LIGHT SCATTERING OF COPOLYMERS
I. EFFECT OF DILUTION DURING COPOLYMERIZATION ON CHAIN COMPOSITION AND MOLECULAR WEIGHT

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
HELEN MARIE KLIMISCH
1970

LIGHT SCATTERING OF COPOLYMERS
I. EFFECT OF DILUTION DURING COPOLYMERIZATION ON CHAIN COMPOSITION AND MOLECULAR WEIGHT

By

Helen Marie Klimisch

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

1970

ABSTRACT

LIGHT SCATTERING OF COPOLYMERS

I. EFFECT OF DILUTION DURING COPOLYMERIZATION ON CHAIN COMPOSITION AND MOLECULAR WEIGHT

by Helen M. Klimisch

Differential refractometry measurements were made on two homopolymers, polyvinylidene chloride and polyisobutylene. A procedure is demonstrated which allows one to determine the specific refractive increment, dn/dc, for a homopolymer in a particular solvent in which the polymer may not be soluble.

Light scattering and differential refractometry measurements were made on two copolymers of vinylidene chloride and isobutylene. The data were treated according to the procedure first described by Stockmayer _et al_[3] and expanded by Bushuk and Benoit[4]. The molecular parameters derived from this treatment were weight-average molecular weight and composition distribution. The composition distribution during copolymerization were used to determine the effect of dilution on the resulting copolymers.

Copolymers I and II were prepared in tetrahydrofuran solutions of 2_M_ and 8.5_M_ concentrations respectively. From the differential refractometry measurements, the weight fraction of each monomer was calculated. These results indicate no difference in weight fraction of vinylidene chloride and isobutylene between the two

copolymers. The weight fraction as calculated from dn/dc measurements was 0.81 vinylidene chloride as compared to 0.87 vinylidene chloride from NMR analysis. The light scattering results also indicate that the two copolymers have approximately the same weight-average molecular weight. The molecular composition parameters, however, do indicate a difference of approximately 18% in the compositional distribution.

ACKNOWLEDGMENTS

The author is indebted to Professor J. B. Kinsinger for the helpful guidance and assistance offered during the course of this investigation.

She also wishes to express thanks to the Dow Corning Corporation for their financial assistance and for their permission to use the light scattering and differential refractometry instruments.

Finally, the author is grateful to Mrs. Ardath Chubb for typing the final draft of this manuscript.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDIX

INTRODUCTION

Light scattering has become one of the standard methods for the determination of molecular weights of polymers. Debye[1] demonstrated the utility of this technique by proving that the amount of light scattered by solutions of high polymers is related to the mass of the solute molecules. It must be emphasized that the polymer molecules must vary only in molecular weight and not in chemical composition to apply this technique with any success. As early as 1952, it was noted[2] that the light scattering molecular weight of a butadiene-styrene copolymer varied with the refractive index of the solvent. It was suggested that this behavior could be due to variations in composition between the polymer chains.

The complications arising from this problem, i.e., heterogeneities in the composition of the polymer chains, were first discussed by Stockmayer et al[3] by considering the light scattered from a copolymer sample containing units A and B. They derived an equation which indicated how the intensity of this scattered light varies with the composition distribution of the copolymer sample. One fundamental assumption made was that the specific refractive index increment of a copolymer in a solvent varies linearly with the composition of the copolymer.

The equation of Stockmayer et al[3] allows one to obtain not only the weight-average molecular weight, but also a measure of the chemical heterogeneity of a copolymer by evaluating light scattering data separately in three solvent media. The validity of this equation has been investigated experimentally by Bushuk and Benoit[4] Krause[5] and Leng and Benoit[6]. These authors have shown the equation to be correct within experimental error. Bushuk and Benoit have also indicated how the parameters of weight-average molecular weight and composition distribution can be used in the interpretation of copolymerization kinetics.

Kinsinger et al[7, 8] have studied the microstructure of isobutylene-vinylidene chloride copolymers by NMR spectroscopy. They have shown that this system is very amenable to NMR analysis and allows one to postulate possible mechanisms for the copolymerization. It was suggested that a light scattering study on the copolymers of isobutylene and vinylidene chloride might also lend some insight into the mechanism of the copolymerization. It was the intent of the author, therefore, to investigate the effect of dilution on the resulting copolymers of isobutylene and vinylidene chloride. It was hoped that this study would provide insight into the sensitivity of this technique as a means of analyzing changes in molecular weight and chain composition heterogeneity. To this end, two copolymers were made at different dilutions but some monomer feed-ratio were analyzed in four solvents. Samples of the two homopolymers were analyzed by differential refractometry to allow the parameters of molecular weight and composition to be calculated.

THEORY

In a homopolymer all the elements scatter in the same manner and the only difference within the sample is due to molecular weight heterogeneity. In a copolymer there may be two or more types of scattering elements depending on the number of monomer types that make up the copolymer. These scattering elements are affected by the molecules of different molecular weight and different chemical composition. The theoretical treatment given here follows that given by Bushuk and Benoit[4]. It is assumed that the refractivity of a copolymer is a simple sum of the refractivities of the two component homopolymers and independent of molecular weight. Stockmayer et al[3] pointed out that this should not introduce a very large error. The light scattering investigations of copolymers by Bushuk and Benoit[4] and Krause[5] agree with the light scattering theory and thus justify this assumption. Bushuk and Benoit also showed that the mole fraction of each mer, as determined from measurements of specific refractive increments, is within 2% of that obtained through chemical analysis. Kinsinger et al[9] have also investigated the colligative nature of the specific refractive increments over a wide range of mer composition. They have shown this technique to be useful and nearly as precise as chemical analysis for carbon. The specific refractive index increment of the copolymer can be calculated from

$$\nu_o = X\nu_A + (1 - X)\ \nu_B \tag{1}$$

where ν is the specific refractive index increment, (dn/dc), of the copolymer; ν_A and ν_B are the (dn/dc) values for the two homopolymers A and B; and X is the weight fraction of component A with concentration in gms/cc.

According to the classical theory on light scattering, the excess scattering due to homogeneous solute particles of mass M, concentration c, and having ν for the specific refractive index increment can be put in the form

$$R = K'\nu^2\ cM, \tag{2}$$

where $K' = (2\ \pi^2\ n_o{}^2)/(\lambda^4\ N)$, in which n_o is the refractive index of solvent, λ is the wavelength of the incident light in vacuum and N is Avogadro's number.

For a solution of a copolymer which may show polydispersity of chain composition in addition to polydispersity of molecular weight, equation (2) can be put in the form

$$R = K'\ \Sigma\nu_i{}^2\ c_i\ M_i \tag{3}$$

where c_i is the concentration of molecules of mass M_i and composition X_i.

The intensity of the scattered light that is measured in a copolymer is given by

$$R = K'\nu_o{}^2\ c\ M_{ap} \tag{4}$$

where ν_o is the average refractive index increment and M_{ap} is the apparent molecular weight obtained from the data.

After equating the intensities given by equations (3) and (4), the apparent molecular weight is given by

$$M_{ap} = (1/\nu_o^2) \quad \Sigma \nu_i^2 \gamma_i M_i \qquad (5)$$

where γ_i is defined as the relative concentration of molecules of composition X_i.

For a copolymer with heterogeneous composition, equation (5) can be expanded by substituting for ν_i the value given by equation (1). The new equation for the apparent molecular weight becomes

$$M_{ap} = (\nu_A \nu_B/\nu_o^2)M_w + \left[\nu_A (\nu_A - \nu_B)/\nu_o^2\right] X M_A + \left[\nu_B(\nu_B - \nu_A)/\nu_o^2\right] (1 - X) M_B \qquad (6)$$

where M_w is the weight-average molecular weight of the copolymer, M_A and M_B are the weight-average molecular weights of the parts of the copolymer formed of monomer A and B respectively and X is the average weight fraction of component A. From measurements in three solvents it is possible to solve for the three parameters M_A, M_B and M_w from which the compositional heterogeneity of the copolymer can be determined.

Bushuk and Benoit[3] also recast equation (5) using

$$\delta X_i = X_i - X_o \qquad (7)$$

where δX_i is the deviation in composition of molecules of type i from the average composition, X_o. Equation (1) for the specific refractive index increment becomes

$$\nu_i = \nu_o + \delta X_i (\nu_A - \nu_B) \tag{8}$$

and the equation for the apparent molecular weight becomes

$$M_{ap} = M_w + 2P\left[(\nu_A - \nu_B)/\nu_o\right] + Q\left[(\nu_A - \nu_B)/\nu_o\right]^2 \tag{9}$$

The two new parameters P and Q are equal to $\Sigma \gamma_i M_i \delta X_i$ and $\Sigma \gamma_i M_i \delta X_i^2$ respectively and are a measure of the degree of heterogeneity of composition.

The values of the parameters of equation (9) can be calculated by either of two methods. One method is to use the data from the measurements in three solvents to solve a set of simultaneous equations. The second method is to plot M_{ap} against $(\nu_A - \nu_B)/\nu_o$. The points of this plot should describe a parabola from which the values of M_w, P and Q can be calculated. The theoretical limits on P and Q are

$$\begin{gathered} -X_o M_w \leq P \leq (1 - X_o)\, M_w, \\ 0 \leq Q \leq M_w \left[1 - X_o\ (1 - X_o)\right] \end{gathered} \tag{10}$$

The parameter Q/M_w for a specific copolymer may be defined as a quantitative measure of the polydispersity of chain composition. Therefore, the ratio of the value of Q/M_w to the maximum possible value, $\left[1 - X_o(1 - X_o)\right]$, seems to be a convenient index of the polydispersity in chain composition which can be used as an additional parameter for characterizing copolymers.

INSTRUMENTS AND MATERIALS

Light Scattering Photometer

A SOFICA PGD (Mechrolab Model 701)[10] light scattering instrument was used for characterization. Optical alignment and calibration of the instrument were accomplished by the scattering of a pure solvent (benzene). Measurements were made using the green mercury line (5460Å) at 35 ± 0.5°C.

Differential Refractometer

All measurements of the specific refractive index increment, (dn/dc), were made with a Brice-Phoenix Differential Refractometer[11]. The instrument was calibrated for the green mercury line (5460 Å) and a temperature of 35 ± 0.05°C with five sucrose solutions.

Polymer Samples

The polyvinylidene chloride used was supplied by Dr. J. B. Kinsinger of Michigan State University.

