THE DEPENDENCE OF DILUTE SOLUTION PROPERTIES ON THE CONFIGURATION OF POLYBUTENE - 1

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Curtis C. Wilkins

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This is to certify that the

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ABSTRACT

THE DEPENDENCE OF DILUTE SOLUTION PROPERTIES ON THE CONFIGURATION OF POLYBUTENE-1

by Curtis C. Wilkins

Fractions of varying molecular weight were obtained from bulk isotactic polybutene-1 by a column elution method. Bulk atactic polybutene-1 was fractionated by a fractional precipitation method.

Phase equilibrium studies were made with the two stereoisomers of polybutene-1 to determine the effect of configuration on the thermodynamic interaction parameters as defined by the Flory-Huggins theory for liquid-liquid phase equilibrium. Phase diagrams were constructed for 4 isotactic and 4 atactic fractions. Theta temperatures were determined for both isomers in α-chloronaphthalene. The interaction parameters established in this study were found to differ for the two stereoisomers and to be very solvent-dependent.

Intrinsic viscosity values were determined for isotactic and atactic fractions in n-nonane at 80°C and over a 34° temperature range in α-chloronaphthalene. Intrinsic viscosity data were obtained for atactic fractions in benzene at 30°C. These data with intrinsic viscosity data at the theta temperature were used to calculate values of the molecular expansion factor, α, for both isomers.

Unperturbed end-to-end dimensions for both isomers were established from intrinsic viscosity values at the theta point. Dimensions appear to be somewhat larger for the atactic isomer.

Light scattering studies were made with isotactic and atactic fractions at the theta temperature in α-chloronaphthalene to establish unperturbed dimensions and molecular weight values. These molecular weight values with intrinsic viscosity data in n-nonane gave an intrinsic viscosity-molecular weight relationship in agreement with previously published results.

THE DEPENDENCE OF DILUTE SOLUTION PROPERTIES ON THE CONFIGURATION OF POLYBUTENE-1

By

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VITA

The author was graduated from Platteville High School, Platteville, Wisconsin in June 1953. He entered Wisconsin State College at Platteville in September 1953 and studied chemistry and mathematics until he received the Bachelor of Science degree in June 1957.

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I. INTRODUCTION

A. Historical

In 1943 Alfrey, Bartovics, and Mark[1] demonstrated that the values of certain constants for polystyrene fractions (characteristic of their thermodynamical and hydrodynamical interaction with a given solvent) were quite dependent on the temperature of polymerization. This unexpected result they interpreted as indicating a "different internal architecture of the macromolecules" in the different samples produced at different temperatures.

A suitable explanation for the existence of this different internal architecture of the macromolecules was proposed by Huggins[2]. He noted that the α-carbon atom in an α-olefin, such as styrene becomes asymmetric once the polymer chain is formed. He further predicted that physical properties of poly α-olefins other than styrene should exhibit a dependence on the nature and extent to which a steroregular structure might be formed during polymerization.

Further advances in this direction were slowed by the difficulty of producing stereoregular polymers. A breakthrough came in 1955 when Natta[3] demonstrated that the polymerization of α-olefins could be controlled by specific catalysts to produce stereoregular polymers.

Natta was able to confirm the earlier experiments of Schildknecht[4] with poly(vinyl-isobutyl ether) and demonstrated the predicted dependence of the physical properties on the stereoconfiguration to be valid. To the

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highly regular all d or all l species, which he was able to identify by x-ray spectroscopy, he gave the name "isotactic". An alternating type (dl dl dl dl ....) polymer was also prepared and named "syndiotactic". Non-crystallizable, amorphous polymers of these types are now generally termed "atactic".

Since that time several studies have been made to compare the molecular dimensions and thermodynamic interaction of the stereoisomeric forms of linear polyolefins. Most of the experimental exploration has involved the measurement of intrinsic viscosities, molecular sizes, and second virial coefficients in thermodynamically good solvents[5-13]. Results of these experiments have shown that isotactic and atactic forms exhibit differences in the second virial coefficients in these solvents, but that perturbed molecular dimensions appear to be indistinguishable.

Very little investigation has, however, involved measurements in thermodynamically poor solvents[13,14] where solvent-segment interactions are diminished. In particular, no results are reported of molecular dimensions for isotactic and atactic forms obtained from light scattering measurements performed in a solvent at the theta temperature*. The comparison of theta temperature values obtained for the different stereoisomers in these two studies[13,14] has suggested that a comparison of thermodynamic parameters in other solvents would be of interest. These two studies have shown that isotactic polypropylene has a lower theta temperature then the atactic form whereas isotactic polybutene-1 has a higher theta temperature than the atactic form in certain solvents.

*At the theta temperature the net energy of polymer-solvent interaction is just balanced by the net polymer-polymer, solvent-solvent interaction--- the average polymer chain dimensions at this temperature are referred to as the unperturbed dimensions.[17]

Recent nuclear magnetic resonance studies by Bovey et. al.[15,16] on poly(methyl methacrylate) samples indicate that a quantitative measure of the degree of tacticity of polymer samples may be established. It would be of interest in future work to correlate the data obtained from nuclear magnetic resonance studies with dilute solution information by performing these measurements concurrently.

B. Statement of Purpose

It was the purpose of this study to investigate dilute solution properties of isotactic and atactic polybutene-1 in a poor solvent, employing phase equilibria, viscosity, and light scattering techniques. The observed physical properties could then be compared for the two isomeric forms and a correlation made between molecular structural features and physical properties. As suggested in the preceding paragraph this study has a further purpose. It represents a portion of the work necessary to establish an eventual correlation of the degree of tacticity with dilute solution properties. In undertaking this study the choice of polybutene-1 seemed attractive because:

1. It was available in various stereoisomeric forms.
2. Its solution properties should not be complicated by interactions of highly polar substituents.
3. Its isotactic isomer melts at a lower temperature (130°) than the corresponding stereoisomers of previously studies polypropylene (176°) or polystyrene (240°). It should therefore be possible to use less severe temperature conditions in solution studies of thermodynamically poor solvents.
4. It would offer information on the role the pendant side group (in this case an ethyl group) plays in determining physical properties.
5. It was available in linear chain form; consequently chain branching would not complicate dilute solution studies.

C. General

Well-developed techniques exist for characterizing the behavior of macromolecules in both bulk polymer systems and dilute solutions. However, dilute solution properties are more amenable to theoretical interpretation than are bulk polymer properties. Consequently, the choice of characterization of polybutene-1 in the dilute solution state was made at the outset of this research.

In undertaking this dilute solution study of samples of polybutene-1 of different tacticity, four main areas of investigation were examined:

1. Fractionation
2. Viscosity
3. Phase Equilibria
4. Light Scattering

1. Fractionation

Fractionation, according to molecular weight, of bulk polymer samples is necessarily the first step in characterizing a polymer by dilute solution methods. Subsequent studies may then be performed on polymer fractions. Well-fractionated samples are required in order to establish a reliable intrinsic viscosity-molecular weight relationship from light scattering and viscosity measurements[17]. Polymer samples with a narrow molecular weight range are necessary in order to obtain accurate precipitation temperatures. Phase separation occurs over a narrower temperature range for a well-fractionated sample than for a sample with a broad molecular weight distribution enabling the precipitation temperature to be established more precisely. Finally, fractionation procedures can be employed to separate the stereoisomeric forms.

2. Viscosity

Viscosity studies of dilute polymer solutions play an important role in the characterization of a polymer. Upon dissolution of a high polymer in a solvent a tremendous increase is observed in the viscosity of the solutions. As a direct result of this large increase, which is a feature common to all macromolecules, a reproducible solution parameter is available for study. One of the most useful relationships obtained from viscosity studies is an empirical intrinsic viscosity-molecular weight relationship which can be established when intrinsic viscosity data is coupled with absolute molecular weight measurements. Subsequent molecular weight determinations of polymer samples can then be based on simple viscosity measurements.

Viscosity data may yield information about the extension of a polymer chain in solution and may therefore be used for studying the configurational* structure of a polymer. Viscosity measurements of randomly coiled polymers at the theta point allow a calculation of the unperturbed root mean square end-to-end dimensions to be made. Unperturbed dimensions have a special significance in current theoretical polymer studies[17,45] which relate the dimensions to the configurational structure of the polymer.

Using intrinsic viscosity data at the theta temperature and at least one other temperature it is possible to describe the effect of a given solvent on the polymer conformation in terms of a molecular expansion factor. Intrinsic viscosity data may also be used to study the temperature effect on polymer conformation in a given solvent.

3. Phase Equilibria

Phase equilibria studies yield thermodynamic information concerning polymer-solvent systems. Previous studies[13,14,18] have shown

* The term configuration refers to the steric orientation of the alternating asymmetric carbon atoms in the polymer chain (e.g., d,l,d,l placement).

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that different stereoisomers of a given polymer may exhibit different thermodynamic interactions with a given solvent. In this particular connection, an entropy of dilution parameter and a heat of dilution parameter for the solvent-polymer system under study may be calculated from phase equilibria data and compared for different stereoisomers.

The theta temperature of a solvent (i.e. the critical miscibility temperature for a polymer of infinite molecular weight) can be established from phase equilibria measurements. Subsequent light scattering measurements at the theta temperature allow direct calculation of the average unperturbed end-to-end dimensions.

4. Light Scattering

Macromolecular systems, by virtue of their large size and subsequent large scattering power of a polymer, may be characterized by the measurement of scattered light. Since a difference in molecular structure of two stereoisomers should be reflected by a difference in the chain dimension of the polymer in solution, light scattering data which yields information about the chain dimension, is pertinent to this study. In particular, structural differences may be examined by comparing molecular dimensions unperturbed by solvent effects. Light scattering measurements made at the θ temperature of a polymer-solvent system appear to offer the best means of obtaining such information. Light scattering data also give the absolute molecular weight values necessary to establish an intrinsic viscosity-molecular weight relationship.

When both light scattering data and intrinsic viscosity data are obtained at the theta temperature on the same polymer fractions it is pos

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possible to deduce information of a general nature on the polymer chain conformation*.

D. Polymer Samples

Samples of atactic and crystalline (isotactic) polybutene-1 were provided by Petro-Tex Division of Food Machinery Corporation of New Jersey. The atactic sample was clear, colorless and rubbery while the isotactic polymer was a white, non-tacky fluffy powder. Infrared spectra, melting point data, and x-ray diffraction patterns are reported in reference 18 for the isotactic polybutene-1 used in this study.

* The term conformation, as used throughout this work, denotes the shape (roughly the alignment of the backbone of the polymer chain) assumed by the polymer. Making use of the earlier definition of configuration, it may be said that for a given polymer sample the conformation may be altered by simple internal rotations whereas the configuration can not be changed (without breaking and re-forming chemical bonds).

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II. FRACTIONATION

A. General

Polymer fractionation is designed to separate the bulk polymer into fractions each of which is more homogeneous in molecular weight than the original polymer.

In suitable solvents the solubility of a homogeneous polymer fraction decreases with molecular weight. Thus the addition of a non-solvent to a heterogeneous polymer progressively precipitates fractions of decreasing molecular weight. Alternatively the polymer can be extracted with progressively better solvents to obtain a series of fractions of increasing molecular weight. The principles involved are the same in both cases. In a "good" solvent a heterogeneous polymer will be miscible in all proportions. If the solubility is reduced by cooling, a stage is reached --- the critical solubility --- where phase separation occurs and two layers form. Fractionation is possible because in such two-phase systems the concentration ratio of high to low molecular weight species is greater in the precipitated phase than in the dilute solution phase.

Equilibrium conditions must be established between the two phases to ensure efficient fractionation. Thus, the temperature control, time of waiting for phase equilibria, and the addition of a non-solvent, influence fractionation efficiency. To assure phase equilibria during non-solvent addition it is necessary to select a non-solvent and solvent pair which will be miscible over the working temperature range.

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Also to assure equilibrium, the addition of a non-solvent should be performed at constant temperature with adequate stirring to prevent local variations in the compositions of the phases. In the case of a crystalline polymer, it is desirable to adopt fractionation conditions which allow the precipitate to separate as an amorphous liquid without formation of polymer in the crystalline state. Liquid-liquid separation from a dilute solution is rapidly reversible whereas liquid-crystalline separation is slowly reversible or irreversible.

B. Solvent, Non-Solvent Selection

In selecting a suitable solvent-non-solvent pair it is helpful to examine the development of the cohesive energy density approach and the use of a subsequent solubility parameter to predict polymer solubility.

A high polymer may interact with a liquid in a manner analagous to the equilibrium interaction between two liquids. For two liquids, solubility occurs if the free-energy of mixing, is negative. For this isothermal reversible process

$$\Delta F_m = \Delta H_m - T\Delta S_m$$

Since ΔS_m, the entropy of mixing, is usually large and positive, the sign of ΔF_m is determined by the sign and magnitude of ΔH_m. If there is some sort of positive interaction between the two liquids (or liquid and polymer) so that ΔF_m is negative then solution will occur.

Following the treatment of Hildebrand[19] and Scratchard[21], the heat of mixing per unit volume is given as

$$\Delta H_m = \phi_s \phi_p \, (\delta_s - \delta_p)^2$$

where ϕ_s and ϕ_p are the volume fractions of solvent and polymer, and δ_s

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and δ_p are solubility parameters such that

$$\delta = (\Delta E/V)^{1/2}.$$

The energy of vaporization per unit volume, $\Delta E/V$, where ΔE is the change in energy for the vaporization process and V is the molar volume of the liquid at the vaporization point, is generally termed the cohesive energy density. For solubility to occur $(\delta_s - \delta_p)$ should be small in magnitude.

C. Experimental-Atactic Isomer

The value of δ_p for polybutene-1 was estimated to be approximately 7.9 from calculated values for polyethylene and polyisobutylene[22]. The selected solvent-non-solvent pair for the atactic polymer fractionation were n-hexane and acetone, respectively.

All atactic samples were fractionated by the addition of a miscible non-solvent to a dilute solution of the polymer following a procedure described by Flory[17,20]. This procedure essentially entails the application of experimental techniques to the fractionation principles set forth in the foregoing discussion.

In Figure 1 a flow diagram including a weight scheme of the atactic fractionation is reported.

Each of the three fractionation stages shown in Figure 1 were conducted under the same experimental conditions. Polymer fractions were recovered by evaporating the polymer-rich phase to dryness on a steam bath under a stream of hot air. The dried polymer was placed on a coarse grade sintered glass filter, washed with copious amounts of distilled acetone, and dried in vacuo at 80°C to constant weight.

Data from the three fractionation stages are listed in Table 1. The weight percentages listed in this table are based on starting sample weights of 10.38, 6.39, and 3.42 grams respectively for the bulk atactic, sample

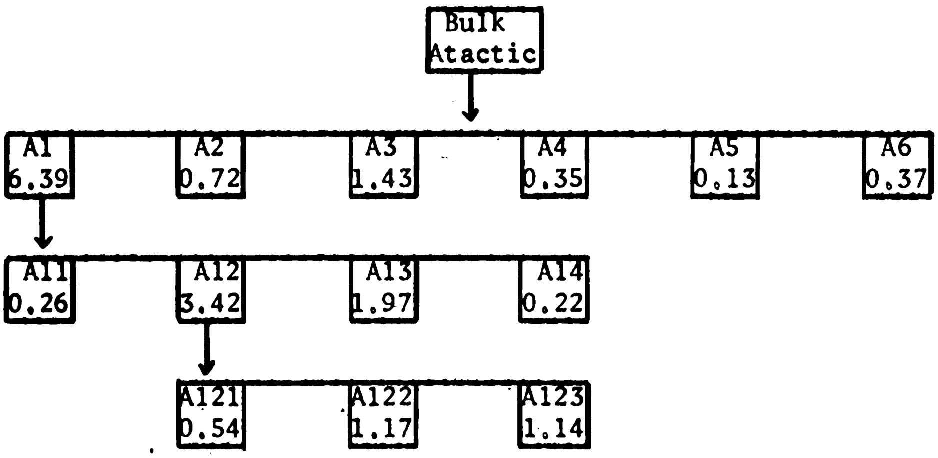

Fig. 1 Flow diagram of atactic fractionation

and sample A12 fractionations.

Intrinsic viscosity data for these fractions indicates molecular weight separation has been effected. A summary of these data for the atactic fractionations appears in Table 3.

D. Experimental - Isotactic Isomer

Rather specialized techniques are employed for the fractionation of high melting crystalline polymers in order to obtain good molecular weight separations. The techniques used in this work for the fractionation of isotactic polybutene-1 represent certain modifications of techniques reported in the literature.

All samples of isotactic polymer were believed to contain some atactic polymer and were consequently subjected to a two stage extraction-fractionation procedure. The first stage, fractionation by extraction, was employed to separate mainly according to tacticity. The second stage, fractionation by column elution techniques, was utilized to separate the polymer according to molecular weight.

Table 1

Fractionation of atactic polybutene-1

Fraction	Weight	Weight %
Bulk Atactic Sample		
A1	6.3919 gms.	61.6 %
A2	0.7197	6.9 %
A3	1.4282	13.8 %
A4	0.3454	3.3 %
A5	0.1273	1.2 %
A6	0.3706	3.6 %
	9.3831 gms.	90.4 %
Atactic Sample A1		
A11	0.2557 gms.	4.0 %
A12	3.4232	53.6 %
A13	1.9738	30.7 %
A14	0.2246	3.5 %
	5.8773 gms.	91.8 %
Atactic Sample A12		
A121	0.5419 gms.	15.8 %
A122	1.1690	34.2 %
A123	1.1365	33.2 %
	2.8474 gms.	83.2 %

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Fractionation by extraction to separate the atactic and isotactic forms of poly α-olefins has been described by Natta[23]. In his experiments boiling hydrocarbons were used at temperatures well below the melting point of the crystalline form of the polymer being extracted. Evidence was cited to show that the poly-α-olefins are separated mainly according to tacticity --- the atactic portion being the only soluble part under these conditions.

Column elution techniques for the molecular weight separation of heterogeneous polyethylene samples have appeared in the literature following the work of Desreux[24,25]. These techniques involved the precipitation of a polymer on an inert support contained in a column, followed by fractional elution. In the elution process, either the solvent composition was held constant while the temperature of the column was increased, or the solvent-non-solvent mixture was varied while the temperature was held constant[25].

In this work, three bulk isotactic samples were fractionated employing the techniques described[24]. In the elution processes of all three samples the temperature of the column was held constant while the composition of the solvent-precipitant mixture used for elution was varied. Two different modifications in the method of depositing the polymer on the inert support were utilized. One modification consisted of precipitating the polymer from a relatively poor solvent by slowly cooling the solution below its precipitation point. A report of a similar process has been given by Francis, Cooke, and Elliott[26] for the column fractionation of polyethylene. The other modification is similar to the methods reported by Kenyon and Salyer[27] and later by Mendelson[28] and consisted of polymer deposition from a theta solvent. As established in the above reports[26,27] molecul

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molecular weight separation of crystalline polymers can be improved if liquid-liquid phase separation can be effected during fractionation. The poor solvent, anisole, used in this study was later shown in phase studies to give liquid-liquid phase separation at the deposition temperature.

Isotactic sample B was extracted with 250 ml. of boiling n-hexane, in a Soxhlet extractor for 100 hours. From an initial 2.56 grams, 0.21 grams were extracted. The portion remaining in the extraction cup was placed in a vacuum oven at 70°C for four hours to drive off all n-hexane. A constant weight of 2.28 was obtained for this portion.

The elution column constructed for use in the second stage of the fractionation of sample B was patterned after a separation column described by Francis et. al.[26].

Sand of #40 mesh size was used as the inert support. Proper precautions were observed to avoid channeling in the column during the packing process.

The extracted sample B (2.28 grams) was dissolved in 100 ml. of o-xylene at 100°C and was introduced at this temperature onto the heated sand column. The column was maintained at 98°C by refluxing n-heptane in the outer jacket. The air pressure applied to the column was regulated so as to assure slow, even, frontal development of the solution. To inhibit oxidative degradation, a commercial antioxidant, Ionol, was added to the o-xylene in an amount equal to 0.1% of the total weight of the polymer sample. The polymer was precipitated by allowing the column to cool to room temperature overnight. To ensure complete precipitation and to remove excess o-xylene, the column, while at room temperature, was rinsed four times with 100 ml. amounts of acetone.

The column was then reheated to 98° by refluxing the n-heptane, and the first 100 ml. of solvent-precipitant mixture (o-xylene-n-hexanol, respectively) was heated to approximately 100 ^{o}C and poured into the solvent holder located just above the sand. The mixture was kept in the solvent holder for approximately ten minutes in order to reach column temperature, and then was introduced onto the column. Normal atmospheric pressure was maintained in the column at all times. After 30 minutes the stopcock on the outlet valve was opened for a 15 minute period and the fraction collected in a tared 150 ml. beaker. Immediately after collection, the valve was closed and the next preheated eluent mixture was introduced onto the column. This process, using solvent-precipitant mixtures made progressively richer by increasing the solvent-precipitant ratio (0:10, 1:9, 2:8, etc.), was continued until nine fractions had been collected. A tenth fraction was obtained by adding pure solvent and allowing the column to drain completely. Each 100 ml. solvent-precipitant mixture contained approximately 3 milligrams of Ionol. To check for complete removal of the polymer from the sand, the sand was removed from the column, placed in a beaker and extracted with boiling p-xylene (138^{o}C). A negligible amount was recovered in this last extraction.

The fractions from isotactic sample B were recovered from the collection beakers in two ways. One method utilized a precipitation technique; the other procedure involved removal of the solvent-precipitant mixture. A volume of acetone equal to the volume of the solution in the collection beaker, was used to precipitate the first four fractions. These fractions were then recovered on a coarse grade sintered glass filter. The last six solutions were evaporated to dryness at 65^{o}C (on a hot plate under a stream of air). A yellowish color which appeared in these six fractions (believed to be caused by impurities in the solvent-precipitant mixture) could be re

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removed by extracting these fractions with acetone.

All ten fractions were dried in vacuo at 70°C to constant weight.

Fractionation data for isotactic polybutene-1 sample B appear in Table 2. The initial weight of sample B used in this fractionation was 2.28 grams.

Intrinsic viscosity data were obtained on several of these fractions. These data are listed in Table 4 and indicate that the fractionation was successful in obtaining a series of increasing molecular weights.

A second isotactic sample was fractionated under nearly the same conditions as have been previously described. This fractionation was undertaken without the use of an antioxidant. The liquid used in the outer refluxing jacket was a mixture of xylenes (b. pt. 138°C). Viscosity data showed that severe degradation occurred in each of the fractions obtained.

A third isotactic sample, designated as sample C, was extracted with 250 ml. of boiling n-hexane in a Soxhlet extractor for 18 hours. An initial amount of 10.965 grams, placed in the extraction cup, yielded 7.466 grams of extracted polymer. The portion remaining in the extraction cup was placed in a vacuum oven at 70°C for four hours to drive off all n-hexane.

The column fractionation procedure for isotactic sample C was altered from that previously described for isotactic sample B; Celite was substituted for sand and the polymer was deposited from a poor solvent. The use of Celite facilitated the use of a slower rate of elution and also the polymer deposition process. It had an added advantage of providing more surface area for polymer deposition than sand provides (thereby enabling the fractionation of a larger sample[29]).

A slurry of 100 grams of Celite; 500 grams of anisole, and 0.1 gram of Ionol was placed in a one liter beaker. This mixture was stirred vigorously

Table 2

Fractionation of isotactic polybutene-1

Fraction	Weight	Weight %
	Isotactic Sample B	
B 1	0.165 gms.	7.2 %
B 2	0.253	11.1
B 3	0.129	5.7
B 4	0.258	11.3
B 5	0.028	1.2
B 6	0.002	.1
B 7	0.172	7.5
B 8	0.616	27.0
B 9	0.422	18.5
B 10	0.162	7.1
	2.207	96.7 %
	Isotactic Sample C	
C 1	0.0936	2.8 %
C 2	0.1999	6.0
C 3	0.4054	12.1
C 4	0.2682	8.0
C 5	0.3220	9.5
C 6	0.4850	14.5
C 7	0.1889	5.6
C 8	0.7507	22.4
C 9	0.5170	15.4
	3.2307	96.3 %

with a mechanical stirrer while being heated to 115^{o}C under a constant blanket of N_2. A polymer sample of 3.35 grams was dissolved in 250 ml. of anisole containing 1 gram of Ionol and then introduced into the above slurry. The stirred mixture was then cooled slowly (1^{o}C per minute) to 40^{o}C, precipitating the polymer onto the Celite support.

To ensure even packing of the support in the column, the entire slurry was poured into the column (at room temperature). The column was brought to 100^{o}C by refluxing water in the outer jacket and the anisole was drained from the column. To prevent the formation of large air bubbles, the column was sparged for two minutes with N_2 prior to draining the anisole.

Elution of the column was performed as previously described for sample B with a few exceptions: fractions C1 and C6 represent double fractions (i.e. two elution runs from the column were collected in the same beaker). The column was allowed to remain at 100^{o}C for an 18 hour period between the collection of fraction C6 and C7. Fraction C8 and C9 were obtained, respectively, from eluent mixtures of 120 ml. xylene and 30 ml. n-hexanol, and 200 ml. of xylene only. The solvent was the standard commercial mixture of xylene isomers, commonly referred to as "xylene". The rate of elution was approximately 1 ml. per minute.

To check for complete removal of the polymer from the support, the Celite was removed from the glass column, and extracted with hot xylene. The amount of polymer recovered in this extraction was very small in comparison to the preceding fraction (C9) obtained during the regular fractionation procedure. It was subsequently combined with fraction C9. The weight of fraction C9 listed in the data of Table 2 represents this combined weight.

After collection from the column, the polymer solutions were evaporated under a N_2 atmosphere to approximately one-half of their starting volume ---

then precipitated by cooling to room temperature. To ensure complete precipitation a volume of acetone equal to the solution volume was added. Polymer fractions were recovered on a coarse grade sintered glass filter and dried in a vacuum oven at 65°C for 13 hours until constant weight was reached.

Fractionation data for isotactic sample C appear in Table 2.

Viscosity data on these fractions appear in Table 4 and indicate that the sample was separated into fractions of increasing molecular weight. The low viscosity values obtained on fractions collected after the column had remained at 100°C for the 18 hour period described above were interpreted as resulting from polymer degradation.

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III. INTRINSIC VISCOSITY

A. Theory

1. Good Solvent[17,30,31]

An empirical relationship between molecular weight and intrinsic viscosity, known as the Mark-Houwink expression, has proved useful for solutions of flexible chain polymer molecules[32,33]. This expression may be written as $[\eta] = KM^a$ where K and a are constants for a given polymer-solvent system at a given temperature.

Before attempting to relate the viscosity of a polymer solution to the molecular weight of the polymer it is necessary to consider what other variables may influence solution viscosity, and then, if necessary, to correct for these effects.

For most polymer-solvent systems the differences between the viscosity of a dilute polymer solution and that of the pure solvent increases more rapidly than the concentration since individual molecules have a greater opportunity for interaction as their concentration increases. Since no satisfactory theoretical treatment exists which can be used to correct for this concentration effect, it is necessary to make measurements at low concentrations and extrapolate to zero concentration.

Huggins[31] found for a series of polymer fractions in the same solvent, that the slopes of the linear portions of the plots of η_{sp}/c

against c were proportional to the square of the intercept where $\eta_{sp} = (\eta-\eta_o)/\eta_o$, and η_o, η, are respectively, solvent and solution viscosities and c is the concentration. The solvent and solution viscosity can be calculated from equation 9v which is discussed on page 25 in reference to kinetic energy effects on viscosities.

Another relationship, similar to the Huggins equation (no. 1v below), attributed to Kraemer shows that the slopes of the linear portions of the plots of $\ln(\eta/\eta_o)/c$ against c are proportional to the square of the intercept. These relationships may be written as:

$$\eta_{sp.}/c = [\eta] + k_1[\eta]^2c \qquad (1v)$$

$$\ln \eta_{rel.}/c = [\eta] - k_2[\eta]^2c \qquad (2v)$$

The constants of equations (1v) and (2v) may be shown to obey[30], to a good approximation, the relationship $k_1 + k_2 = 0.5$ as $c \rightarrow o$.

2. Theta Solvents[17,30,34]

Linear polymers, such as poly α-olefins, are chain structures having valency bonds in the main chain about which certain restrictions to rotation are expected. If the number of bonds in the chain is sufficiently large, the structure is effectively that of a random coil. Random coils can be constructed having a large number of possible conformations of equal energy. The individual conformations adopted by individual molecules will result in a distribution of effective molecular dimensions, even though the molecules may have identical molecular weights. Models have been proposed from which a statistical calculation of this distribution is possible. This distribution is generally expressed as a function of the parameter, $\overline{r^2}$, the mean-square end-to-end distance of the chain. A theoretical derivation has been made which relates $\overline{r^2_{of}}$, the unperturbed mean-square end-to-end distance assuming free rotation about the bonds, to the number of bonds, bond length, and bond angle. A similar expression, for the unperturbed mean-square end-to-end distance, $\overline{r^2_o}$, which includes the effect of restricted bond rotation has been derived. Most theoretical derivations of this type, to date, have included no effects due to thermodynamic interaction between solvent and polymer. Hence they apply only at the "Flory temperature[35] (i.e., Θ) where there is no net thermodynamic interaction. With net interactions present, the real value of the mean-square end-to-end distance, $\overline{r^2}$ differs from $\overline{r^2_o}$. Fox and Flory[36] have described the effect of solvent on conformation in terms of an intramolecular expansion factor, α, such that

$$\alpha = (\overline{r^2}/\overline{r^2_o})^{1/2} \tag{3v}$$

They relate α to the molecular weight, M, and to the parameters characterizing the entropy of dilution of polymer with solvent, ψ_1, and the heat of dilution of polymer with solvent, κ_1, such that

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \Theta/T)M^{1/2} \tag{4v}$$

where Θ is the critical miscibility temperature for a polymer of infinite molecular weight ($\Theta = \kappa_1 T/\psi_1$) and

$$C_M = (27/2^{5/2}\ \pi^{3/2})(\overline{v}_2/N_0V_1)(M/\overline{r^2_o})^{3/2} \tag{5v}$$

In the expression for C_M, $\overline{v}_2$ is the partial specific volume of the polymer molecule, N_o is Avogadro's number and V_1 is the molar volume of the solvent. The term, C_M, accounts for the dependence of α on the density and dimensions of the solute particles.

Fox and Flory[36] have developed a theoretical expression to describe the molecular weight dependence of the viscosity of dilute polymer solutions.

The relationship is:

$$[\eta] = KM^{1/2}\alpha^3 \qquad (6v)$$

where α is defined by equations (3v) and (4v) above and

$$K = \Phi(\overline{r_o^2}/M)^{3/2} \qquad (7v)$$

where Φ is a universal numerical constant. From equations (6v) and (7v)

$$\Phi = [\eta]_\Theta M/(\overline{r_o^2})^{3/2} \qquad (8v)$$

Since M and $\overline{r^2}$ can be determined for fractionated polymers by light scattering measurements Φ can be experimentally evaluated. This has been done for several systems and, according to Flory[17] the best average value for Φ appears to be 2.1 ($\pm$.02)x10^{21}, r being expressed in cm., M in units of molecular weight, and $[\eta]$ in deciliters per gram.

As seen from equations 4v and 6v the intrinsic viscosity and the factor, α^3, are molecular weight dependent. In a theta solvent, $\alpha = 1$ and equation 6v reduces to $[\eta]_\Theta = KM^{1/2}$. A convincing test of the theory then is to measure the intrinsic viscosity at the theta temperature. For a linear, randomly coiled chain, $\overline{r_o^2}$ is directly proportional to M. Thus, if the contribution of the polymer to viscosity is proportional to the cube of its linear dimension, the basis of the Flory-Fox expression, then at the theta temperature the intrinsic viscosity should be proportional to the square root of the molecular weight.

B. Experimental Method

Viscosities were measured in Cannon-Ubbelohde semi-micro dilution viscometers[30]. Since the effective pressure head of the flowing solution remains constant in this viscometer, it was unnecessary to charge the viscometer with the same volume of liquid for each run.

Flow times of solvent and solution were recorded with the aid of a stopwatch registering to 0.1 (or 0.05 by estimation) seconds. As a standard, Onyon[30] has proposed that the flow time should be reproducible to within ±0.1 per cent.

Vertical alignment of the capillary tube was accomplished by plumb line sighting. The viscometer was then fastened securely in two places.

Ordinary filtration methods, using coarse grade sintered glass filters, provided adequate cleaning of solvent and solutions. In all measurements of isotactic solutions, the filter was kept at least 20° above the solution precipitation temperature by heating with electric tape.

Polymer concentrations were formulated such that the relative viscosity of the solution was between the limits of 1.2 to 1.9[17]. Solvent and polymer were weighed on an analytical balance to prepare the first concentration. Different concentrations were formed by consecutive dilutions; concentrations were calculated from a knowledge of the weights of the filter and solvent container preceding and following solvent addition.

Homogeneity was obtained after each dilution by bubbling N_2 through the solution for three minutes. Viscometers were cleaned between runs by rinsing 4 times with boiling xylene, followed by rinsing with warm cyclohexane and drying in an oven at 110°C. This removed all traces of xylene.

No shear corrections were made. An upper limit of 100 sec^{-1} for the mean rate of shear was calculated for one of the viscometers from a knowledge of its geometry. Using this rate of shear with $d \ln \eta_{rel.}/d\,\sigma$* values obtained by Fox et. al.[37] for various polymer solutions, it was determined

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that for intrinsic viscosity values which were less than 4 deciliters per gram the shear rate would not affect the final answer by more than 0.2%.

Calibration data provided by the Cannon Instrument Company are listed below for both viscometers.

Viscometer (designation)	Viscosity Standard	Viscosity (centistokes)	Efflux Time (sec.)	Viscosity Constant (centistokes/sec)
#75, K280	OC	1.861	234.5	0.007936
	OD	3.482	438.6	0.007939
				ave. 0.00794
#50, K414	OC	1.861	499.5	0.003726
	OD	0.9695	260.1	0.003727
				ave. 0.003727

To evaluate the kinetic energy correction, the viscosity, η, may be written as:

$$\eta = \alpha \rho t - \beta\rho/t \qquad (9v)$$

where $\underline{t}$ is the flow time in seconds of the liquid, ρ is the liquid density, and α and β are constants characteristic of a given viscometer operating under a constant head of liquid. The second term of the above equation is essentially the kinetic energy correction. Calibration data given above showed the kinetic energy correction to be negligible.

Normal nonane was used as received from Phillips Hydrocarbons (99 mole% purity) (b. pt. 151°C., $n_D^{20°}$ 1.4052). Eastman White label grade α-chloronaphthalene was not distilled further ($n_D^{20°}$ 1.6255). Literature[38] values are given as (b. pt. 151°C; $n_D^{20°}$ 1.4054) for normal nonane and ($n_D^{20°}$ 1.6332) for α-chloronaphthalene. Diethyl carbitol was used as received from Union Carbide. Peroxides which had formed in the diethyl carbitol during storage were removed by heating and shaking the solvent with powdered copper as a reducing agent[39]. Subsequent testing with mercury[39] revealed all peroxides had been removed.

All solution concentrations were calculated from weight data. The necessary density-temperature relationships were calculated from various sources for the solvents: benzene and η-nonane[40], α-chloronaphthalene[41], and diethyl carbitol[18].

C. Data and Results

Both η_{sp}/c and $\ln \eta_{rel.}/c$ were calculated and plotted against the concentration according to preceding equations (1v) and (2v). These plots are exhibited in Figures 1 to 13 in Appendix A. As may be seen in these figures, intercept values obtained separately from each equation (1v and 2v) gave good agreement with each other.

