

Quasielastic Light Scattering Study of Self-Diffusion and Interaction of Two Homopolymers in an Arbitrary Solvent

Z. Sun and C. H. Wang*

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received: April 7, 1997; In Final Form: June 24, 1997[®]

A method is proposed to show how the self-diffusion coefficients and the Flory–Huggins interaction parameter of two homopolymers in an arbitrary solvent can be determined by using quasielastic light scattering (QELS). The technique does not require one polymer to be isorefractive with solvent. The QELS data of PS/PMMA/dioxane in the semidilute concentration regime obtained in this laboratory are used to illustrate the method. A qualitative expression to predict the critical concentration for phase separation in the ternary polymer solution is also provided.

Introduction

Quasielastic light scattering of polymer–polymer–solvent ternary systems has been the subject of intensive studies in recent years. Systems previously investigated were chosen under special experimental conditions in order to observe particular phenomena or to check theoretical predictions. For example, most of the early work dealt mainly with one polymer as a tracer in a polymer of high concentration which is refractive index matched to the solvent. The object in those studies was to test the reptation model by probing the self- (or tracer) diffusion coefficient of the dilute polymer which is not refractive index matched.^{1–4} Recently, more experimental work has been carried out on polymer solutions in the semidilute and concentrated regimes; however, most experiments have utilized the condition that one polymer is isorefractive with the solvent to simplify data analysis.^{5–8}

General theory for interpreting the QELS spectrum of a ternary polymer solution has been developed by Benmouna et al.^{9–11} However, the general theory cannot be easily used to interpret experimental data because the result contains partial structure factors that cannot be experimentally determined. From the theory, we have found useful expressions and have reduced and simplified Benmouna's result, thereby facilitating data analysis in polymer systems of practical interest.^{12,13} In both ours and Benmouna's theory, the random phase approximation (RPA)^{14,15} is used. The RPA gives a good interpretation of the QELS spectra of ternary polymer solutions over a wide concentration range.¹⁶ Also with the aid of the RPA, Desbrieres et al. have proposed a method to determine the self-diffusion coefficients of two polymers and the Flory–Huggins interaction parameter of the constitute polymers in a ternary polymer solution by QELS.¹⁷ To obtain these quantities, these authors have, however, assumed that they are polymer composition independent. In actual cases, this assumption may not be valid. Recently, we have proposed a method to obtain these important quantities without the need for making this assumption.^{8,12,13} When applied to the ternary solution having one polymer isorefractive with the solvent, such as PDMS/PMMA/toluene and PS/PMMA/benzene solutions,^{8,12} our method allows one to obtain the elements of the diffusivity matrix without needing the RPA. Therefore, our method, which removes the assumption introduced by Desbrieres et al., is general and more versatile.

In ternary solutions with two polymers having arbitrary refractive index increments, as shown in ref 13, the method is, however, rather complex, and computer programs were needed in order to carry out the task. Recently, one of the present authors has succeeded in developing an analytical method that can facilitate the analysis of the QELS data of ternary solutions consisting of two homopolymers with arbitrary optical, hydrodynamic, and thermodynamic properties.¹⁸ In this paper, we employ this method to analyze the QELS data of the polystyrene(PS)/poly(methyl methacrylate)(PMMA)/dioxane system. In the PS/PMMA/dioxane solution, both polymers have different refractive index increments with respect to dioxane.

Theoretical Background

The calculation of the QELS spectrum of an arbitrary ternary polymer solution is given in detail in ref 18. Here we briefly review the theoretical background that is needed for analyzing the QELS data of the polymer-1-polymer-2/solvent (s) ternary system. In the QELS experiment, one deals with the time correlation function $I(q, t)$ defined by

$$I(q, t) = \sum_i \sum_j a_i a_j S_{ij}(q, t) \quad (1)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector; λ is the wavelength of the incident radiation in vacuum; θ is the scattering angle; a_i and a_j are the contrast factors of polymers i and j over the solvent, $i, j = 1, 2$; and n is the refractive index of the polymer solution. $S_{ij}(q, t)$ are the elements of the dynamical scattering matrix $\mathbf{S}(q, t)$, given by

$$S_{ij}(q, t) = \langle \delta \rho_i(q, t) \delta \rho_j(-q, 0) \rangle \quad (2)$$

where $\rho_i(q, t)$ represent the monomer number densities of the component i .

