THE DEPENDENCE OF PHASE EQUILIBRIA ON THE CONFIGURATION OF POLY (BUTENE-1)

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John P. Mullooly

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By

John P. Mullooly

AN ABSTRACT

Submitted to
Michigan State University
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Approved ______________________________

ABSTRACT

THE DEPENDENCE OF PHASE EQUILIBRIA ON THE CONFIGURATION OF POLY(BUTENE-1)

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Phase equilibrium studies were made with isotactic and atactic poly(butene-1) to determine the effect of configuration on the thermodynamic interaction parameters as defined by the Flory-Huggins theory for liquid-liquid phase equilibrium.

The whole atactic polymer was fractionated by a column elution method. Molecular weights of atactic and isotactic fractions of poly(butene-1) were determined from intrinsic viscosity measurement. The polymeric stereoisomers were characterized in the solid state by X-ray and infrared spectroscopy, and melting point determination.

Precipitation temperatures were obtained for isotactic poly(butene-1) in a number of poor solvents, and two solvents where chosen for liquid-liquid phase equilibrium studies. Phase diagrams were constructed for four atactic and three isotactic fractions. Precipitation temperatures were observed visually.

The interaction parameters were found to differ for the two stereoisomers of poly(butene-1). For example, for isotactic poly(butene-1) in diethyl carbitol, $\Psi = 0.941$ and $\Theta = 371.7^{\circ}$A; for atactic poly(butene-1), they are 0.458 and 386.7°A, respectively.

In both systems studied a unique point was found where the Flory-Huggins interaction parameter is equivalent for isotactic and atactic poly(butene-1).

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I. INTRODUCTION

Statement of Purpose

The primary purpose of this investigation was to observe any differences in the thermodynamic interaction parameters of the two stereoisomers of poly(butene-1). Secondarily this work serves as a partial step in the complete characterization of these polymers.

The theta temperature (Θ) and the thermodynamic interaction parameter (χ) are characteristic of a given polymer solvent pair. Θ is defined as the critical miscibility temperature for polymer of infinite molecular weight and may be evaluated by measuring critical miscibility temperatures for a series of polymer fractions and extrapolating to infinite molecular weight. The Flory-Huggins interaction constant is a dimensionless quantity such that χkT measures the difference in energy of a solvent molecule immersed in polymer compared with one immersed in pure solvent. (k is the Boltzmann constant and T the absolute temperature). At the Θ temperature the polymer molecule behaves in an ideal manner and suffers no net interactions.

These parameters enter into many of the thermodynamic equations defining properties of the polymer molecule. For example, according to the simple lattice theory, the reduced osmotic pressure is given by

$$\frac{\pi}{c} = \frac{RT}{M} + \text{constant } \left(\frac{1}{2} - \chi\right)c + \text{higher terms in } c \qquad (1)$$

(π is the osmotic pressure, c the concentration, R the gas constant, and M the molecular weight of the polymer,) so that to obtain the molecular weight one must extrapolate measured values of π/c to infinite dilution. This type of extrapolation is one of the more serious problems encountered in polymer characterization. The better the solvent, the lower the value of χ and so the steeper the slope of π/c versus c. At the Θ temperature χ is almost exactly 0.5, so that $\pi/c = RT/M$. van't Hoff's law is then obeyed and no extrapolation is needed. Similar remarks apply to light scattering measurements. In theory then, a considerable simplification is introduced by using a theta solvent for molecular weight determinations.

According to hydrodynamic theory the polymer chains maintain a minimal size under these conditions. The intrinsic viscosity $[\eta]$ when measured at the Θ temperature is related to the unperturbed chain dimensions($\sqrt{\overline{r_0^2}}$ is the unperturbed root mean square end to end dimension) by the simple expression

$$[\eta]_\Theta = KM^{1/2} \tag{2}$$

where K = constant $(\overline{r_0^2}/M)^{3/2}$. Since this relationship is well established, it is possible to calculate the average dimensions of the chain from the intrinsic viscosity at Θ.

Because interactions between segments of a polymer chain, in solution, are strongest when phase separation takes place, any difference in the properties of a polymer, due to configuration, would be maximized at this point. Therefore phase equilibrium studies may represent a sensitive method for elucidating the differences in solution properties of stereoisomeric polymers.

Liquid-liquid phase equilibrium was chosen to study the solution properties of isotactic (all <u>d</u> or all <u>l</u>) and atactic (random <u>d</u> and <u>l</u>) poly(butene-1).

Theory[1,2,3]

The coexistence curves of two liquid phases can be calculated if an analytical expression for the free energy of mixing is available. 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). When polymer and solvent molecules are mixed there is a non-vanishing heat of mixing due to the interaction of unlike species.

In the Flory-Huggins original derivations it is assumed 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. Using volume fractions, v_i, the heat of mixing of a binary solution of n_1 moles of solvent and n_2 moles of polymer is equated to

$$\frac{\Delta H_M}{RT} = \chi v_1 v_2 (n_1 + x n_2) \qquad (3)$$

(v_1 = volume fraction of solvent, v_2 = volume fraction of polymer,) in analogy to the van Laar-Hildebrand-Scatchard expression for molecules of equal size. The changes of the partial molar heat content on mixing as obtained from (3) are:

$$\frac{\Delta \overline{H}_1}{RT} = \chi v_2^2 \qquad (4)$$

and

$$\frac{\Delta \overline{H}_2}{RT} = \chi x v_1^2 \qquad (5)$$

Assuming that the conformational entropy represents the total entropy change on mixing the free energy of mixing is:

$$\Delta F_M = RT[n_1 \ln v_1 + n_2 \ln v_2 + \chi\, n_1 v_2] \qquad (6)$$

The changes of chemical potential on mixing for the two components are then:

$$\Delta\mu_1 = RT[\ln v_1 + (1 - \frac{1}{x})v_2 + \chi v_2{}^2] \tag{7}$$

$$\Delta\mu_2 = RT[\ln v_2 - (x - 1)v_1 + \chi x v_1{}^2] \tag{8}$$

χ, as defined by (3), is known as the interaction constant and equation (6) as the Flory-Huggins expression.

The conditions for equilibrium between two phases in a binary system are expressed by stipulating equality of the chemical potentials in the two phases; that is

$$\mu_1 = \mu_1{}^1 \tag{9a}$$

$$\mu_2 = \mu_2{}^1 \tag{9b}$$

where the prime denotes the more concentrated phase. Fulfillment of (9a) requires there be two concentrations at which the chemical potential μ_1 has the same value. 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 for (9b) to be satisfied μ_2 must exhibit a maximum and a minimum. Since μ_1 and μ_2 are derived by differentiating the same free energy expression (6) one must pass through a maximum where the other is at its minimum. A point of inflection characterized by the condition of zero curvature

$$\frac{\delta^2\mu_1}{\delta v_2{}^2}{}_{T,P} = 0 \tag{10}$$

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

$$\frac{\delta\mu_1}{\delta v_2}{}_{T,P} = 0 \tag{11}$$

These two conditions then constitute the necessary and sufficient condition for incomplete miscibility. If the curve representing μ_1 as a function of v_2 decreases monotonically with v_2, total miscibility is assured. As the interaction constant is increased, going to poorer solvents, eventually a minimum and a maximum will appear; their appearance signifies incomplete miscibility. Ordinarily a poor solvent for a given polymer becomes poorer with lowering of temperature. A totally miscible system at higher temperatures may be converted to one of limited miscibility by lowering the temperature. At some temperature, T_p, phase separation takes place. At T_p the previously monotonic curve begins to exhibit a minimum, a maximum, and an inflection. These features occur simultaneously at the same concentration.

Differentiating (7) for the chemical potential of the solvent with respect to v_1 and equating the result to zero, we obtain

$$\frac{1}{RT}\frac{\delta\Delta\mu_1}{\delta v_1} = \frac{1}{v_1} - (1 - \frac{1}{x}) - 2\chi v_2 = 0 \qquad (12)$$

and a second differentiation gives

$$\frac{1}{RT}\frac{\delta^2\Delta\mu_1}{\delta v_1^2} = -\frac{1}{v_1^2} + 2\chi = 0 \qquad (13)$$

Denoting critical values with a subscript c, we obtain as the solution of (12) and (13)

$$v_{2c} = \frac{1}{1 + x^{1/2}} \qquad (14)$$

$$\chi_c = \frac{1}{2}(1 + x^{-1/2})^2 \qquad (15)$$

For large values of x, v_{2c} is very small and χ_c very little over 1/2.

Since χ is a free energy parameter it can be written as the sum

of two terms, a temperature independent term χ_s and a term χ_H which varies as $1/T$ and is written β/T. θ, the Flory temperature, is defined as the critical temperature of mixing of an infinitely long polymer, and is given by

$$\theta = \frac{\kappa T}{\psi}$$

where κ is the heat of dilution parameter. ψ , the entropy parameter, is defined as $1/2 - \chi_s$. For this hypothetical polymer (15) becomes upon introduction of these defined quantities

$$\psi = 1/2 - \chi_s = \beta/\theta \tag{16}$$

The Flory-Huggins interaction parameter becomes

$$\chi = 1/2 - \psi\ (1- \frac{\theta}{T}) \tag{17}$$

Equating equations (15) and (17), and rearranging terms, gives a linear relationship between the critical temperature and x, from which ψ and θ can be evaluated experimentally

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\psi\theta}\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right) \tag{18}$$

Quantitative agreement between experiment and (14) is poor. There is no freedom for any deviation from this relationship within the framework of the Flory-Huggins free energy of mixing expression. Tompa has therefore tried to improve the theory by making a mathematical extension. χ, at a given temperature, is assumed to depend linearly on v_2. Mathematically this is equivalent to adding a cubic term to (7). Designating $\partial \chi/ \partial v_2$ by k, the equations obtained for the critical point are

$$\frac{1}{v_1} - (1 - \frac{1}{x}) - 2\chi v_2 - kv_2{}^2 = 0 \tag{19}$$

and

$$-\frac{1}{v_2} + 2\chi + 4kv_2 = 0 \qquad (20)$$

These equations determine, for a given solvent/polymer system, sets of corresponding values of v_{2c} and χ_c for each value of k. Using numerical methods Tompa[4] demonstrates that the influence of any concentration dependence of χ is very much larger on v_{2c} than on χ_c. This then gives at least a formal description of the observation that χ_c is often much better represented by the Flory-Huggins theory than v_{2c}.

At the theta temperature the net interaction between solvent and polymer segments is zero. The polymer molecules are able to penetrate each other freely, and the excluded volume of the molecules is also zero. At this temperature, the polymer molecules assume their unperturbed dimensions, $\overline{r_0^2}$. The expansion factor, α, is defined by

$$\overline{r^2} = \alpha \; \overline{r_0^2} \qquad (21)$$

[$\sqrt{\overline{r^2}}$ is the root mean square end to end distance of the chain in a perturbed state] and is a function of the thermodynamic interaction parameters;

$$\alpha^5 - \alpha^3 = C_m \Psi \left(1 - \frac{\Theta}{T}\right) M^{1/2} \qquad (22)$$

α approaches one as T approaches Θ. C_m is a constant for a given molecular weight and is calculated from the expression

$$C_m = (27/2^{5/2} \pi^{3/2})(\bar{v}^2/NV_1)(\overline{r_0^2}/M)^{-3/2} \qquad (23)$$

($\bar{v}$ is the specific volume of the polymer, V_1 the molar volume of the solvent, and N Avogadro's number).

The interaction parameters are characteristic of the non-ideal behavior of polymer solutions, but their exact significance has not been determined, theoretically. Flory assumes that the same parameters describe both inter- and intra-molecular interactions, although this has been questioned[5]. The dilute solution theory gives different values for Ψ. In dilution solutions, the simple lattice theory predicts that $(\Psi - 1/2) \approx 1/Z$ for intermolecular interactions where Z, as defined, represents the lattice coordination number. Much more complicated expressions for the interaction parameters have been derived by other methods.[6,7,8] These methods consider preferential interactions, molecular size and shape, and chain stiffness.

The effect of stereoregularity has not been directly considered. Therefore, changes in the interaction parameters due to configuration must be postulated by indirect methods. This can be done by making qualitative predictions about the effect of stereoregularity on the quantities which determine the values of the interaction parameters.

Historical

The most thorough investigations of the phase relationships of solvent/polymer systems are those carried out by Schultz and Flory.[9,10,11] These workers studied atactic polystyrene in various solvents. In particular, precipitation temperatures of four well-fractionated samples of polystyrene in solutions of cyclohexane were determined. The experimental binodals agree qualitatively with respect to the shape of the curves with the Flory-Huggins theory. The quantitative agreement is poor; the critical concentrations are higher than those predicted by theory. Similar results were obtained with the cyclohexanol/

polystyrene and diisobutylketone/polyisobutene systems.