The polyisobutylene was purchased from Polysciences, Inc. of Rydal, Pennsylvania.

The two copolymer samples used in this study were prepared by W. C. Page under the direction of Dr. J. B. Kinsinger of Michigan State University. Both samples were solution polymerized using a tetrahydrofuran solvent medium with a one to one mole ratio of vinylidene chloride and isobutylene. The initiator was azo-bis-isobutyronitrile at a concentration of 0.1g per 50 cc reaction mixture. Ultraviolet light was used to promote the decomposition of the azo compound.

Copolymer I was prepared by adding equimolar amounts of isobutylene and vinylidene chloride to a glass bomb. Enough tetrahydrofuran with the initiator dissolved in it was added to the bomb to give a total molarity of 2. After filling, the bomb was freeze-thawed to remove dissolved oxygen and sealed. The bomb was placed in a 30°C thermostat and subjected to uv irradiation. After 4.6% conversion the sample was quenched in a dry ice methanol slush, precipitated from methanol and collected.

Copolymer II was prepared by a similar procedure as copolymer I except that the total molarity was 8.5 with a conversion of 2%.

Solvents

All of the solvents used were reagent grade and distilled prior to use. After two distillations, the 1-bromonaphthalene remained slightly yellow; however, it did not absorb any light at the wavelength used.

The solvents used for polyvinylidene chloride were N, N-dimethylacetamide, cyclohexanone and a 3:1 mixture of cyclohexanone : 1-bromonaphthalene.

The solvents used for polyisobutylene were 1, 1, 1-trichloroethane, chlorobenzene, amyl acetate and o-dichlorobenzene.

The solvents used for the two copolymers were amyl acetate, cyclohexanone, chlorobenzene and o-dichlorobenzene.

The refractive indicies of the solvents were determined at 35 ± 0.05°C on an Abbe Refractometer. These values, which were at the sodium D line, were converted to the green mercury line using dispersion tables. The densities of the solvents at 35 ± 0.05°C were either measured or available in the literature.

PROCEDURE

The experimental procedure discussed below was greatly influenced by the very small quantity of copolymer I available. This small quantity required the author to recover the polymer after each run.

Light Scattering

For each copolymer-solvent system, a stock solution was prepared by weighing polymer and solvent into an acid-washed bottle. The concentration was calculated in g/100 cc using the density of the solvent. Because of the low concentrations used in this work, the density of the copolymer was assumed to have a negligible effect on the concentration.

Several attempts were made to clarify the solvents and stock solutions by pressure filtration through a sintered glass ultra-fine filter. Probably because of the rather viscous nature of most of the solvents, this procedure did not remove enough of the dust.

Success was finally achieved using a pressure filter and a double filtration through three thicknesses of Metricel Filter Type Alpha 8 with pore size of 0.20 micron. A quantity of solvent sufficient for all of the light scattering measurements in a particular solvent was filtered into a carefully cleaned burette. The solvent was again filtered to clarify it sufficiently for the photometer. This freshly filtered solvent was used to dilute the stock solution to four more concentrations.

The stock solution was also filtered through a triple thickness of the membrane filters. The second filtration was made directly into weighed light scattering cells. Each cell was again weighed to determine the amount of stock solution added. A weighed amount of filtered solvent was added to four of the cells to give a total of five concentrations on which the light scattering measurements were made. The concentrations were again calculated from the known density of the solvent.

For all of the copolymer I - solvent systems, except cyclohexanone, a slightly different procedure was necessary. The quantity of copolymer I available for study was too small to prepare enough stock solution for five separate concentrations. For these runs, the second filtration of the stock solution was made into three weighed light scattering cells. The cells were again weighed and diluted as before to give a total of five concentrations, two of the solutions were again diluted by adding a weighed amount of solvent. This dilution was made only after the scattering data were collected on each solution. The concentrations of the solutions were calculated from the known weights of stock solution and solvent added.

The scattering data were collected by placing the cell containing the pure filtered solvent into the constant temperature bath of the SOFICA. The cell was allowed to come to temperature equilibrium for ten minutes. Measurements were made at angles of 37.5° to 142.5° to the incident with duplicate readings at each angle to check the accuracy. The scattering data for each concentration were collected in the same manner.

The parameters, Kc/R and $\sin^2 \theta/2 + kc$, were calculated by a computer. The data was treated according to the extrapolation method of Zimm[12] for the Rayleigh ratio of benzene (16.3×10^{-6} for 5461 Å at 25°C). Depolarization of the scattered radiation was assumed to be negligible.

The relation $Kc/R = m\mathrm{Sin}^2 \theta/2 + 2Bc + (Kc/R)_{\substack{c\,=\,0\\ \theta\,=\,0}}$ relates the parameters obtained from the scattering data, i.e. weight average molecular weight, second virial coefficient, z-average radius of gyration, and the experimental parameters (solution concentration, Rayleigh ratio, and optical constants for the polymer solvent system). The usual procedure consists of plotting the parameter (Kc/R) versus $\mathrm{Sin}^2 \theta/2 + kc$. A grid-like plot (Zimm diagram) is obtained.

The second virial coefficient is obtained from the slope of the zero angle line defined by extrapolation of the data points of constant concentration to zero angle. The radius of gyration is obtained from the initial slope of the zero concentration line defined by extrapolation of data at constant angle to zero concentration. Molecular weights are given by the reciprocal of the ordinate, $(Kc/R)_{\substack{c\,=\,0\\ \theta\,=\,0}}$, determined by the previous extrapolations of the zero angle and zero concentration lines.

Another method was also used to determine the second virial coefficients and molecular weights. This method consists of plotting the parameter (Kc/R) versus $\sin^2 \theta/2$ and extrapolating the constant concentration points to zero angle. The values of $(Kc/R)_{\theta = 0}$ thus determined were plotted versus c (solution concentration). The extrapolation of the zero angle points to zero concentration yields the reciprocal of the molecular weight. The slope of this extrapolation yields the second virial coefficient.

Differential Refractometry

The differential refractometry measurements on the two copolymers were made on the solutions prepared for light scattering measurements. After the scattering data were collected on each solution, the solution was poured into a small vial. The solution side of the refractometry cell was rinsed thoroughly with the solution, filled and allowed to reach temperature equilibrium for ten minutes. Solvent was kept in the other half of the divided cell. Measurements were made by taking at least three readings for each of two positions of the cell. These readings, d_1 and d_2, were subtracted to give a d for the solution from which the reading for pure solvent had to be subtracted to give a Δd. This value can have either a positive or negative sign depending on whether the polymer has a lower or higher refractive index than the solvent. From the relation KΔd = Δn, Δn can be calculated using the calibration constant of the instrument for a wavelength of 5460 Å and temperature of 35 ± 0.05°C.

The relation determined for this instrument is Δn = 0.967Δd. This value of Δn was plotted versus solution concentration in g/100cc. The slope of this plot gives the specific refractive index increment, dn/dc, for a particular polymer-solvent system at a given temperature and wavelength.

The differential refractometry measurements for each of the homopolymers, polyvinylidene chloride and polyisobutylene, were made using a similar procedure to that used with the copolymers. Here, four individual solutions for each polymer-solvent system were prepared. Measurements were taken and plots of Δn versus c were made, from which the specific refractive index increment, dn/dc, was calculated.

Figures 1 through 4 are the plots of Δn versus c for the two homopolymers and two copolymers. Figure 1 shows the data for polyisobutylene in amyl acetate, 1, 1, 1-trichloroethane, chlorobenzene and o-dichlorobenzene. Figure 2 gives the data for polyvinylidene chloride in N, N-dimethylacetamide, cyclohexanone and a 3:1 mixture of cyclohexanone: 1-bromonaphthalene. Figures 3 and 4 give the data for copolymers I and II respectively in amyl acetate, cyclohexanone, chlorobenzene and o-dichlorobenzene.

