INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

SOLUTION PROPERTIES OF POLYMERS

By

Siu Tung Yiu

Thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Applied Science in Chemical Engineering

Department of Chemical Engineering

University of Ottawa

January 1977

M.A.Sc. Candidate

ABSTRACT

Osmometry, viscometry, light scattering and Gel permeation chromatograph are normally used to measure the physical properties of polymer solutions and determine their average molecular weights.

Nine monodisperse polystyrene standards with different molecular weights were used to obtain a conventional calibration curve for GPC. Another five polystyrene standards were used to obtain a universal calibration curve. By use of both calibration curves and the chromatogram of polymer sample from GPC, the number-average molecular weight, $\bar{M}_n$, and the weight-average molecular weight, $\bar{M}_w$, were consequently computed.

Three polystyrene standards were characterized by osmometry, viscometry, light scattering, and GPC. Determinations of molecular weights were generally in agreement with their given molecular weight except for polystyrene of very high molecular weight.

Commercial polybutadiene, polyisoprene, and two types of polystyrene-butadiene were also characterized by means of osmometry, viscometry, light scattering and GPC. $\bar{M}_n$ for the synthetic rubbers as determined by osmometry was found to be in the range from 45,000 to 100,000. Because of some slight turbidity of polystyrene-butadiene-THF solution, the molecular

weight determined by light scattering was found to be extremely high and finally deleted. From GPC analyses, it was found that synthetic rubber polymers had a relatively broad molecular weight distribution.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. W. Hayduk for his kind assistance and guidance in carrying out this work.

Many thanks are also extended to Mr. G. Gasperetti and his staff for their technical assistance.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A	Angstrom, 10^{-8} cms.
a	Mark Houwink exponent
B	second virial coefficient in the power series (osmotic pressure)
c	concentration of solute in solution
G_s	intensity of light scattered at 90°
G_w	intensity of light scattered at 0°
H	light scattering constant
I_0	intensity of incident light
K	Mark Houwink constant relating molecular weight to intrinsic viscosity
K_1	Huggins slope constant
K_2	slope constant in Martin's equation
M	molecular weight of solute
M_i	molecular weight of i-th species
$\overline{M}_n$	number-average molecular weight
$\overline{M}_v$	viscosity-average molecular weight
$\overline{M}_w$	weight-average molecular weight
N	refractive index of solution
N_A	number of particles in polymer solution, Avogadro's number
N_i	number of moles of i-th species
N_0	refractive index of solvent

n_i	mole fraction of i-th species
$\langle \overline{r^2} \rangle^{1/2}$	root mean square end-to-end distance in solvent
$\langle \overline{r_0^2} \rangle^{1/2}$	root mean square end-to-end distance of unperturbed molecules
$\langle \overline{s^2} \rangle^{1/2}$	root mean square radius of gyration in solvent
$\langle \overline{s_0^2} \rangle^{1/2}$	root mean square radius of gyration of unperturbed molecules
V	volume of polymer solution
V_1	molar volume of solvent
V_e	elution volume
V_i	total internal volume
V_i'	internal volume accessible to a particular species
V_0	void volume
V_h	hydrodynamic volume
W_i	weight of i-th species
w_i	weight fraction of i-th species
X_1	mole fraction of solvent
x_1	number of moles of solvent
X_2	mole fraction of solute
x_2	number of moles of solute
η	viscosity of solution
η_0	viscosity of solvent
η_{sp}	specific viscosity

η_r	relative viscosity
$[\eta]$	intrinsic viscosity
π	osmotic pressure
λ	wavelength of light
α	optical polarizability
α_e	expansion factor
ϕ	volume fraction of suspended particles in solution
τ	turbidity of liquid
μ_1	chemical potential of solvent

CHAPTER I

INTRODUCTION

The properties of polymers are largely dependent upon the molecular weight distribution. Until recently, various methods have been established for measuring the physical properties of polymer solutions and determining their average molecular weights. The solution properties which are frequently measured are osmotic pressure, light scattering, viscosity and gel permeation. The measurements are normally made in solution at concentrations of less than 1 % by weight. This low concentration is presumed to give no interaction between individual polymer molecules. The different molecular weight averages are defined as number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$), and viscosity-average ($\bar{M}_v$).

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \sum n_i M_i \qquad \text{--------- (1)}$$

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \sum w_i M_i \qquad \text{--------- (2)}$$

$$\bar{M}_v = \left(\sum w_i M_i{}^a\right)^{1/a} \qquad \text{--------- (3)}$$

The number-average and weight-average molecular weights were determined by means of osmometry, and light scattering photometry, respectively.

Gel Permeation Chromatograph (GPC) was used to determine the number-average and weight-average molecular weights as well as the ratio ($\bar{M}_w/\bar{M}_n$) which is referred to as the polymer polydispersity. Before applying GPC for the analysis of polymers different from monodisperse polystyrene standards, a universal calibration curve was made by plotting the product of $[\eta]M$ against the elution volume. The calibration was established by means of a series of polystyrene standards for which the measurements of intrinsic viscosity and elution volumes were performed.

Viscosities were measured for the determination of the relation between intrinsic viscosities of polymers and their molecular weights. The purpose of this study was to correlate the average molecular weights determined by viscometry and GPC with those determined by osmometry and light scattering.

CHAPTER II

THEORY FOR DETERMINATION OF POLYMER MOLECULAR WEIGHTS IN SOLUTION

(1) Osmotic pressure

The osmotic pressure has been widely used to measure polymer molecuar weights. If a solution is separated from the pure solvent with a semipermeable membrane, the solvent will gradually permeate into the polymer solution because its chmeical potential in the solution is less than that of the pure solvent. In order to keep the solution and the solvent in equilibrium, an excess pressure must be applied to the solution to increase its chemical potential; this excess pressure is called the osmotic pressure and is denoted by . Therefore the relationship between the change in chemical potential and osmotic pressure can be expressed by

$$\Delta\mu_1 = -\pi V_1 \qquad \text{----------(4)}$$

Utilizing Raout's Law for dilute solutions as the mole fraction of solute X_2 approaches zero;

$$\Delta\mu_1 \Big|_{X_2 \to 0} = RT\ln X_1 = -RTX_2 \qquad \text{---------(5)}$$

Since X_2 is very small, $X_2 = \frac{X_2}{X_1 + X_2} \fallingdotseq \frac{X_2}{X_1}$

From equation (4) and (5), one can obtain the following

expression:

$$\pi V_1 = RT\frac{x_2}{x_1} \qquad \text{--------- (6)}$$

Since the product of x_1V_1 is equal to the volume of the solvent V, equation (6) gives

$$\pi V = x_2RT \qquad \text{--------- (7)}$$

The limiting expression for the osmotic pressure can be derived by the substitution of $c = x_2M/V$;

$$\left(\frac{\pi}{c}\right)_{c\to 0} = RT\left(\frac{1}{M}\right) \qquad \text{--------- (8)}$$

This expression for the osmotic pressure is successfully applied only to the solution at infinite dilution. Therefore the limiting value of the reduced osmotic pressure $\left(\frac{\pi}{c}\right)_{c\to 0}$ must be obtained by measuring $\frac{\pi}{c}$ at various concentration and extrapolating its value to zero concentration. This is the basic way for the determination of the number-average molecular weight of polymers by osmotic pressure measurements.

For polymer solution concentrations significantly higher than 1 %, the linear relationship between reduced osmotic pressure and concentration no longer holds. A power series to express the variation of reduced osmotic pressure $(\frac{\pi}{c})$ with concentration was given by McMillan and Mayer (1)

$$\frac{\pi}{c} = \frac{RT}{M} + Bc + Cc^2 + \ldots\ldots \qquad \text{-------- (9)}$$

The constants B, C,----- are known as virial coefficients. The second virial coefficient B is related to the polymer-solvent interaction.

(2) Viscometry

Viscosity measurements are commonly used for characterization of polymers. The viscosity of a polymer solution is significantly greater than that of pure solvent. This can be explained by (i) the large size of polymer molecules relative to that of the solvent in the solution, and (ii) the interaction of the polymer molecules with solvent molecules, which causes the polymer to swell, and thereby increase the resistance of solution to flow. In order to study the effect of the individual polymer molecule in solution, the solution has to be sufficiently diluted. The viscosity of the polymer solution at infinite dilution can be obtained by measuring the viscosity of the solution at a series of concentrations and extrapolating to zero concentration.

The following conventional terms are usually used to express solution viscosities with the first being the relative viscosity:

$$\eta_r = \eta/\eta_0 \qquad \text{--------- (10)}$$

The relative increase of viscosity of the solution when

compared with that of the solvent is known as the specific viscosity η_{sp} :

$$\eta_{sp} = \frac{(\eta - \eta_0)}{\eta_0} = \eta_r - 1 \qquad \text{--------- (11)}$$

The ratio η_{sp}/c is called the reduced viscosity or viscosity number. The value of η_{sp}/c at zero c is the limiting viscosity number or intrinsic viscosity :

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} \qquad \text{------ (12)}$$

Viscosity may also be expressed by a logarithmic relationship, $\ln \eta_r/c$, termed the inherent viscosity or logarithmic viscosity number :

$$[\eta] = \lim_{c \to 0} \ln \frac{\eta_r}{c} \qquad \text{--------- (13)}$$

The intrinsic viscosity is a measure of the contribution of the individual polymer molecules to the solution viscosity and it permits the determination of molecular weight of the dissolved polymer.

A number of empirical relationships have been described for the viscosity number as a function of concentration in the dilute polymer solution. One such expression is Huggins (2) expression :

$$\eta_{sp}/c = [\eta] + K_1[\eta]^2 c \qquad \text{--------- (14)}$$

Another relationship (3), similar to the above equation is :

$$\frac{\ln (\eta/\eta_0)}{c} = [\eta] + K_2 [\eta]^2 c \qquad \text{------- (15)}$$

The constants K_1 and K_2 are related approximately by

$K_1 + K_2 = 0.5$

The intrinsic viscosities of dilute polymer solution are generally determined by plotting either the viscosity number (η_{sp}/c) or the logarithmic viscosity number ($\ln \eta_r/c$) against concentration c and extrapolating to c=0.

Sometimes, it is preferred to combine both plots in the same graph. This procedure facilitates extrapolating since both lines have the same ordinate intercept at zero concentration. If the line does not meet at this point, then the mid-point of the ordinate intercepts of each line is taken as the value of the intrinsic viscosity.

The Mark-Houwink (4) equation has been established for the determination of molecular weight :

$$[\eta] = K M^a \qquad \text{--------- (16)}$$

The two constants a and K can be determined by means of molecular weight determinations for several fractionated samples of the polymer.

(3) Light scattering photometry

Light scattering is probably the most powerful method for the determination of the molecular weight of a polymer and its molecular size and even shape in solution. If a beam of monochromatic light falls on a polymer solution and impinges upon the molecular particles, the electrons of the particles are induced to vibrate, which interfere with the transmission of light, and cause scattering in various directions. The intensity of the scattered light in relation to the intensity of the incident light is usually measured by a photoelectric cell.

If the incident light is non-polarized, the intensity of the scattered light i_θ, at a distance r from the molecule and in the direction which makes an angle θ with the propagation direction of the incident light in a unit volume of a dilute solution, can be expressed by :

$$i_\theta = \frac{8\pi^4\alpha^2 I_0 N_A (1 + \cos^2\theta)}{\lambda^4 r^2 V} \qquad \text{--------- (17)}$$

In the above expression, the polarizability, α , is a function both of molecular weight of particles and the differences in refractive index between the pure solvent and the polymer solution.

$$\alpha = \frac{N_0 M}{2\pi N_A}\left(\frac{dN}{dc}\right) \qquad \text{--------- (18)}$$

In the above expression, N_0 and N, are refractive indices of the solvent, and the solution, respectively.

By integrating the total intensity of scattering, the turbidity (5) may be obtained :

$$\tau = \int_0^{\pi} ({}^{i}\theta/I_0) 2\pi r^2 \sin\theta d\theta \qquad \text{--------- (19)}$$

Substituting equations (17) and (18) into equation (19), another expression is formed :

$$\tau = \frac{128\pi^5}{3\lambda^4} \alpha^2 \frac{N_A}{V}$$

$$= \frac{128\pi^5}{3\lambda^4} \left[\frac{N_0 M}{2\pi N_A} \left(\frac{dN}{dc}\right) \right]^2 \frac{N_A}{V}$$

$$= \frac{32\pi^3}{3\lambda^4 N_A} N_0^2 \left(\frac{dN}{dc}\right)^2 Mc \qquad \text{--------- (20)}$$

Hence the turbidity of a solution is proportional to the molecular weight of the solute. Rearrange equation (20) to make it applicable to the solution at finite concentration:

$$\frac{Hc}{\tau} = F\left(\frac{1}{M}\right) \qquad \text{--------- (21)}$$

where $H = \frac{32\pi^3 N_0^2}{3\lambda^4 N_A} \left(\frac{dN}{dc}\right)^2$

By assuming that $F\left(\frac{1}{M}\right)$ can be expressed as a power series (5) in terms of concentration, c, and the first term is 1/M :

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc + \text{-----} \qquad \text{-------- (22)}$$

Then the molecular weight is found by the reciprocal of the intercept which is determined by measuring $\frac{Hc}{\tau}$ for a number of solutions of different concentration, and extrapolating to zero concentration. The previous expression is restricted to solutions for which the molecular particles can be considered as single isolated dipoles and their molecular diameters are small when compared with the wavelength of the monochromatic light, or specifically, less than $\lambda/20$.

(4) Gel permeation chromatograph

The analytical process of Gel permeation chromatograph applicable to the determination of molecular weight distribution of polymers was initially devised by Moore (7) in 1962.

In this method, the polymer molecules can be separated on the basis of molecular sizes by permeation through the gel. The gel frequently consists of a network of highly crosslinked polystyrenes which form molecular-sized pores of various diameters and are packed in the form of small spherical particles in columns. During the separation process, polymer molecules larger than the maximum pore size of an individual polymer particle can only travel

through the column in the interstitial space between the gel particles. Polymer molecules smaller than the maximum pore size penetrate the gel pores as far as their size permits and are separated accordingly with their sizes.

On the basis of simple models (8), each species of polymer molecules occupies a certain volume which is equal to the sum of the void volume V_0 and of the accessible part of the pore volume. Then the elution volume for each species of molecules is

$$V_e = V_0 + V_i' \qquad \text{--------- (23)}$$

In the above expression, V_i' is part of the total internal volume, V_i, that is accessible to a given molecular species.

The volumetric distribution coefficient K_d is defined as :

$$K_d = \frac{V_i'}{V_i} = \frac{V_e - V_0}{V_i} \qquad \text{--------- (24)}$$

The above equation may be written as

$$V_e = V_0 + K_d V_i \qquad \text{--------- (25)}$$

Experimentally, V_0 is usually found by determining V_e of a substance with totally excluded molecules, that is for $K_d=0$ and hence $V_e=V_0$. For very small molecules, $K_d=1$ and $V_e = V_0 + V_i$.

Laurent and Killander (9) have introduced a different

distribution coefficient, K_{av}, which is related to K_d and involves V_s, the volume of the gel matrix :

$$K_{av} = K_d \frac{V_i}{V_i + V_s} \qquad \text{--------- (26)}$$

The values of K_d and K_{av} are independent of column size and geometry.

For a given gel-solvent system, the molecular species can be characterized by its K_d value, in other words, by its elution volume. Therefore, a number of attempts to relate molecular weight to K_d or to elution volume have been made. Porath (10) was the first one to use a model where the pores were assumed to have equal cone-like shapes. From the model, he developed a theory for polymers involving solvent and gel parameters :

$$K_d = K_1 \left[1 - K_2 \frac{M^{1/2}}{(S_r - \beta)^{1/3}} \right]^3 \qquad \text{------ (27)}$$

In the latter expressions, M is the molecular weight, S_r is the solvent regain which is proportional to the volume of the solvent in the gel, and K_1, K_2 and β are constants for a specified gel.

Because the assumption for the conical gel pore was found to be over-simplified, Laurent and Killander (9) assumed a model involving a network of straight rods with

a radius R_r which were distribution at random in the gel, and of spherical polymer molecules with a radius R_s. The distribution coefficient K_{av} utilized L, the concentration of rod-shaped pores, and was found to be :

$$K_{av} = \exp\left[-\pi L(R_r + R_s)^2 \right] \qquad \text{-------- (28)}$$

These attempts to theoretically relate the solute molecular weight with K_d or with the elution volume were not entirely satisfactory for real polymer solutions. A plot of the logarithm of molecular weight against elution volume, which was usually used to calibrate the instrument and to determine the molecular weight has not yet been fully explained theoretically.

