ELSEVIER

Polymer 40 (1999) 2779–2785

polymer

# Absolute prediction of upper and lower critical solution temperatures in polymer/solvent systems based on corresponding state theory

F. Wang, S. Saeki*, T. Yamaguchi

*Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan*

Received 18 February 1998; revised 4 June 1998; accepted 15 June 1998

---

**Abstract**

The upper critical solution temperature (UCST) and lower critical solution temperature (LCST) have been predicted for 45 polymer/solvent systems based on Patterson's theory. The configurational energy and configurational heat capacity used in the theory are determined by the following thermodynamic relations

$$-U_{\mathrm{conf.}} = \gamma_V T V$$

$$C_{P,\mathrm{conf.}} = \alpha_P T \gamma_V V$$

where the thermal expansion coefficient and thermal pressure coefficient are obtained from our empirical equations

$$\ln(\alpha_P T)^{-1} = 1.1820 + 0.8425 \ln\left(\frac{T_C - T}{T}\right)$$

$$\ln(\gamma_V/\gamma_{V_C}) = 0.8452 + 1.1324 \ln(V/V_C) + 2.8940[\ln(V/V_C)]^2$$

where $T_C$, $V_C$ and $\gamma_{V_C}$ are the critical temperature, critical volume and thermal pressure coefficient at the critical state. The deviations between predicted and experimental UCST and LCST are generally less than 20°C for 28 polymer/solvent systems. The molecular weight dependence of UCST and LCST is predicted for polystyrene (PS)/cyclohexane, PS/methyl cyclohexane and PS/toluene systems, and good agreement with experimental results is obtained. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Upper critical solution temperature; Lower critical solution temperature; Corresponding state theory

---

## 1. Introduction

After Freeman and Rowlinson [1] showed that polymer solutions separate into two liquid phases, not only on lowering the temperature to near the well-known $\theta$-point, but also on raising the temperature, the Flory–Huggins theory faced a great challenge because the theory predicts a monotonic decrease of $\chi_{1,2}$ with temperature and therefore cannot explain the occurrence of a lower critical solution temperature (LCST). Thereafter, much attention has been given to the LCST phenomena. More successful achievements are the free volume theory proposed by Patterson and co-workers [2–6] based on Prigogine's cell theory [7], which can explain both upper critical solution temperature (UCST) and LCST qualitatively. More recently, Prausnitz and co-workers [8–18] have carried much valuable research on the vapour–liquid and liquid–liquid equilibria of polymer solutions, both experimentally and theoretically. They pay special attention to copolymers, highly branched polymers and dendrimer/solvent systems to study the effect of the variation of force field on the properties of polymer solutions. They found that in copolymer/solvent systems the activity coefficient of the solvent does not lie intermediate between those for the two corresponding homopolymer/solvent systems. This unexpected effect is predicted correctly by their perturbed hard-chain-of-spheres theory [11,12].

According to Patterson's free volume theory, the UCST and LCST occurring in many binary polymer solutions [19–23] are due to the differences in intermolecular interaction and free volume between polymer and solvent. For an infinite-molecular-weight polymer, UCST is identified with the Flory $\theta$-point. In the low-temperature

---

* Corresponding author.

PII: S0032-3861(98)00480-7

region (below UCST), systems exhibit phase separation due to the predominant unfavourable intermolecular interactions. Miscibility occurs above the UCST because the entropy of mixing starts to dominant over the intermolecular interactions as the temperature exceeds the UCST. At further elevated temperature, however, the free volume or equation-of-state effect becomes dominant and the mixture again exhibits phase separation. The free volume or equation-of-state effect results from the density or expansivity disparity between the two components in the mixture. A polymeric liquid is much denser than the solvent, and the difference increases with increasing temperature. When the LCST is reached, the unfavourable entropy effect predominates, leading to phase separation. For polymer solutions, the density or expansivity disparity is mainly caused by the difference in molecular sizes.

By taking into account both the intermolecular interactions and free volume effect, Patterson [3,4] derived an expression for the interaction parameter $\chi_{1,2}$ which is essentially the same as that derived by Flory and co-workers [24–27], and both have been used to fit experimental CST data [28–33]. The procedures include evaluation of configurational energy $-U_1$, configurational heat capacity $C_{\mathrm{P},1}$ and the molecular parameter $\tau^2$ by experiment or model. In previous papers [34–36], we have evaluated the thermodynamic coefficients of various amorphous polymers, crystalline polymers and simple liquids, and obtained the universal expressions of $\alpha_P T$ and $\gamma_V$ for amorphous polymers and simple liquids. Our current work aims to predict the solubility, namely, UCST and/or LCST based on the above work and Patterson's theory.

