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DETERMINATION OF PREPOLYMER FUNCTIONALITY AND ITS RELATIONSHIP TO BINDER PROPERTIES

FINAL REPORT

FEBRUARY 3, 1969 - FEBRUARY 2, 1970

Prepared for

Air Force Rocket Propulsion Laboratory
Directorate of Laboratories
Air Force Systems Command
Edwards, California

By

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Contract No. F04611-69-C-0046

Esso Report No. GR-10-FBP-70
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Final Report
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ESSO RESEARCH AND ENGINEERING COMPANY
GOVERNMENT RESEARCH LABORATORY
LINDEN, NEW JERSEY

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FOREWORD

This report summarizes the results on the characterization of selected prepolymers with respect to functionality and functionality distribution and the effect of functionality on mechanical properties of gumstocks carried out under Contract No. F04611-69-C-0046. These studies constitute a continuation of the work carried out under Contract No. F04611-67-C-0012, "Functionality Determination of Binder Prepolymers." The program consisted of two phases. Phase I comprises the adaptation and application of analytical methods developed under Contract F04611-67-C-0012 to other prepolymers. It also provides direct service and support functions to existing solid propellant development programs. Phase II involves the scale-up of the fractionation procedure of prepolymers into pure difunctional and monofunctional components and a study of the effect of monofunctionality on the mechanical properties of the cured binder.

Specific studies relating to Shell's P-BEP prepolymer have already been published in a confidential report entitled "P-BEP Cure Studies," AFRPL-TR-69-179.

The program was sponsored by the Air Force Rocket Propulsion Laboratory, Directorate of Laboratories, Air Force Systems Command, Edwards, California and the program was administered by Captain Raymond Foscante and Dr. James Trout. The work reported was done in the Government Research Laboratory of the Esso Research and Engineering Company, Linden, New Jersey.

Research was carried out by Mr. A. H. Muenker with analytical support by Dr. B. E. Hudson. The project was under the supervision of Dr. D. Grafstein, Program Manager.

This technical report has been reviewed and is approved.

W. W. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Functionality and functionality distribution measurements have been carried out on six different polybutadiene prepolymers containing hydroxy or carboxy functionality which are currently of interest to the Air Force. The specific prepolymers are: Sinclair's Poly B-D R-45M and R-15M, hydroxy-functional butadiene homopolymers prepared by free radical polymerization and General Tire's Telagen prepolymer series, prepared by anionic polymerization. The Telagen prepolymer series comprises the following polymers: the OH-Telagen (nominal M_n=5000) and its low molecular weight (M_n=2000), saturated counterpart, OH-Telagen-S, and the corresponding carboxy-functional analogues, COOH-Telagen and COOH-Telagen-S.

Number average molecular weight measurements of three different lots of the R-45M prepolymer showed little batch to batch variation. Functionality distribution measurements were obtained by elution chromatography on activated silica gel. The difunctional content was found to be approximately 40 to 45 wt % with a nominal molecular weight of 4000, the remainder (55-60 wt %) being trifunctional with a nominal molecular weight of 2000. All three lots of the R-45M have consistently shown this dependence of functionality on molecular weight. The functionality distribution of the R-15M was found to be similar to that of the R-45M, containing more than 50 wt % triol. In contrast to Sinclair's R-45M and R-15M prepolymers which are composed of di- and trifunctional components, the Telagen prepolymers contain non-, mono- and difunctional prepolymers. The total non- and monofunctional content of the four Telagen prepolymers which were analyzed varied from 24 to 32 wt %, the bulk of which is monofunctional.

A sample of Rocketdyne's P-GDEFE prepolymer, lot EII-68, was characterized with respect to functionality distribution and found to contain 12 to 15% monofunctional, 45 to 50% difunctional and 35 to 40% trifunctional prepolymer. Functionality distribution measurements of 3M's new perfluoroalkylene oxide prepolymer, PC2202, showed the presence of 3-5% nonfunctional and 7-9% monofunctional prepolymer, the remainder being difunctional.

Mechanical properties of a gumstock prepared from a pure difunctional HO-polybutadiene prepolymer have been obtained over a temperature range of -65°F to 180°F. The effect of monofunctional prepolymer content on gumstock properties has been quantitatively defined.

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GLOSSARY

COOH-Telagen-S CT-Telagen-S Telagen-CT-S	General Tire and Rubber Company's hydrogenated, carboxy-functional polybutadiene prepolymer
COOH-Telagen CT-Telagen Telagen-CT	General Tire and Rubber Company's unsaturated, carboxy-functional polybutadiene prepolymer
DDI	General Mills' diisocyanate based on a dimer acid
FC2202	3M Company's Perfluoroalkylene oxide prepolymer having hydroxy-functional groups.
HDI	Hexamethylene diisocyanate
$(\bar{M}n)_c$	Number average molecular weight extrapolated to zero concentration
OH-Telagen-S HT-Telagen-S Telagen-HT-S	General Tire and Rubber Company's hydrogenated, hydroxy-functional polybutadiene prepolymer
OH-Telagen HT-Telagen Telagen-HT	General Tire and Rubber Company's unsaturated, hydroxy-functional polybutadiene prepolymer
P-GDNPE	Rocketdyne's nitro-fluoro prepolymer having hydroxy-functional groups
R-15M	Sinclair's Poly B-D hydroxy-functional butadiene homopolymer, molecular weight somewhat greater than R-45M
R-45M	Sinclair's Poly B-D hydroxy-functional butadiene prepolymer.
TDI	2,4-Tolylene diisocyanate
TPMI or TPDMI	Triphenyl dimethylene triisocyanate
TTI	Triphenyl methane triisocyanate

I. INTRODUCTION

Under a previous Contract (F04611-67-C-0012), Esso Research and Engineering Co. developed and/or refined and evaluated test methods for determining molecular weight, equivalent weight, functionality, functionality distribution and molecular weight distribution of selected solid propellant binder prepolymers (1).

Most significantly a method was developed which can determine the functionality distribution of binder prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono-, di- and polyfunctional components.

The ability to determine the functionality distribution of prepolymers and to separate prepolymers into non-, mono- and difunctional prepolymers is a prerequisite in studying the effect of functionality distribution on binder and propellant mechanical properties. It opens up new areas of binder studies such as the establishment of the relationship between mechanical properties and monofunctional prepolymer content. Such experimental investigations were hitherto inaccessible because of lack of appropriate analytical techniques.

Theoretical considerations predict that monofunctional prepolymer components will seriously affect the mechanical properties of the propellant since monofunctional polymer chains will act as chain terminators during the cure process and hence interfere with the formation of a large polymer network needed to impart good mechanical properties to the propellant. The level of monofunctional polymer at which mechanical properties will seriously drop off had not been defined and good quantitative data were needed. The effect of nonfunctional polymer components on cured binder properites was not determined. Nonfunctional prepolymer components cannot participate in the cure process and will therefore merely act as high molecular weight plasticizers.

Prepolymer composition particularly with respect to functionality distribution has long been neglected as a quality parameter in the optimization of solid propellant mechanical properites. Phase II of this program represents an initial step designed to fill this gap. It has established a relationship between functionality, specifically monofunctional prepolymer content, and binder mechanical properites. It has also defined the optimum mechanical properties of a purely difunctional polybutadiene prepolymer. All studies under this program have been restricted to the gumstock. No propellant formulation studies were made.

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(1) Functionality Determination of Binder Prepolymers, Final Report, October 1966—September 1968, AFRPL-TR-68-237, A. H. Muenker and B. E. Hudson, Esso Research and Engineering Co.

II. OBJECTIVE

The objective of this program is to continue the development of methods for the characterization of selected prepolymers with respect to functionality and functionality distribution and to determine the relationship between gumstock mechanical properties and functionality, specifically monofunctional prepolymer content.

The program consisted of two phases:

Phase I entails research aimed at extending and adapting analytical methods developed under Contract F04611-67-C-0012 to new classes of prepolymers of interest to the Air Force.

Phase II involves in part optimization and scale-up of the fractionation procedure to obtain larger quantities of pure difunctional and monofunctional prepolymers. Gumstock formulations employing pure difunctional polymer exclusively and with varying amounts of monofunctional material were made to assess the general effect of functionality distribution on mechanical properties. In addition, gumstock formulations utilizing pure difunctional material were compared with those employing the bulk polymer.

III. SUMMARY

This report discusses functionality and functionality distribution measurements of binder prepolymers currently of interest to the Air Force. The effect of monofunctional prepolymer content on mechanical properties was explored and the mechanical properties of gumstocks prepared from a pure difunctional HO-polybutadiene prepolymer were defined. This is the final report on Contract No. F04611-69-C-0046 and covers the period February 3, 1969 through February 2, 1970. All studies relating to Shell's P-BEP prepolymer have been summarized in AFRPL-TR-69-179, entitled "P-BEP Cure Studies."

A total of eight different prepolymers were characterized with respect to functionality and functionality distribution. All are low molecular weight, liquid polybutadienes containing hydroxy or carboxy functionality.

Sinclair produces two hydroxy-functional butadiene homopolymers which are designated Poly B-D R-45M and R-15M respectively. The R-15M prepolymer has a somewhat higher molecular weight than the R-45M. Interest in these prepolymers stems from two facts: (1) their low cost (48 to 54 cents/pound) and their reportedly high overall functionality which is substantially in excess of 2.0.

Molecular weight and functionality as well as functionality distribution measurements were carried out on three different lots of the R-45M prepolymer to determine whether there were significant differences in these parameters, in particular in the functionality distribution pattern.

The extrapolated number average molecular weights, $(\bar{M}n)_o$, as determined by VPO in chloroform at 37° showed very little batch to batch variation (2740 to 2900). The overall functionalities based on molecular weight and equivalent weight measurements varied from 2.30 to 2.48. In view of this high average functionality level, the R-45M prepolymer should contain significant quantities of polymer components having functionality greater than two. Subsequent functionality distribution measurements have confirmed this. Functionality distribution measurements were obtained by elution chromatography on activated silica gel (100-200 mesh). A comparison of functionality distribution measurements of three lots of the R-45M shows that this prepolymer consists of di- and trifunctional components. The difunctional content is approximately 40 to 45 wt %, with a nominal molecular weight of 4000, the remainder (55 to 60%) being trifunctional with a nominal molecular weight of 2000. All three lots have consistently shown this dependence of functionality on molecular weight. On a molar basis the functionality distribution of the R-45M prepolymer reflects an even higher triol content: 25 mole % diol and 75 mole % triol.

To determine whether there is a substantial difference between the R-45M and the R-15M prepolymer, a single lot of R-15M was also characterized with respect to its functionality and functionality distribution. Molecular weight measurements showed that there is a significant but not dramatic difference in molecular weight between the R-15M (Mn=3400) and the R-45M (Mn=2800). The overall functionality of the R-15M, lot 707203 was found to be 2.40 which is identical to lot 805101 of the R-45M prepolymer. Functionality distribution measurements of the R-15M showed that about 45 wt % of this prepolymer is difunctional with a nominal molecular weight of 6000, the remainder being trifunctional.

A comparison of the functionality distribution of the R-45M and the R-15M prepolymers therefore shows that trifunctional prepolymer is the major component (more than 50 wt %) in both prepolymers. The R-15M appears to have a slightly higher difunctional content than the R-45M. This apparently slight difference in difunctional polymer content may further diminish upon analysis of additional lots of the R-15M prepolymer.

Samples of General Tire's low molecular weight (nominal Mn=2000), hydrogenated OH-Telagen-S had previously been characterized and found to contain non-, mono- and difunctional prepolymer. One additional lot of OH-Telagen-S which is being used on Contract No. F04611-68-C-0045, "Synthesis and Evaluation of Curing Agents," has been analyzed. The functionality distribution of lot 242 AM 273 HH of OH-Telagen-S was found to be as follows: 9% nonfunctional, 15% monofunctional, the remainder being difunctional. Similar functionality distributions were found for previously analyzed lots of OH-Telagen-S.

A sample of the higher molecular weight (nominal Mn=5000), unsaturated OH-Telagen, has also been analyzed. This polymer is the first unsaturated, hydroxy functional prepolymer of the Telagen series of 5000 nominal molecular weight that we have tried to fractionate by functionality. The total non- and monofunctional content of lot 242 AM 292/316 AMS was found to be about 32 wt %. Fractionation of this prepolymer was scaled-up to provide sufficient quantities of pure difunctional and monofunctional material for evaluation of mechanical properties of cured gumstocks. Equivalent weight and molecular weight measurements of the difunctional and monofunctional prepolymer have yielded the following values respectively:

$$\text{difunctional prepolymer:}\quad f = \frac{(\bar{M}n)o}{\text{Eq. Weight}} = \frac{5400}{2720} = 1.99$$

$$\text{monofunctional:}\quad f = \frac{(\bar{M}n)o}{\text{Eq. Weight}} = \frac{6000}{6100} = 0.98$$

Functionality distribution measurements were also carried out on the carboxy-analogues of the OH-Telagen prepolymer series. The COOH-Telagen-S, lot 242 AM 273 CHR, a hydrogenated polybutadiene of 2000 nominal molecular weight was found to contain about 2 wt % nonfunctional and 23 wt % monofunctional prepolymer. This confirms our previous observations that the bulk of the material having less than theoretical functionality (f=2.0) is monofunctional (f=1) rather than nonfunctional (f=0).

The higher molecular weight (nominal Mn=5000), unsaturated COOH-Telagen prepolymer was found to be more strongly adsorbed on the silica gel than any of the previously characterized prepolymers. Polymer recovery upon fractionation on silica gel was only 51 to 69%. Nevertheless, the non- and monofunctional prepolymer components which are less strongly adsorbed on the silica gel were eluted from the column. The total non- and monofunctional content was found to be about 27%.

A sample of Rocketdyne's P-GDNFE prepolymer, lot RII-68, a nitro-fluoro prepolymer having hydroxy functional groups, was characterized with respect to functionality distribution. The monofunctional content which was also the lower molecular weight fraction was found to be 12-15 wt %. Separation of di- and trifunctional components was not realized. However, based on the analysis of the individual fractions the difunctional content is approximately 45 to 50 wt % and the trifunctional content is 35 to 40 wt %.

Functionality distribution measurements of 3M's new perfluoroalkylene oxide prepolymer, FC2202, showed the presence of 3-5% nonfunctional and 7-9% monofunctional prepolymer, the remainder being difunctional.

A series of gumstocks have been prepared from pure difunctional HT-Telagen using three different isocyanate cure systems. Mechanical properties of the pure difunctional gumstock have been compared to gumstocks prepared from HT-Telagen "as received". Mechanical property measurements were made at three temperatures: -65°F, 75° and 180°F.

Gumstocks prepared from pure difunctional HT-Telagen exhibit higher maximum stress levels than those prepared from "as received" HT-Telagen. All three cure systems show the same directional effect. The difference in maximum stress level for the "difunctional" and "as received" gumstocks is most pronounced for the TDI/TPMT cure system. Because of the higher maximum stress level of gumstocks prepared from pure difunctional prepolymer the crosslinker level can be significantly reduced to 10% equivalent triisocyanate or even below.

At comparable triisocyanate levels the pure "difunctional" gumstock exhibits lower maximum strain levels than gumstocks prepared from "as received" HT-Telagen. Because of the monofunctional prepolymer content of the "as received" HT-Telagen the latter gumstock will exhibit lower crosslink density and hence higher strain levels than the pure difunctional gumstock at identical triisocyanate levels.

Gumstocks prepared from the difunctional prepolymer also exhibit significantly higher initial moduli. The gumstock employing a total aromatic cure system (TDI/TPMT) shows the most dramatic effect. The difference in initial moduli between the "difunctional" gumstock and "as received" gumstock diminishes as the temperature is decreased. To obtain low initial moduli in gumstocks prepared from difunctional prepolymer the triisocyanate level should be below 10 equivalent percent.

At comparable triisocyanate levels the pure difunctional gumstock exhibits consistently significantly higher Shore "A" hardness than the "as received" gumstock. The differences in Shore "A" hardness are most pronounced for the TDI/TTI cured gumstocks. The aromatic diisocyanate (TDI) also results in higher hardness than cure systems employing aliphatic diisocyanates.

Monofunctional prepolymer was added to the difunctional prepolymer in increments of 4.9, 9, 18 and 27 mole % to arrive at a quantitative correlation of the effect of monofunctional prepolymer components on gumstock properties. Two cure systems were employed representing an aromatic diisocyanate (TDI) and an aliphatic diisocyanate (DDI) chain extender. In each curative system a triisocyanate crosslinker was used. The di-/triisocyanate ratio was kept constant at 9/1. The addition of monofunctional prepolymer to the difunctional prepolymer reduces the maximum stress level, the initial modulus and the Shore "A" hardness but increases the strain at maximum stress of the cured gumstock.

The percentage decrease in maximum stress level is similar at all three temperatures. The decrease in maximum stress and initial modulus upon addition of the first 5 to 10 mole % monofunctional polymer is more severe for the aliphatic diisocyanate (DDI) chain-extended gumstock.

The Shore "A" hardness shows an essentially linear decrease with increase in monofunctional prepolymer content.

IV. TECHNICAL PROGRESS

A total of eight different prepolymers were characterized with respect to functionality and functionality distribution. All are low molecular weight, liquid polybutadienes. They differ, however, in several respects:

- Different methods of polymerization are employed. The Telagen series, manufactured by General Tire and Rubber Company, uses an anionic polymerization process, whereas Sinclair's Poly B-D prepolymers are prepared by a free radical process. This difference in the method of polymerization results in:

    a. different microstructures and

    b. most significantly in different functionality distributions.

- The anionic process permits some control over the degree of 1,4 and 1,2-addition. The free radical process, however, gives consistently 80% 1,4-addition (60% trans-1,4 and 20% cis-1,4) and 20% 1,2-addition (vinyl groups). This difference in microstructure, however, is not explored on this program. Our objective was to quantitatively determine the functionality distribution of these prepolymers, a parameter which is of particular importance from the standpoint of mechanical properties of the cured gumstock.

- The Telagen prepolymer series is generally composed of non,- mono- and difunctional prepolymer, whereas the Sinclair Poly B-D series comprises di- and trifunctional components.

In addition to this difference in microstructure and functionality distribution, the following differences are reflected by these prepolymers:

- The type of functional group (OH vs COOH)

- Saturated (hydrogenated) vs unsaturated prepolymer (Telagen vs Telagen-S)

- There are also some differences in the molecular weights of these prepolymers.

The saturated Telagen has a lower molecular weight (nominal 2000) than the unsaturated Telagen (nominal 5000). The choice of a lower molecular weight, saturated prepolymer reflects the increased viscosity of the saturated backbone.

In sections A through E the results of functionality and functionality distribution measurements on eight prepolymers are summarized.

Section F discusses the mechanical properties of gumstocks prepared from a pure difunctional HO-polybutadiene and compares these properties with gumstocks prepared from "as received" HT-Telagen. The effect of monofunctional prepolymer content on mechanical properties was explored in detail.

A. Functionality and Functionality Distribution Measurements of Sinclair's POLY B-D Prepolymers

Sinclair's Poly B-D prepolymer series are low molecular weight, liquid butadiene homopolymers or copolymers of butadiene and styrene or acrylonitrile. The two hydroxy-functional homopolymers which are of interest as propellant binders are designated R-45M and R-15M. The R-15M has a somewhat higher molecular weight than the R-45M. The current price per pound (in drum quantities) is 48¢ for the R-15M and 54¢ for the R-45M. These prepolymers have consistently been reported to have overall functionalities substantially in excess of 2.0. In the following sections functionality and functionality distribution measurements of different polymer batches are discussed.

1. Sinclair's R-45M

Three different lots (704211, 805101 and 805201) of the R-45M prepolymer have been characterized with respect to functionality and functionality distribution.

1.1. Functionality Determination

Functionalities were calculated from number average molecular weight measurements and equivalent weight measurements:

$$f = \frac{\text{Number Average Molecular Weight}}{\text{Equivalent Weight}}$$

Number average molecular weights were obtained by VPO in chloroform at 37°C. All measurements were extrapolated to zero concentration to obtain $(\bar{M}n)_o$. The concentration dependence of molecular weight for the three lots of R-45M are shown in Figures 1 through 3. They show a significant negative concentration dependence, the apparent molecular weight increasing with decrease in polymer concentration. The extrapolated molecular weights are summarized in Table I.

TABLE I

SUMMARY OF FUNCTIONALITY MEASUREMENTS OF THREE LOTS OF R-45M

Lot No.	$(\bar{M}n)_o$	Equivalent Weight (Grams of Polymer/Mole of OH)	Functionality
704211	2740	1190	2.30
805101	2800	1130	2.48
805201	2900	1220	2.38

The equivalent weights were determined by reacting the polymer with p-toluenesulfonyl isocyanate in dilute chloroform solution. The reaction is monitored by infrared. Details of this analytical method have been described in AFRPL-TR-68-237 (1). The results of the equivalent

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(1) Functionality Determination of Binder Prepolymers, Final Report, October 66–September 68, A. H. Muenker and B. E. Hudson, Esso Research and Engineering Co.

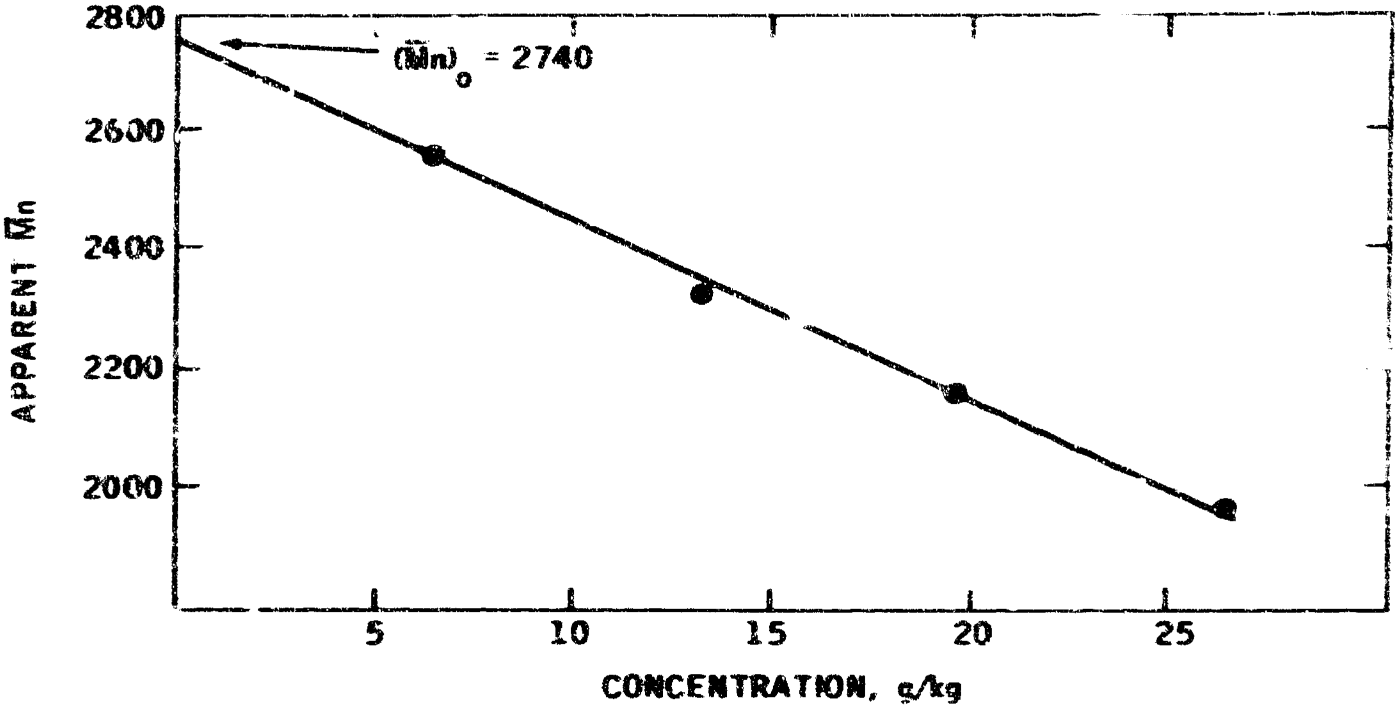


Figure 1. Concentration dependence of number average molecular weight for Poly B-D, R-45M, lot 704211, in chloroform at 37°C by VPO.

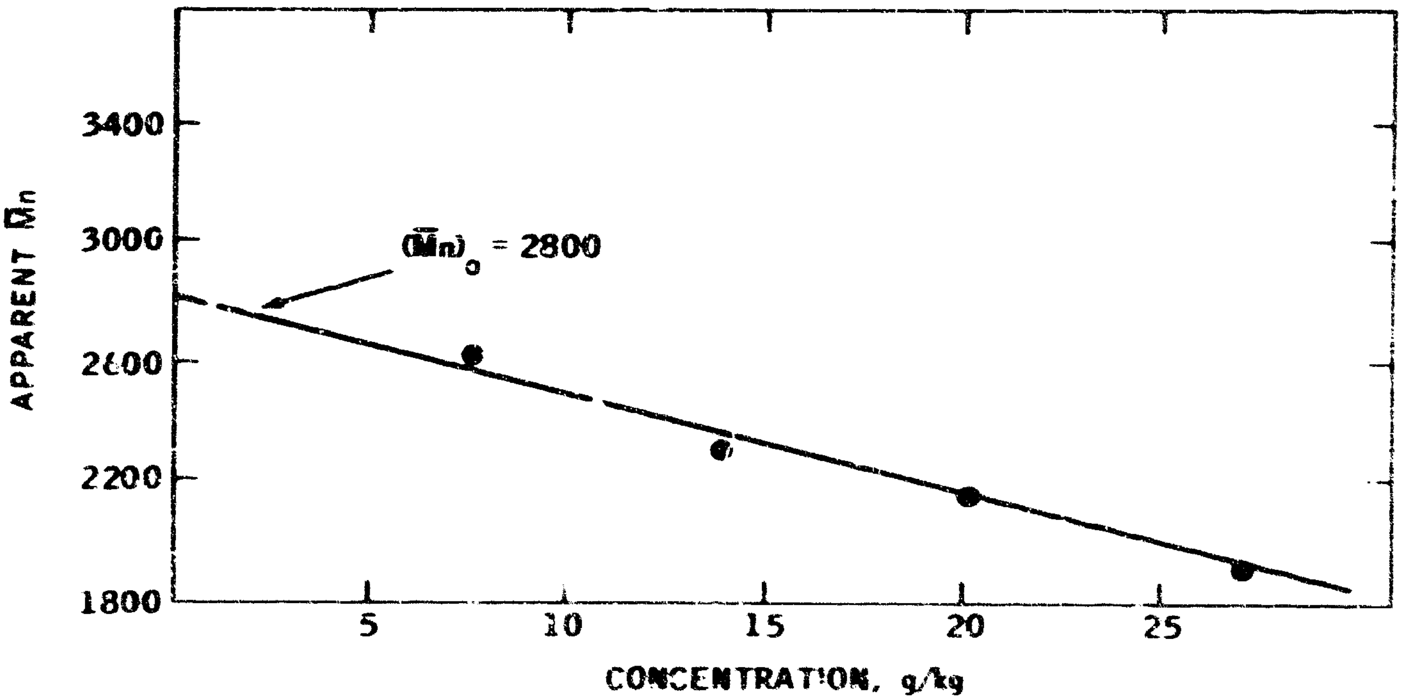


Figure 2. Concentration dependence of number average molecular weight for Poly B-D, R-45M, lot 805101, in chloroform at 37°C by VPO.

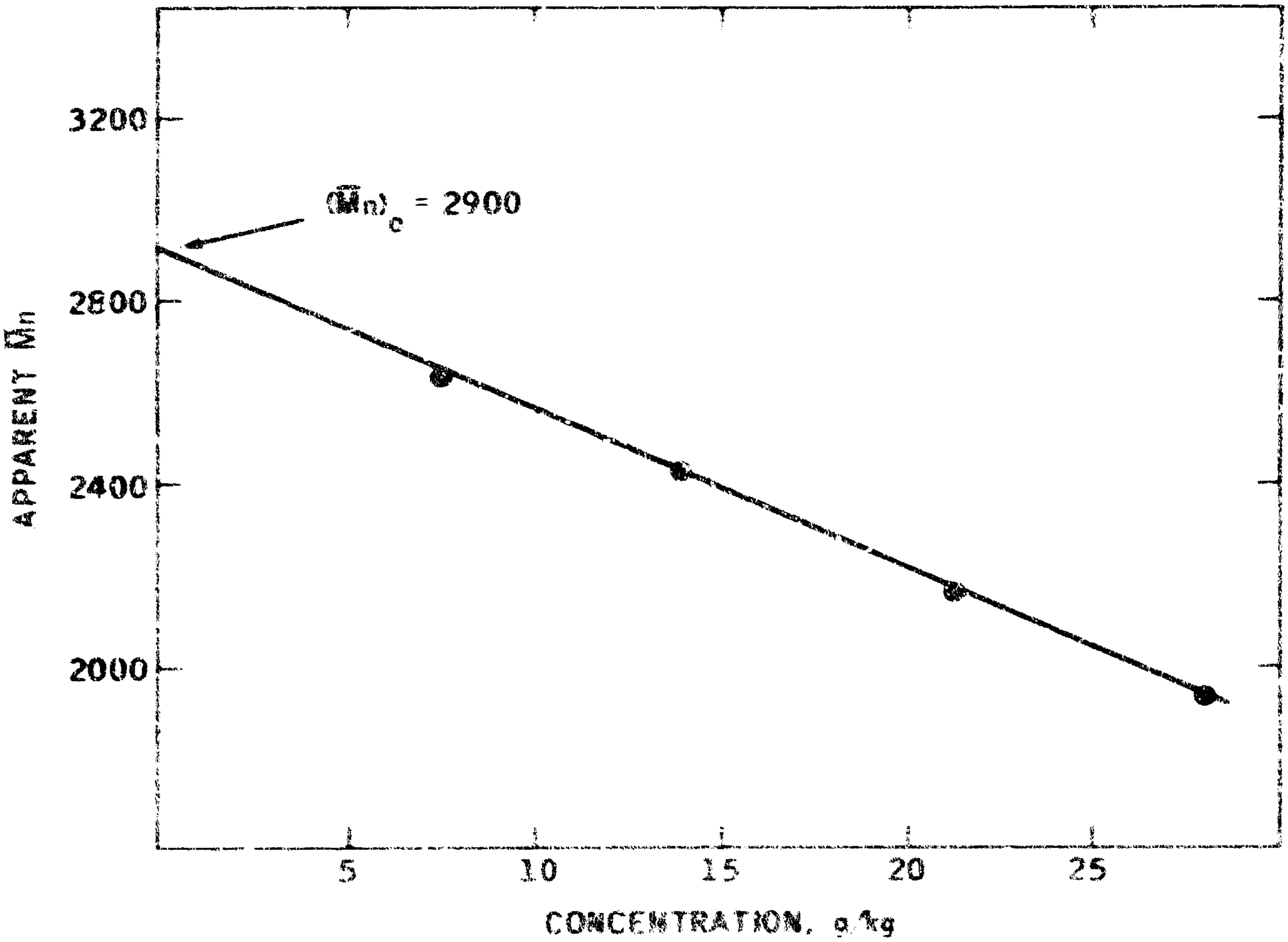


Figure 1 Concentration dependence of number average molecular weight for Poly B-D, R-45M lot 805201, in chloroform at 37°C by VPO.

weight measurements and the functionalities based on molecular weight and equivalent weight measurements are summarized in Table I.

These functionalities for three lots of R-45M are substantially in excess of 2.0. In view of this high average functionality (2.30 to 2.48) the R-45M prepolymer should contain significant quantities of polymer components having functionalities greater than two. Subsequent functionality distribution measurements have confirmed this.

1.2. Functionality Distribution Measurements

Functionality distribution measurements were made on all three lots to determine whether there were significant differences in the distribution pattern. We had previously demonstrated (1) that the R-45M contains no measureable quantities of non- and monofunctional prepolymer components. Our objective was therefore to separate the prepolymer into pure difunctional and polyfunctional components.

a. Lot 704211

The solvent schedule that was found to be particularly effective in separating R-45M by functionality was 100% CH_2Cl_2 followed by solvent mixtures of CH_2Cl_2 and CH_3CN.

Methylene chloride was used as the initial solvent instead of carbon tetrachloride which we have generally used for other prepolymers. Methylene chloride affords greater ease of desorption of the prepolymer. As shown in Figure 4, a fraction accounting for 42% was immediately eluted in response to methylene chloride. Based on the shape of the elution profile we recombined the individual cuts into four major fractions for subsequent analysis. The concentration dependence of molecular weight of the four fractions is shown in Figure 5. Analyses of these fractions are summarized below:

Identification: 447-64
Silica gel/polymer ratio: 87/1
Polymer charged to column: 1.137g
Total polymer recovery: 95.0

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\bar{M}n)c$	Functionality
I	42.2	1930	4000	2.07
II	19.1	790	2400	3.04
III	25.4	730	2150	2.95
IV	8.3	530	1760	3.32
	95.0%			

Functionality data on the individual fractions show that fractionation by functionality has taken place. The prepolymer is clearly composed of di- and trifunctional polymer. About 42 wt % is difunctional, at least 45% is trifunctional, the remainder being trifunctional or tetrafunctional.

