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Phase equilibrium in solutions of star-shaped macromolecules: an improved Okada–Numasawa model☆

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Abstract

The two-region Okada–Numasawa model for solutions of star-shaped polymers has been improved by means of a change in the integration order and introduction of a concentration-dependent and molar-mass-dependent Flory–Huggins interaction parameter (the second and third approximations of the Flory–Huggins theory). To overcome calculation difficulties, a special algorithm for computing coexistence curves of polymeric systems with an UCST has been used. The agreement between the experimental and calculated coexistence curves for the star-shaped polystyrene (PS)–cyclohexane system has been improved: the difference between T_cs is ~0.33 K against ~12 K as given by the original model. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Star-shaped polymer; Coexistence curves; Phase equilibrium

1. Introduction

Flexible-chain polymers with star-shaped macromolecules possess a number of features in comparison with the corresponding linear polymers of the same molar mass. Among these peculiarities is a shift of the coexistence curve downward along the temperature axis [1–3]. Yokoyama et al. [2] observed a 3 K decrease of the critical temperature T_c in going from the linear polystyrene (PS)–cyclohexane system to the 11-arm star-shaped PS–cyclohexane one ($M = 2.05 \times 10^6$). The polymer solubility (the left-hand branch of the coexistence curve, $T < T_c$) correspondingly rose after this change in molecular architecture. This phenomenon cannot be explained in the framework of the classical Flory–Huggins theory [4].

Several attempts have been made to find an explanation of the phenomenon. Okada et al. [3] allowed for the increase in the number of end segments per macromolecule, the Flory–Huggins interaction parameter χ being less for the end segment–solvent interactions than for the middle segment–solvent ones. However, the effect taken into account turned out to be quantitatively insufficient to explain the observed solubility difference.

Saeki [5] approached the problem from the viewpoint of combinatory entropy of mixing. According to his concept, to calculate this quantity for a star-shaped polymer solution, the number of segments per macromolecule should be replaced by that per arm only. Such an operation correctly predicts the direction of the observed changes in the critical concentration ϕ_c but a considerable overestimation takes place, e.g. for the PS–cyclohexane system, the experimental shift of ϕ_c is $0.03 \rightarrow 0.04$ [2] while calculations give $0.0306 \rightarrow 0.0719$ (6.3 arms on the average). Critical temperature was not considered in that paper though it may turn out to be more informative than critical concentration due to a noticeable flatness of the coexistence curve top (see fig. 3 in Ref. [6]).

We have estimated the shift of T_c using the data from Ref. [6]: 11 arms, the number of segments $N = 17,600$, $N/f = 1600$, $\chi = 0.2211 + 85.31/T$. The critical temperature is 297.8 and 280.4 K for the linear and star-shaped polymer, respectively. The difference of 17.4 K seems rather large in comparison with the experimental value (~3 K).

Numasawa and Okada [4] applied the hybrid theory of Koningsveld et al. [7] (also known as the third approximation of the Flory–Huggins theory [8]) to star-shaped polymers. The only account of molecular architecture was in the difference between the values of C in the formula for $h(z)$ [9]

$$h(z) \approx 1 - Cz, \tag{1}$$

z being the dimensionless excluded-volume parameter. Although the hybrid theory provides a good fit between

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theory and experiment in the case of linear chains, it predicts an upward shift of the coexistence curve instead of the actual downward one. A number of other actions undertaken by the authors (variations of the estimated overlap concentration ϕ_2^*, the replacement of the composition of χ for dilute and concentrated solutions as in the original hybrid theory by a composition of the chemical potentials of solvent) brought about no improvement.

The two-region model of Okada and Numasawa [6] proposed for star-shaped polymers with a sufficiently big number of arms and based on the Daoud–Cotton theory [10] seems the most promising one. Its most noteworthy feature is a separate consideration of the internal region (the neighbourhood of the central unit of a star-shaped macromolecule) where the segment concentration is higher than the average one, and of the external region (the other space) where the relation is opposite. For simplicity, the first approximation of the Flory–Huggins theory ($\chi = \chi_c$) and averaging the concentration over the internal region were employed. An 8 K downward shift of the calculated critical point was reported, against the 3 K difference observed in experiments.

