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UPPER AND LOWER CONSOLUTE SOLUTION TEMPERATURES OF THE PSEUDO-BINARY MIXTURES OF POLYDISPERSED POLYMETHYLMETHACRYLATE AND N-BUTYLCHLORIDE

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Abstract—The cloud point curves of upper and lower consolute solutions(UCST, and LCST) have been determined for the solutions of the polydispersed polymethylmethacrylate(PMMA) and n-butyl chloride. Along with the increase of average molecular weights, the equilibrium curves of the lower consolute polymer solutions shifted toward lower temperature regions, but the upper consolute points appeared at higher temperatures. In addition, the shapes of phase boundaries near the consolute solution points became flattened at both temperature regions because of the influence of the polydispersity. In describing the phase diagram of molecular weights, both of the critical consolute temperatures were calculated, incorporating the relative chain length and the temperature dependence for the modified Flory-Huggins interaction parameter χ_1.

INTRODUCTION

The phase behaviors of polymer solutions of both polymer melts and polymer-solvent mixtures are of great importance in investigating the physical properties and the morphological structures for polymer materials[1]. In the temperature-pressure-concentration diagrams(T-P-X) of binary or multicomponent systems included are all the information of phase separation, the loci of critical lines, and the terminal points of upper consolute solution temperature (USCT) and lower consolute solution temperature(LCST) [2]. In describing the solution state of polymer mixtures, the solution theories developed thus far included the lattice-based models[3,4] and the equation of state[5,6]. However, the rigid lattice theories of polymer solutions have been a subject of much criticism and all the experimental features in literatures[7-10] indicated the need of further developments.

For binary systems of polymer-solvent mixtures, the UCST was explained in terms of conformal entropy but the LCST was attributed to the local molecular interactions between the specific orientations[2] or to the free volume effect created by the thermal expansion of polymer molecule and solvent[11,12]. In recent, the closed loop diagrams like polyethyleneglycol-water system were calculated considering the molecular configurations and the strong interactions like hydrogen bond toward one or more directions[13-15]. Further, the solutions of a polydispersed polymer could be counted for a multicomponent mixture with different chain lengths, and the effect of molecular weight distribution for the shape near the critical points was also acknowledged[10].

In this report, polymer solutions of polydispersed polymethylmethacrylate-n-butyl chloride systems having UCST and LCST were investigated by means of phase diagrams, the modified Flory's parameters, and extents of polydispersity.

THEORETICAL BACKGROUNDS

The Gibbs free energy of mixing, ΔG, for a polydispersed polymer solution at constant temperature and pressure can be calculated by

$$\Delta G/NRT = \phi_1 \ln \phi_1 + \Sigma \frac{\phi_r}{r} \ln \phi_r + f(T, P, \phi_1, \phi_r, r, MWD) \qquad (1)$$

where ϕ_1 is the volume fraction of solvent, ϕ_r is the volume fraction of polymer with chain length r and f (T, P, ϕ_1, ϕ_r, r, MWD) represents the enthalpic contribution depending on temperature, pressure, volume fraction, the chain length and molecular weight distribution. The relative chain length r is given by $r = v_1\ M_r/v_r\ M_1$ where v_1 and v_r are the specific volume of solvent and the specific volume of polymer in the liquid state respectively and M, the molecular

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*Cheil Synthetic Textile Co. Seoul Korea weight. In the original Flory-Huggins approach, the residual f can be approximated by neglecting the higher order interactions, i.e., the mer-mer interactions, and by considering the r-mer-solvent interaction to be a pseudo-binary solution with an interaction parameter g depending only on temperature.

From the thermodynamic stability criteria, the activities of solvent(1) and polymer(2) can be obtained from the first derivatives of the equation(1) assuming g is independent of concentrations and r is the average value of chain lengths and is given by,

$$\ln a_1 = \ln \phi_1 + (1 - r^{-1})\,\phi_2 + g(T)\,\phi_2^2 \tag{2}$$

and

$$\ln a_2 = \ln \phi_2 + (1 - r^{-1})\,\phi_1 + g(T)\,r\,\phi_1^2 \tag{3}$$

Then, the spinodal curve and the critical point of r-mer solutions can be obtain such as

$$2g(T) = 1/\phi_1 + 1/\phi_p r_w \text{ (spinodal)} \tag{4}$$

and

$$0 = 1/\phi_1^2 + r_z/\phi_p^2 r_w^2 \text{ (critical)} \tag{5}$$

where r_z and r_w are the z-average and weight-average chain lengths respectively.