## 2. Basic procedures

The equation derived by Patterson [5] is expressed as follows

$$\chi_{12} = \frac{-U_1}{RT}\nu^2 + \frac{C_{P,1}}{2R}\tau^2 \tag{1}$$

where $U_1$ and $C_{P,1}$ are the molar configurational energy and heat capacity of the solvent, $R$ is the gas constant, $\nu^2 = X_{12}/P_1{}^*$, according to Flory's nomenclature, is the intermolecular interaction, $\tau^2$ reflects the difference in free volumes or degrees of thermal expansion of the components and is expressed as

$$\tau^2 = \left(1 - \frac{T_1^*}{T_2^*}\right)^2 \tag{2}$$

where $T_1{}^*$ and $T_2{}^*$ are the temperature reduction parameters of solvent and polymer, respectively. In order to evaluate the polymer/solvent interaction parameter $\chi_{1,2}$ by Eq. (1), $-U_1$, $C_{P,1}$ $\nu^2$ and $\tau^2$ are necessary. We have used the following relations to evaluate the above parameters in this work.

$$-U_{\mathrm{conf.}} = \gamma_V TV \tag{3}$$

$$C_{P,\mathrm{conf.}} = \alpha_P T\gamma_V V \tag{4}$$

$$c_1\nu^2 = \frac{3}{8}\left(\frac{1}{3} - \left(\frac{4c_1\tau^2}{3}\right)^{1/2} + c_1\tau^2\right) \tag{5}$$

Eq. (3) is derived from Flory's relations [24,25] by using the van der Waals model

$$-\tilde{U} = 1/\tilde{V} \tag{6}$$

while Eq. (4) is obtained from the thermodynamic relation

$$C_P - C_V = \alpha_P T\gamma_V V \tag{7}$$

where $C_P$ and $C_V$ are heat capacity at constant pressure and volume, respectively. According to the cell theory [7] and smoothed potential model [5], the cell partition function depends only on volume and the configurational energy is independent of temperature at constant volume. Thus, the configurational $C_V$ is zero, so that Eq. (7) becomes Eq. (4). The $\alpha_P$ and $\gamma_V$ used in Eqs. (3) and (4) can be determined by the following equations [36,37]

$$\ln(\alpha_P T)^{-1} = 1.1820 + 0.8425\,\ln\left(\frac{T_{\mathrm{C}} - T}{T}\right) \tag{8}$$

$$\ln(\gamma_V/\gamma_{V_{\mathrm{C}}}) = 0.8452 + 1.1324\,\ln(V/V_{\mathrm{C}}) + 2.8940[\ln(V/V_{\mathrm{C}})]^2 \tag{9}$$

where $T_{\mathrm{C}}$, $V_{\mathrm{C}}$, and $\gamma_{V_{\mathrm{C}}}$ are the critical temperature, critical volume and thermal pressure coefficient at the critical state. The $\gamma_{V_{\mathrm{C}}}$ used in Eq. (9) can be evaluated by the following relation [38]

$$\gamma_{V_{\mathrm{C}}} = 0.12 + 145.5/V_{\mathrm{C}} \tag{10}$$

The volume can be determined by the Gunn and Yamada [39] equation

$$\frac{V(T_r)}{V(T_r^{\mathrm{R}})} = \frac{V^{(0)}(T_r)\left[1 - \omega\Gamma(T_r)\right]}{V^{(0)}(T_r^{\mathrm{R}})\left[1 - \omega\Gamma(T_r^{\mathrm{R}})\right]} \tag{11}$$

Here $T_r = T/T_C$, $T_r^{\mathrm{R}} = T^{\mathrm{R}}/T_{\mathrm{C}}$, $V(T_r)$ is the volume at temperature $T$, $V(T_r^{\mathrm{R}})$ is the volume at reference temperature $T^{\mathrm{R}}$ (such as 20°C), $\omega$ is the acentric factor, $V^{(0)}$ and $\Gamma$ are functions of $T_r$.

