THE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF SOME STYRENE-MALEIC ANHYDRIDE COPOLYMERS

Thesis for the Degree of M. S.
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ABSTRACT

THE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF SOME STYRENE-MALEIC ANHYDRIDE COPOLYMERS

by Charles E. McCoy Jr.

Methods for preparing styrene-maleic anhydride copolymers with average molecular weights from 5,000 to 35,000 have been developed. The effect on the copolymerization of varying solvent, temperature, and catalyst was studied.

Molecular weights were determined via gel permeation chromatography, vapor pressure osmometry, and viscosity measurements. Number average molecular weights calculated from gel permeation chromatography were contrasted and correlated with number average molecular weights obtained by vapor pressure osmometry.

Molecular weight distributions were derived from the gel permeation chromatograms.

An approximate "K" and "a" were determined for use in estimating molecular weights of styrene-maleic anhydride copolymers by measuring viscosity of the copolymers in acetone solution.

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By

Charles E. McCoy Jr.

A THESIS

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TO SHIRLEY, CAROL, AND LINDA

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INTRODUCTION

Styrene-maleic anhydride copolymers have been of interest to this laboratory for several years. The chemistry of this copolymer system has been the subject of several publications (1).

The purpose of this study was twofold:

1. The synthesis of a broad range of low molecular weight copolymers with number average molecular weights less than 20,000.
2. The characterization of these copolymers by molecular weight and molecular weight distribution.

Little has been published on the molecular weight and molecular weight distribution of equal molar styrene-maleic anhydride copolymers. A better understanding of these properties and methods for controlling them will be important to future work in this laboratory and will fill a void in the existing literature.

HISTORICAL

Copolymerization was first described by Klatte (2) in 1914. Later studies revealed that copolymerization was different from homopolymerization in that some monomers, such as maleic anhydride, homopolymerize with difficulty or not at all but readily copolymerize with monomers like styrene and vinyl chloride (3).

The first studies on the mechanism of copolymerization were conducted by Dostal (4). Three independent publications by Alfrey and Goldfinger (5), Mayo and Lewis (6), and Wall (7) in 1944 described a "copolymerization equation" to account for the observed copolymer composition from any two comonomers. Copolymerization has since been described in many publications.

Several explanations (8) have been advanced for the observed difficulty in the attempted homopolymerization of maleic anhydride and the observed ease of copolymerization with other monomers. Copolymerization with many comonomers favors 1:1 copolymers. Stilbene and maleic anhydride give 1:1 copolymers regardless of the initial monomer composition (9). Styrene and maleic anhydride give essentially 1:1 copolymers except when the monomer mixture contains a high mole percentage of styrene (> 80%) (10). Alfrey and Lanvin (11) have shown that four distinct processes are involved in copolymerization and that these processes are governed by four propagation rate constants. With styrene-maleic anhydride systems, the four propagation rates become three, since maleic anhydride has practically no tendency to add to its own radicals--thus favoring the 1:1 copolymer composition. This conclusion has been supported by Ham, *et al*. (12) and Bartlett and Nozaki (13).

Three sets of r_1 and r_2 values are given for copolymerization of styrene and maleic anhydride:

Styrene is monomer 2

r_1	r_2	reference
0	0.01	(14)
0	0.042	(11)
0	0.02	(15)

If $r_1 r_2 = 0$, each radical prefers to react exclusively with the other monomer and the initial copolymer from any concentration of comonomers will be alternating (16). The relative reactivity of the maleic anhydride radical for styrene is some twenty (17) times greater than the styrene radical for styrene.

Maleic anhydride forms colored molecular complexes with styrene and other aromatic compounds (18). A suggested structure of these materials is one consisting of pairs of radical ions in which styrene has donated an electron to maleic anhydride.

Mayo (14) and co-workers have suggested that the larger the difference in polarity or donor acceptor properties between two comonomers, the greater will be the alternating tendency. They have devised a donor acceptor series in which the substituent groups are ranked as follows:

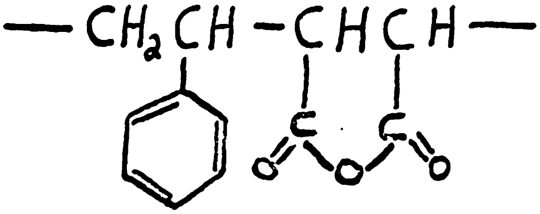
Donor Acceptor Series

decreasing donor ability ↓

R-O-
$H_2C=CH-$
C_6H_5-
$R-CH_2-$
H-
Cl-
R-CO-
R-O-CO-
N≡C-

When two comonomers are well separated in this series, they will have a marked tendency to alternate in copolymerization. Styrene and maleic anhydride are well separated.

The structure of a 1:1 copolymer of styrene and maleic anhydride can be illustrated by the following repeating unit



Alfrey and Price (19) developed the copolymerization parameters Q and e which fill the need for more general and constant factors for characterizing monomers. Q is a measure of general monomer reactivity and e depends on the polar properties. These two parameters should be constant and unique for a given monomer regardless of the copolymerization system. They are calculated as follows (20):

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{\frac{1}{2}}$$

$$Q_2 = Q_1/r_1 \exp \left[-e_1(e_1-e_2)\right]$$

Styrene is taken as the standard for the Q-e scheme and values of Q=1.00 and e=-0.80 are assumed. The r_1 value for maleic anhydride is 0. In such cases, a small finite value must be assumed in order to obtain a reasonable value for e.

Young (20) reports the Q and e values for styrene and maleic anhydride as follows:

	e	Q
Styrene	-0.80	1.00
Maleic Anhydride	2.25	0.23

The positive e value for maleic anhydride indicates that it is an "electron poor" monomer.

The large difference between the two e values (-0.80 to 2.25) suggests that 1:1 copolymers will be obtained when styrene and maleic anhydride are polymerized. This large difference in polarity supports the "radical complex" theory (21) which suggests that polymerization is preceeded by the formation of a "radical complex" which produces 1:1

copolymers virtually independent of any styrene excess available.

While the polymerization parameters for styrene-maleic anhydride systems have been determined by a number of workers, the resultant polymers have not been characterized. The techniques for characterization are known, but apparently have not been applied specifically to styrene-maleic anhydride copolymers.

The recent literature is dominated by process research and techniques (22) which give industrial copolymers for specific uses. The average molecular weights are sometimes reported (23), but not the copolymer distribution.

A polymer or copolymer sample consists of a homologous mixture of molecules having similar or like repeating units. Determination of molecular weight by colligative methods (i.e., osmotic pressure, vapor pressure lowering, freezing point depression, etc..) provides an actual count of the number of solute molecules. The result is a value usually referred to as the number average molecular weight ($\bar{M}n$).

When molecular weight is determined by light scattering, the nature of the process is such that the larger particles contribute more to the scattering than the smaller ones. The molecular weight obtained by this method is usually referred to as the weight average molecular weight, $\bar{M}w$.

$\bar{M}w$ is always greater than $\bar{M}n$ except for monodisperse systems in which they are equal. The ratio $\bar{M}w/\bar{M}n$ has been referred to as a measure of polydispersity.

Neither $\bar{M}n$ or $\bar{M}w$ satisfactorily characterize a polymer system. Values for $\bar{M}n$ and $\bar{M}w$ on a given polymer sample give an indication of the molecular weight distribution, but cannot be used to construct a complete molecular distribution curve.

A new technique, gel permeation chromatography, allows rapid determination of molecular weight and molecular weight distribution. This is a technique for fractionation of samples according to molecular size on a polymer gel column using the principles of liquid phase chromatography.

Gel permeation chromatography was introduced by Moore in 1964 (24). The growth and acceptance of this method has been rapid and commercial units are available (25). The importance that gel permeation chromatography has assumed in polymer chemistry has been paralleled by studies to ascertain the details of the mode of separation. Moore and co-workers have continued their work (26) and have been joined by several others (27). Publications relating to the application and utilization of gel permeation chromatography units have appeared (28).

This method is rapidly supplanting the technique of polymer fractionation from solvent by fractional addition of non-solvent and removal of the precipitated fractions. Average molecular weight values can also be calculated from gel permeation chromatography data.

REAGENTS

(a) Styrene (The Dow Chemical Company) was washed with three successive portions of 10% sodium hydroxide to remove the inhibitor. This was followed by repeated water washings until the washings were neutral to litmus. The resultant styrene was stored over anhydrous sodium sulfate in a refrigerator for one week. The dry styrene was distilled under reduced pressure, and the portion distilling at 36-37°C at 30 mm. of mercury was collected and stored in the refrigerator over anhydrous sodium sulfate until used. Prior to use, the styrene was tested for the presence of polystyrene by addition of methanol to a small sample. Since polystyrene is insoluble in methanol, the absence of a precipitate indicated that the styrene was free of polystyrene.

(b) Maleic Anhydride

Maleic anhydride (Fisher Scientific Company, reagent grade) was further purified by vacuum distillation. The sample used was collected under reduced pressure (15 mm. of mercury) at 56-58°C. The melting point was 52.5±1°C. The sample was ground to a coarse powder, bottled, and stored in a desiccator over calcium chloride.

(c) Benzoyl Peroxide

Benzoyl Peroxide (Eastman Kodak, reagent grade) was used as received. The bottled material was stored in a refrigerator.

(d) 2,2'-azobis (2-methyl propionitrile)

The 2,2'-azobis (2-methyl propionitrile) (Eastman Chemical, reagent grade) was used without further purification.

(e) Benzene

Thiophene free benzene was washed three times with concentrated sulfuric acid. This was followed by a wash with a 10% solution of sodium bicarbonate and then water washings until the washings were neutral to litmus. The resultant benzene was stored over calcium chloride and then over metallic sodium. It was distilled from metallic sodium immediately prior to use. The fraction used distilled at 80°C±0.5°C at atmospheric pressure.

(f) Tetrahydrofuran

Tetrahydrofuran (Eastman Chemical Company) was stored over solid potassium hydroxide for at least one week. It was then refluxed with lithium aluminum hydride for a minimum of 12 hours and was distilled immediately prior to use. The fraction used distilled at 64-65°C at atmospheric pressure.

(g) Carbon Tetrachloride

Carbon tetrachloride (The Dow Chemical Company) was washed with a 10% solution of potassium hydroxide in a 3:1 mixture of water and ethanol. The mixture was stirred vigorously for 30 minutes at 50-55°C. The aqueous layer was separated and the alcohol removed from the carbon tetrachloride by several water washings followed by washing with small portions of concentrated sulfuric acid. Finally the carbon tetrachloride was washed with water to remove the last traces of acid. The resultant carbon tetrachloride was dried over calcium chloride. The product was distilled immediately prior to use. The fraction used distilled at 76-77°C at atmospheric pressure.

(h) Dimethoxymethane

Dimethoxymethane (Eastman Organic Chemicals, reagent grade) was used as received. The boiling point was 44±0.5°C at atmospheric pressure.

(i) Isopropyl Benzene

Isopropyl benzene (The Dow Chemical Company) was dried over calcium chloride, refluxed with lithium aluminum hydride for a minimum of four hours and finally distilled from lithium aluminum hydride under nitrogen. The material used distilled at 152±0.5°C at atmospheric pressure.

(j) Bromochloromethane

Bromochloromethane (The Dow Chemical Company) was dried over calcium chloride and distilled immediately prior to use. The fraction used distilled at 69±0.5°C at atmospheric pressure.

(k) Petroleum Ether

Petroleum ether (Eastman Chemical Company) was dried over sodium and was filtered prior to use. The boiling range was 60-90°C at atmospheric pressure.

(1) Acetone

Acetone (Eastman Chemical Company, spectro grade) was used as received. The boiling point was $56 \pm 0.5^{\circ}C$ at atmospheric pressure.

EXPERIMENTAL

I. Polymerization Technique

The following technique was used for all the copolymerizations conducted during the course of this investigation.

Figure 1 is a drawing of the polymerization apparatus.

The reaction vessel was a one liter, round bottomed, three necked flask. The three necks were fitted with a nitrogen bubbler, stirrer (ground glass joints), and reflux condenser (with calcium chloride drying tube). The temperature was raised to the desired level by means of an oil bath heated with a nichrome heating coil controlled by a variac.

A 50:50 mole ratio of comonomers was used in each copolymerization. This was 21.6 grams of styrene and 20.4 grams of maleic anhydride in 500 milliliters of solvent. Anhydrous conditions were maintained at all times. The type and amount of initiator, the temperature, and the reaction times were varied.

The reaction flask was heated to the desired temperature, and nitrogen was passed through the empty vessel via a nitrogen bubbler. Next 400 milliliters of solvent were added to the reaction vessel and stirring was started. The temperature was equilibrated at the desired level; and the maleic anhydride, initiator, and styrene, all weighed to 0.001 grams, were added quantitatively in the order given. Solvent was used to effect the quantitative addition of the comonomers and the initiator to the reaction flask and to bring the total volume of solvent in the reaction vessel to 500 milliliters.

After the pre-determined time period had elapsed, the heat was removed and the copolymerizations were allowed to cool to room temperature, with stirring, for approximately 30 minutes.

In some reactions, the copolymer precipitated during the course of the polymerization and in others remained in solution. Two procedures were developed for obtaining the copolymers from the reactions as fine white powdered material. These procedures are described in the next section.

II. Purification and Isolation Technique

The copolymers that precipitated from the reaction solvent were vacuum filtered (Buchner). The filter cake was thoroughly washed with the polymerization solvent. The samples were stored in a vacuum desiccator over calcium chloride at room temperature and reduced pressure (0.2mm. of mercury) where most of the polymerization solvent was removed. Then the samples were extracted with benzene for 48 hours by Soxhlet extraction. Finally the copolymers were dried under reduced pressure (0.2mm. of mercury); first at room temperature and then at 56°C. They were stored in a desiccator over calcium chloride at atmospheric pressure while awaiting characterization. The reactions in which the copolymer precipitated were termed "heterogeneous".

The copolymers that remained in solution were precipitated by a seven-fold volume of petroleum ether in a large beaker. The polymer was filtered and treated as is described above. The reactions in which the copolymer remained in solution were termed "homogeneous".

III. Preparation of Samples For Testing

Copolymers were prepared in dimethoxymethane, benzene, tetrahydrofuran, bromochloromethane, and isopropylbenzene. The yields obtained and the copolymer designations are shown in Table 1. All copolymerizations were carried out in 500 milliliters of solvent.

A. Copolymerization in Dimethoxymethane

Two initiators were used, benzoyl peroxide at concentrations of 0.21 and 0.42 grams and 2,2'-azobis (2-methylpropionitrile) also at concentrations of 0.21 and 0.42 grams. All four copolymerizations were conducted at 44±1°C for 24 hours. All were "heterogeneous". The resultant copolymers were labeled 1 through 4 respectively.

The monomers and the initiators were very soluble in dimethoxymethane. All four reactions began as clear solutions but became turbid. Copolymerizations initiated with 2,2'-azobis (2-methylpropionitrile) were definitely turbid within a few minutes, while the benzoyl peroxide initiated reactions appeared hazy only after approximately two hours. After 14 hours, the viscosity of the copolymerization mixtures had increased significantly and the stirrer speed had to be increased to insure proper mixing.

In general, reactions with 2,2'-azobis (2-methylpropionitrile) were much faster and the yields were better.

B. Copolymerization in Benzene

Five copolymers were prepared utilizing three different procedures. The monomers and the initiators were very soluble in benzene. All five reactions were "heterogeneous".

Procedure 1

Two copolymerizations were conducted at 50±1°C for 24 hours. Benzoyl peroxide was the initiator in one at a concentration of 0.21 grams. The other contained 2,2'-azobis (2-methylpropionitrile) also at a concentration of 0.21 grams. The resultant polymers were labeled 5 and 6 respectively.

Both copolymerizations were initially clear. The one initiated with 2,2'-azobis (2-methylpropionitrile) was turbid within 15 minutes, while the one initiated with benzoyl peroxide was turbid within 25 minutes. Formation of copolymer in both was rapid during the course of the reaction, and the stirrer speed had to be increased after two (the 2,2'-azobis 2-methylpropionitrile initiated reaction) and eight (the benzoyl peroxide initiated reaction) hours to maintain proper mixing.

Procedure 2

Two copolymerizations were carried out at 80±1°C for 1.5 hours. One was initiated with 0.84 grams of benzoyl peroxide and the other was initiated with 0.84 grams of 2,2'-azobis (2-methylpropionitrile). These two copolymers were labeled 7 and 8 respectively

Although initially clear, both reactions became turbid within a matter of seconds. Within 30 minutes the copolymers had precipitated to the point where stirring was extremely difficult. The stirrer speeds were increased to the maximum extent, and 50 milliliters of solvent were added to each reaction before a satisfactory stirring rate could be achieved.

One copolymerization was conducted at 80°±1°C for four hours with no added initiator. Turbidity was observed after 58 minutes. The formation of copolymer was very slow. This copolymer was sample 9.

Copolymerization of styrene and maleic anhydride in benzene with initiator was rapid and nearly quantitative. The reaction without initiator was very slow but did proceed at 80°C.

C. Copolymerization in Tetrahydrofuran

Six copolymerizations were carried out using three procedures, two in tetrahydrofuran, two in mixtures of tetrahydrofuran and isopropyl benzene and two in mixtures of tetrahydrofuran and carbon tetrachloride. In each case the temperature was 65±1°C and the reaction time was 5.5 hours.

Procedure 1

Two copolymerizations, both "homogeneous", were conducted in tetrahydrofuran. One was initiated with 0.84 grams of benzoyl peroxide and one was initiated with 0.84 grams of 2,2'-azobis (2-methylpropionitrile). These copolymers were labeled 10 and 11 respectively.

Procedure 2

In this case, combinations of tetrahydrofuran and isopropyl benzene were used as solvents for copolymerization. Two copolymerizations were carried out; one in a 3:2 ratio by volume of tetrahydrofuran to isopropyl benzene (300 milliliters of tetrahydrofuran: 200 milliliters of isopropyl benzene), and one in a 4.5:0.5 ratio by volume of tetrahydrofuran to isopropyl benzene. The initiator in both was 0.84 grams of benzoyl peroxide.

The copolymerization with the 3:2 ratio of solvents was initially clear but became turbid after about one hour. As more polymer precipitated, it began to agglomerate into large particles and was difficult to stir. When the reaction was finished, the copolymer was in a single solid mass, which could not be removed from the flask. The tetrahydrofuran-isopropyl benzene mixture was removed, filtered, and saved. The solids collected were returned to the flask and, along with the single solid mass, were dissolved in tetrahydrofuran. The copolymer was precipitated with petroleum ether and was labeled 12.

The clear tetrahydrofuran-isopropyl benzene solution which was filtered and saved was diluted with petroleum ether and a second copolymer sample was obtained. This was Sample 13.

Thus, two polymers were obtained when a 3:2 ratio of tetrahydrofuran to isopropyl benzene was used as the solvent; the polymer that precipitated and the polymer that remained in solution.

The copolymerization utilizing the 4.5:0.5 ratio by volume of tetrahydrofuran to isopropyl benzene remained clear throughout the 5.5 hour reaction. The copolymer was precipitated with petroleum ether and was labeled 14.

Procedure 3

In this case, combinations of tetrahydrofuran and carbon tetrachloride were used as copolymerization solvents. Two copolymerizations were conducted; one with a 3:2 ratio by volume of tetrahydrofuran to carbon tetrachloride and one with a 4:1 ratio by volume of tetrahydrofuran to carbon tetrachloride. The added initiator in both reactions was 0.84 grams of benzoyl peroxide.

The copolymerization with the 3:2 ratio of solvents was initially clear but became turbid within the first 1.5 hours. The copolymer agglomerated into large particles and stirring was difficult. When finished, the precipitated polymer had formed a single solid mass. The reaction solvent was filtered and saved. The solids on the filter paper were returned to the flask and along with the single solid mass were dissolved in tetrahydrofuran. This copolymer was precipitated with petroleum ether and was labeled 15.

The clear tetrahydrofuran-carbon tetrachloride that passed through the filter was diluted with petroleum ether and a second copolymer was isolated. This was sample 16.

The copolymerization with a 4:1 volume ratio of tetrahydrofuran to carbon tetrachloride as the solvent remained clear throughout the polymerization. The copolymer was precipitated with petroleum ether and was labeled 17.

D. Copolymerization in Bromochloromethane

One copolymerization was carried out in bromochloromethane at 69±1°C for 40 minutes with 0.84 grams of benzoyl

peroxide as the initiator. The comonomers and the initiator were very soluble. The reaction was initially clear but became turbid within 20 minutes. The copolymer from this "heterogeneous" copolymerization was labeled 18.

E. Copolymerization in Isopropyl Benzene

Six copolymers were prepared using four procedures. The comonomers and initiator were very soluble in isopropyl benzene. All six copolymerizations were "heterogeneous".

Procedure 1

Two copolymers were prepared at 80°±1°C for 1.5 hours. One was initiated with 0.84 grams of benzoyl peroxide and the other contained no added initiator. Both reactions were initially clear but became turbid, in both instances, within 11 minutes. The resultant copolymers were labeled 19 and 20 respectively.

Procedure 2

One copolymerization was carried out at 105°±1°C for 1.5 hours with no added initiator. Turbidity was observed within 15 minutes. The resultant copolymer was labeled 21.

Procedure 3

One copolymerization was carried out at 135° ±1°C for 1.5 hours with no added initiator. Turbidity was observed within one minute. The resultant copolymer was labeled 22.

Procedure 4

Two copolymerizations were conducted at $152^{\circ} \pm 1^{\circ}C$ for 1.5 hours. One was initiated with 0.84 grams of benzoyl peroxide and the other polymerized without added initiator. Turbidity was instantaneous in both cases. With these two reactions, the copolymers adhered to the wall of the reaction vessel and were scraped off. The adherence to the wall of the reaction flask does not occur at 135°C or below. The resultant copolymers were labeled 23 and 24 respectively.

Styrene and maleic anhydride copolymerize very readily in isopropyl benzene. The ease of copolymerization is illustrated by the rapid reaction at 80°C without added initiator.

F. Samples From Other Sources

A commercial sample, 1000A from Sinclair (29), was labeled 25 and a sample previously prepared in tetrahydrofuran in this laboratory, 4E (30), was labeled 26.

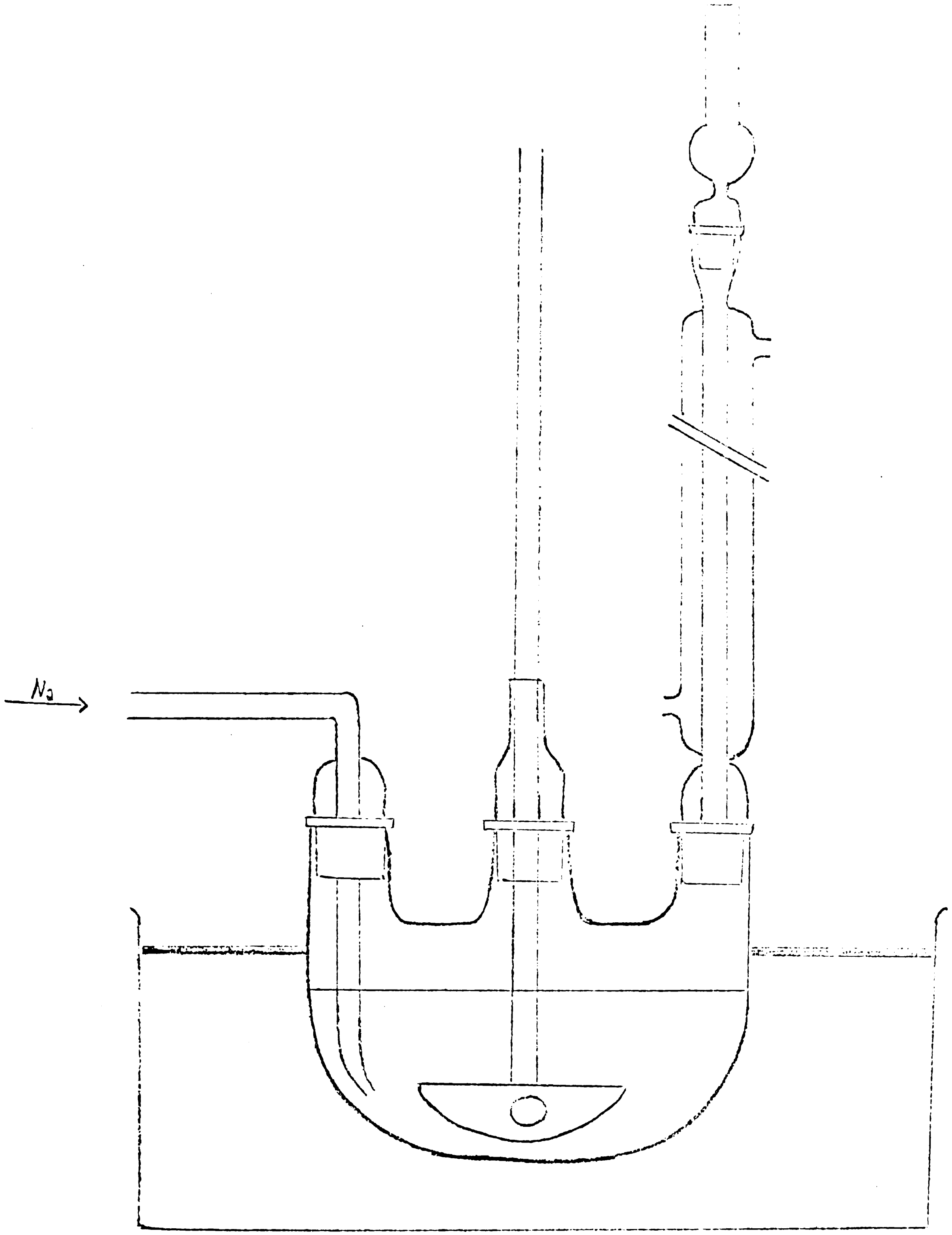


Figure 1. Schematic drawing of the apparatus used for the polymerization experiments.