A number of researchers (11, 12) had investigated the relationship between the elution volume of a sample and the flow rate through the GPC columns. They found little or no change of elution volume with flow rate. Billmeyer and Kelley (13) studied the effect of the injection and detection system on elution volume. They found that the elution volume decreases slightly with increasing flow rate. However, this effect can be eliminated when the operation of GPC is carried out at the same flow rate throughout the experiment.

The concentration, injection time, choice of solvent and operating temperature cause an appreciable shift in

the maximum elution volume and consequently an apparent variation in the molecular weight. To obtain reproducible data, therefore, GPC analyses must be conducted under identical operating conditions.

The concentration effect (14) has been found to become more pronounced for the polymer with high molecular weight. In most cases, it is recommended that GPC should be performed at a low concentration of 0.2% by weight. A finite injection time is required to inject the sample from the sample loop into the solution stream, the flowrate of which has normally been adjusted to a constant rate. It is also desirable to choose a solvent in which the refractive index is quite different from that of the polymer solution even at low concentration. In addition, it is usually desirable to operate at low temperature so that the solvent becomes less volatile, proved that the polymer is soluble at the temperature concerned.

Several theories have been developed for calibrating GPC instruments for analytical purposes. A recent one involves the so-called hydrodynamic volume of the dissolved polymer. When a polymer becomes solvated in the solution, its change of molecular dimensions is totally dependent upon the extent of its interaction with the solvent. This interaction causes the polymer molecules to swell to its

most probable molecular configuration. In a good solvent, the separation of chain ends is increased as the result of the interactions between solvent and polymer molecules. In a poor solvent, polymer chains tend to retain their unperturbed dimensions because the interaction with solvent tends to be small.

For a linear polymer, the polymer molecule is generally arranged in a random configuration and its molecular dimension can be expressed as the root-mean-square radius of gyration $(\overline{s^2})^{1/2}$ or end-toend distance $(\overline{r^2})^{1/2}$. These two parameters (15) are related under a Gaussian distribution by :

$$\left(\overline{s_0^2}\right)^{1/2} = \frac{\left(\overline{r_0^2}\right)^{1/2}}{6} \qquad \text{--------- (29)}$$

The subscript zero is used to indicate an unperturbed dimension for s and r. Concerning the swelling action of the solvent on the polymer molecule in dilute solution, Flory (16) has introduced a parameter, α_e , termed the expansion factor :

$$\left(\overline{r^2}\right)^{1/2} = \alpha_e\left(\overline{r_0^2}\right)^{1/2} \qquad \text{--------- (30)}$$

$$\left(\overline{s^2}\right)^{1/2} = \alpha_e\left(\overline{s_0^2}\right)^{1/2} \qquad \text{--------- (31)}$$

It was shown that $\alpha_e > 1$ in a good solvent and $\alpha_e = 1$ in a theta solvent for the polymer concerned.

A simple functional relationship (17) between the elution volume of a series of standard samples and their molecular weights was found to be invalid when applied to polymers structurally different from the standard samples. Therefore, a new parameter based on the hydrodynamic volumes (18) of polymer molecules has been introduced and referred to as a universal calibration parameter for GPC. The hydrodynamic volume is based on Einstein equation (19) for the viscosity of spherical particles, which can be expressed as :

$$\frac{\eta - \eta_0}{\eta_0} = 2.5\phi \qquad \text{--------- (32)}$$

In the Einstein equation, η_0 is the viscosity of the solvent and ϕ is the volume fraction of suspended particles.

Simha modified the Einstein equation to a more general form involving ϵ , a parameter which depends on the hydrodynamic shape of the particles :

$$\frac{\eta - \eta_0}{\eta_0} = \eta_{sp} = \epsilon\phi \qquad \text{--------- (33)}$$

The last equation can be written in terms of the intrinsic viscosity when the concentration approaches zero, and the hydrodynamic volume V_h :

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c \to 0} = \epsilon \frac{N_A V_h}{M} \qquad \text{------- (34)}$$

This equation shows that the product $[\eta]M$ is a direct measure of the hydrodynamic volume of polymer particles. Consequently, a calibration curve, in which the logarithm of the product $[\eta]M$ is plotted against elution volume for a series of polystyrene standards with known molecular weights and intrinsic viscosities, is considered to be applicable to branched polymers as well as linear polymers.

CHAPTER III

PREPARATION OF SAMPLE SOLUTIONS

Nine polystyrene standards with different molecular weights, supplied by Waters Associates Incorporated, were used to obtain a calibration curve for GPC. Another five polystyrene standards, also supplied by Waters Associates Incorporated, were used not only to obtain a universal calibration curve for GPC but also for the measurement of intrinsic viscosity, osmotic pressure and light scattering.

Commercial polybutadiene (TAKENE 1220), polyisoprene (TRANSPIP 100) and two types of polystyrene-butadiene (KRYLENE 1502 and SS 255) supplied by Polysar Limited were also characterized by means of osmometry, viscometry, light scattering, and GPC.

Tetrahydrofuran (THF) was used as a solvent in the preparation of all polymer solutions. Approximately 1% by weight of polystyrene solution was prepared and filtered through a 10 micron pressure filter system which was entirely resistant to the solvent, using a nitrogen pressure of 40 psig. Portions of the clear solution were diluted to a series of solutions with a concentration range of 10 : 1 and five dilutions were made volumetrically. The exact concentration of the stock solution was determined by evaporating 10 mls of solution to dryness. These solutions

were then used for the measurement of the osmotic pressure and intrinsic viscosity. The polybutadiene and polyisoprene solutions were prepared in the same way as the polystyrene solutions.

For the preparation of polystyrene-butadiene solution approximately 0.5 grams of polystyrene-butadiene was added to 100 mls of THF and was stirred by using a magnetic stirrer for up to eight hours. With this polymer, some undissolved gel substance was invariably dispersed in the solution so that the solution was found to be very cloudy. The solution was then separated from the insoluble gel by means of a centrifuge. The solution was passed through a 10 micron filter under a nitrogen pressure of 50 psig and collected in 100 mls flask, and capped with a stopper. It was found necessary to replace the filter four or five times for filtering 100 mls of solution. Then five solutions, with a concentration range of 10 : 1, were made volumetrically.

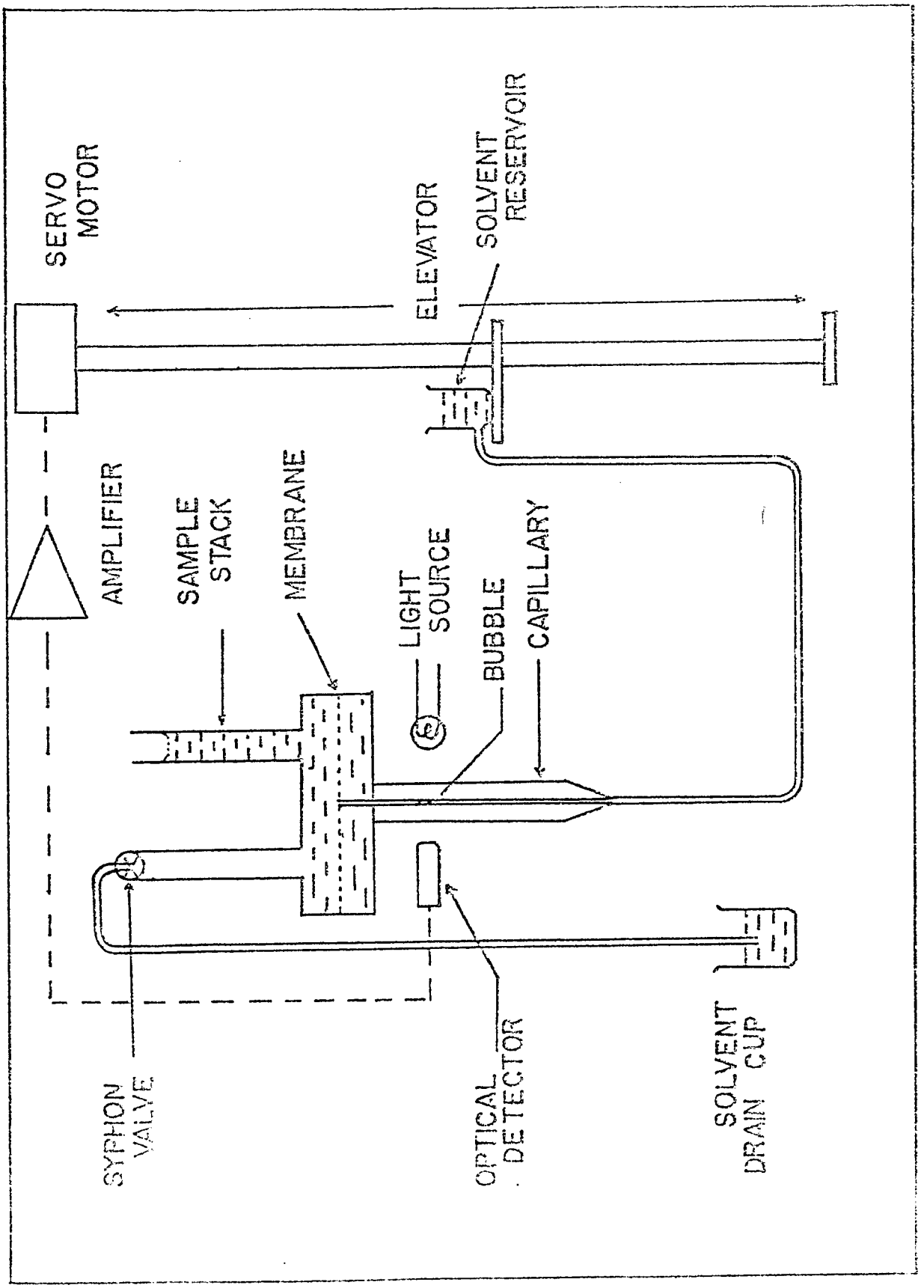
For light scattering measurements, the solutions which were already filtered through a 10 micron filter, had to pass through a 0.45 micron filter again under 50 psig in the filter assembly. Very low solution concentrations of 0.2% by weight were prepared for GPC analyses by diluting the solution which had been used for light scattering measurements. The solutions had to be freshly prepared for all the measurements especially those for the light scattering because polymer gel tended to form on prolonged standing.

CHAPTER IV

OPERATION OF ANALYTICAL INSTRUMENTS

The Hewlett Packard Model 501 high-speed membrane osmometer was used to determine $\overline{M}_n$ of the polymers in the range of 10,000 to 1,000,000. A schematic diagram was shown in figure 1. The osmotic pressure could be obtained automatically with an accuracy of $\pm$ 0.02 cm of solvent in ten minutes after the sample solution had been introduced.

The osmometry consisted of a sample chamber, a servo system, a photocell and an elevator. The sample chamber contained two compartments separated by a semipermeable membrane through which only the solvent molecules could pass. The sample solution was introduced into the upper compartment from a glass sample stack and allowed to drain out through a syphon system. A solvent bottle was mounted on an elevator and connected to the lower solvent compartment through a capillary. A light source was focused on the air bubble which was trapped in the capillary and reflected to a photocell. Any movement of the bubble was detected by the change of light intensity on the photocell. The photocell was connected to an amplifier which activated the servo system and elevator motor thus adjusting the height of the solvent bottle to bring the bubble back to its original



HIGH SPEED MEMBRANE OSMOMETER

Figure 1 Hewlett Packard High Speed Membrane Osmometer, Model 501

position. As a result, the hydrostatic height of the solvent in the solvent bottle was equivalent to the osmotic pressure expressed in cm. of solvent.

The procedure for operating the osmometer was briefly described as follows. First of all, the solvent reference value P_0 had to be established before the measurements with solutions were started. The solvent (THF) was warmed up to 25 °C, introduced into the solvent cup, and drained into the connecting tube and capillary until the lower solvent chamber was completely flooded. Then a small air bubble was injected into the capillary tube and trapped at the bottom of the capillary. A well-conditioned membrane was placed properly on the membrane grid flushed with solvent to keep the membrane wet. The upper clamp with the sample stack was placed upon the membrane and screwed tightly against the lower clamp. Again, the solvent was introduced into the glass sample stack and adjusted to a prescribed height in the sample stack. After an hour for temperature equilibration, measurements were started. The servo system responded automatically to adjust the position of the bubble. The solvent reference pressure P_0, was indicated within 0.01 cm. by a steady reading on the elevator height as determined by the odometer. The time required to achieve a steady pressure required up to five hours or more. The

solution reference pressure P, was then measured. The sample system was drained of solvent and filled with solution. An osmotic pressure reading was usually completed within twenty minutes after the sample solution was introduced.

The membranes, Schleicher and Schuell type o8, obtained from ArRo Laboratories Incorporation were received in a solution of 20% isopropyl alcohol in water. As part of they were soaked in 50% ethanol/water solution for two hours and then in 100% ethanol solution. For further conditioning, they were successively soaked in 75% ethanol/ THF solution, 50% ethanol/THF solution, 25% ethanol/THF solution and 100% THF for two hours in each solution and stored in a closed container of THF.

A Cannon-Fenske viscometer was utilized for viscosity measurements and a schematic diagram was shown in figure 2. Before use, the viscometer was filled with chromic acid to remove any organic substance and then cleaned with THF, distilled water and acetone. Thereafter it was dried with dry air.

A constant volume of liquid was charged into the instrument while it was in an inverted position, by inserting the narrower of the two arms in the solution and applying suction to the opposite arm. The viscometer