For $0.2 \le T_r \le 0.8$

$$V^{(0)} = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4 \tag{12}$$

For $0.8 < T_r < 1.0$

$$V^{(0)} = 1.0 + 1.3(1 - T_r)^{1/2}\log(1 - T_r) - 0.50879(1 - T_r) - 0.91534(1 - T_r)^2 \tag{13}$$

For $0.2 \le T_r < 1.0$

$$\Gamma = 029607 - 0.09045T_r - 0.04842T_r^2 \tag{14}$$

Eq. (5) used to determine $\nu^2$ is given by Patterson [40] in which $c_1$ is one-third the number of external degrees of freedom of the solvent molecule and is expressed as

$$c_1 = \frac{P_1^* V_1^*}{RT_1^*} \tag{15}$$

Here $R$ is the gas constant, and the reduction parameters $P_1$*, $V_1$* and $T_1$* for the solvent are determined by the following equations [24,25]

$$\tilde{V} = \frac{V}{V^*} = \left[\frac{3+4\alpha_P T}{3+3\alpha_P T}\right]^3 \tag{16}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{\tilde{V}^{1/3}-1}{\tilde{V}^{4/3}} \tag{17}$$

$$P^* = \gamma_V T \tilde{V}^2 \tag{18}$$

By using Eqs. (3) and (4), Eq. (1) is reduced to

$$\chi_{1,2} = \frac{\gamma_V V}{R}\left(\nu^2 + \frac{\alpha_P T}{2}\tau^2\right) \tag{19}$$

All of the parameters used in Eq. (19) can be evaluated by the above statement, and the molecular weight dependence of UCST and LCST can also be determined by coupling Eq. (19) with Flory's original equation:

$$\chi_{1,2} = \tfrac{1}{2}\left(1 + \frac{1}{r^{1/2}}\right)^2 \tag{20}$$

where $r$ is the ratio of molar volume of polymer to that of solvent.

## 3. Calculations and results

The UCST and LCST of more than 40 polymer/solvent systems have been predicted in this work based on Eq. (8) for $\alpha_P T$ and Eq. (9) for $\gamma_V$. Taking the polystyrene (PS)/cyclohexane system for example, the calculation procedures are as follows. For cyclohexane, the following quantities are obtained [41]: $T_C = 553.4$ K, $V_C = 308$ cm$^3$ mol$^{-1}$, molecular weight = 84.162, acentric factor $\omega = 0.213$, and volume $V = 1.2837$ cm$^3$ g$^{-1}$ at a reference temperature $T = 293$ K. With the above quantities, the other parameters of cyclohexane are determined at 293 K as follows: $\gamma_{V_C} = 0.5924$ bar K$^{-1}$, $\alpha_P T = 0.3387$, $\gamma_V = 10.089$ bar K$^{-1}$, $V_1{}^* = 1.0069$ cm$^3$ g$^{-1}$, $T_1{}^* = 4803$ K, $P_1{}^* = 4805$ bar and $c_1 = 1.0197$.

For PS, $T_2{}^* = 7205$ K was given by Patterson [40], thus the $\tau^2$ is calculated by Eq. (2) so that $\tau^2 = 0.1111$, and the $\nu^2$ is calculated by Eq. (5) as $\nu^2 = 0.02132$, then the temperature dependence of $\chi_{1,2}$ for the PS/cyclohexane system is expressed as

$$\chi_{1,2} = 1.0123\gamma_V V(0.02132 + 0.05555\alpha_P T) \tag{21}$$

where the coefficient 1.0123 is calculated by 84.162/(10 × 8.314) by considering the dimension. The UCST = 326 K and the LCST = 466 K predicted by Eq. (21) are only 20°C different from the experimental results that UCST = 307 K and LCST = 486 K for an infinite-molecular-weight PS. The UCST, LCST and temperature dependence of $\chi_{1,2}$ predicted by Eq. (21) are shown in Fig. 1 by solid lines. The molecular weight dependence of UCST and LCST are also predicted for PS/cyclohexane by combining Eqs. (19) and (20) in Fig. 2, where good agreement with experimental results is obtained. The same procedures are employed for other polymer/solvent systems, the UCST and LCST of polyethylene (PE)/cyclohexane and polypropylene (PP)/cyclohexane systems for infinite molecular weights of PE and PP predicted by the following equations are shown in Fig. 3.

$$\chi_{1,2} = 1.0123\gamma_V V(0.03997 + 0.030085\alpha_P T) \tag{22}$$

for the PE/cyclohexane system, and

$$\chi_{1,2} = 1.0123\gamma_V V(0.05374 + 0.01866\alpha_P T) \tag{23}$$

for the PP/cyclohexane system. The UCST = 384, LCST = 515 K for the former, and UCST = 415 K, LCST = 530 K

