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LIQUID-LIQUID EQUILIBRIA FOR SOLUTIONS OF POLYDISPERSE POLYMERS. CONTINUOUS THERMODYNAMICS FOR THE LATTICE-FLUID MODEL

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ABSTRACT

A continuous-thermodynamics framework is presented for phase-equilibrium calculations for solutions of polydisperse polymers using a lattice-fluid model. A two-step process is designed to form a real solution containing a solvent and a polydisperse polymer solute at fixed temperature and pressure. In the first step, close-packed pure components are mixed to form a close-packed polymer solution. In the second step, the close-packed mixture, considered to be a pseudo-pure substance, is mixed with holes to form a real polymer solution whose volume depends on temperature and pressure. The simplified Freed model developed previously is adopted for both steps. Besides pure-component parameters, the theory uses a binary size parameter c_r and a binary energy parameter ε_{12}; these binary parameters may be temperature-dependent. The functional approach is adopted to derive expressions for chemical potentials, spinodals and critical points. Computation procedures are established for cloud-point-curve, shadow-curve, spinodal and critical-point calculations for polymer solutions using either a standard distribution or an arbitrary distribution for the polymer molar masses or chain lengths. Calculations are shown for the effect of polydispersity on upper-critical-solution temperature (UCST), lower-critical-solution temperature (LCST) and hour-glass-shaped phase behavior for the system acetone-polydisperse polystyrene.

INTRODUCTION

Synthetic polymers are almost always polydisperse. They consist of a large number of similar chemical species but with different molar masses or chain lengths. An apparent binary solution containing a solvent and a polydisperse polymer is, in fact, a multicomponent system with very many components. Some properties of polymer solutions are not sensitive to the polydispersity of polymers; while vapor-liquid equilibria are nearly independent of polydispersity whenever all chain lengths are large (Krigbaum and Geymer, 1959; Wang et al, 1993), liquid-liquid equilibria are seriously influenced by polymer chain lengths. Not only do critical coordinates vary appreciably, but also the cloud-point curve does not coincide with the coexistance plot for conjugate phases. The latter plot is often called the shadow curve. To characterize a polymer solution with a polydisperse solute, it is necessary to separate the shadow curve from the cloud-point curve.

In many cases, polymer solutions exhibit not only an upper-critical-solution temperature (UCST), but also, at higher temperature, a lower-critical-solution temperature (LCST) and, at different pressures, an hour-glass-shaped phase diagram. It is generally recognized that high-temperature LCSTs and hour-glass-shaped coexistence curves originate from the free-volume effect, which causes demixing at higher temperatures where the solulibity of the polymer is diminished in an expanded solvent (Patterson, 1969).

Although a variety of theories based on an equation of state have been used for describing the phase behavior of polymer solutions at higher temperatures and pressures (Flory et al, 1964; Flory, 1965, 1970; Patterson and Delmas, 1970; Sanchez and Lacombe, 1976, 1978; Kleintjens and Koningsveld, 1980; Kleintjens, 1989; Donohue and Prausnitz, 1978), the literature is sparse in extensions of theories to solutions with a polydisperse polymer solute. Recently, we described a lattice-fluid model (Hu et al, 1991, 1993) based on Freed's theory, which can be used to describe UCST, LCST, miscibility-loop, and hour-glass-shaped phase diagrams for polymer solutions, as well as the molar-mass dependence and the pressure dependence of coexistence curves. In this work, we extend this model to solutions with a polydisperse polymer solute.

In the development of the framework, we use the functional approach pioneered by Kehlen, Rätzsch and Bergmann (1987), Beerbaum et al (1987), Cotterman and Prausnitz (1985), Willman and Teja (1986), and Kang, Lee and Sandler (1989). The derivative method developed previously (Ying Ye and Hu, 1989) is used for polymer solutions with any arbitrary distribution of polymer molar masses or chain lengths. A review of continuous thermodynamics and its applications was published by Cotterman and Prausnitz (1991).

First we introduce the molecular-thermodynamic model and the corresponding equation of state. Then we present the thermodynamic framework to obtain expressions for the Helmholtz and Gibbs energies of mixing, chemical potentials, spinodals and critical points. Finally we present some illustrative examples.

MOLECULAR-THERMODYNAMIC MODEL

Lattice-Fluid Model

Similar to our previous work for a polymer solution with a monodisperse polymer (Hu et al 1991, 1993), we use a two-step process to form a polymer solution containing solvent and polydisperse polymer at a fixed temperature and pressure. In the first step, we form a close-packed mixture from the close-packed pure components. In the second step, we introduce holes, as indicated below:

$$\begin{tikzcd} & N_o \text{ "solvent"} + N_s W(I)dI \text{ "polymer } I\text{"}, \; I = 0 - \infty \\ & \text{close-packed pure components} \arrow[d, "(a)"] \\ & \text{close-packed polymer solution} \arrow[dd, "(b)"] \\ N_h \text{ "hole"} \arrow[r] & {} \\ & \text{polymer solution}, \; V, T, P \end{tikzcd}$$

In the first step (a), we mix N_o molecules of solvent with $N_s W(I)dI$ molecules of polymer species characterized by I where I may vary continuously from zero to infinity. Here N_s stands for the total number of polymer molecules; $W(I)$ is the distribution function for the polydisperse polymer species; I is the distribution variable such as relative molar mass M or chain length r. In the second step (b), the close-packed polymer solution, considered to be a pseudo-pure fluid "u", is mixed with N_h holes to form a real polymer solution with volume V at temperature T and pressure P. Each molecule of solvent, polymer species I occupies r_o and $r(I)$ sites, while each hole occupies one site (r_h=1).

To make the model flexible, r_o and $r(I)$ are treated as effective chain lengths dependent on concentration by

$$r_o = r_o^0 \, (1 + c_r \Phi_s^0) \tag{1}$$

$$r(I) = r^0(I) \, (1 - c_r \Phi_o^0) \tag{2}$$

where r_o^0 and $r^0(I)$ are numbers of sites occupied by a solvent molecule and a molecule of polymer species I in the pure state, respectively. Volume fractions Φ_o^0 and Φ_s^0 refer to the solvent and total polymer; they are defined by

$$\Phi_o^0 = N_o r_o^0 \, / \, N_r \tag{3}$$

$$\Phi_s^0 = N_s \int_0^\infty r^0(I) W(I) dI \, / \, N_r \tag{4}$$

where N_r, the total number of sites occupied by all molecules, is given by

$$N_r = N_o r_o^0 + N_s \int_0^\infty r^0(I) W(I) dI \quad . \tag{5}$$

Substitution of eqs.(1) and (2) into eq.(5) yields

$$N_r = N_o r_o + N_s \int_0^\infty r(I) W(I) dI \quad . \tag{6}$$

Eq.(6) says that the total number of sites occupied by all molecules remains unchanged during mixing. In eqs.(1) and (2) c_r is a binary size parameter.

Helmholtz Energy of Mixing

The total Helmholtz energy of mixing $\Delta_{mix}A$ contains two terms, one contributed by the first, and the other by the second step:

$$\Delta_{mix}A = \Delta_{mix}A_a + \Delta_{mix}A_b \tag{7}$$

where subscripts a and b stand for the first and the second steps.