The polyethylene system as investigated by Richards[12] exhibited a region of liquid-liquid phase separation in the dilute range, with the critical point occuring at a very low polymer concentration. Liquid-crystalline phase separation occurred at higher concentrations; this region extended from a triple point, where three phases are present in equilibrium, to the melting point of pure polyethylene. The size of the liquid-liquid region decreased in better solvents; only liquid-crystalline separation was observed in the best solvent used.

A few papers have appeared recently which have shown that polymer stereoisomers retain their individuality in solution. Light scattering measurements have been made by Kinsinger on the polypropylene system.[13] Small differences in the second virial coefficients of isotactic and atactic polypropylene were observed. In osmotic pressure measurements on isotactic and atactic polystyrene, Danusso and Moraglio found definite differences in the second virial coefficients.[14]

The first study of the phase relationships of polymeric stereoisomers was reported by Kinsinger and Wessling.[15] Phase diagrams of carefully characterized fractions of atactic and isotactic polypropylene were determined and binodals characteristic of liquid-liquid separations for both stereoisomers were obtained in phenyl ether at temperatures near the melting point of the isotactic polymer. Reciprocals of the critical temperatures determined from the phase diagrams were plotted versus $(1/x^{1/2} + 1/2x)$ and the parameters Ψ and Θ were evaluated. Curves for atactic and isotactic polypropylene were found to differ considerably in both slope and intercept. The data reported is summarized in Table I.

Table I. Thermodynamic Interaction Parameters for Polypropylene in Phenyl Ether[15]

Isomer	$\theta(^{o}K)$	Ψ
Isotactic	418.4	1.414
Atactic	426.5	0.986
Difference	8.1	0.426

In a private communication Krigbaum reports differences in the theta temperatures and entropy parameters for atactic and isotactic poly(butene-1) in anisole. Critical miscibility temperature measurements were used and the data reported are summarized in Table II.

Table II. Thermodynamic Interaction Parameters for Poly(butene-1) in Anisole.[16]

Isomer	$\theta(^{o}K)$	Ψ
Isotactic	362.3	0.956
Atactic	359.4	0.740
Difference	2.9	0.216

II. EXPERIMENTAL PROCEDURE

Extraction

Samples of atactic and crystalline (isotactic) poly(butene-1) were provided by the 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. No information was given by the supplier as to the method of preparation used. It was indicated that the samples underwent a solvent treatment subsequent to preparation; no details were given. Initial attempts to obtain phase diagrams with fractions prepared from untreated samples indicated an insoluble content, thought to be inorganic catalyst fragments and suggested that the solvent treatment was incomplete. An extraction method was therefore used, employing isooctane which has been reported by Natta[17] to act as a selective solvent for the atactic isomer. Observation of the samples under a polarized microscope also indicated the need to purify the samples before proceeding with the phase studies.

Fractionation

The atactic polymer was fractionated using an elution sand column method.[18] Butyl cellosolve served as the carrier, cyclohexane and acetone were used as the solvent and non-solvent respectively. The solvent and non-solvent were distilled before use; the observed boiling points and refractive indices were 81°C., 1.4291 and 57°C., 1.3583 respectively. Xylene was refluxed through the outer jacket of the elution column while the butyl cellosolve solution was introduced into the column. The heat was then turned off causing the polymer to precipitate differentially, according to molecular weight, on the sand particles.

Oxidative degradation of the polymer was prevented by the addition of a stabilizer to the butyl cellosolve solutions (2,6-di-t-butyl-p-cresol).

The elution was carried out at room temperature employing a ten ml. increment of solvent-nonsolvent with an elution rate of approximately twenty drops per minute. One hundred ml. portions of the exit eluent were collected, heated to dryness on a steam bath, and the fractions were dried to constant weight in vacuo at 80-90°C. In the initial fractionation 2.8 g. of the extracted atactic sample was used and yielded eight fractions. Fraction four accounted for more than half the weight of the sample. Fractions three and four were returned to the column and the fractionation procedure was repeated. This second fractionation yielded five fractions. The fifth fraction of the first fractionation (designated A-5) and the fourth and fifth fractions of the second fractionation (A'-4, A'-5) were used for the subsequent studies.

Viscosity measurements revealed that all the atactic fractions of sufficient weight were of relatively low molecular weight. The extraction step was suspect of causing degradation since it was carried out at the boiling point of isooctane (118°C.) and involved prolonged exposure (2 days). To check this a 1 g. sample was extracted with hexane at room temperature and the viscosity of the extract was determined. This extract was of comparable molecular weight. The atactic fraction denoted c-2 was obtained by fractional precipitation and was available from previous work in this laboratory.

Three isotactic fractions (designated B-4, B-7 and B-8) were obtained from C. C. Wilkins. They were prepared by a similar column fractionation method, the details of which will be given in his thesis.

Characterization of Isotactic Poly(butene-1) in the Crystalline State

The melting behavior of the isotactic fractions was observed using a Köfler Hot Stage and a polarizing microscope. Samples were prepared for observation by pressing between two microscope slides, melting, quenching and annealing to develop large spherulites. The heating rate was about 0.5°/min. near the melting point.

X-ray spectra were taken using the powder camera and the automatic recording diffractometer. Since the samples could not be ground fine enough to be inserted into the X-ray capillary tube, a film of polymer was cast on the exterior of the tube by dipping it into polymer melt. Cu, Kα radiation was used and the samples were exposed for three hours. The diffractometer samples were prepared by melting the polymer in the sample holder so that a fairly even surface was produced.

Infrared spectra of the stereoisomers were taken with the Perkin Elmer Infrared Spectrophotometer, Model 21. Films were cast on salt plates by placing a few drops of a concentrated cyclohexane solution on the plate and then drying in a vacuum oven at 80-90°C.

Viscosity Measurements

Intrinsic viscosity measurements were carried out for atactic and isotactic poly(butene-1) in benzene at 30°C. and in n-nonane at

80°C. respectively. Pure Grade normal nonane was used as received from Phillips 66 Hydrocarbons (99 mol % minimum)(b.p. 151°C., n_d^{20} 1.4052). Chemically pure benzene was distilled before use (b.p. 80°C., n_d^{20} 1.5014). A Cannon-Ubbelohde Micro Dilution Type viscometer was used for both polymers.

Special techniques were required for handling the crystalline polymer at high temperature. The isotactic samples were weighed to constant weight in 1 ml. volumetrics. Upon addition of the solvent one to two hours of heating at from 80-90° were required to complete the initial solution. The solution was then cooled to room temperature and weighed. The polymer fractions dissolved rapidly in nonane when heated a second time and the solutions were immediately filtered through a heated glass frit into the viscometer immersed in the constant temperature oil bath.

The polymer solutions were prepared so the relative viscosity fell within the limits 1.2 to 1.9. Both η_{sp}/c and $\ln\eta_{rel}/c$ were calculated and plotted against the concentration according to the Huggins viscosity relationships

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$

$$\frac{\ln\eta_{rel}}{c} = [\eta] - \beta[\eta]^2 c$$

A double extrapolation to zero concentration was performed by least squares to give the intrinsic viscosity, $[\eta]$.

The molecular weights were calculated by the empirical Mark-Houwink equation

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

For the atactic polymer in benzene at 30°C. Natta's[19] values of $K = 2.15 \times 10^{-4}$ and $a = 0.685$ were used. Krigbaum's[16] values of $K = 0.585 \times 10^{-4}$ and for $a = 0.80$ for isotactic poly(butene-1) in n-nonane at 80°C. were used.

Phase Studies

Various solvents were investigated to determine their usefulness for liquid-liquid phase equilibrium studies. The following properties were required: the solvent must be sufficiently poor to give liquid-liquid phase separation with isotactic poly(butene-1); it must be inert and high-boiling. Solutions of approximately one percent isotactic poly(butene-1) were prepared and the mode of phase separation was determined. Where liquid-liquid phase separation occurred the precipitation temperatures were reproducible, but this was not the case for liquid-crystalline separation. The endpoint for the latter type of separation was not reproducible because of the dependence of the precipitation on the rate of cooling. When liquid-crystalline phase separation occurred the precipitate formed by cooling would not dissolve until the temperature was raised from 5° to 20° above the endpoint; cooling slightly below the temperature at which the precipitate dissolved would not induce another phase separation.

From this preliminary investigation two solvents were chosen for the phase studies, diethyl carbitol and butyl cellosolve. These two solvents were chosen since they satisfy the requirements given above and differ considerably in solvent power. If differences in the thermodynamic interaction parameters of the two stereoisomers were observed it would be interesting to see whether this difference is dependent solely on the degree of stereoregularity of the polymer or whether there is a solvent effect.

The experimental method for the determination of the phase diagrams consisted of preparing solutions near precipitation and then causing precipitation to take place by lowering the temperature. Polymer samples, which varied from ten to twenty milligrams were weighed into two ml. volumetric sample tubes. The solvent was weighed into the tube from a syringe, and the tube sealed.

The solvents were used as received from Union Carbide. Boiling points and refractive indices were determined (b.p. 188°C., $n_d^{20} = 1.4110$ for diethyl carbitol and b.p. 173°C., $n_d^{20} = 1.4192$ for butyl cellosolve).

Precipitation temperatures were determined, visually, by the following procedure: The bath temperature was lowered at the rate of approximately 1° per minute until turbidity appeared in the solution; the temperature was then raised until the sample cleared. This cycle was repeated at a slower rate (about 0.2°/min) to obtain the endpoint. Oxidative degradation was prevented by adding a stabilizer to the butyl cellosolve solution (2,6-di-t-butyl-p-cresol).

The specific volumes of the polymers were calculated from dilatomètric data reported by Natta.[20] Density temperature relationships for diethyl carbitol and butyl cellosolve were determined by making density measurements at several temperatures with a Gay-Lussac pycnometer which had been calibrated using mercury.

III. DATA AND RESULTS

Extraction

The bulk atactic sample was extracted with isooctane at its boiling point (118°C.) for 48 hours. Of the 4.62 grams of atactic sample used, 0.023 grams of insoluble material remained in the Soxhlet extraction cup after this period.

Fractionation

Table III. Data for Fractionation A of Atactic Poly(butene-1)

Fraction	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	Total	Wt. of Sample
Wt. of Fraction(g)	0.01	0.07	0.28	1.50	0.58	0.03	0.02	0.02	2.51 g.	2.80 g.
% of Sample	0.4	2.5	10.0	53.6	20.7	1.1	0.7	0.7	89.6%	

Table IV. Data for Fractionation A' of Atactic Poly(butene-1)

Fraction	A'-1	A'-2	A'-3	A'-4	A'-5	Total	Wt. of Sample
Wt. of Fraction(g)	0.10	0.24	0.38	0.59	0.40	1.71 g.	1.78 g.
% of Sample	5.6	13.5	21.3	33.1	22.5	96.2%	

Infrared Spectra, Melting Points, X-ray Diffraction Patterns and Photomicrographs

The infrared spectra of isotactic and atactic poly(butene-1) are given in Figs. I and II respectively. These spectra compare well with those reported by Natta[21] except for the 5.84μ peak in the atactic sample which might be indicative of unsaturation.

Samples for melting point determination were pressed between microscope slides, melted, quenched and then annealed. After annealing at 80°C for 48 hours the samples were observed with a polarized microscope. Some crystalline aggregates (spherulites) were found to be present. The samples were then melted and allowed to cool slowly on the Köfler Hot Stage. This treatment resulted in an increased number of large spherulites. The melting point was then determined and was taken as the temperature at which the last trace of birefringence disappeared.

Table V. Melting Point Data for Isotactic Fractions of Poly(butene-1)

Fraction	Melting Range (°C.)	Disappearance of last trace of birefringence	Heating Rate
B-4	121-125.5	125.5	0.5°/min.
B-7	124-128	128	0.5°/min.
B-8	126.5-130	130	0.5°/min.

