Small-angle X-ray scattering and coexistence curve of semidilute polymer solutions

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Small-angle X-ray scattering from semidilute solutions of polystyrene in cyclohexane has been studied in a poor solvent regime. The values of binary and ternary cluster integrals of polymer segments were determined from the concentration dependences of the correlation length and the osmotic compressibility, as obtained from the absolute intensity at zero scattering angle, at various temperatures in the poor solvent regime. By using these interaction parameters the coexistence curve was calculated via a mean field theory. Excellent agreement was achieved between the calculated coexistence curve and the experimental phase separation points which we have measured.

(Keywords: small-angle X-ray scattering; coexistence curve; semidilute solution; poor solvent regime; polystyrene; cyclohexane)

INTRODUCTION

In a previous paper[1] we have calculated the theoretical coexistence curve (binodal curve) of semidilute polystyrene solutions in cyclohexane via a mean field theory using the interaction parameters extracted from SANS (small-angle neutron scattering) and SAXS (small-angle X-ray scattering) measurements. We found a substantial agreement between the calculated coexistence curve and the experimental phase separation points reported in the literature.

The purpose of the present work was twofold: first, to extend the previous studies by providing details of SAXS measurements; second, to describe our own measurements of phase separation points and to compare them with the theoretical coexistence curve, thereby reinforcing the conclusions of the preceding paper.

SMALL-ANGLE X-RAY SCATTERING

Correlation function and scattering law

Let us consider a semidilute polymer solution in which polymer chains fully overlap one another. Further, we focus on the case of a poor solvent regime subject to the conditions:

$$\frac{\beta_1}{\rho b^6}<1 \qquad \frac{\beta_2}{b^6}<1 \tag{1}$$

where b^2 is the mean square length of a polymer segment, β_1 and β_2 are the binary and ternary cluster integrals of segments, ρ is the number of polymer segments in a unit volume of the solution. In this regime, as was first recognized by Edwards[2], the spatial fluctuation of segment density is small, so that one can calculate the density–density correlation function of polymer segments in solution by means of Gaussian approximation in an $n=0$ field theory[3], or by summing up the diagrams of chain type in a cluster expansion theory[4,5]. One obtains the Fourier transform of the correlation function as:

$$G(q)=\frac{12}{b^2}\frac{1}{q^2+\xi^{-2}} \qquad \left(\frac{6}{Nb^2}\right)^{1/2}<q<\frac{1}{b} \tag{2}$$

$$\frac{1}{\xi^2}=\frac{6}{Nb^2}+12\frac{\beta_1}{b^2}\rho+36\frac{\beta_2}{b^2}\rho^2 \tag{3}$$

where N is the number of segments in a polymer chain. If we substitute $\beta_2=0$ in equation (3) we obtain the original Edwards formula[2] for correlation length. Since the size of a polymer segment is not uniquely defined, for the purposes of practical application it is useful to express the above equations in terms of observable quantities defined respectively by[6]:

$$Nb^2=MA^2 \qquad N^2\beta_1=M^2B_1 \qquad N^3\beta_2=M^3B_2 \qquad \frac{\rho}{N}=\frac{c}{M}N_A \tag{4}$$

where M is the molecular weight of a polymer chain, c is the weight concentration of the solution, N_A is Avogadro's number. The angular dependence of the scattered intensity is given by:

$$I(q)=I(0)\frac{1}{1+\xi^2q^2} \tag{5}$$

$$\frac{1}{\xi^2}=\frac{6}{MA^2}+12N_A\frac{B_1}{A^2}c+36N_A^2\frac{B_2}{A^2}c^2 \tag{6}$$

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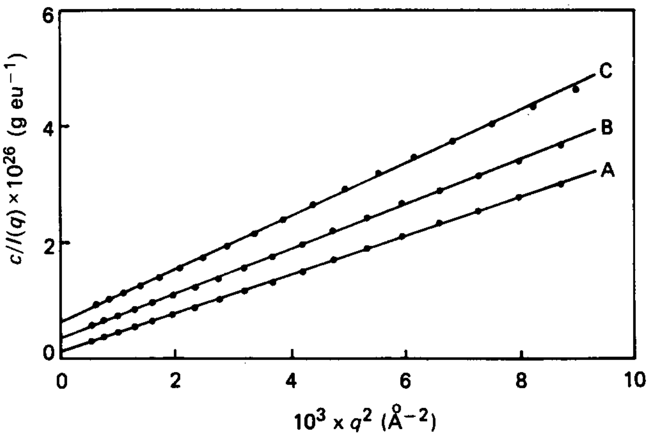

Figure 1 Example of the measured angular dependences of SAXS at 40.5°C: A, 0.0742 g cm^{-3}; B, 0.141 g cm^{-3}; C, 0.174 g cm^{-3}

