LOWER CRITICAL SOLUTION TEMPERATURES FOR POLY-a-OLEFINS

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ABSTRACT

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Lower critical solution temperatures (LCST) were determined for several fractions of five polymers: isotactic polypropylene, atactic polypropylene, isotactic polybutene-1, atactic polybutene-1, and polyoctene-1. The LCST of the first four polymers were determined in n-pentane and that for the last polymer in n-butane. One polyoctene-1 fraction was studied in four hydrocarbon solvents. Finally phase separation temperatures were determined for a polyoctene-1 fraction dissolved in varying mixtures of n-butane and n-pentane.

It was shown that a linear relationship exists between $\frac{1}{\text{LCST}}$ vs $\frac{1}{M^{1/2}}$, where M is the molecular weight of the fraction. This relationship was anticipated from Flory's upper critical solution temperature theory although it does not specifically predict a LCST. A linear relationship also exists between the critical temperature of the solvent and the LCST of the polymer solution. Phase separation temperatures were determined for a three component system. A positive deviation from ideal behavior was observed. No theory as yet exists for such a system; in fact this is the first three component system (2 solvents, 1 polymer) ever studied for a LCST.

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By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

INTRODUCTION

History

It has been known for some time that certain mixed systems exist where the mutual solubility of a pair of liquids decreases with increasing temperature. The minimum temperature at which immiscibility occurs is called the lower critical solution temperature (LCST or T_{CL}). All the early data refer to systems where both components were highly polar and the LCST was related to the increase in entropy associated with the rupture of hydrogen bonds.

Only a few years ago Freeman and Rowlinson[1] observed this same behavior for hydrocarbon polymers in hydrocarbon solvents, a system which is notoriously nonpolar in character. This observation which was not predicted by the Hildebrand-Scatchard solubility theory aroused a great deal of interest. The authors of this initial report associated the decreasing solubility of the polymer with increasing temperature with the expansion of the solvent as it approached its critical temperature and a rapid decrease of its solubility parameter relative to that of the polymer.

Rowlinson and Freeman[2] published simultaneously with the above work their results with ethane solutions of pure liquid hydrocarbons with between 24 and 37 carbon atoms. Their results establish beyond a doubt that LCST are found in mixtures of nonpolar molecules of the same chemical type if the molecular sizes and energies of interaction of the two components are different. They showed that the LCST decreased with increasing molecular weight of the solute and that solute

molecules with saturated rings or with unsaturation gave lower LCST than their corresponding saturated hydrocarbons.

Baker and his coworkers[3] studied the phase equilibria for unfractionated polyisobutene of mean molecular weight from 250 to 2,500,000 in n-pentane. The high molecular weight polymers were precipitated at temperatures slightly above the normal boiling point of the solvent. They showed that the thermodynamic properties change profoundly with molecular weight. In agreement with Freeman and Rowlinson[1] they point out that negative excess heats and excess entropies of mixing are thermodynamic necessities in a binary solution that is close to a LCST, and that these properties are incompatible with the Flory-Huggins equation.

Delmas, Patterson, and Somcynsky[4] used the solubility parameter theory and molecular theory of polymer solutions developed by Prigogine and collaborators to treat quantitatively the negative (exothermic) heats of mixing occurring in some nonpolar polymer-solvent systems and the LCST. Heats of mixing were obtained calorimetrically for unfractionated polyisobutylene (PIB) with solvents in the n-alkane series. Their experimental data are in good agreement with their cell model theory.

The development of their theory leads to the equation:

$$R\chi = A\left(\frac{r_1}{T_{CL}}\right) + B\left(\frac{T_{CL}}{r_1}\right) \qquad (1)$$

where: $r_1 = (n + 1)/2$; n = no. of carbon atoms of the solvent.

A and B = constants.

Subscripts 1 and 2 refer to solvent and polymer respectively.

T_{CL} = LCST in °K; R = gas constant in cal./deg.-mole.

χ = Flory interaction parameter.

A was evaluated from calorimetric heats of mixing of PIB in the n-paraffins and B was chosen to give the best fit with the critical solution temperatures. They used equation (1) to predict a LCST and their calculated values were in fair agreement with the experimental data of Freeman and Rowlinson[1]. However, they assumed a value for χ corresponding to infinite molecular weight polymer, thus eliminating the important molecular weight dependence from their equation.

Ballard[5] determined the LCST for four fractions of polyoctene-1 in n-pentane. Solving equation (1) for T_{CL}/r_1, he obtained

$$\frac{T_{CL}}{r_1} = \frac{R\chi + [(R\chi)^2 - 4AB]^{1/2}}{2B} . \qquad (2)$$

Then he kept the molecular weight dependence in the equation by using the following value for χ.

$$\chi = \frac{1}{2} + \frac{1}{x^{1/2}} + \frac{1}{2x} \qquad (3)$$

where $x = \dfrac{\bar{M}_n v_{sp}}{V_1}$

$\bar{M}_n$ = number average molecular weight

v_{sp} = specific volume of polymer

V_1 = molar volume of solvent.

The parameter χ follows from the Flory-Huggins theory which is useful for upper critical solution temperatures. Using the A and B parameters determined by Delmas, Patterson, and Somcynsky[4], he calculated the LCST for PIB in n-pentane and the calculated values agreed well with Baker's[3] observed data. Also a plot of T_{CL} vs $1/x^{1/2}$ gave a straight line which when extrapolated to infinite molecular weight yielded a temperature which was called θ_L analogous to the familiar Flory theta temperature for upper critical solution temperatures (UCST). Also, Θ_L corresponds to the maximum temperature at which solvent and polymer of infinite molecular weight can coexist in a single phase. Equation (2) was found useful for calculating Θ_L.

In the present work an attempt was made to further elucidate the dependence of LCST on molecular weight by determining the LCST for a number of fractionated poly-α-olefins.

Theory

The stability of a binary phase can be characterized in terms of the chemical potential, μ_p of the components. If we consider a binary system whose two components are in equilibrium, thermodynamic arguments[6] show that for equilibrium with respect to diffusion for a two component system

$$\frac{\partial \mu_1}{\partial n_2} = \frac{\partial \mu_2}{\partial n_1} < 0 \qquad (4)$$

where n = number of moles.

Making use of the Gibbs-Duhem relation, it can be shown that

$$\frac{\partial \mu_1}{\partial n_2} = \frac{x_1}{n}\frac{\partial \mu_1}{\partial x_2} \quad \text{and} \quad \frac{\partial \mu_2}{\partial n_1} = \frac{x_2}{n}\frac{\partial \mu_2}{\partial x_1} \qquad (5)$$

and equation (4) is equivalent to

$$\frac{\partial \mu_1}{\partial x_2} < 0 \quad \text{and} \quad \frac{\partial \mu_2}{\partial x_1} < 0 \qquad (6)$$

These conditions are illustrated in Figure 1, which shows the dependence of the mole fraction on the chemical potential. Below T_{CL} (curve 1) a single phase exists and the conditions of equation (6) are always satisfied. However, at a temperature T_2, the system consists of three parts (curve 3): one rich in solvent, a second rich in solute, and the third portion, the simultaneous presence of two phases. At T_{CL} (curve 2) there is a transition between the two states. The horizontal portion of curve 3 is reduced to a single point of inflection at C which mathematically satisfies the restrictions

$$\frac{\partial \mu_1}{\partial x_2} = \frac{\partial^2 \mu_1}{\partial x_2^2} = 0 \qquad (7)$$

and

$$\frac{\partial^3 \mu_1}{\partial x_2^3} < 0 \qquad (8)$$

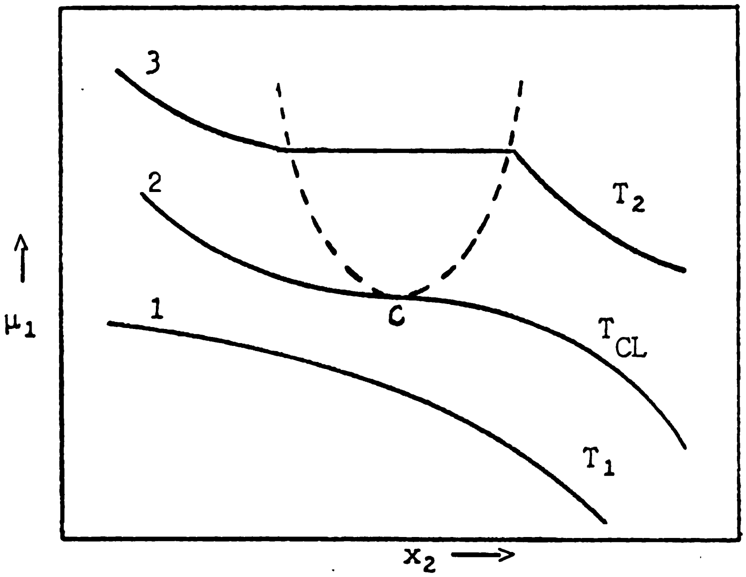


Fig. 1. Chemical potential as a function of x_2

The conditions for stability (4) can be written also in terms of the free energy of mixing since we can write

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = -x_2\left(\frac{\partial^2 \bar{F}_M}{\partial x_2^2}\right)_{T,P} \qquad (9)$$

Therefore, for stability it follows from (4) and (9) that for a stable phase in equilibrium

$$\left(\frac{\partial^2 \bar{F}_M}{\partial x_2^2}\right) > 0 \qquad (10)$$

and at the critical point

$$\left(\frac{\partial^2 \overline{F}_M}{\partial x_2^2}\right)_c = 0 \qquad (11)$$

It can be shown [6a] that $\partial x_2/\partial T$ depends essentially on the change in partial molar enthalpy for both components. At a LCST $\partial x_2/\partial T$ is negative then

$$\left(\frac{\partial^2 \overline{H}}{\partial x_2^2}\right)_c > 0 \qquad (12)$$

and at an UCST $\partial x_2/\partial T$ is positive then

$$\left(\frac{\partial^2 \overline{H}}{\partial x_2^2}\right)_c < 0 \qquad (13)$$

If we consider the relation

$$\overline{F}_M = \overline{H}_M - T\overline{S}_M \qquad (14)$$

and (11), we can write

$$\left(\frac{\partial^2 \overline{H}_M}{\partial x_2^2}\right)_c = T\left(\frac{\partial^2 \overline{S}_M}{\partial x_2^2}\right)_c \qquad (15)$$

From (11), (12), (13), (14), and (15) the curvature of the partial molar heat content and the partial molar entropy must have the same sign at the critical point. This defines these added conditions for a critical point:

$$\left(\frac{\partial^2 \overline{S}}{\partial x_2^2}\right) > 0 \quad \text{for a LCST} \qquad (16)$$

and

$$\left(\frac{\partial^2 \overline{S}}{\partial x_2^2}\right) < 0 \quad \text{for an UCST} \qquad (17)$$

As a first approximation, assume that the LCST has some similarity to the well known UCST. Therefore it seems reasonable that the Flory equation[7] for dilute polymer solutions

$$\frac{1}{T_{CU}} = \frac{1}{\theta_U}\left[1 + \left(\frac{1}{\psi_1}\right)\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right)\right] \tag{18}$$

where: T_{CU} = UCST in ^{0}K

θ_U = Flory theta temperature

ψ_1 = entropy parameter

which predicts an UCST, may apply also for LCST at least with respect to the molecular weight dependence. This equation (18) is the basis for the plots of $1/T_{CL}$ vs $1/M^{1/2}$, where M is the molecular weight. M was used to plot the data rather than x since the molar volume, V_1, of the solvent was not available above its boiling point. Also, the term $1/2M$ was dropped because this factor was negligible compared to $1/M^{1/2}$ for the molecular weight species used in this work.

EXPERIMENTAL

Equipment

A variable temperature bath with Dow-Corning #550 silicone oil was used for all phase separation determinations. The polymer solutions were sealed in "Pyrex" capillary tubes (3 mm. i.d.; 11 mm. o.d.). (It was found that smaller capillaries prevented good mixing which was critical for observing uniform end points.) Four sample tubes were suspended in the bath at one time by means of a wire screen support.

Reagents

Research grade normal pentane, propane and pure grade butane, neopentane, and isobutane were purchased from Phillips Petroleum Co. The supplier claims a purity of 99.84 mol per cent for its research grade and 99 mol per cent for its pure grade. Gas chromatograms were obtained for these reagents to verify their purity. An F. and M. Scient. Corp. Model 609 Flame Ionization Chrom. was used isothermally at 200°C. Table I summarizes the results and Figures 2 through 4 are representations of the chromatograms. Hence it appears according to the chromatographic analysis that the reagents have a purity better than that claimed by the supplier,

Table I. Gas chromatograph analysis of solvents. (Alumina column)

Reagent	Percent impurity based on relative peak heights	Probable impurity
propane	0.097	butane
butane	0.037	propane
isobutane	0.14	some isomer
pentane	0.12	some isomer
neopentane	0.48	propane, butane and others

Figure 2. Gas chromatogram of research grade n-pentane.