Table 1. Samples Prepared for Testing

Sample	Solvent	Initiator g/500ml of sol.	Initiator Type	Reaction Time, Hours	Temp. degrees, C	% Yield
1	DMM	0.21	BZ_2O_2	24.0	44	11.8
2	DMM	0.42	BZ_2O_2	24.0	44	20.5
3	DMM	0.21	AZO	24.0	44	71.5
4	DMM	0.42	AZO	24.0	44	41.2
5	benzene	0.21	BZ_2O_2	24.0	50	93.4
6	benzene	0.21	AZO	24.0	50	95.7
7	benzene	0.84	BZ_2O_2	1.5	80	91.0
8	benzene	0.84	AZO	1.5	80	89.4
9	benzene	none		4.0	80	3.0
10	THF	0.84	BZ_2O_2	5.5	65	47.4
11	THF	0.84	AZO	5.5	65	67.9
12 and 13	3/2 THF-IPB	0.84	BZ_2O_2	5.5	65	54.8 and 7.6
14	4.5/0.5 THF-IPB	0.84	BZ_2O_2	5.5	65	54.3
15 and 16	3/2 THF-CCl_4	0.84	BZ_2O_2	5.5	65	56.0 and 7.4
17	4/1 THF-CCl_4	0.84	BZ_2O_2	5.5	65	51.0
18	BCM	0.84	BZ_2O_2	0.7	69	27.5
19	IPB	0.84	BZ_2O_2	1.5	80	73.0
20	IPB	none		1.5	80	39.5
21	IPB	none		1.5	105	56.5
22	IPB	none		1.5	135	88.5
23	IPB	0.84	BZ_2O_2	1.5	152	88.4
24	IPB	none		1.5	152	88.4

25 & 26 were obtained from other sources (see page 25)

BZ_2O_2 = Benzoyl Peroxide

AZO = 2,2' azobis-(2-methylpropionitrile)

DMM = Dimethoxymethane

THF = Tetrahydrofuran

IPB = Isopropyl Benzene

CCl_4 = Carbon Tetrachloride

BCM = Bromochloromethane

IV. Evaluation of Samples

The samples prepared for testing were evaluated using vapor pressure osmometry, gel permeation chromatography, and viscosity measurements. These techniques and the results obtained are reviewed individually.

A. Vapor Pressure Osmometry

Number average molecular weights were determined using a Mechrolab, High Temperature, Vapor Pressure Osmometer, Model 302. The Mechrolab brochure (31) and other references (32) describe the theory and method of operation in detail.

The vapor pressure osmometer operates on the principal of vapor pressure lowering. Solutions always have a lower vapor pressure than the pure solvent. In this unit a drop of copolymer solution in acetone and a drop of acetone were suspended, side by side, in a closed chamber saturated with acetone vapors. The two drops had different vapor pressures and a differential mass transfer occurred between the two drops and the acetone vapor phase. This resulted in lower evaporation from the copolymer solution drop than from the acetone drop, creating a temperature differential between the two drops. This temperature differential was proportional to the vapor pressure lowering and to the copolymer concentration. This is a colligative effect, dependent only on the number of dissolved molecules.

Acetone was the solvent in all cases. The unit was calibrated with benzoic acid in accordance with the

Mechrolab brochure (31) and a K was determined. Figure 2 is a calibration curve. The data used to construct the calibration curve are in Table 2. The K of calibration from this determination was 419. Recalibrations were made after several (8-10) determinations.

The molecular weights were calculated using the equation:

$$\bar{M}_n = K\left[\frac{1}{\left(\frac{\Delta R}{C}\right)_0}\right]$$

Where C is the concentration of the sample used and Δ R is the dekastat reading obtained for a given concentration, C. The value $\left(\frac{\Delta R}{C}\right)_0$ was obtained by extrapolation to zero concentration.

The number average molecular weights were obtained for samples with molecular weights within the range of the equipment ($\bar{M}n < 20{,}000$). Of the samples prepared, only those made in tetrahydrofuran and isopropyl benzene were in this category. A typical calculation is shown for sample 11, in Table 3. The corresponding plot is shown in Figure 3 along with all the other samples tested.

The resultant $\bar{M}n$ values for all the samples tested are shown in Table 4.

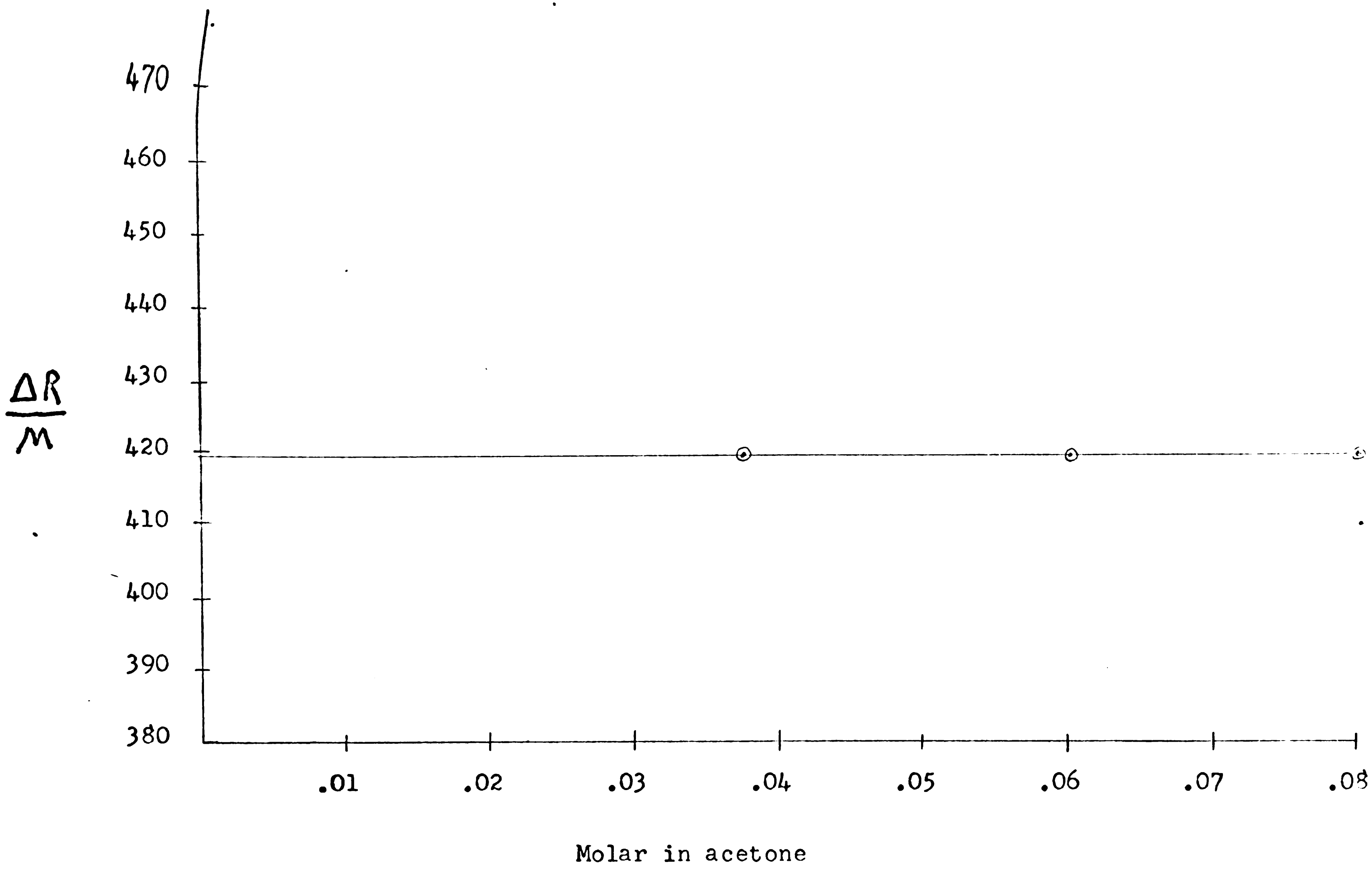


Figure 2. Calibration curve utilizing benzoic acid (K = 419) for the vapor pressure osmometer.

Table 2. Determination of K with Benzoic Acid for the Vapor Pressure Osmometer

	Molar Concentration		
	.04	.06	.08
Δ R reading # 1	16.77	25.14	33.55
Δ R reading # 2	16.78	25.14	33.56
Average Δ R	16.775	25.14	33.555
$\frac{\Delta R}{M}$	419.4	419.0	419.4

Table 3. Vapor Pressure Osmometry Results for Sample 11

	Concentration in grams per liter			
	20	40	60	80
Δ R reading # 1	1.19	2.59	4.08	5.86
Δ R reading # 2	1.18	2.59	4.02	5.78
Average ΔR	1.185	2.59	4.05	5.82
$\frac{\Delta R}{c}$	0.0592	0.0647	0.0675	0.0727

$\left(\frac{\Delta R}{c}\right)_0$ (from figure 3) = 0.04

$$\bar{M}n = K\left[\frac{1}{\left(\frac{\Delta R}{c}\right)_0}\right] = 419\left(\frac{1}{.04}\right) = 10{,}475$$

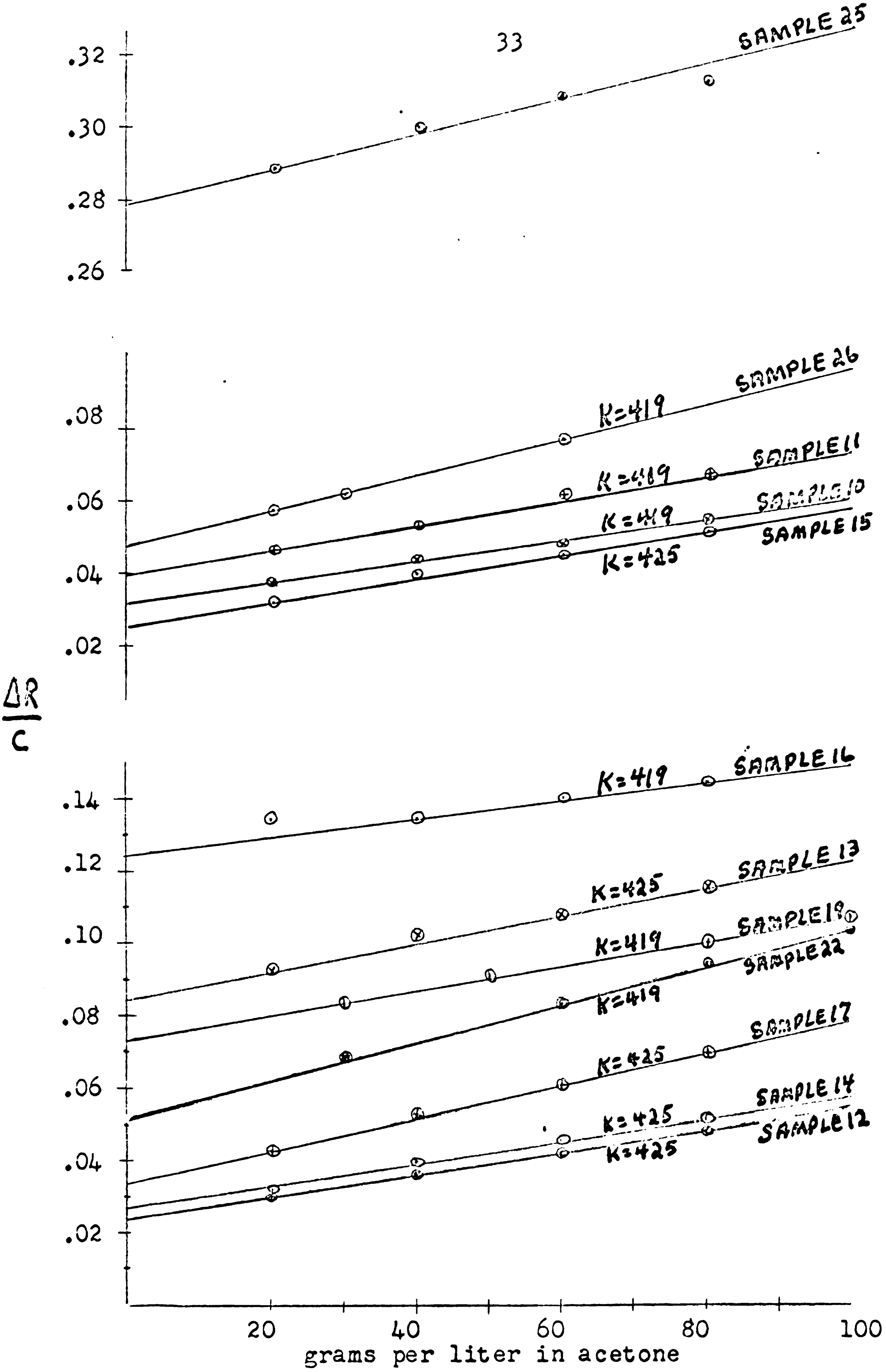


Figure 3. Vapor pressure osmometry plots.

Table 4. $\overline{M}n$ Values From Vapor Pressure Osmometry Data

Copolymer Designation	$\overline{M}n$
10	13,500
11	10,470
12	17,010
13	5,000
14	15,290
15	17,210
16	3,420
17	12,500
23	5,740
24	8,150
25	1,500
26	8,700

B. Gel Permeation Chromatography

A commercial instrument manufactured by Waters Associates was used in this study. The theory and operational procedure for this instrument have been described in the Waters instruction manual (25) and elsewhere (28).

A schematic diagram of the unit used is shown in Figure 4. A four column circuit made up of four foot columns was used. The columns were arranged in series by pore size as follows:

10^6 Å
10^4 Å
10^4 Å
10^3 Å

The sample always passed through the larger pore size first. The columns were high quality with a rating of about 800 plates per foot.

Tetrahydrofuran was used as the solvent for each determination. The sample was prepared by dissolving one weight per cent of the copolymer in tetrahydrofuran. The pumping rate was one milliliter per minute. The sample was injected into the sample valve, and at the proper time, the valve was opened for one minute, introducing one milliliter of the sample solution into the column. The time required for a sample to pass completely through the system was about two and one half hours.

A typical chromatogram is shown in Figure 5. Solvent flow is plotted in increments of five milliliters versus the change in refractive index. The flow rate is maintained constant by a pump. A differential refractometer continuously compared the refractive index of the fraction to the reference solvent and gave a signal proportional to the amount of polymer in the solvent.

The circuit was calibrated with polystyrene of known molecular weight, and the calibration was checked periodically. Two runs, separated by several weeks, were made. The two calibration curves are shown in Figure 6.

The polystyrene used for calibration was polymerized by an anionic mechanism (33) and was made available by The Dow Chemical Company. The calibration samples and their molecular weights are shown below:

Sample	$\bar{M}w$	$\bar{M}n$	$\bar{M}rms$	$\bar{M}w/\bar{M}n$
S-0	10,500	6,400	8,200	1.64
S-102	82,000	78,000	80,000	1.05
S-105	153,000	147,000	150,000	1.04

$$\bar{M}rms = \sqrt{(\bar{M}n)\ (\bar{M}w)}$$

The elution count corresponding to the peak of the calibration sample was assigned the corresponding $\bar{M}rms$ value.

Accordingly, $\bar{M}n$, $\bar{M}w$, and the corresponding $\bar{M}w/\bar{M}n$ values determined by gel permeation chromatography are based on calibration using polystyrene. This should give good estimated of $\bar{M}w$ and $\bar{M}n$ for the molecular weight range desired; however, the relationship between elution count and molecular weight for materials other than pure polystyrene in tetrahydrofuran does not necessarily hold.

The number and weight average molecular weights were determined using a procedure that amounted to tabulating the data on the chromatogram, supplementing it with data from the standard curve, and then following the directions in the following derivation (25) (34).

The height of an increment (i.e., the "height" above the base line), h_i, is proportional to the amount or mass, m_i, of material in the increment.

$$h_i \propto m_i \qquad h_i = K m_i \tag{1}$$

The mass is equal to the number of molecules in the increment, n_i, times the molecular weight of the molecules, M_i (Assume that all molecules in an increment are of the same molecular weight).

$$m_i = n_i M_i \tag{2}$$

Thus

$$n_i = m_i / M_i \tag{3}$$

Number average molecular weight is defined by

$$\bar{M}_n = \frac{\Sigma (n_i M_i)}{\Sigma (n_i)} \tag{4}$$

From (1) and (3) it is known that

$$n_i = K \, {}^{h_i}/_{M_i} \tag{5}$$

By substituting (5) into (4):

$$\bar{M}_n = \frac{\Sigma (K \, {}^{h_i}/_{M_i} \, M_i)}{\Sigma (K \, {}^{h_i}/_{M_i})} = \frac{\Sigma (h_i)}{\Sigma (h_i / M_i)} \tag{6}$$

Weight average molecular weight, $\bar{M}w$, is defined as

$$\bar{M}_w = \frac{\Sigma (m_i M_i)}{\Sigma (m_i)} \tag{7}$$

Substituting

$$\bar{M}_w = \frac{\sum (n_i M_i^2)}{\sum (n_i M_i)}$$

Next, substituting (5)

$$\bar{M}_w = \frac{\sum (n_i M_i)}{\sum (h_i)}$$

With the low molecular weight samples, the data were tabulated on each one-half elution count. With some of the higher molecular weight materials, data were tabulated on the full count. Typical calculations are shown in Table 5. These data were taken from the curve in Figure 5. The results from the gel permeation chromatography work are shown in Table 6.

Data taken from the gel permeation chromatograms were used for plotting distribution curves (28) (35). The refractive indices (see Figure 5) were added to make a table of cumulative heights (see Table 5). The sum of the heights $\sum h_i$ equals $\sum M_i n_i$ since the height of each interval equals the product of the average molecular weight of this interval (M_i) times the number of molecules (n_i). The cumulative heights were normalized and plotted versus the molecular weight data obtained from the calibration curve. Such a plot is shown in Figure 7. All of the chromatograms and some selected distribution plots can be found in appendices 1 and 2 respectively.

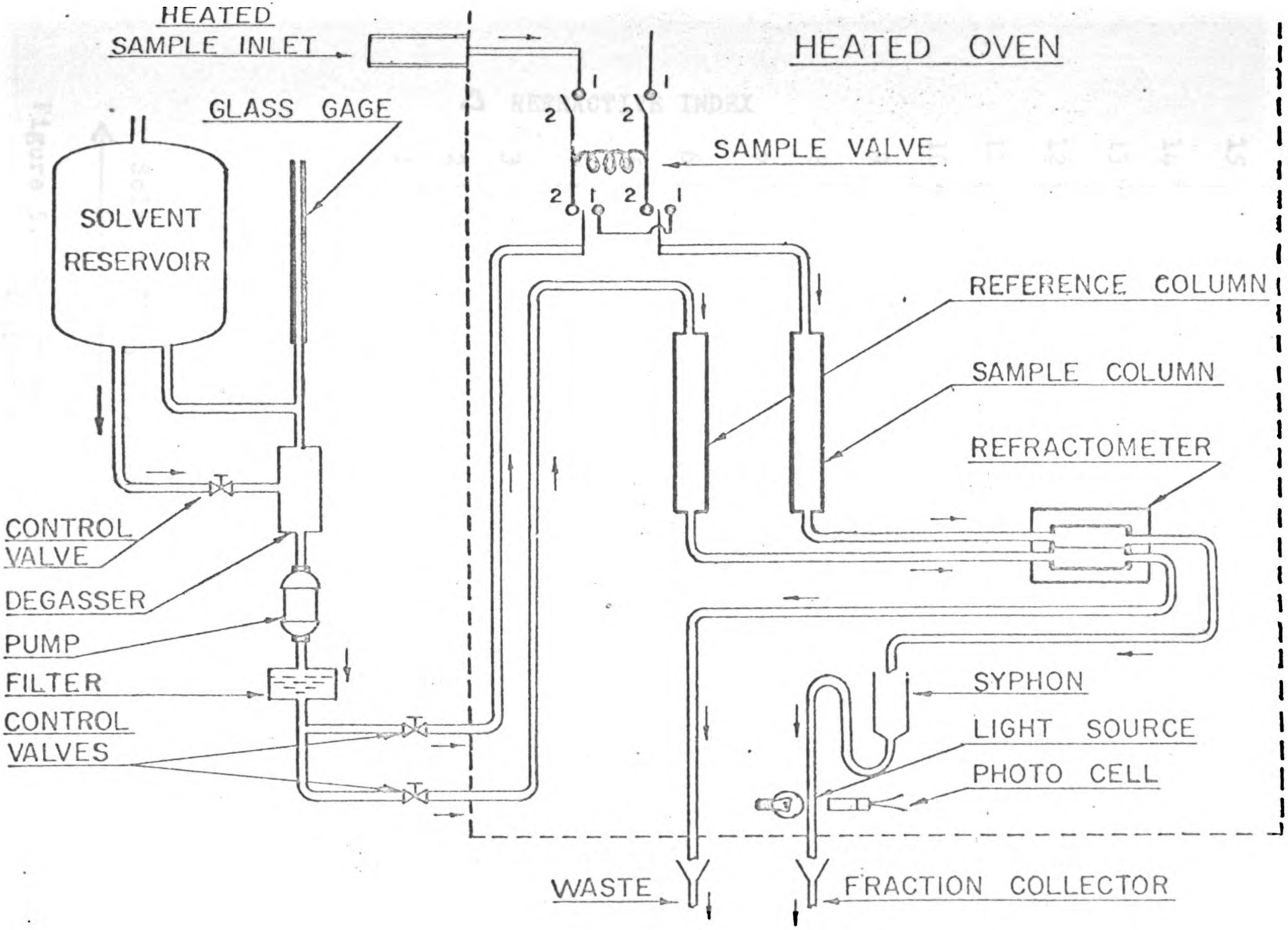


Figure 4. Waters liquid chromatography Assembly.