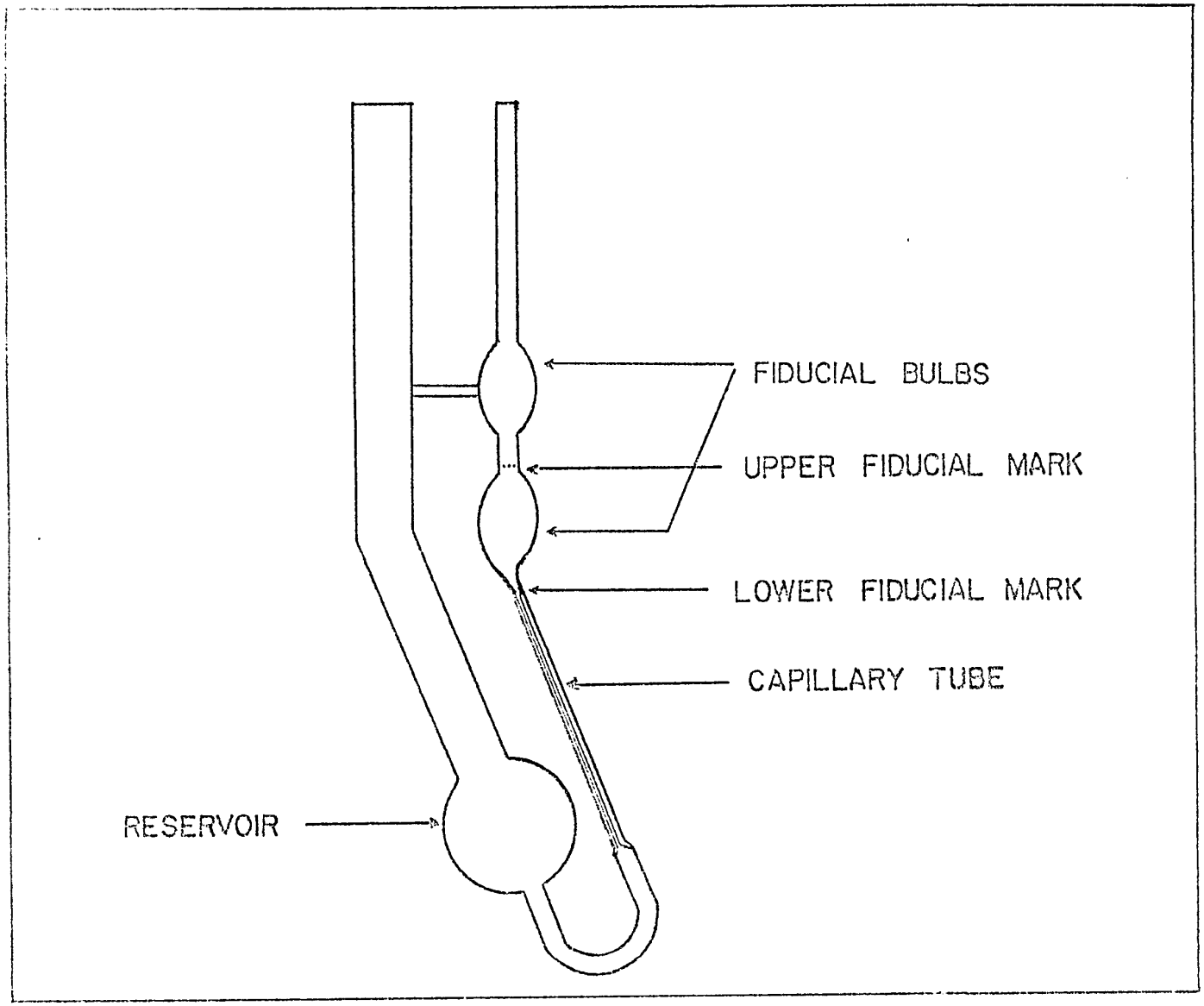


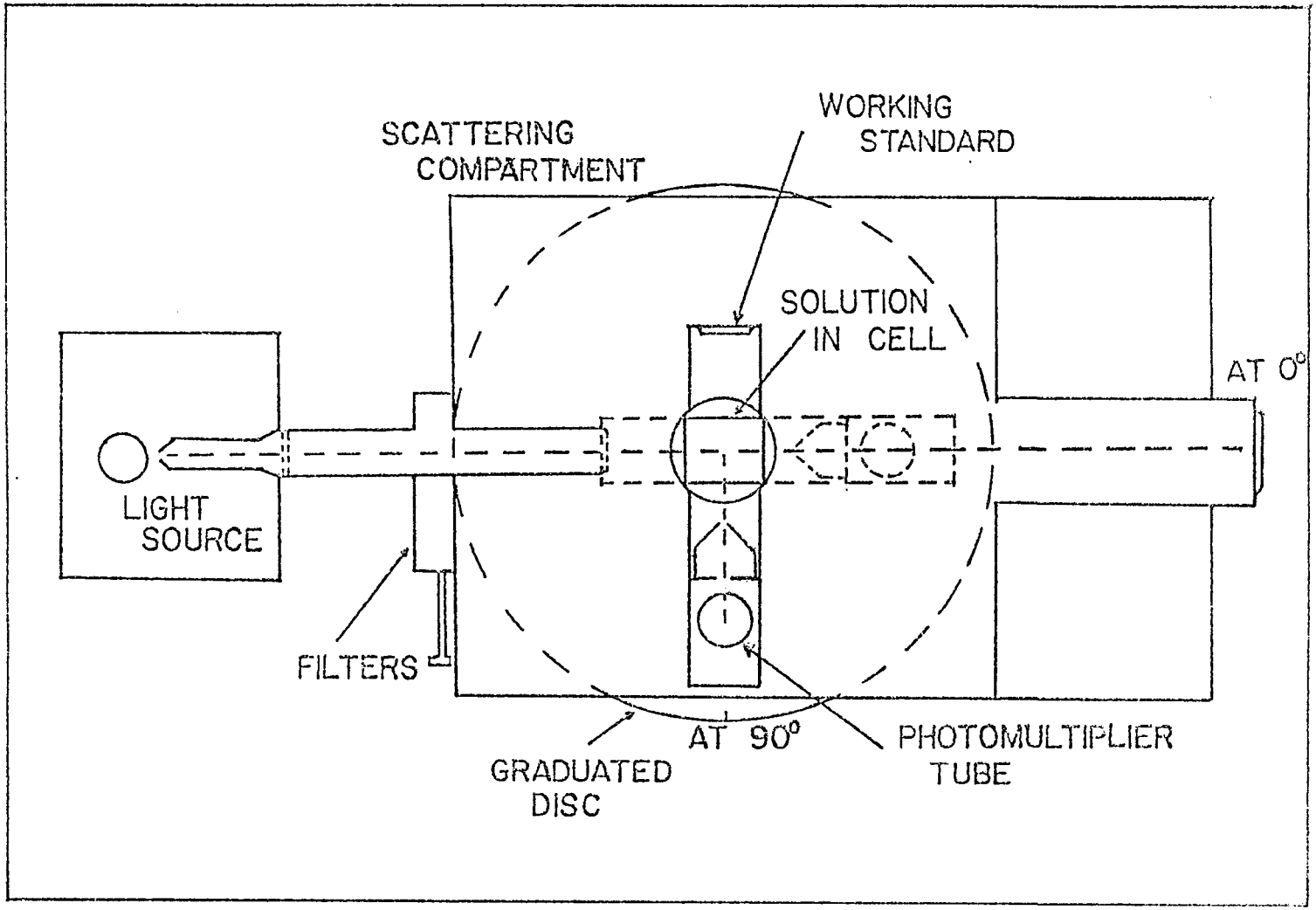
Figure 2 Cannon Fenske Routine Viscometer

was then immersed into the viscosity bath thermostated at 25 $\pm$ 0.1 °C for five to ten minutes until the liquid had reached the bath temperature. A series of five consecutive flow measurements were obtained for each solution. The viscosity was obtained by multiplying the flow time by the calibration constant.

A Brice-Phoenix light scattering photometer model 2000, and the Brice-Phoenix differential refractometer, were used to measure the turbidity, and the differential refractive index of the polymer solution respectively, and consequently $\bar{M}_w$ could be determined.

The light scattering photometer consisted of a mercury-vapor lamp, monochromatic filters, a photographic shutter, a series of push-rod neutral filters with different transmittances, a sample cell, a photomultiplier tube and a graduated disc to indicate the angle at which the photomultiplier tube was orientated with respect to the incident beam. A schematic diagram was shown in figure3.

After the mercury-vapor lamp was heated up for about ten minutes, the filtered sample was charged directly into the 24X24 mm. square sample cell. The 546 mμ green filter was rotated into position. By turning the graduated disc to 0 position, the filter or filter combination, the working



LIGHT SCATTERING PHOTOMETER

Figure 3 Brice-Phoenix Universal Light Scattering Photometer, 2000 Series

standard, the sample solution, and the photomultiplier were in the path of the incident beam. The intensity of light emerging from the solution was detected by the photomultiplier. The deflection was recorded on the chart recorder, and defined as G_w at 0°. Four different readings of G_w at 0° were made by changing the filter or filter combinations. Similarly, the value of G_s at 90° was obtained by setting the graduated disc to the 90° position where the photomultiplier was viewing the scattering light from the solution without filters and working standard in the path of the light. This procedure was repeated to get the readings of G_0 and G_{90} for solutions of different concentration as well as for the pure solvent. Subsequently the apparent turbidity of solution and solvent were calculated from the scattering ratio (G_s / G_w). Hence the excess turbidity for each concentration of solution was found. The excess turbidity of the solutions were also found for blue (436 mμ) light.

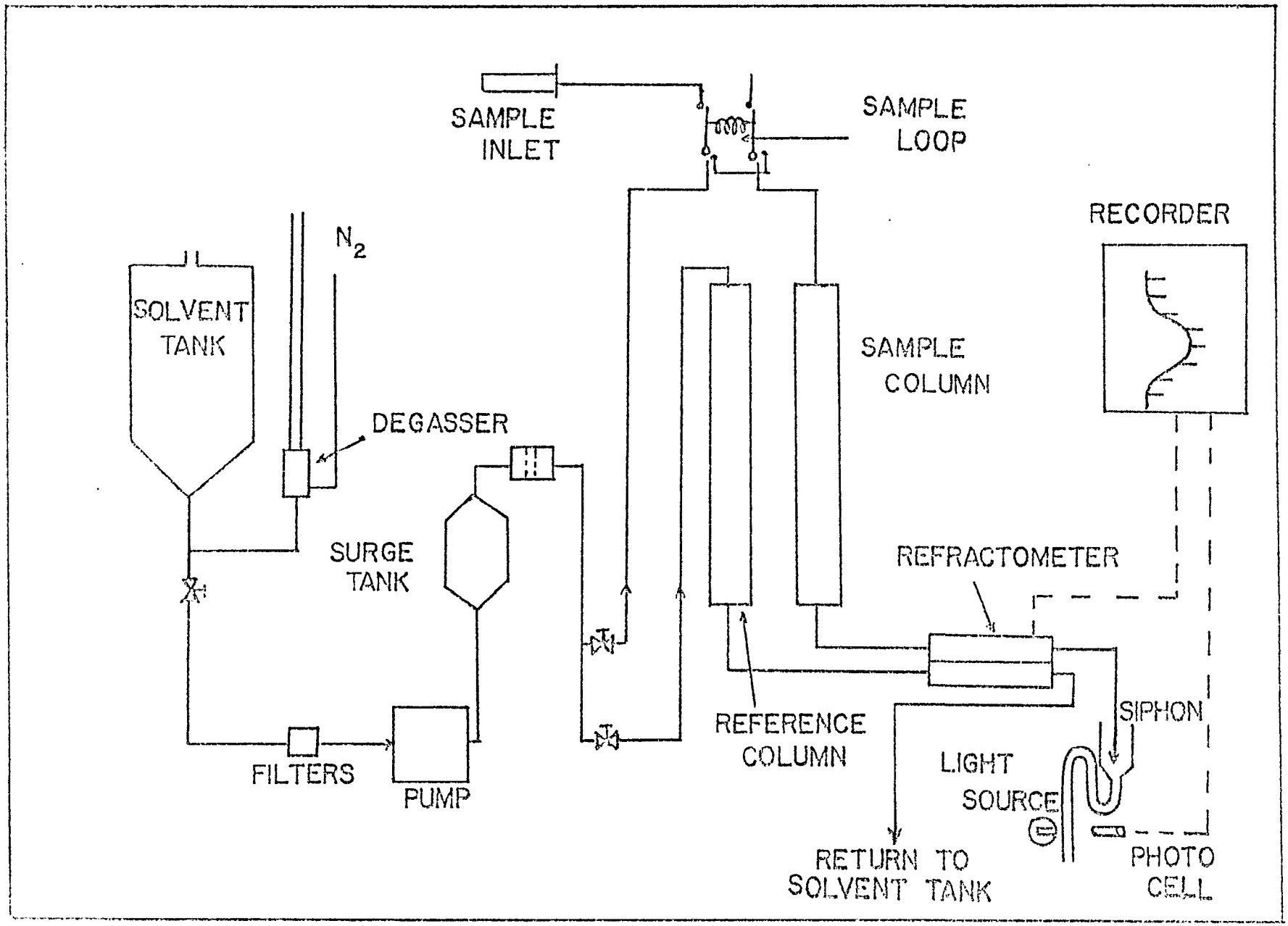
To determine the molecular weight from light scattering measurements, the change of refractive index with concentration was obtained by using the Brice-Phoenix differential refractometer. The latter instrument consisted of a mercury-vapor lamp, blue and green monochromatic filters a jacketed-cell housing, a telescope, an focal image adjusting device and a filar micrometer.

After mercury vapor lamp had been activated about fifteen minutes and constant temperature water at 25°C was circulated through the jacketed housing, the forward compartment was filled with solution and the rear one with solvent. With the cell locked in one position, the telescope was focused on the slit image until the sharpest image was formed. After five readings were made in this position, the cell was turned 180 , and five additional readings were taken in the second position. The displacement correction (d) for the solution was obtained from the difference of the two readings. With the displacement for solvent d^0 initially measured, the total displacement $\Delta d = d - d^0$ could be determined. Hence the differential refractive index was calculated by multiplying the total displacement Δd with the cell constant k which had been originally determined using a potassium chloride solution.

A model 200 GPC developed by Waters Associates Incorporated was used for the determination of $\bar{M}_n$ and molecular weight distributions of polymers. The columns were made of 4 ft. lengths of 3/8 inches stainless steel tubing filled with styragel packing. Two columns sets were available. The combinations of columns in set A in

which the polymer solution was passing through were arranged in series of columns with permeabilities $7X10^5$ — $5X10^6$ Å, 10^4 Å, 10^3 Å, and 700 — 2,000 Å. The columns for the solvent were arranged by two columns with permeabilities $5X10^3$ — $1.5X10^4$ Å and the other two columns with permeabilities $5X10^4$ —$1.5X10^5$ Å. Each column was packed with polystyrene gels of a large range of permeability. A schematic diagram was indicated in figure 4. For analytical purposes, there were three main parts : the injection and pumping system, the detector device, and the electronics systems. The injection and pumping system consisted of an injection valve, syringe, a sample loop, a solvent tank, a mini-pump, a surge tank, a relief valve and the columns. The detector device consisted of a very sensitive differential refractometer which was used to measure the change of refractive index of the solution with respect to the solvent. The signal from the differential refractometer was recorded. The electronics system consisted of a photo-electric detector, connected to an amplifier and a syphon. The discharge of 5 mls volume of solution from the syphon was indicated by means of a vertical pulse on the chart of the recorder.

Three gallons of THF were charged into the solvent tank. Nitrogen was purged through the solvent tank very



GEL PERMEATION CHROMATOGRAPH

Figure 4 Waters Associates Gel Permeation Chromatograph Model 200

slowly for deoxygenation of the solvent THF. The mini-pump was set to 68% of the maximum flowrate in order to get a constant flow rate of 1 ml./min. for the solvent through the instrument. The pressure in the sample stream and solvent stream was adjusted to 55 psig and was checked frequently. Under a fixed condition, the machine was operated continuously as long as a steady baseline appeared on the chart recorder. It usually took at least one day to reach a steady state.

The filtered 0.2% polymer sample solution was injected into the sample loop by means of a syringe. The polymer sample solution was completely delivered from the sample loop to the sample column stream. Both the solvent and polymer solutions were passed through the refractometer system simultaneously. The instantaneous change of refractive index of the polymer solution with respect to that for the solvent was indicated by means of the chart recorder. The polymer solution eluted from the sample columns was collected in a 5 mls syphon and discharged into a waste bottle. The detector device actuated the recorder to make a vertical pulse on the chart paper when 5 mls of solution had been discharged. These pulse marks were used to determine how much solvent had eluted (V_e) The solvent flowing from the solvent columns was returned to the solvent tank.

CHAPTER IV

RESULTS AND DISCUSSION

Molecular weights of several different polymers were determined by osmometry. Polyisoprene (TRANSPIP 100), polybutadiene (TAKENE 1220), two types of polystyrene-butadiene rubbers (SS 255 and KRYLENE 1502) and three polystyrene standards (PS 61970, PS 25170 and PS 25166) were analyzed by means of the high speed membrane osmometer. For the determination of $\bar{M}_n$, as presented in figure 5, a straight line was drawn to find the intercept for the relationship between reduced osmotic pressure (π/c) and concentrations, for each sample. The reduced osmotic pressure values can be seen to increase markedly with concentration. The intercept was generally determined by the method of least squares for accuracy. From figure 5, the slope of the straight lines for polyisoprene and polybutadiene may be observed to be considerably greater than those for polystyrene-butadiene rubbers. It is usually considered that the greater the slope, the greater is the affinity between the polymer and solvent molecules. Hence, it may be considered that the solvent (THF) has a greater affinity for polyisoprene and polybutadiene than for the polystyrene-butadiene polymers.