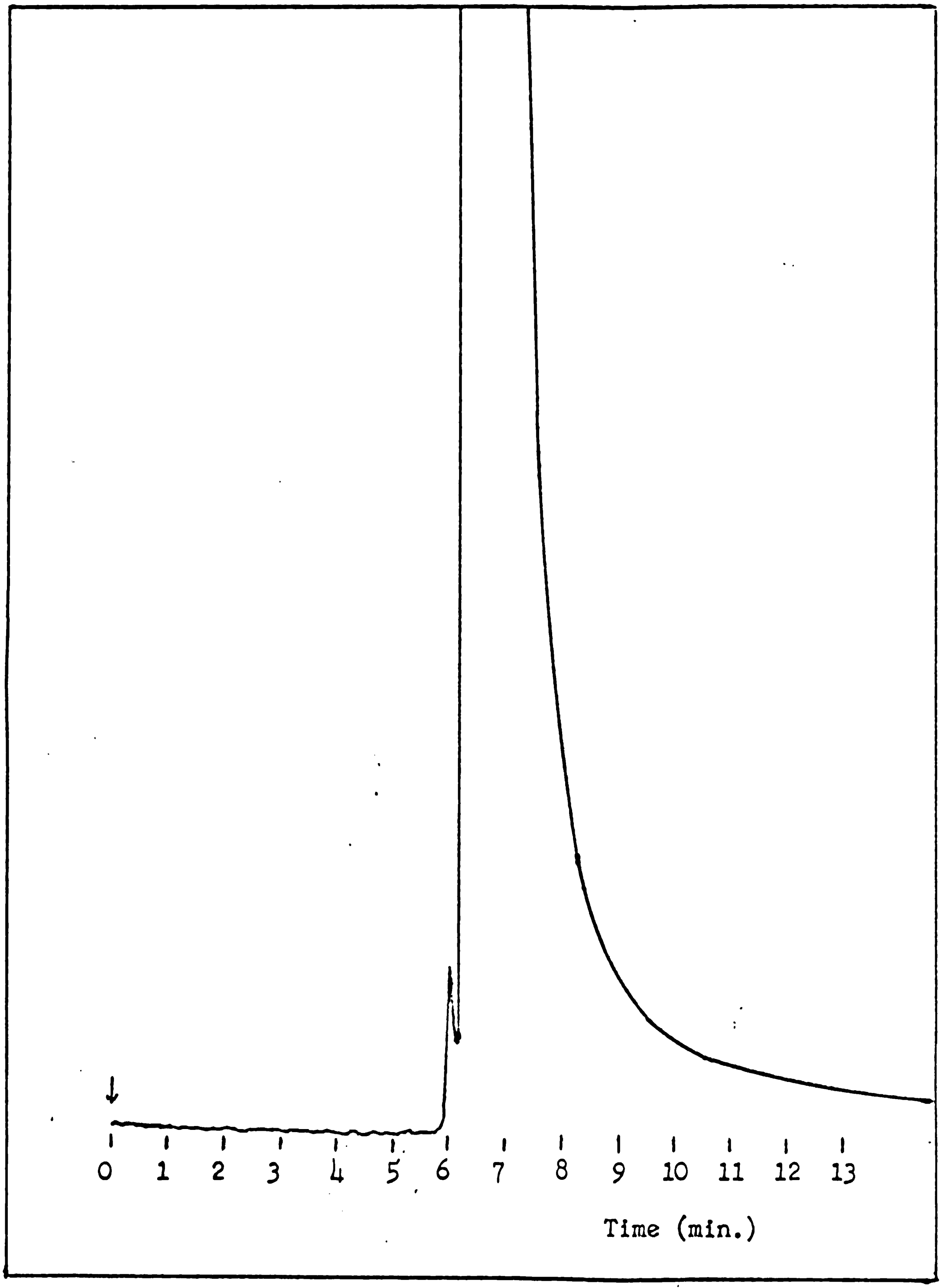


Figure 3. Gas chromatogram of pure grade n-butane.

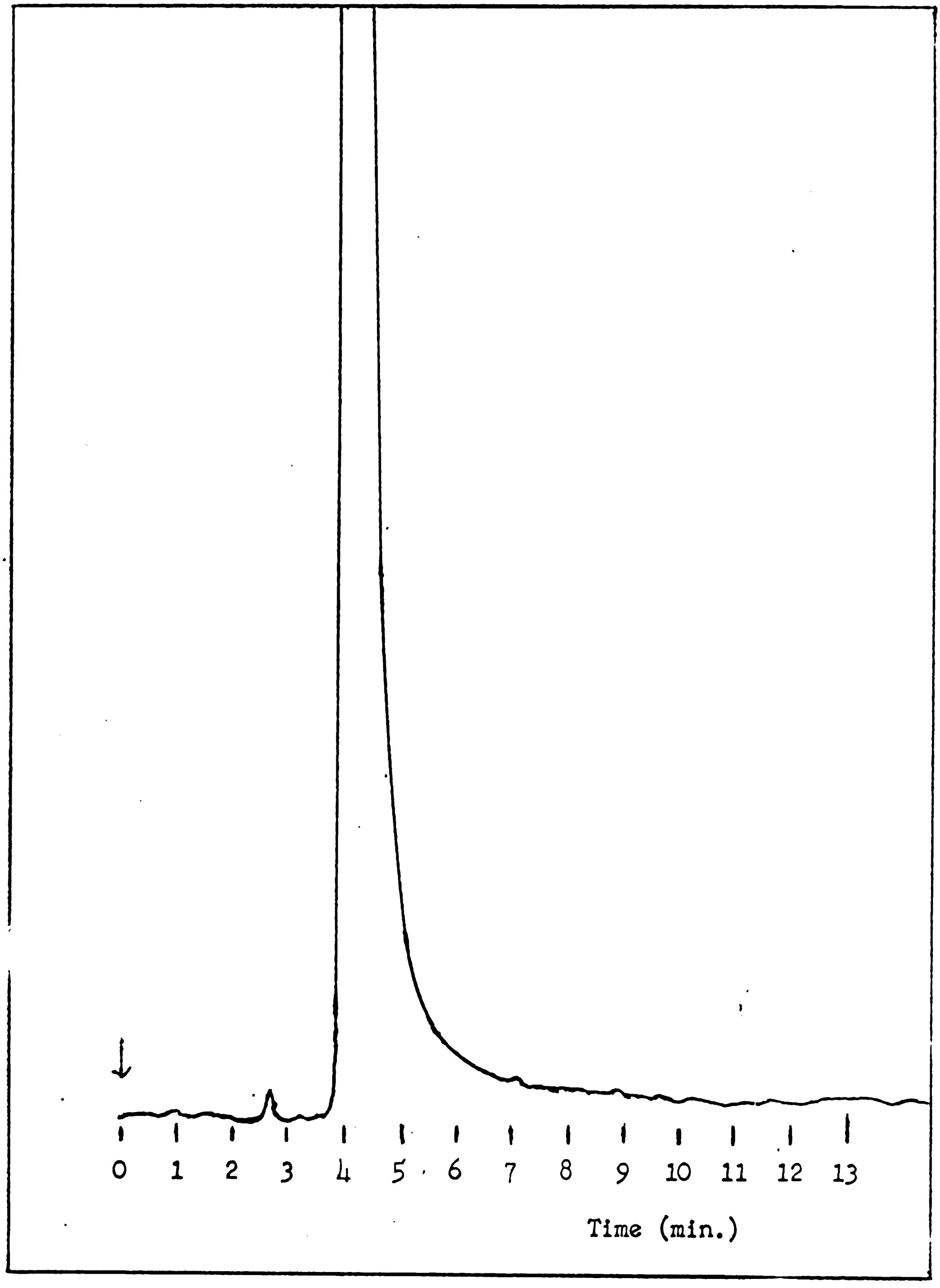
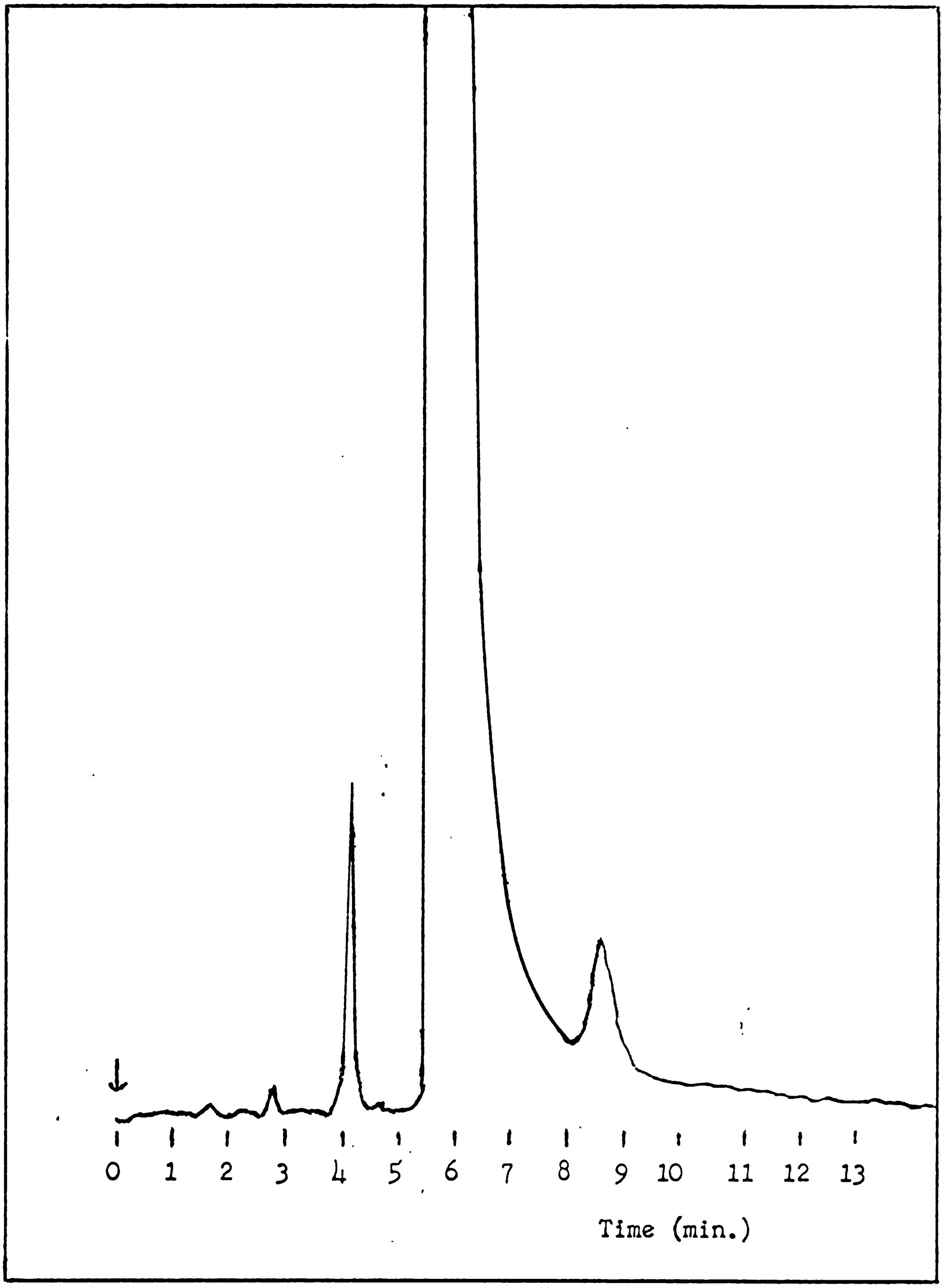


Figure 4. Gas chromatogram of pure grade neopentane.



The polymer fractions used in this research were furnished by Dr. J. B. Kinsinger. Viscosity relationships and number average molecular weights are listed in Table II. The isotactic polypropylene and the polyoctene-1 fractions were used as received. The atactic polypropylene was dissolved in cyclohexane then filtered through a coarse sintered glass funnel. The isotactic polybutene-1 fractions were dissolved in hot tetralin then filtered through a heated coarse sintered glass funnel into methanol. The precipitated polymer was washed three times in methanol and finally dried in a vacuum oven to constant weight. The atactic polybutene-1 fractions were dissolved in cyclohexane then filtered through a coarse sintered glass funnel into methanol. The precipitated polymer was treated similarly to the isotactic fractions.

Preparation of Tubes

The polymer and solvent were added to the capillary tubes in one of four ways:

1. The crystalline fractions were weighed directly into the tubes on a micro balance with a precision of ± 0.03 mg.

2. Since atactic polybutene-1 is soluble in n-pentane at room temperature, solutions of known concentrations were prepared by successive dilutions and a sample of each concentration was added to a tube with a hypodermic syringe.

3. The atactic polypropylene (insoluble in n-pentane at room temperature) and the polyoctene-1 (soluble in n-pentane but used only with gaseous solvents) fractions were dissolved in cyclohexane and this solution was added to the tubes. This latter solvent was removed from the polymer under vacuum and the tubes were brought to constant weight by heating at 50°C in a vacuum oven.

Table II. Viscosity data for polymer fractions.

