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Study of Linear Poly(*p*-chlorostyrene)—Diluent Systems. I. Solubilities, Phase Relationships, and Thermodynamic Interactions

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ABSTRACT: The solubilities of poly(*p*-chlorostyrene) (PPCS) were examined for about ninety solvents. The solvents employed were aliphatic, aromatic and chlorinated hydrocarbons, ethers, esters, ketones, alcohols, and others. The solubilities were successfully interpreted by the three dimensional plots according to Crowley, Teague, and Lowe, in which the solubility parameter, dipole moment, and hydrogen bonding parameter were used as three components, and to Hansen, who devided the solubility parameter into dispersion, polar and hydrogen bonding components. It can be seen that the soluble region is found to be inside the closed surface in the three-dimensional plots. The present systems involve some with either LCST or UCST. The difference between the PPCS—solvent system with LCST and that with UCST is reflected in the relative contribution of the three components rather than in the structure of the solvent. Furthermore, the phase relationships of PPCS were investigated. The eleven theta solvents found in this work contain both the four theta solvent with LCST, *i.e.*, isopropyl acetate (θ=75.7°C), *t*-butyl acetate (θ=65.4°C), ethylcarbitol (θ=27.8°C) and *n*-butylcarbitol (θ=50.1°C), and the seven theta solvents with UCST, *i.e.*, ethylbenzene (θ=−14.7°C), isopropylbenzene (θ=59.0°C), carbon tetrachloride (θ=50.7°C), tetrachloroethylene (θ=44.4°C), methyl chloroacetate (θ=64.6°C), ethyl chloroacetate (θ=−1.8°C), and isopropyl chloroacetate (θ=−8.2°C). It is considered from these phase relationships and from calorimetric measurements in the corresponding monomer solutions for esters that the theta solvent with LCST corresponds to an exothermic solvent and that characterized by UCST to an endothermic one.

KEY WORDS Poly(*p*-chlorostyrene) / Solubility / Theta Solvent / LCST / UCST / Phase Relationship / Thermodynamic Parameter / Three-Dimensional Solubility Parameter /

The solution properties of halogen derivatives of polystyrene have been investigated in order to clarify the effects of a polar group introduced in the side chain in comparison with those of polystyrene itself[1-13,34]. Although much empirical information on the effects of these polar group is available to predict the solubility of halogen derivatives of polystyrene, it is still very difficult to interpret the solubility in any systematic manner. Recently, the concept of a solubility parameter has been extended to polar polymers on the basis of the solubility parameter theory[14]. The studies on solubility are classified in the following two types which are both expressed by three components.

I. The method of Crowley, Teague, and Lowe[15], in which Hildebrand's solubility parameter δ_s is combined with dipole moment μ_s and a value γ_s which is characteristic of the hydrogen bonding of a solvent on the basis of the results by Burrell[16], Lieberman[17], and Gardon[18].

II. The method of Hansen[19], who divided solubility parameter δ_s (or δ_l) into the three components; that is, dispersion component δ_d, polar component δ_p, and hydrogen bonding component δ_h.

The methods described above seem to predict reliably not only the solubility of a polar polymer in an organic solvent but also the results

on theta solvents of the polar polymer.

The phenomenon of the so-called lower critical solution temperature (LCST) except the LCST of Prigogine—Patterson type[20,37-40] has not been explained quantitatively yet. Recently, this type of phenomenon was discovered for the same polymer series. The behavior of polystyrene solution has been explained as the LCST of the Prigogine—Patterson type[20], whilst that for the systems of halogen derivatives of polystyrene and solvent, such as the poly(*p*-iodostyrene)—dimethylformamide[1] and the poly(*o*-chlorostyrene)—methyl ethyl ketone[5] systems cannot be explained as the LCST of the Prigogine—Patterson type. The theory of Prigogine—Patterson predicts that the phase separation will occur well above the normal boiling point of the solvent, while in the latter systems it can take place even at temperatures far below the normal boiling point of the solvent. This genenal behavior also differs from that of the aqueous solution in which hydrogen bonding plays an important role in solubility. Strong interactions such as hydrogen bonding do not exist in the solutions of halogen derivatives of polystyrene in organic solvents, even though hydrophobic and hydrophilic groups in the aqueous solution correspond to lyophobic and lyophilic groups in these solutions.

In this paper, which will be the first of a series of work on poly(*p*-chlorostyrene) (PPCS)—diluent systems, the authors tried to evaluate the solvent power applicable to the polar polymer using the three dimensional solubility parameters mentioned above and to obtain a correlation between the solvent power and the θ solvent. Such arrangements should be convenient to compare with following papers in this series and other related work. Phase relationships in four systems with LCST were also studied, *i.e.*, PPCS in isopropyl acetate, *t*-butyl acetate, ethylcarbitol and *n*-butylcarbitol, and seven systems with upper critical solution temperature (UCST), *i.e.*, PPCS in ethylbenzene, isopropylbenzene, carbon tetrachloride, tetrachloroethylene, methyl chloroacetate, ethyl chloroacetate and isopropyl chloroacetate. The thermodynamic interaction parameters for these θ solvents were determined by using the phase relationships. The results were compared with the calorimetric measurements in ester solutions of the corresponding monomer.

EXPERIMENTAL

Materials

p-chlorostyrene monomer was prepared as follows[21]: *p*-chloroacetophenone was prepared from chlorobenzene and acetyl chloride by the Friedel—Crafts reaction. *p*-chlorophenylmethylcarbinol was obtained by the reduction of *p*-chloroacetophenone with isopropyl alcohol under aluminum isopropoxide. Then, *p*-chlorostyrene was obtained by the dehydration of the carbinol with powdered and fused potassium acid sulfate. The boiling point of the *p*-chlorostyrene obtained was in the temperature range 57—58°C at 6 mmHg.

PPCS designated as type A was prepared by radical polymerization using benzoyl peroxide at 40°C for about ten days and PPCS designated as type L was prepared by thermal polymerization at *ca.* 120°C for about 8 min.[34] The identification[22,23] of the polymers was done by infrared spectra.

PPCS was fractionated from dilute benzene solution by the addition of methanol as a precipitant. Ten fractions of PPCS for type A and eight fractions for type L were obtained by the successive precipitation method. Each fraction was redissolved and precipitated, and dried at 55°C *in vacuo*. Seven fractions in type A and two fractions in type L were used for the measurements.

The solvents employed for the measurements except solubility test were purified according to the standard procedure[24,25], and fractionally distilled just before use. The purity of solvents was checked by means of gas chromatography (Hitachi Ltd., type KGL-2B) and density. The density of solvents was measured using a bicapillary pycnometer[26] calibrated with distilled toluene at each temperature.

Light Scattering

A Shimazu light-scattering photometer type PG—21 was used. The measurements were made for PPCS in ethylbenzene at 30.0°C by using a wavelength of 4358 Å taking 46.5×10^{-6} [27] as Rayleigh's ratio. Solvent and solutions for the optical measurement were centrifuged at

15000 times gravity for 2 hr. The sample temperature was kept within $\pm 0.1°C$ by circulating thermostatted water to the cell housing. The specific refractive index increment measured by a Debye-type differential refractometer was 0.107 cm^3/g at 30.0°C.