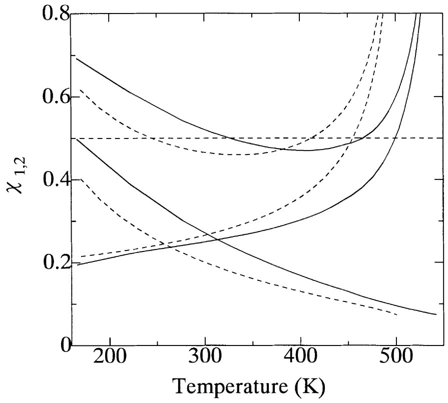

Fig. 1. Temperature dependence of polymer/solvent interaction parameter $\chi_{1,2}$ of the PS/cyclohexane system. (———), predicted in this work with $\nu^2 = 0.02132$, $\tau^2 = 0.1111$; (– – –), fitted by Eq. (24) with $\nu^2 = 0.0159$, $\tau^2 = 0.119$.

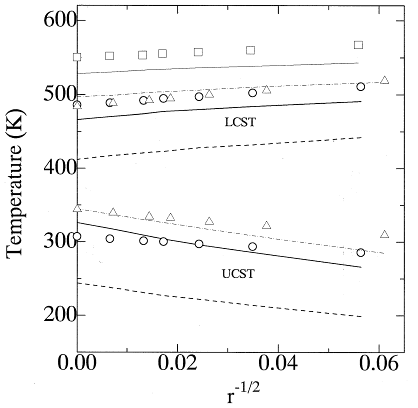

Fig. 2. Molecular weight dependence of UCST and LCST, symbols are experimental data, lines are theoretical prediction. ○ (———), PS/cyclohexane predicted with $\nu^2 = 0.02132$, $\tau^2 = 0.1111$; △ (– · –), PS/methyl cyclohexane predicted with $\nu^2 = 0.01664$, $\tau^2 = 0.09726$; □ (———), PS/toluene predicted with $\nu^2 = 0.02422$, $\tau^2 = 0.08477$; (- - -), PS/cyclohexane fitted by Eq. (24) with $\nu^2 = 0.0159$, $\tau^2 = 0.119$.

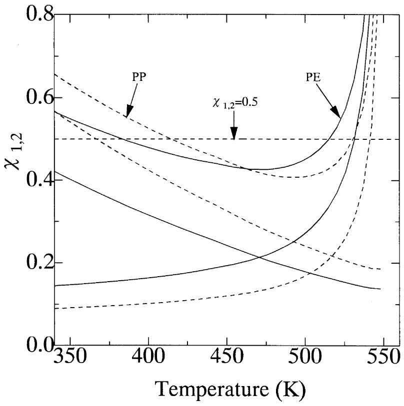

Fig. 3. Temperature dependence of polymer/solvent interaction parameter $\chi_{1,2}$ predicted in this work. (———), PE/cyclohexane system with $\nu^2 = 0.03997$, $\tau^2 = 0.06016$; (- - -), PP/cyclohexane system with $\nu^2 = 0.05374$, $\tau^2 = 0.03732$.

for the latter are predicted by Eqs. (22) and (23), respectively. Since there are no experimental UCST data for these two systems at present, we cannot compare the predicted UCST with the experimental one. But the experimental LCST = 518 K for the former and LCST = 540 K for the latter are almost the same as those predicted in this work. For other systems, the quantities used and obtained for solvents in the present work are given in Table 1, the quantities of polymer used and parameters of polymer/solvent systems determined are listed in Table 2, and the values of UCST and LCST for infinite-molecular-weight polymers predicted in this paper are presented in Table 3, where the experimental UCST and LCST for the corresponding infinite-molecular-weight polymers [19,42,44] are also presented for comparison. The molecular weight dependence of UCST and LCST for PS/methyl cyclohexane and PS/toluene systems is also predicted, and good agreement is obtained as shown in Fig. 2.