Sample No.	Polymer	$[\eta]$ $\left(\frac{\text{deciliter}}{\text{gm}}\right)$	$\bar{M}^*$ (x 10^{-5})
C-5	Isotactic Polypropylene[8]	0.27	0.11
C-4	" "	0.63	0.37
C-3	" "	1.34	0.97
E-2A	" "	4.80	4.91
JK-4	Atactic Polypropylene[9]	0.099	0.031
JK-6	" "	0.133	0.0446
B-2	" "	0.300	0.123
JK-5	" "	0.948	0.520
MI-6	Isotactic Polybutene-1[9]	0.550	0.926
MI-4	" "	0.710	1.34
MI-7	" "	1.200	2.46
MI-5	" "	1.690	3.77
A-3	Atactic Polybutene-1[10]	0.357	1.22
A-2	" "	0.544	3.06
A-121	" "	1.56	23.0
F-11A	Polyoctene-1[5]	0.30	0.60
F-10A	"	1.00	2.50
F- 9A	"	1.75	6.07
F- 7A	"	4.19	16.8
F- 6A	"	5.71	25.0
F- 5A	"	8.60	40.0

*Isotactic PP[8] $[\eta] = 1.38 \times 10^{-4} \bar{M}_n^{0.8}$ in decalin at 135°C.

Atactic PP[8] $[\eta] = 1.60 \times 10^{-4} \bar{M}_n^{0.8}$ in cyclohexane at 25°C.

Isotactic PB[11] $[\eta] = 5.85 \times 10^{-5} \bar{M}_w^{0.8}$ in n-nonane at 80°C.

Atactic PB[11] $[\eta] = 5.85 \times 10^{-5} \bar{M}_w^{0.8}$ in n-nonane at 80°C.

Polyoctene-1[5] $[\eta] = 5.75 \times 10^{-5} \bar{M}_w^{0.78}$ in cyclohexane at 30°C.

In all of the above three methods, after the solvent or solution was added, the tube opening was covered with a rubber cap and the tube was frozen in liquid N_2 until ready for sealing. The tubes were removed from the liquid N_2 one at a time, attached to a vacuum line and sealed. There was no measurable loss of solvent in the sealing process.

4. When the solvent was gaseous at room temperature, the polymer or solution was added to the tube by one of the above methods then the tube was cooled, evacuated, and the gas was condensed into it. The tube was then sealed and weighed to obtain the amount of gas added.

Procedure

After the tubes were immersed in the thermostat and allowed to heat sufficiently to dissolve the polymer, they were manually agitated to insure homogeneity. The temperature of the bath was raised about one degree per minute to determine the approximate temperature range for phase separation. The thermostat was then cooled and the tubes agitated again. This time the bath temperature was raised at a slower rate (about 0.2 degrees per minute) to obtain the endpoint, T_p, which is defined for this work as that temperature where a sharp increase in the solution cloudiness was observed. This endpoint must not be mistaken with that temperature at which the heavier phase starts to settle. At the lower temperatures the solution is clear. As the temperature increases an opalescence gradually appears, then the solution cloudiness increases rapidly, and finally the heavier phase settles. There can be as little as 0.2 degrees or as much as 5 degrees between the sudden increase in cloudiness and the settling of the heavier phase.

RESULTS AND DISCUSSION

Phase Diagrams

Figures 5 through 8 summarize the phase separation data for the polypropylene and polybutene-1 fractions. It was impractical to show the data for the polyoctene-1 fractions in one figure because the curves lie too close to each other and some points overlap.

There are three striking differences between these phase diagrams for the LCST and those corresponding to an UCST[7a] for polymer-solvent binary systems. First, as observed for an UCST, the drift of the critical temperature toward lower weight fraction of polymer as the molecular weight is increased does not appear. In fact the critical weight fraction appears invariant with molecular weight within experimental error. Second, for a LCST the polymer molecular weight dependence of the critical temperature is inverted from that found for UCST, that is, the latter rises with molecular weight whereas the former decreases. Third, the shape of the phase separation curves for the LCST are much more uniform with each molecular weight than is generally found for UCST. Finally it is noted that the temperature range over which the opalescence occurs is much narrower for a LCST than for an UCST and hence the precipitation temperatures are more precise and reproducible.

Some scatter of the data will be noticed in these plots. Some of this results from the dependence of the phase separation temperature on the rate of heating. Since the phase separation temperature is sharp, slight changes in the heating rate cause T_p to change slightly. This change can be traced, at least in part, to temperature gradients in the thermostat.

Figure 5. Phase diagram for atactic polypropylene fractions.

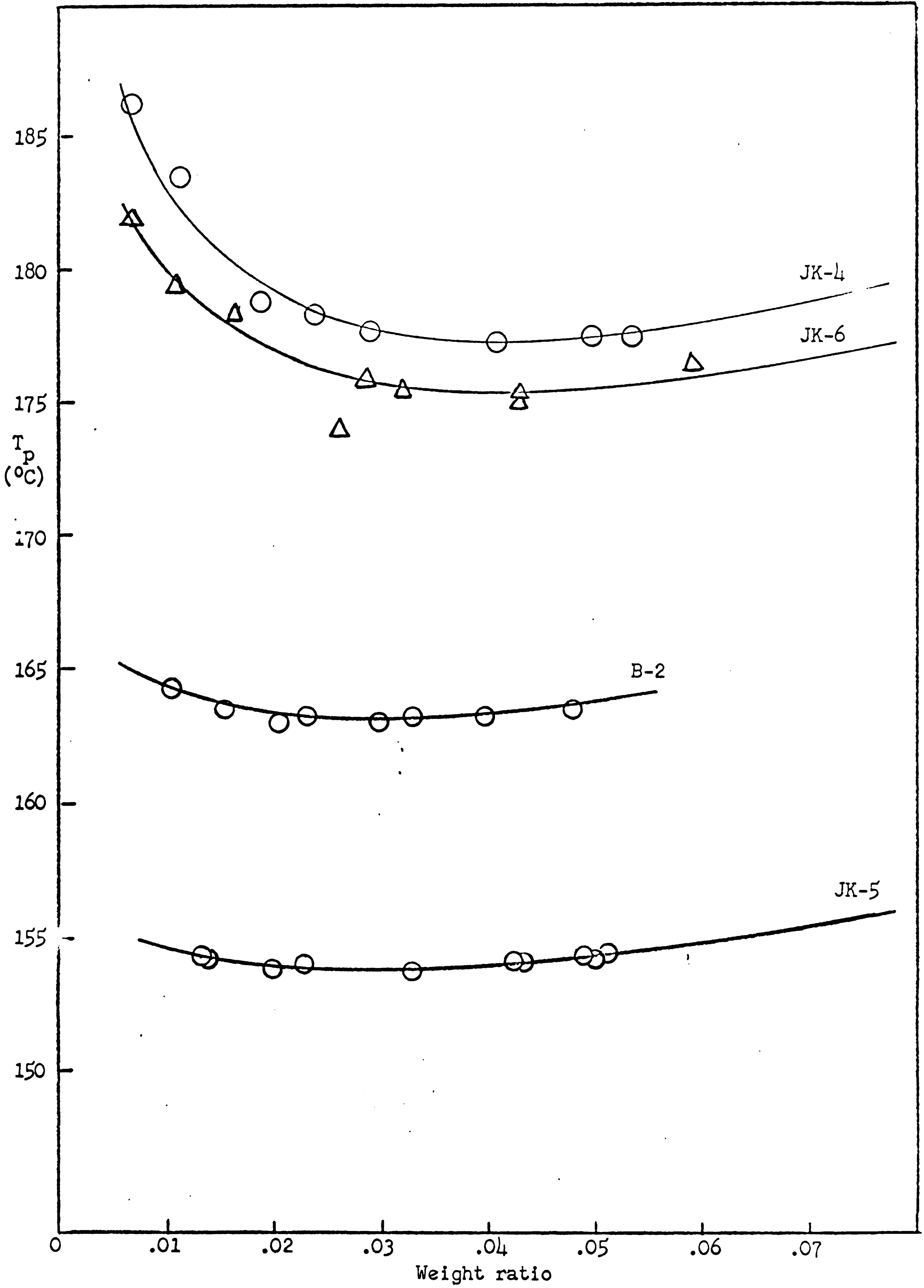


Figure 6. Phase diagram for atactic polybutene-1 fractions.

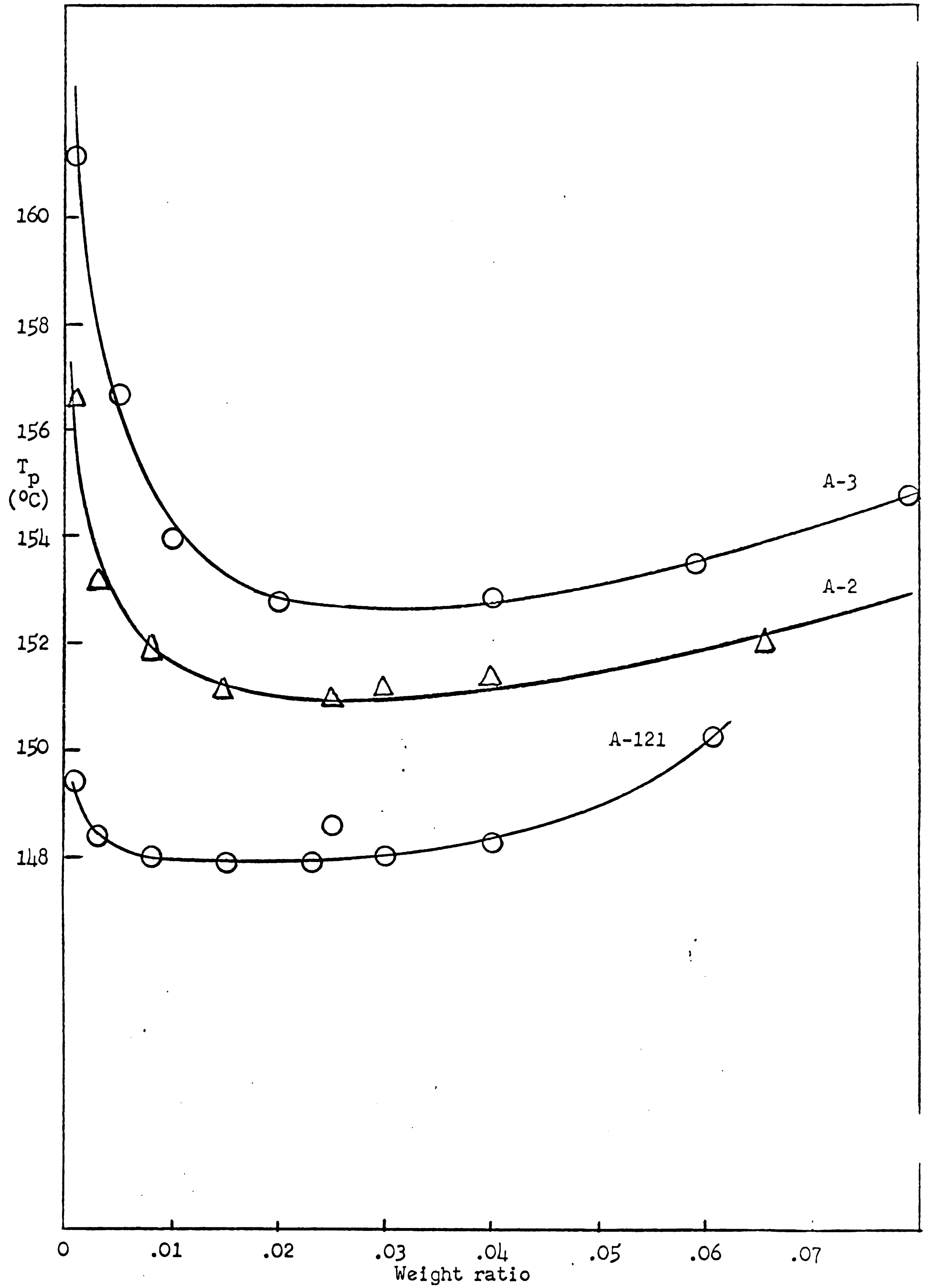


Figure 7. Phase diagram for isotactic polypropylene fractions.

