

Evaluation of Concentration Dependence of χ -Parameter, Flory Temperature and Entropy Parameter for Polymer–Solvent System from Their Critical Solution Temperature and Concentration Data

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ABSTRACT: The critical polymer volume fraction v_p^c and the critical solution temperature T_c were estimated from the threshold cloud point (tcp) for polystyrene (PS) and polyethylene (PE) solutions in literature. The critical points thus obtained, together with those directly determined in literature, of PS in ten solvents and PE in sixteen solvents were analyzed, according to the Shultz–Flory (SF), Koningsveld *et al.* (KKS), and Kamide–Matsuda (KM) methods, to evaluate the Flory temperature θ and the entropy parameter ψ . The concentration dependence parameters p_1 and p_2 of the χ -parameter, as given by $\chi = \chi_0(1 + p_1v_p + p_2v_p^2)$ (χ_0 , a concentration-independent parameter, v_p , polymer volume fraction) were determined by KKS and KM methods, which gave almost the same values of p_1 and p_2 . Except for few solvents, p_1 value for PS solutions can be regarded as constant, which is near to 2/3, theoretically predicted when $A_2 = A_3 = 0$ at θ (A_2 and A_3 , second and third virial coefficients). For lower critical solution point (LCSP), p_2 is always negative, except for PS/cyclopentane and for upper critical solution point (UCSP) p_2 is positive. The very wide variation of p_1 and p_2 with solvents was observed for PE. Application of KM method to the most reliable data on PE/diphenylether by Koningsveld *et al.* led to $p_1 = 0.61$, which is not so far from the theoretical value. θ , obtained by three methods, is practically independent of the method used. ψ estimated by KM method coincides with that by KKS method for a given polymer–solvent system. ψ was found to be positive for UCSP and negative for LCSP, suggesting that the polymer solution should be athermal at a temperature between UCSP and LCSP. The effect of solvent nature on p_1 , p_2 , θ , and ψ are discussed in some detail.

KEY WORDS Critical Polymer Volume Fraction / Critical Solution Temperature / Threshold Cloud Point / Polystyrene / Polyethylene / Flory Theta Temperature / Entropy Parameter / Concentration Dependence Parameter / χ -Parameter /

Koningsveld *et al.* (KKS)¹ and Kamide and Matsuda (KM)² proposed methods for estimating the concentration dependence parameters p_1 and p_2 of the polymer–solvent interaction parameter χ as given by

$$\chi = \chi_0(1 + p_1v_p + p_2v_p^2) \quad (1)$$

from the critical solution temperature T_c and the critical polymer volume fraction v_p^c of the polymer solutions. Here, χ_0 is the concentration independent parameter and v_p is the

polymer volume fraction. The concentration dependence of χ -parameter can also be, from a theoretical point of view, determined by the osmotic pressure, vapor pressure, isothermal distillation, ultracentrifuge, phase equilibrium (the two phase volume ratio R , the partition coefficient σ , the polydispersity of the polymers in two phases etc.) and the cloud point.³ It should be noted that except for the phase equilibrium and cloud point, all methods are limited experimentally to a relatively

lower concentration range and do not enable us to evaluate p_2 accurately. The phase equilibrium method is applicable up to a concentrated solution range, but the experimental accuracy is not high enough to estimate p_2 . The remaining two methods (the critical and cloud points) are the most suitable for determining p_1 and p_2 . Kamide and Matsuda have shown for polystyrene/cyclohexane system $p_1=0.643$ and $p_2=0.200$ from the cloud point curve data of themselves³ and $p_1=0.642$ and $p_2=0.190$ from literature data on the critical point using KM method.² Using p_1 and p_2 parameters thus estimated and the critical solution data, the Flory theta temperature θ and the entropy parameter at θ , ψ can also be determined.^{1,2}

Kamide and Matsuda² applied these two methods to the systems of polystyrene(PS)/cyclohexane(CH) and PS/methylcyclohexane (MCH), concluding the two methods to give similar results on p_1 , p_2 , θ , and ψ for a given system and that ψ values obtained by these methods are remarkably smaller than those by the Shultz and Flory (SF)⁴ method hithertofore widely utilized, lying in the range of variation of ψ values evaluated from the temperature dependence of the second virial coefficient A_2 .⁵ In other words, Kamide and Matsuda clarified the unconditioned superiority of the KKS and KM methods over the SF method, in which $p_1=p_2=0$ was assumed. In this article, as an extension of the previous study,² an attempt is made by applying the above mentioned methods (*i.e.*, KKS, KM, and SF) to the literature data on the critical points of the polymer solutions in a very systematic manner to compare the reliability of these methods and disclose, if possible, the dependence of p_1 , p_2 , θ , and ψ parameters on the solvent nature.

THEORETICAL BACKGROUND

Equation 1 can be generalized in the form:⁶

$$\chi = \chi_0 \left(1 + \sum_{i=1}^n p_i v_p^i \right) \quad (2)$$

with

$$\begin{aligned} \chi_0 &= \chi_{00} (1 + k' / X_n) \\ &= (a + b/T) \left\{ 1 + \frac{k_0}{X_n} \left(1 - \frac{\theta}{T} \right) \right\} \end{aligned} \quad (3)$$

Here, χ_{00} is a parameter independent of v_p and of the molar volume ratio of j -th component of multicomponent polymers to the solvent X_j ($j=1, 2, \dots, m$; m =total number of the components constituting the polymer), k' and p_i , the molecular weight- and concentration-dependence parameters, both independent of v_p and X_j , T is Kelvin temperature, a , b , and k_0 are coefficients independent of X_n , v_p , and T .

The chemical potential of the solvent $\Delta\mu_0$, in the Flory-Huggins polymer solution theory,⁷ can be given by

$$\begin{aligned} \Delta\mu_0 &= RT \left\{ \ln(1 - v_p) + \left(1 - \frac{1}{X_n} \right) v_p \right. \\ &\quad \left. + \chi_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{i=1}^n p_i v_p^i \right) v_p^2 \right\} \end{aligned} \quad (4)$$

Here, R is the gas constant. The chemical potential of X_j -mer, $\Delta\mu_j$, which satisfies the Gibbs-Duhem relation with $\Delta\mu_0$ in eq 4, is

$$\begin{aligned} \Delta\mu_j &= RT \left[\ln v_j - (X_j - 1) + X_j \left(1 - \frac{1}{X_n} \right) v_p \right. \\ &\quad \left. + X_j (1 - v_p)^2 \chi_{00} \left[\left(1 + \frac{k'}{X_n} \right) \right. \right. \\ &\quad \left. \left. \times \left\{ 1 + \sum_{i=1}^n \frac{p_i}{i+1} \left(\sum_{q=0}^i (q+1) v_p^q \right) \right\} \right. \right. \\ &\quad \left. \left. + k' \left(\frac{1}{X_j} - \frac{1}{X_n} \right) \left\{ \frac{1}{1 - v_p} \right. \right. \right. \\ &\quad \left. \left. \left. + \sum_{i=1}^n \frac{p_i}{i+1} \left(\sum_{q=0}^i \frac{v_p^q}{1 - v_p} \right) \right\} \right] \right] \end{aligned} \quad (5)$$

