for the scattering experiment to obtain precise $q$ dependences of this function.

IV. Conclusion

The neutron small-angle scattering data show the distinct long-range organisations in polymer coil systems, subject to different environments and external stresses. Contrast matching and $q$ dependence associated with this technique offer a unique possibility for a detailed investigation, which has only recently begun.

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References


Small-Angle X-ray Scattering by Polymer Solutions at Intermediate Concentrations

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SAXS by solutions of monodisperse polystyrene at intermediate concentrations has been studied for the solvents having only a small volume-exclusion effect, such as methyl ethyl ketone (MEK) and cyclohexane (CH). Both the density-density correlation function of segments in solution and the osmotic compressibility, as obtained from the absolute intensity at zero angle, were measured for different concentrations and the results were successfully analysed by means of the recent theory of Moore [J. Phys. (Paris), (1977), 38, 265–271]. According to the theory, in the semi-dilute poor-solvent regime the concentration $C$, dependence of the screening length $\xi$, and the scattered intensity at zero angle $I(0)$ are given by

$$\frac{1}{\xi^2 C} = 12 N_A B_1 \frac{A^2}{M} + 36 N_A B_2 \frac{A^2}{M^2} C$$

and

$$\frac{(A^2)}{I(0)} = B_1 + 3 N_A B_2 C,$$

where $M$ is the molecular weight of a polymer molecule, $N_A$ Avogadro’s number and $A^2 M$ the mean square end-to-end distance of an unperturbed chain; $m^2 B_1$ and $m^2 B_2$ are respectively the binary and ternary cluster integrals (or the first and the second irreducible integrals) for segments in solution, $m$ being the molecular weight of a segment. $AZ$ is the number of excess mole electrons per unit mass of segments. The measured concentration dependences were in agreement with the above prediction and the values of $B_1$ and $B_2$ were obtained.

Introduction

The theory of polymer solutions at intermediate concentrations (semi-dilute solutions), in which polymer chains fully overlap one another was initiated by Edwards (1966) and extended by Jannik & de Gennes (1968) for a poor-solvent system. The concept of screening length of the density correlation of polymer segments in solution was introduced. In the mean-field approximation the osmotic equation of state is given by

$$\frac{\pi}{kT} = \frac{1}{2} \beta_1 \varrho^2,$$

where $\pi$ is the osmotic pressure, $\varrho$ the number density of polymer segments in solution, $\beta_1$ the binary cluster integral of polymer segments, $k$ the Boltzmann constant and $T$ the absolute temperature. In the random-phase approximation the density–density correlation function of polymer segments is given by

$$G(q) = \frac{12}{q b^2} \frac{1}{q^2 + \xi^{-2}},$$
where $G(q)$ is the spatial Fourier transform of the correlation function, and $b^2$ is the mean square length of a polymer segment. The screening length $\xi$ is given by

$$\xi^{-2} = 12 \frac{q^6}{b^2} \beta_1.$$  

(3)

Subsequent advances both in theoretical methods, i.e. the application of scaling method and renormalization group theory to the chain statistics, and in experimental investigations by small-angle neutron scattering (SANS), mainly by the French group, are remarkable and the density–density correlation function of polymer segments in a semi-dilute good-solvent system were fully investigated (Daoud et al., 1975). Recently, using the scaling analysis based upon the analogy between the $\theta$ point of polymer solutions and the tricritical point (de Gennes, 1975), Daoud & Jannink (1976) have classified polymer solutions with respect to the concentration and temperature. They showed in particular that for a semi-dilute poor-solvent system, region III in their notation, the asymptotic behavior of the osmotic pressure and the screening length are given respectively by

$$\zeta^{-2} = 12 \frac{q^6}{b^2} \beta_1.$$  

(4)

$$\zeta^{-2} \sim q^3.$$  

(5)

These results, however, differ from those of the earlier theories of Edwards (1966) and Jannink & de Gennes (1968).

