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Polymer–Cosolvent Systems. 8. Free Volume and Contact Energies in Two Cosolvent Mixtures for Polystyrene and an Interpretation in Terms of a Site Model[†]

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ABSTRACT: Cosolvency in the ternary system methylcyclopentane (1) + acetone (2) + polystyrene (3) has been demonstrated by establishing the demixing behavior of the polymer as a function of temperature and solvent composition. Enhanced solvation of the polymer occurs at all intermediate compositions as evidenced by an increased separation of the critical solution temperatures. An analysis of the phase behavior in terms of the free volume theory of polymer solutions reveals that cosolvency has an enthalpic origin, both in this and in a second ternary system acetone (1) + diethyl ether (2) + polystyrene (3). A possible mechanism for cosolvent action by binary liquid mixtures is discussed.

Introduction

The demixing behavior of a polymer dissolved in a binary solvent mixture may be used to study possible cosolvent (or synergistic) action of the liquid pair. If cosolvency occurs the resulting phase diagram will reflect the enhanced solvation of the polymer coil through an increased separation of the demixing temperatures at the upper and lower critical solution temperatures (UCST and LCST). In the case where each of the single liquids is itself a poor solvent, i.e., capable of dissolving only low molecular weight polymers, so-called "classic" cosolvency occurs. In such a system the demixing contours in the composition–temperature plane form a series of closed loops, and examples of this type of behavior are afforded by polystyrene dissolved in mixtures of acetone and diethyl ether[1] and in mixtures of acetone and various n-alkanes.[2]

Explanations of cosolvent action in liquid (1) + liquid (2) + polymer (3) systems have been given in terms of an averaging of the solubility parameters δ_1 and δ_2 to a value closer to that of the polymer, δ_3. This implies that $\delta_1 < \delta_3 < \delta_2$, but it has been shown that cosolvency can occur when both δ_1 and δ_2 are greater and smaller than δ_3.[3–5] The modifying effect of a third component on binary systems, in which order may be present, has also been suggested as a possible origin of cosolvent action.[6–8] This may indeed be the case in mixtures which are significantly polar, but it is unlikely in the essentially nonpolar classic systems mentioned above.

Some degree of antipathy between the components of binary cosolvent mixtures has been noted[1,2,4,9] and it has been proposed that unfavorable solvent (1)–solvent (2) contacts may be offset by mutual interaction of the liquids with the polymer and that this will provide the drive for cosolvent action. This concept, through the single-liquid approximation of Scott,[10] has been used as a basis of a semiquantitative description of the acetone (1) + diethyl ether (2) + polystyrene (3) system.[11] However, since polymer–poor solvent contacts must themselves by unfavorable, it is difficult to see this as a complete explanation of cosolvency at the molecular level.

The consequences of unfavorable solvent (1)–solvent (2) interactions have been examined by us, in terms of the Prigogine–Patterson–Flory theory[12,13] of polymer solutions, using a series of cosolvent mixtures for polystyrene formed from acetone and n-alkanes ranging from hexane to eicosane.[2] For each of the binary liquid pairs the excess heat of mixing H^E is both large and positive and the mixtures were treated as single fluids whose interaction with the polymer could be characterized by a mixed-solvent interaction parameter χ_{ms}, where

$$\chi_{ms} = \frac{T^* c \nu^2}{T\tilde{V}} + \frac{c\tau^2}{2(\frac{4}{3}\tilde{V}^{-1/3} - 1)} = \tfrac{1}{2}(1 + r^{-1/2})^2 \tag{1}$$

with

$$T^* = T\tilde{V}/(1 - \tilde{V}^{-1/3}) \tag{2}$$

and

$$c = p^* V^*/RT^* \tag{3}$$

T^*, p^*, and $V^* = V/\tilde{V}$ are the temperature, pressure, and volume reduction parameters for the solvent mixture and were evaluated according to Flory's theory of binary liquid mixtures.[14] Here, a tilde indicates a reduced quantity. $\tau^2 = (1 - T^*/T_3^*)^2$ quantifies the free volume difference between the polymer (3) and the solvent mixture, and r is the ratio of the hard-core volume of polymer to that of solvent mixture. The free volume difference was found

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[†] Dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday.