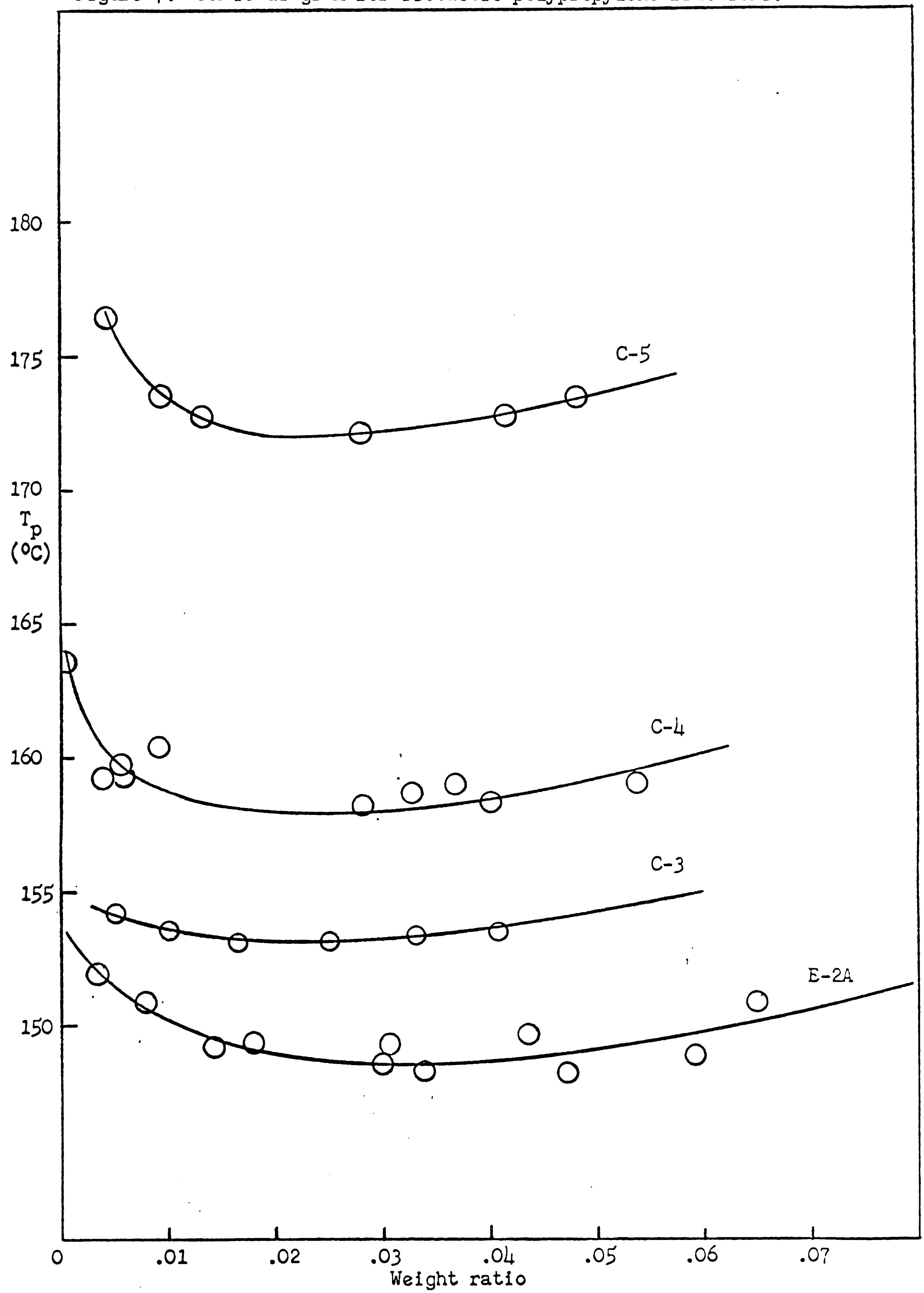
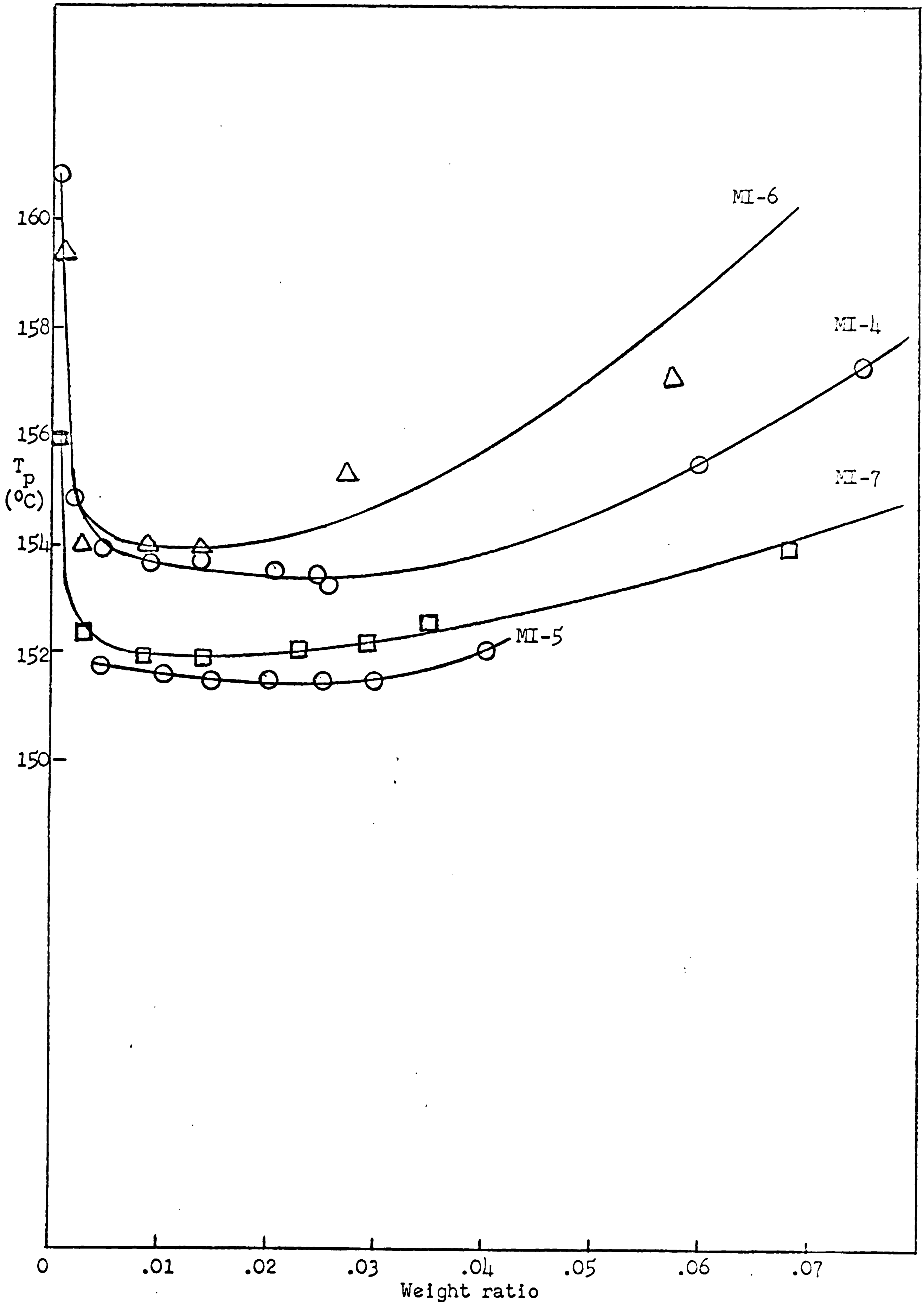


Figure 8. Phase diagram for isotactic polybutene-1 fractions.



The LCST and the molecular weights for all polymer fractions studied are listed in Table III. An indication of the reproducibility of these LCST's is shown from the data for isotactic polybutene-1 fraction, MI-7. The author obtained 424.9°K as compared to Ballard's 424.4°K.[5]

Molecular Weight Dependence of T_{CL}

If it is assumed there is a similarity in the molecular weight dependence for a LCST and an UCST, equation (18) implies that a plot of $1/T_{CL}$ vs $1/M^{1/2}$ should give a straight line. Figures 9 through 11 indicate that this is the case. These results then confirm the idea that some aspects of the UCST theory may apply, within our error limits, to LCST. On the other hand, a combination of the Delmas, Patterson, and Somcynsky and the Flory theories, equation (2), gives the expression, assuming $A = 0$

$$T_{CL} = R\frac{r_1}{B}\chi \qquad (19)$$

A plot of T_{CL} vs $1/M^{1/2}$ should give a straight line also and Figure 12 confirms the usefulness of this relationship. It was on the assumption that the parameter A is zero that Ballard[5] found fair agreement between calculated and observed T_{CL} values. Therefore we cannot distinguish between the two treatments on the basis of this experimental data because we are probably on a linear portion of both theoretical curves. Figure 17 is a plot of the Delmas, Patterson, and Somcynsky equation (1) without elimination of A, and it can be seen that the data fall in the linear portion of the curve.

The upper critical miscibility temperature for polymer of infinite molecular weight, now called the "Flory temperature", and given the

Table III. LCST data for poly-α-olefins.

Polymer	Fraction	Molecular Weight (x 10^{-5})	LCST (°K)
isotactic polypropylene	C-5	0.11	445.0
" "	C-4	0.37	430.8
" "	C-3	0.97	426.0
" "	E-3	1.24	424.9^{5}
" "	E-2A	4.91	421.5
Atactic polypropylene	JK-4	0.0309	450.2
" "	JK-6	0.0446	448.3
" "	B-2	0.123	436.0
" "	JK-5	0.520	426.8
isotactic polybutene-1	MI-4	1.79	426.4
" "	MI-5	3.76	424.4
" "	MI-6	4.33	426.9
" "	MI-7	5.00	424.9
" "	MI-7	5.00	424.4^{5}
atactic polybutene-1	A-3	1.22	425.6
" "	A-2	3.06	423.9
" "	A-121	23.0	420.9
polyoctene-1*	F-11A	0.60	393.3
"	F-10A	2.50	388.3
"	F- 9A	6.07	386.8
"	F- 7A	16.0	386.5
"	F- 6A	25.0	386.6
"	F- 5A	40.0	386.3

*In butane.

Figure 9. LCST for polymer of infinite molecular weight, in n-pentane

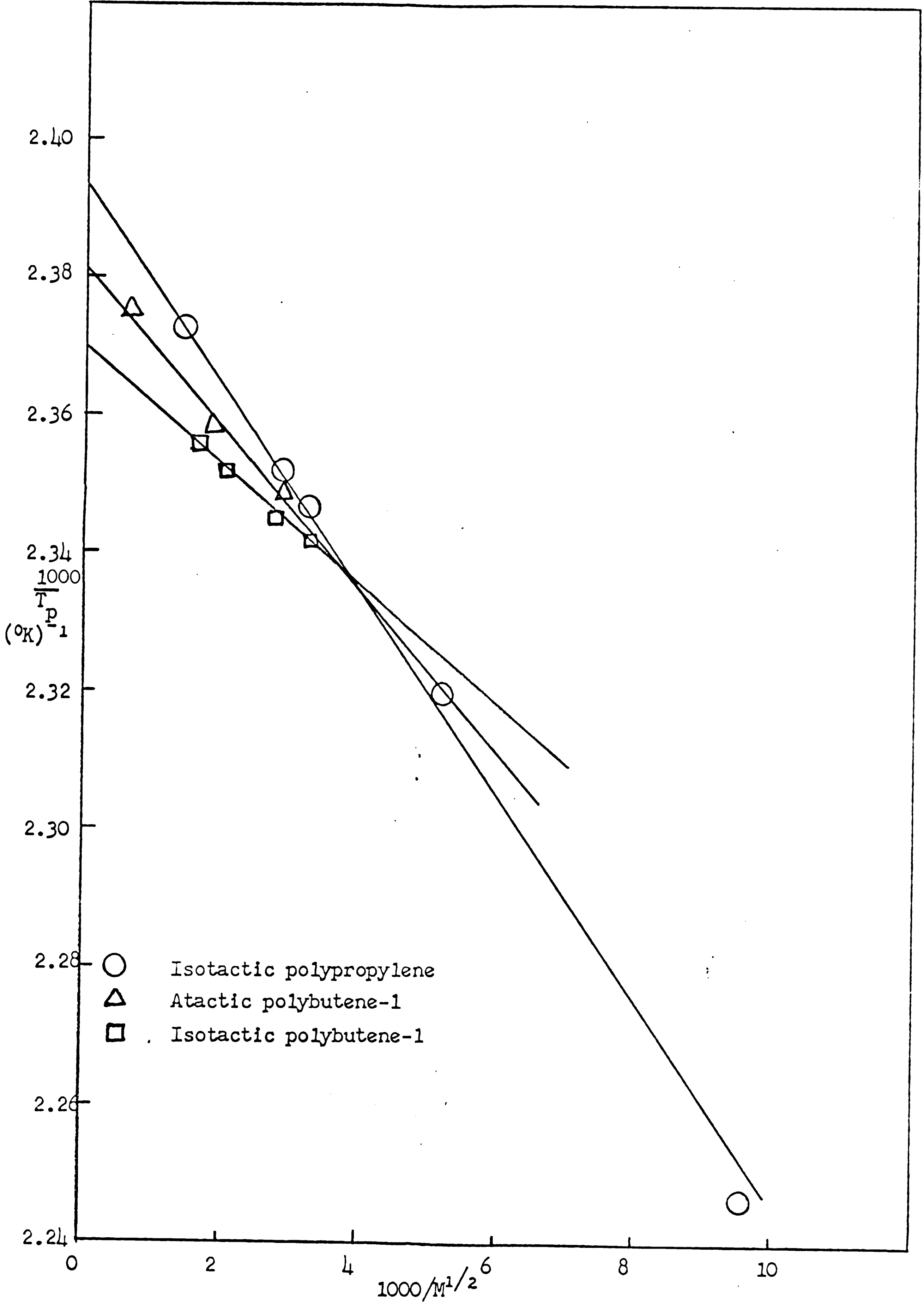


Figure 10. LCST for infinite molecular weight atactic polypropylene.