Fraction B-7 was unusual in its melting behavior. After the 48 hour period of annealing the spherulites morphology was different than the other fractions. The Maltese Crosses appeared to be imperfectly formed. Upon initial melting the observed melting point was about

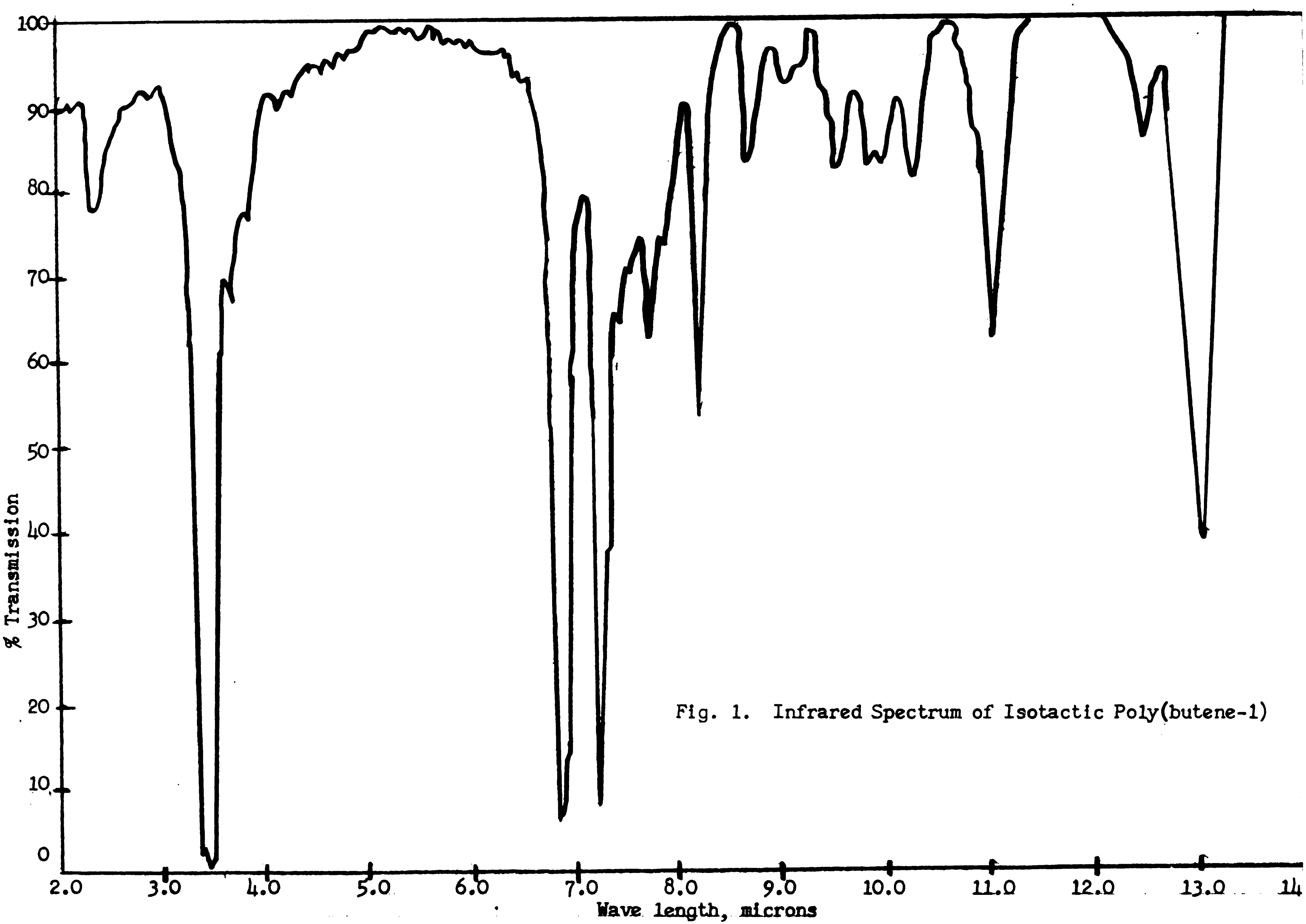


Fig. 1. Infrared Spectrum of Isotactic Poly(butene-1)

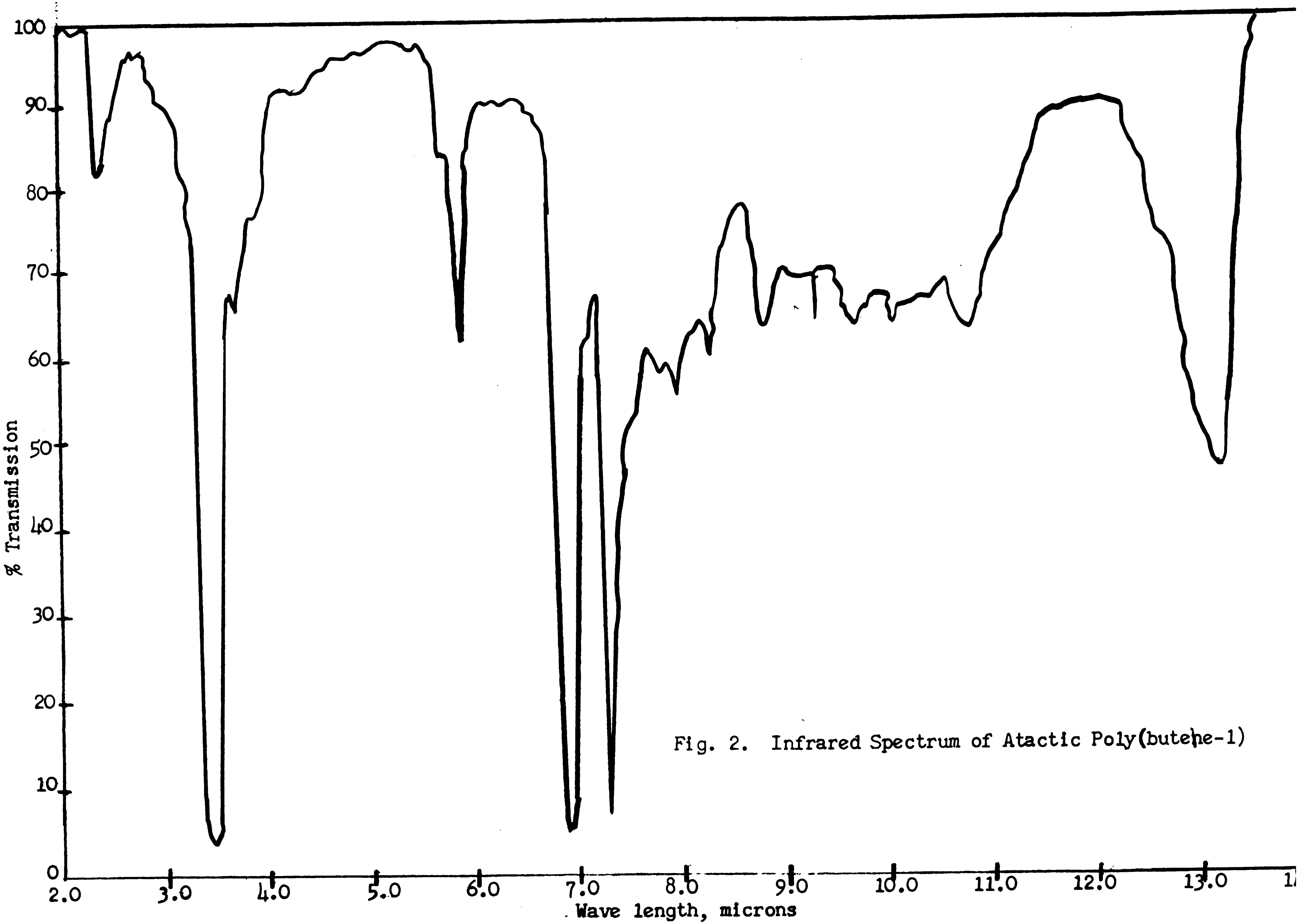


Fig. 2. Infrared Spectrum of Atactic Poly(butene-1)

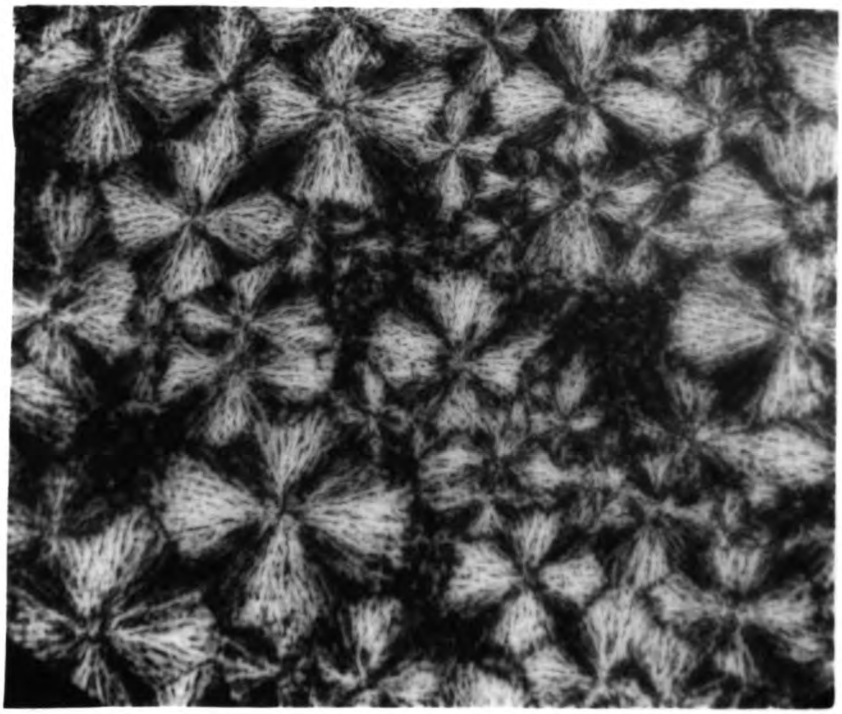
105°C. Slow cooling resulted in growth of the aggregates but no morphological change was noted. The melting point was again determined and was found to be from 105 - 110°C. This sample was returned to the 80°C. annealing oven and investigated periodically. The observed melting point increased with annealing time and only after about 100 hours was a constant value obtained, at which time the crosses seemed well formed and resembled fractions B-4 and B-8. The metastable aggregates of fraction B-7 are compared photographically with the stable form in Fig. 3.

Slight differences will be noted in the X-ray spectra of fractions B-7 and B-8 as given in Fig. 4. All these spectra were taken approximately one hour after crystallization from the melt. Marked differences are noted when Geiger counter registration of the X-ray spectra is used (Figs. 5 and 6). These spectra agree well with those given by Natta.[21]

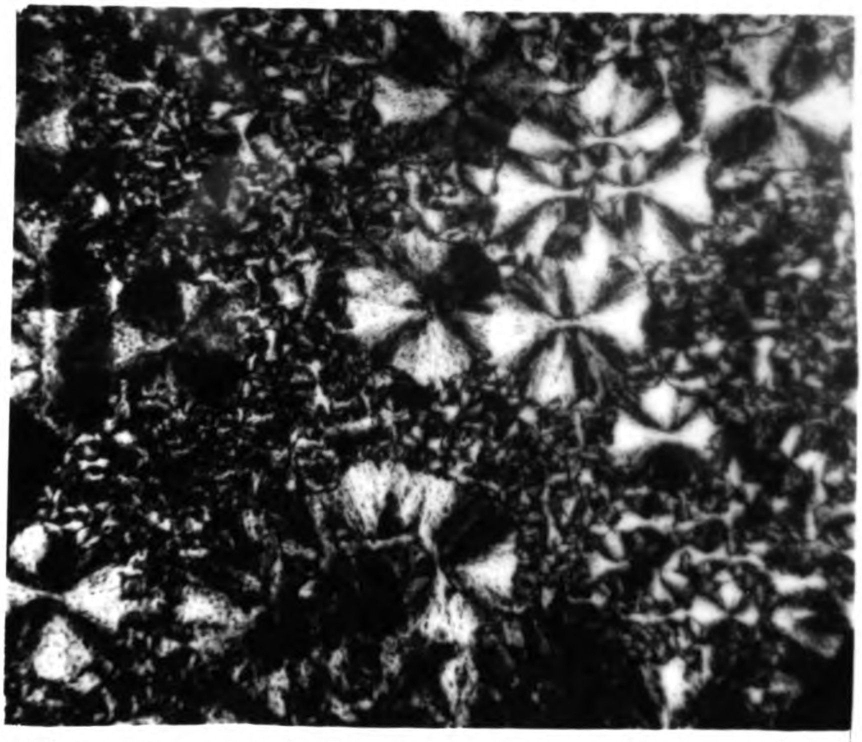
Natta[21,22] reports crystal dimensions for two polymorphic species of isotactic poly(butene-1). The unstable species as reported consists of four monomeric units per repeating unit with a repeating unit along the fiber axis of 6.85°A. The stable form consists of 3 monomeric units per repeating unit with a 6.50°A repeating unit along the fiber axis. Natta reported 126-128°C. as the melting point of the stable form of isotactic poly(butene-1).