$\bar{M}_n$ for the synthetic rubbers as determined by osmometry

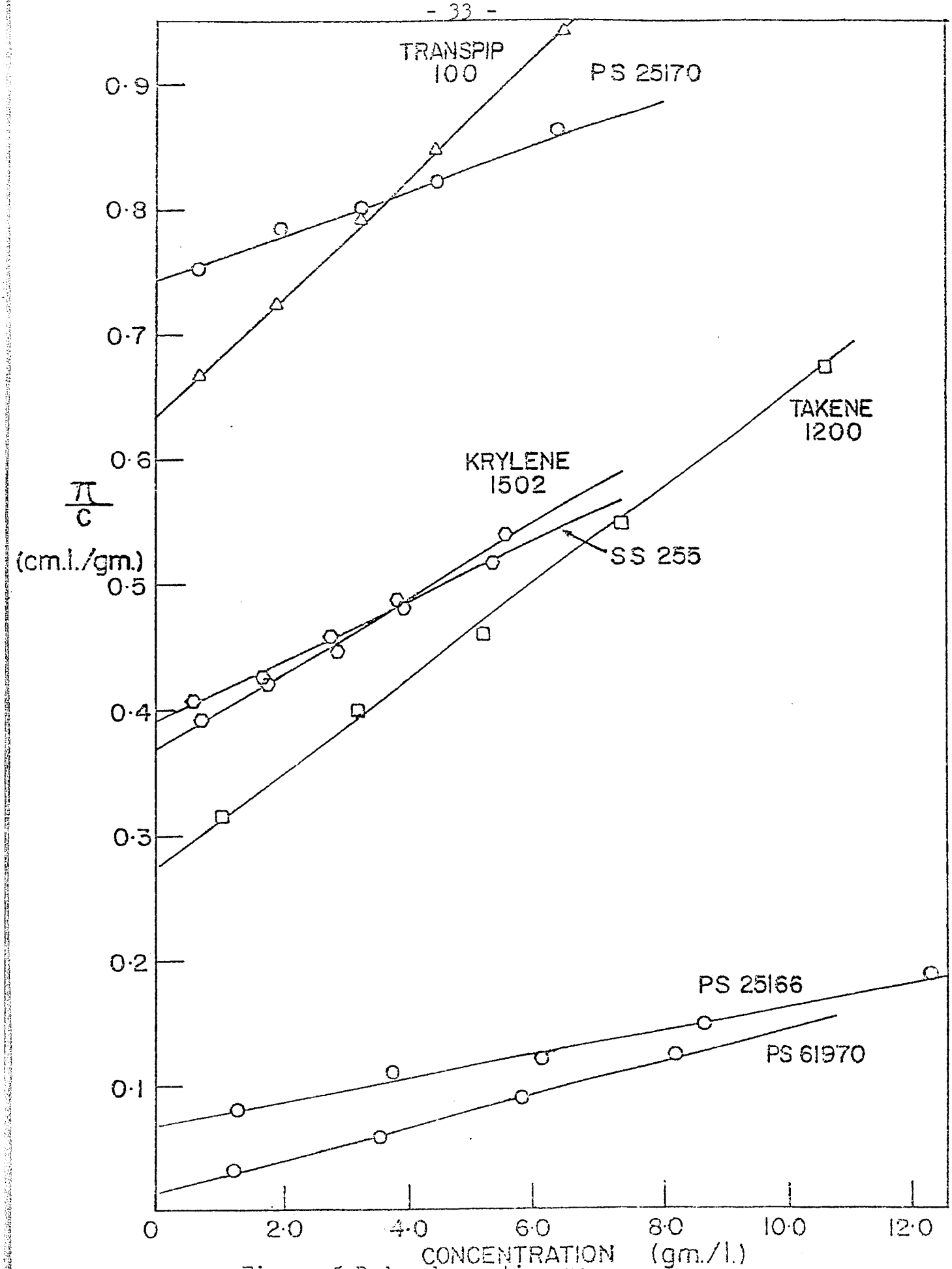


Figure 5 Reduced osmotic pressure versus concentration

was found to be in the range from 45,000 to 100,000. $\bar{M}_n$ for the polystyrene standards (PS 61970 and PS 25170) were found to be up to 10% greater than those given by the supplier. Usually, the high speed osmometer is capable of a good performance for the range of molecular weights between 10,000 and 1,000,000. For those samples having molecular weights above the upper limit, the deviation is possibly caused by experimental error as well as the reliability of the instrument itself. It is more likely that the membrane was not sufficiently impermeable for the $\bar{M}_n$ being determined. Since the membrane used for the instrument was not exactly semipermeable, some minute solute molecules of low molecular weights may have passed through the membrane and caused a decrease of concentration in the solution. Consequently, this could have resulted in an increase in observed molecular weight for certain samples, particularly those of low molecular weight.

$\bar{M}_n$ as determined by osmometry for all samples are listed in table 1.

TYPE OF POLYMER	REDUCED OSMOTIC PRESSURE $(\pi/c)_0$	NUMBER AVE. MOLECULAR WEIGHT	
PS 25170	0.7424	38,420	(35,000)*
PS 25166	0.0704	405,240	(470,000)*
PS 61970	0.0118	2,377,000	(2,700,000)*
POLYSTYRENE-BUTADIENE (SS 255)	0.3912	72,900	
POLYSTYRENE-BUTADIENE (KRYLENE 1502)	0.3723	76,600	
POLYBUTADIENE (TAKENE 1220)	0.2784	102,440	
POLYISOPRENE (TRANSPIP)	0.6323	45,100	

*$\bar{M}_n$ as specified by supplier.

Five monodisperse polystyrene standards, were used for determining the relationship between the intrinsic viscosity and molecular weight in THF solvent at 25 °C. Plots of reduced specific viscosity (η_{sp}/c) and concentration for the polystyene standards are shown on figure 6. The relation between intrinsic viscosity and concentration was calculated by the least squares methods. Figure 6 also indicates that the value of the intrinsic viscosity and the slope of the straight line plot of η_{sp}/c versus concentration is dependent on the sample molecular weight. As commonly observed, the positive slope of the straight line increases as the molecular weight increases, showing the greater dependence of reduced viscosity on concentration for polymers of high molecular weight. This increase in slope may be explained by chain entanglement which may occur with high molecular weight polymer in dilute solutions. By contrast , the reduced viscosities of low molecular weight polymers are only slightly affected by a variation in concentration.

The molecular weights of polystyrene standards and their measured intrinsic viscosities as listed in table 2, were used to determine the Mark-Houwink parameters "a" and "K". The logarithm of the intrinsic viscosity was plotted against the logarithm of the molecular weight as shown in figure 7. A linear relationship between the intrinsic viscosity and the molecular weight existed and the constants were found to be

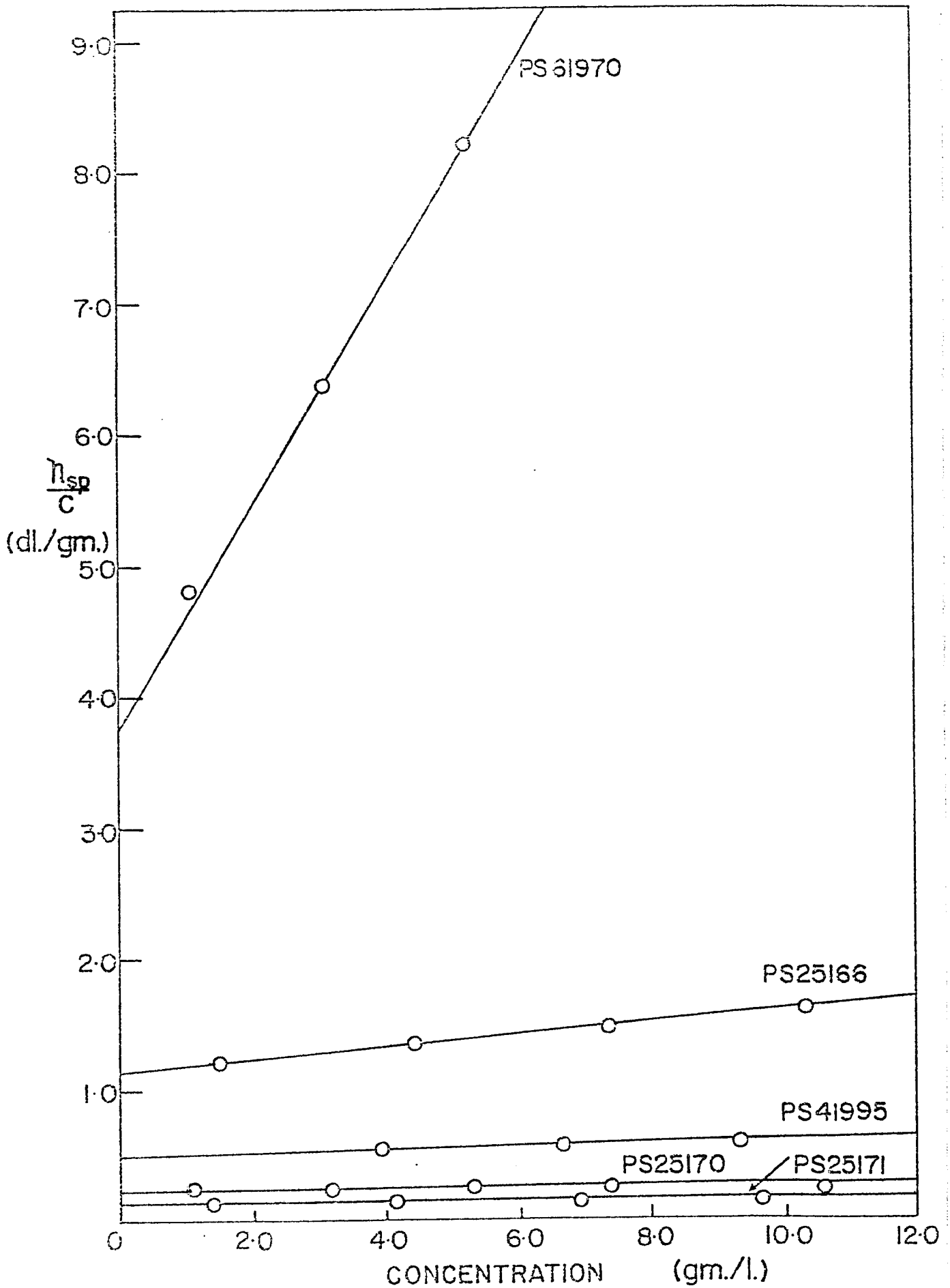


Figure 6 Reduced specific viscosity versus concentration for polystyrenes

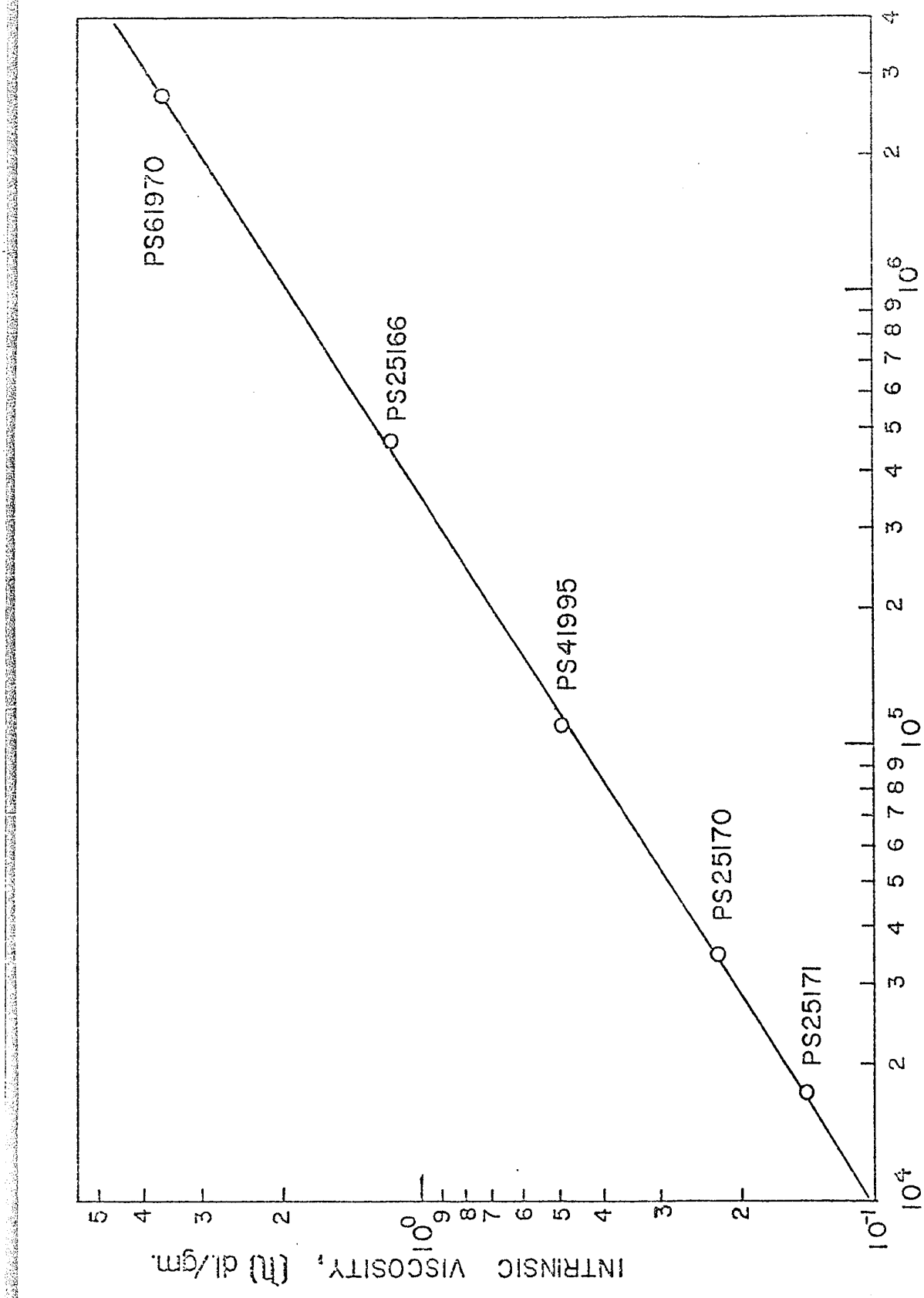


Figure 7 Intrinsic viscosity versus molecular weight for polystyrene standards

$a=0.6334$ and $K=3.04\times10^{-4}$ dl./gm.

Table 2 Intrinsic viscosity and molecular weight for polystyrene standards in THF at 25 °C

POLYSTYRENE STANDARDS NUMBER	MOLECULAR WEIGHT M*	INTRINSIC VISCOSITY dl./gm.
PS 61970	2,700,000	3.6355
PS 25166	470,000	1.1335
PS 41995	110,000	0.5011
PS 25170	35,000	0.2266
PS 25171	17,500	0.1384

* It is given by supplier

In figure 8, the viscosity-concentration relations for polybutadiene, polyisoprene, and two types of polystyrene-butadiene rubbers all in THF solvent are shown. Instrinsic viscosities were determined by the least square method. A rather low value of intrinsic viscosity was obtained for polystyrene-butadiene (SS 255) when compared with the other type (KRYLENE 1502) as shown in figure 8. The low intrinsic viscosity $[\eta]$ is probably caused by the presence of highly branched molecules as well as microgel in polystyrene-butadiene-THF solution. As a result of extensive chain-branching, polymer molecules are considered to occupy a smaller volume than linear ones of the same type and molecular weight, hence intrinsic viscisities of such polymers will be less.

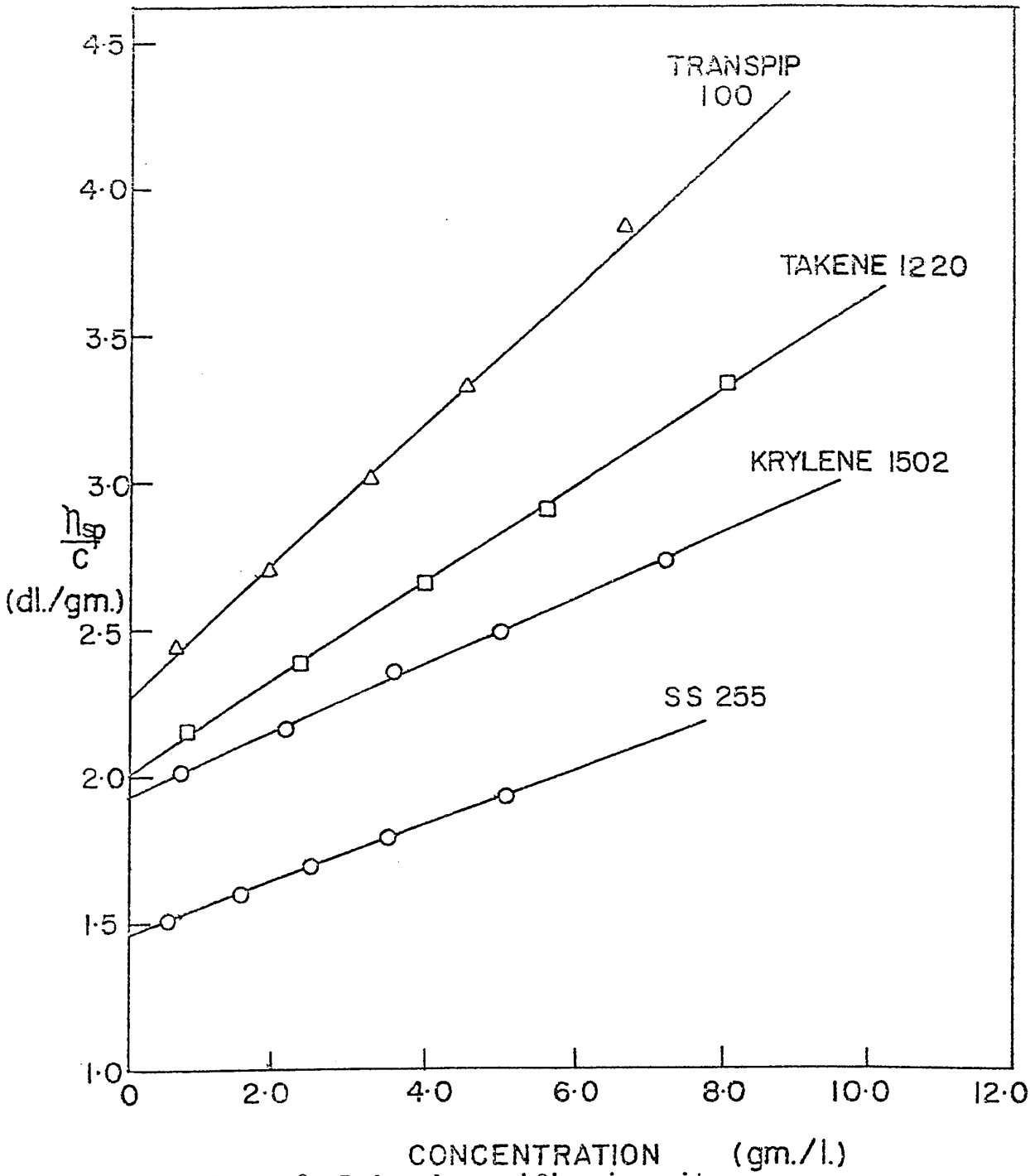


Figure 8 Reduced specific viscosity versus concentration for synthetic rubbers

Three polystyrene standards were analyzed by light scattering to determine $\bar{M}_w$. Scattering ratio (G_s / G_w) of pure solvent and each solution concentration were traced on the recorder chart. The excess turbidity of each solution, denoted by τ, was then determined from the difference between the apparent turbidity of solution and the apparent turbidity of pure solvent. A plot of Hc/τ against concentrations was drawn and extrapolated to zero concentration . The molecular weight was obtained either from the reciprocal of the intercept or analytically by the method of least squares. The results are listed in table 3.

