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On the Dynamic Scattering of Linear and Cyclic Copolymers in Solution

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ABSTRACT: In this paper, a comparative study of the dynamic scattering properties of some linear and cyclic copolymers in solution is presented. This investigation is prompted by the recent elastic and quasi-elastic light scattering measurements reported by Amis and co-workers on polystyrene−polydimethylsiloxane cyclic diblock copolymers and their linear triblock counterpart. A formalism is presented which could provide a theoretical framework for the analysis of some aspects of these data. The model predicts that two relaxation modes characterize the dynamics of both the cyclic diblock and the linear triblock copolymers. The amplitudes and decay rates of these relaxation modes are investigated as a function of the polymer architecture, the concentration, and the scattering wavevector. Questions related with phase transitions via aggregation or micellar formation are not addressed here.

1. Introduction

In the last decade, the dynamic scattering properties of block copolymers were the subject of particular attention for both theoreticians[1−3] and experimentalists.[4−8] In the bulk state, besides the fast motions of side chain groups, the dynamics of linear block copolymers is believed to be made of a single mode which would describe the relaxation of the composition fluctuations within a volume equivalent to the volume occupied by a single chain. This mode is highly dependent both upon the architecture of the copolymer and the degree of compatibility of the monomer species entering into its composition. This mode is sometimes referred to as the structural, internal, or interdiffusive mode of the copolymer. For solution properties, in the presence of a low molecular weight solvent, the situation is different and somewhat more subtle. In the simplest picture, however, one admits at least one additional mode describing the relaxation of the total polymer concentration fluctuations and known as the cooperative process. This mode is similar to the one obtained in the case of a binary homopolymer/solvent mixture where relevent quantities such as the second virial coefficient and the friction coefficient are some sort of average of the corresponding quantities for the constituant polymers.

These two relaxation processes have been discussed theoretically and observed experimentally using light scattering[4] and neutron spin-echo techniques.[5,6] The situation is of course not always simple even for linear block copolymers in solution. Other processes have been suggested due either to aggregation, micelles formation,[7] polydispersity[8] in composition, and/or in molecular weight. These additional processes are still the subject of active research in different laboratories but will not be considered in the present paper. Here, we will be concerned more with the classical interdiffusive−cooperative processes or fast−slow modes. We examine the particular effects of chain architectures by considering linear and cyclic homopolymers and copolymers under similar conditions and compare their dynamics as it would be revealed by quasi-elastic light scattering or neutron spin-echo techniques.

Recently, Amis and co-workers[9,10] reported elastic and quasi-elastic light scattering measurements on polystyrene (PS)−polydimethylsiloxane (PDMS) block copolymers in cyclohexane. They considered two types of copolymers: The first one is a linear triblock copolymer in which the middle block is a PS block and the wings are PDMS blocks. The second copolymer is a diblock cyclic copolymer which essentially corresponds to the same triblock in which the two ends are joined together by a chemical bond. The main goal of this investigation is to analyze the static and dynamic behaviors of these two copolymers and perform a comparative study of their properties when the temperature is lowered from 35 to 12 °C. The concentration was also changed from 0.05 to 30 mg/mL for the static measurements and from 5 to 20.8 mg/mL for the dynamic measurements, and the average molecular weight was approximately $M = 4 \times 10^4$ g/mol. The system cyclohexane/PS−PDMS is characterized by two properties which are important from the point of view of light scattering. First, the Θ temperature of polystyrene (PS) in cyclohexane is 35 °C, whereas that of PDMS is estimated to be as low as −81 °C. Second, the increment of refractive index of PDMS in cyclohexane is approximately zero, which means that the scattered light is practically entirely due to the PS blocks. Several interesting observations were made from the measurements of Amis et al. In the static experiments, it was found that the molecular weight obtained from the Zimm plots in a temperature range way below 35 °C corresponds to the total molecular weight of the copolymer chain in spite of the fact that only the PS block contributes to the scattered intensity. Furthermore, the apparent second virial coefficient for the cyclic copolymer, $A_{2\mathrm{app}}$ is found to be constant at all temperatures from 35 to 12 °C. This means that the

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apparent Θ temperature of this polymer has undergone a shift of more than 23 °C below the Θ temperature of PS, the visible component. For the linear triblock copolymer, a sharp decrease of the virial coefficient is observed at 20 °C, indicating a shift of the Θ temperature of only 15 °C below that of PS. In fact, $A_{2\mathrm{app}}$ for the linear triblock drops suddenly at 20 °C and takes negative values, suggesting the formation of aggregates or micelles.