A double extrapolation of η_{sp}/c and $\ln \eta_{rel.}/c$ was performed to give the intrinsic viscosity, $[\eta]$. Values of k_1 and k_2 were calculated from equations 1v and 2v.

Table 3 lists values of $[\eta]$, k_1, and k_2, for atactic polybutene-1 fractions in benzene at 30°C and n-nonane at 80°C. Table 4 lists this same information for isotactic polybutene-1 fractions.

Table 3

Intrinsic viscosities for atactic polybutene-1

Fraction	Benzene (30°C) (η) (dl./g)	k_1	k_2	n-Nonane (80°c) (η) (dl./g)	k_1	k_2
A2	1.23	.46	.09	1.44	.60	-.02
A3	0.655	.39	.11	.730	.42	.10
A4	0.34	.32	.15			
A121	4.9	.38	.12			
A122	3.94	.16	.28	2.46*	.36	.14

Values of $[\eta]$, k_1, and k_2 were calculated for isotactic and atactic fractions (in α-chloronaphthalene and in diethyl carbitol) in the same manner as previously described in n-nonane and benzene viscosity data. These

* measured after light-scattering run

Table 4

Intrinsic viscosities for isotactic polybutene-1 in n-nonane at 80^oC

Fraction	$[\eta]$(dl./g.)	k_1	k_2
	Sample B		
B2	1.025	.36	.14
B3	1.35	.31	
*B4	1.364	.38	
*B7	1.784	.39	
*B8	1.904	.34	
	Sample C		
C2	.932	.41	.10
C3	1.69	.31	.17
C4	1.89	.31	.17
C5	2.12	.31	.17
C6	2.19	.32	.17
C7	1.38	.38	.13
C8	1.60	.48	.00
C9	2.20	.40	.12

*** Data from reference 18, k_2 values not given**

appear in Tables 5 and 6. Values of the theta temperatures of diethyl carbitol for the two stereoisomers are taken from reference 18. Values of the theta temperatures of α-chloronaphthalene for the two stereoisomeric forms were obtained from phase studies performed as a part of this work. Molecular weights in Table 5, as will be discussed later, were obtained from viscosity data in benzene and n-nonane.

Table 5

Values of $(\eta)_\Theta$ for polybutene-1 isomers

Isomer	Fraction	$(\eta)_\Theta$(dl./g.)	Solvent	Temp.(°C)	$M_w \times 10^{-5}$
Isotactic	C5	.57	α-chloronaphthalene	85.1	4.9
	C5	.55	diethyl carbitol	98.5	---
	C4	.55	α-chloronaphthalene	83.7	4.5
	C2	.35	α-chloronaphthalene	83.7	1.7
Atactic	A3	.35	α-chloronaphthalene	81.7	1.2
	A3	.40	diethyl carbitol	113.5	---
	A2	.54	α-chloronaphthalene	81.7	3.0
	* A121	1.56	α-chloronaphthalene	83.8	23.0

* Calculated using α^3 value of 1.06 to correct data at 83.8°C.

Table 6

Intrinsic viscosities of polybutene-1 in α-chloronaphthalene

Isomer	Fraction	Temperature (°C)	(η) (dl./g)	k_1	k_2
Atactic	A2	81.5	0.54	1.06	-.40
		85.9	0.61	.68	-.10
		90.9	0.63	.74	-.13
		96.1	0.70	.48	.14
		100.9	0.72	.51	.04
Isotactic	C5	85.1	0.58	.48	.06
		95.2	0.65	.57	.00
		105.7	0.70	.57	.00
		115.6	0.75	.55	.02
	C4	87.3	0.61	.93	-.24
	C2	87.3	0.36	.97	-.30

D. Conclusions

Values of the molecular expansion (α) in n-nonane at 80° were calculated from measurements made at the theta temperature in α-chloronaphthalene and at 80°C in n-nonane according to the expression $\alpha^3 = [\eta]/[\eta]_\Theta$. These results are shown in Table 7 and indicate α^3 increases in magnitude with molecular weight as expected from theory. The molecular expansion factor (α) is larger for the isotactic isomer in n-nonane (when comparing equal molecular weights) since it is observed that $[\eta]_\Theta$ is less for the isotactic form but the Mark-Houwink expression in n-nonane is the same for both isomers.

According to equation (4v), the quantity $(\alpha^5 - \alpha^3)/M^{1/2}$ should be independent of molecular weight. Values of this quantity are exhibited in Table 7 and appear to increase with increasing molecular weight. A similar increase in the quantity $(\alpha^5 - \alpha^3)/M^{1/2}$ with increasing molecular weight has been observed for the polystyrene-benzene system[36]. Orofino and Flory[42] have proposed a refinement to the theoretical expression of Fox and Flory which accounts for this observation. They have pointed out that the original relationship, 4v, can be made more generally applicable by the addition of a term involving a higher order thermodynamic interaction parameter, χ_2. Inclusion of this parameter, which is a function of the molecular weight, results in a variation of $(\alpha^5 - \alpha^3)/M^{1/2}$ with molecular weight.

Also, according to equation 4v, the function $(\alpha^5 - \alpha^3)/M^{1/2}$ should vary in a linear fashion with 1/T. The value of α depends on the intensity of the thermodynamic interaction as expressed by $\psi_1(1 - \Theta/T)$, which is equal to $\psi_1 - \kappa_1$. If the expansion factor (α) is sufficiently large over the temperature range used, an accurate evaluation of $\alpha^5 - \alpha^3$ can be made. If the theory holds, then evaluation of the slope and intercept of a plot of $(\alpha^5 - \alpha^3)/M^{1/2}$ versus 1/T should yield ψ_1 and κ_1. These values then may be compared to the values obtained from phase equilibrium studies.

Table 7

Expansion factor values in n-nonane at 80°C

Isomer	Fraction	$M_w \times 10^{-4}$	α^3	$\alpha^5 - \alpha^3$	$\left(\frac{\alpha^5 - \alpha^3}{M_w^{1/2}}\right) \times 10^3$
Atactic	A2	30	2.7	2.5	4.6
	A3	12	2.0	1.2	3.5
Isotactic	C5	49	3.6	5.0	7.2
	C4	45	3.5	4.8	7.1
	C2	17	2.6	2.6	6.2

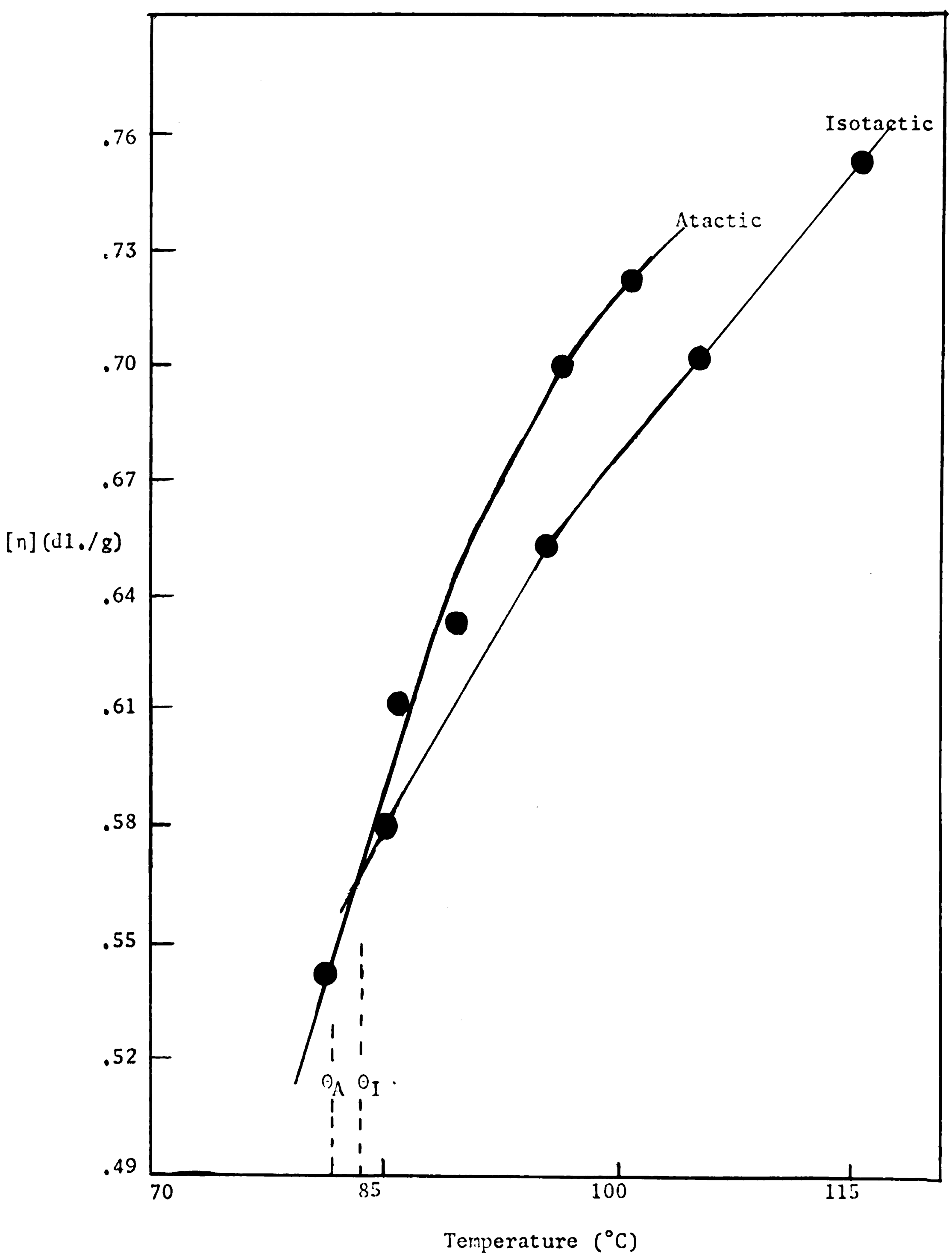

Figure 2. Variation of [η] in α-chloronaphthalene near theta point for isotactic fraction C5 and atactic fraction A2.

The constant C_M in equation 5v contains the quantity, $(\overline{r_0^2}/M)^{3/2}$, which may vary with temperature. Values of $(\overline{r_0^2}/M)^{3/2}$ for polybutene-1, obtained at different temperatures in various theta solvents, are given in Table 8 and permit $(\overline{r_0^2}/M)^{3/2}$ to be corrected for temperature.

Intrinsic viscosities obtained in α-chloronaphthalene for both isomers at various temperatures are presented in Figure 2 and collected in Table 6. The corresponding values of α^3 are given in Table 9.

The uncertainty involved in calculating $\alpha^3(\alpha^2 - 1)$ was estimated for each individual temperature by allowing a 3% error in individual intrinsic viscosity results. Values of the quantity $\alpha^2 - 1$ appear in Table 9. The data indicate that the expansion of polybutene-1 in α-chloronaphthalene is of such small magnitude in the temperature range used here as to preclude evaluation of ψ_1 and κ_1 from intrinsic viscosities and inference of differences between isomers is not justified.

These low values obtained for α^3 indicate that (η) values taken two or three degrees removed from the theta temperature are essentially the same as $(\eta)_\Theta$. Thus the (η) value for C5 and 85.1°C as shown in Figure 2 was taken to be $(\eta)_\Theta$.

The first derivative $(d(\eta)/dT)$ obtained from figure 2 is positive as expected from equation 4v and the fact that Θ is positive. The variation of $d(\eta)/dT$ with temperature appears to be greatest in the vicinity of the theta point as predicted by equation 4v.

Table 8

Calculated $(\bar{r}_o^2/M)^{1/2}$ values at various temperatures

Isomer	Fraction	Temp(°C)	$*10^{10}(\bar{r}_o^2/M)^{1/2}$	$*10^{10}(\bar{r}_o^2/M)^{1/2}$
Isotactic	C5	83.7	72.9	
	C4	83.7	72.9	73.1
	C2	83.7	73.5	
	C5	99.6	72.0	72.0
Atactic	A3	81.7	78.8	
	A2	81.7	77.0	78.2
	A121	81.7	78.8	
***Isotactic	B2-121	89.2	86	
	B6-2	89.2	81	84
***Atactic	AB-11	86.2	87	
	AB-12	86.2	76	
	AB-122	86.2	77	80
**Atactic	RR4222	23.0	81.1	
	R322	23.0	81.6	
	R4222	23.0	81.1	
	R52	23.0	80.8	81.4
	R63	23.0	81.5	
	R82	23.0	82.1	
	R83	23.0	81.6	

* $\bar{r}_o^2$ is given in units of cm.^{2}

** Data taken from reference 43 ($(\eta)_\Theta$ data taken in iscamyl acetate)

*** Data taken from reference 13 ($(\eta)_\Theta$ data taken in anisole)

E. Discussion

A comparison can be made between the unperturbed end-to-end dimensions for the two isomers through the use of intrinsic viscosity data at

Table 9

Functions of expansion factor (α) for two stereoisomers near theta temperature in α-chloronaphthalene

Isomer	Fraction	α^3	$\alpha^2 - 1$	Temp.(°C)
Atactic	A2	1.12±.07	.08±.07	85.9
		1.17±.07	.11±.07	90.9
		1.28±.08	.18±.08	96.1
		1.33±.08	.21±.08	100.9
Isotactic	C5	1.13±.07	.09±.07	95.2
		1.22±.07	.14±.07	105.7
		1.31±.07	.17±.07	115.6

the theta point. Within experimental error the established intrinsic viscosity-molecular weight relationship for isotactic and atactic fractions in α-chloronaphthalene at the theta point is $(\eta) = KM^{1/2}$. A graph of this data appears in Figure 3 in the form of log $(\eta)_\Theta$ versus log M_w. From equation 7v a value can be obtained for $(\bar{r}_o^2/M)^{1/2}$ by knowing $(\eta)_\Theta$ and $M^{1/2}$. Values of $M^{1/2}$ were obtained from a Mark-Houwink expression for atactic polybutene-1 in benzene at 30°C published by Natta[43] and for isotactic polybutene-1 in n-nonane from a relationship established by Krigbaum et. al.[13] and confirmed in this laboratory. Intrinsic viscosities measured for both isomers in α-chloronaphthalene at their respective theta temperatures are presented in Table 5. Values of $(\bar{r}_o^2/M)^{1/2}$ calculated from intrinsic viscosity measurements in different solvents under theta conditions are shown in Table 8.

These ratios of $(\bar{r}_o^2/M)^{1/2}$ obtained from significantly different theta conditions for atactic polybutene-1 appear to be nearly independent of the solvent and of the temperature. The data available for isotactic polybutene-1

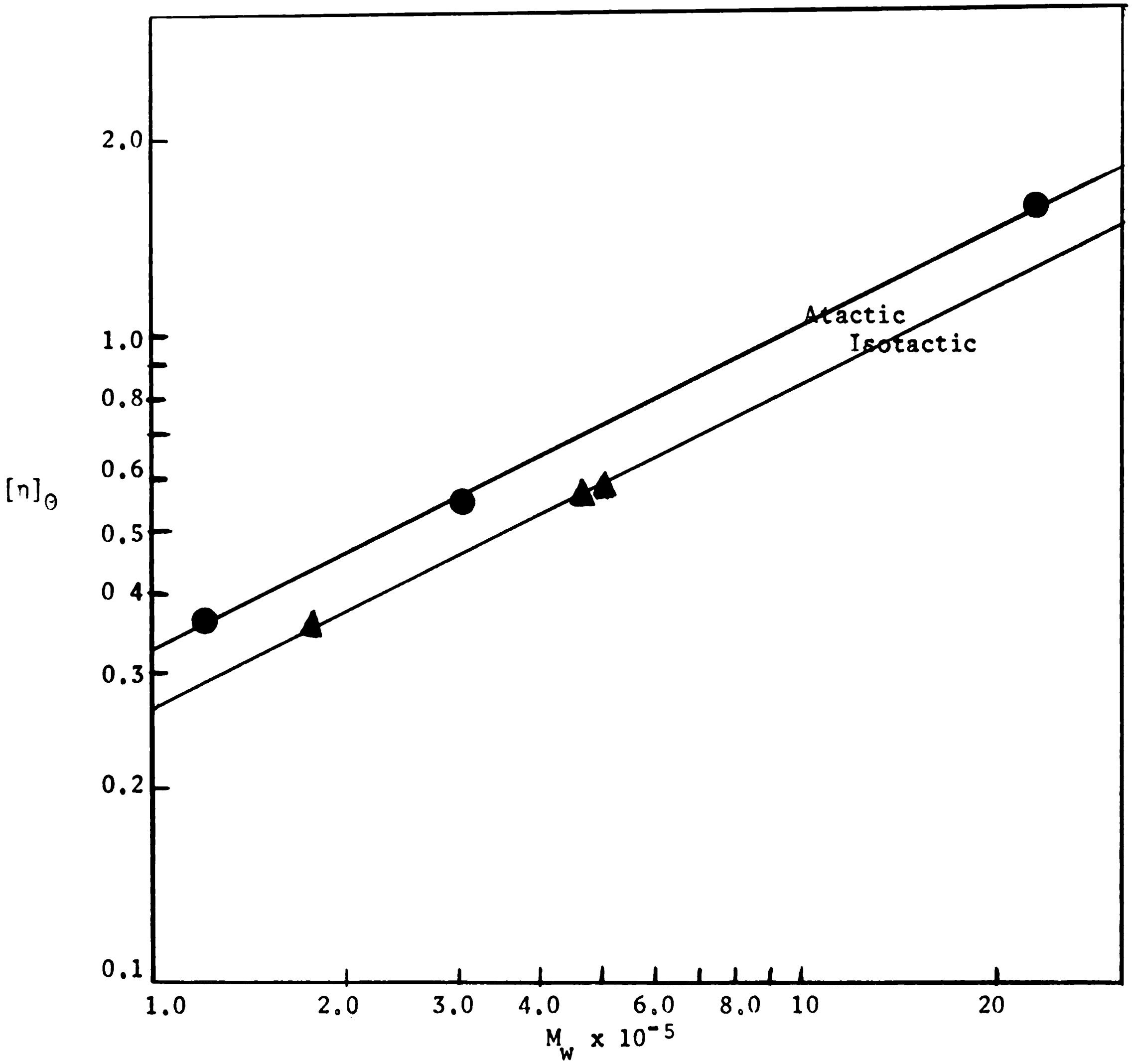

Figure 3. Double logarithmic plot of $[\eta]_\Theta$ against M_w for three fractions each of isotactic and atactic polybutene-1.

are not sufficient to establish reliable comparisons of $(\overline{r}_o^2/M)^{1/2}$ in different theta solvents. However, calculated ratios of $(\overline{r}_o^2/M)^{1/2}$ for the isotactic form do appear to vary considerably. This behavior may represent a specific influence of the theta solvent on the restrictions to rotation about the valence bonds of the polymer chain.

Examination of unperturbed dimensions in this manner has revealed an interesting and perhaps significant feature. Krigbaum[13] has reported unperturbed dimensions of isotactic polybutene-1 which appear to be larger than those of atactic polybutene-1.

The data of Krigbaum[13] were obtained from light scattering measurements performed in a good solvent where thermodynamic interaction occurs. It is necessary to account for this interaction through the use of the second virial coefficient. Second virial coefficients obtained in the above study[13] exhibited considerable scatter due to high temperature experimental difficulties and were not plotted. Perturbed dimensions were converted to unperturbed dimensions using a statistical thermodynamic treatment. The polymer chain was assumed to have a random coil conformation.

Unperturbed dimensions in the present study were obtained using a value of Φ of 2.1×10^{21} for both isomers. The use of equation 8v is based on hydrodynamic theory assuming a random coil conformation[17,44].

It has been suggested from light scattering and osmotic pressure data obtained for the somewhat similar stereoisomers of polypropylene[11], that isotactic and atactic polypropylene do adopt a random coil conformation. The type of conformation polybutene-1 adopts in dilute solutions has not been established, however.

A possible theoretical explanation for the above-mentioned results was considered; however, at present the number of parameters required

to establish the end-to-end dimensions from conformational theory are too numerous to permit a comparison with experiment. The calculation of dimensions for an atactic vinyl-like polymer chain for example requires more parameters than are available from the experimental data[45].

Since the various samples used in these two studies come from different sources it is of interest to speculate on the possible relationship of the degree of tacticity to the unperturbed dimensions. To examine this, consider the possible stereoisomers; the syndiotactic and isotactic isomers are the limiting stereoregular forms and the atactic isomer lies between these limits. As the degree of tacticity varies from an isotactic to a syndiotactic polymer chain, corresponding unperturbed dimensions* may exhibit maxima and/or minima. If the isotactic polymer chain were smaller than the syndiotactic polymer chain the occurrence of a minima in the variation of $\overline{r_0^2}$ with tacticity would allow the measured relationships of isotactic and atactic to be consistent. If, however, the syndiotactic polymer chain were smaller than the corresponding isotactic polymer chain, then the difference shown in the two sets of data could be explained by the occurrence of a maxima in the variation of $\overline{r_0^2}$ with tacticity.

* No comparison of unperturbed dimensions for isotactic and syndiotactic polybutene-1 has appeared to date in the literature.

IV. PHASE EQUILIBRIA

A. Theory[17]

As the critical miscibility temperature for a polymer of infinite molecular weight is approached, the excluded volume (a result of long range segment-segment interaction) of a polymer molecule decreases. Finally, at the theta temperature, the excluded volume becomes zero and the dilute solution theory, which takes account of the inherent nonuniformity of the polymer segment concentration, converges to the general theory of polymer solutions. Consequently, it is legitimate to use the simpler general solution theory for treatment of liquid-liquid phase equilibria at Θ.

The condition that the Gibbs free energy of a closed system be a minimum at a given temperature and pressure can be used to obtain conditions for the phase relationships of a two component phase. The binary system studied here consists of a solvent and a polymer characterized by the ratio of the molar volumes of polymer and solvent (denoted by x).

In the Flory-Huggins original derivations it is assumed that the entropy of mixing in any polymer solution can be equated to the conformational entropy of mixing. Any possible influence of the energies of interaction on the entropy of mixing is neglected.

The entropy of mixing of n_1 moles of solvent with n_2 moles of polymer is, accordingly, $\Delta S_M = -R(n_1 \ln v_1 + n_2 \ln v_2)$ (1p)

where n_1 and n_2 are the number of moles of solvent and solute and

$\left(v_1 = \frac{n_1}{n_1+xn_2}\right)$ and $\left(v_2 = \frac{xn_2}{n_1+xn_2}\right)$ are the volume fractions of solvent and solute.

When polymer and solvent molecules are mixed there is a non-vanishing heat of mixing due to the interaction of unlike species. Flory[46] expressed the heat of mixing of n_1 moles of solvent and n_2 moles of polymer as,

$$\Delta H_M = RT\ \chi_1 v_1 v_2 (n_1 + xn_2) \qquad (2p)$$

where χ_1 is a dimensionless quantity which characterizes the interaction energy per solvent molecule, divided by kT, in analogy to the Van Laar-Hildebrand-Scratchard expression for molecules of equal size.

Combining equations (1p) and (2p) the free energy of mixing may be obtained. Thus,

$$\Delta F_M = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 n_1 v_2) \qquad (3p)$$

The chemical potential μ_1, of the solvent relative to its chemical potential μ_1^o, in the pure liquid state is obtained by differentiating the free energy of mixing, ΔF_M, with respect to the number n_1 of moles of solvent. Then

$$\mu_1 - \mu_1^o = RT[\ln(1-v_2) + (1-1/x)v_2 + \chi_1 v_2^2] \qquad (4p)$$

Differentiation of equation (3p) with respect to n_2 gives the chemical potential μ_2 of the polymeric solute relative to the pure liquid polymer as standard state. Thus

$$\mu_2 - \mu_2^o = RT[\ln v_2 - (x-1)(1-v_2) + \chi_1 x(1-v_2)^2] \qquad (5p)$$

The conditions for equilibrium between two phases in a binary system are expressed by setting the chemical potentials in the two phases equal; that is,

$$\mu_1 = \mu_1' \qquad (6p_1)$$

$$\mu_2 = \mu_2' \qquad (6p_2)$$

where the prime denotes the more concentrated phase. Fulfillment of $(6p_1)$ requires that there be two concentrations at which the chemical potential μ_1 has the same value, and this requires that μ_1 pass through a minimum and then a maximum as v_2 is increased from zero to unity. Similarly in order to comply with $(6p_2)$, μ_2 must exhibit a maximum and a minimum. Since μ_1 and μ_2 (see equations (4p) and (5p)) were both derived by differentiating the same free energy function, it can be shown that the one must pass through a maximum where the other is a minimum, hence it will suffice to consider either chemical potential alone. A point of inflection, characterized by the condition of zero curvature

$$\left(\frac{\partial^2 \mu_1}{\partial v_2^2}\right)_{T,P} = 0 \tag{7p}$$

must necessarily occur between the minimum and the maximum in the curve. At both the minimum and maximum

$$(\partial\mu_1/\partial v_2)_{T,P} = 0 \tag{8p}$$

These characteristics in the function representing μ_1 constitute the necessary and sufficient conditions for incomplete miscibility. Equations (7p) and (8p) are satisfied simultaneously at the critical points, and, conversely, equations (7p) and (8p) determine the critical points.

Applying these critical conditions by differentiating the chemical potential of the solvent with respect to v_1 from equation (4p) we obtain

$$1/v_1 - (1 - 1/x) - 2\chi_1 v_2 = 0 \tag{9p}$$

and

$$1/v_1{}^2 - 2\chi_1 = 0$$

Denoting critical values with a subscript c, we obtain

$$v_{2c} \cong 1/(1 + x^{1/2}) \tag{10p}$$

$$\chi_{1c} = (1 + x^{1/2})^2/2x \tag{11p}$$

Flory[17] has shown that it is possible to relate χ_1, the free energy parameter, to the heat of dilution parameter, κ_1, and ψ_1 the entropy of dilution parameter, where κ_1 and ψ_1 are defined by the relationships of partial molar enthalpy and entropy

$$\overline{\Delta H}_1 = RT\kappa_1 v_2^{\,2} \tag{12p}$$

$$\overline{\Delta S}_1 = R\psi_1 v_2^{\,2} \tag{13p}$$

The relationship obtained by Flory is,

$$\kappa_1 - \psi_1 = \chi_1 - 1/2 \tag{14p}$$

It is frequently useful to define another parameter, the "ideal" temperature, Θ*, in order to express this relationship. It is defined as

$$\Theta = \kappa_1 T/\psi_1 \tag{15p}$$

From this, it follows that

$$\chi_1 - 1/2 = -\psi_1(1-\Theta/T). \tag{16p}$$

Under critical conditions, using equation 11p, we may write

$$-\psi_1(1-\Theta/T_c) = 1/x^{1/2} + 1/2x \tag{17p}$$

or

$$1/T_c = (1/\Theta)\left[1 + (1/\psi_1)(1/x^{1/2} + 1/2x)\right] \tag{18p}$$

Both Θ and ψ_1 can be evaluated experimentally from the linear relationship between the critical temperature and x as expressed in (18p).

The interaction parameters are characteristic of the non-ideal behavior of polymer solutions, but their molecular significance has not been determined, theoretically. Flory assumes that the same parameters describe both inter- and intra-molecular interactions[17], but Huggins[47] has pointed out that inter- and intra-molecular interactions may give rise to different entropy parameters.

The effect of stereoregularity on the interaction parameters has not been explicitly expressed in the theory; therefore this effect must be postulated in an indirect and qualitative manner.

* The "ideal" temperature, Θ, is identical with the theta temperature referred to earlier (footnote, page 2) in this thesis.

B. Solubility Studies

Several solvents were examined to assess their usefulness as theta solvents. To conduct theta point light scattering studies, two requirements were imposed; the solvent should give liquid-liquid phase separations near room temperature, and it should have a refractive index value as far removed from the polymer value as possible. A theta point near room temperature (or not more than 20°C above) substantially reduces the necessity to perform high temperature light scattering. The greater the value of dn/dc, the specific refractive increment, the more likely the data will be reproducible. A value for dn/dc of .08 ml./g. or greater was sought. It was further necessary that the solvent be sufficiently non-volatile, inert and stable to yield reproducible solution phase separation temperatures.

Preliminary tests were made with 1% mixtures of isotactic polymer samples, primarily fraction B10. An approximate value of the precipitation temperature and the mode of phase separation was determined. When liquid-liquid phase separation occured, the precipitation temperatures were reproducible, but this was not the case for liquid-crystalline separation. When liquid-crystalline separation occured, the precipitate formed by cooling would not dissolve until the temperature was raised from 5° to 20° above the endpoint; cooling slightly below the point at which the precipitate dissolved would not induce phase separation. The results of these tests are listed in Appendix B. From these tests α-chloronaphthalene was selected for phase equilibrium studies.

C. Experimental

Experimental methods for determining precipitation temperatures for a polymer-solvent system have been thoroughly described by Shultz and Flory[48].

Experimental conditions used for the α-chloronaphthalene-polybutene-1 system were largely adapted from one method described by these authors.

Solutions were weighed on the analytical balance and prepared in 4 inch Pyrex test tubes. Each test tube was stoppered and was equipped with a stirring rod of nichrome wire. Temperature of the solutions was varied by suspending the different fractions in a controlled thermostat. A thermometer calibrated to 0.1°C was used to record bath temperatures.

Light from a 100 watt bulb shining through a window in the insulation provided adequate illumination of solution turbidity. A light path oriented 90° from the line of observation afforded the best view. A white paper, cross-hatched with sharp black lines, placed at a bath window directly behind the solutions provided a suitable background for viewing the haziness characteristic of incipient phase separation for all atactic solutions. For all isotactic solutions this background was provided by wrapping a wire ring about the test tube and extending the wire in a vertical line the length of the tube. This background modification resulted from difficulty in viewing incipient phase separation in fraction C9 due to the presence in this fraction of a small amount of highly refractive, insoluble impurity. Unlike the other fractions, fraction C9 was obtained, as previously described, in part by extracting the Celite support with hot xylene and filtering the extract through a coarse-grade sintered-glass filter. It was believed that this may have resulted in the retention of a few extremely fine particles of Celite in the polymer fraction.

First concentrations were prepared by weighing approximately 100 milligrams of polymer fraction, in 1 gram of solvent. Subsequent concentrations were formed by dilution. Dilution was continued beyond the experimentally determined critical volume fraction to obtain 3 or 4 additional points on the phase diagram. To account for changes due to evaporation, the concentration of atactic samples was obtained as follows: after each precipitation temperature was measured, the sample tube was withdrawn, the oil carefully removed, and the tube weighed before addition of solvent. The amount of solvent added was measured by the difference in weight of the test tube. The small concentration correction for solvent evaporation (α-chloronaphthalene has a very low vapor pressure even at 80°C) did not justify this laborious procedure. Accordingly, solutions of isotactic samples were diluted by use of a syringe which could be weighed more conveniently.

Precipitation temperatures were determined, visually, by the following procedure: the bath temperature was lowered at a rate of about 1°C per minute until the solution appeared turbid; the temperature was then raised until the solution cleared. The temperature was then lowered at a slower rate (about 0.3°C per min) until the endpoint was reached. Incipient phase separation started 0.5 - 3.0°C above the actual endpoint. The endpoint was taken as the temperature at which the greatest change in turbidity occured.

The specific volumes of the two isomeric polymer forms were computed from dilatometric data reported by Natta[49]. Density-temperature relationships for α-chloronaphthalene were obtained from a density-temperature plot made by Fuchs[41].

D. Data and Results

Temperatures at which precipitation occurs upon cooling α-chloronaphthalene solutions are collected in Table 1 and Table 2 of Appendix C and are shown in Figures 4 and 5 for four isotactic and four atactic polybutene-1 fractions. Abscissa values express the concentration as volume fraction of polymer. Volume fraction values were obtained from weight fraction values by assuming negligible volume changes on mixing; hence $v_2 = (W_2V_{sp})/(W_1/d_1 + W_2V_{sp})$ where the specific volume and density values were taken at the precipitation temperature. Precipitation temperatures were reproducible to $\pm$.3°C and were independent of the cooling rate. The scatter exhibited for the lowest volume fraction of both samples A2 and A3 was attributed to experimental error. As may be seen in the phase diagrams for these two fractions, this scatter does not affect the value obtained for the critical temperatures. Consequently these points were not re-examined. Maxima in the phase diagrams (Figures 4 and 5) correspond to critical solution temperatures for various polymer fractions. These phase diagrams for both forms of polybutene-1 in α-chloronaphthalene exhibit quite pronounced slopes in contrast to phase diagrams for both isomers of polybutene-1 in anisole[13]. Such behavior indicates, with respect to polybutene-1, that the solvent power of α-chloronaphthalene varies more with temperature than does the solvent power of anisole.

Table 10

Critical data for atactic and isotactic polybutene-1 in α-chloronaphthalene

Isomer	Fraction	T_c (°K)	x
Atactic	A121	351.5	20,000
	A122	350.6	11,870
	A2	345.4	2,633
	A3	341.5	1052
Isotactic	C9	353.4	4513
	C4	352.9	3936
	C3	351.5	3250
	C2	350.3	1523

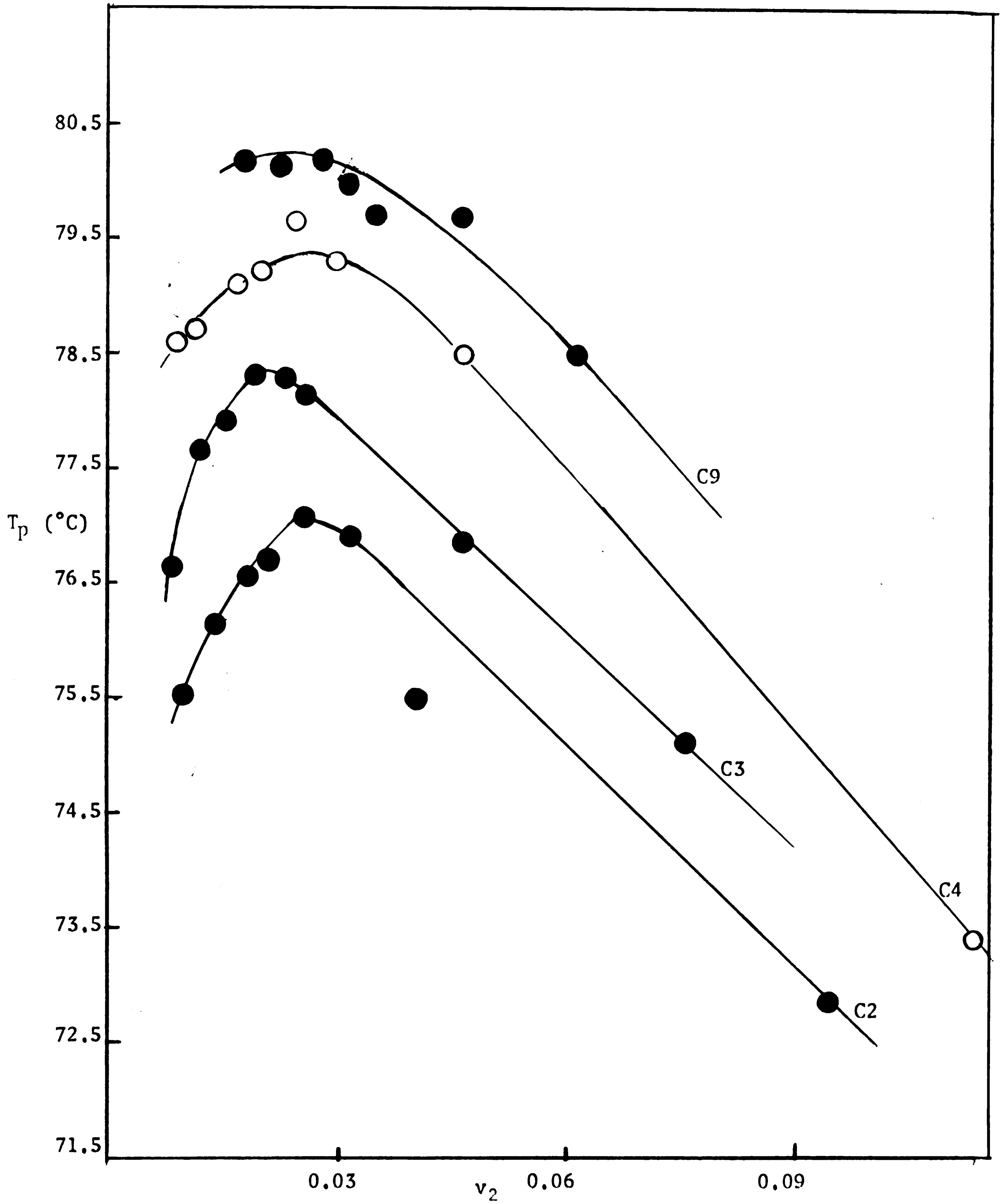

Figure 4. Phase diagrams of isotactic polybutene-1 in α-chloronaphthalene.