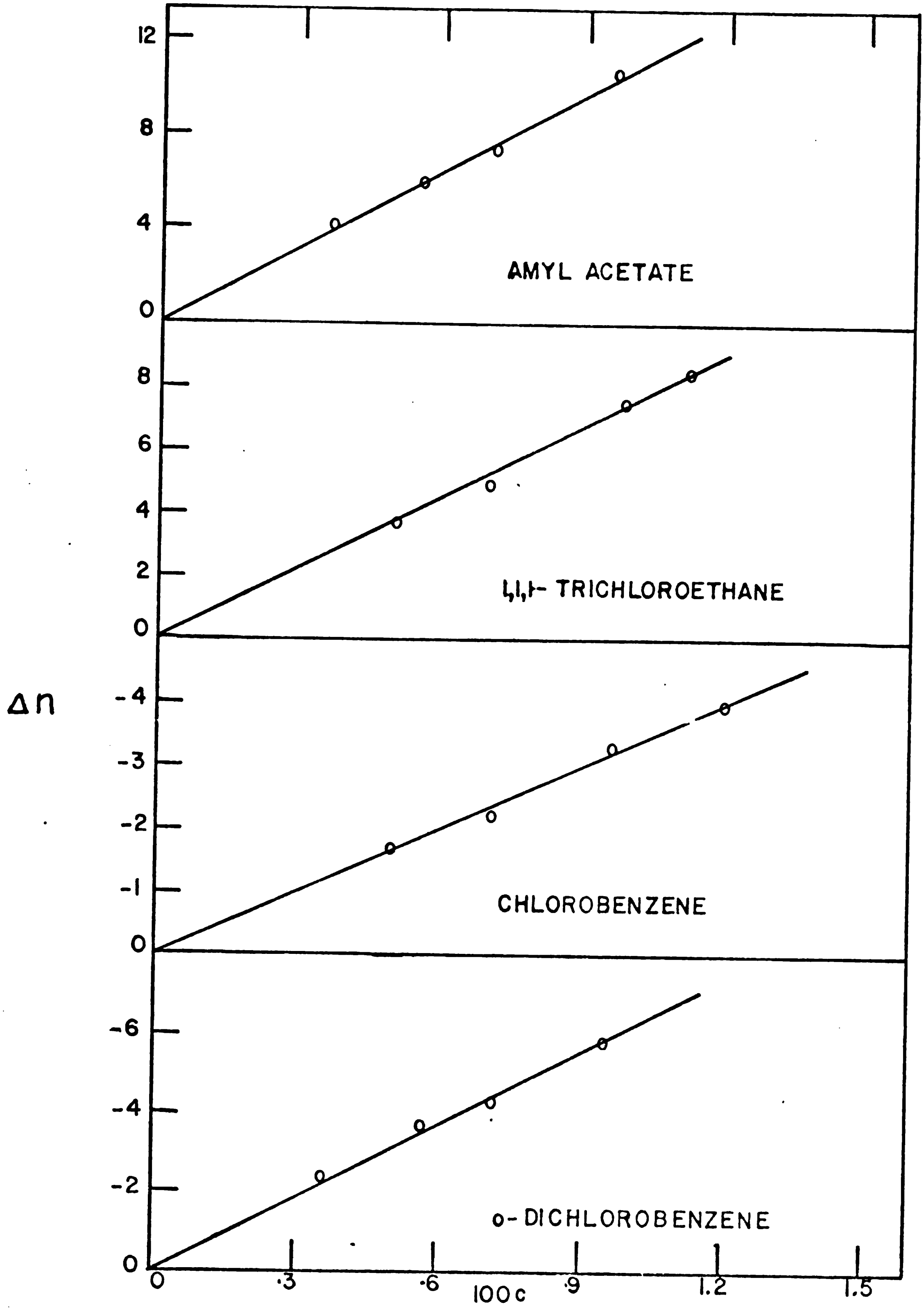

Figure 1. Refractive Increment Data for Polyisobutylene at 5460 Å and 35°C

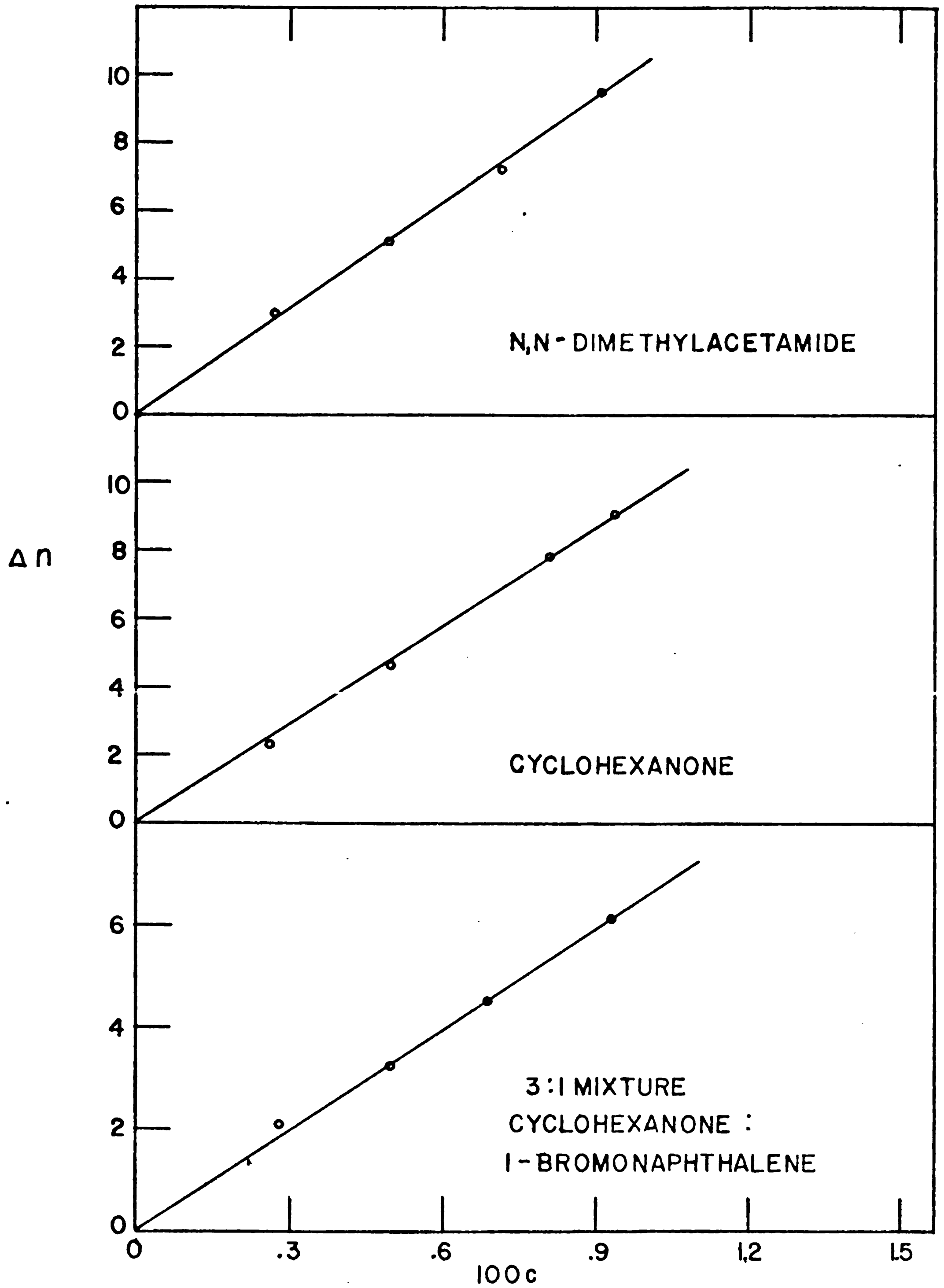

Figure 2. Refractive Increment Data for Polyvinylidene Chloride at 5460Å and 35°C