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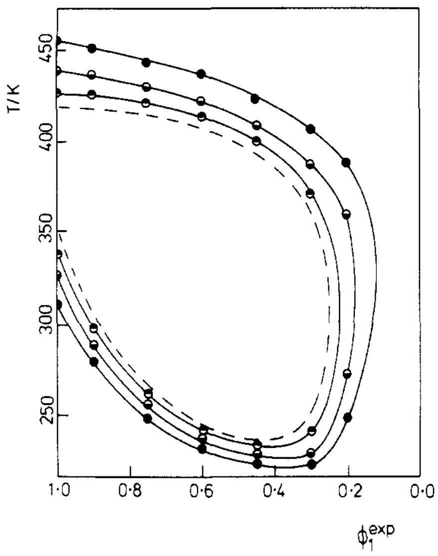

Figure 1. Phase contour diagram for the cosolvent system methylcyclopentane (1) + acetone (2) + polystyrene (3). ϕ_1^{exp} is the volume fraction of methylcyclopentane. Polystyrene molecular weights ($\bar{M}_n$) and volume fractions (ϕ_3^{exp}) are as follows: (●) 6.3 × 10^4, 0.075; (◒) 2.39 × 10^5, 0.065; (◓) 2.0 × 10^6, 0.033.

to be a nonlinear function of solvent composition and showed a maximum with respect to the polymer + single-solvent systems. It was concluded that this should generally be the case in binary solvent systems where H^E is appreciably positive and will result in an unfavorable entropic contribution to χ_{ms} which opposes cosolvent action in the mixture. Cosolvency in the acetone + *n*-alkane series was found to originate from enhanced enthalpic interactions, characterized by the ν^2 term of eq 1, achieving a minimum value at intermediate compositions of the liquid mixtures. ν^2 represents the contact energy differences between the mixture and its components.

These ideas are examined further in this paper, which presents a similar analysis of two other cosolvent systems for polystyrene. These are acetone (1) + diethyl ether (2) (whose phase behavior has been published previously[1]) and methylcyclopentane (1) + acetone (2), a new system whose phase behavior will be presented here.

Experimental Section

The polystyrene samples used were narrow molecular weight distribution fractions ($\bar{M}_w/\bar{M}_n$ < 1.04) supplied by Pressure Chemical Co. The solvents were dried and distilled before use. The phase contour diagram for polystyrene in the binary solvent mixture methylcyclopentane + acetone was established as described previously.[2] The heat of mixing of equimolar amounts of the two solvents was measured at 298 K using an LKB 10700-2 batch calorimeter which was calibrated electrically.

Results and Discussion

The Ternary System Methylcyclopentane (1) + Acetone (2) + Polystyrene (3). The demixing of the polystyrene both in acetone alone and in methylcyclopentane alone is described elsewhere.[1,13,15] Three fractions were selected to study the demixing in several methylcyclopentane/acetone mixtures, each of which is insoluble in acetone. The resulting phase contour diagram is shown in Figure 1, where the demixing temperatures for each fraction have been joined to give a series of loops which are "open" at the methylcyclopentane side of the diagram. The polymer concentrations for demixing measurements were chosen so as to correspond closely to the maximum and minimum of the cloud point curves in the single solvents. The demixing temperatures are thus close to the expected critical temperatures for each system.

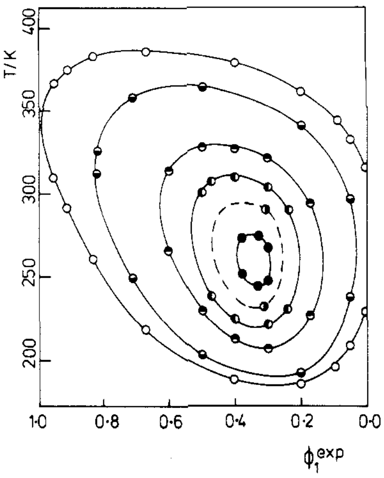

Figure 2. Phase contour diagram for the cosolvent system acetone (1) + diethyl ether (2) + polystyrene (3).[1] ϕ_1^{exp} is the volume fraction of acetone. Polystyrene molecular weights ($\bar{M}_n$) are as follows: (○) 2.0 × 10^4; (◒) 3.7 × 10^4; (◓) 1.1 × 10^5; (◐) 2.7 × 10^5; (◑) 4.1 × 10^5; (●) 8.6 × 10^5.