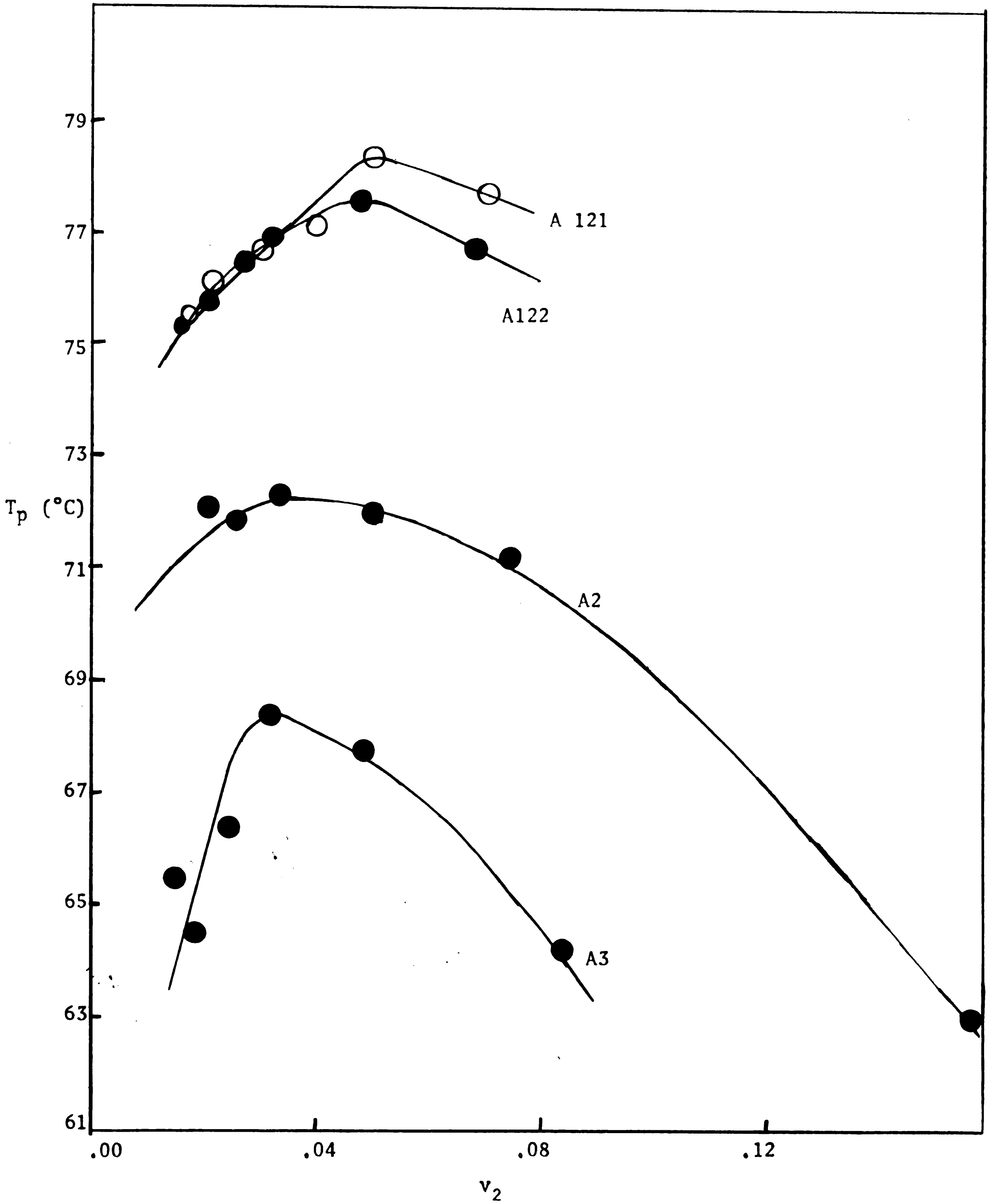

Figure 5. Phase diagrams of atactic polybutene-1 in α-chloronaphthalene.

The critical data for atactic and isotactic polybutene-1 are summarized in Table 10. Values of x, the ratio of molar volumes of polymer and solvent were calculated from $x = M.W.\ \bar{v}/V_1$ where V_1 is the molar volume of the solvent, M.W. is the polymer molecular weight and $\bar{v}$ is the specific volume of the polymer. The values of $\bar{v}$ were taken at the critical temperature.

Reciprocals of the critical temperatures are plotted against the function $[\frac{1}{x^{1/2}} + \frac{1}{2x}]$ in Figure 6 according to equation. As predicted by theory, both isomers exhibited linear plots within experimental error. The best slope and intercept were obtained by the method of least squares. As expressed in equation 18p, the intercepts of the two lines in Figure 6 represent values of Θ. Entropy of dilution parameters, ψ_1, according to equation 18p can be calculated from the slopes of the lines.

Both the slopes and intercepts of these lines are different for the two stereoisomers. This results in a difference in the thermodynamic interaction parameters for the two forms. For comparison of the two isomeric forms these interaction parameters appear in Table 11.

Table 11

Thermodynamic interaction parameters in α-chloronaphthalene

Isomer	Θ (°C)	ψ_1
Isotactic	83.7	1.3442
Atactic	81.7	0.7486
Difference	2.0	0.5956

Heat of dilution parameters, κ_1, in α-chloronaphthalene as defined in equation 12p may be obtained from equation 15p for both isomers. For a given system at a fixed temperature, κ_1, depends only on Θ and ψ_1.

According to theory (equation 16p) the temperature dependence of χ_1 can be obtained from the interaction parameters. For the α-chloronaphthalene system $\chi_1 = -.844 + 479.5(1/T)$ for isotactic polybutene-1 and $\chi_1 = -.249 + 266.6\ (1/T)$ for atactic polybutene-1. These functions are plotted in Figure 7.

Values of χ_1 at various temperatures are collected in Table 12.

Table 12

Calculated values of the Flory-Huggins interaction parameter for the system α-chloronaphthalene-polybutene-1

Isomer	Temp. (^{o}A)	χ_1
Isotactic	1000	-0.365
	500	+0.115
	355	+0.505
	333	+0.595
	250	+1.075
Atactic	1000	+0.017
	500	+0.283
	355	+0.505
	333	+0.549
	250	+0.814

A comparison of various solvent systems for both isomers can be made by reference to Table 13 where published values of Θ and ψ_1 appear for polybutene-1 in these systems.

E. Discussion

Although the values of χ_1 are for a polymer of infinite molecular weight, they may be used for comparison purposes of the two isomers for any molecular weight. This parameter which expresses the interaction energy, divided by kT, for solvent with polymer can be interpreted as a measure of

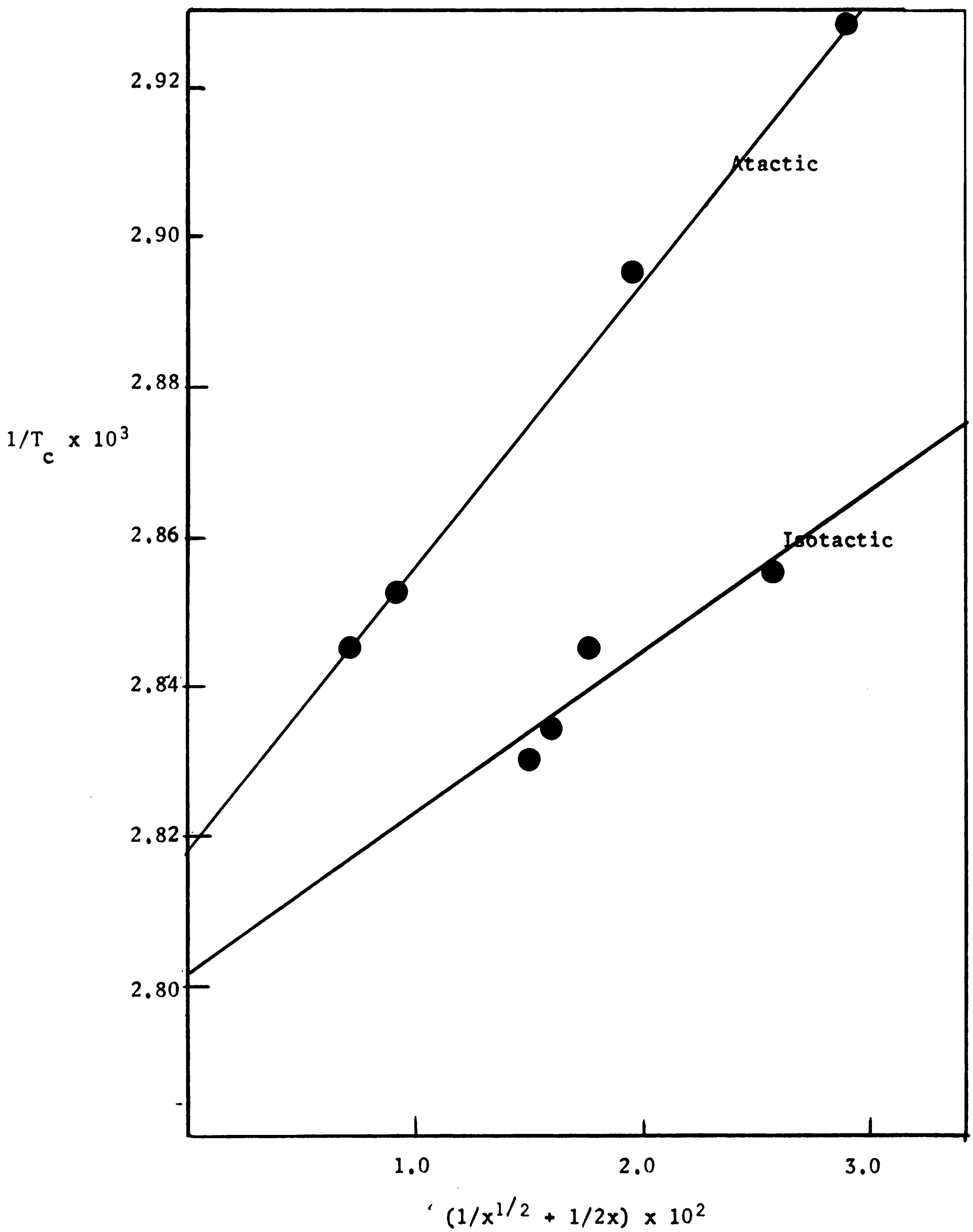

Figure 6. The dependence of T_c on x for the system α-chloronaphthalene.

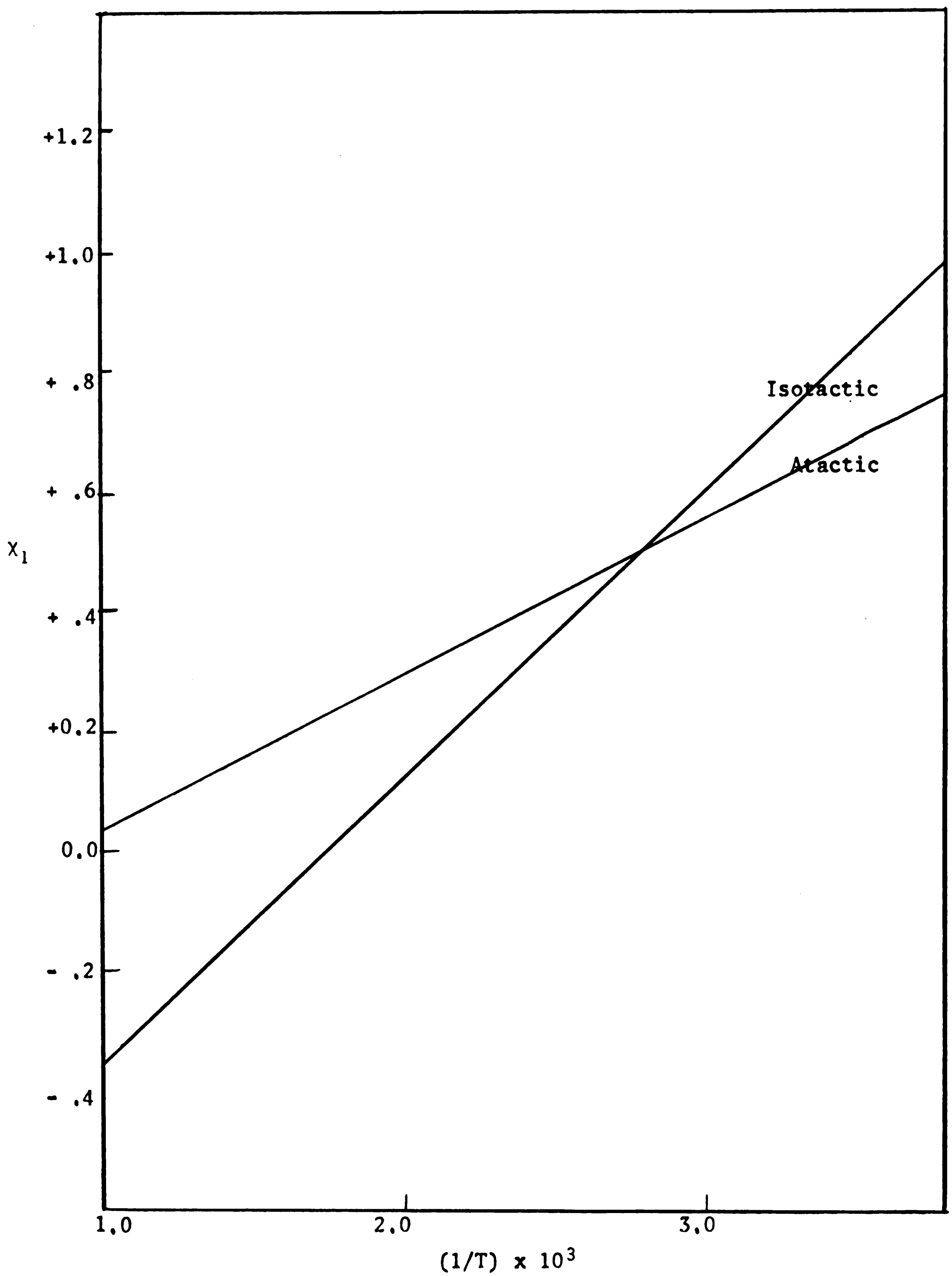

Figure 7. The dependence on temperature of the Flory-Huggins interaction, χ_1, parameter for the system polybutene-1 α-chloronaphthalene.

Table 13

Comparison of thermodynamic parameters for polybutene-1 and polypropylene

Isomer	Theta Solvent	Θ (°C)	ψ_1
Isotactic polybutene-1	α-Chloronaphthalene	83.7	1.344
Atactic polybutene-1	α-Chloronaphthalene	81.7	0.749
Difference		2.0	0.595
[1]Isotactic polybutene-1	Diethyl carbitol	98.5	0.941
Atactic polybutene-1	Diethyl carbitol	113.5	0.458
Difference		-15.0	0.483
[1]Isotactic polybutene-1	Butyl Cellosolve	187.2	0.203
Atactic polybutene-1	Butyl Cellosolve	198.1	0.308
Difference		-10.9	-0.105
[2]Isotactic polybutene-1	Anisole	89.1	0.956
Atactic polybutene-1	Anisole	86.2	0.740
Difference		2.9	0.216
[3]Isotactic polypropylene	Phenyl ether	145.2	1.414
Atactic polypropylene	Phenyl ether	153.3	0.986
Difference		-8.1	0.428

[1]Data taken from reference 18

[2]Data taken from reference 13

[3]Data taken from reference 14

solubility. Therefore some statement can be made about the relative solubilities of the two stereoisomers.

Consider the dependence of χ_1 on temperature as given in Figure 7. At temperatures above the point of intersection which corresponds to 82°C, isotactic polybutene-1 is the more soluble and below it the less soluble. This is a hypothetical situation, of course, since the solubility at any temperature is a function of the molecular weight.

The heat of dilution parameter, κ_1, is positive for both isomers in α-chloronaphthalene as is expected in poor solvents. In an ideal solution, the heat of mixing is zero; consequently κ_1 can be used as a measure of deviation from ideality. Since isotactic polybutene-1 has a larger κ_1 value its solution behavior can be considered to be less ideal than that of the atactic modification. The heat of dilution parameter is proportional to the energy associated with segment-solvent interaction. The difference in segment-solvent interaction shown to result here from macromolecules of different stereochemical structure suggests the use of the parameter, κ_1, as a quantitative measure of the stereoregularity.

A knowledge of both the conformation and configuration of the polymer chain is required to correlate polymeric structure with thermodynamic parameters. The heat of dilution is dependent on both the configuration (d or l placement) and conformation (roughly, the orientation of the backbone chain). Any correlation of the influence of configurational differences upon κ values requires some knowledge of the conformation assumed by the polymer chain (e.g. random coil model, planar zig-zag model, etc.). The present state of knowledge about the conformation assumed by a polymer in a dilute solution is limited. Radii of gyration obtained from light scattering data permit a knowledge of overall molecular structure (e.g. random coil, rigid rod, solid sphere, etc.) but at present no known experimental method gives a picture of the detailed conformation or microstructure of the polymer segments.

Values of ψ_1, the entropy of dilution parameter, obtained in α-chloronaphthalene show a difference between the stereoregular and random polymers.

A rather unexpected feature of the thermodynamic behavior of the stereoisomers, as expressed by the entropy of dilution parameter, was discovered in the course of this work. This aspect is the unusual comparison that can be made between different solvents in which phase studies of isotactic and atactic polybutene-1 have been made.

To examine the role of solvent in these studies, results obtained in various theta solvent systems from various laboratories are compared in Table 13. The results are all in agreement on one point, i.e., that differences are observed between the stereoregular and random polymers. A further conclusion is that the thermodynamic interaction parameters are dependent on the solvent. The solvent used must therefore be considered in any comparison of ψ_1, values between the isomers. The effect of solvent influence is especially highlighted by the observation that the isotactic modification does not exhibit a higher entropy parameter than the atactic form in all cases. The various aspects emphasized by these data illustrate some complications posed by macromolecule-solvent systems in contrast to monomer-solvent systems. To consider the increase in entropy which results from decreasing the segment concentration in any given volume element of the system, a liquid lattice model may be used in both the macromolecule-solvent system and the monomer-solvent system to derive a statistical expression for the entropy of mixing. In this model the solution has a structural arrangement approximated by a lattice. To derive an expression for the entropy of mixing, a solvent molecule and a solute molecule (for monomers) or a segment (for macromolecules) being of virtually the same size, are allowed to replace one another in the liquid lattice. The polymer solution differs from that containing an equal proportion of monomeric solute in that sets of contiguous cells in the lattice are required to accommodate the segments of a polymer molecule, whereas no such restriction applies to the monomeric solute. This difference between the two types of systems must be recognized in considering the results expressed by the entropy parameters.

If the entropy parameter represents the "drive" of the polymer chain to achieve a random conformation, then for the α-chloronaphthalene-polybutene-1 system it appears that the isotactic isomer has a greater tendency to achieve randomness than does the atactic form. It seems reasonable that this "drive" toward "randomness" would be different for two polymer chains of different configuration in a given solvent. It seems logical, too, that the entropy for the process of forming a dilute polymer solution would be dependent on the solvent. In attempting to achieve a state of "randomness" a certain ordering will always be present because of the contiguous nature of the polymer segments. This partial ordering will be affected by both the segment-segment and segment-solvent interaction, hence it is concluded that the entropy parameter will be solvent dependent. These conclusions are consistent with the data.

It might be expected that the above-mentioned "drive" toward "randomness" which is greater for the isotactic form than for the atactic isomer in α-chloronaphthalene would be greater for the isotactic form in any solvent. Such is not the case as exhibited by the smaller entropy parameter for isotactic polybutene-1 in butyl cellosolve. The conclusion drawn is that, for the two stereoisomers, the effect of segment-segment interactions (which are inherently of the same relative order of magnitude in the dilution process) is overshadowed by the effect of the solvent-segment interactions. Further, the solvent-segment interaction seemingly depends quite strikingly on the stereospecific nature of the polymer.

Such data suggest a study of the role of solvent in future phase studies of polybutene-1. It is interesting to note for the particular solvent (butyl cellosolve) in which $\psi_{\text{isotactic}} < \psi_{\text{atactic}}$, that the theta point is considerably higher than for the other solvents. The conclusion which is suggested here is that the thermal motion of the molecules, which should be greater at a higher temperature, is also a factor in entropy considerations.

The possible dependence of ψ_1 on the degree of tacticity was also considered. (It should be recognized that polymers of different origin used in different laboratories most likely have a different degree of tacticity.) In the foregoing discussion it has been implied that in progressing from one stereospecific extreme to the other (syndiotactic to isotactic) the value of ψ_1 should either increase or decrease in a monotonic fashion. It can be speculated that the value of ψ_1 may instead exhibit maxima and minima in going from a syndiotactic to a completely isotactic case. The data referred to in Table 13 were examined more closely to see if ψ_1 seemed to indicate such behavior. Data obtained in two different solvents for identical atactic fractions show a different relative order of magnitude in comparing ψ_1 values of the two isomers.

Thus, either ψ_1 does not exhibit maxima or minima as the degree of tacticity is varied, or if such an effect is present, it probably is a comparatively minor factor in governing the relative order of magnitude of ψ_1 exhibited by the stereoisomers.

V. LIGHT SCATTERING

A. Theory[17,30]

A theory of light scattering was originally derived by Rayleigh for the case of isotropic particles whose dimensions are small compared to the wavelength, λ, of the light. The intensity of light I_θ scattered by a particle through an angle θ depends on the intensity of incident light I_0, the distance r from the scattering volume, and the polarizability α of the particle. For unpolarized light, this relation is

$$R_\theta = I_\theta r^2/I_0 \tag{1s}$$

where:

$$R_\theta = \frac{8\pi^4\alpha^2}{\lambda^4}(1 + \cos^2\theta) \tag{2s}$$

The quantity R_θ is termed the Rayleigh ratio.

In 1944 Debye[50] extended the Rayleigh theory to apply to a solution of macromolecules. In his treatment he indicated how the method of light scattering could lead to an absolute value of the weight average molecular weight $\overline{M}_w$, and under some circumstances give information concerning the size of the polymer molecules in solution.

The polarizability α is related to the optical dielectric constants ε_0 and ε of the solvent and solution respectively, in the following manner: $(4\pi N/V)\alpha = \varepsilon - \varepsilon_0$ where N/V is the number of particles per unit volume. The dielectric constants may be replaced by the squares of the respective refractive indexes of solution and solvent, which yields $\alpha = (V/4\pi N)(\tilde{n}^2 - \tilde{n}_0^2)$. Since the solution is dilute

$$\alpha = (V/4\pi N)c\,(d\tilde{n}^2/dc)_0 = (\tilde{n}_0 c\frac{V}{2\pi N})\,(d\tilde{n}/dc)_0 \tag{3s}$$

where c is the concentration in grams per cc. Noting that $c = NM/N_0V$ where N_0 is Avogadro's number, substituting equation (3s) into (2s), and rearranging terms, we obtain

$$I_\theta/I_0 = (2\pi^2/N_0\lambda^4r^2)\ \tilde{n}_0^{\ 2}\ (d\tilde{n}/dc)_0^2\ (1 + \cos^2\theta)Mc \qquad (4s)$$

The quantity r^2I_θ/I_0, i.e. R_θ, may then be written

$$R_\theta = K(1 + \cos^2\theta)Mc \qquad (5s)$$

where

$$K = 2\pi^2\tilde{n}_0^{\ 2}(d\tilde{n}/dc)_0^{\ 2}/N_0\lambda^4 \qquad (6s)$$

D e b y e preferred to consider the fraction of the light scattered in all directions from the primary beam per cm. of path. A beam of intensity I decreases, due to scattering, by the amount τIdx in traveling the distance dx through the solution of turbidity τ. After traveling a distance x, the incident beam will have been reduced from the initial intensity I_0 to I, where $I/I_0 = e^{-\tau x}$, or, since the reduction in intensity will be extremely small, $\tau x = (I_0 - I)/I_0$. The turbidity may be obtained by integrating the total intensity of radiation scattered in all directions by the N/V particles per unit volume, i.e. $\tau = \int_0^\pi \frac{I_\theta}{I_0} 2\pi r^2 \sin\theta d\theta$.

If I_θ is the intensity which would be observed if intraparticle interference were negligible, then on substituting from equation (4s) for I_θ/I_0 and integrating we obtain for the turbidity

$$\tau = HcM \qquad (7s)$$

where

$$H = \frac{32\pi^3}{3\lambda^4N_0}\tilde{n}_0^2\left(\frac{d\tilde{n}}{dc}\right)_0^2 \qquad (8s)$$

Comparing equation (7s) and (8s) with (5s) and (6s) it can be seen that

$$\tau = \frac{\left(\frac{16\pi}{3}\right)R_\theta}{(1 + \cos^2\theta)} \qquad (9s)$$

Thus either the turbidity or the Rayleigh ratio is readily calculated from the other.

In theory, then, the molecular weight may be calculated from equation (5s) or (7s). In practice, it is not so simple for it is necessary to consider two complications not dealt with so far. One complication is the non-ideal behavior of the solution at finite concentrations. To account for this it is necessary to extrapolate c/τ values obtained at finite concentrations to a $(c/\tau)_0$ value at infinite dilution. The other difficulty arises because polymer molecules in solution often have dimensions which are not small compared with the wavelength of the incident light, as has been assumed in the derivation thus far. In such cases it is necessary to correct for the angular dependence of the intensity of the scattered light.

A derivation due to Debye[50] can be used to treat light scattering by non-ideal solutions at finite concentrations. First, it might be pointed out that the scattering from a solution arises in two parts: that due to density fluctuations which are assumed to be the same as those in the pure solvent and that due to concentration fluctuations which result from the thermal motion of the solute molecules. Debye compares the average thermal energy of the solute with that required to cause a concentration change, i.e. $kT/c(\delta\Pi/\delta c)$ where k is Boltzmann's constant and Π the osmotic pressure. The excess turbidity due to the solute is similar in form to equation (8s):

$$\tau = \frac{32\pi^3}{3\lambda^4}\frac{kT}{c(\partial\Pi/\partial c)}\, n_0^2\, c^2\, (d\tilde{n}/dc)_0^2 \tag{10s}$$

Using the van't Hoff relationship for an ideal solution, $\Pi/c = N_0kT/M$ where M is the molecular weight of the solute, then

$$\tau = \frac{32\pi^3}{3\lambda^4} n_0{}^2 \left(\frac{d\tilde{n}}{dc}\right)_0^2 \frac{Mc}{N_0} \tag{11s}$$

However, polymer solutions of finite concentrations do not generally exhibit ideal behavior. These deviations from ideal behavior are primarily due to the non-ideal entropy of mixing of polymer molecules with solvent molecules. It is therefore necessary to use the expression

$$\Pi/c = RT(1/M + A_2c + \text{higher terms in } c) \qquad (12s)$$

Then, combining (12s) and (10s) we can write

$$Hc/\tau = Kc/R_\theta = 1/M + 2A_2c + \ldots\ldots\ldots\ldots \qquad (13s)$$

where H is given by (8s) and K by (6s).

The treatment thus far has been restricted to systems where the solute particles are regarded as single isolated dipoles, their dimensions being small compared with the wavelength of the incident light. When the dimensions of the scattering particle exceed about one-twentieth of the wavelength of the light, it is no longer permissible to consider the particle as a simple source of scattered radiation. As the scattering angle θ increases there is an increasing path difference between the light received from the different parts of the molecule, and, as a result, the intensity of the scattered radiation is reduced because of destructive interference.

If the refractive index of the molecule is nearly identical with that of the surrounding medium, then the problem is similar to that encountered in X-ray and electron scattering. Debye[51] showed that if the particle scattering factor P_θ is defined as R_θ/R_0, i.e. the ratio of the intensity at the angle θ to that at zero angle, then, for randomly coiled polymer molecules,

$$P_\theta = 2/u^2\ [e^{-u} - (1-u)] \qquad (14s)$$

where

$$u = 2/3(\overline{r^2}/\lambda'^2)\ [2\pi\sin(\theta/2)]^2 \qquad (15s)$$

and $\overline{r^2}$ = the mean square end-to-end distance between the ends of the polymer chains,

λ' = the wavelength of the light in solution (λ/n_0).

The value of P_θ approaches unity when $u \to 0$, that is, when $(\overline{r^2})^{1/2}/\lambda' \to 0$ and/or $\theta \to 0$. It follows that, in order to measure molecular weights under conditions where $P_\theta \neq 1$, then either P_θ must be known, or the results evaluated in such a way that P_θ approaches unity. A method of treating the data originally proposed by Zimm[52] shall be considered.

In the method of Zimm, the intensity of the scattered light is measured at several angles for each concentration of the polymer and the results are plotted using as axes Kc/R_θ and $\sin^2\theta/2 + kc$ where k is an arbitrary constant chosen for convenience. A double extrapolation is carried out. Points at constant concentration are extrapolated to zero angle. These extrapolated points of various concentrations now at zero angle are then extrapolated to zero concentration. The other extrapolation is performed in a reverse manner, extrapolation first to zero concentration at constant angle; then, an extrapolation is made to zero angle. Both lines should meet at a common intercept, which is $(Kc/R_\theta)_{c=0,\ \theta=0}$ From this the weight average molecular weight can be calculated without making any assumptions, such as a random-coil configuration, about the shape of the molecule.

The limiting gradient of the zero concentration line (kc_o) is a measure of the size of the polymer molecule. Assuming that kc_o is linear, its equation is of the form

$$(Kc/R_\theta)_{c=o} = (Kc/R_\theta)_{c=o,\ \theta=o} + K'\sin^2\theta/2 \qquad (16s)$$

Dividing by $(Kc/R_\theta)_{c=o,\ \theta=o}$ gives

$$1/P_\theta = 1 + \frac{K'}{(Kc/R_\theta)_{c=o,\ \theta=o}} \sin^2\theta/2 \qquad (17s)$$

Substituting the value of P_θ from (14s) and noting that $(Kc/R_\theta)_{c=o,\ \theta=0}$ is the intercept of kc_o we can write

$$K'/\text{intercept} = 1/3\ (u/\sin^2\theta/2) \qquad (18s)$$

Substituting u from (15s) gives

$$\overline{r}^2 = \frac{9\lambda'^2}{8\pi^2}\ \frac{\text{slope}}{\text{intercept}} \qquad (19s)$$

B. Light Scattering Solvent Studies

It has been shown in equation (7s) that the turbidity, τ, of a polymer solution can be related to the molecular weight of the polymer, M_w, by the expression: $Hc/\tau = 1/M_w$. It follows that the sensitivity of the light scattering method depends on the magnitude of H, which depends in turn on the square of the difference between the refractive indices of the solute and of the solvent, i.e. $(dn/dc)^2$. A reasonable working range for the quantity, (dn/dc), according to Stacey[53] seems to be 0.08 to 0.20 ml./g. In systems having dn/dc values of less than 0.1 ml./g. it may be difficult to obtain reproducible results.

The empirical rule of Gladstone and Dale[53], $dn/dc = K_2 - \frac{d_1 K_1}{d_2}$, in which d is the density, n, the refractive index, and K a constant independent of temperature and the subscripts 1 and 2 refer to solvent and polymer respectively, was used to calculate approximate values of dn/dc at room temperature for various solvent-polybutene-1 systems. Since no dn/dc values of any solvent-polybutene-1 system were known to be published at the time of this research, the dn/dc value of a solvent-polyethylene system was used as a guide. It was believed that polyethylene should closely approximate polybutene-1 in its refractive index since earlier work by Chiang[9] indicated polyethylene and polypropylene were very similar in this respect.

Limiting $n_D^{20°}$ values of the solvent were obtained by using Chiang's[9] comparison of polyethylene and polypropylene in conjunction with dn/dc values for polyethylene-α-chloronaphthalene given by Billmeyer[54] at various temperatures. Calculated limits, which would give a dn/dc value with polybutene-1 of 0.1 ml./g. or greater, were $n_D^{20°} = 1.35$ or less and $n_D^{20°} = 1.55$ or greater.

A non-volatile solvent was required since the relationship $Hc/_\tau = 1/M_w$ is valid only for conditions of thermal equilibrium. The use of a relatively volatile solvent precludes the attainment of thermal equilibrium and may also give rise to concentration changes which lead to erroneous molecular weight calculations.

More than 50 chemicals of widely varying chemical structure were examined in an attempt to find a room temperature solvent. No entirely satisfactory solvent was found. On the basis of its high $n_D^{20°}$, α-chloronaphthalene was chosen as a light scattering solvent.

In the solubility tests, approximately 1% by weight of polymer was added to each liquid and set aside for 2-4 days. On the basis of their ability to swell the polymer fibers, liquids were rated very good, good, fair, poor, etc. Those liquids which seemed most promising were subjected to a more quantitative-type test and were rated, accordingly, as soluble at 40°-50°C, etc. Results of these tests are presented in tabular form in Appendix D.

C. Measurements of dn/dc

Attempts to measure dn/dc for the polybutene-bromobenzene system were made on the Zeiss interferometer at 55°C. The reservoir enclosing the sample cell was thermostatted by completely surrounding it with styrofoam. Viewing windows were provided by boring holes in the styrofoam. A liquid (at first water, later butyl phthalate) was heated conductively in a two foot section of spiralled 1/4" copper tubing positioned in an externally regulated bath. A commercial pump was employed to circulate the liquid through the reservoir. All attempts, even at temperatures as low as 30°C, to obtain a reliable dn/dc value proved unsuccessful. One of the chief problems seemed to arise from the convection currents produced in the reservoir bath liquid surrounding the sample cell. The "fringes" viewed through this medium of constantly varying refractive power appeared wavy and indiscernable. An effort was made to control temperature by forcing heated air (heated by a copper tube wound with nichrome wire which was regulated thermally by a powerstat) through the reservoir surrounding the sample cell. This too was unsuccessful.

To overcome the problems encountered in measuring the dn/dc value at elevated temperatures, the following improvements were provided: a more closely regulated bath, a better method of transport for the heating liquid, and more adequate reservoir insulation.

A Brice-Phoenix differential refractometer was utilized, subsequently, and proved satisfactory in providing dn/dc values at elevated temperatures.

Insulation was provided for the differential refractometer cell in the following manner: the metal reservoir surrounding the cell was entirely lined with sheet asbestos and provided with a 3/8" Plexiglass top; this unit was then completely enclosed by a cardboard box, 2 ft. x 2 ft. x 1 ft., which was packed, except for the connecting hoses to the reservoir and the viewing space, with glass wool. Constant temperature within the cell was maintained by circulating ethylene glycol through the reservoir from a regulated, well-agitated external bath. The glycol was transported entirely through silicone rubber tubing. Solution temperature within the cell lagged eleven degrees below that of the external bath but once thermal equilibrium was established the cell temperature did not appear to vary more than ±.3°.

