I. Polymer solutions

Polymer solutions are binary mixtures for which the molecular weights of solute and solvent are very different. The similarity in behaviour of polymer solutions (PS) and liquid binary mixtures (LB) in the vicinity of the critical concentration \( C_c \) and temperature \( T_c \), of demixing, is well known (Kuwahara et al., 1971) (Fig. 1a). A difference in behaviour emerges in the high-temperature limit and this is ascribed to the excluded-volume interaction, specific to polymer coils. The excluded-volume effect was once considered to be an intrinsic property of polymer coils, the behaviour of the latter is nevertheless very sensitive to environment. We show this dependence by considering successively polymer coils in neutral solution, as electrolytes and finally in the bulk under stress.

Although the configuration fluctuation is an intrinsic property of polymer coils, the behaviour of the latter is nevertheless very sensitive to environment. We show this dependence by considering successively polymer coils in neutral solution, as electrolytes and finally in the bulk under stress.

Perhaps the most far-reaching theory for the understanding of polymer behaviour has been developed recently by de Gennes (1972) and de Cloizeaux (1975) for the case of neutral solutions. The experimental evidence related to this theory is best given by neutron scattering data.

Neutron scattering data are presented for polymer coils in three different environments: neutral semi-dilute solutions, concentrated polyelectrolyte solutions and stretched bulk. Each of these environments provides a specific constraint to the coil. The short-range volume interactions swell the chains in neutral solutions. The long-range Coulomb interactions stretch the chains to a considerable size. Mechanical stretching of bulk material also modifies the Brownian coil shape. In the first two cases, the structure factor is discussed as a function of momentum transfer. This factor reflects characteristic long-range organization. For the bulk material, the form factor is discussed which is obtained directly from the scattering data, with isotropic labelling used in the protonated matrix.

A polymer solution in the high-temperature limit is in fact a critical system. Spatial distribution is scale invariant, the characteristic length being \( \xi \propto C^{-3/4} \). In fact, \( \xi \) replaces the characteristic long-range organization (Daoud et al., 1975).

A non-classical behaviour (Fig. 1b, c). This is not found for LB mixtures, for which we have, far enough from \( T_c \)

\[
I_0, \text{ given the virial expansion along the isotherm (1.3)}
\]

\[
I(q) = 1/(q^2 + \xi_{LB}^2) \cdot \xi_{LB}^2 \chi(T-T_c)^{(qT-T_c)^2} \]

A polymer solution in the high-temperature limit is in fact a critical system. Spatial distribution is scale invariant, the characteristic length being \( \xi \propto C^{-3/4} \). In fact, \( \xi \) replaces the step length \( l \) introduced in an earlier description of the coil and remains the only significant quantity apart from the average square end-to-end distance \( R^2 \). The osmotic pressure \( \pi \) scales like \( \xi^{-3} \). Polymer coils in solution show a distinct long-range organization (Daoud et al., 1975).
II. Structure of polyelectrolyte solutions

A large class of polymer coils has ionizable side groups distributed along the chain, for example sulfonated polyvinyls. When these are dissolved in water, dissociation occurs, separating polyions of charge $Ze$ from counterions for charge $e$. The mobility of the counterions is much greater than that of the polyions. This difference accounts for characteristic configurations and distributions of the coils, especially if no simple electrolyte is added to the solution. The chains are more extended than random coils, although still flexible. The spatial distribution among coils is more rigid than in the case of neutral polymers. What the structure of the solution is the purpose of the experimental investigation and will be resolved by small-angle scattering. At this stage we wish to show evidence of the incompressibility of the structure, as predicted by several authors (de Gennes, Pincus, Velasco & Brochard, 1976) and hinted at by earlier light-scattering experiments (Alexandrowicz, 1960).

The result is given in Fig. 2, where intensities scattered by polyelectrolytes and neutralized polymers in semi-dilute solutions are compared. The osmotic compressibility of the solution is directly observable from the extrapolation of the scattered intensity at zero angle (as in equation I.1). We have

$$I_0 = K C \frac{dC}{d\eta}, \quad \text{(II.1)}$$

where $K$ is a constant for instrumentation and solvent solute contrast.

