

Reconsiderations on The χ -Parameter in Thermodynamics of Polymer Solutions

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SYNOPSIS: Historical evolution of the χ -parameter, a characteristic parameter in thermodynamics of polymer solutions is reconsidered. For this purpose, five solution models are classified in the route of evolution. A general formula for χ , in which the concentration- and molecular weight dependences are taken into account, is semi-empirically derived. Formulas for the chemical potentials of the solvent and the solute, $\Delta\mu_0$ and $\Delta\mu_1$, are derived for polydisperse polymer solutions. The concentration-dependence coefficients are experimentally evaluated by various methods. Cloud point curve (CPC) method and critical solution point (CSP) method, both established by the Kamide and his coworkers, are described in some details. The both methods are proved to be the best for accurate estimation of the first and second coefficients of the polymer concentration ϕ_1 , p_1 and p_2 . By use of accurate p_1 and p_2 values we can determine ϕ_1 at CSP ϕ_1^c which agrees with experimental ϕ_1^c . Phase-separation theory by Kamide, in which the polymolecularity of polymer and p_1 are considered, is compared with experiments. By simulation of polymer solutions, based on the lattice model, the concentration dependence of χ is examined. The theory for quas-binary (polydisperse polymer/solvent) system is extended to the cases of polymer blend and quasi-ternary system, compared with actual experiments.

1. Introduction

In the thermodynamics of the solutions (or the mixture) the most fundamental physical quantity is the chemical potential of the solvent $\Delta\mu_0$ and of the solute $\Delta\mu_1$, (i.e., the partial molar change of Gibbs energy of mixing of the solute and the solvent). Then, **the determination of $\Delta\mu_0$ (more generally, $\Delta\mu_i$ ($i=1\sim m$)) as function of pressure P and temperature T is our financial goal of the study of thermodynamics of polymer solutions.**

There are various methods for evaluating $\Delta\mu_0$ as demonstrated in Fig.1.^{5,6}

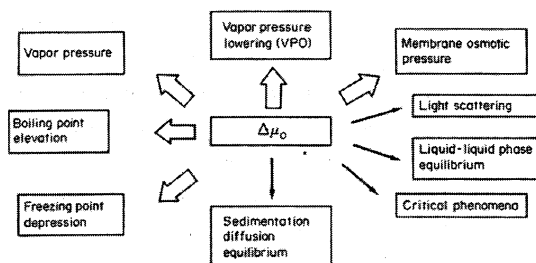


Figure 1 Various thermodynamic properties closely correlated with the chemical potential of the solvent $\Delta\mu_0$ in a polymer solution. Unfilled arrows denote colligative properties; filled arrows denote other properties.

At embryo stage of the polymer science (the 1920s–the 1930s) the colligative properties of polymer solution was particularly important to characterize the molecular mass (molecular weight) and $\Delta\mu_0$.

For this purpose, vapor pressure, boiling point elevation, and freezing point depression, were utilized (Fig.1). They were rather less accurate. In the 1940~60s membrane osmometry and light scattering method became popular. The liquid phase-separation and the critical phenomena were studied later. In 1990 Kamide stated in his book⁶, 'However, we dare say that a more comprehensive study on the thermodynamics of phase equilibria and critical phenomena of polymer solutions, the main topics of this book, started only in the late 1960s, because this kind of study requires computer technology, which only at that time became readily available to polymer scientists. In particular, the establishment of the theory, which permits the accurate theoretical prediction of the spinodal, binodal, cloud point and critical point for multicomponent polymer solutions is undoubtedly one of the most significant milestones achieved in polymer science over the last 20 years.'

If once $\Delta\mu_i$ or $\Delta\mu_0$ is determined experimentally by some method we can calculate other quantities such as vapor pressure, osmotic pressure, and critical point from μ_0 or $\Delta\mu_i$ determined in advance.

The above mentioned physical quantities are not only very important from the standpoint of pure science but also play significant role in industrial production of membranes by casting methods, fibers by wet spinning, and paints, all of which are dominated by the thermodynamics of phase separation of polymer solutions. The establishment of this kind of science is of paramount importance for the process control, development of the new innovative processes and control of the polymer supermolecular structure which governs the performance of membranes, fibers, and paints.

Thermodynamics of polymer solution had, of course, its root in the classical thermodynamics which had emerged in the late 19th century. Then, the first model of the polymer solutions was used an ideal solution. Fig.2 demonstrates the routes of evolution of the polymer solution models, from which the chemical potentials, $\Delta\mu_0$ and $\Delta\mu_1$, could be evaluated. Models were improved from Model I to Model V so as to minimize the disparity between the theoretical prediction and the actual experiments. Note that rapid and eminent progress, in particular since 1950s, of measuring technology enabled to get useful information from accurate measurements to judge adequacy of the theory. The χ -parameter was at first time introduced in the 1940s by Flory⁸²⁻⁸⁶ and Huggins⁸⁷⁻⁹² in Model III to represent the gap of $\Delta\mu_0$ between real polymer solution and Model II. Then, χ -parameter is a characteristic parameter for the polymer solutions. The physical meaning of χ -parameter changed during evolution of model. Now, in Model V, χ -parameter is not simply the polymer-solvent interaction parameter as Flory first supposed.

I had a keen interest in the phase equilibria of the polymer solutions when I was a university student at Kanazawa in 1905s and my interest was strongly and continuously motivated to carry out the theoretical and experimental studies on phase equilibria of the polymer solutions. This has resulted in the publication of two books,^{6,7} five book chapters¹⁻⁵ and more than 50 papers⁸⁻⁶⁵ since 1968. As an extension of the basic theory, the thermodynamics of membrane formation by solvent casting method was proposed.⁶⁶⁻⁷⁵

In 1972 I had an opportunity of being invited to speak of some theoretical and experimental results on the phase-equilibrium as one of main lecturers at IUPAC International Polymer symposia, Helsinki.^{2,8-17} Prof. P.J.Flory and Dr. M. L. Huggins, both the founders of the thermodynamics of polymer solution, sat on fore front seats of a lecture room at The Finlandia Hall. Afterwards Huggins told me that you did what I had wanted to do.

In this article the historical development of the thermodynamics of polymer solution, particularly the χ -parameter, will be briefly reviewed.

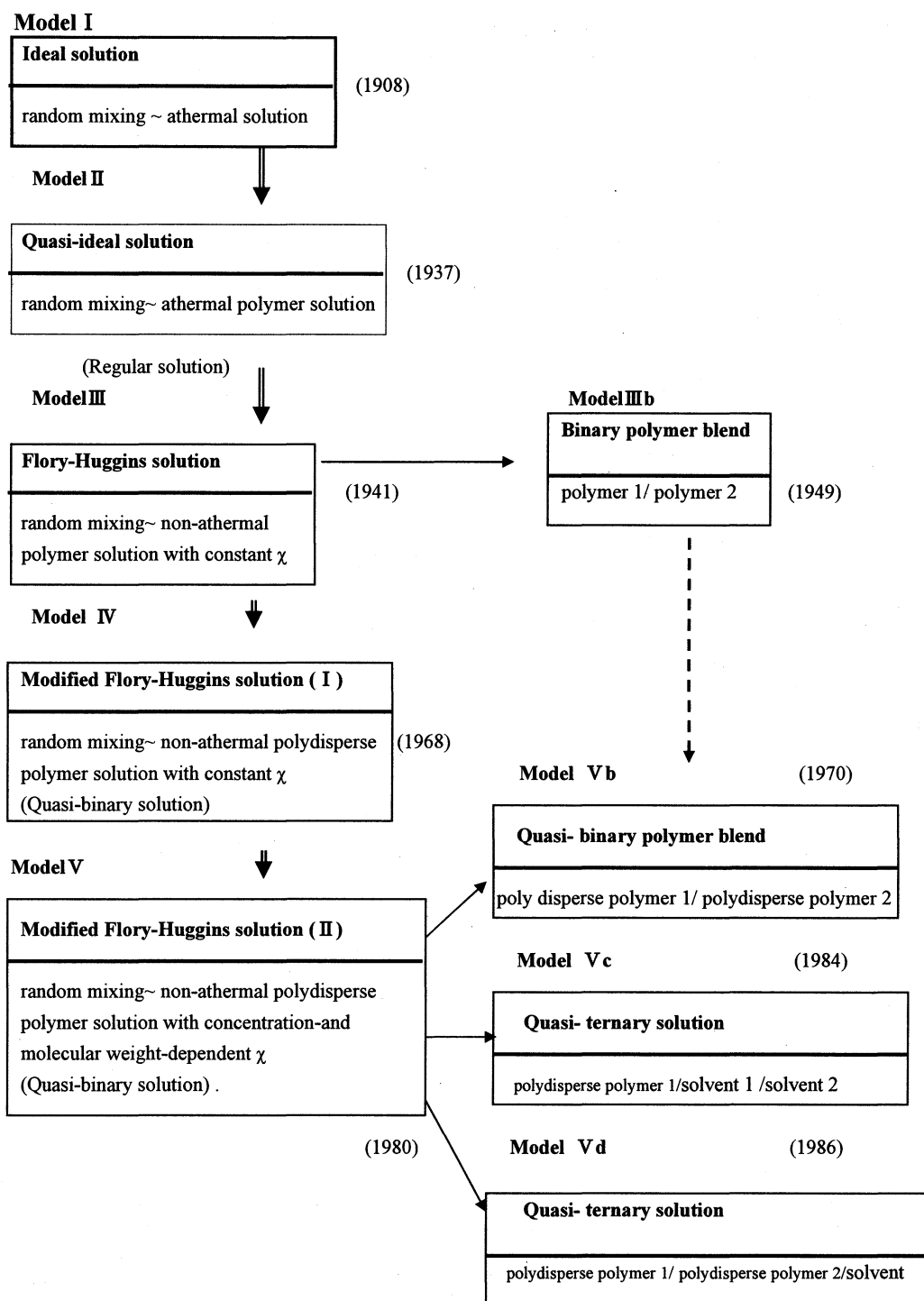


Figure 2 Evolution of the solution model employed in thermodynamics of polymer solutions

2. General equations of chemical potentials for non-ideal solutions consisting of multicomponent polymer homologue and single solvent

2.1 Model I : Ideal solution^{6,7}

When the chemical potential μ_i of a solution is expressed as

$$\mu_i(T, P) = \mu_i^0(T, P) + RT \ln x_i \quad (1)$$

the solution is defined as **ideal solution**⁷⁶. Here, $\mu_i^0(T, P)$ means the chemical potential of species i at pure state, which is a function of temperature T and pressure P , and x_i is the relative proportion of i th component in the solution (known as the mole fraction of species i),

$$x_i = \frac{N_i}{\sum_i N_i} \quad (2)$$

$R = kN_A$ is the gas constant, N_i the number of moles of species i , $\sum_i N_i (=N)$ the total number of moles, k the Boltzmann constant and N_A the Avogadro's number. Gilvert Newton Lewis named the solution which satisfies eq. (1), as **ideal solution**.⁷⁶

Difference of the partial molar enthalpies H_i in the solution and H_i^0 in the pure state ΔH_i^{id} is given by

$$\Delta H_i^{id} = H_i - H_i^0 = 0 \quad (3)$$

and difference of the partial molar entropy S_i in the solution and S_i^0 in the pure state ΔS_i^{id} is

$$\Delta S_i^{id} = S_i - S_i^0 = -R \ln x_i \quad (4)$$

The molar heat of mixing $\Delta \bar{Q}_{mix}$ and the molar entropy of mixing $\Delta \bar{S}_{mix}$ are defined by:

$$\Delta \bar{Q}_{mix} = \sum x_i (H_i - H_i^0) \quad (5)$$

and

$$\Delta \bar{S}_{mix} = \sum x_i (S_i - S_i^0) \quad (6)$$

For ideal solution

$$\Delta \bar{Q}_{mix}^{id} = 0 \quad (7)$$

and

$$\Delta \bar{S}_{mix}^{id} = R \sum x_i \ln x_i \quad (8)$$

Solution of $\Delta \bar{Q}_{mix}^{id} = 0$ is called as **athermal solution**. Guggenheim⁷⁷ wrote in his book that 'it was commonly believed that all athermal solution should be ideal'. This view was openly challenged in a discussion held by the Faraday Society in 1936, at which Fowler then suggested that this view could be proved or disproved by a statistical analysis of a mixture of two kinds of molecules arranged on a lattice, each molecule of the one kind occupying two neighbouring sites of the lattice and each

molecule of the other kind occupying one site. This problem was attacked by Fowler and Rushbrooke⁷⁸ and by Guggenheim.^{77,79}

In an ideal solution the entropy change of mixing (i.e the mixing entropy) ΔQ_{mix} depends only on the mole fraction x_i (eq.2) and neither a volumetric change nor a thermal change occurs on mixing. In other words, an ideal solution, in which all components are randomly mixed, is absolutely athermal. A more exact treatment suggests that the molecules of solvent and solute should have the same size if Raoult's Law holds.⁷⁹

Comparison with experiments : (a) For example, the methanol-ethanol system at 24.95°C follows, within the precision of the experiment, Raoult's law. This system is not an ideal solution due to an extremely small, but significant, nonzero heat of mixing.⁵ (b) The partial molar entropy change of mixing of the solvent ΔS_0 , estimated for rubber-toluene at 30°C from the temperature dependence of the chemical potential $\Delta\mu_0$, is some 15 ~ 20 times of ΔS_0 of ideal solution, ΔS_0^{id} .¹⁵⁰

Gilbert Newton Lewis defined a 'perfect solution' as one which obeys $(p_i/p_i^0 = x_i)(p_i$, the vapor pressure of i th component in solution : p_i^0 , that in pure i th component liquid)⁷⁶ and Washburn called a solution which obeys Raoult's law throughout the whole range of compositions as 'ideal'.⁸⁰ Mixture of benzene and ethylene chloride obeys Raoult's law throughout the whole range of compositions.⁸¹

2.2 Model II : Quasi-ideal polymer solution (random mixing ~ athermal polymer solution)^{6,7}

(a) non-ideal solution

Solutions whose components greatly differ in chemical structure and in polarity exhibit remarkable deviations from ideal solution.

The chemical potential of the component i in non-ideal solutions is generally given by

$$\mu_i = \mu_i^0(T,P) + RT \ln a_i \quad (9)$$

with $a_i = \gamma_i x_i$. Here, a_i and γ_i are the activity and the activity coefficient of the component i , respectively. γ represents the extent of deviation from the ideality and is a complicated function of x_j ($j \neq i$) or the interaction between solutes and solvent.