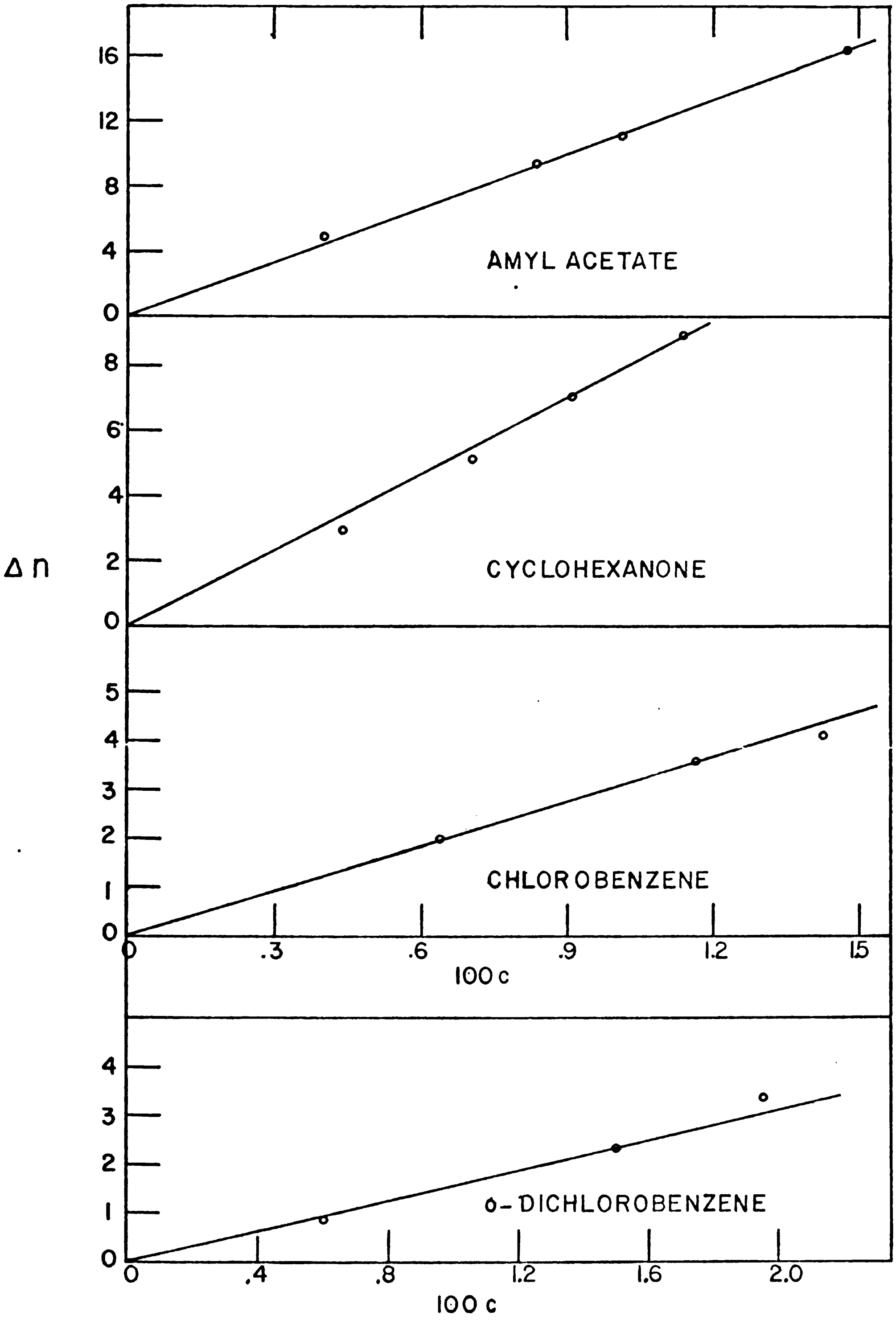

Figure 3. Refractive Increment Data for Copolymer I at 5460Å and 35°C

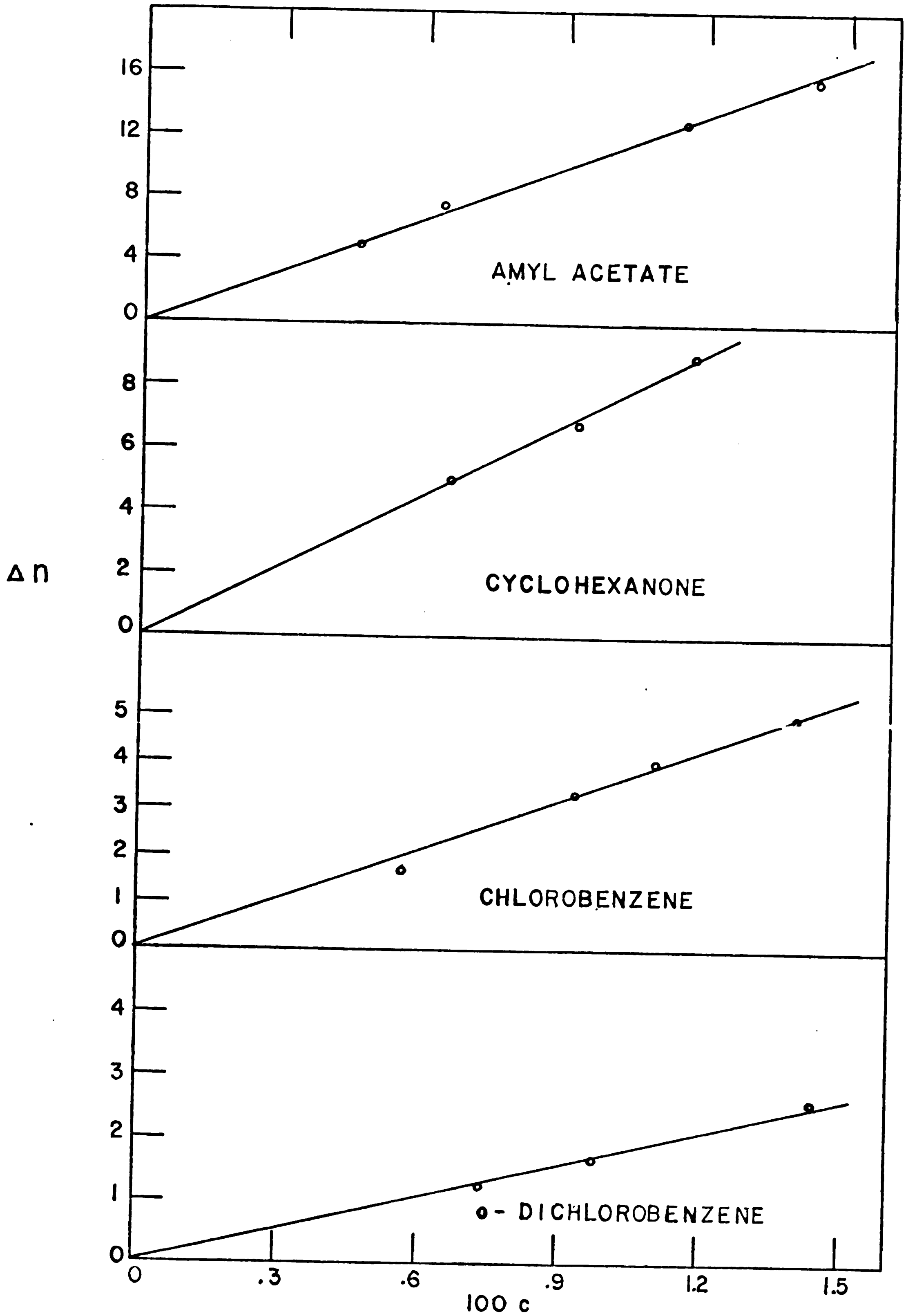

Figure 4. Refractive Increment Data for Copolymer II at 5460 Å and 35°C

RESULTS AND DISCUSSION

Differential Refractometry

Differential refractometry measurements were made on the two homopolymers and the two copolymers at a wavelength of 5460 Å and a temperature of 35 ± 0.05°C.

Table I gives the refractive indicies of the solvents used in this study. The list contains both measured values at 35°C with the sodium D line and those calculated for 35°C at 5460 Å.

TABLE I

Refractive Index Values of Solvents Used in This Study

Solvent	n_o - 35°C	$n^{a}_{5460\ \text{Å}}$ - 35°C
Amyl Acetate	1.3952	1.3969
1, 1, 1-Trichloroethane	1.4282	1.4303
N, N, -Dimethyacetamide	1.4308	1.4333
Cyclohexanone	1.4439	1.4461
3:1 Mixture of Cyclohexanone:		
1-Bromonaphthalene	1.4952	1.4987
Chlorobenzene	1.5159	1.5202
o-Dichlorobenzene	1.5446	1.5490

a. Calculated from dispersion tables

Table II lists the specific refractive index increments for the two homopolymers in the various solvents.

Table III lists the specific refractive index increments for the two copolymers in the four solvents used in the light scattering study.

TABLE II

Refractive Index Increments of Polyvinylidene Chloride and Polyisobutylene

Solvent	Polyvinylidene Chloride		Polyisobutylene	
	ν_A (Meas.)	ν_A^a(Extrap.)	ν_B (Meas.)	ν_B^a(Extrap.)
Amyl Acetate		0.123	0.108	0.110
1, 1, 1-Trichloroethane			0.074	
N,N-Dimethyacetamide	0.104			
Cyclohexanone	0.097	0.095		0.053
3:1 Mixture of Cyclohexanone:				
1-Bromonaphthalene	0.066			
Chlorobenzene		0.054	-0.034	-0.031
o-Dichlorobenzene		0.039	-0.061	-0.063

a. Determined from plot of dn/dc vs. n_o for homopolymers

TABLE III

Refractive Index Increments of Copolymers I and II

Solvent	Copolymer I ν_0 (Meas.)	 ν_0 a (Extrap.)	Copolymer II ν_0 (Meas.)	 ν_0 a (Extrap.)
Amyl Acetate	0.111	0.115	0.114	0.115
Cyclohexanone	0.078	0.082	0.076	0.083
Chlorobenzene	0.031	0.033	0.035	0.035
o-Dichlorobenzene	0.015	0.014	0.017	0.017

a. Determined from plot of dn/dc vs n_0 for copolymers

The two copolymers and homopolymers were not soluble in the same solvents, so an extrapolation technique was used to determine the specific refractive index increments, dn/dc, for the four polymers in the same four solvents. The technique used was to measure the specific refractive index increments for the homopolymers in at least three solvents with a broad range of refractive indicies. The dn/dc of the homopolymer for each solvent was plotted against the refractive index of that solvent at 35°C and a wavelength of 5460 Å. Figure 5 is such a plot of dn/dc versus n for polyvinylidene chloride and polyisobutylene. It was from this plot that the values of the specific refractive index increments were determined for those solvents in which the two homopolymers were not soluble. These values are listed in Table II. A least squares analysis was done on the homopolymer data to

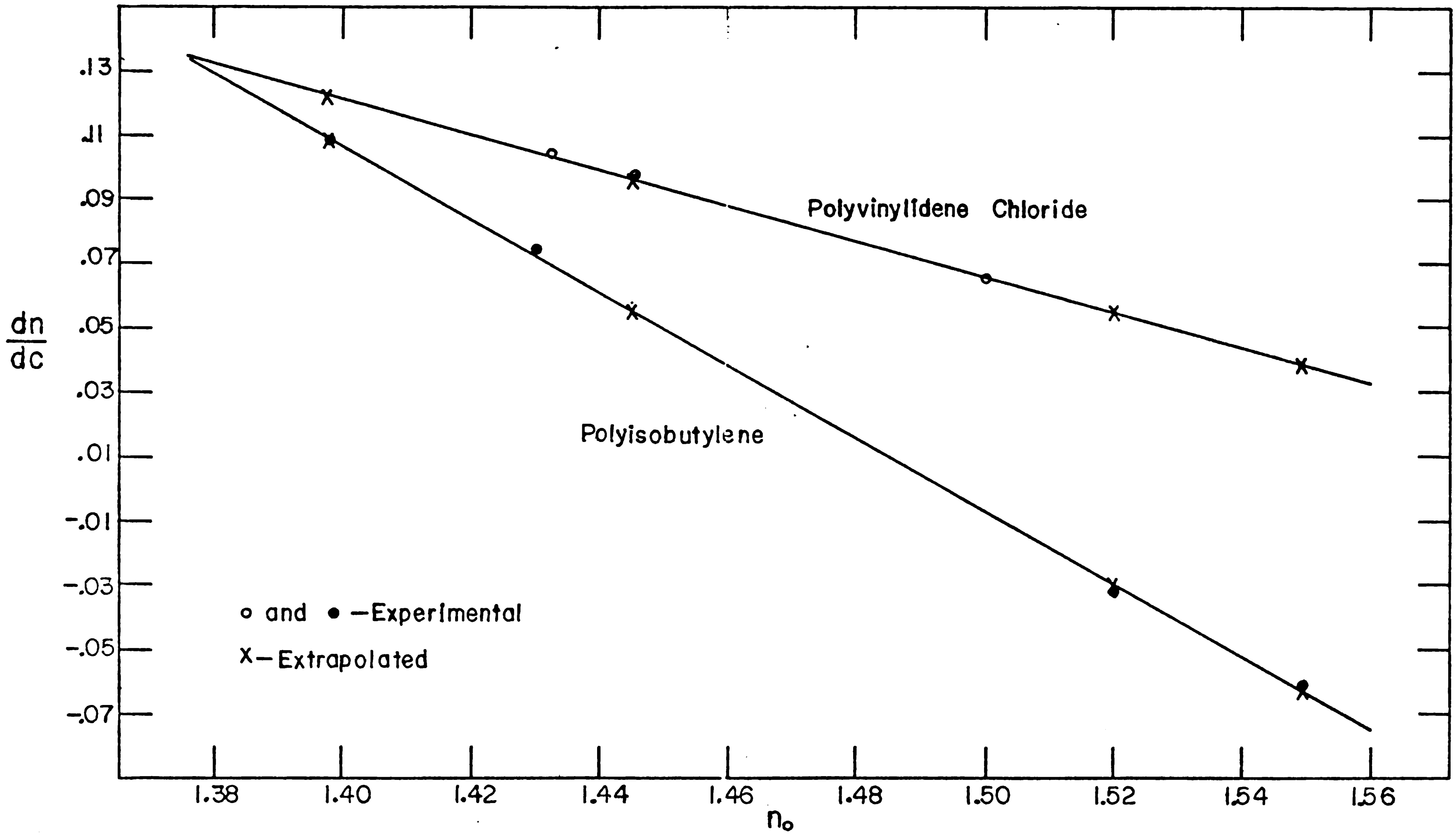

Figure 5. Specific Refractive Index Increment, dn/dc, vs Refractive Index of Solvent, n_o, for Polyvinylidene Chloride and Polyisobutylene at 5460 Å and 35° C

give the curves shown in Figure 5. The equations of the lines are

$$\nu_A = -0.547\ n_o + 0.888 \tag{11}$$

for polyvinylidene chloride and

$$\nu_B = -1.14\ n_o + 1.71 \tag{12}$$

for polyisobutylene.