Shultz and Flory[16] approximated the maximum separation temperature with the model interaction function $g(T) = g_s + g_H/T$, and derived a linear relationship in $1/T_c$ vs $(1/\sqrt{r} + 1/2r)$ curves by

$$\theta/T_c = 1 + (1/\Phi)\,(1/\sqrt{r} + 1/2r) \tag{6}$$

where θ is the temperature determined by an extrapolation to the infinite chain length, and Φ is the entropic parameter.

Meanwhile, Patterson model used two different temperature-dependent coefficients of g(T). Patterson and Delmas[17,18] have extended the statistical thermodynamic theory based on the corresponding state principle developed by Prigogine and his co-workers [19]. This theory can describe the existence of the LCST and the interaction parameter χ_1 can be given by

$$\frac{\chi_1(P,T)}{C_1} = \frac{-\widetilde{U}(\widetilde{P},\widetilde{T})\,\mu^2}{T} + \frac{\widetilde{C}_p(\widetilde{P},\widetilde{T})\,\tau^2}{2} \tag{7}$$

where $\widetilde{U}$ is the reduced configurational energy of the solvent, and $\widetilde{C}_p$ the reduced configurational heat capacity. μ^2 is a energy parameter describing differences in force fields and τ^2 the free volume parameter of segment sizes between polymer and solvent and C_1 is the number of external degree of freedom of the solvent molecule. μ^2 is normally treated as an adjustable parameter although it can be defined by the theory[20]. C_1 and τ are measured directly from experimental expansion coefficients, α_i, and thermal pressure coefficients, γ_i[21]. The first term may be regarded as an alternative expression of the Flory-Huggins dependence of χ_1 on temperature. The second term expresses the effect of free-volume differences between the components[22]. Using the equation (7) the behavior of the LCST and UCST can be described, although the closed loop diagrams of polyethyleneglycol(PEG)-water, polyvinylalcohol (PVA)-water can not.

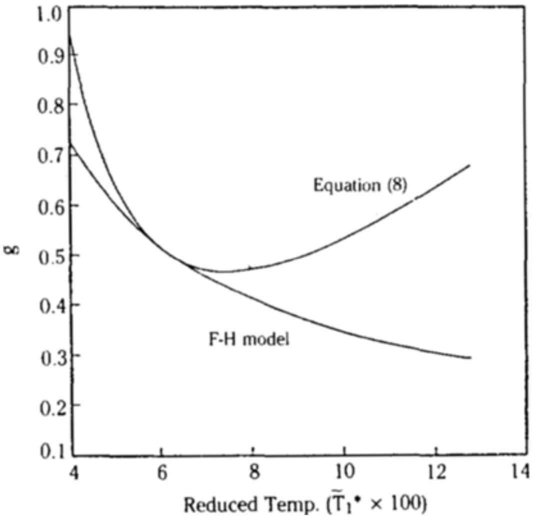

Fig. 1. Interaction parameter g for polymethylmethacrylate(PMMA) in n-butyl chloride. g was plotted against reduced temperature, $\widetilde{T}_1^*$ ($=T_c/T_1^*$) by the equation (8) and by the original Flory-Huggins model, where T_1^* is 5065 for PMMA-n-butylchloride systems [22].

Considering the temperature dependence of ΔG with the specific heat, the enthalpy and entropy of mixing, more generalized form for g(T) can be given by

$$g(T) = a + b/T + cT + d\ln T \tag{8}$$

where the terms with c and d come from the temperature-dependence of ΔC_p (assumed linear) [23]. The second and third terms, which are the main contributions to g(T), show an identical temperature-dependence to those arising from molecular theory[24]. Depending the constants the several different type of miscibility diagrams can be calculated(also with or without the fourth term). In Figure 1, the Flory-Huggins model and the generalized model of the equation (8) have demonstrated in calculating the energy parameter g(T). While the original Flory-Huggins model shows only the upper critical points, the equation (8) can have two critical points as temperature increases.