## 4. Discussion

Up to the present, the van der Waals model (Eq. (6)) and Flory's equation of state [24,25] are always used to evaluate $-U_1$, $C_{P,1}$ and $\tau^2$, thus Eq. (1) is reduced to Eq. (24) under critical conditions

$$\frac{c_1\nu^2}{1-\tilde{V}_1^{-1/3}}+\frac{c_1\tau^2}{2\left[(4/3)\tilde{V}_1^{-1/3}-1\right]}=\tfrac{1}{2}\left(1+\frac{1}{r^{1/2}}\right)^2 \qquad (24)$$

where $\tau$ and $r$ have the same meaning as those used in Eqs. (19) and (20), $\tilde{V}_1$ is the reduced volume of the solvent and can be determined by Eq. (16). The parameter $\nu^2$ (sometimes also $c_1$) is chosen such that the separation of UCST and LCST, determined by experiment, is reproduced by Eq. (24). But the values of UCST and LCST predicted in this way are very different from the experimental results, and it is generally found [19–21,31,42–44] that a temperature shift is necessary in order that the fitted CST coincides with experimental results. For the PS/cyclohexane system, a shift of 76°C is necessary as is shown in Figs 1 and 2 by the dashed lines. In the case of polypentene-1 (PP1) and poly(4-methylpentene-1) (P4MP1), the LCST predicted by the model are 40–60°C lower than the experimental results [44], while for the PS/toluene and PS/methylcyclohexane systems, shifts of 110 and 71°C are necessary for both UCST and LCST [19].

More recently, Cowie and McEwen [29,45–47] have illustrated an absolute prediction of CST by using a reference temperature other than 298 K. They gave an empirical relation that [45]

$$T^*/\mathrm{K} = -17491 + 74.774T_\mathrm{C} - 0.061085T_\mathrm{C}^2 \qquad (25)$$

They claimed that $T^*$ can be determined by the above relation in the critical temperature $T_\mathrm{C}$ range of 490–600 K and then gave an absolute prediction of CST. They used

Table 1
Quantities used and obtained in this work for solvents

| Solvent | $T_\mathrm{C}$[a] (K) | $V_\mathrm{C}$[a] (cm$^3$ mol$^{-1}$) | $M_\mathrm{w}$[a] | $\omega$[a] | $V$[a] (cm$^3$ g$^{-1}$) at 293 K | $\gamma_{V_\mathrm{C}}$[b] (bar K$^{-1}$) | $\gamma_V$[c] (bar K$^{-1}$) | $\alpha_P T$[d] | $c_1$[e] | $V_1$*[f] (cm$^3$ g$^{-1}$) | $T_1$*[g] (K) | $P_1$*[h] (bar) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *n*-Pentane | 469.6 | 304 | 72.151 | 0.251 | 1.5974 | 0.5986 | 7.072 | 0.4698 | 0.9439 | 1.1790 | 4123 | 3804 |
| *n*-Octane | 568.8 | 492 | 114.232 | 0.394 | 1.4225 | 0.4157 | 9.628 | 0.3227 | 1.4152 | 1.1251 | 4926 | 4510 |
| 2,2-Dimethyl butane | 488.7 | 359 | 86.178 | 0.231 | 1.5408 | 0.5253 | 6.945 | 0.4308 | 1.0117 | 1.1565 | 4280 | 3612 |
| 2,3-Dimethyl pentane | 537.3 | 393 | 100.205 | 0.299 | 1.4388 | 0.4902 | 6.732 | 0.3574 | 0.9419 | 1.1179 | 4674 | 3267 |
| Cyclohexane | 553.4 | 308 | 84.162 | 0.213 | 1.2837 | 0.5924 | 10.089 | 0.3387 | 1.0197 | 1.0069 | 4803 | 4805 |
| Methyl cyclohexane | 572.1 | 368 | 98.189 | 0.233 | 1.3072<br>at 298 K | 0.5154 | 9.033 | 0.3290 | 1.0629 | 1.0305 | 4959 | 4332 |
| Benzene | 562.1 | 259 | 78.114 | 0.212 | 1.1376 | 0.6818 | 12.969 | 0.3294 | 1.0576 | 0.8966 | 4873 | 6117 |
| Toluene | 591.7 | 316 | 92.141 | 0.257 | 1.1534 | 0.5804 | 12.228 | 0.3017 | 1.1210 | 0.9226 | 5107 | 5599 |

[a] From Ref. [41].
[b] Calculated by Eq. (10).
[c] Calculated by Eq. (9) at reference temperature 293 K.
[d] Calculated by Eq. (8) at reference temperature 293 K.
[e–h] Calculated by Eqs. (15)–(18) respectively at reference temperature 293 K.