With regards to the quasi-elastic scattering data, it is found that the autocorrelation function for the cyclic copolymer decays following a single exponential for all the wavevectors, concentrations, and temperatures scanned in these experiments. In the case of the linear triblock, however, a different behavior is found consistent with the observations made in the static measurements. A single relaxation mode is observed between 35 and 20 °C. At the latter temperature, a second slow mode appears, and at temperatures below 20 °C, a multimodal correlation function prevails, but it was possible to fit the data reasonably well with two exponential decay functions. All the modes were diffusive and their relaxation frequencies proportional to q^2, the squared amplitude of the wavevector.

In a preceeding paper,[11] we discussed the static scattering properties of these copolymers, and the purpose of the present paper is to extend these discussions to the dynamic properties which are probed by quasi-elastic light scattering measurements. For completeness, we also consider the case of a linear diblock PS($^1/_3$)−PDMS($^2/_3$) (see Figure 1b of ref 11). Theoretical predictions are made for these systems by analyzing the relaxation modes of their dynamic correlation functions. Certain aspects of the data are compared with the predictions of this work, but no attempt is made to account for all the trends revealed by the experiments. In particular, the possibility of phase transition due to aggregation or micelle formation when the temperature is lowered is not considered.

2. Theoretical Background: the Dynamic Scattering Properties

Since we are dealing with a system involving two monomer species, it is convenient to use a matrix formulation which is more general since it could be applied to multicomponent systems. The matrices and vectors are represented using bold letters and the starting point is to assume that the dynamic scattering matrix $\mathbf{S}(q,t)$ decays following a single exponential:

$$\mathbf{S}(q,t) = \mathrm{e}^{-\mathbf{\Omega}(q)t}\mathbf{S}(q) \tag{1}$$

where t is the time and q, the amplitude of the wave vector, can be expressed in terms of the index of refraction of the solution, n; the scattering angle, θ', and the wavelength of the incident radiation, λ:

$$q = 4\pi n \sin(\theta/2)/\lambda \tag{2}$$

Equation 1 neglects the effects of memory due to random fluctuations which may become important at long times. Discussions of the approximation which consists of neglecting memory effects can be found in several classical papers by Akcasu and co-workers.[1,3] A list of references and a detailed review of the dynamic properties of multicomponent polymer mixtures can be found in these two references. Dynamic scattering data of copolymer and homopolymer mixtures in solution were often analyzed satisfactorily using intermediate scattering functions which were calculated by neglecting the memory function.[12,13] In this paper, we follow the same procedure and assume that the information we need is contained within the relaxation frequency matrix $\mathbf{\Omega}(q)$ and the static structure matrix $\mathbf{S}(q)$. In a system with several components, the elements of the dynamic scattering matrix are sums of eigenmodes. For example, its ij component is

$$S_{ij}(q,t) = \sum_{k}^{p} A_{ijk}(q)\mathrm{e}^{-\Gamma_k(q)t} \tag{3}$$

where p is the number of components, Γ_k ($k = 1, 2, ..., p$) are the eigenvalues of the frequency matrix $\mathbf{\Omega}(q)$ and $A_{ijk}(q)$ are the amplitudes of the kth mode for the ij component of the dynamic structure matrix $\mathbf{S}(q,t)$. $\mathbf{\Omega}(q)$ can be expressed in terms $\mathbf{S}(q)$ and the mobility matrix $\mathbf{M}(q)$ using the standard formula[1−3,14]

$$\mathbf{\Omega}(q) = q^2 k_{\mathrm{B}} T \mathbf{M}(q)\mathbf{S}^{-1}(q) \tag{4}$$

where k_{B} is the Boltzmann constant and T the absolute temperature. For multicomponent systems, in general, the elements of $\mathbf{S}(q)$ can be obtained from the general equation[15]

