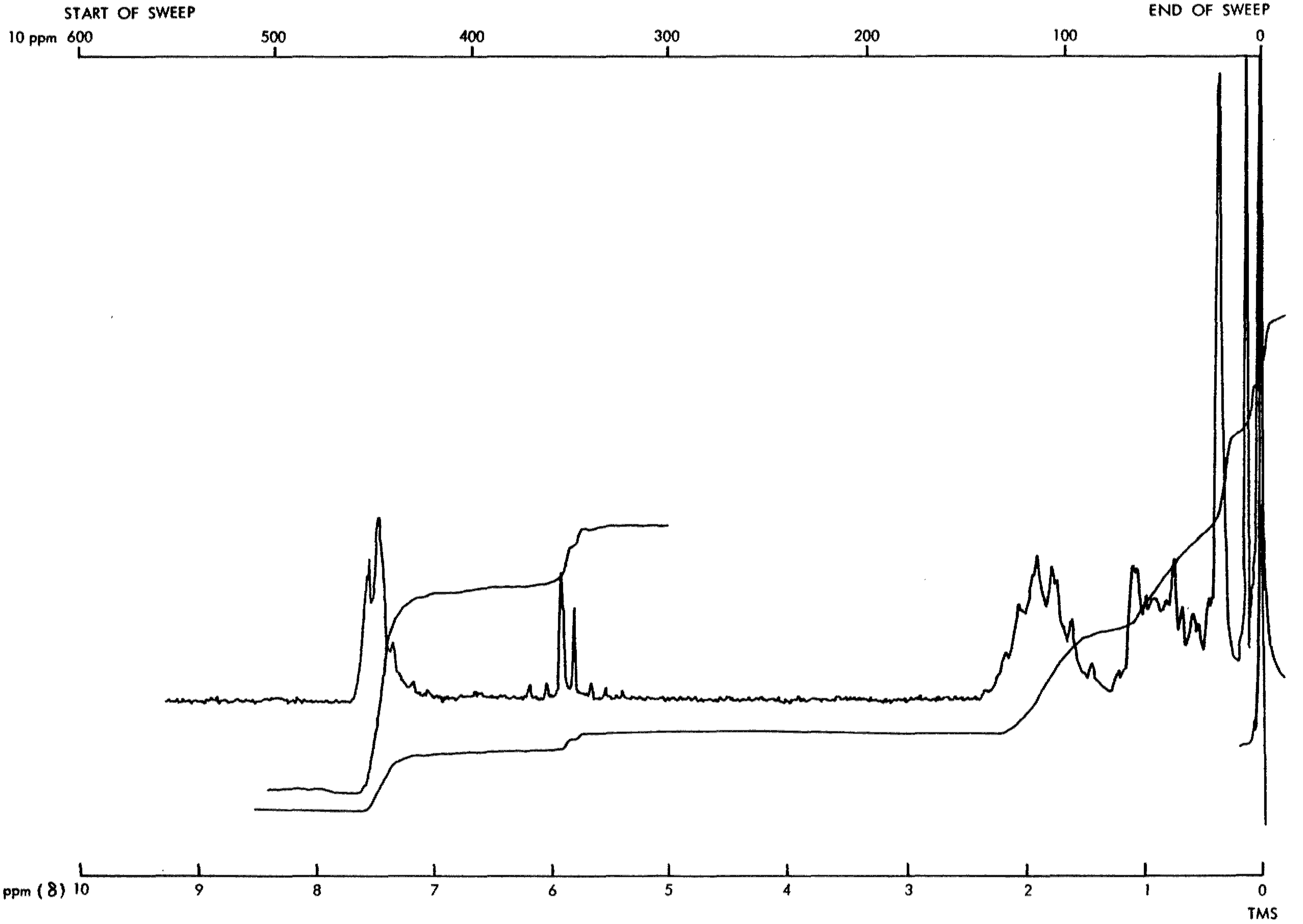


Figure 23 - GPC Curve of Oligomer Sample No. 3 (250 g)