Table 3 Results of Light scattering for polystyrene

(i) Green light

TYPE OF POLYMER	$\bar{M}_w$ FILTER COMBINATIONS F(1,2,3,4)	F(2,3,4)	F(3,4)	AVERAGE $\bar{M}_w$
PS 61970	2,813,370	2,763,000	2,675,330	2,750,600 (2,700,000)*
PS 25166	655,780	667,990	642,320	655,360 (470,000)*
PS 25170	48,840	47,130	46,420	47,460 (35,000)*

*$\bar{M}_w$ as given by supplier

(ii) Blue light

TYPE OF POLYMER	$\bar{M}_w$ FILTER COMBINATIONS F(1,2,3,4)	F(2,3,4)	F(3,4)	AVERAGE $\bar{M}_w$
PS 61970	2,051,420			2,051,420 (2,700,000)*
PS 25166	571,120	563,400	521,800	552,110 (470,000)*
PS 25170	52,920	53,280	49,720	51,970 (35,000)*

The molecular weight of the polystyrene standard for which $\overline{M}_w$ was given as 2,700,000, as measurement agreed well with the given value when green light was provided for the measurement of light scattering. By using blue light, the scattering value (G_s) was found to slowly decrease. This was probably caused by interference or dissymmetry of the scattered light passing through the polymer solution in which the polymer molecular dimension was not sufficiently small when compared with the wavelength of the light. It appears possible that as a consequence of destructive interference, the molecular weights determined by blue light were erroneously low compared with those obtained using green light.

For the polystyrene of medium molecular weight, both green light and blue light were found to give $\overline{M}_w$ which was slightly larger than the listed molecular weight of the sample. It is considered possible that certain impurities and gel patricles which were not completely removed by the 0.45 micron filters caused a large increase in turbidity of the polymer solution. It is suggested that a filter of sufficiently small pore size should be used, and that the scattering cell should be scrupulously cleaned with solvent before starting each measurement. A high speed centrifugation followed by filtration was found helpful to get some improvement in clarification of the polymer solutions.

However, the simple plot of Hc/τ against concentrations can be appropriately applied only to polymers of molecular dimensions much less than the wavelength of the light but not to high molecular weight polymers. Since the effect of destructive interference on the intensity of scattered light for high molecular weight polymer solutions has to be taken account to obtain correct molecular weights, the more precise procedure known as the Zimm double extrapolating method might have been used. This method, however, requires measurements of scattered intensity at a series of angles and for a series of solution concentrations. This more complex procedure was not considered warranted for this work.

Nine monodisperse polystyrene standards were used for the purpose of calibrating the GPC. The peak elution volume of each sample was measured by means of GPC at a concentration of 0.2% by weight and at a constant flow rate of 1 ml/min. Three or four runs for each sample were made and the elution volume was found to be very consistent at the same operating conditions. The results are listed in table 4 and the chromatograms for all samples are shown in figure 9. A plot of the logarithms of molecular weights of the polystyrene standards against peak elution volumes was then obtained as shown in figure 10, and is sometimes referred to as the conventional calibration curve.

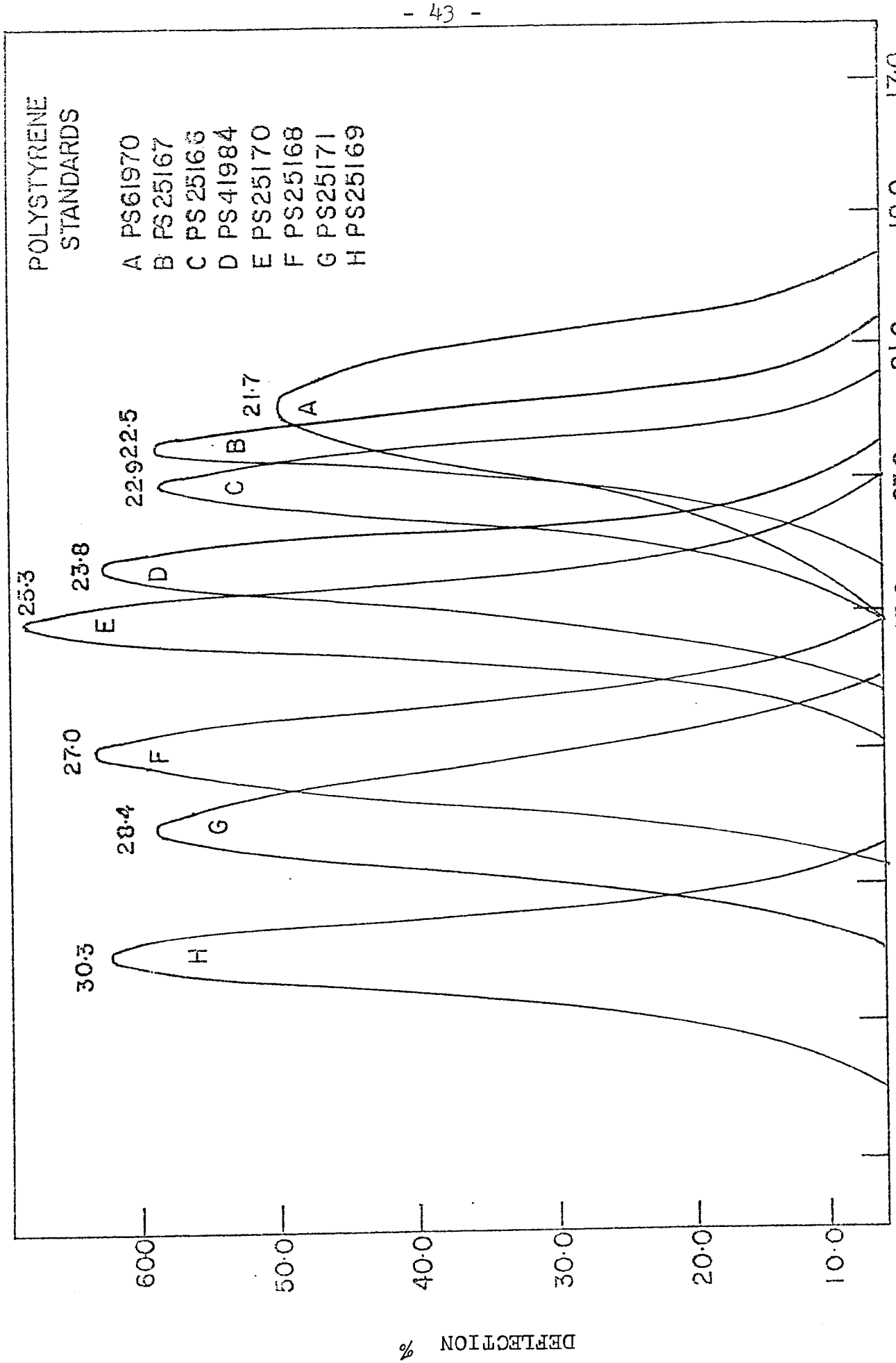


Figure 9 Chromatograms of polystyrenes used for calibration

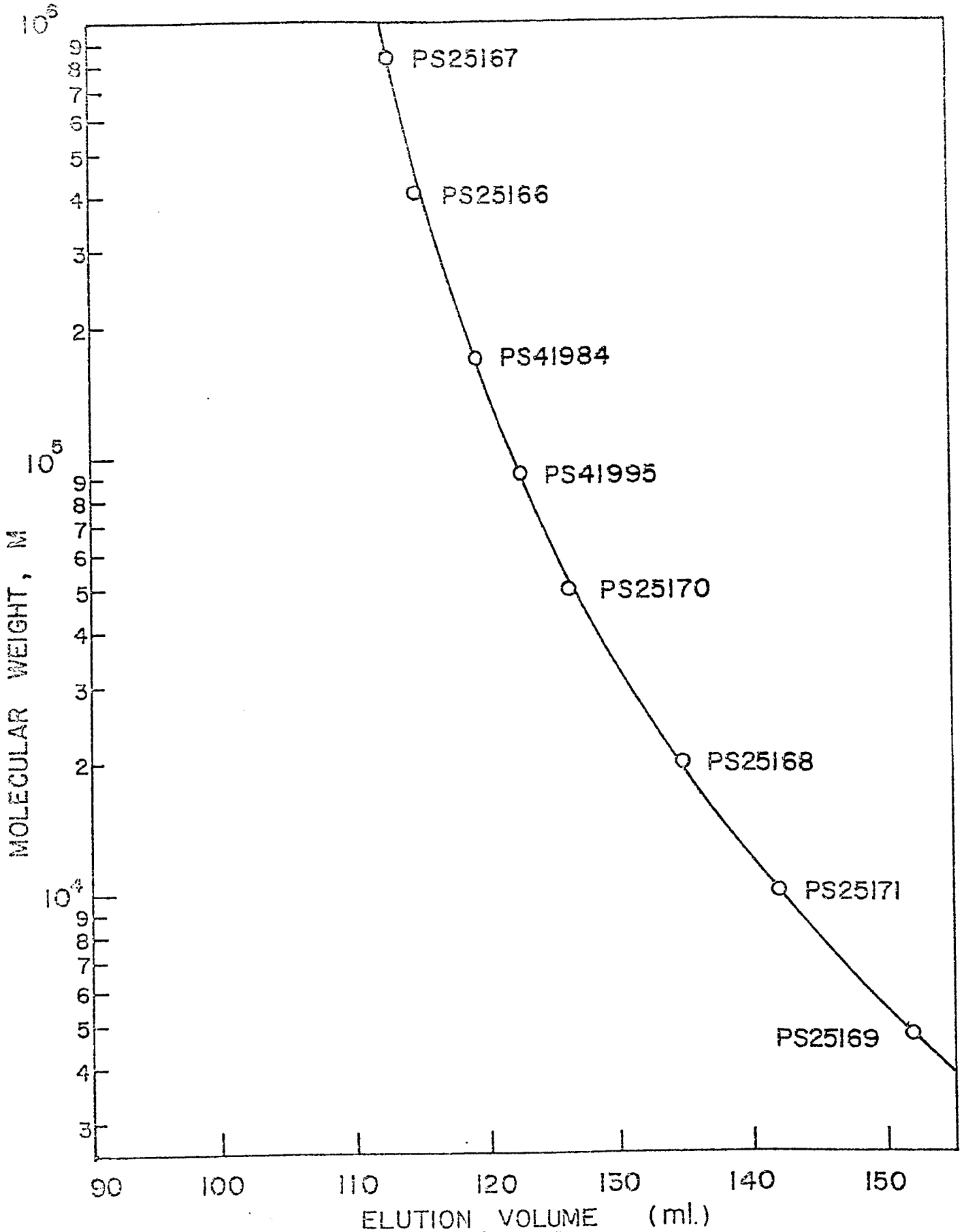


Figure 10 Peak elution volume versus molecular weight

Table 4 Data for conventional calibration curve in GPC

POLYSTYRENE STANDARDS	WEIGHT AVE. MOL. WEIGHT $\bar{M}_w$*	NUMBER AVE. MOL. WEIGHT $\bar{M}_n$*	PEAK MOL. WEIGHT $\bar{M}$*	ELUTION VOL. V_e ml
PS 25166	411,000	392,000	402,000	114.5
PS 25167	867,000	773,000	830,000	112.5
PS 25168	19,850	19,650	19,750	135.0
PS 25169	5,000	4,600	4,800	151.5
PS 25170	51,000	49,000	50,000	126.5
PS 25171	10,300	9,700	10,000	142.0
PS 41984	173,000	164,000	171,000	119.0
PS 41995	98,200	96,200	97,200	122.5
PS 61970	2,145,000	1,780,000	1,987,000	108.5

* As specified by the supplier.

Another five polystyrene standards, which were a little bit different in molecular weights from those used for the conventional calibration were used for defining a second calibration curve sometimes called a universal calibration. With the intrinsic viscosities from viscometry measurements and the GPC respective peak elution volumes for each sample as listed in table 5, a plot of the logarithm of the product $[\eta]M$ against elution volumes was made. The resulting universal calibration curve is shown in figure 11.

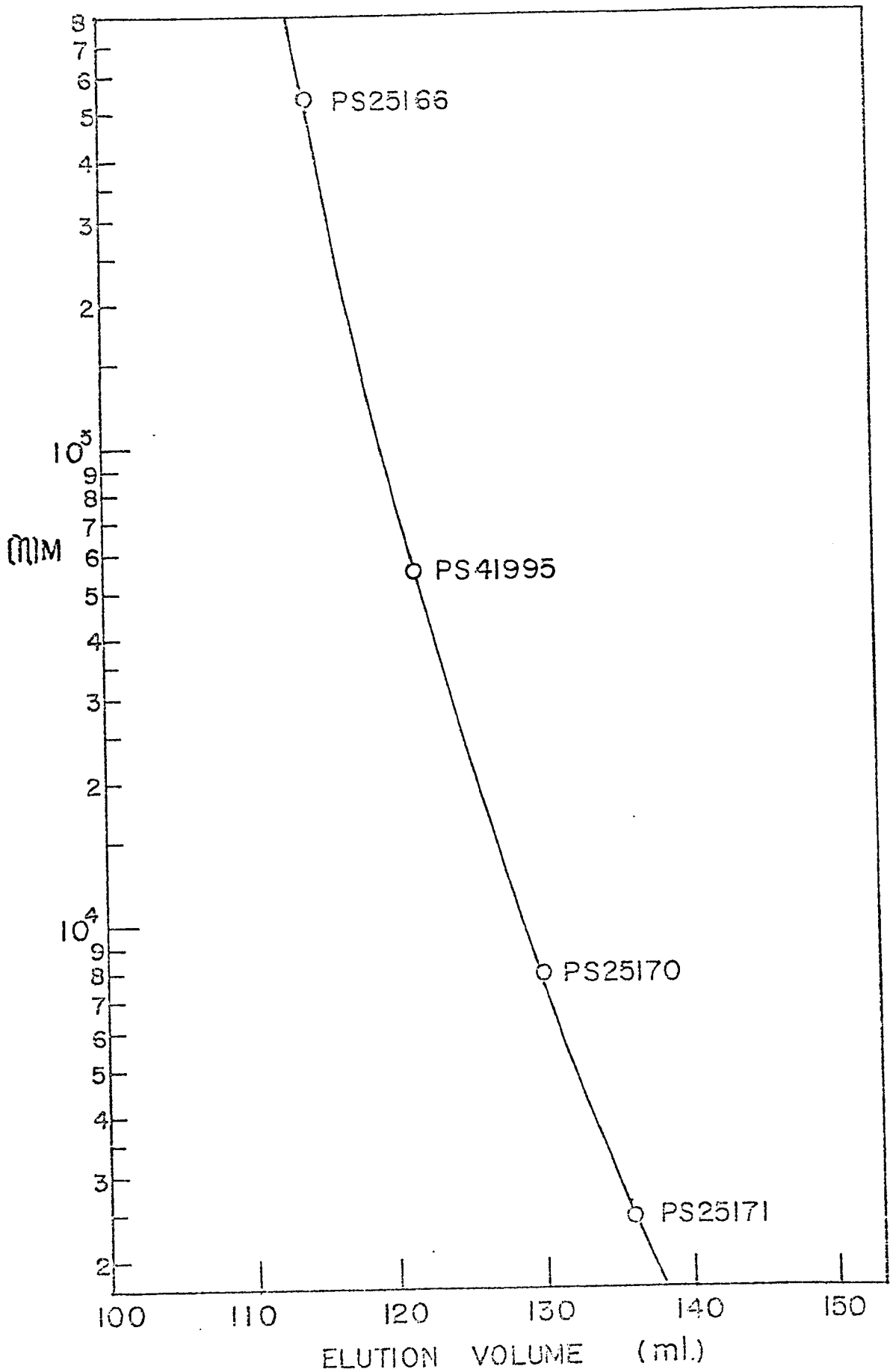


Figure 11 Peak elution volume versus product of intrinsic viscosity and molecular weight

Table 5 Data for the universal calibration curve by GPC

POLYSTYRENE STANDARDS	PEAK MOL. WEIGHT M*	INTRINSIC VISCOSITY dl/gm	MOL. WEIGHT x INTRINSIC VISC. $M[\eta] \times 10^{-4}$	ELUTION VOLUME V_e
PS 61970	2,700,000	3.6355	981.6	106.8
PS 25166	470,000	1.1335	53.27	114.1
PS 41995	110,000	0.5011	5.512	121.3
PS 25170	35,000	0.2266	0.793	129.8
PS 25171	17,500	0.1384	0.242	135.8

* It is given by the supplier.