Viscosity Measurements

The viscosity data for the atactic and isotactic fractions are plotted in Figures 7 and 8 respectively.

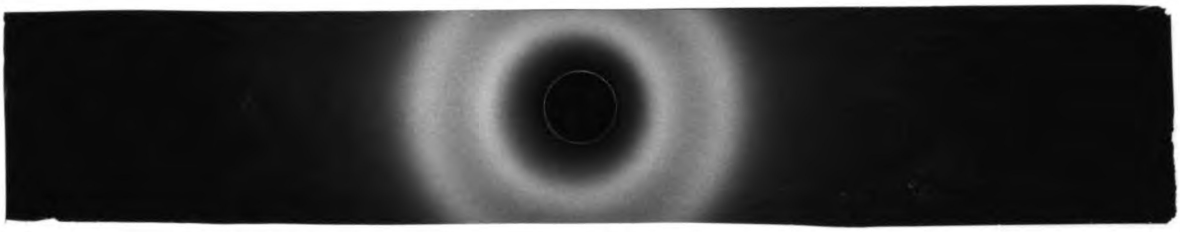


(a) Fraction B-8

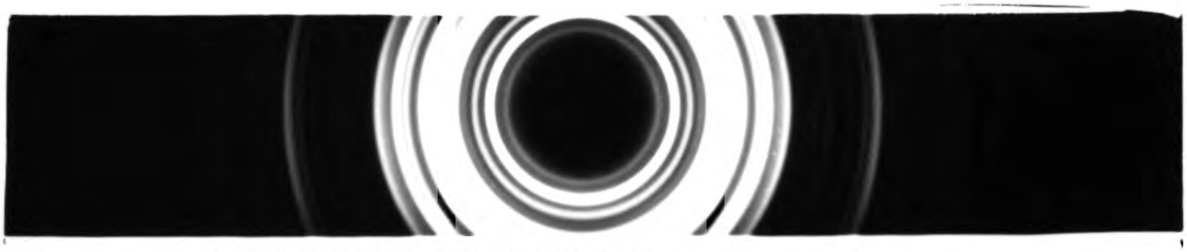


(b) Fraction B-7 (after initial annealing period).

Fig. 3. Photomicrographs of Isotactic Poly(butene-1).



(a) Atactic Poly(butene-1)



(b) Unextracted Isotactic Sample

(c) Isotactic Poly(butene-1) Fraction B-7

(d) Isotactic Poly(butene-1) Fraction B-8

Fig. 4. X-Ray Powder Spectra of Poly(butene-1)

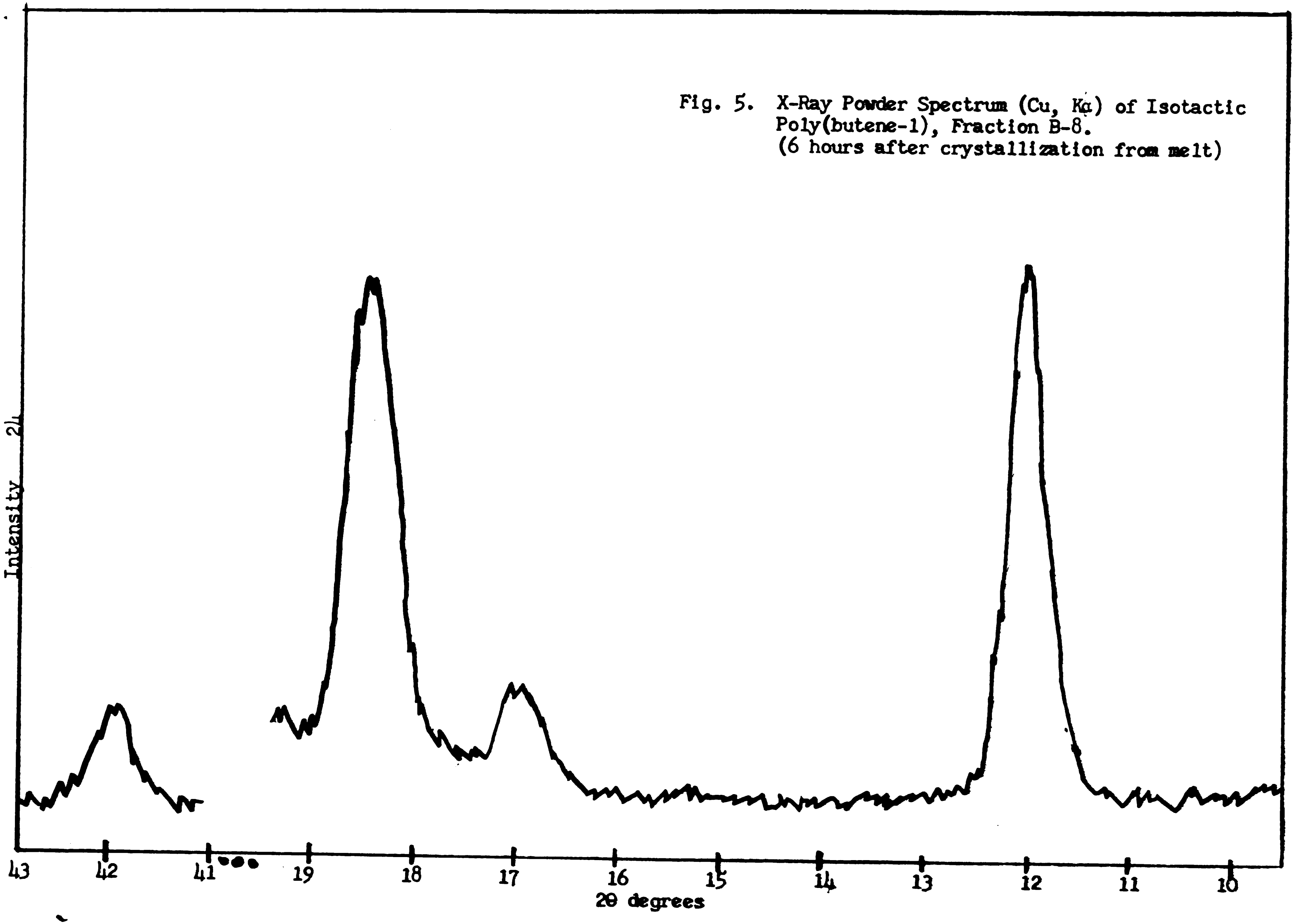


Fig. 5. X-Ray Powder Spectrum (Cu, Kα) of Isotactic Poly(butene-1), Fraction B-8. (6 hours after crystallization from melt)

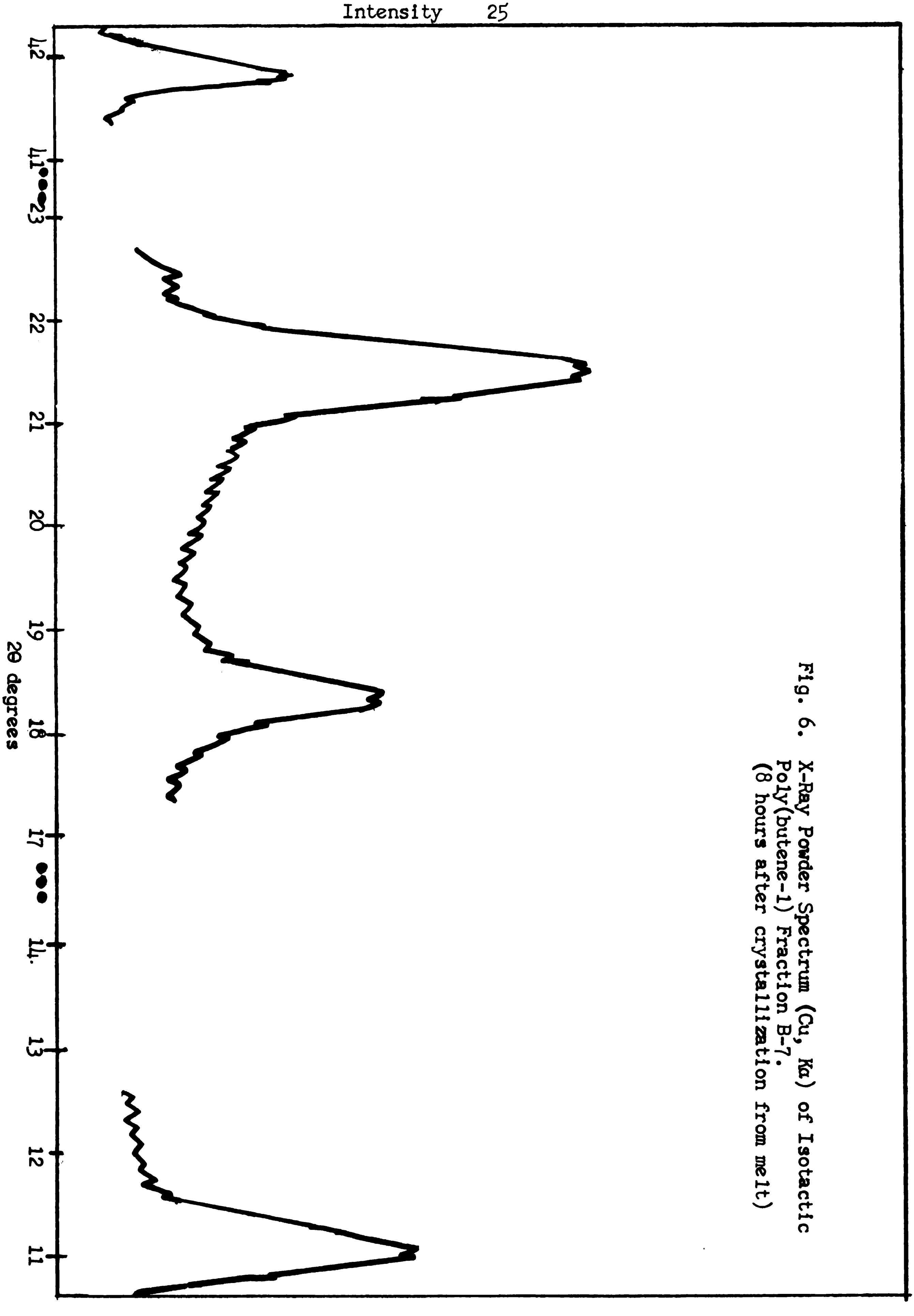


Fig. 6. X-Ray Powder Spectrum (Cu, Kα) of Isotactic Poly(butene-1) Fraction B-7. (8 hours after crystallization from melt)