The close-packing contribution of the first step is expressed using the simplified Freed model on a cubic lattice developed previously (Hu et al, 1991):

$$\frac{\Delta_{mix}A_a}{N_r kT} = \frac{\Phi_o}{r_o}\ln\Phi_o + \int_0^\infty \frac{\Phi_s W(I)}{r(I)}\ln[\Phi_s W(I)]dI + \Phi_o \int_0^\infty \Phi_s W(I) g_a(I) dI \tag{8}$$

where

$$g_a(I) = \frac{1.2}{9}\left(\frac{1}{r_o}-\frac{1}{r(I)}\right)^2 + 2\tilde{\varepsilon}_a(I) + \frac{\tilde{\varepsilon}_a(I)}{r_o}\Phi_s + \frac{\tilde{\varepsilon}_a(I)}{r(I)}(1-\Phi_s) - \frac{3}{2}1.074\tilde{\varepsilon}_a^2(I)\Phi_s(1-\Phi_s) \quad . \tag{9}$$

Parameter $\varepsilon_a(I)$ can be molar-mass (or chain-length) dependent. Effective volume fractions Φ_o and Φ_s refer to the solvent and to the total polymer, respectively. They are defined by

$$\Phi_o = N_o r_o \,/\, N_r \tag{10}$$

$$\Phi_s = N_s \int_0^\infty r(I) W(I) dI \,/\, N_r \quad . \tag{11}$$

From eqs(1) and (2), we have

$$\Phi_o = \Phi_o^0\,(1 + c_r \Phi_s^0) \tag{12}$$

$$\Phi_s = \Phi_s^0\,(1 - c_r \Phi_o^0) \quad . \tag{13}$$

If $\tilde{\varepsilon}_a$ is independent of molar mass (or chain length),

$$\tilde{\varepsilon}_a(I) = \tilde{\varepsilon}_a = \varepsilon_a/kT = (\varepsilon_{oo}+\varepsilon_{ss}-2\varepsilon_{os})/kT \tag{14}$$

where ε_{oo}, ε_{ss} are (positive) energy parameters for pure solvent and pure polymer, respectively, while ε_{os} is a binary interaction energy parameter. These parameters may be temperature-dependent.

The contribution of the second step can also be expressed by the simplified Freed model for a pseudo binary of the pseudo-pure substance "u" and holes.

$$\frac{\Delta_{mix}A_b}{N_l kT} = \frac{\phi_h}{r_h}\ln\phi_h + \frac{\phi_u}{r_u}\ln\phi_u + \phi_h\phi_u g_b \tag{15}$$

$$g_b = \frac{1.2}{9}\left(\frac{1}{r_h}-\frac{1}{r_u}\right)^2 + 2\tilde{\varepsilon}_b + \frac{\tilde{\varepsilon}_b}{r_h}\phi_u + \frac{\tilde{\varepsilon}_b}{r_u}\phi_h - \frac{3}{2}1.074\tilde{\varepsilon}_b^2\phi_h\phi_u \tag{16}$$

where N_l is the total number of sites occupied by molecules and holes,

$$N_l = N_r + N_h \quad . \tag{17}$$

Here ϕ_h and ϕ_u are volume fractions of holes and pseudo substance, respectively. They are defined by

$$\phi_h = N_h/N_l \ ; \qquad \phi_u = N_r/N_l \quad . \tag{18}$$

The chain length of the pseudo substance r_u can be estimated by the following mixing rule,

$$r_u^{-1} = \Phi_o r_o^{-1} + \Phi_s \int_0^\infty r^{-1}(I)W(I)dI = \Phi_o^0(r_o^0)^{-1} + \Phi_s^0\int_0^\infty [r^0(I)]^{-1}W(I)dI \quad . \tag{19}$$

Because $r(I)$ is much larger than r_o, eq.(19) can be simplified to

$$r_u^{-1} = \Phi_o r_o^{-1} = \Phi_o^0(r_o^0)^{-1} \quad . \tag{20}$$

Parameter $\tilde{\varepsilon}_b$ is estimated by the mixing rule

$$\tilde{\varepsilon}_b = \varepsilon_b/kT$$

$$= (\Phi_o^2\varepsilon_{oo} + 2\Phi_o\Phi_s\varepsilon_{os} + \Phi_s^2\varepsilon_{ss})(\Phi_o^2 + 2\Phi_o\Phi_s\xi + \Phi_s^2)/kT \tag{21}$$

where ξ is a binary parameter close to unity. Calculated results are not sensitive to ξ provided that it lies within a fairly broad specified range.

Eqs.(15) and (16) are rearranged to the following form:

$$\frac{\Delta_{mix}A_b}{N_l kT} = \frac{\phi_h}{r_h}\ln\phi_h + \frac{\phi_u}{r_u}\ln\phi_u + \sum_m\sum_n a_{mn}^0\tilde{\varepsilon}_b^n\phi_u^m \tag{22}$$

where

$$a_{10}^0 = 1.2(r_h^{-1}-r_u^{-1})^2/9 \ , \quad a_{20}^0 = -a_{10}^0$$

$$a_{11}^0 = 2+r_u^{-1} \ , \quad a_{21}^0 = -2+r_h^{-1}-2r_u^{-1} \ , \quad a_{31}^0 = -a_{11}^0-a_{21}^0$$

$$a_{22}^0 = -1.611 \ , \quad a_{32}^0 = 3.222 \ , \quad a_{42}^0 = a_{22}^0 \tag{23}$$

All a_{mn} other than those listed above are zero. Coefficients in eq.(23) can be further simplified by setting $a_{11}^0 = 3$ and $a_{21}^0 = -3$ with all others equal to zero. This means using the Flory-Huggin theory for the second step.

In summary, this model uses pure-component size parameters r_o, $r(I)$, pure-component energy parameters ε_{oo}, ε_{ss}, and binary size parameter c_r, binary energy parameter ε_{os}, and an additional binary parameter ξ.

Equation of State

We first define reduced temperature $\tilde{T}$, reduced pressure $\tilde{P}$ and reduced desity $\tilde{\rho}$:

$$\tilde{T} = kT/\varepsilon_b = 1/\tilde{\varepsilon}_b \tag{24}$$

$$\tilde{P} = P/P^* = Pv^*/\varepsilon_b \tag{25}$$

$$\tilde{\rho} = V^*/V = N_r v^*/V \tag{26}$$

where v^* is the volume of one site and V^* is the hard-core volume of all molecules. Because the close-packed first step makes no contribution to volume-dependent properties, only ε_b, an energy parameter in the second step, appears in eqs(24) and (25). Combining with eq.(18), we have

$$\tilde{\rho} = \phi_u \ , \quad 1-\tilde{\rho} = \phi_h \quad . \tag{27}$$

The reduced Helmholtz energy of mixing $\Delta\tilde{A}_b$ for the second step, and the reduced Gibbs energy of mixing $\Delta\tilde{G}$ for the second step, are defined by

$$\Delta\tilde{A}_b = \Delta_{mix}A_b/N_r\varepsilon_b \ , \quad \Delta\tilde{G}_b = \Delta_{mix}G_b/N_r\varepsilon_b \tag{28}$$

Substitution of eqs.(24) and (26) into eq.(22) yields

$$\frac{\Delta_{mix}A_b}{N_l kT} = \frac{1-\tilde{\rho}}{r_h}\ln(1-\tilde{\rho}) + \frac{\tilde{\rho}}{r_u}\ln\tilde{\rho} + \sum_m\sum_n a^0_{mn}\tilde{T}^{-n}\tilde{\rho}^m \quad . \tag{29}$$

Using eq.(27) and r_h=1, eq.(29) becomes

$$\frac{\Delta_{mix}A_b}{N_r kT} = \frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{1}{r_u}\ln\tilde{\rho} + \sum_m\sum_n a^0_{mn}\tilde{T}^{-n}\tilde{\rho}^{m-1} \quad . \tag{30}$$

The reduced Helmholtz energy of mixing for the second step can then be expressed as

$$\Delta\tilde{A}_b = \tilde{T}\{\frac{(1-\tilde{\rho})}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{1}{r_u}\ln\tilde{\rho} + \sum_m\sum_n a^0_{mn}\tilde{T}^{-n}\tilde{\rho}^{m-1}\} \quad . \tag{31}$$

We notice that $\Delta\tilde{A}_b$ is volume-dependent but $\Delta\tilde{A}_a$ is not.