An additional three monodisperse polystyrene standards were used for testing both the conventional calibration curve as well as the universal calibration curve. The chromatograms of these standards shown in figure 12, were obtained. Estimates of the molecular weights were made using both calibration curves. The molecular weights of two polystyrene standards (PS 25170 and PS 25166) as estimated from both calibration curves were found to be quite close to their given molecular weights. For the polystyrene standards of high molecular weight, there was a great deviation between the molecular weights computed by means of both calibration curves and that given by the supplier. In other words, both calibration curves would appear to be of questionable accuracy for polystyrene of extremely high molecular weight. Probably, the efficiency of polystyrene gel packed in the column was not good enough for

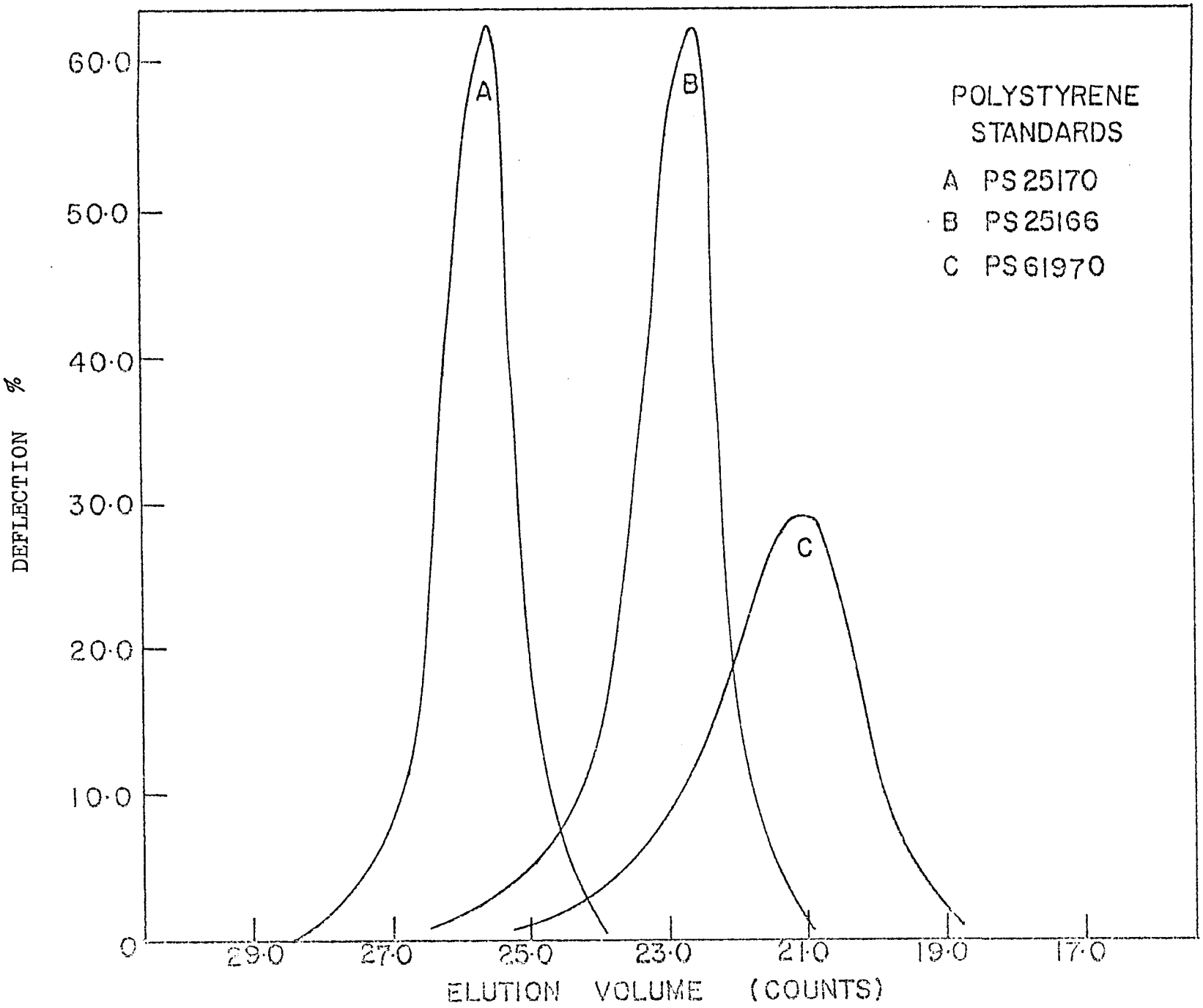


Figure 12 Chromatograms of polystyrene samples

separating the polymer having molecular weights of up to several million. Or, on the other hand, the calibration curve itself may not be applicable to polymers having such a large range of molecular weights. This comparison is shown in tables 6 and 7.

The synthetic rubber polymers, polybutadiene, polyisoprene, and two types of polystyrene-butadiene polymers were also characterized by GPC. Their chromatograms shown in figure 13, were used to determine elution volumes. Molecular weights were determined by using both calibration curves. The molecular weights for these samples estimated by means of the conventional calibration curve were found to be larger than those estimated by means of the universal calibration curve. This occurrance may be explained by the structures of these sythetic rubber polymers which are different from polystyrene. For branched polymers and linear polymers with more complicated structures, the time retained in the GPC columns is always longer than those of linear polymer of the same molecular weight. This would appear to be the reason why the conventional calibration curve yielded a relatively high molecular weight. On the other hand, the universal calibration curve utilizes the intrinsic viscosity which can be related to the polymer chain dimensions and to the interaction between polymer and solvent. Therefore this calibration curve can be used with greater confidence for most polymers for the determinations

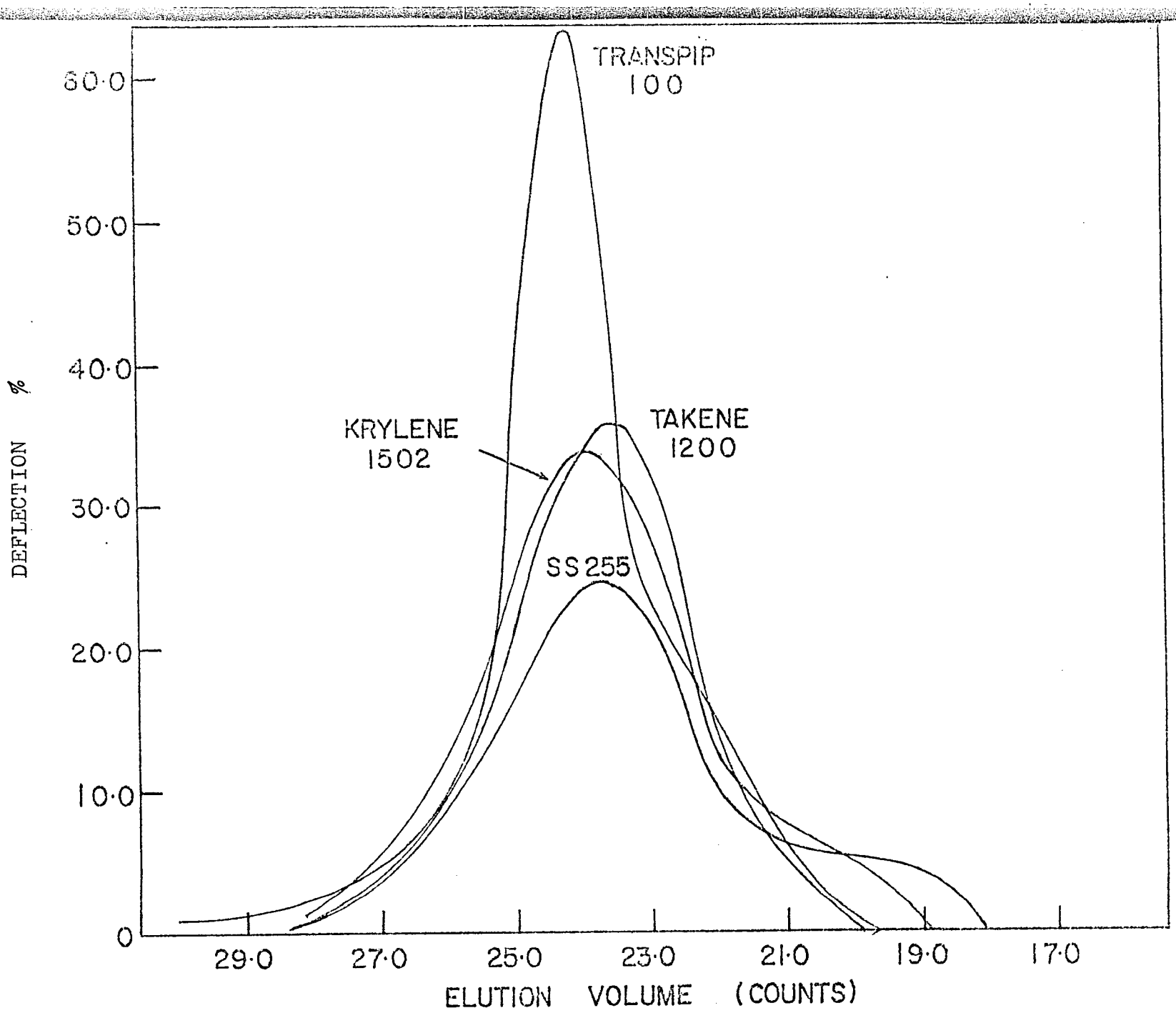


Figure 13 Chromatograms of synthetic rubber samples

of molecular weights from GPC chromatograms. The results of this comparison are listed in tables 6 and 7.

Table 6 Application of conventional calibration curve in determining $\overline{M}_n$ and $\overline{M}_w$

TYPE OF POLYMER	NUMBER AVERAGE MOLECULAR WEIGHT $\overline{M}_n$	WEIGHT AVERAGE MOLECULAR WEIGHT $\overline{M}_w$	POLY-DISPERSITY $\overline{M}_w / \overline{M}_n$
PS 25170	31,720	36,460	1.15
PS 25166	252,410	448,620	1.78
PS 61970	740,080	3,498,140	4.73
POLYSTYRENE-BUTADIENE (SS 255)	119,530	1,479,110	12.37
POLYSTYRENE-BUTADIENE (KRYLENE 1502)	123,760	671,530	5.43
POLYBUTADIENE (TAKENE 1220)	138,120	740,870	5.36
POLYISOPRENE (TRANSPIP)	83,550	318,430	3.81

Table 7 Application of universal calibration curve in determining $\overline{M}_n$ and $\overline{M}_w$

TYPE OF POLYMER	NUMBER AVERAGE MOLECULAR WEIGHT $\overline{M}_n$	WEIGHT AVERAGE MOLECULAR WEIGHT $\overline{M}_w$	POLY-DISPERSITY $\overline{M}_w / \overline{M}_n$
PS 25170	31,750	38,410	1.21
PS 25166	246,530	428,460	1.74
PS 61970	716,770	4,257,320	5.94
POLYSTYRENE-BUTADIENE (SS 255)	77,720	968,550	12.46
POLYSTYRENE-BUTADIENE (KRYLENE 1502)	80,470	410,890	5.11
POLYBUTADIENE (TAKENE 1220)	87,150	411,730	4.73
POLYISOPRENE (TRANSPIP)	59,130	193,190	3.27

CHAPTER V

CONCLUSION

Several types of monodisperse polystyrene standards were characterized by osmometry, viscometry, light scattering and GPC. Determinations of molecular weights were generally in agreement with their given molecular weights except for polystyrene of very high molecular weight. This indicates that these instruments can provide measurements with good accuracy. In addition, a universal calibration curve was obtained by plotting the product, $[\eta]M$ versus elution volume. The universal calibration curve was found to be applicable for the determination of molecular weights for polystyrene polymers.

Osmometry, viscometry, light scattering and GPC measurements were attempted for polyisoprene, polybutadiene, and two types of polystyrene-butadiene polymers. Because of some slight turbidity of polystyrene-butadiene-THF solutions, The determination of molecular weight by light scattering, yielded incredibly high molecular weights which were consequently deleted. On the other hand, analyses for $\bar{M}_n$ by osmometry were still possible in spite of the turbidity. By use of the universal calibration curve and the chromatogram from GPC, the weight-average molecular weight, $\bar{M}_w$, was

computed and hence the polydispersity of the polymer. The polydispersity of polyisoprene, polybutadiene, and polystyrene-butadiene polymers as analyzed by GPC showed a relatively broad molecular weight distribution.

REFERENCES

1. McMillan and Mayer, J. Chem. Phys. 13 (1945) 276
2. Huggins, M. L., J. Amer. Chem. Soc. 64, 2716 (1942)
3. Kraemer E. O., Ind. Eng. Chem. 30, 1200 (1938)
4. Brandrup, J. and Immerent, E. H., "Polymer Handbook", John Wiley and sons, N. Y., (1967)
5. Flory, P. J., "Principle of Polymer Chemistry", Cornell University Press, Ithaca, N. Y., 1953
6. Tompa, H., "Polymer Solutions", Butterworths Scientific Publications, London, (1956)
7. Anon, Chem. Engng. News, 17 December 1962
8. Cazes J., J. Chem. Education, 43, A625 (1966)
9. Laurent, T. C. and Killander, E. P., J. Chromatog., 16, 89 (1964)
10. Porath, J., Pure Appl. Chem. 6, 233 (1963)
11. Brewer, P. I., Polymer 6, 603 (1965)
12. Le Page, M., Beau, R. and DE Vries, A. J., J. Polym. Sci. C21, 119 (1968)
13. Billmeyer, F. W., Jr. and Kelley, R. N., J. Chromatog. 34, 322 (1968)
14. Hazell, J. E., Prince, L.A. and Stapelfeldt, H. E., J. Polym. Sci. C21, 43 (1968)
15. Debye, P., J. Chem. Phys., 14, 636 (1946)
16. Flory, P. J., and Fox, T. G., J. Am. Chem. Soc., 73, 1904, 1915 (1951)

17. Hendrickson, J. G. and Moore, J. C., J. Polym. Sci. A1, 4, 167 (1966)

18. Grubisic, Z., Rempp, P. and Benoit, H., J. Polym. Sci. B5, 753 (1967)

19. Allen P. W., "Technique of Polymer Characterization" Butterworths Scientific Publications, London, 1959

20. Simha, R., J. Phys. Chem. 44, 25 (1940)

21. Jenkins A. D., "Progress in Polymer Science" Vol. I and II, Pergamon Press, (1970)

22. Morris, M. C., J. Chromatog. 55, (1971) 203-210

23. Hayduk, W., Laudie, H., J. Polym. Sci. 16, 3003 (1972)

24. Booth, C., and Beason, L. R., J. Polym. Sci., 42, 81 (1960)

25. Blackley, D. C., and Smith, D. A., "Addition Polymers: Formation and Characterization", Butterworths Scientific Publications, London, 1968

26. White, J. L., Salladay, D. G., Quisenberry, D. O., and Maclean, D. L., J. Applied Poly. Sci. 16, 2811(1972)

27. Van Krevelen, D. W., and Hoftyzer, P. J., J. Applied Poly. Sci., 2, 2189(1967)

APPENDIX I

CALCULATIONS AND CALIBRATED CONSTANTS FOR LIGHT SCATTERING

The general equation used to calculate the absolute turbidity of a solution for the Brice-Phoenix light scattering photometer is :

$$\tau = \frac{16TD}{3(1.049)xh}\left[N^2\,\frac{R_w}{R_c}\right]\left[a\,F\,\frac{G_s}{G_w}\right]$$

Where :

G_s / G_w is the scattering ratio

F is the product of transmittances of the neutral filters used in determining the scattering ratio.

a is a constant relating the working standard to the opal glass reference standard.