The entropy of mixing for ideal solution is expressed as

$$\Delta S_{\text{mix}}^{\text{id}} = -R \sum_i N_i \ln x_i \quad (8)'$$

According to the definition of the excess entropy of mixing,

$$\Delta S_{\text{mix}}^{\text{E}} \equiv S_{\text{mix}} - S_{\text{mix}}^{\text{id}} \quad (10)$$

the excess Gibbs free energy of mixing per mole is derived as

$$\Delta S_{\text{mix}}^{\text{E}} = \Delta \mu_{\text{mix}}^{\text{E}} = \frac{\Delta G_{\text{mix}}^{\text{E}}}{\sum_i N_i} = RT \sum_i x_i \ln \gamma_i \quad (11)$$

(b) quasi-ideal solution ; random mixing ~ athermal polymer solution

In ideal solution, the cohesive energy is completely homogeneous. If any heat of mixing is neglected, the mixtures are called athermal solutions.

Consider a system consisting of N_i polymer molecules, each occupying n sites, and N_0 solvent

molecules, each occupying one site, the total number of sites being $N = nN_1 + N_0$. The entropy of mixing of disorientated polymer and solvent is given by

$$\Delta \bar{S}_{\text{mix}} = -k(N_0 \ln \phi_0 + N_1 \ln \phi_1) \quad (12)$$

Here, ϕ_0 and ϕ_1 are the volume fractions of the solvent and the polymer, respectively.

The partial molar entropies of mixing of the solvent and the polymer ΔS_0 and ΔS_1 are obtained by differentiating the entropy of mixing eq.(8') with respect to the number of moles N_0/N_A of solvent molecules and to the number of moles N_1/N_A of polymer molecules, as given by

$$\Delta S_0 = \frac{\partial \Delta S_{\text{mix}}}{\partial N_0} N_A, \quad \Delta S_1 = \frac{\partial \Delta S_{\text{mix}}}{\partial N_1} N_A \quad (13)$$

respectively. From eq.(10) we obtain

$$\frac{\partial \Delta S_{\text{mix}}}{\partial N_0} N_A = -R \left\{ \log \frac{N_0}{N_0 + n N_1} \right\} + \frac{n N_1}{N_0 + n N_1} - \frac{N_1}{N_0 + n N_1} = -R \left\{ \log(1 - \phi_1) + \left(1 - \frac{1}{n}\right) \phi_1 \right\} \quad (14)$$

$$\frac{\partial \Delta S_{\text{mix}}}{\partial N_1} N_A = -R \left\{ \log \frac{-n N_0}{N_0 + n N_1} \right\} + \log \frac{n N_1}{N_0 + n N_1} + \frac{N_0}{N_0 + n N_1} \cdot \left\{ (1 - n) \phi_0 + \log(1 - \phi_0) \right\} \quad (15)$$

accordingly,

$$\Delta S_0 = -R \left\{ \log(1 - \phi_1) + \left(1 - \frac{1}{n}\right) \phi_1 \right\} \quad (16)$$

$$\Delta S_1 = -R \left\{ (1 - n) \phi_0 + \log(1 - \phi_0) \right\} \quad (17)$$

Note that eq.(16) and (17) are valid for the solution of random mixing.

Excess Gibbs free energy of mixing ΔG_{mix}^E is given by eq.(11).

Comparison with experiments ; (a) Guggenheim noted that the plots of ratio P_1/P_1^0 (P_1 , the vapor pressure of the solvent in solution, P_1^0 , that of pure solvent) versus ϕ_1 (the volume fraction of solute) for rubber - benzene, polystyrene(PS) -toluene, and PS - various solvents^{110,111,152,153} could be represented by a single line which departs widely from Raoult's law.¹⁵¹ (b) The experimental data for PS/toluene at three different temperatures lie within the experimental error on a single curve, indicating that the heat of mixing ΔQ_{mix} of these solutions must be very small. (c) In 1952 accurate measurements of the heat of mixing did not exist¹⁵¹.

2.3 Random mixing~ non-athermal polymer solution

In fact, an extraordinarily solute mole fraction was observed in the 1920s to early 1930s in polymer solutions and these experimental facts motivated theoretical study by Flory,⁸²⁻⁸⁶ Huggins⁸⁷⁻⁹² et al., based on the lattice model, of the thermodynamics of polymer solutions. Usefulness of the lattice theory in study of the mixing entropy of polymer solutions were suggested also by Meyer and Mark.^{93,94} The so-called Flory-Huggins thermodynamic theory of the polymer solutions was derived on the basis of the combinatory entropy of mixing,

corresponding to the effect of dilution in the configurational entropy calculated on the lattice model and the enthalpy of mixing of van Laar-Scatchard type.

(a) van Laar-Scatchard approximation ^{6,7}

van Laar and Scatchard showed that the **heat of mixing for regular solution** which consists of N_0 solvent molecules and N_1 solute molecules is given by

$$\Delta H_{\text{mix}} = \varepsilon z N_0 N_1 / (N_0 + N_1) \quad (18)$$

where ε is the change in energy for formation of an unlike contact pair (0-1 pair) and z is the lattice coordination number. Now consider N_1 polymer molecules, each consisting of n segments as solute. The heat of mixing ΔH_{mix} and the partial molar heat of dilution of the solvent and of the polymer ΔH_0 and ΔH_1 , respectively are

$$\Delta H_{\text{mix}} = \varepsilon z N_0 n N_1 / (N_0 + n N_1) \quad (19)$$

ΔH_0 and ΔH_1 are defined by

$$\Delta H_0 = N_A \frac{\partial \Delta H}{\partial N_0} \quad (20)$$

$$\Delta H_1 = N_A \frac{\partial \Delta H}{\partial N_1} \quad (21)$$

respectively. Combination of eq.(19) and eq.(20) or eq.(21) leads to

$$\Delta H_0 = B N_A \frac{n^2 N_1^2}{(N_0 + n N_1)^2} = B N_A \phi_1^2 \quad (22)$$

$$\Delta H_1 = B N_A \frac{n N_0^2}{(N_0 + n N_1)^2} = B N_A n \phi_0^2 \quad (23)$$

Here $B \equiv \varepsilon z$.

Note that van Laar-Scatchard equation (eq.(18)) is derived on the assumption of random mixing.⁹⁵

(b) Gibbs free energy of mixing of polymer solution ΔG_{mix} ^{6,7}

Suppose the heat of mixing ΔH_{mix} and the entropy of mixing ΔS_{mix} are given by the relations eq.(19) and (12), respectively. Here the volumetric change of mixing ΔV_{mix} is implicitly assumed to be zero.

Substituting eq. (19) for ΔH_{mix} and eq. (12) for ΔS_{mix} in the equation

$$\Delta G_{\text{mix}} = \Delta F_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (24)$$

at constant pressure and temperature, we obtain

$$\Delta G_{\text{mix}} = kT(N_0 \log \Phi_0) + \varepsilon z N_0 \Phi_1 \quad (25)$$

The chemical potential of the solvent for the random mixing~non-athermal polymer solutions $\Delta \mu_0$ is derived from eqs.(16) and (20) and the chemical potential of polymer $\Delta \mu_1$ is obtained from eq.(17) and eq.(23). Substituting eqs.(14) and (18) into eq.(26) gives eq.(27) for $\Delta \mu_0$ and that of eqs.(15) and (21) into eq.(28) we obtain eq.(29) for $\Delta \mu_1$.

$$\Delta \mu_0 = \Delta H_0 - T \Delta S_0 \quad (26)$$

$$\begin{aligned}
 &= RT \left\{ \log(1 - \phi_1) + \left(1 - \frac{1}{n}\right) \phi_1 + \frac{B}{kT} \phi_1^2 \right\} \\
 &= RT \{ \log(1 - \phi_1) + (1 - 1/n)\phi_1 + \chi \phi_1^2 \} \quad (27)
 \end{aligned}$$

$$\Delta\mu_1 = \Delta H_1 - T\Delta S_1 \quad (28)$$

$$\Delta\mu_1 = -RT \left\{ n\phi_0 + \left(\frac{1}{2} - \frac{Bn}{kT}\right) \phi_0^2 + \frac{\phi_0^3}{3} + \dots \right\} - RT \left\{ n\phi_0 + \left(\frac{1}{2} - \chi_n\right) \phi_0^2 + \frac{\phi_0^3}{3} \right\} \quad (29)$$

Thus, the χ -parameter was first introduced into the thermodynamic theory for the random mixing-non-athermal polymer solution. Definition of χ is some what difference between Flory and Huggins.

For examples ;

$$\chi = B/RT \quad (\text{Flory})^{82,83} \quad (30)$$

$$\chi = \frac{1}{z} \left(1 - \frac{1}{n}\right)^2 + B/RT \quad (\text{Huggins})^{87,88} \quad (31)$$

The lattice theory of polymer solutions has following great advantages:⁶⁵

- (1) The structural regularity postulated in the theory has sound experimental diffraction evidences (at least, with respect to the short-range regularity).
- (2) The theory has explicit continuity with the theory of solutions of low molecules.
- (3) Phase separation and critical phenomena of polymer solutions can be quantitatively interpreted by the lattice theory (eq 16).

Comparison with experiments : Plots of $\log P_0/P_0^0 \cdot \log(1 - \phi_1) \cdot (1 - 1/n)\phi_1$ vs. ϕ_1^2 for PS/toluene and methylethylketone are represented by a straight line with positive slope. which gives χ .¹¹⁰

Assumption in Flory's 0th approximation theory

Flory's theory of the zeroth approximation^{65,82-86} assumes :

- (1) There is no volume change on mixing.
- (2) The lattice possesses a definite coordination number (i.e., the number of nearest neighbours of each segment per solvent molecule in the solution) z .
- (3) The entropy of mixing ΔS_{mix} can be calculated without reference to the possible energy change caused by the pair formation (i.e., **Bragg-Williams approximation**⁹⁷). In other words, the polymer segments mix with solvent randomly and ΔS_{mix} is the entropy of mixing of athermal solution.
- (4) In the calculation of the total number of configurations ω , from which the combinatory entropy of mixing is derived, the possibility that the nearest neighbour lattice point to the lattice point in question has been already occupied by polymer segment equals the probability of the case where all the polymer segments are uniformly distributed over all the lattice points (i.e., the **average concentration approximation of the chain segment**). This means that the two segments belonging to the same polymer molecule are allowed to occupy the same lattice site. For

rearrangement of the expression for ω , Stirling's approximation is applicable.

- (5) The potential energy of the mixture is the sum of contributions from each pair of the closest neighbouring segments (**van Laar-Scatchard approximation**^{95,96}).
- (6) The heat of mixing ΔH_{mix} can be calculated from the average contact numbers where all the segments comprising polymer chains are completely disconnected and randomly mixed with solvents (i.e., the **average concentration approximation**). In this case, the total number of polymer-solvent contact pairs n_c is given by

$$n_c = z\phi_0\phi_1L \quad (\text{Average concentration approximation}) \quad (32)$$

where L is the total number of lattice sites, ϕ_0 is the volume fraction of the solvent and ϕ_1 the volume fraction of the polymer expressed by eqs.(25) and (27), respectively. Here, χ in the equation is empirical parameter.

Difference of the thermodynamic quantities(in this case, ΔG) between real polymer solution and the quasi-ideal solution

The pseudo-excess chemical potentials for the solvent and n-mer,

$\Delta\mu_0^{\text{PE}}$ and $\Delta\mu_n^{\text{PE}}$ respectively are given by eqs.(33) and (34).

$$\Delta\mu_0^{\text{PE}} = RT\chi/\phi_p^2 \quad (33)$$

and

$$\mu_{ni}^{\text{PE}} = RT \left\{ \chi\phi_p(1-\phi_p) + \int_{\phi_p}^1 \chi d\phi_p \right\} \quad (34)$$

Flory regarded $\Delta\mu_0^{\text{PE}}$ as $\Delta\mu_0^{\text{E}}$ (in this notation)(see eq.41 of reference 85)). This is apparently overestimation of the excess chemical potential and should be subtracted with $RT\ln N_0$. Kamide's treatment, given in his book(chapter 12)⁶ is rather obscure because he did not keep strict distinction between ideal and quasi-ideal solutions throughout the chapter. Note that in derivation of eq.(25) van Laar-Scatchard type heat of dilution is assumed and in other words ΔG^{PE} is regarded to be exclusively caused by the heat of dilution $\Delta H(\equiv \Delta H_{\text{mix}} = \Delta H_{\text{mi}}^{\text{PE}}, \Delta H_{\text{mix}}^{\text{PE}}$ is the excess fraction).⁶³ χ -parameter is considered to be a constant independent of the concentration ϕ_0 in the Flory-Huggins (FH) theory. The actual experiments, however, show the concentration dependence of χ for numerous polymer solutions(see, Fig 2). In this sense, χ should be considered to be an empirical parameter, defined by the equation.

Real polymer solutions have, in general, the following characteristics.⁷

- (1) Heat of mixing ΔQ_{mix} is not zero.
- (2) Volumetric change in mixing ΔV_{mix} is not zero.
- (3) Excess entropy of mixing $\Delta S_{\text{mix}}^{\text{E}}$ is not zero.
- (4) Π/C , $\Delta T/C$ and P_0/P_0^0 depends on concentration, where Π is the osmotic pressure, ΔT , the boiling point elevation or freezing point depression, P_0 the vapor pressure of the solvent in solution and P_0^0 , vapor pressure of pure solvent.

The departure of the chemical potentials in real polymer solution from those eq.(16) reflects unquestionably on the χ -parameter(See, eq.(27)). Then, the concentration dependence of the χ -parameter may be, even not totally, but partly at least, due to inadequate hypothesis and mathematical approximations employed in the original lattice theory⁷.

First approximation theory (Non-athermal solution)⁷

For non-athermal solutions($\Delta H_{\text{mix}} \neq 0$), Bragg-Willams and van Laar-Scatchard approximations

(hypotheses (3) and (6), respectively) might seem more or less unrealistic and less appropriate. Then several attempts to improve the Flory's zeroth approximation theory were made by calculating the total number of configurations ω through the use of quasi-chemical equilibria method, which is equivalent to the mathematical technique originally developed by Bethe⁹⁸ for the treating order-disorder transitions in alloys. This method was occasionally referred to as the Flory-Huggins first approximation theory. The disparity of values of ΔH_0 for polymethylmethacrylate/trichloroethylene⁹⁹ and ΔS_0 for rubber/ethylacetate¹⁰⁰, both calculated on the basis of the first approximation theory from their corresponding experimental data is significantly larger than those by the zeroth approximation theory, indicating that the first approximation is less reliable and cannot be recommended to use it for analysis^{94,101}. This might appear to be somewhat surprising to note that allowance for hypotheses (3) and (6) does nothing to improve the agreement with experiments.