It should be noted that in fig. 3 from Ref. [6] the calculated and experimental coexistence curves for the linear polymer are rather far apart (the difference in T_c is about 7 K). It seems desirable to adjust these curves nearer to each other prior to calculations for the star-shaped polymer. To this end, a concentration-dependent χ parameter must be introduced [7,11], which may well make calculations enormously difficult.

To overcome the problem, the method of computing coexistence curves should be modified. At present, a set of non-linear equations expressing the equality of the chemical potential of each component in each phase is written and then solved numerically [11]. Such an algorithm requires a happy choice of the initial point (two concentrations) or else convergence will not be achieved. Since the critical point, as a rule, is not calculated separately but a whole coexistence curve is plotted from higher χs (lower Ts) to lower ones (higher Ts), a divergence of the computational processes, once met, can be interpreted ambiguously: either the critical temperature has been exceeded or the initial point has been chosen unlucky. By the way, the initial point comprises two concentrations (according to the number of equations in the set), which leaves a too wide field for manoeuvre to improve the choice of the initial point.

As both equations in the set originate from one, namely, the formula for the Gibbs free energy of mixing ΔG_m (ϕ; params), it seems reasonable to develop an algorithm involving this equation only (perhaps, with several derivatives). Besides, two sought variables should be replaced by one, easily estimated initially; the algorithm should indicate immediately whether the critical temperature is exceeded.

Such an algorithm is described in Appendix A and has enabled the two-region Okada–Numasawa model to be improved. Here we propose a number of corrections to this model.

2. Model

Okada and Numasawa [6] accepted the following expression for the radial density of segments:

$$\phi_s(r) = \frac{Nl^3}{4\pi R_g^2}\frac{1}{r}\exp\left(-\frac{r}{R_g}\right), \tag{2}$$

where N is the total number of segments, l^3 the volume of a segment or a lattice cell, R_g the radius of gyration, r the distance to the centre. When $r \to 0$, $\phi_s(r) \to \infty$ while physical sense dictates $\phi_s(r) \to 1$. So, as a first correction we restrict the rise of $\phi_s(r)$ to unity. A quantity R_1 was introduced and (Fig. 1, cf. fig. 1 from Ref. [6])

$$\phi_s(r) = \begin{cases} 1, & r \le R_1; \\ \dfrac{R_1}{r}\exp\left(\dfrac{R_1 - r}{R_g}\right), & r \ge R_1. \end{cases} \tag{3}$$

The algorithm of calculating ΔG_m has therefore been supplemented by the determination of R_1 (straightforward). It is interesting that R^* (the radius at which $\phi_s(r)$ falls to the concentration ϕ_{out} in the external region) undergoes no change. The volume $4\pi R^{*3}/3$ where $\phi_s(r) = 1$ does not contribute to the enthalpy of mixing, which, under phase separation conditions, must increase the polymer solubility.

A second correction concerns the order of integration. As was mentioned above, the original model averages the segment concentration over the whole internal region