EXPERIMENTAL

1. Chemicals

Two polymethylmethacrylates with different molecular weights were purchased from Aldrich Co., Ltd. and used without further purification. The 1-chlorobutane from Wako Chem. was in purity over 98%, with density of 0.885-0.890 g/cc at 20°C.

2. Characterization of sample polymers

The molecular weight, molecular distribution, tacticity and glass transition temperature, T_g were characterized for the polymers. Viscosity was measured by Cannon-Fenske viscometer at 25°C in the solution of benzene and toluene and viscosity-averaged molecular weights were determined from the equation in the Polymer Handbook[25]. Glass transition temperature were determined by Du Pont 910 differential scanning calorimeter(DSC) and molecular weight distribution by gel permeation column, HPLC Waters with RI detector. The column was packed with μ-Styragel, 10^3, 10^4 and 10^5 Å in a serial connection and tetrahydrofuran carrier was used with the rate 1 cc/min after preconditioning for 40 hrs at 20°C. Calibration was done by five points of polystyrene standards at 0.25, 0.1 wt% in solution. The tacticity was determined by PMX-60 NMR spectrometer for 15 wt% in $CDCl_3$ solution at room temperature.

In Table 1, the characteristic properties of PMMA's, the viscosity-averaged molecular weight M_v, glass transition temperature, Tg, determined by DSC, tacticity from the NMR spectra by way of triad analysis of Bovey[26], and polydispersity from gel permeation column were given respectively.

3. Determination of cloud points

3-1. Sample preparation

Ampoules of heavy wall Pyrex with the inner diameter of 5.5 mm and the height of 150 mm, having a hourglass neck at the position of 100 mm from the bottom were used. The volumes of sampling bottles were calibrated by water, filled at 20°C and the amount of samples were fixed at the 70% of the net volumes. After the polymer solutions were filled, the ampoules were slightly evacuated to remove unnecessary air and sealed with flame. To obtain the homogeneous sample, the samples were incubated for 2 days at 75°C.

Table 1. Polymer characterization

properties	PMMA A	PMMA B
M_v	5.12×10^5	1.03×10^5
Tg (°C)	128	114
Mw/Mn	3.308	3.78
tacticity	s = 0.48 h = 0.41 i = 0.11	s = 0.48 h = 0.35 i = 0.17

* s (syndiotactic), h (heterotactic), i (isotactic)

3-2. Cloud points

The cloudiness was observed visually or by photosensor of Kodenshi Co HP-3KR III diode and the temperature is determined by the Chromel-Alumel thermocouple compensated with a cold junction. The optical source was 60 W bulb and the optical path fixed with guideline. In order to avoid the mass transfer effect at the phase interface, all the data were taken when the homogeneous solutions were separated. For UCST's the samples were directly cooled at the rate of 1°C/30 min in the water bath with the accuracy of 0.05°C and for LCST's the clouding points were determined at the varying rate of heating of 0.1 to 1°C/min under the silicon oil bath and extrapolated to the zero rates of heating with the accuracy of 0.25°C. The clouding points were determined by the intensity change of the transmitted light and the data were taken at the intersection of the tangential slope extended from the inflection point to the base line since the points gave consistent values with the visual observations.

RESULTS AND DISCUSSION

1. Determination of cloud points

In Figure 2, the cloud points of PMMA solution at the various rates of heating were given for the samples of the several concentrations. The rate of heating near the extreme concentration like 2.23, significantly affect the phase separation, since the viscosities and the diffusivities were greatly affected near the critical solution concentration[27,28]. In UCST, the difference was 3 to 4 K when the sample was heated or cooled, and for LCST, 1 to 2 K, which is within ranges of the mixing effect on agitated or static cases[27]. To differentiate the effect of transport properties, the cloud points were determined extrapolating the rate of heating or cooling to zero. However, it is not clear whether the sensitivity on the rate should be a maximum near the extreme point.