In general, the solution for $\mathbf{S}(q, t)$ can be written as¹¹

$$\mathbf{S}(q, t) = e^{-q^2 \mathbf{D} t} \mathbf{S}(q) \quad (3)$$

where \mathbf{D} is the diffusivity matrix given by

$$\mathbf{D}(q) = kT \mathbf{M}(q) \cdot \mathbf{S}(q)^{-1} \quad (4)$$

$\mathbf{M}(q)$ is the generalized mobility matrix,^{10,11} and $\mathbf{S}(q)$ is the matrix of the static structure factor.

For two monodisperse polymers in a small molecular weight solvent, \mathbf{D} can thus be approximated as a two by two matrix.

* To whom all correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

The resolution of eq 3 in terms of the eigenvalues of the diffusivity matrix \mathbf{D} is straightforward. In terms of the eigenvalues and eigenvectors of \mathbf{D} , one obtains for $S_{ij}(q,t)$ ^{10,18}

$$S_{ij}(q,t) = A_-^{ij} e^{-q^2 D_- t} + A_+^{ij} e^{-q^2 D_+ t} \quad (5)$$

where D_+ and D_- are the eigenvalues of \mathbf{D} , and specific expressions for amplitudes A_-^{ij} and A_+^{ij} are given by

$$A_-^{11} = \frac{(D_- - D_{22})S_{11}(q) + D_{12}S_{21}(q)}{D_- - D_+} \quad (6)$$

$$A_+^{11} = \frac{(D_+ - D_{22})S_{11}(q) + D_{12}S_{21}(q)}{D_+ - D_-} \quad (7)$$

$$A_-^{21} = \frac{(D_- - D_{11})S_{21}(q) + D_{21}S_{11}(q)}{D_- - D_+} \quad (8)$$

$$A_+^{21} = \frac{(D_+ - D_{11})S_{21}(q) + D_{21}S_{11}(q)}{D_+ - D_-} \quad (9)$$

A_-^{22} , A_+^{22} , A_-^{12} , and A_+^{12} can be obtained from the above equations by interchanging indices 1 with 2. Using the above results, we can write the time correlation function given by eq 1 as

$$I(q,t) = A_- e^{-q^2 D_- t} + A_+ e^{-q^2 D_+ t} \quad (10)$$

where A_- and A_+ can be derived from A_-^{ij} and A_+^{ij} , respectively.

Experimentally one can determine eigenvalues D_+ and D_- as well as the relative amplitude $A_-/(A_+ + A_-)$ factor of the two eigenmodes. These quantities are related to the elements of the \mathbf{D} matrix as

$$D_+ + D_- = D_{11} + D_{22} \quad (11)$$

$$D_+ D_- = D_{11} D_{22} (1 - XY) \quad (12)$$

where

$$X = D_{21}/D_{22}, \quad Y = D_{12}/D_{11} \quad (13)$$

We can relate the relative amplitude factor to the quantities D_{ij} , X , and Y , by using two approximations that we shall next describe.