$$\phi_{in} = \frac{3}{R^{*3}}\int_0^{R^*} \phi_s(r) r^2 \, dr, \tag{4}$$

then the value obtained is substituted into the expression for

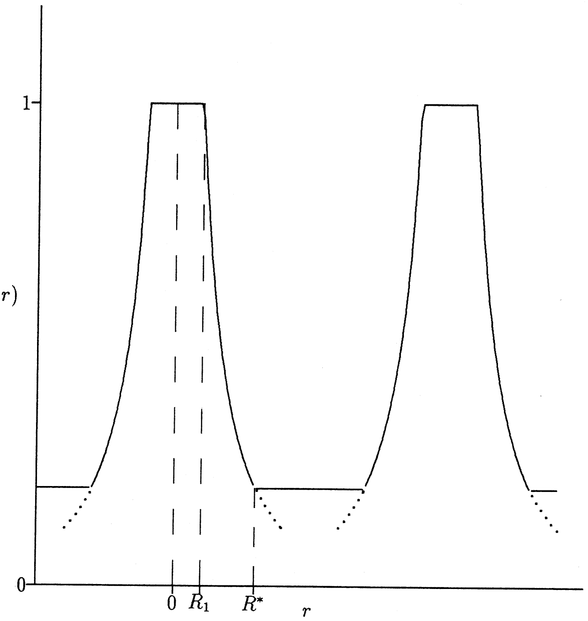

Fig. 1. Unity-corrected schematic representation of local segment concentration $\phi_s(r)$ in a semidilute solution of a star-shaped polymer (cf. fig. 1 from Ref. [6]).

the enthalpy of mixing

$$\frac{\Delta H_{\mathrm{m}}}{RT} = \cdots + \frac{4\pi}{3}\frac{R^{*3}\phi}{Nl^3}\chi\phi_{\mathrm{in}}(1-\phi_{\mathrm{in}}) + \cdots \tag{5}$$

This simplifies calculations drastically but integration of the r-dependent enthalpy term with no averaging of concentration is more rigorous

$$\frac{\Delta H_{\mathrm{m}}}{RT} = \cdots + \frac{\phi}{Nl^3}\chi\int_{R_1}^{R^*}\phi_{\mathrm{s}}(r)(1-\phi_{\mathrm{s}}(r))4\pi r^2\,\mathrm{d}r + \cdots \tag{6}$$

Integration is performed analytically with the given form of $\phi_{\mathrm{s}}(r)$ (Eq. (2)).

Thereby ground has been prepared for introducing a third (a concentration-dependent χ or g) and a fourth corrections (the hybrid theory):

$$\frac{\Delta H_{\mathrm{m}}}{RT} = \cdots + \frac{\phi}{Nl^3}\int_{R_1}^{R^*} g(\phi_{\mathrm{s}}(r))\phi_{\mathrm{s}}(r)(1-\phi_{\mathrm{s}}(r))4\pi r^2\,\mathrm{d}r + \cdots \tag{7}$$

This time we have to integrate by quadratures (the Gauss–Legendre quadratures [12]). However, this simplifies the differentiation required by the algorithm (see Appendix A).

As was mentioned in Section 1, the hybrid theory of Koningsveld was already used to calculate the coexistence curve of star-shaped polymers [4], but the authors confined themselves to the change of the coefficient C in $h(z)$ (Eq. (1)). Here we have a choice: to use either the original set of formulas for linear chains (FKOm, S, KY, CM) as in Ref. [7] or Eq. (1) used by Numasawa and Okada [4]. There is an additional variant (which produces the best results), namely, to modify each formula from the set (except KY which is a two-parameter one) in view of an altered coefficient C

$$C = \frac{32}{15f^{1/2}}[7 - 4\times 2^{1/2} + (f-1)(17\times 2^{1/2} - 9\times 3^{1/2} - 8)], \tag{8}$$

$$h(z) = 1 - Cz \qquad \text{(Trivial)}, \tag{9}$$

$$h(z) = \frac{\log(1+2Cz)}{2Cz} \qquad \text{(FKO, m)}, \tag{10}$$

$$h(z) = \frac{1}{1+Cz} \qquad \text{(S)}, \tag{11}$$

$$h(z) = \frac{1-\exp(-2Cz)}{2Cz} \qquad \text{(CM)}. \tag{12}$$

As z takes on negative values under phase separation conditions, the FKOm formula works within a too narrow temperature range near the critical point and therefore has been excluded from consideration.