Figure 6 is a plot of dn/dc versus n for the two copolymers. The scale is displaced slightly for Copolymer I because of the small differences in the dn/dc values. A least squares analysis was also done on the data for Copolymers I and II which yields the curves as shown. The equations of the lines are

$$\nu_1 = -0.670\ n_o + 1.06 \tag{13}$$

for Copolymer I and

$$\nu_2 = -0.623\ n_o + 0.985 \tag{14}$$

for Copolymer II.

The compositions of the copolymers were calculated using equation (1) and the equations for the homopolymers and copolymers relating the dn/dc to the refractive index of the solvent. The weight fraction of vinylidene chloride can be calculated from equation (1) by

$$X = \frac{\nu_o - \nu_B}{\nu_A - \nu_B} \tag{15}$$

Instead of using the dn/dc values as calculated from the equations, the equations for the data expressed as $\nu = k\ n_o + c$ were used. After substituting these values for dn/dc into equation (1), the weight fraction is

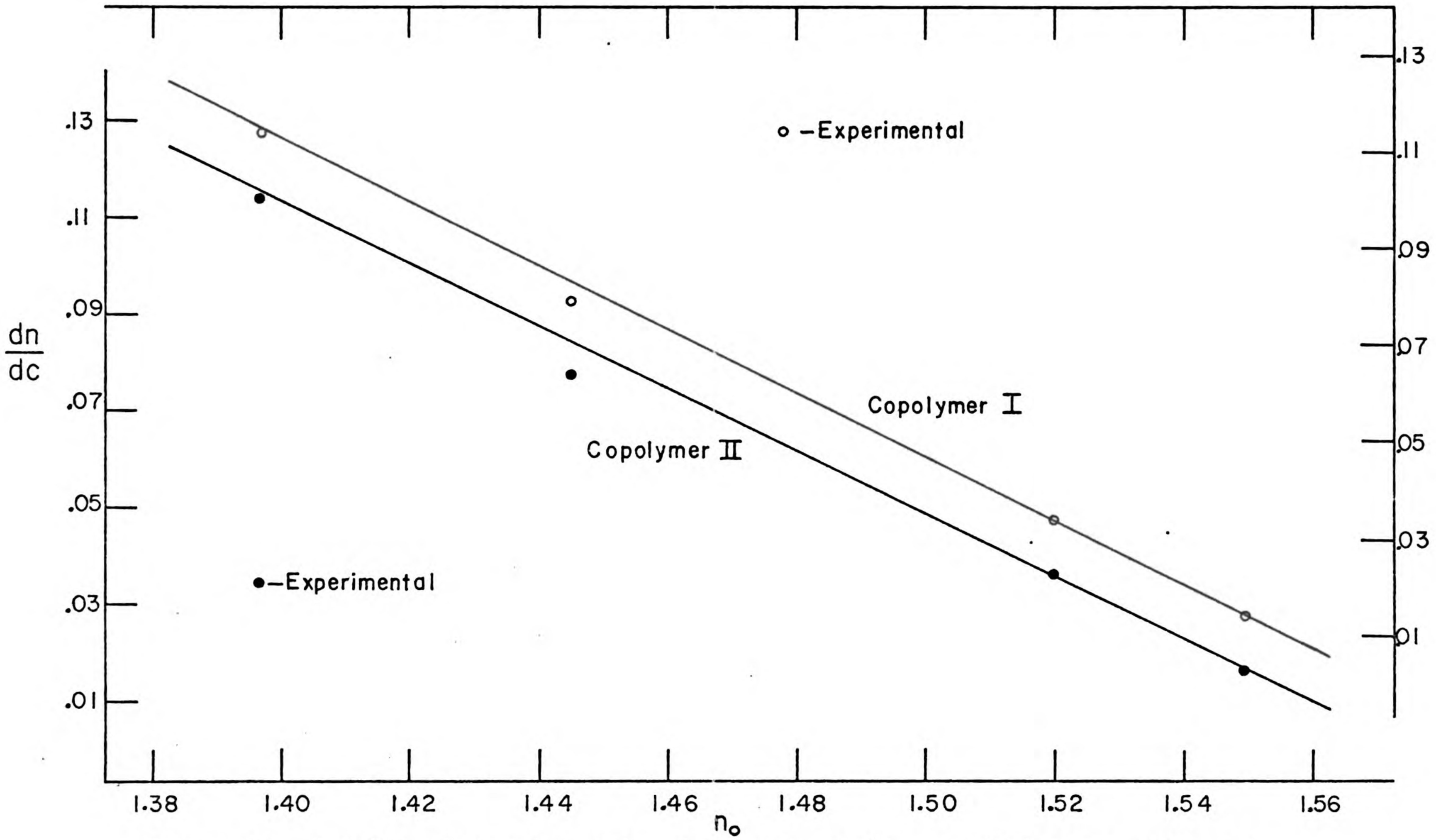

Figure 6. Specific Refractive Index Increment, dn/dc, vs Refractive Index of Solvent, n_o, for Copolymers I and II at 5460 Å and 35°C

defined as

$$X = \frac{n_o(k_C - k_B) + (C_C - C_B)}{n_o(k_A - k_B) + (C_A - C_B)} \qquad (16)$$

Using the equations as determined from the data for the homopolymers and copolymers, the compositions of the Copolymers I and II are the same within experimental error and are calculated to be 81% vinylidene chloride and 19% isobutylene.

The accuracy of the data can also be analyzed using equation (16) defining the weight fraction, X. The composition of a copolymer must be independent of the refractive index of the solvent in which a series of measurements may be made. This fact allows one to set the first derivative of X with n equal to zero that is dX/dn = 0. Equation (17) gives this derivative of the weight fraction, X, with respect to the refractive index, n,

$$\frac{(k_C - k_B)(C_A - C_B) - (k_A - k_B)(C_C - C_B)}{\left[n_o(k_A - k_B) + (C_A - C_B)\right]^2} = 0 \qquad (17)$$

The numerator therefore must be equal to zero for the equality to hold,

$$(k_C - k_B)(C_A - C_B) = (k_A - k_B)(C_C - C_B) \qquad (18)$$

Using the k's and c's as calculated from the dn/dc data and substituting these values into equation (18) gives an agreement of better than 1% for both Copolymers I and II.

The composition of the copolymers can also be determined by NMR analysis. From this analysis, the weight fraction of vinylidene chloride was determined to be 87%, which is in reasonable agreement with the value of 81% determined from differential refractometry. The NMR data and spectra for the two copolymers can be found in the Appendix.

Light Scattering Measurements

Light scattering measurements were made on the copolymers in four solvents: amyl acetate, cyclohexanone, chlorobenzene and o-dichlorobenzene. Figures 7, 8 and 9 are representative Zimm plots of the light scattering data. Figures 7 and 8 are plots of Kc/R versus $\mathrm{Sin}^2\,\theta/2 + C$ and illustrate the usual method of displaying the data. Figure 9 illustrates an alternative method for determining the molecular weight. It is a double plot of Kc/R versus $\mathrm{Sin}^2\,\theta/2$ and then a plot of $(Kc/R)\ \theta = 0$ versus c.

Figure 7 is a plot of the data for Copolymer II in cyclohexanone. The data points are in good agreement for the scattering angles from 75° to 142.5°. The data for the lower angles of 37.5° to 60° showed a very pronounced downward curvature and are not on the plot. The reason for the curvature is not completely understood.

Figure 8 is a Zimm plot for Copolymer I in o-dichlorobenzene. For this case the data points define a sinusoidal curvature, however, the extrapolation is quite straightforward.

Figure 9 is the double plot for Copolymer I in amyl acetate. Here again some scatter is evident at the lower