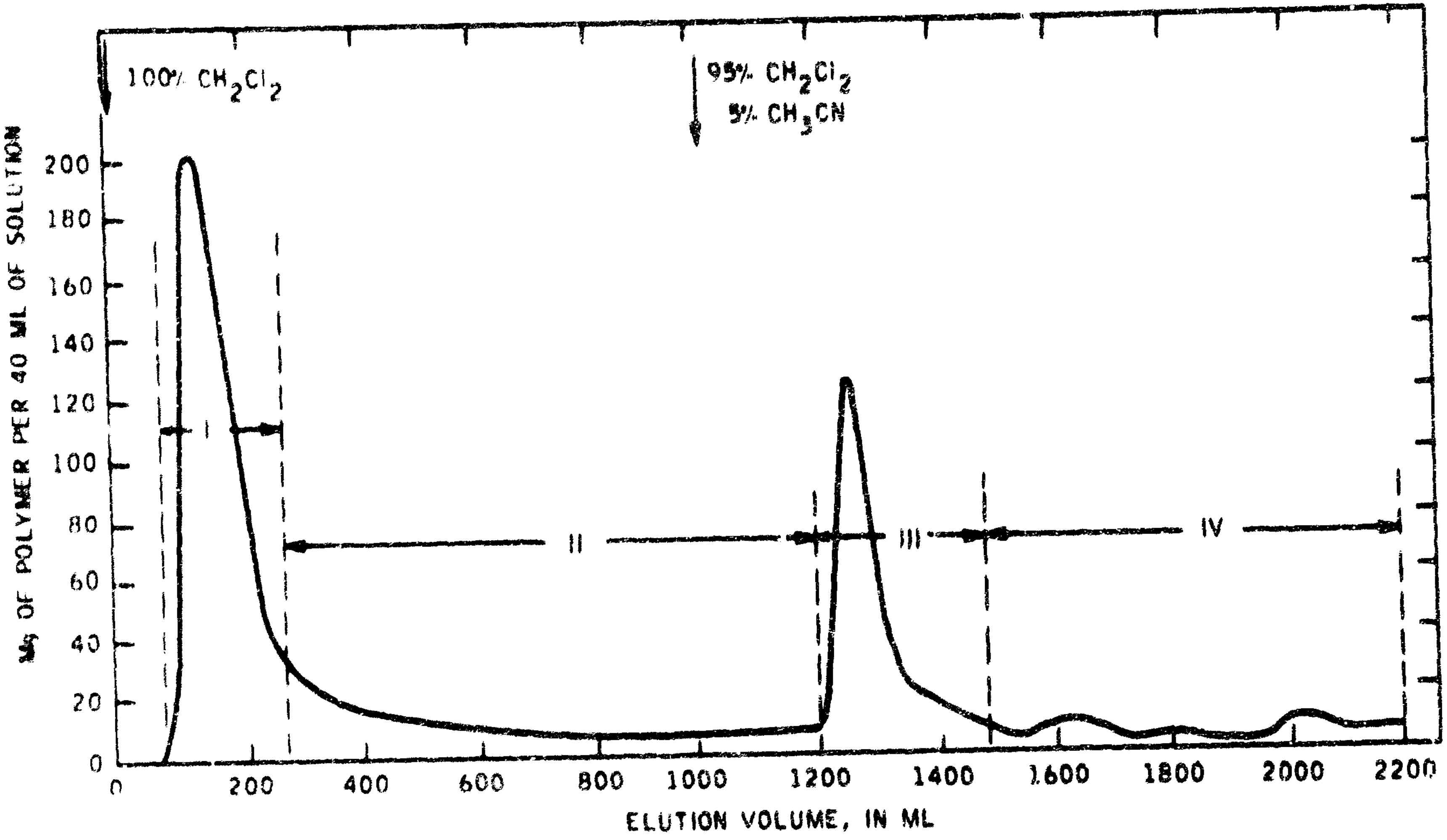


Figure 4. Elution Profile for Poly B-D, R-45M, Lot 704211. Stepwise elution from silica gel.

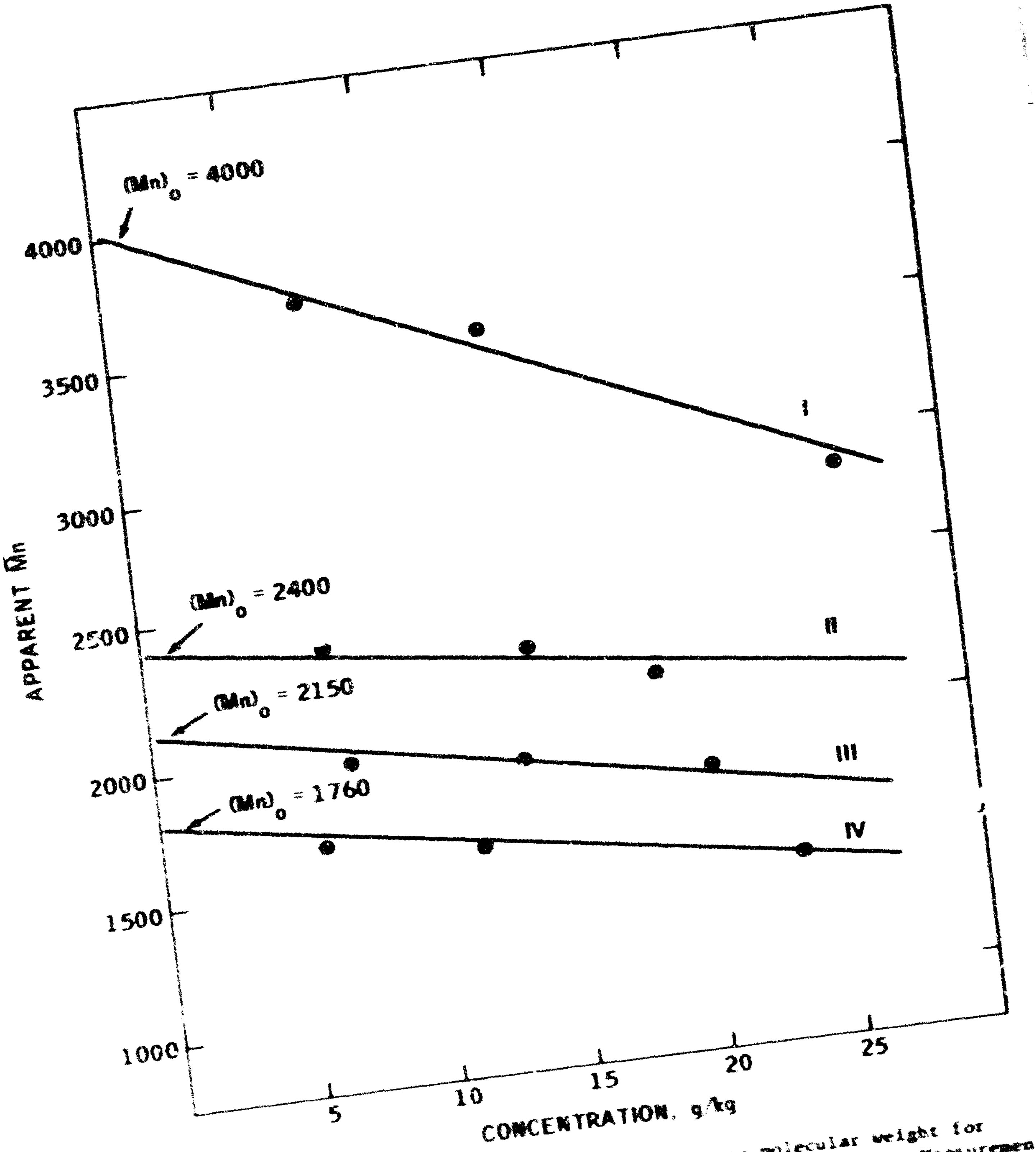


Figure 5. Concentration dependence of number average molecular weight for fractions I through IV of Sinclair's R-45M, lot 704211. Measurements were made by VPO in chloroform at 37°C.

Analysis of Fraction IV has raised the possibility that this prepolymer contains tetrafunctional components. The interesting finding is that functionality is a function of molecular weight, the low molecular weight components being trifunctional and the higher molecular weight fraction being difunctional.

Lots 805101 and 805201 were subsequently fractionated to determine the variation in functionality distribution among different batches.

b. Lot 805101

The solvent schedule was similar to that used for lot 704211 (100% CH_2Cl_2 followed by a solvent mixture of 95% CH_2Cl_2 and 5% CH_3CN). However, the profile was shortened by switching to the 95/5 CH_2Cl_2/CH_3CN mixture earlier in the elution schedule.

The resulting elution profile is shown in Figure 6. The individual cuts were recombined into four major fractions. During the recombination of Fractions I and II and subsequent stripping at 40°C we observed that these polymer fractions became insoluble. Apparently, oxidative crosslinking took place making the polymer insoluble. Therefore, no analyses could be obtained on Fractions I and II. Fractions III and IV did not show evidence of crosslinking and were therefore analyzed. Analyses of these fractions are summarized below:

Identification: 447-82
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.18 g
Total polymer recovery: 95.4%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\overline{M}_n)_o$	Functionality
I	37.2		*	
II	10.0		*	
III	37.9	860	2600	3.02
IV	10.3	570	1780	3.12
	95.4%			

---

*Samples had become insoluble due to oxidative crosslinking.

Analyses of Fractions III and IV showed that these fractions are trifunctional. Based on functionality distribution measurements of the previous lot of R-45M (lot 740211) and the similarity between the two profiles it can be assumed that Fraction I is difunctional and Fraction II is trifunctional. We therefore assign the following functionality distribution to lot 805101:

- 37% difunctional
- 58% trifunctional
- remainder (5%) trifunctional or above

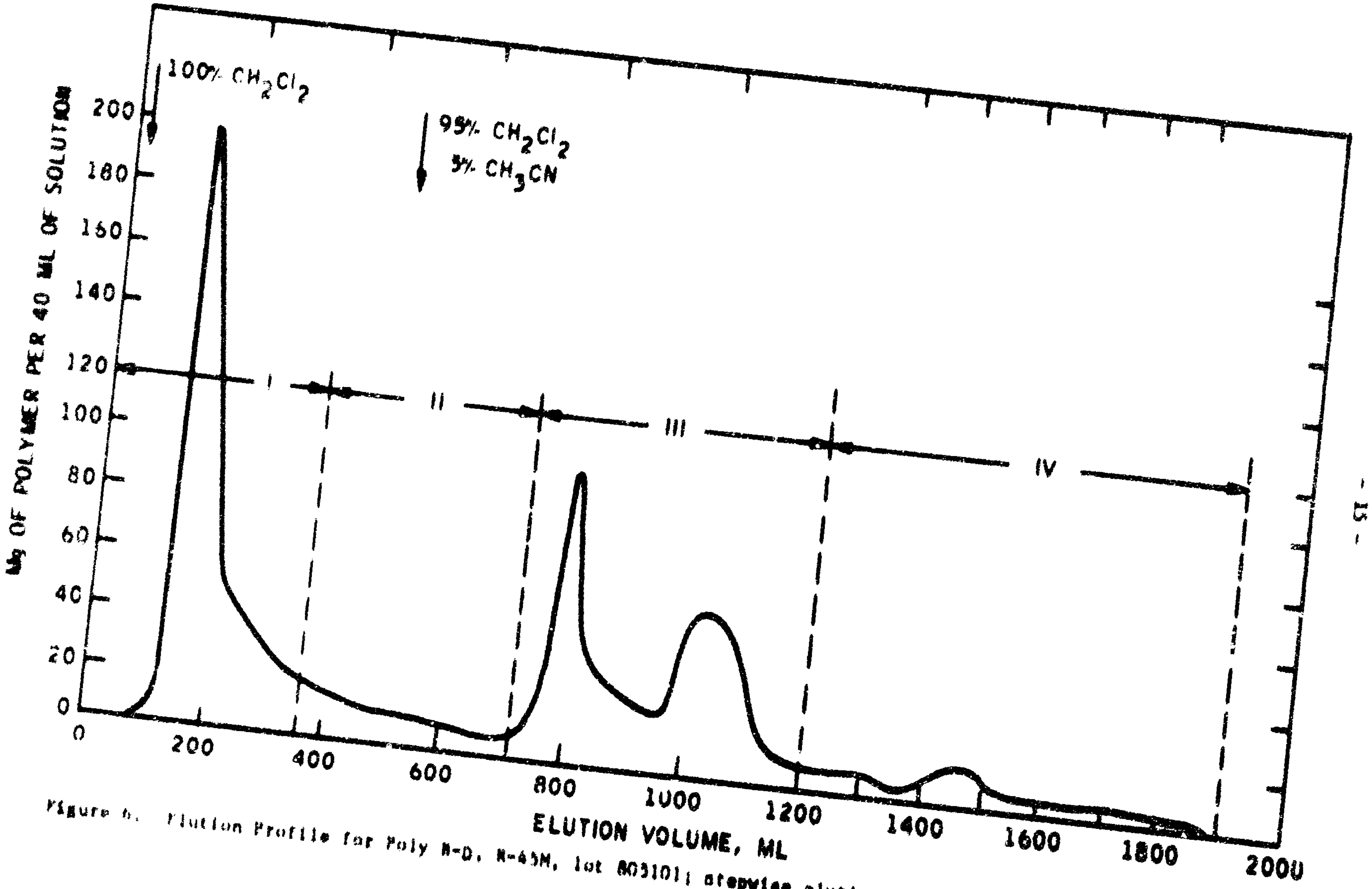


Figure 6. Elution Profile for Poly B-D, R-45M, lot 803101; stepwise elution from silica gel.

c. Lot 805201

The solvent schedule was again the same employed for lots 704211 and 805131 except for increasing the CH_3CN content to 20%. Increasing the CH_3CN solvent content did not, however, speed up the elution of the trifunctional polymer. The elution profile is shown in Figure 7. The individual cuts were recombined into three major fractions. Oxidative crosslinking again prevented the analysis of Fraction II. Based on elution profiles of previously analyzed R-45M samples this fraction is believed to be trifunctional. Analyses are summarized below:

Identification: 447-108
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.20 g
Total polymer recovery: 92.8%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\bar{M}_n)_o$	Functionality
I	43.0	2005	4100	2.04
II	7.4		*	
III	42.4	720	2100	2.92
	92.8%			

---

*Sample had become insoluble due to oxidative crosslinking before analyses could be obtained.

Lot 805201 therefore contains approximately 43% difunctional polymer of $(\bar{M}_n)_o = 4100$, the remainder being trifunctional, having a molecular weight of about 2100.

A comparison of functionality distribution measurements of three lots of R-45M shows that the difunctional content is approximately 40 to 45% with a nominal molecular weight of 4000, the remainder being trifunctional with a nominal molecular weight of 2000. All three lots have consistently shown this dependence of functionality on molecular weight.

On a molar basis, the functionality distribution of the R-45M prepolymer reflects an even higher triol content:

Functionality Distribution of R-45M on a Molar Basis:

Diol: 25 Mole %

Triol: 75 Mole %

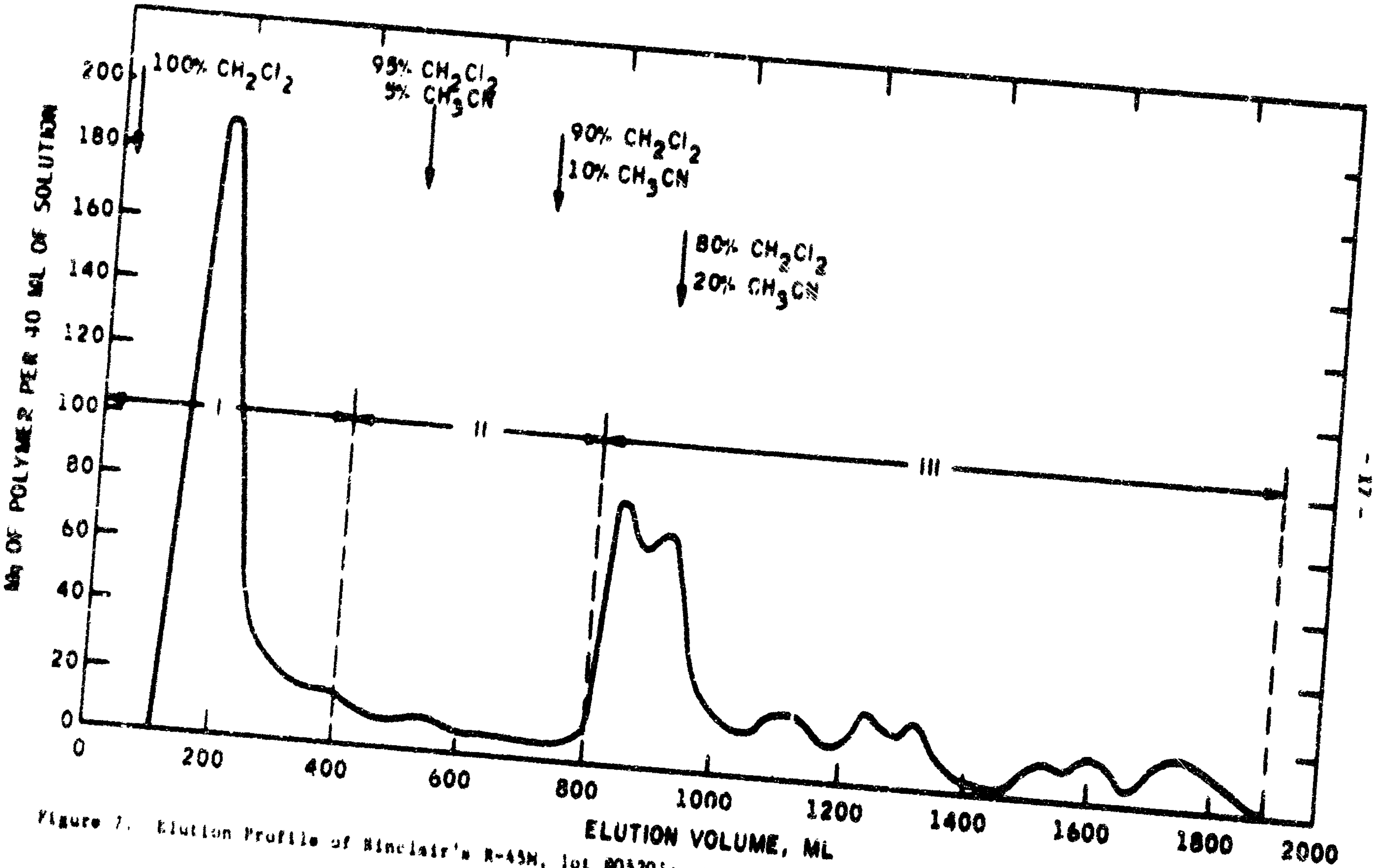


Figure 7. Elution Profile of Sinclair's R-45M, lot 803201; stepwise elution from silica gel.

1.3. Effect of Silica Gel/Polymer Ratio on Separation Efficiency

The two major parameters which largely control the fractionation efficiency of prepolymers into their functional components are (1) the silica gel/polymer ratio, and (2) the desorbing power of the eluting solvent. We have explored the effect of the silica gel/polymer ratio in the case of the R-45M prepolymer. The ratio was varied from 10/1 to 100/1 using 100% CH_2Cl_2 as the eluting solvent. As the criterion of fractionation efficiency, we chose the wt % of the prepolymer eluted after a total elution volume of 400 ml. This fraction generally accounts for 42-43 wt % for this particular batch of R-45M if separation between di- and trifunctional prepolymer has been achieved. If this fraction is greater than 43%, then trifunctional prepolymer has been eluted together with the difunctional prepolymer. Figure 8 shows the wt % of this first fraction as a function of silica gel/polymer ratio.

It is apparent that at a silica gel/polymer ratio somewhat less than 40/1, separation is incomplete and trifunctional polymer is eluted together with the difunctional prepolymer. The minimum silica gel/polymer ratio required for fractionation of R-45M into its functional components using CH_2Cl_2 as the eluting solvent is therefore about 40/1. It should be realized, though, that the optimum ratio is a function of the solvent schedule and the prepolymer.

2. Sinclair's R-15M

To determine whether there is a substantial difference between R-45M and R-15M, a sample of R-15M, lot 707203, was also characterized.

2.1. Functionality Determination

Based on number average molecular weight measurements by VPO and equivalent weight measurements based on the reaction of the prepolymer with p-toluenesulfonyl isocyanate the following functionality was calculated:

$$f = \frac{(Mn)o}{Eq.\ Wt} = \frac{3420}{1380} = 2.48$$

This functionality is identical to lot [illegible]1, of the R-45M prepolymer. There is a significant, but not dramatic difference in molecular weight between the R-15M (3400) and the R-45M (2800).

2.2. Functionality Distribution Measurements

The elution schedule was identical to the one used for the R-45M prepolymer. The resulting elution profile is shown in Figure 9. Oxidative crosslinking was again in evidence when the individual cuts comprising Fraction I were combined and stripped under vacuum at 40°C and subsequently exposed to air. The initial part of the profile (see dotted line of Fraction I, Figure 9) was therefore repeated. Fraction I of the repeat fractionation accounts for 44.0 wt % of the total polymer as compared to 47.6% of the initial fractionation.

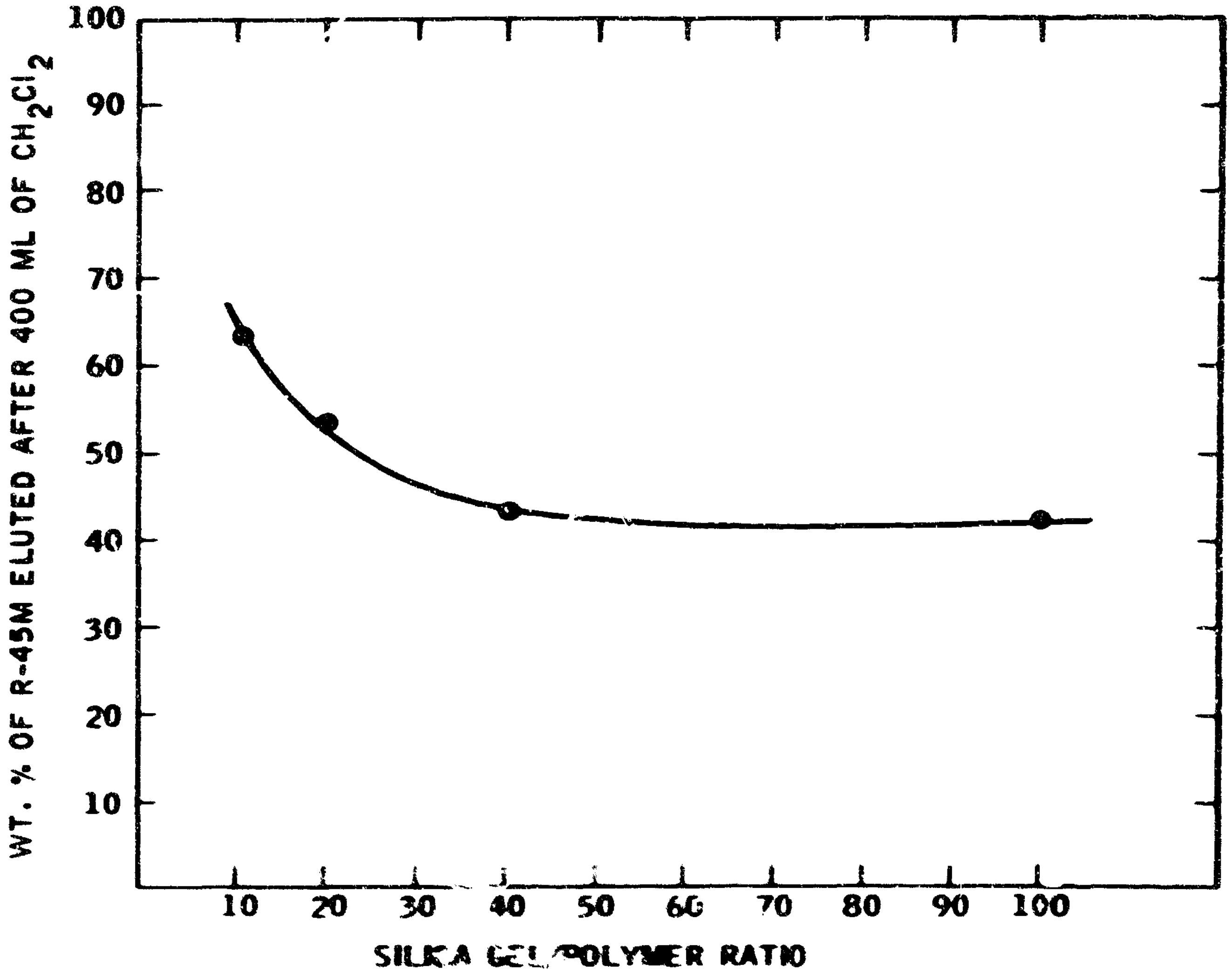


Figure 8. DEPENDENCE OF THE WT. % OF R-45M, LOT 805201, ELUTED WITH 400 ML OF CH_2Cl_2 AS A FUNCTION OF THE SILICA GEL/POLYMER RATIO.

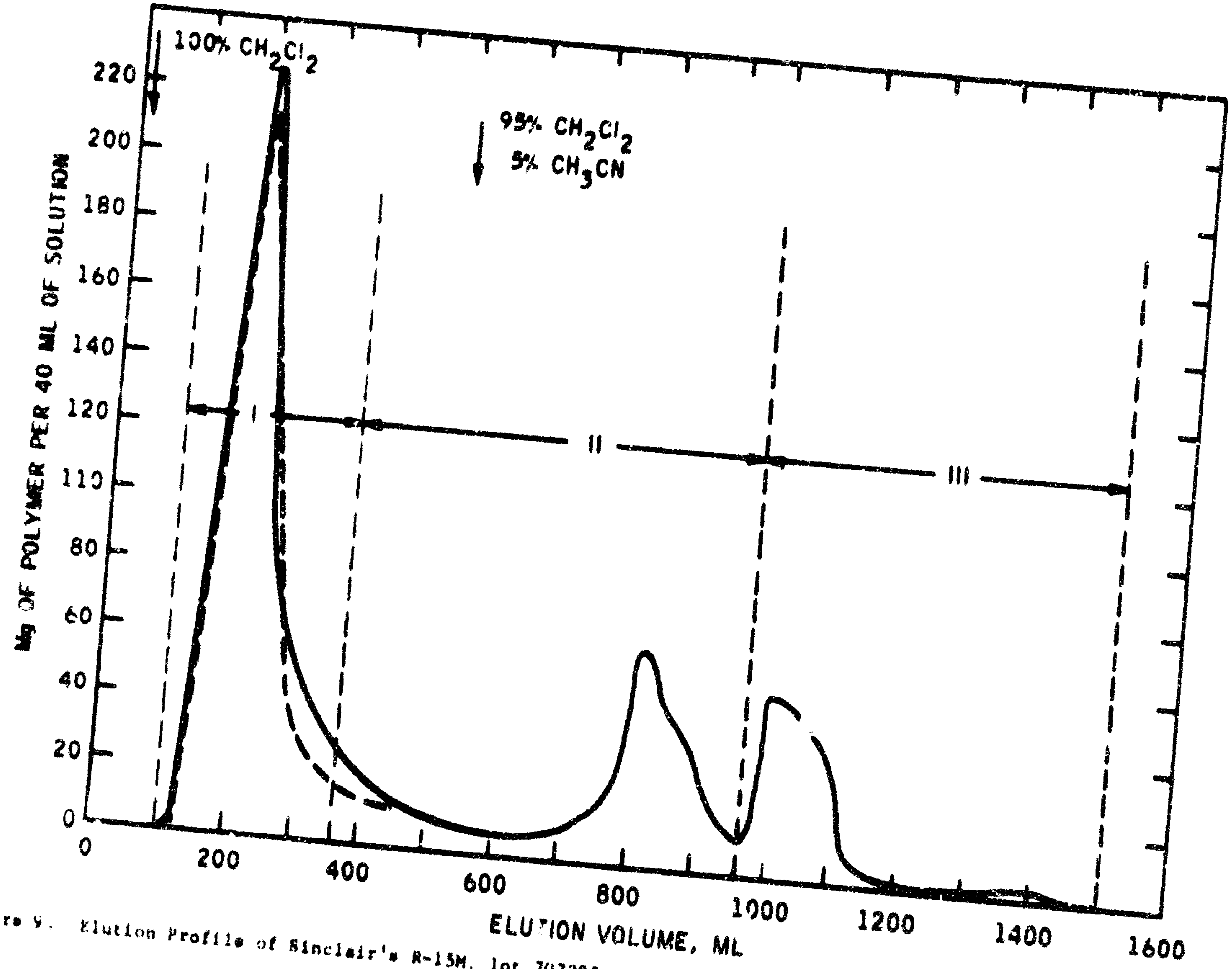


Figure 9. Elution Profile of Sinclair's R-15M, lot 707203; stepwise elution from silica gel.

Analysis of Fraction I showed that this fraction was difunctional as had been expected. Fractions II and III were found to be trifunctional.

Complete analyses are given below:

Identification: 447-90 and 447-112
Silica gel/polymer ratio: 100/1
Polymer charged to column: 1.20 g
Total polymer recovery: 86.5%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole of OH)	$(\bar{M}n)_o$	Functionality
I	47.6	————————	*	————————
	44.0**	2750	5700	2.07
II	24.1	810	2450	3.02
III	14.8	716	2180	3.04

---

* This fraction could not be analyzed because of oxidative crosslinking

** Repeat of initial segment of profile

Based on the above data we can conclude that about 45% of this prepolymer is difunctional, about 40 wt % is trifunctional and the remaining prepolymer (15%) which could not be desorbed is also presumed to be trifunctional.

A comparison of the functinality distribution of the R-45M and the R-15M prepolymers shows that trifunctional prepolymer is the major component (morethan 50%) in both prepolymers. The R-15M appears to have a slightly higher difunctional content than the R-45M. This apparently slight difference in difunctional polymer content may further diminish upon analysis of additional lots of R-15M.

B. Functionality and Functionality Distribution Measurements of General Tire's OH-TELAGEN Prepolymers

Samples of the low molecular weight, hydrogenated, OH-Telagen-S, had previously been characterized (1) and found to contain non-, mono- and difunctional prepolymer. We have analyzed one additional lot of OH-Telagen-S which is being used in a program on the evaluation of curing agents. A sample of the higher molecular weight, unsaturated OH-Telagen, has also been analyzed for the first time on this program. Fractionation of this prepolymer was scaled-up to provide sufficient quantities of pure mono- and difunctional material for evaluation of mechanical properties of cured gumstocks.

1. OH-TELAGEN-S (Nominal Mn=2000), Lot [illegible]-JAM [illegible]38h

This lot of OH-Telagen-S was purchased from General Tire and Rubber Company for use on Contract F04611-68-C-[illegible], "Synthesis and Evaluation of Curing Agents."

1.1. Functionality Determination

Equivalent weight measurements were made by reaction of the prepolymer with p-toluene sulfonyl isocyanate. The following results were obtained:

Equivalent Weight (Grams mole of OH)
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

Average [illegible] g mole of OH

Number average molecular weight [illegible] see Figure [illegible]. The [illegible] molecular weight [illegible] Based on these measurements [illegible]

[illegible]

[illegible]

[illegible]

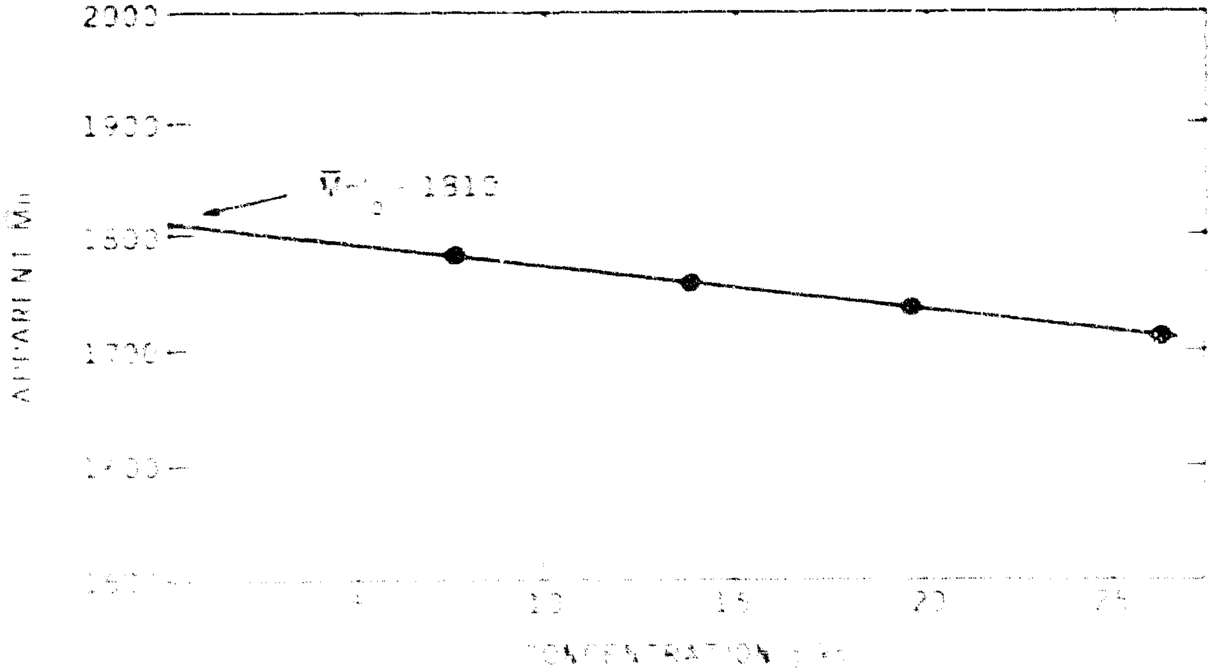
Identification: 447-84
Silica gel polymer ratio: 79:1
Total polymer charged: 1.27 g
Total polymer recovery: 92.6%

Fraction	Wt % Total	Equivalent Weight (Grams/mole of OH)	$(\overline{M}n)c$	Functionality
I	17.9	4525	2340	0.52
II	6.0	1730	1760	1.02
III	30.8	1010	2010	1.99
IV	37.9	770	1580	2.05
	92.6%			

Fraction I and II comprise non- and monofunctional components. They account for about 24% of the total prepolymer. The remainder (fractions III and IV) is difunctional. Fraction I is apparently a 50:50 mixture of non- and monofunctional polymer. The functionality distribution of this lot of OH-Telagen-S is therefore as follows:

- 9% nonfunctional
- 15% monofunctional
- remainder difunctional

Similar functionality distributions were found for previously analyzed lots of OH-Telagen-S.