2. Phase diagram and behavior

Figure 3 summarized the curve of cloud points determined by turbidity measurements. The phase separation regions were shown to increase as the molecular weight increased[3,10]. Since the polymer A and B were polydispersed, the extreme points might not be unique critical points(often called by threshold point), but a representative extreme for the pseudo-binary mixtures(especially for homologue series) could correspond to the critical point specified on a critical line

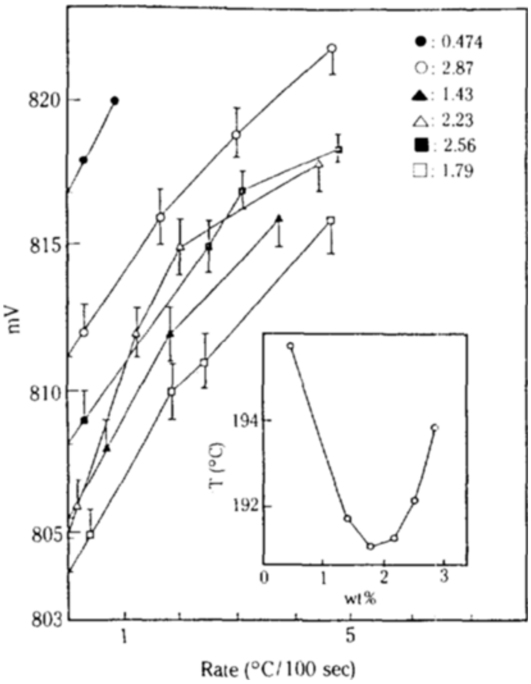

Fig. 2. The cloud points of PMMA-n-butylchloride mixtures at various compositions, wt %. The phase diagram(small box) was constructed by extrapolating the cloud point curves to the values at zero heating rate.

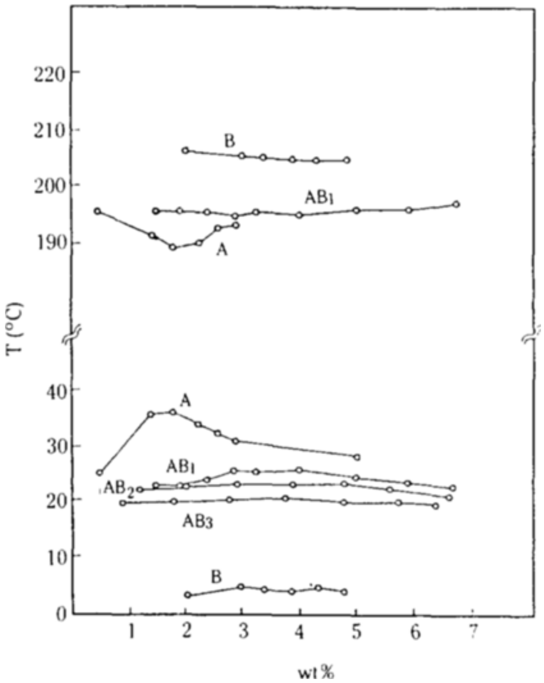

Fig. 3. The cloud point curves of upper and lower consolute temperatures for PMMA-n-butylchloride mixtures.
A: $M_v = 512000$, B: $M_v = 103000$,
AB_1: $M_v = 408000$, AB_2: $M_v = 323000$,
AB_3: $M_v = 243000$

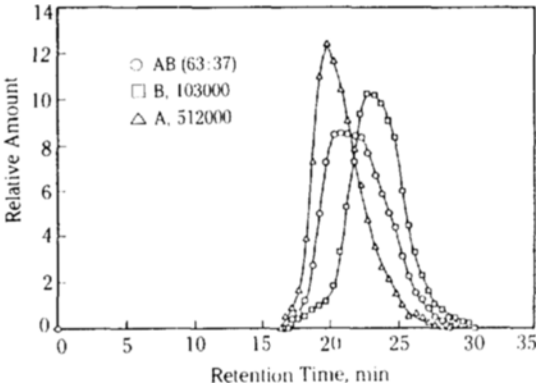

Fig. 4. Molecular weight distribution obtained from GPC curve.
A: PMMA $M_v = 512000$, B: PMMA $M_v = 103000$,
AB(A:B = 63:37) $M_v = 408000$

of a multicomponent system or at least very close to the true critical points. The critical concentrations calculated from the Flory-Huggins model are 1.91, 4.20 and 2.13 for the PMMA A, B, and AB1(mixture of A:B = 63:37) respectively. The Flory volume fractions were calculated, assuming that the molecular volume of the repeating unit of polymer and solvent are equal. For the weight fractions, the volume of polymer, 0.813 cm^3/g and n-butyl chloride, 1.1320 cm^3/g at 298 K were used[21].