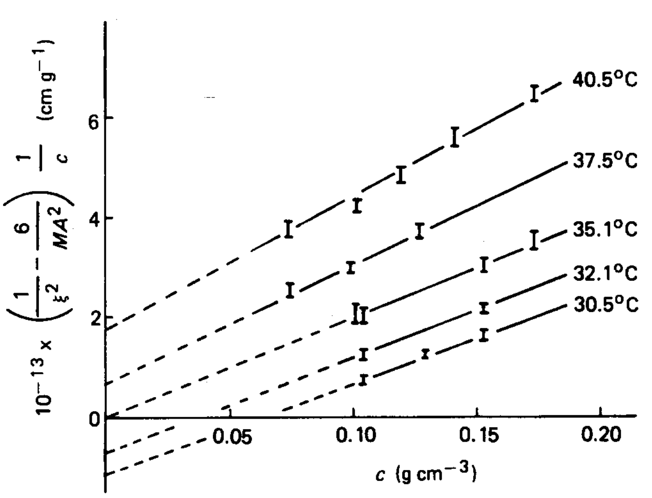

Figure 2 Concentration dependence of ξ for several temperatures near the θ point

$$\frac{1}{I(0)} = \frac{1}{(\Delta z)^2}\left(\frac{1}{2N_A Mc} + B_1 + 3N_A B_2 c\right) \qquad (7)$$

where q is now the scattering vector and Δz is the number of excess electrons per mol polymer.

We have already shown[6] that equations (5), (6) and (7) in fact work well in analysing SAXS measurements of semidilute poor-solvent solutions. In this paper we have obtained interaction parameters B_1 and B_2 of a polystyrene–cyclohexane system based on the above equations.

Measurement and analysis of SAXS

The X-ray generator used was a rotating copper anode type (Rigaku RU-200) and was operated at 50 kV, 180 mA with $\lambda = 1.54$ Å filtered by Ni foil of 14 μm thickness. A Kratky U-slit camera was used with an entrance slit of 100 μm, counter slit of 300 μm, and height-determining slit of 16 mm. Photon counting was done by a scintillation counter with a pulse-height analyser. Slit correction was done by the variation–function method[7]. Absolute scattered intensity was determined by the Lupolen method.

Samples used were cyclohexane solution of monodisperse polystyrene (from Pressure Chemical Co.; molecular weight 6×10^5; $M_w/M_n \leqslant 1.10$). The temperature of the sample was controlled within ± 0.03°C by a thermocouple placed in the solution.

The measured angular dependence of the scattered intensity showed Lorentzian form (*Figure 1* and equation 5), and we could determine the correlation length, ξ, and scattered intensity at zero angle, $I(0)$, for each concentration and temperature. *Figures 2* and *3* show the concentration dependences of ξ and $I(0)$ at several temperatures near the θ point. The results agree well with the prediction of equations (6) and (7), respectively. These equations enable us to determine B_1 and B_2 separately. The B_1 and B_2 values obtained from ξ agree with the values from $I(0)$ within the experimental error.

Throughout the course of the analysis we have assumed that the parameter A related to the unperturbed dimension of polystyrene has a value of 0.7 Å and is independent of temperature[6]. This procedure is allowed because the temperature dependence of unperturbed dimension is generally very weak. For atactic polystyrene it is reported that[8]:

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln A^2 \simeq 4 \times 10^{-4}\,\mathrm{deg}^{-1}$$

Therefore, we can safely neglect the temperature dependence of A within the accuracy of the SAXS measurements over the measured temperature range. *Figure 4* shows the temperature dependences of B_1 and B_2 determined thus. From the Figure it is clear that B_1 increases monotonically with temperature from negative to positive values and vanishes at about 35°C, the θ

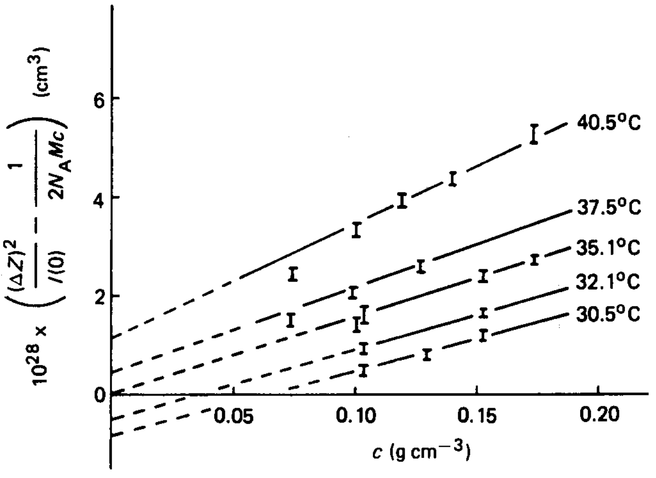

Figure 3 Concentration dependence of $I(0)$ for several temperatures near the θ point