For polymer solutions in semidilute and concentrated regimes, the hydrodynamic interactions associated interchains are screened,¹⁹ and the off-diagonal elements of the mobility matrix can be neglected. Writing the diagonal mobility matrix elements²⁰ as $M_{ii} = \phi_i/\xi_i$, with $i = 1$ or 2 , we obtain from eq 4 the diffusivity matrix $\mathbf{D}(q)$ as

$$\mathbf{D} = \frac{kT}{\Delta(S)} \begin{bmatrix} \frac{\phi_1 S_{22}(q)}{\xi_2} & -\frac{\phi_1 S_{12}(q)}{\xi_1} \\ -\frac{\phi_2 S_{21}(q)}{\xi_2} & \frac{\phi_2 S_{11}(q)}{\xi_2} \end{bmatrix} \quad (14)$$

where $\Delta(S) = S_{11}S_{22} - S_{12}S_{21}$. Here $\phi_i = n_i N_i$ is the number of monomers per unit volume of type i . N_i is the degree of polymerization, n_i is the number of chains per unit volume, and ξ_i is the friction coefficient of monomer of type i .

From eq 14, one finds

$$X = D_{21}/D_{22} = -S_{21}/S_{11} \quad (15)$$

$$Y = D_{12}/D_{11} = -S_{12}/S_{22} \quad (16)$$

These results allow us to simplify eqs 6–9, leading to the

expression for the relative amplitude factor¹⁸

$$\frac{A_-}{A_- + A_+} = \frac{D_+}{(D_+ - D_-)} \left[1 - D_- \left(\frac{a_2^2 X/D_{11} + a_1^2 Y/D_{22}}{a_1^2 Y - 2a_1 a_2 XY + a_2^2 X} \right) \right] \quad (17)$$

In the above equation, if $a_2 = 0$ (solvent is index matched to polymer-2) is assumed, one reduces eq 17 to $A_-/(A_- + A_+) = (D_+ D_- / D_{22} - D_+) / (D_- - D_+)$, which was obtained previously.^{8,12} On the other hand, if $a_1 = a_2$ (two polymers differ only in molecular weight), one obtains

$$A_-/(A_- + A_+) = \left[1 - D_- \frac{Y/D_{22} + X/D_{11}}{X + Y - 2XY} \right] \frac{D_+}{D_+ - D_-}$$

which was previously used in analyzing the ternary system consisting of PS-1/PS-2/toluene.¹⁶

It should be noted that a_i is the contrast factor equal to the increment of the refractive index for polymer i with the polymer concentration expressed in terms of number density. Due to the fact that $S_{ij}(q,t)$ is the correlation function of the number density fluctuation between component i and j , it is more convenient to write

$$a_i = \left(\frac{\partial n}{\partial c} \right)_i m_i \quad (18)$$

where $(\partial n / \partial c)_i$ is the increment of refractive index for polymer i with the polymer concentration expressed in grams per unit volume; m_i is the monomer molecular weight per mole of polymer i . This conversion will not affect the results for the special cases when one polymer is isorefractive with the solvent or when two polymers differ only in molecular weight. In those cases, the refractive index increment factor cancels out in the relative amplitude factor expression. However, in an arbitrary ternary system, the refractive index increment enters in the final relative amplitude expression (cf. eq 17); the difference in the definition of a_i is important when two polymers have different values of m .

The second approximation we shall need is the random phase approximation (RPA). The RPA allows one to relate D_{ij} to the single-chain structure factors, molecular weights, concentration, and the second-virial coefficients as follows:^{8,9,14,15}

$$D_{11} = \frac{D_{s1}}{P_1(q)} [1 + 2x A_{2,11} M_{w1} C_T P_1(q)] \quad (19)$$

$$D_{22} = \frac{D_{s2}}{P_2(q)} [1 + 2(1-x) A_{2,22} M_{w2} C_T P_1(q)] \quad (20)$$

$$D_{12} = D_{s1} C_T 2A_{2,12} M_{w1} (m_2/m_1) \quad (21)$$

$$D_{21} = D_{s2} (1-x) C_T 2A_{2,12} M_{w2} (m_1/m_2) \quad (22)$$

where x is the fraction of polymer 1 of the total polymer. It is related to the weight fraction of polymer 1 in total polymer (w) as $x = w/[w + (1-w)m_1/m_2]$. $P_i(q)$ is the form factor of a simple chain in the bare system, which for $qR_g \ll 1$, reduces to unity; R_g is the radius of the gyration.