From thermodynamics,

$$\tilde{P} = \tilde{\rho}^2(\frac{\partial\Delta\tilde{A}}{\partial\tilde{\rho}})_{\tilde{T}} \quad . \tag{32}$$

We then have the equation of state,

$$\tilde{P} = \tilde{T}\{-\ln(1-\tilde{\rho}) - (1-1/r_u)\tilde{\rho} + \sum_m\sum_n a^0_{mn}\tilde{T}^{-n}\tilde{\rho}^m\} \quad . \tag{33}$$

FRAMEWORK FOR USING CONTINUOUS THERMODYNAMICS

Helmholtz and Gibbs Energies of Mixing

We now make a further rearrangement for $\Delta_{mix}A$. For converting effective volume fractions Φ_o and Φ_s into normal volume fractions Φ^0_o and Φ^0_s, we substitute eqs.(12) and (13) into eq.(8) of the first step. We obtain

$$\begin{aligned}\frac{\Delta_{mix}A_a}{N_r kT} &= \frac{\Phi^0_o}{r^0_o}\ln\Phi^0_o + \int_0^\infty \frac{\Phi^0_s W(I)}{r^0(I)}\ln[\Phi^0_s W(I)]dI + \frac{\Phi^0_o}{r^0_o}\ln(1+c_r\Phi^0_s) \\ &+ \int_0^\infty \frac{\Phi^0_s}{r^0(I)}\ln(1-c_r\Phi^0_o)W(I)dI + \Phi^0_o\int_0^\infty \Phi^0_s(1+c_r\Phi^0_s)(1-c_r\Phi^0_o)W(I)g_a(I)dI \\ &= \frac{\Phi^0_o}{r^0_o}\ln\Phi^0_o + \int_0^\infty \frac{\Phi^0_s W(I)}{r^0(I)}\ln[\Phi^0_s W(I)]dI + \Phi^0_o\int_0^\infty \Phi^0_s W(I)g^*_a(I)dI\end{aligned} \tag{34}$$

where

$$g^*_a = \frac{1}{\Phi^0_s r^0_o}\ln(1+c_r\Phi^0_s) + \frac{1}{\Phi^0_o r^0(I)}\ln(1-c_r\Phi^0_o) + (1+c_r\Phi^0_s)(1-c_r\Phi^0_o)g_a(I) \quad . \tag{35}$$

For the second step, if we take the simplified eq.(20) for r_u, the equation of state [eq.(33)] and the Helmholtz energy of mixing [eq.(30)] are then independent of the distribution of polymer species.

Therefore, the total Helmholtz energy of mixing can be expressed in a form that is the same as that for the close-packed first step, i.e., eq.(34).

$$\frac{\Delta_{mix}A}{N_r kT} = \frac{\Phi^0_o}{r^0_o}\ln\Phi^0_o + \int_0^\infty \frac{\Phi^0_s W(I)}{r^0(I)}\ln[\Phi^0_s W(I)]dI + \Phi^0_o\int_0^\infty \Phi^0_s W(I)g^*(I)dI \tag{36}$$

where

$$g^*(I) = g_a^*(I) + \Delta_{mix}A_b \,/\, N_r\Phi_o^0\Phi_s^0 kT \quad . \tag{37}$$

For the Gibbs function of mixing,

$$\frac{\Delta_{mix}G}{N_rkT} = \frac{\Delta_{mix}A}{N_rkT} + \frac{\Delta pV}{N_rkT} = \frac{\Delta_{mix}A}{N_rkT} + \tilde{p}\tilde{T}^{-1}\tilde{\rho}^{-1} \quad . \tag{38}$$

The contribution of the close-packed lattice to the pressure is zero. Both $\Delta_{mix}A$ and $\Delta_{mix}G$ are functionals.

Chemical Potentials

For the discrete solvent component o, the chemical potential can be derived by

$$(\mu_o - \mu_o^*)/kT = \partial(\Delta_{mix}A/kT) \,/\, \partial N_o$$

$$= \ln\Phi_o^0 + \Phi_s^0(1 - r_o^0/r_n^0) + r_o^0(\Phi_s^0)^2[\int_0^\infty g^*(I)W(I)dI - (1-\Phi_s^0)\int_0^\infty g^{*\prime}(I)W(I)dI\ ] \tag{39}$$

where $g^{*\prime}(I) = [\partial g^*(I) \,/\, \partial\Phi_s^0]_{T,V}$.

For continuous components, the chemical potential of solute I is defined as:

$$\mu(I) = \partial A \,/\, \partial[N_r\Phi_s W(I)/r(I)] \tag{40}$$

where the denominator is physically comparable with ∂N_i in the discrete approach. But now it is a variation of a functional. In the theory of functionals, for an integral $\Psi = \int f(N_I)dI$, the derivative of Ψ with respect to the functional N_I is defined by

$$\frac{\partial\Psi}{\partial N_I} = \frac{\partial f(N_I)}{\partial N_I} \quad . \tag{41}$$

An expression for the chemical potential of a continuous component I can then be derived by

$$[\mu(I) - \mu^*(I)]/kT = \partial(\Delta_{mix}A/kT) \,/\, \partial[N_r\Phi_s^0W(I)/r^0(I)]$$

$$= \ln[\Phi_s^0W(I)] + 1 - r^0(I)/r_o^0 + r^0(I)\Phi_s^0(1 - r_o^0/r_n^0)/r_o^0 + (1-\Phi_s^0)r^0(I)g^*(I)$$

$$-r^0(I)\Phi_s^0(1-\Phi_s^0)[\int_0^\infty g^*(I^+)W(I^+)dI^+ - (1-\Phi_s^0)\int_0^\infty g^{*\prime}(I^+)W(I^+)dI^+] \tag{42}$$

where r_n^0 is the number-average chain length.

Spinodal Criterion and Critical-Point Criterion

We need the reduced Gibbs energy of mixing per site, $\tilde{G}_v = \Delta_{mix}G \,/\, N_rkT$. We rearrange eq.(38):

$$\tilde{G}_v = \frac{\Delta_{mix}G}{N_rkT} = \frac{\Phi_o^0}{r_o^0}\ln\Phi_o^0 + \int_0^\infty \frac{\Phi_s^0W(I)}{r^0(I)}\ln[\Phi_s^0W(I)]dI + \Phi_o^0\int_0^\infty \Phi_s^0W(I)g^{**}(I)dI \tag{43}$$

where

$$g^{**}(I) = g^*(I) + \tilde{p}\tilde{T}^{-1}\tilde{\rho}^{-1} \,/\, \Phi_o^0\Phi_s^0 \quad . \tag{44}$$

$\tilde{G}_v$ is also a functional. For deriving the spinodal criterion and the critical-point criterion, we need expressions for $\delta^2\tilde{G}_v$ and $\delta^3\tilde{G}_v$. Kehlen, Rätzsch, Bergmann (1987) and Beerbaum et al (1987) suggested

$$\delta^k \tilde{G}_v = \partial^k \tilde{G}_v \{\Phi_o^0 + t\,\delta\Phi_o^0,\ \Phi_s^0 W(I) + t\,\delta[\Phi_s^0 W(I)]\} / \delta t^k \,|_{t=0} \quad . \tag{45}$$

The relation between the two dependent variations $\delta\Phi_o^0$ and $\delta[\Phi_s^0 W(I)]$ in eq.(45) is determined by using the Lagrange method of undetermined multipliers. Finally, $\delta^k \tilde{G}_v / (\delta\Phi_o^0)^k$ can be obtained.