The Brice-Phoenix differential refractometer was calibrated with sodium chloride at 546 mμ using values given by Kruis[55] at various wavelengths and tabulated at 546 mμ by Stamm[56]. Since the relative positions of component parts on the optical bench gave different calibration constants, dn/dc measurements were made at only one setting of the various component parts and were made simultaneously with the calibration measurements.

It was possible to decrease the solvent scale deflection reading to less than 3 scale divisions (in contrast to a deflection of more than 300 scale divisions for the solutions) by carefully aligning the component parts on the optical bench.

Results are presented in Table 14. Values of dn/dc obtained for both isomeric forms were the same within experimental error.

D. Experimental

Light scattering measurements were performed in a Brice-Phoenix Light Scattering Photometer[57] fitted with a high temperature thermostat after a design by Trementozzi[58]. The double walled thermostat was built from seamless brass tubing and lagged on the outside with sheet asbestos. Constant temperature was maintained within the unit by pumping ethylene glycol through the thermostat from a well-regulated insulated external bath. The hot glycol was successfully transported through silicon rubber tubing by a commercial centrifugal pump. The polymer solution temperature lagged approximately six degrees below that of the external bath, but once equilibrium was established the solution temperature did not appear to vary more than ±.3°C during a complete measurement.

Table 14

Measurement of dn/dc for α-chloronaphthalene-polybutene-1 at 85°C

Polymer Sample	Conc. (g./100ml. of solution)	No. of measurements	dn/dc ave. value (ml./g.)
Atactic fraction A	1.553	32	-.198
Atactic fraction A*	1.553	16	-.196
Atactic fraction A	1.170	20	-.191
Atactic fraction A*	1.170	22	-.211
Isotactic bulk	1.286	20	-.202

$$dn/dc = -.200 \pm .006$$

* Indicated measurements performed on previous fraction after 24 hour period

Temperature was measured by a thermistor probe which made contact with the back side of the outer wall of the light scattering cell. The probe served also as a temperature sensing device for a commercial electronic controller, which actuated the heater in the external bath. The probe was sensitive to changes of ±.1°C. A bimetallic thermoregulator, sensitive to changes of ±.2°C. controlled a second knife blade heater (250 watts) in the external bath. Use of a stainless steel beaker to contain the bath fluid permitted a constant heat source to be supplied to the glycol by a pre-set electrical hot plate. The sides of the 5 liter beaker were insulated with a heavy layer of glass wool with an outer layer of aluminum foil. The top was covered with 1/4" sheet asbestos with openings cut for the hose connections, heaters, regulator, and thermometer.

The photomultiplier tube housing was lagged with thin sheet asbestos to insulate the tube from excess heat radiated by the thermostat. Galvanometer readings showed no erratic behavior nor excessive drift, which indicated the photomultiplier tube was not affected by the small temperature rise it sustained during measurements. Data taken over a 30-60 minute period were reproducible.

Light scattering measurements were carried out over the angular range 45°-135° using unpolarized light of 546 mμ wave length. A cylindrical Witnauer[59] type cell from the Phoenix Instrument Company was used throughout. To correct for optical imperfections a fluorescein factor was used. This factor was obtained for each angle by viewing the green fluorescence (through a yellow filter) produced by illuminating a dilute aqueous solution of fluorescein with blue light[60] and comparing this reading (when corrected for the volume viewed by the detector --- the sinθ correction) with that obtained at 90°.

The photometer was calibrated by two methods: by comparison with Cornell polystyrene in toluene and the standard opal glass reference. A value of 1.31×10^{-3} cm.$^{-1}$ was used for the excess turbidity with light of 546 mμ wavelength when using the Cornell polystyrene[58]. Calibration with Cornell polystyrene was used to check the standard opal glass. During the actual operation of the instrument only the calibration with the standard opal glass reference as explained in the Brice-Phoenix handbook was performed. Comparison of the two calibration methods showed agreement within 1%.

Eastman White Label α-chloronaphthalene was distilled through a short Vigreux column at 20mm. pressure for use in measurements on fractions B7 and B8. Other light scattering measurements were made with Eastman White Label α-chloronaphthalene which was not further distilled. The refractive index of each batch of solvent was taken with an Abbe refractometer at 20°C. These values were found to agree with the literature values within seven units in the fourth decimal place[38].

Solvent and polymer were cleaned in a dual filter arrangement consisting of a coarse-grade sintered glass filter mounted on an ultrafine-grade sintered glass filter. The entire apparatus was wound with heating tape. The nichrome wire leads were connected to a direct 110 volt line source through a powerstat. For accurate temperature control, a calibration was made by plotting filter temperature versus powerstat setting.

Visual examination for dust was nearly impossible when the cell was enclosed in the thermostat. Dust particles were detected by fluctuations (bouncing) of the galvanometer and by dissymmetry increases. Any concentration which exhibited a greater apparent solution dissymmetry value than its predecessor or showed other signs of dust particles being present was refiltered until free of dust. Between measurements on different fractions the filter was cleaned by rinsing several times with hot (110°C) xylene. The solvent, α-chloronaphthalene, was used as a final rinse before the filter was dried with N_2.

Warm xylene was used between runs to remove any remaining traces of polymer from the scattering cell. The cell was scoured with water and detergent and then rinsed with dried, distilled acetone. The outer surface of the cell was wiped clean with special lens tissue. A radioactive polonium brush removed any remaining dust particles from the outer surface. The inner glass surfaces of the cell were cleaned by rinsing with α-chloronaphthalene which had been filtered through an ultrafine filter. Rinsing was continued until examination of the cell under strong light revealed no dust particles.

Solutions were forced through the filter with approximately 10 lbs. gauge pressure. The tip of the dual filter was cut extremely short to circumvent earlier precipitation difficulties which occured when hot solution passed through this air cooled tip on its way into the cell. Precipitation in the cell itself was avoided by filtering directly into the cell while it remained within the thermostat.

To prevent severe clogging in the ultrafine filter, which ensued when the filter temperature was within five or ten degrees of the precipitation temperature, solutions were filtered at approximately 20° above their precipitation temperature.

Changes in concentration of a polymer fraction were made by successive dilutions. Prior to dilution, polymer and solvent were weighed on an analytical balance to make up the first concentration. First concentrations were made approximately one per cent by weight of polymer with a total volume of either 10 or 25 ml. After each run the entire cell and its contents were weighed, the hot solvent filtered in, the cell reweighed, and the added amount of solvent calculated by weight difference. Each weighing was performed by removing the cell from the thermostat. To prevent dust contamination which would result from the use of a glass stirring rod, solution homogeneity was achieved by swirling the cell while holding the lid tightly in place.

Except for atactic samples A122 and A121, all of the solutions measured appeared colorless. The color of these samples, a pale yellow, was attributed to some impurity, soluble in the solvent, since the polymer upon precipitation appeared colorless while the solvent retained its faint yellow tinge. Light absorption during scattering measurements due to color was insignificant. The presence of color did cause a change in the amount of fluorescence exhibited by the solutions at 546mμ.

Solutions were examined for fluorescence as described in the Brice-Phoenix instrument handbook. In all colorless solutions examined, no detectible fluorescence was present. The fluorescence exhibited by the two colored samples was negligible.

Galvanometer readings were made at angles of 45°, 50,60,70,80,90, 100,110,120,130,135°. From the plot of $\sin^2\theta/2$ vs. Kc/R_θ for this range of galvanometer readings, presence of dust in the solution could be detected very sensitively by a rapid change in slope at low angles.

E. Data and Results

For measurements made at the Θ temperature the second virial coefficient was zero. To obtain the angular data at zero concentration it was necessary then only to obtain average values for the galvanometer ratios at each of the angles from the galvanometer ratios obtained for the different concentrations used. Galvanometer ratios were converted to Kc/R_θ values and the data were plotted as Kc/R_θ vs. $\sin^2\theta/2$ for both finite and zero concentrations. These data appear in Appendix E, Figures 1-7. The method of conversion of galvanometer reading to Kc/R_θ values is described in Appendix F.

To obtain values for $(Kc/R_\theta)_{c=o}$ at each of the angles for measurements made at temperatures slightly higher than the theta temperature, it was necessary to extrapolate Kc/R_θ values obtained at three or more concentration (for a given angle) to zero concentration. Extrapolations for a few representative angles are given in Figures 8-10 in Appendix E.

All fractions examined gave linear plots of Kc/R_θ vs. $\sin^2\theta/2$. In the case of the low molecular weight atactic fractions A2 and A3 and for some concentrations of the isotactic fractions it was necessary to correct for a slight downward curvature corresponding to the low angle (45° and 50°) readings. The downward curvature for these data was interpreted as arising from the incomplete removal of dust particles. Light scattering data obtained for high molecular weight atactic fractions A121 and A122 confirmed this interpretation. The greatly increased turbidity resulting from use of these high weight fractions substantially reduced the "dust error", and the subsequent plotting of Kc/R_θ versus $\sin^2\theta/2$ for fractions A121 and A122 revealed no downward curvature at low angles (45° and 50°).

The value of the intercept of these curves of $\sin^2\theta/2$ versus $(Kc/R_\theta)_{c=o}$ gave the reciprocal of the molecular weight as shown in equations 16s and 5s. From equation 19s the end-to-end dimensions, $\overline{r}^2$ or $\overline{r}^2_z$, may be calculated from the slope and intercept of the $(Kc/R_\theta)_{c=o}$ versus $\sin^2\theta/2$ curve for each polymer fraction. Values of the slope, intercept, and $\overline{r}^2_z$ obtained from these curves are collected in Table 15. Plots of $(Kc/R_\theta)_{c=o}$ versus $\sin^2\theta/2$ are given in Appendix E in Figures 11-13.

To obtain the second virial coefficient, A_2, for the measurements not at theta, $(Kc/R_\theta)_{\theta=0}$ values were plotted versus concentration. These are shown in Figures 19-21 for A2, B3, B8. Values of A_2 were obtained by use of equation 13s. The values of the intercept (equation 13s) yielded the reciprocal of the molecular weight. Values of $(Kc/R_\theta)_{\theta=0}$ for each concentration were obtained by plotting Kc/R_θ against $\sin^2\theta/2$ and extrapolating the resulting curves to $\theta = 0$. These curves are shown in Appendix E as Figures 14-18. Values of A_2 are collected in Table 16.

An intrinsic viscosity-molecular weight relationship $(\eta) = KM^a$, may be established by combining the viscosity data in n-nonane at 80°C and

Table 15

Data from $(Kc/R_\theta)_{c=o}$ versus $\sin^2\theta/2$ curves

Fraction	Slope(a)	Intercept(b)	$M_w(\times10^{-5})$	$(\overline{r_z^2})^{1/2}$ (Å)
C3	189	266	3.8	969
C4	188	203	4.9	1100
A2	231	351	2.9	932
A3	418	735	1.4	867
B3	331	348	2.9	1130
B8	174	228	4.4	1000

(a) Expressed as $(M_w \times 10^8)$

(b) Expressed as $(M_w \times 10^8)^{-1}$

Table 16

Second virial coefficients in α-chloronaphthalene

Fraction	Temperature (°C)	$M_w(\times10^{-5})$	A_2(cc.moles/g^2)
A2	85	2.9	3.4×10^{-7}
B3	86	2.9	7.6×10^{-8}
B8	86	4.4	6.0×10^{-8}

the molecular weight values obtained from light scattering data in α-chloronaphthalene. The relationship (i.e. Mark-Houwink expression) established here confirms an earlier intrinsic viscosity-molecular weight expression obtained from light scattering data in n-nonane and viscosity data on n-nonane at 80°C. Results from both laboratories are collected in Table 17. These data are presented as a plot of log (η) versus log M_w in Figure 8. The value obtained for "a" from the slope of this plot is 0.80. The value of K which may be calculated from the intercept of this curve is 5.85×10^{-5}.

Table 17

Intrinsic viscosity (n-nonane at 80°C) and molecular weight values for polybutene-1

Fraction	M_w (x 10^{-5})	(η)(dl./g)
B8	4.4 (1)	1.90
C3	3.8 (1)	1.69
B3	2.9 (1)	1.35
C4	4.9 (1)	1.89
A3	1.4 (1)	0.655
A2	2.9 (1)	1.44
AB-11	13.0 (2)	4.75
AB-12	1.42 (2)	0.725
B2-121	9.35 (2)	3.33
B2-122	4.12 (2)	1.87
B6-13	1.70 (2)	0.946
B6-2	1.05 (2)	0.612

(1) Obtained from light scattering data in α-chloronaphthalene
(2) Taken from reference 13 using n-nonane as light scattering solvent

As previously noted[13] both isomers obey an identical intrinsic viscosity-molecular weight relationship under these conditions.

Prior to beginning light scattering studies on fractions in α-chloronaphthalene, a bulk sample of isotactic polybutene-1 was studied for degradation. The solution of bulk polymer was placed in the light scattering cell and measurements were made at approximately 90°C. The same solution was maintained at 90°C for a period of 24 hours by sealing and placing in an oven. The measurements were then repeated under identical experimental conditions. The turbidity was identical (within experimental error) for both runs, thereby indicating no degradation had occured. A comparison of galvanometer ratios for these two light scattering runs is presented in Appendix G.

The light scattering study of a somewhat similar polymer, polyethylene[61] revealed that α-chloronaphthalene (at 105°C) gave rise to the problem of molecular association. Molecular weights and dimensions obtained in this solvent-polymer system appeared too high by approximately a factor of two.

Light scattering data in two different solvents, n-nonane[13] and α-chloronaphthalene were compared to resolve this question. Since molecular weights obtained from both solvents revealed an identical Mark-Houwink expression in n-nonane at 80°C it was concluded that no significant molecular association occurred in the fractions studied here. These results are presented in Figure 8.

F. Discussion

One task undertaken in this study was an attempt to find a solvent in which light scattering studies could be made at the theta temperature for isotactic and atactic polybutene-1. The requirements of such a solvent have been mentioned in the introductory remarks on light scattering. As a result of this work α-chloronaphthalene has been shown to be a suitable solvent for this purpose. Light scattering measurements for both isotactic and atactic fractions in α-chloronaphthalene at the theta temperature are shown in Figures 1-4 in Appendix E. End-to-end dimensions (Z average)[52] for these fractions have been calculated from the relationship given in equation 19s and these appear in Table 15. Values of the parameter, Φ, may be calculated from the expression given by equation 8v. These are tabulated and appear in Table 18. Molecular weights may be computed, as

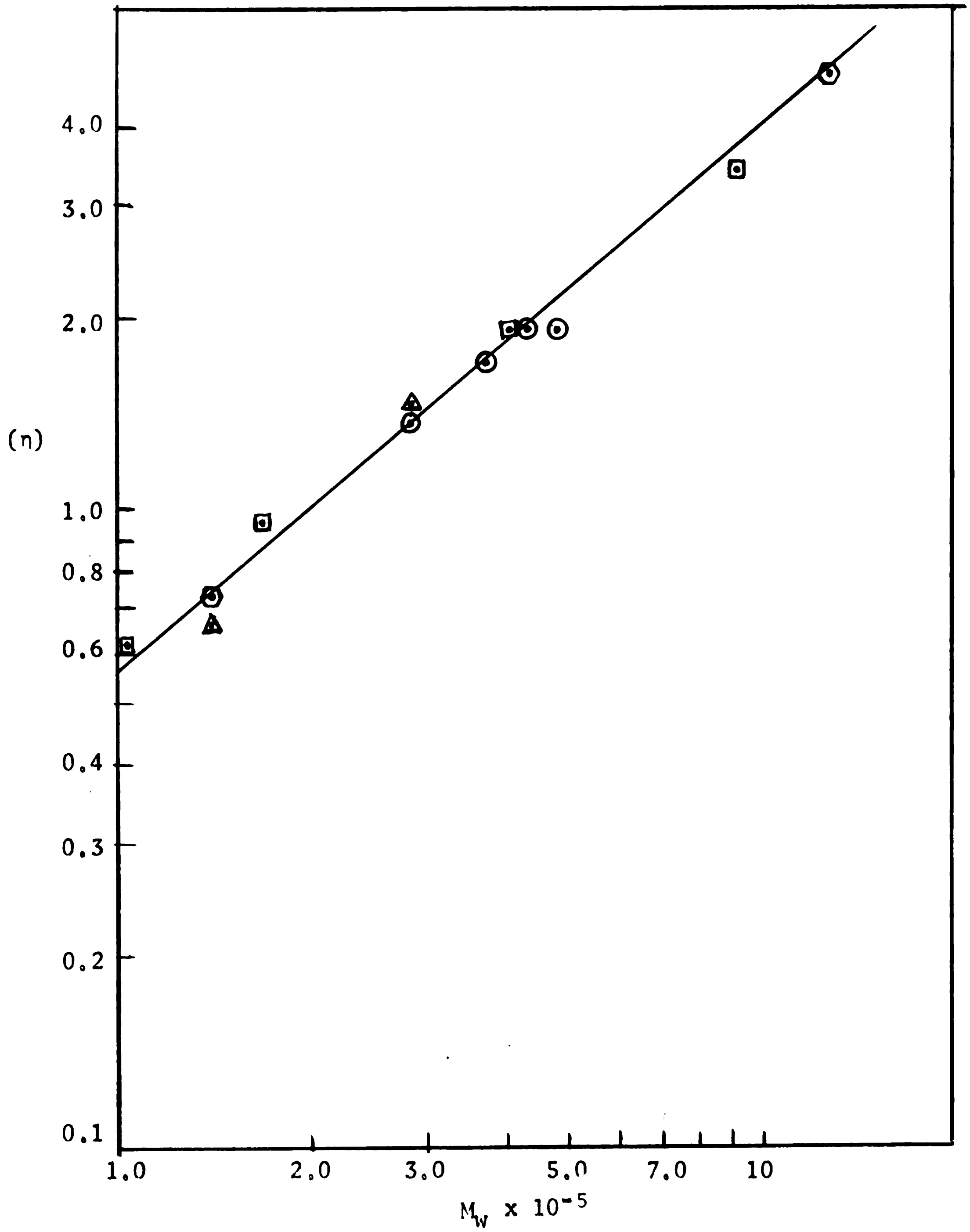

Figure 8. Double logarithmic plot of (η) against M_w for polybutene-1 fractions in n-nonane at 80°C.

□ ref. 13 Isotactic; ⬡ ref. 13 Atactic
O Isotactic; **Δ** Atactic.

described previously, from equation 16s and these are also presented in Table 15.

Thus far no determination of the unperturbed dimensions of polybutene-1 from light scattering data in theta solvents has appeared in the literature. A calculation of dimensions has been made from light scattering data obtained in a good solvent[13]. A calculation of dimensions made from light scattering data obtained in a good solvent[13] was referred to earlier in this thesis when discussing unperturbed dimensions obtained from intrinsic viscosity data.

The calculation of unperturbed dimensions from light scattering data in a theta solvent can be made directly. At the theta point there is no net polymer-solvent interaction. The second virial coefficient of the system is zero and no correction of chain dimensions for thermodynamic interaction effects is necessary.

The root-mean-square end-to-end distance calculated above for the various polybutene-1 fractions in α-chloronaphthalene represent the so-called "Z-average dimensions" described by Zimm[52]. On the other hand, the calculated molecular weights represent weight average quantities. The "Z-average" dimensions may be converted to weight average dimensions from a knowledge of the heterogeneity of the polymer fractions. A polydispersity parameter[52], h, may be established from a knowledge of the number average molecular weight (usually obtained from osmometry). Osmotic pressure measurements were not made in the present study. A further complication, characteristic of any light scattering study, is the presence of dust. Such particles cause the calculated root-mean-square end-to-end dimensions to be too high.

The particle scattering factor $P(\theta)$ or its reciprocal $P^{-1}(\theta)$ was examined as a possible source of information about the polydispersity and shape of the polymer. The $P(\theta)$ function can be written[62] as:

$$P(\theta) = 1 - A^*u^2/3 - B^*u^4/60 + \text{higher order terms}$$

where $u = (4\pi n/\lambda o)\sin\theta/_2$, A^* gives the radius of gyration, B^* varies with shape and polydispersity, and the other symbols are as previously defined.

Doty and Benoit[62] have attempted the explicit evaluation of B^* for ellipsoids, cylinders, and Gaussian coils. They found that the variation of this function with the amount of coiling is very small and in practice is probably swamped by the effects of polydispersity. Information about polydispersity (apart from the study of shape) from light scattering data was considered by Benoit, Holtzer, and Doty[63]. They have examined the theoretical curves of $1/P(\theta)$ over the whole practical range of polydispersity using scattering angles of 30° to 135° and a value of $\lambda o/\eta = 3220$Å. They found that polydispersity does not lend itself to interpretation for molecules possessing an end-to-end dimension of less than about 1000 Å.

On the basis of the work by these authors and in compliance with the experimental findings ($\sqrt{\overline{r_z^2}}$ ca. 1000 Å), the particle scattering factor for the α-chloronaphthalene-polybutene-1 system was not examined further for polydispersity information.

Since values of the polydispersity parameter, h, were not available, no further discussion of chain dimensions will be made here. It should be emphasized, however, that by obtaining suitable osmotic pressure measurements on each of the fractions for which light scattering data in α-chloronaphthalene at the theta temperature have been taken it would be possible to obtain corrected unperturbed end-to-end dimensions (or the "weight average" type) for each fraction.

VI. CONFORMATION DISCUSSION

Information concerning the conformation of a polymer in solution may be obtained by comparing unperturbed dimensions from intrinsic viscosity and light scattering measurements at the theta point[34]. The conclusion as to the shape polybutene-1 assumes in dilute solution (in this case in α-chloronaphthalene) is deduced in part from use of the ratio $(\overline{r_o^2}/M)$. The end-to-end dimensions and molecular weight in this ratio should be of the same average. The same considerations stipulated previously for converting the experimentally obtained "Z average" dimensions to weight average dimensions apply here. Any final conclusion as to the conformation adopted by polybutene-1 must be based therefore on a consideration of the polydispersity parameter. Evidence obtained in this study, however, does allow several deductions to be made about polybutene-1 conformation in solution.

Light scattering and viscosity evidence seem to indicate that polybutene-1 exhibits many of the features characteristic of polymer chains of low flexibility. The following evidence is cited: low Φ values, the relatively small change with increasing temperature of α^3 values in α-chloronaphthalene, the trend of $(\overline{r_o^2}/M)^{1/2}$ to increase with decreasing molecular weight (in the low molecular weight range). Values of $(\overline{r_{oz}^2}/M)^{1/2}$ and Φ from light scattering data in α-chloronaphthalene are collected in Table 18 for four isotactic fractions and four atactic fractions of polybutene-1. Values of α^3 in α-chloronaphthalene are presented in Table 9.

Probably the most reliable indication of chain flexibility is the value

Table 18

Values of Φ and $(\overline{r^2_{oz}}/M_w)^{1/2}$ for four fractions of atactic and isotactic polybutene-1

Fraction	$M_w(x10^{-5})$	$10^{10}(\overline{r^2_{oz}}/M_w)^{1/2}$	$10^{-21}\ \Phi$*
A121	**	92	1.8
A122	**	82	2.5
C4	4.9	158	0.29
B8	4.4	151	0.34
C3	3.8	157	0.29
A2	2.9	175	0.34
B3	2.9	176	0.28
A3	1.4	237	0.29

* Calculated from estimated $M_w/M_n = 1.3$

** Not reported -- see discussion

obtained for the parameter, Φ. Since the "stiffness" of the chain is reflected in the value of $\overline{r^2_o}$ it may be examined as shown in equation (6v) from values of Φ. With reference to the viscosity relationship shown in equation (6v), non-Gaussian chains cannot satisfy the premise of the Fox-Flory relationship[36], that is, that the effective hydrodynamic volume of the polymer molecule is spherical and can be characterized by a radius that varies directly with a linear parameter of the Gaussian distribution.

In particular, a non-Gaussian coil should exhibit substantially less frictional resistance than a random coil of equal end-to-end dimensions: hence the apparent value of Φ will be lowered. Thus the low Φ values calculated for the following systems: polyethylene-tetralin[61] and isotactic polypropylene-α-chloronaphthalene[64], have in each case been interpreted as a departure from a Gaussian distribution. Based on the rather low Φ values obtained in α-chloronaphthalene it appears that the same interpretation could be applied to polybutene-1.

The low α^3 values are contrary to observed viscosity behavior in a poor solvent for polymers possessing a random coil conformation[36,44]. Caution must be exercised in using α^3 values in deducing any conformation properties since these values are very solvent-dependent. Thus from equation (2v) it can be seen that in an athermal solvent ($\kappa_1 = 0$, $\Theta = 0$) that no change in α^3 should occur with temperature.

The inherent resistance to flow of the random coil suggests $[\eta]$ values will be sensitive to changes in temperature and in solvent power. Thus, for example, it has been observed that a threefold change in $[\eta]$ occurs in polyisobutylene over a 25° temperature range near the theta point[36]. As shown by equations (2v) and (4v) this change in $[\eta]$ should be greatest near the theta temperature of the solvent. The rather small observed change in $[\eta]$ near the theta point in α-chloronaphthalene suggests that polybutene-1 possesses a rather rigid conformation.

It is to be expected that as the number of chain segments in the polymer increases the chain should more closely approximate Gaussian statistics. If fraction A3, having considerably lower molecular weight than the other atactic fractions, can be considered to be somewhat more non-Gaussian than the others, it follows that it should have a more extended conformation. Perhaps even more significantly, the fractionation data shows that A3 has a higher weight fraction than the other fractions studied by light scattering. This indicates perhaps that A3 has a greater heterogeneity than normal. Both considerations predict that fraction A3 would have a lower calculated value of Φ than the other atactic fractions A121, A122, and A2. This is the case as shown in Table 18.

The intrinsic viscosity data measured in α-chloronaphthalene are not sufficient to establish a reliable intrinsic viscosity-molecular weight relationship; however, a plot made assuming a molecular weight exponent of 0.5 for both isomers does seem to fit the data satisfactorily for both isomers. Other existing intrinsic viscosity data for polybutene-1 in theta solvents are presented in Table 19. The wide variation in reported "a" values and the lack of sufficient supporting evidence for any given set of data suggest further investigation of intrinsic viscosities of polybutene-1 at the theta point.

Unfortunately, a reliable intrinsic viscosity-molecular weight relationship was not established from light scattering runs performed on the very high molecular weight fractions, A121 and A122. For this reason the $\sin^2\theta/2$ versus Kc/R_θ and the concentration versus Kc/R_θ curves for these fractions are not published here. Both samples were partially retained on the filter during the clarification procedure. However, since the plots of $\sin^2\theta/2$ versus Kc/R_θ and concentration versus Kc/R_θ for both A121 and A122 exhibited excellent agreement with theory, the data were used to estimate the molecular dimensions. A value for the concentration which would correct the light scattering molecular weight to the viscosity molecular weight was assumed in each case. Values of M_w and the "Z-average" dimensions calculated on this basis for these fractions appear in Table 18. Values of Φ obtained from this type of calculation also appear in Table 18. The magnitude of the Φ values calculated in this manner indicates a Gaussian distribution for these fractions.

The "dust error" for these fractions (A121 and A122) should be considerably less (because of their greatly increased turbidity) and the

Table 19

Critical solvent data for polybutene-1

Polymer	Critical solvent	a[1]
Atactic polybutene-1*	Isoamyl acetate (23°C)	0.50
Isotactic polybutene-1**	Anisole (89.2°C)	0.59
Atactic polybutene-1**	Anisole (86.3°C)	0.64
Isotactic polybutene-1	α-Chloronaphthalene (83.7°C)	0.50
Atactic polybutene-1	α-Chloronaphthalene (81.7°C)	0.50

"a" is the molecular weight exponent for the Mark-Houwink expression

* Data taken from reference 43
** Data taken from reference 13

heterogeneity effect should be substantially reduced (both fractions were obtained from a triple-stage fractionation procedure). These additional data lend support to the previous conclusions about molecular shape. Thus if the semi-flexible polybutene-1 chain does exhibit non-Gaussian behavior in the low molecular weight regions in contrast to the somewhat similar polypropylene chain[11] it might be expected to exhibit Gaussian behavior with increased polymer segments. Also, if the apparent non-Gaussian behavior arises from residual hetereogeneity and from experimental difficulties with dust, it should vanish as these factors are corrected. In either interpretation these high molecular weight fractions should appear to be Gaussian.

The speculation that lower molecular weight species may behave in a non-Gaussian behavior takes on an additional significance in the determination of the unperturbed dimensions. It suggests that previous calculation not based on light scattering measurements at the theta point are invalid.

Previous calculations [13,43] of dimensions have had to rely on the light scattering data performed in good solvents and data obtained from viscosity measurements --- neither of which is reliable except for a Gaussian distribution.

For the reasons put forth in the preceding discussion it appears that high molecular weight species do obey Gaussian statistics. Although low molecular weight species may obey Gaussian statistics, it would be premature to assume so on the basis of information obtained in this study.

VII. PROPOSAL FOR FURTHER STUDY

It would be desirable to ultimately correlate the observed physical properties of poly-α-olefins with their structure. The present study has established physical properties of fractions of polybutene-1 of varying degrees of stereoregular order. With this information now available a proposed future problem would be to evaluate the degree of stereoregular order of these polymer fractions. Up to the present time, x-ray, infrared and nuclear spin resonance spectra have been employed to determine the stereochemical configuration and conformation of polymers. Nuclear spin resonance spectra obtained by Bovey and Tiers[16] on polymethylmethacrylate samples of different stereochemical configuration demonstrate the applicability of nuclear spin resonance to the determination of stereochemical configuration and conformation in a system similar to polybutene-1.

Additional thermodynamic information could be obtained from osmotic pressure studies on the same polybutene-1 fractions used for the present study. Osmotic pressure data would yield second virial coefficient values for the particular combinations of solvent-polymer fraction used and in addition give the number average molecular weight for the fraction. The number average molecular weight of a fraction coupled with its weight average molecular weight enable a determination of its heterogeneity and thus would enable $\overline{r^2_{oz}}$ values obtained from light scattering to be corrected.

VIII. SUMMARY

Isotactic and atactic polybutene-1 were compared in phase equilibrium, light scattering, and intrinsic viscosity studies to determine the effect of configuration on physical properties.

Thermodynamic interaction parameters as defined by the Flory-Huggins theory were found to differ for the two stereoisomers and to be very solvent-dependent.

Molecular weight values (from light scattering) with intrinsic viscosity data in n-nonane gave an identical intrinsic viscosity-molecular weight relationship for the two stereoisomers in agreement with previously published results. However, the intrinsic viscosity-molecular weight relationship from viscosity data in the theta solvent differed for the isotactic and atacic forms.

Unperturbed end-to-end dimensions for both isomers were established from light scattering studies at the theta temperature and also from intrinsic viscosity data at the theta temperature. Dimensions appear to be somewhat larger for the atactic form.