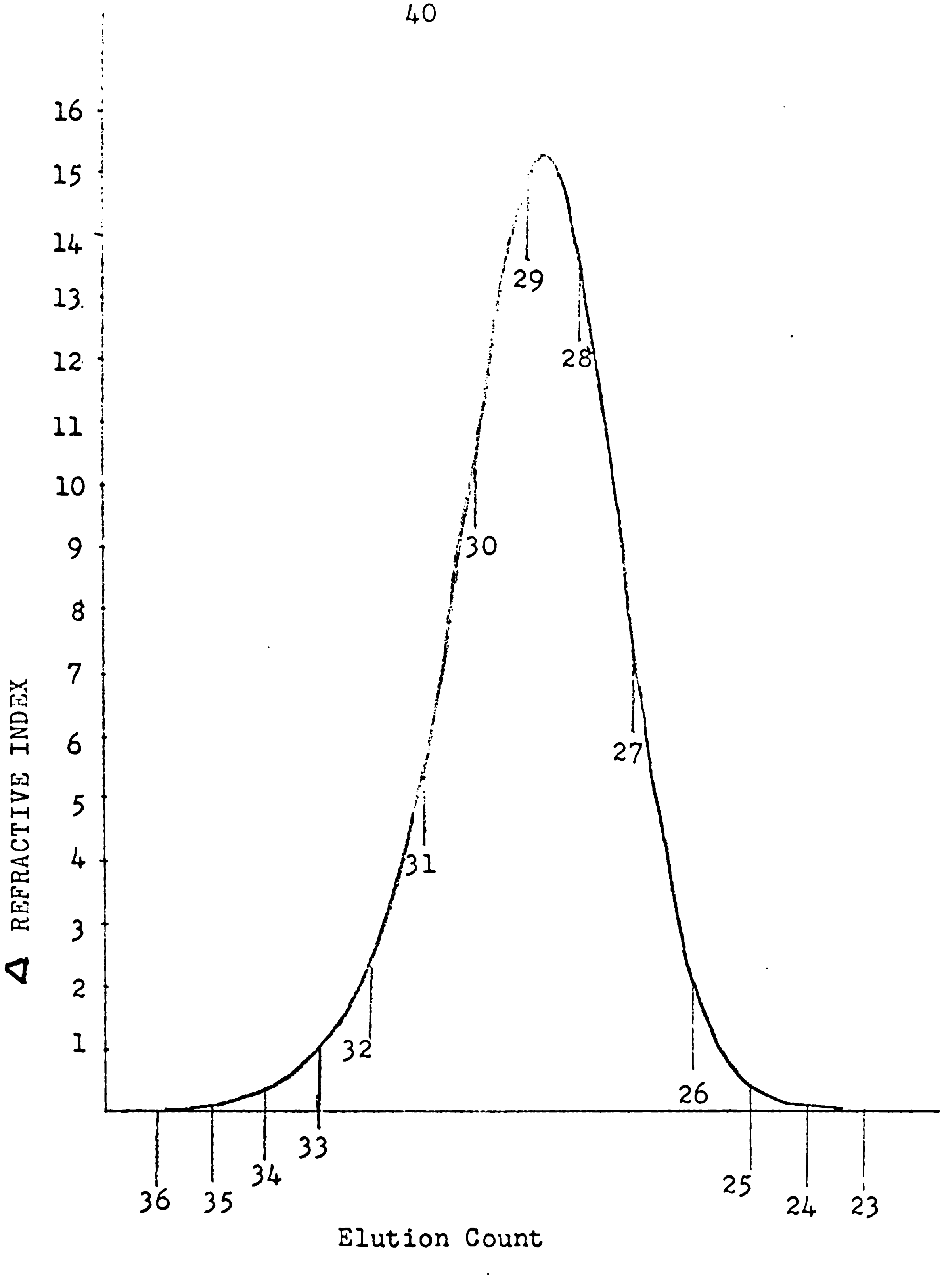


Figure 5. Gel permeation chromatogram of sample 12, calibration curve number 2.

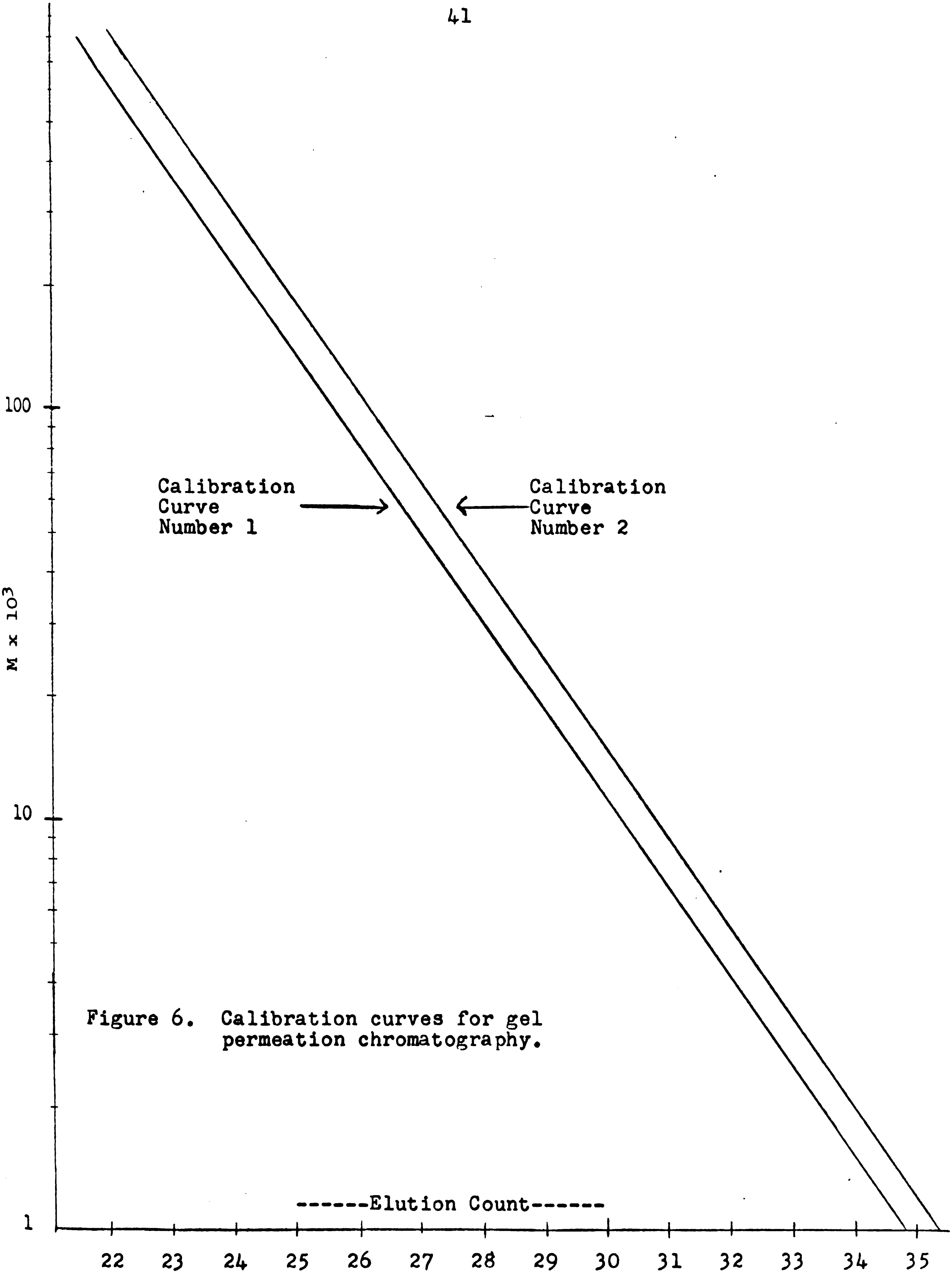


Figure 6. Calibration curves for gel permeation chromatography.

Table 5. Molecular Weight Calculations for Sample 12

Counts	Mi	hi	Cumulative hi	Normalized Cumulative hi	hi/Mi	hiMi
23	490,000	0.00	116.20			
23.5	380,000	0.05	116.20	100.0	.0000001	14,700
24	297,000	0.10	116.15	99.9	.0000003	22,750
24.5	230,000	0.25	116.05	99.8	.0000010	45,000
25	178,000	0.45	115.80	99.7	.0000025	80,100
25.5	140,000	1.00	115.35	99.4	.0000071	140,000
26	108,000	2.09	114.35	98.4	.0000193	225,720
26.5	85,000	4.40	112.26	96.8	.0000517	374,000
27	67,000	7.17	107.86	93.8	.0001070	480,390
27.5	51,000	10.88	100.69	86.5	.0002133	554,880
28	40,000	13.50	89.81	77.2	.0003375	540,000
28.5	30,800	15.19	76.31	65.6	.0004931	467.852
29	24,000	14.75	61.12	52.6	.0006145	354,000
29.5	18,600	12.98	46.37	39.8	.0006978	241,428
30	14,500	10.38	33.39	28.7	.0007158	150,510
30.5	11,300	7.83	23.01	19.8	.0006929	88,479
31	8,700	5,30	15.18	13.1	.0006091	46,110
31.5	6,800	3.72	9.88	8.5	.0005470	25.296
32	5,150	2.32	6.16	5.3	.0004504	11,948
32.5	4,050	1.52	3.84	3.3	.0003753	6,156
33	3,040	0.95	2.32	2.0	.0003125	2,888
33.5	2,500	0.60	1.37	1.2	.0002400	1,500
34	1,950	0.35	0.77	0.7	.0001794	682
34.5	1,500	0.20	0.42	0.4	.0001333	300
35	1,160	0.12	0.22	0.2	.0001034	139
35.5	900	0.10	0.10	0.1	.0001111	90
36		0.00	0.00	0.0		
		116.20			.0070154	3874918

$$\bar{M}n = \frac{\sum (h_i)}{\sum (h_i/M_i)} = 16,563 \qquad \bar{M}w = \frac{\sum (h_i M_i)}{\sum (h_i)} = 33,347$$

$\bar{M}w/\bar{M}n = 2.01$

Table 6. Molecular Weights From Gel Permeation Chromatography Data

Copolymer	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
1	37,600	123,300	3.28
2	50,200	224,600	4.47
3	82,700	245,600	2.97
4	77,300	222,100	2.87
7	42,100	214,400	5.10
8	36,300	145,900	4.00
10	13,600	25,000	1.84
11	9,100	15,900	1.75
12	16,560	33,350	2.01
13	5,720	11,200	1.96
14	13,750	30,180	2.19
16	4,100	6,780	1.65
23	4,400	8,520	1.91
25	3,080	5,770	1.87
26	8,800	18,600	2.11

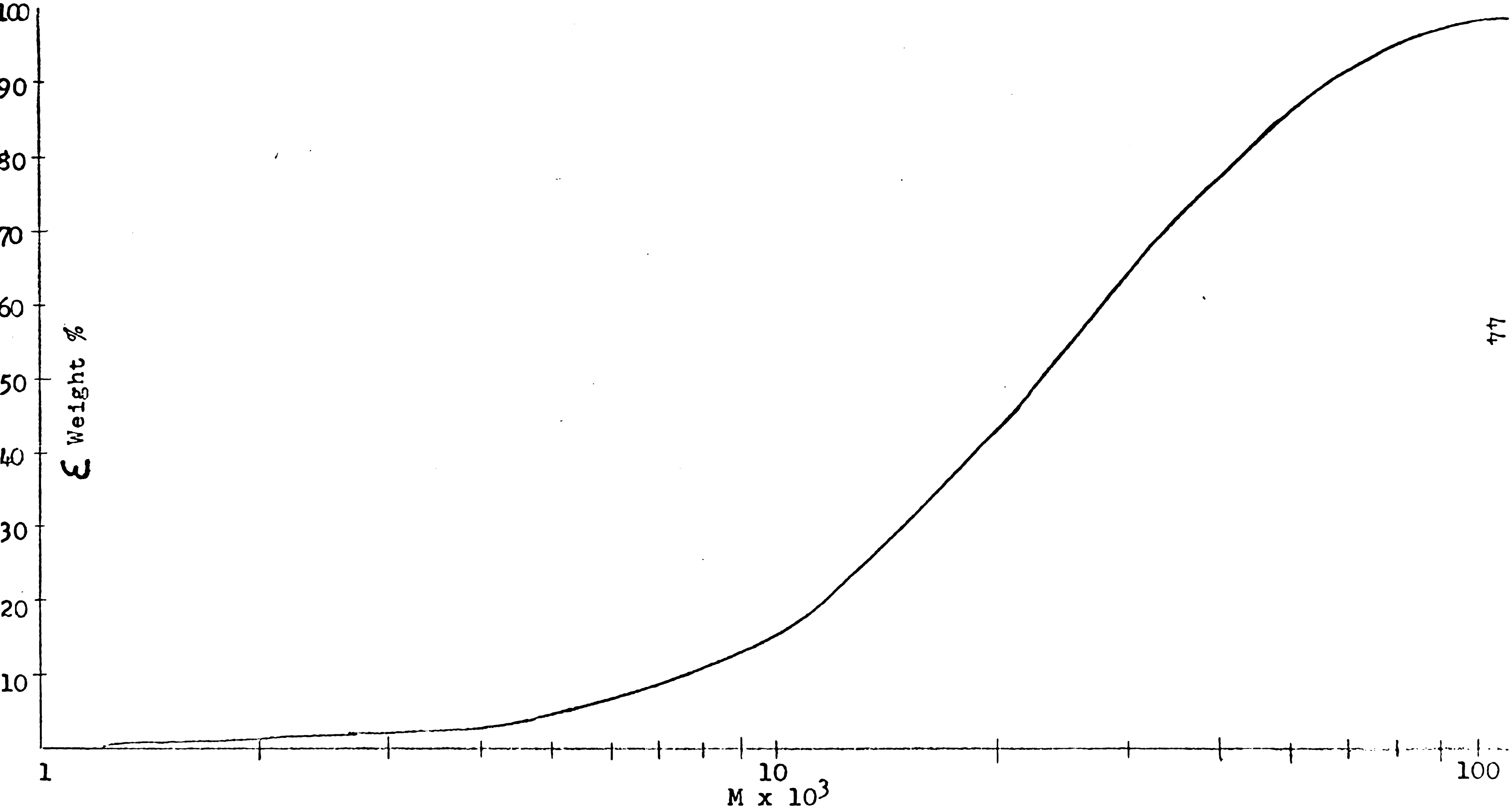


Figure 7. Integral distribution curve for sample 12.

C. Viscosity Measurement

Viscosity measurements were made on dilute solutions in acetone at concentrations of 0.5, 1.0, 1.5, and 2.0 grams per 100 milliliters. A Cannon-Fenske viscometer with 0.50 millimeter capillary diameter was utilized at 25°C. Previously published procedures (36) were followed with regard to cleaning, filling, alignment, and measurement.

The solution viscosities were measured by comparing the "efflux time t" required for a specified volume of polymer solution to flow through the capillary tube with the corresponding "efflux time t_o" for the solvent. The specific viscosity (η_{sp}) was determined at several concentrations where:

$$\eta_{sp} = t/t_o - 1$$

Values for η_{sp}/c were plotted versus the concentration in grams per 100 milliliters and extrapolated to infinite dilution to give the intrinsic viscosity, $[\eta]$. The results from the viscosity measurements on sample 12 are shown in Table 7. The plot of sample 12 is shown in Figure 8 along with the others.

Evaluation of molecular weight for a polymer from viscosity measurements is usually made from the equation:

$$[\eta] = KM^a$$

This requires an evaluation of "K" and "a" for a specific polymer solvent system using polymer samples of known molecular weight by an absolute method.

The log of the intrinsic viscosity is a linear function of the logarithm of the molecular weight:

$$\log[\eta] = \log K + a \log M$$

$\bar{M}n$ values for samples 10, 11, 12, 15, 17, and 24 had been previously determined by vapor pressure osmometry. The intrinsic viscosity was determined for these same samples and a plot of log M versus Log $[\eta]$ yields a straight line. The slope (0.79) is "a" and the intercept, when extrapolated to zero molecular weight, is K. The plot is shown in Figure 9. The extrapolation is not shown. The values of log M and log $[\eta]$ were taken from a point on the straight line and $K = 0.64 \times 10^{-4}$ was calculated using equation 1 (see Figure 9). Extrapolation to the intercept gives the same value of K.

The intrinsic viscosities and the $\bar{M}n$ values calculated from them are shown in Table 8. A typical calculation is also shown.

Billmeyer (37) points out the possibility of estimating molecular weight from the specific viscosity at one concentration. A plot of $\eta_{sp/c}$ at 0.5g/100 milliliters versus molecular weight is shown in Figure 10. This appears to be a quick, easy method to get a relative molecular weight value on styrene-maleic anhydride copolymers for comparative purposes. This was used to estimate the $\bar{M}n$ of three copolymers with the results shown in Table 9.

Table 7. Results From Viscosity Measurements on Sample 12

t_o = 93.6 seconds

Concentration	Efflux Times	Average t	η_{sp}	$\eta_{sp/c}$
2g/dl	126.1 126.2 126.4	126.2	0.348	0.174
1.5g/dl	116.8 116.8 116.8	116.8	0.248	0.165
1g/dl	108.4 108.4 108.4	108.4	0.158	0.158
0.5g/dl	100.6 100.4 100.5	100.5	0.074	0.148

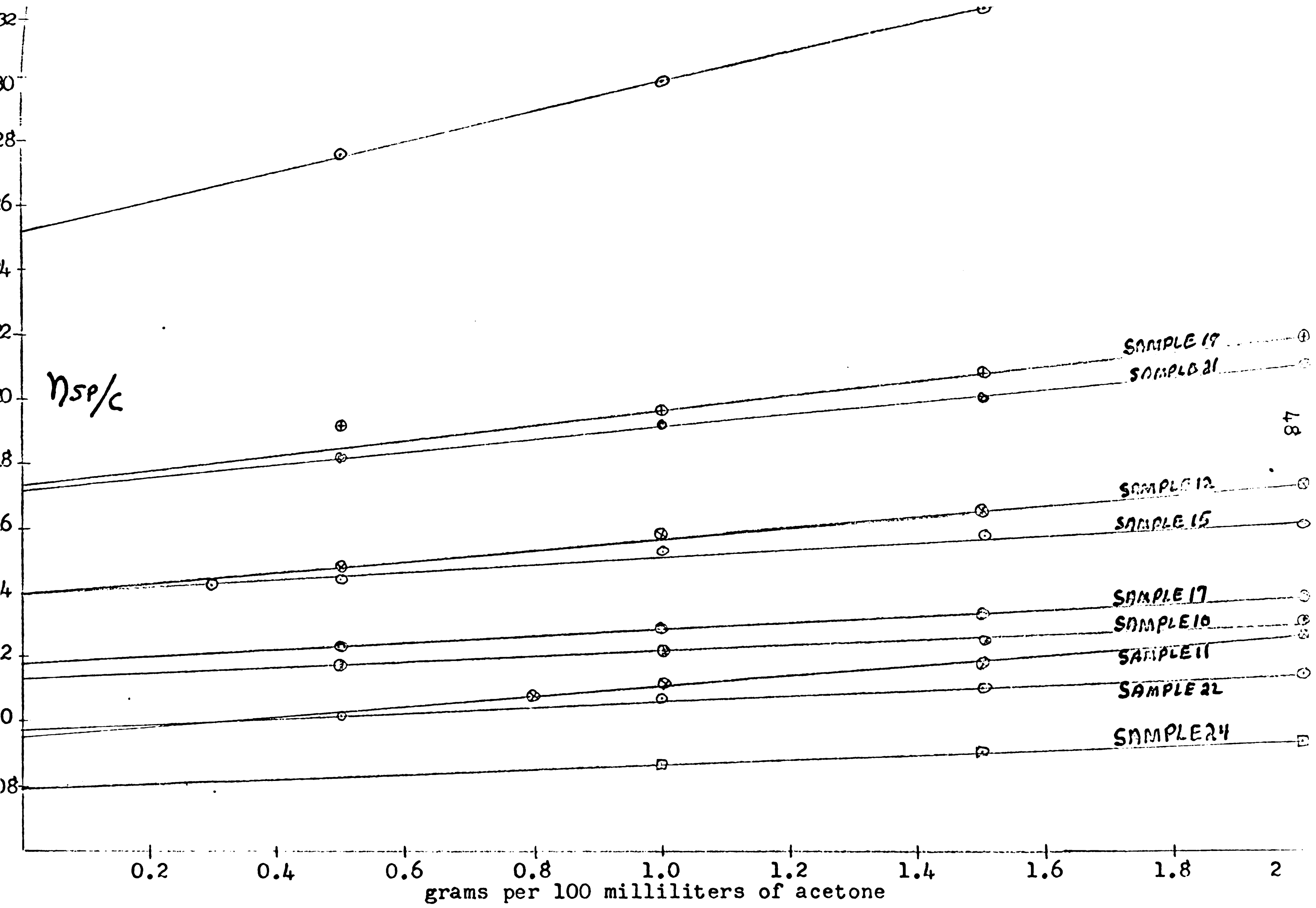


Figure 8. Intrinsic viscosity extrapolations

Table 8. Intrinsic Viscosity Results and Calculated $\overline{M}n$ Values

Copolymer	$[\eta]$	$\overline{M}n$ Calculated From
10	0.1140	13,290
11	0.0955	10,620
12	0.1400	17,240
15	0.1398	17,210
17	0.1178	13,850
19	0.174	22,710
20	0.2525	36,410
21	0.1725	22,460
22	0.0975	10,650
24	0.0800	8,480

Typical Calculation, Sample 24

$$0.08 = 0.64 \times 10^{-4} M^{.79}$$

$$M^{.79} = 1257.86$$

$$.79 \log M = \log 1257.86$$

$$\log M = 3.92855$$

$$M = 8,483$$

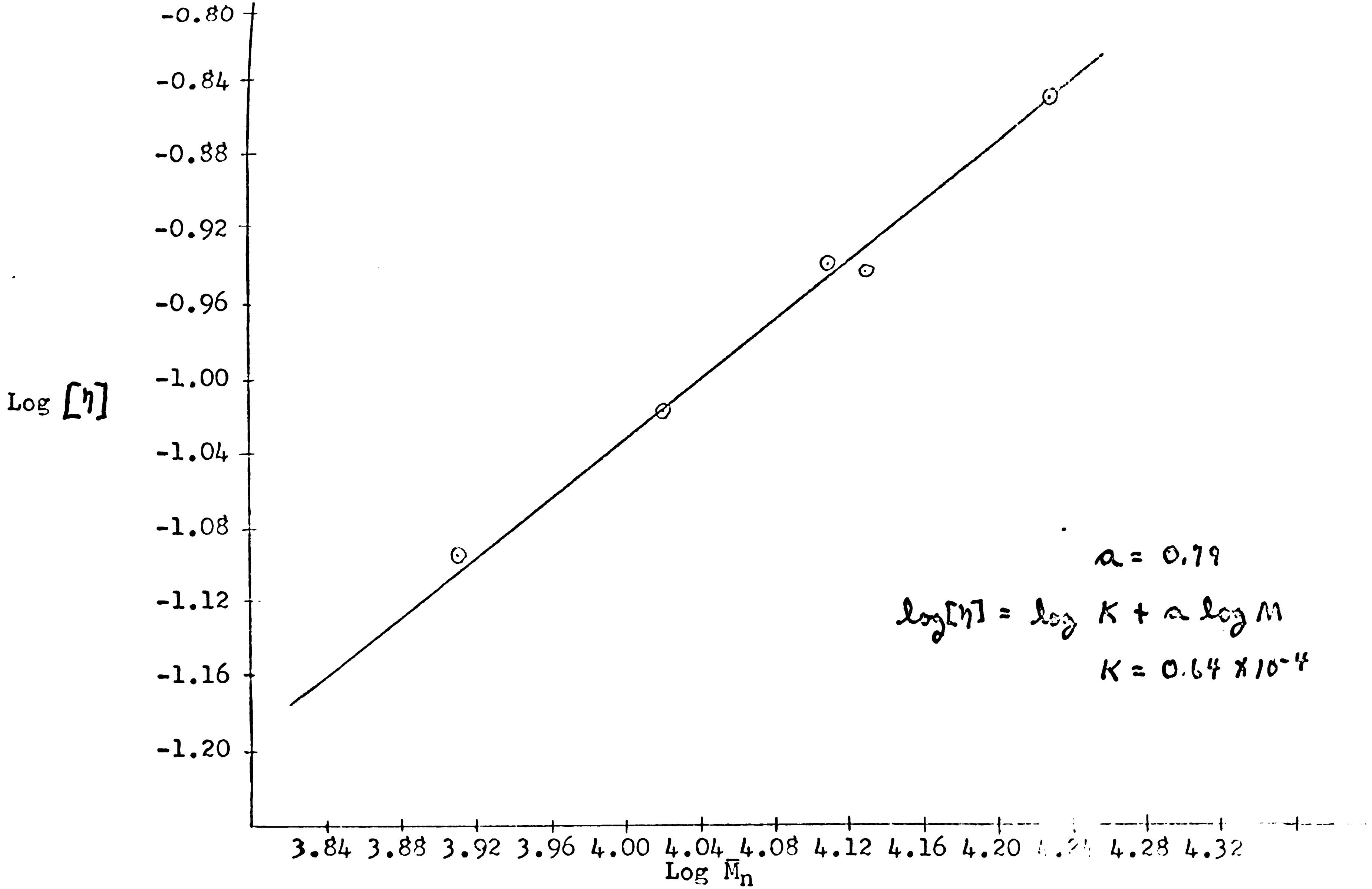


Figure 9. Log $[\eta]$ versus Log K for samples 10, 11, 12, 15, 17, and 24.