For the spinodal criterion, we obtain:

$$F_{sp} = \frac{\delta^2 \tilde{G}_v}{(\delta\Phi_o^0)^2} = \frac{1}{r_o^0 \Phi_o^0} + \frac{1}{r_w^0 \Phi_s^0} + \Phi_s^0 \frac{(<g^{**} r> - \Phi_o^0 <g^{**\prime} r>)^2}{r_w^0} - 2\frac{<g^{*} r> - \Phi_o^0 <g^{**\prime} r>}{r_w^0}$$
$$- \Phi_s^0(<g^{**2} r> - 2\Phi_o^0 <g^{**} g^{**\prime} r> + (\Phi_o^0)^2 <g^{**\prime 2} r>) - 2\Phi_s^0(<g^{**\prime}> - \Phi_o^0 <g^{**\prime\prime}>/2) = 0 \tag{46}$$

where r_w^0 is the weight-average chain length.

$$<g^{**l} g^{**\prime m} g^{**\prime\prime n} r> = \int_0^\infty g^{**l}(I) g^{**\prime m}(I) g^{**\prime\prime n}(I) r(I) W(I) dI \quad . \tag{47}$$

Here, $g^{**\prime}(I) = [\partial g^{**}(I)/\partial\Phi_s^0]_{T,P}$, $g^{**\prime\prime}(I) = [\partial^2 g^{**}(I)/\partial(\Phi_s^0)^2]_{T,P}$. Notice that $g^{**\prime}(I)$ and $g^{**\prime\prime}(I)$ are different from $g^{*\prime}(I)$ in eqs(39) and (42) for chemical potentials. The subscript of the latter derivative is T,V, while that of the former is T,P. For obtaining partial derivatives $g^{**\prime}(I)$ and $g^{**\prime\prime}(I)$, we need partial derivative $(\partial\tilde{\rho} / \partial\Phi_s^0)_{T,P}$. For details see Appendix.

Similar expression can be obtained for the critical-point criterion.

$$F_{cr} = \frac{\delta^3 \tilde{G}_v}{(\delta\Phi_o^0)^3} = 0 \quad . \tag{48}$$

PHASE-EQUILIBRIUM CALCULATIONS

When two liquid phases α and β are at equilibrium,

$$\mu_o^{(\alpha)} = \mu_o^{(\beta)} \tag{49}$$

$$\mu^{(\alpha)}(I) = \mu^{(\beta)}(I) \tag{50}$$

We define

$$S_o = \int_0^\infty g^{*}(I) W(I) dI - (1-\Phi_s^0) \int_0^\infty g^{*\prime}(I) W(I) dI \tag{51}$$

and

$$\sigma_o = \ln(1-\Phi_s^0) + \Phi_s^0(1 - r_o^0/r_n^0) + r_o^0(\Phi_s^0)^2 S_o \quad . \tag{52}$$

Substitution into eqs.(39) and (42) yields

$$(\mu_o - \mu_o^*)/kT = \sigma_o \tag{53}$$

$$[\mu(I) - \mu^*(I)]/kT = \ln[\Phi_s^0 W(I)] + 1 - r^0(I)/r_o^0 + (1-\Phi_s^0) r^0(I) g^*(I)$$
$$- r^0(I)\Phi_s^0 S_o + r^0(I)(\sigma_o - \ln\Phi_o^0)/r_o^0 \quad . \tag{54}$$

Eqs.(49) and (50) become

$$\sigma_o^{(\alpha)} = \sigma_o^{(\beta)} \tag{55}$$

$$\ln K(I) = \ln \frac{\Phi_s^{0(\beta)} W^{(\beta)}(I)}{\Phi_s^{0(\alpha)} W^{(\alpha)}(I)}$$

$$= r^0(I)\{[(1-\Phi_s^0)g^*(I)-(r_o^0)^{-1}\ln(1-\Phi_s^0)-\Phi_s^0 S_o]^{(\alpha)} - [(1-\Phi_s^0)g^*(I)-(r_o^0)^{-1}\ln(1-\Phi_s^0)-\Phi_s^0 S_o]^{(\beta)}\} \quad . (56)$$

where $K(I)$ is the partition coefficient for polymer species I. We also define

$$\kappa = \int_0^\infty K(I)W^{(\alpha)}(I)dI \tag{57}$$

Substituting $K(I) = \Phi_s^{0(\beta)}W^{(\beta)}(I)/\Phi_s^{0(\alpha)}W^{(\alpha)}(I)$ into eq.(57) and accounting for the normalization constraint $\int_0^\infty W(I)dI = 1$, we have

$$\kappa\Phi_s^{0(\alpha)}/\Phi_s^{0(\beta)} = 1 \tag{58}$$

We then define two objective functions F_o and F_s.

$$F_o = 1 - \sigma_o^{(\alpha)}/\sigma_o^{(\beta)} = 0 \tag{59}$$

$$F_s = 1 - \kappa\Phi_s^{0(\alpha)}/\Phi_s^{0(\beta)} = 0 \tag{60}$$

By solving eqs.(61) and (62), we can obtain the cloud-point curve and the shadow curve.

If we want spinodals and critical points, we solve eq.(46) $F_{sp} = 0$ and eq.(48) $F_{cr} = 0$.

Computation programs have been established for systems having a standard distribution for I and for systems having an arbitrary distribution for I. In the latter case, the derivative method developed previously (Ying, Ye and Hu, 1989) is used.

Calculations for the system acetone-polydisperse polystyrene provide an example. Binary parameters c_r,ε_{os} and ξ as well as corresponding pure-component parameters are taken from our previous work (Hu et al, 1993):

$$r_o^0 = 4.7340\ , \qquad r(I) = M(I)/0.0165435$$

$$\varepsilon_{oo}/k = 167.626 + 15619.98/T\ , \qquad \varepsilon_{ss}/k = 263.279$$

$$c_r = 4.94309 - 4078.12/T + 1166686/T^2 - 111546900/T^3$$

$$\varepsilon_{os}/k = 206.124 + 7826.574/T - 184482/T^2 + 56521010/T^3$$

$$\xi = 1.04489$$

where T and ε/k are in kelvins. These parameters, obtained from data for the same system with monodisperse polystyrene, can accurately simulate the experimental liquid/monodisperse-liquid equilibria including UCST, LCST and hour-glass phase diagrams covering a temperature range 260-460K and a pressure range 0 to 10 MPa.

Figures 1, 2 and 3 show the dependence of spinodals on the polydispersity expressed by $M_w\ /\ M_n$ at different pressures. Calculation results show that the shape and location of spinodal curves are dependent on polydispersity. When M_w is kept constant, the location of the spinodal curve is virtually independent of polydispersity. Figures 4,5 and 6 show the dependence of cloud-point curves and shadow curves on the polydispersity at different pressures. Generally, the lower the pressure, the closer the UCST is to the LCST. On the other hand, the greater the polydispersity, the wider the coexistence curve.