The ternary mixture is quite evidently a cosolvent system, as evidenced by the fact that the miscibility range of any fraction is increased considerably at intermediate solvent compositions. The data in Figure 1 may be compared with the established "classic" cosolvent system acetone (1) + diethyl ether (2) + polystyrene (3), whose phase diagram is reproduced here as Figure 2 for the reader's convenience. We would prefer to describe the present system as "pseudoclassic" in order to contrast with the case shown in Figure 2, where both of the liquid components are very poor solvents and where completely closed loops are obtained, but this distinction is essentially one of degree. A related phase contour diagram of polystyrene in mixtures of methylcyclohexane and diethyl ether[4] is similarly composed of open-ended loops, but the miscibility range is not enhanced in that mixture; i.e., little cosolvent action can be detected.

The dashed line in Figure 1 shows the extrapolated temperatures of demixing for infinite molecular weight polymer, which is soluble from 239 to 398 K at an optimum composition of $\phi_1^{exp} = 0.5$. It also reveals that, for $\phi_1^{exp} \sim 0.3$, Θ-conditions pertain over the temperature range ~280 to ~330 K, as the phase contour is almost vertical in the region of this composition.

Examination of the Cosolvent Systems in Terms of Free Volume Theory. The application of the Prigogine–Patterson–Flory theory to the cosolvent systems acetone (1) + diethyl ether (2) + polystyrene (3) and methylcyclopentane (1) + acetone (2) + polystyrene (3) necessitates the evaluation of the solvent mixture reduction parameters[14] via

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \qquad (4)$$

$$T^* = p^*/(\phi_1 p_1^*/T_1^*) + (\phi_2 p_2^*/T_2^*) \qquad (5)$$

and

$$V^* = x_1 V_1^* + x_2 V_2^* \qquad (6)$$

The hard-core volume fraction and site fraction are defined by, respectively

$$\phi_1 = 1 - \phi_2 = x_1 V_1^*/(x_1 V_1^* + x_2 V_2^*) \qquad (7)$$

$$\theta_2 = 1 - \theta_1 = \phi_2/\phi_1(s_1/s_2) + \phi_2 \qquad (8)$$

x_i is the mole fraction and s_i the surface area to hard-core ratio, calculated as noted in Table I. X_{12}, the Flory interaction term, was calculated[16] for the acetone–ether

Table I
Equation of State Parameters (298 K) Used in the Calculations

	T^*/K	p^*/(J cm^{-3})	V^*/(cm^3 mol^{-1})	c	$10^{-8}s$/ cm^{-1} [a]	X_{12}/(J cm^{-3})	ref [b]
acetone	4355	597	55.54	0.91_6	1.07	30	21, 22
diethyl ether	4106	502	76.50	1.12_6	1.11		21, 22
methylcyclopentane	4600	424	86.91	0.96_4	0.92	160	21, 23
polystyrene	7420		84.33				24

[a] s, the surface to hard-core volume ratio, calculated assuming acetone and methylcyclopentane to be spheres of volume V^* and diethyl ether to be a right cylinder of radius 2.5 Å and volume V^*. [b] Sources of expansion and compressibility data for the calculation of T^*, p^*, and V^*.

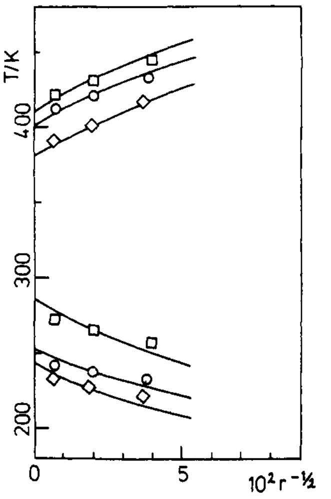

Figure 3. Precipitation temperatures vs. $r^{-1/2}$ in the methylcyclopentane (1) + acetone (2) + polystyrene (3) system. Volume fraction of methylcyclopentane: (□) 0.8; (○) 0.6; (◇) 0.4. The full lines represent the corresponding theoretical dependence of critical temperature on $r^{-1/2}$.

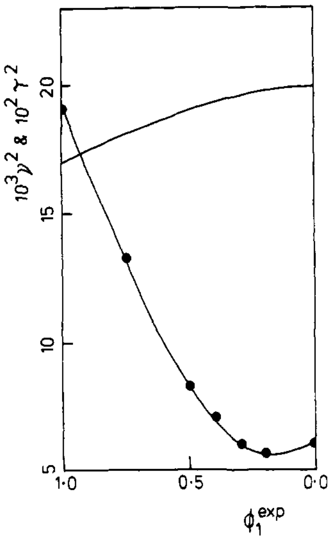

Figure 4. Variation of the free volume parameter τ^2 (full line) and the interaction parameter ν^2 (●) in the system acetone (1) + diethyl ether (2) + polystyrene (3).