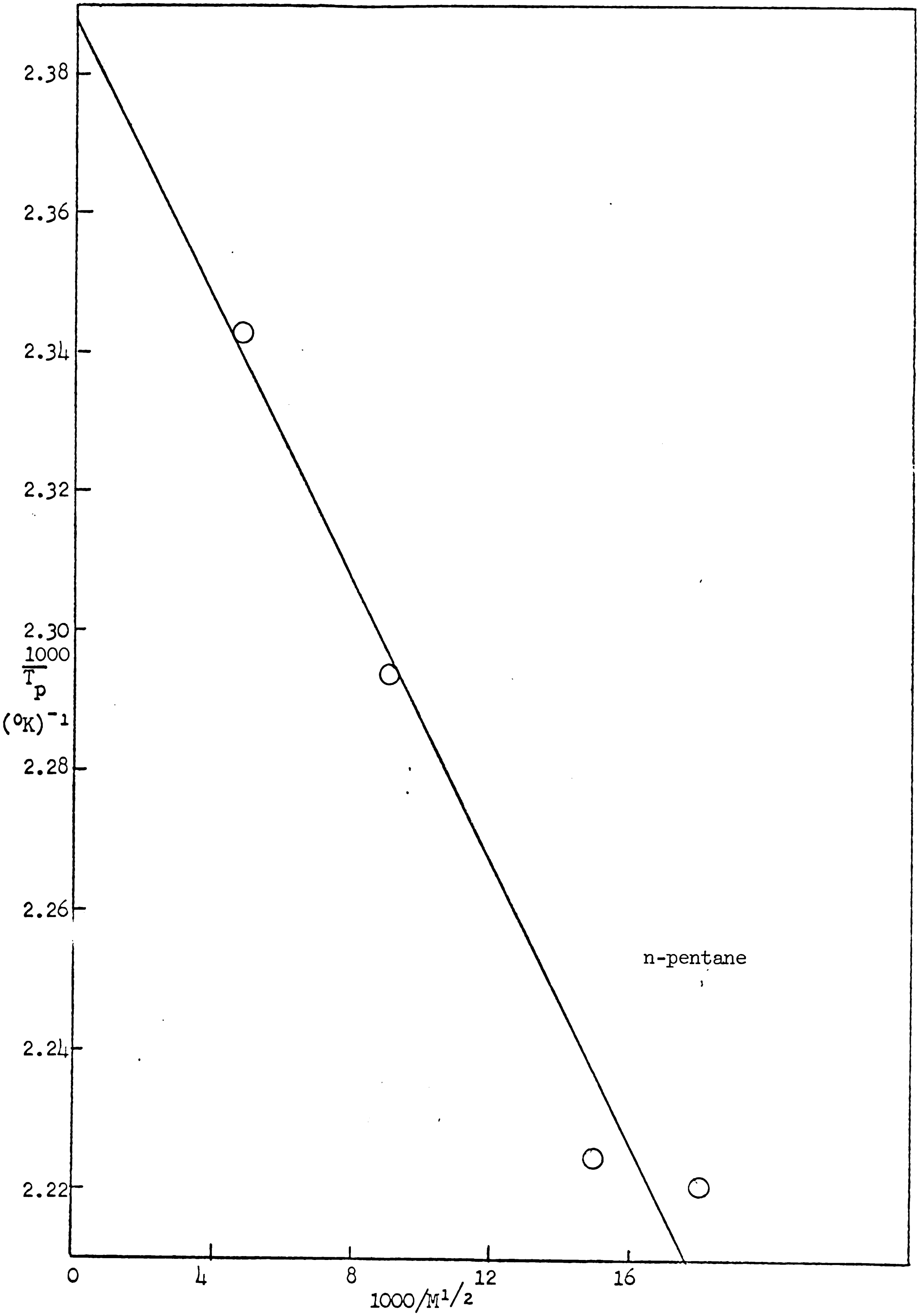


Figure 11. LCST for infinite molecular weight polyoctene-1 in n-pentane and in n-butane.

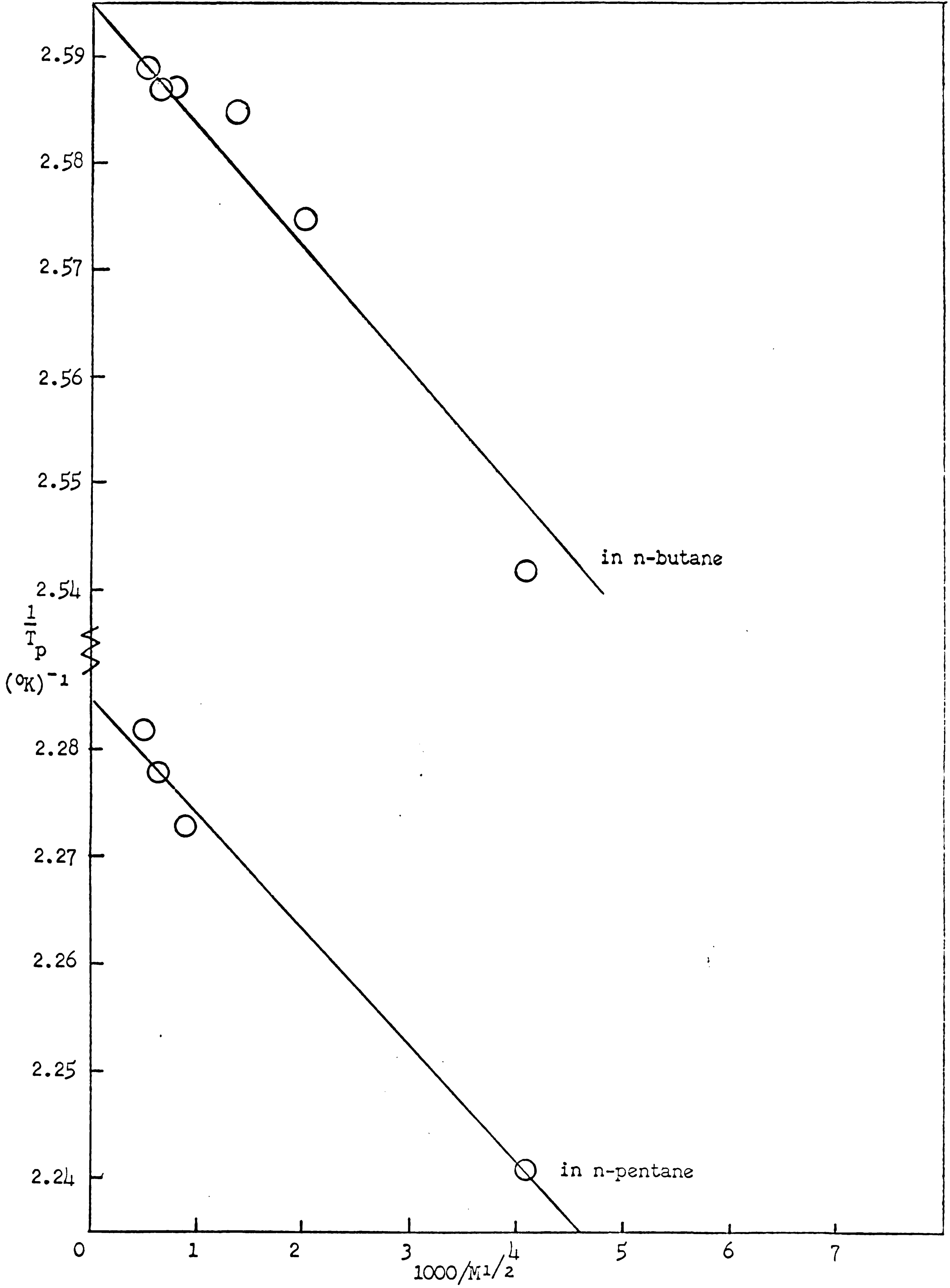
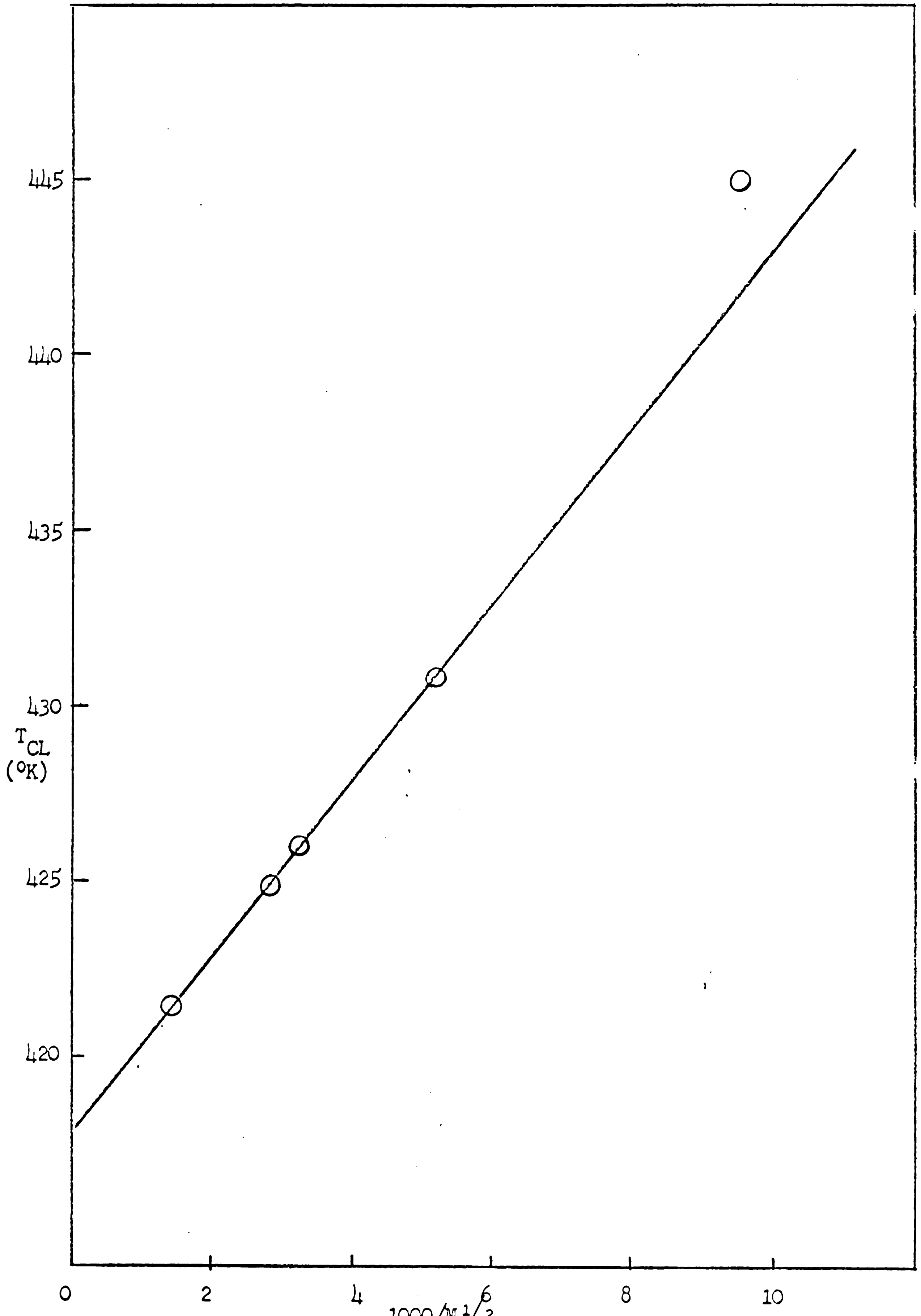


Figure 12. LCST for isotactic polypropylene of infinite molecular weight.



symbol θ, is the solution analogue of the Boyle temperature for a gas. That is, at θ the intermolecular forces which cause the polymer to expand are exactly counterbalanced by the intra-molecular segment-segment forces which cause the polymer to contract. At this special temperature, polymer solutions become ideal in their behavior and the second virial coefficient vanishes. We now propose the Flory temperature be symbolized by θ_U and the new temperature extrapolated to infinite molecular weight for a LCST (Figures 9 through 11) be symbolized by θ_L[5] and defined as the maximum temperature at which solvent and polymer of infinite molecular weight can be maintained in a single phase. At this temperature we suggest the intra-molecular forces which cause the solvent to expand are just counterbalanced by the intermolecular forces which prevent this expansion. That is, if these solutions have a negative ΔH_M, the solvent-polymer interactions are extremely favorable and should oppose the general expansion in the solvent as it approaches its critical temperature.