CONCLUSION

It has been known for about 25 years that the free-volume effect plays an important role in phase equilibria of polymer solutions and polymer blends. Even at moderate temperatures the free-volume effect cannot be neglected. LCST and hour-glass-shaped phase diagrams can only be reasonably interpreted by thermal volume expansion, which causes a decrease in the solubility of the polymer in the solvent. The effect of volume expansion depends on the pressure and on the molar mass of the polymer. Generally, the higher the molar mass of the polymer, the higher the UCST and the lower the LCST and correspondingly, the narrower the intermediate soluble region. On the other hand, increasing the pressure increases the region of mutual solubility.

Introducing both the volume effect and polydispersity very much complicates the theoretical framework. However, the functional method described here offers a procedure for generating cloud-point and shadow curves. That procedure may be particularly useful for determining characteristic binary parameters from experimental cloud-point and shadow-curve data. It may also be useful for predicting the effect of the molar-mass distribution on a polymer-solvent phase diagram as required for process design.

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List of Symbols

A	Helmholtz energy
a_{mn}	coefficient in expression for $\Delta_{mix}A$
c_r	binary size parameter
F	criterion for stability
G	Gibbs energy
g	Flory parameter
I	distribution variable
K	partition coefficient
k	Boltzmann constant
M	molar mass
N	number of molecules or number of sites
N_r	total number of sites, holes not accountd
N_t	total number of sites including holes

P	pressure
r	chain length
T	temperature
V	volume
v^*	volume of one site
W	distribution function

Greek

β	compressibility
ε	binary energy parameter or interaction energy
Φ	volume fraction not accounting for holes
ϕ	volume fraction accounting for holes
λ	defined by eq.(A2)
κ	defined by eq.(57)
Ψ	defined by eq.(A6)
ρ	density
σ	reduced solvent chemical potential
μ	chemical potential
ξ	additional binary parameter

subscripts

a	first step
b	second step
cr	critical point
h	hole
n	number average
o	solvent
s	total polymer
sp	spinodal
u	pseudo-pure fluid
v	per site
w	weight average

superscripts

0	pure component, second step
α, β	liquid phase
$\sim$	reduced function

$'$ first-order derivative with respect to Φ_s

$''$ second-order derivative with respect to Φ_s

Appendix : Derivation of $(\frac{\partial\tilde{\rho}}{\partial\Phi_s^0})_{T,P}$

We first take the derivative of $\tilde{P}$ in eq.(33) with respect to Φ_s^0 at constant temperature and pressure.

$$(\frac{\partial\tilde{P}}{\partial\Phi_s^0})_{T,P} = -\tilde{P}\tilde{T}\lambda + \tilde{T}\sum_m\sum_n n(m-1)a_{mn}^0\tilde{T}^{-n+1}\tilde{\rho}^m\lambda - \frac{\tilde{T}\tilde{\rho}}{r_o}$$

$$+ \tilde{T}[\frac{1}{1-\tilde{\rho}}-1+\frac{1}{r_a}+\sum_m\sum_n m(m-1)a_{mn}^0\tilde{T}^{-n}\tilde{\rho}^{m-1}]\,(\frac{\partial\tilde{\rho}}{\partial\Phi_s^0})_{T,P} + \sum_m\sum_n(m-1)(\frac{\partial a_{mn}^0}{\partial\Phi_s^0})\tilde{T}^{-n+1}\tilde{\rho}^m \quad \text{(A1)}$$

where

$$\lambda = (\frac{\partial\tilde{T}^{-1}}{\partial\Phi_s^0})_{T,P} \quad \text{(A2)}$$

On the other hand, because $\tilde{P} = Pv^*/\varepsilon_b = Pv^*\tilde{T}/kT$ from eq.(25), that derivative can be obtained directly.

$$(\frac{\partial\tilde{P}}{\partial\Phi_s^0})_{T,P} = -\tilde{P}\tilde{T}\lambda \quad \text{(A3)}$$

Combine eqs. (A1) and (A2), we have

$$(\frac{\partial\tilde{\rho}}{\partial\Phi_s^0})_{T,P} = \tilde{T}\tilde{\rho}^2\beta P^*\psi \quad \text{(A4)}$$

where

$$\beta P^* = \frac{1}{\tilde{\rho}}(\frac{\partial\tilde{\rho}}{\partial\tilde{P}})_T$$

$$= \{\tilde{\rho}\tilde{T}[\frac{1}{1-\tilde{\rho}} -1+\frac{1}{r_a} + \sum_m\sum_n m(m-1)a_{mn}^0\tilde{T}^{-n}\tilde{\rho}^{m-1}]\}^{-1} \quad \text{(A5)}$$

$$\psi = \frac{1}{r_o^0} - \sum_m\sum_n[n(m-1)a_{mn}^0\tilde{T}^{-n+1}\tilde{\rho}^{m-1}\lambda + (m-1)(\frac{\partial a_{mn}^0}{\partial\Phi_s^0})\tilde{T}^{-n}\tilde{\rho}^{m-1}] \quad \text{(A6)}$$

Figure Captions

Figure 1. Dependence of spinodals on the polydispersity of the polymer for acetone-polystyrene systems, P = 2MPa, M_n = 20.4kg/mol.

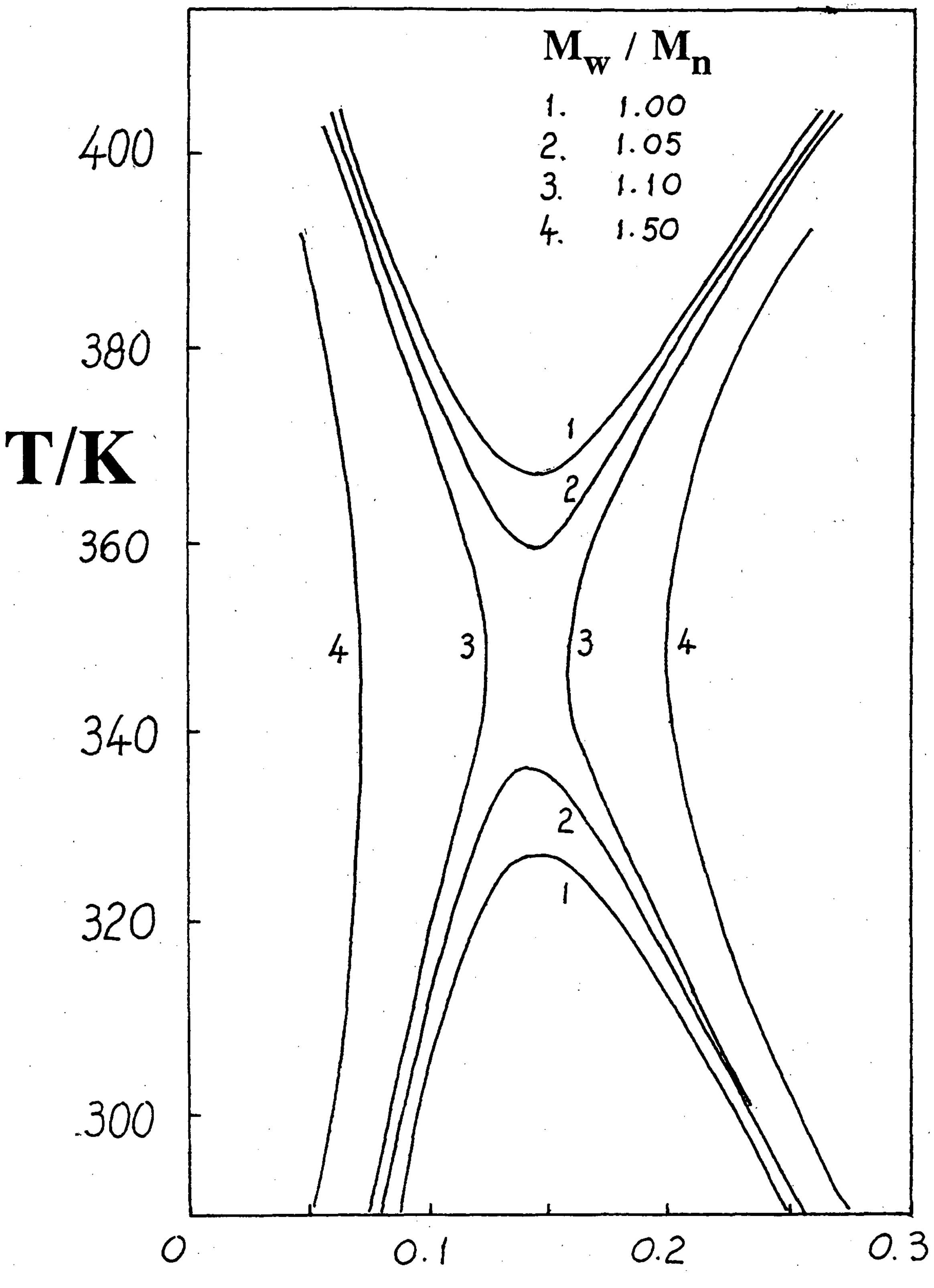
Figure 2. Dependence of spinodals on the polydispersity of the polymer for acetone-polystyrene systems, P = 5MPa, M_n = 20.4kg/mol.