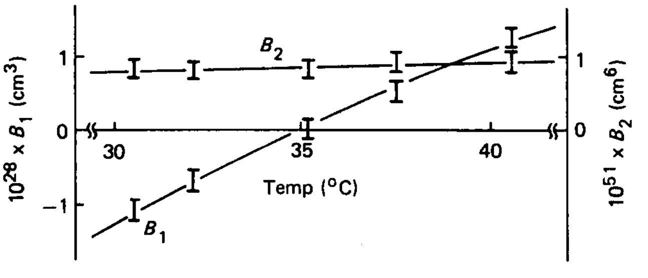

Figure 4 Temperature dependence of binary (B_1) and ternary (B_2) cluster integrals of polymer segments

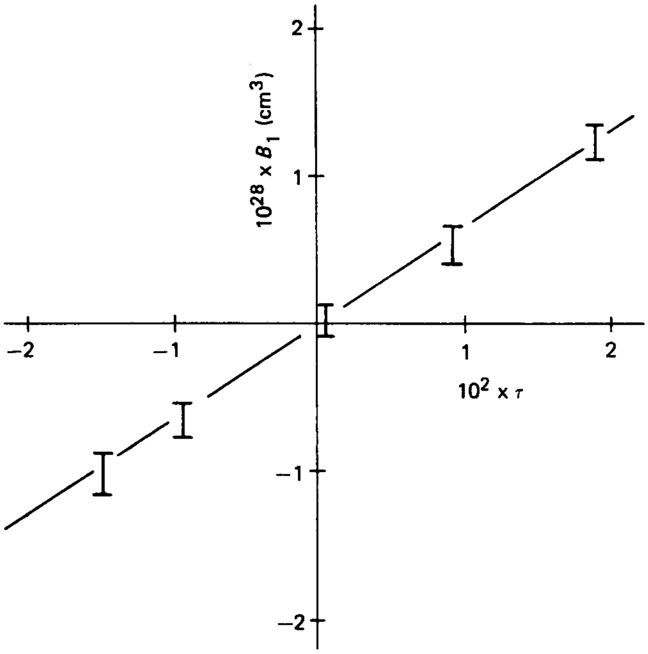

Figure 5 Binary cluster integral B_1 plotted against τ, with $\theta = 35°C$

temperature, while B_2 is almost independent of temperature in the measured temperature range. In *Figure 5* the values of B_1 are replotted against reduced temperature τ defined by:

$$\tau = 1 - \frac{\theta}{T} \tag{8}$$

We thus obtain the empirical equations:

$$B_1 = B_{10}\tau \quad \text{where } B_{10} = 6 \times 10^{-27}\,\text{cm}^3 \tag{9}$$

$$B_2 = 0.8 \times 10^{-51}\,\text{cm}^6 \tag{10}$$

These empirical equations for the polystyrene–cyclohexane solution coincide well with those of a polystyrene-deuterated cyclohexane solution obtained by SANS[4] in spite of the difference in the θ temperature.

COEXISTENCE CURVE

Theoretical coexistence curve

As pointed out by de Gennes[9], the semidilute branch of the coexistence curve can be calculated by equating the osmotic pressure, π, of the semidilute solution to zero. In a mean field approximation, π is given by[3,9]:

$$\frac{\pi}{RT} = \frac{c}{M} + \frac{1}{2}N_A B_1 c^2 + N_A^2 B_2 c^3 \tag{11}$$

where R is the universal gas constant and T is the absolute temperature. In the case where the temperature dependences of B_1 and B_2 are, respectively, given by:

$$B_1 = B_{10}\tau \qquad (B_{10}\text{independent of } \tau) \tag{12}$$

$$B_2 \qquad \text{independent of } \tau \tag{13}$$

the coexistence curve is given by:

$$\tau = -2\frac{1}{N_A B_{10} M}\frac{1}{c} - 2N_A\frac{B_2}{B_{10}}c \tag{14}$$

In the reduced variables defined by:

$$\tilde{\tau} = \sqrt{M}\tau \qquad \tilde{c} = \sqrt{M}c \tag{15}$$

the theoretical coexistence curve becomes:

$$\tilde{\tau} = -2\frac{1}{N_A B_{10}}\frac{1}{\tilde{c}} - 2N_A\frac{B_2}{B_{10}}\tilde{c} \tag{16}$$

As has already been reported[1] and described above in detail, the temperature dependences of the interaction parameters of polystyrene in cyclohexane in fact take the form of equations (12) and (13), respectively, with the numerical values mentioned above, equations (9) and (10). Equation (16) now reduces to[1]:

$$\tilde{\tau} = -5.6 \times 10^2\frac{1}{\tilde{c}} - 1.6 \times 10^{-1}\tilde{c} \tag{17}$$

which is to be compared with experiments. In contrast to the preceding paper[1], we now compare the above theoretical equation with our own measurements of phase separation points.