The temperature, θ_L and the slopes for the curves in Figures 9 through 11 are listed in Table IV. The slopes of these curves are quite significant for UCST in that they permit the calculation of ψ_1, the solvent entropy of interaction parameter [see equation (18)]. However, the slopes in Table IV cannot be definitively interpreted since the change in the molar volume of the solvent in this temperature range is unknown. However, it is interesting that the sign of the slopes is constant and their values fall within a narrow range. It is also significant that the slopes and θ_L for atactic polypropylene is greater than the corresponding values for isotactic polypropylene whereas these are reversed for the atactic and isotactic polybutene-1 system. This

Table IV. LCST for polymer of infinite molecular weight

Polymer	Solvent	Slope $[(\frac{gm}{mole})^{1/2}(^{o}K)^{-1}]$	Intercept $[\frac{1000}{T_{CL}(^{o}K)}]$	θ_L (^{o}K)	$\frac{\theta_L}{T_C}$
Isotactic P.P.	pentane	-0.0144	2.3935	417.8	0.889
Atactic P.P.	pentane	-0.0101	2.388	418.8	0.891
Isotactic P.B.	pentane	-0.00862	2.370	421.9	0.898
Atactic P.B.	pentane	-0.0117	2.3815	419.9	0.893
Polyoctene-1	pentane	-0.0142	2.285	437.6	0.931
Polyoctene-1	butane	-0.0112	2.595	385.4	0.907

behavior has also been observed in UCST studies[13,14] and give additional evidence that the thermodynamic interaction between solvent and polymer depends on the chain geometry but the magnitude of the effect is wholely solvent dependent.

Although these polymer-solvent systems are distinctly nonpolar, the molecular weight dependence gives a reasonable fit to the data[12] for polyethyleneoxide in water solutions also. Figure 13 illustrates that aqueous solutions of polar polyethyleneoxide also obey equation (18). The LCST found in this system undoubtedly involve hydrogen-bond rupture.

The Dependence of LCST on Solvent

To study the dependence of the LCST on solvent, phase diagrams were obtained for a single polyoctene-1 fraction in four different hydrocarbon solvents. This data is illustrated in Figure 14 and the LCST are summarized in Table V. We have seen that the LCST is invariant with polymer weight fraction (Figures 5 through 8) for different molecular weight fractions. Figure 14 shows that the LCST for the same polymer fraction in different solvents is also invariant with the weight fraction of the polymer. Therefore the LCST appear somewhat insensitive to solvent also. An attempt was made to find a relationship between the LCST and the critical temperature, T_C, of the solvent (see Tables IV and V) but a constant ratio does not exist, although the solvent appears to be within 9/10 of its critical temperature before the phase break.

"It is presumably the decreasing configurational energy and increasing molar volume of the pure solvent as it approaches its own gas-liquid critical point that makes it a 'poorer' solvent for the polymer."[1] The

Figure 13. LCST for infinite molecular weight polyethyleneoxide.

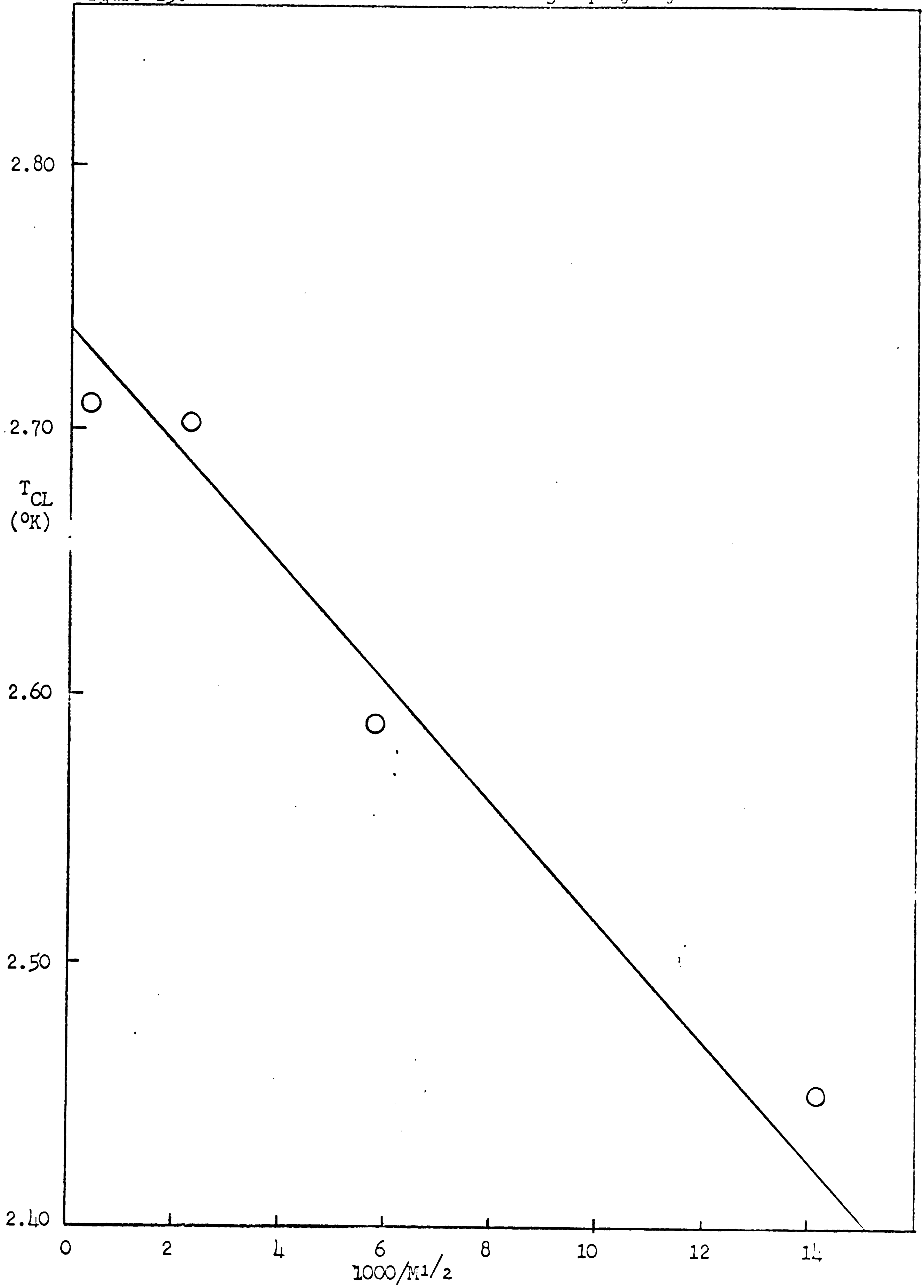
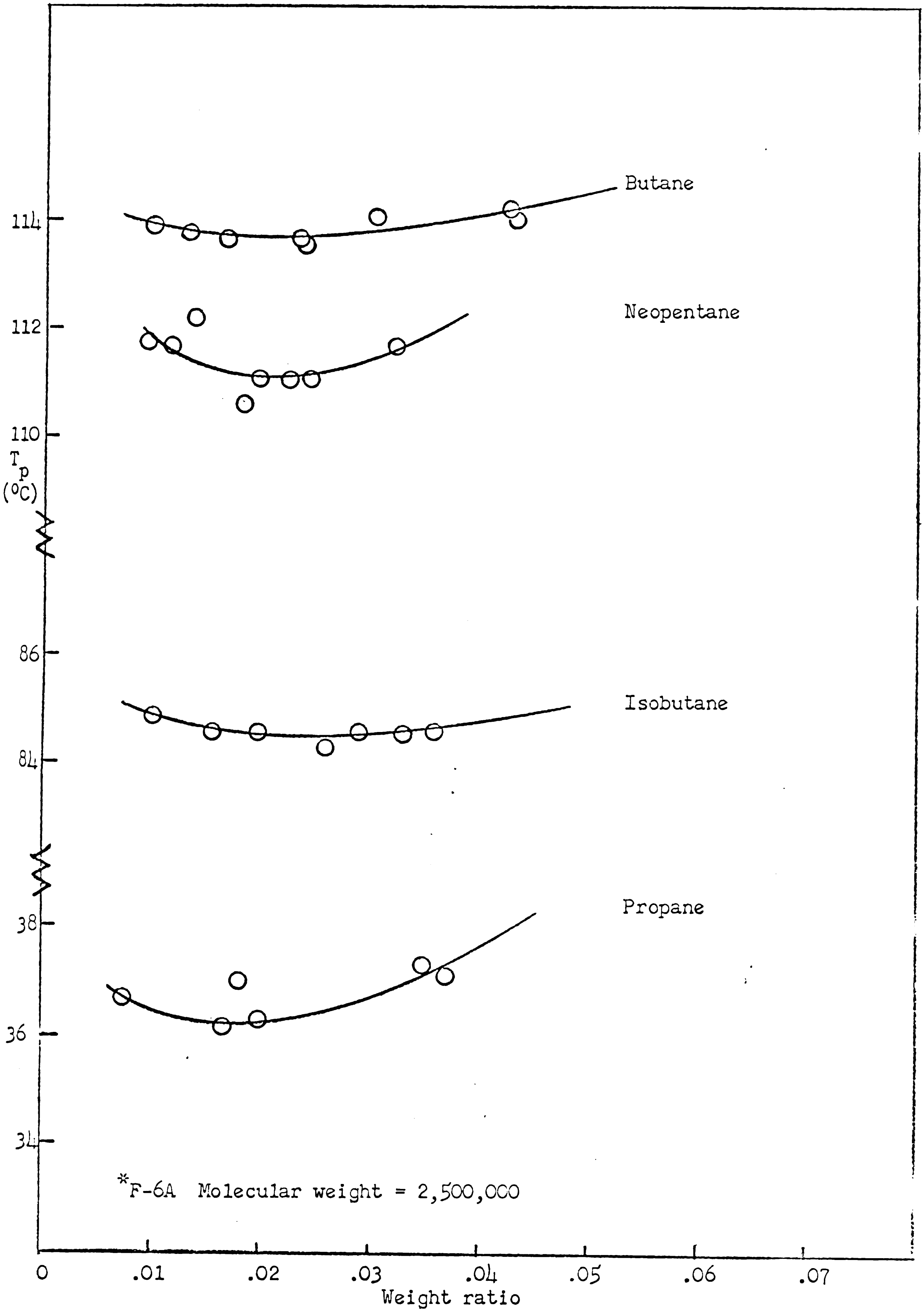


Figure 14. Phase diagram for a polyoctene-1 fraction* in different solvents.



*F-6A Molecular weight = 2,500,000

Table V. LCST data of one polyoctene-1 fraction (F-6A) in several solvents.

Solvent	δ[15]	T_C (°K)	T_{CL} (°K)	$\frac{T_{CL}}{T_C}$	$T_C - T_{CL}$
Propane	~6.3	370	309	0.835	61
Isobutane	6.25	408	357	0.875	51
n-butane	6.7	425	387	0.911	38
Neopentane	6.2	434	384	0.885	50
Pentane	7.1	470	439[5]	0.934	31

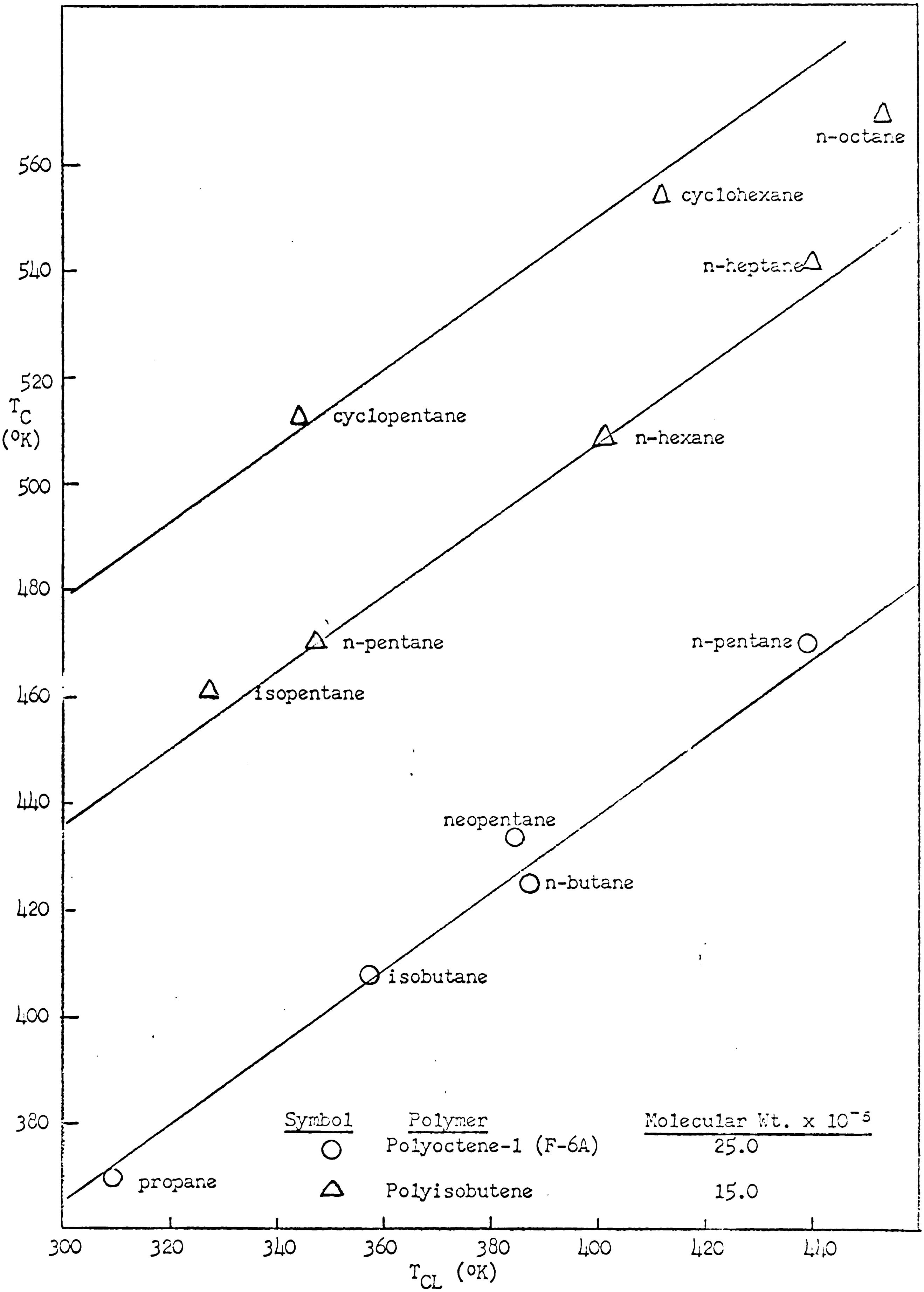
LCST of polyoctene-1 does not follow the Hildebrand δ parameter of the solvent just as Freeman and Rowlinson[1] demonstrated with polyisobutylene and n-alkanes. If immiscibility occurred whenever δ had decreased to some critical value one would expect the LCST to fall in the same order as the solubility parameter. However, the order of increasing δ is neopentane < isobutane < propane < n-butane < n-pentane, while the order of increasing LCST is propane < isobutane < neopentane < n-butane < n-pentane. The miss-match in δ reported by Rowlinson and Freeman[1] for PIB were much greater than for polyoctene-1.