Spectrum Ampl 100/7
Filter 0.1 sec
RF Power 0.05 mG

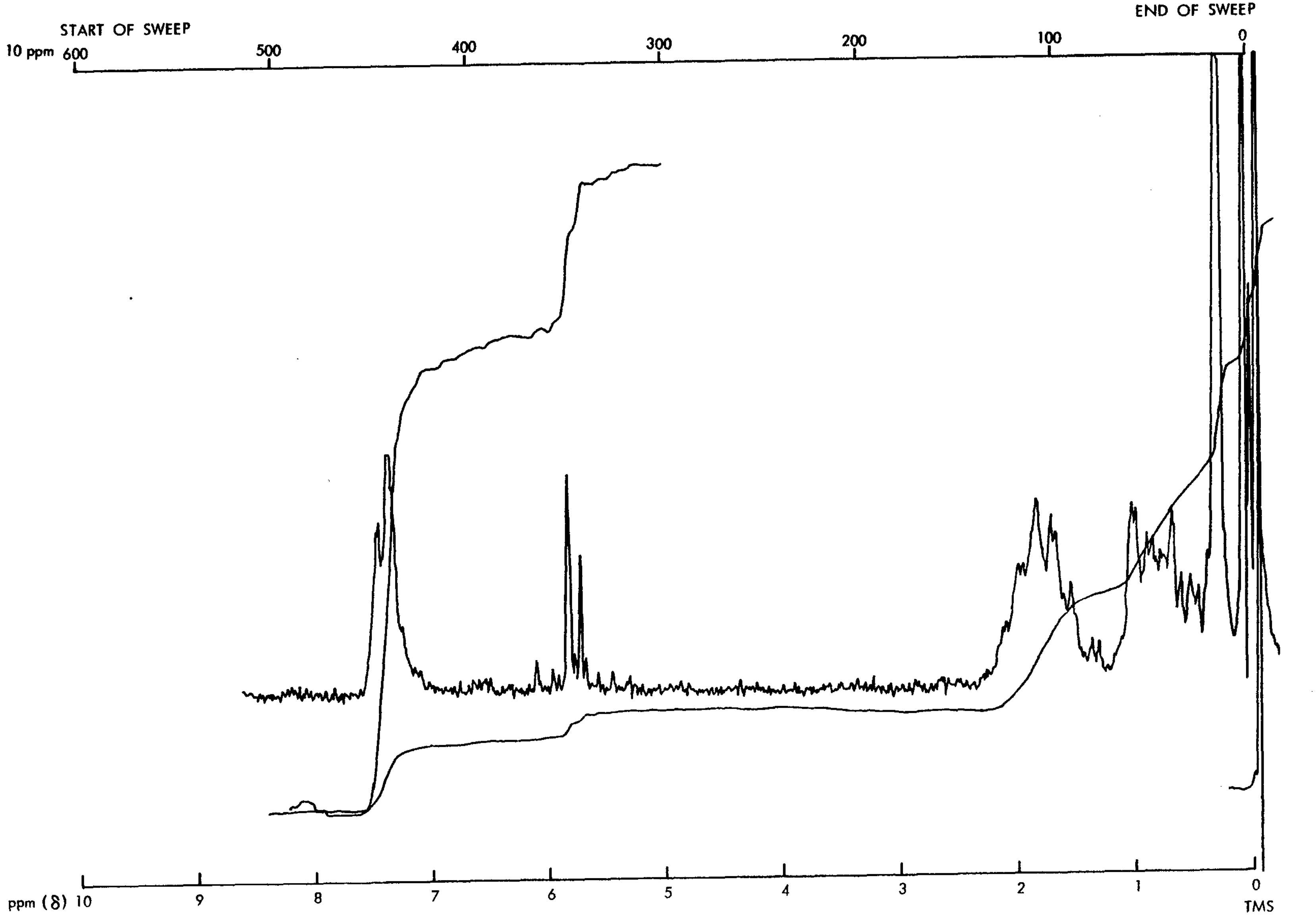
Sweep Time 5 min
Sweep Width 10 ppm or Hz
End of Sweep 0 ppm or Hz

Sample: N = 0.03
Vinyl End Capped Fasil Polymer
Solvent: CCl_4

Remarks: External Std. TMS

Operator TJB
Date 6/6/78

Figure 24 - NMR Spectrum of Oligomer Sample No. 1 (250 g)