Huggins' 'new' theory (1964)^{7,68}

In his 'new' theory, Huggins¹⁰¹ assumed as basic tenet that the interior segments of a convoluted molecule are partially shielded from contact with interior segments of other polymer molecules and the shielding factor depends on the concentration. He derived theoretical equations for χ_h and χ_s (see eq (49)) in closed form and as expansions in powers of the concentration, introducing a number of physical quantities, such as molecular surface area, effective surface area, multiple contact factor, shielding factor and empirical constant relating to shielding factor's concentration dependence. All of which cannot be determined by independent absolute method, although he described that these quantities are "observable". He considered that from experimental data of χ and its dependence on concentration and temperature one can evaluate all the parameters introduced. That is, the parameters introduced in his theory are only adjustable parameters to fit the experimental relations between χ , ϕ_1 and T. Note that in mid-1960s the methods based on phase separation and critical phenomena were not yet established and there was lack of extensive and reliable experimental data to judge the theories. Huggins¹⁰¹ described "Testing of the equations presented in the paper, using published experimental data, has been begun. The results will be reported in due course". Unfortunately as far as we know, there is no his succeeding paper.

Validity of hypothesis 6⁷

The most probable inadequate hypothesis in the Flory-Huggins theory is that the total number of solvent-polymer contacts is strictly proportional to the product $\phi_0\phi_1$ (hypothesis 6). For example, κ defined by $\Delta H_0/(RT\phi_1^2)$ (eq.(64)) is expected, if the above hypothesis is accepted, to be constant over wide ranges of T and ϕ_1 , but it was confirmed by numerous experiments that κ directly measured by accurate calorimetry, depends strongly on both T and ϕ_1 .¹⁰² Validity of the application of overall average concentration approximation of polymer segment to estimate the heat of mixing has never hitherto been tried to examine thoroughly due to mathematically extreme difficulty, although the first approximation, of course, did also treat this problem in rather rough and insufficient manner.

Strictness and adequacy of the model, and mathematical complexity and approximation

As Flory¹⁰³ pointed out at Fifteenth Spiers Memorial Lectures in 1970, sponsored by the Royal Society, that "to be effective, any conceptual scheme, or theory of liquids and solutions must entail approximations, either in model or in mathematical technique, even for the simplest of real liquids".

Mathematical approximations become more serious in the first approximation theory than in the zeroth approximation theory and this is the reason why introduction of more adequate concepts into the first approximation theory failed, on the contrary, to get rid of the disparity between the theory and actual experiments. This means that even if seemingly more adequate models are used, we cannot always derive accurate theoretical relations between the time-average observable physical quantities like ΔG , ΔS and ΔH , and the structural, molecular and thermodynamic parameters (for example, z , n and the enthalpy change of formation of an unlike contact pair $\Delta \epsilon$) from the models by traditional method of statistical mechanics, because the system in question is too complicated. Since then, serious limit of further evolution of the lattice theory was widely recognized, although it was largely successful in semi-quantitatively accounting for unusual (from the stand point of low molecular weight solutions) behavior of ΔG , observed in polymer solutions, by differences in size and shape of the species that make up the solution, and there has been no generally accepted explanation of physical significance of the concentration- and molecular weight-dependences of χ -parameter, in spite of its experimentally unquestionable existence.

3. χ -Parameter

3.1 Semi-empirical expression of χ -parameter

The parameter χ can be expressed in a power series of concentration as

$$\chi = \chi_0 (1 + p_1 \phi_1 + p_2 \phi_1^2 + \dots + p_n \phi_1^n) = \chi_0 \left(1 + \sum_j p_j \phi_1^j \right) \quad (35)$$

The condition that all the virial coefficients are concurrently zero at θ point is given by⁴⁷

$$\chi_0 = \frac{1}{2} \quad (36)$$

$$p_1 = \frac{2}{3}, \quad p_2 = \frac{2}{4}, \quad p_3 = \frac{2}{5}, \quad \dots, \quad p_n = \frac{2}{n+2} \quad (37)$$

The molecular weight dependence of χ is phenomenologically given by

$$\chi_0 = \chi_{00} (1 + k'/n_n) \quad (38)$$

The temperature dependence of k' and χ_{00} in eq.(36) can be empirically expressed as

$$k' = k_0 (1 - \theta/T) \quad (39)$$

and

$$\chi_{00} = a + b/T \quad (40)$$

where k_0 , a and b are the constants independent of temperature and θ , the Flory temperature. Eq (39) was first proposed by Kamide et al.^{36,41}

Equation (41), which is simplified form of equation (35), is an adequate expression of χ from the experimental point of view.

$$\chi = (a' + b'/T + c'/T^2)(1 + p_1 \phi_1 + p_2 \phi_1^2) \quad (41)$$

The chemical potential of n -th polymer component $\Delta \mu_n$ in multicomponent polymer solutions

with constant χ can be expressed as

$$\Delta\mu_n = RT \left\{ \log \phi_n - (n-1) + \phi_1 n \left(1 - \frac{1}{n_n} \right) + \chi n (1 - \phi_1)^2 \right\} \quad (42)$$

Here, n_n is the number-average chain length (average number of segments in a polymer).

Then, eq.(42) can be generalized to this case as

$$\Delta\mu_n = RT \left\{ \log \phi_n - (n-1) + \phi_1 n \left(1 - \frac{1}{n_n} \right) + \chi_0 n (1 - \phi_1)^2 + \chi_0 p_1 n \left(\frac{1}{2} - \frac{3}{2} \phi_1^2 + \phi_1^3 \right) \right\} \quad (43)$$

with

$$\chi = \chi_0 (1 + p_1 \phi_1) \quad (44)$$

Eqs. (43) is a practical equations to describe the thermodynamic properties of multicomponent polymer solutions. Eq. (43) was derived by Huggins-Okamoto¹⁰⁴ and Kamide-Sugamiya¹³.

When χ parameter of i th polymer component χ_i is expressed by eqs. (35) and (38), the heat of dilution ΔH of the solution and the chemical potential of the solvent $\Delta\mu_0$ can be written by

$$\Delta H = RT \left\{ \chi_{00} \left(1 + \frac{k'}{n_n} \right) \left(1 + \sum_{j=1}^n p_j \phi_1^j \right) \right\} \phi_0 \phi_1 \quad (45)$$

$$\Delta\mu_0 = RT \left\{ \ln(1 - \phi_1) + \left(1 + \frac{1}{n_n} \right) \phi_1 + \chi_{00} \left(1 + \frac{k'}{n_n} \right) \left(1 + \sum_{j=1}^n p_j \phi_1^j \right) \phi_1^2 \right\} \quad (46)$$

Using the Gibbs-Duhem relation

$$\sum_i N d\mu_i = 0 \quad (47)$$

(*J. Willard Gibbs deduced eq(47) in 1885^{105,106} and later, P. Duhem independently derived the same equation^{107,108})

The chemical potential of n_i -mer, $\Delta\mu_i$, is expressed as

$$\begin{aligned} \Delta\mu_i = RT & \left[\ln \phi_i - (n_i - 1) + n_i \left(1 + \frac{1}{n_n} \right) \phi_1 \right. \\ & + n_i (1 - \phi_1)^2 \chi_{00} \left[\left(1 + \frac{k'}{n_n} \right) \left(1 + \sum_{j=1}^n \frac{p_j}{j+1} \left(\sum_{q=0}^j (q+1) \phi_1^q \right) \right) \right] \\ & \left. + k' \left(\frac{1}{n_i} + \frac{1}{n_n} \right) \left[\frac{1}{1 - \phi_1} + \sum_{j=1}^n \frac{p_j}{j+1} \left(\sum_{q=0}^j \frac{\phi_1^q}{1 - \phi_1} \right) \right] \right] \quad (48) \end{aligned}$$

where ϕ_n is the partial molar volume of i component of the polymer and $\phi_n = \sum \phi_n$.

If all the parameters in equations (46) and (48) are determined accurately by some adequate methods, $\Delta\mu_0$ and

$\Delta \mu_i$, calculated using these parameters, can represent satisfactorily the thermodynamical properties of the polymer solutions over the entire range of T , ϕ_1 and r (or n_n)²⁵ Note that the applicability of eq. (48) is not restricted only to the lattice model used originally in the Flory-Huggins theory.

χ can be assumed to be divided into an entropy term and an enthalpy term as

$$\chi = \chi_S + \chi_H \quad (49)$$

where

$$\chi_S = \frac{1}{2} - \Psi \quad (50)$$

$$\chi_H = \kappa = \frac{\Psi\theta}{T} \quad (51)$$

κ (accordingly, χ_S) in eq.(51) can be semi-empirically expressed as

$$\kappa = \kappa_0 + \kappa_1\phi_p + \kappa_2\phi_p^2 + \dots \quad (52)$$

with

$$\kappa_0 = \lim_{\phi_1 \rightarrow 0} \{ \Delta H_0 / (RT\phi_1^2) \} \quad (53)$$

κ_0 is the Flory enthalpy parameter at infinite dilution, ΔH_0 , the partial molar heat of dilution, κ_1, κ_2 , concentration-dependence parameters.

Table 1 summarizes some characteristics of three typical solutions

Table 1 Some characteristics of three typical solutions^{7,64}

Solutions	Characteristics	Equation
ideal (Model I)	random mixing (solute=solvent in size)	(4)
	zero heat of mixing	(3)
quasi-ideal (Model II)	'random' mixing (solute>solvent in size)	(12)
	zero heat of mixing	(3)
FH (Model III)	'random' mixing (solute>>solvent in size)	(3)
	non- zero heat of mixing	(34)
real (Model V)	non- 'random' mixing non- zero heat of mixing	(46)

3.2 Traditional method for experimental determination of χ -parameter

χ in the Flory-Huggins theory (see eq. (27)) can be experimentally evaluated by the following steps.

- (1) Determination of the activity of solvent a_0 by vapor pressure depression;

$$P_0 = a_0 P_0^0 \quad (54)$$

or membrane osmometry,

$$\Pi = - \frac{RT}{V_0} \log a_0 \quad (55)$$

(2) Substitution of a_0 , determined by the above methods into the equation:

$$\log a_0 = \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 + \chi \phi_1^2 \quad (56)$$

Originally, χ was assumed to be independent of the polymer concentration ϕ_1 . χ in the Flory-Huggins theory (see eq. (25)) can be experimentally evaluated by the following methods.

4. Concentration dependence coefficients p_1 and p_2 of the χ -parameter

4.1 Experimental determination of the concentration dependence of the χ -parameter

In the original Flory-Huggins theory, the χ -Parameter was taken as constant. During the late 1940s and early 1950s, the vapor pressure measurements and the isothermal distillation equilibration were applied for some polymer / solvent systems, including polydimethylsiloxane (PDMS) in benzene¹⁰⁹, polystyrene (PS) in methylethylketone (MEK)¹¹⁰, PS in toluene¹¹⁰ and rubber in benzene.¹¹¹ Flory constructed plots of χ against ϕ_1 for these systems (Fig. 111 of ref.86) and he stated that "in no other system so far investigated is the agreement so good as for the rubber / benzene system for which χ is remarkably constant over a very wide concentration range", and that "in those cases where either the polymer unit or the solvent possesses a dipole, as in the PDMS / benzene and in PS / MEK systems, χ appears to vary throughout the concentration range". Flory also agreed that the available data is too little to justify generalization. Surprisingly, Flory's figure (Fig. 111 of ref. 86) has been occasionally cited without serious modifications in many text books published later. It should be noted that the experimental data cited in Flory's book is less accurate: p_1 values estimated from Fig.111 of ref.86 are 0.15 for PS/MEK, 0.17 for PS / toluene and these values are compared with the values accepted as most probable (0.618 and 0.494), both evaluated by analyzing the critical solution points (see, Table 2).

At present the parameter p_1 and p_2 in eq.(35) can be experimentally determined by (1) temperature dependence of vapor pressure and membrane osmometry, (2) temperature dependence of second virial coefficient in the vicinity of the Flory theta temperature θ , (3) calorimetry, (4) isothermal distillation, (5) ultracentrifuge, (6) coexisting curve (i.e., binodal curve), (7) phase separation and cloud point curve and (8) critical solution point (temperature T_{cc} and concentration ϕ_p^c).

Applicability of methods(1)~(5) are severely limited to rather rough estimation of p_1 only and the method (7) by Kamide et al. and the method (8) proposed by Koningsveld et al.¹¹² and by Kamide and his coworkers⁴⁷ give the most accurate and reliable values of p_1 and p_2 . The method 8 was successfully applied by Kamide et al. to the literature data on the upper and /or lower critical solution points of ten polystyrene-solvent pairs and sixteen polyethylene-solvent pairs in very systematic manner.⁴⁸

In the above methods, p_1 and p_2 are assumed to be temperature independent. In fact this assumption seems to be experimentally acceptable: over a wide temperature range covering both the upper critical solution point (UCSP) and the lower critical solution point (LCSP).

Note that other methods than methods(6)–(8) are limited experimentally to a relatively low concentration range and do not enable us to evaluate p_2 accurately. This is the main reason why in Flory's milestone text book,⁸⁶ the values of the χ -parameter obtained using the vapor pressure and (in part) the isothermal distillation equilibrium for poly(dimethylsiloxane), polystyrene and natural rubber were constant with $p_2 = p_3 = \dots = 0$. The phase separation method is applicable up to a moderately concentrated solution range, but the experimental accuracy is unfortunately not high enough to estimate p_2 satisfactorily.

4.2 (a) Method 7: Cloud point curve (CPC) method (Kamide et al. method)^{7,47}

There is method for determining the parameters a , b and p_j ($j=1, \dots, n$) from the cloud-point curve and an empirical relationship between temperature and relative amount of polymers partitioned in polymer-rich phase ρ_p with the corresponding theoretical ones.

Parameters a , b , p_j ($j=1, \dots, n$) can be determined when the cloud point temperature $T_{cp,e}$, experimentally determined, coincides with that calculated by a computer simulation for phase equilibrium due to eqs.(35) and (38)–(40), $T_{cp,c}$.