Table 2
Quantities of polymers used and parameters of polymer/solvent systems determined in this work[a]

| | Polymer | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PS | | PE | | PP | | P4MP1 | | PP1 | | PB1 | |
| $d$ (g cm$^{-3}$) | | | 0.887 | | 0.858 | | 0.838 | | 0.86 | | 0.86 | |
| $\alpha_P$ (K$^{-1}$) | | | 0.00072 | | 0.000801 | | 0.00078 | | 0.00079 | | 0.000755 | |
| $T_2^*$ (K) | 7205 | | 6364 | | 5953 | | 6052 | | 6004 | | 6176 | |
| Solvent | $\tau^2$ | $\nu^2$ | $\tau^2$ | $\nu^2$ | $\tau^2$ | $\nu^2$ | $\tau^2$ | $\nu^2$ | $\tau^2$ | $\nu^2$ | $\tau^2$ | $\nu^2$ |
| *n*-Pentane | 0.1830 | 0.01040 | 0.1240 | 0.02199 | 0.09450 | 0.03086 | 0.1016 | 0.02847 | 0.09815 | 0.02961 | 0.1105 | 0.02571 |
| *n*-Octane | 0.1001 | 0.01071 | 0.05107 | 0.02522 | 0.02977 | 0.03669 | 0.03463 | 0.03358 | 0.03225 | 0.03506 | 0.04097 | 0.03001 |
| 2,2-Dimethyl butane | 0.1648 | 0.01058 | 0.1073 | 0.02278 | 0.07901 | 0.03218 | 0.08575 | 0.02964 | 0.08248 | 0.03084 | 0.09427 | 0.02673 |
| 2,3-Dimethyl pentane | 0.1234 | 0.02225 | 0.07053 | 0.04067 | 0.04616 | 0.05416 | 0.05185 | 0.05056 | 0.04908 | 0.05228 | 0.05915 | 0.04638 |
| Cyclohexane | 0.1111 | 0.2132 | 0.06016 | 0.03997 | 0.03732 | 0.05374 | 0.04259 | 0.05007 | 0.04001 | 0.05182 | 0.04942 | 0.04579 |
| Methyl cyclohexane | 0.09718 | 0.02311 | 0.04875 | 0.04315 | 0.02789 | 0.05792 | 0.03262 | 0.05397 | 0.03030 | 0.05585 | 0.03884 | 0.04939 |
| Benzene | 0.1048 | 0.02118 | 0.05493 | 0.04011 | 0.03294 | 0.05412 | 0.03798 | 0.05038 | 0.03552 | 0.05216 | 0.04455 | 0.04603 |
| Toluene | 0.08477 | 0.02422 | 0.03900 | 0.04537 | 0.02018 | 0.06097 | 0.02437 | 0.05680 | 0.02231 | 0.05879 | 0.02994 | 0.05197 |

[a] The values of $d$ and $\alpha_P$ are from Ref. [42], $T_2^*$, $\tau^2$ and $\nu^2$ are calculated by Eqs. (17), (2) and (5), respectively.
PS, polystyrene; PE, polyethylene; PP, polypropylene; P4MP1, poly(4-methylpentene-1); PP1, polypentene-1; PB1, polybutene-1.

Table 3
Comparison of UCST and LCST (K) predicted in this work with experimental data

| Solvent | | | Polymer | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | PS | PE | PP | P4MP1 | PP1 | PB1 |
| *n*-Pentane | UCST | pred. | ins. | 295 | 312 | 307 | 309 | 301 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | | 369 | 410 | 403 | 407 | 393 |
| | | exp. | / | 353 [42] | 422 [42] | 441 [44] | 433 [44] | 421 [44] |
| *n*-Octane | UCST | pred. | / | 363 | 400 | 391 | 396 | 379 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | / | 537 | 552 | 548 | 550 | 543 |
| | | exp. | / | 496 [42] | 542 [42] | 553 [44] | 556 [44] | 540 [44] |
| 2,2-Dimethyl butane | UCST | pred. | ins. | / | 328 | 322 | 325 | 315 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | | / | 438 | 432 | 435 | 425 |
| | | exp. | / | / | 441 [42] | 462 [44] | 457 [44] | 444 [44] |
| 2,3-Dimethyl pentane | UCST | pred. | / | 373 | 403 | 396 | 399 | 387 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | / | 487 | 504 | 501 | 502 | 495 |
| | | exp. | / | 463 [42] | 513 [42] | / | 529 [44] | 517 [44] |
| Cyclohexane | UCST | pred. | 326 | 384 | 415 | 406 | 410 | 397 |
| | | exp. | 307 [19] | / | / | / | / | / |
| | LCST | pred. | 466 | 515 | 530 | 527 | 529 | 522 |
| | | exp. | 486 [19] | 518 [42] | 540 [42] | / | / | / |
| Methyl cyclohexane | UCST | pred. | 345 | 407 | 440 | 432 | 437 | 422 |
| | | exp. | 344 [19] | / | / | / | / | / |
| | LCST | pred. | 497 | 540 | 554 | 551 | 552 | 547 |
| | | exp. | 484 [19] | 537 [42] | 564 [42] | / | / | / |
| Benzene | UCST | pred. | 330 | 388 | 420 | 412 | 416 | 403 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | 487 | 530 | 543 | 541 | 542 | 536 |
| | | exp. | 525 | / | / | / | / | / |
| Toluene | UCST | pred. | 370 | 431 | 465 | 457 | 461 | 446 |
| | | exp. | / | / | / | / | / | / |
| | LCST | pred. | 528 | 567 | 579 | 576 | 578 | 573 |
| | | exp. | 550 [19] | / | / | / | / | / |