Figure 3. Dependence of spinodals on the polydispersity of the polymer for acetone-polystyrene systems, P = 10MPa, M_n = 20.4kg/mol.

Figure 4. Dependence of cloud-point curves and shadow curves on the polydispersity of the polymer for acetone-polystyrene systems, P = 2MPa, M_w = 20.4kg/mol.

Figure 5. Dependence of cloud-point curves and shadow curves on the polydispersity of the polymer for acetone-polystyrene systems, P = 5MPa, M_w = 20.4kg/mol.

Figure 6. Dependence of cloud-point curves and shadow curves on the polydispersity of the polymer for acetone-polystyrene systems, P = 10MPa, M_w = 20.4kg/mol.



Weight Fraction of Polystyrene

Fig. 1

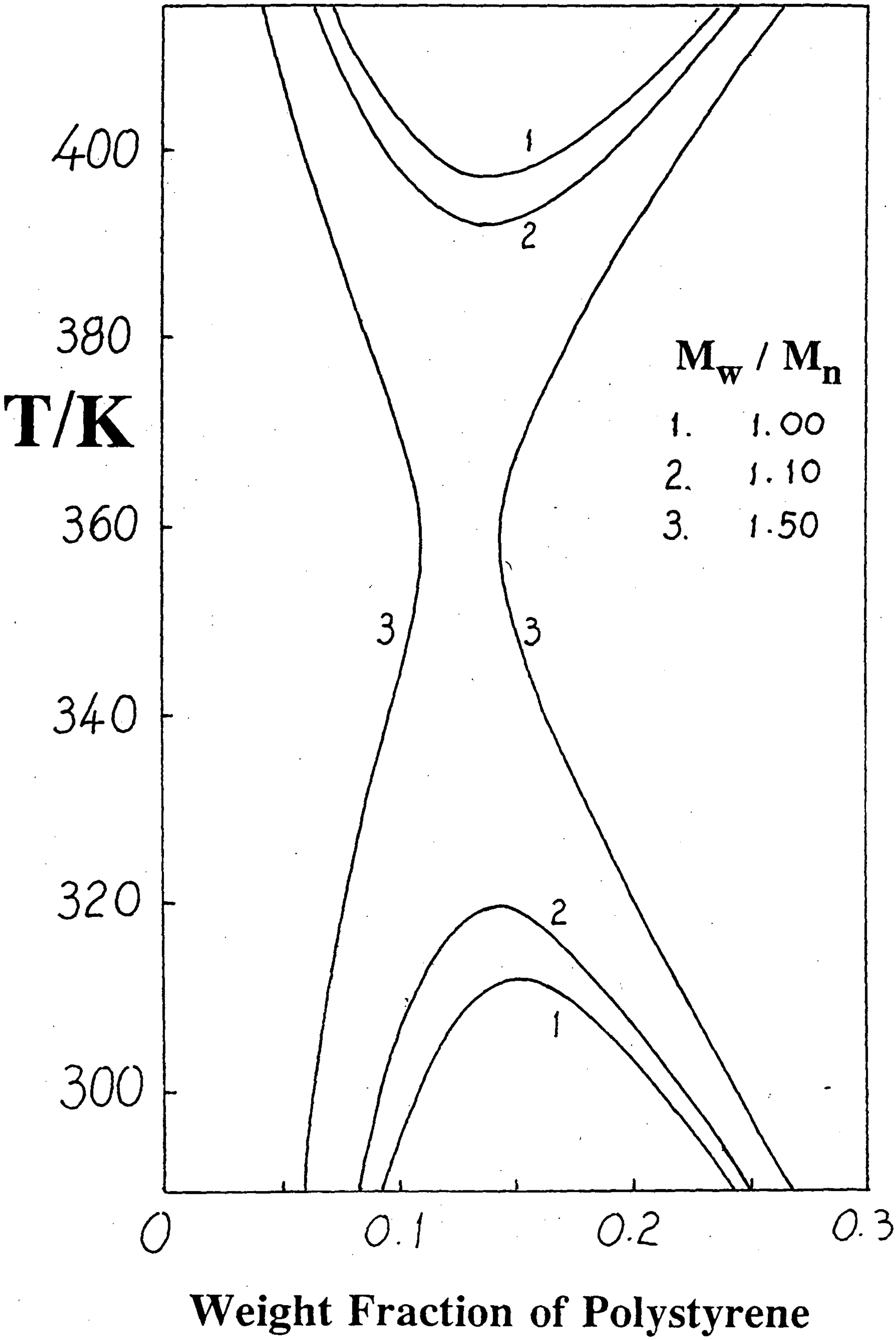

T/K
400
380
360
340
320
300
0
0.1
0.2
0.3
Weight Fraction of Polystyrene
M_w / M_n
1. 1.00
2. 1.10
3. 1.50
1
2
3
3
2
1