The Gibbs free energy $\Delta G'$ per unit volume of the solution

$$\Delta G' = (1 - v_p) \left(\frac{\Delta\mu_0}{V_0} \right) + \sum_{j=1}^m v_j \left(\frac{\Delta\mu_j}{X_j V_0} \right) \quad (6)$$

can be calculated from eq 4 and 5. Here, V_0 is the solvent molar volume and v_j is the volume fraction of X_j -mer. Substitution of eq 6 into the equation for the spinodal and that for the condition, under which the equilibrium is neutral, gives⁸

$$\frac{1}{X_w v_p} + \frac{1}{1 - v_p} + \chi_{00} \left\{ 1 + k' \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right\} \times \left\{ 2 + \sum_{i=1}^n p_i (i+2) v_p^i \right\} = 0 \quad (7)$$

$$\frac{1}{(1 - v_p)^2} - \frac{X_z}{X_w^2 v_p^2} - \chi_{00} \left\{ 1 + k' \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right\} \times \left\{ \sum_{i=1}^n p_i i (i+2) v_p^{i-1} \right\} = 0 \quad (8)$$

where X_w and X_z are the weight- and z-average X . At the critical point, eq 7 and 8 should be satisfied simultaneously. χ_{00} at the critical point (χ_{00}^c) is related to T_c , θ , and ψ through the relation,⁸

$$\chi_{00}^c = \left(\frac{1}{2} - \psi \right) + \frac{\theta \psi}{T_c} \quad (9)$$

with

$$\psi = \frac{1}{2} - \chi_{00,s} \quad (10)$$

and

$$\theta = \chi_{00,h} T_c / (1/2 - \chi_{00,s}) \quad (11)$$

$\chi_{00,s}$ and $\chi_{00,h}$ are entropy and enthalpy terms of χ_{00} , respectively (*i.e.*, $\chi_{00} = \chi_{00,s} + \chi_{00,h}$).

Substituting eq 9 into eq 3, we obtain

$$\chi_0^c = a' + \frac{b'}{T_c} + \frac{c'}{T_c^2} \quad (12)$$

with

$$a' = \left(\frac{1}{2} - \psi \right) \left(1 + \frac{k_0}{X_n} \right) \quad (13)$$

$$b' = \theta \psi + \theta \left(\psi - \frac{1}{4} \right) \frac{2k_0}{X_n} \quad (14)$$

$$c' = - \left(\frac{k_0}{X_n} \right) \psi \theta^2 \quad (15)$$

The effect of the molecular weight dependence of χ -parameter on the critical point can be considered to be relatively small and then, the critical point is expected to be explained in terms of the concentration-dependence parameters alone. In this case ($k' = 0$, $k_0 = 0$), eq 9 reduces to

$$\frac{1}{T_c} = \frac{\chi_0^c}{\theta \psi} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi} \right) \quad (16)$$

Assuming p_i ($i = 1, 2, \dots, m$) = 0 and $X_w = X_z$, eq 16 coincides with the equation of Shultz and Flory.⁴

$$\frac{1}{T_c} = \frac{1}{\theta \psi} \left(\frac{1}{2X_w} + \frac{1}{X_w^{1/2}} \right) + \frac{1}{\theta} \quad (17)$$

$\Delta\mu_0$ in eq 4 can be rewritten by expanding the term $\ln(1 - v_p)$ in Taylor expansion form, and by expressing v_p by the weight concentration, by

$$\Delta\mu_0 = -RTcV_0 \left\{ \frac{1}{M_n} + \frac{\bar{v}^2}{V_0} \left(\frac{1}{2} - \chi_0 \right) c + \sum_{i=1}^n \frac{\bar{v}^{i+2}}{V_0} \left(\frac{1}{i+2} - \chi_0 p_i \right) c^{i+1} \right\} \quad (18)$$

Here, \bar{v} is the polymer specific volume, and M_n , the number-average molecular weight.

Osmotic pressure π is given in virial expansion form,

$$\pi = - \frac{\Delta\mu_0}{V_0} = RTc \left(\frac{1}{M_n} + A_2 c + A_3 c^2 + A_4 c^3 + \dots \right) \quad (19)$$

where A_2, A_3, A_4, \dots are the second, third, fourth, \dots virial coefficients, and are given using eq 18 as follows,

$$A_2 = \frac{\bar{v}^2}{V_0} \left(\frac{1}{2} - \chi_0 \right) \quad (20)$$

and

$$A_{i+2} = \frac{\bar{v}^{i+2}}{V_0} \left(\frac{1}{i+1} - \chi_0 p_i \right) \quad (i=1, 2, \dots, n) \quad (21)$$

If we can assume that $A_2 = A_3 = A_4 = \dots = 0$ at $T = \theta$ for UCSP, we obtain

$$\begin{aligned} \chi_0 &= \frac{1}{2}, \\ p_1 &= \frac{2}{3}, \quad p_2 = \frac{2}{4}, \quad p_3 = \frac{2}{5}, \quad \dots, \quad p_n = \frac{2}{n+2} \end{aligned} \quad (22)$$

These are the theoretically predicted values for χ_0 and p_j ($j=1, \dots, n$). In LCSP region, p_1 is not influenced by free volume in contrast with χ_0 ,^{23,24} and $\chi_0 p_1 = 1/3$ is also satisfied.

Determination of p_1 , p_2 , θ , and ψ

Kamide and Matsuda² showed that the terms more than or equal to v_p^3 can be neglected to make the theoretical critical concentration $v_p^c(\text{theo})$ coincident with the experimental value $v_p^c(\text{exp})$. First calculate χ_0^c and $v_p^c(\text{theo})$ by solving eq 7 and 8 with assumed values of p_1 and p_2 . Evaluate the square average of the difference between $v_p^c(\text{theo})$ and $v_p^c(\text{exp})$, δ , defined by

$$\delta = \sum_{i=1}^N (v_p^c(\text{exp}) - v_p^c(\text{theo}))_i^2 / N_0 \quad (23)$$

(N_0 , total number of samples)

for a given combination of p_1 and p_2 . Finally determine the most probable p_1 and p_2 as a pair which gives minimum δ . Substituting χ_0^c , calculated for the most probable p_1 and p_2 , and the experimental critical temperature $T_c(\text{exp})$ into eq 16, and plotting the relation of $1/T_c(\text{exp})$ vs. $\chi_0^c(\text{theo})$, we obtain θ and ψ .