- (1) Determine the relationships between ρ_p (ρ_p is the weight fraction of the polymer partitioned into the polymer-rich phase to the polymer dissolved in the initial solution) and the temperature T from the two-phase equilibrium experiments.
- (2) Carry out a computer simulation assuming arbitrarily chosen values of p_j ($j=1, \dots, n$) to obtain the relationship between χ_{00} and ρ_p .
- (3) Construct the relationship between χ_{00} and $1/T$ by using ρ_p vs. T relationship obtained in step (1) and χ_{00} vs. ρ_p relations obtained in step (2) and a and b determined as the intercept and slope of χ_{00} vs. T plot, respectively.
- (4) Calculate CPC ($T_{cp,c}$ vs. ϕ_1 relationship) using a and b obtained in step (3)
- (5) Compute $\delta \equiv \sum_N (T_{cp,c} - T_{cp,e})^2 / N$ (N is the total number of the solutions, for which the cloud point was determined) and determine a set of p_j ($j=1, \dots, n$) to minimize δ (where $N \gg n$).
- (6) Repeat steps 2-5 and evaluate a , b and p_j where δ is below the permissible limit. See <<Problem 4-21.d>> in ref.7 for the details of the simulation.

Fig.3 shows the relationship between ρ_p and T (a), and between χ_0 and T (b), both obtained by an actual phase separation experiment for the system polystyrene (PS) in cyclohexane(CH). The relationship (a) can be roughly approximated by a part of circle arc with ρ_p approaching zero. The most appropriate set of p_1 and p_2 , giving the minimum δ ($\equiv \sum_N (T_{cp,c} - T_{cp,e})^2 / N$ (N is the total number of the solution: $T_{cp,c}$, calculated T at SCP ; $T_{cp,e}$ experimental T at SCP)) (~ -0.1), could be determined as $p_1 = 0.643$ and $p_2 = 0.200$. These values are very close to the corresponding values evaluated from the critical point data.⁴⁶ The cloud point curve, calculated with using these values of a , b , p_1 and p_2 can express accurately the experimental data except for the threshold point region ($\phi_1 \sim 0.07$) (see, Fig.11). The concentration dependence of the parameter χ , evaluated for PS/CH system by many investigators, is plotted in Fig.5. In the figure, the curves have been calculated from the p_1 and p_2 values evaluated from the critical points. The experimental data points can be reasonably represented by eqs. (38), (39) and (35) for $n=2$, in which terms higher than ϕ_1^2 are neglected. That is, in the ϕ_1 range of 0-0.15, both p_2 and p_1 are necessary to represent the concentration dependence of χ and in a comparatively dilute range, there is no sharp distinction in χ between the investigators.

Table 2 shows the parameter determined for the system of polystyrene in cyclohexane.

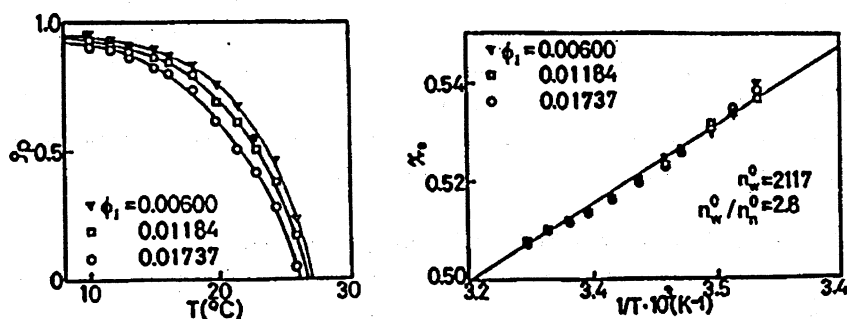


Fig. 3(a) experimental relationship between ρ_p and T and (b) temperature dependence of χ_0 in eq. (33) for solution ϕ_1^0 are 0.6×10^{-2} (∇), 1.184×10^{-2} (\square) and 1.737×10^{-2} (\circ), respectively. Full line in (b) is the theoretical curve calculated by assuming $p_1=0.62$, $p_2=0.20$ and $k_0=0$.⁴⁷

4.2(b) Method 8 : Critical solution point(CSP) method^{7,46}

The composition at the critical solution point ϕ_1^c is given by eq.(57)~(62)

(1) For single component polymer~single solvent system with constant χ (Model III)

$$\phi_1^c = \frac{1}{1 + \sqrt{n}} \quad (57)$$

$p_i=0; i>0; m=1$

Eq.(57) was first derived by Shultz-Flory and applied to the systems of polystyrene in cyclohexane and polyisobutylene/diisobutyl ketone.¹¹³

(2) For multicomponent polymer~single solvent system with constant χ (Model IV)

$$\phi_1^c = \frac{1}{1 + n_w/n_z^{1/2}} \quad (\text{Stockmayer}) \quad (58)$$

where n_w and n_z are the weight- and z-average degree of polymerization.¹¹⁴

Note that in Shultz-Flory and Stockmayer equations the concentration dependence of χ -parameter are not taken into account ($p_i=0, i>0; i=1-m$)

(3) For multicomponent polymer~single solvent system with χ obeying eq.(33) : Model V

The parameter χ can be phenomenologically expressed as eq. (33). At the critical point, the following equations can be derived:⁴⁶

$$\frac{1}{n_w \phi_1^c} + \frac{1}{1 - \phi_1^c} - \chi_0^c (2 + \sum_{j=1}^n p_j (j+2) \phi_1^{c,j}) = 0 \quad (59)$$

and

$$\frac{1}{(1 - \phi_1^c)^2} - \frac{n_z}{(n_w \phi_1^c)^2} - \chi_0^c \sum_{j=1}^n p_j j (j+2) \phi_1^{c,j+1} = 0 \quad (60)$$

Both χ_0^c and ϕ_1^c can be obtained concurrently through the application of eqs.(59) and (60), using a numerical method, to the data of n_w , n_z and p_j ($j=1,2$).

Whether the concentration dependence of the parameter χ and the polymolecularity of the polymer should be taken into account to explain the critical point and, in the former case, what would be the most reasonable values of p_1, p_2, \dots, p_n , can be decided by comparing the experimental critical volume fraction of the total polymer ($\phi_1^c(\text{exp})$) and the theoretical one ($\phi_1^c(\text{theo})$) calculated using eqs. (59) and (60) (Kamide-Matsuda), eq. (58) (Stockmayer), and eq.(57)(Shultz-Flory). An analysis of the data on $\phi_1^c(\text{exp})$, n_z and n_w would provide the most ideal values of $p_1, p_2 \dots p_n$ as a combination yielding the minimum δ , defined by

$$\delta = \sum_{i=1}^{N_0} (\phi_1^c(\text{exp}) - \phi_1^c(\text{theo}))_i^2 / N \quad (61)$$

where N_0 is the total number of samples.

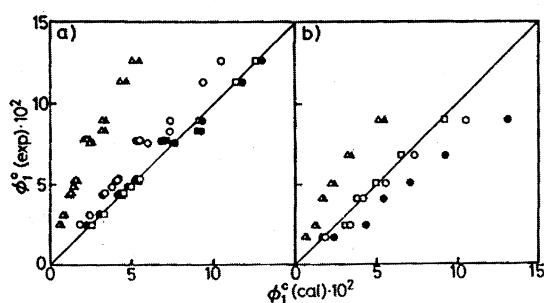


Fig.4 The critical concentration experimentally determined, $\phi_1^c(\text{exp})$, plotted against the critical concentration theoretically calculated, $\phi_1^c(\text{theo})$ for UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. (Δ)Shultz-Flory [eq.58]; (O) Kamide-Matsuda eq.(61,62), $p_1=0.6, p_2=0$; (\bullet) Kamide-Matsuda [$p_1=0.623, p_2=0.290$]; (\square) Kamide-Matsuda [$p_1=0.642, p_2=0.190$ for UCSP and $p_1=0.602, p_2=0.347$ for LCSP]. (See, Ref.46)

Fig.4 shows the plot of $\phi_1^c(\text{exp})$ vs. $\phi_1^c(\text{theo})$ calculated for some typical combinations of p_1 and p_2 for the UCSP and LCSP of a PS / CH system. Evidently, the methods of Shultz-Flory (eq. (57)) and Stockmayer (eq (58)) can not give reasonable ϕ_1^c ; ϕ_1^c calculated by the above two methods overstimulates and is almost twice of the experimental data. Even if p_1 only is considered in Kamide-Matsuda method the difference between $\phi_1^c(\text{exp})$ and $\phi_1^c(\text{theo})$ remains significant, although improved remarkably. p_2 as well as p_1 is necessary to calculate ϕ_1^c .

4.3. Reliability of the experimental methods for determining p_1 and p_2

The reliability of the methods can be confirmed by comparing p_1 and p_2 values estimated by various methods. Table 2 demonstrates the parameters p_1 and p_2 together with a, b, ψ_0 and θ for the PS/CH system. p_1 for atactic polystyrene (PS) in cyclohexane (CH) system was determined to be 0.630 by osmotic pressure (34°C)¹, 0.534 by ultracentrifuge (34°C)², 0.610 by solution critical point (SCP) (34°C)³, 0.622 by SCP(34°C)⁴, 0.607 by threshold cloud point⁵, 0.642 by SCP⁶, and 0.600 by cloud point curve combined with relationship between the relative amount of polymer partitioned in a polymer-rich phase and the phase separation temperature⁷. The results indicate that no significant difference in p_1 exists among various methods and p_1 values for atactic PS-CH system are averaged to 0.619 ± 0.023 , except for the ultracentrifuge data.¹¹⁷

Table 2 Temperature-dependence (a and b in the equation $\chi = a + b/T$ or $a = 0.5 \cdot \psi_0$, $b = \Psi_0 \theta$) and concentration-dependence (p_1 and p_2 in eq.(33)) parameters of thermodynamic interaction parameter χ , Flory entropy parameter ψ_0 and Flory theta temperature θ for atactic polystyrene/cyclohexane system (T=299K).^{7,47,62}

Author(s)	Method	a	b	p_1	p_2	ψ_0	θ/K
Krigbaum and Geymer(1959) ¹¹⁶	Osmotic Pressure	0.2469	76.67	0.630 ₄	0.480 ₈	0.25	302.9
Scholte(1970) ¹¹⁷	Ultracentrifuge	0.2631	74.31	0.534 ₄	0.430 ₄	0.24	313.7
Koningsveld(1970) ¹¹⁸	Critical point	0.2035	90.50	0.610 ₆	0.920 ₇	0.30	305.2
Koningsveld(1970)	Critical point	0.2211	85.31 ₃	0.6.22 ₂	0.289 ₁	0.28	305.9
Kuwahara et al.(1973) ¹¹⁹	Threshold cloud	0.2798	67.50	0.607 ₃	0.512 ₁	0.22	306.5
Kamide and Matsuda(1984) ⁴⁶	Critical point	0.23	82.37 ₇	0.642	0.190	0.27	305.1
Kamide et al.(1995) ⁶²	Cloud point curve and ρ_p vs.T.relationship	0.23	82.89	0.600	0.460	0.27	307.0

* ρ_p , the relative amount of polymer partitioned in polymer-rich phase

*T temperature

Figure 5 shows the plots of χ experimentally determined, against ϕ_1 for polystyrene in cyclohexane. The figure shows a significant ϕ_1 dependence of χ . χ is not constant, but should be considered to be an empirical parameter.

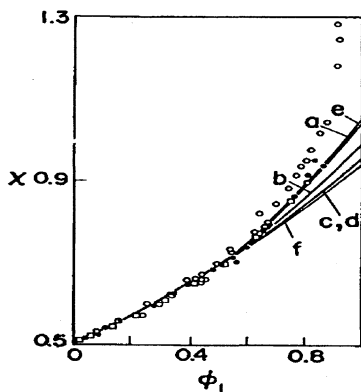


Fig.5 Concentration dependence of χ parameter for polystyrene in cyclohexane.⁵⁻⁷ (○) osmotic pressure, isothermal distillation by Krigbaum and Geymer¹¹⁵, (●) vapor pressure by Krigbaum and Geymer¹¹⁵, (□) ultracentrifuge by Scholte¹¹⁶. Lines a to f are calculated using p_1 and p_2 , in the equation $\chi = \chi_0(1 + p_1\phi_1 + p_2\phi_1^2)$, obtained by experiment, (a) Krigbaum and Geymer¹¹⁶; (b) Scholte¹¹⁷; (c) Koningsveld et al.¹¹⁷; (d) Koningsveld et al.¹¹⁸; (e) Kuwahara et al.¹¹⁹; (f) Kamide et al.⁴⁷. This expression for χ yields a better fit compared with eq.(44).

In the figure, the curves have been calculated from the p_1 and p_2 values evaluated from the critical points. The experimental data points can be reasonably represented by eqs. (38), (39) and (35) for $n=2$, in which terms higher than ϕ_1^2 are neglected. That is, in the ϕ_1 range of 0-0.15, both p_2 and p_1 are necessary to represent the concentration dependence of χ and in a comparatively dilute range, there is no sharp distinction in χ between the investigators. Similar results have been obtained for polystyrene/methylcyclohexane system.⁴⁶

4.4 p_1, p_2 values of polystyrene in various solvents⁴⁸

Parameters in χ determined by KM methods for PS/ in various solvents are summarized in Table 3. The best and most widely used method for estimating p_1 and p_2 are SCP method. p_1 values for atactic PS in various non-polar or less polar solvents, whose upper or lower critical solution points (UCSP or LCSP) data in literature were analyzed systematically by Kamide et al.⁴⁸ according to Kamide-Matsuda method⁴⁶, are 0.618 (methyl ethyl ketone, LCSP), 0.615 (cyclopentane, UCSP), 0.631 (cyclopentane, LCSP), 0.642 (cyclohexane, UCSP), 0.638 (cyclohexane, LCSP), 0.602 (methylcyclohexane, UCSP), 0.649 (methylcyclohexane, LCSP), 0.673 (isopropylacetate, UCSP), 0.839 (isopropylacetate, LCSP), 0.643 (n-propylacetate, UCSP), 0.797 (n-propylacetate, LCSP), 0.650 (dimethoxymethane, LCSP), and 0.630 (trans-decalin, UCSP). p_1 values are averaged to 0.663 for all the above systems or 0.636 except two LCSPs of PS in iso- and n-propylacetates. It can therefore be concluded that p_1 values of PS in non-polar solvents are close to 2/3, eq. (37), and are slightly higher than the value (ca. 0.6) obtained in a computer experiment, but no significantly so.