The high incompressibility, seen in Fig. 2, of the polyelectrolytes in solution is accounted for by the distribution of the counterions. We shall discuss this effect in terms of a different experiment, namely the osmotic-pressure measurement, which is distantly related to the scattering experiment, but easier to understand. We now have a requirement of electrical neutrality on each side of the semipermeable wall. For a mobile ion population of identical charges, whose sign is opposite to the pollyon charge, this requirement has a drastic effect on the coil distribution. In the case of added simple electrolyte, the mobile ion population contains charges of both signs, and as a result the coil distribution is much less dependent upon its interaction with the ions. This is a consequence of the Donnan effect (Tanford, 1967), usually associated with the osmotic-pressure experiment: let all $m_p$ polyions be on one side $V$ of the semipermeable wall which allows the flow of all molecules but the polyions.

1. In the absence of simple polyelectrolytes all the $m^- = Zm_p$ counterions of negative charge are inside the volume $V$ and will not migrate through the membrane because of the electrical neutrality requirement.

2. In the presence of simple electrolyte, a population of mobile counter- and coions is distributed across the membrane.

Let $m^-$ and $m^+$ be the number of coions, and $m^-$ and $m^+$ be the number of counterions, respectively inside and outside $V$. We have

$$m^- = m^+ + Zm_p \quad \text{(II.2)}$$

and from the equality of the ion chemical potentials across the membrane

$$m^- = [m^- (m^- - Zm_p)]^{1/2} = [m^+ (m^+ + Zm_p)]^{1/2}. \quad \text{(II.3)}$$

The osmotic pressure is

$$\pi \beta = (m_p + m^- + m^+ - m^- - m^-) \quad \text{(II.4)}$$

In the limit of zero added simple electrolyte, $m^+ = 0$ and

$$\pi \beta = m_p (1 + Z). \quad \text{(II.5)}$$

For a large concentration of added simple electrolyte, $m^+ \gtrsim Zm_p$,

$$\pi \beta \sim m_p. \quad \text{(II.6)}$$

Let $m_s$ be the total number of added simple electrolyte molecules ('salt')

$$m_s = m^+ + m^- = m^+ [1 + \left(1 + \frac{Zm_p}{m^+}\right)^{1/2}]. \quad \text{(II.7)}$$

As a function of salt and coil concentrations the osmotic pressure is

$$\frac{\pi \beta}{m_p} = 1 + Z - 2 \frac{m_s}{m_p} \left[1 - \frac{2}{1 + \left(1 + \frac{Zm_p (2m_p + 2m_s)}{m_p^2}\right)^{1/2}}\right]. \quad \text{(II.8)}$$

The osmotic pressure, and therefore the inverse scattered intensity at zero angle, varies by a factor 1 to $Z$ as the salt concentration increases. For a pollyon of molecular weight $M_w = 78 000$, the effective charge $Z$ is approximatively 150. The effect of added salt on the structure of the polyions is seen in Fig. 2.

The low scattered intensity at zero angle for $m_s = 0$ in Fig. 2 confirms earlier light-scattering observations. The new information given by the neutron scattering experiment is the maximum intensity at $q \approx 10^{-2}$ Å. The full significance of the structure associated with this peak will be given by the observation of labeled polyions in unlabeled pollyon solutions.
III. Coil configuration in hot-stretched polymer samples

One of the first results of the neutron small-angle scattering experiments applied to polymer physics was to confirm the prediction made by Flory that the polymer coil in bulk has a configuration which is similar to the random configuration in two respects:

1. the dependence of the squared end-to-end distance on molecular weight $M$ is
   \[ R^2 \propto M; \]  
   (III.1)
2. the asymptotic scattering law is
   \[ S_1(q) \propto 2/(q^2 R^2 + 1), \]  
   (III.2)
where $S_1$ is the 'labelled' coil scattering law. The bulk state produces a subtle balance of interactions, which leads to a characteristic configuration very different from that of a coil in a good solvent.