PS, polystyrene; PE, polyethylene; PP, polypropylene; P4MP1, poly(4-methylpentene-1); PP1, polypentene-1; PB1, polybutene-1.

$T^* = 5208$ K for cyclohexane which corresponds to a reference temperature of 433 K. In this work, however, a reference temperature 293 K is selected as usual, and all of the molecular parameters, i.e. $P^*$, $V^*$, $T^*$ and $c_1$, are determined at this temperature. With these data, the UCST and LCST of more than 40 polymer/solvent systems are predicted based on Eq. (3) for $U_{\mathrm{conf.}}$ and Eq. (4) for $C_{P,\mathrm{conf.}}$. Eq. (3) is also derived from the van der Waals model, so the first term in the Eq. (19) is essentially the same as that in Eq. (24), but the configurational heat capacity used in the two equations is different. It is well known that the van der Waals model for $U_{\mathrm{conf.}}$ is theoretically wrong because it predicts a monotonically decreasing function of $U_{\mathrm{conf.}}$ with decreasing volume, which is different from the experimental facts, but it is mathematically simple and empirically correct in a narrow volume range, so is used extensively. However, if the configurational heat capacity is derived from an incorrect model, a larger error will be caused, which is the primary reason why Eq. (24) cannot give an accurate prediction of UCST and LCST. In this work, Eq. (4) which is derived from Eq. (7) represents the expansion energy due to the volume change, and hence has the same meaning as the configurational heat capacity defined by Prigogine and Patterson, and can give a good prediction of UCST and LCST. It has been noted that the UCST and LCST predicted by this method are very sensitive to $\tau^2$ and $\nu^2$. For example, if $\tau^2 = 0.099$ and $\nu^2 = 0.0223$ replace $\tau^2 = 0.1111$ and $\nu^2 = 0.02132$ in Eq. (21) for the PS/cyclohexane system, UCST = 306 K and LCST = 488 K are obtained, which are almost the same as the experimental UCST = 307 K and LCST = 486 K, while the variation in $\tau^2$ and $\nu^2$ is very small. Therefore, the accurate determination of $\tau^2$ and $\nu^2$ is vital.

## 5. Conclusions

The method outlined in this work can give an absolute prediction of the UCST and LCST of polymer/solvent systems. The configurational energy is derived from the van der Waals model, and is therefore the same as that usually used. But the configurational heat capacity is obtained from thermodynamic relation and cell theory, which is the main difference from the traditional method. The configurational energy, heat capacity, and molecular parameters $c_1$, $\tau^2$ and $\nu^2$ are determined from the thermal expansion coefficient $\alpha_{\mathrm{P}}$ and the thermal pressure coefficient $\gamma_{\mathrm{V}}$ which can be determined accurately from our empirical equations

$$\ln(\alpha_P T)^{-1} = a_0 + a_1 \ln\left(\frac{T_{\mathrm{C}} - T}{T}\right)$$

and

$$\ln(\gamma_V/\gamma_{V_{\mathrm{C}}}) = b_0 + b_1 \ln(V/V_{\mathrm{C}}) + b_2 \left[\ln(V/V_{\mathrm{C}})\right]^2$$

and only the critical temperature $T_{\mathrm{C}}$ and volume $V_{\mathrm{C}}$ are necessary. Most of the deviations of UCST and LCST predicted by this method are less than 20°C.

## Acknowledgements

We are grateful to Mr. Tsubokawa for his assistance.