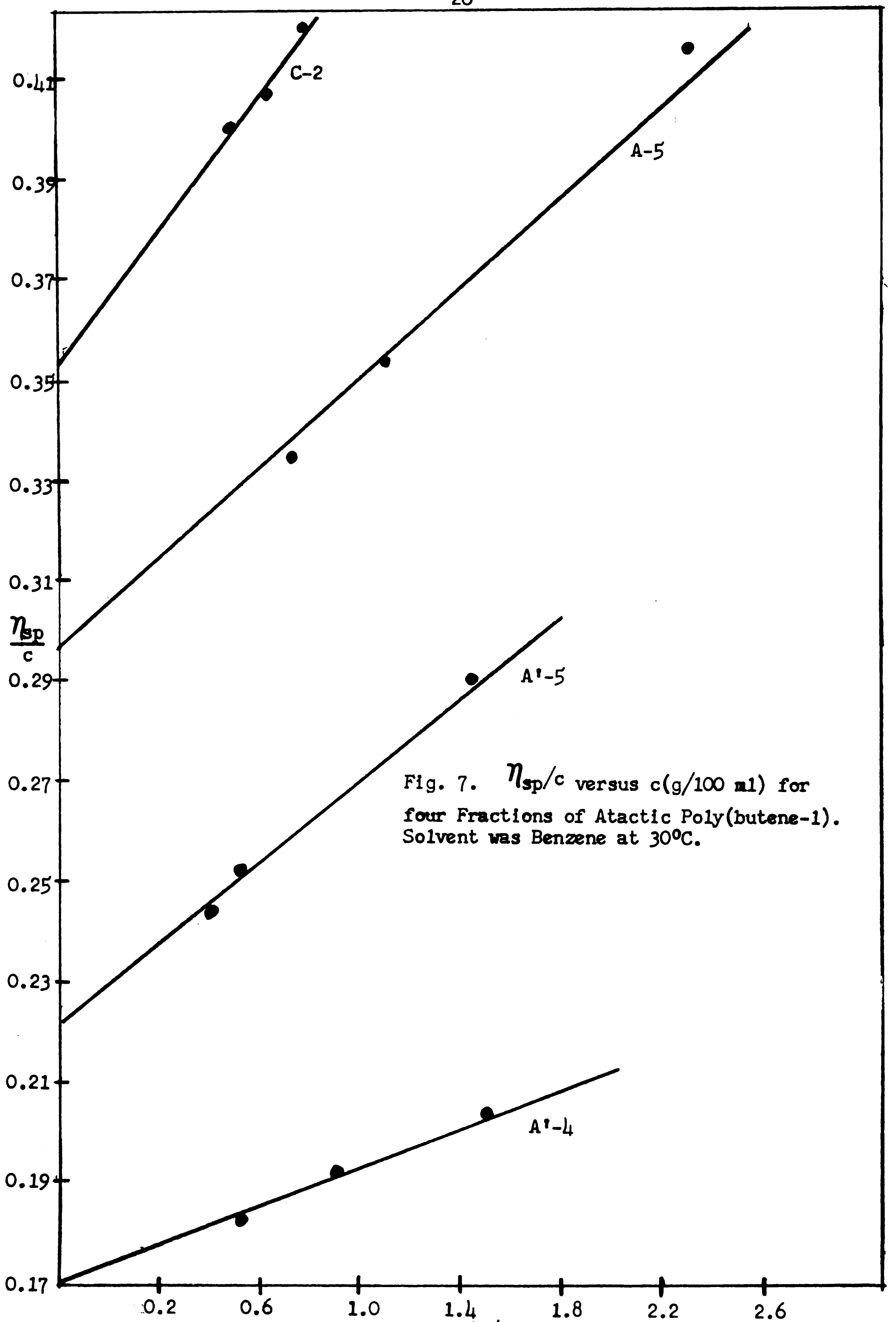


Fig. 7. η_{sp}/c versus c(g/100 ml) for four Fractions of Atactic Poly(butene-1). Solvent was Benzene at 30°C.

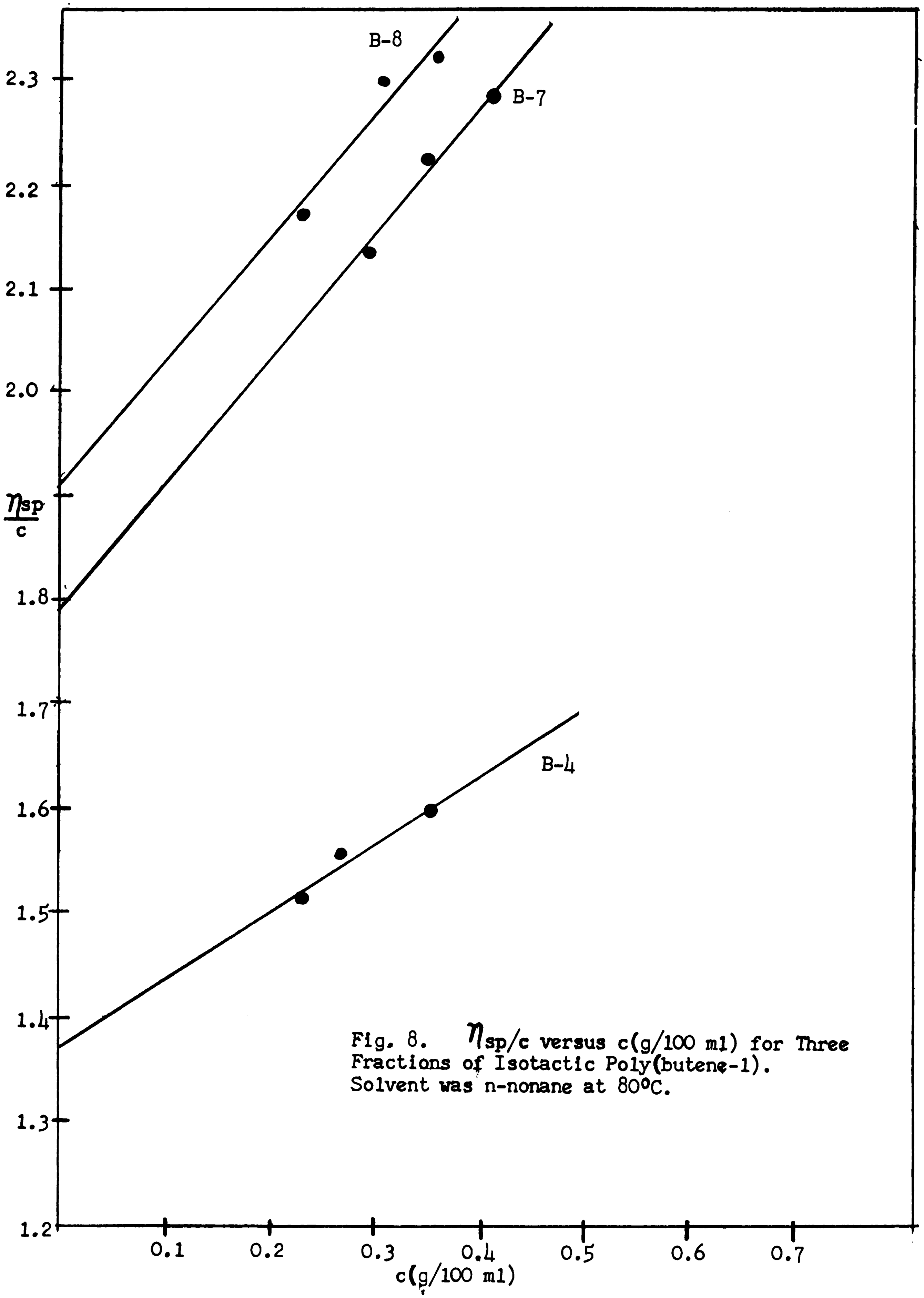


Fig. 8. η_{sp}/c versus c(g/100 ml) for Three Fractions of Isotactic Poly(butene-1). Solvent was n-nonane at 80°C.

Table VI. Intrinsic Viscosities and Molecular Weights for Fractions of Isotactic and Atactic Poly(butene-1)

Isomer	Fraction	$[\eta]$	M.W.*
Atactic	A'-4	0.170	17,010
	A'-5	0.221	24,950
	A -5	0.296	38,600
	C -2	0.352	49,210
Isotactic	B-4	1.364	287,800**
	B-7	1.784	402,500
	B-8	1.904	436,700

*Calculated from Natta's relationship for atactic poly(butene-1) in benzene at 30°C.

**Calculated from Krigbaum's relationship for isotactic poly(butene-1) in n-nonane at 80°C.

Phase Diagrams

Preliminary tests were made with approximately 1 percent mixtures of unfractionated isotactic polymer. The modes of phase separation are designated L - L for liquid - liquid separation and L - C for crystallization.

Phase diagrams in the dilute range were obtained for both stereoisomers in diethyl carbitol and butyl cellosolve.

Weight fractions, obtained experimentally, were converted to volume fractions by assuming negligible volume change on mixing; therefore

$$v_2 = (W_2V_{sp})/(W_1d_1 + W_2V_{sp})$$

where the values of the specific volume and density were taken at the

Table VII. Precipitation Temperatures of Approximately 1% Mixtures of Isotactic Poly(butene-1) in Different Solvents.

Solvent	δ*	T_p (°C)	Phase Separation
Phenyl Ether		140	L - L
Butyl Cellosolve	8.9	150	L - L
Decyl Alcohol		80	L - C
Octanol	10.3	82	L - C
Anisole		85	L - L
Phenetole		50	L - L
Diethyl Carbitol		90	L - L
Cyclohexanone	9.7	95	L - C

*δ is a solubility parameter defined as the square root of the cohesive energy density

$$\delta = (CED)^{1/2} = (Evap./V)^{1/2}$$

Table VIII. Phase Diagram Data for the System Atactic Poly(butene-1) - Diethyl Carbitol

Fraction	Volume fraction (v_2)	T_p (°C.)
A'-4	0.131	41.8
	0.0752	43.9
	0.0508	43.7
	0.0389	43.4
	0.0285	41.8
	0.0204	40.4
A'-5	0.0998	53.5
	0.0650	55.0
	0.0516	55.4
	0.0392	55.3
	0.0309	55.2
	0.0240	53.5
A-5	0.120	56.5
	0.0580	60.5
	0.0382	60.4
	0.0270	59.5
	0.0174	57.5
C-2	0.130	70.0
	0.0622	72.6
	0.0359	72.7
	0.0273	72.3
	0.0197	71.3
	0.0139	70.2
	0.00950	68.8

Table IX. Phase Diagram Data for the System Isotactic Poly(butene-1) - Diethyl Carbitol

Fraction	Volume fraction (v_2)	T_p (°C.)
B-4	0.0776	90.4
	0.0355	90.2
	0.0206	90.3
	0.0143	89.6
	0.0960	88.2
	0.00800	87.7
B-7	0.0776	89.2
	0.0373	90.5
	0.0214	90.7
	0.0174	90.6
	0.0130	90.1
	0.009600	89.5
B-8	0.0732	89.0
	0.0377	90.7
	0.0250	91.0
	0.0191	91.0
	0.0152	90.4
	0.0119	90.2
	0.0102	90.0
	0.00890	88.9

Table X. Phase Diagram Data for the System Atactic Poly(butene-1) - Butyl Cellosolve

Fraction	Volume fraction (v_2)	T_p (°C.)
A'-4	0.0994	95.1
	0.0657	95.1
	0.0507	95.0
	0.0355	94.0
	0.0108	90.9
	0.00990	89.6
A'-5	0.108	109.0
	0.0831	110.2
	0.0610	111.8
	0.0496	111.7
	0.0364	111.5
	0.0333	111.0
	0.0255	110.5
	0.0201	109.8
	0.0146	108.5
A-5	0.0822	117.5
	0.0465	118.8
	0.0379	119.5
	0.0300	119.5
	0.025	119.0
	0.0203	118.2
	0.0157	117.6
C-2	0.0731	132.8
	0.0428	134.5
	0.0338	134.5
	0.0292	134.0
	0.0224	132.9

Table XI. Phase Diagram Data for the System Isotactic Poly(butene-1) - Butyl Cellosolve

Fraction	Volume fraction (v_2)	T_p(°C.)
B-4	0.0329	143.6
	0.0162	145.2
	0.0107	145.4
	0.00870	145.0
	0.00470	143.1
B-7	0.0471	146.6
	0.0246	150.0
	0.0158	150.4
	0.0124	150.6
	0.00890	147.7
	0.00660	146.1
B-8	0.0163	150.9
	0.0131	151.0
	0.0102	151.1
	0.00887	151.0
	0.00680	150.8
	0.00610	150.6
	0.00470	150.0
	0.00372	148.5

precipitation temperature. The precipitation temperatures were plotted against volume fractions to obtain the phase diagrams. Critical points were determined from rectilinear diameters.

Precipitation temperatures were reproducible to ±0.3°C. and were independent of the cooling rate. The endpoint varied with the viewing angle; all of the endpoints in this work were obtained by sighting through the sample perpendicular to the light path.

The critical data for atactic and isotactic poly(butene-1) are summarized in Tables XII and XIII.

Table XII. Critical Data for Atactic and Isotactic Poly(butene-1) in Diethyl Carbitol

Isomer	Fraction	T_c(°C)	x	v_{2c}(exp)	v_{2c}(calc)*
Atactic	A'-4	44.1	108.0	0.0675	0.0878
	A'-5	55.4	157.5	0.0517	0.0738
	A-5	60.6	243.1	0.0510	0.0603
	C-2	72.8	308.0	0.0480	0.0539
Isotactic	B-4	90.4	1815	0.0261	0.0229
	B-7	90.8	2537	0.0245	0.0195
	B-8	19.1	2751	0.0235	0.0187

*Calculated from the Flory-Huggins expression

$$v_{2c} = \frac{1}{1 + x^{1/2}}$$

An odd feature of the phase diagrams for poly(butene-1) in diethyl carbitol was the deviation of the critical volume fractions from ideality. Whereas the deviations were negative for the atactic fractions they were positive for the isotactic samples.