Very recently Moore (1977) has carried out a detailed calculation of the density correlation of segments in a semi-dilute poor-solvent solution by the field-theoretical formalism of des Cloizeaux (1975). Moore has invoked the ternary cluster integral $\beta_2$ of polymer segments in addition to the ordinary binary cluster integral $\beta_1$. Based upon the mean-field free energy, Moore has obtained the following equation for the osmotic pressure:

$$\frac{\pi}{kT} = \frac{1}{\beta_1} q^2 + \frac{1}{\beta_2} q^4.$$  

(6)

and for the correlation function:

$$G(q) = 12 \frac{q^6}{b^2} \frac{1}{q^2 + \xi^{-2}}$$  

(7)

$$\xi^{-2} = 12 \frac{\beta_1}{b^2} q + 36 \frac{\beta_2}{b^2} q^2$$  

(8)

in the Gaussian approximation. The correlation function $G(q)$ has exactly the same form as that of the earlier paper (Jannink & de Gennes, 1968) except for the expression for the screening length. Moore has thus shown that if $\beta_2$ is very small the theories of Edwards (1966) and of Jannink & de Gennes (1968) hold good; otherwise the expression by Daoud & Jannink (1976) is appropriate near the $\theta$ point.

A systematic investigation by SANS of a poor-solvent system has also been performed by the French group (Cotton et al., 1976). These authors found that the measured temperature dependence of $\xi$ of polystyrene in cyclohexane in the vicinity of the $\theta$ temperature is in good agreement with the theoretical prediction of Daoud & Jannink (1976).

With these recent developments in mind, we intended to measure the density–density correlation function of polymer segments in a semi-dilute poor-solvent system by small-angle X-ray scattering (SAXS), and to obtain the value of the ternary cluster integral of segments, $\beta_2$, in addition to the ordinary binary cluster integral, $\beta_1$, based upon the theory of Moore (1977).

**SAXS by polymer solution in the semi-dilute poor-solvent regime**

We define the semi-dilute poor-solvent regime of polymer solution by the following inequalities

$$\frac{4\pi}{3} (N b^3)^{3/2} \geq \frac{N}{q},$$  

(9)

$$z_1 = \frac{\beta_1}{b^3} N^{1/2} < 1.$$  

(10)

and

$$z_2 = \frac{\beta_2}{b^6} < 1.$$  

(11)

Let us define the overall correlation function of segments in solution by

$$G(R) = \frac{1}{q^3} \left< (v(r) - \rho)(v(r + R) - \rho) \right> - \delta(R),$$  

(12)

where $v(r)$ is the instantaneous number density of segments in solution, so that

$$\rho = \langle v(r) \rangle.$$  

(13)

We also define the Fourier transform of the correlation function:

$$G(q) = \int G(R) \exp(iqR) dR.$$  

(14)

Then Moore's theory leads to equations (7) and (8). Equations (9) to (11) are equivalent to the Ginzburg-Kadanoff criterion (Kadanoff et al., 1967) for the validity of the mean-field theory:

$$G(R = \xi) \ll 1^{*}$$  

(15)

or

$$\frac{\beta_1}{q b^6} \ll 1$$  

(16)

and

$$\frac{\beta_2}{b^6} \ll 1.$$  

(17)

The intensity† of SAXS is generally related to the Fourier transform of the correlation function as

$$I(q) = (\Delta n)^2 \rho \left[ 1 + q G(q) \right],$$  

(18)

where we have used the electron unit (Hendricks, 1972) for the intensity of SAXS so that $\Delta n$ is the number of excess electrons per segment, and $\lambda$ the wavelength of X-rays and $\theta$ the scattering angle.

* The correlation function $G(R)$ in real space corresponding to equation (7) is given by

$$G(R) = \frac{3}{2 \pi} \frac{1}{q b^3} \frac{1}{R} \exp \left( -R \xi \right), |R| = R.$$  

† We mean by 'intensity' the excess intensity of solution over that of solvent.
We are interested in the so-called 'intermediate momentum range' of $q$:

$$\left(\frac{1}{b} N b^2\right)^{1/2} < q < b^{-1}. \quad (20)$$

Then we have from equations (7) and (18) the Lorentzian or the Ornstein-Zernike form of scattering function:

$$\frac{1}{I(q)} = \frac{1}{I(0)} \left[ 1 + q^2 \xi^2 \right], \quad (21)$$

where

$$I(0) = (\Delta n)^2 \frac{12}{b^2} \xi^2. \quad (22)$$

Putting equation (8) into equation (22), we obtain

$$\frac{1}{I(0)} = \frac{1}{(\Delta n)^2} \left[ \beta_1 + 3 \beta_2 \xi^2 \right]. \quad (23)$$

If we measure the angular dependence of the absolute intensity we may obtain the values of $\beta_1$ and $\beta_2$, either via $\zeta$, equation (8), or via $I(0)$, equation (23). By the 'compressibility equation',

$$I(0) = (\Delta n)^2 qT \left( \frac{\partial \pi}{\partial \rho} \right)_T^{-1}, \quad (24)$$

the latter amounts to a measurement of the osmotic compressibility, $(\partial \pi/\partial \rho)_T^{-1}$.