Fig. 2

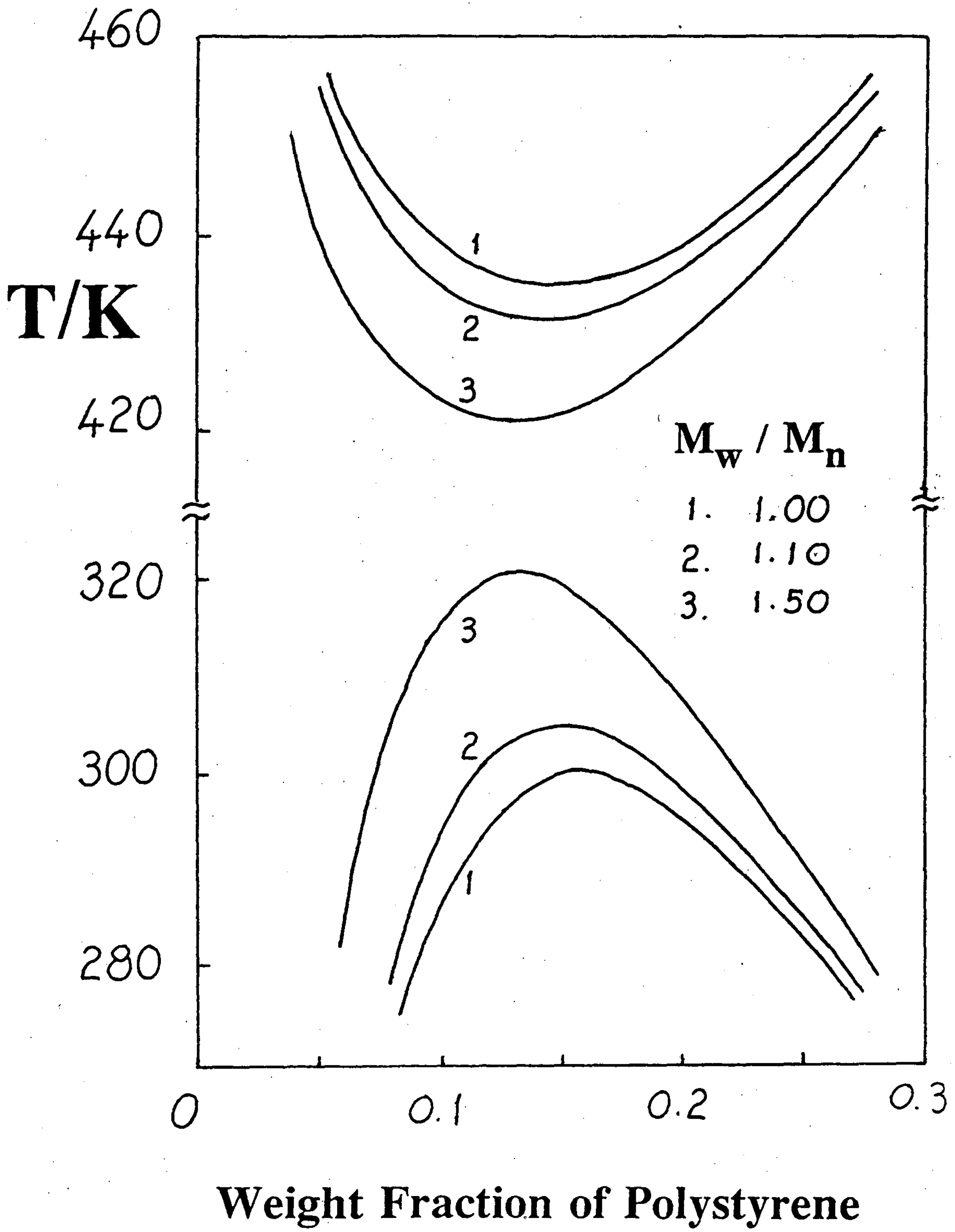

460
440
420
320
300
280
T/K
1
2
3
3
2
1
M_w / M_n
1. 1.00
2. 1.10
3. 1.50
0
0.1
0.2
0.3
Weight Fraction of Polystyrene

Fig. 3

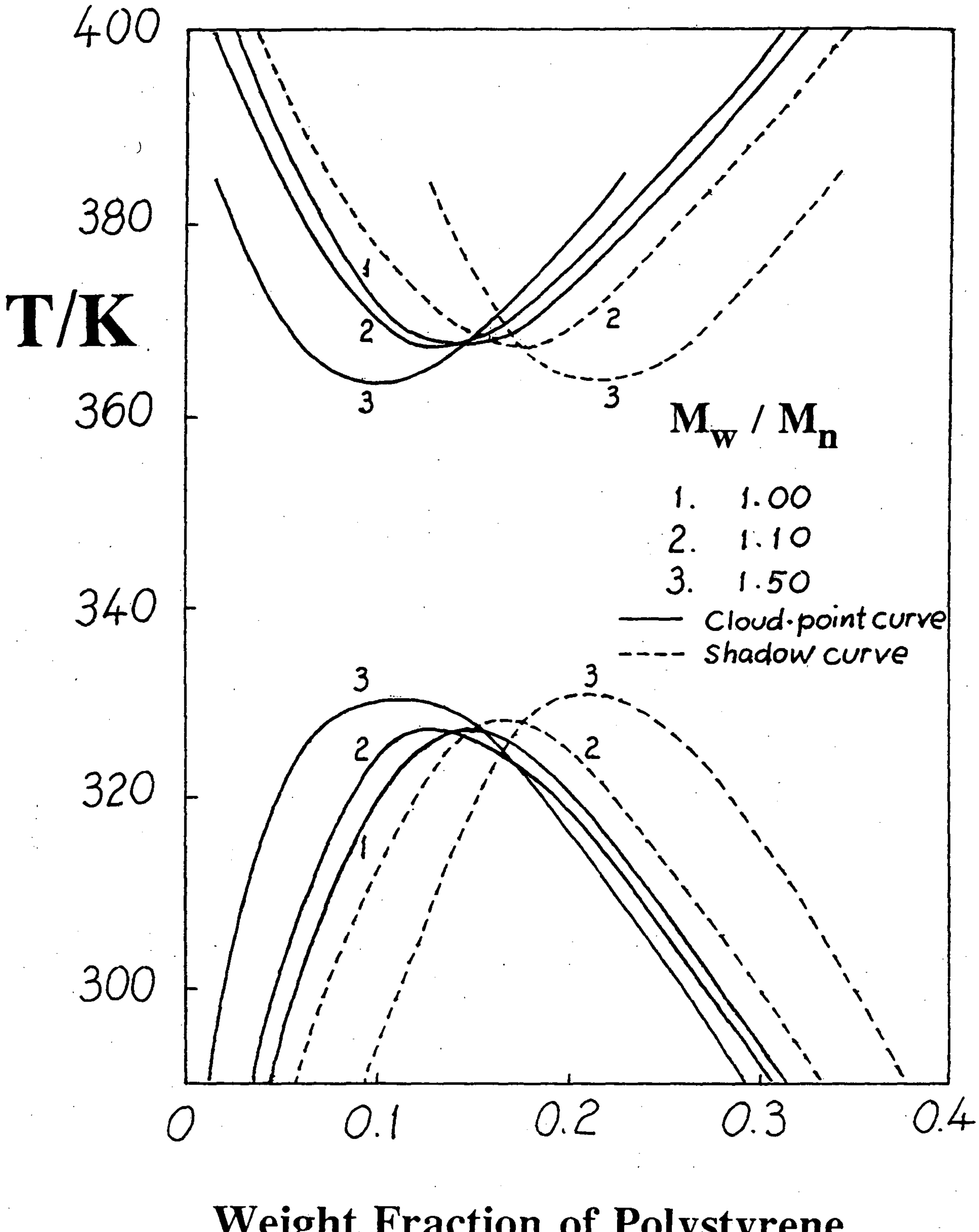

400
380
360
340
320
300
T/K
0
0.1
0.2
0.3
0.4
Weight Fraction of Polystyrene
1
2
3
2
3
3
2
1
3
2
M_w / M_n
1. 1.00
2. 1.10
3. 1.50
Cloud-point curve
Shadow curve