Koningsveld *et al.*^{1,9} defined the polymer-solvent interaction parameter g by eq 24,

$$g = \sum_{i=0}^n g_i v_p^i \quad (24)$$

where g_i is the concentration dependent parameter. Equation 8 can be rearranged using

eq 24 into

$$\begin{aligned} Y &\equiv g_1 - g_2 + 4g_2 v_p^c \\ &= \frac{1}{6} \left[\frac{1}{(1 + v_p^c)^2} - \frac{X_z}{(X_w v_p^c)^2} \right] \end{aligned} \quad (25)$$

for the case of $n=2$. Substituting X_w and $v_p^c(\text{exp})$ into eq 25 we obtain the relation of T and v_p^c , from which g_1 and g_2 can be determined using curve fitting method. g_0 depends on the temperature through the relation,

$$\begin{aligned} g_0 &\equiv g_{00} + g_{01}/T_c \\ &= \frac{1}{2} \left[\frac{1}{1 - v_p^c} + \frac{1}{X_w v_p^c} \right. \\ &\quad \left. + 2g_1(1 - 3v_p^c) + 6g_2(1 - 2v_p^c)v_p^c \right] \end{aligned} \quad (26)$$

Substitution of X_w , X_z , $T_c(\text{exp})$ data into eq 26 enables us to estimate g_{00} and g_{01} .

The following relation holds between χ and g

$$\chi = g - (1 - v_p) \frac{\partial g}{\partial v_p} \quad (27)$$

and the parameters χ_0 , p_1 , and p_2 in eq 1 can be expressed in terms of g_{00} , g_{01} , f_1 and g_2 as follows:

$$\chi_0 = g_{00} - g_1 + \frac{g_{01}}{T} \quad (28)$$

$$p_1 = 2 \frac{g_1 - g_2}{g_{00} - g_1 + g_{01}/T} \quad (29)$$

$$p_2 = 3 \frac{g_2}{g_{00} - g_1 + g_{01}/T} \quad (30)$$

Comparing eq 16 with eq 28, we obtain

$$\psi = \frac{1}{2} - g_{00} + g_1 \quad (31)$$

$$\theta = g_{01}/\psi \quad (32)$$

APPLICATION TO EXPERIMENTAL DATA

The literature data on the critical solution

points ($v_p^c(\text{exp})$ and $T_c(\text{exp})$) on polystyrene (PS),^{1,10-16} and polyethylene(PE)¹⁷⁻²² in single solvents were analyzed. It should be remembered that except for dimethoxy methane by Siow *et al.*¹⁵ and cyclohexane (in part) by Koningsveld and his coworkers,¹ all the data on PS solutions were made by Kaneko, Kuwahara, and their collaborators at Sapporo,^{10-14,16} who used PS samples with $X_w/X_n < 1.10$ (in particular for samples with the weight-average molecular weight $M_w \times 10^{-4} = 3.7$ to 40, $X_w/X_n < 1.06$) manufactured by Pressure Chemical Co. (Pittsburg, USA) and the majority of literature data on PE solutions was cited from works by Nakajima, Hamada *et al.* at Kyoto,^{19,20} who employed PE fractions isolated by successive precipitation fractionation or solid extraction (column) method from whole polymers.

Here, in the case where $v_p^c(\text{exp})$ and $T_c(\text{exp})$ are described in the literature, we employed these data without recalculation and in the case where neither $v_p^c(\text{exp})$ nor $T_c(\text{exp})$ are given in the literature, we regarded the threshold cloud point (v_p^{tcp} and T_{tcp}) as the critical point and if no threshold cloud point data are available, we estimated from the cloud point curve in the literature. For the polymer with the large molecular weight and sharp distribution, the difference between $v_p^c(\text{exp})$ and $v_p^{\text{tcp}}(\text{exp})$ can become small enough to be neglected.³ However, for the polymer with small molecular weight and broad distribution, special attention should be paid, because the difference becomes of the order of 0.01. In addition, the temperature dependence of specific volumes of the polymer and the solvent should be carefully taken into account to convert the cloud point curve, usually expressed in terms of the weight fraction. Of course, p_1 , p_2 , θ , and ψ determined by KKS and KM method are significantly affected by the accuracy of $g_p^c(\text{exp})$ and $T_c(\text{exp})$.

Tables I and II show data for the

polymer-solvent systems used for analysis, the number of samples for each system and the method, by which the critical solution data are estimated. In these tables, R denotes the case when $v_p^c(\text{exp})$ is determined as v_p of the two phase volume ratio $R=1$, diameter and tcp denotes the case when $v_p^c(\text{exp})$ is determined from diameter and the threshold cloud point curve, respectively. These tables contain also the correlation coefficients r of $1/T_c$ vs. χ_0^c (eq 16) or Y vs. v_p^c (eq 25) or g_0 vs. $1/T_c$ (eq 26). Obviously accuracy of $v_p^c(\text{exp})$ is lower than that of $T_c(\text{exp})$ for any polymer-solvent systems.

RESULTS AND DISCUSSION

Tables III and IV summarized p_1 , p_2 , θ and ψ values for PS- and PE-solvent systems, evaluated by KM, KKS, and SF methods. The values in parenthesis are cited from literature.

Polystyrene

For PS/methyl ethyl ketone(LCSP), PS/toluene(LCSP), PS/isopropyl acetate(UCSP), PS *n*-propyl acetate(UCSP), and PS/dimethoxy methane(LCSP), the correlation coefficient r between Y and v_p^c is low (< 0.55) and in consequence, the reliability of p_1 and p_2 obtained by KKS method is not high for these systems (Table I). In contrast to this, r between $1/T_c$ and χ_0^c (by KM method) is without exception larger than 0.98. Except for PS/toluene(LCSP), PS/benzene(LCSP), PS/isopropyl acetate(LCSP), PS/*n*-propyl acetate(LCSP), the p_1 value determined for PS solutions by KM method can be almost regarded as constant (0.638 ± 0.035). This value is near to the theoretically expected value ($2/3$). The range of variation (± 0.035) in p_1 may contain the solvent effect together with the experimental uncertainty. Except for PS/cyclopentane, the p_2 value for LCSP is always negative, lying between -2.0 and -0.202 and, except PS/isopropyl acetate and *n*-propyl acetate systems, in which p_2 is slightly nega-

Table I. Method for determining the critical point, number of samples and correlation coefficient r of Shultz–Flory Koningsveld *et al.* and Kamide–Matsuda plots for polystyrene–solvent systems

Polymer: Polystyrene					Correlation coefficient r				Reference	
Solvent	Number of samples	X_w/X_n	UCSP or LCSP	Method for determining critical point	Shultz–Flory	Koningsveld <i>et al.</i>		Kamide–Matsuda		
					$1/T_c$ vs. χ_0^c (eq 17)	Y vs. v_p^c (eq 25)	g_0 vs. $1/T_c$ (eq 26)	$1/T_c$ vs. χ_0^c (eq 16)		
Methyl ethyl ketone	6	<1.06	LCSP	tcp	−0.99	0.39	−0.99	−0.98	13	
Cyclopentane	6	1.10	UCSP	tcp	0.99	0.97	0.99	0.99	13	
	6	1.10	LCSP	tcp	−0.99	0.87	−0.99	−0.99	13	
Cyclohexane	6	1.02–1.4	UCSP	R	0.99	0.87	0.99	0.99	1	
	6	1.10	UCSP	Diameter						10
	4	1.02–1.44	UCSP	tcp						11
	5	1.10	LCSP	tcp	−0.99	−0.78	−0.98	−0.99	11	
Methylcyclohexane	9	1.06	UCSP	Diameter	0.99	0.97	0.99	0.99	12	
	6	1.10	UCSP	tcp						11
	6	1.10	LCSP	tcp	−0.99	−0.85	−0.99	−0.99	11	
Toluene	6	1.10	LCSP	tcp	−0.99	−0.54	−0.99	−0.99	11	
Benzene	6	1.10	LCSP	tcp	−0.99	−0.94	−0.99	−0.99	13	
Isopropyl acetate	6	1.06–1.15	UCSP	tcp	0.99	−0.17	0.99	0.99	14	
	6	1.06–1.15	LCSP	tcp	−0.97	−0.55	−0.95	−0.95	14	
<i>n</i> -Propyl acetate	4	1.06–1.15	UCSP	tcp	0.99	0.40	0.99	0.99	14	
	5	1.06–1.15	LCSP	tcp	−0.99	−0.77	−0.99	−0.99	14	
Dimethoxy methane	5	1.06	LCSP	tcp	−0.99	−0.41	−0.99	−0.99	15	
<i>trans</i> -Decalin	6	1.06	UCSP	tcp	0.99	0.96	0.99	0.99	16	