Analysis of the scattering data was carried out according to the procedure of Zimm and Berry, plotting the square root of Kc/R_θ against $c+\sin^2(\theta/2)$ where R_θ is Rayleigh's ratio, c the polymer concentration in conventional units, θ the scattering angle, and K the well-known constant involving the refractive index and its increment.

Viscosity

Viscosities were measured with Ubbelohde-type viscometers maintained at constant temperature kept within $\pm 0.01°C$. The correction for kinetic energy and the density ratio was unnecessary. In order to determine the intrinsic viscosity the data were extrapolated to infinite dilution according to Huggins' and Kraemer' equations[35,36].

Solubility

The solutions or the mixtures of 2 wt% were prepared from PPCS sample and solvents of reagent grade, and put in glass tubes. Aliphatic, aromatic and chlorinated hydrocarbons, esters, ethers, ketones, alcohols, and others were used as solvents. The solutions or the mixtures were shaken and heated until the solutions became homogeneous or the mixtures showed no further change. The solubilities were determined at room temperature after the samples had been allowed to stand quietly for several days at the same temperature.

The iodine bonding number γ_s, used as the qualitative measure for specific interactions (such as hydrogen bonding), was estimated by Small's method[28]. Tricresylphosphate was used as a standard substance instead of trioctylphosphate. Values of solubility parameters of the solvents δ_s were calculated from the literature[15-19,25,29]. The symbol δ_1 was used to designate the solubility parameter calculated according to Hansen,[19] although the difference between δ_s and δ_1 values is generally small for the same solvent. Values of dipole moment μ_s were cited from the literature[25,29].

Phase Separation

Each glass tube, in which small glass chips were inserted to aid stirring, was filled with a solution and sealed off. The glass tubes, in which the solutions of various concentrations were enclosed, were fixed on a black board of Bakelite and put in a water or methanol bath. The board was often rotated to stir the samples in the glass tubes. Measurements were carried out over the temperature range from −30° to 90°C.

The temperature of incipient phase separation and the dissolution temperature at which the solution became clear again were determined by slowly lowering or raising the temperature of the bath. In order to repeat easily the procedure mentioned above, a thin white thread was tightly strung between the glass tubes and the black board. The temperature was checked at which the thread became dim or clear when viewed by the naked eye while raising or lowering the temperature, because the incipient phase separation began to appear or disappear according to the temperature change. The precipitation and dissolution temperatures agreed within $\pm 0.2°C$ except for systems of ethylcarbitol and *n*-butylcarbitol, for which the accuracy of the measurement was worse on account of the high viscosity (*ca.* $\pm 0.4°C$). The temperature of phase separation was given by the average value of the precipitation and the dissolution temperatures.

Calorimetric Measurements

The twin calorimeter for high temperatures (made by Agne Technical Center Co., Ltd.) was used to measure the heat of mixing at room temperature. It consists of two glass cell holders, into which are put a mixing cell and a reference cell. The mixing cell is made of glass and consists of an outer cell (A) and an inner cell (B), as shown in Figure 1. The outer cell (A) is filled with the solvent and the inner cell containing some glass chips is filled with solute (*p*-chlorotoluene), and then both cells are sealed off. The solute and the solvent are mixed by shaking the glass rod (C) and by breaking only the inner cell (B) which is made of very thin glass. The reference cell is the same type of cell as the mixing cell and is used as the standard for one side of the thermocouples wound around the outside surface of the cell holders.

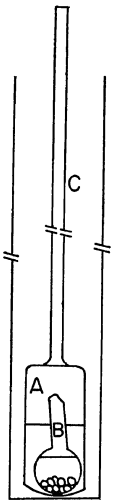


Figure 1. Calorimetric cell: (A) an outer cell; (B) an inner cell; (C) glass rod.

ANALYTICAL

Evaluations of Solvent Power and Soluble Region

The heat of mixing for a system containing polar molecules may be written by the following equation in the most general form, according to the Hildebrand—Scatchard regular solution theory[14,31,42].

$$\Delta H_m = V_1 A_{12}(n_1 + x n_2)\phi_1\phi_2 \quad (1)$$

where A_{12} is the interchange energy density for the solvent—solute pair; n_1 and n_2 are the number of moles of solvent and polymer, respectively; ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively; x is the ratio of the molar volume of polymer and that of solvent; V_1 is the molar volume of the solvent. Using eq 1 together with the Flory—Huggins expression for the athermal configurational entropy of mixing, the polymer—solvent interaction parameter χ, which reflects the intermolecular forces between polymer and solvent, is given by[14]

$$\chi = \chi_S + \chi_H = \chi_S + (V_1/RT)A_{12} \quad (2)$$

(The empirical constant χ_S has usually a value of approximately 0.3 to 0.4[28]). The interchange energy density A_{12} is given by

$$A_{12} = c_{11} + c_{22} - 2c_{12} \quad (3)$$

where the c_{ij}'s characterize the intermolecular forces acting between molecules i and j. c_{11} and c_{22} are the cohesive energy densities of pure components 1 and 2, respectively. According to Blanks, *et al.*[31], and Hansen[19], the c_{ij}'s are rewritten by

$$c_{ii} = \Delta E_i^V / V_i = \delta_i^2 = \delta_{id}^2 + \delta_{ia}^2 \quad (4)$$

$$\delta_{ia}^2 = \delta_{ip}^2 + \delta_{ih}^2 \quad (5)$$

where ΔE_i^V is the molar energy of vaporization of substance i at zero pressure; δ_{id}, δ_{ia}, δ_{ip}, and δ_{ih} are defined as the dispersion, association, polar and hydrogen-bonding solubility parameters of substance i, respectively; the quantity c_{12} represents the intermolecular force acting between solvent molecule 1 and segment of polymer 2. In this paper, it is assumed that c_{12} is given by

$$c_{12} = \delta_{1d}\delta_{2d} + \delta_{1p}\delta_{2p} + \delta_{1h}\delta_{2h} \quad (6)$$

where $\delta_{1d}\delta_{2d}$ represents the nonpolar dispersion forces acting between the solute and the solvent, $\delta_{1p}\delta_{2p}$ the interaction between permanent dipole of the solute and that of the solvent, and $\delta_{1h}\delta_{2h}$ the pair interaction involved in any solvation which may occur in the solution except the interactions mentioned above. Using eq 4, 5, and 6, eq 3 can be put in the form

$$A_{12} = (\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2 = r_A^2 \quad (7)$$

On the other hand, an empirical equation proposed by Hansen[19] is

$$R_A^2 = 4(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2 \quad (8)$$

It might be expected from eq 7 or 8 that various polymer—solvent systems with the same value of r_A or R_A would show the same solubility (or solvent power), even if the three solubility parameters δ_d, δ_p, and δ_h are different in each system. Equations 7 and 8 are also in the form of the surface of the second order characterized by the values r_A and R_A in three dimensional space of the solubility parameter, δ_d, δ_p, and δ_h, respectively. This fact indicates that r_A or R_A have inherent values $r_{A,2}$ or $R_{A,2}$ for a given polymer. The inherent value satisfies the condition that the systems are soluble, for r_A (or R_A) $\langle r_{A,2}$ (or $R_{A,2}$) and are insoluble, for r_A (or R_A)$\rangle$ $r_{A,2}$ (or $R_{A,2}$).