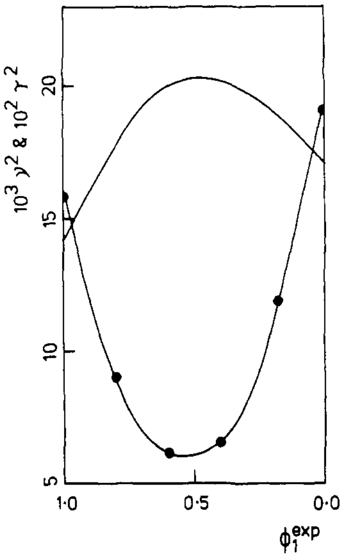

Figure 5. Variation of the free volume parameter τ^2 (full line) and the interaction parameter ν^2 (●) in the system methylcyclopentane (1) + acetone (2) + polystyrene (3).

system from the H^E data of Sameshita,[17] and for the methylcyclopentane–acetone system its value was estimated[18] from the heat of mixing of equimolar amounts of the two liquids. Along with the other parameters listed in Table I, these values were used to calculate T^* and τ^2 as a function of composition for the two mixtures.

The corresponding variation of the interaction term ν^2 was obtained as follows. In the acetone–ether system the UCST and LCST coalesce for all compositions of the liquid mixture, and under these conditions eq 1 may be rewritten as

$$2c\nu^2 = 3/4(c\tau^2) + 1/4(1 + r_{co}^{-1/2})^2 \pm \{3/4(c\tau^2)(1 + r_{co}^{-1/2})^2\}^{1/2} \tag{9}$$

where r_{co} is the value of r at which the UCST and LCST merge. Equation 9 may then be used to evaluate ν^2 at chosen values of ϕ_1^{exp} where r_{co} is obtained by extrapolation of the UCST and LCST data. In order to evaluate ν^2 for the methylcyclopentane–acetone system, the demixing temperatures at various compositions of the solvent mixture are identified with the corresponding critical temperatures and fitted to eq 1, as described elsewhere.[4,15,19,20] Examples of the fits obtained are shown in Figure 3.

Figures 4 and 5 show the variation of both τ^2 and ν^2 with solvent mixture composition for the two systems. τ^2 passes through a maximum with respect to the linear interpolations between the pairs of solvents. This demonstrates that the solvent mixture is more expanded than either component separately and hence the difference in free volume between the polymer and the mixture is greater than expected. This effect is large for the methylcyclopentane–acetone system and reflects the high X_{12} value characterizing the mixture. Since demixing at the LCST is free volume controlled, the behavior here should oppose cosolvent action in both mixtures and result in the LCST appearing at lower temperatures. However, as observed previously in the series of acetone + n-alkane cosolvent mixtures for polystyrene,[2] the values of ν^2 obtained from this analysis pass through minima compared with the single solvents. Thus cosolvency is clearly enthalpic in origin, arising from more favorable polymer–solvent interactions which are made available in the mixtures, and this factor outweighs the entropic parameter.

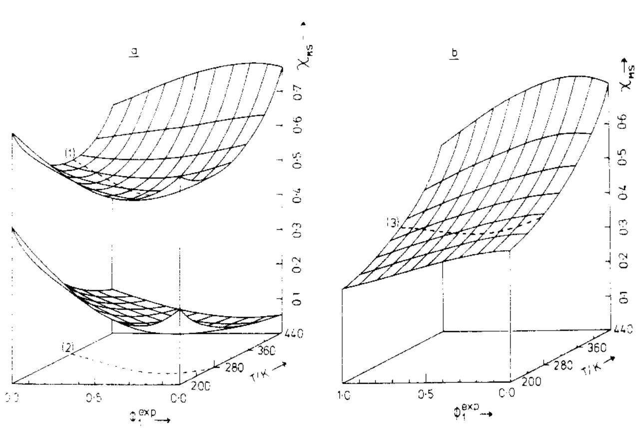

Figure 6. χ surfaces for the system acetone (1) + diethyl ether (2) + polystyrene (3). (a) χ_{ms} (top) and χ_{ms}^H (bottom) surfaces; (b) χ_{ms}^S surface. The broken line is the pathway along which χ is a minimum on (1) the χ_{ms} surface, (2) in the ϕ_1^{exp}–T plane, and (3) on the χ_{ms}^S surface.