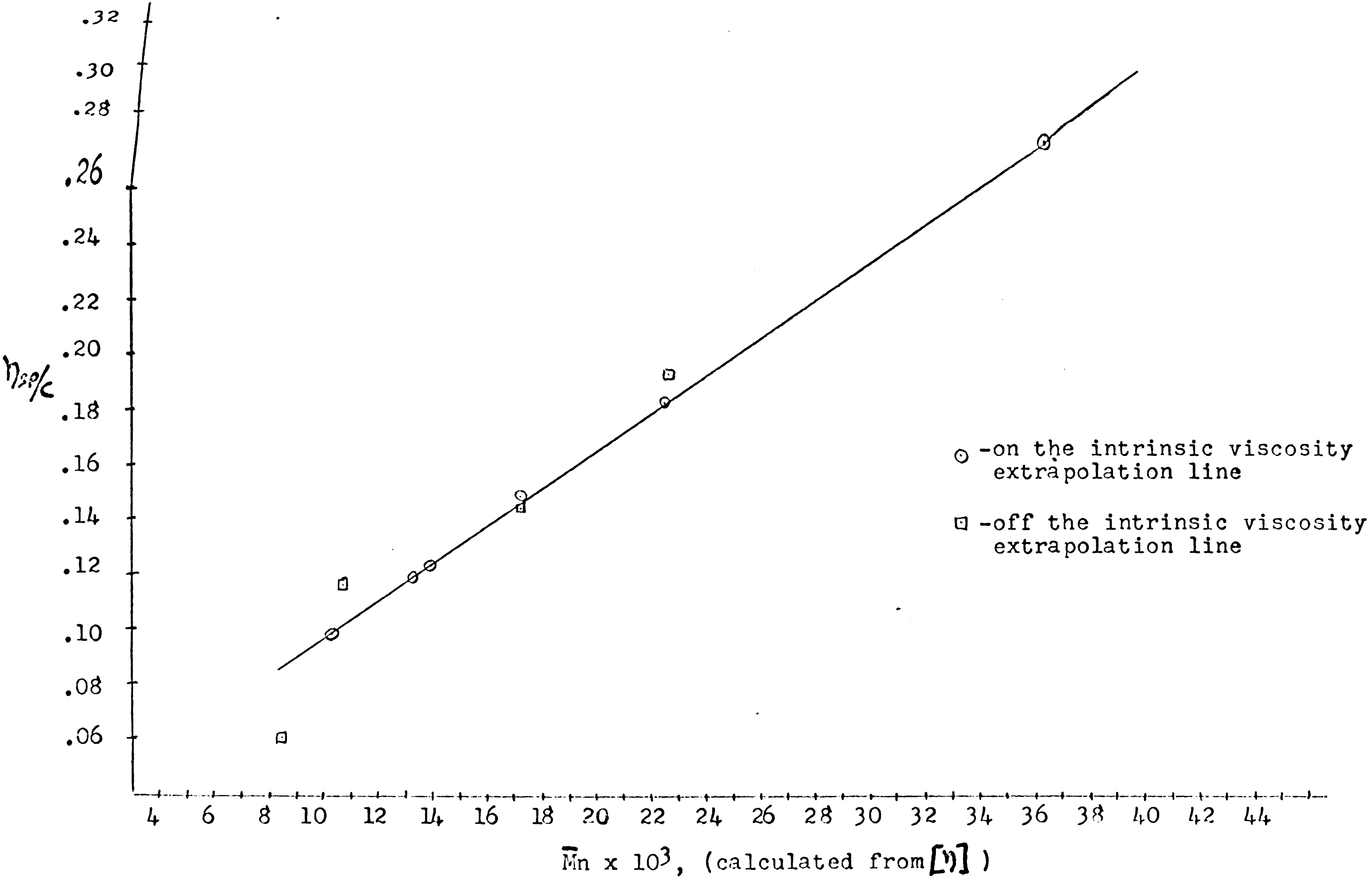


Figure 10. η_{sp}/c versus $\bar{M}n$ at concentrations of 0.5 grams per 100 milliliters in acetone.

Table 9. $\overline{M}n$ Estimated From η_{sp}/c at C = 0.5g/100 milliliters

Copolymer	η_{sp}/c	Estimated $\overline{M}n$
5	2.24	200,000
18	1.400	150,000
19	0.070	6,300

CORRELATION OF RESULTS AND DISCUSSION

I. General

The choice of solvent in which the copolymerization occurs is a critical factor in determining the molecular weight of alternating styrene-maleic anhydride copolymers. Of the solvents used, only tetrahydrofuran and isopropyl benzene resulted in low molecular weight polymers within the desired range ($\bar{M}n < 20,000$).

The preparation of low molecular weight styrene-maleic anhydride samples in dimethoxymethane has been previously reported (37). However, all of the copolymers prepared in dimethoxymethane during this study had $\bar{M}n$ values in excess of 37,000.

In dimethoxymethane, the reactions initiated with 2,2'-azobis (2-methylpropionitrile) were much faster and the yields were better than when benzoyl peroxide was used as the initiator. The chromatograms in Appendix 1 and the $\bar{M}w/\bar{M}n$ ratios in Table 6 show a broad molecular weight distribution for all four copolymers (samples 1 through 4). The two samples initiated by 2,2'-azobis (2-methylpropionitrile) (samples 3 and 4) have a much narrower distribution than the corresponding copolymers initiated with benzoyl peroxide (samples 1 and 2).

The copolymers prepared in benzene were also of high molecular weight. Sample 7 with an $\bar{M}n$ value of 36,300 was the lowest molecular weight sample of the five prepared. Gel permeation chromatograms are shown for samples 7 and 8 in Appendix 1. The benzoyl peroxide initiated sample (sample 8) has the higher molecular weight ($\bar{M}n = 42,000$), but its distribution is highly unsymmetrical as is evidenced by the shape of the chromatogram and by the $\bar{M}w/\bar{M}n$ value of 5.1.

The rate of reaction in benzene, (at comparable temperatures) was much faster than in dimethoxymethane. This is evidenced by higher yields, shorter reaction times, and reaction without added initiator.

The one reaction in bromochloromethane resulted in an $\bar{M}n$ greater than 150,000 (estimated from one $\eta_{sp/c}$ value, see Table 9). High molecular weights ($\bar{M}n > 100,000$) have been reported for copolymerization of styrene and maleic anhydride in methylene chloride (39).

In the polymerization of styrene, halogenated hydrocarbons are reported to be active chain transfer agents (40); much more active than simple hydrocarbons. This is not the case in styrene-maleic anhydride copolymerizations. The comparison of the molecular weight of copolymers prepared in bromochloromethane and isopropyl benzene is illustrative (samples 5 and 19, Table 9). This aspect will be discussed further under chain transfer.

The use of tetrahydrofuran as a solvent resulted in low molecular weight ($\bar{M}n < 15,000$) copolymers. The copolymers initiated with benzoyl peroxide and 2,2'-azobis (2-methylpropionitrile) had similar distributions (see the chromatograms and distribution curves for samples 10 and 11 in Appendices 1 and 2) but significantly different molecular weights. A 30% difference was observed in the $\bar{M}n$ values of samples 10 and 11, with the benzoyl peroxide initiated polymerization (sample 10) giving the higher molecular weight.

Isopropyl benzene and carbon tetrachloride were evaluated as portions of the solvent in combination with tetrahydrofuran. The technique by which two polymers, one soluble and the other insoluble, are produced in mixed solvents has been termed "insitu fractionation". Table 10 reports the results from polymerization in both of the above mentioned mixtures to include data on homogeneous copolymerizations in which the ratio of the mixture has been varied enough to keep the copolymers in solution. The molecular weight difference between samples 13 and 16 indicates that styrene-maleic anhydride copolymers are more soluble in isopropyl benzene than they are in carbon tetrachloride. Obviously, the combination of various non-solvents with solvents can result in the isolation of polymers with varying molecular weights.

This same technique is also useful for preparing polymers with narrow distribution. The narrow distributions of samples 12 and 15 are shown on the gel permeation chromatograms and distribution plots in the appendices. The chromatogram of sample 14 is essentially a composite of samples 12 and 13, assuming equal concentrations. The lack of symmetry in sample 13 is due to the loss of the higher molecular weight portion by fractionation.

The polymerization of styrene and maleic anhydride proceeds rapidly in isopropyl benzene with and without added initiator. Low molecular weight polymers with $\bar{M}n$ values varying from 6,000 to 36,000 are readily obtained. The results with no added initiator are shown graphically in Figure 11. It may be noted that the molecular weight decreases substantially as the temperature increases. This is an excellent method for preparing polymers with a predetermined molecular weight. The results with initiator are similar near reflux temperatures but differ at lower temperatures. The following is illustrative:

Sample		$\bar{M}n$ 152°C	 80°C
23	Initiated with 0.84 grams benzoyl peroxide	6500	22,750
24	No added initiator	7500	36,000

II. Gel Permeation Chromatography

In gel permeation chromatography a dilute solution of polymer is injected into a solvent stream flowing through a column packed with porous beads of inert, cross-linked, polymer gel of controlled porosities. Under a constant total flow rate, the permeation rate of the molecular species of different sizes in the polymer sample differ. The smaller molecules have greater accessible volumes in the gel packed column and permeate more slowly than large molecules. The larger species permeate the gel least and are eluted first.

Styrene-maleic anhydride copolymers were not expected to permeate the gel at the same rate as polystyrene; however, this did occur. Table 11 compares the $\bar{M}n$ values from vapor pressure osmometry data with those calculated from gel permeation chromatography data. These same data are shown graphically in Figure 12. The correlation between the two methods is obvious. In tetrahydrofuran at $\overline{M}n$ values less than 20,000 styrene-maleic anhydride copolymers appear to have the same "effective" size as polystyrene on the column utilized.

As was mentioned earlier, such a correlation was not expected. Just recently, Meyerhoff (41) evaluated polystyrene, cellulose nitrate, and polymethyl methacrylate and in a paper on molecular parameters and gel permeation noted that neither molecular weight, intrinsic viscosity, radius of gyration, or diffusion coefficient permits any general correlation with the evolution volume independent of the chemical nature of the polymer.

It is reasonable that different polymer structures will pass through the columns at different rates. The fact that styrene-maleic anhydride copolymers, with $\overline{M}n$ values less than 20,000, acted like polystyrene samples is at present unexplained.

For the column circuit used, the optimum resolution of polymers differing in molecular size occurred between elution counts 21 and 28. Only reasonable resolution was possible between counts 28 and 36. It was fortunate that the low molecular weight samples tested eluted largely in the area of reasonable resolution.

The copolymers with $\overline{M}n$ values less that 20,000 have narrower distributions and lower $\overline{M}w/\overline{M}n$ values that the higher molecular weight copolymers. This trend is apparent from the data in Table 6. It may also be reflecting the loss of resolution due to the transition into the reasonable resolution area; however, even though this is a factor it would not be expected to account for the entire trend.

The samples with $\bar{M}n$ below 20,000 have similar $\bar{M}w/\bar{M}n$ values (see Table 6) , samples 14 and 16 being exceptions.

Sample 14 ($\bar{M}w/\bar{M}n$ = 2.10) resulted when a 4.0/0.5 ratio of tetrahydrofuran to isopropyl benzene was utilized as the solvent. The $\bar{M}n$ value was similar to that obtained for a copolymer prepared in pure tetrahydrofuran (sample 10); however, $\bar{M}w$ was larger by 5000. Thus, isopropyl benzene used in this fashion appears to broaden the distribution. This is readily observed from the chromatograms in Appendix 1 (samples 12 and 14).

III. Viscosity Measurements

Viscosity measurements cannot be used as an "absolute" method of molecular weight determination. The most general equation expressing the dependence of the intrinsic viscosity on molecular weight (42) is:

$$[\eta] = KM^{a}$$

"K" and "a" are usually determined from data based on solution viscosity of narrow polymer fractions of known molecular weight. In this case, the copolymers used for determination of "K" and "a" were not fractionated. The molecular weights of the samples were determined by vapor pressure osmometry. Gel permeation chromatography data indicated that these copolymers had $\bar{M}w/\bar{M}n$ values varying from 1.75 to 2.01. The use of $[\eta]=KM^{a}$ and the experimentally determined values of "K" and "a" for styrene-maleic anhydride copolymers of similar polydispersity should result in reasonable $\bar{M}n$ values. Figure 13 is a plot of intrinsic viscosities versus $\bar{M}n$ values calculated, using "K" = 0.64 x 10^4 and "a" = .79. The values calculated from intrinsic viscosity data correlate well with the $\bar{M}n$ values from vapor pressure osmometry in the range investigated ($\bar{M}n < 20,000$). This correlation is shown in Table 12.

IV. Chain Transfer

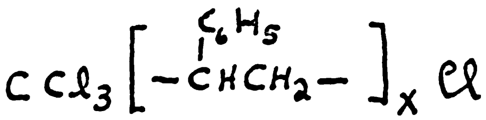
Isopropyl benzene and carbon tetrachloride were tried as chain transfer agents in tetrahydrofuran. Their effectiveness as chain transfer agents for styrene has been noted by Flory (43). Since they were examined in tetrahydrofuran, the combination must be more effective than tetrahydrofuran to be noticeable. There was no molecular weight reduction with either compound under the conditions utilized.

Benzene, isopropyl benzene, and carbon tetrachloride have all been reported (43) as chain transfer agents for styrene with relative effectiveness of approximately 1:4:360 respectively.

The molecular weights of copylymers obtained in benzene (samples 7 and 8) at 80°C indicated that benzene is not sufficiently effective as a chain transfer agent to produce low molecular weight styrene-maleic anhydride copolymer.

The effectiveness of isopropyl benzene in reducing the molecular weight of the copolymers was apparent at 80°C and was very significant at 152°C (see Figure 11). A mixture with tetrahydrofuran gave results similar to those obtained with pure tetrahydrofuran (both conducted at 65°C), indicating that isopropylbenzene is not noticeable over tetrahydrofuran as a chain transfer agent under the conditions used.

Polystyrene prepared in the presence of carbon tetrachloride has four chlorine molecules per molecule (43). The resultant polymer has been represented by the formula:



$$CCl_3\left[-\overset{C_6H_5}{\overset{|}{C}}HCH_2-\right]_x Cl$$

and a transfer mechanism assumed

$$CCl_3-M_x\cdot + CCl_4 \longrightarrow CCl_3-M_x-Cl + CCl_3\cdot$$

$$CCl_3\cdot \xrightarrow{+M} CCl_3-M\cdot \xrightarrow{+M} etc. \longrightarrow CCl_3M_x\cdot$$

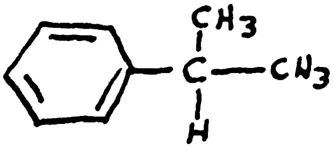
A telomer is a compound capable of forming the terminal part of the polymer. The telomerization of styrene by carbon tetrachloride and chloroform have been reported (8). In addition, carbon tetrachloride has been shown to telomerize divinyl benzene to solid fusable polymers (8).

In spite of all of the above, the data show the complete lack of participation by carbon tetrachloride in the copolymerization of styrene and maleic-anhydride. This is verified by the lack of chlorine in the following copolymers prepared in the presence of carbon tetrachloride.

Sample	%C	%H	%Cl	% Maleic anhydride moiety based on carbon content
15	71.30	5.19	trace	50
17	71.29	5.20	trace	50

The results with carbon tetrachloride are surprising in light of what has previously been reported. Generally, aliphatic hydrocarbons become more reactive (43) when substituted with halogens, and carbon tetrachloride is very reactive with styrene, vinyl acetate, and to a lesser extent methyl methacrylate. However, it is clearly indicated that carbon tetrachloride is not a chain transfer agent for styrene-maleic anhydride in tetrahydrofuran.

Aromatic hydrocarbons with benzylic hydrogens are active chain transfer agents (43). Isopropyl benzene is such a compound and did act as a chain transfer agent. The plot of $\bar{M}n$ versus temperature in Figure 11 indicates the effect of temperature. As a general rule, benzylic hydrogens

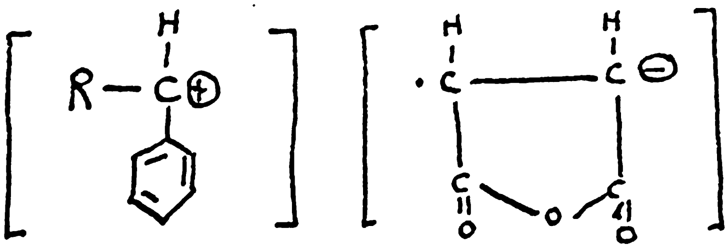


are easy to abstract, resembling allylic hydrogens.

The molecular weights obtained in tetrahydrofuran indicate that it is an effective chain transfer agent. The structure of tetrahydrofuran suggests transfer through a hydrogen.

The available data suggest that chain transfer with styrene-maleic anhydride systems through hydrogen is effective; however, chain transfer through halogen is non-existent or difficult. This statement is supported by some recent work in this laboratory, copolymerization in dioxane gave low molecular weights ($\bar{M}n$ = 8,000) at moderate temperatures (44).

Walling and co-workers (21) explain the particularly high reactivity of maleic anhydride for styrene in terms of an intermediate:

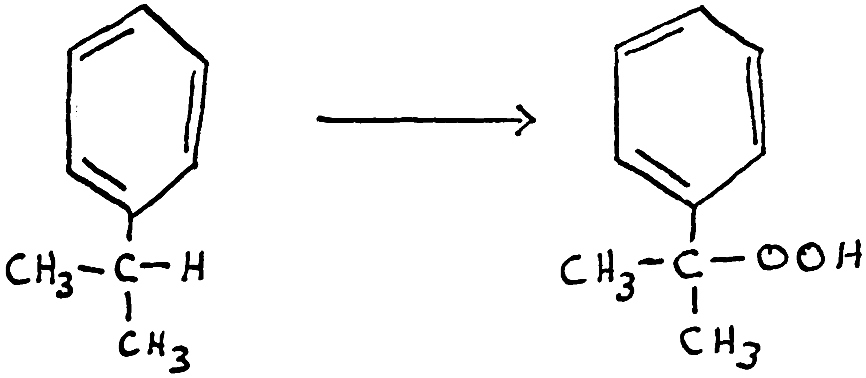


The e values reported earlier for styrene and maleic anhydride support this concept. Other intermediates have been suggested (8) and the "intermediate" concept has been the subject of much discussion.

If copolymerization of styrene and maleic anhydride does go through an "intermediate", the structure of the "intermediate" is one that does not allow chain transfer with halogenated hydrocarbons like carbon tetrachloride, methylene chloride, and bromochloromethane. However, chain transfer through hydrogen does occur and is quite rapid at elevated temperatures.

V. Isopropyl Benzene Stability

Isopropyl benzene is oxidized in the presence of air and heat to cumene hydroperoxide.



This is an initiator and if formed could account for the low molecular weight obtained in isopropyl benzene. Care was taken to see that this did not happen (see under reagents).

The reactions in isopropyl benzene without initiator proceeded easily and rapidly. This further suggested formation of cumene hydroperoxide. Polymerizations without initiator were carried out in benzene to show that this could be accomplished in a solvent where peroxides would not be a problem. Thus demonstrating that copolymerization of styrene-maleic anhydride proceeds in the absence of initiator if the proper procedure and technique are utilized.

VI. Benzene Extraction

All of the styrene-maleic anhydride copolymers were extracted by benzene before they were characterized as to molecular weight and molecular weight distribution. Some of the existing literature on styrene-maleic anhydride copolymers reports characterization without benzene extraction. Benzene removes the residual monomer, polystyrene and catalyst fragments. The removal of residual monomer is important. Extraction puts all samples on a common basis.

For example, the osmometry data on sample 10 before and after extraction (both samples dried) were:

	$\overline{M}n$
Sample 10, not extracted	12,300
Sample 10, extracted	13,500

A similar check was made on a higher molecular weight sample,(sample 7 with and without extraction), via gel permeation chromatography. The extracted sample gave the expected parabolic type curve with a smooth decline from elution count 30 through 37. The non-extracted sample is almost the same but the decline curve starts back up after touching down at elution count 34. This small peak is low molecular weight material, probably monomer. Figure 14 has one curve superimposed on the other showing that the low molecular weight peak is the only difference.

Both samples were dried; however, it is apparent that drying (55°C at 0.2mm. for 8 hours) did not remove all of the low molecular weight constituents. The principle contaminant is believed to be maleic anhydride.

VII. Structure of the Polymer

When styrene and maleic anhydride are copolymerized under the conditions used, the result is a 50:50 copolymer (11). Recent high frequency titration work by Meyer (38) on similar polymers confirms this. This has been further confirmed on many occasions by carbon-hydrogen analysis on samples prepared in this laboratory.

A technique (34) utilizing gel permeation chromatography on styrene-maleic anhydride copolymers shows that the styrene and maleic anhydride moieties are equally distributed throughout the polymer distribution. The method consisted of catching the 5 milliliter eluants from the gel permeation chromatography unit and analyzing each by ultra-violet for styrene. The normalized styrene data were plotted on the gel permeation chromatography curve and conformed very well, indicating an equal distribution of styrene throughout the polymer distribution.

Table 10: Results from Copolymerization in Mixed Solvents

Solvent	Copolymer Designation	$\overline{M}n$ (VPO)
Tetrahydrofuran	10	13,500
3/2 blend of tetrahydrofuran and isopropyl benzene	12 and 13	17,010 5,000
4.0/0.5 blend of tetrahydrofuran and isopropyl benzene	14	15,290
3/2 blend of tetrahydrofuran and carbon tetrachloride	15 and 16	17,210 3,420
4/1 blend of tetrahydrofuran and carbon tetrachloride	17	12,500

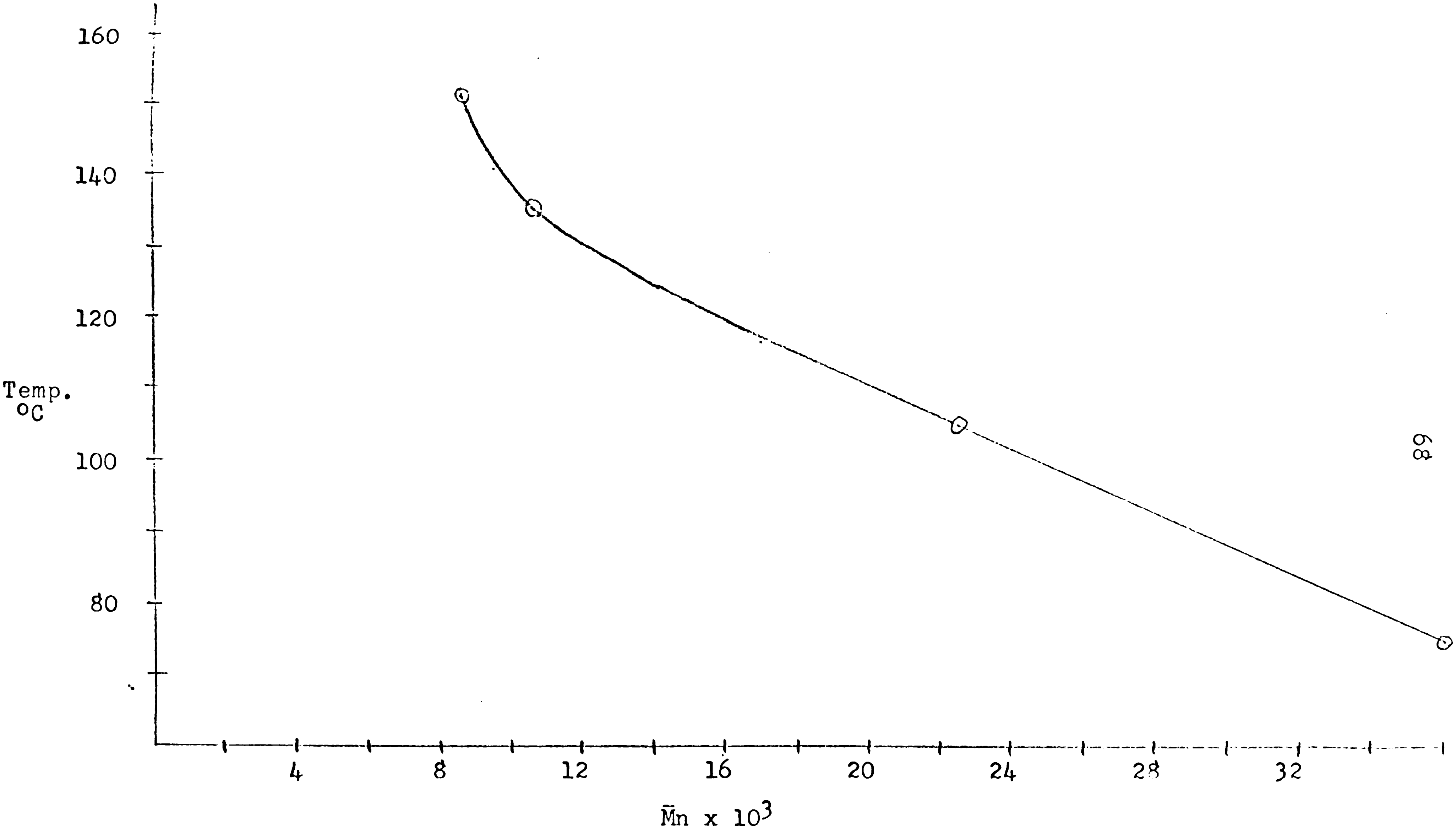


Figure 11. $\bar{M}n$ versus polymerization temperature in isopropyl benzene, no added initiator.