Accordingly, r_A or R_A may be used as a measure of the solubility (or solvent power),

provided that a polymer—solvent system is represented by a point in the three-dimensional space of the solubility parameters δ_d, δ_p, and δ_h. The numerical factor 4 of the first term in eq 8 means that the dispersion term in the solubility parameter contributes twice as much as the other terms. In other words, the δ_d axis is elongated twice in the three-dimensional space of solubility parameters. By this procedure, eq 8 gives the equation of spherical surface with radius R_A.

Division of Solubility Parameter into Three Components According to Method II[19,31,42]

δ_i^2, as shown in eq 4, is divided into δ_{id}^2 and δ_{ia}^2 according to Blanks and Prausnitz[31,42] on the basis of the homomorph concept of Brown[44]. (The homomorph of a polar molecule corresponds to a nonpolar molecule with almost the same size and shape as those of the polar molecule, as in the case of a normal paraffin carbon for a linear polar molecule.)

The separation of δ_{ia}^2 into δ_{ip}^2 and δ_{ih}^2 in eq 5 has been done by a trial and error plotting technique assuming that the representative points for solvents dissolving a polymer should fall in the region characterized by the inherent length $r_{A,2}$ or $R_{A,2}$ of the polymer according to eq 7 or eq 8. The procedure will be mentioned in the following section.

Although δ_i^2 is divided accurately, the division of δ_{ia}^2 is thought to be reasonable by virtue of the fact that the evaluated values are in agreement with the values calculated by[19,33]

$$\delta_h=(5000N/V_1)^{1/2} \qquad (9)$$

$$\delta_p^2=W/V_1=\frac{12108}{V_1^2}\frac{\varepsilon-1}{2\varepsilon+n_D^2}(n_D^2+2)\mu_s^2\ , \qquad (\mathrm{cal/cm^3}) \quad (10)$$

where W is the interaction energy between spherical molecules with the dipole moment μ_s (Debye unit) at the center of the molecule, N the number of alcohol groups in the molecule, d the density (g/cm^3), ε the dielectric constant (the static value) and n_D the index of refraction for sodium D line.

Determination of Theta Temperature

The theta temperature was determined by plotting the reciprocal critical precipitation temperature (exactly, threshold precipitation temperature) $1/T_c(°K^{-1})$ measured with fractions of different molecular weights against the molecular size function $(x^{-1/2}+1/2x)$ according to the Flory formula[30]:

$$1/T_c=(1/\theta)[1+(1/\psi_1)(1/x^{1/2}+1/2x)] \qquad (11)$$

where ψ_1 is the entropy parameter.

RESULTS AND DISCUSSION

Light Scattering and Viscosity

The results of light scattering and viscosity measurements are summarized in Table I. The

Table I. Light-scattering and viscosity data for PPCS at 30°C[a]

Fractions	M_w $\times 10^{-4}$	Ethylbenzene		Toluene	
		$[\eta]$	k'	$[\eta]$	k'
(Type A)					
PF 1	179	1.240	0.42	1.453	0.48
2	123	0.957	0.48	1.100	0.50
3	72.1	0.723	0.52	0.855	0.48
4	57.0	0.605	0.56	0.709	0.50
5	42.3	0.517	0.50	0.586	0.44
6	30.5[b]	—	—	0.460	0.47
7	18.9	0.320	0.50	0.338	0.48
		Average	0.50		0.48
(Type L)					
LPF 6	4.52[b]	—	—	0.122	—
7	2.16[b]	—	—	0.076_5	—

[a] M_w, weight-average molecular weight; $[\eta]$, intrinsic viscosity (dl/g); k', Huggins constant.
[b] Values calculated from eq 12.

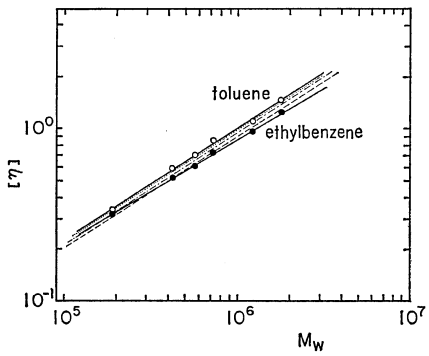


Figure 2. Double logarithmic plots of $[\eta]$ against M_w for PPCS in ethylbenzene (filled circles) and in toluene (open circles) at 30°C. Dotted, broken and chained lines represent the relationships obtained by Davis, Saito, and Noguchi, respectively.

Table II. Solubilities and solubility parameters for PPCS—Diluent systems at 25°C[a]

No.	r_A	R_A	Diluents	Solubilities	δ_s	δ_{ds}	δ_{ps}	δ_{hs}	μ_s	γ_s
1	0.45	0.64	1,2-Dichloroethane	+	9.76	8.85	2.6	2.0	2.06	0
2	0.63	1.66	1,1,2,2-Tetrachloroethane	+	9.85	9.15	2.5	2.56	0.0	0
3	0.72	1.63	*o*-Dichlorobenzene	+	9.98	9.39	3.1	1.6	—	—
4	0.85	1.03	Dichloromethane	+	9.93	8.71_5	3.1	3.0	1.55	0
5	0.89	1.61	Bromobenzene	+	9.78	9.25	2.2	2.5	—	—
6	1.16	1.58	2,2-Dichlorodiethyl ether	+	10.33	9.20	3.9	1.5	2.58	—
7	1.22	1.61	Methyl isoamyl ketone	+	8.55	7.80	2.8	2.0	—	—
8	1.25	1.12	Acetophenone	+	9.68	8.55	4.1	1.8	—	—
9	1.50	1.60	Chloroform	+	9.21	8.75	1.65	2.8	1.15	0
10	1.50	2.05	Pyridine	+	10.61	9.25	4.3	2.9	2.20	—
11	1.50	1.94	Butylcarbitol	+(∓)	8.96	7.80	3.1	3.1	—	6.37
12	1.52	2.36	Chlorobenzene	+	9.57	9.24	2.1	1.0	1.56	0
13	1.53	2.22	Methyl isobutyl ketone	+	8.57	7.49	3.1	2.0	—	—
14	1.63	2.16	Diethyl ketone	+	8.86	7.66	3.7	2.8	—	—
15	1.66	1.75	Trichloroethylene	+	9.28	8.78	1.4	2.6	0.9	0
16	1.68	1.55	1,1,1-Trichloroethane	+	8.57	8.19	2.15	1.0	1.79	0
17	1.73	2.05	Diisobutyl ketone	+	8.17	7.77	1.8	2.0	2.7	1.58
18	1.85	1.44	Cyclohexanone	−	9.88	8.65	4.35	2.5	2.8	23.98
19	1.88	2.06	Tetrahydrofuran	+	9.52	8.22	2.7	3.9	—	—
20	1.90	2.12	1,2-Dibromoethane	+	10.40	8.10	2.5	3.8	1.12	0
21	1.92	1.50	Methyl ethyl ketone	+	9.27	7.77	4.45	2.5	2.75	4.03
22	2.04	2.47	Butyl acetate	+	8.46	7.67	1.8	3.1	1.84	1.36
23	2.18	2.63	Tetraline	+	9.50	9.4	1.0	1.4	—	—
24	2.22	2.73	*n*-Propyl acetate	+	8.74	7.61	2.2	3.7	1.86	—
25	2.23	2.68	*n*-Amyl acetate	+	8.5	7.66	1.6	3.3	1.91	—
26	2.36	3.51	Isopropyl acetate	+(∓)	8.45	7.04	3.0	3.6	1.9	1.41
27	2.38	3.27	*tert*-Butyl acetate	+(∓)	8.1[b]	7.20	1.8	3.2	—	1.19
28	2.43	3.06	Isoamyl acetate	+	8.32	7.45	1.55	3.4	1.8	1.01
29	2.55	2.56	*o*-Xylene	+	9.0	8.61	0.5	2.53	—	—
30	2.54	3.52	Ethyl ether	−	7.62	7.05	1.4	2.5	1.15	—
31	2.56	3.25	Isobutyl acetate	+	8.42	7.35	1.8	3.7	1.85_4	1.17
32	2.61	2.73	Styrene	+	9.30	9.01	0.4	2.0	—	—
33	2.62	2.55	Xylene (Commercial)	+	8.80	8.65	0.5	1.5	—	0
34	2.66	3.10	Ethylcarbitol	+(∓)	9.6	7.57	5.1	3.0	—	7.75
35	2.74	2.66	Toluene	+	8.91	8.74_5	0.55	1.0	0.39	0
36	2.74	2.92	*p*-Dioxane	+	9.87	8.92_5	0.65	3.6	0.45	3.92
37	2.75	2.72	*m*-Xylene	+	8.80	8.51	0.3	2.3	0.37	0
38	2.77	2.80	Benzene	+	9.15	8.99	0.5	1.0	0	0
39	2.81	3.43	Ethyl acetate	+	9.10	7.44	2.6	4.5	1.81	1.42
40	2.81	3.24	Acetone	−	9.77	7.58	5.1	3.4	2.72	4.93
41	2.84	2.69	Isopropylbenzene	−(±)	8.52	8.15	0.5	2.4	0.75	0
42	2.86	3.00	Ethylbenzene	+(±)	8.80	8.66_5	0.4	0.7	0.35	0
43	2.90	3.57	Aniline	+	11.02	9.53	2.45	5.0	1.51	—
44	3.01	3.39	Nitrobenzene	+	10.62	9.16_5	6.2	2.0	3.99	0
45	3.05	3.03	*p*-Xylene	+	8.75	8.45	0	2.3	0.00	0
46	3.07	4.31	Isopropyl ether	−	7.03	6.69	1.0	1.9	1.22	—
47	3.08	3.57	Methyl acetate	−	9.49	7.56	2.9	4.9	1.75	1.70
48	3.10	3.32	Tetrachloroethylene	−(±)	9.36	9.25	0	1.44	0.0	0
49	3.36	3.80	Ethyl formate	−	9.55	7.58	3.2	5.2	1.94	1.81
50	3.48	3.95	Diethyl malonate	−	9.5[b]	7.57	2.3	5.3	2.54	1.25
51	3.68	4.34	*n*-Propyl formate	−	9.56	7.33	2.6	5.5	1.89_3	—