However, as is usual in the theory of polymer solution, the size of a polymer segment is not uniquely defined; a theory must be constructed so as to be independent of the size of segment. So that, instead of the quantities $N$, $b^2$, $\beta_1$, $\beta_2$, and $\Delta n$, we use the measurable quantities $M$, $A^2$, $B_1$, $B_2$ and $\Delta Z$, defined respectively as follows. $M$ is the molecular weight of a polymer and

$$M A^2 = Nb^2 \quad (25)$$
$$M^2 B_1 = N^2 \beta_1 \quad (26)$$
$$M^3 B_2 = N^3 \beta_2 \quad (27)$$
$$M \Delta Z = N \Delta n. \quad (28)$$

Then equations (8) and (23) become

$$\frac{1}{\zeta^2} = 12 N A B_1 C + 36 N A^2 B_2 C^2 \quad (29)$$

and

$$\frac{1}{I(0)} = \frac{1}{(\Delta Z)^2} [B_1 + 3 N A B_2 C], \quad (30)$$

where $C$ is the weight concentration (g cm$^{-3}$) of polymer in solution.

The purpose of the present exposition is to test experimentally the theoretical equations (21), (29) and (30) by using SAXS, and to determine the values of $B_1$ and $B_2$.

Experimental and results

The X-ray generator was operated at 47-5 kV, 28 mA with $\lambda = 1.54$ Å filtered by Ni foil of 14 μm in thickness. A Kratky monitor camera (Fig. 1) was used with entrance slit of 150 μm, counter slit of 300 μm, and height-determining slit of 16 mm. Photon counting was done by a scintillation counter with pulse-height analyser. Slit correction was done by the variation-function method (Glatter, 1974).

Sample solutions were monodisperse polystyrene (PS) of Pressure Chemical Co., with molecular weight $6 \times 10^5$. 

Fig. 1. Kratky monitor camera. T: X-ray tube, C: collimation system, S: sample, V: vacuum chamber, A: adjusting spindle, BS: beam stop, M: reference detector (monitor), DS: detector slit, D: detector.

Fig. 2. An example of an Ornstein-Zernike plot of SAXS.

Fig. 3. Concentration dependence of $1/\zeta^2 C$ for PS-MEK at 30°C.

Fig. 4. Concentration dependence of $\Delta Z^2/I(0)$ for PS-MEK at 30°C.
(M_w/M_x < 1.1), in methyl ethyl ketone (MEK) at 30°C and in cyclohexane (CH) at 56°C of several concentrations in the semidilute range satisfying the inequality (9).

In the range of scattering vector defined by the inequalities (20), 1/I(q) was found to be linearly dependent on q^2 in all cases, which is in accordance with the theoretical equation (21). An example is shown in Fig. 2. From the angular dependence of SAXS intensity we have calculated the values of ξ and I(0) for several concentrations, which are shown in Tables 1 and 2. Figs. 3 and 4 show respectively the concentration dependence of ξ and I(0) thus obtained for the case of PS in MEK. The results are consistent with the theoretical prediction, equations (29) and (30). Therefore we can evaluate the values of B_1 and B_2 from the lines in the figures and the results of which are shown in Table 3. The last column of the table is cited from the reference (Yamakawa, 1971). The concentration dependences of ξ and I(0) for the case of PS in CH are shown in Figs. 5 and 6 respectively. The values of B_1 and B_2 obtained from these figures are shown in Table 4. We have also analysed in the same way the values of ξ measured by SANS by Cotton et al. (1976), the results of which are shown in the last column of Table 4. We find substantial agreement of SAXS measurement with the SANS data.

We have also calculated the parameters z_1 and z_2 as defined respectively by the relations (10) and (11) from the values of B_1 and B_2 just obtained, together with the value of A as given by Yamakawa (1971). The results are shown in Table 5, which demonstrates the smallness of the relevant parameters. Thus, we may say that we were actually dealing with semidilute poor-solvent systems.

### Conclusion

SAXS by semi-dilute solutions of PS (M = 6 x 10^5) in MEK at 30°C and in CH at 56°C, 'poor-solvent' systems, were successfully analysed by the recent theory by Moore (1977), and the values of ternary as well as binary cluster integrals were estimated. To the best of the authors' knowledge, the value of the ternary cluster integral has not been previously reported in the literature.

### References