BIBLIOGRAPHY

1. T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. 65, 2319 (1943)

2. M. L. Huggins, J. Am. Chem. Soc., 66, 1991 (1944)

3. G. Natta, Makromol. Chem., 16, 77, 213, (1955)

4. C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert, and A. O. Zoss, Ind. Eng. Chem. 40, 2104 (1948)

5. G. Natta, F. Danusso, and G. Moraglio, Makromol. Chem., 20, 37 (1956)

6. F. W. Peaker, J. Polymer Sci., 22, 25 (1956)

7. F. Danusso and G. Moraglio, J. Polymer Sci. 24, 161 (1957)

8. W. R. Krigbaum, D. K. Carpenter, and S. Newman, J. Phys. Chem. 62, 1586 (1958)

9. R. Chiang, J. Polymer Sci., 28, 235 (1958)

10. F. Danusso and G. Moraglio, Makromol. Chem. 28, 250 (1958)

11. J. B. Kinsinger and R. E. Hughes, J. Phys. Chem. 63, 2002 (1959)

12. F. Danusso and G. Moraglio, Rend. accad. naz. Lincei, 25, 509 (1958)

13. W. R. Krigbaum, J. E. Kurz, and P. Smith, J. Phys. Chem. 65, 1984 (1961)

14. J. B. Kinsinger and R. A. Wessling, J. Am. Chem. Soc. 81, 2908 (1959)

15. F. A. Bovey, G. V. D. Tiers, and G. Filipovich, J. Polymer Sci. 38, 73 (1959)

16. F. A. Bovey and G. V. D. Tiers, J. Polymer Sci. 44, 173 (1960)

17. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N. Y., 1953

18. J. P. Mullooly, Masters Thesis, Michigan State University, 1961

19. J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electroytes", 3rd ed., Reinhold, New York, New York, (1950)

20. P. J. Flory, J. Am. Chem. Soc., 65, 372 (1943)

21. G. Scatchard, Chem. Rev. 8, 321 (1931)

22. P. A. Small, J. Appl. Chem. 3, 71 (1953)

23. G. Natta, G. Marzanti, G. Crespi, and G. Moraglio, Chimicia e industria (Milan) 39, 275 (1957)

24. V. Desreux, Rec. trav. chim. 68, 789 (1949)

25. V. Desreux, and M. C. Spiegels, Bull. soc. chem. Belges 59, 476 (1950)

26. P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, J. Polymer Sci. 31, 453 (1958)

27. A. S. Kenyon and I. O. Salyer, J. Polymer Sci. 43, 437 (1960)

28. R. A. Mendelson, presented at the 141st National American Chemical Society Meeting, Washington, D. C., March 1962

29. P. M. Henry, J. Polymer Sci. 36, 3 (1959)

30. P. W. Allen, "Techniques of Polymer Characterization", Butterworths Scientific Publications, London, England, 1959

31. M. L. Huggins "Physical Chemistry of High Polymers", John Wiley and Sons, Inc., New York, N. Y. 1958, Chapt. 8

32. H. Mark, Der feste Korper, Hirzel, Leipzig, 1958 p. 103

33. R. Houwink, J. prakt. Chem. 157, 15 (1940)

34. C. Tanford "Physical Chemistry of Macromolecules", John Wiley and Sons, Inc., New York, N. Y., 1961, Chapt. 6

35. P. J. Flory, J. Chem. Phys., 17, 303 (1949)

36. P. J. Flory and T. G. Fox, J. Am. Chem. Soc. 73, 1904, 1915 (1951)

37. T. G. Fox, J. C. Fox, and P. J. Flory, J. Am. Chem. Soc. 73, 1901 (1951)

38. Handbook of Chemistry and Physics, 35th edition, 1953-54

39. C. R. Noller "Chemistry of Organic Compounds", W. B. Saunders Company, Philadelphia, Pa., 1951 p. 139

40. Volume 3, International Critical Tables, McGraw Hill Book Co., New York, N. Y. 1928

41. O. Fuchs, unpublished results

42. T. A. Orofino and P. J. Flory, J. Chem. Phys. 26, 1067 (1957)

43. G. Moraglio and G. Gianotti, Rend. accad. naz. Lincei, 27, 374 (1959)

44. P. J. Flory and T. G. Fox, J. Polymer Sci., 5, 745 (1950)

45. S. J. Yoo and J. B. Kinsinger, J. Chem. Phys. 36, 1371 (1962)

46. P. J. Flory, J. Chem. Phys. 10, 51 (1942)

47. M. L. Huggins, J. Am. Chem. Soc. 64, 2716 (1942)

48. A. R. Shultz, and P. J. Flory, J. Am. Chem. Soc., 74, 4760 (1952)

49. G. Natta, F. Danusso, G. Moraglio, Angew. Chem. 69, 686 (1957)

50. P. Debye, J. Appl. Phys. 15, 338 (1944)

51. P. Debye, J. Phys. and Colloid Chem. 51, 18 (1947)

52. B. H. Zimm, J. Chem. Phys. 16, 1093, 1099 (1948)

53. K. A. Stacey "Light Scattering in Physical Chemistry", Academic Press Inc., New York, N. Y., 1956

54. F. W. Billmeyer, Jr., J. Am. Chem. Soc. 75, 6118 (1953)

55. A. Kruis, Z. physik. Chem. B34, 13 (1936)

56. R. F. Stamm, J. Opt. Soc. Amer. 40, 788 (1950)

57. B. A. Brice, M. Halwer, and R. Speiser, J. Opt. Soc. Amer. 40, 768 (1950)

58. Q. A. Trementozzi, J. Polymer Sci. 22, 187 (1956)

59. L. P. Witnauer and H. J. Scherr, Rev. Sci. Instr. 23, 99 (1952)

60. E. F. Casassa and S. Katz, J. Polymer Sci. 14, 385 (1954)

61. Q. A. Trementozzi, J. Polymer Sci. 36, 113 (1959)

62. H. Benoit, and P. Doty, J. Phys. Chem. 57, 958 (1953)

63. H. Benoit, A. M. Holtzer, and P. Doty, J. Phys. Chem. 58, 635 (1954)

64. A. Kotera, K. Takamizawa, T. Kamata, and H. Kawaguchi, Reports on Progress in Polymer Physics in Japan, 4, 131 (1961)

APPENDICES

APPENDIX A

Intrinsic Viscosity Data

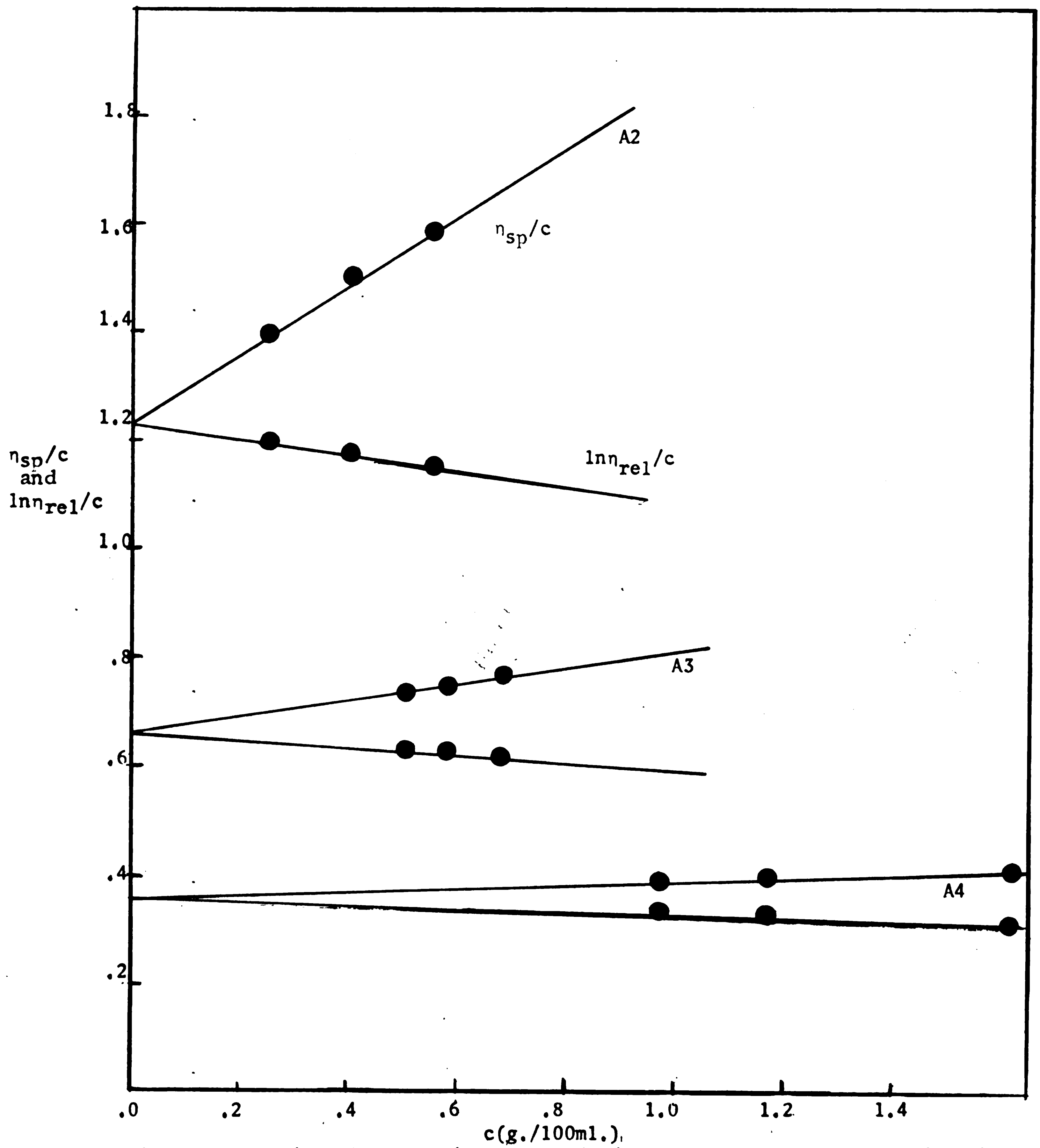

Figure 1. η_{sp}/c and $\ln\eta_{rel}/c$ versus c(g./100ml.) for three atactic fractions in benzene at 30°C

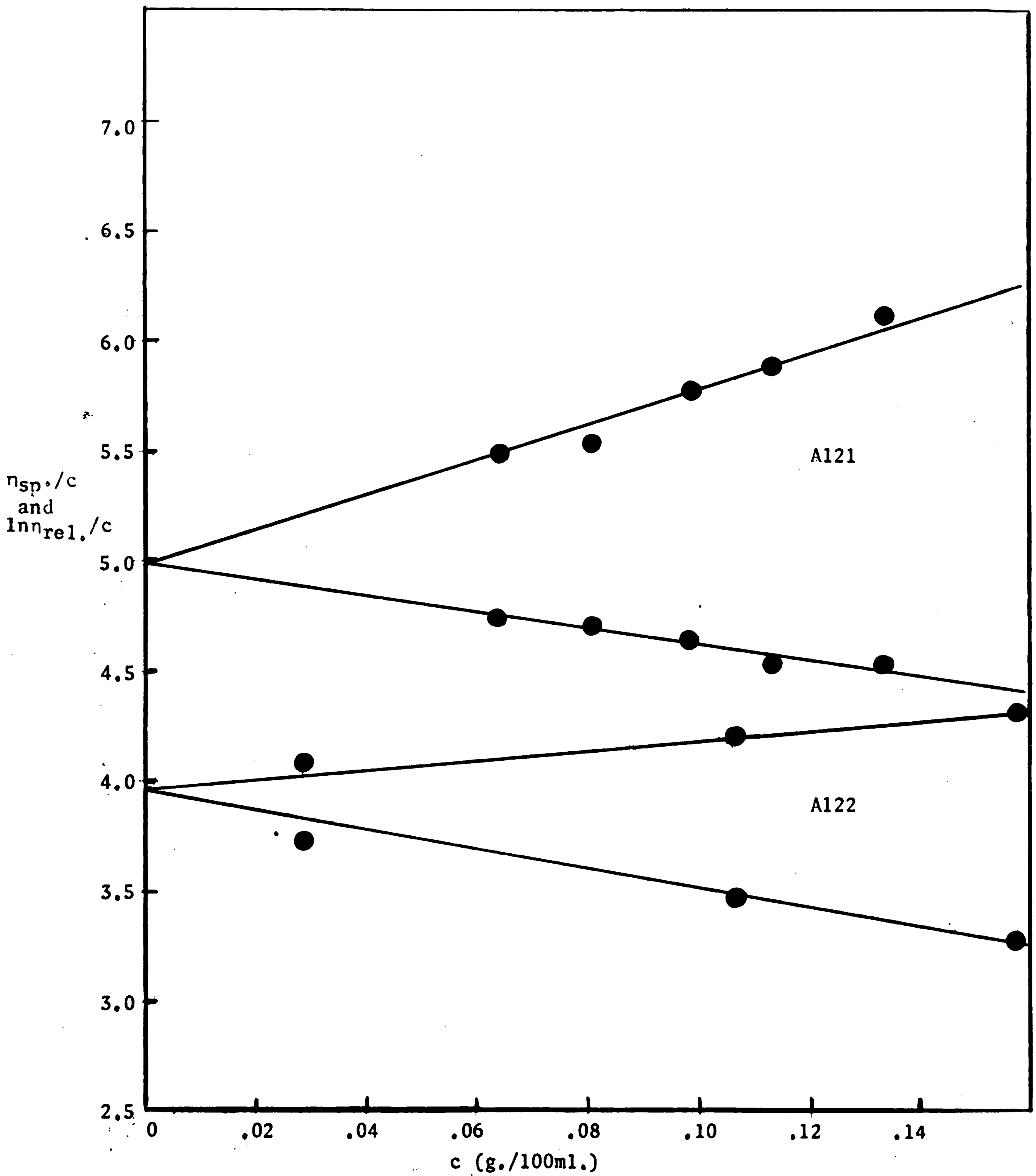

Figure 2. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c(g./100ml.) for two atactic fractions in benzene at 30°C

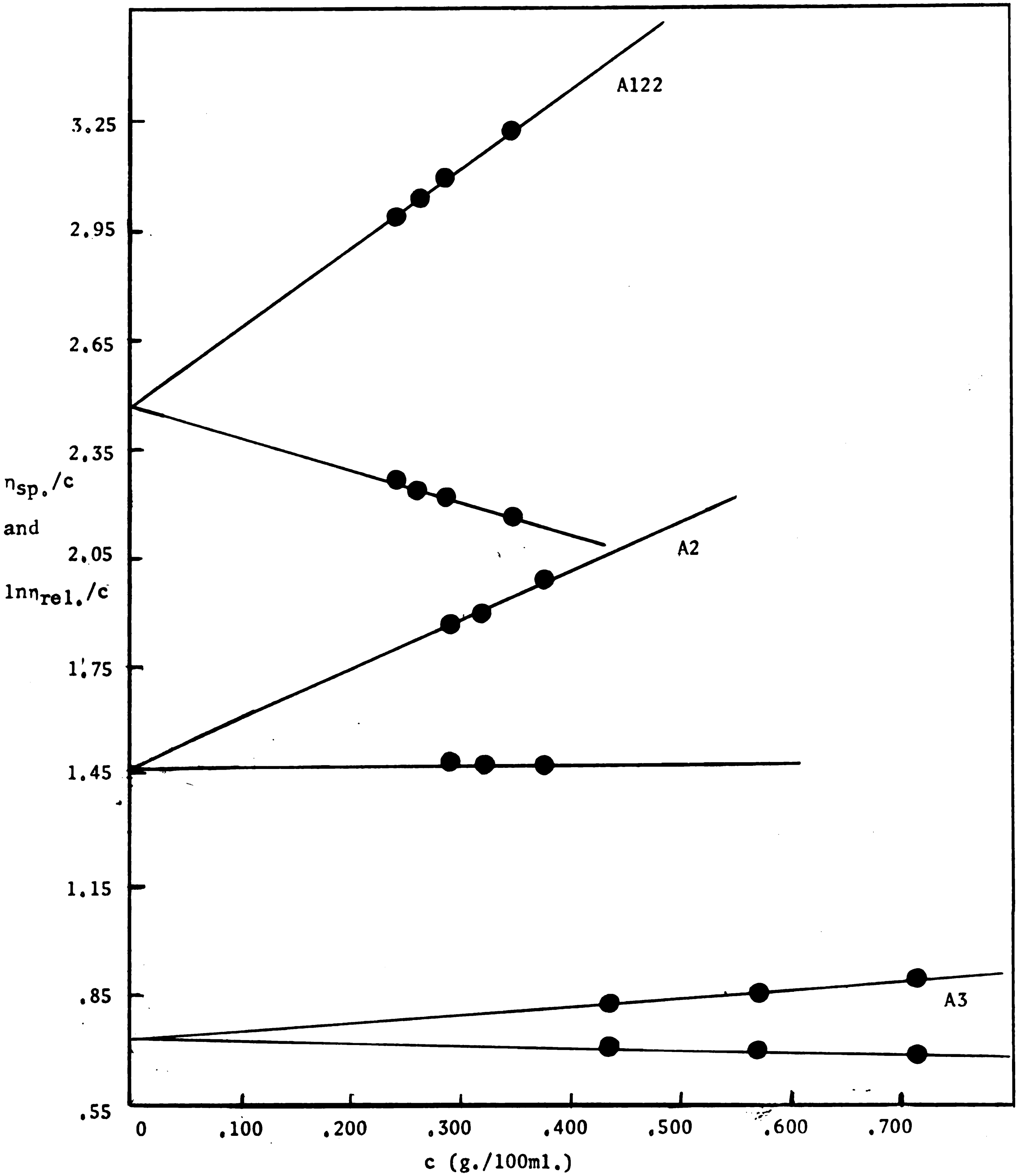

Figure 3. η_{sp}/c and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for three atactic fractions in n-nonane at 80°C

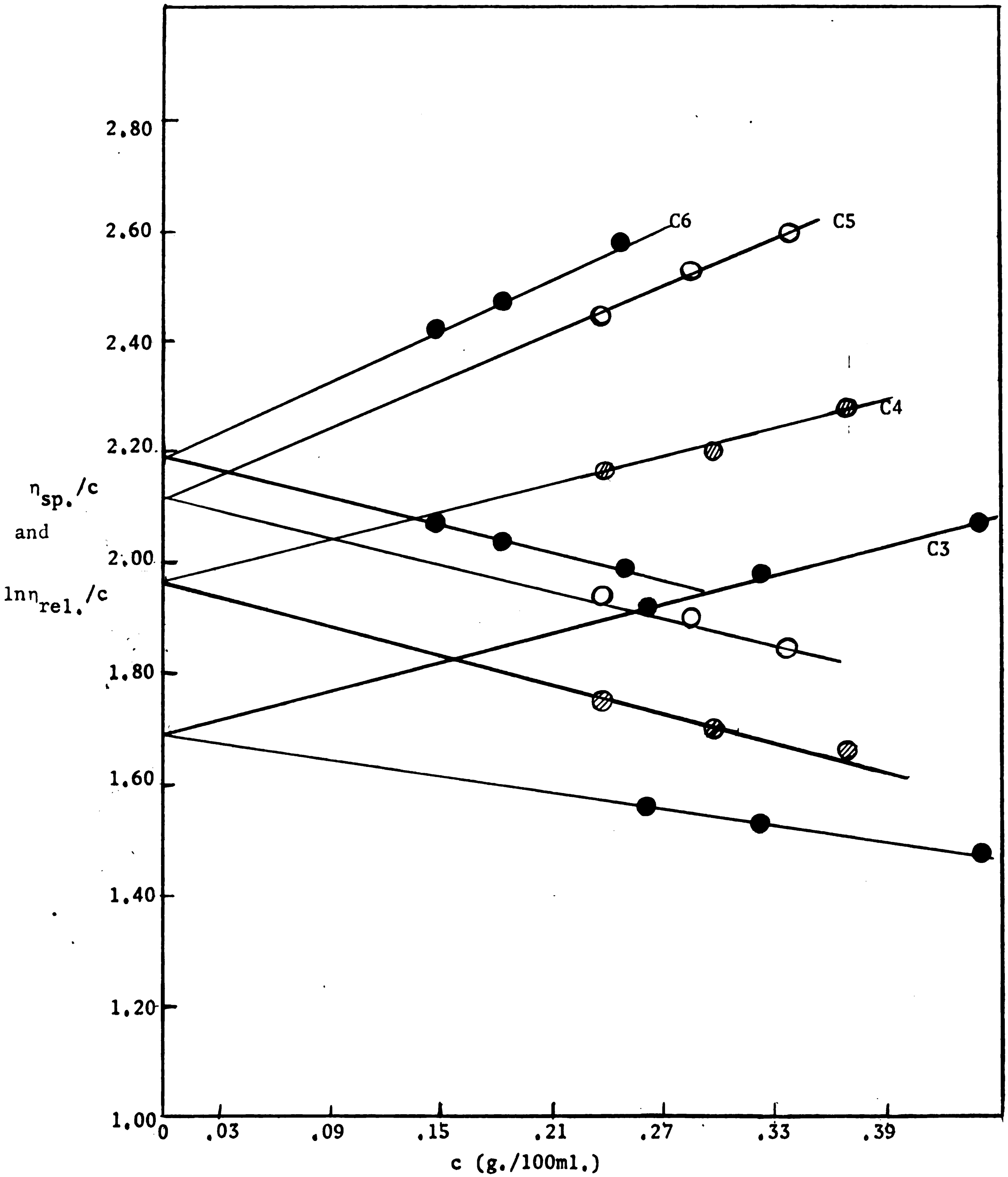

Figure 4. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for four isotactic fractions in n-nonane at 80°C

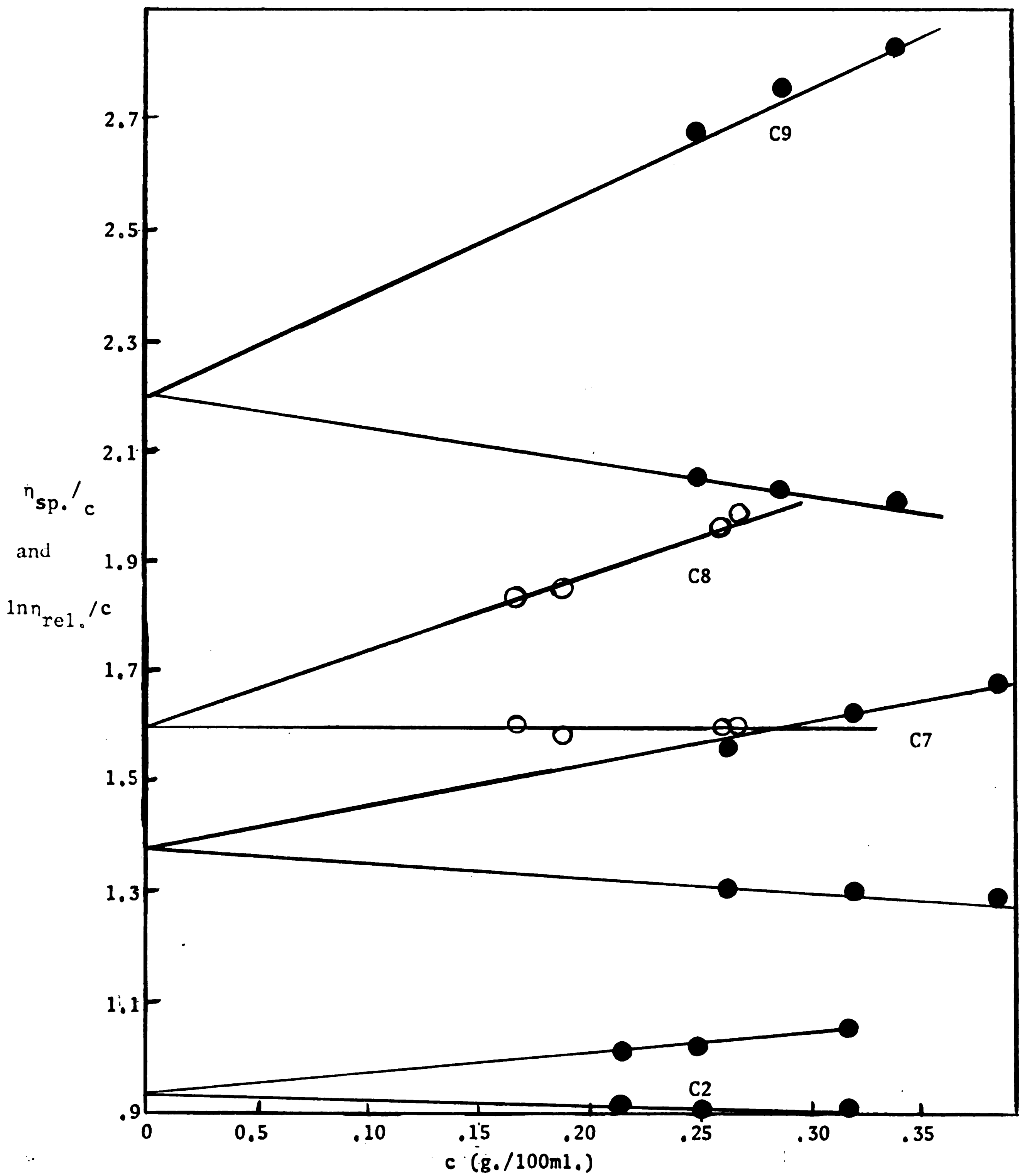

Figure 5. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for four isotactic fractions in n-nonane at 80°C

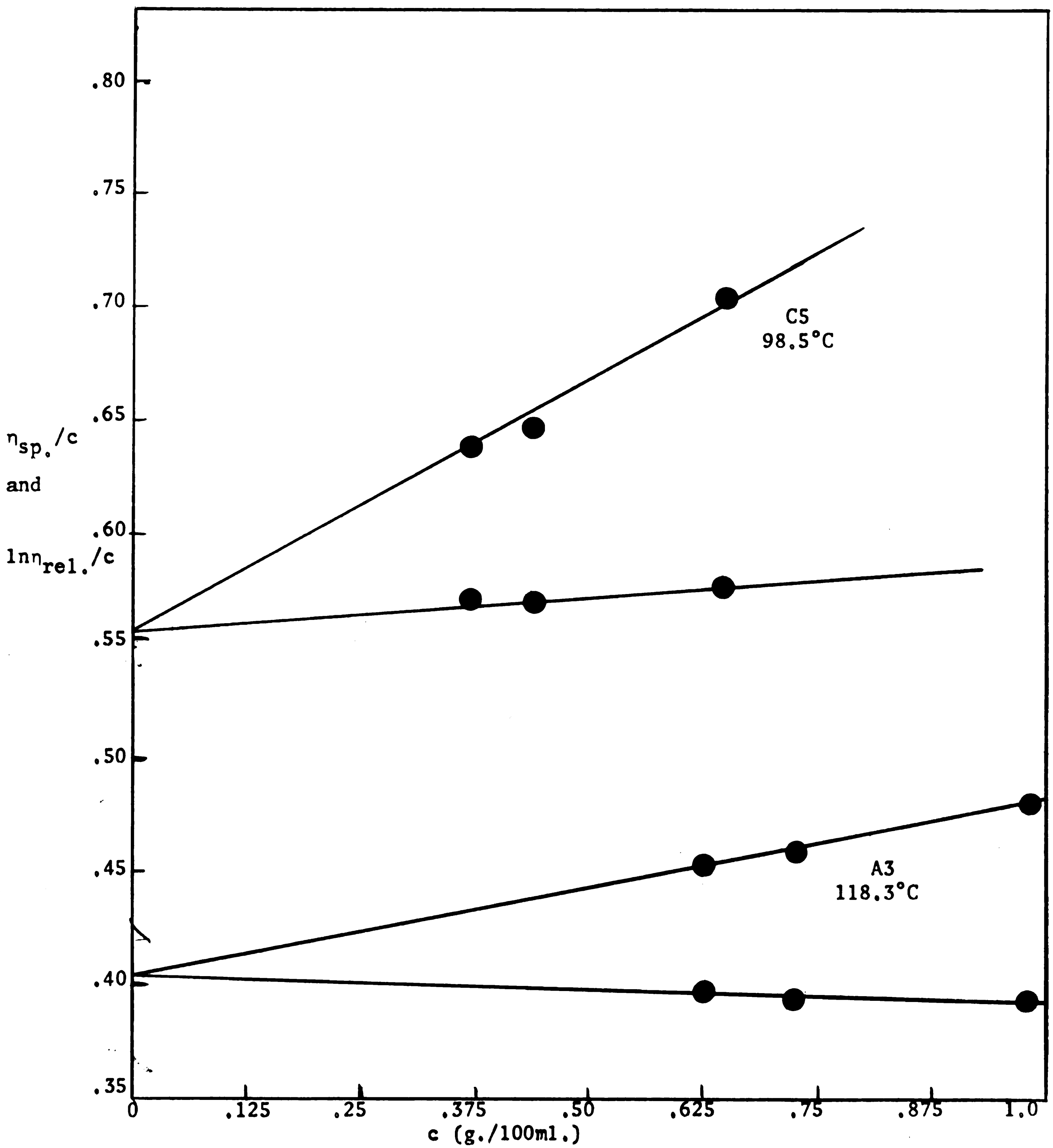

Figure 6. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for isotactic fraction C5 and atactic fraction A3 in diethyl carbitol at the respective Θ temperatures.

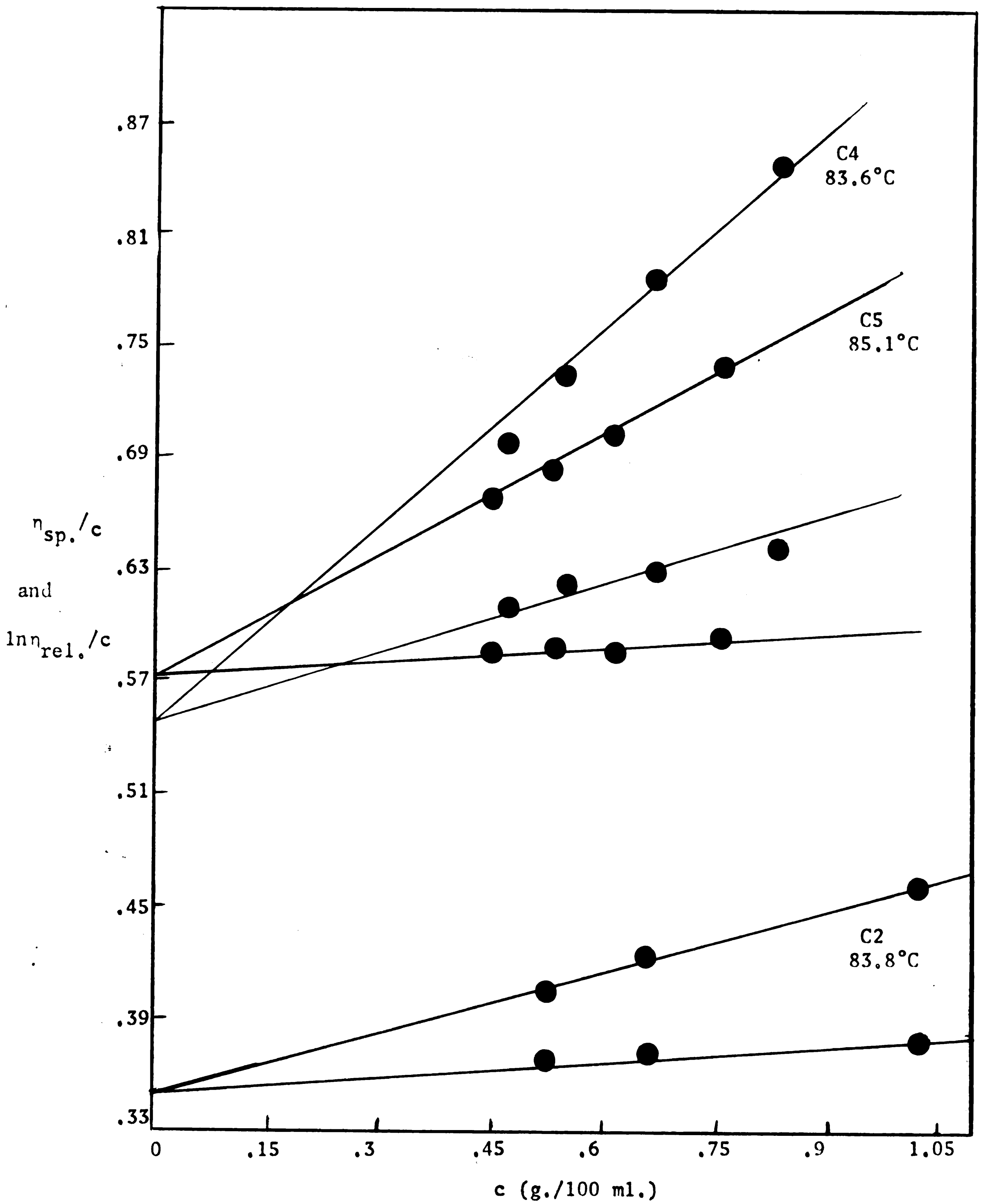

Figure 7. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100 ml.) for three isotactic fractions in α-chloronaphthalene.

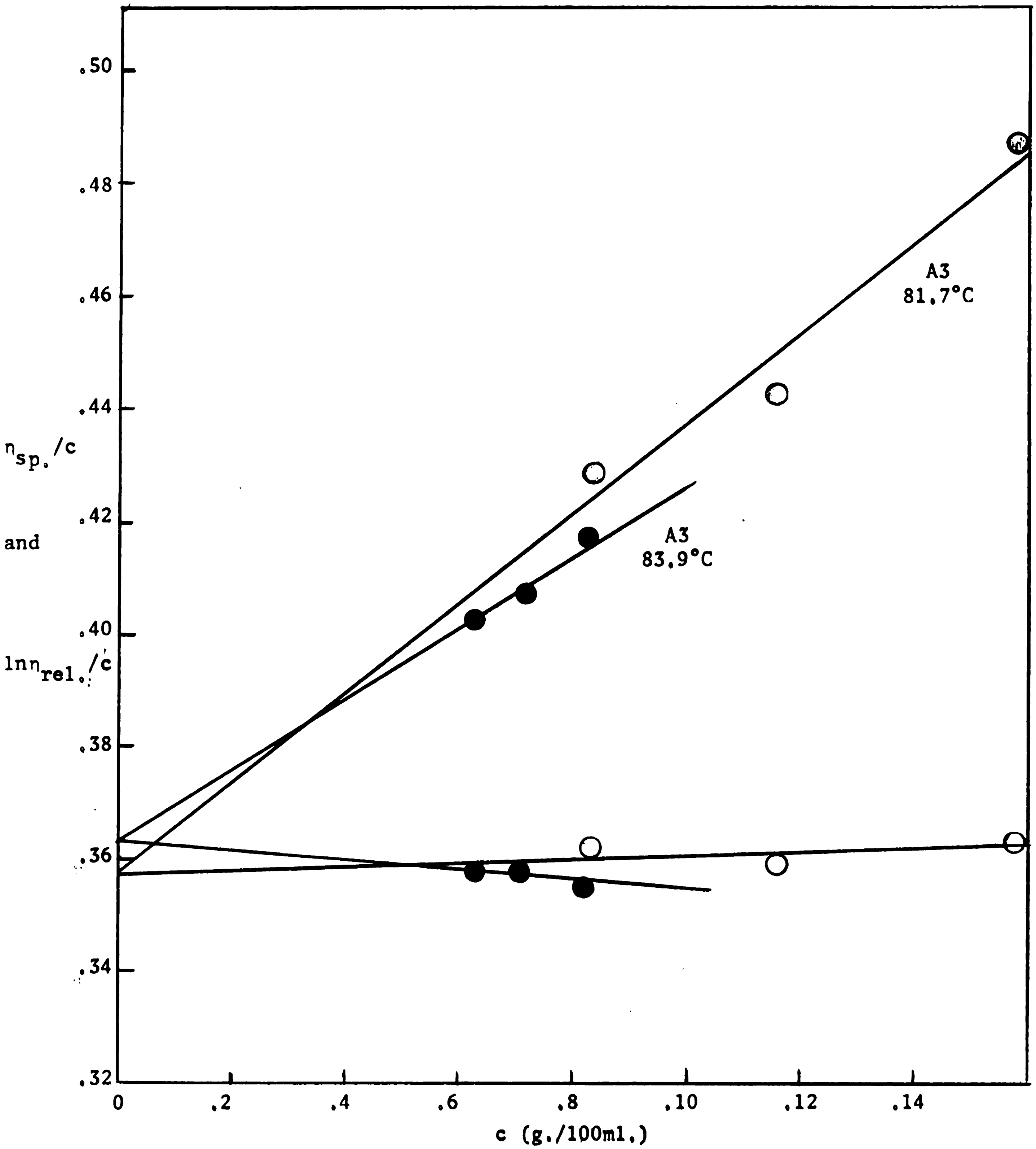

Figure 8. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for atactic fraction A3 in α-chloronaphthalene

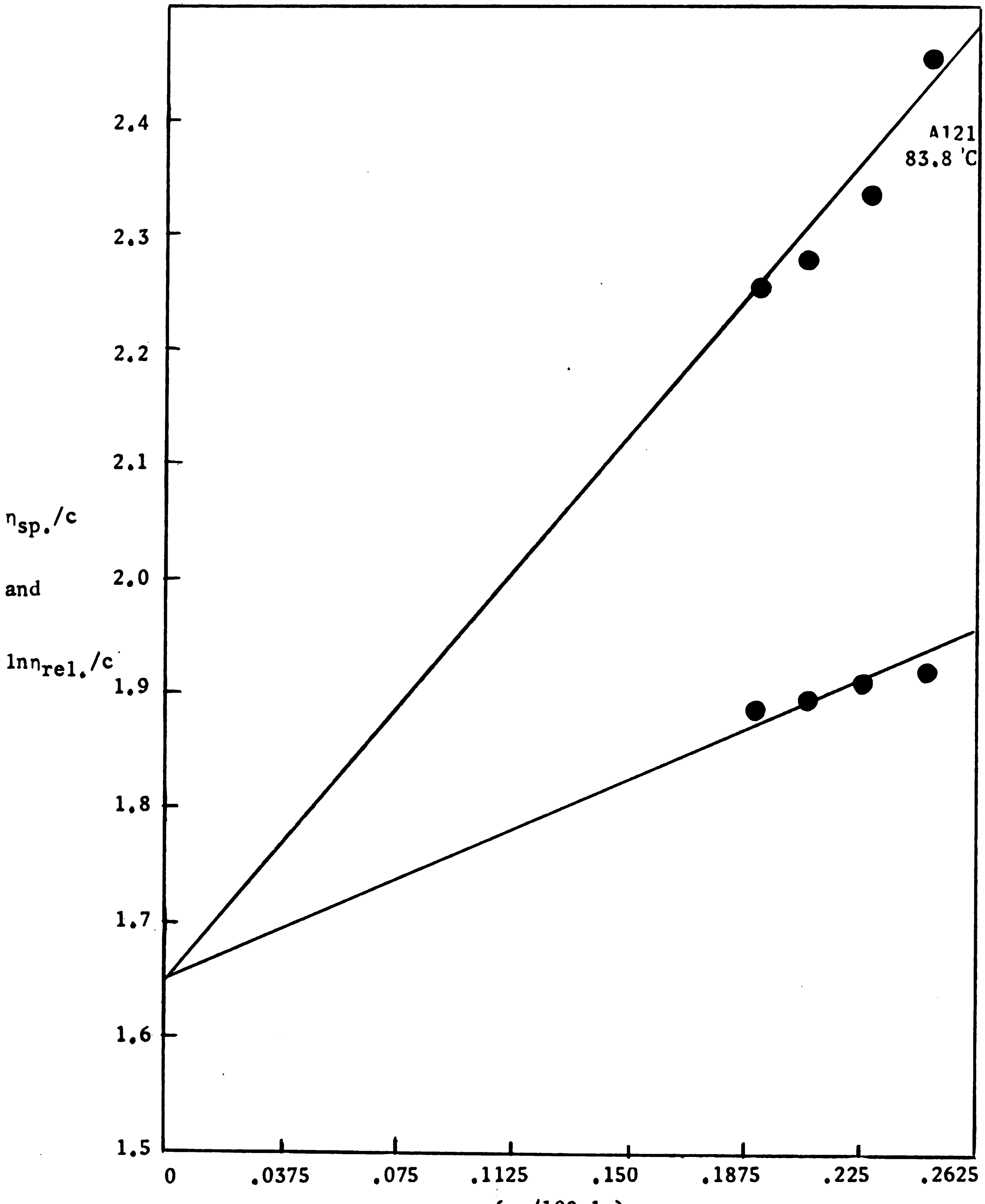

Figure 9. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for atactic fraction A121 in α-chloronaphthalene