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Table II. Method for determining the critical point, number of samples and correlation coefficient r of Shultz-Flory Koningsveld *et al.* and Kamide-Matsuda plots for polyethylene-solvent systems

Polymer : Polyethylene					Correlation coefficient r				Reference
Solvent	Number of samples	X_w/X_n	UCSP or LCSP	Method for determining critical point	Shultz-Flory	Koningsveld <i>et al.</i>		Kamide-Matsuda	
					$1/T_c$ vs. χ_0^c (eq 17)	Y vs. v_p^c (eq 25)	g_0 vs. $1/T_c$ (eq 26)	$1/T_c$ vs. χ_0^c (eq 16)	
<i>n</i> -Butyl acetate	4	F ^c	UCSP	tcp	0.98	-0.91	0.99	-0.99	18
	4	F ^c	LCSP	tcp	-0.97	-0.86	-0.97	-0.97	18
<i>n</i> -Pentane	3	F ^b	LCSP	tcp	-0.99	-0.98	-0.99	-0.99	19
<i>n</i> -Hexane	4	F ^b	LCSP	tcp	-0.99	-0.93	-0.99	-0.99	19
<i>n</i> -Heptane	4	F ^b	LCSP	tcp	-0.99	0.89	-0.99	-0.98	19
<i>n</i> -Octane	4	F ^b	LCSP	tcp	-0.99	0.96	-0.97	-0.98	19
<i>n</i> -Octyl alcohol	4	W & F	UCSP	tcp	0.99	-0.87	0.99	0.99	21
	4	W & F	LCSP	tcp	-0.98	-0.86	-0.99	-0.98	21
	4	F ^a	UCSP	tcp	0.99	-0.93	0.99	0.99	20
<i>n</i> -Decyl alcohol	3	F ^a	UCSP	tcp	0.99	0.79	0.99	0.99	20
<i>n</i> -Lauryl alcohol	3	F ^a	UCSP	tcp	0.99	-0.98	0.99	0.99	20
<i>p</i> - <i>tert</i> -Amyl phenol	4	F ^a	UCSP	tcp	0.99	-0.49	0.99	0.99	20
<i>p</i> -Octyl phenol	4	F ^a	UCSP	tcp	0.99	0.09	0.99	0.99	20
<i>p</i> -Nonyl phenol	3	F ^a	UCSP	tcp	0.99	-0.30	0.99	0.99	20
Anisole	3	F ^a	UCSP	tcp	0.99	-0.99	0.99	0.99	20
Benzyl phenyl ether	3	F ^a	UCSP	tcp	0.97	-0.30	0.99	0.98	20
Diphenyl	4	F ^b	UCSP	tcp	0.96	0.96	0.99	0.99	22
Diphenyl methane	6	F ^b	UCSP	tcp	0.97	0.72	0.99	0.99	22
Diphenyl ether	3	W & F	UCSP	R	0.98	-0.47	0.99	0.99	17
	6	F ^b	UCSP	tcp	0.99	0.07	0.99	-0.99	22

W, Whole polymer; F, Fractionated polymer (F^a, by SPF; F^b, by column fractionation (solid extraction); F^c, by SSF)

Evaluation of p_1 , p_2 , θ , and ψ for Polymer-Solvent System

Table III. Concentration dependence of χ -parameter p_1 , p_2 , Flory temperature θ , and entropy parameter ψ of the critical point for polystyrene-solvent systems

Polymer: Polystyrene		Methods									
Solvent	UCSP or LCSP	Kamide-Matsuda				Koningsveld <i>et al.</i>				Shultz-Flory	
		p_1	p_2	θ	ψ	p_1	p_2	θ	ψ	θ (θ ref)	ψ (ψ ref)
Methyl ethyl ketone	LCSP	0.618	-0.208	423.6	-0.44	0.550	-0.262	423.8	-0.31	423.1 (422 ^a)	-0.63 (-0.529 ^a)
Cyclopentane	UCSP	0.615	0.404	292.1	0.16	0.606	0.497	292.1	0.18	292.7 (293 ^a)	0.53 (0.548 ^a)
	LCSP	0.631	0.331	428.5	-0.25	0.611	0.468	428	-0.27	427.4 (427 ^a)	-0.81 (-0.858 ^a)
Cyclohexane	UCSP	(0.642)	0.190	305.1	0.27 ^e)	(0.623)	0.308	305.2	0.29 ^e)	306.5 (306.2 ^b)	0.75 (0.78 ^b)
		—	—	—	—	(0.623)	0.290	306.4	0.30 ^e)	— (307.0 ^d)	— (0.79 ^d)
	LCSP	0.638	-0.498	488.6	-0.58	0.621	-0.305	488.3	-0.60	486.8 (486.0 ^d)	-1.21 (-1.19 ^d)
		(0.602)	0.347	487.2	-0.42 ^e)	(0.571)	-0.047	487.5	-0.61 ^e)	— (486.0 ^e)	— (-1.20 ^e)
Methyl cyclohexane	UCSP	(0.602)	0.234	340.2	0.25 ^e)	(0.602)	0.363	339.6	0.27 ^e)	342.3 (344 ^d)	0.61 (0.56 ^d)
	LCSP	(0.649)	-1.183	487.9	-0.54 ^e)	(0.643)	-1.008	487.8	-0.56 ^e)	485.1 (484 ^d)	-0.96 (-0.94 ^d)
Toluene	LCSP	0.494	-0.922	550.4	-1.36	0.501	-0.475	550.3	-1.20	549.8 (550 ^d)	-2.02 (-1.92 ^d)
Benzene	LCSP	0.388	-1.781	524.3	-1.81	0.382	-1.655	524.2	-1.82	523.7 (523 ^a)	-2.19 (-1.79 ^a)
Isopropyl acetate	UCSP	0.673	-0.034	240.8	0.11	0.673	-0.082	240.6	0.13	245.3 (246 ^f)	0.29 (0.32 ^f)
	LCSP	0.839	-2.000	398.1	-0.46	0.773	-1.594	394.6	-0.46	389.5 (380 ^f)	-0.71 (-0.46 ^f)
<i>n</i> -Propyl acetate	UCSP	0.643	-0.018	192.3	0.21	0.623	0.168	192.7	0.22	193.2 (193 ^f)	0.60 (0.63 ^f)
	LCSP	0.797	-1.440	456.3	-0.47	0.769	-1.204	455.6	-0.49	451.1 (451 ^f)	-0.96 (-0.85 ^f)
Dimethoxy methane	LCSP	0.650	-0.202	389.1	-0.25	0.642	-0.083	388.0	-0.24	386.0 (—)	-0.61 (—)
<i>trans</i> -Decalin	UCSP	0.630	0.240	292.7	0.33	0.623	0.338	292.5	0.36	293.7 (—)	0.95 (—)

^a ref 13. ^b ref 3. ^c ref 2. ^d ref 4. ^e ref 1. ^f ref 14.