From the above results, we also find that

$$\frac{X}{Y} = \frac{S_{22}(q)}{S_{11}(q)} = \frac{(1-x)N_2 P_2(q)}{xN_1 P_1(q)} \frac{1 + 2x A_{2,11} M_{w1} C_T P_1(q)}{1 + 2(1-x) A_{2,22} M_{w2} C_T P_2(q)} \quad (23)$$

One notes that this quantity is completely determined by

TABLE 1: Properties of Polymers Used in the Experiment

sample	$10^{-3}M_w$	$I = M_w/M_n$	10^4A_2 (mol cm ³ g ⁻²)	dn/dc (mL/g)	R_g (nm)	m (g/mol)
PMMA	244	1.13	2.80	0.069	26.5	100.12
PS	181	1.05	3.65	0.166	15.2	104.15

thermodynamic and structural properties of polymer-1 and polymer-2 in solution and hence can be determined from dilute binary solution static light scattering experiments. Here $D_{si} = kT/N_i\zeta_i$ is the self- (or tracer) diffusion coefficient. $A_{2,11}$ and $A_{2,22}$ are the second-virial coefficients of polymers 1 and 2 in solvent, respectively. $A_{2,12}$ is the second-virial coefficients between polymers 1 and 2 and is related to the Flory–Huggins polymer–polymer interaction parameter χ_F by^{8,12}

$$\chi_F = \frac{2V_s}{\bar{v}_1\bar{v}_2}A_{2,12} - \frac{V_s}{\bar{v}_1^2}A_{2,11} - \frac{V_s}{\bar{v}_2^2}A_{2,22} \quad (24)$$

where \bar{v}_i is the specific volume of polymer i , V_s is the molar volume of the solvent. To obtain eqs 19–24, we have converted excluded volume matrix elements v_{ij} to the second-virial coefficient, $A_{2,ij}$, by the expression $v_{ij} = 2A_{2,ij}m_i m_j$.

As mentioned above, $A_-/(A_- + A_+)$, D_+ , and D_- are experimentally determinable quantities. By setting $X = \alpha Y$, where α is a known number that can be calculated from eq 23, we obtain from eq 17 an equation consisting of three unknowns, D_{11} , D_{22} , and Y , provided that contrast factors a_1 and a_2 are known. This equation together with eqs 11 and 12 give three equations with three unknowns: D_{11} , D_{22} , and Y . One can thus solve these three simultaneous equations to obtain the unknowns. After D_{11} , D_{22} , and Y are obtained, one can obtain the values of D_{s1} , D_{s2} , and $A_{2,12}$ (or χ_F) uniquely with the help of eqs 19–22. Comparing with the one previously used,¹³ the present method provides us with a much simpler technique to obtain the self-diffusion coefficients (D_{s1} , D_{s2}) and the Flory–Huggins interaction parameter (χ_F) from the experimental data. We next illustrate the application of this new method by using it to analyze the experimental QELS data on PS/PMMA/dioxane ternary solution, in which neither PS nor PMMA is isorefractive with dioxane.

Results and Discussion

A detailed QELS experimental study of the PS/PMMA/dioxane has been carried out in our laboratory, and parts of the data have been reported in ref 13. To illustrate the method outlined above, we choose a set of samples whose composition is fixed with $w = 0.3$ but have different total polymer concentrations. Physical data of PS and PMMA needed for the analysis are given in Table 1.