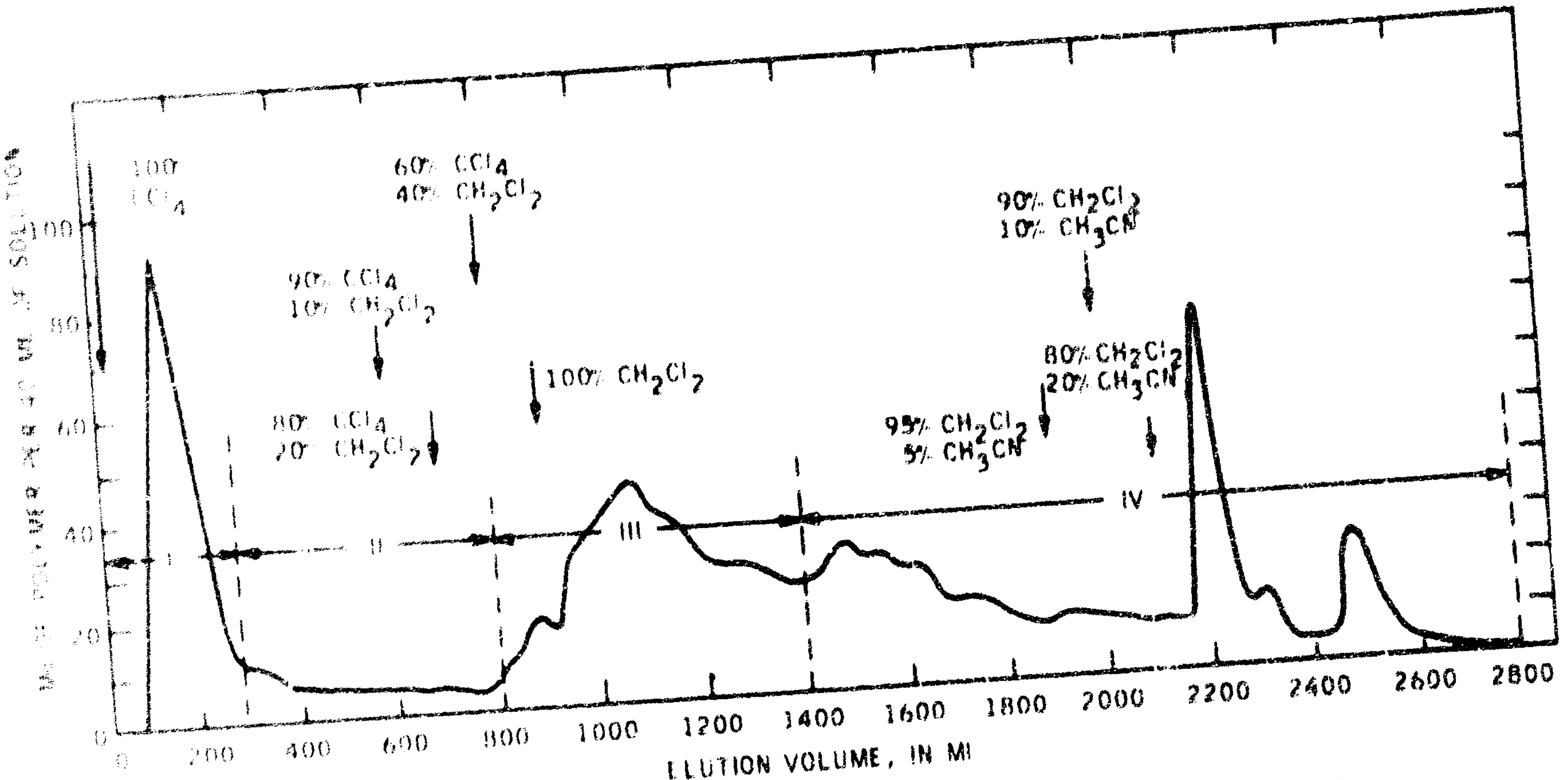


Figure [illegible]. Elution Profile for OH Telagen S, lot 242 AM 273 BH; stepwise elution from silica gel.

2. OH-TELAGEN (Nominal Mn=5000), Lot 241 AM 292/316 AM6

This lot of OH-Telagen (nominal molecular weight 5000) was purchased from General Tire and Rubber Company for use on both Contracts F04611-69-C-0046 and F04611-68-C-0045. This polymer is the first unsaturated, hydroxyfunctional prepolymer of the Telagen series of 5000 nominal molecular weight that we have tried to fractionate by functionality. Fractionation of this prepolymer was scaled-up for evaluation of mechanical properties of a gumstock prepared from a pure difunctional hydroxy-terminated polybutadiene prepolymer.

2.1. Functionality Determination

Number average molecular weights were determined in chloroform at 37°C (see Figure 12), yielding an extrapolated molecular weight by VPO of $(\bar{M}_n)_o = 4260$.

Equivalent weight measurements based on the reaction of the prepolymer with p-toluene sulfonyl isocyanate are as follows:

Equivalent Weight (Grams mole of OH)
3064
3015
3024

Average: 3034 g mole of OH

Based on these measurements, the calculated functionality is:

$$f = \frac{4260}{3034} = 1.40$$

This calculated overall-functionality suggests the presence of very substantial quantities of non- and monofunctional components.

2.2. Functionality Distribution Measurements

This OH-Telagen prepolymer differs from previously characterized prepolymers of the OH-Telagen-S series in both molecular weight (4300 vs [illegible]) and unsaturation (OH-Telagen-S is the hydrogenated analogue of OH-Telagen). The OH-Telagen prepolymer also differs from Sinclair's R-45M, another hydroxy-functional polybutadiene. OH-Telagen is reportedly a mixture of non-, mono- and difunctional polymer whereas R-45M has been shown to be composed of di- and trifunctional prepolymer.

The first series of experiments were concerned with the development of an optimum solvent schedule for fractionation of the polymer by stepwise elution from silica gel. Also the minimum silica gel polymer ratio required to achieve satisfactory separation of non-, mono- and difunctional prepolymer must be defined. [illegible]

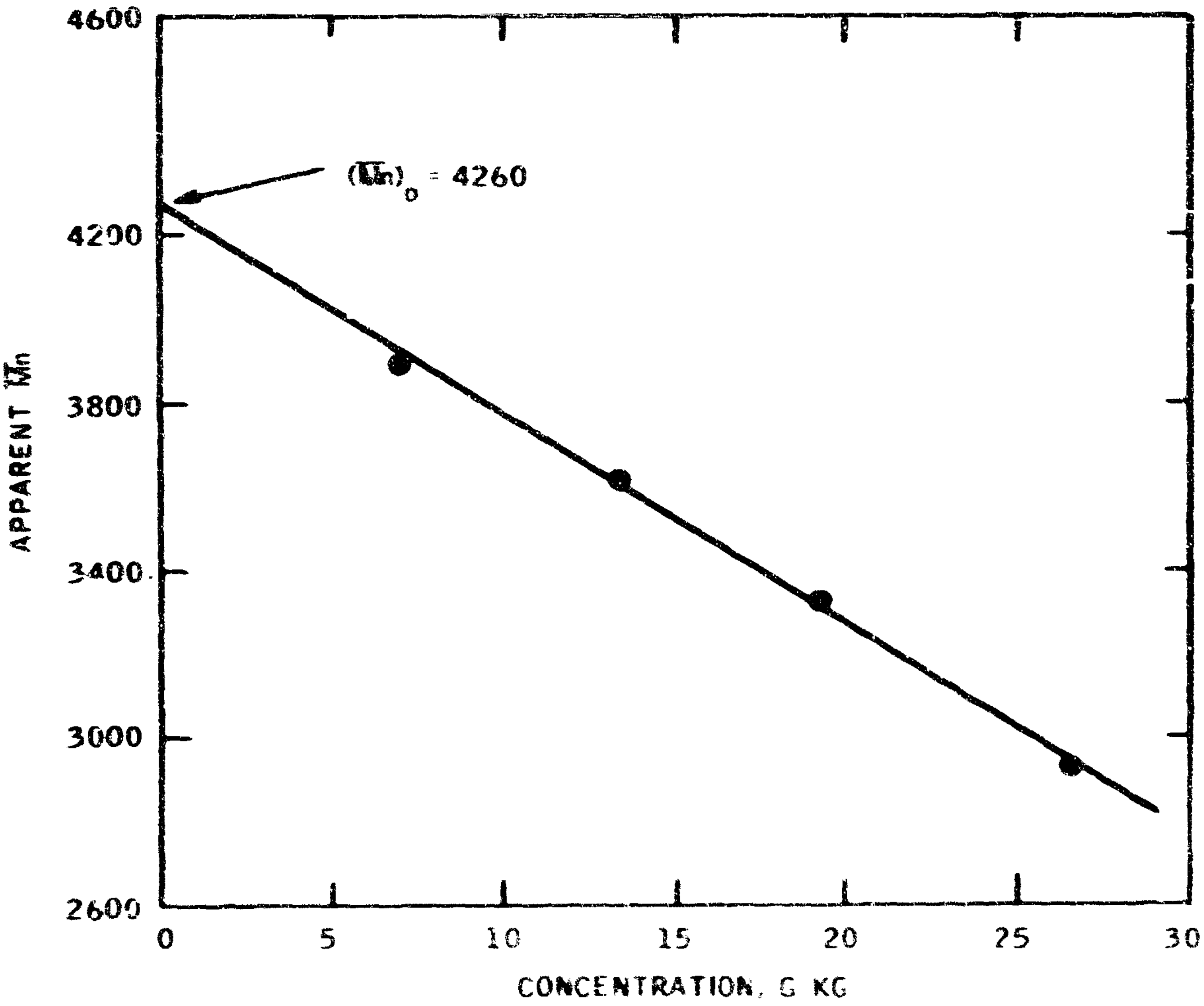


Figure 11- Concentration dependence of number average molecular weight by VPO for OH-Telagen, lot [illegible] AM 293 [illegible] AM, in chloroform at [illegible]°C.

The first fractionation study was carried out at a silica gel/polymer ratio of 95/1 using CCl_4 and mixtures of CCl_4 and $CHCl_3$ of progressively higher $CHCl_3$ content. The resulting elution profile is shown in Figure 13. It is apparent from this profile that no significant amount of polymer was eluted from the column in response to CCl_4. The first significant elution (fraction II) was in response to mixtures of $CCl_4/CHCl_3$ and/or 100% $CHCl_3$. Fraction II was followed immediately by the major fraction (major peak of fraction III) in response to 100% $CHCl_3$. The fractionation was terminated after 83.6% of the polymer had been recovered. Analyses of the fractions shows some separation by functionality. Fraction III apparently contained some monofunctional material in addition to the difunctional polymer.

Identification: 447-116
Silica gel/polymer ratio: 95/1
Total polymer charged: 1.372g
Total polymer recovery: 83.6%

Fraction	Wt % Total	Equivalent Weight (Grams/mole of OH)	$(\overline{M}n)_o$	Functionality
I	0.4	———	* ———	———
II	16.4	6000	4800	0.80
III	66.8	2600	4540	1.75
	83.6			

---

* Analysis could not be obtained because of small sample size.

The profile indicated that CCl_4 lacked sufficient desorbing action whereas $CHCl_3$ was too strong a desorbing agent to permit separation by functionality. To confirm the strong desorbing power of $CHCl_3$, a fractionation study was carried out using only $CHCl_3$ as the eluting solvent. The resulting profile is depicted in Figure 14. The profile very clearly demonstrates the desorbing action of $CHCl_3$ and the lack of separation of the polymer into distinct peaks. Elution from the column was terminated after 81.2% recovery.

Specific conditions are summarized below.

Identification: 447-12[illegible]
Silica gel/polymer ratio: 100/1
Total polymer charged: 0.956g
Total polymer recovery: 81.2%

No analyses were carried out.

On the basis of these two experiments, it was concluded that CCl_4 should be used as the initial solvent to allow adsorption of the polymer on the silica gel. It was further noted that a suitable mixture of CCl_4 and $CHCl_3$ should give adequate separation of the polymer by functionality. It was also apparent that the silica gel/polymer ratio could be significantly reduced from the current level of 100/1.

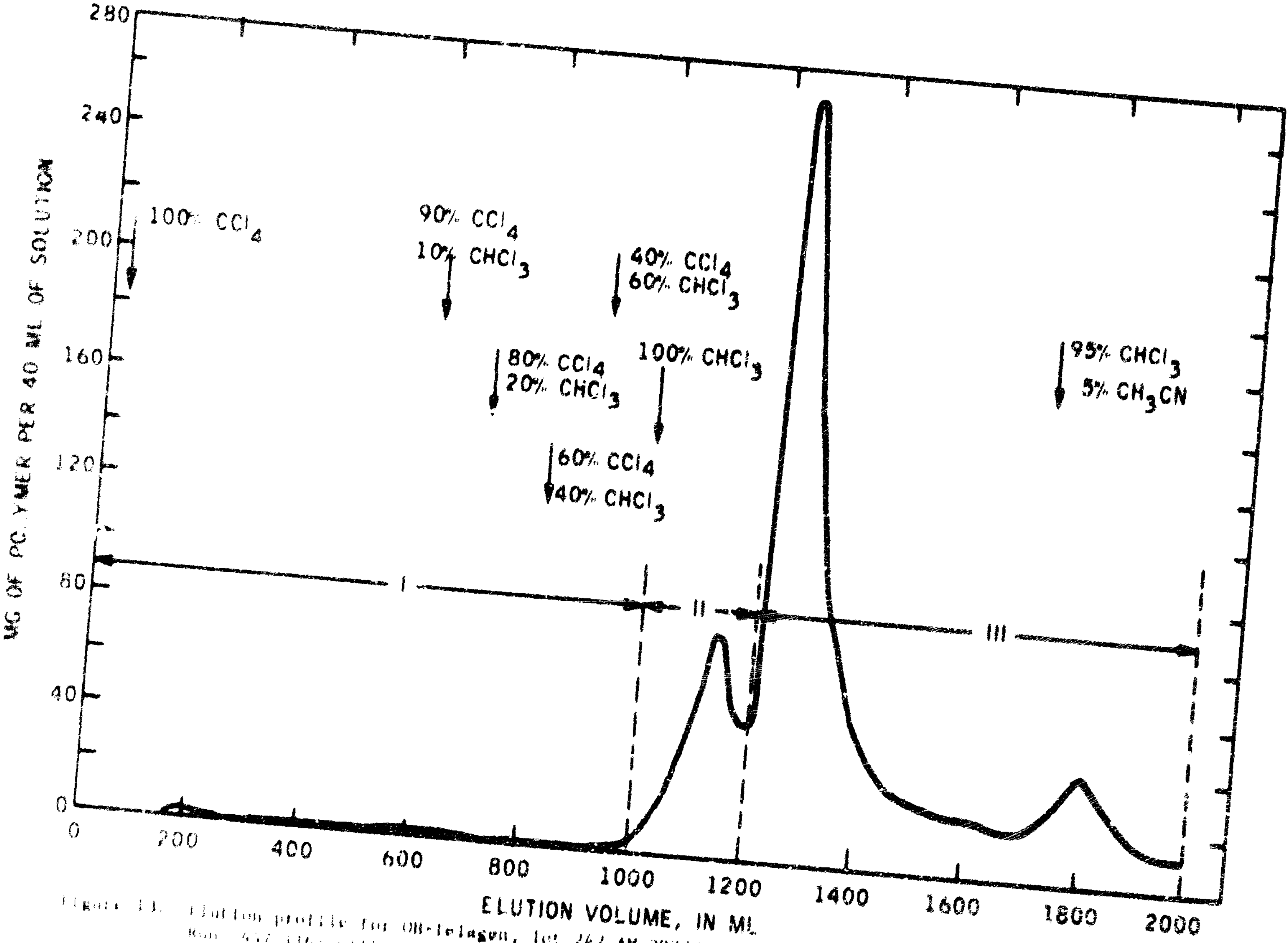


Figure 11. Elution profile for OH-Telagen, lot 242 AM 292/116 AM6 by stepwise elution from silica gel. Run [illegible]; silica gel/polymer ratio = [illegible].

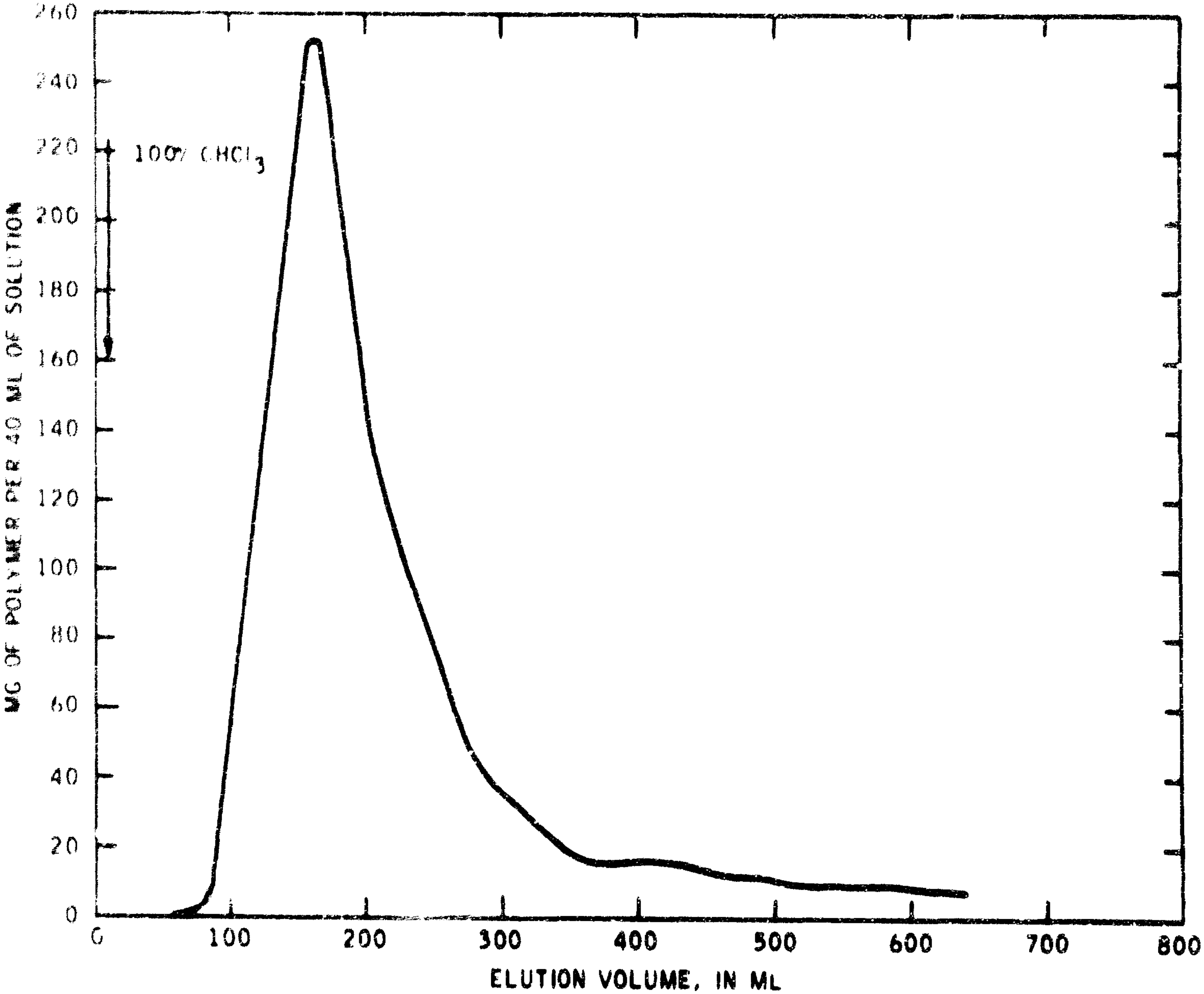


Figure 14. Elution profile for OH-Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel. Run: 647-134; silica gel/polymer ratio: 100/1

In subsequent studies, we lowered the silica gel/polymer ratio and also investigated the effect of the chloroform content of the carbon tetrachloride/chloroform solvent mixture on the efficiency of polymer fractionation. Figure 15 shows the elution profile at a silica gel/polymer ratio of 26/1. Even at this considerably lower ratio, less than 1% of the polymer is eluted by CCl_4 and $CCl_4/CHCl_3$ mixtures containing up to 20% chloroform. There is a significant response to the 60/40 $CCl_4/CHCl_3$ solvent mixture which elutes about 26% (Fraction II) of the total polymer from the column. The bulk of the polymer is subsequently eluted in response to 100% chloroform. Fractionation was terminated after 89.1% of the polymer had been recovered. Analyses of the fractions are summarized below:

Identification: 447-138
Silica gel/polymer ratio: 26/1
Total polymer charged: 3.869 g
Total polymer recovery: 89.1%

Fraction	Wt %	Equivalent Weight (Grams/mole of OH)	$(\bar{M}_n)_o$	Functionality
I	0.9	---------------------- *	----------------------	----------------------
II	25.9	5800	4900	0.84
III	10.3	3140	4700	1.50
IV	52.0	2620	5200	1.98
	89.1			

---

* No analysis could be obtained because of the small sample size.

Based on these data the total non- and monofunctional prepolymer content is in excess of 27% (total of I and II). Fraction III is approximately a 50/50 mixture of mono- and difunctional prepolymer. The total non- and monofunctional content is therefore about 32%.

2.3. Scale-up of the Fractionation of OH-Telagen

The two major parameters which largely control the fractionation of the OH-Telagen prepolymer into its functional components are (1) the silica gel/polymer ratio, and (2) the desorbing power of the eluting solvent. These variables were explored on a small scale before scale-up of the chromatographic separation was attempted. Fractionations have been carried out at silica gel/polymer ratios of 15.6/1 and 10/1. As the silica gel/polymer ratio is reduced the $CHCl_3$ content of the $CCl_4/CHCl_3$ eluting solvent is similarly decreased to reduce the desorbing power of the solvent mixture.

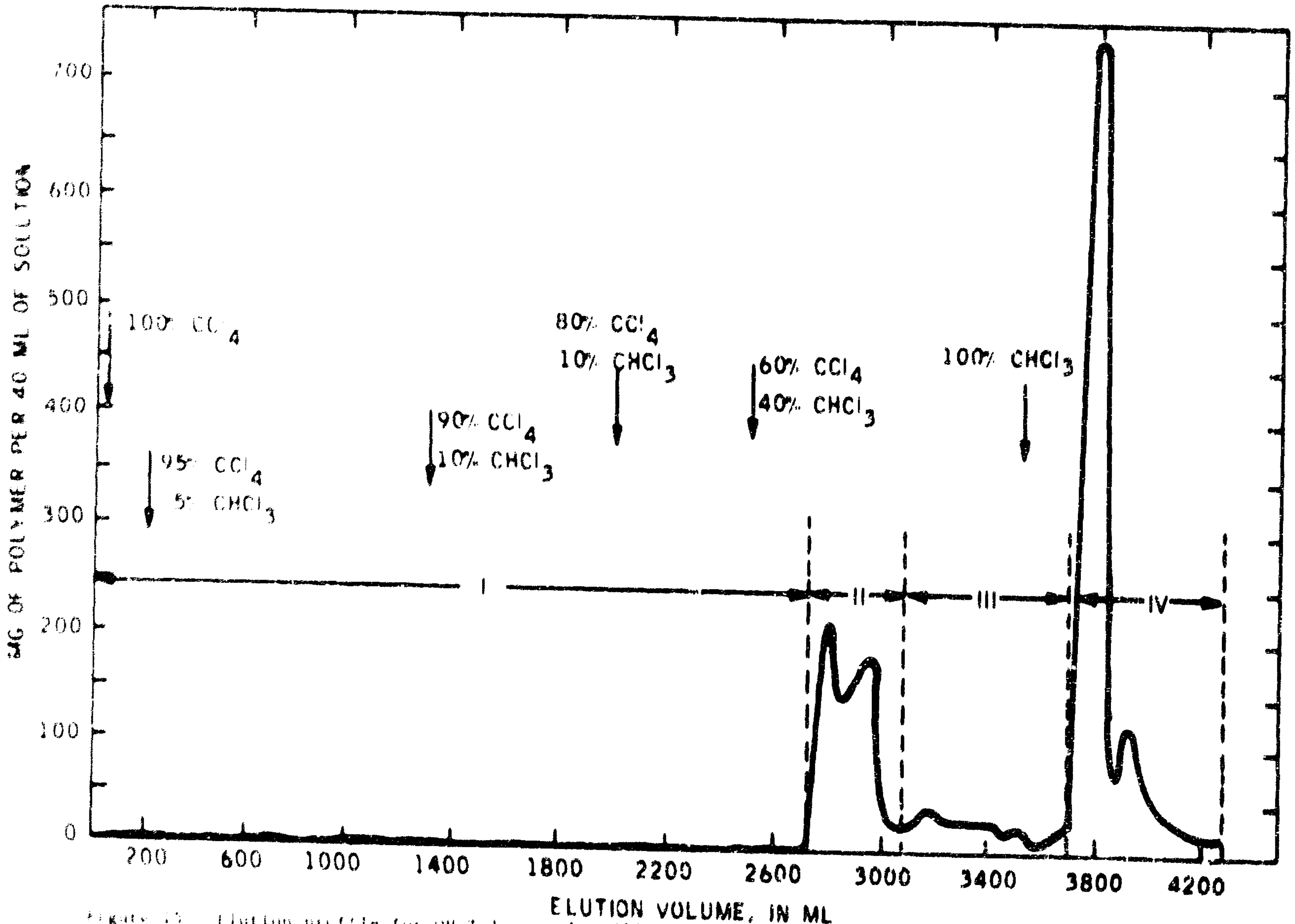


Figure 15. Elution profile for OH-Telagen, lot 242 AM 292/316 AM 6; stepwise elution from silica gel. Run 447 138, silica gel/polymer ratio = 26/1.

Figure 16 shows the elution profile at a gel/polymer ratio of 15.6/1 using 100% CCl_4, 70/30 $CCl_4/CHCl_3$ and 100% $CHCl_3$ in succession. Analyses of the three major fractions are summarized below:

Identification: 447-160
Silica gel/polymerization: 15.6/1
Polymer charged to column: 6.415 g
Total polymer recovery: 92.1%

Fraction	Wt. %	Equivalent Weight (Grams/Mole of OH)	$(\bar{M}n)_c$	Functionality
I	0.3	—	*	—
II	24.7	4540	4700	1.04
III	10.5	4790	4900	1.02
IV	56.6	2620	5000	1.91

---

*Sample size too small for analysis

It appears that some difunctional prepolymer may have been included in fraction II as a result of the reduced silica gel/polymer ratio.

Figure 17 illustrates the elution profile at a further reduced silica gel/polymer ratio (10/1). The solvent schedule was 100% CCl_4 and 80/20 $CCl_4/CHCl_3$. The profile has been considerably condensed and there is less separation between major peaks. Analyses are summarized below.

Identification: 471-8
Silica gel/polymer ratio: 10/1
Total polymer charged: 12.737 g
Polymer Recovery: 88.2%

Fraction	Wt. %	Equivalent Weight (Grams/Mole of OH)	$(\bar{M}n)_c$	Functionality
I	31.9	4015	4500	1.12
II	6.6	6200	5700	0.92
III	49.7	2660	4600	1.73
	88.2%			

These data confirm the trend indicated in run 447-160 that at progressively lower silica gel/polymer ratios some difunctional polymer is initially washed through the column without getting adsorbed on the gel (see functionality of fraction I). To counteract this trend, the chloroform content of the $CCl_4/CHCl_3$ eluting solvent was further reduced to 90/10.

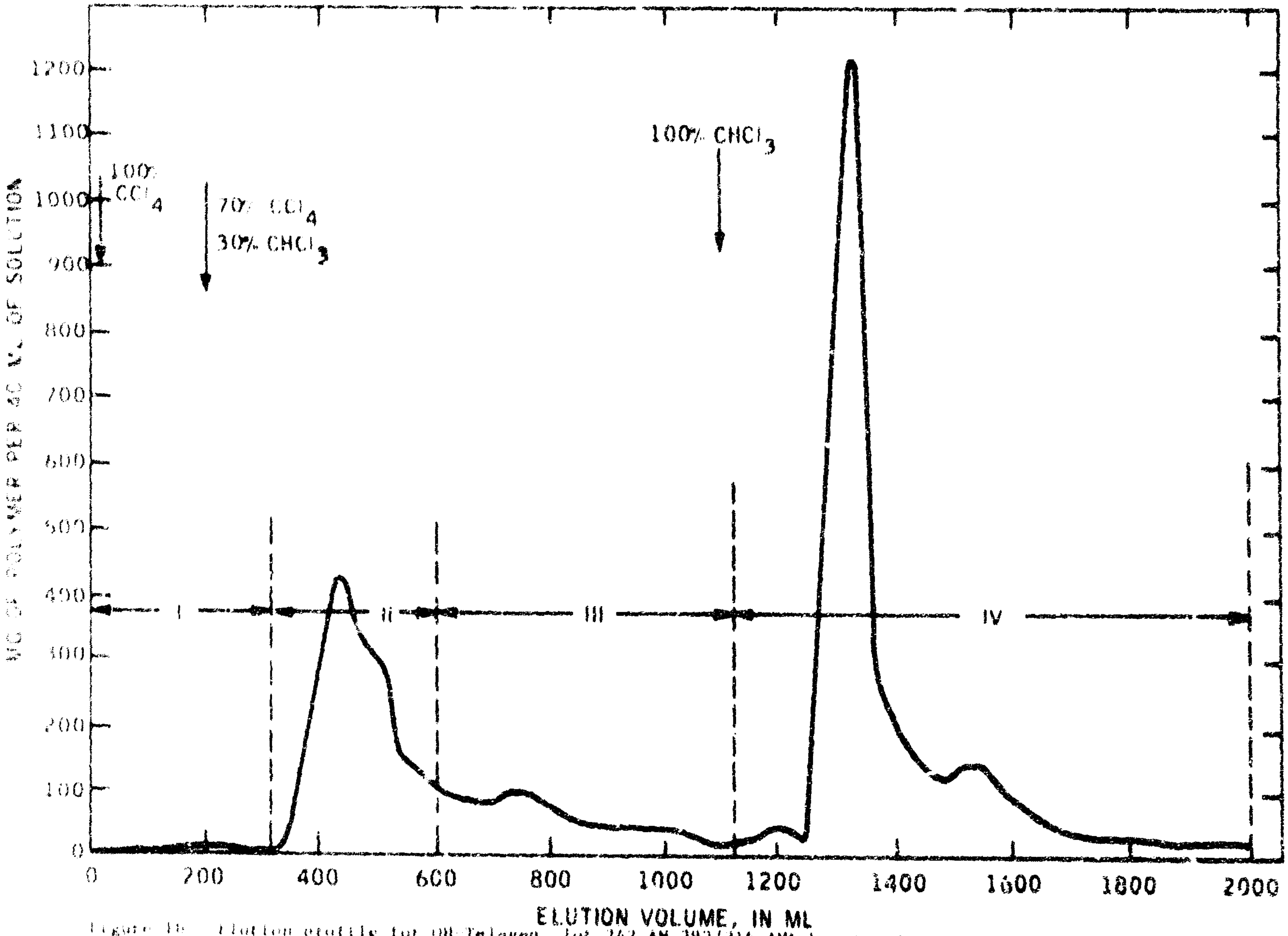


Figure 16. Elution profile for OH-Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel. Run: 447-160, silica gel/polymer ratio = 15.5/1.

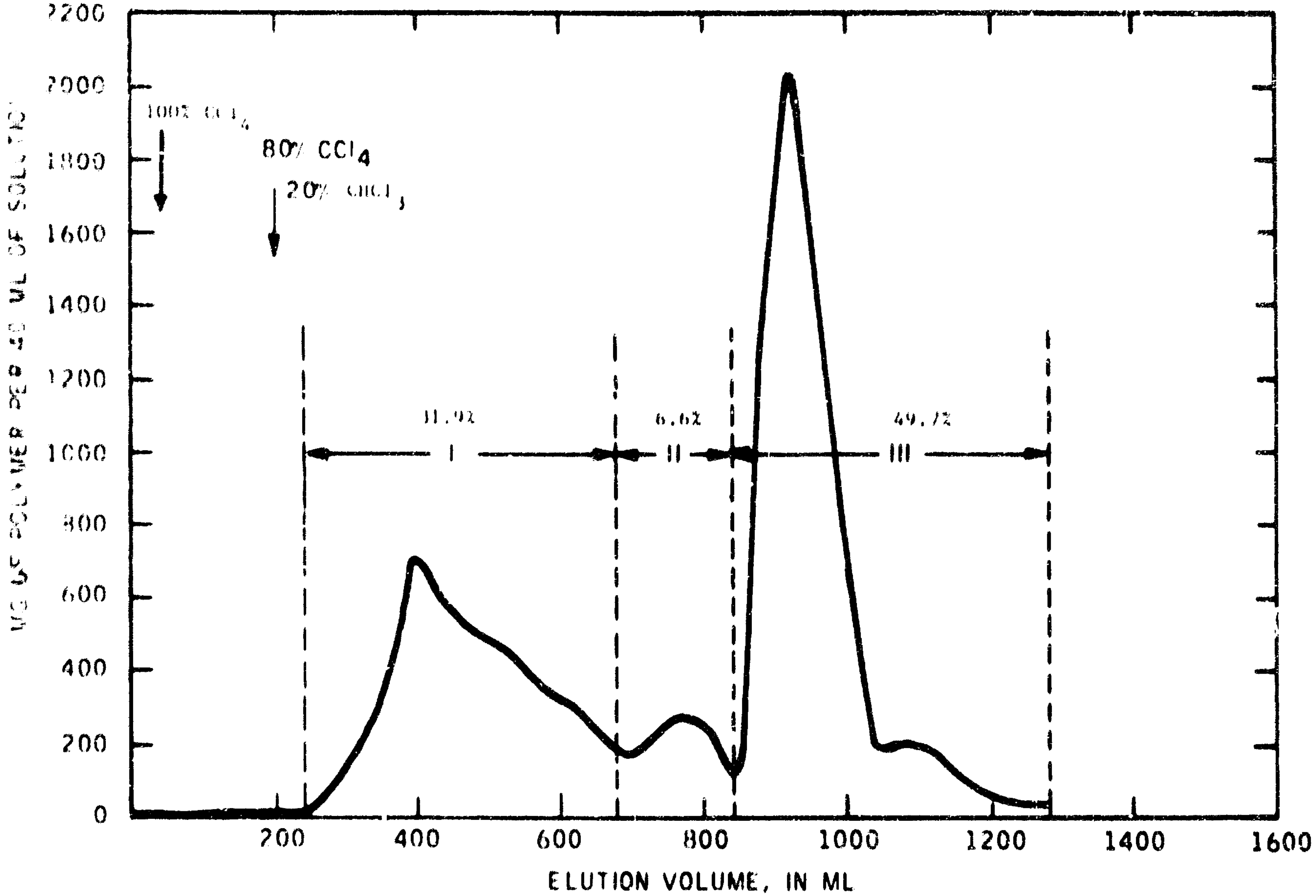


Figure 17. Elution profile for OH Telagen, lot 242 AM 292/316 AM6 by stepwise elution from silica gel. Run 671 8, silica gel/polymer ratio = 10/1.