Table IV. Concentration dependence of χ -parameter p_1 , p_2 , Flory temperature θ , and entropy parameter ψ of the critical point for polyethylene-solvent systems

Polymer : Polyethylene		Methods									
Solvent	UCSP or LCSP	Kamide-Matsuda				Koningsveld <i>et al.</i>				Shultz-Flory	
		p_1	p_2	θ	ψ	p_1	p_2	θ	ψ	θ (θ ref)	ψ (ψ ref)
<i>n</i> -Butyl acetate	UCSP	2.98	-34.6	453.8	0.89	3.100	-36.6	453.8	0.93	482.1 (483**a)	0.61 (0.65**a)
	LCSP	4.63	-38.0	506.5	-1.15	3.742	-31.59	499.9	-1.27	474.9 (471**a)	-1.17 (-1.12**a)
<i>n</i> -Pentane	LCSP	1.95	-23.4	366.7	-1.82	4.529	-42.69	376.2	-1.78	351.8 (353**b)	-1.06 (-1.3**b)
<i>n</i> -Hexane	LCSP	0.662	-6.53	410.4	-0.93	0.675	-6.54	410.3	-0.95	407.3 (406.3**b)	-0.98 (-1.0**b)
<i>n</i> -Heptane	LCSP	-1.5	12.9	446.5	-1.89	-3.76	34.60	446.5	-2.68	447.1 (446.9**b)	-1.16 (-1.2**b)
<i>n</i> -Octane	LCSP	-1.0	7.7	482.9	-1.64	-2.873	26.12	481.6	-2.14	484.4 (483.0**b)	-1.22 (-1.1**b)
<i>n</i> -Octyl alcohol	UCSP	1.7	-33.7	440.9	1.53	3.435	-59.0	436.7	1.52	445.0 (444**c)	1.21 (1.16**c)
	LCSP	1.8	-37.0	621.9	-7.40	2.712	-51.43	622.4	-7.13	620.6 (621**c)	-5.76 (-5.4**c)
	UCSP	0.48	-25.6	446.3	2.59	1.440	-43.79	445.8	2.47	452.9 (453.1**d)	1.15 (1.15**d)
<i>n</i> -Decyl alcohol	UCSP	-1.82	6.02	425.7	2.82	-2.688	11.24	427.6	2.65	425.5 (426.3**d)	1.47 (1.44**d)
<i>n</i> -Lauryl alcohol	UCSP	-0.304	-3.40	409.0	2.47	-0.249	-5.036	409.2	2.39	410.1 (410.3**d)	1.67 (1.64**d)
<i>p</i> - <i>tert</i> -Amyl phenol	UCSP	-2.13	2.30	470.2	2.54	-1.923	-6.158	472.0	2.17	472.1 (472.2**d)	1.07 (1.07**d)
<i>p</i> -Octyl phenol	UCSP	-1.52	-0.912	446.1	3.26	-2.744	0.997	450.6	2.89	448.2 (447.5**d)	1.47 (1.48**d)
<i>p</i> -Nonyl phenol	UCSP	0.175	-2.71	434.1	1.78	-0.095	-1.277	435.7	1.77	435.8 (435.4**d)	1.55 (1.62**d)
Anisole	UCSP	1.15	-39.1	422.6	2.61	1.655	-49.63	422.1	2.59	426.3 (426.5**d)	1.45 (1.41**d)
Benzyl phenyl ether	UCSP	-0.823	-20.1	461.6	2.95	-1.945	-12.17	464.2	2.74	464.0 (464.5**d)	1.32 (1.38**d)
Diphenyl	UCSP	-1.32	9.32	400.5	1.84	-2.064	15.86	401.1	1.95	399.8 (400.5**e)	1.19 (1.17**e)
Diphenyl methane	UCSP	-0.89	3.1	414.5	1.61	-1.970	10.66	418.6	1.58	413.7 (415.2**e)	1.13 (1.06**e)
Diphenyl ether	UCSP	0.611	-2.483	427.5	1.04	0.400	-1.50	431.4	0.98	431.9 (—)	0.96 (—)
	UCSP	-0.31	-1.6	433.0	1.53	-0.698	0.471	435.1	1.49	434.1 (436.9**e)	1.12 (1.00**e)

^a ref 18. ^b ref 19. ^c ref 21. ^d ref 20. ^e ref 22.

Evaluation of p_1 , p_2 , θ , and ψ for Polymer-Solvent System

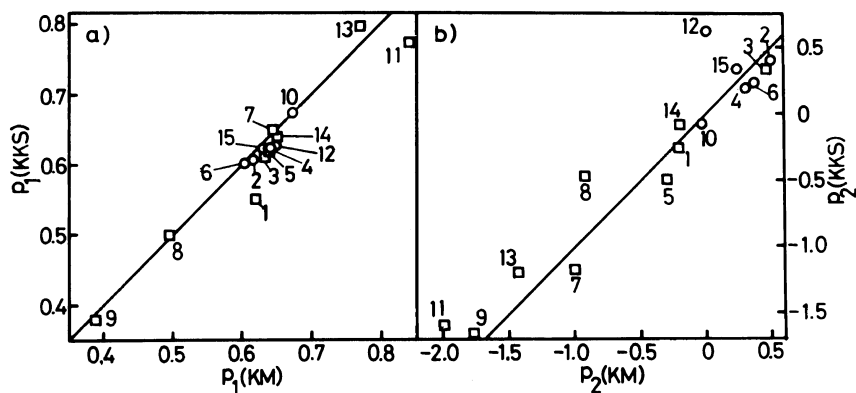


Figure 1. Correlations between $p_1(\text{KKS})$ and $p_1(\text{KM})$ and correlations between $p_2(\text{KKS})$ and $p_2(\text{KM})$, both for polystyrene solutions: rectangle, LCSP; circle, UCSP: 1, methyl ethyl ketone (LCSP)¹³; 2, cyclopentane (UCSP)¹³; 3, cyclopentane (LCSP)¹³; 4, cyclohexane (UCSP)^{1,10,11}; 5, cyclohexane (LCSP)¹¹; 6, methylcyclohexane (UCSP)^{11,12}; 7, methylcyclohexane (LCSP)¹¹; 8, toluene (LCSP)¹¹; 9, benzene (LCSP)¹³; 10, isopropyl acetate (UCSP)¹⁴; 11, isopropyl acetate (UCSP)¹⁴; 11, isopropyl acetate (LCSP)¹⁴; 12, *n*-propyl acetate (UCSP)¹⁴; 13, *n*-propyl acetate (LCSP)¹⁴; 14, dimethoxy methane (LCSP)¹⁵; 15, *trans*-decalin (UCSP).¹⁶

tive (-0.03 and -0.02), the p_2 value for UCSP is positive (0.297 ± 0.107). This mean value is slightly smaller than the theoretical value ($1/2$).