Figure 15 indicates there may be a linear relationship between the critical temperature of solvents of similar structure and the LCST. Freeman and Rowlinson's[1] data for PIB are also plotted in Figure 15 in support of this proposed relationship. The PIB points for n-heptane and n-octane were not weighted strongly in drawing the line because the authors[1] state that these points are uncertain. Within experimental error, the lines have a similar slope.

Three-Component System

Finally, the phase separation temperature was determined for a polyoctene-1 fraction (F-7A) dissolved in mixtures of n-pentane and n-butane. This data is illustrated in Figure 16. The straight line joins the LCST for each of the pure solvents, which may be considered as ideal behavior for the mixtures. The intermediate points are phase separation temperatures for a given mole fraction of n-butane within a narrow range (0.02 to 0.04) of polymer weight fraction. The data were limited to this range of polymer weight fraction since it is in the region of the critical weight fraction (see Figures 5 through 8).

Figure 15. LCST for two polymer fractions vs solvent critical temperature.



The solvent effect on the phase separation temperature is much greater than the variation of polymer weight fraction. For example consider the T_p of the following two solutions:

Pentane W.F.	Butane W. F.	Polymer W. F.	T_p(°C)
0.450	0.516	0.0324	140.3
0.402	0.565	0.0322	135.8

The consistent positive deviation from the straight line (Figure 16) indicates that the T_p of the mixtures are not additive in the mole fraction of the solvent components. This is the first work on LCST of three-component systems (containing polymer as one species) and no theory has been carried far enough to understand the significance of these data.

Analysis Based on the Cell Model

The Delmas, Patterson, and Somcynsky LCST theory led to equation (1). The usefulness of this theory lies in the quadratic relationship between the critical solution temperatures and χ, the molecular weight dependent interaction parameter. The roots of this equation then define both an upper and lower critical solution temperature.[4] Delmas and coworkers[4] discuss three methods of determining the constants A and B for equation (1). These methods were not feasible here, so the values of the parameters A and B were determined for each polymer by a least squares fit of the experimental data to equation (1). Table VI lists the values thus obtained. The least squares fitting of the data was accomplished by solving simultaneously the following two equations:

$$A \sum_{i=1}^{N} x_i^2 + NB = \sum_{i=1}^{N} x_i y_i \qquad (20)$$

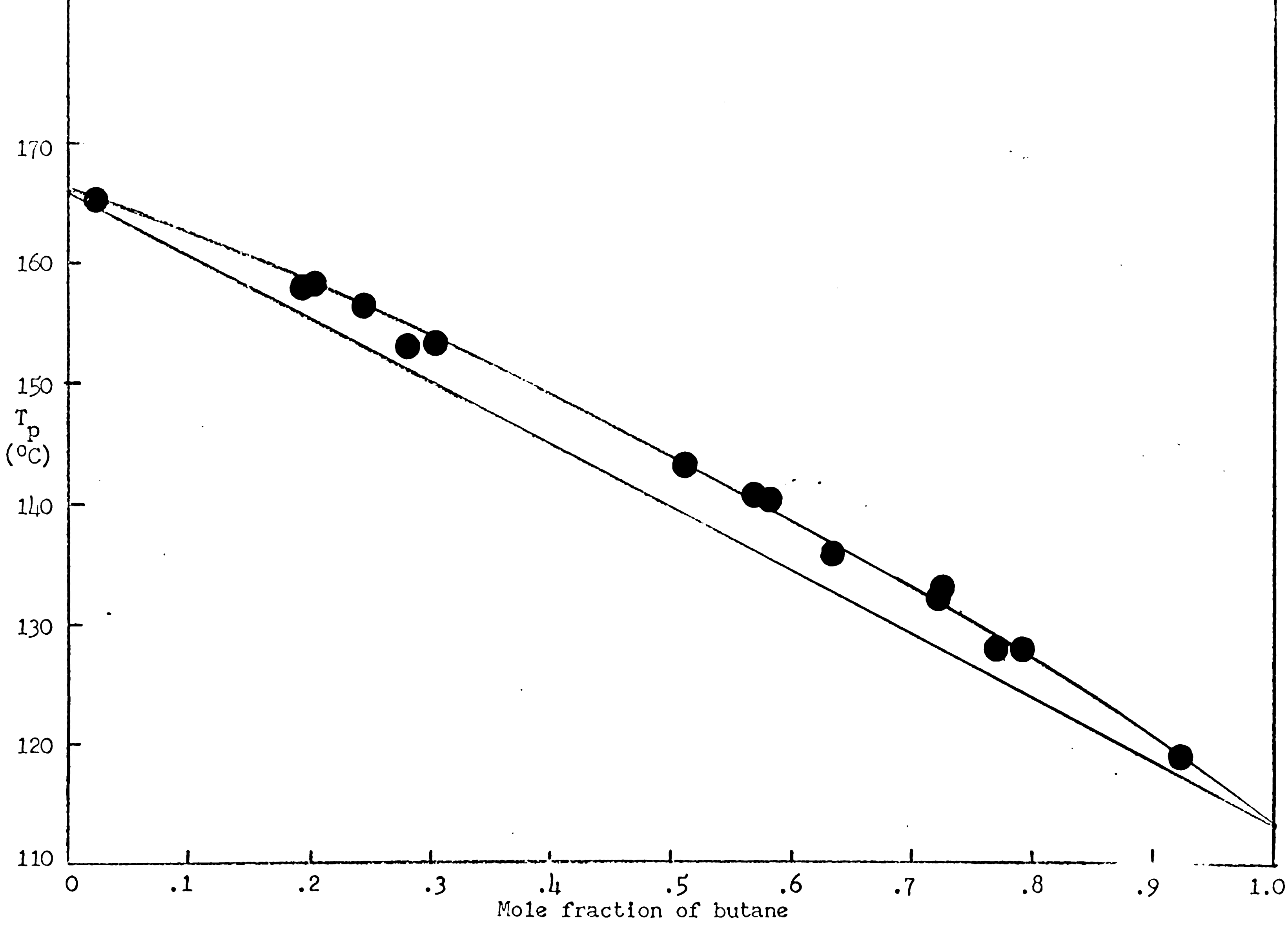


Figure 16. Phase separation temperatures for solutions of polyoctene-1 (F-7A) in mixtures of pentane and butane.

Table VI. Delmas, Patterson, and Somcynsky constants calculated by least squares fit of the experimental data.

Polymer	Solvent	A (cal/base mole)	B (cal/deg^2 base mole)
polyoctene-1	n-butane	40.43	0.00474
atactic polypropylene	n-pentane	69.28	0.00357
isotactic polypropylene	n-pentane	67.45	0.00365
atactic polybutene-1	n-pentane	67.92	0.00363
isotactic polybutene-1	n-pentane	66.42	0.00371

$$NA + B \sum_{i=1}^{N} \frac{1}{x_i^2} = \sum_{i=1}^{N} \frac{y_i}{x_i} \qquad (21)$$

where; $x = \frac{r_i}{T_{CL}}$

$y = R\chi$

N = number of data points.

Figure 17 is a plot of equation (1) using the constants A and B calculated by a least squares fit of the polyoctene-1 data in n-butane. All the experimental data points lie within the small rectangle on the curve.

Notice in Table VI that the values of A and B for atactic and isotactic polypropylene follow the same trend as the atactic and isotactic polybutene-1. A reverse trend was noted earlier (Table IV). Also the values of A and B are surprisingly constant for the range of polymers that were studied.

According to the Delmas[4] theory

$$A = z\epsilon_{11}^{*}\delta^{2} N/8 \qquad (22)$$

$$B = 10.5\,(k^{2}/z\epsilon_{12}^{*})N \qquad (23)$$

where: $\epsilon_{i,j}$ = minimum potential energy of interaction of 2 segments of type i and j.

z = coordination number

N = Avogadro's number

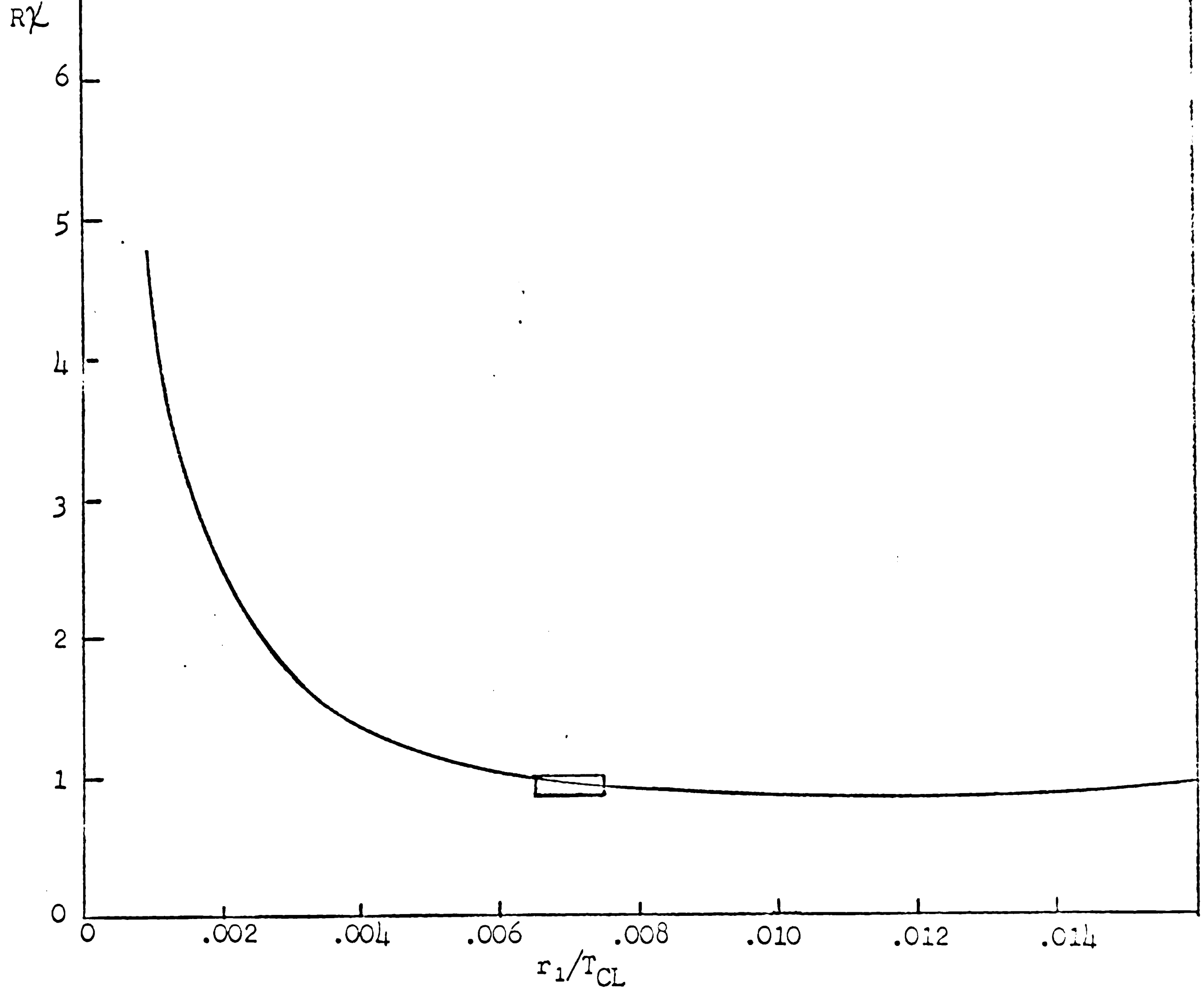
k = Boltzman constant

$$\delta = \frac{\epsilon_{22}^{*} - \epsilon_{11}^{*}}{\epsilon_{11}^{*}}$$

Therefore, A is the parameter that takes into account the solvent-solvent interactions while B takes care of the solvent-polymer interactions. Ballard had some success predicting the LCST and θ_L by assuming A was

Figure 17. Plot of Delmas, Patterson, and Somcynsky equation* for LCST using constants calculated by least squares fit of experimental data.

$$^{*}R\chi = 40.43\left(\frac{r_1}{T_{CL}}\right) + 0.00474\left(\frac{T_{CL}}{r_1}\right)$$



zero. This assumption is reasonable according to the authors[1] of the theory, when the polymer and solvent differ only in chain lengths. First of all, a polyoctene-1 chain with its six-carbon pendant group on every other carbon may not be very similar to n-pentane. Secondly, a fairly large (Delmas'[4] values range from 10 to 22) value of A was obtained by the least squares fit of the experimental data for the same polymer in n-butane (Table VI). Thirdly, an attempt was made to predict θ_L with A equal to zero and these calculated values are approximately twice the observed values (see Table VIII).