Table 3 Concentration dependence of χ -parameter p_1, p_2 , Flory temperature θ , and the entropy parameter ψ at the critical point for polystyrene-solvent systems at critical point⁴⁸

Solvent	UCSP or LCSP	p_1	p_2	θ/κ	ψ	Remarks
Methyl ethyl ketone	LCSP	0.618	-0.208	423.6	-0.44	Aliphatic
Cyclopentane	UCSP	0.615	0.404	292.1	0.16	Aliphatic
	LCSP	0.631	0.331	428.5	-0.25	Aliphatic
Cyclohexane	UCSP	(0.642)	0.190	305.1	0.27)	Aliphatic
		-	-	-	-	
	LCSP	0.638	-0.498	488.6	-0.58	Aliphatic
		(0.602)	0.347	487.2	-0.42)	
Methyl cyclohexane	UCSP	(0.602)	0.234	340.2	0.25)	Aliphatic
	LCSP	(0.649)	-1.183	487.9	-0.54)	
Toluene	LCSP	0.494	-0.922	550.4	-1.36	Aromatic
Benzene	LCSP	0.388	-1.781	524.3	-1.81	Aromatic

In Contrast to the systems of non-polar polymer in non-polar solvent, for PS-aromatic solvent systems p_1 value at CSP deviates significantly from 2/3. ⁴⁸ For examples, $p_1=0.494$ (toluene) and 0.388 (benzene) were obtained.⁴⁸ Kamide et al. pointed out, from an analysis of ¹H NMR spectra

with the aid of infra-red spectra and adiabatic compressibility, that the PS phenyl ring is stacked in parallel to the solvent phenyl ring for PS/aromatic solvent system. This strongly suggests that marked difference in the thermodynamic parameters, including the concentration dependence coefficients p_1 and p_2 of the parameter χ , and the **Flory entropy parameter at infinite dilution** Ψ_0 , observed for atactic PS in aromatic and aliphatic solvents, are accounted for, at least in part, by the formation of some supermolecular structure in the former solutions, which may affect the entropy term in the parameter χ , and the entropy of mixing.¹²⁰ Fig. 6 shows the plot of p_2 against p_1 , both estimated by the KM method, for PS solutions. Here, the unfilled circle and rectangle correspond to UCSP and LCSP, respectively. The point theoretically expected when $A_2 = A_3 = A_4 = 0$ at $\theta : 1$ 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 .

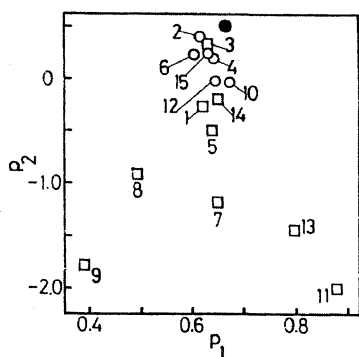


Fig. 6 Plot of p_1 (KM) versus p_2 (KM) for polystyrene solutions: rectangle, LCSP; unfilled circle, UCSP; filled circle, the point theoretically expected when $A_2 = A_3 = A_4 = 0$ at $\theta : 1$, methylethylketone (LCSP)¹²¹; 2, cyclopentane UCSP¹²¹; 3, cyclopentane (LCSP)¹²¹; 4, cyclohexane (UCSP)^{117,119,122}; 5, cyclohexane (LCSP)¹²²; 6, methylcyclohexane (UCSP)^{122,123}; 7, methylcyclohexane (LCSP)¹²²; 8, toluene (LCSP)¹²²; 9, benzene (LCSP)¹²¹; 10, isopropyl acetate (UCSP)¹²⁴; 11, isopropyl acetate (LCSP)¹²⁴; 12, n-propyl acetate¹²⁴; 13, n-propyl acetate (LCSP)¹²⁴; 14, dimethoxy methane (LCSP)¹²⁵; 15, trans-decalin¹²⁶.

4.5 Role of concentration-dependence of χ on phase-separation and critical phenomena.

By lowering or rising the temperature of quasi-binary solution or by adding a non-solvent to the solution (resulting in quasi-ternary solution), the polymer-rich (or lean) phase particles separate from the mother solution (i.e. cloud point) and, after settling for a long time, the total solution separates into a two-liquid phase. At constant temperature and constant pressure these two phases are in equilibrium with each other. We define hereafter the phase of smaller ϕ_p as the polymer-lean phase and the phase of larger ϕ_p as the polymer-rich phase.

When the two phases are in equilibrium under constant T and constant P, the well-known Gibbs' law applies, that is^{105,106},

$$\Delta\mu_0(1) = \Delta\mu_0(2) \quad (62)$$

$$\Delta\mu_{ni}(1) = \Delta\mu_{ni}(2) \quad (i = 1, \dots, m) \quad (63)$$

Here, the suffixes (1) and (2) denote the polymer-lean and -rich phases, respectively: Gibbs discussed "the conditions of equilibrium for heterogeneous masses in contact when uninfluenced by gravity, electricity, distortion of the solid mass, or capillary tensions", showing that "the

potential, defined by eqs. for $\Delta\mu_0$ and $\Delta\mu_n$, for each component substance must be constant throughout the whole mass" ^{105,106} of osmotic pressure or vapor pressure. From the vapor pressure and osmotic pressure measurements, $\Delta\mu_0$ can be calculated using eqs (9),(54),(55) and putting $\Delta\mu_0$ into eq. (27) allows n_n and χ to be evaluated. In phase equilibrium studies, an accurate knowledge of $\Delta\mu_{ni}$ is necessary in addition to that of $\Delta\mu_0$. $\Delta\mu_{ni}$ can be estimated from $\Delta\mu_0$ through use of the Gibbs-Duhem relation* (see, eq. (47)), which, even for polymer solutions, should hold its validity at constant T and constant P (see, for example, eq. (33)). For a single component polymer / single solvent system numerous researchers, including Flory, performed theoretical studies on two-phase equilibrium mainly in 1950s. In these studies, the theory employed was based on a lattice model and the calculations were only made under very specific conditions. No comparisons were made with actual experimental data. For long time it has been considered without any doubt that the solution theory does not permit the exact calculation of the partition coefficient σ and that σ is a kind of underestimated parameter¹²⁷. It is interesting to note that Flory stated in his classical book "*Principle of Polymer Chemistry*" (1953)⁸⁶ that "we need not undertake the incomparably more involved calculation of the theory." From this statement, it is clear that Flory did not consider his theory to be fully quantitative in nature.

In order to carry out the accurate simulation of two-phase equilibrium of actual polymer / solvent systems for all components (m is usually of order of 10^2 - 10^5) eqs (62) and (63) should be solved concurrently. As early as 1968 Kamide and his coworkers ^{8,9} and Koningsveld and Staverman ¹²⁸⁻¹³⁰ independently succeeded in carrying out accurate computer simulations of these equations. Thereafter, Kamide and his collaborators^{2,31-33,35,36,39,41} and Koningsveld et al.¹³¹⁻¹³⁵ developed more advanced and more rigorous theories for the quasi-binary(multicomponent polymers/single solvent) system than those first published in 1968 and they established the necessary computer simulation techniques in a more systematic way.

In Fig.7 the molecular weight distribution (MWD) curve of the polymer remaining in the polymer-rich phase is compared with theoretical curves assuming varying values of the parameter p_1 in eq. (45) (here, $k' = 0$ and $p_2 = \dots = p_n = 0$ are assumed), when atactic PS / methylcyclohexane(MCH) solution is cooled to bring about the two-phase separation. As just described before for computer experiment on model polymer solutions ($k' = 0$ and $p_2 = \dots = p_n = 0$ in eq. (45)), the MWD curve markedly depends on p_1 values chosen ²⁹. It is generally accepted from these figures that, PS / MCH can be reasonably approximated by a theoretical curve with $p_1 = 0.7$ (dotted line) ²⁹. An adequate value of p_1 , with which the experimental MWD coincides with the theoretical one, clearly varies in the range $p_1 = 0.6 \sim 0.7$ depending on the operating conditions (ϕ_p^0 and ρ_p) for PS / MCH and PS / cyclohexane (CH) systems. The large discernible solvent effect on the MWD of the fractions is evident and an increase in p_1 value is just equivalent to lowering the initial polymer concentration, ϕ_p^0 .⁽²⁹⁾

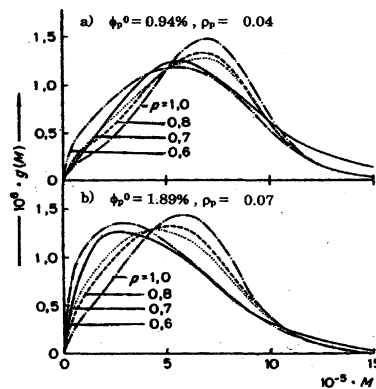


Fig. 7 Molecular weight distribution of polymer partitioned into polymer-rich phase $g(M)^{(2)}$ obtained from a solution of polystyrene in methylcyclohexane: Full line, experiment; double chain line, computer simulation with $p_1=0.6$; dotted line, computer simulation with $p_1=0.7$; broken line, computer simulation with $p_1=0.8$; chain line, computer simulation with $p_1=1.0$; $k'=0$ and $p_2 = \dots = p_n = 0$; a), $\phi_p^0 = 0.0094$, $\rho_p = 0.04$; b) $\phi_p^0 = 0.0189$, $\rho_p = 0.07$.

Fig.8 shows the plot of the polymer fraction in the polymer-rich phase $\phi_p^{(2)}$ vs. the relative amount of polymer in polymer-rich phase $\rho_p^{6,29}$. The broken, chain and full lines mean the theoretical calculations at $\phi_p^0 = 1.89, 0.94$ and 0.47% , respectively. The magnitude of $\phi_p^{(2)}$ depends largely on p_1 (ref.29).

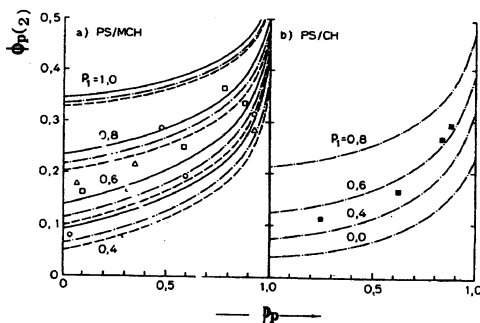


Fig.8 Effect of the relative amount of polymer in polymer-rich phase ρ_p on the polymer volume fraction $\phi_p^{(2)}$ remaining in the polymer-rich phase: Full line, theoretical curve at initial polymer volume fractions $\phi_p^{(2)} = 0.0047$; chain line, 0.0094 ; broken line, $\phi_p^0 = 0.0189$; numbers on curves denote the values of p_1 (cf. eq (43); $k'=0$ and $p_2 = \dots = p_n = 0$); Δ , \square , \circ , experimental data for $\phi_p^{(2)} = 0.0189, 0.00942$ and 0.0047 : a) polystyrene (PS)/ methylcyclohexane; b) PS / cyclohexane.

The volume ratio R of the two phases decreases drastically as ρ_p increases. Fig.9 is an illustrative case for a 0.94% solution. The difference in the experimental R values and the theoretical curve with $p_1 = 0.7$ for PS / MCH and $p_1 = 0.6$ for PS / CH is within experimental uncertainty in the range $\phi_p^0 = 0.47$ to 1.89% , irrespective of ϕ_p^0 .

By the use of figures like Figs. 8 and 9 the magnitude of p_1 can be more precisely estimated in such a manner that the experimental point coincides well with the theoretical value at a given ρ_p .²⁹

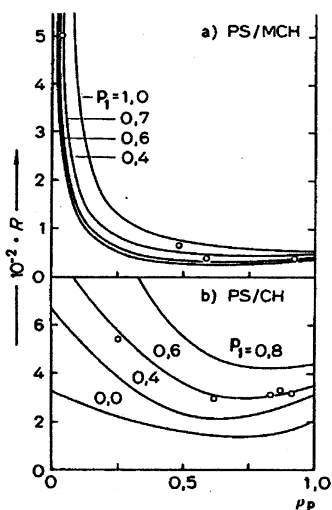


Fig.9 Effect of the relative amount of polymer in polymer-rich phase ρ_p on the volume ratio of two phases R for a) polystyrene (PS)/ methylcyclohexane and b) PS/ cyclohexane for initial polymer volume fraction $\phi_p^0=0.0094$: Full line, theoretical curves; \circ , experimental data for initial polymer volume fraction $\phi_p^0 = 0.0094$; numbers on curves denote p_1 value ($k' = 0$ and $p_2 = \dots, p_n = 0$).

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 to more concentrated solution, but the experimental accuracy is not high enough to estimate p_2 . Now, if one can employ the value of p_1 , estimated by other experiments such as osmotic pressure, critical phenomena etc., for a given polymer / solvent system, the MWD (molecular weight distribution) of the fraction and any other characteristics of phase separation can be completely calculated by using an electronic computer for the given experimental conditions (the MWD of the original polymer, fractionation scheme, initial polymer volume fraction ϕ_p^0 , ρ_p) without any ambiguity.²⁹

Table 4 summarizes the value of p_1 evaluated.

Table 4 Values of p_1 evaluated by phase separation phenomena and by successive fractionation for the polystyrene (PS) / methylcyclohexane (MCH) and PS / cyclohexane (CH) systems.^{6,29}

From ^{a)}	p_1	
	PS/MCH	PS/CH
MWD	0.6~0.7	ca.0.6
$\phi_p^{(2)}$ (Fig.8)	0.66 ± 0.10	0.56 ± 0.05
R (Fig.9)	0.69 ± 0.10	0.58 ± 0.05
SPF	0.74 ± 0.10	-
SSF	0.72 ± 0.10	-

a) SPF and SSF: successive precipitational and successive solutional fractionations, respectively; $\phi_p^{(2)}$, volume fraction of polymer-rich phase; R, volume ratio of polymer-lean phase to polymer-rich phase.