Figure 1a) shows the plot of p_1 , evaluated by KKS method ($p_1(\text{KKS})$) versus p_1 , evaluated by KM method ($p_1(\text{KM})$) and Figure 1b) is similar plot of p_2 . KM and KKS methods give almost the same values of p_1 and p_2 (hereafter referred to as $p_1(\text{KM})$, $p_1(\text{KKS})$, $p_2(\text{KM})$, and $p_2(\text{KKS})$).

$$p_1(\text{KKS}) = 0.889 p_1(\text{KM}) + 0.052, \\ r = 0.9813$$

$$p_2(\text{KKS}) = 0.927 p_2(\text{KM}) + 0.150, \\ r = 0.9714$$

The Flory temperature, obtained by three methods, is practically independent of the methods employed. ψ is positive for UCSP and negative for LCSP as expected, irrespective of the methods used for evaluation. These are observed not only for PS, but also for PE, strongly suggesting that ψ cannot be regarded as temperature-independent over wide range of temperature, which is assumed in KKS and KM methods and the

polymer solution should be athermal at a temperature between UCSP and LCSP. Absolute values of ψ , $|\psi|$ increases in the order:

$$|\psi(\text{KM})| \cong |\psi(\text{KKS})| < |\psi(\text{SF})|$$

As pointed out for PS/CH and PS/MCH systems in the previous paper,² the fact that $|\psi(\text{SF})|$ is larger than $|\psi(\text{KM})|$ and $|\psi(\text{KKS})|$ is mainly caused from the ignorance of the concentration dependence of χ parameter in SF method. Among three methods the following relations hold:

$$\psi(\text{KKS}) = 0.983 \psi(\text{KM}) + 0.017, \quad r = 0.9963$$

$$\psi(\text{SF}) = 1.554 \psi(\text{KM}) + 0.076, \quad r = 0.9553$$

$$\psi(\text{SF}) = 1.578 \psi(\text{KKS}) + 0.094, \quad r = 0.9571$$

For PS/cyclopentane (CP), /CH, and /MCH systems, p_1 values for LCSP or UCSP are very similar to each other, but difference in ψ values between CP and CH is much larger than that between CH and MCH for both CSP. In other words, the skeleton structure of the solvent (*i.e.*, five- or six-membered ring structure) is a more important factor than the substituent group to the skeleton, covering the thermody-

namic interaction between the polymer and solvent.

Even if the solvents have similar molecular weights and almost the same molecular shapes, p_1 and also p_2 differ remarkably depending on whether the solvent is aliphatic or aromatic. For PS/CH and PS/MCH systems, p_1 for LCSP was found to be 0.64–0.65 by KM method. In contrast to this, for PS/benzene and PS/toluene systems p_1 for LCSP was 0.39 and 0.49 by KM method, respectively. An aromatic solvent acts as a better solvent against PS.

Figure 2 shows the plot of p_2 against p_1 , both estimated by KM method, for PS solutions. Here, unfilled circle and rectangle correspond to UCSP and LCSP, respectively. The point theoretically expected when $A_2 = A_3 = A_4 = 0$ at θ temperature, is denoted as a filled circle. It is obvious that the experimental points for UCSP are not far from the theoretical point. On the other hand, the data points scatter for LCSP, showing negative p_2 .

Figure 3 shows ^1H NMR spectra of PS (the weight-average molecular weight $M_w = 23.2 \times 10^4$ by the light scattering method in benzene at 25°C)³ solutions in hexadeutero benzene (benzene- d_6) and in CH. In the former system, the spectra consists of five peaks, as denoted in the figure by a–e. Peaks a and b are due to the proton attached to benzene ring, in racemic and meso configurations, of PS, respectively. Here, the intensity ratio of a to b was 2.28. Peak c is attributed to methin proton in the PS main chain. The NMR peak of the methylene proton splits into two peaks d and e, corresponding to their racemic and meso configurations, respectively. In the meso configuration (peak b), the direction of the magnetic field induced by a circular current of benzene ring is exactly anti-parallel to that of the external field and then the magnetic shielding effect is weakened, resulting in a significant shift of the peak to higher than that in racemic configuration. The peaks c, d, and e, observed in higher magnetic field (< 3 ppm) for PS/CH

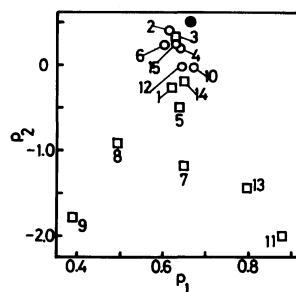


Figure 2. Plot of p_1 (MK) versus p_2 (KM) for polystyrene solutions: rectangle, LCSP; unfilled circle, UCSP; filled circle, the point theoretically expected when $A_2 = A_3 = A_4 = 0$ at θ . Key number has the same meaning as those in Figure 1.

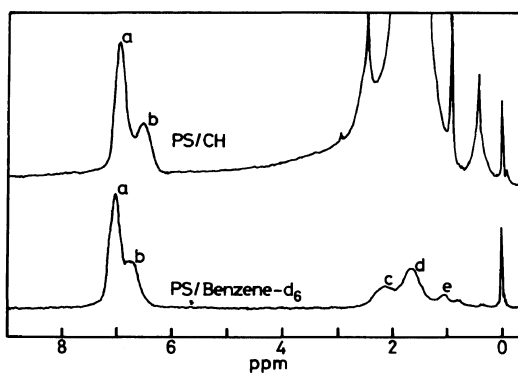


Figure 3. ^1H NMR spectra of polystyrene in benzene- d_6 and in cyclohexane: for assignment of peaks a, b, c, d, and e see the text.

system, are overlapped by those of the solvent and only peaks a and b are separately detected. Chemical shift of the proton attached to the benzene ring of PS in racemic configuration was observed at 7.04 ppm in benzene and at 6.95 ppm in CH. Similar difference in the chemical shift for meso configuration (0.21 ppm) was observed between benzene and CH. This kind of shift of peak a or b to lower magnetic field can be explained as follows: The magnetic shielding effect induced by circular electric current is strengthened by planar interaction between the benzene ring of PS and benzene as solvent. The interaction makes benzene a better solvent than CH.