TD is the experimentally determined product of the diffuse transmittance of the opal glass and a correction factor.

h is the width of the diaphragm.

N is the refractive indew of the solution.

R_w / R_c is an experimentally determined correction for incomplete compensation for refraction effects.

Since the photometer number 2416 is used, the above equation comes to be :

$$\tau = 1.17\left[N^2\frac{R_w}{R_c}\right]\left[aF\ \frac{G_s}{G_w}\right] \quad \text{------- for blue light}$$

$$\tau = 1.28\left[N^2\frac{R_w}{R_c}\right]\left[aF\ \frac{G_s}{G_w}\right] \quad \text{------- for green light}$$

The calibration constants for Photometer No. 2416 are listed in the following table.

CONSTANTS		WAVELENGTH mμ BLUE 436	GREEN 546
Diffuse transmittance of reference opal times diffusor correction factor (TD)		0.275	o.302
Width of primary beam, cm	h	1.20	1.20
Working standard constant	a	0.0310	0.0445
Transmittance of neutral filter 1.	F_1	0.460	0.486
2.	F_2	0.239	0.257
3.	F_3	0.108	0.129
4.	F_4	0.0374	0.0489

Then the molecular weight is determined by calculating Hc/τ for a number of solutions of different concentration, plotting Hc/ versus c, extrapolating to zero concentration.

$Hc/\tau = 1/M + 2Bc$

where : $H = 15.2 \times 10^{-5} N^2 (N - N_0)^2 / c^2$ --- for blue light

$H = 6.18 \times 10^{-5} N^2 (N - N_0)^2 / c^2$ --- for green light

The quantity $(N - N_0)/c$ is a constant for a given solute-solvent solution, and is measured by the Brice-Phoenix Differential Refractometer.

Hence the calibration constants for the differential refractometer were already determined by using Potassium Chloride solution and their values were $K=909.635 \times 10^{-6}$ (green light) and $K=908.287 \times 10^{-6}$ (blue light)

The quantity $(N - N_0)/c$ determined by means of differential refractometer for polystyrene standards are :

TYPE OF POLYMER	$(N - N_0)/c$ (10^6) GREEN LIGHT	BLUE LIGHT
PS 61970	190.02	205.258
PS 25166	186.611	194.978
PS 25170	187.36	198.074

Determination of calibration constant for the Differential Refractometer by using KCl, Potassium Chloride solution

Solvent (distilled water) zero reading

$d_2 - d_1 = -0.019$ ------ Green light

$d_2 - d_1 = -0.04$ ------ Blue light

GREEN LIGHT

CONCENTRATION gm/100ml	SOLUTION d_1'	SOLUTION d_2'	Δ d	N x 10^6	CALIBRATION CONSTANT Kx10^6
0.05	4.632	4.674	0.061	68	1114.8
0.15	4.555	4.755	0.219	205	936.1
0.25	4.483	4.845	0.381	342	897.6
0.35	4.404	4.915	0.531	480	904
0.50	4.272	5.035	0.779	682	875.5
1.50	3.543	5.775	2.251	2040	906.3
2.50	2.816	6.495	3.698	3365	910
3.50	2.064	7.214	5.169	4685	906.4
5.00	0.986	8.215	7.248	6610	912

CALIBRATION CONSTANT = 909.635 x 10^{-6}

BLUE LIGHT

CONCENTRATION gm/100ml	SOLUTION d_1'	SOLUTION d_2'	Δ d	N x 10^6	CALIBRATION CONSTANT Kx10^6
0.05	4.635	4.685	0.09	75	833.3
0.15	4.564	4.764	0.24	220	916.7
0.25	4.475	4.853	0.418	359	858.8
0.35	4.404	4.933	0.569	502	882.2
0.50	4.264	5.055	0.831	715	860
1.50	3.515	5.813	2.338	2130	911
2.50	2.784	6.556	3.812	3500	918.2
3.50	2.013	7.276	5.303	4865	917.4
5.00	0.883	8.354	7.611	6865	902

CALIBRATION CONSTANT = 908.287 x 10^{-6}

APPENDIX II

MATHEMATICAL BASIS FOR UNIVERSAL CALIBRATION AND ITS APPLICATION

The method for using the GPC with the universal calibration curve to obtain $\bar{M}_n$, $\bar{M}_w$, and the polydispersity of the polymer ($\bar{M}_w$ / $\bar{M}_n$) is simply derived by the following expressions :

Assume a parameter Z as the product of the intrinsic viscosity and the molecular weight

$$Z_i = [\eta]_i M_i \qquad \text{---------- (1)}$$

Using the Mark-Houwink relationship for a polymer :

$$[\eta]_i = KM_i^a \qquad \text{--------- (2)}$$

Then a expression for M_i is written as :

$$M_i = \left(\frac{Z_i}{K}\right)^{1/(a+1)} \qquad \text{--------- (3)}$$

where M_i, $[\eta]_i$ and Z_i are the molecular weight, the intrinsic viscosity, and the product of molecular weight and intrinsic viscosity, respectively, of the i-th species.

Finally, $\bar{M}_n$ and $\bar{M}_w$ are calculated by the following expressions :

i)

$$\bar{M}_n = \frac{K^{-1/(a+1)}}{\sum_i \frac{W_i}{Z_i^{1/(a+1)}}} \qquad \text{--------- (4)}$$

ii)

$$\bar{M}_w = K^{-1/(a+1)} \sum_i w_i Z_i^{1/(a+1)} \qquad \text{--------- (5)}$$

where : w_i, the weight fraction of the i-th species

The contants K and "a" found in reference (26,27) are listed in the table below.

TYPE OF POLYMER	MARK-HOUWINK CONSTANTS	
	K (10^4) dl/gm	a
POLYSTYRENE	3.04	0.6334
POLYSTYRENE-BUTADIENE (SS 255 and KRYLENE 1502)	2.984	0.7043
POLYBUTADIENE (TAKENE 1220)	2.12	0.739
POLYISOPRENE (TRANSPIP)	2.0	0.728

APPENDIX III

OSMOMETRY DATA

Solvent : THF
Membrane : S & S 08
Temperature : 25 C
Solvent density : 0.885 gm/ml
RT = 28,520

POLYSTYRENE (PS 25170)

CONCENTRATION, c (gm/l)	0.6384	1.9152	3.192	4.4688	6.384
SOLVENT PRESSURE P_0	17.29	17.31	17.31	17.33	17.34
SAMPLE PRESSURE	17.75	18.78	19.88	21.01	22.83
SAMPLE PRESSURE	17.78	18.83	19.84	20.98	22.84
AVERAGE PRESSURE P	17.77	18.81	19.86	21.00	22.84
$\pi = P - P_0$ (cm solvent)	0.48	1.50	2.55	3.67	5.50
π/c	0.7519	0.7832	0.799	0.8212	0.8615

INTERCEPT = 0.7424

$\bar{M}_n$ = 38,420

POLYSTYRENE (PS 25166)

CONCENTRATION,c (gm/l)	1.229	3.687	6.145	8.603	12.29
SOLVENT PRESSURE P_0	17.54	17.52	17.50	17.50	17.48
SAMPLE PRESSURE	17.63	17.93	18.22	18.73	19.72
SAMPLE PRESSURE	17.64	17.94	18.24	18.71	19.83
AVERAGE PRESSURE P	17.64	17.94	18.23	18.72	19.78
$\pi = P - P_0$ (cm solvent)	0.10	0.42	0.73	1.22	2.30
π/c	0.08	0.114	0.118	0.148	0.187

INTERCEPT = 0.0704

$\bar{M}_n$ = 405,240

POLYSTYRENE (PS 61970)

CONCENTRATION, c (gm/l)	1.1654	3.4962	5.8270	8.1578
SOLVENT PRESSURE P_0	17.92	17.94	17.94	17.96
SAMPLE PRESSURE	17.95	18.13	18.43	18.96
SAMPLE PRESSURE	17.96	18.14	18.49	18.99
AVERAGE PRESSURE P	17.96	18.14	18.46	18.98
$\pi = P - P_0$ (cm solvent)	0.04	0.20	0.52	1.02
π/c	0.0343	0.0572	0.0891	0.125

INTERCEPT = 0.0118

$\bar{M}_n$ = 2,377,000

POLYSTYRENE-BUTADIENE (SS 255)

CONCENTRATION, c (gm/l)	0.5378	1.6134	2.689	3.7646	5.378
SOLVENT PRESSURE P_0	18.40	18.38	18.37	18.36	18.35
SAMPLE PRESSURE	18.62	19.06	19.58	20.18	21.12
SAMPLE PRESSURE	18.61	19.06	19.61	20.20	21.16
AVERAGE PRESSURE P	18.62	19.06	19.60	20.19	21.14
$\pi = P - P_0$ (cm solvent)	0.22	0.68	1.23	1.83	2.79
π/c	0.409	0.421	0.457	0.486	0.519

INTERCEPT = 0.3912

$\bar{M}_n$ = 72,900

POLYSTYRENE-BUTADIENE (1502)

CONCENTRATION, c (gm/l)	0.557	1.671	2.785	3.899	5.57
SOLVENT PRESSURE P_0	18.92	18.91	18.91	18.90	18.89
SAMPLE PRESSURE	19.15	19.60	20.12	20.75	21.86
SAMPLE PRESSURE	19.13	19.61	20.17	20.79	21.92
AVERAGE PRESSURE P	19.14	19.61	20.15	20.77	21.89
$\pi = P - P_0$ (cm solvent)	0.22	0.70	1.24	1.87	3.00
π/c	0.395	0.419	0.445	0.480	0.539

INTERCEPT = 0.3723

$\bar{M}_n$ = 76,600

POLYBUTADIENE (TAKENE 1220)

CONCENTRATION, c (gm/l)	1.0586	3.1758	5.2930	7.4102	10.586
SOLVENT PRESSURE P_0	17.83	17.81	17.81	17.80	17.79
SAMPLE PRESSURE	18.16	19.06	20.17	21.85	24.97
SAMPLE PRESSURE	18.15	19.09	20.21	21.88	25.02
AVERAGE PRESSURE P	18.16	19.08	20.19	21.87	25.00
$\pi = P - P_0$ (cm solvent)	0.33	1.27	2.38	4.07	7.21
π/c	0.312	0.40	0.45	0.549	0.681

INTERCEPT = 0.2784

$\bar{M}_n$ = 102,440

POLYISOPRENE (TRANSPIP)

CONCENTRATION, c (gm/l)	0.6298	1.8894	3.1490	4.4086	6.298
SOLVENT PRESSURE P_0	17.85	17.83	17.81	17.78	17.76
SAMPLE PRESSURE	18.28	19.19	20.29	21.52	23.70
SAMPLE PRESSURE	18.25	19.19	20.30	21.49	23.72
AVERAGE PRESSURE P	18.27	19.19	20.30	21.51	23.71
$\pi = P - P_0$ (cm solvent)	0.42	1.36	2.49	3.73	5.95
π/c	0.667	0.72	0.791	0.846	0.945

INTERCEPT = 0.6323

$\bar{M}_n$ = 45,100

APPENDIX IV

INTRINSIC VISCOSITY DATA

Solvent : THF
Solvent density : 0.885 gm/ml
Solvent viscosity : 0.469 cp
Temperature : 25 °C

POLYSTYRENE (PS 61970)

CONCENTRATION	1.046	3.138	5.230	7.322	10.460
TUBE NUMBER	50,M795	50,M795	50,M795	100,M532	100,M532
TUBE CONSTANT	0.004026	0.004026	0.004026	0.01593	0.01593
SOLVENT DENSITY	0.88516	0.88549	0.88582	0.88615	0.88664
	199.3	395.6	698.0	275.7	505.5
TIME	199.5	395.5	698.2	275.6	505.7
(sec.)	199.5	395.7	698.3	275.8	505.5
	199.6	395.7		276.0	505.7
AVERAGE TIME	199.38	395.63	698.17	275.8	505.6
η (cp.)	0.7105	1.4104	2.4899	3.8933	7.1411
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.5149	2.0072	4.3089	7.3012	14.226
$\frac{\eta_{sp}}{c}$ (l/gm)	0.4923	0.6396	0.8239	0.9972	1.360

INTRINSIC VISCOSITY = 0.36355 l/gm

POLYSTYRENE (PS 25166)

CONCENTRATION	1.475	4.425	7.375	10.325	14.750
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88523	0.88584	0.88616	0.88662	0.88732
	155.3	209.8	273.2	348.6	489.4
TIME	155.2	209.8	273.3	348.7	489.5
(sec.)	155.2	209.7	273.0	348.6	489.8
	155.2	209.9	273.3	348.8	
AVERAGE TIME	155.23	209.8	273.2	348.68	489.57
η (cp.)	0.5523	0.7482	0.9747	1.2446	1.7489
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.1796	0.5953	1.0782	1.6538	2.7290
η_{sp}/c (1/gm)	0.1218	0.1345	0.1462	0.1602	0.1850

INTRINSIC VISCOSITY = 0.11335 1/gm

POLYSTYRENE (PS 41995)

CONCENTRATION	3.9984	6.6640	9.3296	13.3280
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88563	0.88607	0.88647	0.8871
	159.6	180.1	202.5	238.3
TIME	159.6	180.4	202.5	238.5
(sec.)	159.5	180.2	202.4	238.6
	159.7	180.2	202.5	238.6
AVERAGE TIME	159.6	180.23	202.48	238.5
η (cp.)	0.5691	0.6429	0.7226	0.8518
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.2134	0.3709	0.5408	0.8162
η_{sp}/c (1/gm)	0.0534	0.0557	0.058	0.0612

INTRINSIC VISCOSITY = 0.05011 1/gm

POLYSTYRENE (PS 25170)

CONCENTRATION	3.1866	5.311	7.4354	10.622
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.8855	0.88583	0.88617	0.88667
	141.3	148.0	155.0	165.6
TIME	141.3	148.0	155.0	165.8
(sec.)	141.2	148.1	155.1	165.7
	141.3	148.1	155.1	165.8
AVERAGE TIME	141.28	148.05	155.05	165.73
η (cp.)	0.5037	0.528	0.5532	0.5916
$\eta_{sp}=(\eta-\eta_0)/\ _0$	0.0739	0.1258	0.1795	0.2614
η_{sp}/c (1/gm)	0.0232	0.0237	0.0241	0.0246

INTRINSIC VISCOSITY = 0.02266 1/gm

POLYSTYRENE (PS 25171)

CONCENTRATION	1.3794	4.1382	6.8970	9.6558	13.7940
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88522	0.88565	0.88608	0.88652	0.88717
	134.1	139.3	144.3	149.5	158.0
TIME	134.1	139.2	144.4	149.6	158.0
(sec.)	134.2	139.2	144.3	149.6	158.0
	134.1	139.2	144.4	149.6	158.1
AVERAGE TIME	134.13	139.23	144.35	149.58	158.03
η (cp.)	0.4780	0.4964	0.5149	0.5339	0.5644
$\eta_{sp}=(\eta-\eta_0)/\ _0$	0.01924	0.05851	0.0980	0.1383	0.2035
η_{sp}/c (1/gm)	0.01395	0.01414	0.0142	0.01432	0.01475

INTRINSIC VISCOSITY = 0.01384 1/gm

POLYISOPRENE (TRANSPIP)

CONCENTRATION	0.6696	2.0088	3.348	4.6872	6.696
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88503	0.88509	0.88516	0.88523	0.88532
	153.2	203.5	264.6	336.8	474.4
TIME	153.2	203.5	264.5	336.9	474.7
(sec.)	153.3	203.4	264.7	336.8	474.8
	153.3	203.6	264.7	337.2	
AVERAGE TIME	153.25	203.5	264.63	336.93	474.63
η (cp.)	0.546	0.7251	0.9430	1.2008	1.6917
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.1643	0.5461	1.0107	1.5603	2.607
η_{sp}/c (l/gm)	0.2453	0.2719	0.3019	0.3329	0.3893

INTRINSIC VISCOSITY = 0.22525 l/gm

POLYBUTADIENE (TAKENE 1220)