In the PS/PMMA/dioxane sample, two relaxation modes are found in the homodyne intensity autocorrelation function covering the dynamic range 10^{-6} to 10^2 s and scattering angles ranging from 30° to 150° . The faster mode is the D_+ mode, and the other is the D_- mode. The relaxation time distribution for samples with different concentration and composition can then be obtained from QELS data by using either the CONTIN program or stretched exponential analysis. Both methods yield results that agree within experimental uncertainty. Results obtained from the analysis of the QELS data are given in Table 2. It can be clearly seen that, at a fixed composition ($w = 0.3$, w is the weight fraction of PMMA with respect to the total polymer), D_+ and $A_-/(A_- + A_+)$ increase, but D_- decreases with the increase of total polymer concentration. The calculated values of D_{11} , D_{22} , X , and Y using the procedure described above are also given in Table 2. It can be seen that D_{11} and D_{22} both

TABLE 2: QELS Data of PS/PMMA/Dioxane System

C_T (g/mL)	$10^{12}D_C$ (m ² /s)	$10^{12}D_{11}$ (m ² /s)	$A_-/(A_- + A_+)$	$10^{12}D_{11}$ (m ² /s)	$10^{12}D_{22}$ (m ² /s)	X	Y
0.025	30.7	6.51	0.48	19.1	18.2	0.65	0.65
0.033	33.2	4.53	0.56	18.6	19.1	0.74	0.78
0.041	36.7	3.46	0.68	22.4	17.7	0.79	0.86
0.050	41.3	2.37	0.75	23.2	20.5	0.84	0.94
0.058	44.2	2.26	0.78	26.1	20.3	0.84	0.96

TABLE 3: Self-Diffusion Coefficients and Interaction Parameter of PS and PMMA in Dioxane

C_T (g/mL)	$10^{12}D_{s1}$ (m ² /s)	$10^{12}D_{s2}$ (m ² /s)	$10^4A_{2,12}$ (mol cm ³ /g ²)	χ_F
0.025	9.28	5.54	3.48	0.006
0.033	7.77	4.77	3.67	0.010
0.041	8.17	3.71	3.72	0.011
0.050	7.41	3.67	3.82	0.013
0.058	7.61	3.24	3.73	0.011

increase with the increase of total polymer concentration, meanwhile X and Y also increase with increasing the concentration. This result shows that the off-diagonal elements of the diffusivity matrix D_{12} and D_{21} increase with the increase of the total polymer concentration. These results are similar to those obtained from PS/PMMA/benzene system.

With the aid of the data shown in Table 2, and eqs 19, 20, and 23, we have calculated the values of $A_{2,12}$ (and χ_F) and D_{si} ($i = 1$ and 2) at different polymer concentrations. The concentration dependences of D_{s1} , D_{s2} , $A_{2,12}$, and χ_F are given in Table 3. One notes that the χ_F value is positive, which is consistent with the fact that PS and PMMA are immiscible in the dry state. This suggests that the PS–PMMA interaction in dioxane is repulsive. The repulsive interaction results in the increase of D_{12} and D_{21} as the polymer concentration is increased. However, $A_{2,12}$ and χ_F remain nearly constant, except for the case of the lowest concentration, which decreases significantly.

The concentration dependence of the self-diffusion coefficient of polymer in solutions can be described by a simple blob diffusion arguments,²¹ as discussed in ref 13.

It is important to point out the effect of increasing X and Y with increasing total polymer concentration. In eq 12, if XY approaches 1, then D_+D_- becomes zero. Since D_+ always increases with the total polymer concentration, D_- must become zero in this case. The fact that D_- becomes zero suggests that the solution approaches phase separation.²² We can predict the critical concentration for the phase separation for the solution at the fixed composition. From eqs 19–22, we obtain $(P_1(q) = P_2(q) = 1)$

$$XY = \frac{2xA_{2,12}M_{w1}C_T}{1 + 2xA_{2,12}M_{w1}C_T} \frac{2(1-x)A_{2,12}M_{w2}C_T}{1 + 2(1-x)A_{2,12}M_{w2}C_T} \quad (25)$$

Thus, given the value of XY , we can solve for C_T from eq 25. Using the data of Table 2, we set the value of A_{12} equal to 3.73×10^{-4} mol cm³ g⁻², and from eq 25, we then obtain for $XY = 1$ $C_T = 0.103$ g/mL, which is the critical concentration.