Table II. (continued)

No.	r_A	R_A	Diluents	Solubilities	δ_s	δ_{ds}	δ_{ps}	δ_{hs}	μ_s	γ_s
52	3.74	3.61	Carbon tetrachloride	−(±)	8.65	8.65	0	0	0.00	0
53	3.81	3.70	Cyclohexane	−	8.18	8.18	0	0	0	0
54	3.88	4.16	1-Octanol	−	9.66	7.88	1.5	5.6	1.68	2.98
55	3.91	3.94	Methylcyclohexane	−	7.8	7.8	0	0	0	0
56	4.05	4.33	Heptane	−	7.4	7.4	0	0	0.00	0
57	4.12	5.27	Hexane	−	7.24	7.24	0	0	0.08	0
58	4.26	4.59	Butylcellosolve	−	10.24	7.77	2.2	6.2	—	7.69
59	4.33	4.83	Diacetone alcohol	−	10.18	7.65	4.0	5.8	2.5	13.72
60	4.36	4.69	1-Hexanol	−	10.70	7.75	3.8	6.3	1.7	—
61	4.50	4.67	*m*-Cresol	−	11.11	9.14	2.35	6.6	—	—
62	4.64	4.92	Benzyl alcohol	−	11.97	9.04	2.4	6.8	1.66	—
63	4.70	4.67	Cyclohexanol	−	10.95	8.50	2.2	6.6	1.9	5.78
64	4.82	5.12	1-Pentanol	−	10.61	7.81	2.2	6.8	1.8	4.23
65	4.88	5.32	3-Methyl-1-butanol	−	10.43	7.49	2.4	6.8	1.82	—
66	4.97	5.44	2-Methyl-2-butanol	−	9.70	7.42	2.0	6.8	—	—
67	4.98	5.10	*N,N*-Dimethylformamide	+	12.14	8.52	6.7	5.5	3.37	40.98
68	5.35	5.80	2-Methyl-2-propanol	−	10.82	7.45	2.5	7.3	1.66	—
69	5.44	5.91	2-Methyl-1-propanol	−	11.12	7.40	2.8	7.4	—	—
70	5.47	5.79	2-Butanol	−	10.85	7.72	1.9	7.4	—	4.15
71	5.49	5.96	1-Butanol	−	11.30	7.81	2.75	7.55	1.68	4.27
72	5.70	6.07	Diethyl oxalate	−	11.1[b]	7.59	2.5	7.7	2.49	0.59
73	6.04	6.36	2-Propanol	−	11.52	7.70	3.2	8.1	1.68	—
74	6.05	6.29	Ethylcellosolve	−	11.88	7.85	5.2	7.2	2.08	7.81
75	6.09	6.34	Methylcellosolve	−	12.06	7.90	4.5	8.0	2.04	8.33
76	6.28	6.58	1-Propanol	−	11.97	7.75	3.25	8.35	1.65_7	5.21
77	6.41	6.53	Acetonitrile	+	11.9	7.50	8.8	3.0	3.37	2.26
78	7.43	7.71	Ethanol	−	12.92	7.73	4.3	9.4	1.68	8.47
79	9.43	9.78	Methanol	−	14.28	7.42	6.1	11.0	1.66_4	—
80	9.52	9.71	1,2-Propandiol	−	14.80	8.24	4.6	11.55	—	—
81	11.23	11.42	1,2-Ethanediol	−	16.30	8.25	5.8	13.05	—	—
82	12.35	12.54	1,2,3-Propantriol	−	21.10	8.46	5.4	14.3	—	—
83	—	—	*sec*-Butyl acetate	+	8.2	—	—	—	—	1.17
84	—	—	*sec*-Amyl acetate	+	8.3	—	—	—	—	—
85	—	—	Carbitol acetate	+	8.5	—	—	—	—	1.90
86	—	—	Isopropyl chloroacetate	+(±)	9.3[b]	—	—	—	—	1.3
87	—	—	Ethyl chloroacetate	+(±)	10.0[b]	—	—	—	—	1.1
88	—	—	Benzyl acetate	+	10.1[b]	—	—	—	1.80	—
89	—	—	Methyl chloroacetate	−(±)	10.6[b]	—	—	—	—	0.95
90	—	—	Dibutyl phthalate	+	9.3	—	—	—	2.4	0.63
91	—	—	Diethyl phthalate	+	10.0	—	—	—	—	0.73
92	—	—	Dimethyl phthalate	−	10.7	—	—	—	—	0.80
93	—	—	Diisopropyl ketone	+	8.0	—	—	—	2.7	—
94	—	—	Methyl *n*-amyl ketone	+	8.5	—	—	—	2.7	1.42
95	—	—	Methyl propyl ketone	+	8.9	—	—	—	2.7	—
96	—	—	Phenetol	+	9.1[b]	—	—	—	1.0	—
97	—	—	Anisole	+	9.4[b]	—	—	—	1.20	—