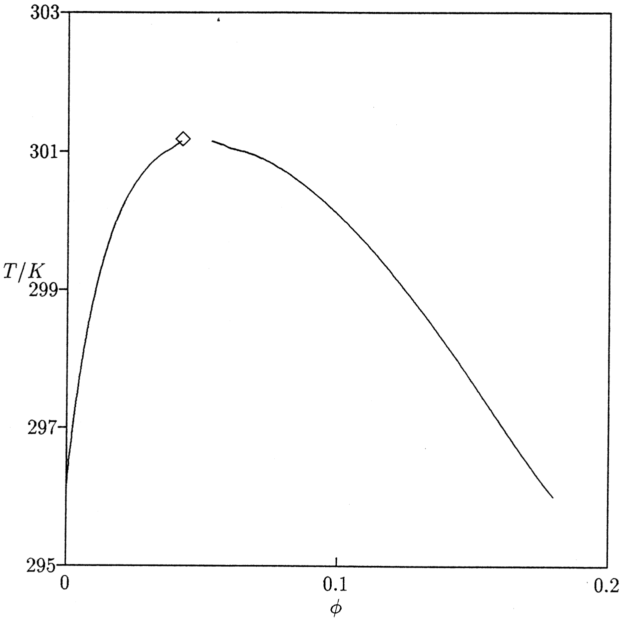

Fig. 2. Calculated coexistence curve of the 6.3-arm star-shaped PS–cyclohexane system and the experimental critical point [2] (experimental data adapted from Ref. [2]).

3. Results and discussion

The best results have been achieved with the Stockmayer (S) formula for $h(z)$ with the f-dependent C. The calculated coexistence curves for the star-shaped PS–cyclohexane system are shown in Fig. 2 ($f = 6.3$) and Fig. 3 ($f = 11$). Fig. 2 also includes the critical point ($\phi_{\mathrm{c}} = 0.0393$, $T_{\mathrm{c}} = 28\,°C$ [2]) while the whole experimental coexistence curve

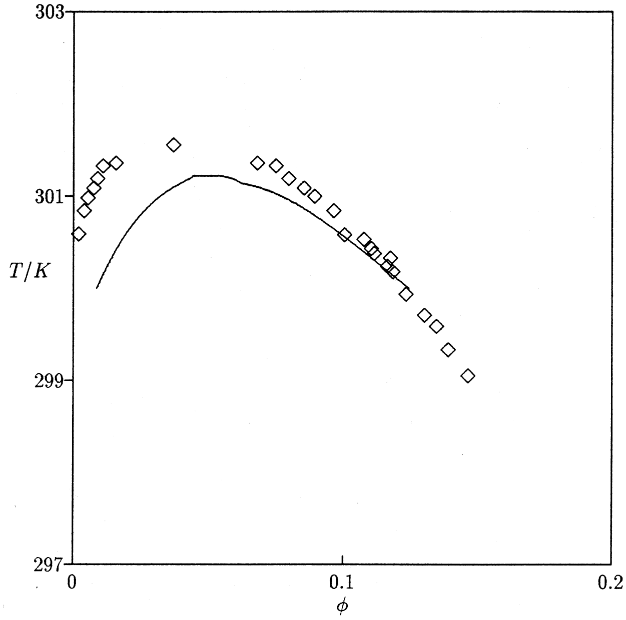

Fig. 3. Calculated (solid line) and experimental (◇) [2] coexistence curves of the 11-arm star-shaped PS–cyclohexane system (experimental data adapted from Ref. [2]).

from the same paper is placed on Fig. 3. One can see an obvious improvement in comparison with the predictions of the original theory: the experiment–calculation difference of ~12 K ($f = 11$) is reduced to ~0.33 K; for $f = 6.3$, agreement is very good (experimental $T_c = 301.15$ K, calculated $T_c = 301.157$ K). Such is the overall effect of all the four corrections.

The critical concentration ϕ_c is reproduced much worse: the experimental values are 0.0393 and 0.0371 for $f = 6.3$ and 11 [2], respectively, while the calculated values lying within 0.05 and 0.06. In this connection, one can notice that the tops of the coexistence curves look rather flat, which makes difficulties in estimating ϕ_c. Besides, classical theories fail in the critical region, and ϕ_c does not seem a reliable criterion for experiment–theory comparison.