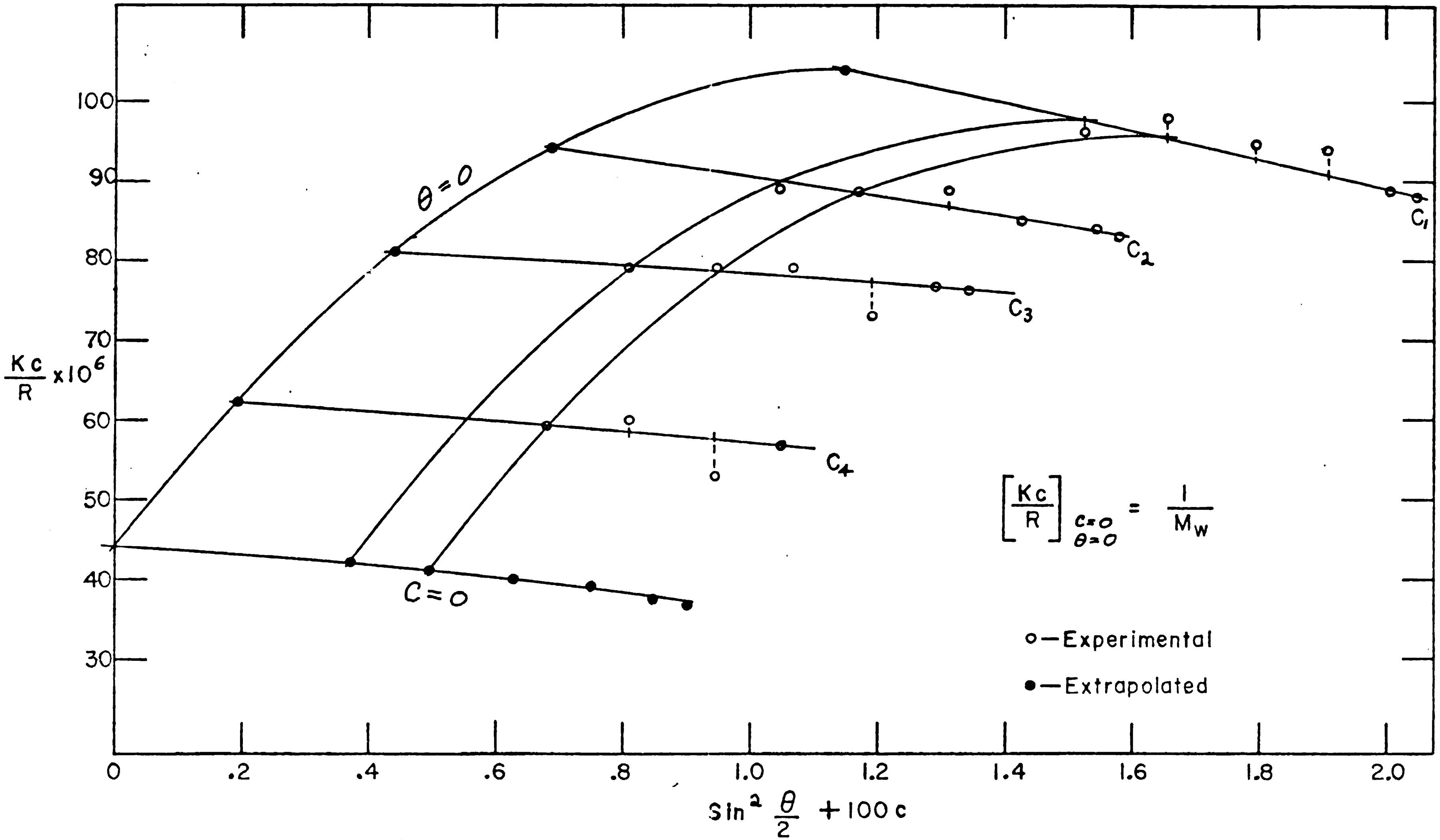

Figure 7. Zimm Plot for Copolymer II in Cyclohexanone at 5460 Å and 35 °C

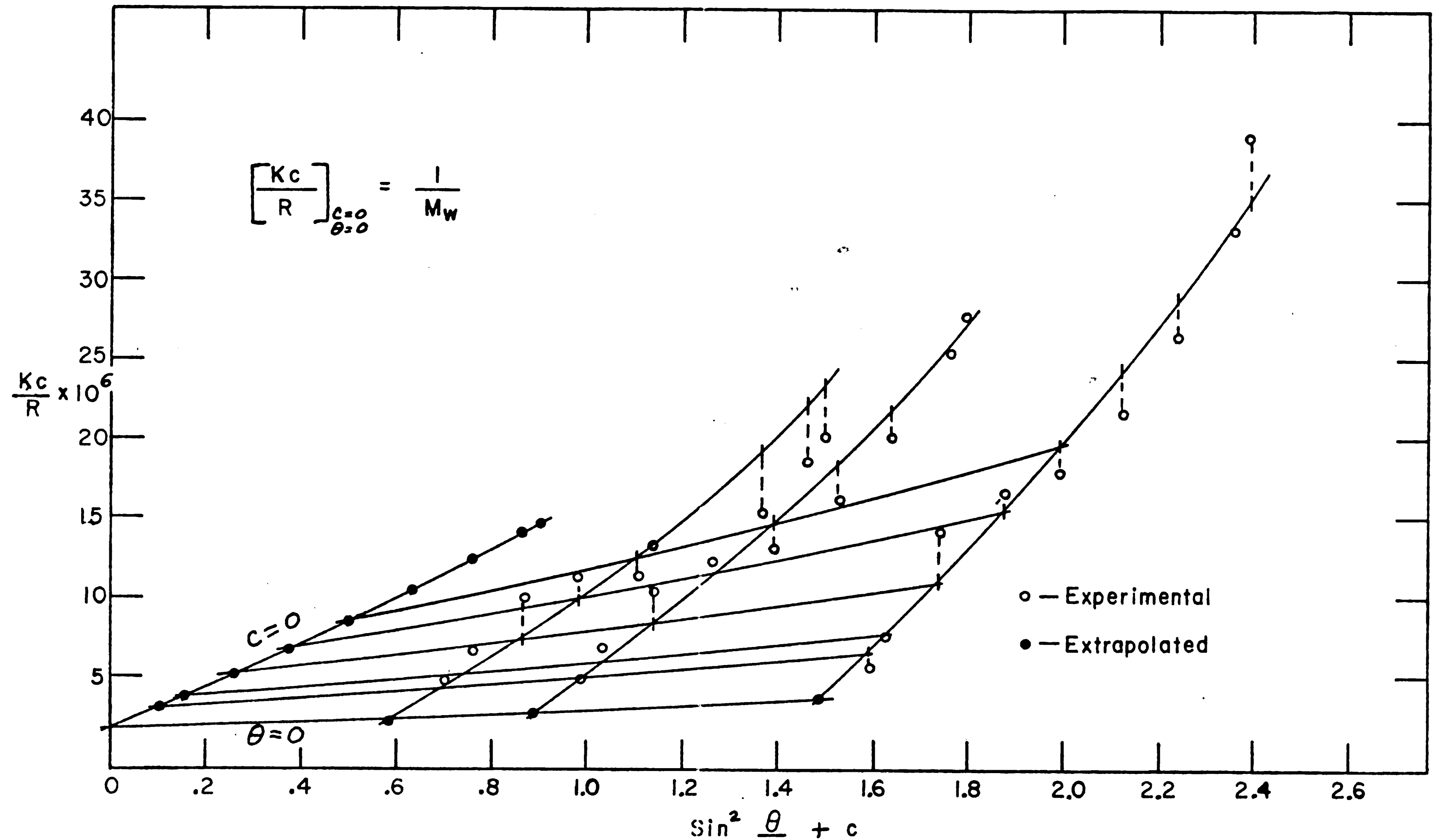

Figure 8. Zimm Plot for Copolymer I in o-Dichlorobenzene at 5460 Å and 35°C

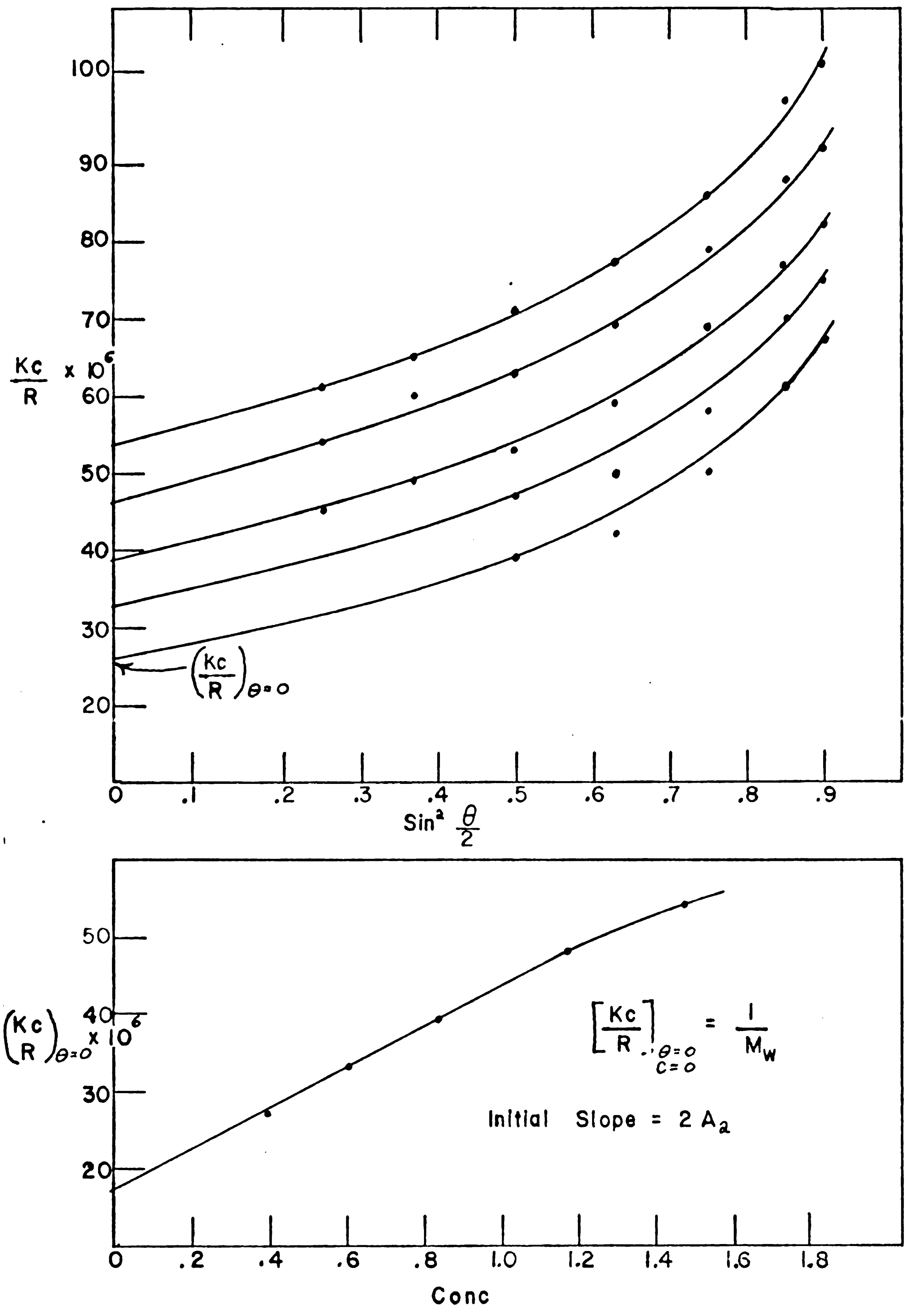

Figure 9. Alternative Method of Plotting Light Scattering Data — Copolymer I in Amyl Acetate at 5460 Å and 35°C

scattering angles. The second plot of $(Kc/R)_{\theta = 0}$ versus c illustrates the ease with which the second virial coefficient can be determined. The curve for this plot is very nearly linear and thus the slope can be calculated with less error.

The light scattering results for the two copolymers are summarized in Table IV.

TABLE IV

Light Scattering Results for Copolymers I and II

Solvent	Copolymer I		Copolymer II	
	$M_{ap} \times 10^{-4}$	$A_2 \times 10^4$	$M_{ap} \times 10^{-4}$	$A_2 \times 10^4$
Amyl Acetate	5.57	0.14	4.02	-0.08
Cyclohexanone	1.62	1.50	1.87	0.51
Chlorobenzene	4.20	0.03	3.76	0.15
o-Dichlorobenzene	83.9	0.02	50.8	0

This table lists the values of the molecular weight and second virial coefficient for each solvent. The molecular weights were calculated using the refractive indicies as determined at 5460 Å and the specific refractive increments as determined from the best fit on the dn/dc versus n plot.