Table XIII. Critical Data for Atactic and Isotactic Poly(butene-1) in Butyl Cellosolve

Isomer	Fraction	T_c(°C)	x	v_{2c}(exp)	v_{2c}(calc)*
Atactic	A'-4	95.1	145.3	0.0590	0.0766
	A'-5	111.8	211.0	0.0520	0.0644
	A-5	119.5	324.9	0.0350	0.0526
	C-2	134.6	409.9	0.0410	0.0471
Isotactic	B-4	145.5	2384	0.0125	0.0201
	B-7	150.6	3309	0.0140	0.0171
	B-8	151.1	3588	0.0110	0.0164

*Calculated from the Flory-Huggins expression (see **Table** XII).

x, the ratio of the molar volumes of polymer and solvent is calculated from

$$x = \frac{\text{M.W.}\ V_{sp}}{V_1}$$

where V_1 is the molar volume of the solvent. The values of the specific volume of the polymer and the molar volume of the solvent were taken at the critical temperatures.

Figures 9 through 12 give the phase diagrams of the stereoisomers in the solvents studied.

As predicted by theory, plots of $1/T_c$ versus $[1/x^{1/2} + 1/2x]$ were linear within experimental error for both systems. Straight lines were obtained by a least squares fit. Figures 13 and 14 give the dependence of the critical temperature on the ratio of molar volumes, x, for the diethyl carbitol and butyl cellosolve systems respectively.

In both solvents the slopes and intercepts are different for the two stereoisomers; this results in a sizable difference in the thermodynamic interaction parameters.

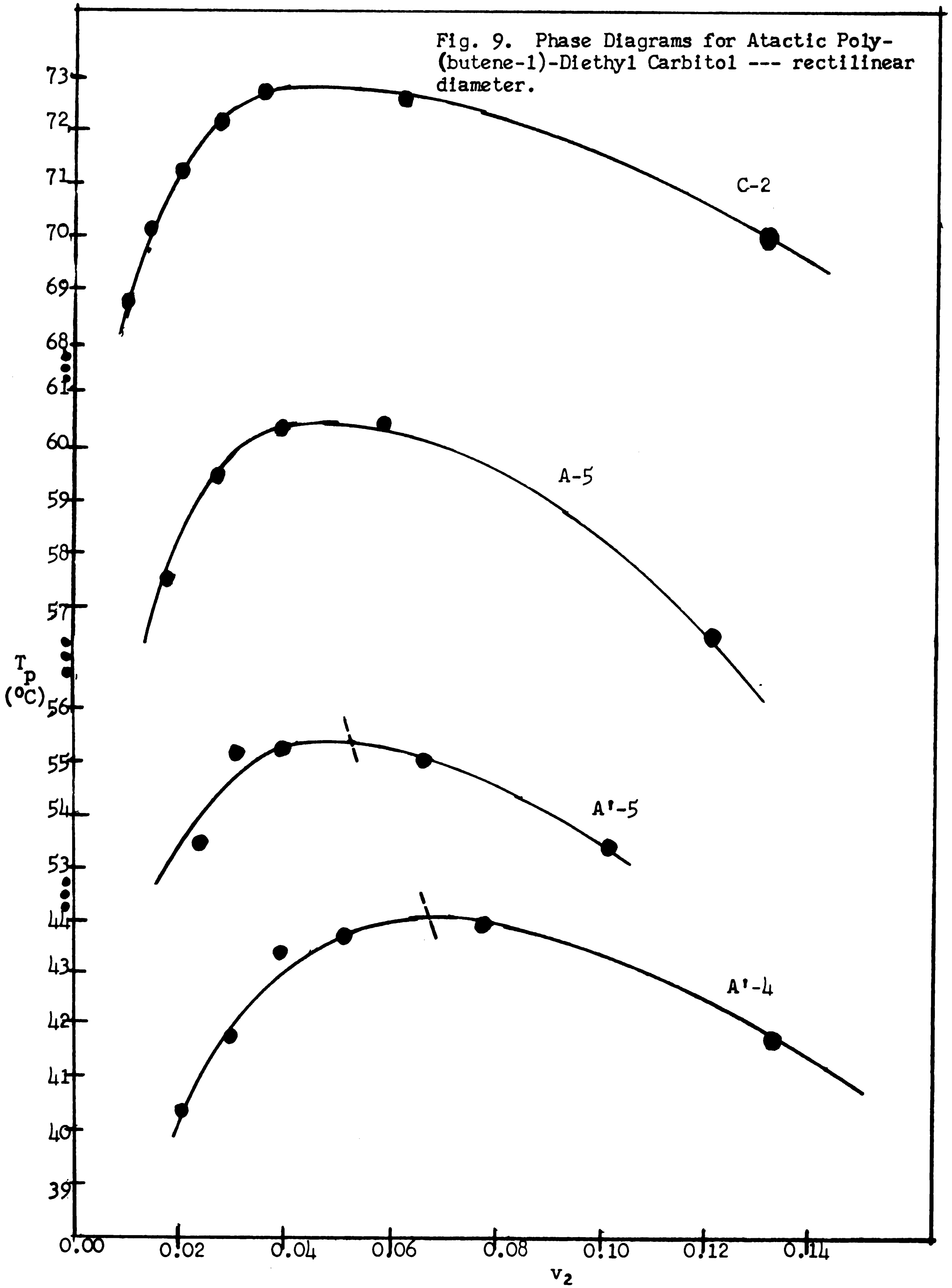
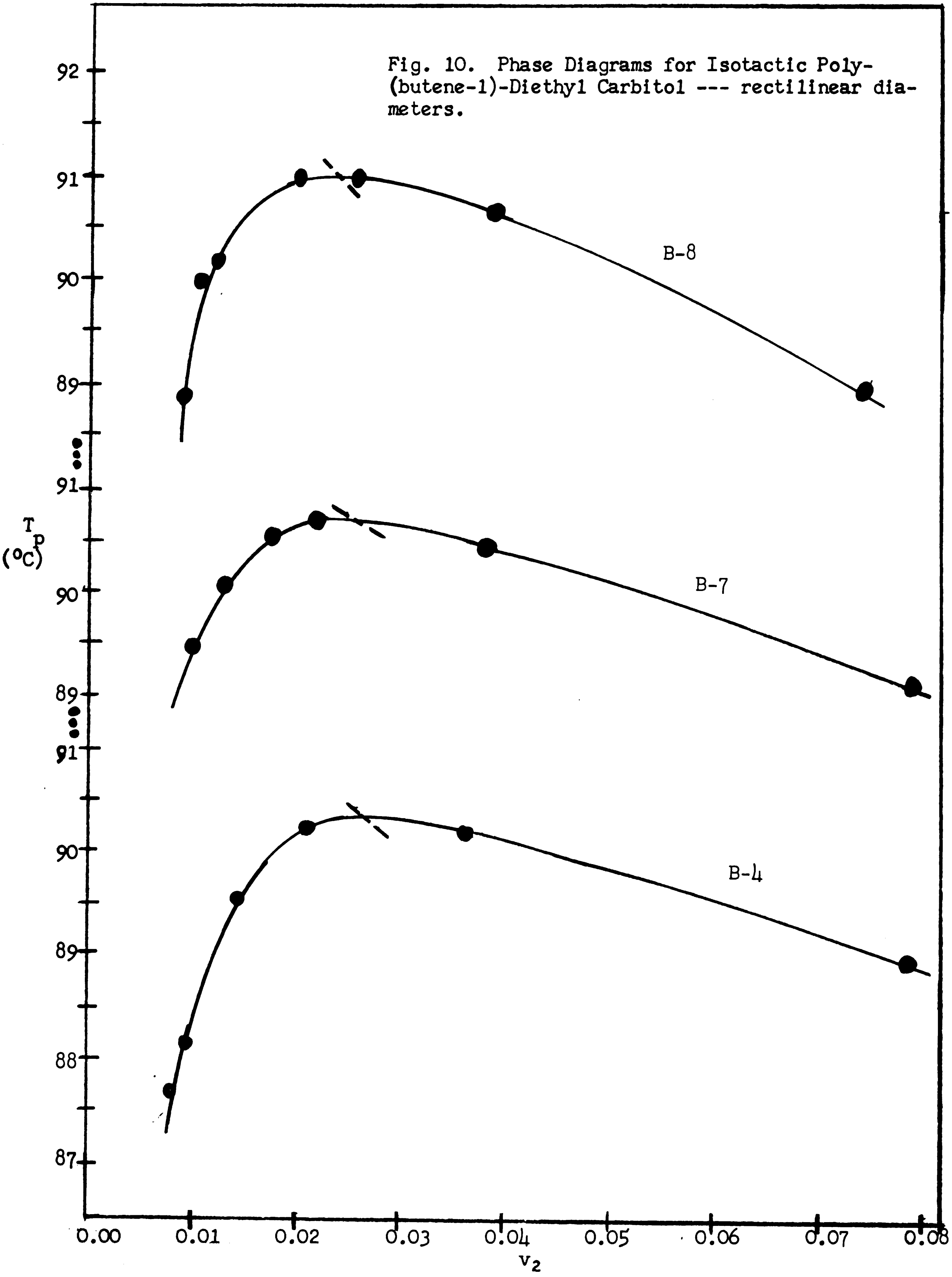


Fig. 9. Phase Diagrams for Atactic Poly-(butene-1)-Diethyl Carbitol --- rectilinear diameter.

Fig. 10. Phase Diagrams for Isotactic Poly-(butene-1)-Diethyl Carbitol --- rectilinear diameters.



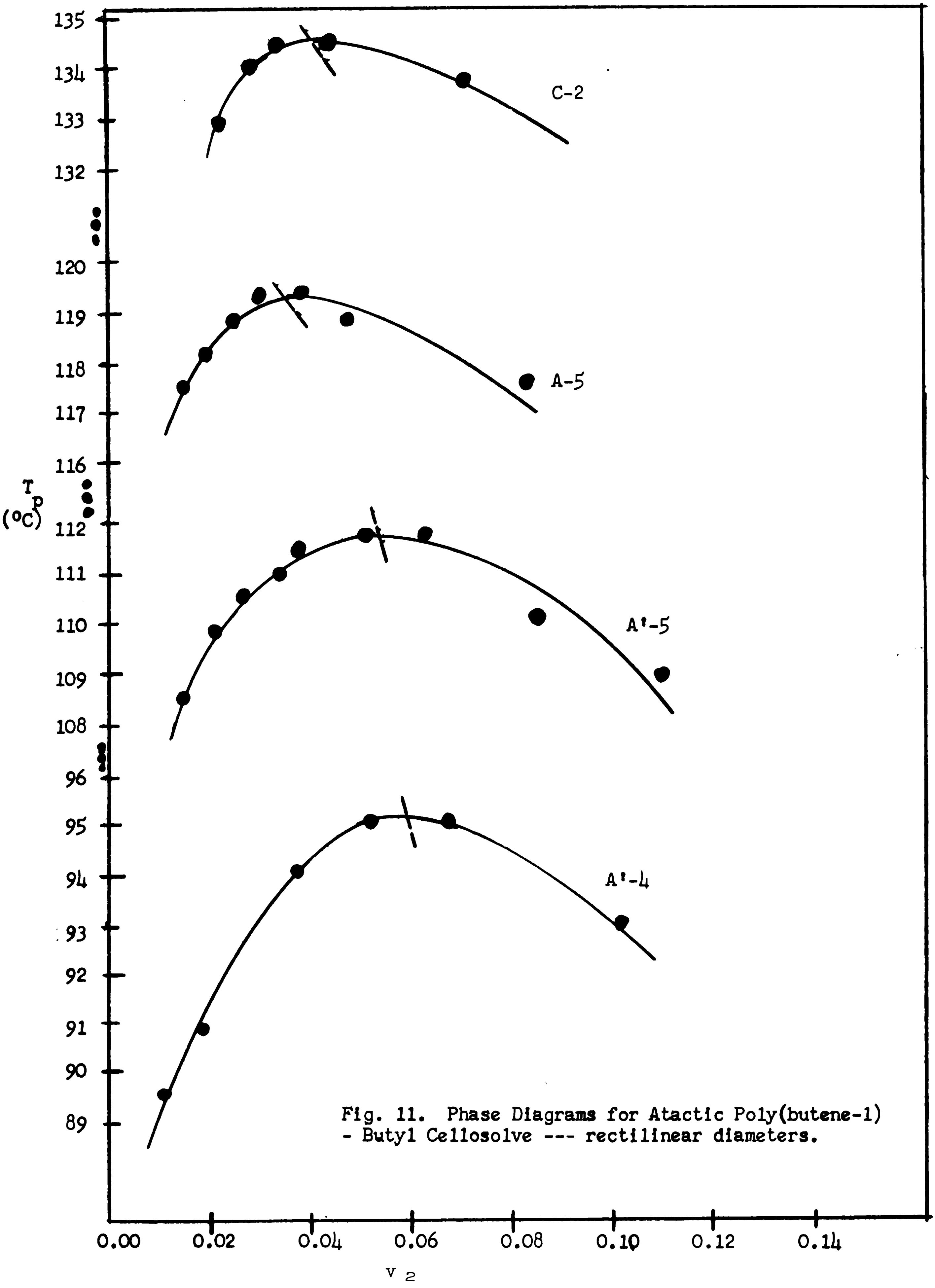


Fig. 11. Phase Diagrams for Atactic Poly(butene-1) - Butyl Cellosolve --- rectilinear diameters.