CONCENTRATION	0.8134	2.4402	4.067	5.6938	8.134
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88504	0.88512	0.8852	0.88528	0.88539
	154.7	208.3	273.6	348.8	489.5
TIME	154.8	208.2	273.6	348.7	489.3
(sec.)	154.7	208.4	273.8	349.0	489.4
	154.8	208.2	273.9	349.0	489.6
AVERAGE TIME	154.75	208.28	273.73	348.88	489.45
η (cp.)	0.5514	0.7422	0.9755	1.2434	1.7446
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.1757	0.5825	1.08	1.6513	2.7199
η_{sp}/c (l/gm)	0.216	0.2387	0.2656	0.29	0.3344

INTRINSIC VISCOSITY = 0.20057 l/gm

POLYSTYRENE-BUTADIENE (SS255)

CONCENTRATION	0.5106	1.5318	2.553	3.5742	5.106
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88504	0.8851	0.88517	0.88524	0.88535
	141.8	163.8	188.4	215.4	261.0
TIME	141.8	163.7	188.4	215.6	261.3
(sec.)	141.7	163.8	188.4	215.6	261.4
	141.8	163.8	188.3	216.0	
AVERAGE TIME	141.78	163.78	188.38	215.53	261.23
η (cp.)	0.5052	0.5836	0.6713	0.7681	0.9311
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.0771	0.2444	0.4314	0.6378	0.9853
η_{sp}/c (1/gm)	0.1511	0.1595	0.169	0.1784	0.193

INTRINSIC VISCOSITY = 0.14588 1/gm

POLYSTYRENE-BUTADIENE (KRYLENE 1502)

CONCENTRATION	0.7248	2.1744	3.624	5.0736	7.248
TUBE NUMBER	50,M795	50,M795	50,M795	50,M795	50,M795
TUBE CONSTANT	0.004026	0.004026	0.004026	0.004026	0.004026
SOLVENT DENSITY	0.88505	0.88515	0.88525	0.88535	0.88549
	151.0	193.3	243.7	297.6	392.5
TIME	151.0	193.2	243.6	297.4	392.8
(sec.)	150.9	193.3	243.8	297.8	392.5
	150.9	193.2	243.7		
AVERAGE TIME	150.95	193.25	243.7	297.6	392.6
η (cp.)	0.5379	0.6887	0.8685	1.0608	1.3996
$\eta_{sp}=(\eta-\eta_0)/\eta_0$	0.1468	0.4684	0.8519	1.2618	1.9842
η_{sp}/c (1/gm)	0.2026	0.2154	0.2351	0.2487	0.2738

INTRINSIC VISCOSITY = 0.19355 1/gm

APPENDIX V

GEL PERMEATION CHROMATOGRAPH DATA

POLYSTYRENE (PS 25170)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
125	19	0.1919	62,000	24,800
130	61	0.6162	34,000	8,100
135	18	0.1818	19,200	2,700
140	1	0.0101	12,000	920
	H_i = 99			

i. Universal calibration curve

$\bar{M}_n$ = 31.750 $\bar{M}_w$ = 38,410

ii. Conventional calibration curve

$\bar{M}_n$ = 31,720 $\bar{M}_w$ = 36,460

POLYSTYRENE (PS 25166)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
105	1	0.0087	4,100,000	20,500,000
110	14	0.1212	1,150,000	2,400,000
115	71.5	0.619	390,000	355,000
120	24	0.2078	143,000	79,000
125	4	0.0346	62,000	24,800
130	1	0.0087	34,000	8,100
	H_i=115.5			

i. Universal calibration curve

$\bar{M}_n$ = 246,530 $\bar{M}_w$ = 428,460

ii. Conventional calibration curve

$\bar{M}_n$ = 252,410 $\bar{M}_w$ = 448,620

POLYSTYRENE (PS 61970)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
100	7	0.0986	17,000,000	350,000,000
105	24	0.338	4,100,000	20,500,000
110	22	0.3099	1,150,000	2,400,000
115	12.5	0.1761	390,000	355,000
120	5.5	0.0775	143,000	79,000

$H_i = 71$

i, Universal calibration curve

$\overline{M}_n = 716,770$ $\overline{M}_w = 4,257,320$

ii. Conventional calibration curve

$\overline{M}_n = 740,080$ $\overline{M}_w = 3,498,140$

POLYSTYRENE-BUTADIENE (SS 255)

ELUTION VOLUME	HEIGHT H_i	WEITHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
100	5	0.0546	17,000,000	350,000,000
105	5.5	0.0601	4,100,000	20,500,000
110	12.5	0.1366	1,150,000	2,400,000
115	23	0.2514	390,000	355,000
120	23	0.2514	143,000	79,000
125	14	0.153	62,000	24,800
130	6	0.0656	34,000	8,100
135	2.5	0.0273	19,200	2,700

$H_i = 91.5$

i. Universal calibration curve

$\overline{M}_n = 77,720$ $\overline{M}_w = 968,550$

ii. Conventional calibration curve

$\overline{M}_n = 119,530$ $\overline{M}_w = 1,479,110$

POLYSTYRENE-BUTADIENE (KRYLENE 1502)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
100	1.5	0.0128	17,000,000	350,000,000
105	4	0.034	4,100,000	20,500,000
110	15	0.1277	1,150,000	2,400,000
115	34	0.2894	390,000	355,000
120	34.5	0.2936	143,000	79,000
125	20	0.1702	62,000	24,800
130	7	0.0596	34,000	8,100
135	1.5	0.0128	19,200	2,700

$H_i = 117.5$

i. Universal calibration curve

$\overline{M}_n = 80,470$ $\overline{M}_w = 410,890$

ii. Conventional calibration curve

$\overline{M}_n = 123,760$ $\overline{M}_w = 671,530$

POLYBUTADIENE (TAKENE 1220)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
100	1.5	0.0132	17,000,000	350,000,000
105	4.5	0.0396	4,100,000	20,500,000
110	18	0.1583	1,150,000	2,400,000
115	35.7	0.314	390,000	355,000
120	31	0.2726	143,000	79,000
125	16	0.1407	62,000	24,800
130	5.5	0.0484	34,000	8,100
135	1.5	0.0132	19,200	2,700

$H_i = 113.7$

i. Universal calibration curve

$\overline{M}_n = 87,150$ $\overline{M}_w = 411,730$

ii. Conventional calibration curve

$\overline{M}_n = 138,120$ $\overline{M}_w = 740,870$

POLYISOPRENE (TRANSPIP)

ELUTION VOLUME	HEIGHT H_i	WEIGHT FRACTION, w_i	MOLECULAR WEIGHT, M_i	INTRINSIC VISCOSITY x MOLECULAR WEIGHT
105	3.5	0.0232	4,100,000	20,500,000
110	12.5	0.0829	1,150,000	2,400,000
115	21.5	0.1426	390,000	355,000
120	24.8	0.3634	143,000	79,000
125	42.5	0.2818	62,000	24,800
130	10	0.0663	34,000	8,100
135	4	0.0265	19,200	2,700
140	2	0.0133	12,000	920
	H_i = 150.8			

i. Universal calibration curve

$\bar{M}_n$ = 59,130 $\bar{M}_w$ = 193,190

ii. Conventional calibration curve

$\bar{M}_n$ = 83,550 $\bar{M}_w$ = 318,430

APPENDIX VI

LIGHT SCATTERING DATA

POLYSTYRENE (PS 61970) GREEN LIGHT
FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	1.25	-	-	-
0.6204	118E-06	52.7	1.22	3.6829E-03	4.4070E-12	7.4238E-07
1.8612	354E-06	80.6	1.08	6.4753E-03	4.4070E-12	1.2667E-06
3.1020	589E-06	89.0	1.125	6.8734E-03	4.3921E-12	1.9822E-06
4.3428	824E-06	95.0	1.175	7.0733E-03	4.3963E-12	2.6992E-06

INTERCEPT = 0.35545E-06 M_w = 2,813,370

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	2.54	-	-	-
0.6204	118E-06	52.7	2.49	3.7122E-03	4.4070E-12	7.3652E-07
1.8612	354E-06	80.6	2.225	6.4650E-03	4.4070E-12	1.2687E-06
3.1020	589E-06	89.0	2.31	6.8861E-03	4.3921E-12	1.9785E-06
4.3428	825E-06	95.0	2.39	7.1551E-03	4.3963E-12	2.6684E-06

INTERCEPT = 0.36193E-06 M_w = 2,763,000

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	2.54	-	-	-
0.6204	118E-06	52.7	2.49	3.5388E-03	4.4070E-12	7.7261E-07
1.8612	354E-06	80.6	2.225	6.2192E-03	4.4070E-12	1.3189E-06
3.1020	589E-06	89.0	2.31	6.5552E-03	4.3921E-12	2.0784E-06
4.3428	825E-06	95.0	2.39	6.8163E-03	4.3963E-12	2.8010E-06

INTERCEPT = 0.37379E-06 M_w = 2,675,330

POLYSTYRENE (PS 61970)

BLUE LIGHT

FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.472	-	-	-
0.6204	127E-06	120.4	0.428	8.6348E-03	1.2556E-11	9.0211E-07
1.8612	382E-06	215.0	0.376	1.7909E-02	1.2622E-11	1.3117E-06
3.102	637E-06	268.5	0.396	2.1300E-02	1.2635E-11	1.8401E-06
4.3428	891E-06	296.0	0.416	2.2369E-02	1.2612E-11	2.4486E-06

INTERCEPT = 0.48747E-06 M_w = 2,051,420

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.996	--	-	-
0.6204	127E-06	120.4	0.908	8.8463E-03	1.2556E-11	8.8055E-07
1.8612	382E-06	215.0	0.816	1.7929E-02	1.2622E-11	1.3102E-06
3.102	637E-06	268.5	0.844	2.1722E-02	1.2635E-11	1.8043E-06
4.3428	891E-06	296.0	0.886	2.2829E-02	1.2612E-11	2.3992E-06

INTERCEPT = 0.58859E-06 M_w = 1,698,960

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	4.52	-	-	-
0.6204	127E-06	120.4	4.12	8.1574E-03	1.2556E-11	9.5491E-07
1.8612	382E-06	215.0	3.75	1.6320E-02	1.2622E-11	1.4394E-06
3.102	637E-06	268.5	3.86	1.9870E-02	1.2635E-11	1.9725E-06
4.3428	891E-06	296.0	4.02	2.1053E-02	1.2612E-11	2.6017E-06

INTERCEPT = 0.64743E-06 M_w = 1,544,580

POLYSTYRENE (PS 25166)

GREEN LIGHT

FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	1.25	-	-	-
2.1438	400E-06	38.8	1.085	3.0223E-03	4.2411E-12	3.0083E-06
3.573	667E-06	48.0	1.11	3.6870E-03	4.2453E-12	4.1140E-06
5.0022	933E-06	52.1	1.08	4.1310E-03	4.2380E-12	5.1318E-06
7.146	1333E-06	54.3	1.015	4.5980E-03	4.2389E-12	6.5880E-06

INTERCEPT = 1.52491E-06 M_w = 655,780

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	1.25	-	-	-
2.1438	400E-06	38.8	2.2	3.0672E-03	4.2411E-12	2.9642E-06
3.573	667E-06	48.0	2.24	3.7604E-03	4.2453E-12	4.0337E-06
5.0022	933E-06	52.1	2.185	4.2020E-03	4.2380E-12	5.0451E-06
7.146	1333E-06	54.3	2.055	4.6734E-03	4.2389E-12	6.4816E-06

INTERCEPT = 1.49703E-06 M_w = 667.990

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	1.25	-	-	-
2.1438	400E-06	38.8	8.9	2.9502E-03	4.2411E-12	3.0818E-06
3.573	667E-06	48.0	9.08	3.6094E-03	4.2453E-12	4.2025E-06
5.0022	933E-06	52.1	8.82	4.0509E-03	4.2380E-12	5.2333E-06
7.146	1333E-06	54.3	8.32	4.4914E-03	4.2389E-12	6.7442E-06

INTERCEPT = 1.55687E-06 M_w = 642,320

POLYSTYRENE (PS25166)

BLUE LIGHT

FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.472	-	-	-
2.1438	418E-06	104.4	0.388	8.2442E-03	1.1391E-11	2.9621E-06
3.573	697E-06	133.0	0.406	1.0112E-02	1.1402E-11	4.028E-06
5.0022	975E-06	149.6	0.39	1.190E-02	1.1383E-11	4.785E-06
7.146	1393E-06	157.6	0.354	1.3476E-02	1.1386E-11	6.0373E-06

INTERCEPT = 1.75096E-06 M_w = 571,120

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.996	-	-	-
2.1438	418E-06	104.4	0.83	8.3732E-03	1.1391E-11	2.9164E-06
3.573	697E-06	133.0	0.87	1.0253E-02	1.1402E-11	3.9733E-06
5.0022	975E-06	149.6	0.844	1.1945E-02	1.1383E-11	4.7669E-06
7.146	1393E-06	157.6	0.77	1.3848E-02	1.1386E-11	5.8752E-06

INTERCEPT = 1.77495E-06 M_w = 563,400

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	4.52	-	-	-
2.1438	418E-06	104.4	3.74	7.7774E-03	1.1391E-11	3.1399E-06
3.573	697E-06	133.0	3.95	9.4489E-03	1.1402E-11	4.3115E-06
5.0022	975E-06	149,6	3.8	1.1103E-02	1.1383E-11	5.1283E-06
7.146	1393E-06	157.6	3.48	1.2822E-02	1.1386E-11	6.3454E-06

INTERCEPT = 1.91646E-06 M_w = 521,800

POLYSTYRENE (PS 25170)

GREEN LIGHT

FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	1.25	-	-	-
0.7768	146E-06	4.58	1.265	1.6706E-04	4.3034E-12	2.001E-05
2.3304	437E-06	8.45	1.28	4.3188E-04	4.2838E-12	2.3115E-05
3.884	728E-06	12.14	1.165	7.7115E-04	4.2798E-12	2.1556E-05
5.4375	1019E-06	15.22	1.155	1.0161E-03	4.2783E-12	2.2895E-05

INTERCEPT = 2.04748E-05 M_w = 48,840

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	2.54	-	-	-
0.7768	146E-06	4.58	2.605	1.6485E-04	4.3034E-12	2.0278E-05
2.3304	437E-06	8.45	2.585	4.410E-04	4.2838E-12	2.3990E-05
3.884	728E-06	12.14	2.385	7.7391E-04	4.2798E-12	2.1479E-05
5.4375	1019E-06	15.22	2.34	1.0324E-03	4.2783E-12	2.2533E-05

INTERCEPT = 2.12192E-05 M_w = 47,130

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	2.175	10.28	-	-	-
0.7768	146E-06	4.58	10.56	1.5799E-04	4.3034E-12	2.1158E-05
2.3304	437E-06	8.45	10.5	4.2191E-04	4.2838E-12	2.3661E-05
3.884	728E-06	12.14	9.7	7.3968E-04	4.2798E-12	2.2473E-05
5.4375	1019E-06	15.22	9.48	9.9142E-04	4.2783E-12	2.3465E-05

INTERCEPT = 2.15427E-05 M_w = 46,420

POLYSTYRENE (PS 25170)

BLUE LIGHT

FILTERS(1,2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.472	-	-	-
0.7768	154E-06	12.72	0.48	5.0036E-04	1.1776E-11	1.8283E-05
2.3304	462E-06	24.35	0.48	1.2739E-03	1.1776E-11	2.1543E-05
3.884	769E-06	36.0	0.426	2.3522E-03	1.1746E-11	1.9395E-05
5.4375	1077E-06	45.9	0.43	3.0621E-03	1.1755E-11	2.0874E-05

INTERCEPT = 1.88979E-05 M_w = 52,920

FILTERS(2,3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	0.996	-	-	-
0.7768	154E-06	12.72	1.022	5.077E-04	1.1776E-11	1.8018E-05
2.3304	462E-06	24.35	1.034	1.2783E-03	1.1776E-11	2.1469E-05
3.884	769E-06	36.0	0.914	2.3774E-03	1.1747E-11	1.9189E-05
5.4375	1077E-06	45.9	0.916	3.1215E-03	1.1755E-11	2.0476E-05

INTERCEPT = 1.87692E-05 M_w = 53,280

FILTERS(3,4)

CONCENTRATION	ΔN	G_s 90°	G_w 0°	TEXCESS	H	Hc/τ
THF	-	5.11	4.52	-	-	-
0.7768	154E-06	12.72	4.63	4.6947E-04	1.1776E-11	1.9485E-05
2.3304	462E-06	24.35	4.62	1.2022E-03	1.1776E-11	2.2828E-05
3.884	769E-06	36.0	4.13	2.2028E-03	1.1746E-11	2.0709E-05
5.4375	1077E-06	45.9	4.15	2.8833E-03	1.1755E-11	2.2167E-05

INTERCEPT = 2.01118E-05 M_w = 49,720