There is another demerit of the calculated curves, namely, their branches going more steep than it is observed for the experimental coexistence curves. A similar observation was made by Okada and Numasawa [6] for their results, they attributed this narrowness to that disadvantage of the Flory–Huggins theory which is overcome by providing for the dilute solution peculiarities [7]. Having compared Fig. 3 with fig. 3 from Ref. [6], the reader can see that the calculated curves have indeed become somewhat wider though, qualitatively, a difference in the slopes remains. In our opinion, it should be attributed to the fact that the formulas for $h(z)$ used (including the Stockmayer one) were derived mainly for positive values of z (a good solvent, no phase separation). Figs. IV-3, 5–7 from Ref. [13] contain only the positive abscissa semiaxis, all the formulas for $h(z)$ (except the CM one) fail at a certain negative z—all this confirms our supposition. Therefore, the accuracy of these formulas diminishes as temperature goes from T_c to lower values (in our case; in general, as the excluded-volume parameter z becomes more negative), the error of estimating ϕs in the coexisting phases increases, the calculated coexistence curve's branches get a slope different from that of the experimental curves.

Thus, the improved Okada–Numasawa model described in this paper, having been calibrated against the corresponding linear polymer, predicts the critical temperature well while the critical concentration and the shape of coexistence curves are less well reproduced.

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Appendix A. Algorithm for the calculation of binodals of polymer–solvent systems with a UCST

As is known (e.g. Ref. [8]), if the free Gibbs energy of mixing ΔG_m is plotted against the volume fraction of polymer ϕ and a bitangent line is drawn to this curve (Fig. 4, solid lines), the abscissae of the points of tangency will be equal to the volume fractions of polymer in the coexisting phases.

The algorithm used in the present work is based on the observation that if the slope of the bitangent line (say, K) multiplied by ϕ is subtracted from both $\Delta G_m(\phi)$ and the bitangent line equation, this straight line will become parallel to the abscissa axis, the tangency will take place at the two minima of the modified $\Delta G_m(\phi)$ curve, the deepness of these minima will become equal, and the abscissae of the points of tangency will not be altered (Fig. 4, dotted lines). So, the task is reduced to finding such a value of K (negative) at which the elevated curve will possess two minima of an equal depth.

To be used, the algorithm requires a subroutine to calculate $\Delta G_m(\phi)$ itself and its first and second derivatives with respect to ϕ (the third derivative is welcome but not mandatory). Before its use in the present work, it had been tested on the $\Delta G_m(\phi)$ formulae from the first, second, and third approximations of the Flory–Huggins theory [8,15]. The Flory theory for rod-like macromolecules [16] was also involved (a bill-looking binodal). Of course, in the case of the possibility of more than one bitangent line existing, the Gibbs curve requires a more thorough analysis than that done by the algorithm used here.

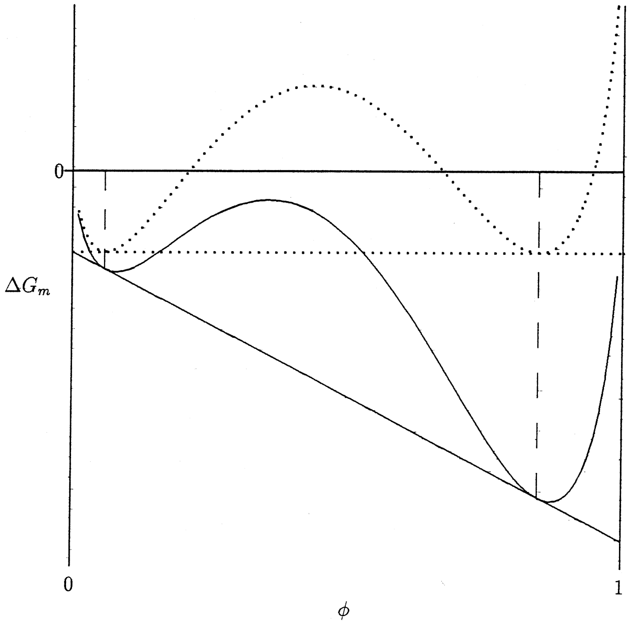

Fig. 4. Illustration of the technique used for binodal computation.

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