Fig. 4

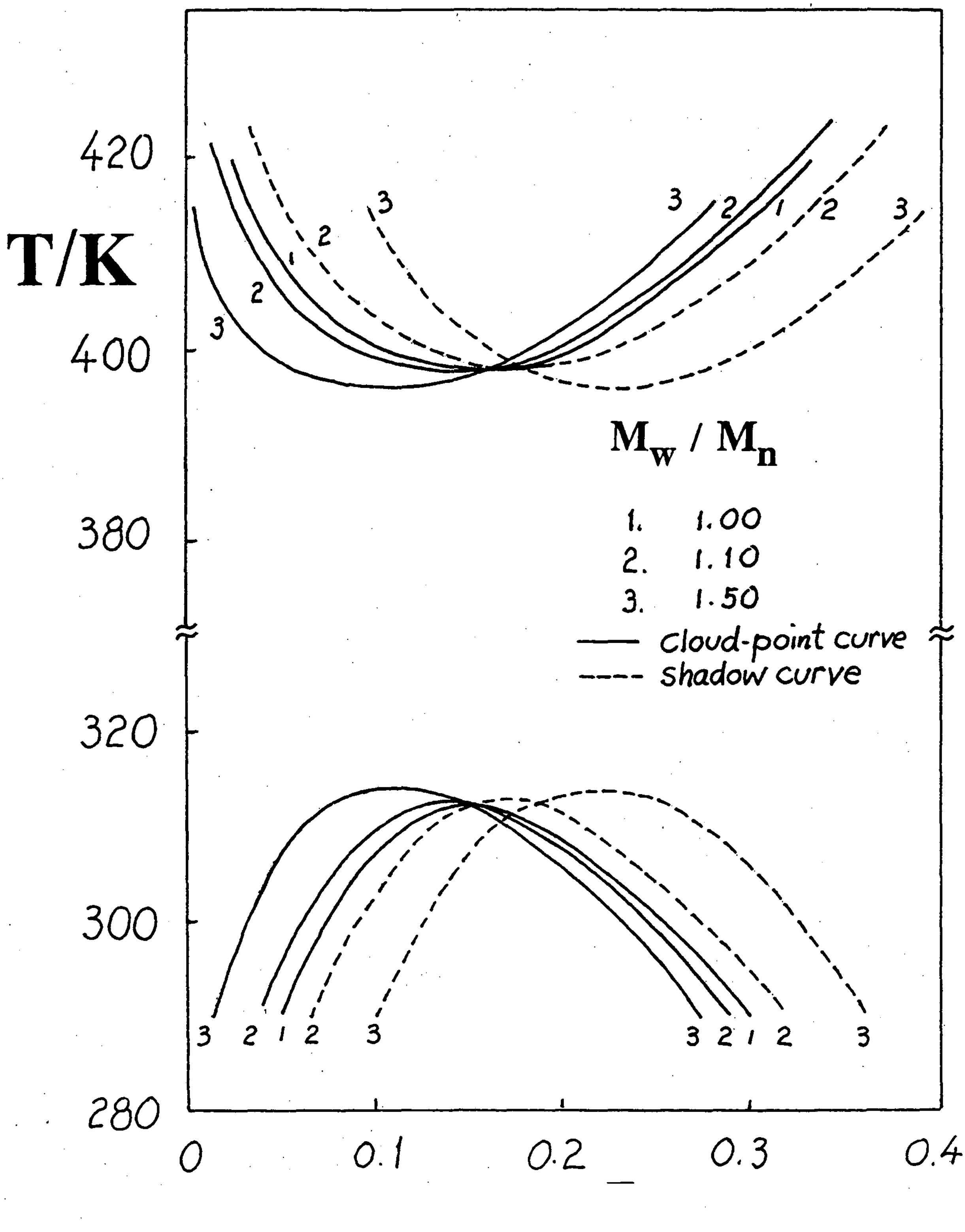

T/K
420
400
380
320
300
280
0
0.1
0.2
0.3
0.4
Weight Fraction of Polystyrene
Mw / Mn
1. 1.00
2. 1.10
3. 1.50
cloud-point curve
shadow curve
3
2
1
2
3

Fig. 5

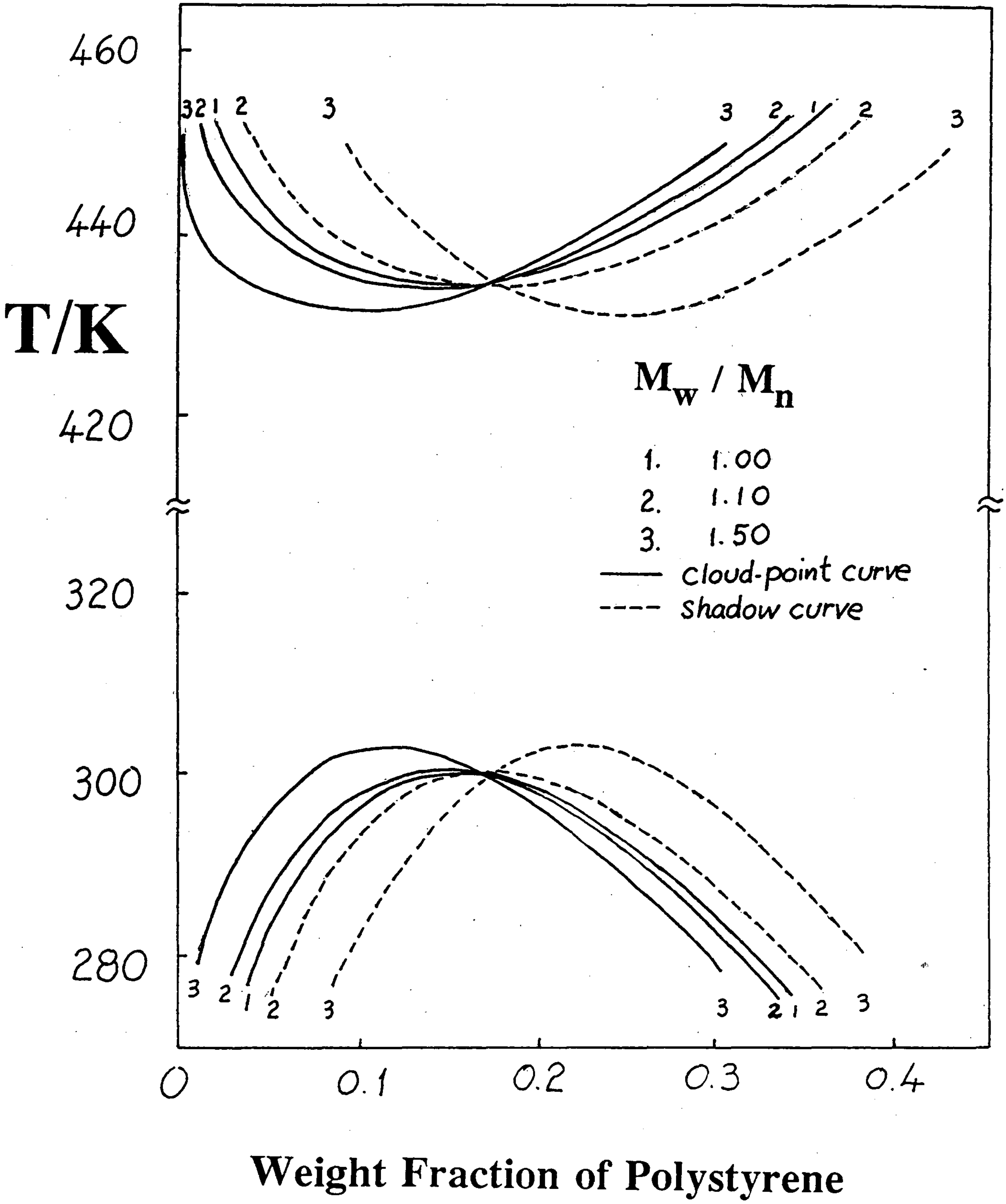

460
440
420
320
300
280
T/K
0
0.1
0.2
0.3
0.4
Weight Fraction of Polystyrene
M_w / M_n
1. 1.00
2. 1.10
3. 1.50
cloud-point curve
shadow curve
3
2
1

Fig. 6

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