Table 11. Comparison of $\bar{M}n$ by Vapor Pressure Osmometry with $\bar{M}n$ by Gel Permeation Chromatography

Copolymer	$\bar{M}n$ (VPO)	$\bar{M}n$ (GPC)
10	13,500	13,500
11	10,500	9,100
12	17,010	16,560
13	5,000	5,720
14	15,290	13,750
16	3,420	4,100
23	5,740	4,400
25	1,500	3,080
26	8,700	8,800

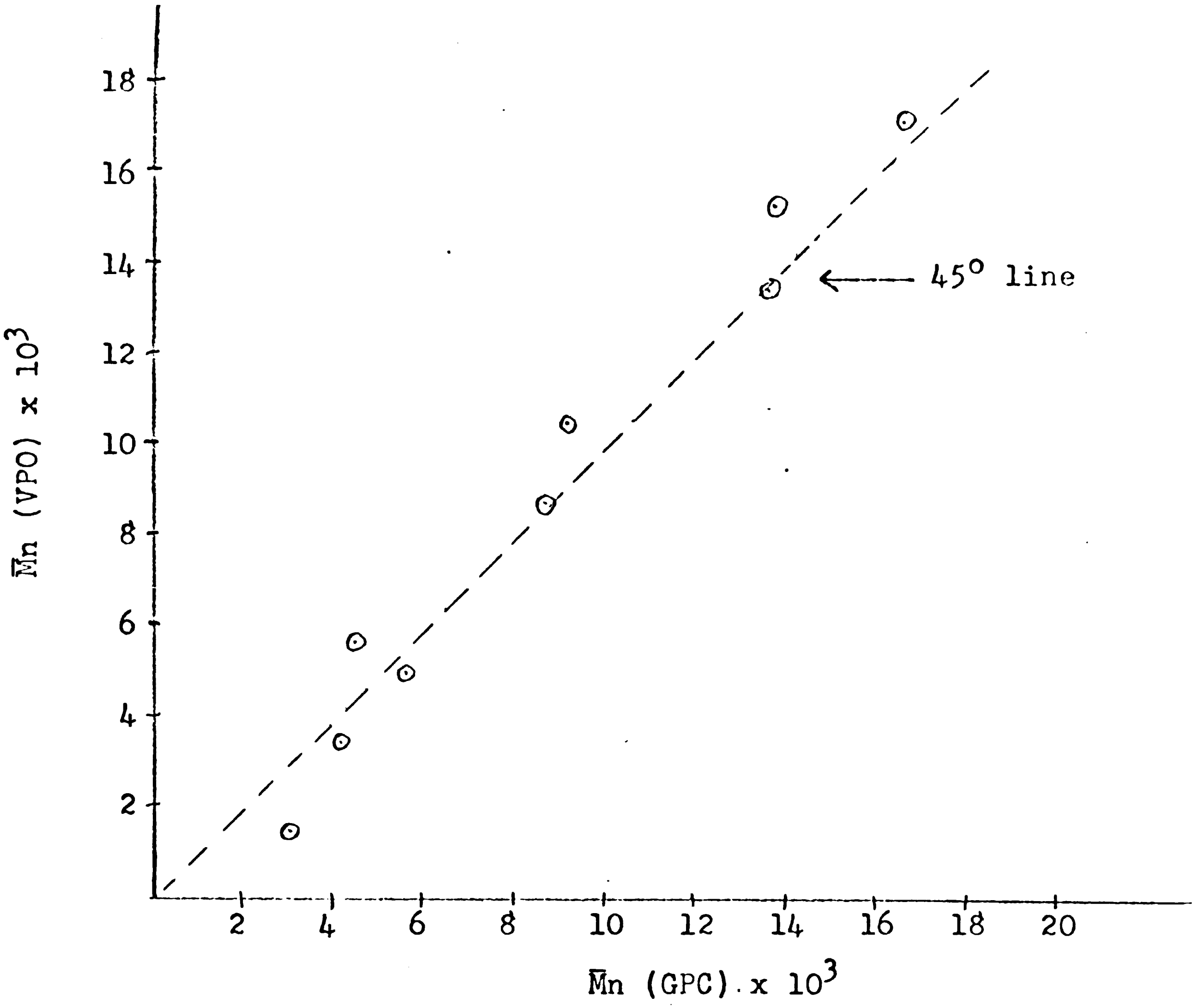


Figure 12. $\overline{M}$n by vapor pressure osmometry versus $\overline{M}$n by gel permeation chromatography.

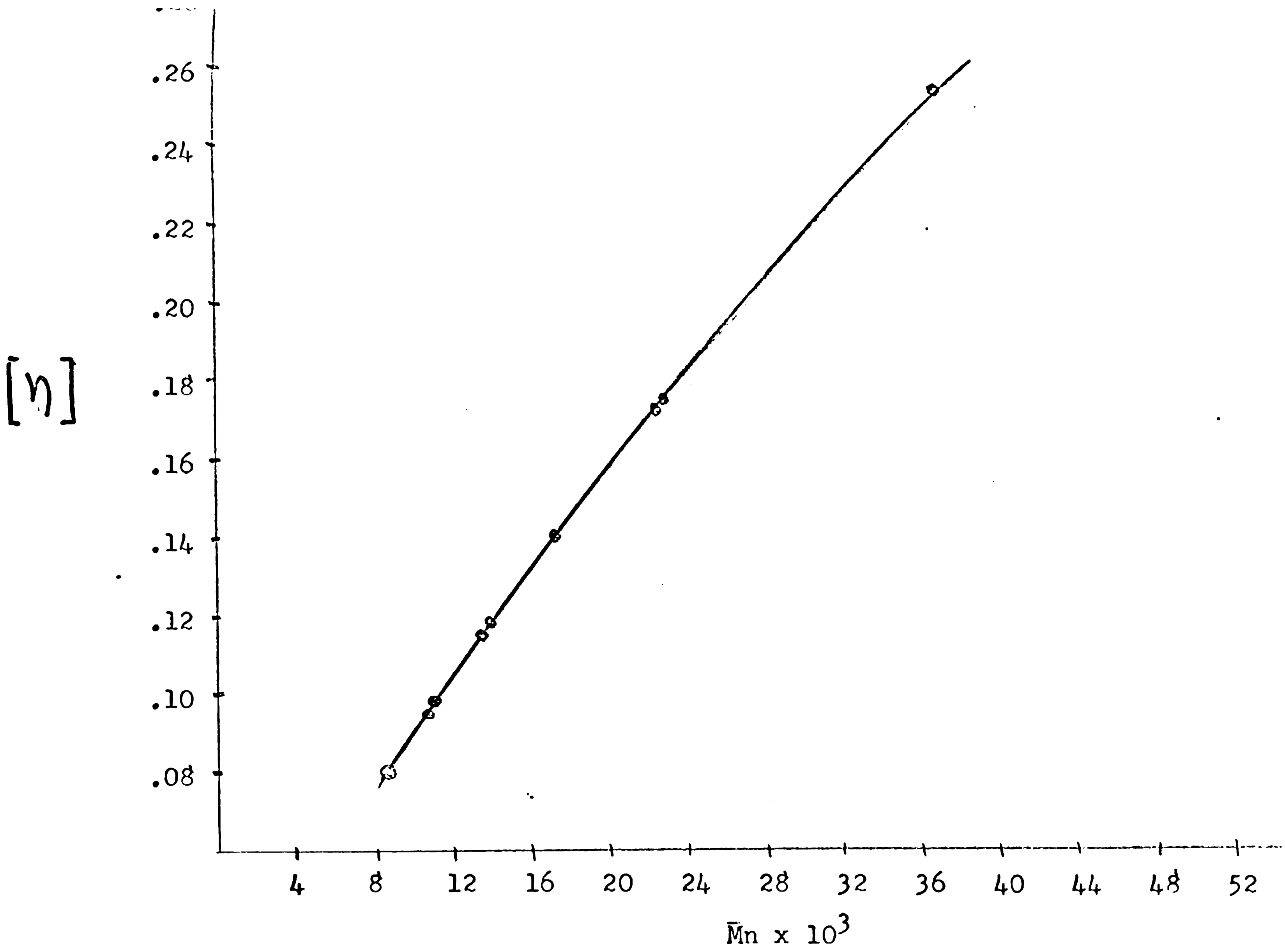


Figure 13. Intrinsic viscosity versus $\bar{M}n$

Table 12. A Comparison of $\overline{M}n$ Values Obtained From Intrinsic Viscosity Data with $\overline{M}n$ Values for Vapor Pressure Osmometry Data

Sample	$\overline{M}n$ (VPO)	$\overline{M}n$ (Vis)
10	13,500	13,290
11	10,470	10,620
12	17,010	17,240
15	17,210	17,210
17	12,500	13,850
24	8,150	8,480

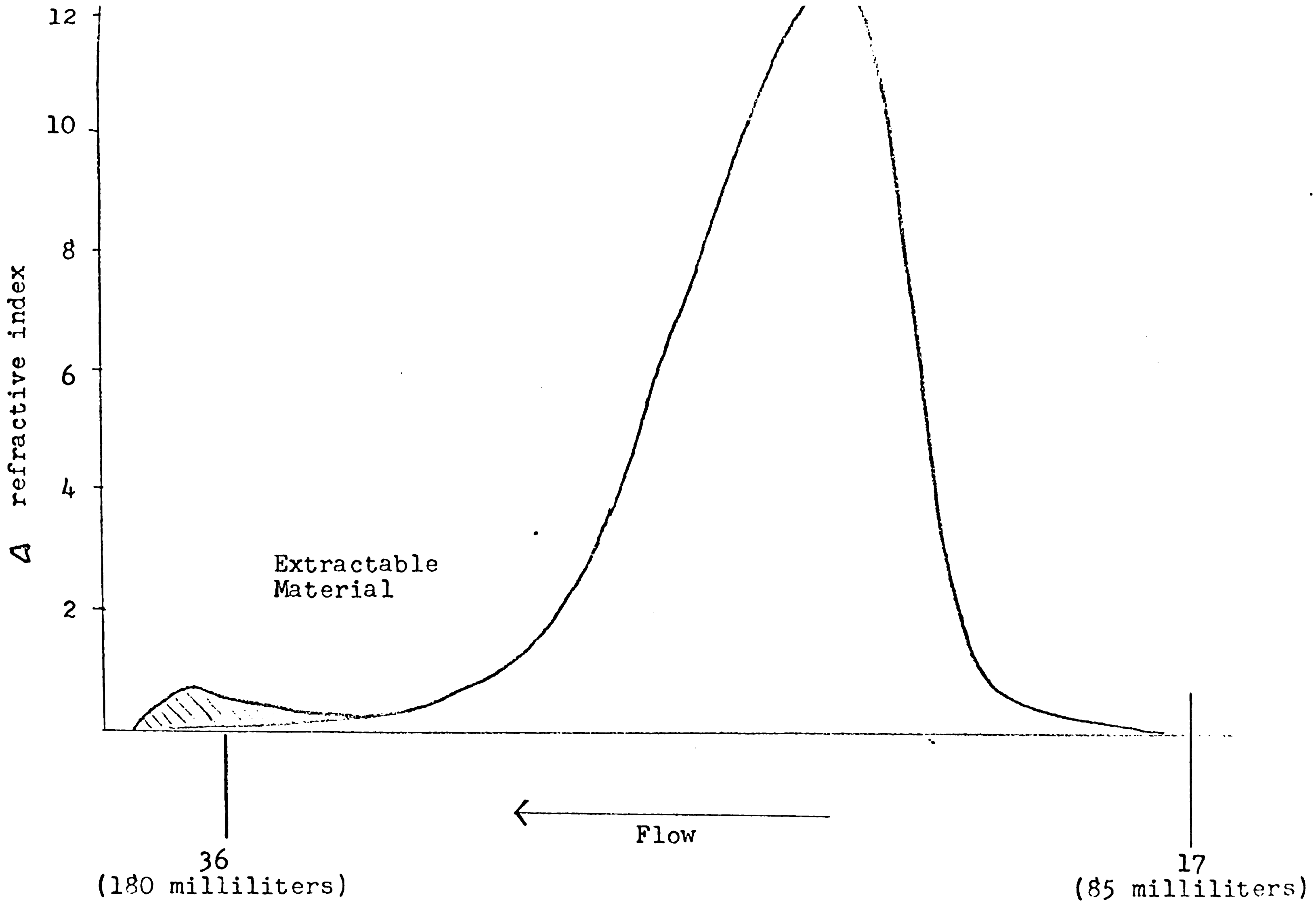


Figure 14. Detection of non-polymeric materials in polymers via gel permeation chromatography.

SUMMARY

1. Styrene-maleic anhydride copolymers were prepared with number average molecular weights varying from 3,000 to 36,000. The molecular weights within this range were varied as desired by varying catalyst concentration, temperature, and solvent.

2. Number average and weight average molecular weights were calculated from data obtained from a polystyrene calibrated gel permeation chromatography unit with a general purpose column.

3. Number average molecular weights were determined via vapor pressure osmometry.

4. The number average molecular weights determined by gel permeation chromatography correlated well with those determined by vapor pressure osmometry.

5. Molecular weight distributions were determined from the gel permeation chromatography data.

6. Low molecular weight styrene-maleic anhydride copolymers are readily prepared in isopropyl benzene without added initiator. $\bar{M}n$ can be varied from 8,000 to 36,000 by varying the polymerization temperature.

7. The polymerization of styrene-maleic anhydride in tetrahydrofuran results in low molecular weight polymers ($\bar{M}n$ = 10 to 13,000). $\bar{M}n$ can be varied by the choice of initiator.

8. Carbon tetrachloride, a very effective chain transfer agent in homopolymerization of styrene, did not act as chain transfer agents in the preparation of styrene-maleic anhydride copolymers.

9. Viscosity measurements were made on a series of styrene-maleic copolymers ($\overline{M}w/\overline{M}n$ values ranging from 1.75 to 2.01). The constants in the equation

$$[\eta] = KM^{a}$$

were evaluated using samples with $\overline{M}n$ values determined by vapor pressure osmometry and were

$$K = 0.64 \times 10^{-4}$$

$$a = 0.79.$$

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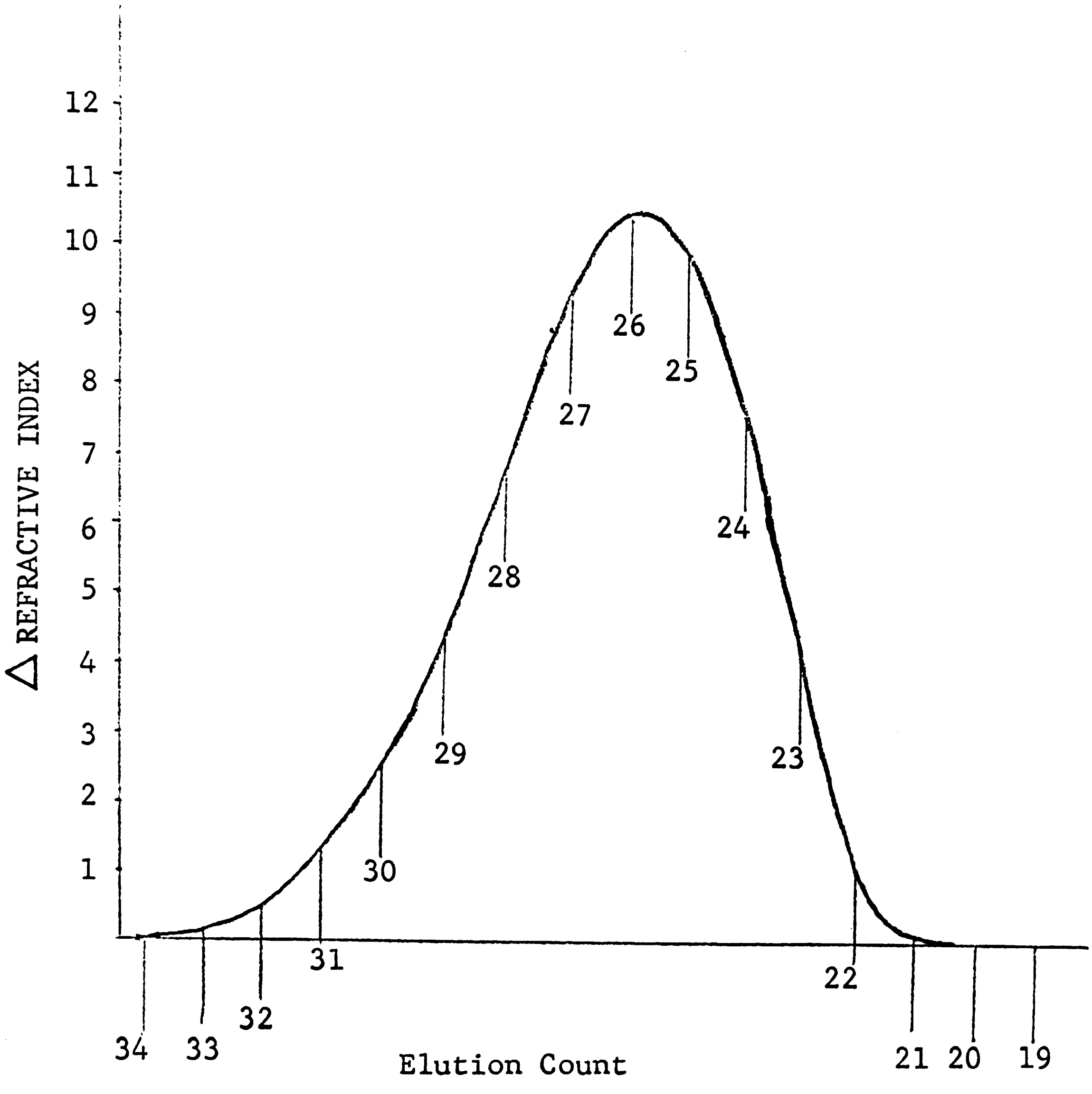
APPENDICES