Therefore, Ballard apparently was not justified in letting A = 0. The reason he found fair agreement with experimental values is probably because he determined B from one of his experimental points and this latter value corrected for the null A value.

The constants A and B in Table VI were used in equation (1) to calculate the LCST and θ_L for some of the systems studied. The results of these calculations are in Tables VII and VIII. The agreement for the LCST of fraction F-6A in propane is excellent while the agreement of the same fraction in n-pentane is within 6%.

A comparison of the observed and calculated θ_L is presented in Table VIII. Here also the worst agreement is for polyoctene-1 in n-pentane but even then the error is less than 6%. θ_L is an interesting value in that it represents a combination of the Flory theory, equation (18) and the Delmas theory, equation (1), i.e., θ_L is determined from a plot resulting from the Flory equation and it is calculated from the Delmas theory. The agreement appears very good.

A calculated θ_L for atactic polypropylene is not found in Table VIII because the calculation produced imaginary roots. This resulted

Table VII. Comparison of calculated and experimentally determined LCST for polyoctene-1 (F-6A) in different solvents.

Solvent	T_{CL} (°K) calc.	exp.	UCST (°K) calc.
propane	309.4	309.2	110.2
n-pentane	464.2	439.0[5]	165.6

Table VIII. Comparison of the calculated and experimentally determined θ_L for all the polymers studied.

Polymer	Solvent	θ_L (°K)			θ_U(°K)
		calc.	obs.	calc w. A=0	(calc.)
polyoctene-1	propane	308.5	--	--	110.5
polyoctene-1	butane	385.6	385.4	523.8	138.2
polyoctene-1	pentane	462.7	437.6	--	165.8
isotactic polypropylene	pentane	422.4	417.8	815.6	393.3
atactic polypropylene	pentane	--	418.8	835.6	--
isotactic polybtene-1	pentane	422.1	421.9	804.3	382.1
atactic polybutene-1	pentane	417.7	419.9	820.7	403.0

from too large a magnitude in either A or B. For example, subtracting the small quantity 0.277 from A, 69.277, gives a real root very close to the experimental value.

Tables VII and VIII also list calculated UCST and θ_U. Apparently these calculated values do not predict experimental fact. For example, the calculated values predict that atactic polybutene-1 of infinite molecular weight will go into solution only above 130°C, yet it is soluble at room temperature. The calculated values, θ_U, could not be checked experimentally for the isotactic fractions because the theory calls for liquid-liquid separation and the isotactic polymers separate as a crystalline phase at a higher temperature than that predicted. A solution of atactic polybutene-1 and one of atactic polypropylene each in n-pentane were cooled to the freezing point of the solvent (142°K) without observing any precipitation. For some reason the Delmas theory predicts very well LCST and θ_L (within 6%) but does not agree with experiment for UCST.

From the above then, it can be seen that the existing theories of polymer solutions are inadequate to treat accurately LCST and fail completely to predict both an UCST and a LCST. Obviously this is an area where experimental work is ahead of theoretical development.

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APPENDICES

APPENDIX I

Phase separation temperatures for polymer fractions in n-pentane.

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
Fraction C-3		
8.30	265.45	154.4
4.21	58.81	154.0
2.95	49.20	153.7
1.20	59.40	153.4
0.95	72.20	154.1
0.95	65.85	154.2
2.95	49.20	154.3
1.20	59.40	155.1
5.56	130.36	153.8
4.40	104.50	153.7
0.45	89.54	154.2
2.66	106.17	153.1
6.60	199.27	153.4
2.98	180.20	153.1
2.40	59.00	153.5
0.97	96.63	153.5
Fraction C-4		
0.10	232.55	163.8
0.61	101.69	160.8
0.77	83.92	160.4
0.14	35.53	158.9
0.98	30.12	158.4
1.19	42.55	158.3
7.13	33.62	158.9
3.17	79.57	158.0
0.98	30.12	158.9
3.17	79.57	158.3
0.08	141.82	163.5
0.50	84.91	159.3
2.52	46.90	159.0
2.12	57.79	159.0
1.76	62.71	158.2
0.61	101.69	159.8
Fraction C-5		
2.15	121.30	175.3
2.15	90.90	172.3
0.93	117.36	176.8
1.47	101.25	172.7
3.39	121.41	172.0

Appendix I (cont.)

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
	Fraction C-5 (cont.)	
4.21	101.31	172.7
3.58	74.49	173.4
1.00	106.40	173.5
0.58	127.70	176.5
	Fraction E-2A	
0.49	151.10	151.9
1.28	162.14	150.9
0.13	135.37	153.2
1.89	132.13	149.2
2.68	149.16	149.4
3.50	116.40	148.6
5.24	154.36	148.3
4.35	73.69	148.9
1.60	52.25	149.3
2.60	59.92	149.7
2.99	63.20	148.2
5.18	80.00	150.9
	Fraction JK-4	
1.62	248.5	186.2
4.98	263.6	178.8
5.17	218.1	178.3
2.88	257.7	183.5
5.24	105.7	177.5
5.10	125.0	177.3
4.11	141.5	177.7
6.96	130.3	177.5
	Fraction JK-5	
6.31	145.8	154.1
4.91	150.0	153.8
4.25	188.0	154.0
3.30	239.4	154.2
6.39	131.1	154.4
7.46	146.6	154.4
3.74	188.0	153.8
2.87	221.0	154.3
10.21	311.6	153.7
11.97	273.6	154.1
11.95	239.4	154.2
9.66	288.1	154.5

Appendix I (cont.)

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
	Fraction JK-6	
3.85	237.5	178.3
1.52	230.0	182.0
2.21	208.5	179.4
2.41	92.7	174.1
4.00	140.1	176.0
3.97	93.1	175.1
5.46	92.0	176.6
7.99	83.2	178.0
1.85	129.0	182.5
3.74	158.2	179.0
4.43	138.5	175.5
5.76	135.1	175.3
	Fraction B-2	
1.76	170.4	164.3
2.20	143.0	163.5
2.61	128.7	163.0
3.07	133.1	163.3
4.12	138.3	163.1
4.28	130.8	163.2
5.34	134.5	163.3
5.76	120.5	163.5
	Fraction MI-4	
1.32	142.80	153.7
1.43	103.22	153.8
0.82	80.93	153.6
1.47	71.30	153.5
3.05	119.85	153.3
1.12	251.74	153.9
5.53	73.92	157.3
0.36	174.06	154.9
0.55	296.70	155.6
0.22	285.51	160.9
2.76	112.35	153.4
5.68	94.69	155.5
	Fraction MI-5	
0.53	115.67	151.7
2.82	190.10	151.5
2.55	245.25	151.6
2.76	137.76	151.5
2.90	114.80	151.5
3.23	108.85	151.5
5.42	134.63	152.1

Appendix I (cont.)

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
	Fraction MI-6	
0.10	121.38	159.4
0.29	100.34	154.0
1.65	120.55	153.9
0.80	89.55	154.0
2.92	50.98	157.1
2.40	88.50	155.3
	Fraction MI-7	
0.49	164.16	152.3
0.12	150.65	156.0
1.21	141.99	151.9
2.06	146.89	151.9
2.22	97.23	152.1
2.86	97.94	152.2
3.59	102.21	152.6
6.93	101.75	153.9
	Fraction A-121	
63.5	1046.1	150.3
34.3	854.7	148.3
16.3	549.5	148.0
10.4	418.3	148.6
6.9	458.6	147.9
3.1	387.6	148.0
1.7	575.1	148.4
1.0	1246.1	149.4
	Fraction A-2	
212.2	3516.7	152.0
207.4	5219.5	151.4
193.3	6443.5	151.2
12.9	869.2	151.2
9.5	1194.6	151.9
7.1	2368.0	153.2
5.6	7022.9	156.6
170.2	6814.3	151.0
	Fraction A-3	
257.2	2419.6	155.0
17.8	225.2	154.8
65.1	1096.0	153.5
44.3	1104.5	152.9
27.6	1382.5	152.8
16.1	1610.4	154.0
7.9	1578.7	156.7
4.3	4282.3	161.2

APPENDIX II

Phase separation temperatures for polyoctene-1 fractions in n-butane.

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
Fraction F-5A		
1.26	133.4	113.9
1.50	101.1	113.6
2.16	99.7	113.5
2.89	114.3	113.6
3.07	114.3	113.4
4.70	113.7	113.5
5.37	88.0	113.8
1.90	190.4	113.6
3.00	158.4	113.7
3.43	129.6	113.3
4.00	108.5	113.1
Fraction F-6A		
1.50	154.5	113.9
2.19	168.7	113.8
2.26	136.0	113.7
2.55	107.5	113.6
3.56	83.6	114.2
3.55	117.0	114.1
4.24	98.3	114.1
3.32	141.5	113.7
Fraction F-7A		
4.13	206.5	113.5
5.05	169.4	113.7
5.91	183.4	113.4
7.59	155.4	113.7
7.03	190.0	113.8
1.27	255.6	114.1
2.44	259.4	113.9
3.07	152.3	113.0
3.71	132.1	113.8
Fraction F-9A		
1.26	139.7	114.1
1.55	109.0	113.8
1.97	113.6	113.8
3.10	96.9	113.9
3.09	84.3	114.4
2.70	83.5	114.1

Appendix II (cont.)

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
	Fraction F-10A	
1.34	133.6	116.4
1.85	119.2	115.3
3.02	118.7	115.2
2.85	143.4	115.9
4.06	147.0	115.2
4.05	126.5	115.3
6.18	144.3	115.1
2.95	154.2	115.7
3.75	151.3	115.5
5.27	153.9	115.4
	Fraction F-11A	
1.88	195.4	121.9
2.29	149.1	121.2
2.56	133.9	120.7
3.57	122.1	120.4
3.75	116.9	120.3
5.20	125.2	120.5
5.64	111.4	120.7

APPENDIX III

Phase separation temperatures for the polyoctene-1 fraction, F-6A, in different solvents.

Wgt. of Pol. (mg)	Wgt. of Solv. (mg)	T_p (°C)
	Neopentane	
2.40	257.9	111.8
2.64	230.2	111.7
3.81	210.7	110.6
3.30	242.3	112.2
3.86	197.1	111.1
3.87	160.2	111.1
6.50	203.0	111.7
4.85	216.1	111.1
	Isobutane	
2.04	201.7	84.9
2.09	135.9	84.6
3.06	156.3	84.6
4.47	156.0	84.6
4.08	159.9	84.3
4.53	137.3	84.6
4.52	126.0	84.6
5.31	139.2	84.5
	Propane	
1.14	158.4	36.7
2.42	135.9	37.0
2.35	142.0	36.2
2.97	149.0	36.3
4.72	135.9	37.3
4.70	127.1	37.1

See Appendix II for F-6A in n-butane.

APPENDIX IV

Phase separation temperatures for the polyoctene-1 fraction, F-7A, in mixtures of n-pentane and n-butane.

Wgt. of Pol. (mg)	Wgt. of Pent. (mg)	Wgt. of But. (mg)	T_p (°C)
0.95	47.4	54.6	140.9
1.89	60.5	59.1	142.4
2.85	83.3	78.1	142.7
4.49	62.3	71.4	140.3
3.32	68.4	58.1	143.2
3.32	56.4	59.5	140.8
5.40	58.1	75.5	137.0
5.04	62.9	88.2	135.8
1.47	112.9	30.4	156.9
2.54	125.4	28.6	155.8
2.52	90.4	31.7	153.4
2.61	78.0	15.0	158.0
3.30	82.2	21.2	156.5
3.74	71.3	22.6	152.9
3.58	71.5	14.8	158.4
4.77	77.6	14.6	158.7
1.56	44.2	127.9	126.1
1.66	38.4	100.3	128.4
2.75	35.2	74.1	132.1
3.08	40.5	108.8	127.9
4.25	27.4	73.2	129.2
3.55	26.4	80.4	127.8
3.07	24.5	52.5	133.0
4.67	23.4	62.5	130.0
3.99	130.1	2.2	165.2
4.48	21.3	234.1	118.9