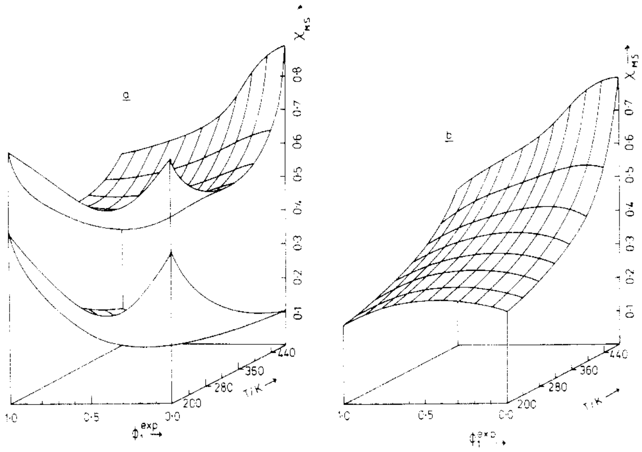

Figure 7. χ surfaces for the system methylcyclopentane (1) + acetone (2) + polystyrene (3). (a) χ_{ms} (top) and χ_{ms}^H (bottom) surfaces; (b) χ_{ms}^S surface.

χ Surfaces. It is convenient to think of the ν^2 and τ^2 terms of eq 1 as enthalpic and entropic components of the polymer–mixed solvent interaction parameter χ_{ms} and to recast the equation as

$$\chi_{ms} = \chi_{ms}^H + \chi_{ms}^S \tag{10}$$

Using the data in Figures 4 and 5, one may evaluate the variation of χ_{ms}, χ_{ms}^H, and χ_{ms}^S as functions of solvent composition and temperature, which can be translated into the "χ surfaces" shown in Figures 6 and 7. These reveal that cosolvent action is characterized by a χ_{ms} surface which is concave upward in all directions. The surface for acetone–diethyl ether (Figure 6a) lies completely above the critical value of χ, whereas that for methylcyclopentane–acetone is intersected by the $\chi = 0.5$ plane, reflecting the fact that Θ-conditions exist in this latter system.

The shape of the χ_{ms} surfaces reflects the corresponding concavity, in the composition direction, of the respective χ_{ms}^H surfaces. This indicates that the two mixtures provide more favorable polymer–solvent interactions than the pairs of single solvents. In contrast, examination of an isothermal traverse on the χ_{ms}^S surface reveals that it will always pass over an unfavorable maximum with respect to the composition extremes.

The path along which χ_{ms} is a minimum in the acetone + ether mixture is shown as a dashed line on Figure 6, and its projection onto the ϕ_1^{exp}–T plane reveals that the temperature locus of maximum cosolvent action in this system is nonlinear. The reprojection of this locus onto the χ_{ms}^S surface defines a traverse along which χ_{ms}^S now passes through a shallow minimum as a function of solvent composition. The temperature locus of maximum cosolvent action is found to be one along which both χ_{ms}^H and χ_{ms}^S are minimized, as was observed previously for the acetone + n-alkane series of polystyrene cosolvents.[2]

Figures 6 and 7 embody the conclusion that the drive toward cosolvent action has an enthalpic rather than an entropic origin. This is in accord with the findings of Schuster and Cantow,[6] who have investigated the thermodynamics of the equilibrium swelling of cross-linked polystyrene in acetone + cyclohexane mixtures, which also exhibit a cosolvent action. The liquid components of this system also mix with a positive H^E.

A Possible Molecular Interpretation of Cosolvency. Cosolvent mixtures for polystyrene are obtained from acetone in combination with linear alkanes[2] and cycloalkanes[5,6,15] and with diethyl ether.[1] Schuster and Cantow have proposed[6] that the origin of the cosolvent effect is the production of a "monomeric" acetone by (in their case) dilution with cyclohexane and they assert that acetone itself is a poor solvent because of self-aggregation. No direct evidence can be supplied to support the existence of aggregates and, if indeed this were a possibility, then methyl ethyl ketone would also be expected to show little affinity for polystyrene, and this is not the case. Additionally, such an explanation does not account for the varying extent of cosolvency obtained when acetone is in combination with a homologous series of n-alkanes, and it seems reasonable that the interaction of both components with the polymer should be considered.