Molecular Parameters

The values of the weight-average molecular weights, $\bar{M}_w$, and the composition distribution functions, P and Q, for the two copolymers were calculated using equation (9). The data from Tables II, III and IV were used to solve a set of simultaneous equations to determine these parameters. A computer program for linear regression analysis was used with an IBM 360 to perform the calculations. This program calculates the values of $\bar{M}_w$, P, Q and also the value of a correlation coefficient which indicates how the experimental points fit the calculated curve. The correlation coefficient for Copolymer I is 0.9998 and for Copolymer II it is 0.9996. The maximum value for the coefficient is of course 1, thus the agreement between calculated and experimental points is very good. This agreement indicates that the procedure used to determine the specific refractive increment values was an acceptable one. This agreement also indicates that the extrapolation procedures used on the Zimm plots are also acceptable. Table V lists the parameters as determined for Copolymer I and II.

TABLE V

Molecular Parameters for Copolymers I and II

Copolymer	$M_w \times 10^{-4}$	$P \times 10^{-4}$	$Q \times 10^{-4}$	P/M_w	Q/M_w
I	5.61	-3.46	2.44	-0.62	0.44
II	5.27	-2.81	1.97	-0.53	0.37

The parameter P, which is the same as the Stockmayer et al[3] (MΔX), is a measure of the drift in the composition of the copolymer molecules with molecular weight. This quantity can be either positive or negative depending on which monomer predominates in the higher molecular weight molecules in the sample. Both of the copolymers in this case have a negative sign for P which indicates that the higher molecular weight molecules in the sample contain a larger proportion of isobutylene than the lower molecular weight molecules. This phenomenon was also noted by Krause[5] in a study of the block copolymer of styrene and methyl methacrylate.

The parameter Q is the same as the Stockmayer et al[3] $M(\Delta X)^2$ and is a measure of the width of the composition distribution of the sample, somewhat weighted toward high molecular weights. This quantity must be positive and is for both of the copolymers.

Table V also lists the values of the normalized forms for P and Q which are P/M_w and Q/M_w. These calculated values indicate an 18% difference between Copolymers I and II. This would tend to indicate that Copolymer I has a broader compositional distribution than Copolymer II.

According to equation (9), if one were to plot M_{ap}/M_w as a function of $(\nu_A - \nu_B)/\nu_o$ the points should fall on a parabola. Figures 10 and 11 are such plots of M_{ap}/M_w versus $(\nu_A - \nu_B)/\nu_o$ for Copolymers I and II respectively. The lines represent the data as calculated from equation (9) with the values of P and Q as given in Table V. The circles represent the experimental data for the four solvents used in the study. It should be pointed out that a linear plot indicates a polymer of homogeneous composition. The data for Copolymer I yields a parabola with more curvature than that for Copolymer II

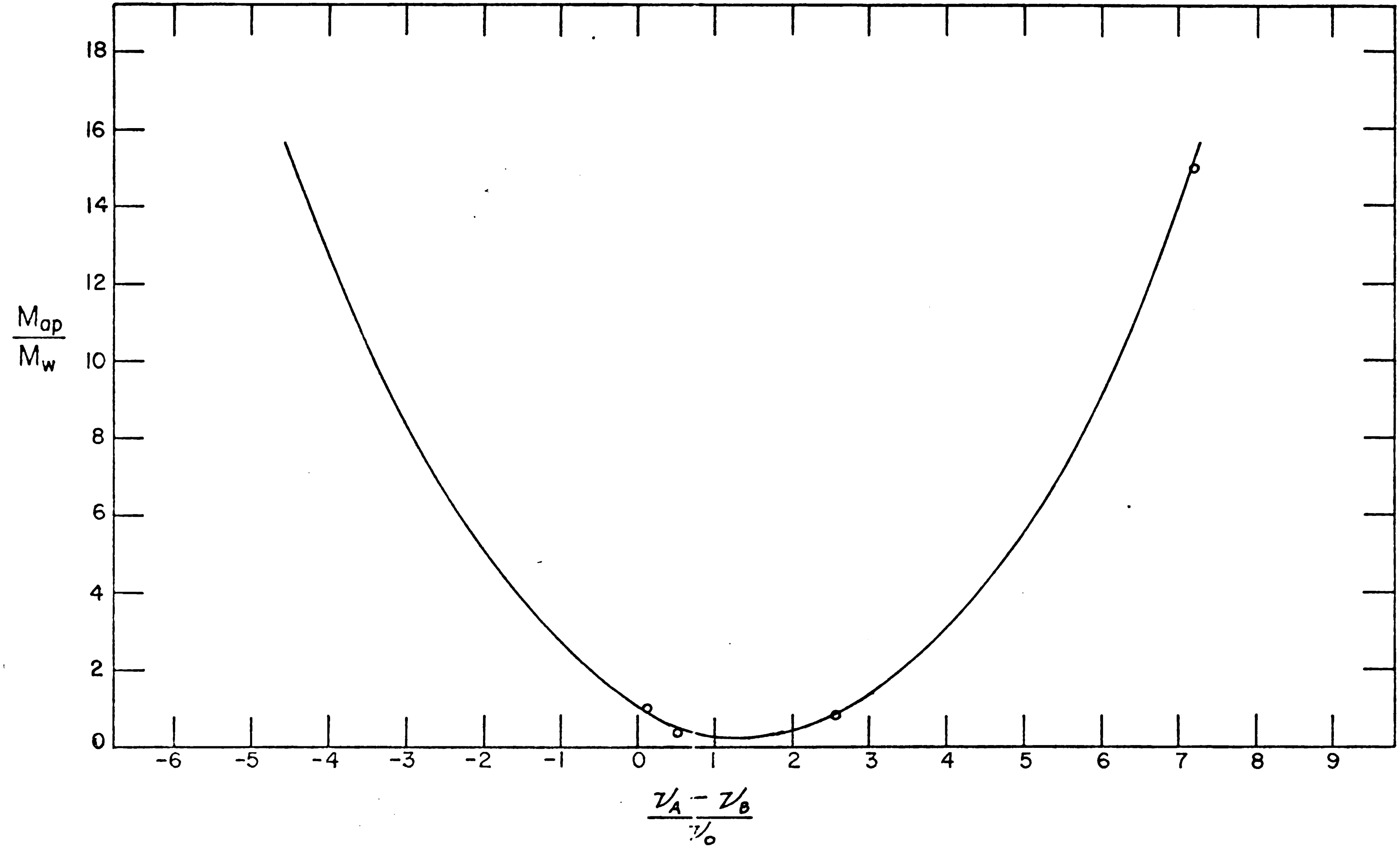

Figure 10. Apparent Molecular Weight (M_{ap}/M_w) vs. $(\nu_A - \nu_B)/\nu_0$ for Copolymer I. Lines Represent Data Calculated from Equation (9). Experimental Data: Circles.

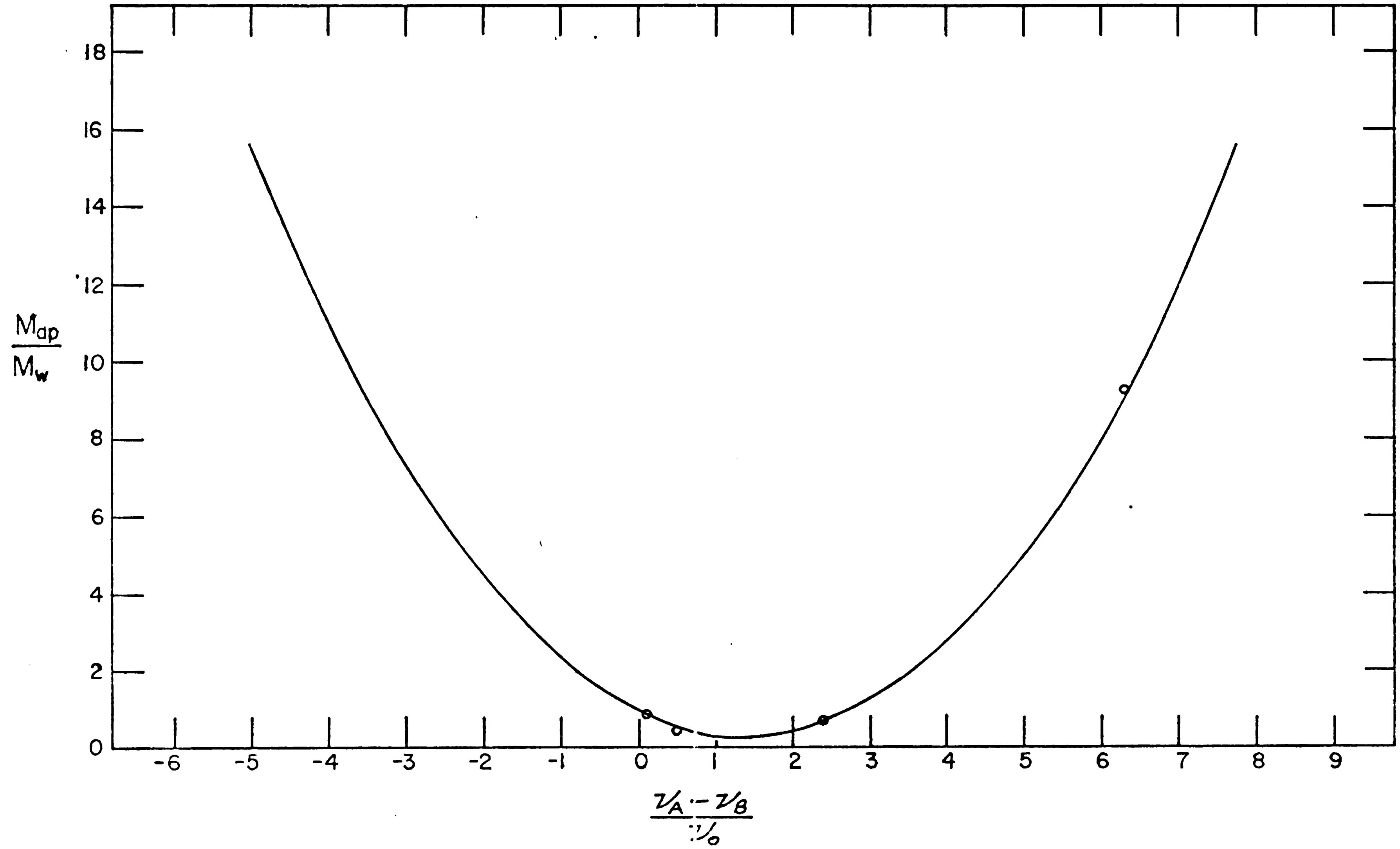

Figure II. Apparent Molecular Weight (M_{ap}/M_w) vs. $(\nu_A - \nu_B)/\nu_0$ for Copolymer II. Lines Represent Data Calculated from Equation (9). Experimental Data: Circles.

which also indicates a broader composition distribution. A plot such as this can also be used to determine the values of P and Q. For P, the slope of the curve at $(\nu_A-\nu_B)/\nu_0 = 0$ is equal to 2P. A qualitative examination of the plots indicate a negative value of P is required which has been shown to be the case. Another aspect of copolymers is illustrated by Figures 10 and 11. These plots demonstrate the dependence of molecular weight on the refractive index of the solvent. The degree of heterogeneity of the copolymer is the cause for this dependence and even allows one to measure an apparent molecular weight that is lower than the true weight average molecular weight.