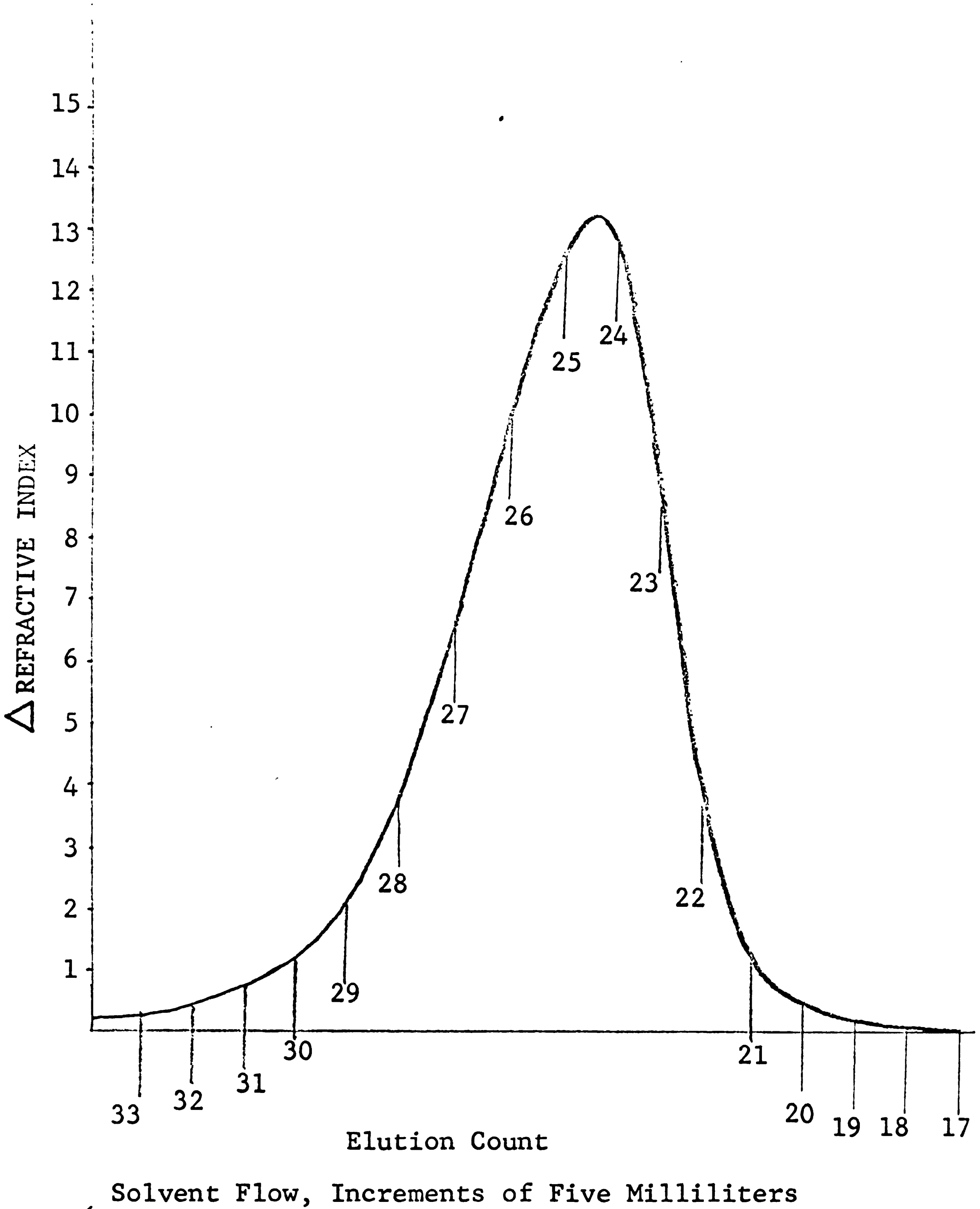
APPENDIX 1

Gel Permeation Chromatograms

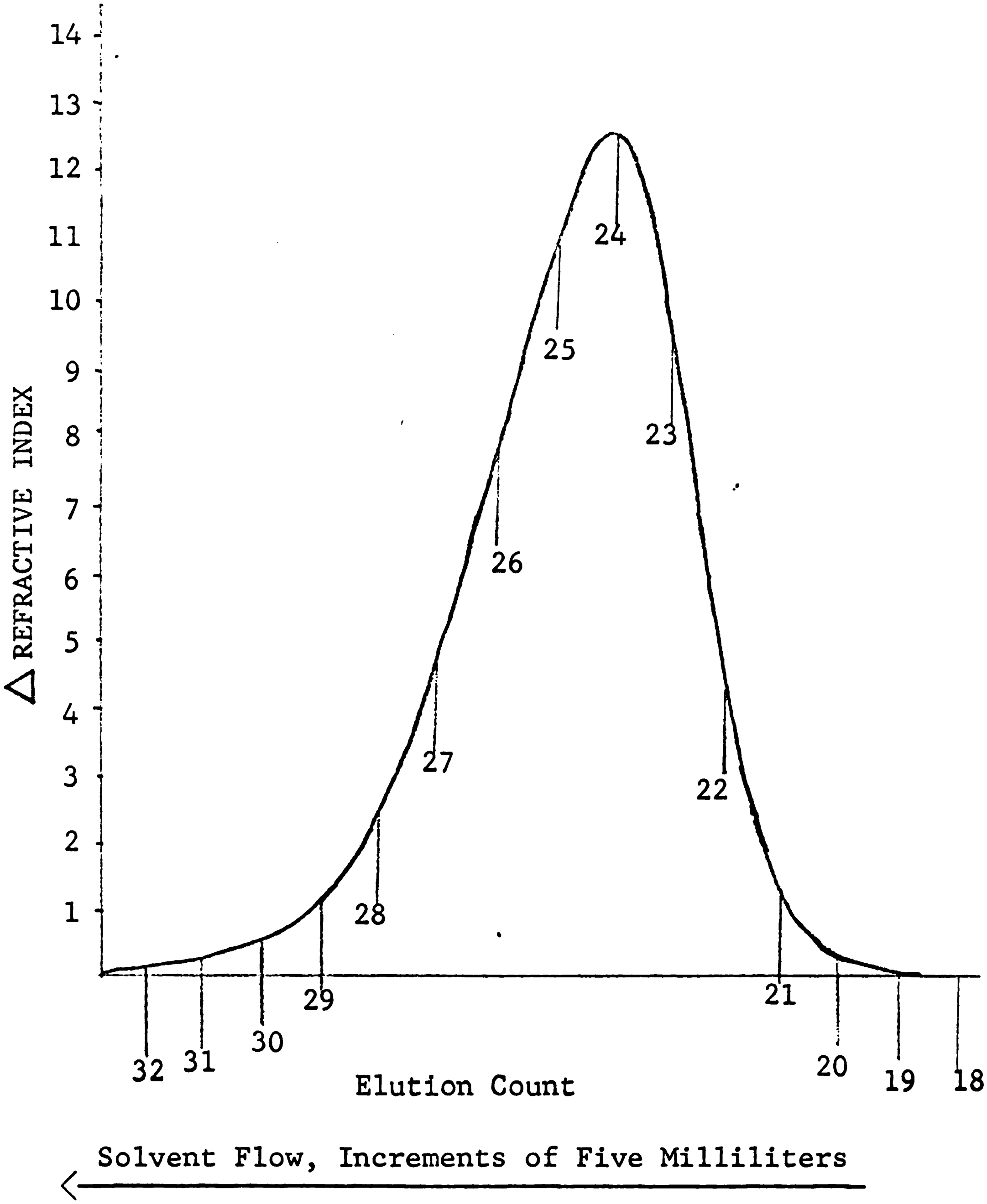


Solvent Flow, Increments of Five Milliliters

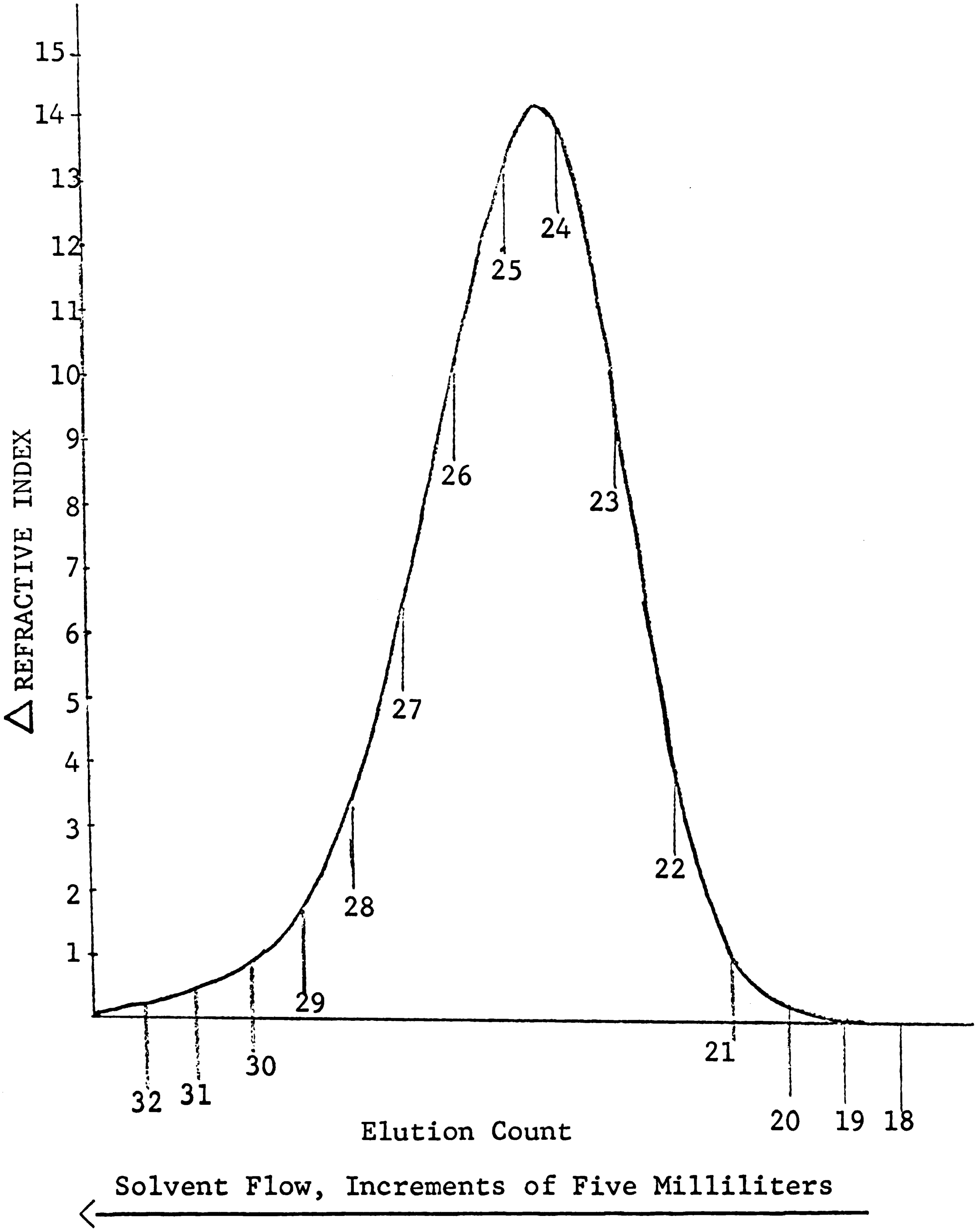
GEL PERMEATION CHROMATOGRAM OF SAMPLE 1
(calibration curve #1)



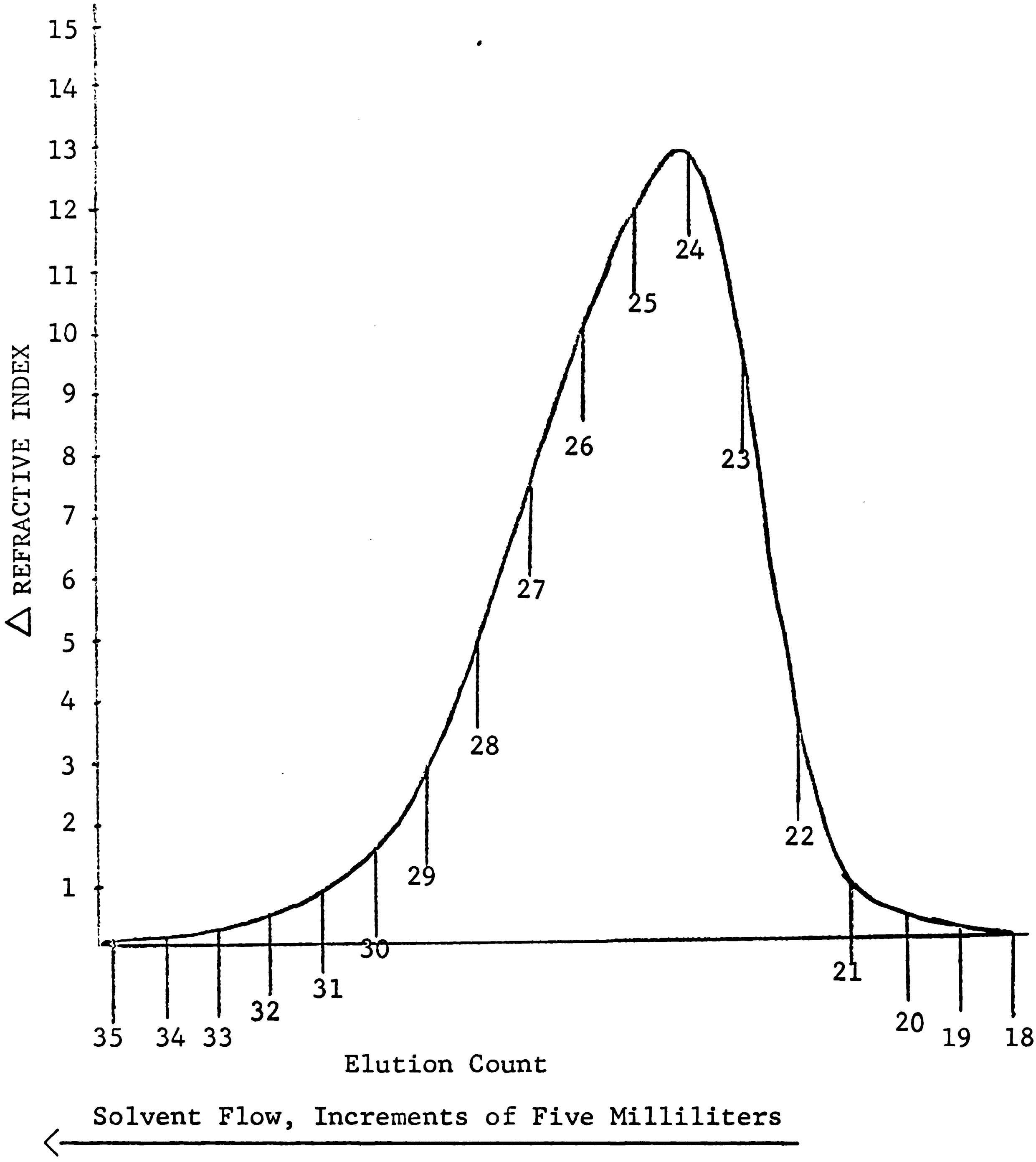
GEL PERMEATION CHROMATOGRAM OF SAMPLE 2
(calibration curve #1)



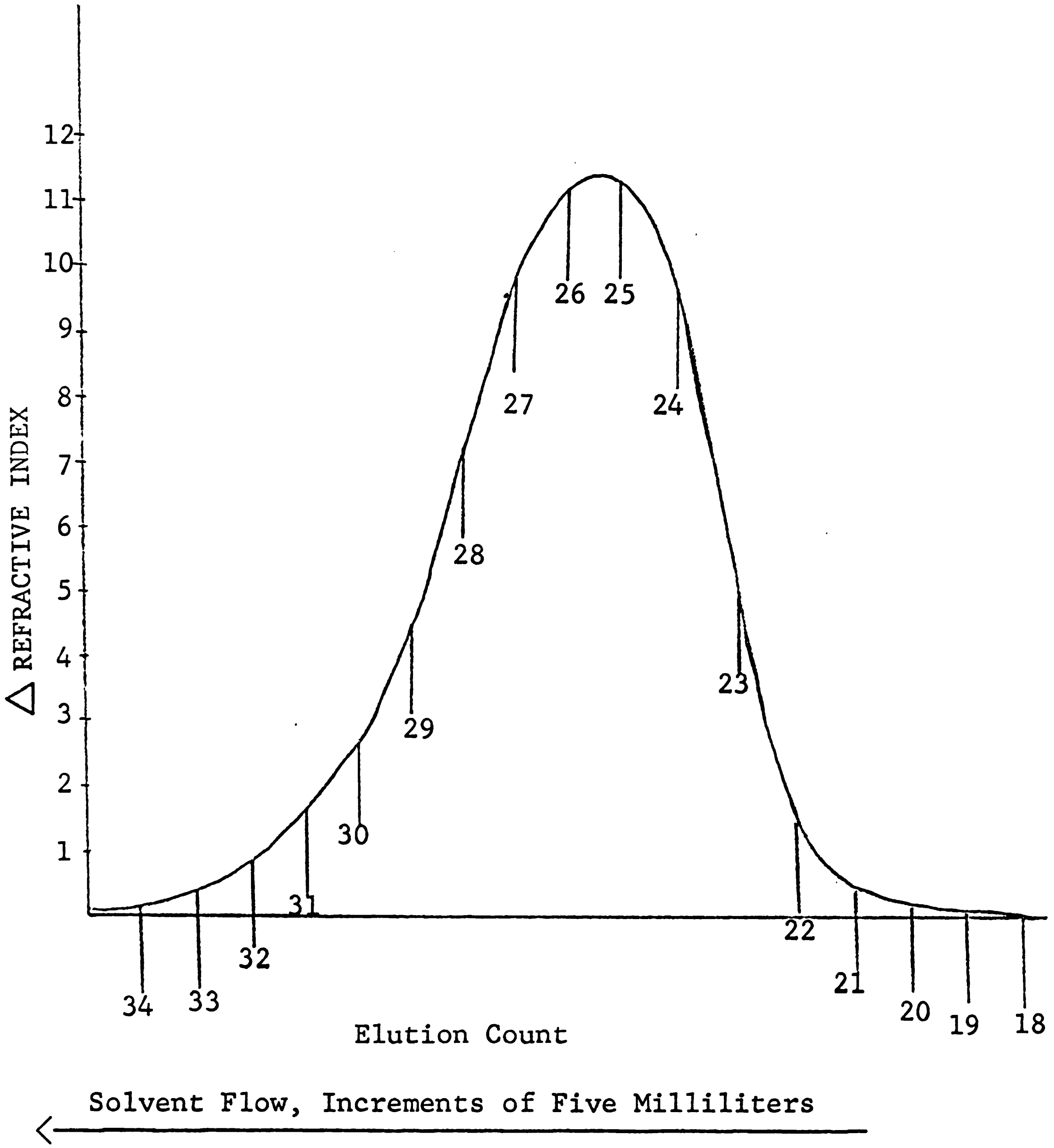
GEL PERMEATION CHROMATOGRAM OF SAMPLE 3
(calibration curve #1)



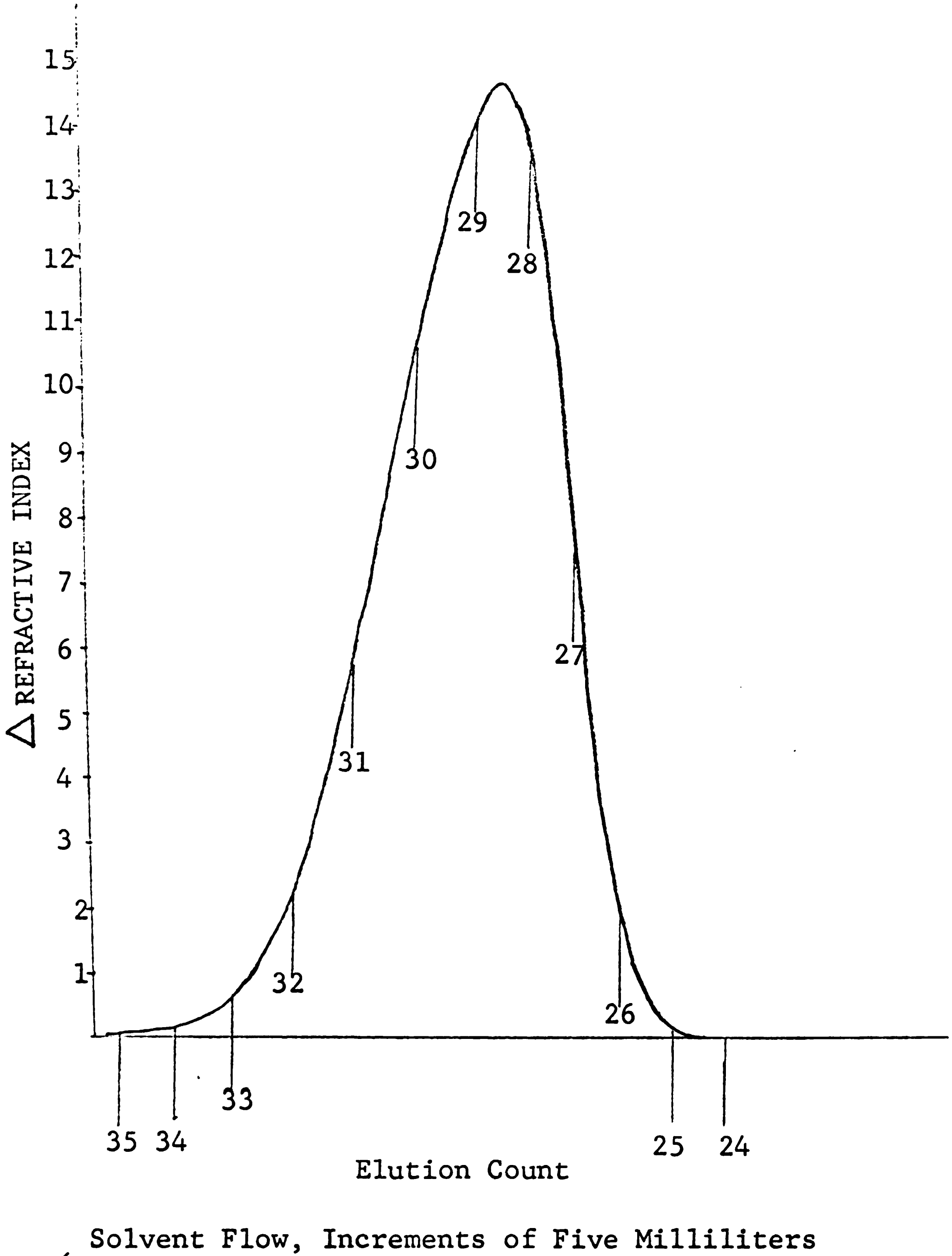
GEL PERMEATION CHROMATOGRAM OF SAMPLE 4
(calibration curve #1)



GEL PERMEATION CHROMATOGRAM OF SAMPLE 7
(calibration curve #1)

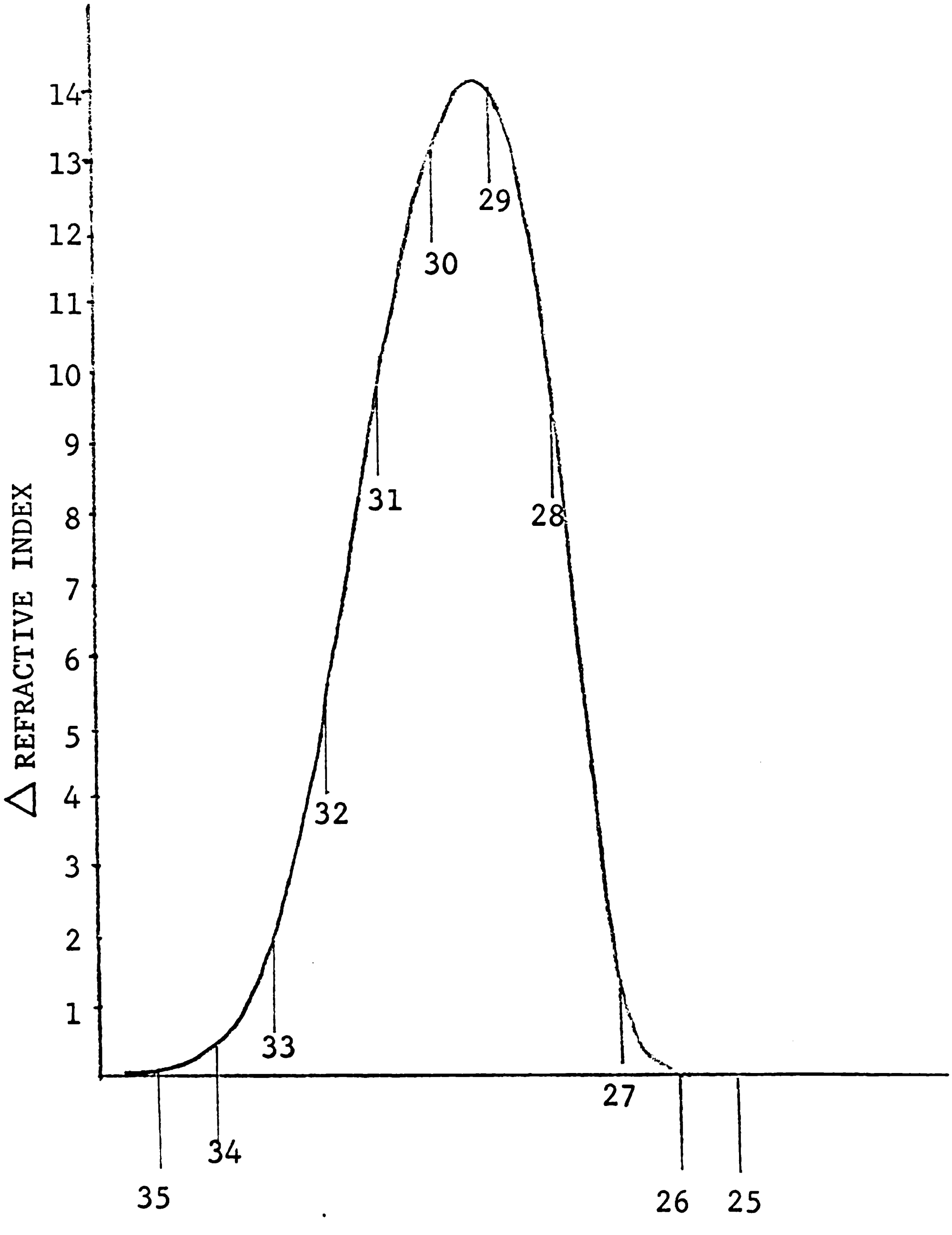


GEL PERMEATION CHROMATOGRAM OF SAMPLE 8
(calibration curve #1)



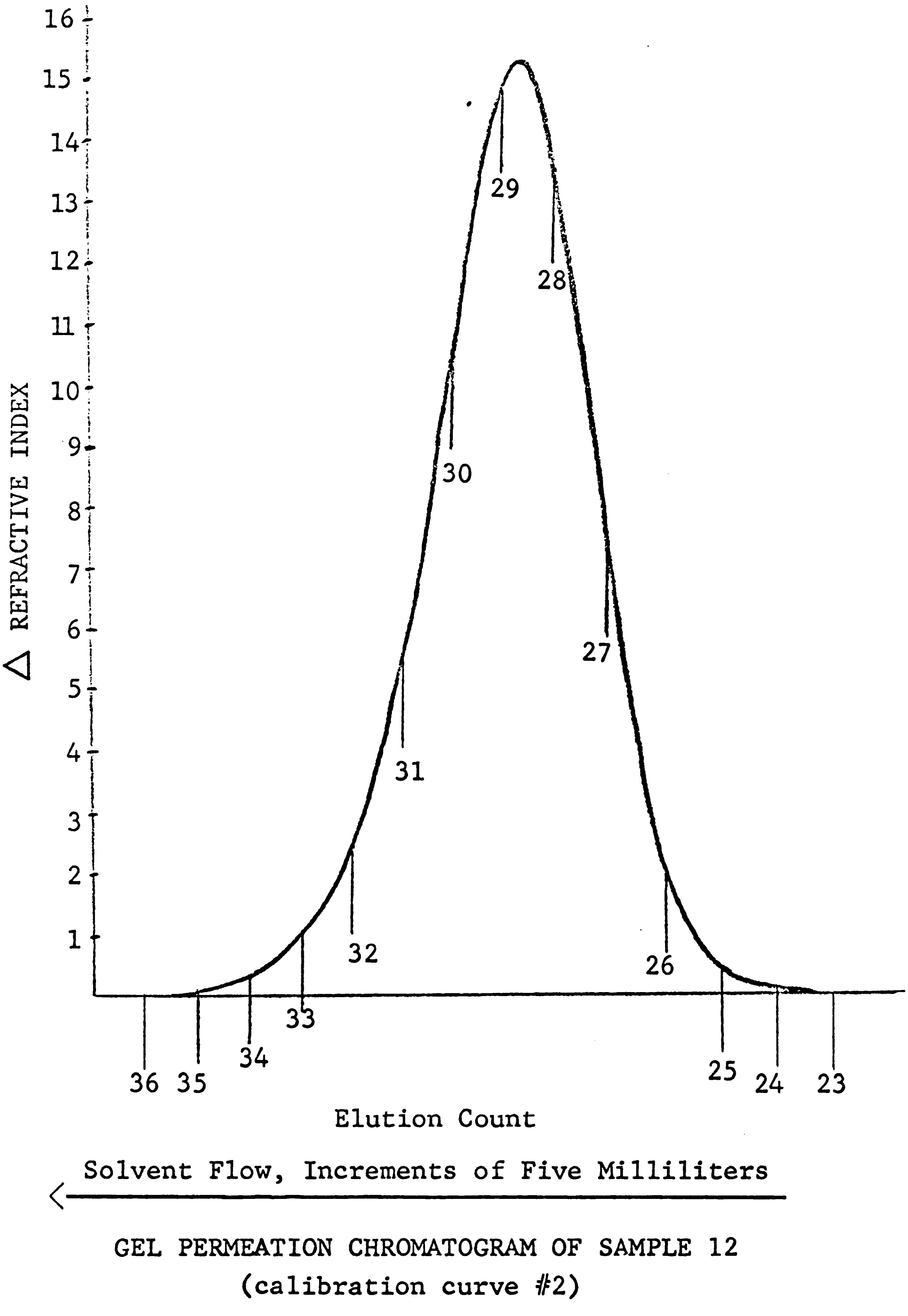
Solvent Flow, Increments of Five Milliliters

GEL PERMEATION CHROMATOGRAM OF SAMPLE 10
(calibration curve #1)