We tend to favor a different and more general explanation for cosolvency. The model proposed is a simple one and is based on the following assumptions: (a) solvent molecules will tend to solvate a polymer chain at preferred sites; (b) solvents, which differ in terms of shape, polarity, and orientational preferences will select sets of different sites at which solvent–polymer contact energies are minimized; (c) synergism is observed in a liquid (1) + liquid (2) + polymer (3) system when the liquids select different sites, therby enhancing polymer solvent contacts; (d) liquids which compete for the same site on the polymer chain will not tend to form cosolvent pairs.

Thus, in a "classic" cosolvent system, the liquids are separately both very poor solvents for the polymer and the number of polymer–liquid contacts formed in each binary system is insufficient to stimulate dissolution of the polymer except at very short chain lengths. Mixing to produce a ternary system results in a combination of liquid (1)–polymer (3) and liquid (2)–polymer (3) contacts, which is sufficient to cause the polymer to dissolve if these contacts are of a different nature, i.e., if the two liquids tend to solvate the polymer at different "sites" along the chain and so lead to a reinforcement of solvation. If this occurs then it is also likely that the expanded coil will allow further liquid–polymer contacts to develop even though these may be energetically weak.

This idea of a favorable solvation sheath is in accord with observations made during preferential adsorption studies in ternary systems exhibiting cosolvency. Maximum coil expansion is usually found to occur at a mixed-solvent composition where there is no preferential adsorption. A change in liquid composition by increasing liquid component (1) leads to preferential adsorption of liquid (2) and vice versa. In other words, the driving force is an attempt to maintain the most favorable composition, thereby minimizing polymer–polymer contacts. Thus the

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combined polymer–solvent interactions are more favorable than either set singly and there is a minimization of the free energy when the mixed solvent has a specific composition.

We are continuing work in this area in order to provide further evidence in favor of this simple interpretation for cosolvency, which appears to depend largely on the enthalpic interactions associated with each system rather than entropic ones.

Registry No. Polystyrene (homopolymer), 9003-53-6; methylcyclopentane, 96-37-7; acetone, 67-64-1; diethyl ether, 60-29-7.

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Dynamic Scattering from Bimodal Polymer Solutions. 1. Apparent Diffusion Coefficient

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ABSTRACT: The dynamic scattering matrix $\mathbf{S}(q,t)$ for scattering from multimodal systems is formulated, and explicit results in the case of bimodal systems are presented in the small-q limit. The total dynamic scattering function is expressed in this limit as a weighted sum of two exponentials with decay rates Γ_1 and Γ_2. Both the decay rates and the weighting factors are calculated in terms of the concentrations and molecular weights of the two components. The dependence of the apparent diffusion coefficient D_{app} on the concentrations of both components is calculated, and the results are compared to experimental data for polystyrene ($M_w = 1.79 \times 10^5$ and 1.05×10^6) in cyclohexane at the Θ point. The magnitude of the interference effect on the concentration dependence of D_{app} is studied quantitatively. The concentration dependence of the apparent diffusion coefficient and the collective diffusion coefficient in a single-component system is expressed in terms of the pair correlation function for polymer molecules.

Introduction

The purpose of this paper is to investigate dynamic scattering from polydisperse polymer solutions and to provide tractable theoretical formulas to interpret quantities that can be extracted from the scattering data with sufficient precision, such as the apparent diffusion coefficient and the decay rates of the scattering function. Specifically, we consider a solution containing chemically identical polymers with different molecular weights. The continuous molecular weight distribution is assumed to be lumped into groups such that N_g is the number of polymers with molecular weights in a narrow interval ΔM about M_g. The number of groups G is not restricted. In the small-q region where $qR_G \ll 1$ is satisfied in all groups, the measured dynamic scattering function $S(q,t)$ can be represented as

$$S(q,t) = S(q)\sum_{g=1}^{G} A_g \exp(-\Gamma_g t) \tag{1}$$

where $S(q)$ is the static structure factor. The coefficients A_g and the decay rates Γ_g are determined experimentally by appropriate data analysis such as the histogram technique[1,2] or least-squares curve fitting. In the zero-concentration limit, $\Gamma_g \rightarrow q^2 D_g$, where D_g is the translational diffusion coefficient of an isolated polymer with molecular weight M_g, and

$$A_g = C_g M_g \Big/ \sum_{g=1}^{G} C_g M_g \tag{2}$$

where C_g is the mass concentration of the polymers in the gth group.

At finite concentrations, the above simple interpretation of $S(q,t)$ based on linear superposition is no longer strictly valid due to the interference effects among different components. For example, $q^{-2}\Gamma_g$ can no longer be identified

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