Spectrum Ampl 100/7
Filter 0.1 sec
RF Power 0.05 mG

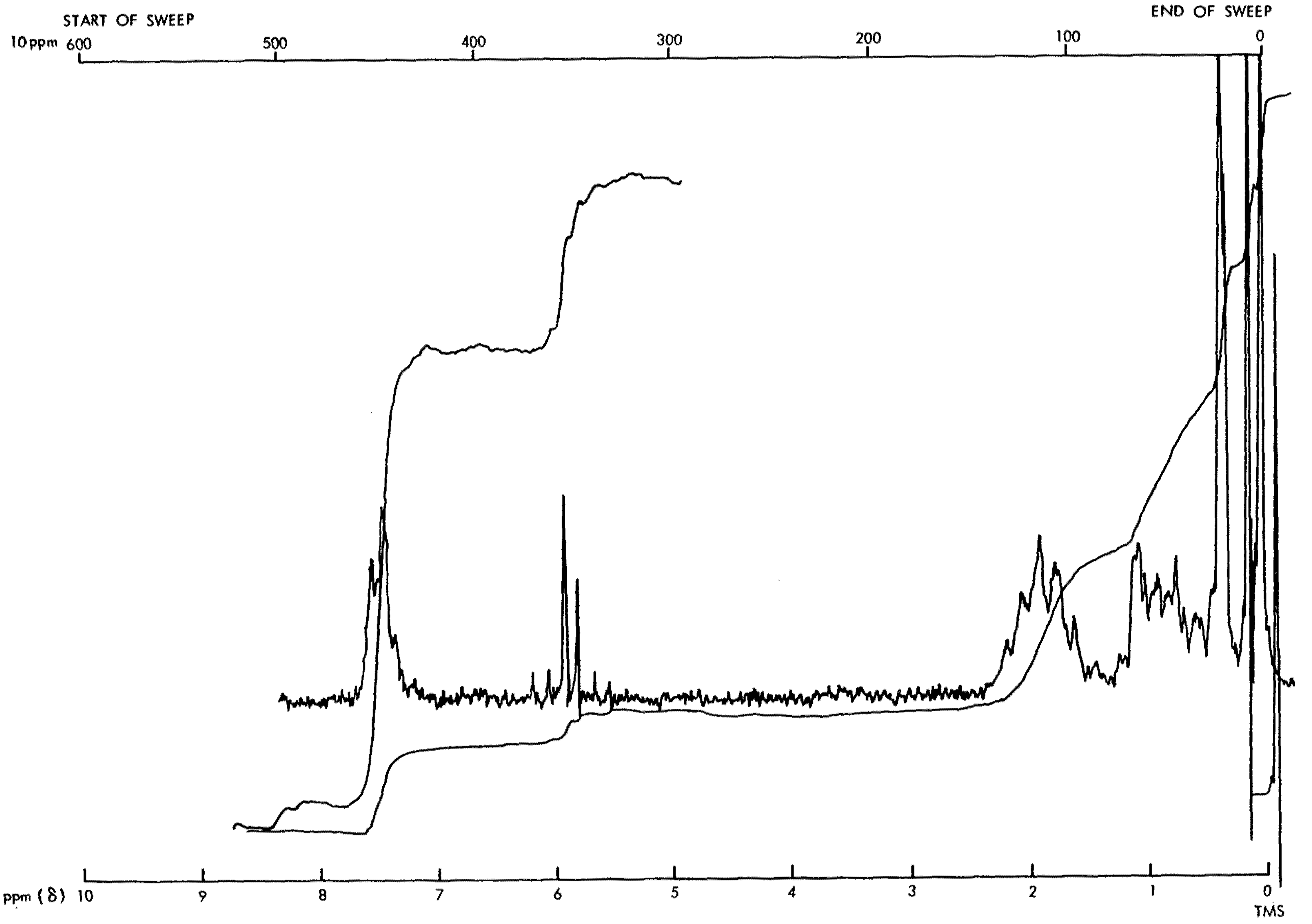
Sweep Time 5 min
Sweep Width 10 ppm or Hz
End of Sweep 0 ppm or Hz

Sample: N = 0.04
Vinyl End Capped Fasil Polymer
Solvent: CCl_4

Remarks: External Std. TMS

Operator TJB
Date 6/6/78

Figure 25 - NMR Spectrum of Oligomer Sample No. 1 (250 g)



Spectrum Ampl 100/7
Filter 0.1 sec
RF Power 0.05 mG

Sweep Time 5 min
Sweep Width 10 ppm or Hz
End of Sweep 0 ppm or Hz

Sample: N = 0.05
Vinyl End Capped Fasil Polymer
Solvent: CCl_4

Remarks: External Std. TMS

Operator TJB
Date 6/6/78

Figure 26 - NMR Spectrum of Oligomer Sample No. 3 (250 g)

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