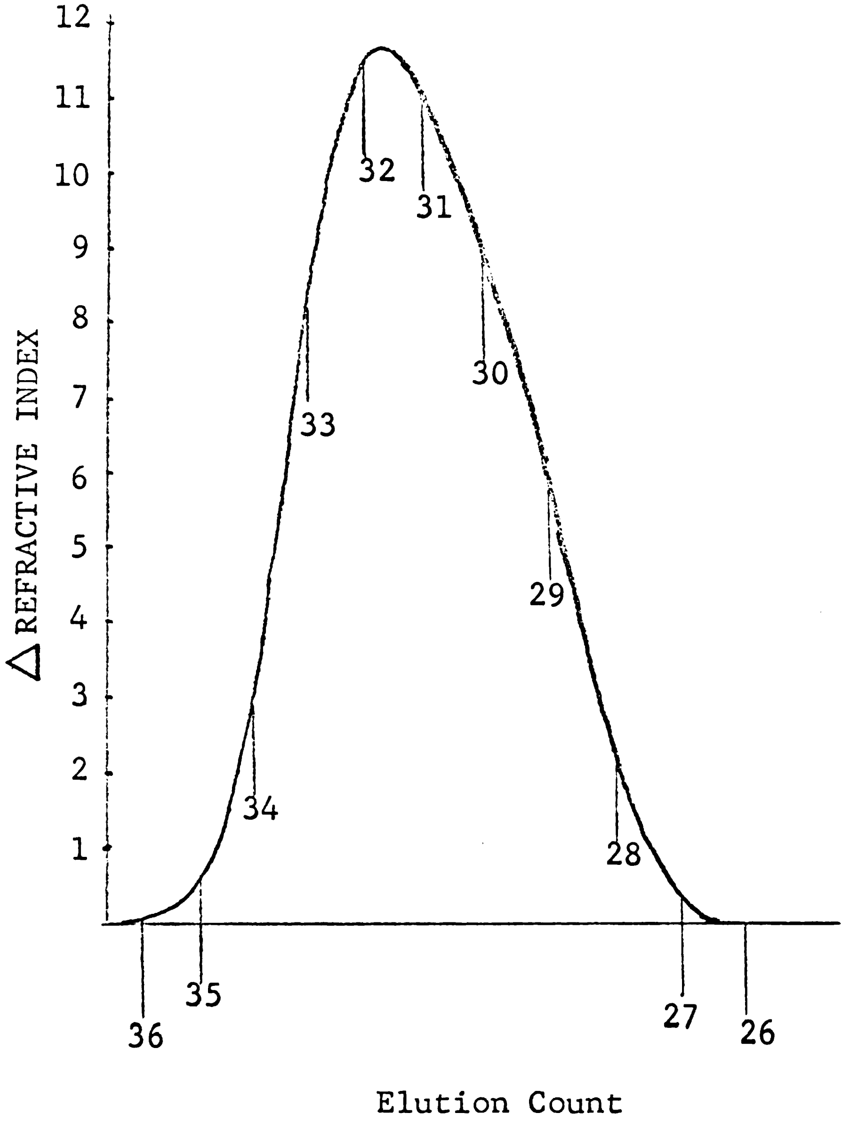


Solvent Flow, Increments of Five Milliliters

GEL PERMEATION CHROMATOGRAM OF SAMPLE 11
(calibration curve #1)

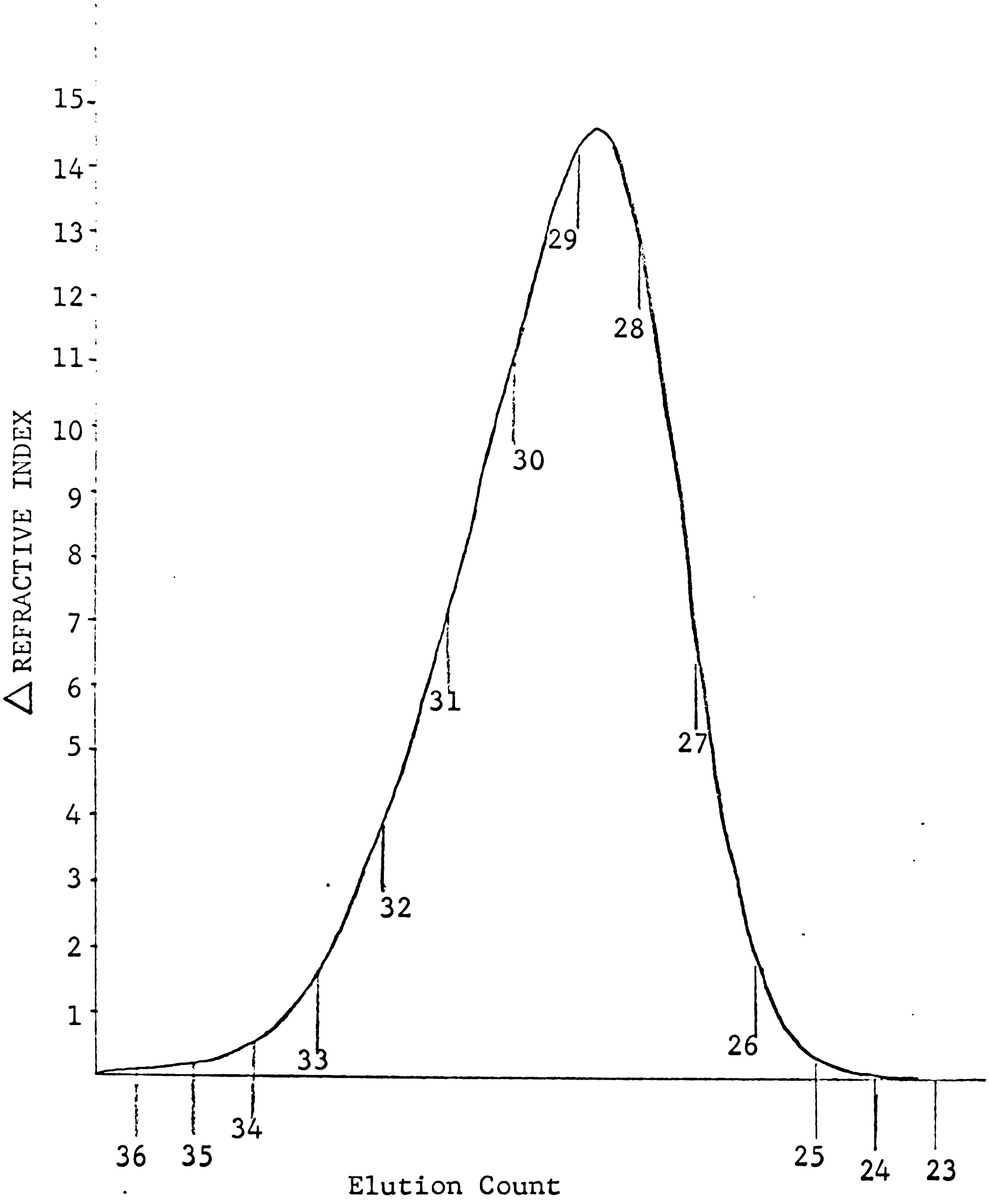


GEL PERMEATION CHROMATOGRAM OF SAMPLE 12
(calibration curve #2)



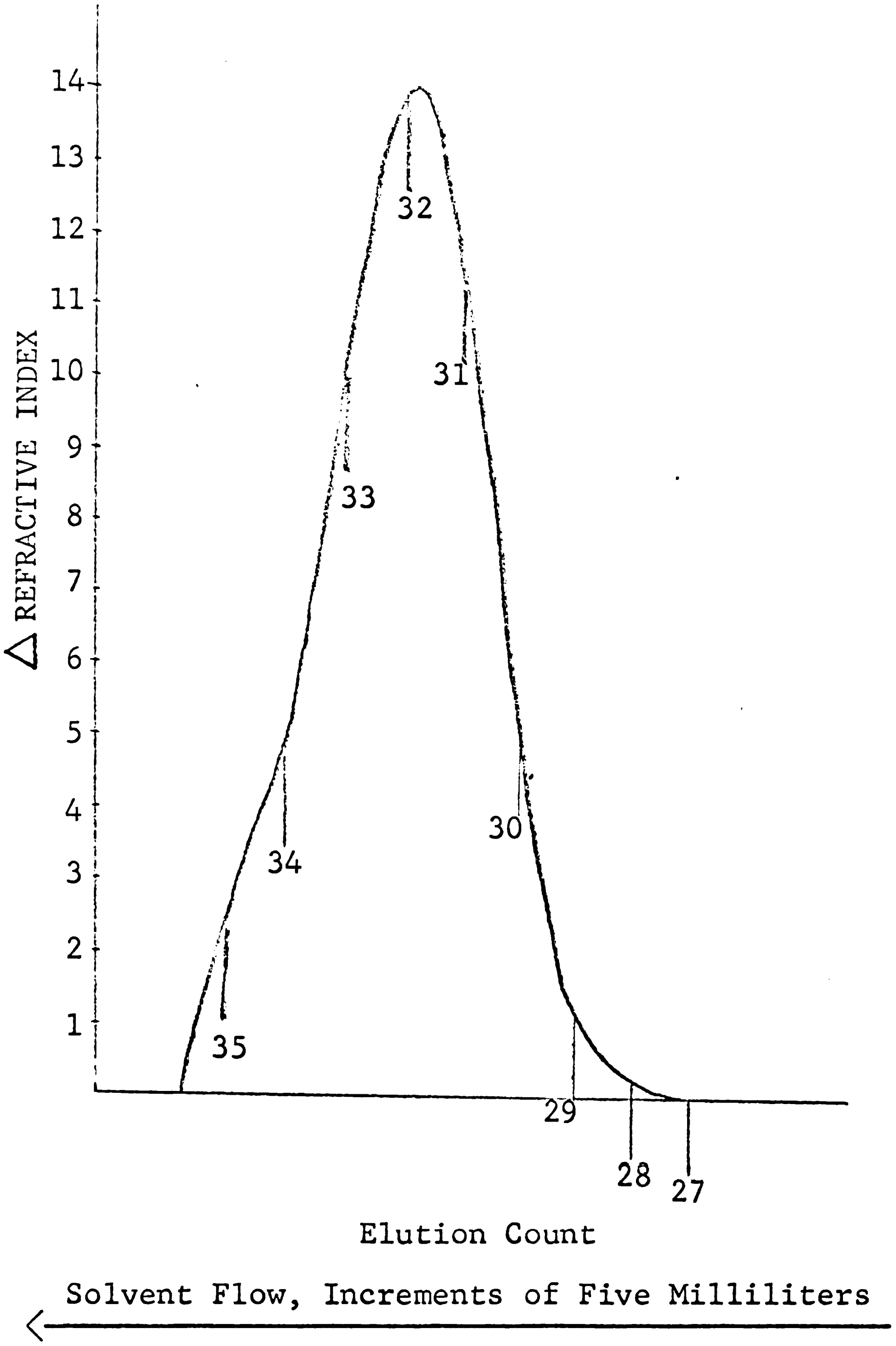
Solvent Flow, Increments of Five Milliliters

GEL PERMEATION CHROMATOGRAM OF SAMPLE 13
(calibration curve #2)

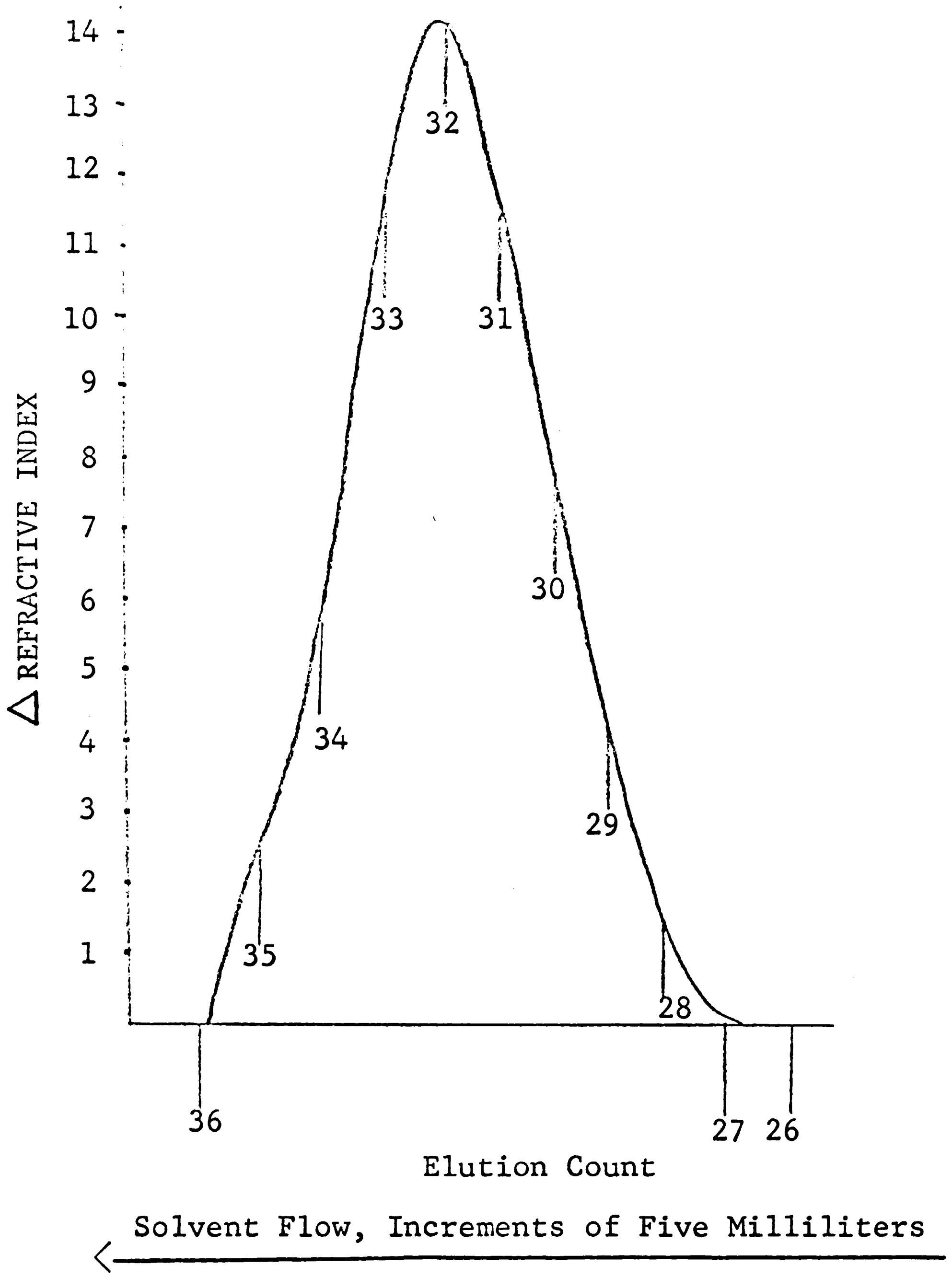


Solvent Flow, Increments of Five Milliliters

GEL PERMEATION CHROMATOGRAM OF SAMPLE 14
(calibration curve #2)



GEL PERMEATION CHROMATOGRAM OF SAMPLE 16
(calibration curve #2)



GEL PERMEATION CHROMATOGRAM OF SAMPLE 23
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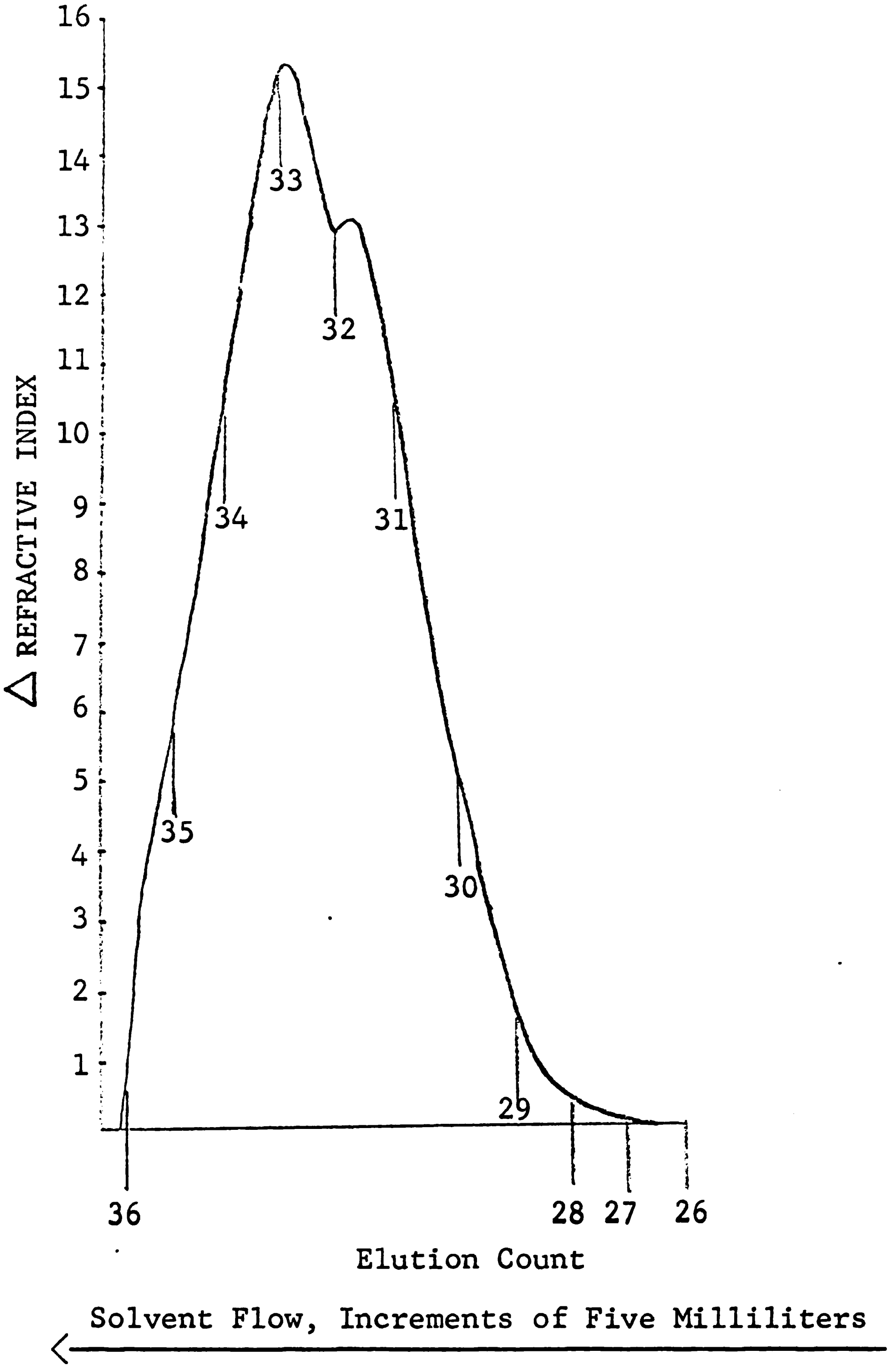
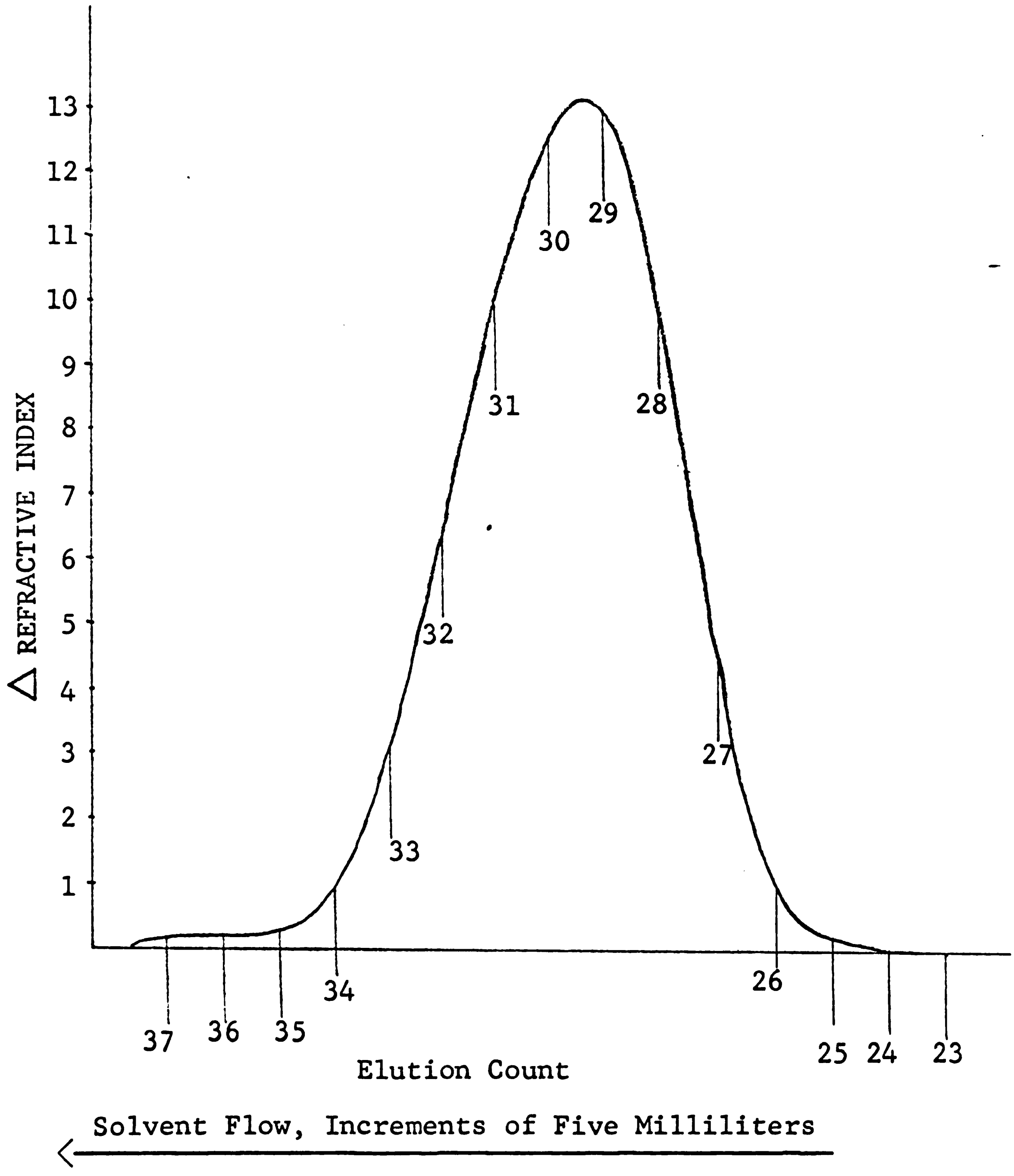


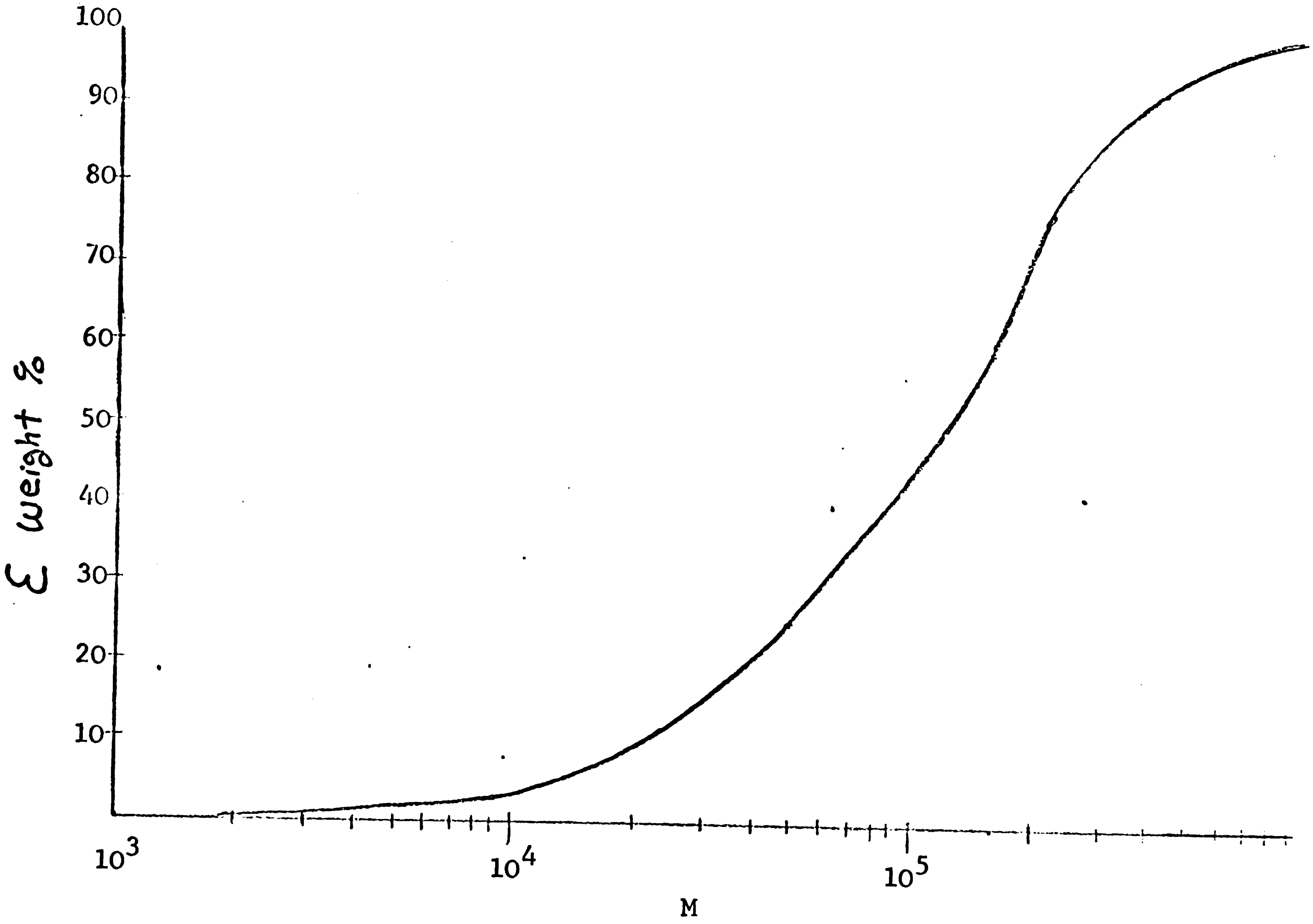
GEL PERMEATION CHROMATOGRAM OF SAMPLE 25
(calibration curve #2)