There is an extremely large gap between oversimplified theories of phase equilibria of polymer solutions and operational conditions of the fractionation in practice. In particular, the study of operational conditions of the fractionation from the standpoint of solution theory, even though qualitative, was limited to very special cases. The main reason for this limitation is that the theory of the phase equilibrium on rigorous monodisperse polymer/single solvent system cannot be generalized by simple mathematical analysis to polydisperse polymer/single solvent system, corresponding to the fractionation. It was only after many years, that by the use of electronic computers, the principal mechanism underlying the fractionation was well understood.^{1,2} In 1968 Kamide et al.^{8,9} and Koningsveld et al.¹²² bridged this gap by using large (at that time) electronic digital computers.⁷

5. Molecular weight dependence of χ -parameter k'

5.1 Experimental determination of k'

k' (eq. (38)) can be evaluated by the following means:⁶

(1) **Comparison of the theoretical and experimental relations between the partition coefficient σ ($\equiv (1/n)\log(\phi_{n(2)}/\phi_{n(1)})$), where ϕ_n is the volume fraction of n -mer and the suffixes 1 and 2 refer to the polymer-lean, and polymer-rich phases respectively, both in phase equilibrium, and $1/n$, (2) **direct determination of χ or A_2 , by light scattering or membrane osmometry.** However, we need χ values accurate to four significant digits in order to evaluate k' with two significant figures. Such precision is undoubtedly beyond the accuracy of actual experiments at present,⁶ (3) **comparison of molecular weight distributions (MWD) of the polymer in the two phases with the theoretical curves** calculated assuming various values for k' .**

5.2 Temperature dependence of k'

Fig. 10 shows the temperature dependence of k' for the PS / MCH system⁴¹. In this figure, Kamide et al. data for PS / MCH¹³⁶ except for $\rho_p \geq 0.88$ and those for PS / CH¹³⁶ are shown for comparison. The k' parameter increases linearly with an increase in $1/T$. In other words, this parameter becomes small as the temperature T approaches the Flory theta temperature. Kamide and his coworkers demonstrated for the PS / CH and PS / MCH systems that k' vanished at Flory theta temperatures (307K and 343K, respectively). Therefore, it may be concluded that the molecular weight dependence of χ changes its sign at the Flory theta temperature θ and that k' can be expressed by eq. (39): k_0 in eq. (39) is estimated to be -104.2 for PS / CH system and -132.0 for PS / MCH system.

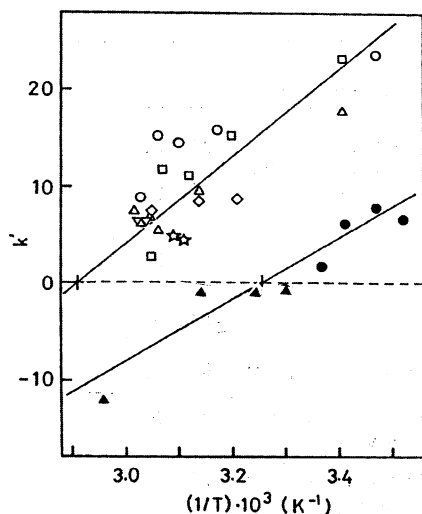


Fig.10 Changes in the k' parameter with temperature T : closed and half closed mark, polystyrene (PS) / cyclohexane system: ●, Kamide-Miyazaki¹³⁶; half closed circle, Scholte by light scattering^{137,138}; open mark, PS/ methylcyclohexane system: □, $\phi_p^0=0.50 \times 10^{-2}$; ◇, $\phi_p^0=0.47 \times 10^{-2}$; ○, $\phi_p^0=0.86 \times 10^{-2}$; ☆, $\phi_p^0=0.94 \times 10^{-2}$; △, $\phi_p^0=2.0 \times 10^{-2}$; ▽, $\phi_p^0=1.86 \times 10^{-2}$.

5.3 Role of the concentration and the molecular weight dependences in phase separation phenomena⁶

Summarizing, the molecular weight dependence of the χ parameter has a minor effect, when compared with its concentration dependence, on the phase separation phenomenon of polymer solutions, but this effect is not always negligible and comes into play with the following characteristics: the partition coefficient σ , the molecular weight distribution (MWD) of the polymer with small ρ_p in the polymer-rich phase and/or with small ρ_p in the polymer-lean phase, the M_w/M_n (M_w , the weight-average molecular weight; M_n , the number-average molecular weight) vs. M_w relations for the fractions isolated by successive precipitational fractionation (SPF). It should be noted at the limit $\rho_p \rightarrow 1$, the polymers remaining in the polymer-lean phase are absolutely independent of the p_1 parameter and in the above regions, the k' parameter may play an important role. We can interpret the previously observed small discrepancy between the actual experiments on the PS / CH and PS / MCH systems and the theory, by the molecular weight dependence of the χ parameter. The fractionation efficiency decreases with an increase in the molecular weight dependence of the χ parameter.

The effect of the k' and p_1 parameters on the phase equilibrium characteristics is very complicated, but the comparative role of the two parameters is summarized in Table 5.^{20,29,136}

Table 5 Comparison of the effect of k' and p_1 parameters on phase equilibrium characteristics.⁶

Phase equilibrium characteristics	Comparative role	
Partition coefficient	At limit of $\rho_p \rightarrow 0$	$k' < p_1$ ^a
Volume ratio R	At limit of $\rho_p \rightarrow 1$	$k' > p_1$ ^b $k' \ll p_1$
Polymer volume fraction in polymer-rich phase $v_{p(2)}$		$k' \ll p_1$
Polymer volume fraction in polymer-lean phase $v_{p(1)}$		$k' \approx p_1$
$\bar{n}_w(2) / \bar{n}_n(2)$	At limit of $\rho_p \rightarrow 0$	$k' < p_1$
	At limit of $\rho_p \rightarrow 0$ and large p_1	$k' > p_1$
	At limit of $\rho_p \rightarrow 0$ and small p_1	$k' < p_1$
	At limit of $\rho_p \rightarrow 1$ and large p_1	$k' > p_1$
	SPF Initial few fractions	$k' < p_1$
	End few fractions	$k' > p_1$
$\bar{n}_w(1) / \bar{n}_n(1)$	At limit of $\rho_s \rightarrow 0$	$k' > p_1$
	At limit of $\rho_s \rightarrow 1$ and large p_1	$k' > p_1$
	At limit of $\rho_s \rightarrow 0$ and small p_1	$k' < p_1$
	SSF Initial few fractions	$k' > p_1$

^a p_1 parameter is much more effective than k' parameter.

^b k' parameter is much more effective than p_1 parameter.

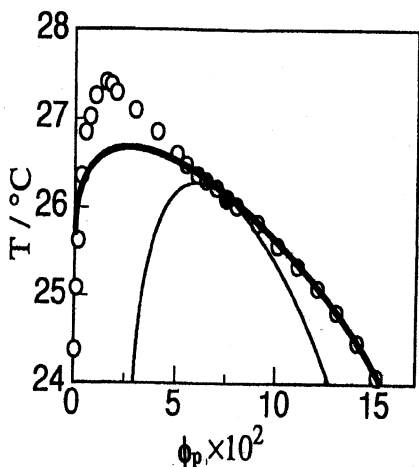


Figure 11. Cloud point curve of polystyrene($M_w=2.4 \times 10^5$ and $M_w/M_n=2.8$)/cyclohexane system⁶²: \circ , experimental data;¹ broad full line, theoretical curve calculated using $p_1=0.60$, $p_2=0.46$, $\Psi_0=0.27$ and $\theta=307.0$ K. Fine full line, theoretical spinodal curve; \bullet , theoretical critical solution point. Here, $a=0.23$, $b=82.89$, $p_1=0.60$ and $p_2=0.46$ were utilized for calculation of spinodal curve and critical solution point.

Figure 11 shows the experimental CPC (open circle) and the theoretical CPC (bold line), calculated by Kamide et al.'s method⁴⁷ using the value of a , b , p_1 and p_2 estimated in reference 65. In the figure, the critical solution point (CSP) (filled circle) and spinodal curve (SC) (narrow full line) also calculated by Kamide et al.'s procedure⁴⁶⁻⁴⁸ using the same a , b , p_1 and p_2 data, are shown. As the theory requests, CPC and SC coincides at CSP. The theoretical CPC agrees well with the experimental CPC except the threshold point region. Although as early as 1984 Kamide et al. suggested that the above inconsistency at lower ϕ_p region may be due to the neglect of the molecular weight dependence of χ -parameter⁴⁷. Any effort to dissolve this disagreement in the line of the above suggestion has ended in failure although Kamide was too optimistic in his monograph in 1989.⁵ So, this is even now undissolved problem.⁶⁵

6. Flory Enthalpy Parameter

6.1. κ and κ_0

The pair interaction Flory enthalpy parameter κ is defined by the van Laar-Scatchard type relation⁸⁶:

$$\kappa = \frac{\Delta H_0}{RT \phi_p^2} \quad (64)$$

where ΔH_0 is the partial molar heat of dilution with respect to the solvent.

Calorimetry allows direct determination of ΔH_0 , and thus κ . The calorimetric experiments, made by Fujishiro and his students, showed that κ was not independent of T and ϕ_p , which was firstly assumed in the original Flory-Huggins theory, but that it is a purely phenomenological parameter, which depends on both T and ϕ_p ¹³⁹.

$$\kappa = \kappa_0 + \kappa_1 \phi_p + \kappa_2 \phi_p^2 + \dots \quad (65)$$

κ_0 in eq. (65) is given by

$$\kappa_0 = \lim_{\phi_1 \rightarrow 0} \{ \Delta H_0 / (RT\phi_1^2) \} \quad (66)$$

and $\kappa_1, \kappa_2 \dots$ are the 1st, 2nd, \dots order concentration-dependence parameters of κ . Theoretically, κ or simply κ_0 can be evaluated by various methods, directly or indirectly as will be described later. In other words, if good agreement between κ or κ_0 values evaluated by various methods is confirmed, the theory, on which the principles of the methods are based, is considered thoroughly acceptable to explain all the thermodynamic properties of polymer solutions.⁴⁸

6.2 Experimental determination of κ_0

(a) **The temperature dependence of the chemical potential of the solvent**, estimated from vapor pressure and osmotic pressure, through use of the relation⁸⁶,

$$\kappa_0 = \lim_{\phi_1 \rightarrow 0} \{ 1 / (RT\phi_1^2) \} \{ \partial(\Delta\mu_0/T) / \partial(1/T) \}_{p,\phi} \quad (67)$$

where $\Delta\mu_0$ is given by eq. (46). The partial differentiation of $\Delta\mu_0/T$ with respect to $1/T$ is carried out under constant pressure and constant composition except the polymer.

(b) **The critical phenomena (critical solution temperature T_c and critical polymer concentration ϕ_p^c)**. κ_0 is related to the Flory theta temperature θ and the Flory entropy parameter Ψ_0 through the definition of θ ⁸⁶.

$$\kappa_0 = \theta \Psi_0 / T_c \quad (68)$$

with

$$\Psi_0 = \lim_{\phi_1 \rightarrow 0} (\Delta S_0 - \Delta S_0^{\text{comb}}) / (R\phi_1^2) = \lim_{\phi_1 \rightarrow 0} (\Delta\mu_0 - \Delta H_0 - T\Delta S_0^{\text{comb}}) / (RT\phi_1^2) \quad (69)$$

ΔS_0 is the partial molar entropy of dilution and ΔS_0^{comb} , the combinatorial entropy term.

θ and Ψ_0 can be evaluated from T_c (and θ_p^c) for a series of solution of polymers having different molecular weights by the method described in section 2.7 [SF¹¹³, Stockmayer¹¹⁴, Kamide - Matsuda(KM)⁴⁶, and Koningsveld - Kleintjens - Schultz(KKS)¹¹⁷].

(c) **Temperature dependence of A_2 by membrane osmometry or light scattering measured in vicinity of the θ temperature.** Ψ_0 is determined by

$$\Psi_0 = (V_0^0 / v^2) \theta (\partial A_2 / \partial T)_0 \quad (\text{Here, } v \text{ is the specific volume of polymer}) \quad (70)$$

Then, it is possible to evaluate κ_0 by putting θ and Ψ_0 obtained thus into eq.(70).

(d) **Calorimetry**

The heat of dilution ΔH and accordingly ΔH_0 can be directly measured by calorimetry.

Fig. 12 demonstrates schematic routes of determination for κ_0 .⁵³

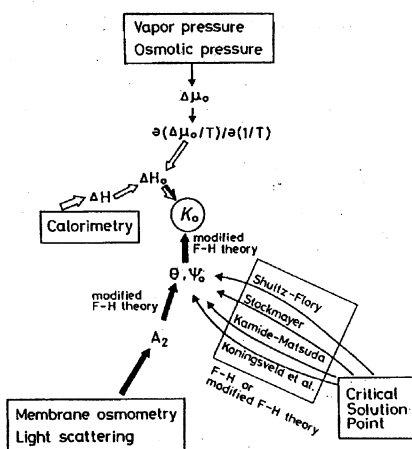


Fig.12

Routes of calculation of the Flory enthalpy parameter κ_0 from experimental data of vapor pressure, osmotic pressure, light scattering and critical solution points.

6.3 Molecular weight dependence of κ_0 (polystyrene/ cyclohexane)

Table 6 summarizes κ_0 and Flory θ temperature for polystyrene-cyclohexane system.⁵³

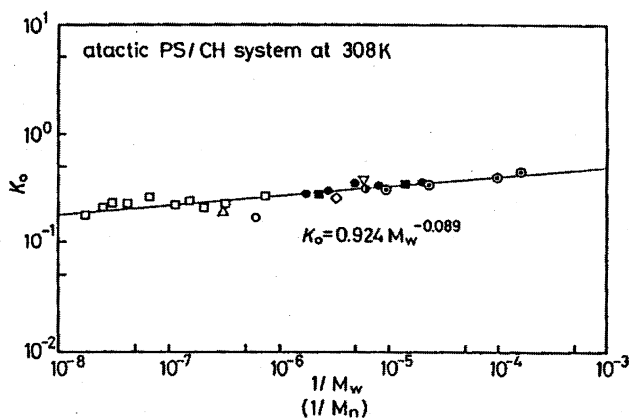


Fig.13 Log-log plot of Flory enthalpy parameter at infinite dilution κ_0 , evaluated by the temperature dependence of the chemical potential and second virial coefficient A_2 in the vicinity of the theta temperature and by calorimetry versus the reverse of weight-(or number-) average molecular weight $M_w(M_n)$ for the atactic polystyrene / cyclohexane system: ●, Krigbaum(membrane osmometry (MO)); ■, Krigbaum-Geyner (MO)¹¹⁶; half black circle, Scholte (ultracentrifuge)¹¹⁶; △, Krigbaum-Carpenter (light-scattering (LS))¹⁴¹; ▽, Schulz-Baumann (LS)¹⁴²; ◇, Kotera et al. (LS)¹⁴³; ○, Outer et al. (LS)¹⁴⁰; □, Miyaki-Fujita (LS)¹⁴⁴; ⊙, Fujihara (calorimetry)¹⁴⁷. Solid line, the equation(71).