When the bulk sample is stretched (above the glass temperature) it is also expected that these interactions will lead to a coil configuration very different from that of a free coil stretched by forces acting on its two ends. We consider next this case. The main feature of this configuration is the non-Gaussian character of the end-to-end probability distribution, $P_{1N}(x)$, in the stretch direction $X$: this function is no longer centered about $X = 0$ (Fig. 3a), but about a finite value $\bar{a}_{1N}$. A possible (Benoit et al., 1975) formation of $P_{1N}(x)$ is
\[ P_{1N}(x) = \frac{1}{N_{1/2}} \exp \left[ -(x-\bar{a}_{1N})^2/R_5^2 \right]. \]  
(III.3)
The length $\bar{a}_{1N}$ is related to the retractive force $f$,
\[ f = \frac{a_{1N}}{R_5^2}, \]  
(III.4)
where $R_5^2$ is the average square end-to-end distance before stretching. The dependence of $\bar{a}_{ij}$ upon $|i-j|$ is an interesting problem which is answered in Pincus’s (1976) formula of the coil scattering law
\[ S_1(q) \propto \hat{q}^{1/2} \Sigma \{q \xi_p\}, \]  
(III.5)
where $q^2 = q^2 + 4 \xi_p^{-2} \cos^2 \delta$,
\[ \xi_p = (\beta f)^{-1}. \]  
(III.6)
and $\delta$ is the angle between the applied force and $q$. The function $\Sigma$ is such that $\Sigma(y) = y^{2/3}$ for $y \to \infty$, and $\Sigma(0) = 1$. This implies
\[ \bar{a}_{ij} \propto |i-j|, \quad R_{ij} > \xi_p^{-1} \]
\[ \bar{a}_{ij} \propto |i-j|^{2}, R_{ij} < \xi_p^{-1}. \]

Returning to the bulk problem, we know that the configuration of the deformed coil is very different, although not yet known in such detail as given by equation (III.5). Consider a uniaxial stretching of the sample, such that the ratio of final to initial length is $\lambda$. The most current hypothesis is the 'affine deformation', by which $x_i = \lambda x_i^0$, etc. This leads to
\[ \bar{a}_{ij} = 0 \]  
whenever $f$ and $ij$ (Fig. 3b). The average orientation of a segment with $\hat{x}$ is such that:
\[ \langle \cos \omega \rangle = 0 \quad \text{and} \quad \langle \cos^2 \omega \rangle = \frac{1}{3} + (\lambda - 1). \]  
(III.9)
The affine hypothesis is however not verified experimentally. From birefringence data Kuhn (1941) had already pointed out that $\langle \cos^2 \omega \rangle$ is much nearer to $\frac{1}{3}$ than given by (III.9).

This is confirmed and shown in greater detail by the neutron scattering data (Fig. 4). The degree of affinity of the deformation, at a given scale $q$, is given by the slope of the intensity dependence versus $q^2$. In the affine deformation hypothesis, this slope is uniformly $R_5^2 \lambda^2$, over the entire interval $R_5^{-1} \leq q \leq R_5^{-1} N^{-1/2}$. Thus Fig. 4 indicates that for $q \geq q^*$, the deformation is not affine, whereas for $q < q^*$ the deformation is affine. A possible interpretation of this figure is to assume the relations
\[ \bar{a}_{ij} = 0, \quad |i-j| > n_1, \]
\[ \bar{a}_{ij} > 0, \quad |i-j| < n_1. \]
where $n_1$ is a function of $\lambda$. A positive value of $\bar{a}_{ij}$ for a coil in the bulk is a somewhat disturbing proposition, which may be clarified by considering a coil with one fixed end: $\omega_{ij}$ is then the average of $\omega_{ij}$ over all possible configurations of that coil. Pearson (1977) pointed out recently that the fluctuations of $\bar{a}_{ij}$ are an important parameter, which reflects the entanglement effects and which determines the shape of the $S_1(q)$ function between the two extreme situations $\bar{a}_{ij} = 0$ and $\bar{a}_{ij} = |i-j|a$ (where $a$ is a constant). It remains

Fig. 3. End-to-end probability distribution as a function of the distance $x$ parallel to the stretch direction. Full line: Gaussian configuration; broken line: non-Gaussian extended configuration.

Fig. 4. Inverse scattering laws in the direction parallel (●) and perpendicular (+) to the stretch direction, as a function of $q^2$. The affine deformation model is shown by the full line. The broken line is the scattering law for the unoriented sample.
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 methy 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

\[
\frac{1}{\xi^2 c} = 12N_A \frac{B_1}{A^2} + 36N_A \frac{B_2}{A^2} C
\]

and

\[
\frac{(\Delta Z)^2}{I(0)} = B_1 + 3N_A B_2 C,
\]

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. \( \Delta Z \) 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

\[
\frac{\pi}{kT} = \frac{1}{2} \beta_1 \rho^2,
\]

where \( \pi \) is the osmotic pressure, \( \rho \) 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

\[
G(q) = \frac{12}{q b^2} \frac{1}{q^2 + \xi^{-2}},
\]