p_1 , p_2 , θ , and ψ values of UCSP for the

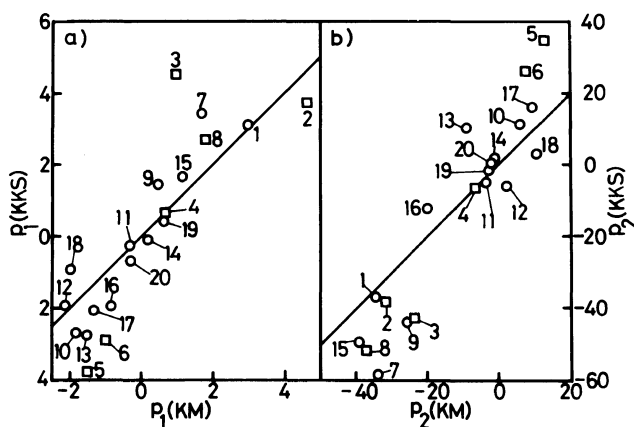


Figure 4. Correlations between p_1 (KKS) and p_1 (KM) and correlations between p_2 (KKS) and p_2 (KM), both for polystyrene solutions: rectangle, LCSP; circle, UCSP: 1, *n*-butyl acetate (UCSP)¹⁸; 2, *n*-butyl acetate (LCSP)¹⁸; 3, *n*-pentane (LCSP)¹⁹; 4, *n*-hexane (LCSP)¹⁹; 5, *n*-heptane (LCSP)¹⁹; 6, *n*-octane (LCSP)¹⁹; 7, *n*-octyl alcohol (UCSP)²¹; 8, *n*-octyl alcohol (LCSP)²¹; 9, *n*-octyl alcohol (UCSP)²⁰; 10, *n*-decyl alcohol (UCSP)²⁰; 11, *n*-lauryl alcohol (UCSP)²⁰; 12, *p*-*tert*-amyl phenol (UCSP)²⁰; 13, *p*-octyl phenol (UCSP)²⁰; 14, *p*-nonyl phenol (UCSP)²⁰; 15, anisole (UCSP)²⁰; 16, benzyl phenyl ether (UCSP)²⁰; 17, diphenyl (UCSP)²²; 18, diphenyl methane (UCSP)²²; 19, diphenylether (UCSP)¹⁷; 20, diphenyl ether (UCSP).²²

PS/CH system were calculated from whole data on v_p^c and T_c , obtained by three different methods. The data of Kuwahara *et al.*¹⁰ by the diameter method gave $p_1=0.593$, $p_2=0.551$, $\theta=306.9$ and $\psi=0.22$. The threshold cloud point method¹¹ gave $p_1=0.645$, $p_2=0.165$, $\theta=305.1$, and $\psi=0.27$. The phase volume ratio method¹ yielding $p_1=0.631$, $p_2=0.221$, $\theta=305.8$, and $\psi=0.27$. Obviously, from the latter two methods, we can obtain the same results, giving p_1 value similar with the theoretical value and also ψ value, practically identical with the average value (0.264) estimated from the second virial coefficient.

Polyethylene

For PE/*p*-*tert*-amyl phenol(UCSP), PE/*p*-octyl phenol(UCSP), PE/*p*-nonyl phenol (UCSP), PE/benzyl phenyl ether (UCSP), and PE/diphenyl ether(UCSP), the correlation between Y and v_p^c is low ($|r|<0.5$). Even for these systems, $|r|$ between $1/T_c$ and χ_0^c in KM method is larger than 0.97. p_1 and p_2 , determined by KM method vary in the range $p_1 = -1.82$ — 2.98 , $p_2 = -39.1$ — 9.32 for

UCSP, and $p_1 = -1.5$ — 4.63 , $p_2 = -38.0$ — 12.9 for LCSP. Obviously, the range of variation in p_1 and p_2 is much wider for PE than for PS, and only two system, PE/*n*-hexane(LCSP) and PE/diphenyl ether(UCSP), have p_1 values in the vicinity of the theoretical value (2/3).

Figure 4a) and b) show the relations between p_1 (KKS) and p_1 (KM) and between p_2 (KKS) and p_2 (KM), respectively. From the figure, we obtain

$$p_1(\text{KKS}) = 1.322 p_1(\text{KM}) - 0.265,$$

$$r = 0.913$$

and

$$p_2(\text{KKS}) = 1.436 p_2(\text{KM}) - 0.398,$$

$$r = 0.942$$

$|\psi|$ decreases in the order;

$$|\psi(\text{KM})| \cong |\psi(\text{KKS})| > |\psi(\text{SF})|$$

In PE solutions, p_2 often has an unexpectedly large negative value, which brings about larger $|\psi(\text{KM})|$ than $|\psi(\text{SF})|$. Therefore, if ψ value, deduced from the temperature dependence of

A_2 of PE solutions, $\psi(A_2)$ becomes available in the future, we can predict $|\psi(A_2)| > |\psi(\text{SF})|$.

$$\psi(\text{KKS}) = 0.987 \psi(\text{KM}) - 0.114, \quad r = 0.996$$

$$\psi(\text{SF}) = 0.680 \psi(\text{KM}) - 0.196, \quad r = 0.980$$

$$\psi(\text{SF}) = 0.684 \psi(\text{KKS}) - 0.115, \quad r = 0.977$$

Among the literature data on PE/solvent systems, those by Koningsveld *et al.*¹⁷ for PE/diphenylether are believed to have the highest accuracy, because the cloud point curves they constructed for three PE samples were constituted of 28, 42, and 48 data points and the critical points were determined by using the two phase volume ratio R , which gives directly the critical point, irrespective of the polymolecularity of the sample. It is well-known that PE as polymerized whole polymers have extremely wide molecular weight distributions and PE fractions isolated by successive precipitation fractionation using proper solvent/non-solvent the system can never be regarded as monodisperse. Unfortunately, with exception of Koningsveld *et al.*'s experiments,¹⁷ no experiment was carried out to determine v_p^c and T_c using R . The results, obtained by analyzing Nakajima *et al.*'s threshold cloud point curves for PE/diphenyl ether system are different remarkably from the data by Koningsveld *et al.* for the same polymer/solvent system. This means that the threshold cloud points, at least for PE fractions, do not coincide with the critical points with good accuracy and the wide variation of p_1 and p_2 is mainly due to low accuracy of the experiments.

By analyzing Koningsveld *et al.*'s data¹⁷ for the PE/diphenylether system, we obtain $p_1 = 0.61$, using the KM method, which is close to the theoretical value. Koningsveld *et al.*¹⁷ concluded, only considering g_1 , that the most reasonable supposition for PE/diphenyl ether system appears to be g_1 (accordingly, $p_1 = 0$, and δ (in eq 23), calculated assuming $p_1 = p_2 = 0$ for the same data, is about 60% larger than that obtained using the values of p_1 and p_2 ,

estimated by KM method for this system ($p_1 = 0.61$ and $p_2 = -2.483$). Similar analysis of Nakajima and his coworkers' data for the same system gave $p_1 = -0.31$ by KM method. Note that the cloud point curves in Nakajima *et al.*'s study were constructed from only 4–8 (average 5) different concentration solutions. The large difference in p_1 indicates the experimental difficulty (and accordingly, the experimental uncertainty) contained in determination of the critical point of PE solutions, and as far as PE/diphenyl ether sys-

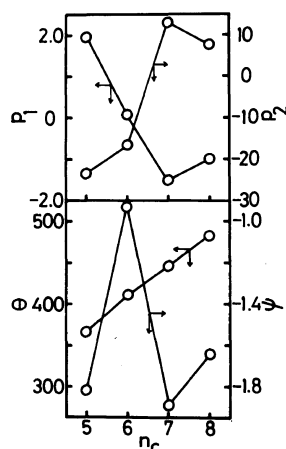


Figure 5. p_1 , p_2 , θ , and ψ plotted against the carbon number n_c constituting linear aliphatic hydrocarbons as LCSP solvent for polyethylene.