Table 6 Flory θ temperature and enthalpy parameter κ_0 at infinite dilution for the upper critical solution point of atactic polystyrene-cyclohexane system

Method		$\frac{\theta}{K}$	$\kappa_0(M_n \text{ or } M_w \times 10^{-4})$ at 308°C	(Data)
(1) Chemical potential	Membrane osmometry	—	0.21(44)	(Krigbaum-Geymer) ¹¹⁴
	Sedimentation equilibrium	—	0.32(15.4)	(Scholte) ¹¹⁶
(2) Critical point	Shultz-Flory	306.2	0.75(-)	[0.28] ^a (Koningsveld et al. ¹¹⁸ , Kuwahara et al. ¹¹⁹ , Saeki et al.) ¹²⁴ 0.26(∞)
	Stockmayer	306.5	0.80(-)	
	Koningsveld et al.	305.2	0.29(-)	
	Kamide-Matsuda	305.1	0.27(-)	
(3) Second virial coefficient	Membrane osmometry	307.6	0.28(∞)	[0.28] ^a (Krigbaum) ¹³⁹ (Krigbaum-Geymer) ¹¹⁶
		307.6	0.27(∞)	
	Light scattering	308.0	0.19(163)	[0.26] ^a (Outer et al.) ¹⁴⁰ (Krigbaum-Carpenter) ¹⁴¹ (Schulz-Baumann) ¹⁴² (Kotera et al.) ¹⁴³ (Miyaki-Fujita) ^{144,145} (Tong et al.) ¹⁴⁶ (Fujihara) ¹⁴⁷
		308.4	0.19(320)	
		307	0.39(17)	
		307.4	0.26(30)	
		307.4	0.22(∞)	
		308	0.30(∞)	
		307.7	0.28(∞)	
(4) Heat of dilution	Calorimetry	—		(Fujihara) ¹⁴⁷

^a Averaged value (See K.Kamide, S.Matsuda and H.Shirataki, *Polym. J.* 20, 31 (1988))

A log-log plot of κ_0 against M_w^{-1} or M_n^{-1} for atactic PS / CH systems at 307.2K is shown in Fig. 13. All data points available yielded a straight line given by (ref. 48).

$$\kappa_0 (\equiv \Psi_0) = 0.924 M_w \text{ (or } M_n) ^{-0.089} \quad (71)$$

Eq. (71) is valid over the entire molecular range which is accessible experimentally from 6.2×10^3 to 5.680×10^7 . Eq.(71) is represented by the full line in Fig.13⁵³. Therefore, we can conclude that the most probable κ_0 value is, in a strict sense, dependent on M_w (or M_n), irrespective of the method employed and that if eq. (71) can be expanded its applicability to $M_w = \infty$, κ_0 at the infinite molecular weight may be zero. This is an experimental indication that both the randomness in the mixing of a polymer and solvent and the special homogeneity of the polymer segment density in solution are expected to be realized in dilute solutions of polymer with infinitely large molecular weight (i.e., $\Delta S_0 = \Delta S_0^{\text{comb}}$). The fact that methods (1) - (4) give essentially identical κ_0 values within ± 0.02 for a given PS sample in CH, strongly supports the validity of the modified Flory-Huggins theory (Model V)⁴⁸.

6.4 Flory entropy parameter Ψ_0 .

The Flory entropy parameter Ψ_0 can also be evaluated from the critical point data as well as the

temperature dependence of A_2 [6.2.(c)] as follows :

(1) Kamide-Matsuda method⁴⁶

$$\frac{1}{T_c} = \frac{\chi_0^c}{\theta\psi} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi}\right) \quad (72)$$

Using χ_0^c , calculated from eqs. (59) and (60) and experimental T_c , we can determine θ and Ψ from the plot of $1/T_c$ against χ_0^c .⁴⁶

(2) Stockmayer method¹¹⁴

$$\frac{1}{T_c} = \frac{1}{\theta\psi} \left\{ \frac{1}{2} \left(\frac{1}{n_w^{1/2}} + \left(\frac{n_z}{n_w}\right)^{1/2} \right) \times \left(\frac{1}{n_w^{1/2}} + \left(\frac{n_w}{n_z}\right)^{1/2} \right) \right\} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi}\right) \quad (73)$$

(3) Shultz-Flory method¹¹³

When $n_w = n_z$ is assumed, eqs. (58) and (74) are reduced to the well known equations derived by Shultz and Flory.

$$\frac{1}{T_c} = \frac{1}{\theta\psi} \left\{ \frac{1}{2} \left(\frac{1}{n_w^{1/2}} + 1 \right)^2 \right\} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi}\right) = \frac{1}{\theta\psi} \left(\frac{1}{n_w^{1/2}} + \frac{1}{2n_w} \right) + \frac{1}{\theta} \quad (74)$$

7. New strategy to give theoretically reasonable explanation to χ -parameter: Computer simulation of lattice model

(a) Preface

Kamide and Shirataki⁶² attempted to examine the validity of average concentration approximation in hypotheses (4) and (6), employed in the Flory-Huggins lattice theory of polymer solution, and investigated the concentration- and molecular weight-dependences of χ (accordingly, the reliability of the expression of χ (eqs. (33), (36) and (37)) for quasi-strictly regular solution (i.e., random mixing~non-athermal polymer solution⁶⁴ (Model III). For this purpose, computer experiments by applying Monte Carlo simulation method to the lattice model, where hypotheses (1), (2) and (5) are strictly adopted, were carried out.

(b) Computer simulation⁶²

1) Suppose a long flexible linear polymer chain consisting of n identical repeating units, whose size is equal to that of solvent molecules and are freely movable under the condition that these segments are linearly connected. In this case, the repeating units are regarded as the segments. Then, the number of segments comprising a polymer chain is for simplicity the degree of polymerization, n . Define the first segment by the segment at the chain end, the second segment by the segment nearest neighbour of the first chain segment, \dots , n th segment by the segment of the another opposite chain end.

2) Consider the case where N_1 polymer molecules and N_0 solvent molecules are to be arranged on $L (=N_1n + N_0)$ lattice sites in three dimensional most closely packed hexagonal lattice space (the lattice co-ordination number $z=12$). In this case, the total number of lattice site of L is chosen as $40 \times 40 \times 40 = 64000$. Assign one segment, which constitutes a polymer chain whose n is constant ($n = 5 \sim 700$), to one lattice site initially empty. Assign at random the second, third, fourth, \dots , n th segments of the first polymer chain to the lattice in the same manner as the first segment under the condition that all the segments constituting a polymer chain is linearly connected in the order of first, second, \dots , n th. This means that the succession of segments comprising the first polymer chain must occupy a series of consecutively contiguous lattice sites and is a kind of self-avoiding walk.

- 3) Repeat this kind of assignment of polymer chains. Total number of polymer chains to be assigned in the space is given by the ratio $\phi_p L/n$. After all the polymer chains are assigned to the lattice sites, place $L(1 - \phi_p)$ solvent molecules on the hence left unfulfilled lattice sites (i. e., one solvent molecule to one site). Then, the polymer solution having a specific configuration (in other words, at a specific instant) is hypothetically prepared. Count the number of the closest neighbor solvent - segment contacts existing in the above solution, n_c .
- 4) Apply first the reptation movement to all the polymer molecules simultaneously and apply next the crankshaft movement to them. Each polymer chains may be rearranged to another internal configurations. The reptation and crank shaft movements are schematically demonstrated in Figure 14. This operation is defined as one step. Avoid any possible multiplicative arrangement of two or more segments belonging to the same or different chain.

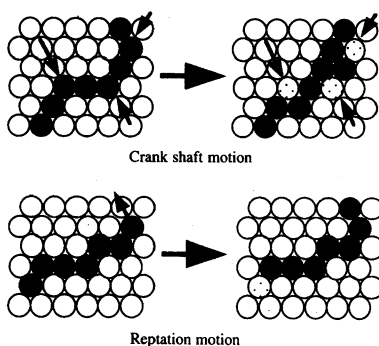


Fig. 14 Schematic representation of two types of chain motion in hexagonal lattice.

The total number of polymer segment-solvent pairs at equilibrium state $n_{c,e}$ as functions of the concentration ϕ_1 and the degree of polymerization n of the polymer solutes. Two types of chain motions (crankshaft motion and then reptation motion) were applied to all the polymer molecules in the lattice simultaneously and this operation (crankshaft-reptation motions) was repeated 1500 times. Any possible multiplicative arrangement of two or more segments belonging to the same or different chain was avoided.

(c) Theoretical background ^{62,7}

$n_{c,e}$ is given by

$$n_{c,e}/(\phi_0\phi_1L) = C_x (1 + \sum p_i \phi_1^i) \quad (75)$$

with

$$C_x \equiv \lim_{\phi_1 \rightarrow 0} n_{c,e} / (\phi_0\phi_1L) = C_0(1 + k'/n) \quad (76)$$

$$C_0 = Rb/\Delta\epsilon \quad (77)$$

When the average concentration approximation (hypothesis (4)) is applied, C_x and p_i are given

by

$$C_x = z \quad (78)$$

$$p_i = 0 \quad (79)$$

Then, from the plots of C_x vs. $1/n$ and the plots of $n_{c,e}/(\phi_0 \phi_1 L)$ against ϕ_1 the validity of the expression of χ (eqs. (33), (36) and (37)) could be confirmed by the computer experiments (Figs. 4a, 4b and 5 of reference 65). If eqs. (33), (36) and (37) are applicable, k' and p_1 can be determined from the above plots, respectively.

(d) Results⁶²

The plots of n_c as a function of step number $n=10$ in the ϕ_p range 0.02 to 0.24 show that n_c increases with step number i , approaching to an asymptotic value. The step, at which n_c attains its asymptotic value, i_a , is smaller for solutions with lower n (degree of polymerization) and of lower ϕ_p . For example, $i_a < 50$ for $n=10$ and $\phi_p = 0.24$, $i_a < 15$ for $n=10$ and $\phi_p = 0.10$, $i_a < 400$ for $n=100$ and $\phi_p = 0.24$ and $i_a < 65$ for $n=100$ and $\phi_p = 0.10$. It was confirmed that $i_a < 500$ holds without exception under the whole conditions employed. Therefore, approximately constant values are obtained within probable experimental uncertainty. $n_{c,e}$ was evaluated as average n_c between 500 - 1500 steps. It can be considered that an equilibrium state is attained quickly for solutions, with smaller n , of lower ϕ_p .

Fig. 15 shows the relations between $n_{c,e}/(\phi_0 \phi_p L)$ and ϕ_p for given n ($n = 5 \sim 700$). $n_{c,e}/(\phi_0 \phi_p L)$ is, to a fairly good approximation, in linear proportion to ϕ_p over wide range of n , suggesting a significant concentration dependence of χ -parameter. Then, eq 75 can be simplified into

$$\frac{n_{c,e}}{\phi_0 \phi_p} = c_n (1 + p_1 \phi_p) \quad (75')$$

Experimentally it has been confirmed for polyisobutylene (PIB) - benzene (10, 24.5, 25 and 40°C¹⁰³), atactic polystyrene (PS) - methyl ethyl ketone (25 °C)⁵⁸, atactic PS - cyclohexane^{6,47} that χ -Parameter is linearly proportional to ϕ_p in the range $0 < \phi_p \sim 0.3$ and p_1 is obtained as an initial slope of the plots of χ vs. ϕ_p . Note that in this study the upper limit of ϕ_p was 0.24. Therefore, it is expected that only p_1 should be a major significant factor contributing to the plots in Fig.15⁶². Full line in the figures were obtained by applying the least-square methods to the data, using eq 75. Table 7 collects the values of C_n and p_1 estimated from Fig.15.

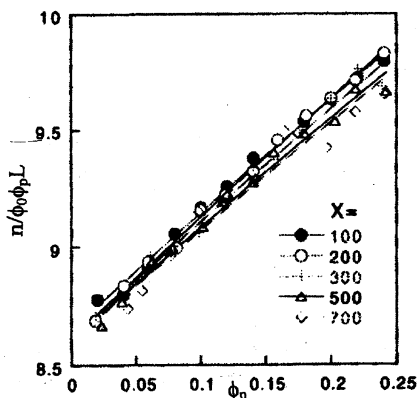


Fig.15 Relationship between $n_{c,e}/(\phi_0 \phi_p L)$ and ϕ_p for $n=100-700$.⁶²

p_1 first increases rapidly with an increase in n , then slowly approaching an asymptotic value (ca. 0.6) at $n \approx 200$. Inspection of the table shows that successive connection of the polymer segments brings about the concentration dependence of χ -parameter. p_1 values of PS in non-polar solvents are close to 2/3, theoretically predicted at $T = \theta$ for random mixing-non zero heat of mixing solution^{6,7} and are little higher than the value (ca. 0.6) obtained in this computer experiments, but no significantly so.

Computer experiments on random mixing-non-athermal polymer solutions indicated that the average concentration approximation hypothesis cannot be approved even if random mixing is assumed and eqs. (35), (38) and (39) appears to be of correct form to represent the χ -parameter. In other words, the hypothesis employed in Flory-Huggins theory can never be accepted even in the quasi-regular solutions and the concentration- and molecular weight-dependences of the χ -parameter, observed in actual experiments, can be explained reasonably, if the consecutive characteristics of linear chain molecules is strictly considered.