In order to examine the effect of polydispersity of polymers with the same interaction energy, the PMMA's of different molecular weight A and B were mixed to prepare the mixtures AB1, AB2 and AB3. The weight-averaged molecular weights of mixed polymers were 408000, 323000, 243000 respectively. In Figure 3, the UCST's and LCST's were located at the temperatures between those of two PMMA A and B. The molecular weight distribution of the mixtures determined by GPC were shown in Figure 4. The mixed polymers apparently have the bimodal type distribution in molecular weight. In fact, the phase behaviors of mixed polymers in Figure 3 were greatly influenced, in all concentrations observed, by the polymer with higher molecule weight.

In Figure 5, the UCST's of the mixed PMMA solutions(line 2) have been shown with those of polystyrene(line 1) solutions of A (MW = 1,270,000) and B

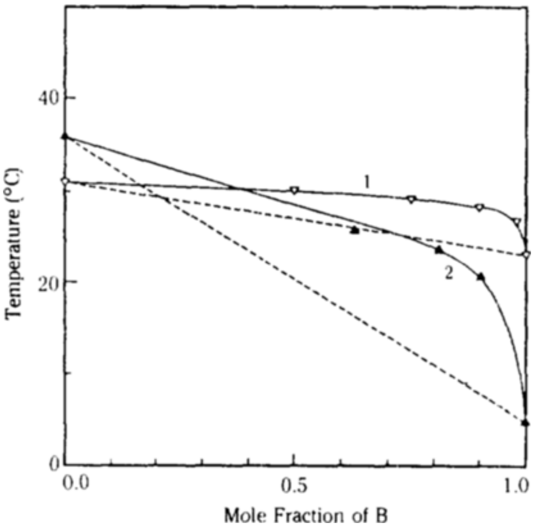

Fig. 5. Upper consolute solution temperatures of the mixed polymers with different molecular weights for the system 1, polystyrene-cyclohexane mixtures (▽)[16]and for the system 2, PMMA-n-butylchloride mixtures (▲).

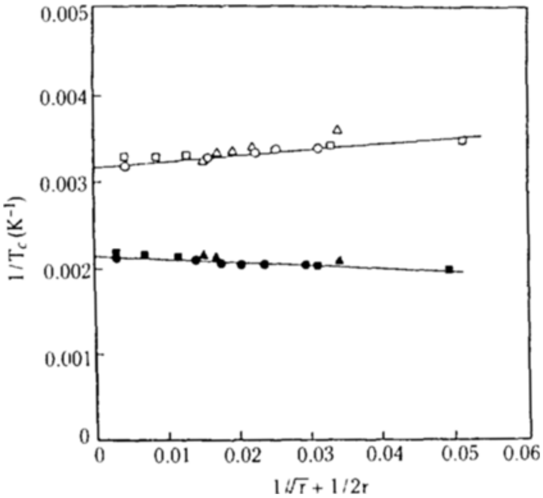

Fig. 6. Dependence of critical temperatures for the upper and lower phase separations on molecular weight for PMMA in n-butyl chloride. Filled symbols represent for the lower consolute solution temperatures.
atactic (○) and isotactic (□)[21] this works (△)

(MW = 89,000). In any cases, the UCST's or the phase behavior can largely be influenced by the polymer of higher molecular weight up to 95 wt% and then rapidly approaches those of low molecular weight polymer. Further, the flattening of the cloud point curve of the mixtures of the bimodal distribution can be accounted for the effects of the multiplicity discussed by Koningsveld et al. [10].