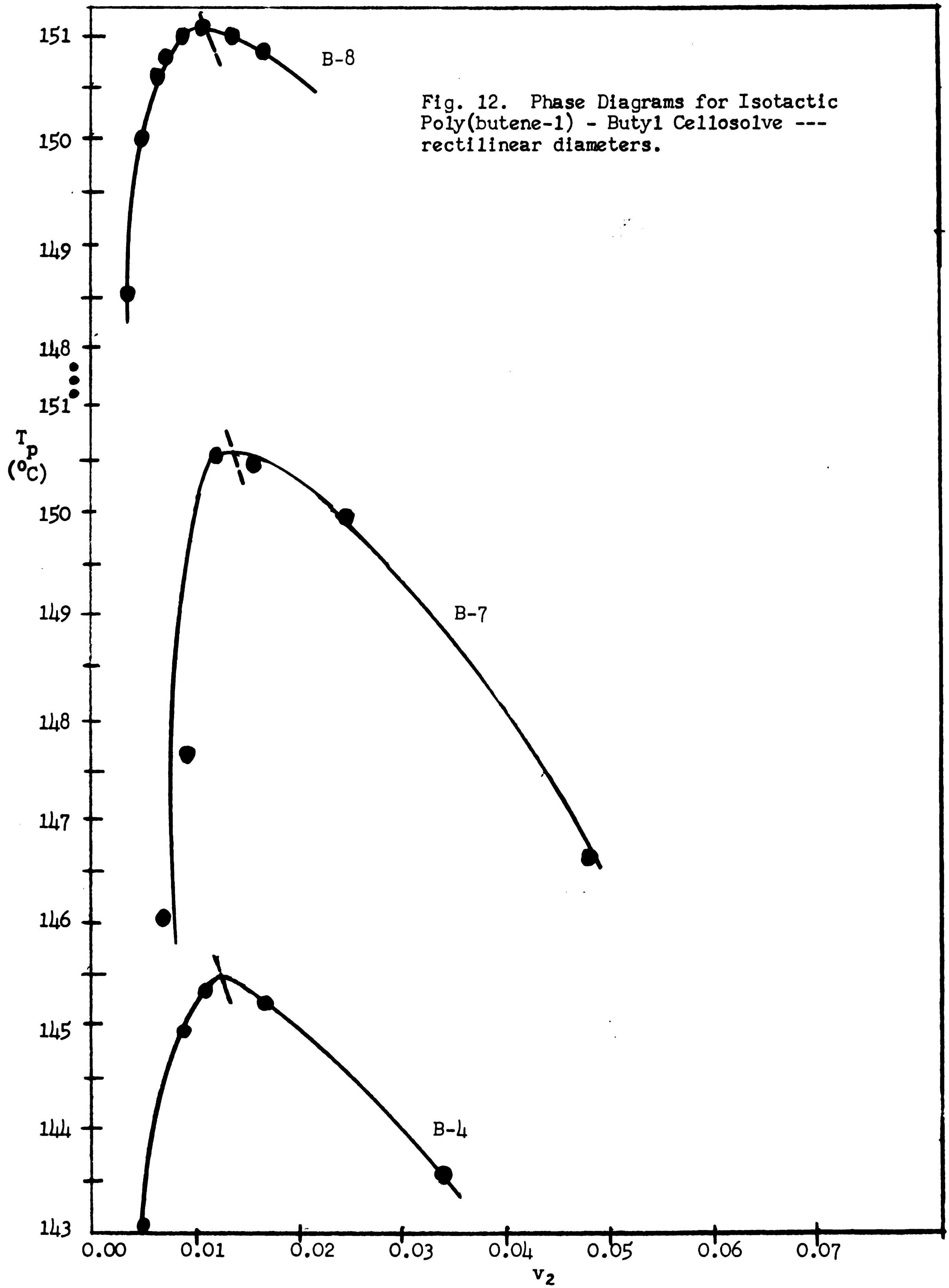


Fig. 12. Phase Diagrams for Isotactic Poly(butene-1) - Butyl Cellosolve --- rectilinear diameters.

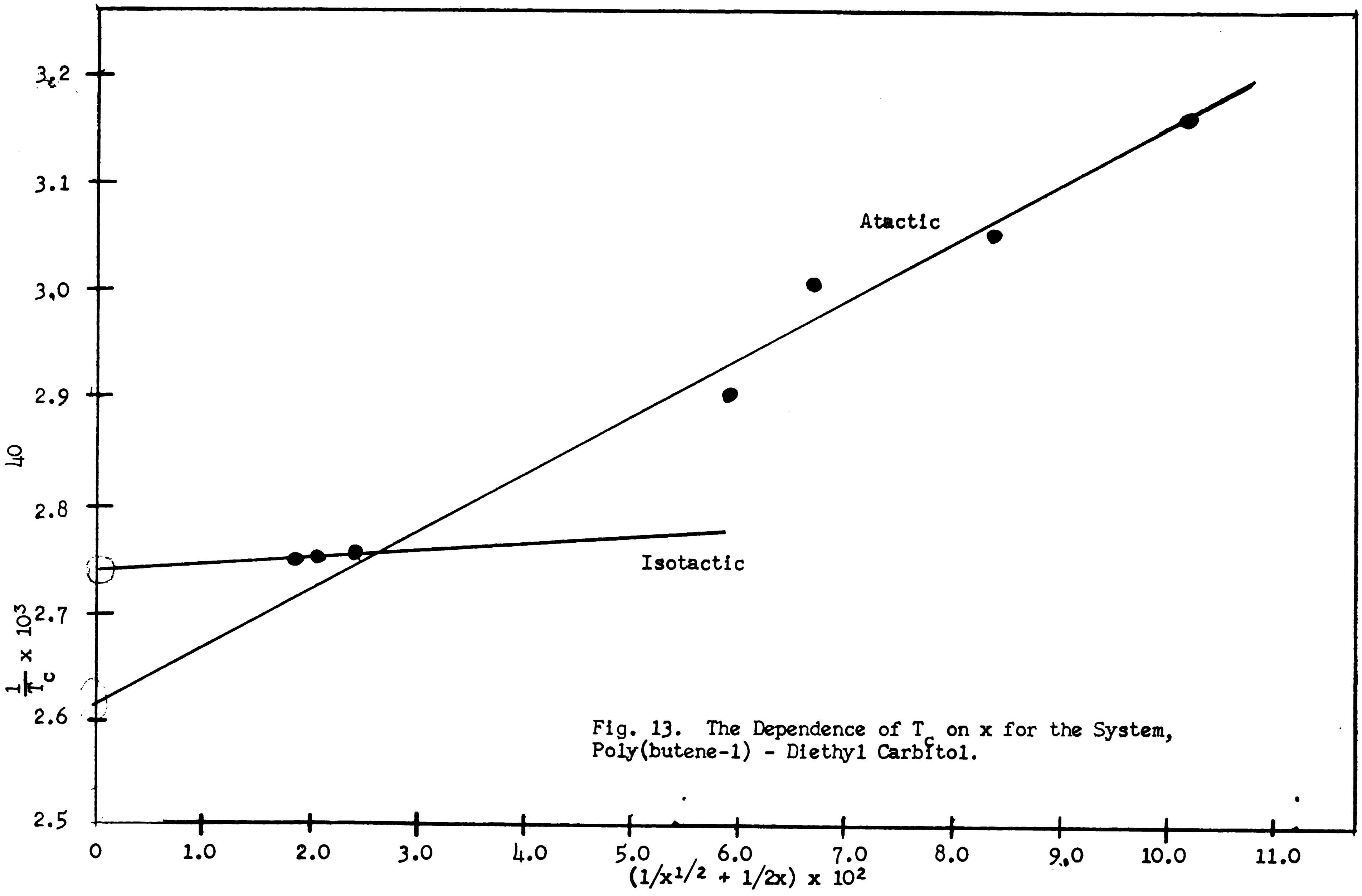


Fig. 13. The Dependence of T_c on x for the System, Poly(butene-1) - Diethyl Carbitol.

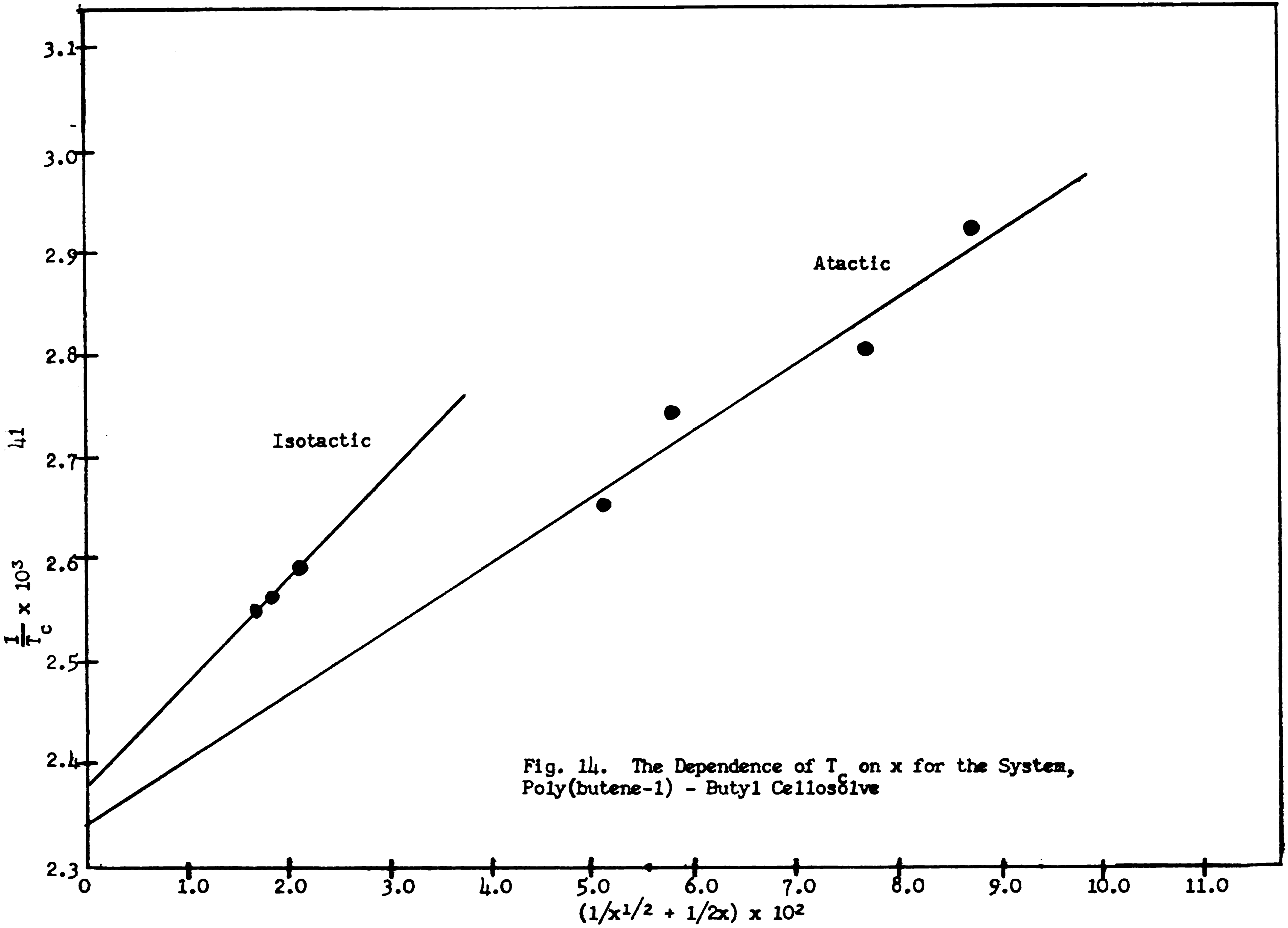


Fig. 14. The Dependence of T_c on x for the System, Poly(butene-1) - Butyl Cellosolve

The values of the interaction parameters in the diethyl carbitol system are $\theta = 371.7^\circ$K, $\psi = 0.941$ for isotactic poly(butene-1) and $\theta = 386.7^\circ$K, $\psi = 0.458$ for atactic poly(butene-1).