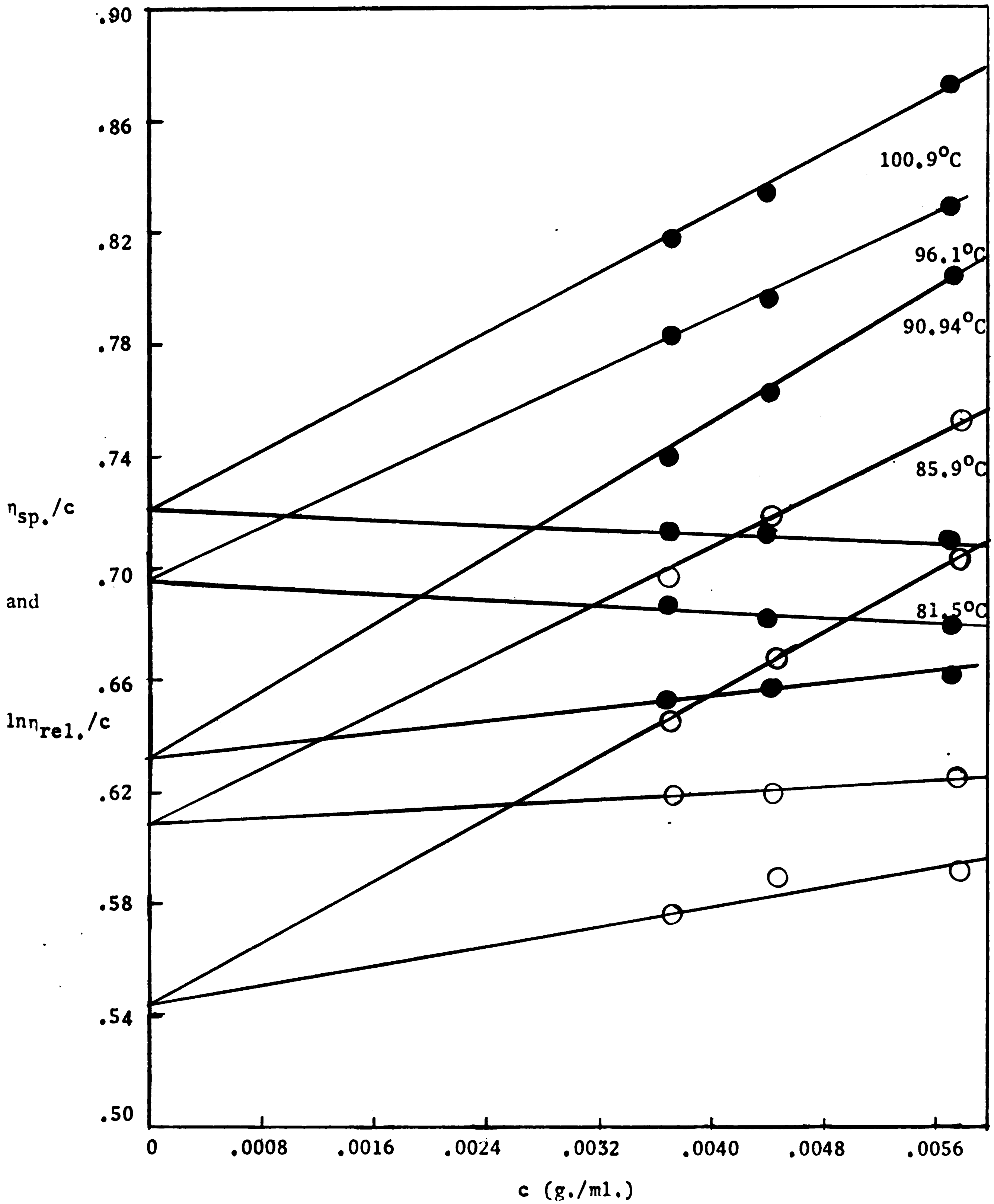

Figure 10. η_{sp}/c and $\ln\eta_{rel.}/c$ versus c (g./ml.) for atactic fraction A2 in α-chloronaphthalene at various temperatures

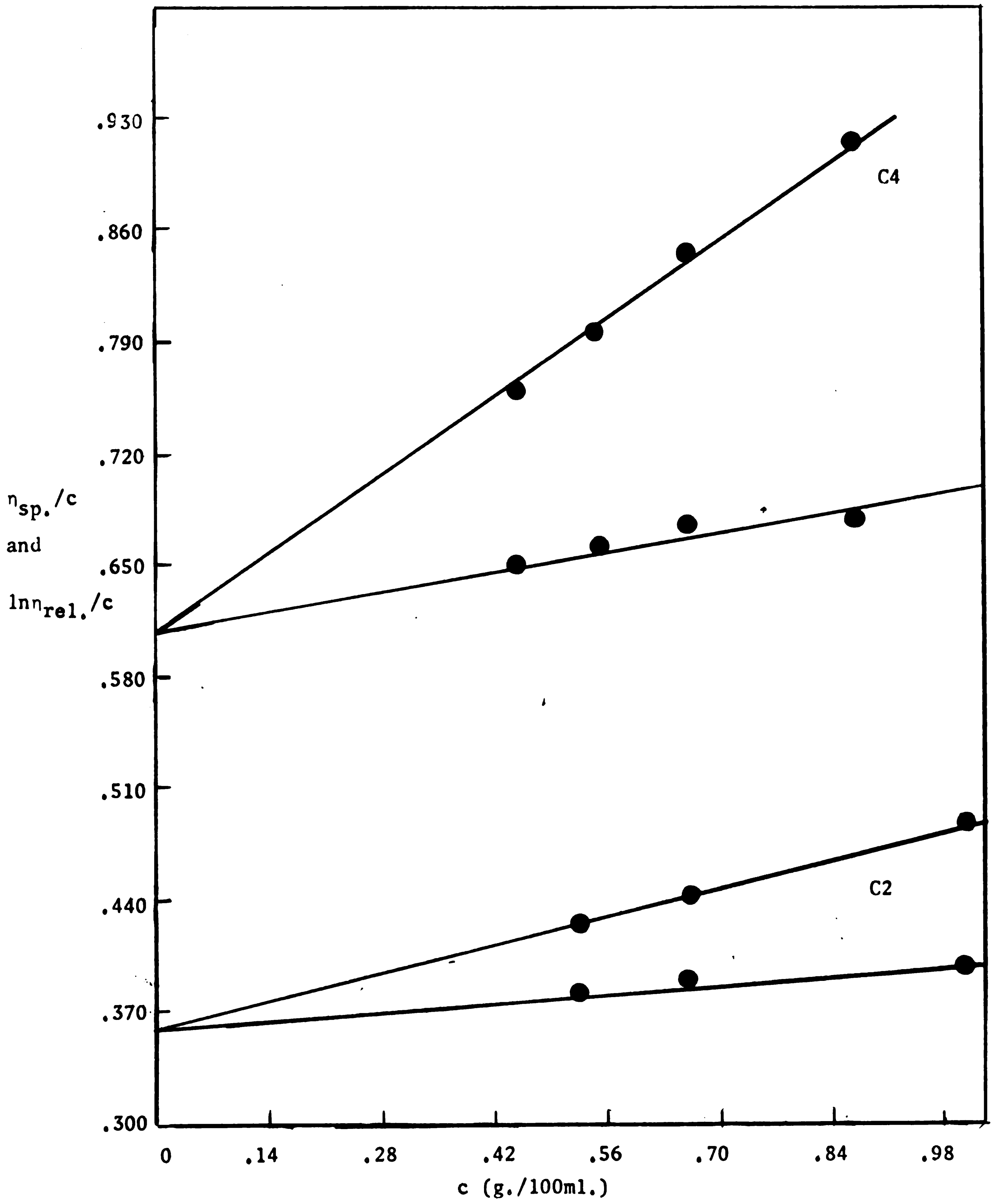

Figure 11. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for two isotactic fractions at 87.3°C in α-chloronaphthalene

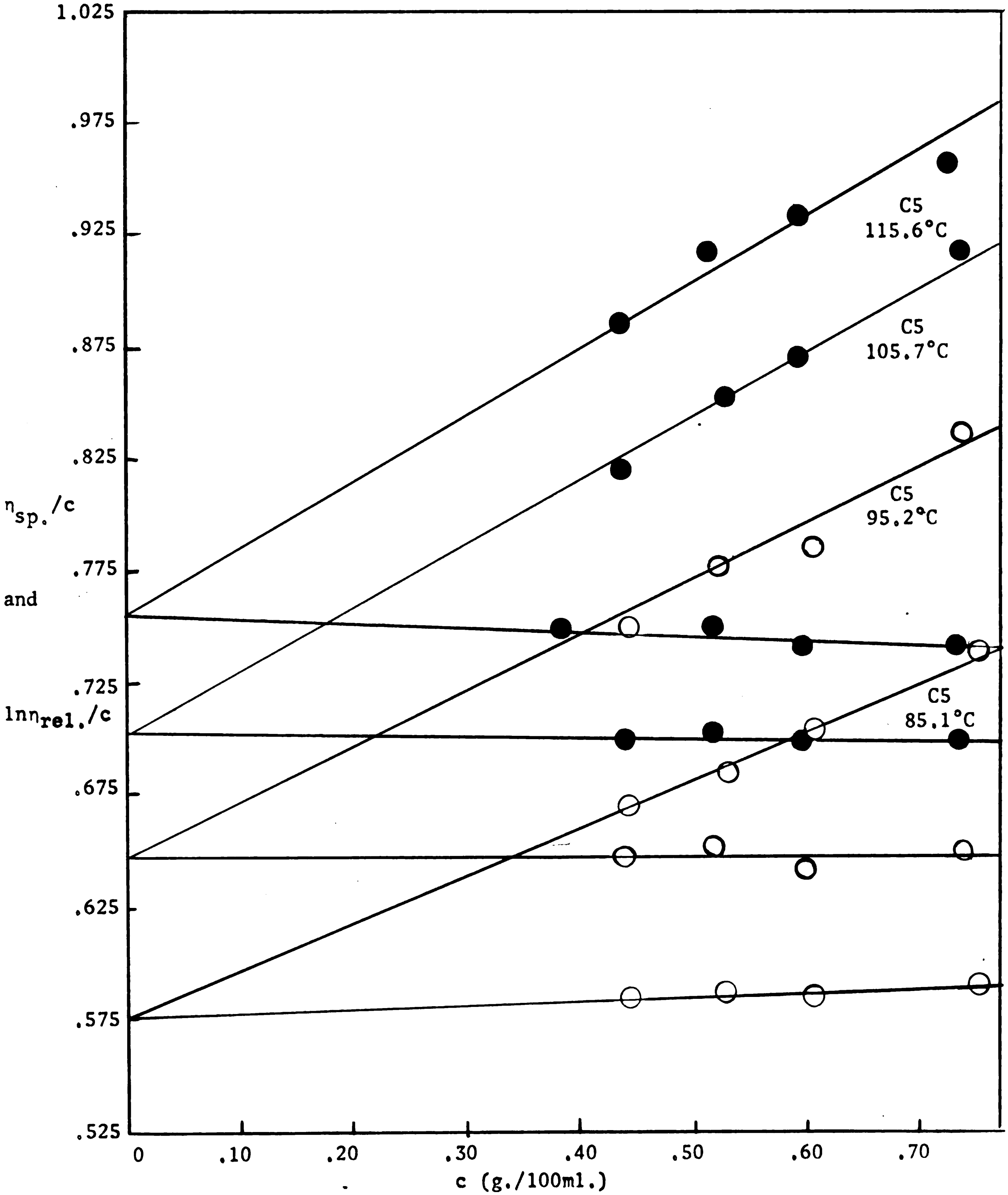

Figure 12. η_{sp}/c versus $\ln\eta_{rel.}/c$ versus c for isotactic fraction C5 in α-chloronaphthalene at various temperatures.

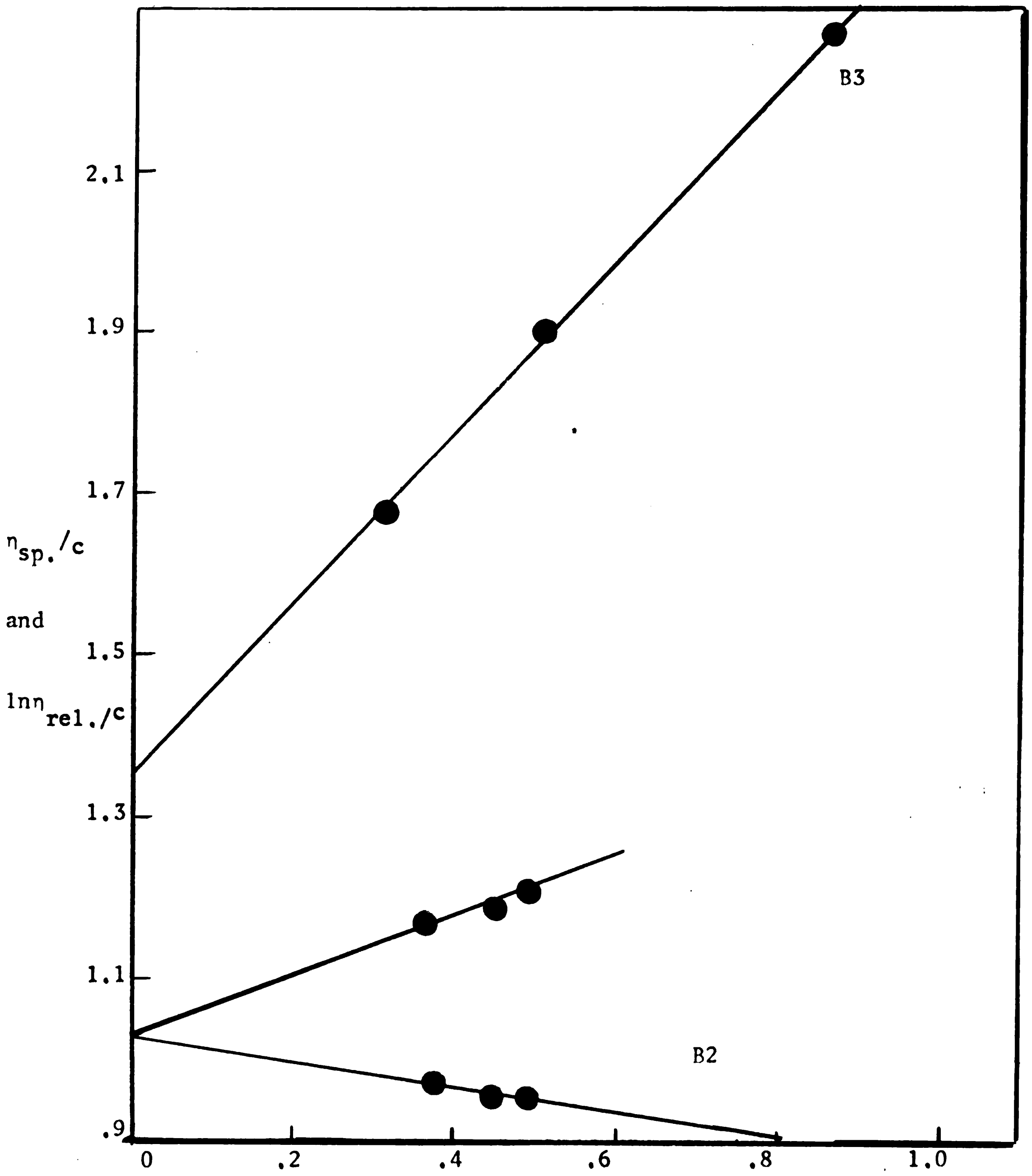

Figure 13. $\eta_{sp.}/c$ and $\ln\eta_{rel.}/c$ versus c (g./100ml.) for two isotactic fractions in n-nonane at 80°C.

APPENDIX B

Precipitation Temperature of 1% Mixture of Isotactic Polybutene-1 in Various Solvents.

Precipitation temperature of 1% mixture of isotactic polybutene-1 in various solvents

Solvent	δ	T_p (°C)	Phase separation
Bromobenzene		35-40	L-C
Tetralin	8.40 (1)	40-45	L-C
Orthobromotoluene		45-50	L-C
Orthodichlorbenzene	10.0 (3)	50-60	L-C
Ortho-xylene	8.99 (1)	25-30	L-C
Chlorobenzene	9.53 (2)	25-35	L-C
Benzene	9.16 (1)	25-35	L-C
Toluene	8.91 (1)	25-35	L-C
Phenetole		56	L-L
Chloroform		25-35	L-C
Cyclohexane	8.20 (1)	25	L-C
Butyl ether		23	L-C
Butyl ether		50-55	indistinct -- may be L-L
Cyclohexyl methyl acetate		60-65	L-C
n-Heptanol		80-90	L-C
Methyl nonyl ketone		70-75	L-C
Anisole		87.0-88.5	L-L
Diethyl ketone		75-80	L-C
Phenyl cyclohexane		45-55	L-C
α-Chloronaphthalene		78	L-L

(1) Dr. W. R. Krigbaum, Duke University
(2) Walker, E. E., Journal of Applied Chemistry, 2, 470 (1952)
(3) Burrel, H., Interchem. Rev., 14, 1 (spring 1955)

APPENDIX C

Phase Data

Table 1

Phase diagram data for the system isotactic polybutene-1 α-chloronaphthalene

Fraction	Volume fraction (v_2)	T_p ($^oC.$)
C9	.0610	78.5
	.0466	79.7
	.0350	79.7
	.0311	80.0
	.0274	80.2
	.0223	80.15
	.0174	80.2
C4	.1129	73.4
	.0461	78.5
	.0300	79.3
	.0245	79.7
	.0201	79.2
	.0167	79.1
	.0129	78.7
	.0094	78.6
C3	.0754	75.15
	.0462	76.9
	.0259	78.15
	.0231	78.3
	.0194	78.3
	.0161	77.9
	.0123	77.65
	.0090	76.65
C2	.0945	72.9
	.0408	75.5
	.0305	76.9
	.0255	77.1
	.0218	76.6
	.0183	76.55
	.0144	76.15
	.0104	75.55

Table 2

Phase diagram data for the system atactic polybutene-1 α-chloronaphthalene

Fraction	Volume fraction (V_2)	T_p (°C)
A122	.0706	76.7
	.0493	77.5
	.0327	76.9
	.0279	76.5
	.0217	75.8
	.0162	75.4
A121	.0622	77.7
	.0512	78.4
	.0410	77.1
	.0313	76.8
	.0224	76.2
	.0180	75.6
A2	.1601	63.0
	.0768	71.2
	.0513	72.0
	.0347	72.3
	.0262	71.8
	.0210	72.1
A3	.0858	64.2
	.0499	67.8
	.0323	68.4
	.0249	66.4
	.0192	64.5
	.0152	65.5

APPENDIX D

Light Scattering Solvent Study

Light scattering solvent study

Compound	$n_D^{20°}$ (1)	Qualitative(2) test	Solubility(3) temperatures (°C)
Acetonitrile	1.3459	p	
Acetophenone	1.5342	g	
Allyl chloride	1.415	g-vg	
Aniline	1.586	f	
Anisole	1.5179		soluble 87.0-88.5
Benzene	1.5014	g-vg	soluble 25-35
Benzyl ether		f-g	
Bromobenzene	1.5597	vg	soluble at 40
Bromoform	1.5980	g-vg	
Bromotrichloromethane	1.5300	vg	soluble at 50
Butyl cellosolve		f	
Butyl ether			soluble at 55
Carbon disulfide	1.6295	vg	
Chlorobenzene	1.5248	vg	soluble 25-35
1-Chloro-2-ethylbenzene		vg	
α-Chloronaphthalene	1.6332	f-g	soluble 78
Chloroform	1.4464		soluble 25-35
Cyclohexane	1.4290	vg	soluble at room temp.
Cyclohexene	1.4451	vg	
Cyclohexyl methyl acetate		vg	soluble 60-65
Dichlorobenzene 1,2	1.5518	g	soluble 50-60
Diethyl ketone	1.3939	f	insoluble below 65
Diisobutyl ketone	1.412	g	soluble at 60
Dimethyl phthalate	1.515	p-f	
Ethyl acetate		p	
Ethyl alcohol	1.3624	p	
Ethyl bromide	1.4239	f	
Hexane	1.3754	g-vg	
Iodo benzene	1.6214	g-vg	not soluble at 40
Isoamyl acetate	1.4017		soluble 25-35
Mesitylene	1.4967	vg	
m-Xylene	1.4996	g-vg	
Methanol	1.3312	p	
Methyl cellosolve		f	
Methyl ethyl ketone	1.38071	p-f	
Methyl nonyl ketone	1.4300	f-g	soluble 65-75
Neohexane		f-g	
Nitrobenzene	1.55291	f-g	

(1) Data taken from Langes* Handbook of Chemistry or CEM Rubber Handbook
(2) Designation indicates ability of solvent (20°C) to swell polymer fibers (g = good; f = fair; vg = very good; p = poor)
(3) Temperature at which 1% polymer sample is soluble

Nitromethane	1.3818	p	
n-Amyl acetate		f	
n-Butyl chloride	1.4015	g	better solvent than diisobutyl at room temperature
n-Decanol	1.4368	f-g	
n-Heptanol	1.4241		insoluble below 85
o-Bromotoluene		g	soluble 45-50
o-Chloroaniline	1.5895	f-g	
o-Chlorobenzaldehyde	1.5614	f	
o-Toluidine	1.5728	p-f	
o-Xylene	1.5078		soluble 25-30
p-Xylene	1.4942	g-vg	
Phenetole	1.5076		soluble at 56
Phenyl cyclohexane	1.589		soluble at 55
Propylene chloride	1.4388	p-f	
Quinoline	1.6245	f-g	
Tetrabromoethane(1,1,2,2)	1.6379	g-vg	
Tetrachloroethane(1,1,1,2)	1.4817		not soluble at room temp.
Tetrachloroethylene	1.505		soluble at room temp.
Tetralin	1.5461	g	
Toluene	1.4978	vg	soluble 25-35
Trichlorobenzene(1,2,4)	1.5671	g	
Xylene		g-vg	

APPENDIX E

Light Scattering Data

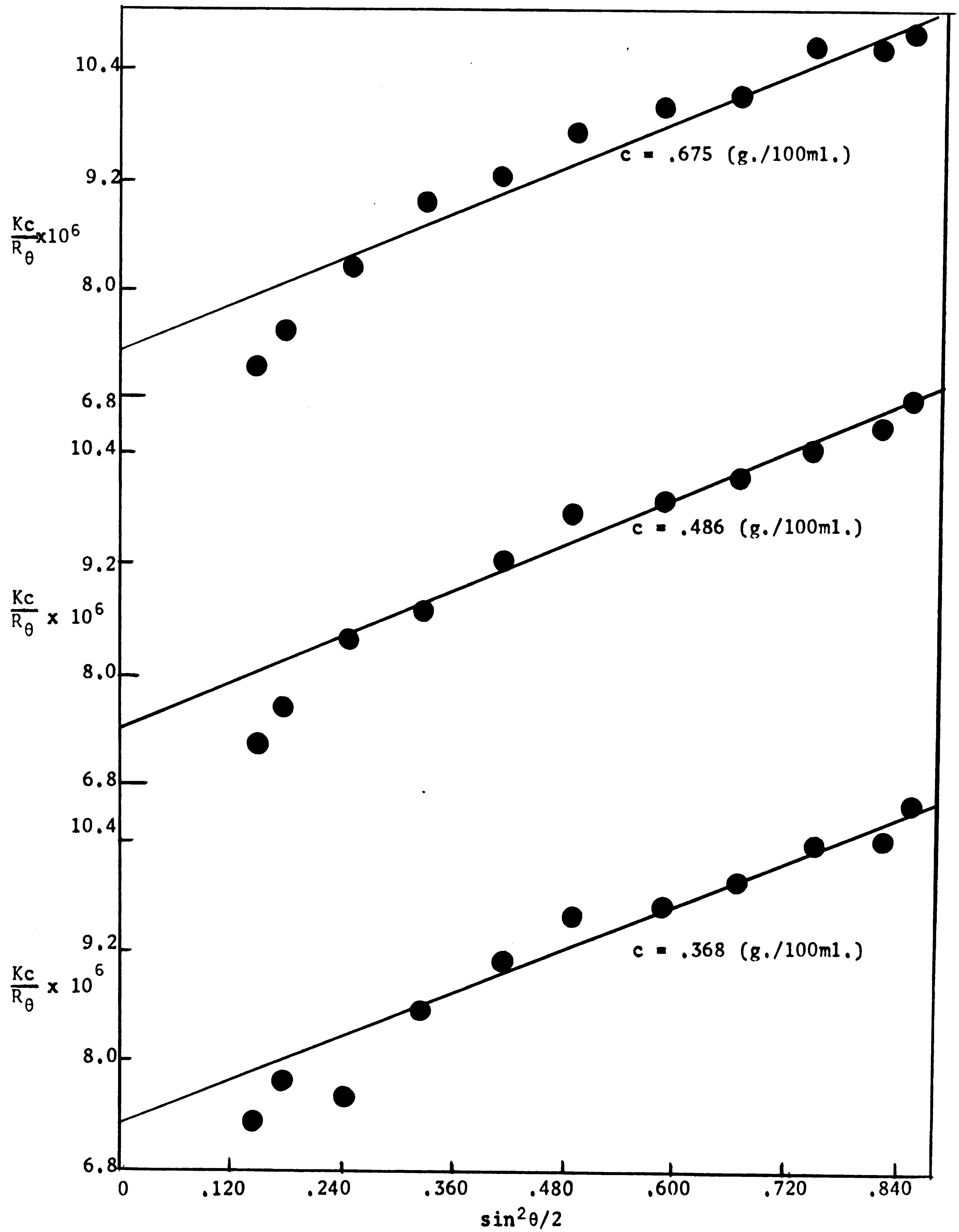

Figure 1. Angular light scattering data for atactic fraction A3 in α-chloronaphthalene at 81.7°C at various concentrations.

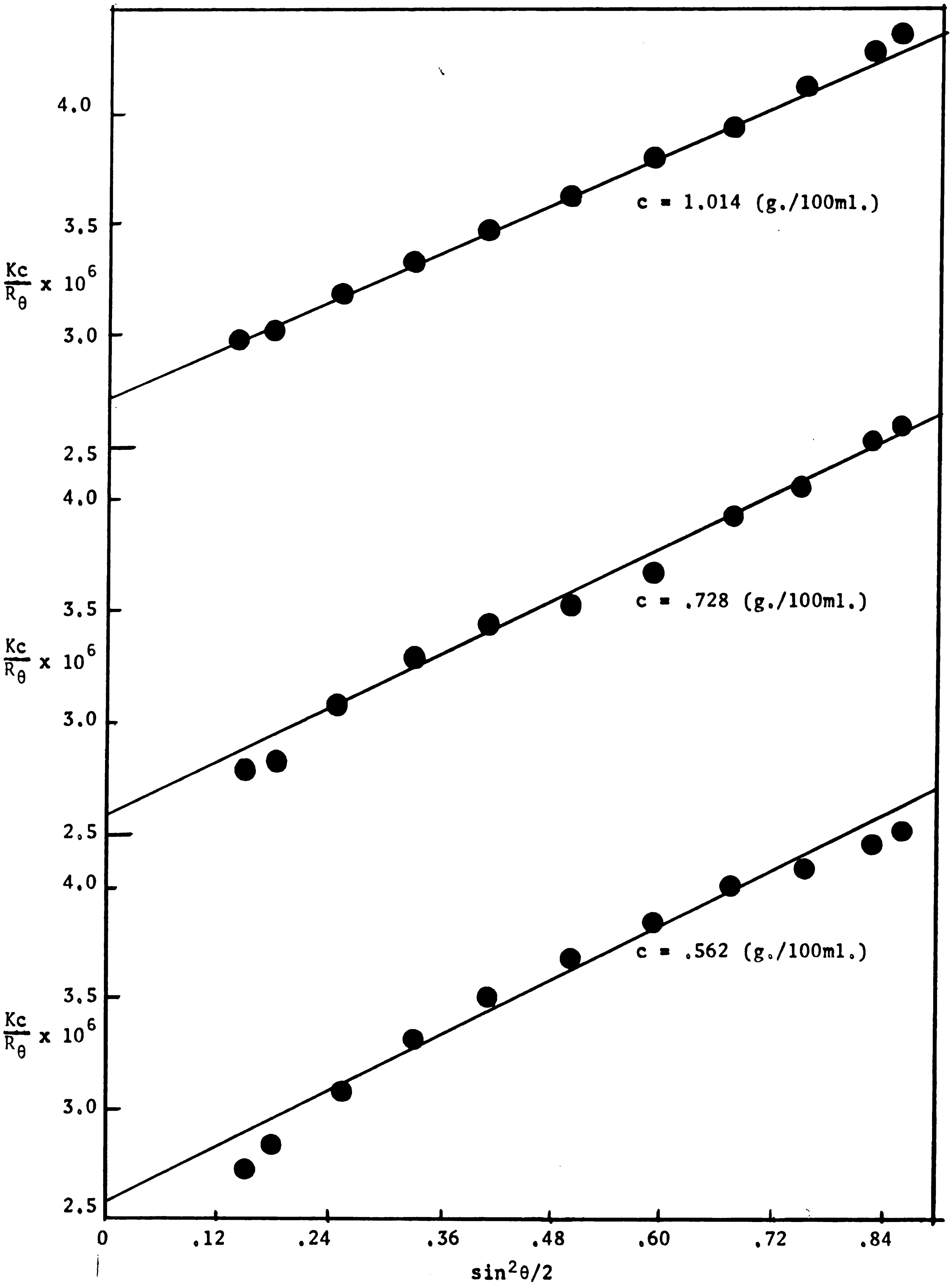

Figure 2. Angular light scattering data for isotactic fraction C3 in

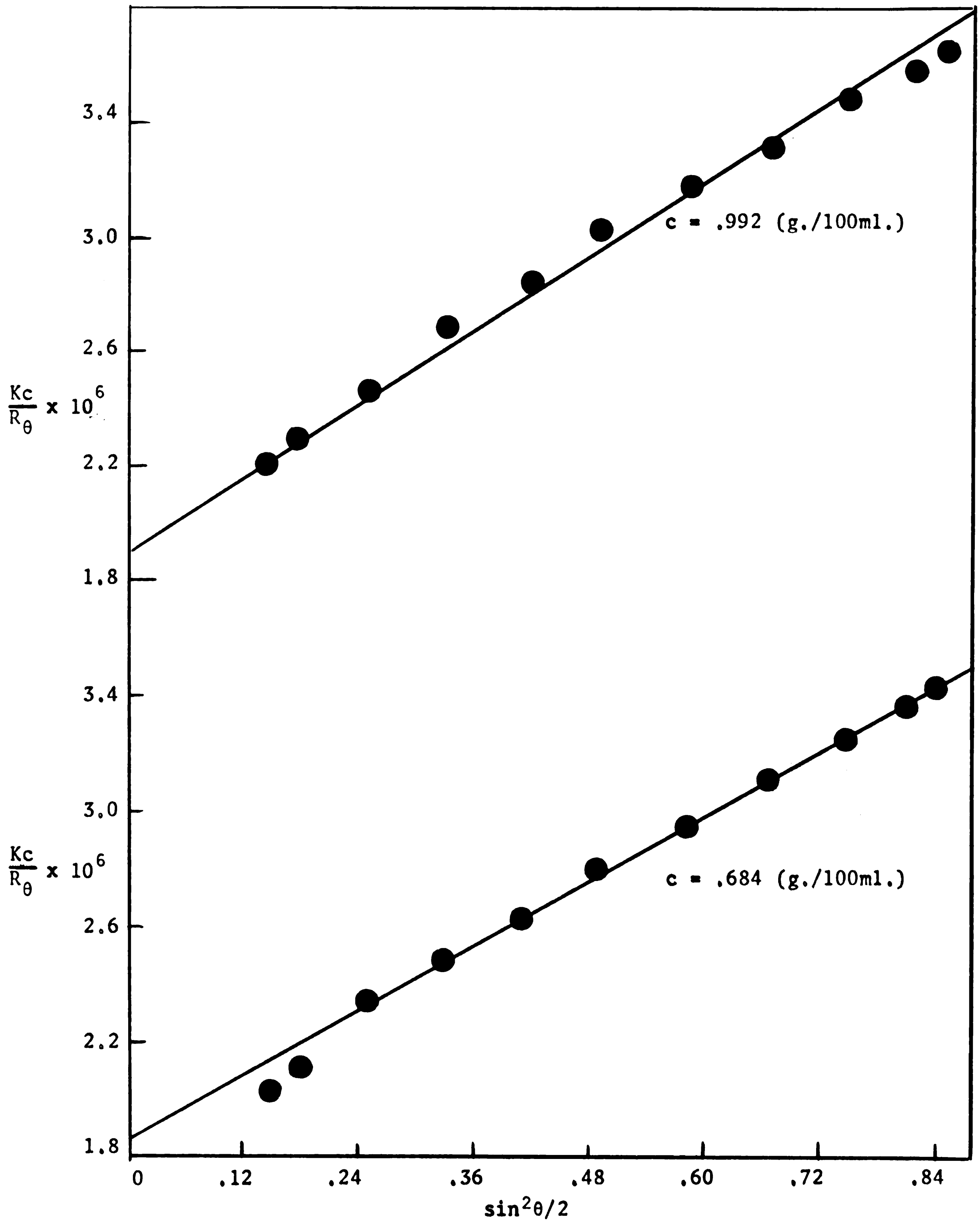

Figure 3. Angular light scattering data for isotactic fraction C4 in α-chloronaphthalene at 83.7°C at various concentrations.

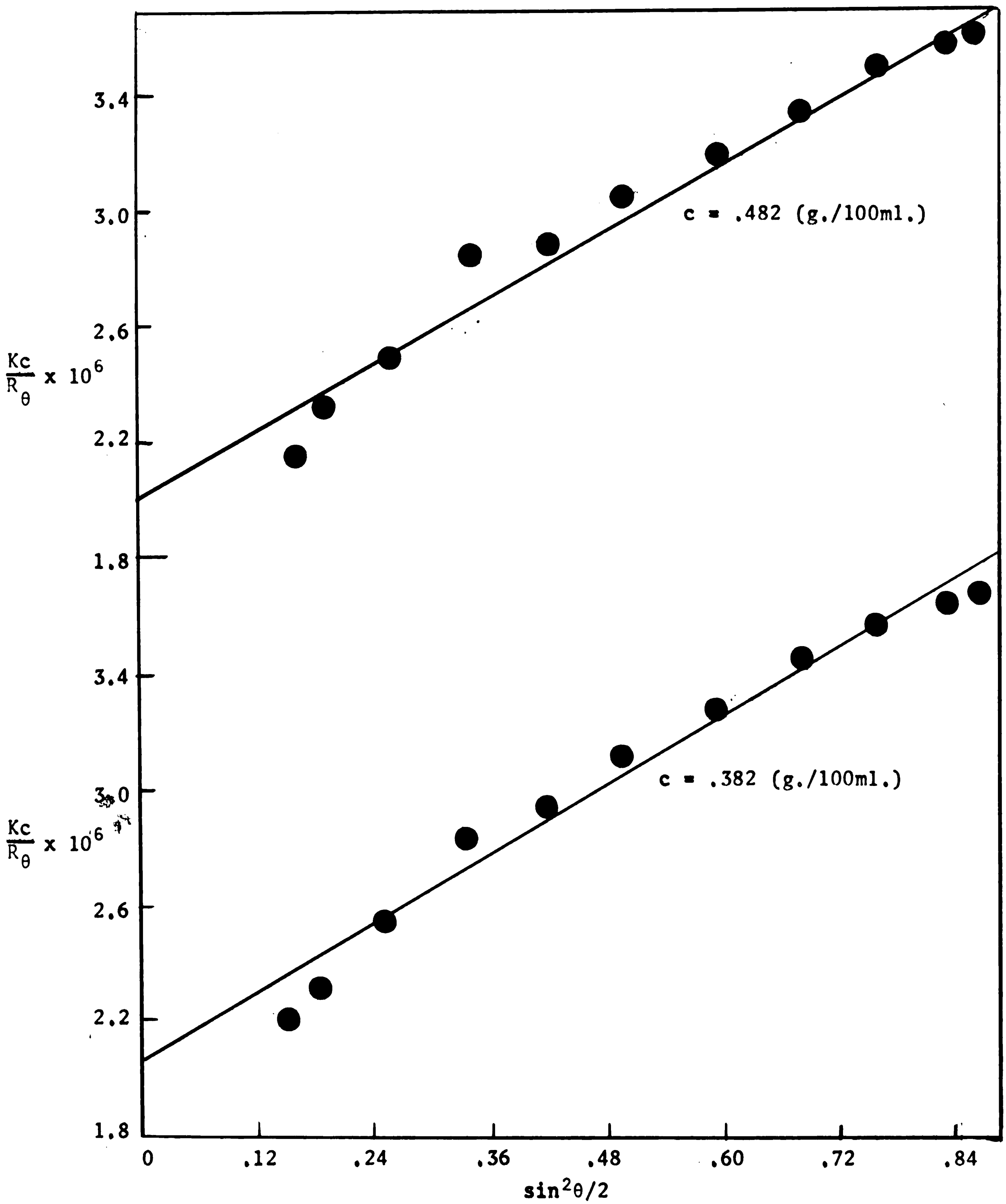

Figure 4. Angular light scattering data for isotactic fraction C4 in α-chloronaphthalene at 83.7°C at various concentrations.