[a] +, soluble; −, insoluble; ±, U.C.S.T.; ∓, L.C.S.T.
[b] Calculated values from Small's method.

plots of $\log[\eta]$ against $\log M_w$ for PPCS in toluene and ethylbenzene at 30°C are shown in Figure 2. The straight full lines are represented by

$$[\eta]=12.3_5\times10^{-5}M_w^{0.653} \quad \text{in toluene} \tag{12}$$

$$[\eta]=21.7_9\times10^{-5}M_w^{0.601} \quad \text{in ethylbenzene} \tag{13}$$

The dotted, broken, and chained lines in Figure 2, represent the $[\eta]$—M_w relationships obtained by Davis[6] (at 25°C), by Saito[7] (at 30°C), and by Noguchi, *et al.* (at 30°C), respectively, for PPCS in toluene. It is seen that result in this paper is in good agreement with the one obtained by Davis[6]. The exponents of M_w in eq 12 and 13 indicate that toluene is an intermediate solvent and ethylbenzene is a rather poor solvent.

Solubility Relationships

According to the concept in the previous sections, the results are shown as representative points in the three-dimensional space of solubility parameters in Figures 3 (a, b, c, and d), 4 (a, b, and c) and 5 (a, b, and c). Figure 3 shows the results analyzed according to Method I and Figures 4 and 5 are analyzed by Method II. The numbers described in these figures mean the numbers of solvents given in Table II. r_A and R_A values obtained from both eq 7 and 8 are also listed in Table II with the numerical

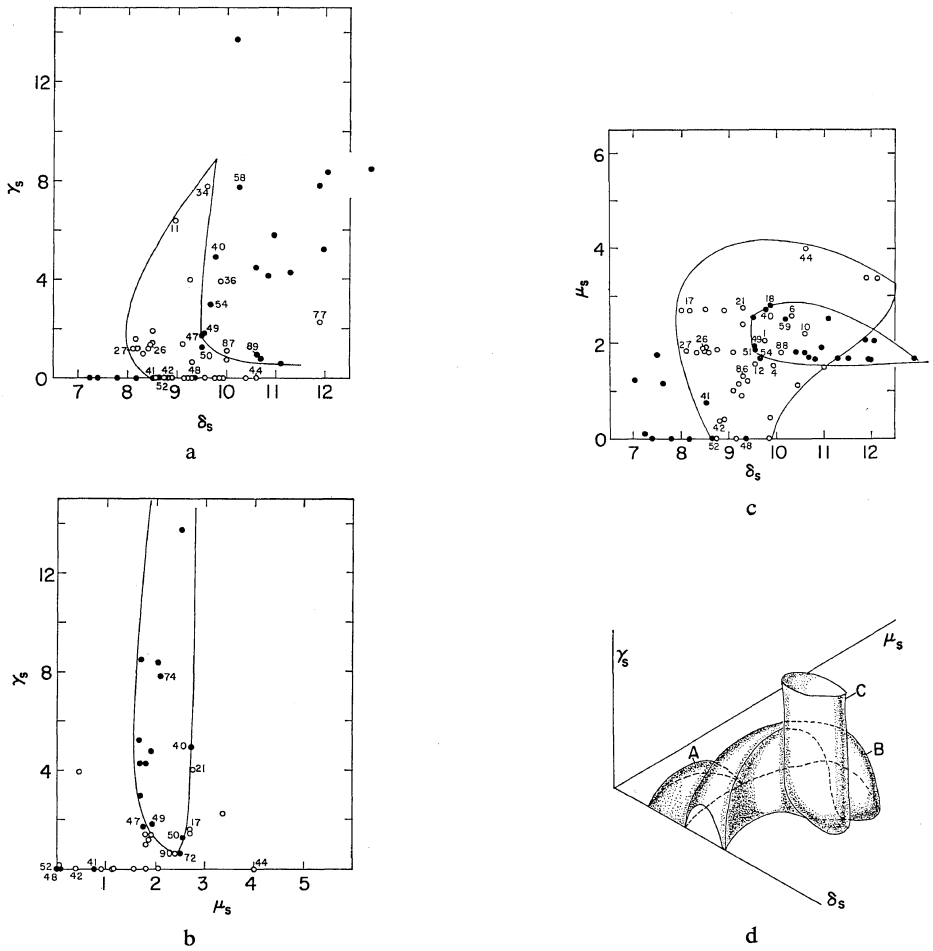


Figure 3. Solubility of PPCS in diluents (Method I): (a) γ_s *vs.* δ_s; (b) γ_s *vs.* μ_s; (c) μ_s *vs.* δ_s; (d) the stereograph of solubility for PPCS—diluents. Numbers described in Figures 3, 4 and 5 show the solvent' number given in Table II.

values of three components of the solubility parameter. Table II indicates that the solubility for the PPCS—solvent systems is not always predicted by the parameter δ_s alone, because some of solvents dissolve PPCS but others do not, even though the values for their solubility parameters, δ_s, are almost the same. This fact leads to the introduction of other additional parameters for the prediction of solubility.

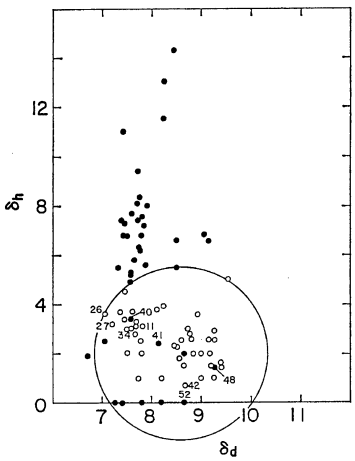
The Analysis of the Solubility by Method I[15]

Figure 3a corresponding to Small's diagram[28] is the correlation of γ_s *vs.* δ_s, Figure 3b for that of γ_s *vs.* μ_s and Figure 3c for that of μ_s *vs.* δ_s. The full lines in these figures show the boundaries which distinguish solvents dissolving PPCS (open circles) from non-solvents (filled circles) for PPCS at room temperature. The stereograph is schematically shown in Figure 3d, where the soluble region B exists between the insoluble regions A and C. From these figures and Table II, it is seen that the introduction of the concepts of μ_s and γ_s is successful in the interpretation of solubility, qualitatively, in spite of the demerit that the surface of soluble region is a very complex shape. The results obtained from the above discussion are summarized as follows

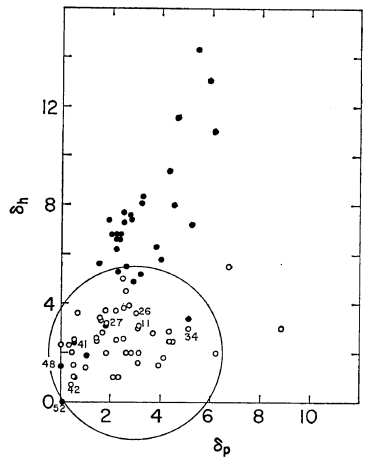
(1) the contribution of δ_s is large for a non-polar θ solvent ($\mu_s=0$, $\gamma_s=0$).