In addition to the polydispersity, and molecular distribution, the molecular structures and tacticities also affect the phase behavior significantly. In case of PMMA, though it depends on the solvent selected, the effect of tacticity on the observed phase behavior was significant such that the isotactic structure has much broader than those of atactic shape, where the UCST and the LCST of PMMA-n-butyl chloride are 320, and 463 K for atactic and 309, and 454 K for isotactic[21]. The effect of side chain also, as reported by Koningsveld[29] is significant for the irregularity of the spinodal curve of polyethylene. The specific conformational transition and structural transition of PMMA-benzene, toluene solution was reported[30].

3. Interaction parameter

The critical lines of LCST and UCST in terms of chain length were shown in Figure 6. The symbols represent for the experimental data of PMMA-n butyl chloride and line for the calculated from the equation (8) with optimized parameters using Marquardt method[31].

Following Figure 1, the appearance of two critical lines can be explained by either Patterson model[17] or the equation (8) for the curve B. A closer look at the Patterson model (7) consisting of χ_1(cohesive energy, CE) and χ_1(free volume, FV) shows that it can be expressed as follows

$$\chi_1\,(\mathrm{CE}) = \left(\frac{3}{\alpha \mathrm{T}} + 4\right) c_1 \mu^2 \tag{10}$$

$$\chi_1\,(\mathrm{FV}) = \left(\frac{3}{2} + 2\,\alpha \mathrm{T}\right) c_1 \tau^2 \tag{11}$$

where α stands for thermal expansion coefficient. Then the equation (7) can be reduced to be

$$\chi_1 = \chi_1\,(\mathrm{CE}) + \chi_1\,(\mathrm{FV}) \tag{12}$$

$$= \mathrm{A} + \mathrm{B}/\mathrm{T} + \mathrm{CT} \tag{13}$$

which results in nearly similar form with equation (8). Here, A is the constant which represents mixed effect of the cohesive energy and free volume. The constant B and C represent for the temperature-dependence of cohesive energy contribution and free volume contribution respectively.

In our calculations of UCST and LCST, the variations of phase diagrams in temperature, can be described regardless of molecular weights and molecular distributions by the modified Flory-Huggins interaction parameter. However, it is not clear whether the temperature dependence of interaction parameter, the equation (8), can also describe the closed loop of polymer-solvent mixtures[13] as well as the hour-glass type. Recent developments[14,15] suggested that further modifications are required for the contribution of the cohesive energy of hydrogen-bonding.

CONCLUSIONS

The cloud point curves of upper and lower consolute solution temperatures have been determined for the solutions of the polydispersed polymethylmethacrylate(PMMA) and n-butyl chloride.

Depending on the rate of heating or cooling, the clouding points of the solutions of the atactic polydispersed PMMA and n-butyl chloride varied abruptly near the extreme points. For polydispersed polymers, the equilibrium curves of the upper consolute polymer solution shifted to lower temperature regions as molecular weight decreased, but the lower consolute points appeared at higher temperatures.

For the polymer solutions with molecular weight distribution, the shapes of phase boundaries near the consolute solution points became flattened at both temperature regions and the curvatures near the extreme points were small because of the influence of the polydispersity.

In describing the phase diagram of molecular weights, both of the critical consolute temperatures were calculated, incorporating the relative chain length and the temperature dependence for the modified Flory-Huggins interaction parameter χ_1.

NOMENCLATURE

a : activity
C_1 : number of external degree of freedom of the solvent molecules
Cp : heat capacity, Kcal/g·°C
g : interaction energy constant
G : Gibbs free energy, Kcal
M : molecular weight
MWD : molecular weight distribution
r : relative chain length
T : temperature, K
T_1^* : temperature reduction parameter of solvent
$\tilde{U}$: reduced configuration energy of solvent
v_i : specific volume, cm^3/g
α : thermal expansion coefficient, K^{-1}
χ : interaction energy constant
μ : parameter describing the difference of force field
ϕ_r : volume fraction of r-mer
Φ : entropic parameter
τ : free volume parameter in equation (7)

Subscripts
c : critical
i : i species
p : polymer
w : weight-averaged
z : z-averaged

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