Figure 18 shows the elution profile (471-32) at the identical gel ratio as run 471-8 (i.e., 10/1) but using 100% CCl_4 followed by 90/10 $CCl_4/CHCl_3$ as the elution schedule. The effect is very dramatic. A fraction accounting for 24 wt % of the total polymer charged is eluted in response to the 90/10 $CCl_4/CHCl_3$ solvent mixture. However, the 90/10 $CCl_4/CHCl_3$ mixture failed to elute the major peak (difunctional polymer). Even the subsequent use of a 80/20 $CCl_4/CHCl_3$ solvent brought only little additional response. There is apparently a very significant difference in the eluting power of a 90/10 and 80/20 $CCl_4/CHCl_3$ solvent mixture. No analyses have been carried out on run 471-32.

Identification: 471-32
Silica gel/polymer ratio: 10/1
Total polymer charged: 12.960 g
Total polymer recovery: 30.3%

The fractionation of OH-Telagen by column chromatography was subsequently scaled-up to the 400 g level. A large glass column having the following dimensions was employed: length=4 feet, diameter=100 mm.

Three scale-up runs of the fractionation of OH-Telagen were made. Two of the runs were carried out at a 20/1 silica gel/polymer ratio and one at a 15/1 ratio. All three elution profiles are very similar (see Figures 19 through 21). The appropriate fractions were characterized with respect to equivalent weight. Based on the equivalent weights, a nominal functionality was assigned to each fraction. Details of runs 471-70, 82 and 94 are given below.

Identification: 471-70
Silica gel/polymer ratio: 15/1
Total polymer charged: 416.5 g
Polymer Recovery: 92.1%

Fraction	Wt. % Total	Equivalent Weight (Grams/Mole of OH)	Nominal Functionality
I	0.1	*	0
II	5.5	8,600	0-1
III	22.7	5,600	1
IV	3.2	--	
V	0.9	--	
VI	19.7	2,990	2
VII	42.0	2,750	2
VIII	6.0	2,350	2

---

*No hydroxyl band in the infrared; functionality = 0

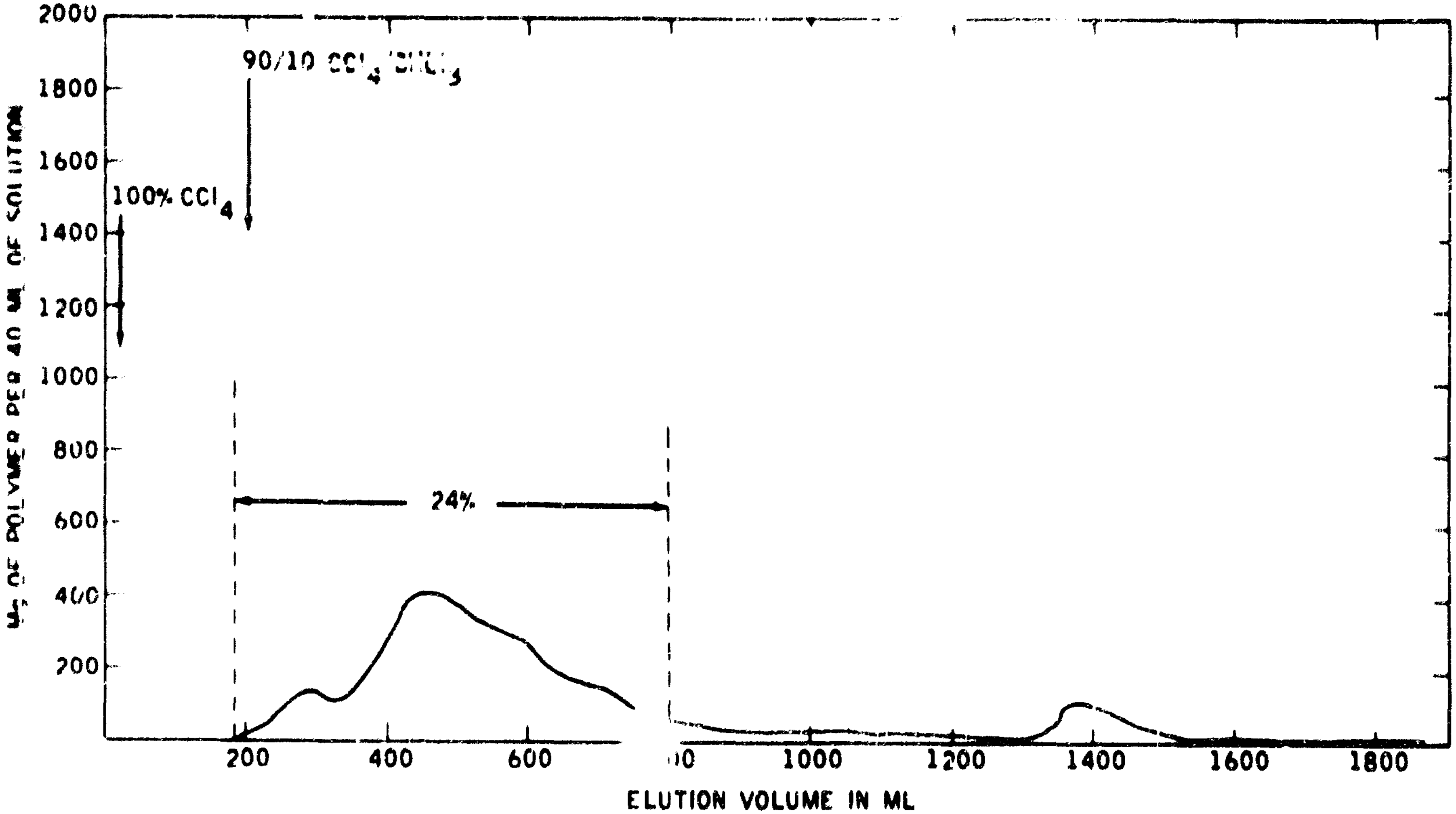


Figure 18. ELUTION PROFILE FOR OH-TELAGEN, LOT 242 AM 292/316 AM6 BY STEPWISE ELUTION FROM SILICA GEL. RUN 471-32, SILICA GEL/POLYMER RATIO = 10/1.

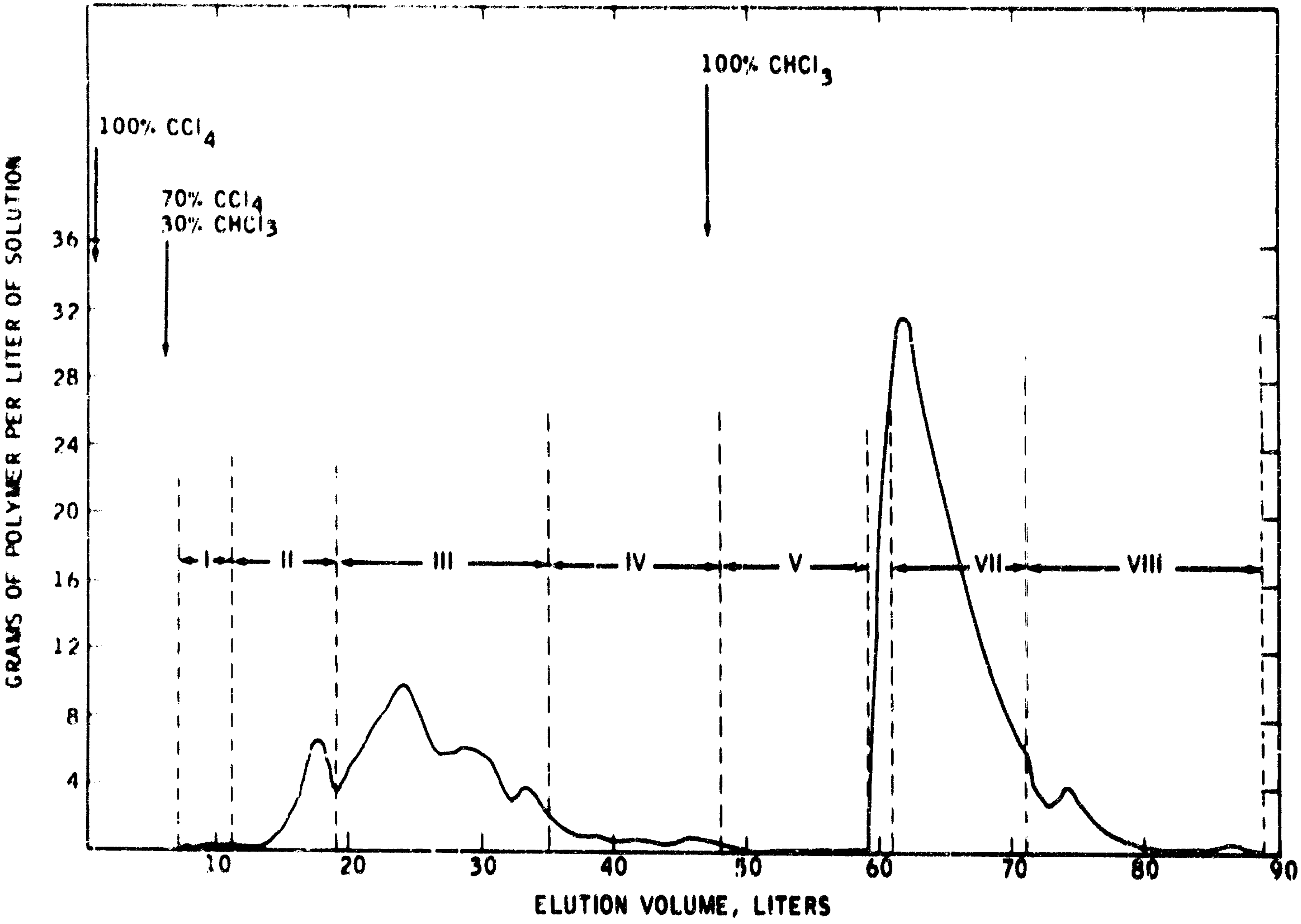


Figure 19. ELUTION PROFILE OF THE SCALEUP OF THE FRACTIONATION OF TELAGEN-HT, LOT 292 AM/316 AM6. RUN 471-70; SILICA GEL/POLYMER RATIO = 15/1.

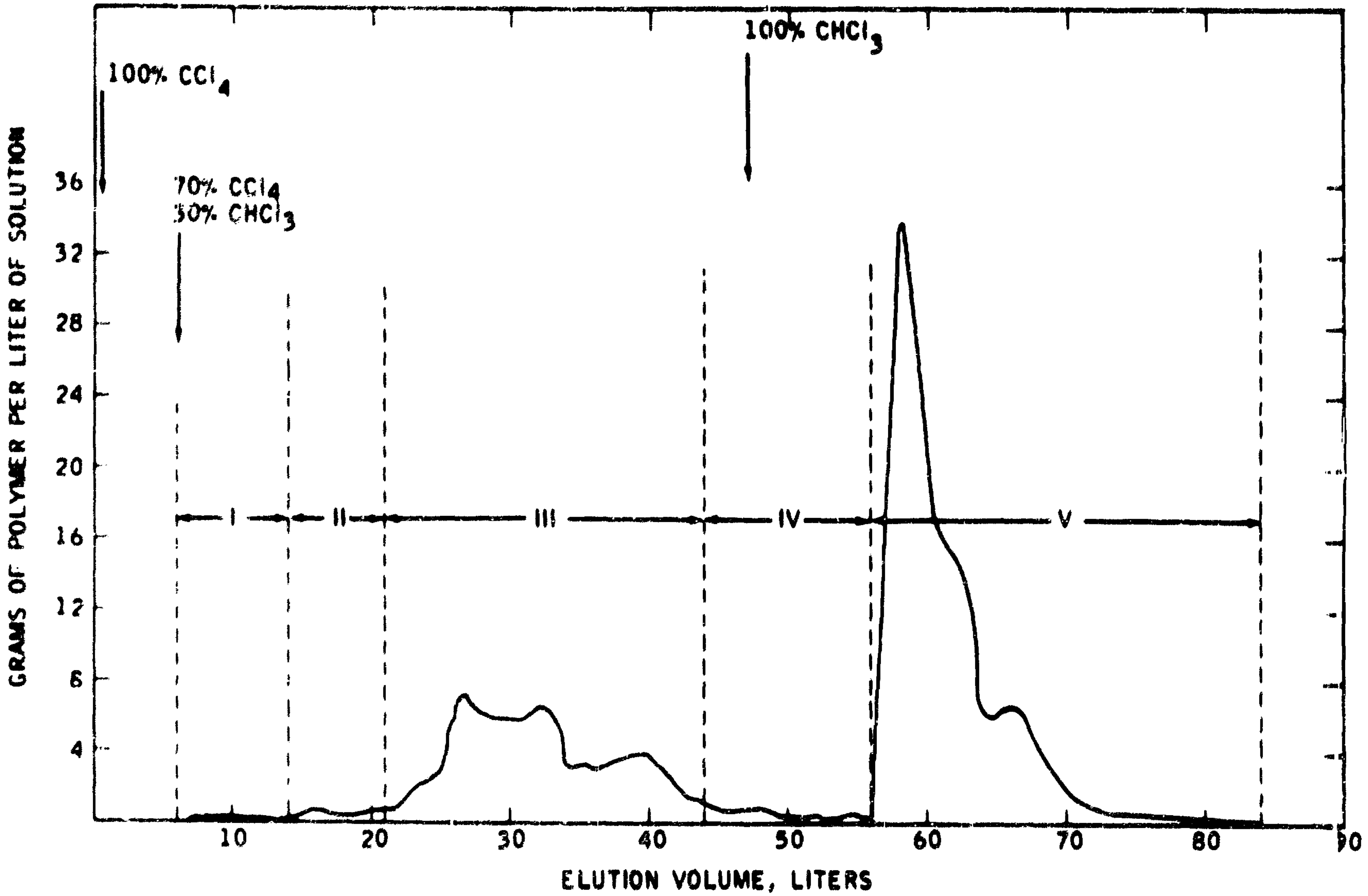


Figure 20. ELUTION PROFILE OF THE SCALEUP OF THE FRACTIONATION OF TELAGEN-HT, LOT 292 AM/316 AM6. RUN 471-82; SILICA GEL/POLYMER RATIO = 20/1.

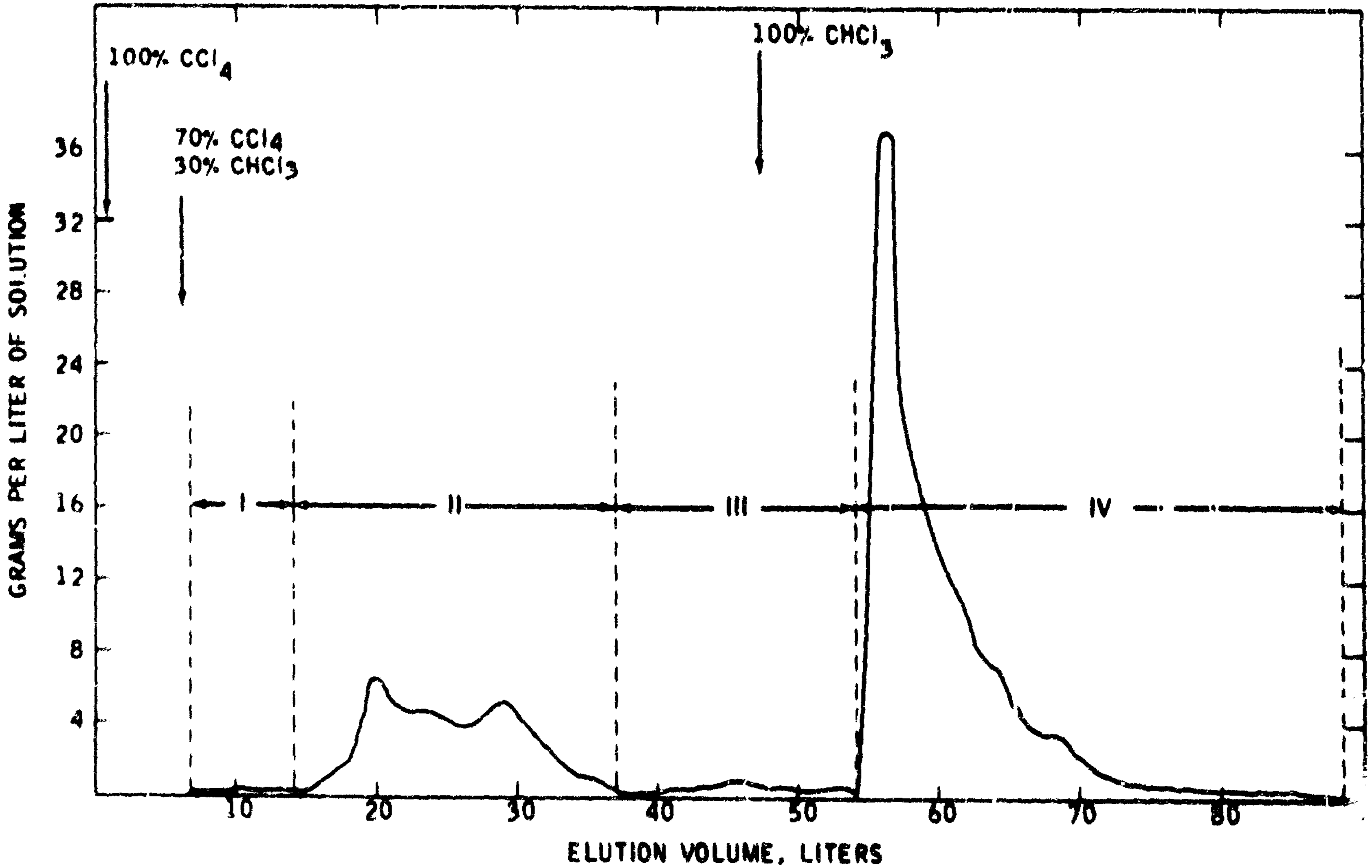


Figure 21. ELUTION PROFILE OF RUN 471-94; SILICA GEL/POLYMER RATIO = 20/1.

Identification: 471-82
Silica gel/polymer ratio: 20/1
Total polymer charged: 315 g
Polymer recovery: 91.7%

Fraction	Wt. % Total	Equivalent Weight (Grams/Mole of OH)	Nominal Functionality
I	0.3	*	0
II	1.2	37,000**	0
III	29.3	4,880	1
IV	2.8	3,700	2
V	58.1	2,680	2
	91.7%		

---

*No hydroxyl band in the infrared; functionality = 0
**Essentially nonfunctional

Identification: 471-94
Silica gel/polymer ratio: 20/1
Total polymer charged: 314.3
Polymer recovery: 90.5%

Fraction	Wt. % Total	Equivalent Weight (Grams/Mole of OH)	Nominal Functionality
I	0.2	*	0
II	23.1	5300	1
III	2.8	3610	1-2
IV	64.4	2560	2
	90.5%		

---

*No hydroxyl band in the infrared; functionality = 0

The appropriate "difunctional fractions" from the three scale-up runs of the fractionation of OH-Telagen have been rechromatographed to yield about 200 grams of pure difunctional prepolymer for gumstock studies.

Equivalent weight and molecular weight measurements of this difunctional polymer have yielded the following values.

$$f = \frac{(\bar{M}n)o}{\text{Eq. Weight}} = \frac{5400}{2720} = 1.99$$

To further confirm the purity of this difunctional prepolymer, we have rechromatographed a small sample on an analytical-size column. Any monofunctional components that are present would be concentrated in the front segment of the elution profile. Fractionation was carried out at a silica gel/polymer ratio of 100/1 and yielded the elution profile shown in Figure 22.

Analysis of the first fraction eluted from the column gave the following analysis.

$$f = \frac{(\bar{M}n)o}{\text{Eq. Weight}} = \frac{5700}{2840} = 2.01$$

Based on these data it can be concluded that the polymer is pure difunctional. This material was subsequently used for gumstock studies to determine the mechanical properties of a purely difunctional OH-prepolymer.

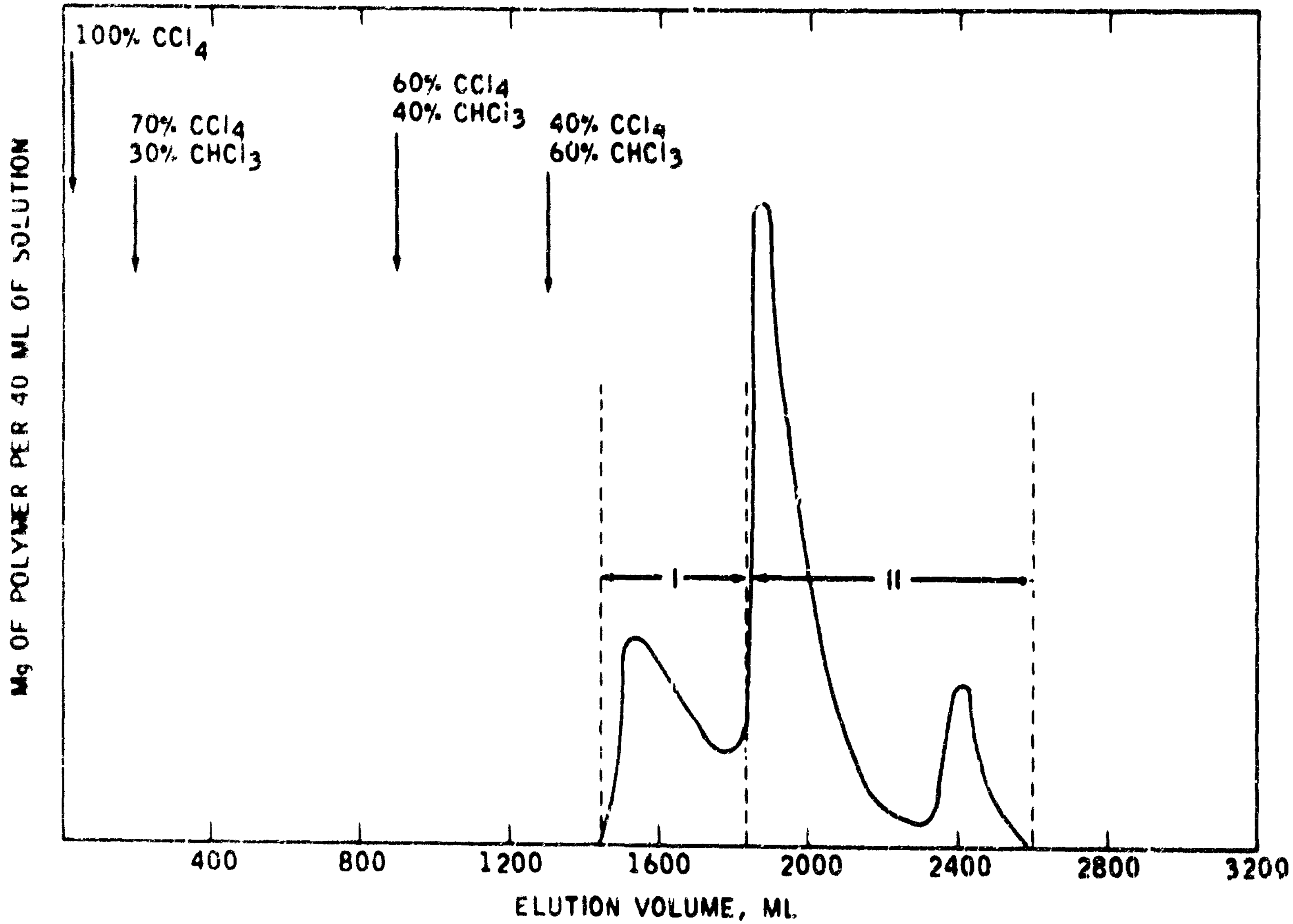


Figure [illegible]. ELUTION PROFILE FOR DIFUNCTIONAL OH-TELAGEN. RUN 471-100; SILICA GEL/POLYMER RATIO = 80/1.

C. Functionality and Functionality Distribution Measurements of General Tire's COOH-TELAGEN

General Tire and Rubber Company produces also the carboxy analogue of the OH-Telagen prepolymer series. Again both a hydrogenated, COOH-Telagen-S, and the unsaturated analogue, COOH-Telagen are available. Samples of both prepolymers were analyzed on this program.

1. COOH-TELAGEN-S (Nominal 2000). Lot 242AH 273CHR

Previous lots (1) of COOH-Telagen-S prepolymer which had been analyzed had varied in total non- and monofunctional polymer content from 18 to 38%, the bulk of this fraction being monofunctional. This latest lot of COOH-Telagen-S had a non- and monofunctional prepolymer content of 25%.

1.1. Functionality Determination

This prepolymer lot was found to contain about 0.45% volatiles. Molecular weights were obtained after removal of the volatile components. The concentration dependence of apparent molecular weight by VPC in chloroform at 37°C is shown in Figure 23. Of particular interest is the positive slope of the molecular weight dependence on concentration, the molecular weight decreasing with decrease in polymer concentration. This reflects at least in part the association of the prepolymer through its carboxy-functional groups. Some of the OH-prepolymers show this type of concentration dependence. The extrapolated molecular weight, $(\bar{M}n)_0 = 2220$. The equivalent weight of this prepolymer was determined by potentiometric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol yielding a value of 1170 g/mole of COOH.

Based on these measurements, the calculated functionality is:

$$f = \frac{2220}{1170} = 1.89$$

1.2. Functionality Distribution Measurements

To determine its functionality distribution the polymer was fractionated on silica gel using the following solvent schedule: 100% CCl_4, mixtures of CCl_4 and $CHCl_3$, 100% $CHCl_3$ and mixtures of $CHCl_3$ and CH_3CH_2OH. The resulting elution profile is shown in Figure 24. Analyses of the recombined fractions are summarized below:

Identification: 447-41
Silica gel/polymer ratio: 36/1
Polymer charged to column: 1.57g
Total Polymer Recovery: 91.9%

Fraction	Wt % of Total	Equivalent Weight (Grams/mole COOH)	$(\bar{M}n)_c$	Functionality
I	6.6	7100	2300	0.32
II	18.1	2830	2800	0.99
III	62.7	1060	2150	2.03
IV	4.5	1050	2120	2.02
	91.9			

The first fraction accounting for 6.6 w. % is a mixture of non- and monofunctional prepolymer. Based on its overall functionality of 0.32, approximately 1/3 is nonfunctional (2.2%) and 2/3 is monofunctional (4.4%). Fraction II (18.1%) is clearly monofunctional and fractions III and IV are difunctional. The residual 8% which could not be desorbed are presumably also difunctional. The functionality distribution of this prepolymer is therefore as follows:

Nonfunctional: 2.2%
Monofunctional: 4.4 + 18.1 ≈ 22-23%
Difunctional: >67%

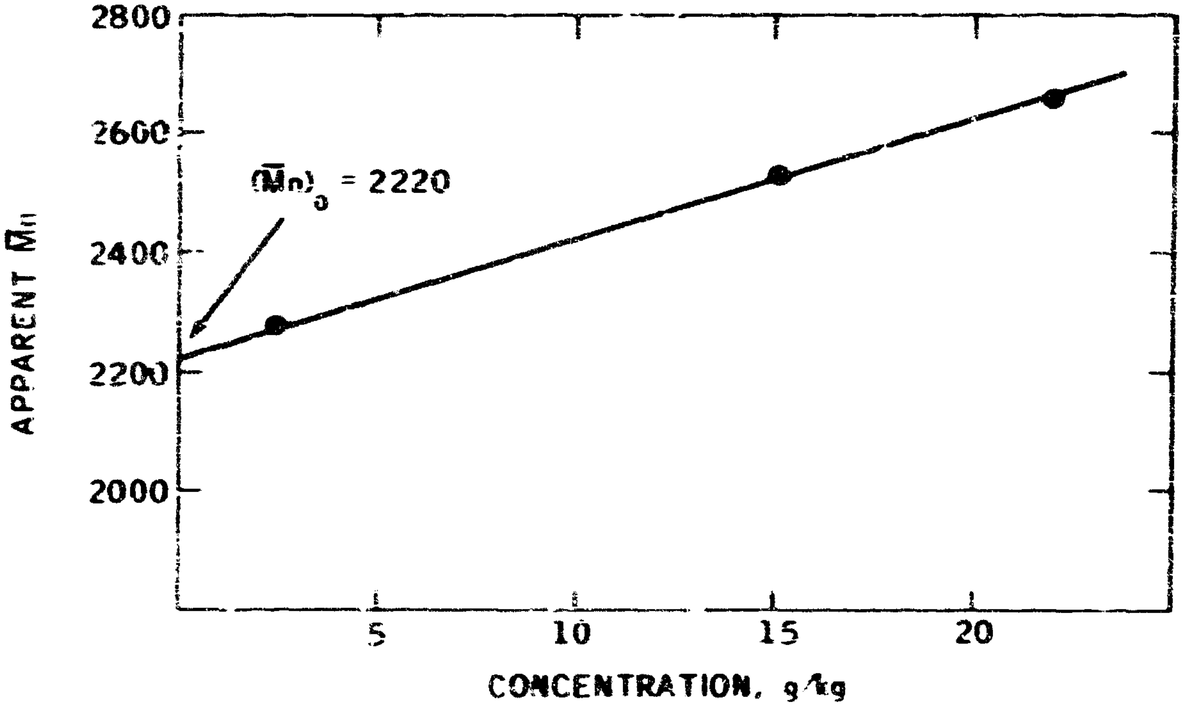


Figure 23. Concentration dependence of molecular weight for OHOH-Telagen-S, batch no. 242 AM 273 CHR by VPO in chloroform at 37°C.

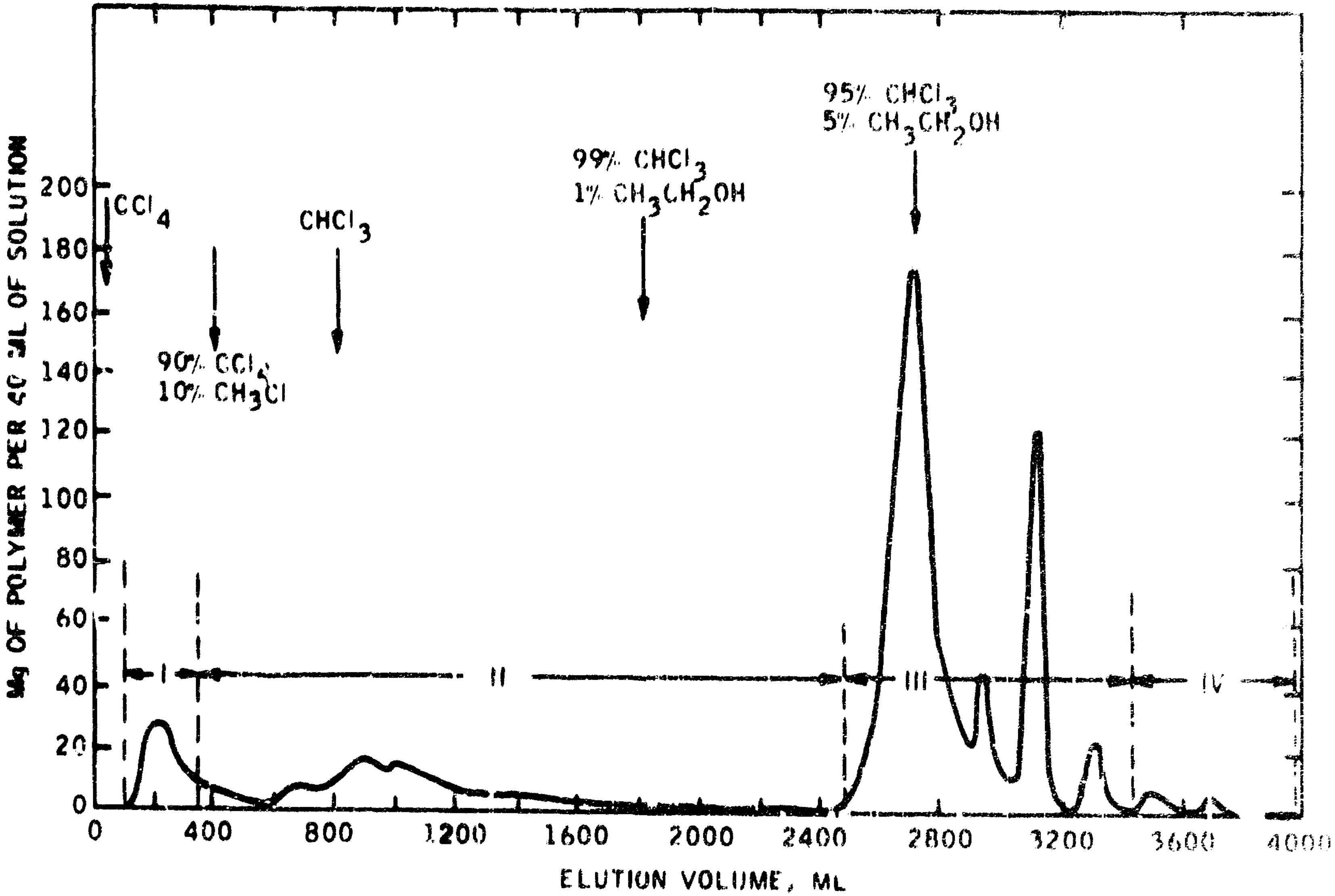


Figure 44. Elation Profile for COOH Telagen-S, Batch No. 242AM 271 CHR, by Stepwise Elution from Silica Gel. Run 447-41 silica gel/polymer ratio = 96/1.