(2) that of γ_s is large for the strong polar θ solvent, such as carbitols ($\gamma_s=6$—8).

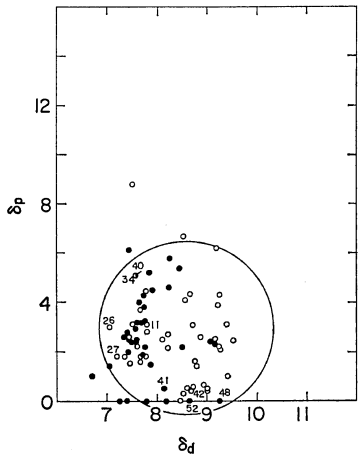
(3) esters to become θ solvents have the intermediate property between (1) and (2).



a



b



c

Figure 4. Solubility of PPCS in diluents (Method II): (a) δ_h *vs.* δ_d; (b) δ_h *vs.* δ_p; (c) δ_p *vs.* δ_d.

The complex appearance of the boundary surface may be due to the following:

(1) δ_s always contains the contribution of both μ_s and γ_s for the solvent having more or less polarity.

(2) The value of μ_s used in present procedure is a rough measure of the polar component of solubility parameter.

(3) The estimation of γ_s depends on the method of measurements and there are no definable correlations[32] amongst the values estimated by the different methods.

The Analysis of the Solubility by Method II[19]

Correlation of δ_{1h} *vs.* δ_{1d} is shown in Figure

4a, that of δ_{1h} *vs.* δ_{1p} in Figure 4b and that of δ_{1p} *vs.* δ_{1d} in Figure 4c. In Figures 4a and 4b, almost all the open circles are separated from the filled circles by a large circle which means that that is the boundary of the soluble region, while, in Figure 4c, both circles are placed almost in the same region. However, it is evident from Figures 4a and 4b, and the values of r_A in Table II that the filled circles in Figure 4c are actually located outside the sphere which represents the soluble region, because this figure is one of the projection charts. These figures correspond to Figures 3a, 3b, and 3c, respectively. δ_{1d}, δ_{1p}, and δ_{1h} in eq 7 and 8 are already known parameters whose values are given in Table II, while values of δ_{2d}, δ_{2p}, δ_{2h} and $r_{A,2}$ (or $R_{A,2}$) are determined by a trial and error method from Figures 4a, 4b, and 4c, according to Hansen[19]. As a result, almost all the solvents dissolving PPCS are involved in the spherical region which is expressed by eq 7 with $r_{A,2}=3.06$, $\delta_{2d}=9.0$, $\delta_{2p}=3.0$, and $\delta_{2h}=2.2$ or by eq 8 with $R_{A,2}=3.51$, $\delta_{2d}=8.6$, $\delta_{2p}=3.0$, and $\delta_{2h}=2.0$. Solubility parameters obtained from these three components for PPCS are $\delta_2=(\delta_{2d}^2+\delta_{2p}^2+\delta_{2h}^2)^{1/2}=9.7$ from eq 7 and 9.3 from eq 8, respectively. The value calculated by Small's method is close to the value obtained from eq 7 (*i.e.*, $\delta_2=ca.$ 9.7). In particular, the solubility relationships for PPCS—esters systems are shown in Figure 5a, 5b, and 5c, because these systems have both UCST and LCST. Figures 4 and 5, and Table II seem to indicate that these solubility relationships for PPCS can be more satisfactorily explained by Method II than by Method I.

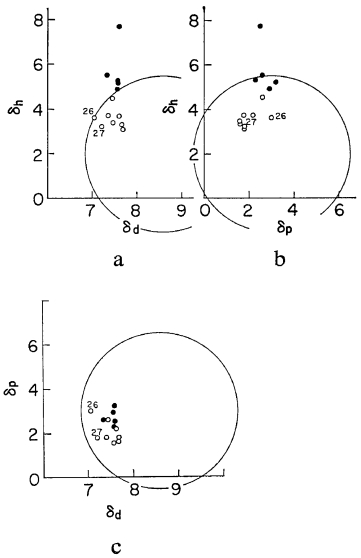


Figure 5. Solubility of PPCS in esters (Method II): (a) δ_h *vs.* δ_d; (b) δ_h *vs.* δ_p; (c) δ_p *vs.* δ_d.

The result of the analysis by Method II suggests that the difference between the PPCS—solvent system with LCST and that with UCST is reflected in the relative contribution of the three components, δ_d, δ_p and δ_h, rather than in the structure of solvent, as seen in Table II and Figure 5. Almost all θ solvents are nearly on the surface of the soluble region shown by the sphere whose radius corresponds to $R_{A,2}$. The correlation[45] between $R_{A,2}$ and δ_2 is shown in Figure 6 with the published data[19]. $R_{A,2}$ increases

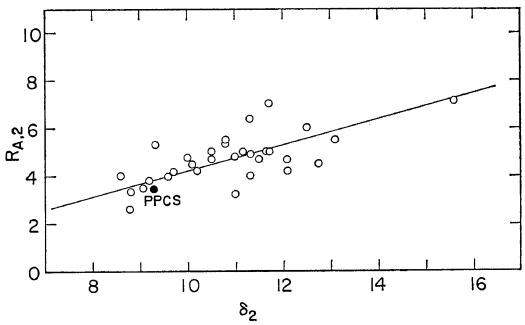


Figure 6. The relationship between $R_{A,2}$ and δ_2. Filled circle denotes that of PPCS.

with increasing δ_2, although the points scatter somewhat about the full straight line. The concept that the soluble region for a polymer lies within the sphere of the radius $R_{A,2}$ corresponds to the conventional Hildebrand idea that the difference between the solubility parameter of a solvent and that of a polymer is within a constant value. Thus, $R_{A,2}$, the maximum radius of the soluble region where θ solvents exist in general, is presumed from the value of δ_2, if if the δ_2 value is known.

Equations 7 and 8, however, have the following faults: (i) the solubility of the solvent containing a large polar component, such as some nitrogen compounds and ketones, is not adequately explained. (ii) The assumption of eq 6 to derive eq 7 and the empirical constant in eq 8 are

uncertain on the theoretical basis, although the reasonable values of solubility parameters evaluated from eq 9 and 10 are used. R_A value in the empirical equation (eq 8) is not directly related to χ (or χ_H). r_A value in eq 7 is related to χ (or χ_H) rigorously but gives a value of χ (or χ_H, *e.g.*, χ_H=*ca.* 0.6—2.2 for θ solvents) larger than the expected value. (iii) The sign of the heat of mixing described in the following section cannot be explained. In spite of these faults in eq 7 and 8, r_A or R_A plays an important role in the prediction of solubility as seen in above discussion.