Table 7 Dependence of χ on ϕ_p and n for random mixing-non-athermal polymer solution (computer simulation)

n	Cn	p_1	k'	n	Cn	p_1	k'
1	12 ^a	~	0.39	100	8.65	0.556	0.49
5	9.821	0.247	0.70 ₉	200	8.61	0.591	0.23
10	9.25	0.343	0.76	300	8.62	0.564	0.70
20	8.92	0.439	0.74	500	8.61	0.544	0.58
30	8.80	0.480	0.70	700	8.60	0.539	---
40	8.75	0.518	0.70
50	8.72	0.522	0.70
60	8.67	0.556	0.49	∞	8.6(=C ₀) ^b	0.54	0.6~0.7

a: estimated

b: estimated

8. Phase equilibria of polymer blend (P₁/P₂)

8.1 Monodisperse polymer P₁/ monodisperse polymer P₂

Scott¹⁴⁸ is probably the first who carried out a theoretical study on the phase equilibria of the polymer solutions consisting of two kinds of polymer with the different chemical compositions (polymer 1 and polymer 2), without solvent (i.e., quasi-binary polymer mixture). He derived, based on the Flory-Huggins solution theory, the relationships giving the chemical potentials of monodisperse polymer 1 and monodisperse polymer 2, $\Delta\mu_X$ and $\Delta\mu_Y$:

$$\Delta\mu_X = RT[\ln\phi_1 + (1 - X/Y)\phi_2 + X\chi_{12}\phi_2^2] \quad (80)$$

$$\Delta\mu_Y = RT[\ln\phi_2 + (1 - Y/X)\phi_1 + Y\chi_{12}\phi_1^2] \quad (81)$$

where χ_{12} is the thermodynamic interaction parameter between polymers 1 and 2, X and Y are the degree of polymerization, DP (in a strict sense, the molecular volume ratio of the polymer and the lattice unit (the polymer segment)), and ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2 ($\phi_1 + \phi_2 = 1$). The equations for χ_{12} , ϕ_1 and ϕ_2 at the critical solution point (CSP) are:

$$\partial \Delta\mu_X / \partial \phi_1 = 0 \text{ and } \partial^2 \Delta\mu_X / \partial \phi_1^2 = 0 \text{ (or } \partial \Delta\mu_Y / \partial \phi_2 = 0 \text{ and } \partial^2 \Delta\mu_Y / \partial \phi_2^2 = 0) \quad (82)$$

and finally we obtain

$$\chi_{12}^c = 1/2(X^{-1/2} + Y^{-1/2})^2 \quad (83)$$

$$\phi_1^c = Y^{1/2} / (X^{1/2} + Y^{1/2}) \quad (84)$$

$$\phi_2^c = X^{1/2} / (X^{1/2} + Y^{1/2}) \quad (85)$$

Note that at CSP the spinodal curve (SC) and the neutral equilibrium conditions should be satisfied concurrently, for the P_1/P_2 system.

Scott predicted that values of χ_{12} for these systems are several digits smaller than those for a mixture of two low molecular weight liquids ($\chi_{12} \sim 2.0$) and those for polymer-solvent systems ($\chi_{12} \sim 0.5$).¹⁴⁸

8.2 Polydisperse polymer/ polydisperse polymer (P_1/P_2)

(1) Theory

An attempt to generalize CSP equations (eqs.(83)~(85)) for two monodisperse polymer mixture to the case of multicomponent polymer 1/ multicomponent polymer 2 systems was made by Koningsveld et al.¹⁴⁹ They derived the equations of spinodal and neutral equilibrium conditions (Eqs. (12) and (13) in their paper) for systems of multicomponent polymer 1/ multicomponent polymer 2/ single solvent. As Kamide et al. pointed out,⁵⁷ they did not show the detailed mathematical derivation of the equations. Koningsveld et al. described that the spinodal condition for the multicomponent polymer 1/ multicomponent polymer 2 system was derived as Eq. (23) of their paper after multiplying Eq. (12) of their paper by ϕ_0 and reducing ϕ_0 to zero. But we should first define the mean Gibbs free energy of mixing ΔG_m (See eq. (86))^{57,7}

$$\Delta G_{\text{mix}} = \text{RTL} \left[\sum_{i=1}^{m_1} \frac{\phi_{X_i}}{X_i} \ln \phi_{X_i} + \sum_{j=1}^{m_2} \frac{\phi_{Y_j}}{Y_j} \ln \phi_{Y_j} + \chi_{12} \phi_1 \phi_2 \right] \quad (86)$$

where L is the total number of lattice site ($= \sum_i X_i N_{X_i} + \sum_j Y_j N_{Y_j}$; N_{X_i} and N_{Y_j} are the numbers of X_i -mer of polymer 1 and that of Y_j -mer of polymer 2, respectively), m_1 and m_2 are the total numbers of the components consisting polymer 1 and polymer 2, ϕ_{X_i} is the volume fraction of X_i -mer of multicomponent polymer 1, ϕ_{Y_j} is the volume fraction of Y_j -mer of multicomponent polymer 2, and ϕ_1 and ϕ_2 are the total volume fractions of polymer 1 and polymer 2 as defined by the relations $\phi_1 = \sum_i \phi_{X_i}$ and $\phi_2 = \sum_j \phi_{Y_j}$. The first and the second terms in the right-hand side of eq. (86) are the combinatory terms and the third term is the term relating to the mutual thermodynamic interaction. Shirataki et al.⁵⁷ derived straightforwardly the equation of spinodal from the determinant (eq.(87))

$$|\Delta G_v| = 0 \quad (87)$$

constructed using ΔG_m (eq.(86)). They described that the equation of the neutral equilibrium conditions (eq. (24) in their paper) for two different multicomponent polymers can be derived using a method analogous to the spinodal condition. The equation should be rigorously derived from the determinant (Eq. (88)) of the neutral equilibrium conditions.

$$|\Delta G^2| = 0 \quad (88)$$

We can take into consideration the concentration (in this case composition) dependence of χ_{12} ,

$$\chi_{12} = \chi_{12}^0 \left[1 + \sum_{t=1}^{n_t} (p_{1,t} \phi_1^t + p_{2,t} \phi_2^t) \right] \quad (89)$$

where $t=1,2,\dots,n_t$, and n_t is the highest order number of concentration dependence parameter taken into account in the calculation. Eq. (86) is symmetrical with respect to the exchange of polymer 1 and polymer 2. The coefficient χ_{12}^0 in Eq. (86) is a parameter, independent of ϕ_1 and ϕ_2 and inversely proportional to T . The coefficients $p_{1,t}$ and $p_{2,t}$ are the parameters of concentration dependence. After combining eq. (83) with eq. (86), we can obtain $\Delta\mu_{X_i}$ and $\Delta\mu_{Y_j}$ in the case when χ_{12} is concentration-dependent are expressed as for polydisperse polymer 1/polydisperse polymer 2.⁷

$$\Delta\mu_{X_i} = RT \left[\ln \phi_{X_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) \phi_1 + X_i \left(1 - \frac{1}{Y_n} \right) \phi_2 + X_i \chi_{12} \phi_2^2 \right] \quad (90)$$

$$\Delta\mu_{Y_j} = RT \left[\ln \phi_{Y_j} - (Y_j - 1) + Y_j \left(1 - \frac{1}{X_n} \right) \phi_1 + Y_j \left(1 - \frac{1}{Y_n} \right) \phi_2 + Y_j \chi_{12} \phi_1^2 \right] \quad (91)$$

When both polymer 1 and polymer 2 are monodisperse (i.e., single component), eqs.(90) and (91) straightforwardly reduce to eq.(80) and (81).

(2) Comparison with experiments

To confirm the reliability of the theory of phase equilibria of multicomponent polymer 1/multicomponent polymer 2 systems (i.e., quasi-binary systems) and the method of computer experiment based on Shirataki et.al's theory (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 285 (1990); *ibid.* **23**, 299 (1990); *Polym. Int.* **29**, 219 (1992)), CSP has been determined experimentally for the quasi-binary mixtures of poly(ethylene oxide) ($M_w=647$, $M_w/M_n=1.15$) and poly(propylene oxide) ($M_w=2028$, $M_w/M_n=1.08$ and $M_w=2987$, $M_w/M_n=1.13$)(Table 8). χ_{12} and the concentration dependence parameters for the above quasi-binary systems were determined and cloud point curve (CPC), phase volume ratio R and CSP values calculated on the basis of the theory are in good agreement with the values determined experimentally (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 299 (1990)). Figure 16 shows the experimental and theoretical CPCs and CSPs for the system A and B in Table 8. The full lines are the theoretical CPCs calculated taking into consideration the concentration dependence of χ_{12} . The theoretical CPCs are in excellent agreement with the actual experiments for both systems. The parameters in eq. (89) were found to be $p_{1,1}=-0.0917$, $p_{1,2}=0.0022$, $a=-0.3125$ and $b=131.59$ for System A and $p_{1,1}=-0.1120$, $p_{1,2}=0.0027$, $a=-0.2045$ and $b=98.09$ for system B.

Table 8 Comparison of experimental and calculated CSPs

System	Polymer	ϕ_1^c (exp.)	ϕ_2^c (calc)	$T^{CSP}(\text{exp.})/^\circ\text{C}$	$T^{CSP}(\text{calc.})/^\circ\text{C}$
A	E-600/P-2000	0.5875	0.5841	46.3	47.0
B	E-600/P-3000	0.613	0.6264	59.8	61.2

(See H. Shirataki and K. Kamide, *Polym.Int.* **34**,73(1994)).

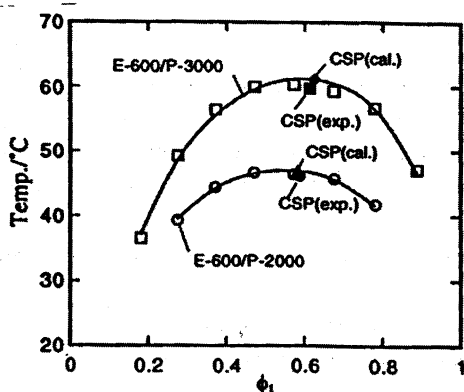


Fig.16 Theoretical CPC and CSP for PEO/PPO systems. Solid lines, Theoretical CPC with $p_{1,1}=0.0917$ and $p_{1,2}=0.0022$ for E-600/P-2000, and with $p_{1,1}=0.1120$ and $p_{1,2}=0.0027$ for E-600/P-3000; (\square) and (\circ) experimental CPC for E-600/P-3000 and E-600/P-2000. (\blacksquare) and (\bullet) experimental CSP for E-600/P-3000 and E-600/P-2000. (\blacklozenge) and (\blacktriangle) theoretical CSP for E-600/P-3000 and E-600/P-2000. (See H. Shirataki and K. Kamide, *Polym. Int.* **34**, 73 (1994)).⁶¹

9. Phase equilibrium of quasi-ternary system: polydisperse polymer in mixed solvent ($P_1/S_2/S_1$)

Kamide and his coworkers developed the theory of phase phenomena, including chemical potential, spinodal condition, neutral equilibrium, and critical condition for quasi-ternary mixtures such as polydisperse polymer(P_1)/solvent(S_1)/solvent(S_2); polydisperse polymer(P_2)/polydisperse polymer(P_1)/solvent(S_0), and polydisperse polymer(P_2)/polydisperse polymer(P_1)/polymer (P_0). Here, they assumed that (a) χ_{01} , χ_{02} and χ_{12} are independent of concentration and molecular weight of polymers, (b) the molar volume of solvent and the segment of polymers 1 and 2 are the same, (c) solvent, polymers 1 and 2 are volumetrically additive, and (d) the density of solvent is the same as that of polymers 1 and 2.

Fig.17 demonstrates the phase diagram, theoretically constructed for $P_2/P_1/S_1$ system.

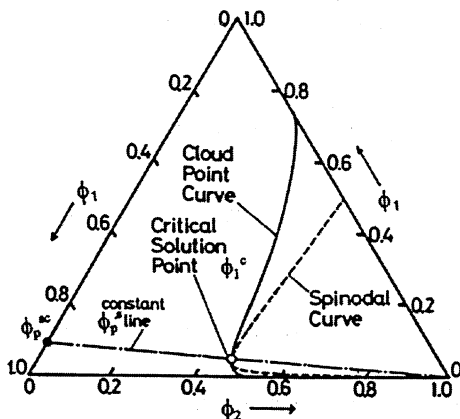


Fig.17 Cloud point curve (full line), spinodal curve (broken line) and critical solution point (unfilled circle) of a quasi-ternary system. Original polymer, Schulz-Zimm type distribution ($n_w^0=300$, $n_w/n_n=2.0$); $\chi_{12}=0.5$, $\chi_{13}=0.2$ and $\chi_{23}=1.0$. (See K. Kamide and S. Matsuda, *Polym. J.* **18**, 347 (1986)).⁴⁹

10. Conclusion

1. χ -parameter is not a constant, but functions of ϕ_1 and n as expressed as eqs.(33), (36-38) .
2. Model V (in Fig.1) is recommended to utilize for further study.
3. Colligative properties including osmotic pressure, vapor pressure, and light scattering are significantly influenced by p_1 (i.e, the first term of ϕ_1). On the other hand, phase equilibrium, critical phenomena are explained in terms of p_1 and p_2 .
4. Experimental method for determining with high reliability and accuracy are methods, based on critical phenomena (cloud point, solution critical point).
5. Formula for the chemical potential of solvent $\Delta\mu_0$ is most adequately expressed by eq.(46).
6. Using $\Delta\mu_0$ expressed by eq.(46) we can describe all colligative solution properties and phase equilibrium very consistently.
7. The critical phenomena, in particular, critical point (ϕ_1^c) is overestimated and the Flory's entropy parameter Ψ_0 , derived from the phenomena , is much larger than that by other methods , if the concentration-dependence is not considered.
8. Ψ_0 , obtained by analysis on critical point with consideration of p_1 and p_2 coincide with that by light scattering.
9. Effect of the polymolecularity is smaller than that of concentration-dependence of χ -parameter on critical point of the solution.
10. The Flory's enthalpy parameter at infinite dilution κ_0 , estimated for PS/CH by various methods and various authors, yields a straight line of long-long plot of κ_0 vs. M_w ; the weight-average molecular weight.
11. κ_0 at infinite M_w may be zero.
12. Successive connection of the polymer chain contributes significantly to the concentration-dependence of χ -parameter. In other words, average concentration approximation hypothesis cannot be approved even if random mixing is assured.
13. Even at present time more than 60 years after the first paper of the Flory-Huggins theory, the atactic polystyrene(PS/CH) system is almost the only system for which all the thermodynamic parameters necessary for describing $\Delta\mu_0$, such as p_1 , p_2 , θ , Ψ_0 and κ_0 are determined comprehensively.
14. Then, χ for PS/CH system can be expressed as function of temperature(T in °K) and polymer concentration (volume fraction) as

$$\chi = \{0.23 + 82.89/T\}(1 + 0.6000\phi_p + 0.460\phi_p^2)$$
15. The chemical potential of the solvent in polymer solution $\Delta\mu_0$ is generally given¹⁶ by

$$\Delta\mu_0 = RT \left\{ \ln(1-\phi_p) + \left(1 - \frac{1}{n_n}\right) v_p + \chi \phi_p^2 \right\} \quad (27)$$

16. Theory of thermodynamics for quasi-binary polydisperse polymer/solvent system was established and applied successfully to phase-equilibrium.
17. The theory was extended to the cases of polymer blend system and quasi-ternary system.

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