## References

[1] Freeman PI, Rowlinson JS. Polymer 1960;1:20.
[2] Patterson D. Rubber Chem Technol 1967;40:1.
[3] Patterson D. J Polym Sci, Part C 1968;16:3379.
[4] Patterson D. Macromolecules 1969;2:672.
[5] Patterson D, Delmas G, Somcynsky T. Polymer 1967;8:503.
[6] Patterson D, Delmas G. Trans Faraday Soc 1969;65:708.
[7] Prigogine I, Bellemans A, Mathot V. The molecular theory of solutions. Amsterdam: North-Holland, 1957.
[8] Hu Y, Ying X, Wu DT, Prausnitz JM. Macromolecules 1993;26 (25):6817.
[9] Hino T, Lambert SM, Soane DS, Prausnitz JM. Polymer 1993;34 (22):4756.
[10] Hino T, Song Y, Prausnitz JM. Macromolecules 1994;27:5681.
[11] Song Y, Lambert SM, Prausnitz JM. IEC Research 1994;33:1047.
[12] Song Y, Lambert SM, Prausnitz JM. Macromolecules 1994;27: 441.
[13] Lambert SM, Song Y, Prausnitz JM. Macromolecules 1995;28: 4866.
[14] Hino T, Song Y, Prausnitz JM. Macromolecules 1995;28:5717.
[15] Hino T, Song Y, Prausnitz JM. Macromolecules 1995;28:5725.
[16] Gupta RB, Prausnitz JM. Fluid Phase Equilibria 1996;117:77.
[17] Hino T, Song Y, Prausnitz JM. J Polym Sci: Part B: Polym Phys 1996;34:1961.
[18] Hino T, Song Y, Prausnitz JM. J Polym Sci: Part B: Polym Phys 1996;34:1977.
[19] Saeki S, Kuwahara N, Konno S, Kaneko M. Macromolecules 1973;63:24.
[20] Saeki S, Kuwahara N, Konno S, Kaneko M. Macromolecules 1973;6:589.
[21] Saeki S, Konno S, Kuwahara N, Nakata M, Kaneko M. Macromolecules 1974;7:52.
[22] Bae YC, Lambert SM, Soane DS, Prausnitz JM. Macromolecules 1991;24:4403.
[23] Delmas G, Patterson D. J Polym Sci, Part C 1970;30:1.
[24] Flory PJ, Orwoll RA, Vrij A. J Am Chem Soc 1964;86:3507.
[25] Flory PJ, Orwoll RA, Vrij A. J Am Chem Soc 1964;86:3515.
[26] Flory PJ. J Am Chem Soc 1965;87:1833.
[27] Abe A, Flory PJ. J Am Chem Soc 1965;87:1838.
[28] Cowie JMG, Maconnachie A, Ranson RJ. Macromolecules 1971;4:57.
[29] Cowie JMG, McEwen IJ. Polymer 1975;16:244.
[30] Cowie JMG, McEwen IJ. J Polym Sci 1974;12:441.
[31] Siow KS, Delmas G, Patterson D. Macromolecules 1972;5:29.
[32] Nakajima A, Hamada F, Yasue K, Fujisawa K, Shiomi T. Makromol 1974;175:197.
[33] Hamada F, Fujisawa K, Nakajima A. Polym J 1973;4:316.
[34] Wang F, Saeki S, Yamaguchi T. Polymer 1997;38(14):3485.
[35] Wang F, Saeki S, Yamaguchi T. Polymer, in press.
[36] Wang F, Saeki S, Yamaguchi T. Polymer, in press.
[37] Wang F. Doctoral dissertation, Fukui University, 1998.
[38] Saeki S. J Supercritical Fluids 1995;8 (1):30.
[39] Gunn RD, Yamada T. AIChE J 1971;17:1341.
[40] Delmas G, Patterson D. In: Int Symp Macromol Chem, Toronto, 1968.

[41] Reid RC, Prausnitz JM, Sherwood TK. The properties of gases and liquids, 3rd edn. New York: McGraw-Hill, 1977.

[42] Charlet G, Delmas G. Polymer 1981;22:1811.

[43] Cowie JMG, McEwen IJ. J Chem Soc, Faraday Trans 1 1974;70:171.

[44] Charlet G, Ducasse R, Delmas G. Polymer 1981;22:1190.

[45] Cowie JMG, McEwen IJ. J Chem Soc, Faraday Trans 1 1976;72:1675.

[46] Cowie JMG, McEwen IJ. Macromolecules 1974;7:291.

[47] Cowie JMG, McEwen IJ. J Chem Soc, Faraday Trans 1 1976;72: 526.