For the butyl cellosolve system θ is again higher for the atactic isomer but the relative values of the entropy parameter are reversed. The values obtained are $\theta = 460.4^\circ$K, $\psi = 0.203$ for isotactic poly(butene-1) and $\theta = 471.3^\circ$K, $\psi = 0.308$ for the atactic polymer.

Refering to Figure 13 it will be noted that the curves have a point of intersection at which the critical temperature is the same for both stereoisomers.

According to theory (equation 7), the temperature dependence of can be obtained from the interaction parameters. For atactic poly-(butene-1) in diethyl carbitol $\chi = 0.042 + 177.1(1/T)$ and in butyl cellosolve $\chi = 0.192 + 145.2(1/T)$ for this isomer. The relationship for isotactic poly(butene-1) is $\chi = -0.441 + 349.8(1/T)$ in diethyl carbitol and $\chi = 0.297 + 93.46(1/T)$ in butyl cellosolve. These functions are plotted in Figures 15 and 16.

For comparison of the two systems, the parameters are collected in Table XIV.

Table XIV. The Thermodynamic Interaction Parameters for Isotactic and Atactic Poly(butene-1) in Diethyl Carbitol and Butyl Cellosolve

Isomer	Diethyl Carbitol		Butyl Cellosolve	
	$\theta(^\circ K)$	ψ	$\theta(^\circ K)$	ψ
Atactic	386.7	0.458	471.3	0.308
Isotactic	371.7	0.941	460.4	0.203
Difference	15.0	0.583	10.9	0.105

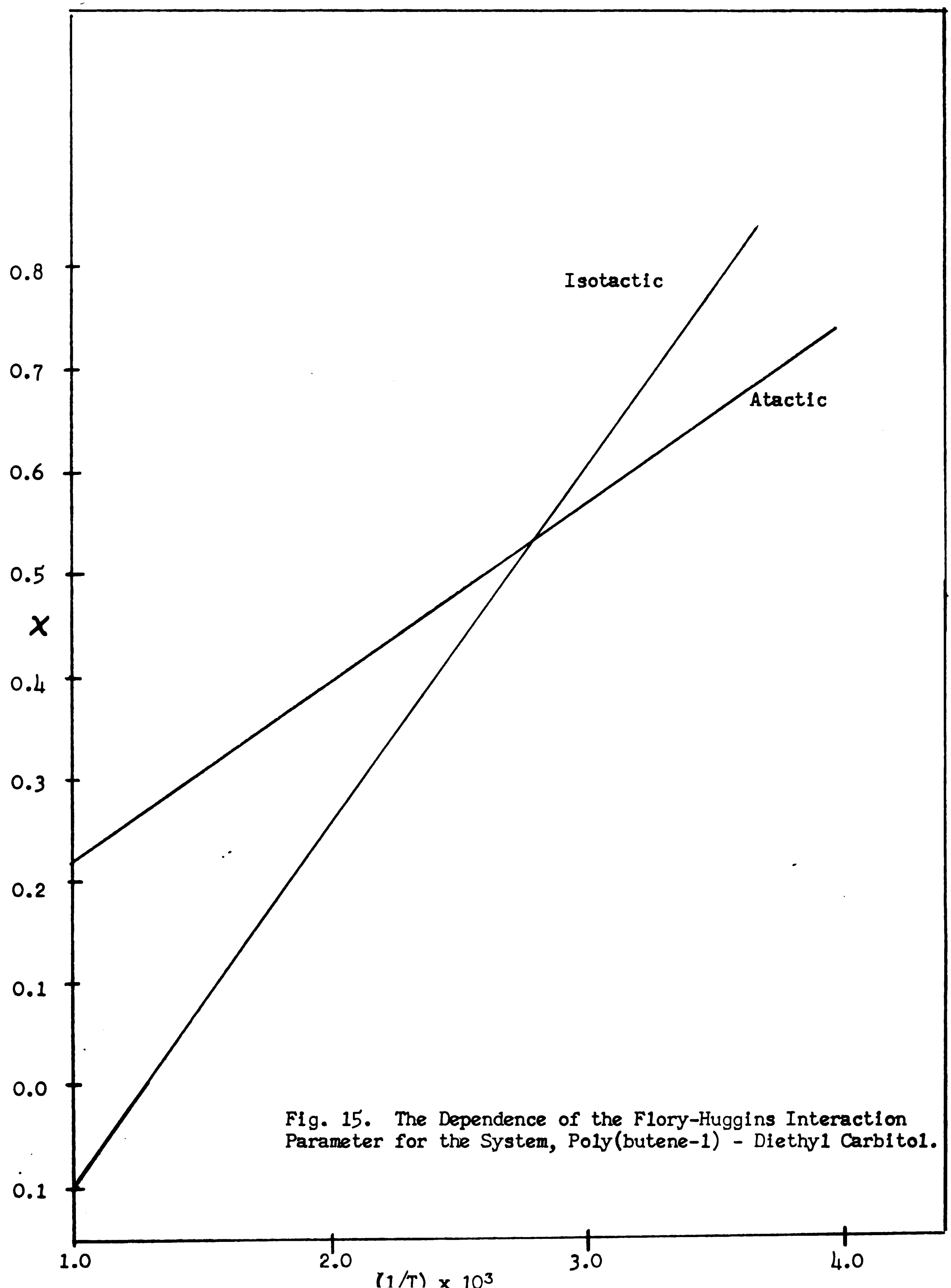


Fig. 15. The Dependence of the Flory-Huggins Interaction Parameter for the System, Poly(butene-1) - Diethyl Carbitol.

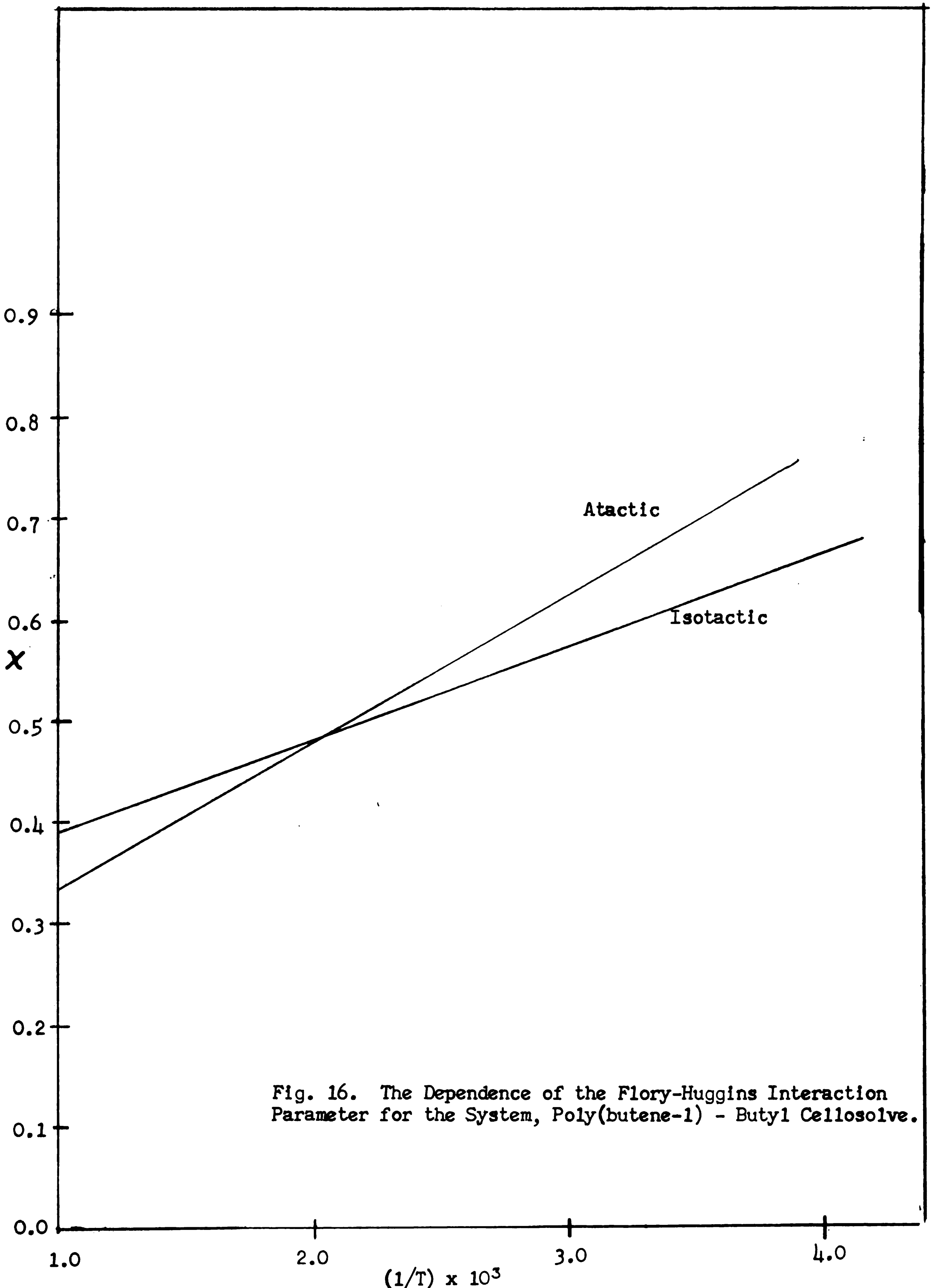


Fig. 16. The Dependence of the Flory-Huggins Interaction Parameter for the System, Poly(butene-1) - Butyl Cellosolve.

The weights of known volumes of diethyl carbitol were determined at 45°C., 61°C., 75°C. and 85°C. The calculated densities were fitted by least squares giving the relationship

$$d = 0.931 - 0.001T(^{\circ}C).$$

The weights of known volumes of butyl cellosolve were determined at 90°C., 104°C., 132°C. and 140°C. Least squares gave the density temperature relationship

$$d = 0.937 - 0.001T(^{\circ}C).$$

Specific volumes of the isomers as calculated from Natta's dilatometric data are

$$v_{sp}(\text{atactic}) = 1.154 + 9.0 \times 10^{-4}\ (T(^{\circ}C) - 30)$$

$$v_{sp}(\text{isotactic,liquid}) = 1.20 + 3.8 \times 10^{-4}\ T(^{\circ}C).$$

IV. DISCUSSION

Although the values of χ are for a polymer of infinite molecular weight, they can be used to show the trend for any molecular weight. χ can be interpreted as a measure of solubility; therefore some statement can be made about the relative solubilities of the two stereoisomers.

Consider first the diethyl carbitol system as given in Figure 15. At temperatures above the point of intersection, which corresponds to 84°C., isotactic poly(butene-1) is the more soluble isomer and below it the less soluble.

This situation is reversed in butyl cellosolve (Figure 16). The atactic isomer is the more soluble at temperatures above the point of intersection. Intersection here occurs at a much higher temperature, 213°C., which would be impossible to obtain experimentally since it is above the boiling point of the solvent. These are hypothetical situations, of course, because the solubility at any temperature is a function of the molecular weight.

Although Krigbaum reports a higher theta temperature for isotactic poly(butene-1) than for the atactic isomer in anisole, the χ versus $1/T$ curves are similar to the diethyl carbitol system as reported here. An intersection occurs at 89°C. in this system and the differences in solubility at other temperatures aren't as large as reported here for diethyl carbitol.

The root mean square end to end distance cannot be calculated from these data, but must be determined from light scattering measurements. These phase studies do give an indication of what differences might exist. At the Θ temperature, the polymer assumes its unperturbed

dimensions. Since in both solvents investigated θ is higher for atactic poly(butene-1), its expansion factor, α, is smaller at a given temperature; eg., at θ for atactic its α is unity but the α for the isotactic species is greater than one (above its θ).

The heat of dilution parameter, κ, is positive for both polymers as is expected in poor solvents. In an ideal solution, the heat of mixing is zero, and κ can be used as a measure of deviation from ideality. In diethyl carbitol isotactic poly(butene-1) has a larger κ and so is less ideal. There is a reversal in the relative values of the heat of dilution and entropy parameters in butyl cellosolve. These differences in the two systems studied are thought to reflect differences in size and polarity of the solvent molecules.

These experiments indicate that differences in the thermodynamic interaction parameters of stereoisomeric polymers are dependent on the solvent as well as on the degree of stereoregularity of the polymer.

If the dependence on solvent is clarified and it is possible to separate variables, differences in the thermodynamic interaction parameters might represent a quantitative measure of the degree of stereoregularity.

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