In our experiment, it is found that when the total polymer concentration of the PS/PMMA/dioxane is higher than 0.064 g/mL, the solution gradually becomes cloudy, suggesting the onset of phase separation. This concentration corresponds to $XY = 0.848$. However, it should be pointed out that the present calculation assumes that the off-diagonal elements of the mobility matrix can be neglected. In the vicinity of phase transition, particles are corrected dynamically and structurally over a long distance; the neglect of the off-diagonal elements

is probably not justified. This thus suggests that $C_T = 0.103$ g/mL is an estimate of the critical concentration.

In summary, we have provided a method for analyzing the QELS spectrum of a ternary solution consisting of two homopolymers with arbitrary optical properties. Using this method, we have shown how the polymer–polymer interaction and self-diffusion coefficients in the ternary system can be obtained from the QELS spectrum of a ternary polymer solution. We have used QELS experimental results on the PS/PMMA/dioxane ternary solution in the semidilute concentration regime to illustrate the method. We have also provided a qualitative expression to predict the critical concentration for phase separation for solutions with repulsive polymer–polymer interaction.

Acknowledgment. This work is supported by a grant from NSF Polymer Division (DMR9112993).

References and Notes

- (1) Lodge, T. P. *Macromolecules* **1983**, *16*, 1393; **1986**, *19*, 2986.
- (2) Nemoto, N.; Inoun, T.; Makita, Y.; Tsunashina, Y.; Kurata, M. *Macromolecules* **1985**, *18*, 2516.
- (3) Aven, M. R.; Cohen, C. *Macromolecules* **1990**, *23*, 476.
- (4) Numasawa, N.; Kuwamoto, K.; Nose, T. *Macromolecules* **1986**, *19*, 2593.
- (5) Borsali, R.; Duval, M.; Benoit, H.; Benmouna, M.; *Macromolecules* **1987**, *20*, 1112.
- (6) Giebel, L.; Borsali, R.; Fisher, E. W.; Benmouna, M. *Macromolecules* **1992**, *25*, 4379.
- (7) Borsali, R.; Duval, M.; Benmouna, M. *Macromolecules* **1989**, *22*, 816.
- (8) Sun, Z.; Wang, C. H. *Macromolecules* **1996**, *29*, 2011.
- (9) Benoit, H.; Benmouna, M. *Macromolecules* **1984**, *17*, 535.
- (10) Benmouna, M.; Benoit, H.; Duval, H.; Akcasu, Z. *Macromolecules* **1987**, *20*, 1107.
- (11) Akcasu, Z. *Dynamic Light Scattering*; Brown, W., Ed.; Oxford University Press: Oxford, U.K., **1993**; p 1.
- (12) Sun, Z.; Wang, C. H. *J. Chem. Phys.* **1995**, *103*, 3762.
- (13) Sun, Z.; Wang, C. H. *J. Chem. Phys.* **1997**, *106*, 3775.
- (14) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
- (15) Farnoux, B. *Ann. Phys. (Paris)* **1978**, *39*, 77.
- (16) Sun, Z.; Wang, C. H. *Macromolecules* **1997**, *30*, 4939.
- (17) Desbrieres, J.; Borsali, R.; Rinaudo, M.; Milas, M. *Macromolecules* **1993**, *26*, 2592.
- (18) Wang, C. H. *J. Chem. Phys.* **1997**, *107*, 3675.
- (19) Doi, M.; Edwards, S. F. *Theory of Polymer Dynamics*; Clarendon Press: Oxford, U. K., 1986.
- (20) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
- (21) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: London, 1979.
- (22) Benmouna, M.; Seil, J.; Meier, G.; Patkowski, A.; Fischer, E. W. *Macromolecules* **1993**, *26*, 668.