2. COOH-TELAGEN (Nominal 5000), Lot 126

This prepolymer is also being used on the curative program for evaluation of aziridine curing agents. It is the carboxy-functional analogue of the OH-Telagen discussed in Section B2.

2.1. Functionality Determination

Number average molecular weight measurements by VPO in chloroform at 37°C yielded an extrapolated molecular weight of (Mn)c = 4400 (see Figure 25).

The equivalent weight of the prepolymer was determined by potentiometric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol yielding a value of 2650 g/mole of COOH.

Based on these measurements, the calculated functionality is:

$$f = \frac{4400}{2650} = 1.66$$

2.2. Functionality Distribution Measurements

In our first fractionation study with the COOH-Telagen prepolymer we employed the same solvent schedule that had previously been applied successfully to the lower molecular weight (2300), hydrogenated prepolymer, COOH-Telagen-S. Polymer recovery in excess of 95% had been realized with the COOH-Telagen-S. The unsaturated, higher molecular weight COOH-Telagen, however, upon fractionation gave only 50% recovery.

Figure 26 shows the resulting elution profile after the particular solvent schedule used. Fraction I could not be analyzed because of the small quantity involved. The infrared spectrum, however, showed a weak COOH absorption band. Since the following fraction was found to be composed of non- and monofunctional polymer, Fraction I is also believed to be a mixture of non- and monofunctional material. Inspection of individual cuts comprising Fraction II revealed the presence of a crystalline material which is believed to be additive (antioxidant). These cuts were not included in Fraction II but are reflected in the total percentage of Fraction II. Analyses of the fractions showed that Fraction II is a mixture of non- and monofunctional material whereas Fraction III is purely monofunctional. Fraction IV was essentially difunctional. The remaining 49% which could not be desorbed are also believed to be difunctional. The total non- and monofunctional content is therefore about 27%. The results of the fractionation are summarized on the following page.

Identification: 447-114
Silica gel/polymer ratio: 100/1
Total polymer charged: 1.302 g
Total polymer recovery: 51.4%

Fraction	Wt %	Equivalent Weight (Grams/Mole of COOH)	$(\bar{M}n)o$	Functionality
I	2.3	----------	*	----------
II	18.6	6720	5100	0.76
III	5.7	3810	3800	1.0
IV	24.8	1950	3800	1.95
	51.4			

---

* Because of small sample size no analysis could be obtained.

In attempts to improve polymer recovery, 100% $CHCl_3$ was used as the initial solvent. Figure 27 depicts the elution profile using 100% $CHCl_3$ and subsequently 95/5 $CHCl_3/CH_3CH_2OH$. Although polymer recovery was somewhat improved (68.8% vs 51.4%) separation efficiency was adversely affected. Fraction I (33%) was a mixture of non-, mono- and difunctional polymer. Fraction II was a mixture of mono- and difunctional polymer and Fraction III was difunctional. Results of fractionation 447-146 are summarized below.

Identification: 447-146
Silica gel/polymer ratio: 100/1
Total polymer charged: 1.338 g
Total polymer recovery: 68.8%

Fraction	Wt %	Equivalent Weight (Grams/Mole of COOH)	$(\bar{M}n)o$	Functionality
I	33.0	6200	5300	0.85
II	21.2	2380	3800	1.60
III	14.6	2000	4100	2.05
	68.8			

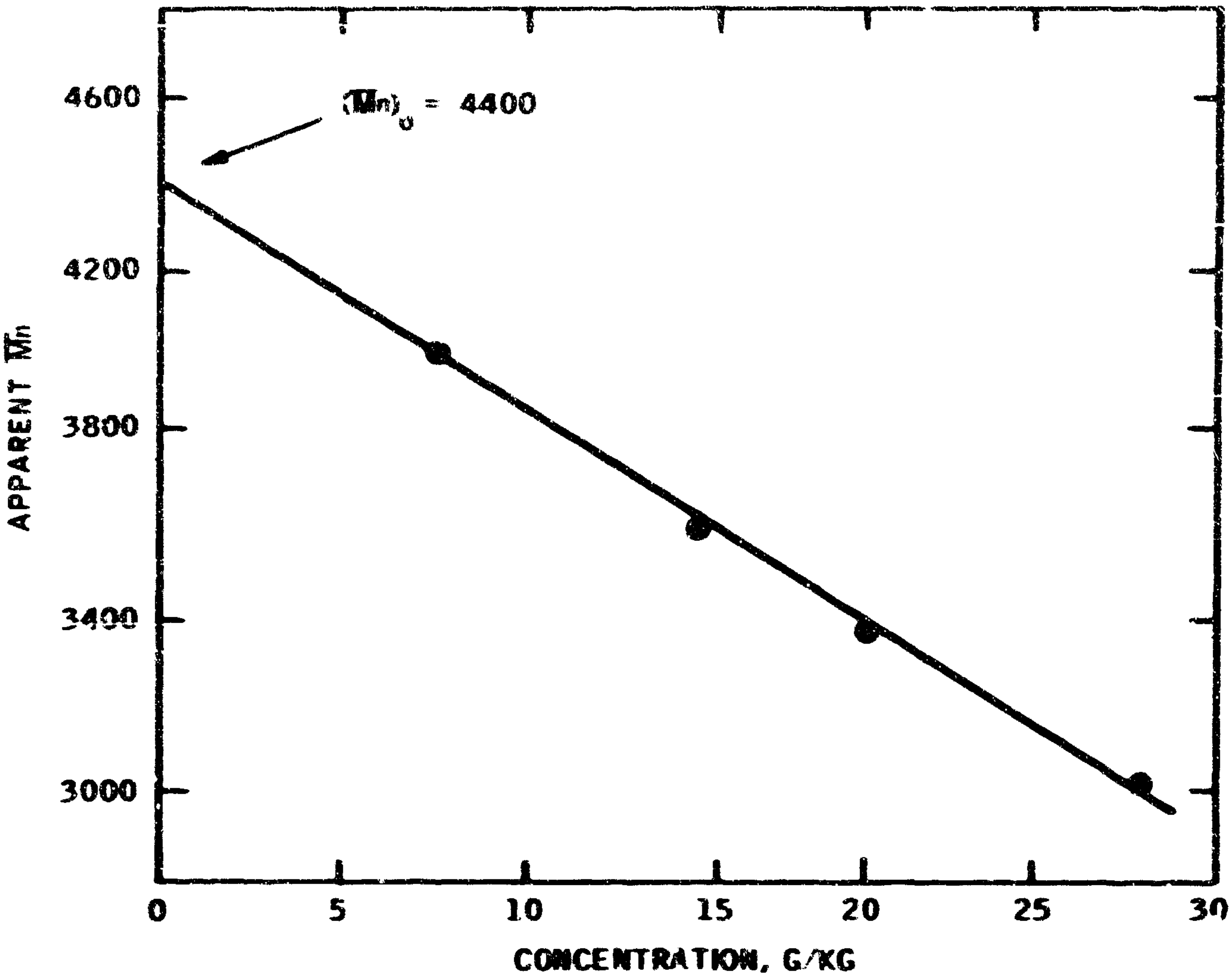


Figure 25. Concentration dependence of number average molecular weight by VPO for COOH-Telagen, lot 126, by VPO in chloroform at 37°C.

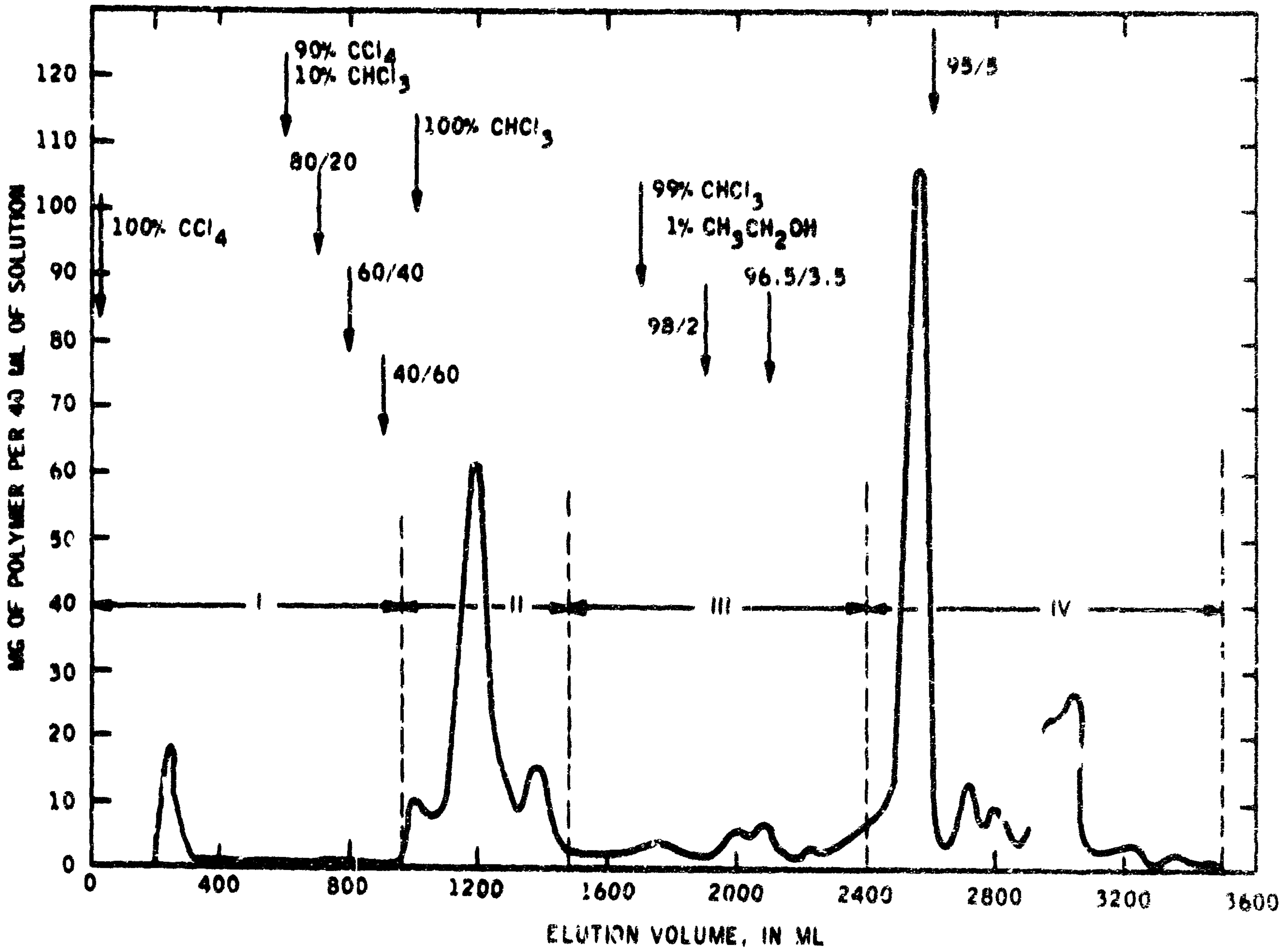


Figure 26. Elution profile for COOH-Telagen, lot 126 by stepwise elution from silica gel. Run: [illegible]47-114; silica gel/polymer ratio = 100/1

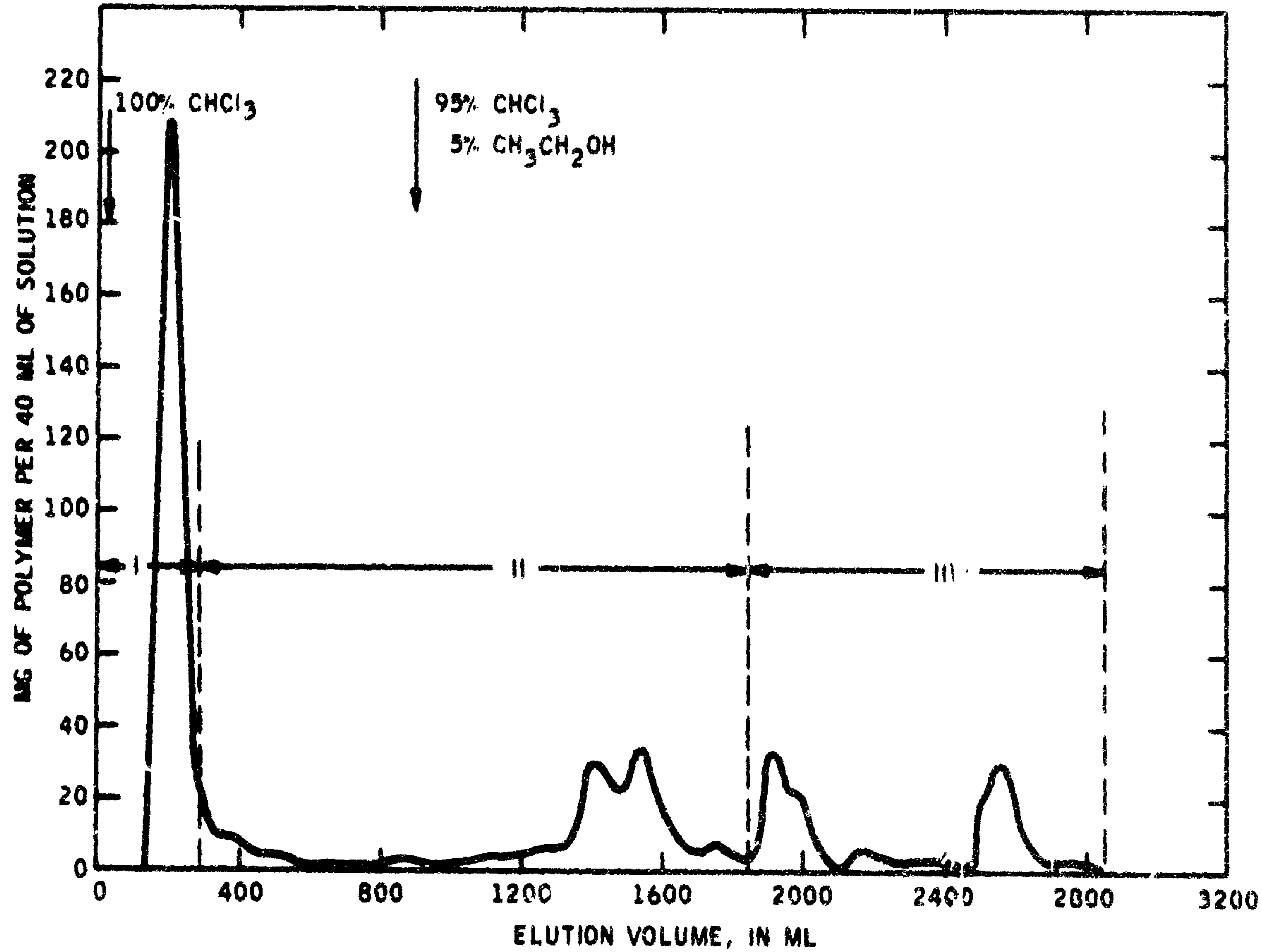


Figure 27. Elution profile for COOH-Telagen, lot 126 by stepwise elution from silica gel. Run: 447-140; silica gel/polymer ratio = 100/1

D. Functionality and Functionality Distribution Measurements of Rocketdyne's P-GDMFE Prepolymer

About 15 grams of Rocketdyne's P-GDMFE prepolymer, lot EII-68 were received for functionality distribution measurements. P-GDMFE is a nitro-fluoro prepolymer having hydroxy-functional groups. Only one lot (EII-68) was characterized on this program.

1. Functionality Determination

Equivalent weight determinations of P-GDMFE, lot EII-68 were made in duplicate by reaction of the prepolymer with toluenesulfonyl isocyanate in chloroform solution. A typical reaction profile of P-GDMFE with excess toluenesulfonyl isocyanate as monitored by IR is shown in Figure 28. The reaction is essentially complete after [illegible] hours at ambient temperature. Excellent reproducibility was obtained as shown by the following equivalent weight determinations:

	Equivalent Weight (Grams/Mole of OH)
	1288
	1294
Average:	1290

Molecular weight measurements of P-GDMFE lot EII-68 were obtained by VPO in chloroform at 37°C. As shown in Figure 29 this polymer exhibits only a slight concentration dependence of apparent molecular weight. The extrapolated molecular weight is $(\bar{M}_n)_0 = 2800$ which is in excellent agreement with the data reported by Rocketdyne ($\bar{M}_n = 2794$). Based on these measurements the calculated functionality is:

$$f = \frac{2800}{1290} = 2.17$$

These data suggest the presence of components having greater than difunctionality.

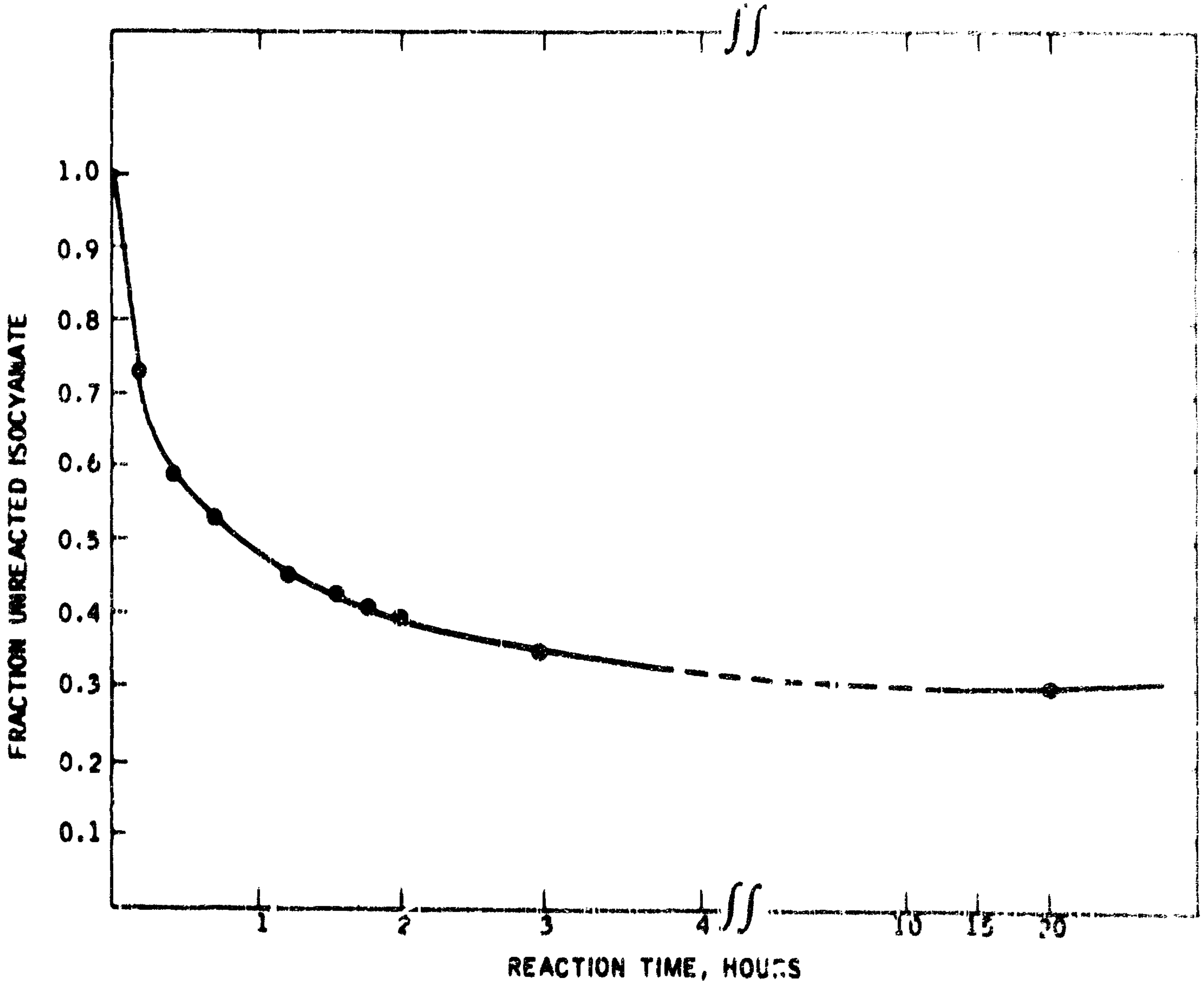


Figure 28. REACTION PROFILE OF ROCKETDYNE'S P-GDKFE, LOT E11-68, WITH EXCESS TOLUENESULFONYL ISOCYANATE IN CHLOROFORM AT ROOM TEMPERATURE. REACTION WAS MONITORED BY INFRARED.

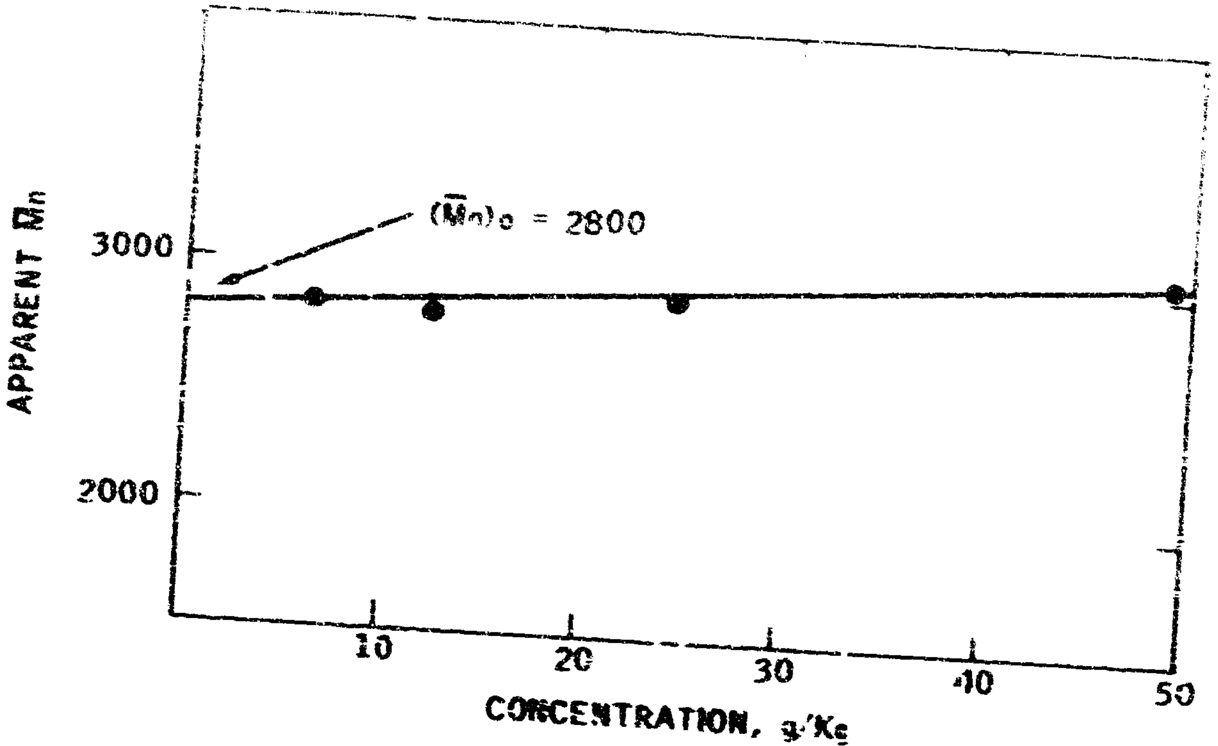


Figure 29. CONCENTRATION DEPENDENCE OF NUMBER AVERAGE MOLECULAR WEIGHT FOR ROCKETDYNE'S P-GDMFE, LOT EII-68, IN CHLOROFORM AT 37°C BY VPC.

2. Functionality Distribution Measurements

The fractionation of prepolymers into their functional components by elution chromatography on activated silica gel has been extended to the P-GDMFE. The development of a suitable solvent system is the key factor which determines the efficiency of separation by functionality.

In our first experiment the following solvent schedule was used: 100% $CHCl_3$, $CHCl_3/CH_2Cl_2$ mixtures, 100% CH_2Cl_2 and finally an 80/20 mixture of CH_2Cl_2/CH_3CN. These studies indicated that this prepolymer is very strongly adsorbed on activated silica gel. As shown in Figure 30, chloroform and methylene chloride which have been used in the past to fractionate conventional prepolymers such as CH-Telagen, have failed to elute the polymer. However, a solvent mixture of 20% CH_3CN and 80% CH_2Cl_2 immediately eluted the polymer with no apparent fractionation. Based on these observations the solvent schedule was subsequently modified by slowly increasing the CH_3CN content in methylene chloride from zero percent to 25 vol. %. The resulting elution profile is shown in Figure 31. Individual polymer fractions were recombined into four major fractions for subsequent analysis. The analyses of these fractions are summarized on the next page.

Identification 471-109
Silica gel/polymer ratio: 82/1
Total polymer charged: 1.460 g.
Polymer recovery: 92.6%

Fraction	Wt. % of Total	Equivalent Weight (Grams/Mole of OH)	$(\overline{M}n)o$	Functionality
I	12.6	1610	1550	0.96
II	46.1	1410	3400	2.41
III	20.2	1260	3080	2.44
IV	13.7	1100	2700	2.45
	92.6%			

In a subsequent third fractionation, the elution schedule was further modified by eliminating solvent compositions of 98/2, 96/4, 94/6 and 92/8% CH_2Cl_2/CH_3CN. Instead the acetonitrile content of the solvent mixture was stepwise increased from 90/10 to 88/12 and finally to 85/15 CH_2Cl_2/CH_3CN. As a result, the elution profile was expanded as shown in Figure 32. The individual cuts were recombined into six fractions for analysis. Fraction I which accounts for only 0.3 wt % could not be analyzed because of sample size limitation. The equivalent weights of Fraction II through VI show the same trend of increasing hydroxyl content that was observed in fractionation 471-109.

Identification 471-116
Silica gel/polymer ratio: 96/1
Total polymer charged: 1.40 g
Polymer recovery: 95.7%

Fraction	Wt. % of Total	Equivalent Weight (Grams/Mole of OH)	$(\overline{M}n)o$	Functionality
I	0.3			
II	16.0	1640	1860	1.13
III	23.9	1490	3720	2.50
IV	22.2	1400	3350	2.39
V	14.6	1220	3000	2.46
VI	18.7	1150	2900	2.52
	95.7%			

Functionality data on the individual fractions show that monofunctional components have been separated from the total polymer. The monofunctional components which account for about 12-15 wt % are also the lower molecular weight components. Separation of di- and trifunctional components was not realized. However, based on the analysis of the individual fractions the approximate functionality distribution of P-GDMFE, lot EII-68 is as follows:

- 12-15 wt % monofunctional (including a small fraction of nonfunctional material)
- 45-50 wt % difunctional
- 35-40 wt % trifunctional

This functionality distribution is only representative of lot EII-68 and may not reflect the typical distribution of P-GDMFE prepolymer lots.

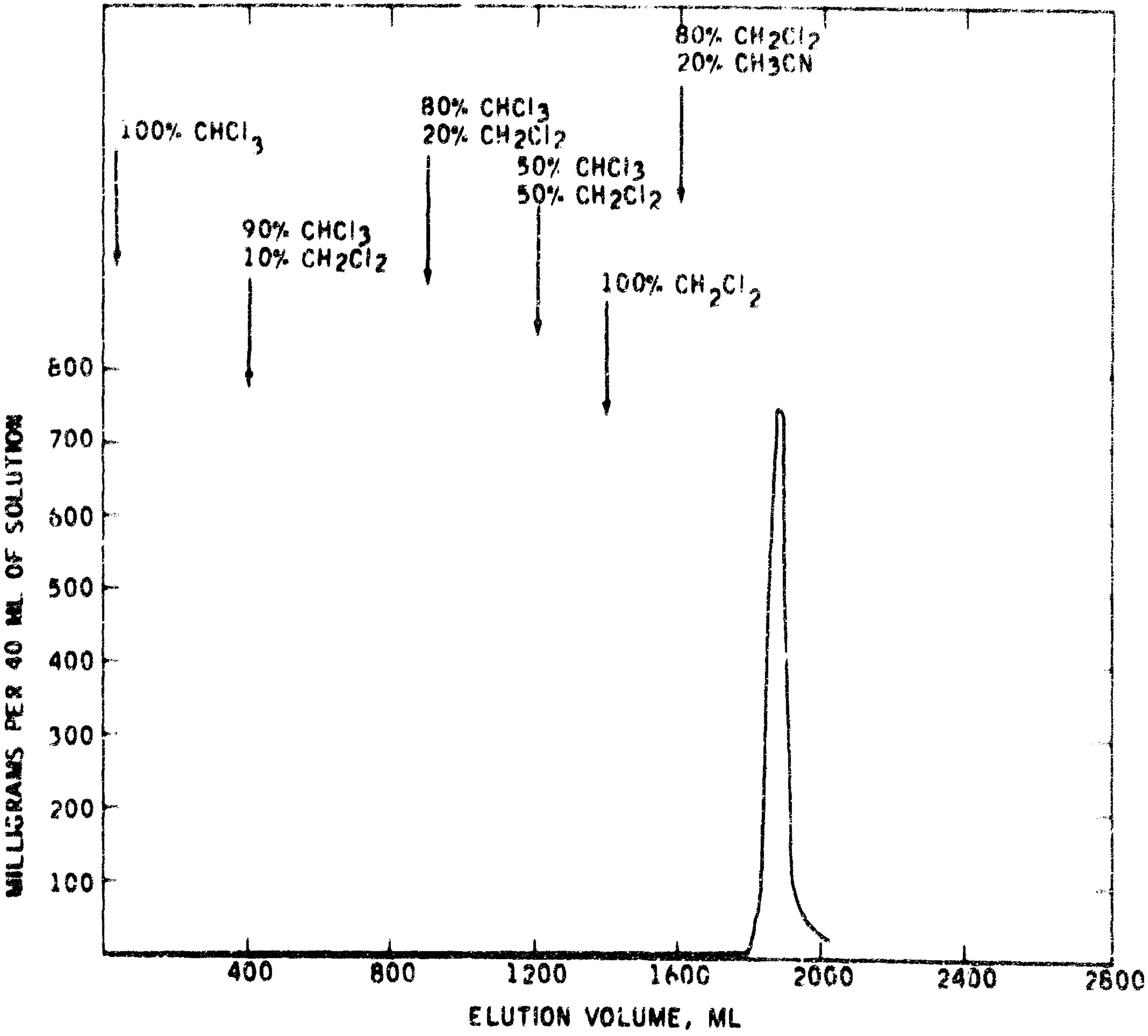


Figure 30. ELUTION PROFILE OF ROCKETDYNE'S P-GDNFE, LOT EII-68. RUN 471-104; SILICA GEL/POLYMER RATIO = 90/1.

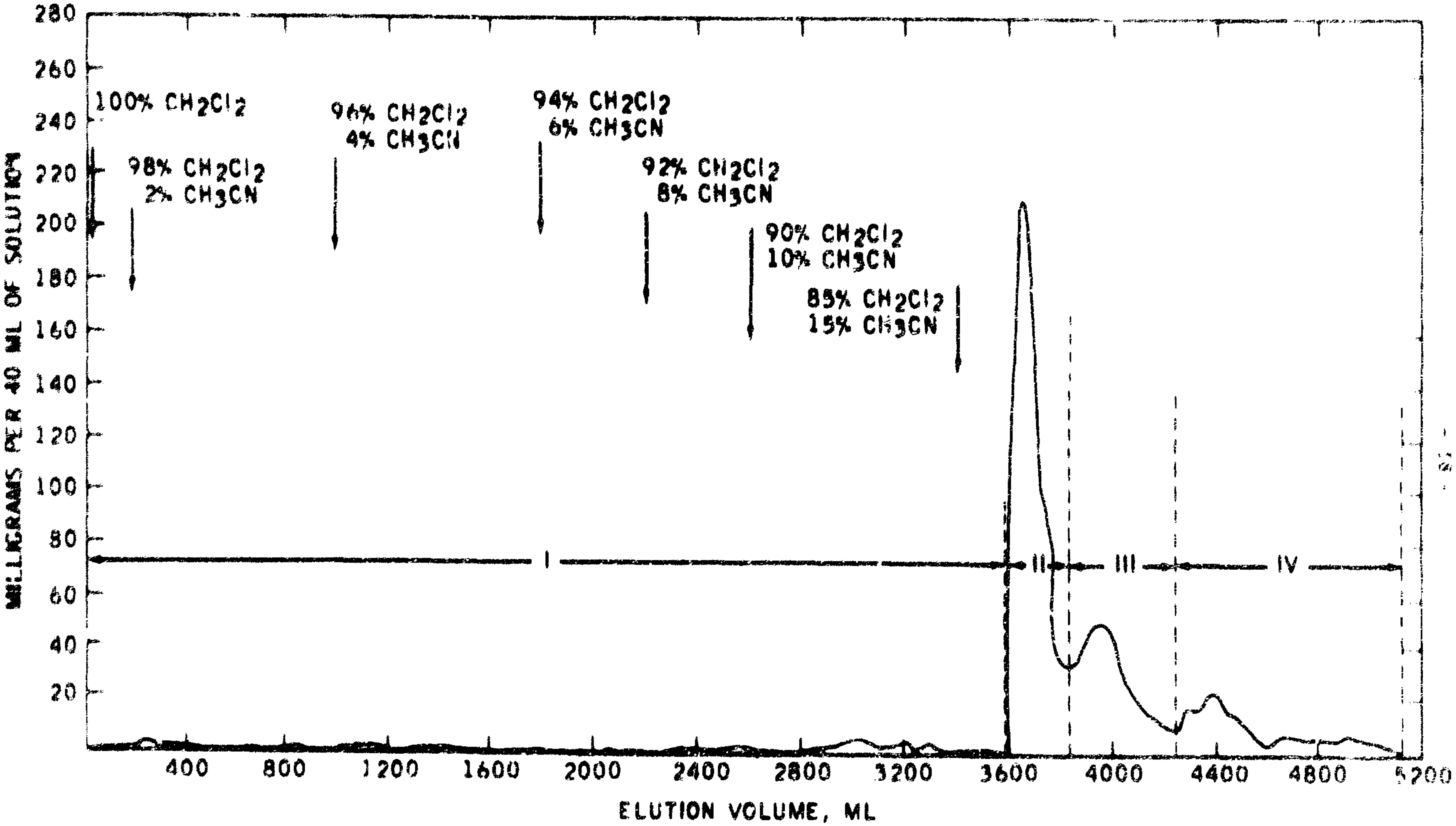


Figure 11 ELUTION PROFILE OF ROCKETDYNE'S P-GDNFE, LOT E11-68. RUN 471-109; SILICA GEL/POLYMER RATIO - 82/1.