As indicated in the theoretical section, it is possible to determine the weight-average molecular weights of the two fractions comprising part A and B of the copolymer. Table VI lists the values obtained for the two copolymers used in this study.

TABLE VI

Summary of Derived Data for Copolymers I and II

Copolymer	$M_A{}^{a} \cdot x\ 10^{-4}$	$M_B{}^{b} x\ 10^{-4}$	$M_W\ x\ 10^{-4}$	P/M_W	Q/M_W	Q/Q_{max}
I	0.74	21.3	5.61	-0.62	0.44	0.54
II	1.17	17.4	5.27	-0.53	0.37	0.44

a. A-Polyvinylidene Chloride

b. B-Polyisobutylene

The values for M_A and M_B listed were calculated using an approach of Leng and Benoit[6] which uses the following equations

$$2P = (1 - X_o)(M_W - M_B) - X_o(M_W - M_A)$$
$$Q = X_o(1 - X_o)(M_A + M_B - M_W). \qquad (19)$$

Table VI is a summary of the derived data for Copolymers I and II. The table includes all of the molecular parameters determined in this study.

The last column of Table VI gives the ratio Q/Q_{max}, where Q_{max} is the upper limit on Q. Q_{max} is calculated from the relation $\left[1 - X_o(1 - X_o)\right]$ which for both copolymers is approximately 0.82. This ratio can be used as a measure of the heterogeneity of chain composition as compared to the maximum value of unity.

To summarize the results of this study, it should be noted that the techniques of differential refractometry and light scattering are very useful for analyzing copolymers. The extrapolation technique used to determine the specific refractive increments of the homopolymers has been shown to be an effective one. The only limitation on this technique is the refractive index difference between the two homopolymers. As the difference between the refractive indicies of the homopolymers decreases, the accuracy of the compositions calculated from the data also decreases. The technique of plotting dn/dc vs n_o and using the equations of the lines as determined from a least squares analysis does allow one to minimize the experimental error. The compositions of the copolymers have been calculated from the differential refractometry data. Copolymer I, which was prepared in a 2M solution, consists of 81% vinylidene chloride and 19% isobutylene. Copolymer II, which was prepared in an 8.5M solution, also consists of 81% vinylidene chloride and 19% isobutylene.

Theory[3] predicts that the apparent molecular weight of a copolymer, as measured by light scattering, should be dependent on the refractive index of the solvent used in the measurement. This refractive index dependence is readily apparent from equations (6) and (9) which define the relationship between apparent molecular weight, refractive index increment, weight fraction, true molecular weight and composition functions. Table IV summarizes the light scattering results and indicates a wide variation in apparent molecular weight with solvent. The extreme cases are for Copolymer I in cyclohexanone, $M_{ap} = 1.62 \times 10^4$, and o-Dichlorobenzene, $M_{ap} = 83.9 \times 10^4$.

The molecular parameters, P and Q, as calculated for the two copolymers indicate a difference of approximately 18% in the compositional distribution parameters. Table V lists the normalized values for P and Q with Copolymer I having a broader compositional distribution than Copolymer II. However, both copolymers are quite broad and have a larger quantity of isobutylene in the higher molecular weight molecules, as indicated from the negative values of P. The breadth of the composition distributions is also indicated from the ratio of Q/Q_{max} which are 0.54 and 0.44 for Copolymers I and II respectively. The maximum value for this ratio is unity which indicates the heterogeneous nature of the copolymers. Theory also allows one to calculate the weight-average molecular weights of the two fractions comprising part A and B of the copolymer. For copolymers of homogeneous composition, the sum of the molecular weights of the components is equal to the true weight-average molecular weight. As the data in Table VI indicates, the sum of the components does not equal the true molecular weight. The predominating fraction is isobutylene and also points to a heterogeneous composition. Again, Copolymer I has a somewhat broader distribution than Copolymer II.

The theory of copolymerization predicts that high conversion copolymers will in general be of heterogeneous chain composition. However, these are low conversion copolymers. Copolymers I and II have conversions of 4.6% and 2.0% respectively. All of the differential refractometry and light scattering results indicate copolymers with heterogeneous compositions. Copolymer I, with the highest percentage conversion, does appear approximately 18% broader in composition than Copolymer II. The explanation for the heterogeneous nature of these copolymers must lie in the kinetics of the copolymerization of isobutylene and vinylidene chloride. Perhaps some type of equilibrium exists which influences the composition of the chains during copolymerization.

In conclusion, the findings of this work indicate how the differences in two copolymers prepared as a function of dilution can be analyzed by light scattering. However, much more work could be done to determine the exact sensitivity of this technique in measuring differences in composition distribution.

BIBLIOGRAPHY

1. Debye, P., J. Phys. & Colloid Chem. 51, 18 (1947).
2. Tremblay, R., Rinfret, M. and Rivest, R., J. Chem. Phys. 20, 523 (1952).
3. Stockmayer, W. H., Moore, L. D., Jr., Fixman, J. and Epstein, B. N., J. Polymer Science, 16, 517 (1955).
4. Bushuk, W. and Benoit, H., Can. J. Chem., 36, 1616 (1958).
5. Krause, S., J. Phys. Chem., 65, 1618 (1961).
6. Leng, M. and Benoit, H., J. Polymer Science, 57, 263 (1962).
7. Kinsinger, J. B., Fischer, T. and Wilson, C. W. III, J. Polymer Science B, 4, 379 (1966).
8. Kinsinger, J. B., Fischer, T. and Wilson, C. W. III, J. Polymer Science B, 5, 285 (1967).
9. Kinsinger, J. B., Bartlett, J. S., and Rauscher, W. H., J. Applied Polymer Science, 6, 529 (1962)
10. Whippler, C. and Scheibling, G., J. Phys. Chimie 51 (4) 201 (1954)
11. Brice, B. A. and Halwer, J., J. Opt. Soc. AM. 41, 1033 (1951).
12. Zimm, B. H., J. Chem. Phys. 16 (12) 1093 (1948).
13. Carr, C. I., Jr. and Zimm, B. H., J. Chem. Phys. 18, 1616 (1950).

APPENDIX

APPENDIX I

NMR Analysis of Vinylidene Chloride-Isobutylene Copolymers

Kinsinger et al[7, 8] have illustrated the utility of NMR in studying the microstructure of vinylidene chloride-isobutylene copolymers. The NMR spectra were taken with a Varian HR-100 NMR spectrometer with TMS as an internal standard. The spectra were taken at ambient temperatures in bromobenzene as solvent at approximately 8 wt. % copolymer. The spectra are shown in Figures 12 and 13.

Kinsinger et al[7] have given the formulas to be used in calculating the mole fractions of the monomer units from the spectra. The mole fraction of pairs is

$$f_{AA} = \frac{X}{X + \frac{5Y}{8} + \frac{Z}{4}}$$

$$2f_{AB} = \frac{Y}{X + \frac{5Y}{8} + \frac{Z}{4}}$$

$$f_{BB} = \frac{Z}{4} - \frac{3Y}{8} / (X + 5Y/8 + Z/4)$$

where X, Y and Z are the areas under the spectra as designated in Figures 12 and 13.

The mole fraction of monomer units is

$$f_A = f_{AA} + f_{AB} \quad \text{and} \quad f_B = f_{BB} + f_{BA}$$

The experimental data as calculated from these formulas are:

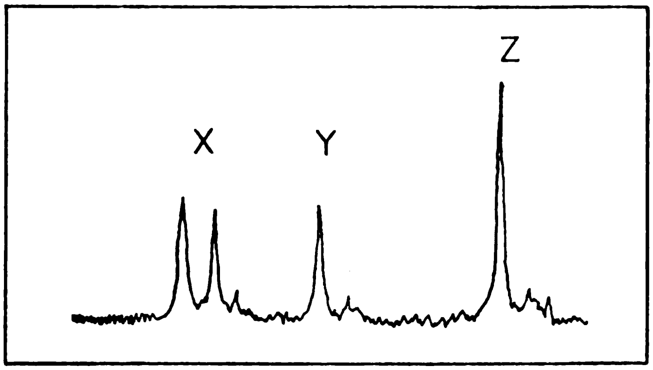

Figure 12. NMR Spectra of Copolymer I

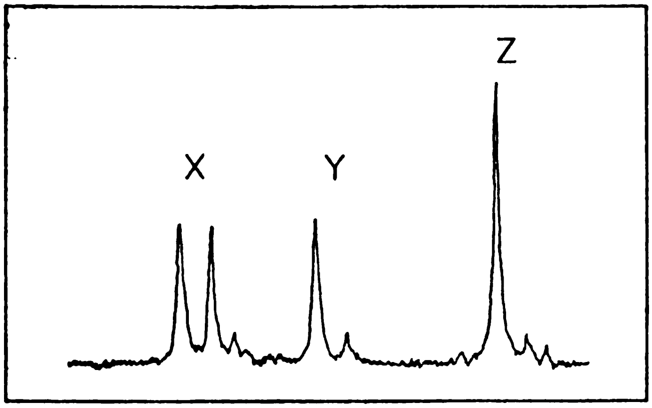

Figure 13. NMR Spectra of Copolymer II

Copolymer	Mole Fraction of VCl_2	f_{AA}	f_{AB}	f_{BB}
I	0.80	0.64	0.16	0.03
II	0.81	0.64	0.17	0.02

The mole fraction of vinylidene chloride, M_A, can be converted to weight fraction, X_A, with the following equation

$$M_A = \frac{X_A \ MW_B}{X_A \ MW_B + X_B \ MW_A}$$

where MW_B is the monomer molecular weight of isobutylene and MW_A is the monomer molecular weight of vinylidene chloride. Using this formula, the weight fraction of vinylidene chloride in Copolymers I and II is 87%.