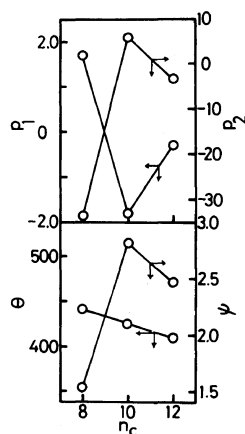


Figure 6. p_1 , p_2 , θ , and ψ plotted against the carbon number n_c constituting linear aliphatic hydrocarbons as UCSP solvent for polyethylene.

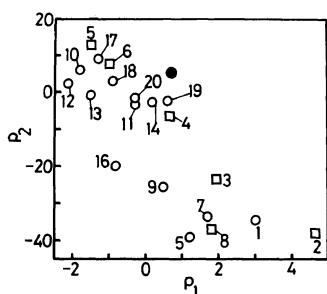


Figure 7. Plot of $p_1(\text{KM})$ versus $p_2(\text{KM})$ for polyethylene solutions: rectangle, LCSP; unfilled circle, UCSP; filled circle, the point theoretically expected when $A_2 = A_3 = A_4 = 0$ at θ : Number has the same meaning as those in Figure 3.

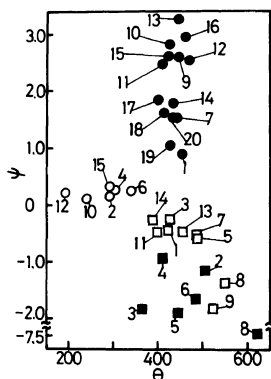


Figure 8. Plot of ψ as a function of θ for polystyrene (unfilled mark) and polyethylene (filled mark) solutions: circle, UCSP; rectangle, LCSP. Number has the same meaning as those in Figures 1 and 3.

tem is concerned, we can obtain $p_1 \cong 2/3$ as in the case of PS/solvent systems.

Figure 5 shows the plot of p_1 , p_2 , θ , and ψ as a function of the carbon number n_c constituting linear aliphatic hydrocarbons as LCSP solvent systems investigated. In short, increase in n_c and then slowly increases after passing through minimum at n -heptane. n_c dependence of p_2 is just reverse to that of p_1 . Although ψ does not show a systematic change with n_c , θ increases with n_c .

Figure 6 demonstrates the plot of p_1 , p_2 , θ , and ψ against the carbon number n_c constituting linear aliphatic alcohols as UCSP solvent for PE. p_1 shows maximum and both p_2 and ψ

attain maximum at $n_c = 10$ (i.e., n -decyl alcohol). θ decreases linearly with n_c .

Figure 7 illustrates the relationship between p_1 and p_2 , both estimated by KM method, for PE solutions. The theoretical point predicted where $A_2 = A_3 = A_4 = 0$ at θ temperature is denoted as a filled circle. It is interesting to note that, unlike PS solutions, p_1 cannot be regarded as nearly constant and p_2 has a tendency to decrease with an increase in p_1 , satisfying $p_1 p_2 \lesssim 0$.

Figure 8 shows the correlations between ψ and θ of PS (unfilled mark) and PE (filled mark). For PS solutions, the solvent dependence of ψ is much smaller than that of θ in the both ranges of UCSP and LCSP. In contrast to this, for UCSP of PE solutions ψ variation with solvent is remarkable as compared with the solvent dependence of θ . The difference in ψ between UCSP and LCSP is very significant in PE solution and the following relations holds:

$$\psi_{\text{PE}}^{\text{UCSP}} > \psi_{\text{PS}}^{\text{UCSP}} > \psi_{\text{PS}}^{\text{LCSP}} > \psi_{\text{PE}}^{\text{LCSP}}$$

For convenience, we express the Flory temperature evaluated by KM, KKS, and SF methods as $\theta(\text{KM})$, $\theta(\text{KKS})$, and $\theta(\text{SF})$, respectively. For the UCSP of PS/single solvent system, $\theta(\text{SF})$ is on the average *ca.* 1.8 K higher than $\theta(\text{KM})$ and $\theta(\text{KKS})$. For LCSP of the same system $\theta(\text{SF})$ is 2–3 K lower than $\theta(\text{KM})$ and $\theta(\text{KKS})$. For the PE/single solvent system $\theta(\text{SF})$ is *ca.* 3–4 K higher in UCSP and *ca.* 8 K lower in LCSP than $\theta(\text{KM})$ and $\theta(\text{KKS})$. The difference between $\theta(\text{KM})$ and $\theta(\text{KKS})$ is practically insignificant for all the polymer-solvent systems investigated. In short, $\theta(\text{KM}) \cong \theta(\text{KKS}) < \theta(\text{SF})$ for UCSP and $\theta(\text{KM}) \cong \theta(\text{KKS}) > \theta(\text{SF})$ for LCSP. The Flory temperature is believed the most reliable when it is determined as the temperature at which the second virial coefficient A_2 by the membrane osmometry or the light scattering method becomes zero (hereafter referred to as $\theta(A_2)$). $\theta(A_2)$ was found to be in the range 307.0 and 308.4 K (Table II of ref 2) and averaged to 307.6 K for UCSP

of PS/CH system. For this system, $\theta(\text{KM})$, $\theta(\text{KKS})$ and $\theta(\text{SF})$ are by 2.5, 2.4, and 1.1 K underestimated. $\theta(A_2)$ was determined for LCSP of PS/MCH system to be 340.4 and 341 K (Table IV of ref 2) and averaged to be 340.7 K which is 0.5 and 1.1 K higher than $\theta(\text{KM})$ and $\theta(\text{KKS})$ and 1.6 K lower than $\theta(\text{SF})$. From a theoretical point of view, KM and KKS methods are superior as compared with SF method. But, to estimate θ more accurately using KM or KKS method, the temperature dependence of p_1 and p_2 should be taken into account.

Summarizing, literature data on the cloud point curve and the critical solution point for PS solutions are accurate enough to be analyzed by KKS and KM methods and p_1 was found to be fairly near to the theoretical value (2/3), expected when $A_2=A_3=0$ at θ . However, p_2 for these polymer/solvent systems deviates occasionally to a large extent, from the theoretical value (1/2), calculated when $A_2=A_3=A_4=0$ at θ and p_2 is positive for UCSP and negative for LCSP. This suggests that the fourth virial coefficient A_4 does not always become zero even at θ . The corresponding literature data for PE solutions are unfortunately rather qualitative and more reliable data for this polymer is highly anticipated. The entropy parameter ψ for PS and PE solutions is negative at the LCSP region and positive at the UCSP region and an athermal solution will be realized, at least, for these polymers in any solvent at a specific temperature between LCSP and UCSP.

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