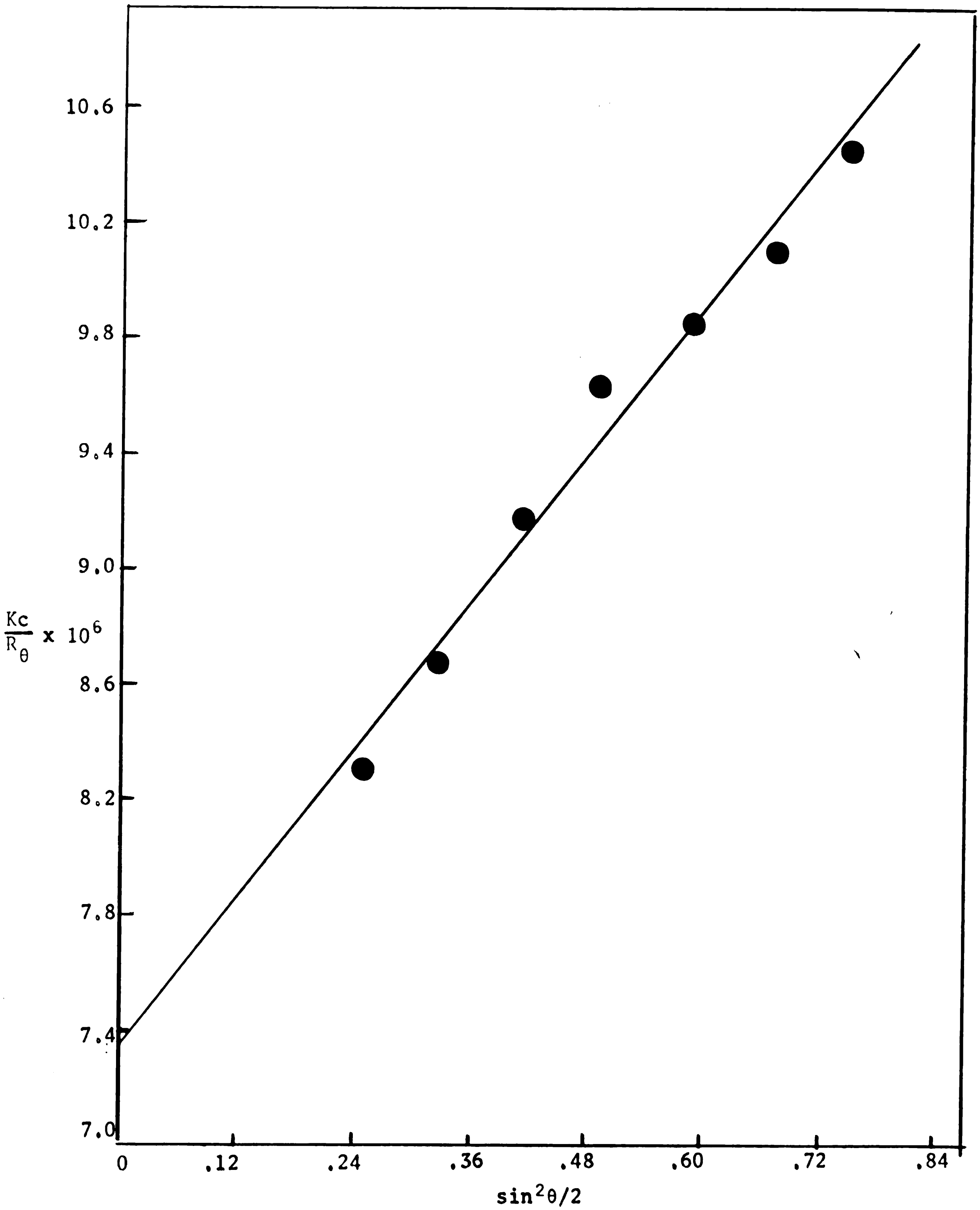

Figure 5. Angular light scattering data for atactic fraction A3 in α-chloronaphthalene at 81.7°C at zero concentration.

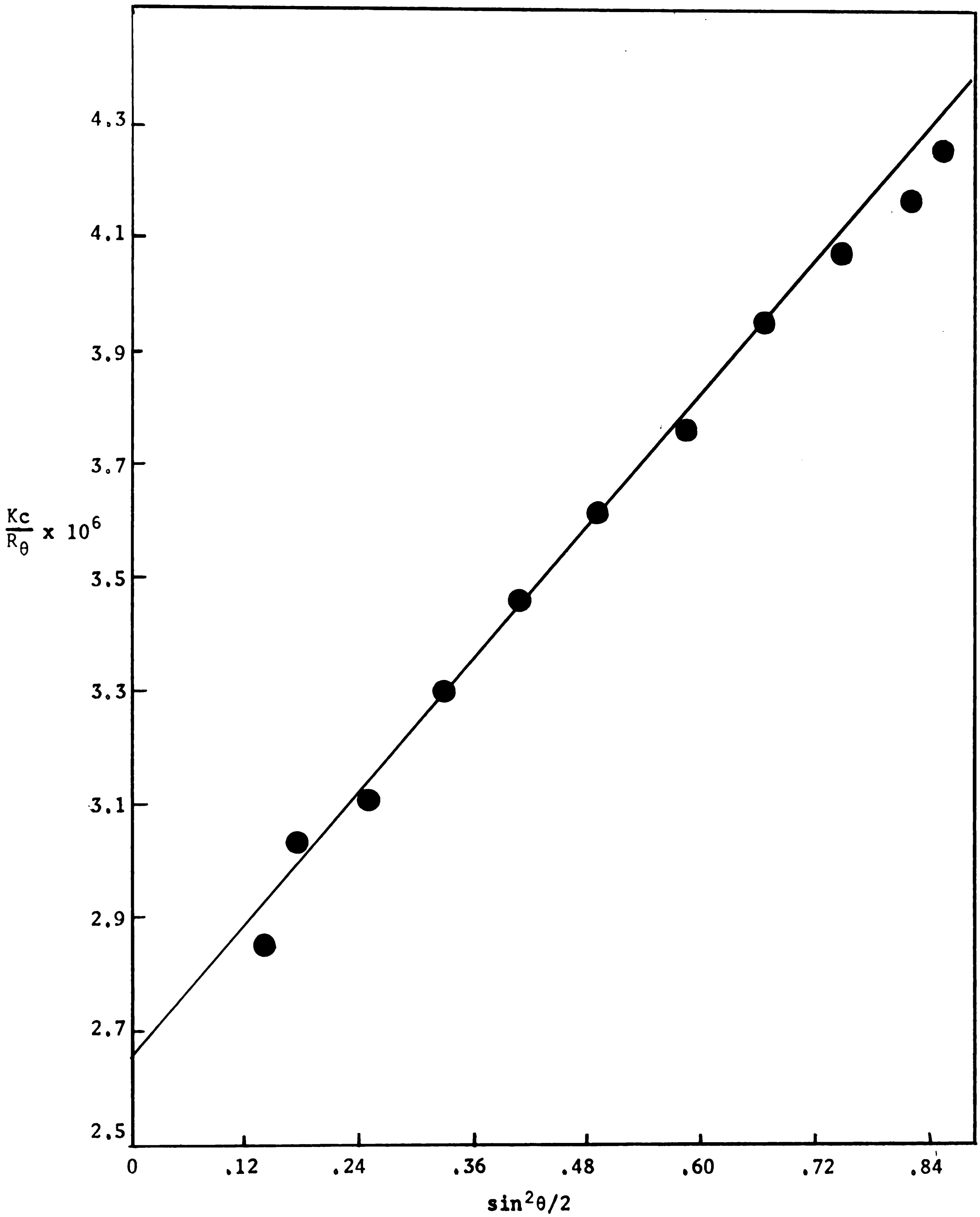

Figure 6. Angular light scattering for isotactic fraction C3 in α-chloronaphthalene at 83.7°C at zero concentration.

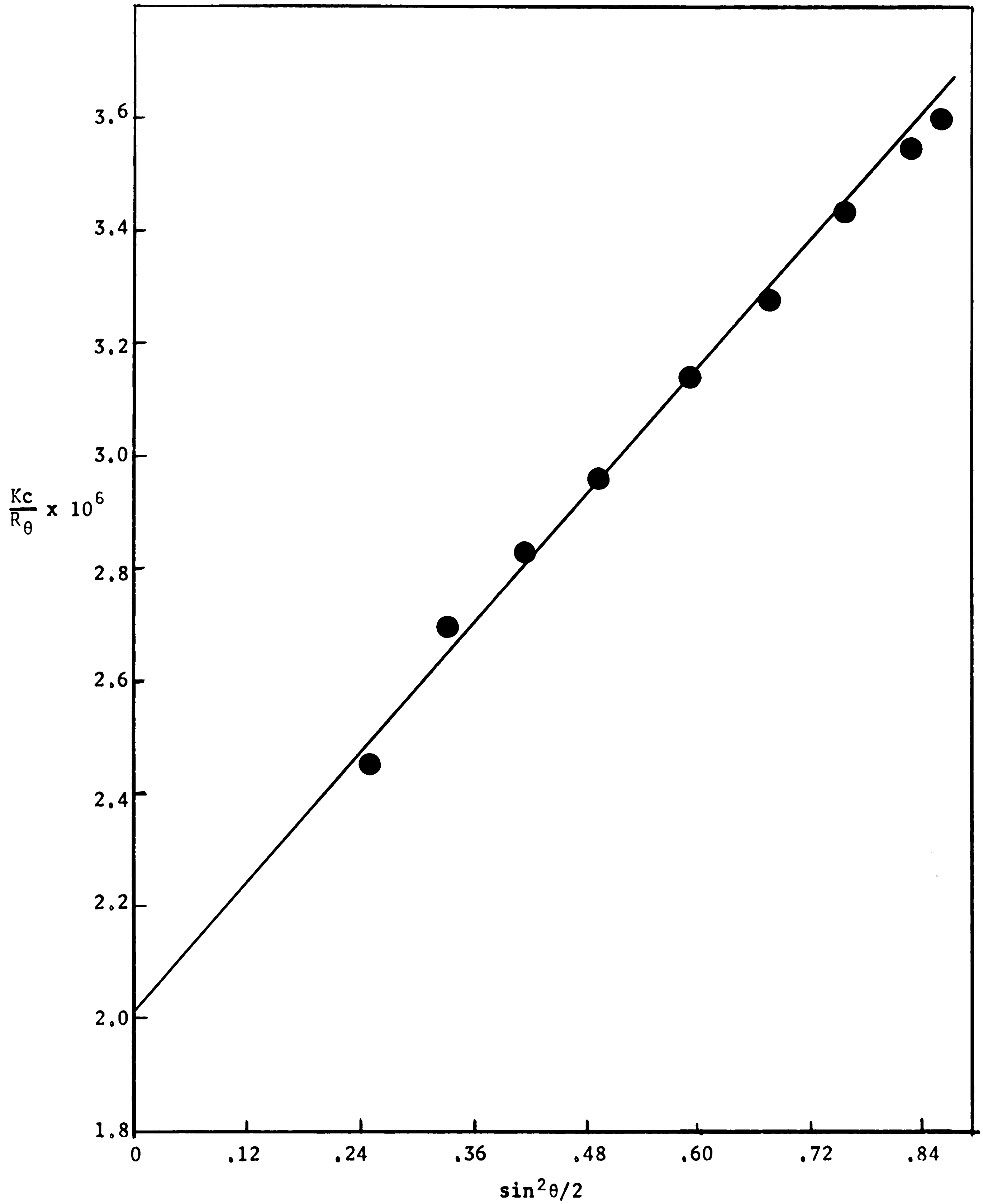

Figure 7. Angular light scattering for isotactic fraction C4 in α-chloronaphthalene at 83.7°C at zero concentration.

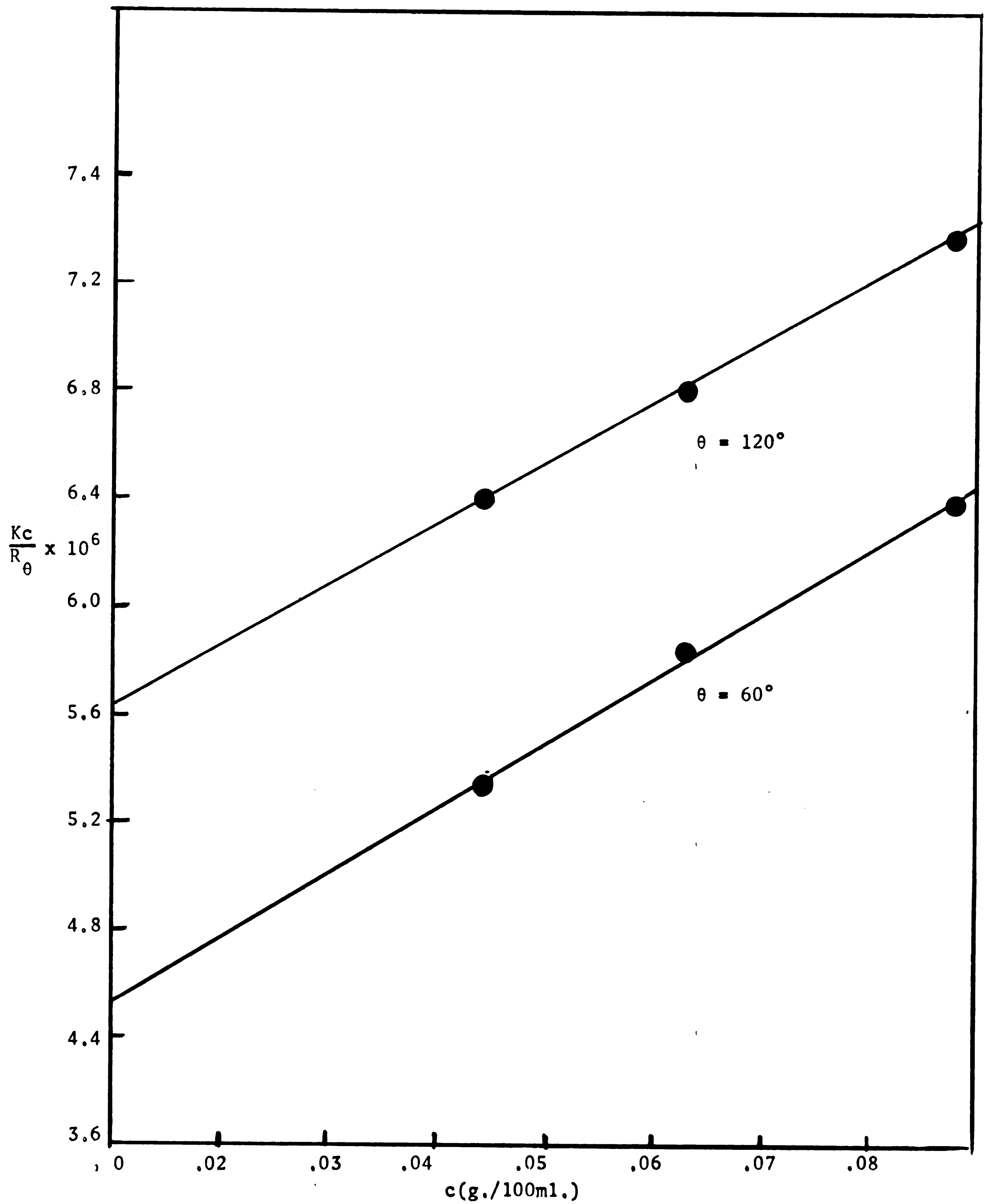

Figure 8. Light scattering data of $\sin^2\theta/2$ values extrapolated to zero concentration for atactic fraction A2 in α-chloronaphthalene at 85°C.

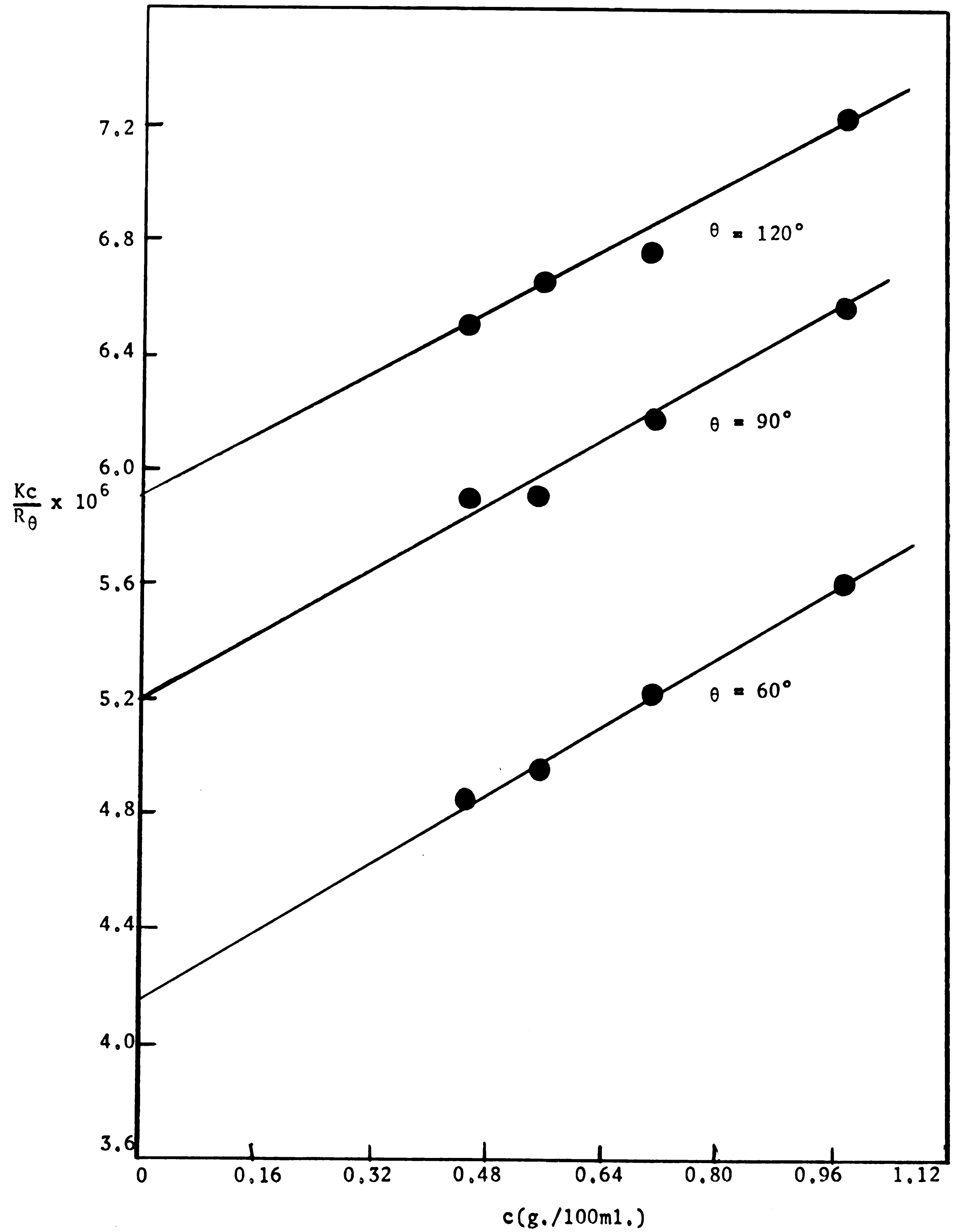

Figure 9. Light scattering data of $\sin^2\theta/2$ values extrapolated to zero concentration for isotactic fraction B3 in α-chloronaphthalene at 86°C.

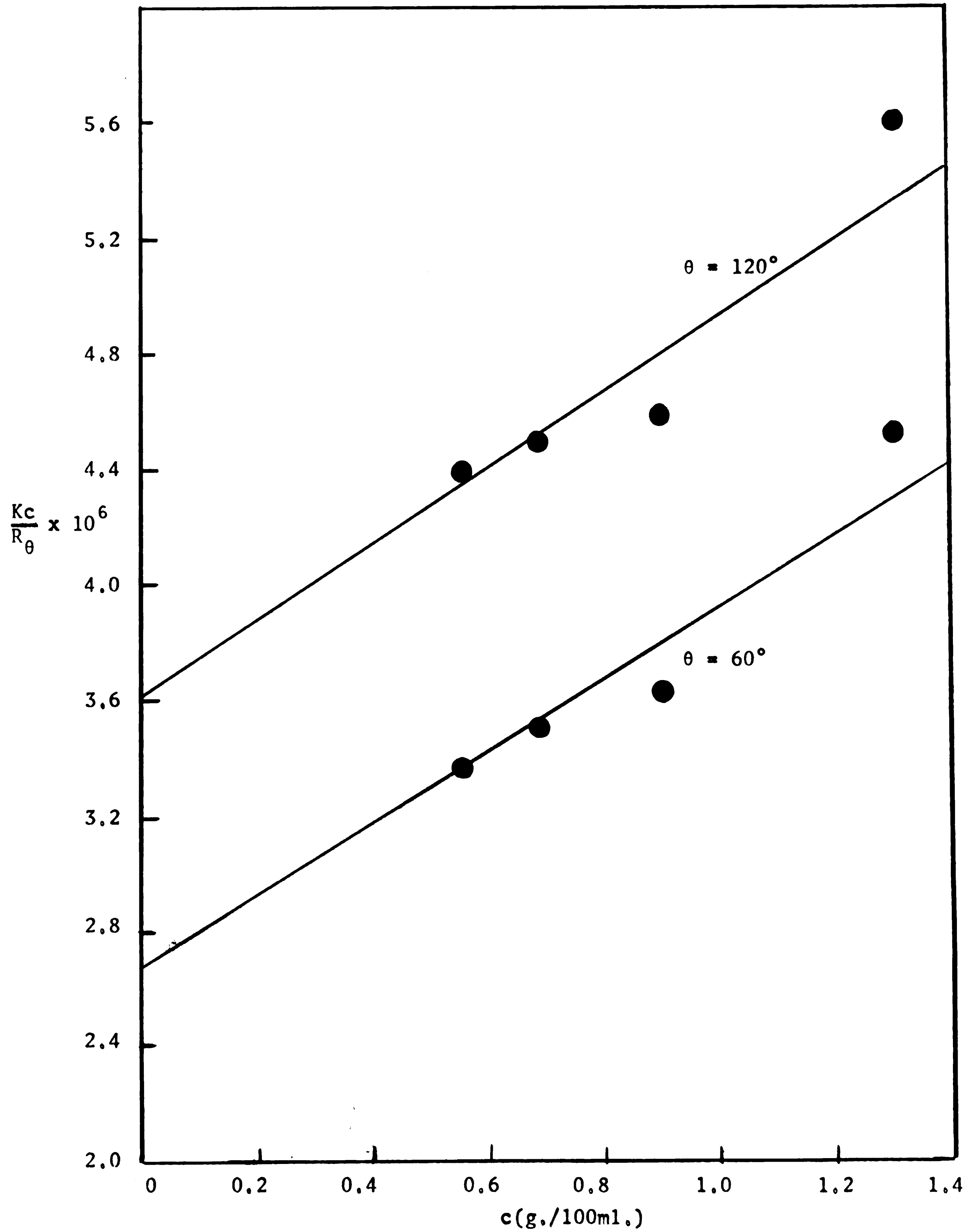

Figure 10. Light scattering data of $\sin^2\theta/2$ values extrapolated to zero concentration for isotactic fraction B8 in α-chloronaphthalene at 86°C.

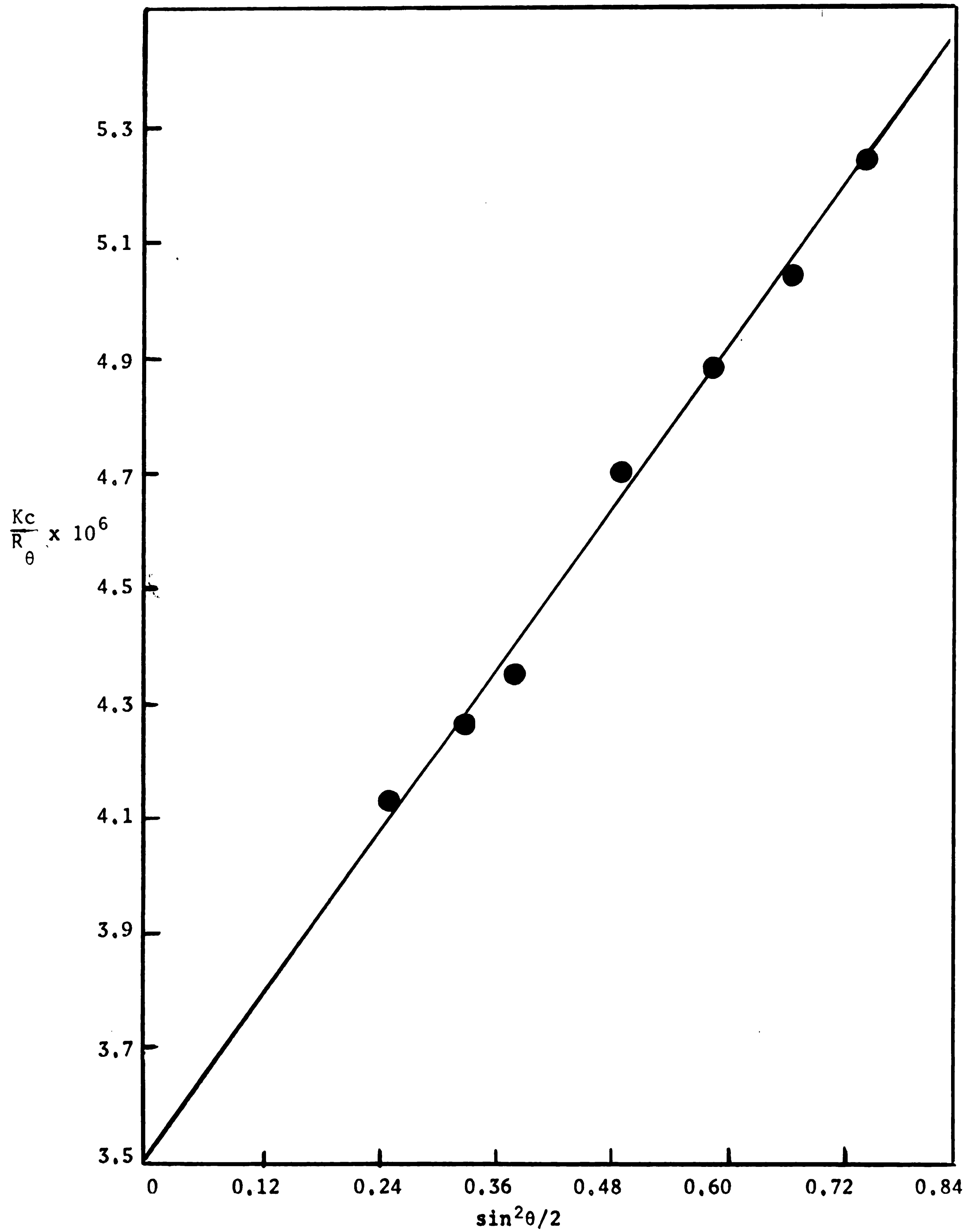

Figure 11. Angular light scattering data for atactic fraction A2 in α-chloronaphthalene at 85°C at zero concentration.

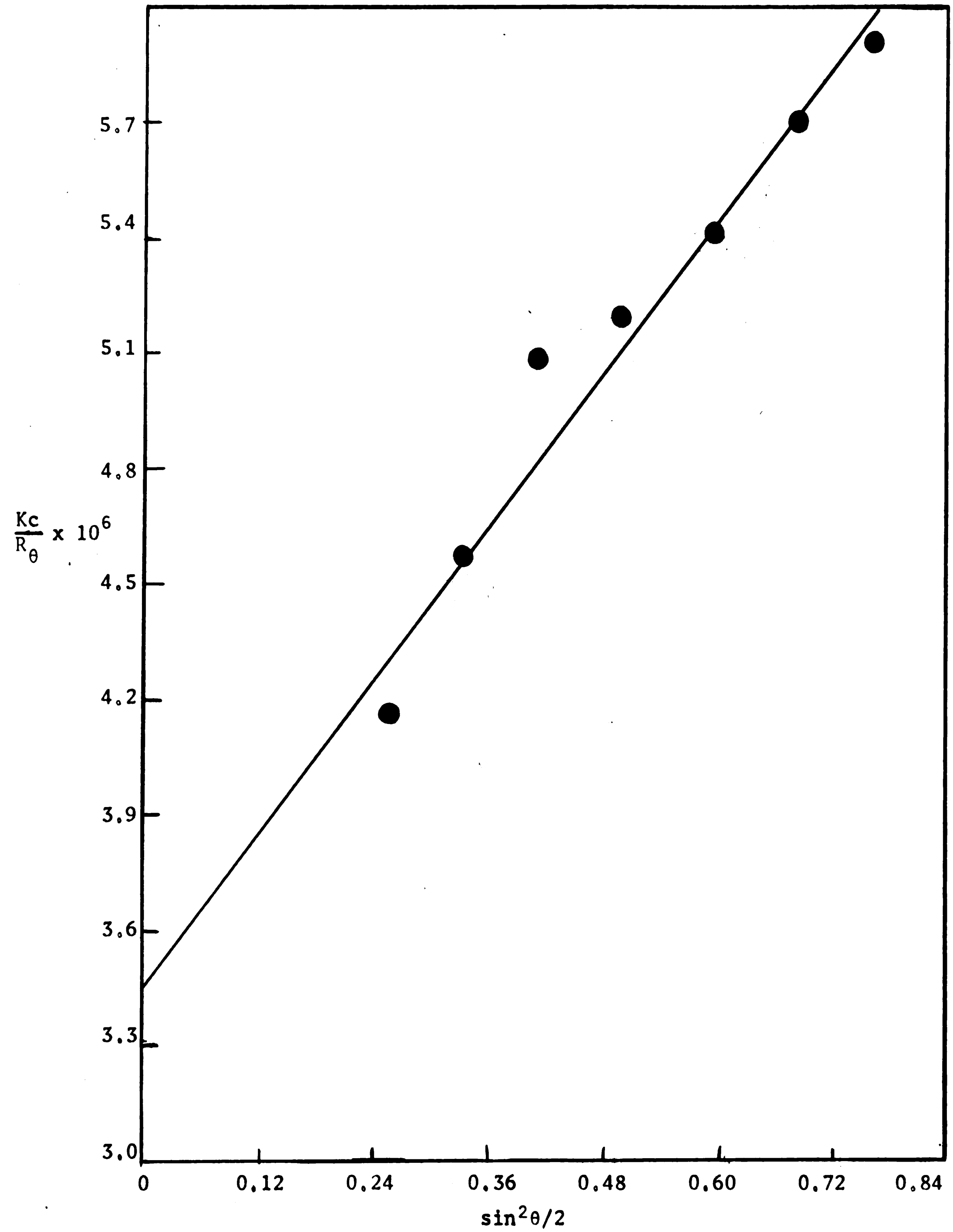

Figure 12. Angular light scattering data for isotactic fraction B3 in α-chloronaphthalene at 86°C at zero concentration.

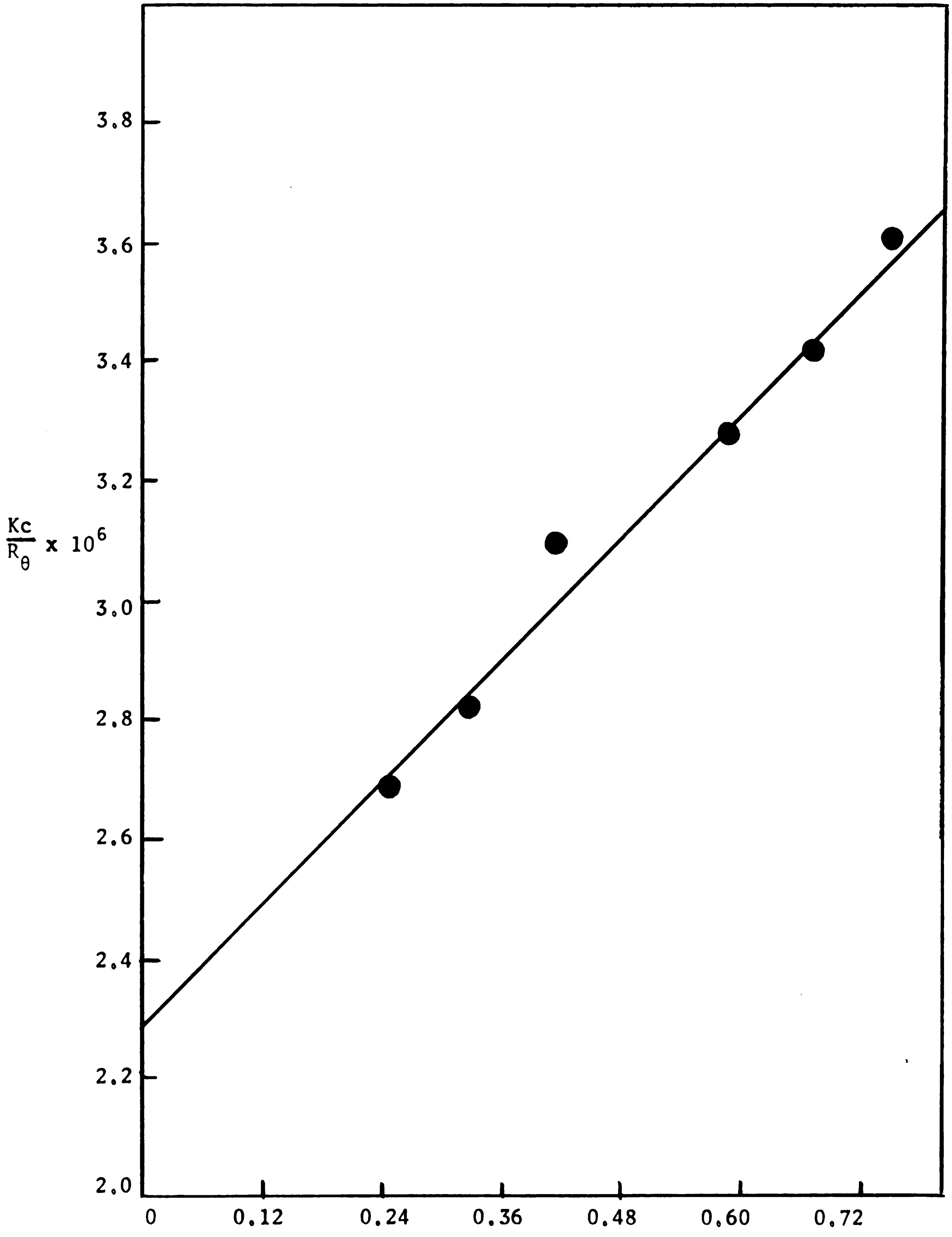

Figure 13. Angular light scattering for isotactic fraction B8 in α-chloronaphthalene at 86°C at zero concentration.