As pointed out recently by Patterson[37], the entropy of mixing in polymer solutions is strongly affected by differences in free volume between the polymer and the solvent. In most typical cases, the solvent is more closely packed than the polymer. The effect of free volume, which has been discussed in detail by

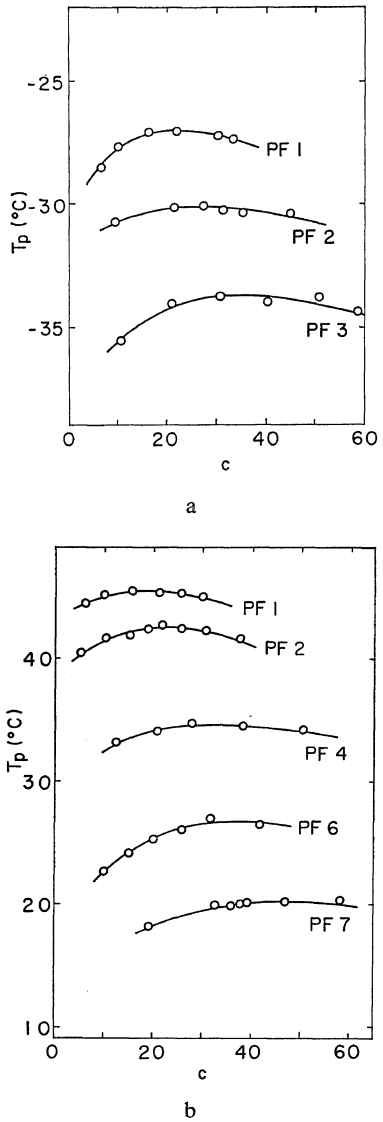


Figure 7. Phase diagrams for PPCS in aromatic hydrocarbons: (a) in ethylbenzene; (b) in isopropylbenzene.

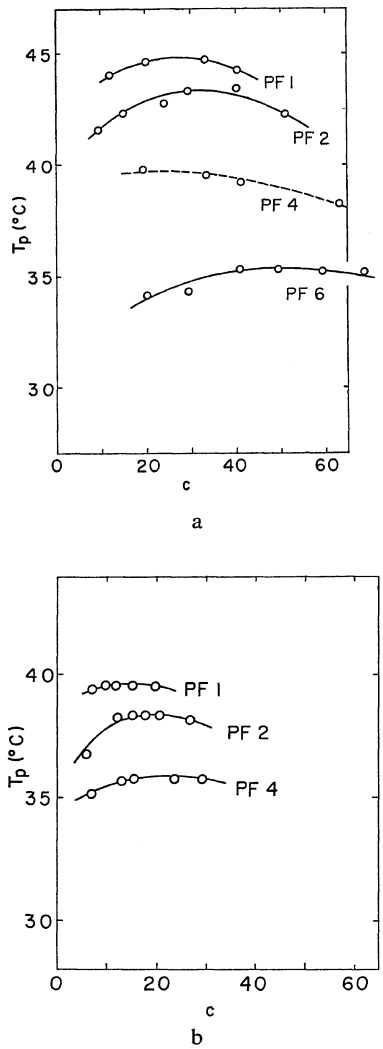


Figure 8. Phase diagrams for PPCS in chlorinated hydrocarbons: (a) in carbon tetrachloride; (b) in tetrachloroethylene.

Prigogine[38], Flory[39], and Patterson[40], is not apparently taken into account in the solubility parameter theory mentioned above. Patterson[40,41] has also pointed out that the empirical success achieved by the solubility parameter theory may be due to the fact that the solubility parameter is a single quantity which reflects both the intermolecular forces and the free volume of a liquid, and remarkably similar predictions are actually obtained from the solubility parameter theory and the corresponding state theory on the Flory model of liquid state[41], and that, as a result, the great popularity of the solubility parameter approach is entirely justified.

In connection with Patterson's suggestions, it is worth-while considering the χ parameter,

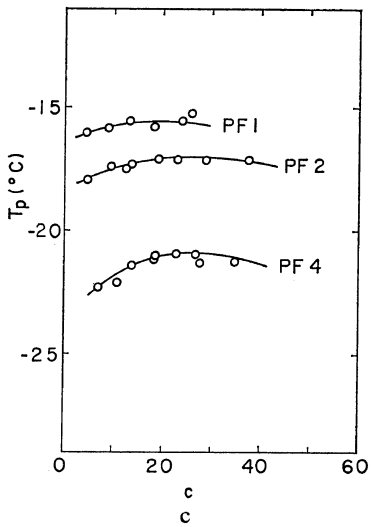
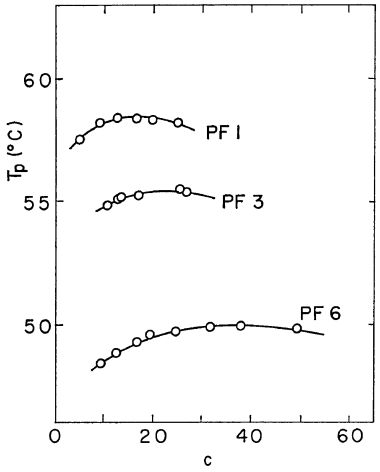
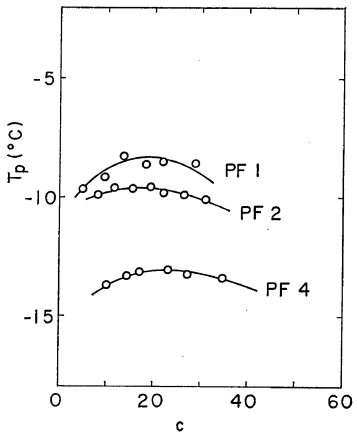


Figure 9. Phase diagrams for PPCS in chlorinated esters: (a) in methyl chloroacetate; (b) in ethyl *m*-chloroacetate; (c) in isopropyl chloroacetate.



a



b

which is rewritten into a similar form of a normal solubility parameter with eq 4, 5, and 7 by

$$\chi=\chi_S+(V_1/RT)\sum_{j=d,p,h}(\delta_{1j}-\delta_{2j})^2 \qquad (2')$$

$$\delta_i^2=\Delta E_i^v/V_i=\sum_{j=d,p,h}\Delta E_{ij}^v/V_i$$
$$=\sum_{j=d,p,h}\delta_{ij}^2 \qquad (i=1 \text{ or } 2) \qquad (4')$$

If each general solubility parameter δ_{ij}^2 plays the same role in a solution as well as a normal solubility parameter does, Patterson's indications will also fit the general solubility parameter theory. In spite of this situation, the phenomena on LCST in PPCS—diluent systems cannot be sufficiently explained, especially the appearance of LCST below the normal boiling point of the solvent, because this LCST is not corresponding to the behavior of Prigogine—Patterson type. Hence, it is necessary to introduce another model for the explanation of this LCST.

Phase Relationships

Phase diagrams of PPCS in aromatic and chlorinated hydrocarbons, chlorinated esters, esters and carbitols are shown in Figures 7—11. It should be noted that some of PPCS—ester systems have UCST and others show LCST in spite of being the same chemical type.