Measurement of phase separation temperature

We focused our attention on the semidilute concentration range and endeavoured to measure the equilibrium phase separation points with sufficient accuracy for our purpose.

The polystyrene fractions used were furnished by Pressure Chemical Co. and Toyo Soda Inc. The characteristics of the fractions are compiled in *Table 1*. The polystyrene sample had been dried for 3 days in a vacuum box and was dissolved in cyclohexane. The cells were made of Pyrex tubing (inner diameter 8 mm) and were flame sealed. The measurements were carried out in a water thermostat controlled within ±0.03°C.

Phase separation temperature was determined by observing, on a screen, the intensity of transmitted light beam (He–Ne laser; $\lambda = 632.8$ nm) through the sample solution placed in the thermostat. It takes many hours for a phase separation process to achieve equilibrium, and it is not practicable to wait for a long time for each solution. We therefore set up the following criterion for detecting the equilibrium phase separation temperature. As the temperature of the solution was reduced gradually (0.1°C h^{-1}), the intensity suddenly decreased at a certain temperature T_p. At $T_p + 0.05°C$, the meniscus showing the phase separation did not appear on leaving the solution for 2 weeks, while at $T_p - 0.05°C$, the meniscus was seen

Table 1 Molecular weight (M_w) and polydispersity M_w/M_n of the polymers used

$M_w \times 10^{-6}$	M_w/M_n
0.60	$\leqslant 1.10$
1.80	$\leqslant 1.3$
3.84	$\leqslant 1.04$

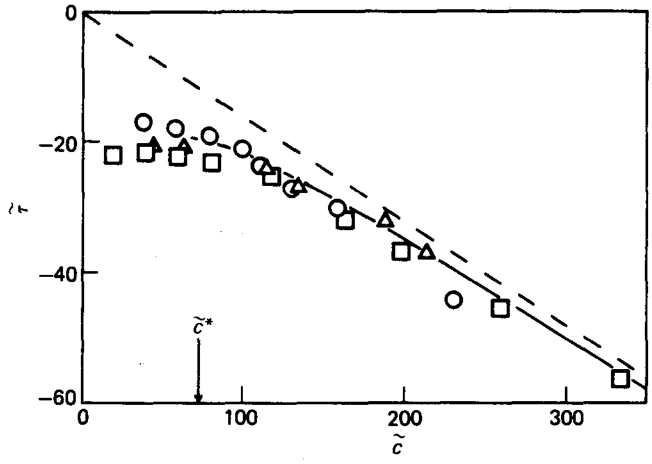

Figure 6 Theoretical coexistence curve (solid line) and the experimental phase separation points: ○, $M=6.0\times10^5$; △, $M=1.8\times10^6$; □, $M=3.84\times10^6$. Broken line represents the asymptote to the theoretical coexistence curve

after 24 h. Thus, we defined the phase separation temperature as T_p.

The measured phase separation points are shown in *Figure 6*, in which the theoretical coexistence curve is also drawn. The measured points agree well with the theoretical curve. This result implies that the theoretical coexistence curve, equation (16), is valid and the values of interaction parameters, equations (9) and (10), are reasonable.

CONCLUSION

We conclude from this work and also from the results described in the preceding paper[1] that in a semidilute poor solvent regime a mean field approximation is adequate to calculate the equation of state and the coexistence curve. We also conclude that equations (5), (6) and (7), which are based on the Gaussian approximation or its equivalent in describing the fluctuation of segment density, work well for semidilute poor solvent solutions and we can obtain the interaction parameters from small-angle scattering experiments via these equations. All these features are the consequences of smallness of spatial fluctuations of segment density in the regime.

REFERENCES

1 Okano, K., Ichimura, T., Kurita, K. and Wada, E. *Polymer* 1987, **28**, 693
2 Edwards, S. F. *Proc. Phys. Soc. (London)* 1966, **88**, 265
3 Moore, M. A. *J. Phys. (Paris)* 1977, **38**, 265
4 Okano, K., Kurita, K., Nakajima, S., Wada, E., Furusaka, M. and Ishikawa, Y. *Physica* 1983, **120B**, 413
5 Benoit, H. and Benmouna, M. *Polymer* 1984, **25**, 1059
6 Okano, K., Wada, E., Kurita, K. and Fukuro, H. *J. Appl. Crystallogr.* 1978, **11**, 507
7 Glatter, O. *J. Appl. Crystallogr.* 1974, **7**, 147
8 Orofine, T. A. and Ciferri, A. *J. Phys. Chem.* 1964, **68**, 3136
9 de Gennes, P. G. 'Scaling Concepts of Polymer Solutions', Cornell University Press, 1979