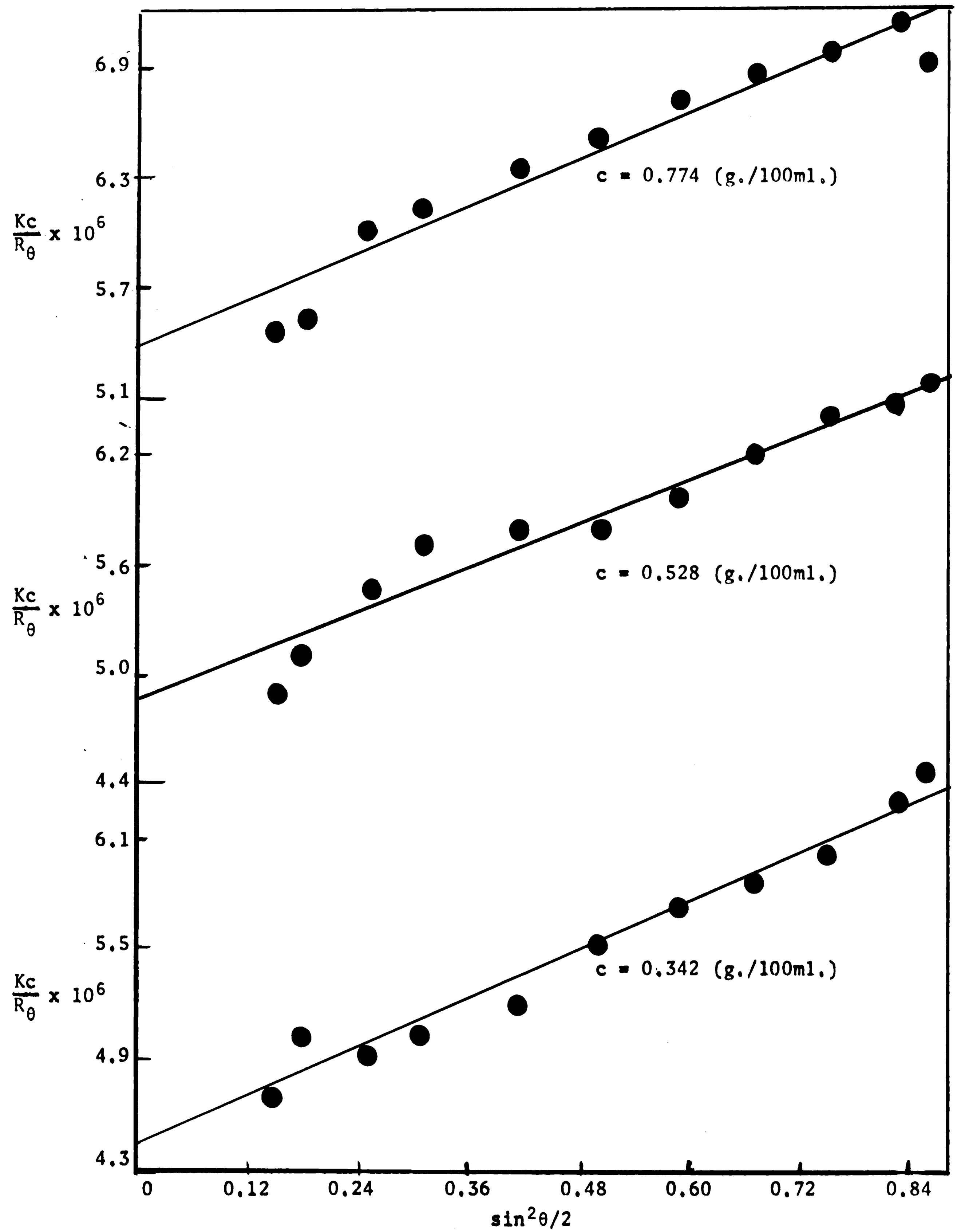

Figure 14. Angular light scattering data for atactic fraction A2 in α-chloronaphthalene at 85°C at various concentrations.

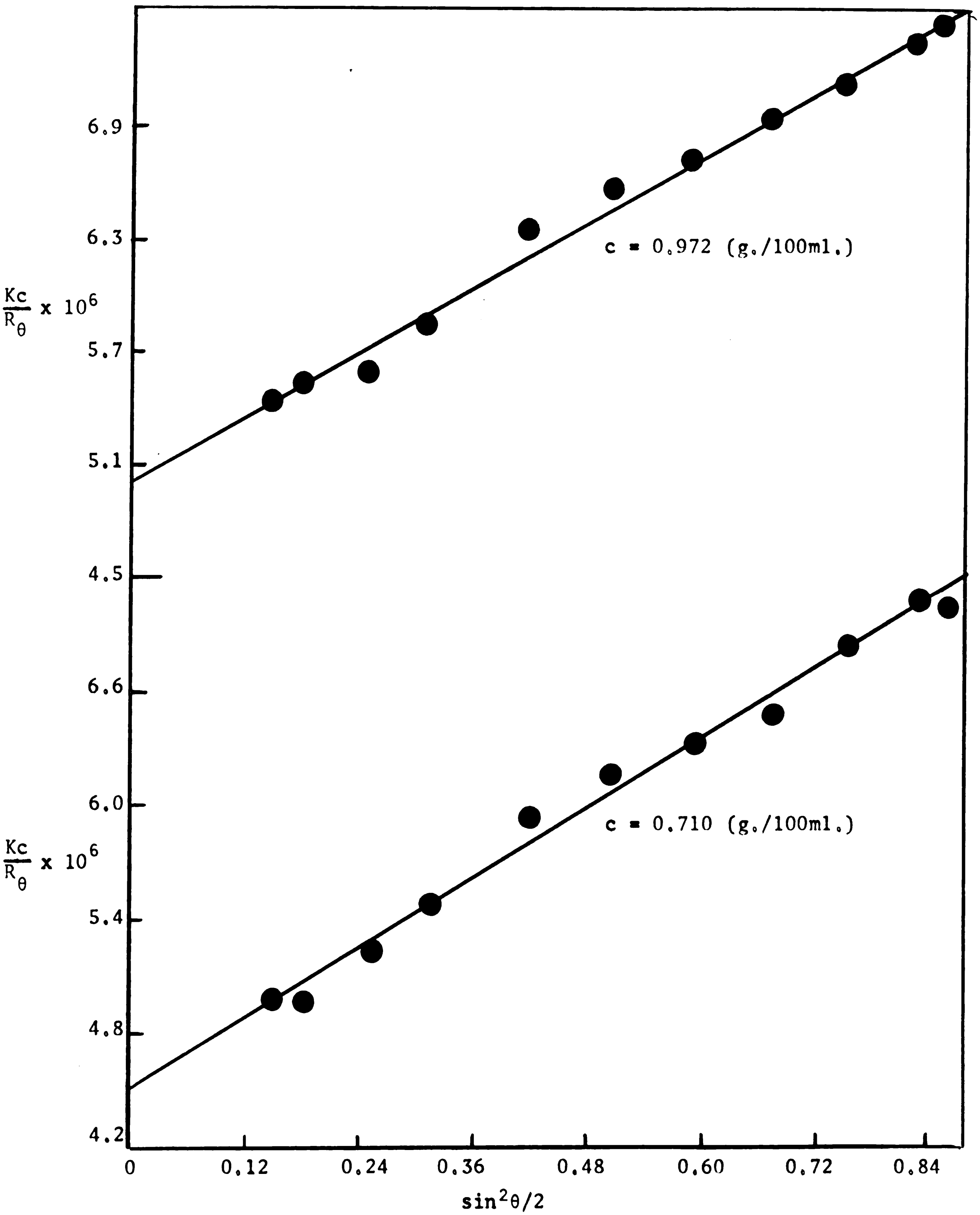

Figure 15. Angular light scattering data for atactic fraction B3 in α-chloronaphthalene at 86°C at various concentrations.

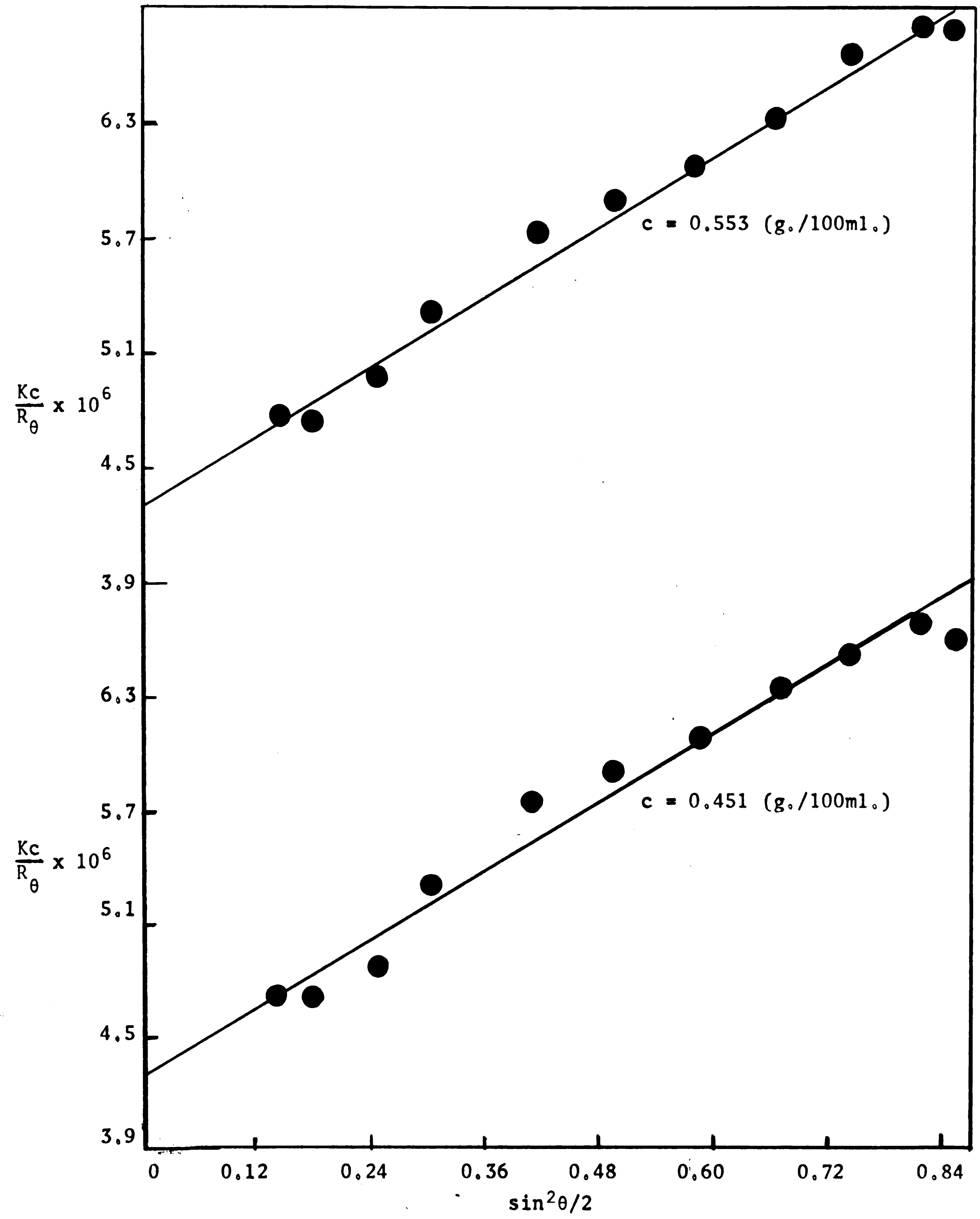

Figure 16. Angular light scattering data for isotactic fraction B3 in α-chloronaphthalene at 86°C at various concentrations.

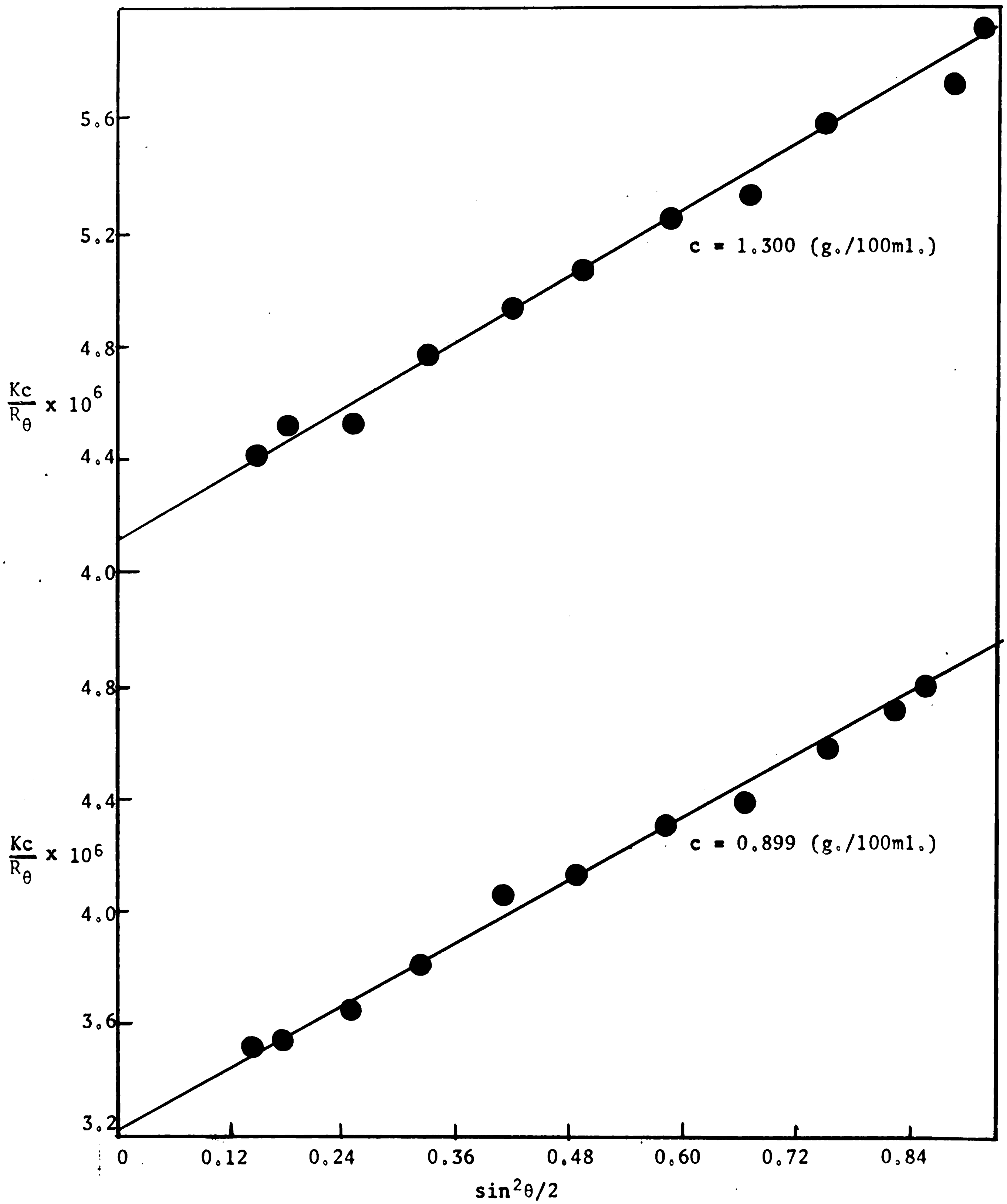

Figure 17. Angular light scattering data for isotactic fraction B8 in α-chloronaphthalene at 86°C for various concentrations.

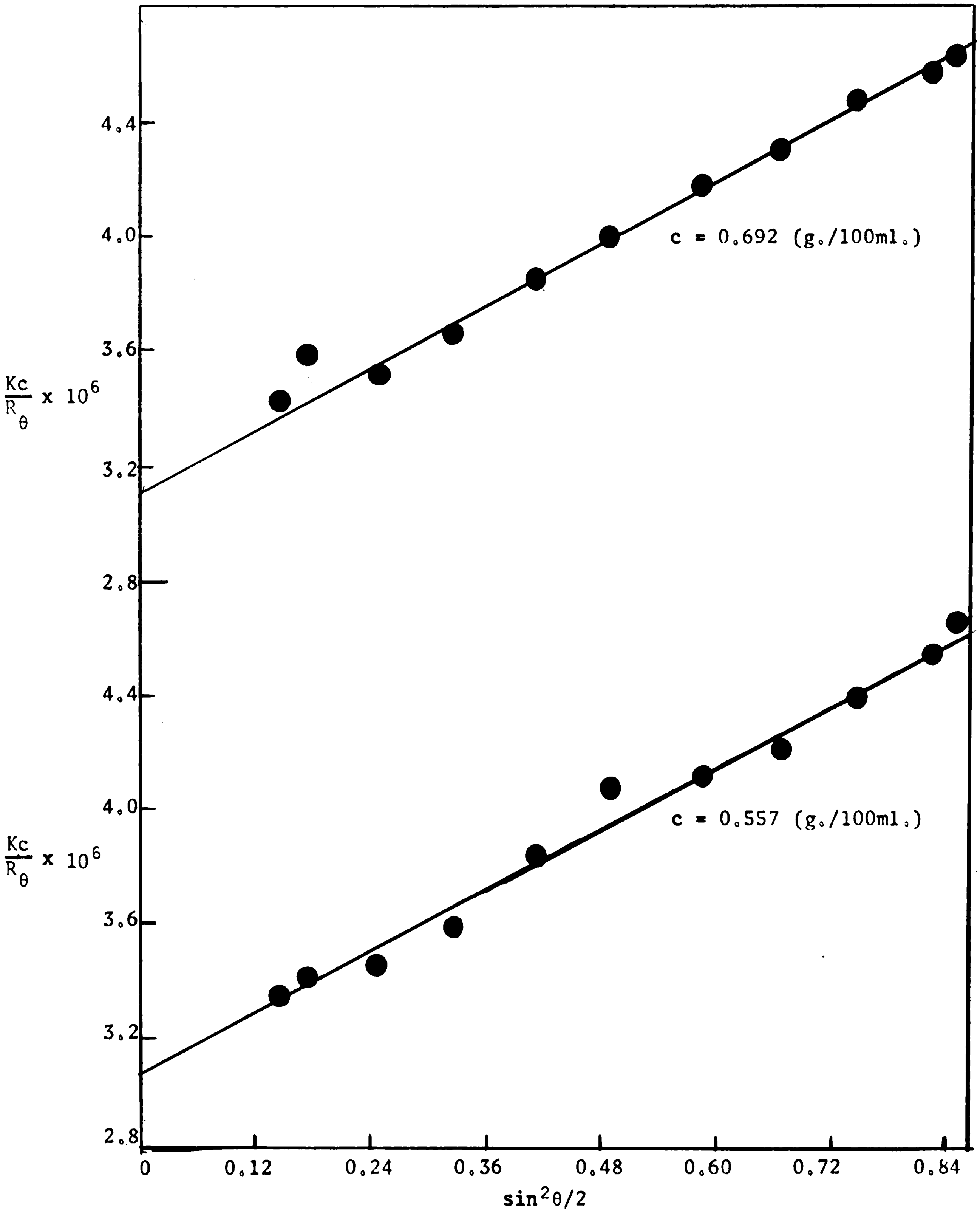

Figure 18. Angular light scattering data for isotactic fraction B8 in α-chloronaphthalene at 86°C for various concentrations.

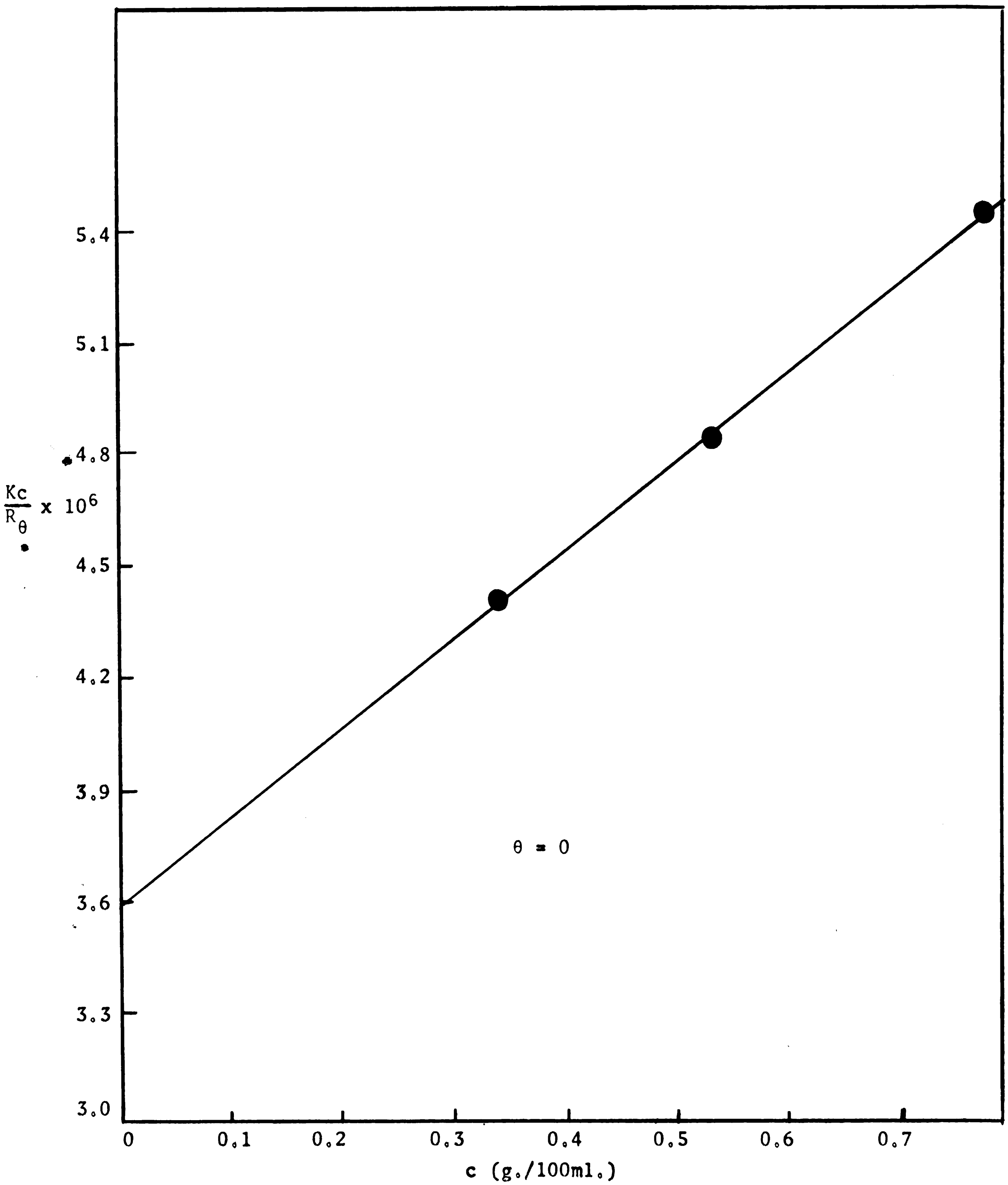

Figure 19. Light scattering data at θ = 0 for atactic fraction A2 in α-chloronaphthalene at 85°C.

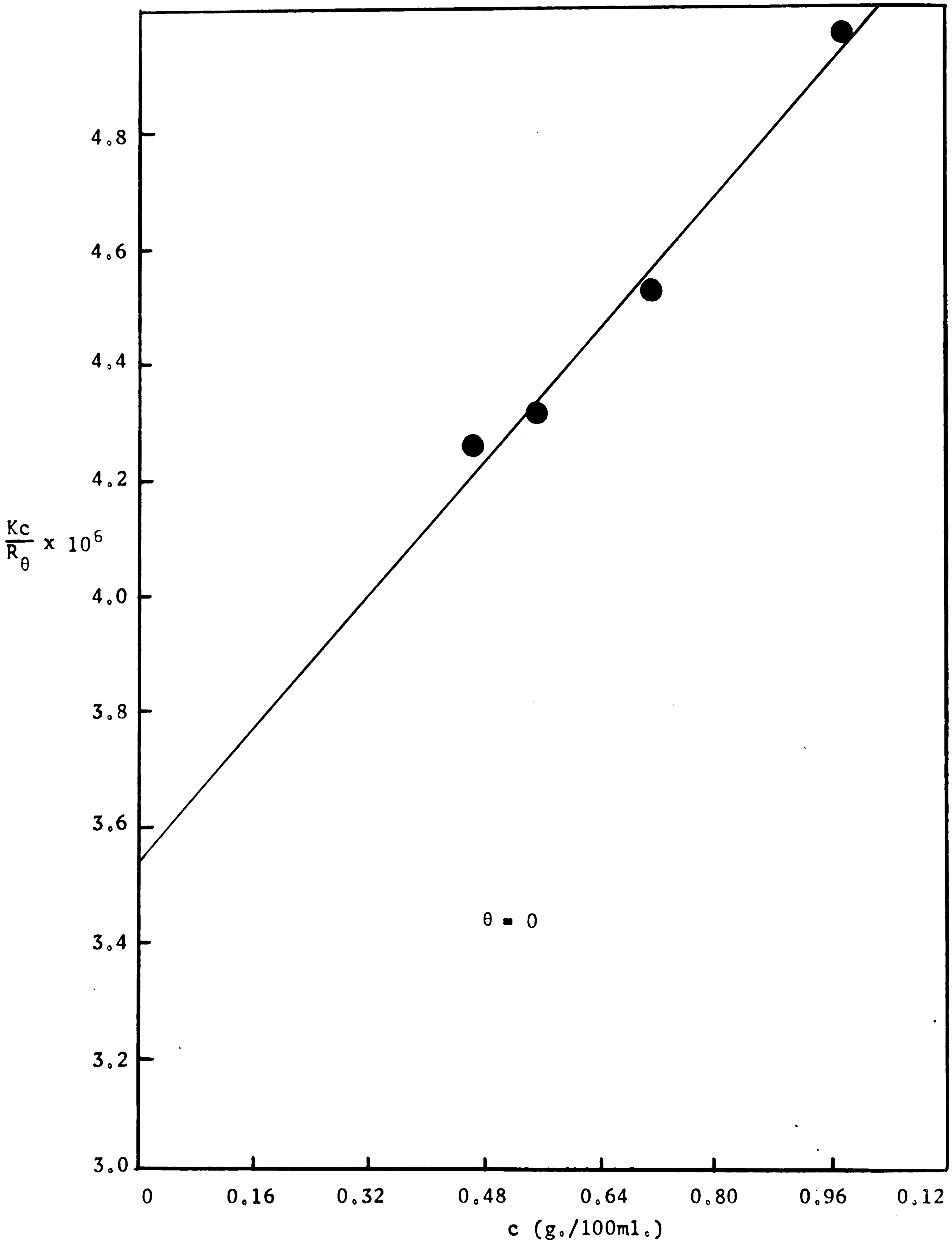

Figure 20. Light scattering data at θ = 0 for isotactic fraction B3 in α-chloronaphthalene at 86°C.

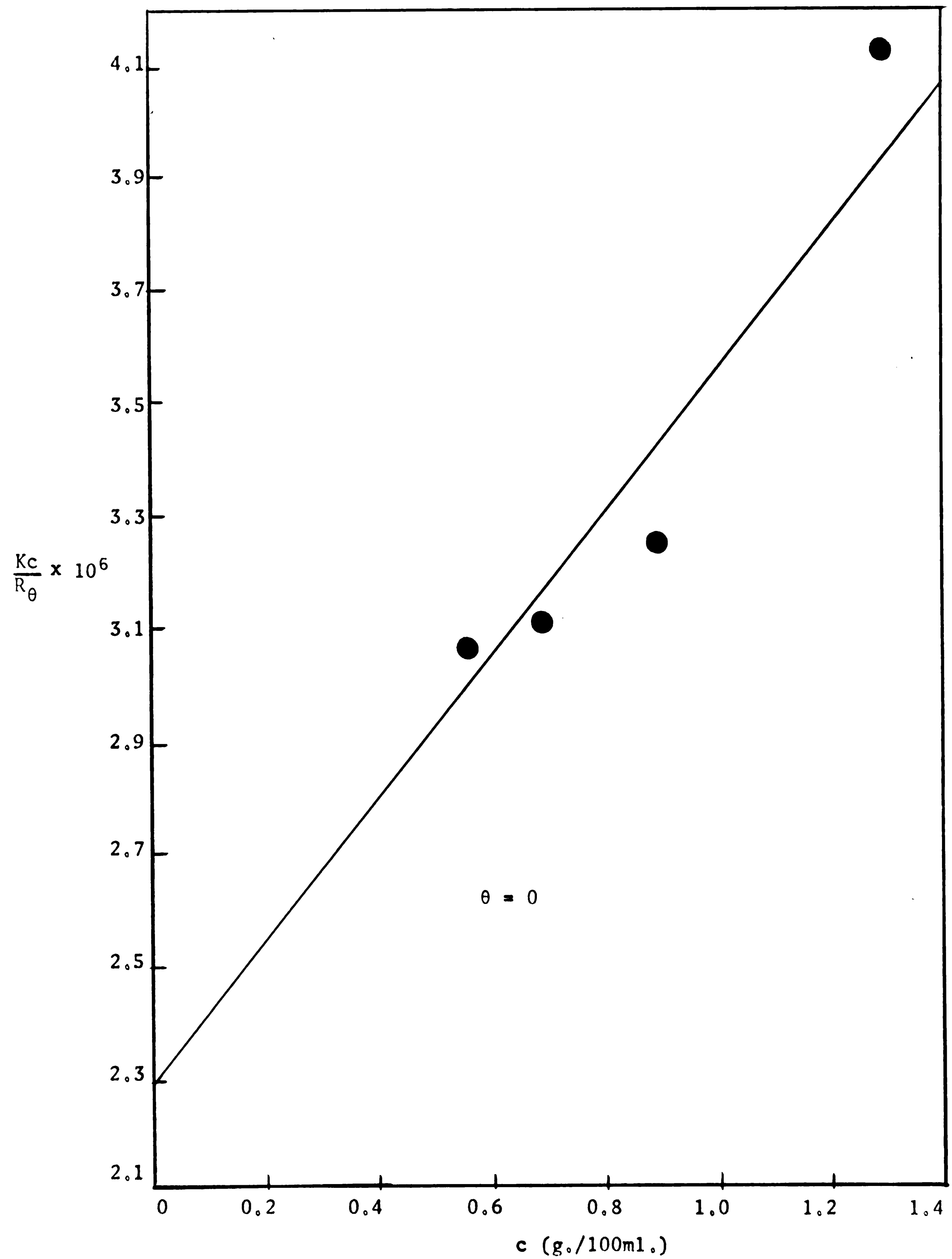

Figure 21. Light scattering data at $\theta = 0$ for isotactic fraction B8 in α-chloronaphthalene at 86°C.

APPENDIX F

Calculation of Light Scattering Data

Calculation of light scattering data[1]

To convert galvanometer readings to Kc/R_θ it is necessary to use the following constants: the Brice constant (B), the cell constant (C), the working standard constant (a), K and c. Since these constants are independent of angle they may be combined at the end of the calculations. To begin the calculation J_θ which is proportional to R_θ is computed according to (1).

$$\Delta J_\theta = (FG_\theta/G_o)_{\text{total}} - (FG_\theta/G_o)_{\text{solvent}}\,[\sin\theta/(1 + \cos^2\theta)] \qquad (1)$$

where G_o and G_θ are the galvanometer readings at 0° and θ° respectively, and F is the appropriate filter factor.

For Pyrex cells with walls normal to the incident beam, i.e. cylindrical cells, a back reflection correction must be made. Once J_θ has been computed it may be corrected as follows: $\Delta J_{\theta\ (\text{correct})} + 1.039\ [J_{(\text{observed})} - 0.039\ J_{180-\theta\,(\text{observed})}]$.

From $\Delta J_{\theta(\text{correct})}$ the value of Kc/R_θ can be obtained as follows:

$$Kc/R_\theta = Kc/(aBC \times \Delta J_\theta)$$

or

$$Kc/R_\theta = \frac{\left[\begin{array}{c}\text{K-Constant}\\ \dfrac{2\pi n_0^2\left(\frac{dn}{dc}\right)^2}{N_o\quad \lambda^4}\end{array}\right]\cdot c}{\left[\begin{array}{l}\dfrac{TC\qquad n_0^2\left(\frac{R_w}{R_c}\right)}{1.045\ (\pi h)}\\ \text{Brice}\\ \text{Constant}\end{array}\right]\left[\begin{array}{c}\dfrac{G_{ws}\ F_{sd}}{G_{sd}\,{}_{\text{"a"}}\,F_{ws}}\\ \text{Constant}\end{array}\right]\left[\begin{array}{c}\dfrac{\Delta J_{90°},\ \text{square cell wide slite}}{\Delta J_{90°},\ \text{Erlenmeyer cell narrow slite}}\\ \text{Cell}\\ \text{Constant}\end{array}\right]\left[\begin{array}{c}J_\theta\dfrac{\sin\theta}{1=\cos^2\theta}\\ \text{Normalized}\\ \text{Excell}\\ \text{Angular}\\ \text{Intensity}\end{array}\right]}$$

in which: R_θ = the absolute Raleigh scattering ratio at an angle relative to the incident intensity

n_o = refractive index of the solvent

$\frac{dn}{dc}$ = refractive index increment of the solution

N_o = Avogadro's number

λ^0 = wavelength of the incident light

T = diffuse transmittance of an opal glass reference standard

D = diffusor correction factor (near unity)

$\frac{R_w}{R_c}$ = correction for incomplete compensation of refraction effects

c = concentration of polymer (gm./cc.)

1.039 = the correction for the reflection of the incident light at the emergent face of the cell

h = the width of the slit diaphragm

$\frac{G_{ws}}{G_{sd}}$ = scattering ratio relating the working standard to the opal reference standard diffuser, measured at 0^o to the incident beam

F = the product of the neutral filters used in determining the scattering ratios

ΔJ = the difference in scattering ratios, at the angles θ, between the solution and the solvent, both normalized to the scattering at 0^o

$\sin\theta$ = the correction for the volume element observed by the photomultiplier

$1+\cos^2\theta$ = the polarization correction for the unpolarized incident light

(1) From unpublished light scattering notes compiled by Professor P. Doty, Harvard University

APPENDIX G

Light Scattering Data on Bulk Isotactic Polybutene-1 in α-chloronaphthalene

Light scattering data
on bulk isotactic polybutene-1 in α-chloronaphthalene
during 24 hour period

(high temperature run)

Angle of measurement	G_θ/G_o Arbitrary[(1)] units*	G_θ/G_o Arbitrary[(1)] units
90	160	167
45	964	974
50	836	836
60	139	140
70	111	112
80	963	978
90	156	164
100	162	164
110	985	1010
120	116	118
130	145	148
135	164	167

* Run made after sample maintained at 90°C in α-chloronaphthalene for 24 hours

(1) Units used here are for comparison for a given angle only --- they may differ for different angles