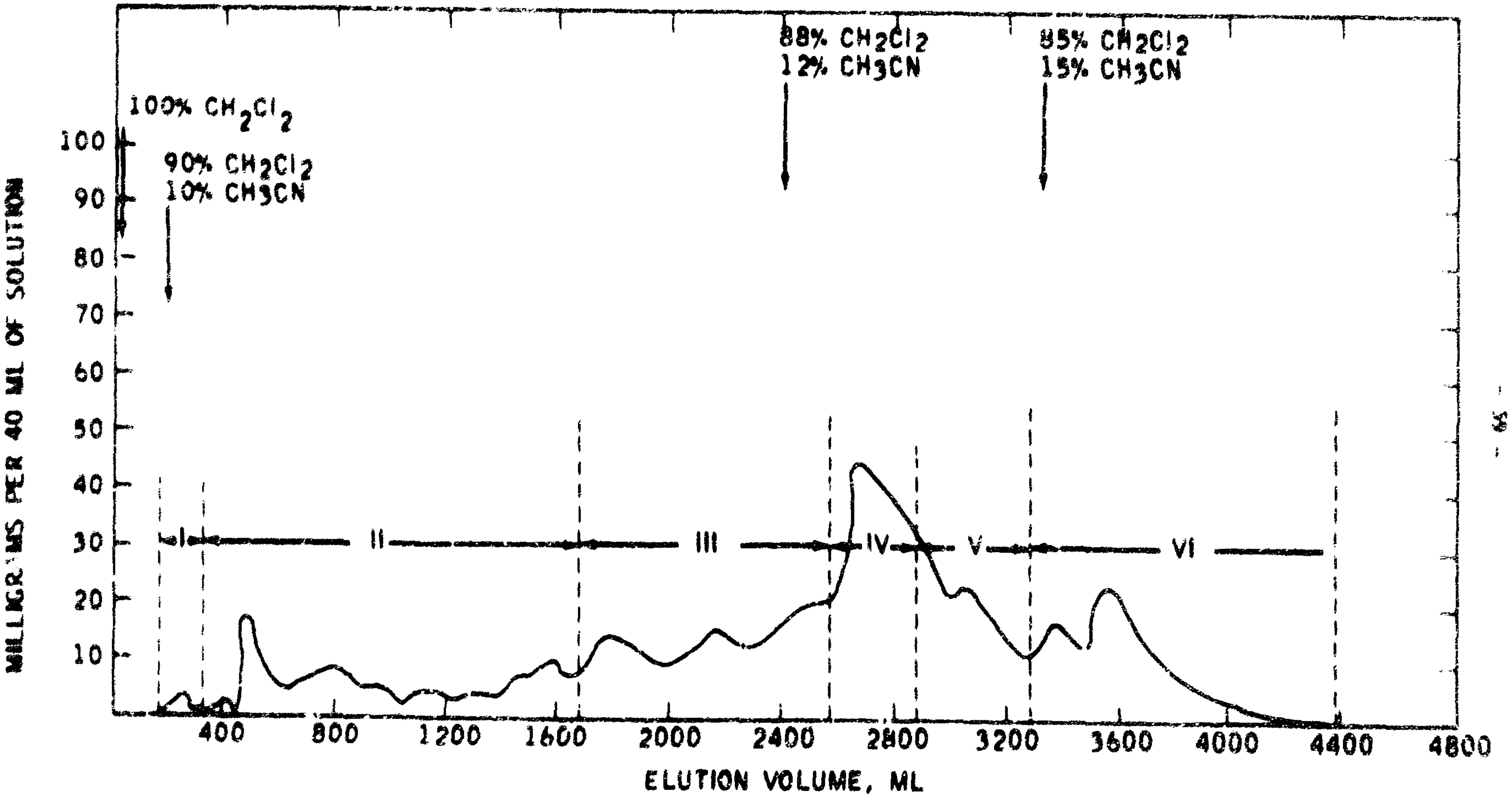


Figure 12. ELUTION PROFILE OF ROCKETDYNE'S P-GDNFE, LOT E11-68. RUN 471-116; SILICA GEL/POLYMER RATIO = 86/1.

E. Functionality and Functionality Distribution Measurements of 3M's Perfluoroalkylene Oxide Prepolymer (FC2202)

A sample of 3M's FC2202, lot 2, was received from Allegheny Ballistics Laboratory for characterization. The functionality distribution of this new 3M prepolymer is of particular interest since it reportedly differs significantly in functionality from 3M's old prepolymer (HYPFO). A sample of the old HYPFO prepolymer had previously been analyzed by Esso (1) and found to have a functionality of 3.5. Functionality distribution measurements showed that the major components (>65 wt %) were polyfunctional ($f \geq 3$).

1. Functionality Determination

Equivalent weight measurements of 3M's FC2202 prepolymer, lot 2 have been carried out by reaction of the prepolymer with toluenesulfonyl isocyanate. Since the prepolymer is not soluble in chloroform, our standard solvent, a new calibration was established in Freon-215 (trichloropentafluoropropane). Figure 33 shows the linear calibration plot relating toluenesulfonyl isocyanate absorbance at 4.46μ to wt % concentration of the isocyanate in Freon 215.

Equivalent weight measurements were made in duplicate yielding the following values:

	Equivalent Weight (Grams/Mole of OH)
	1100
	1120
Average	1110

This value is in good agreement with data reported by the 3M Company (1090 grams/mole of OH).

Molecular weight measurements were obtained by VPO in Freon-215 at 37°C. The extrapolated molecular weight was found to be $(\bar{M}n)_o = 2300$. Based on these measurements the calculated functionality is:

$$f = \frac{2300}{1110} = 2.07$$

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(1) A. H. Muenker and B. E. Hudson, "Functionality Determination of Binder Prepolymers", Esso Research and Engineering Company, Sept. 1968, AFRPL-TR-68-237.

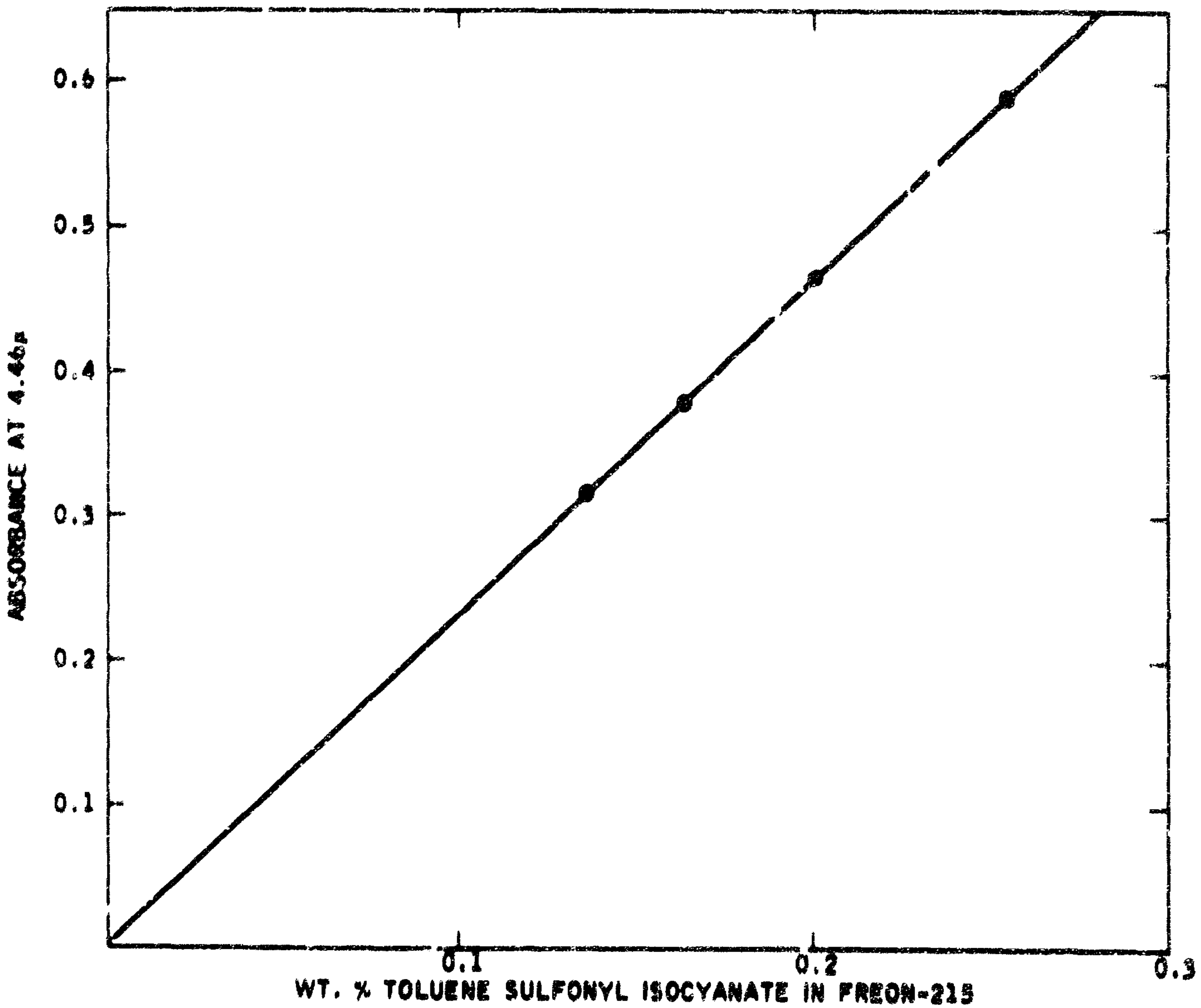

Figure 33. CALIBRATION PLOT OF TOLUENESULFONYL ISOCYANATE (TSNCO) IN FREON 215 RELATING ISOCYANATE ABSORBANCE AT 4.46μ TO WT. % CONCENTRATION; 0.1 mm THICK MATCHED LIQUID ABSORPTION CELLS.

2. Functionality Distribution Measurements

To find a suitable solvent system for the fractionation of the FC2202 prepolymer on silica gel we initially studied the system Freon 113 and mixtures of Freon 113 with diethyl ether. Prepolymer solubility limits the number of potential solvent systems. The above solvent system has resulted in the elution profile shown in Figure 34. Recovery was 95%. The eluted polymer was recombined into four major fractions for analysis:

Identification: 471-118
Silica gel/polymer ratio: 84/1
Total polymer charged: 1.186 g
Polymer recovery: 95.3%

Fraction	Wt. % of Total	Equivalent Weight (Grams/Mole of OH)	$(M_n)_0$	Functionality
I	12.7	6040	2200	0.36
II	40.2	1510	3100	2.05
III	19.1	860	1800	2.09
IV	23.3	620	1300	2.1
	95.3%			

Analysis of the individual fractions shows that the non- and monofunctional content is about 12-13 wt %, the remainder being difunctional.

One additional fractionation of FC2202, lot 2, has been carried out on activated silica gel using Freon 113 and mixtures of Freon 113 and acetonitrile as the eluting solvent (see Figure 35). Fractionation has again yielded fractions of increasing hydroxyl content. However, only 69% of the polymer charged was eluted from the column. Three major fractions were isolated for analysis:

Identification: 471-133
Silica gel/polymer ratio: 60/1
Total polymer charged: 1.[illegible]34 g
Polymer recovery: 69.2%

Fraction	Wt. % of Total	Equivalent Weight (Grams/Mole of OH)
I	3.4	18,000
II	7.3	2,900
III	58.5	980
	69.2%	

Fraction I which accounts for 3.4 wt. % of the total polymer is essentially nonfunctional. Based on the analysis of the two fractionations (471-133 and 471-118) the nonfunctional content is about 3-5% and the monofunctional prepolymer content is 7-9%.

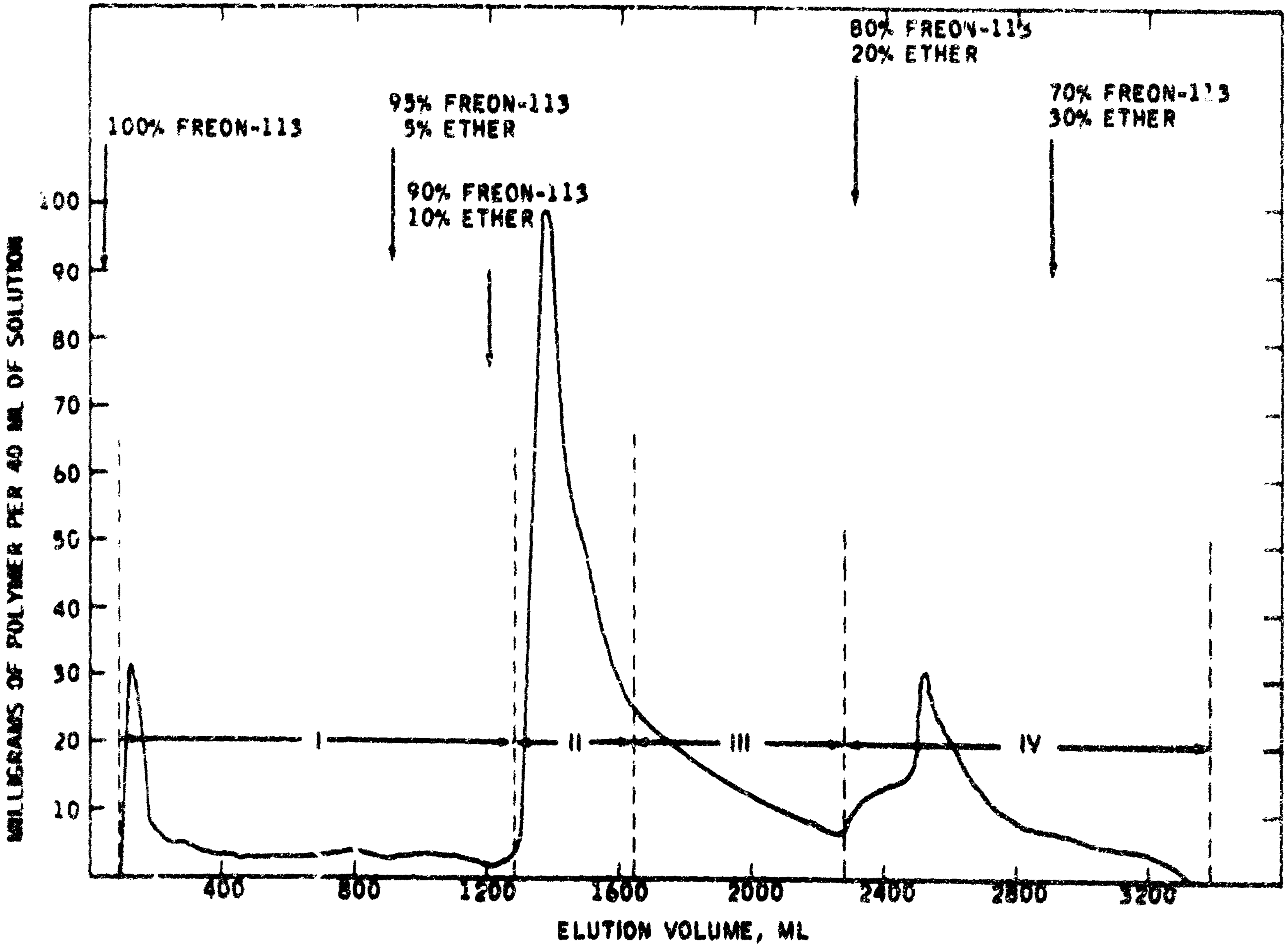

Figure 34. ELUTION PROFILE OF THE FRACTIONATION OF 3M'S FC2202, LOT 2, PREPOLYMER.
RUN 471-118; SILICA GEL/POLYMER RATIO = 84/1.

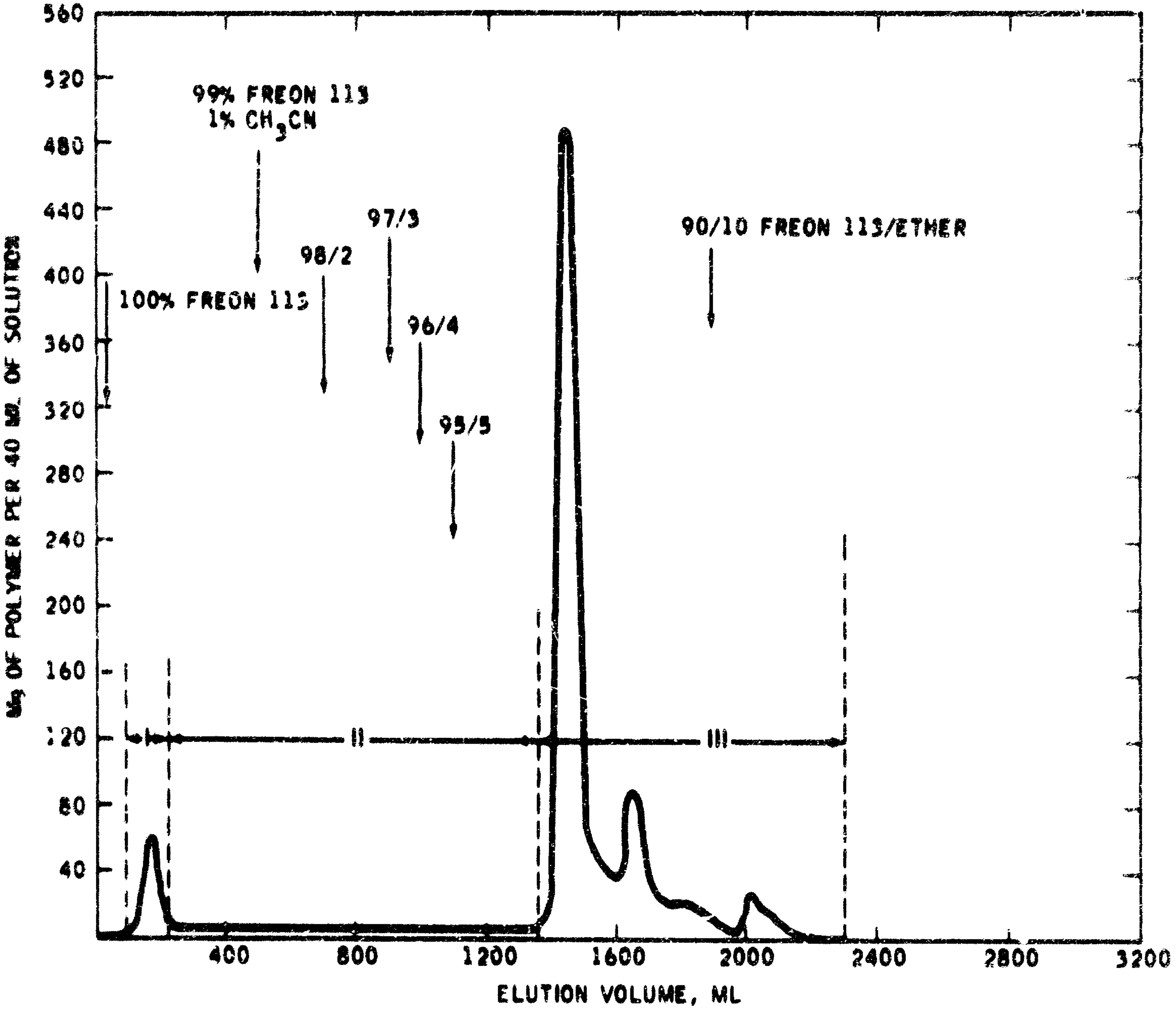

Figure 15. ELUTION PROFILE OF THE FRACTIONATION OF 3M'S FC2202, LOT 2, PREPOLYMER: RUN 471-133; SILICA GEL/POLYMER RATIO ~ 60/1.

F. Effect of Prepolymer Functionality on Mechanical Properties of HT-Telagen Gumstocks

The ability to determine the functionality distribution of prepolymers and to separate prepolymers into non-, mono- and difunctional components has opened up new areas of binder studies. The following sections deal with the mechanical properties of gumstocks prepared from a purely difunctional polybutadiene prepolymer and compare these properties to gumstocks from "as received" prepolymer. Also the relationship between mechanical properties and monofunctional prepolymer content has been explored.

1. Mechanical Properties of Gumstocks Prepared from Pure Difunctional HT-Telagen and "As Received" HT-Telagen

Gumstocks have been prepared from the pure difunctional HT-Telagen prepolymer previously isolated by silica gel chromatography (see Section B-2.3) and compared to gumstocks prepared from "As Received" HT-Telagen, lot 242 AM 292/316 AM6. Three isocyanate cure systems were evaluated representing one aromatic and two aliphatic diisocyanates. In all cases, triisocyanates were used as crosslinkers:

- 2,4-Tolylene diisocyanate/triphenyl methane triisocyanate
- Hexamethylene diisocyanate/triphenyl methane triisocyanate
- DDI/triphenyl dimethylene triisocyanate

The diisocyanates, except General Mills' DDI, were distilled prior to use. The two triisocyanates, triphenyl methane triisocyanate and triphenyl dimethylene triisocyanate, were purified by precipitation and subsequent vacuum distillation (1). All gumstocks were prepared at stoichiometric (1/1) NCO/OH ratio and cured at 150°F for seven days. Uniaxial tensile-strain properties were measured at 2 inches/minute crosshead speed using micro-dumbbells.

Mechanical property measurements were made at three temperatures: -65°, 75° and 180°F. Data for the pure difunctional gumstocks and gumstocks prepared from "As Received" HT-Telagen prepolymer are tabulated in Tables II through VII and graphically presented in Figures 36 through 47.

Figures 36 through 38 show the effect of di/triisocyanate ratio on the <u>maximum stress</u> of a "pure difunctional" HT-Telagen gumstock as compared to HT-Telagen as received. All three cure systems show the same directional effect:

- Gumstocks prepared from pure difunctional HT-Telagen exhibit significantly higher maximum stress levels than those prepared from HT-Telagen as received.

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(1) Muenker, A. H., C. A. Rowe, et al., "Synthesis and Evaluation of Curing Agents," Esso Research and Engineering Company, Annual Report, March 1969, AFRPL-TR-69-136.

- The pure "difunctional" gumstocks and gumstocks prepared from "as received" HT-Telagen show essentially a parallel dependence of maximum stress on triisocyanate level except at -65°F for the TDI/TTI and HDI/TTI cure systems.

- The difference in maximum stress level for the "difunctional" and "as received" gumstocks is most pronounced for the TDI/TPMT cure system (Figure 36).

- Because of the higher maximum stress level of gumstocks prepared from pure difunctional prepolymer the crosslinker level can be significantly reduced to 10% equivalent triisocyanate or even lower.

The effect of di-/triisocyanate ratio on the strain level at maximum stress is depicted in Figures 39 through 41:

- In each case the strain values of the pure "difunctional" gumstock are displaced to the left (towards lower triisocyanate levels).

- At comparable triisocyanate levels the "pure difunctional" gumstock exhibits lower maximum strain levels. In practice this implies that the pure difunctional gumstock will require lower triisocyanate levels. Because of the monofunctional content of the HT-Telagen "as received" the latter gumstock will exhibit lower crosslink density and hence higher strain levels than the pure difunctional gumstock at identical triisocyanate levels.

- The three cure systems show essentially the same dependence of strain at maximum stress on triisocyanate level.

- At -65°F the dependence of strain at maximum stress on triisocyanate level is less pronounced which reflects the increased stiffness of the backbone at this low temperature.

Figures 42 through 44 show that the pure difunctional HT-Telagen gumstocks exhibit significantly higher initial moduli:

- The gumstock employing a total aromatic cure system (TDI/TPMT) (see Figure 42) shows again the most dramatic effect.

- The two aliphatic diisocyanate chain-extended gumstocks show essentially the same dependence on triisocyanate level.

- At -65°F all three "difunctional" gumstocks show only a slight dependence of initial modulus on triisocyanate level at the level of interest to propellants (5 to 40% equivalent triisocyanate).

- Also the difference in initial moduli between the "difunctional" gumstock and "as received" gumstock diminishes as the temperature is decreased.

- To obtain low initial moduli in gumstocks when using a pure difunctional prepolymer, triisocyanate levels below 10 equivalent % are indicated.

Figures 45 through 47 compare the Shore "A" hardness values at 75°F for the pure "difunctional" HT-Telagen with those obtained from HT-Telagen "as received". At comparable triisocyanate levels the pure difunctional gumstock exhibits consistently significantly higher hardness. This obviously reflects the higher crosslink density of the pure difunctional gumstock. The differences in Shore "A" hardness are most pronounced for the 2,4-tolylene diisocyanate/triphenyl methane triisocyanate cured gumstocks (see Figure 45). A comparison of Figures 46 and 47 shows that the aliphatic diisocyanate cure systems (HDI and DDI) give essentially identical hardness values at comparable triisocyanate levels. The aromatic diisocyanate (TDI, Figure 45), results in higher hardness values than cure systems employing aliphatic diisocyanates.

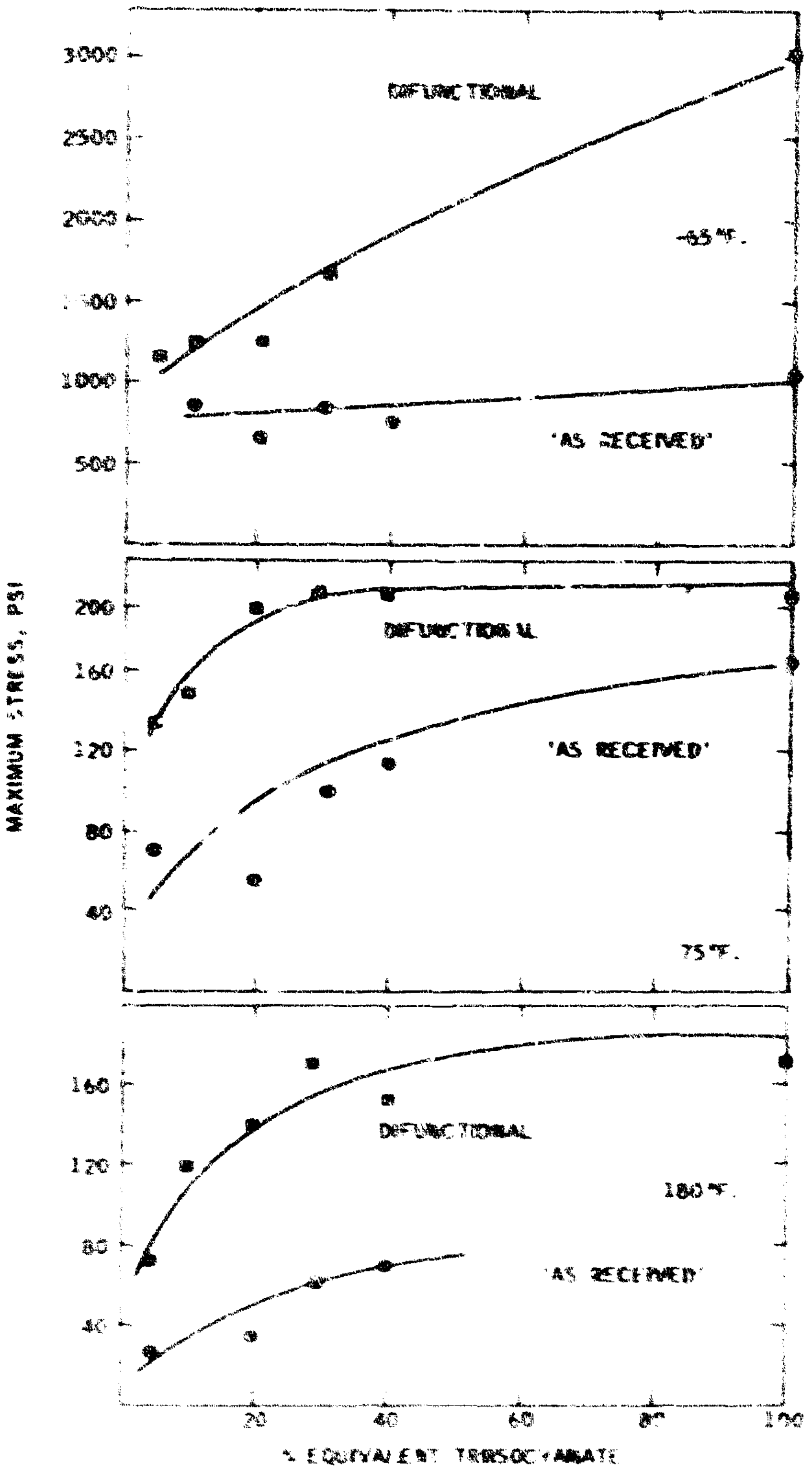

Figure 36. <u>MAXIMUM STRESS</u> OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN "AS RECEIVED". DEPENDENCE OF MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM <u>2,4-TOLYLENE DIISOCYANATE TRIPHENYL METHANE TRIISOCYANATE</u>

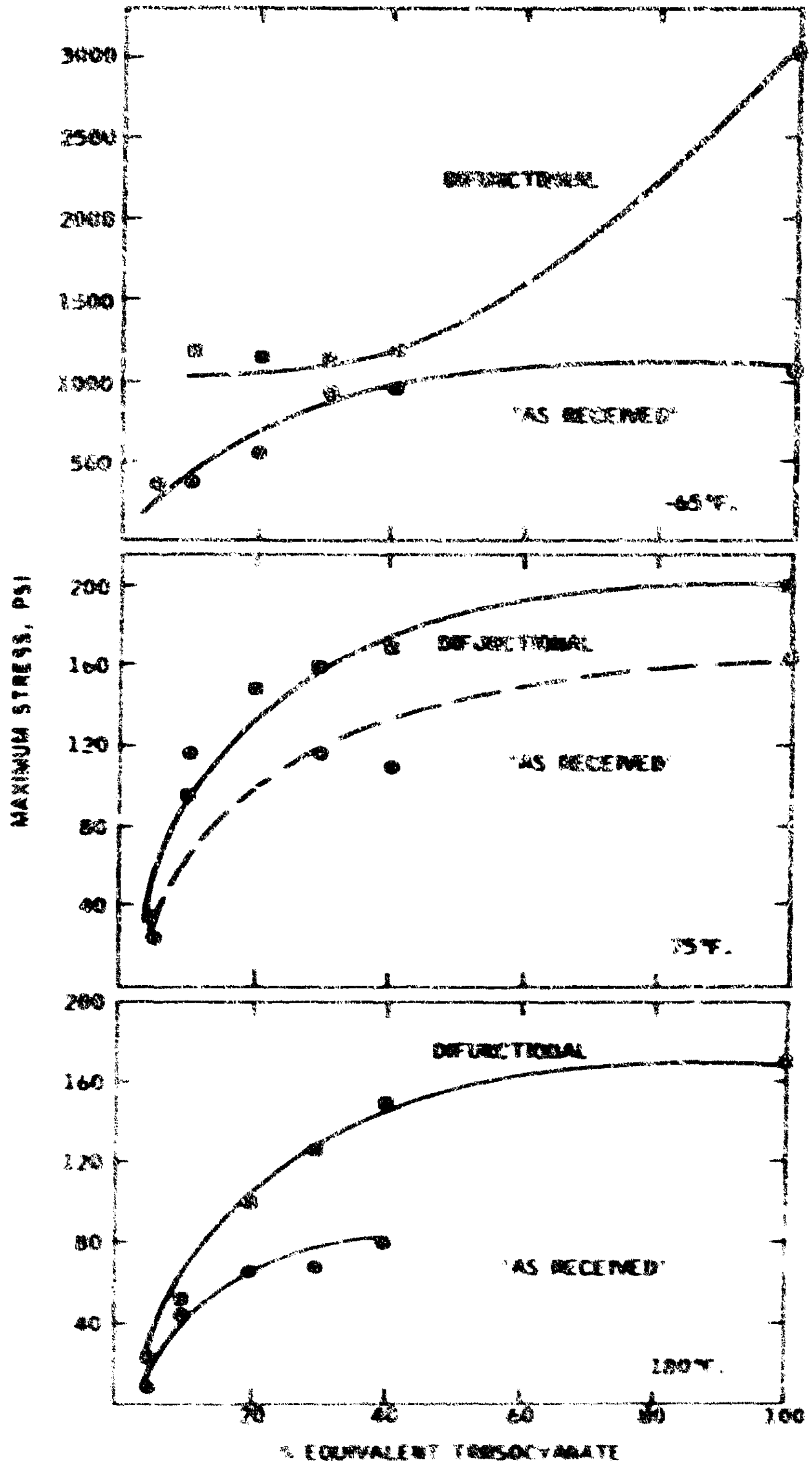

Figure 37. MAXIMUM STRESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN AS RECEIVED. DEPENDENCE OF MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: HEXAMETHYLENE DIISOCYANATE TRIPHENYL METHANE TRIISOCYANATE.