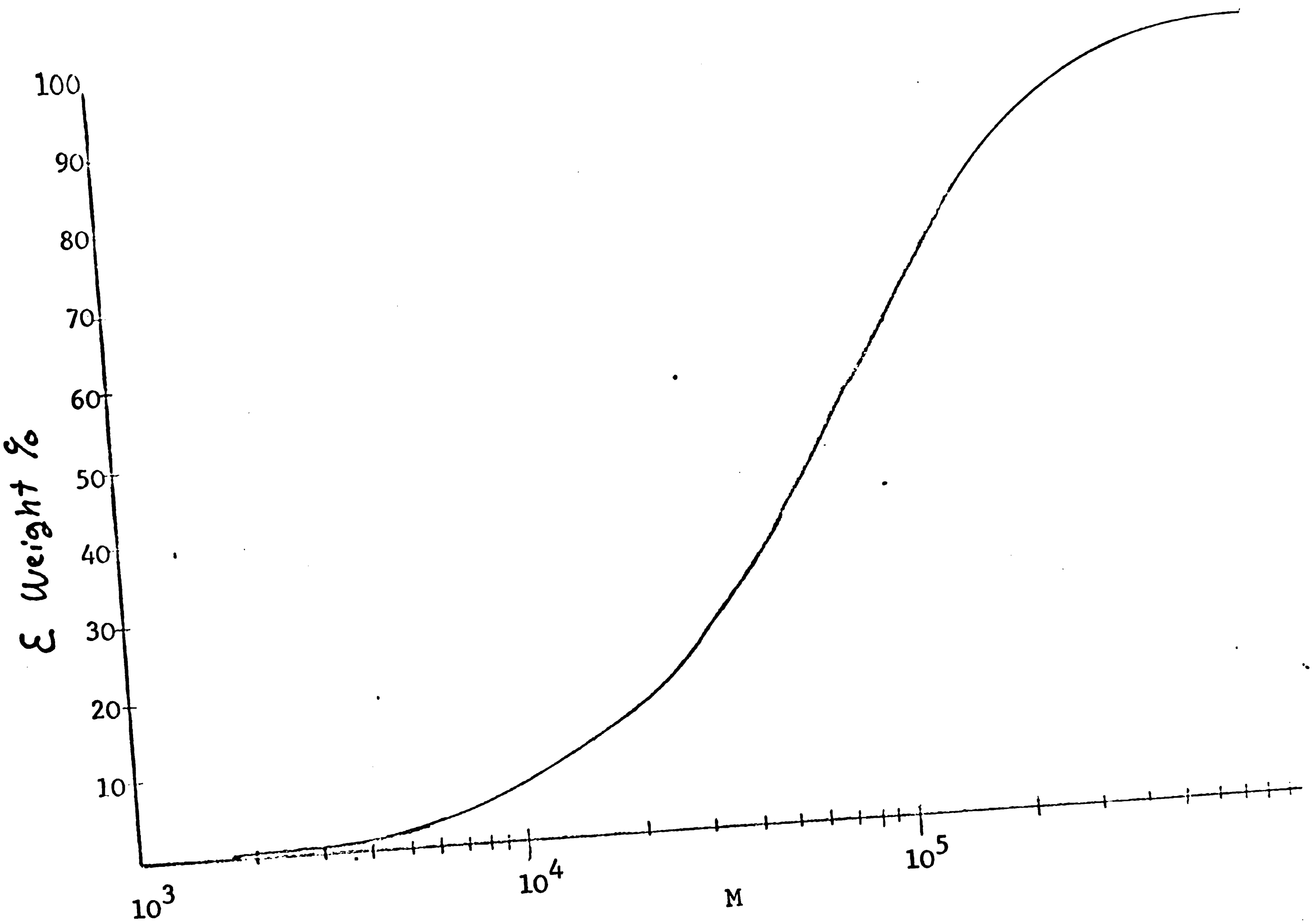
GEL PERMEATION CHROMATOGRAM OF SAMPLE 26
(calibration curve #1)

APPENDIX 2

Integral Distribution Curves



INTEGRAL DISTRIBUTION PLOT FOR SAMPLE 7



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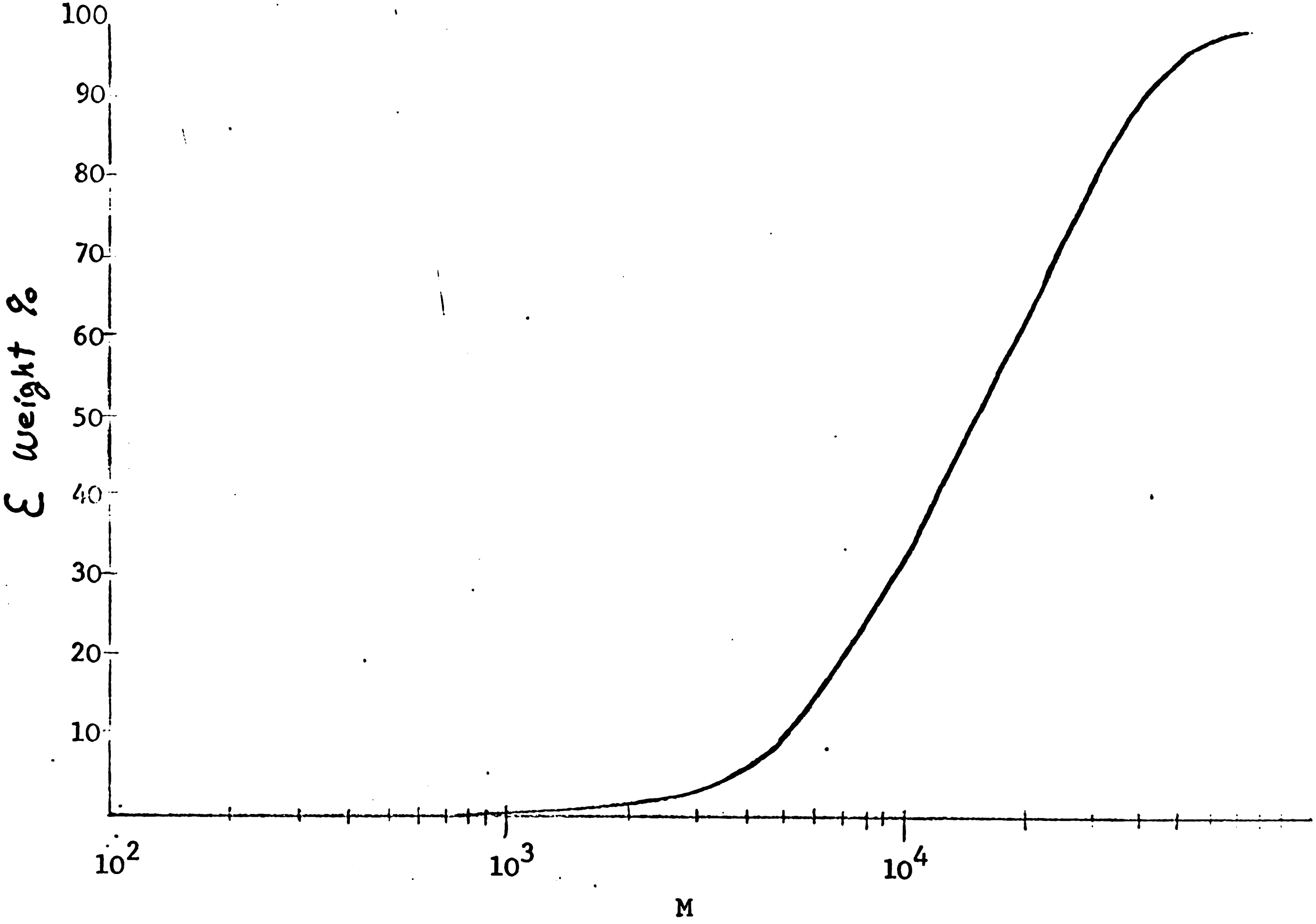
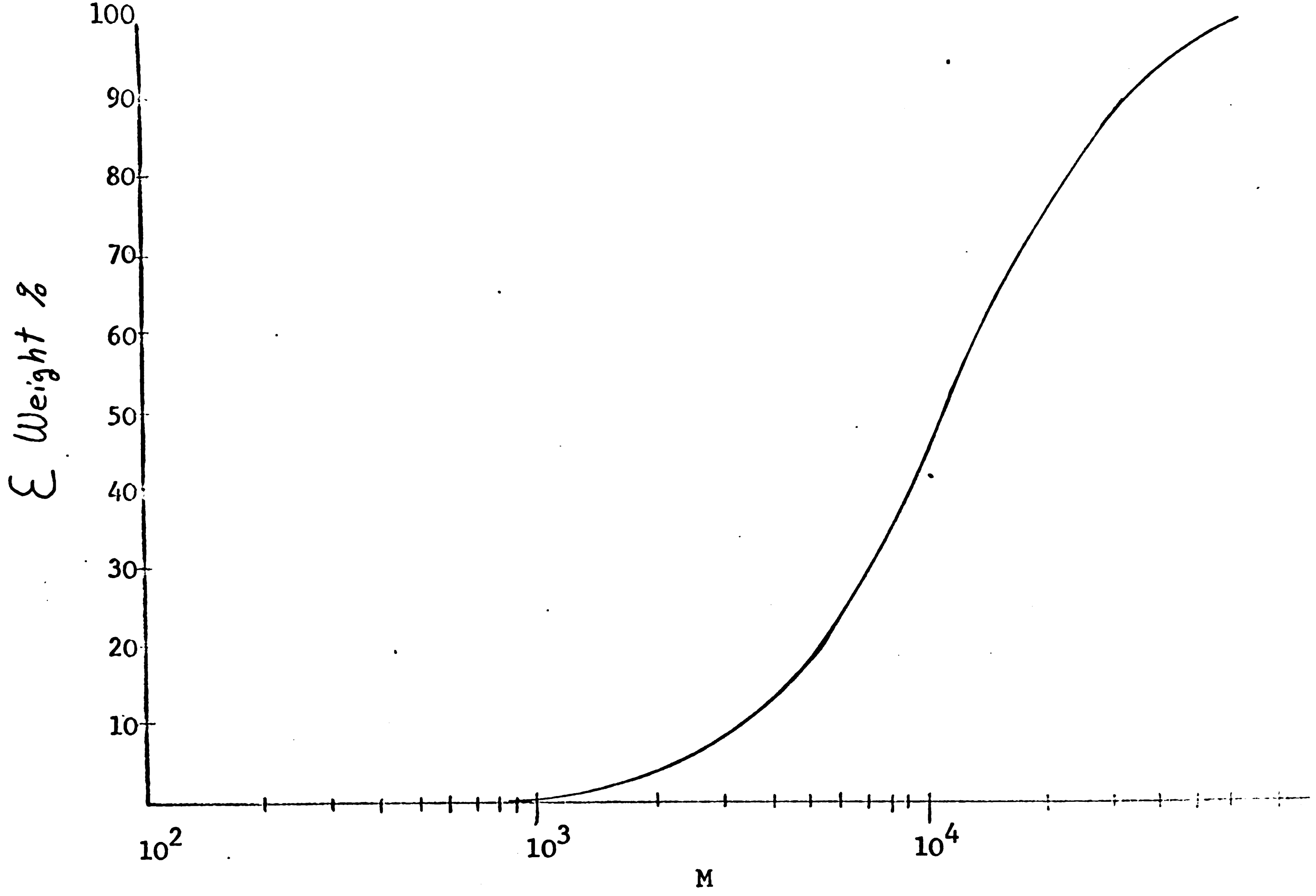


INTEGRAL DISTRIBUTION PLOT FOR SAMPLE 10



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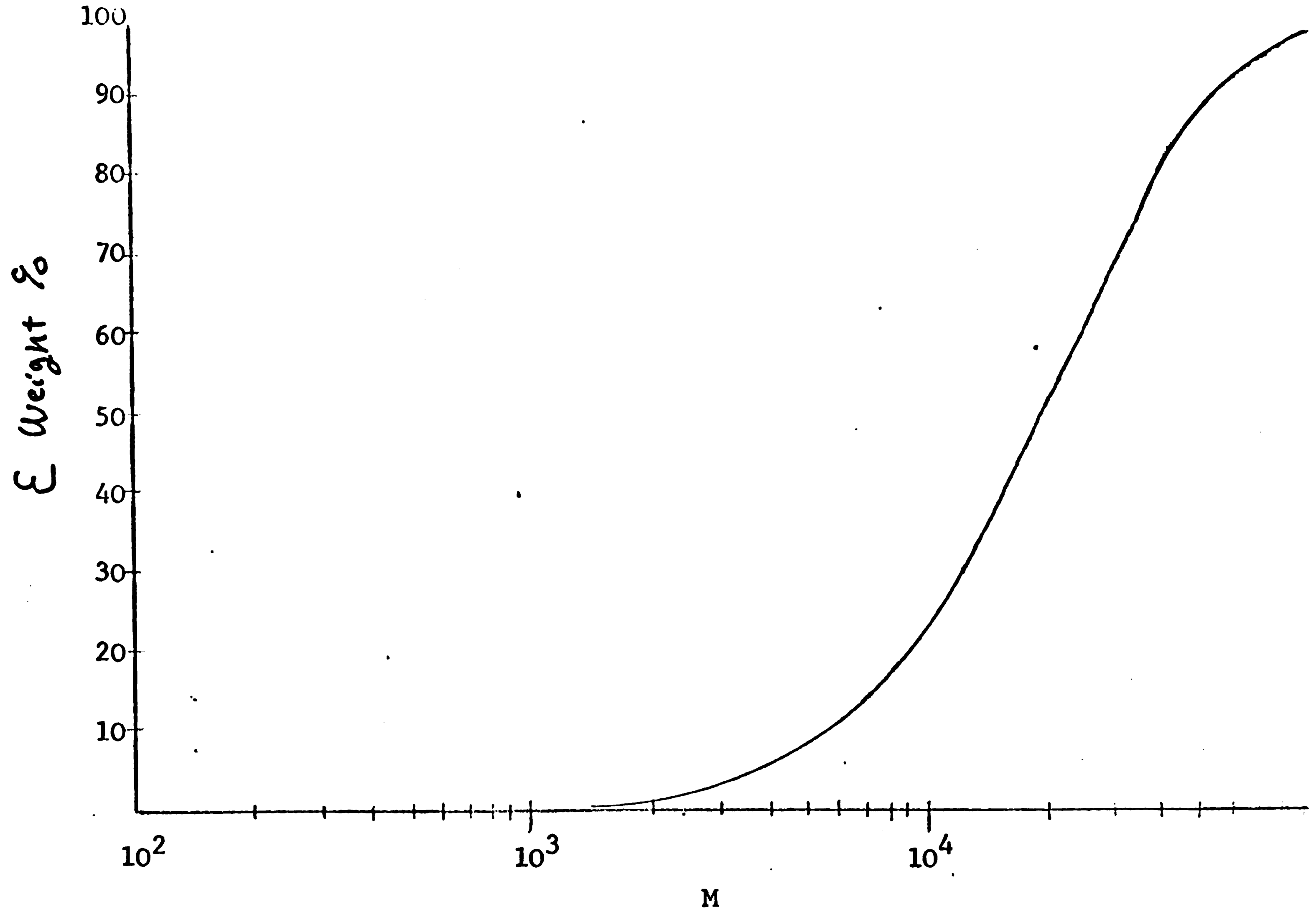

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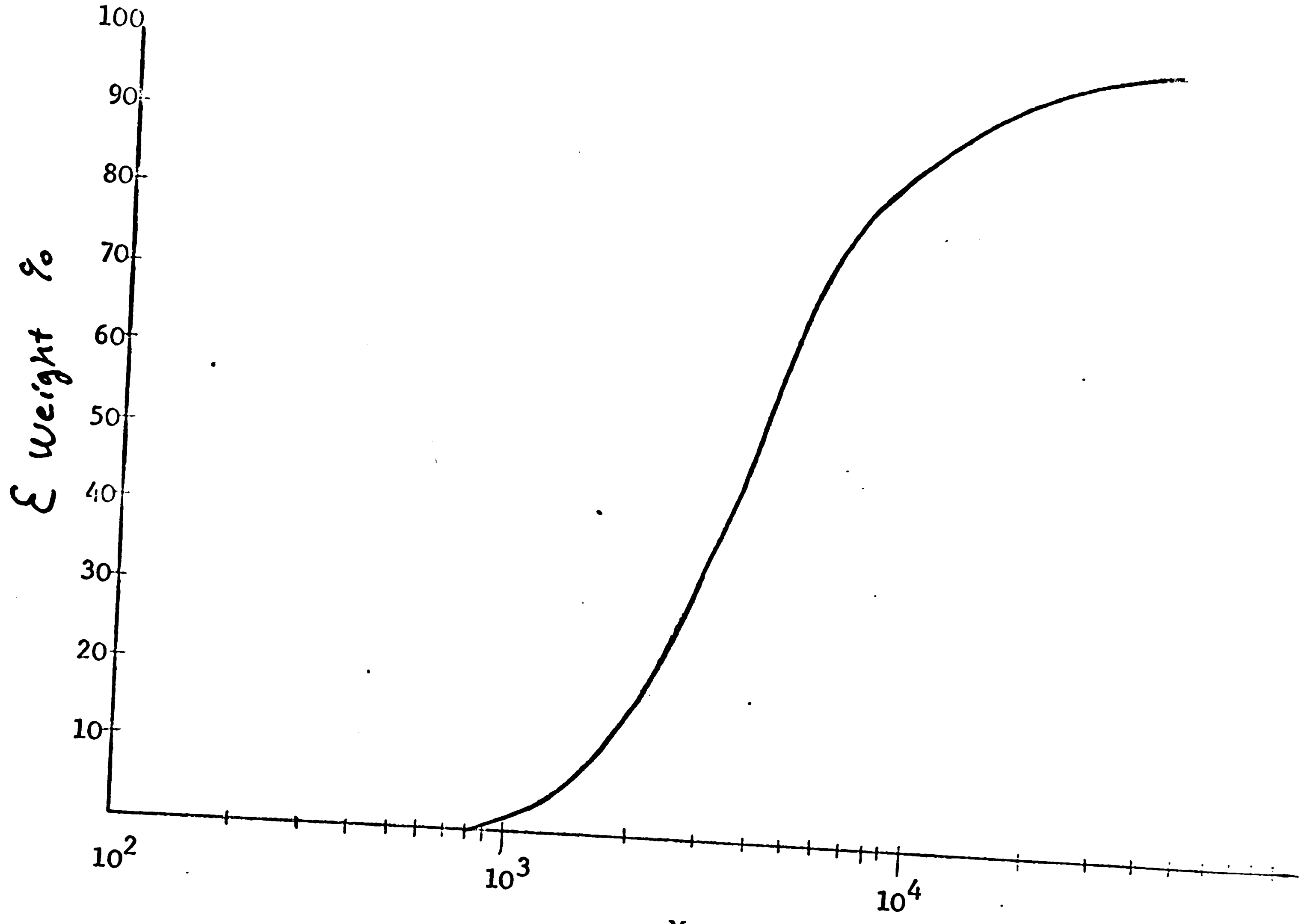

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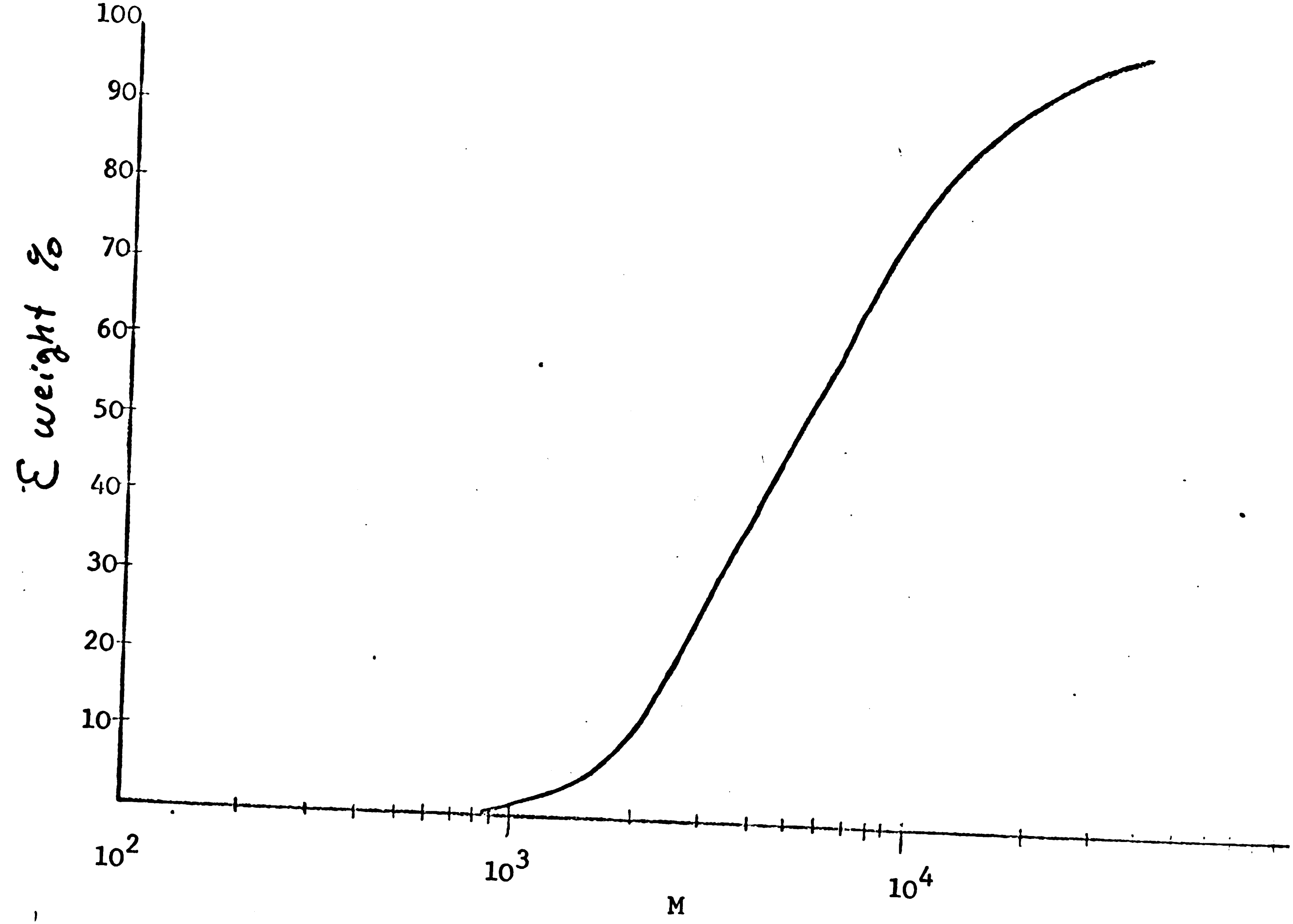

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