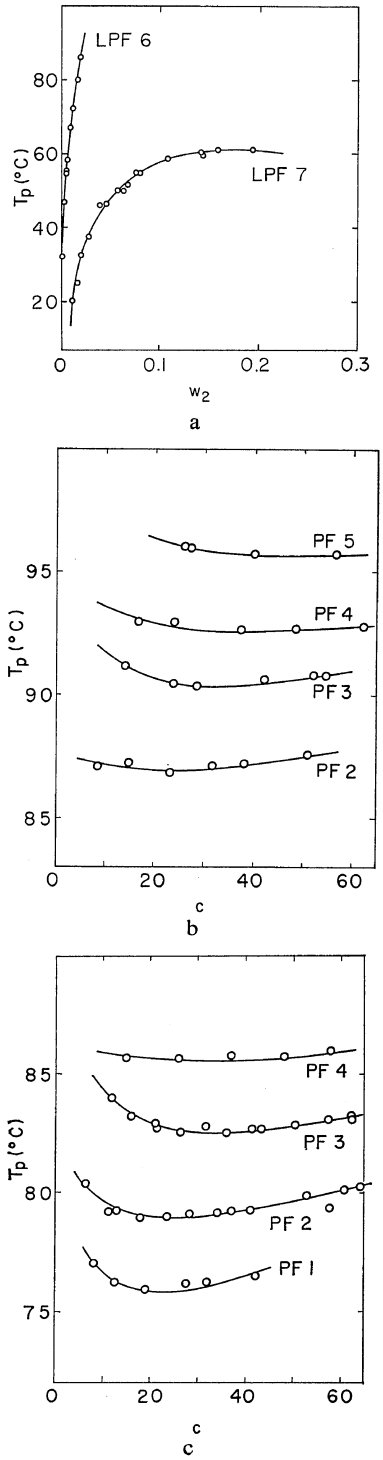


Figure 10. Phase diagrams for PPCS in esters: (a) in methyl acetate (w_2, weight fraction); (b) in isopropyl acetate; (c) in *tert*-butyl acetate.

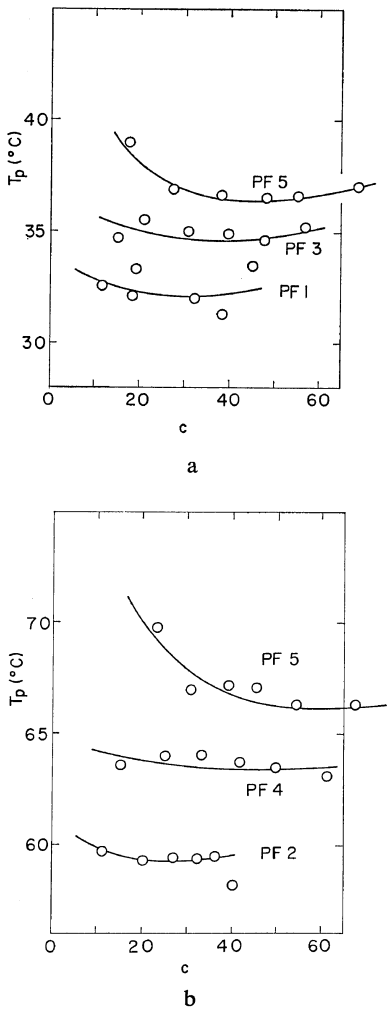


Figure 11. Phase diagrams for PPCS in carbitols: (a) in ethylcarbitol; (b) in *n*-butylcarbitol. T_p denotes precipitation temp; c denotes weight concentration.

The reciprocal critical precipitation temperature, $1/T_c$, is plotted against $(x^{-1/2}+1/2x)$ in Figure 12, from which the θ temperature and the entropy parameter ψ_1 were determined according to eq 11. This figure seems to indicate that eq 11 can be also applied to LCST system[43]. Using the values of θ and ψ_1, the enthalpy parameter κ_1 and the free energy parameter χ_1 were estimated according to the Flory expressions, $\kappa_1=\theta\psi_1/T$ and $\chi_1=0.5+\kappa_1-\psi_1$. The numerical values of these parameters are also shown in Table III. Both ψ_1 and κ_1 are negative for

Table III. Theta temperatures and thermodynamic parameters of theta solvents for PPCS

Theta solvents	θ, °C	ψ_1	κ_1(30°C)	χ_1(30°C)
Aromatic hydrocarbons				
Ethylbenzene	−14.7	0.176	0.150	0.474
Isopropylbenzene	59.0	0.226	0.204	0.478
Chlorinated hydrocarbons				
Carbon tetrachloride	50.7	0.412	0.440	0.528
Tetrachloroethylene	44.4	0.546	0.572	0.618
Chlorinated esters				
Methyl chloroacetate	64.6	0.433	0.482	0.549
Ethyl chloroacetate	−1.8	0.348	0.312	0.464
Isopropyl chloroacetate	−8.2	0.317	0.277	0.460
Esters				
Isopropyl acetate	75.5	−0.360	−0.414	0.446
tert-Butyl acetate	65.4	−0.323	−0.361	0.462
Carbitols				
Ethylcarbitol	27.8	−0.696	−0.691	0.505
n-Butylcarbitol	50.1	−0.489	−0.521	0.468

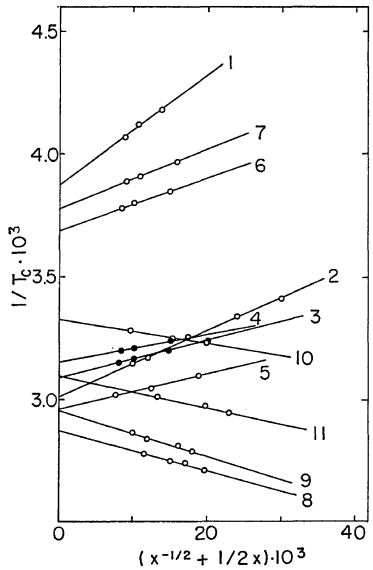


Figure 12. Reciprocal critical precipitation temperature of PPCS in diluent, $1/T_c$, plotted against $(x^{-1/2}+1/2x)$: (1) ethylbenzene; (2) isopropylbenzene; (3) carbon tetrachroride; (4) tetrachloroethylene; (5) methyl chloroacetate; (6) ethyl chloroacetate; (7) isopropyl chloroacetate; (8) isopropyl acetate; (9) *tert*-butyl acetate; (10) ethylcarbitol; (11) *n*-butylcarbitol.

LCST systems and positive for UCST ones. The heat of mixing for the corresponding monomer in ester systems is shown in Table IV. It

Table IV. Heat of mixing ΔH of *p*-chlorotoluene solutions at room temperature

Systems	w_2[a]	ΔH(arb.)[b]
p-Chlorotoluene —Methyl acetate	0.31	3.18±0.02
p-Chlorotoluene —Ethyl acetate	0.31	−0.04±0.02
p-Chlorotoluene —Isopropyl acetate	0.31	−0.25±0.02

[a] w_2, weight fraction of *p*-chlorotoluene.
[b] (arb.), arbitrary unit.

is considered from these results that LCST system corresponds to an exothermic solution, while the UCST system to an endothermic one. χ_1 value, one of factors deciding the solubility, does not differ greately, irrespective of the difference between the endothermic solution and the exothermic one.

CONCLUSIONS

It is concluded that in predicting the solubility of polar polymers such as PPCS in diluent, a three-dimensional plot employing three components on the basis of the solubitity parameter theory is more reliable than the conventional plot with only one solubility parameter δ_s, though the treatment is somewhat trouble some. In particular, the prediction by Method II is quantitatively better than that by

Method I. According to the former treatment, the difference between LCST and UCST seems to be reflected in the relative contribution of the three components rather than in the structure of solvent.

From the signs of thermodynamic interaction parameter and the heat of mixing for the corresponding monomer—esters, it is considered that LCST and UCST systems correspond to exothermic and endothermic solutions, respectively. Another interpretation on this problem has been attempted on the basis of the statistical thermodynamics and will be presented in this series in future.

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