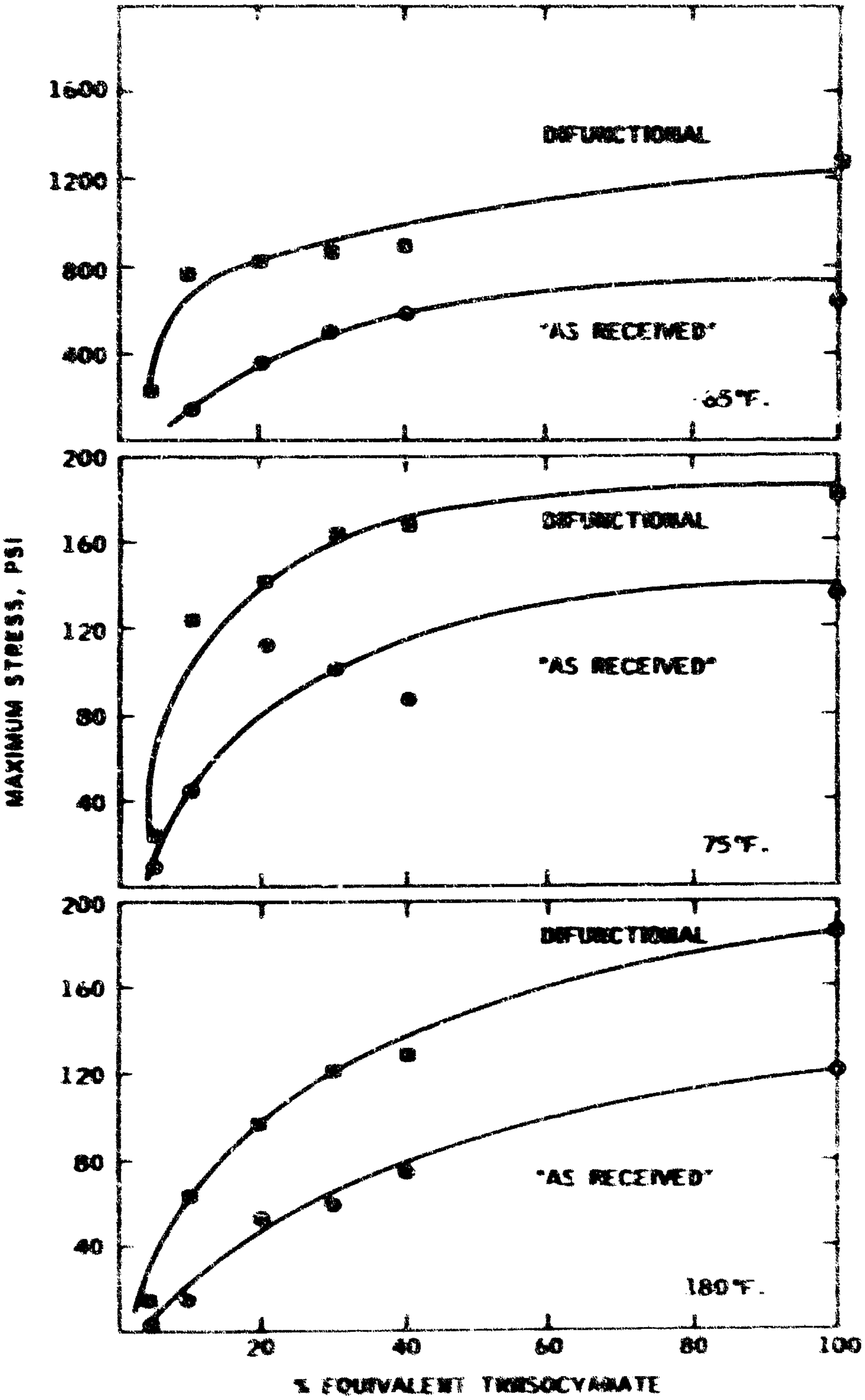

Figure 38. MAXIMUM STRESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN "AS RECEIVED". DEPENDENCE OF MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: DDI/TRIPHENYL DIMETHYLENE TRIISOCYANATE.

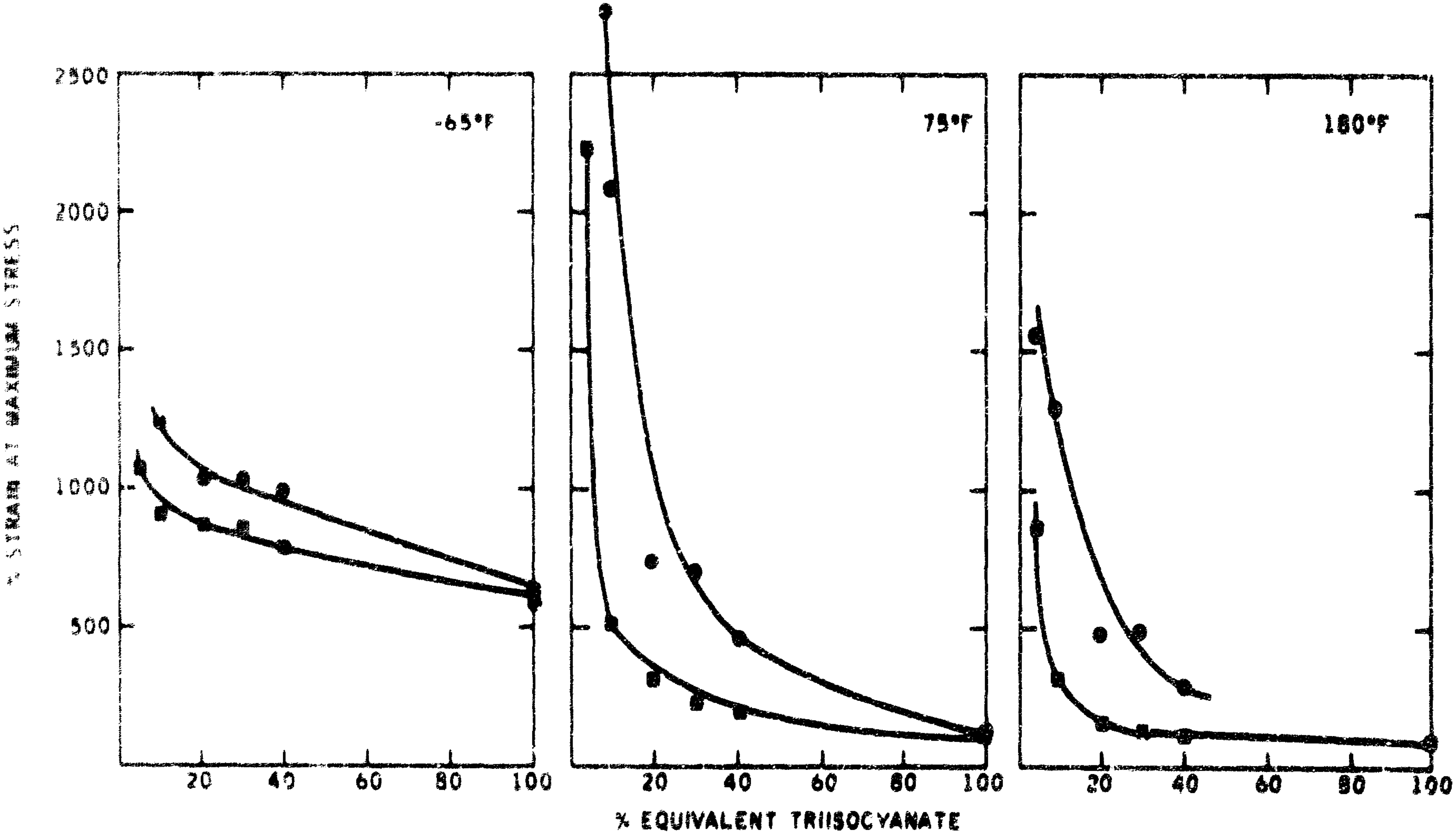

Figure 19 STRAIN AT MAXIMUM STRESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN AS RECEIVED. DEPENDENCE OF STRAIN AT MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE.

■ DIFUNCTIONAL
● "AS RECEIVED"

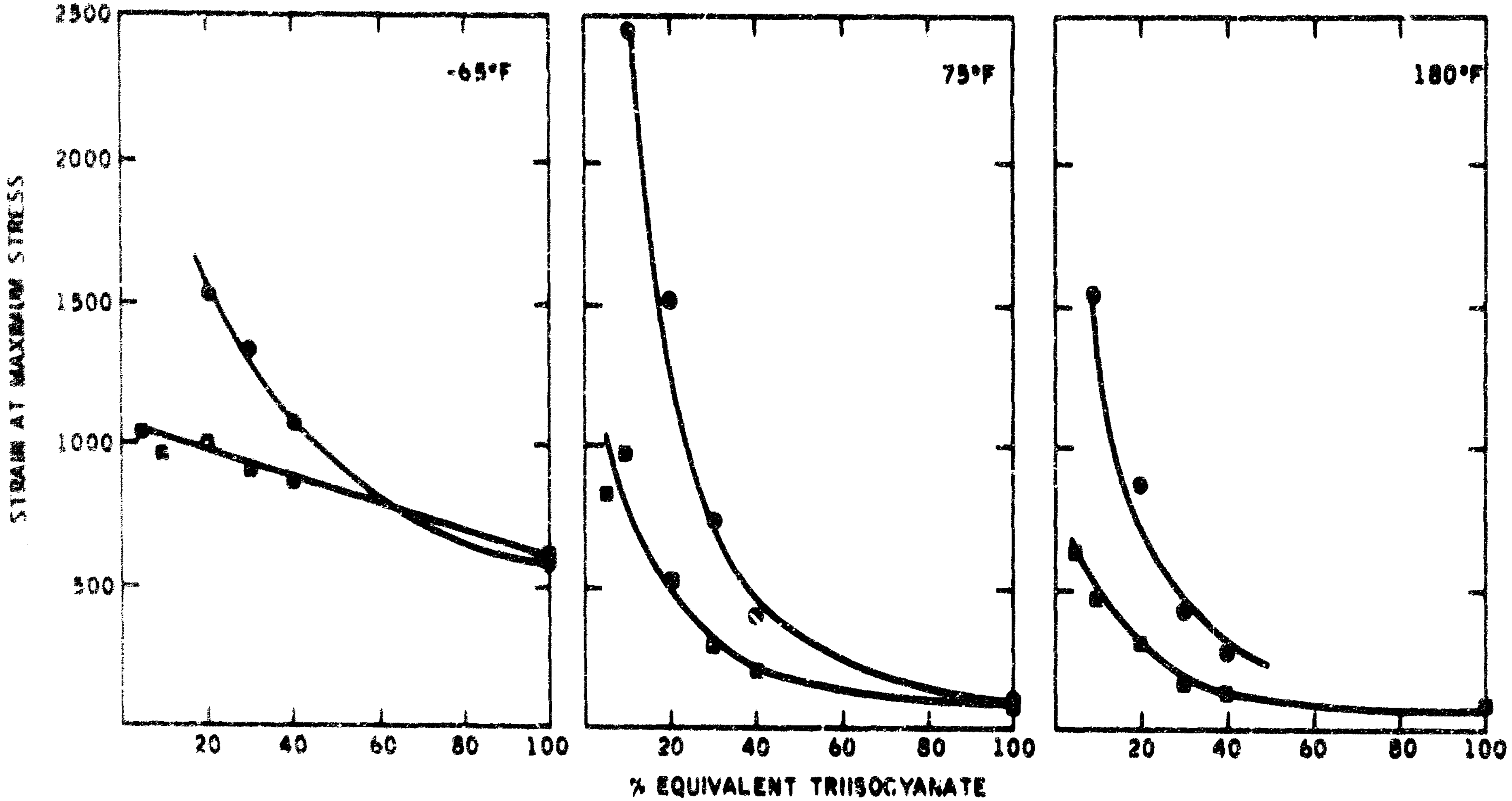

Figure 40. STRAIN AT MAXIMUM STRESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN AS RECEIVED. DEPENDENCE OF STRAIN AT MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: HEXAMETHYLENE DIISOCYANATE/TRIPHENYLMETHANE TRIISOCYANATE.

■ DIFUNCTIONAL
● "AS RECEIVED"

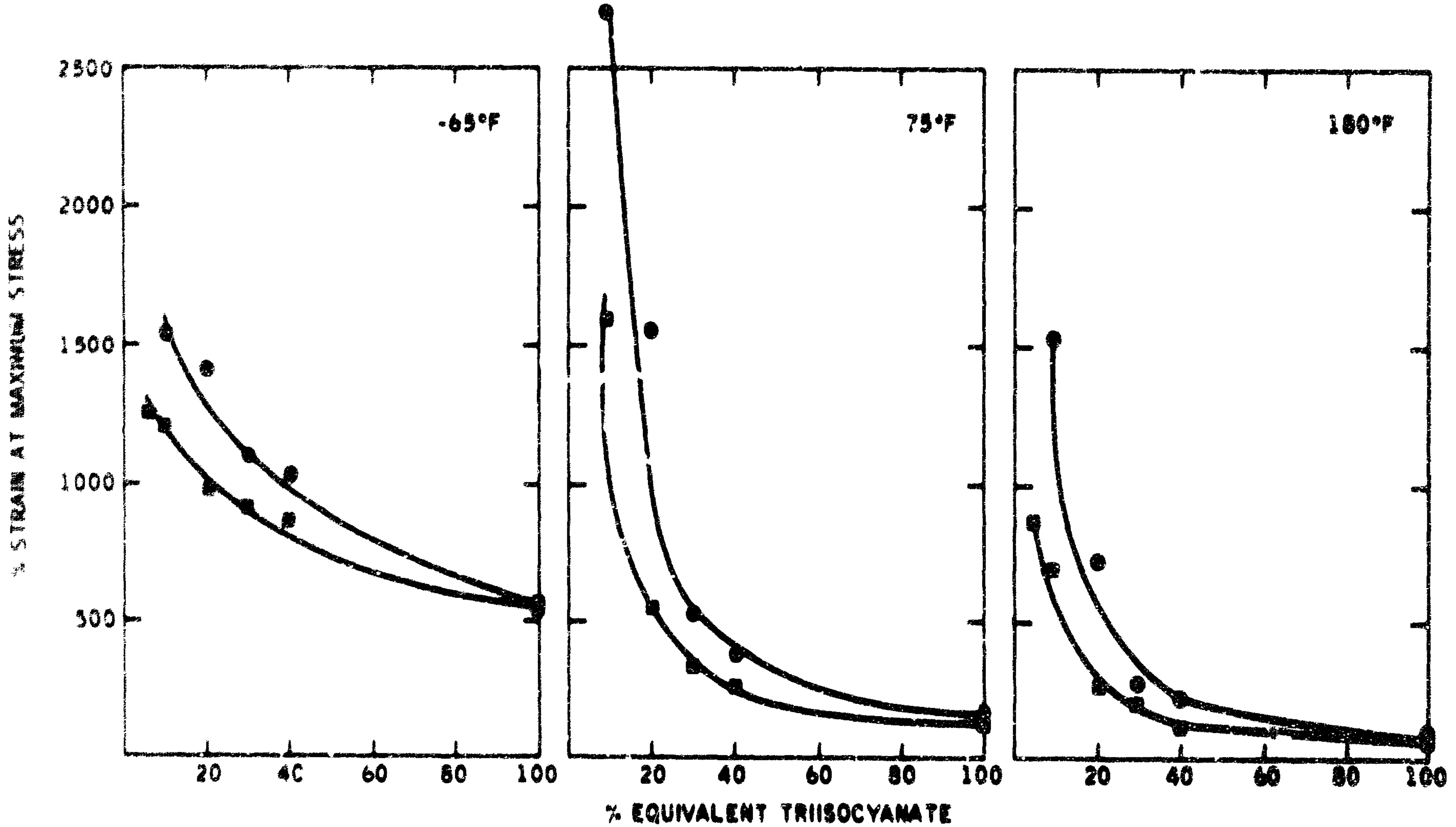

Figure 41. STRAIN AT MAXIMUM STRESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN AS RECEIVED. DEPENDENCE OF STRAIN AT MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: DDI/TRIPHENYL DIMETHYLENE TRIISOCYANATE.

■ DIFUNCTIONAL
● "AS RECEIVED"

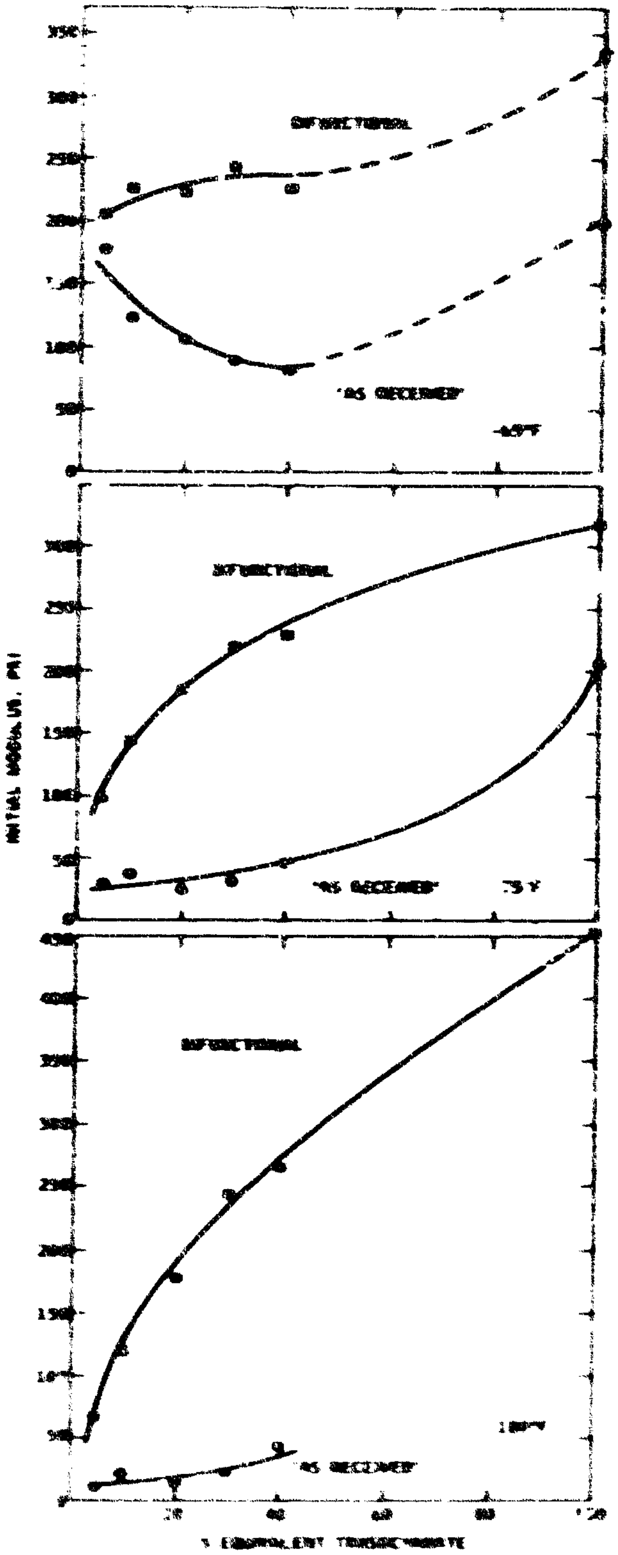

Figure 42. INITIAL MODULUS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN AS RECEIVED. DEPENDENCE OF INITIAL MODULUS ON TRIISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: 2,4-TOLYLENE DIISOCYANATE TRIPHENYLMETHANE TRIISOCYANATE

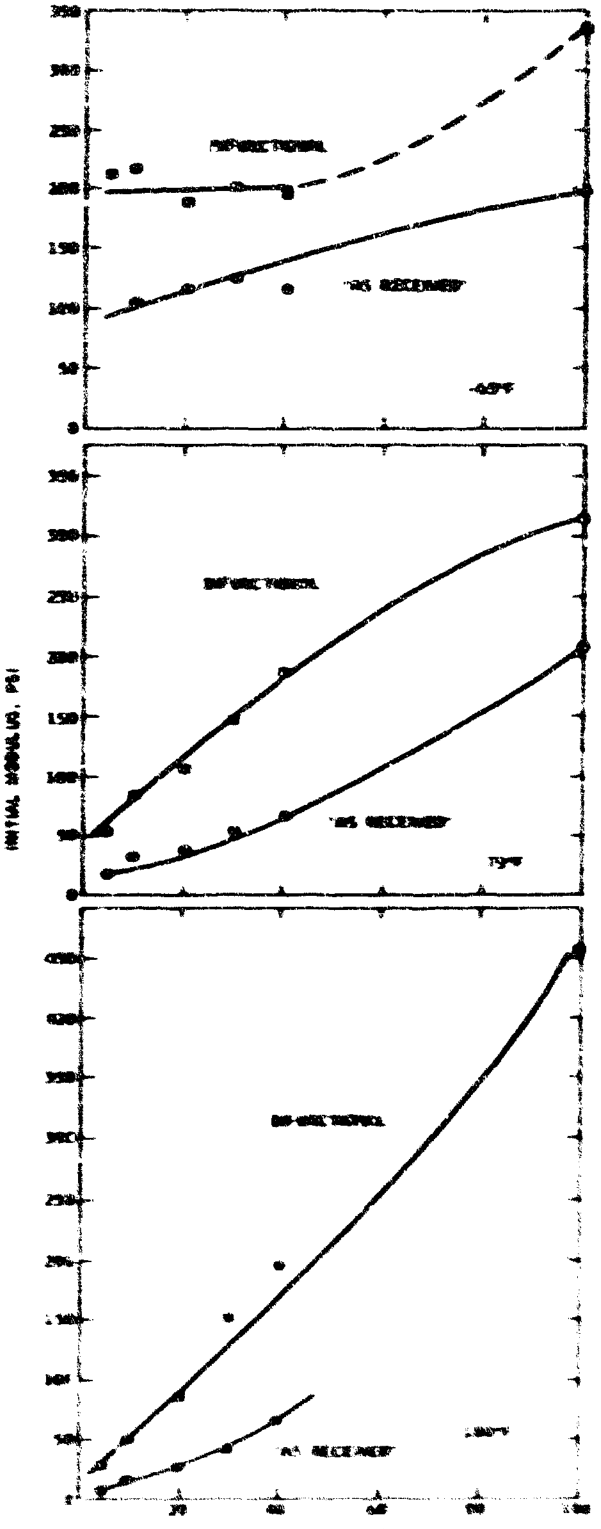

Figure 43 INITIAL MODULUS OF [illegible] PREPARED FROM PURE BIFUNCTIONAL [illegible] AND [illegible] AS RECEIVED. DEPENDENCE OF INITIAL MODULUS ON TRIFUNCTIONALITY LEVEL AT THREE TEMPERATURES [illegible]

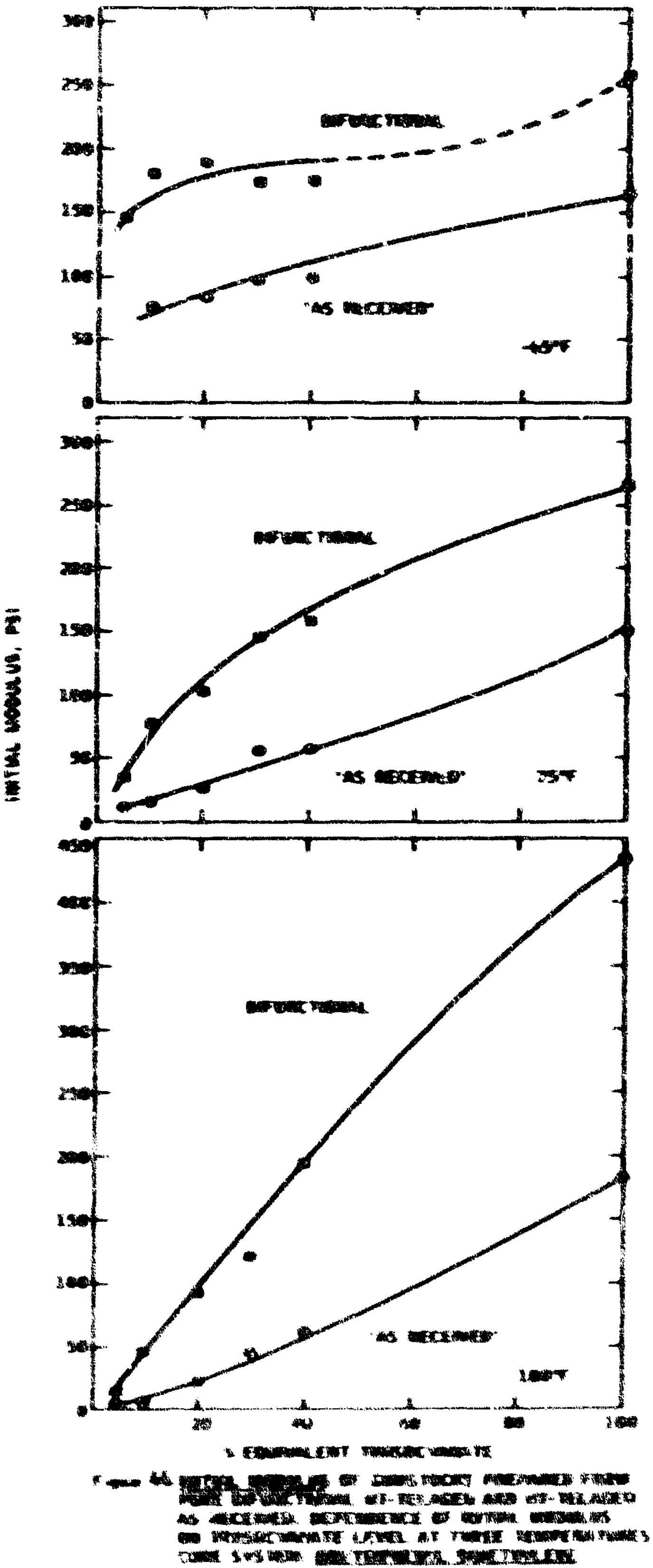

Figure 46 INITIAL MODULUS OF ELASTOMERS PREPARED FROM PURE BIFUNCTIONAL [illegible]-RELAXED AND [illegible]-RELAXED AS RECEIVED. DEPENDENCE OF INITIAL MODULUS ON POLYISOCYANATE LEVEL AT THREE TEMPERATURES. CURE SYSTEM: [illegible] TRIISOCYANATE

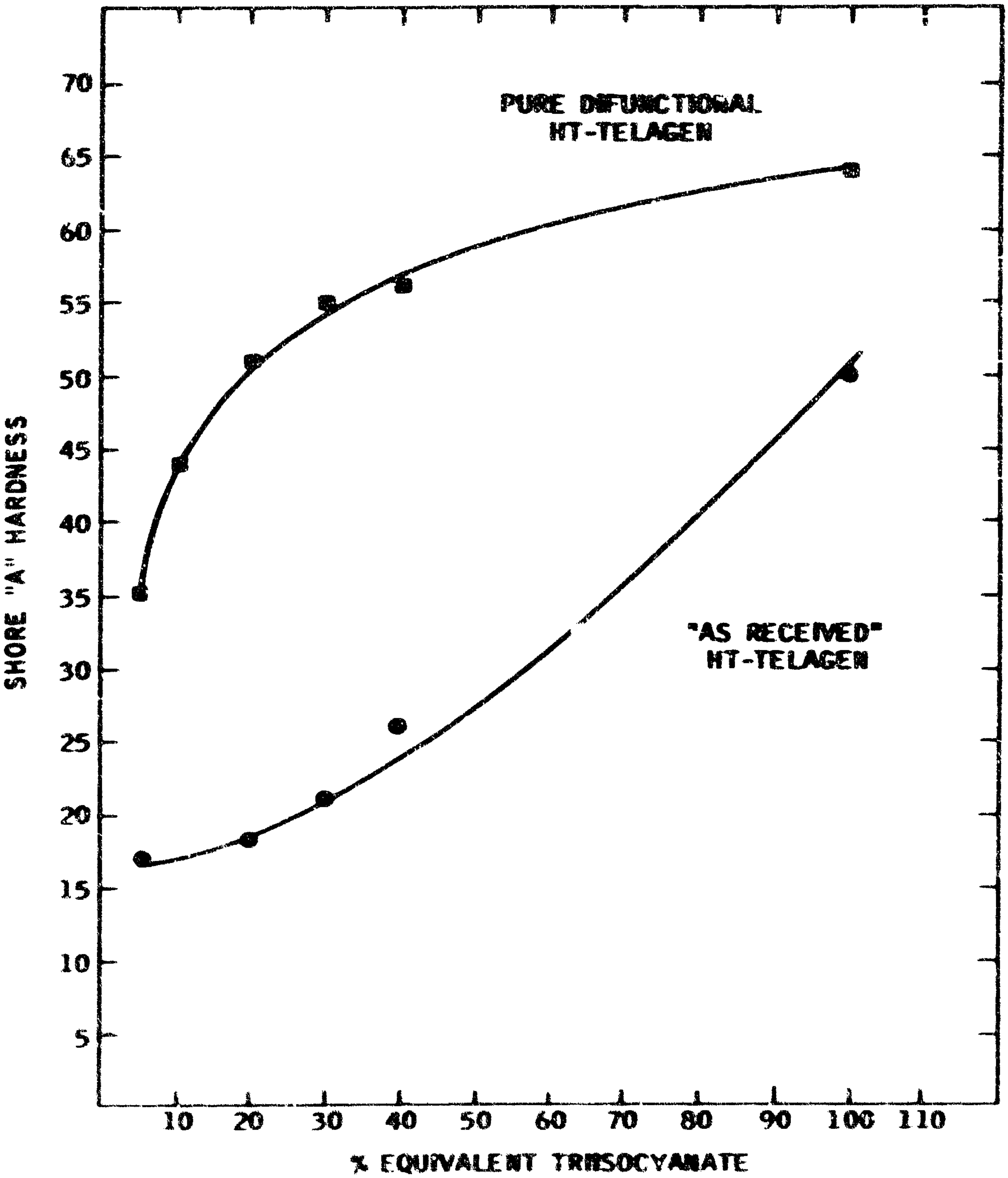

Figure 45. SHORE "A" HARDNESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN "AS RECEIVED". DEPENDENCE OF SHORE "A" HARDNESS ON TRIISOCYANATE LEVEL AT 75°F.. CURE SYSTEM: 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRI-ISOCYANATE.

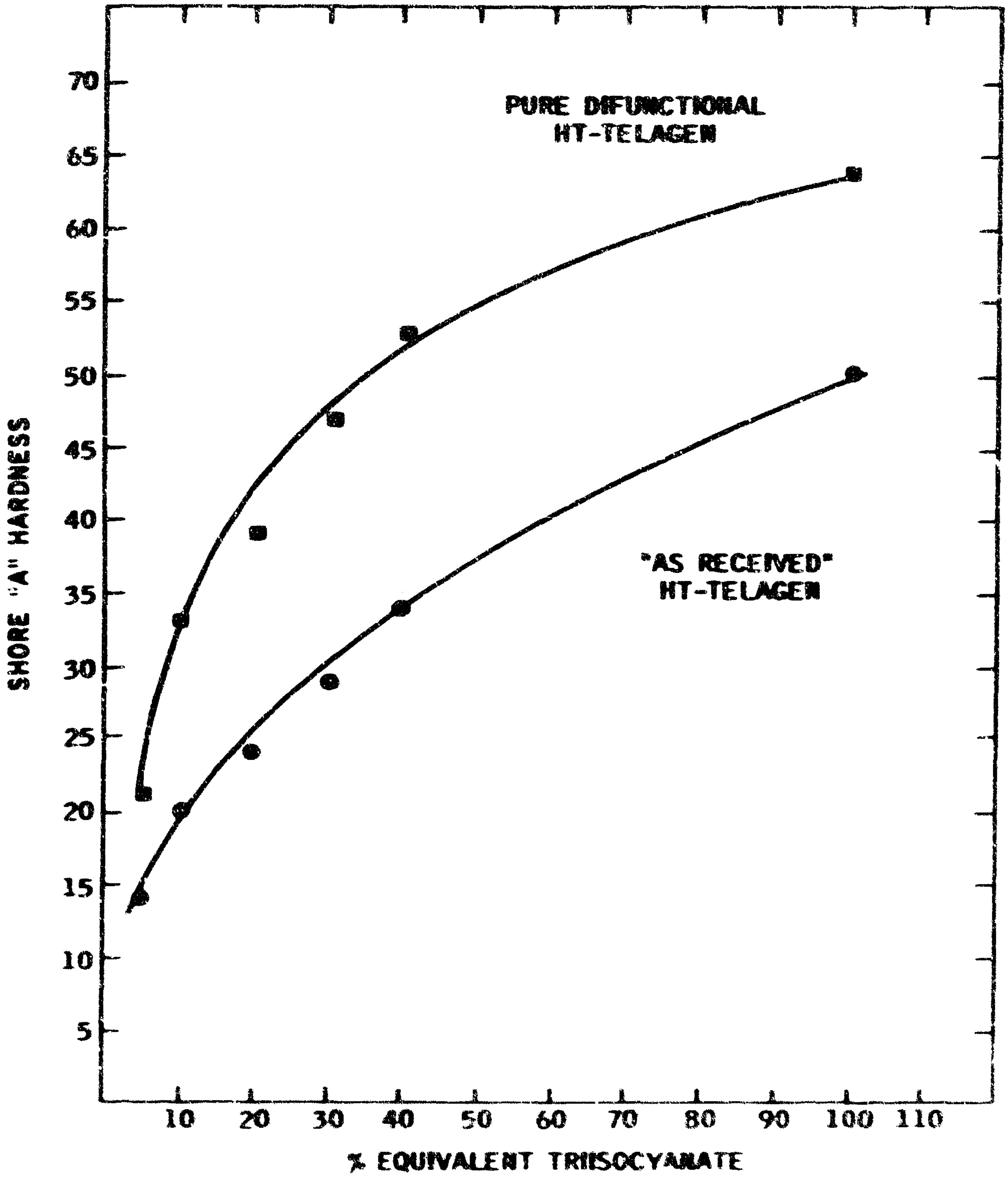

Figure 46. SHORE "A" HARDNESS OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN "AS RECEIVED". DEPENDENCE OF SHORE "A" HARDNESS ON TRIISOCYANATE LEVEL AT 75°F.. CURE SYSTEM: HEXAMETHYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE.

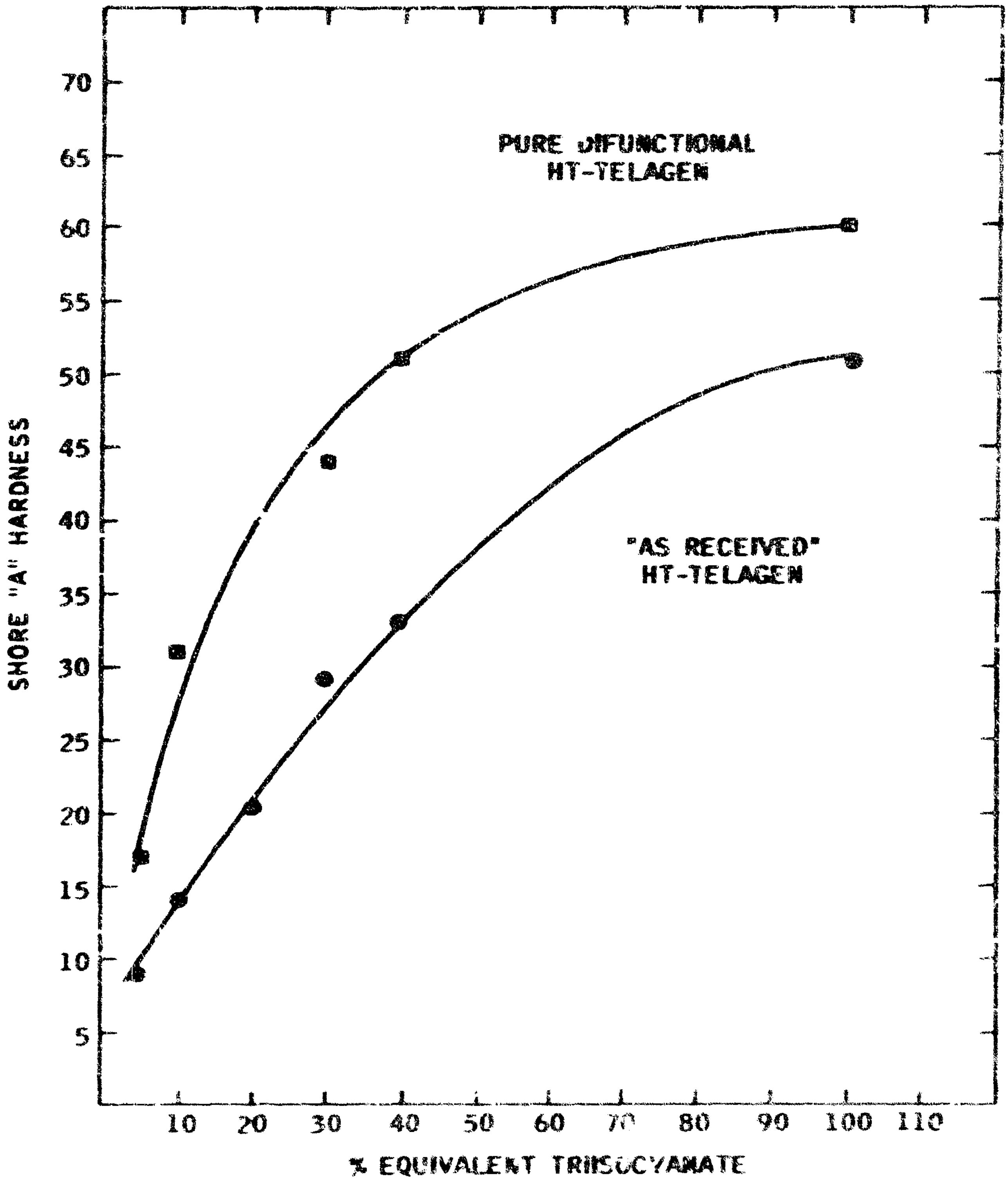

Figure 47. <u>SHORE "A" HARDNESS</u> OF GUMSTOCKS PREPARED FROM PURE DIFUNCTIONAL HT-TELAGEN AND HT-TELAGEN "AS RECEIVED". DEPENDENCE OF SHORE "A" HARDNESS ON TRIISOCYANATE LEVEL AT 75°F.. CURE SYSTEM: DDI/ TRIPHENYL DIMETHYLENE TRIISOCYANATE.

3. Effect of Monofunctional Prepolymer Components on the Mechanical Properties of HT-Telagen Gumstocks

In the preceding section the mechanical properties of gumstocks prepared from pure difunctional HT-Telagen were compared to gumstocks prepared from "as received" HT-Telagen prepolymer. In order to arrive at a quantitative correlation of the effect of monofunctional prepolymer components on gumstock mechanical properties we have added controlled amounts of monofunctional HO-polybutadiene to the pure difunctional HT-Telagen. Monofunctional prepolymer was added in increments of 4.5, 9, 18, and 27 mole % respectively.

The monofunctional prepolymer used in these studies had been isolated from the total HT-Telagen by silica gel chromatography (see Section B-2.3). Molecular weight and equivalent weight analysis yielded the following functionality:

$$f = \frac{(\overline{Mn})c}{Eq.\ Wt} = \frac{6000}{6100} = 0.98$$

Two cure systems were employed representing an aromatic diisocyanate (2.4-tolylene diisocyanate) and an aliphatic diisocyanate (General Mills' DDI). In each curative system a triisocyanate crosslinker was used (triphenylmethane triisocyanate and triphenyl dimethylene triisocyanate respectively). The di-/triisocyanate ratio was kept constant at 9/1. Mechanical property measurements were made at three temperatures. The results are tabulated in Tables VIII and IX and graphically represented in Figures 48 through 51.

The addition of monofunctional prepolymer to the difunctional prepolymer reduces the <u>maximum stress level</u> at a given di-/triisocyanate ratio. Figure 48 shows quantitatively the effect of mole % monofunctional prepolymer level on the maximum stress level for two cure systems:

- The percentage decrease in maximum stress level is similar at all three temperatures.
- The decrease in maximum stress upon addition of the first 5 to 10 mole % monofunctional polymer is more severe for the aliphatic diisocyanate (DDI) chain-extended gumstock.
- The aromatic diisocyanate (TDI) chain-extended gumstocks exhibit higher maximum stress levels at all temperature levels at comparable monofunctional polymer levels.

The addition of monofunctional prepolymer reduces the crosslink density of the gumstock at a given di-/triisocyanate curative ratio and consequently increases the <u>strain at maximum stress</u>. This effect is graphically shown in Figure 49. The increase in the maximum strain level is similar at the three temperatures except for the TDI/TTI curative system at 75°F which shows an initial sharp increase in maximum strain level with monofunctional prepolymer content.

The effect of monofunctional prepolymer content on the initial modulus at three temperatures is shown in Figure 50. The conclusions that can be drawn from these data can be summarized as follows:

- The initial modulus decreases with increase in monofunctional prepolymer content.
- The decrease is most significant upon addition of the first 5 to 10 mole % of monofunctional polymer, then levels off.
- As expected, the initial modulus increases with decrease in temperature showing only minor changes at temperatures between 75°F and 180°F but a more significant change between 75°F and -65°F.
- The two curative systems show parallel behavior. However, the aromatic (TDI) chain extended gumstock has a higher initial modulus at all three temperatures and at comparable monofunctional polymer levels.

Figure 51 shows an essentially linear decrease in Shore "A" hardness at 75°F with increase in monofunctional prepolymer content. The two cure systems show a similar behavior. However, the aromatic diisocyanate chain extended polymer shows clearly a higher Shore "A" hardness at comparable monofunctional prepolymers levels as compared to the corresponding aliphatic diisocyanate extended system. For instance, the gumstock, cured with a 9/1 TDI/TTI curative system in the presence of about 17 mole % monofunctional polymer has essentially the same hardness as a 9/1 DDI/TPDMI cured gumstock containing no monofunctional prepolymer. These data confirm similar studies on a related program (1) which have shown that aromatic diisocyanates have consistently resulted in gumstocks of greater hardness.

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(1) A. H. Muenker, C. A. Rowe et al., Esso Research and Engineering Company, "Synthesis and Evaluation of Curing Agents", Annual Technical Report, AFRPL-TR-69-136, March 1969.

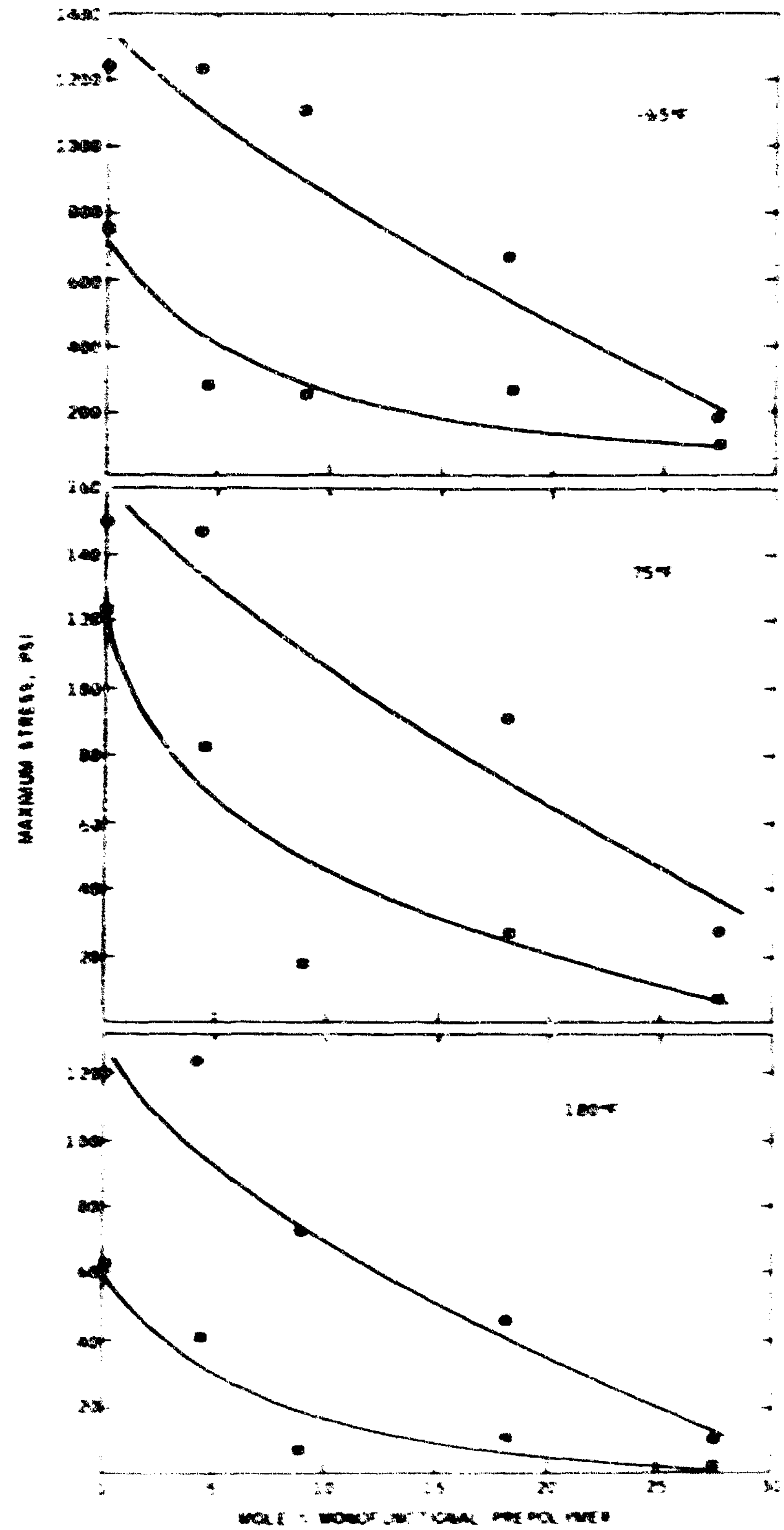

Figure 48 EFFECT OF MONOFUNCTIONAL PREPOLYMER CONTENT ON MAXIMUM STRESS OF A HYDROXY-FUNCTIONAL POLYBUTADIENE PREPOLYMER WITH TELAGEN AT THREE TEMPERATURES. CURE SYSTEM (○ POINTS) [illegible] 2,4-TOLYLENE DIISOCYANATE, TRIPHENYL METHANE TRIISOCYANATE (● POINTS) [illegible] TRIPHENYL [illegible] TRIISOCYANATE

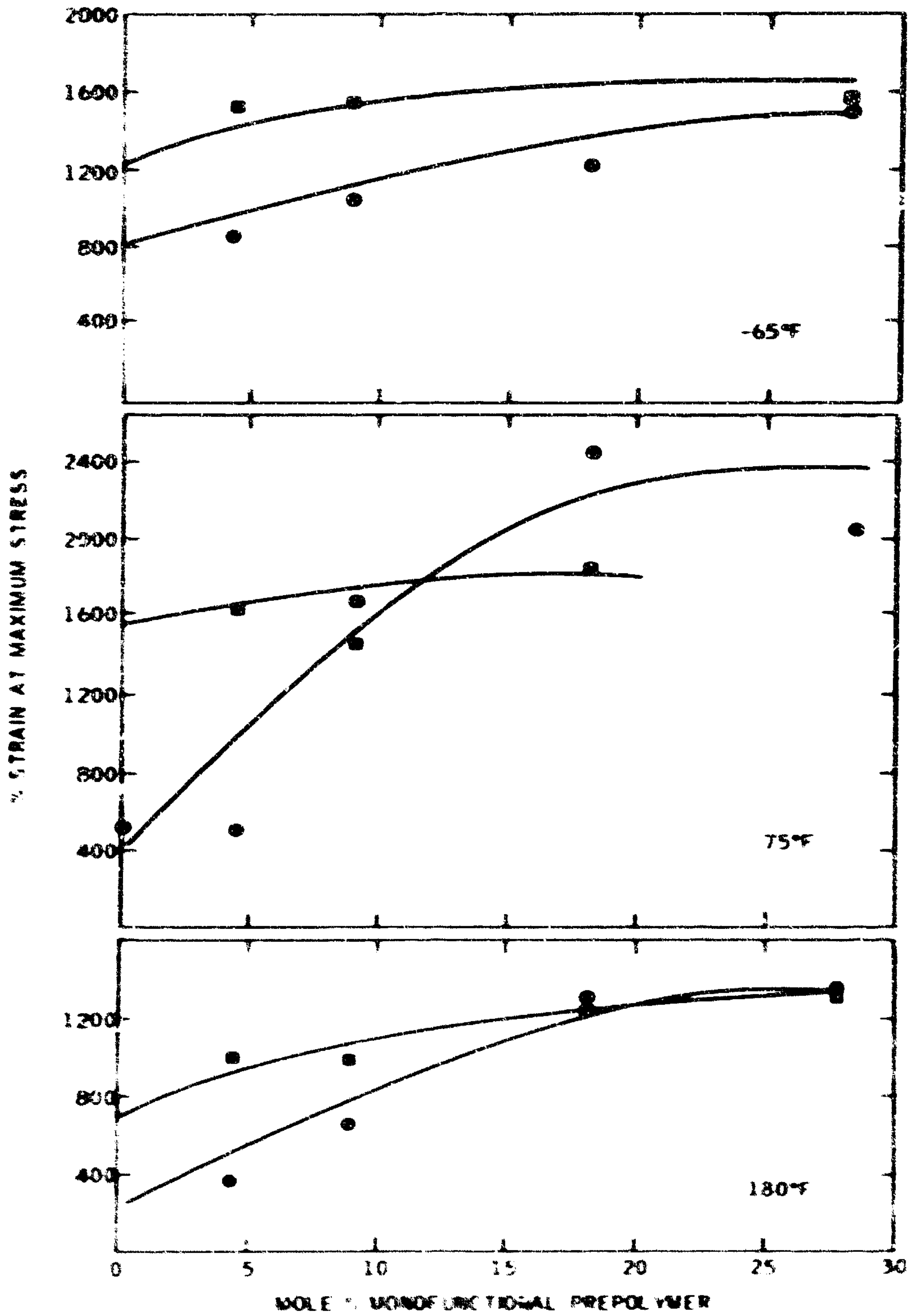

Figure 39. EFFECT OF MONOFUNCTIONAL PREPOLYMER CONTENT ON STRAIN AT MAXIMUM STRESS OF A HYDROXY-FUNCTIONAL POLYBUTADIENE PREPOLYMER (HT-TELAGEN) AT THREE TEMPERATURES. CURE SYSTEM (● POINTS): TOLUYLENE DIISOCYANATE TRIPHENYL METHANE TRIISOCYANATE (■ POINTS) 9:1 DDI TRIPHENYL DIMETHYLENE TRIISOCYANATE

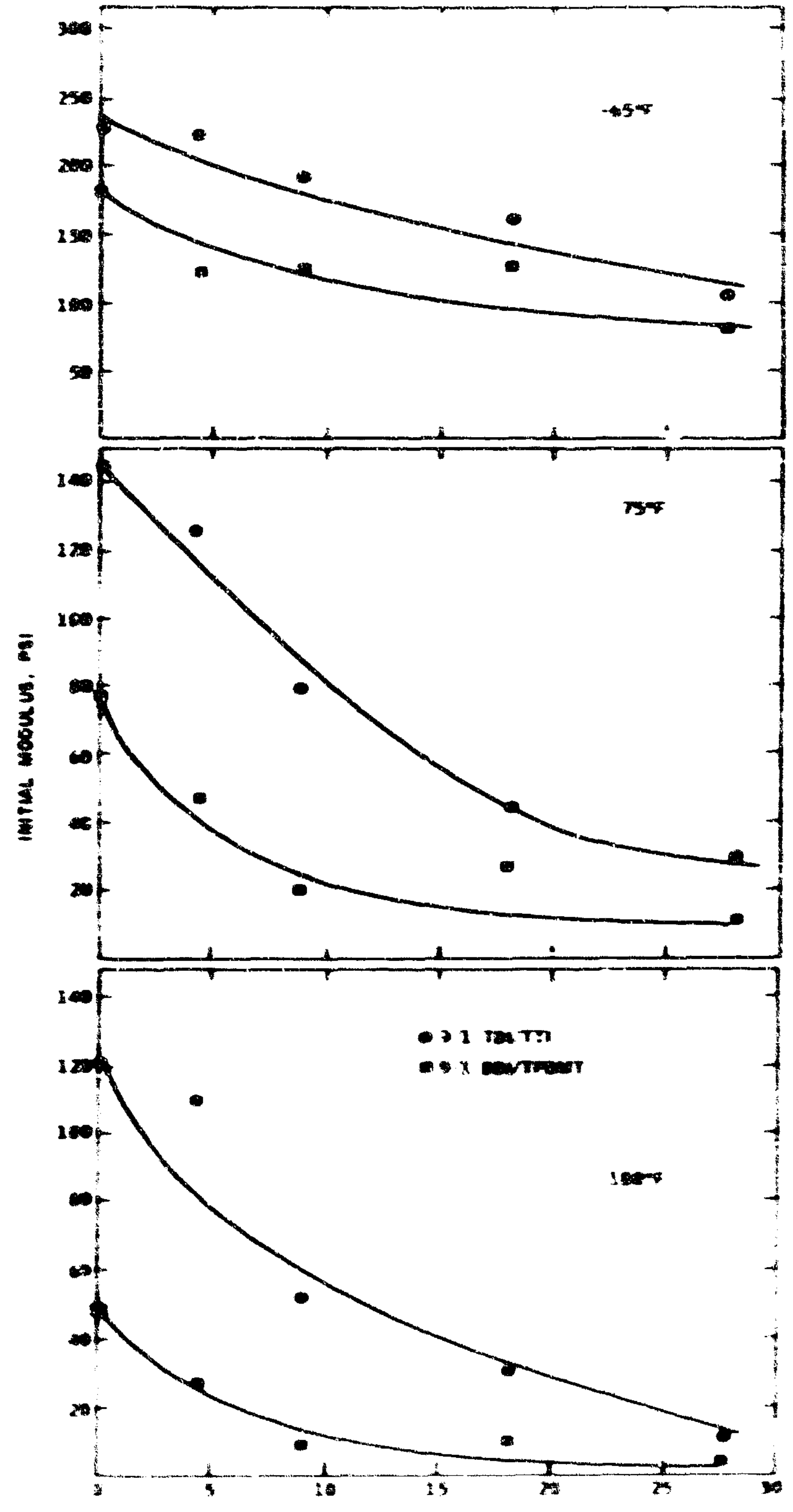

Figure 50. EFFECT OF MONOFUNCTIONAL PREPOLYMER CONTENT ON INITIAL MODULUS OF A HYDROXY-FUNCTIONAL POLYBUTADIENE PREPOLYMER [illegible] AT THREE TEMPERATURES. CURE SYSTEM: ● POINTS: 2,4-TOLYLENE DIISOCYANATE TRIPHENYL METHANE TRIISOCYANATE; ■ POINTS: [illegible] TRIPHENYL [illegible] TRIISOCYANATE

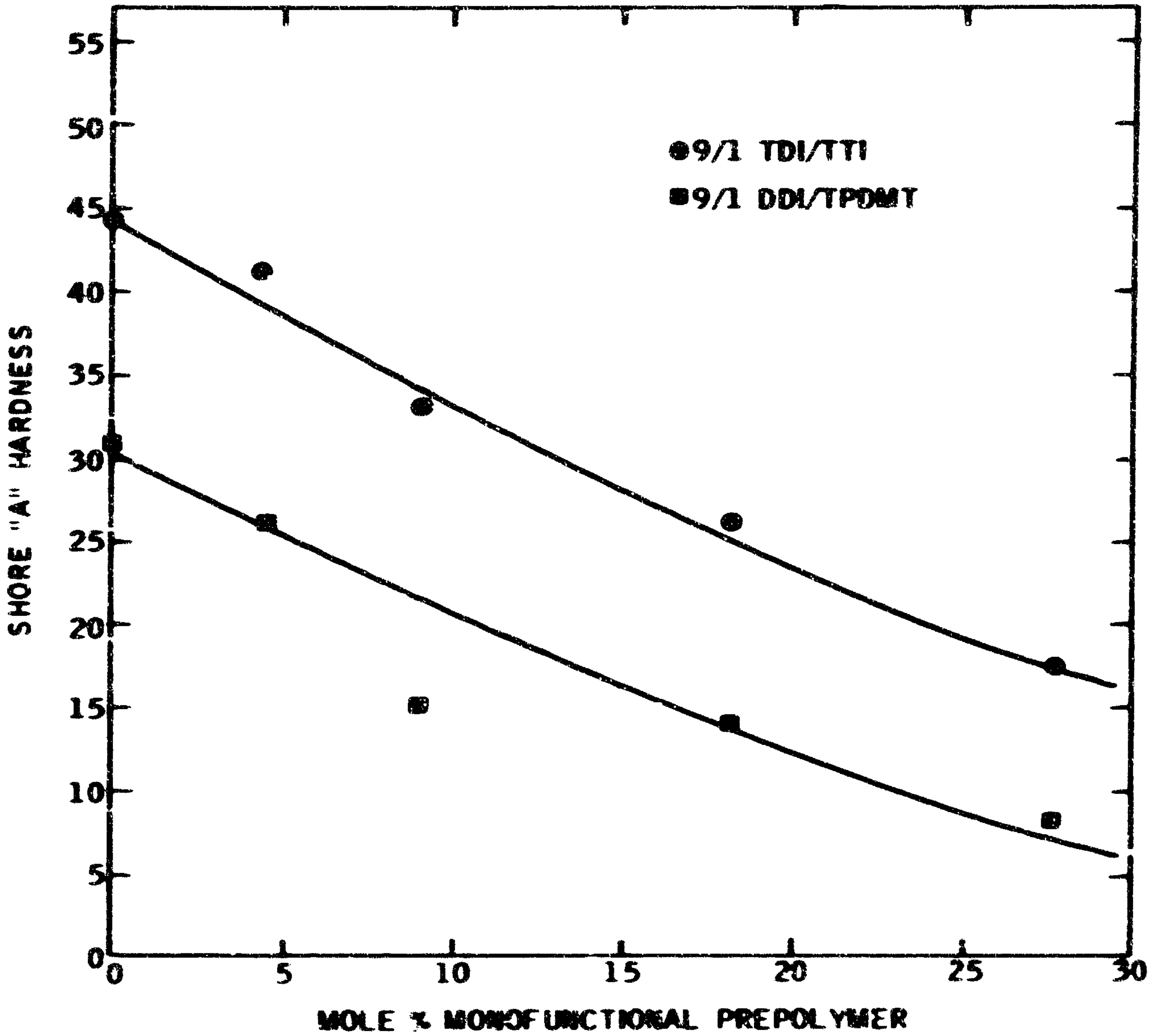

Figure 51. EFFECT OF MONOFUNCTIONAL PREPOLYMER CONTENT ON SHORE "A" HARDNESS OF A HYDROXY-FUNCTIONAL POLYBUTADIENE PREPOLYMER (HT-TELAGEN) AT 75°F. CURE SYSTEM: (● POINTS) = 9/1 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE; (■ POINTS) = 9/1 DDI/TRIPHENYL DIMETHYLENE TRIISOCYANATE.

TABLE II

MECHANICAL PROPERTIES OF DIFUNCTIONAL HI-TELAGEN GUMSTOCKS, 471-114-VI CURED WITH 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	35	134	2240	98
1/9	44	168	510	144
2/8	51	190	320	184
3/7	55	200	230	220
4/6	56	195	200	229
100% Triisocyanate	64	197	105	313

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	72	860	67.6
1/9	119	315	120
2/8	139	160	177
3/7	169	135	245
4/6	153	113	262
100% Triisocyanate	159	80	455

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	1170	1070	204
1/9	1270	905	226
2/8	1270	870	[illegible]
3/7	1690	865	242
4/6	1290	795	225
100% Triisocyanate	3020	615	33

TABLE III

MECHANICAL PROPERTIES OF DIFUNCTIONAL HT-TELAGEN GUMSTOCKS, 471-114-VI CURED WITH HEXAMETHYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	21	36	830	53
1/9	33	95	975	82
2/8	39	147	540	106
3/7	47	159	300	145
4/6	53	168	215	187
100% Triisocyanate	64	197	105	313

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	22	630	27.7
1/9	53	465	49.5
2/8	98	310	83
3/7	126	170	150
4/6	149	145	196
100% Triisocyanate	169	80	455

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	1630	1040	212
1/9	1170	970	217
2/8	1115	1000	189
3/7	1130	900	202
4/6	1140	875	195
100% Triisocyanate	1020	615	331

TABLE IV

MECHANICAL PROPERTIES OF BIFUNCTIONAL HT-TELAGEN GUMSTOCKS, 471-114-VI CURED WITH MDI DIISOCYANATE/ TRIPHENYL METHYLENE TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	17	24	1130	37
1/9	31	123	1590	77
2/8	40	142	550	102
3/7	44	163	340	145
4/6	51	168	270	158
100% Triisocyanate	60	181	135	266

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	13.5	860	16.7
1/9	63	700	47.5
2/8	96	270	92.5
3/7	120	205	121
4/6	128	125	194
100% Triisocyanate	186	95	433

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	230	1250	147
1/9	760	1210	180
2/8	810	970	190
3/7	870	910	174
4/6	900	870	176
100% Triisocyanate	1270	535	256

TABLE V

MECHANICAL PROPERTIES OF OH-TELAGEN GUMSTOCKS, LOT 242 AN 292/316 ANG, AS RECEIVED, CURED WITH 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	17	>70.4	>2720	30
1/9	21	154	2080	36.1
2/8	18-19	65	745	23.0
3/7	20-21	99	715	30.8
4/6	25-26	114	460	46.4
100% Triisocyanate	50	163	120	206

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	>25.5	>1560	13
1/9	63	1290	22
2/8	33	475	14.3
3/7	60	495	22.0
4/6	68	285	44.0
100% Triisocyanate	--	--	--

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	1250	1700	178
1/9	870	1330	123
2/8	665	1030	104
3/7	830	1045	90
4/6	755	980	81
100% Triisocyanate	1070	580	199

TABLE VI

MECHANICAL PROPERTIES OF OH-TELAGEN GUMSTOCKS, LOT 242 AM 292/316 AM6, AS RECEIVED, CURED WITH HEXAMETHYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	14	>24	>2720	19.4
1/9	20	117	2450	33.2
2/8	24	150	1510	37.7
3/7	29	115	750	51.8
4/6	34	107	400	66.5
100% Triisocyanate	50	163	120	206

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	>9	>1560	8
1/9	>43	>1530	16.5
2/8	65	870	27
3/7	67	415	40
4/6	80	260	65
100% Triisocyanate	—	—	—

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	365	2225	142
1/9	>360	1530	104
2/8	>620	>1530	117
3/7	930	1330	124
4/6	940	1070	119
100% Triisocyanate	1070	580	152

TABLE VII

MECHANICAL PROPERTIES OF OH-TELAGEN GUMSTOCKS, LOT 242 AM 292/316 AMG, AS RECEIVED, CURED WITH DDI/TRIPHENYL [illegible] TRIISOCYANATE

At Ambient Temperature (75°F)

Tri-/Diisocyanate Equivalent Ratio	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	9	8.9	1860	10.7
1/9	14	>44	>2720	16.8
2/8	20	112	1550	27.5
3/7	29	102	530	56.5
4/6	33	86	375	56.7
100% Triisocyanate	31	136	160	149

At 180°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	>3	>1560	4
1/9	>15	>1130	7.0
2/8	52	730	23.3
3/7	58	270	[illegible]
4/6	73	230	62
100% Triisocyanate	121	100	181

At -65°F

Tri-/Diisocyanate Equivalent Ratio	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0.5/9.5	440	1225	158
1/9	>150	>2530	76
2/8	360	1410	81
3/7	500	1100	48
4/6	560	1030	38.5
100% Triisocyanate	630	530	166

TABLE VIII

MECHANICAL PROPERTIES OF DIFUNCTIONAL HT-TELAGEN GUMSTOCKS CONTAINING VARYING AMOUNTS OF MONOFUNCTIONAL PREPOLYMER AND CURED WITH 9/1 2,4-TOLYLENE DIISOCYANATE/TRIPHENYL METHANE TRIISOCYANATE

At Ambient Temperature (75°F)

Mole % Monofunctional Prepolymer	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	44	148	510	144
4.3	41	146	540	125
9.0	33	200	1700	78.8
18.2	26	91	2440	44.8
27.6	17	27	2020	28.7

At 180°F

Mole % Monofunctional Prepolymer	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	119	325	120
4.3	123	370	110
9.0	72	650	51.3
18.2	46	1300	29.4
27.6	11.5	1350	10.8

At -65°F

Mole % Monofunctional Prepolymer	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	1270	935	226
4.3	1230	870	223
9.0	1100	1050	192
18.2	660	1130	160
27.6	>187	>1475	106

TABLE IX

MECHANICAL PROPERTIES OF DIFUNCTIONAL HT-TELAGEN GUMSTOCKS CONTAINING VARYING AMOUNTS OF MONOFUNCTIONAL PREPOLYMER AND CURED WITH 9/1 DDI/TRIPHENYL METHYLENE TRIISOCYANATE

At Ambient Temperature (75°F)

Mole % Monofunctional Prepolymer	Shore "A" Hardness (15 Sec. Reading)	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	31	123	1590	77
4.5	26	82	1630	47
9.0	15	18	1450	20
18.2	14	27	1840	27
27.6	8	6.8	1180	10.8

At 180°F

Mole % Monofunctional Prepolymer	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	63	700	47.5
4.5	41	1010	26.7
9.0	6.9	980	8.4
18.2	10.2	1230	9.7
27.6	1.8	1330	2.8

At -65°F

Mole % Monofunctional Prepolymer	Max. Stress Psi	% Strain at Max. Stress	Initial Modulus (Psi)
0	760	1410	180
4.5	>280	>1540	123
9.0	250	>1550	125
18.2	>270	>1420	129
27.6	96	>1550	81

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13. ABSTRACT

Functionality and functionality distribution measurements have been carried out on six different polybutadiene prepolymers containing hydroxy or carboxy functionality which are currently of interest to the Air Force. The specific prepolymers are: Sinclair's Poly B-D R-45M and R-15M, hydroxy-functional butadiene homopolymers prepared by free radical polymerization and General Tire's Telagen prepolymer series, prepared by anionic polymerization. The Telagen prepolymer series comprises the following polymers: the OH-Telagen (nominal Mn=5000) and its low molecular weight (Mn=2000), saturated counterpart, OH-Telagen-S, and the corresponding carboxy-functional analogues, COOH-Telagen and COOH-Telagen-S.

Number average molecular weight measurements of three different lots of the R-45M prepolymer showed little batch to batch variation. Functionality distribution measurements were obtained by elution chromatography on activated silica gel. The difunctional content was found to be approximately 40 to 45 wt % with a nominal molecular weight of 4000, the remainder (55-60 wt %) being trifunctional with a nominal molecular weight of 2000. All three lots of the R-45M have consistently shown this dependence of functionality on molecular weight. The functionality

13. **Abstract (Cont'd)**

distribution of the R-15M was found to be similar to that of the R-45M, containing more than 50 wt % triol. In contrast to Sinclair's R-45M and R-15M prepolymers which are composed of di- and trifunctional components, the Telagen prepolymers contain non-, mono- and difunctional prepolymers. The total non- and monofunctional content of the four Telagen prepolymers which were analyzed varied from 24 to 32 wt %, the bulk of which is monofunctional.

A sample of Rocketdyne's P-CDMFE prepolymer, lot EXI-68, was characterized with respect to functionality distribution and found to contain 12 to 15% monofunctional, 45 to 50% difunctional and 35 to 40% trifunctional prepolymer. Functionality distribution measurements of 3M's new perfluoroalkylene oxide prepolymer, PC2202 showed the presence of 3-5% nonfunctional and 7-9% monofunctional prepolymer, the remainder being difunctional.

Mechanical properties of a gumstock prepared from a pure difunctional HO-polybutadiene prepolymer have been obtained over a temperature range of -65°F to 180°F. The effect of monofunctional prepolymer content on gumstock properties has been quantitatively defined.

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	ROLE	WT	ROLE	WT	ROLE	WT
VPO						
Number Average Molecular Weight Determination						
Equivalent Weight Determination						
Functionality						
Functionality Distribution Measurements						
Prepolymers						
Binders						
Elution Chromatography						
Sinclair's Poly B-D, R-45M and R-15M Prepolymer						
OH-Telagen, HT-Telagen						
OH-Telagen-S, HT-Telagen-S						
COOH-Telagen, CT-Telagen						
COOH-Telagen-S, CT-Telagen-S						
P-CDBPE						
FC2202						
Pure Difunctional Polybutadiene						