$$\mathbf{S}^{-1}(q) = \mathbf{S_0}^{-1}(q) + \mathbf{v} \tag{5}$$

where $\mathbf{S_0}(q)$ is the bare structure matrix elements S_{0ij} depend upon the architecture of the chains. In the general case where we have a mixture of homopolymers and copolymers, S_{0ij} are given by

$$S_{0ii} = \varphi_{i\mathrm{h}} N_{i\mathrm{h}} P_{i\mathrm{h}}(q) + \varphi_{i\mathrm{c}} N_{i\mathrm{c}} P_{i\mathrm{c}}(q) \quad \text{for} \quad i = j \tag{6}$$

$$S_{0ij} = [\varphi_{i\mathrm{c}} N_{i\mathrm{c}} \varphi_{j\mathrm{c}} N_{j\mathrm{c}}]^{1/2} P_{ij\mathrm{c}}(q) \quad \text{for} \quad i \neq j \tag{7}$$

where $\varphi_{i\mathrm{h}}$ is the volume fraction of homopolymer i and the subscripts h and c designate the homopolymer and the copolymer components, respectively. The matrix $\mathbf{v}$ in eq 5 describes the excluded volume interactions between different monomers. Its elements are the excluded volume parameters, which can be written in terms of the Flory−Huggins interaction parameters χ_{ij}[15,16]

$$v_{ij} = (v_{0i} v_{0j}/v_{0\mathrm{s}})(1/\varphi_{\mathrm{s}} - \chi_{i\mathrm{s}} - \chi_{j\mathrm{s}} + \chi_{ij}) \qquad i, j = \mathrm{a, b} \tag{8}$$

where φ_{s} is the volume fraction of solvent, χ_{ij} is zero for $i = j$ and v_{0i} is the molar volume of the component i = a, b, s, etc. A common assumption is to let the three volumes $v_{0\mathrm{a}}$, $v_{0\mathrm{b}}$, and $v_{0\mathrm{s}}$ equal to the volume of a unit cell in the Flory−Huggins lattice model.[16] The same assumption is made here for simplicity in the notations.

The matrix mobility $\mathbf{M}(q)$ depends upon the system under consideration and relies on a particular choice of the dynamical model. It is, in general, a nondiagonal matrix and its elements are sums of Rouse terms describing the short range frictional forces and Zimm terms describing the long range hydrodynamic interactions. Calling ζ_i the friction coefficient of monomer i and η the viscosity of the solution, one obtains:

$$M_{ij} = [\delta_{ij}]\varphi_i/\zeta_i + [1 - \delta_{ij}][1/(4\pi^2\eta)]\int_0^\infty \mathrm{d}k\, f(k/q) S_{ij}(k) \tag{9}$$

where we have used the Kroneker δ function ($\delta_{ij} = 1$ if

$i = j$ and 0 otherwise) and $f(x)$ is the hydrodynamic or mode coupling function. In the absence of hydrodynamic screening, $f(x)$ is[3,14,17]

$$f(x) = x^2\{[(x^2 + 1)/(2x)] \log |(x + 1)/(x - 1)| - 1\} \quad (10)$$

One observes that even in its nonscreened version, this function introduces a tremendous complication, especially in the cases where the structure factors $S_{ij}(q)$ do not have a simple form, as is the case here. A substantial simplification is obtained if one neglects the effects of hydrodynamic interactions and considers only the q-independent Rouse mobilities. This is a crude assumption which can become questionable in the dilute range where hydrodynamic screening is weak. Nevertheless, for the sake of simplifcation, we shall neglect the hydrodynamic interactions and assume that all off diagonal elements of the mobility matrix are zero. The ith diagonal element is expressed in terms of the friction coefficient ζ_i and the volume fraction φ_i:

$$M_{ii} = \varphi_i/\zeta_i \quad (11)$$

As pointed out earlier, the matrix formalism can be applied to a multicomponent mixture with an arbitrary number of homopolymer or copolymer constituents. In the present work, we are interested in solutions of block copolymers made of two monomer species, A and B. Therefore, in the next section, we write the formulae for this case but without making a specific reference to the architecture of the copolymer. This specification will be made only at a later stage.

Blockcopolymers Made of Monomers A and B. For a block copolymer A–B, eq 5 simplifies substantially and becomes a two-by-two matrix:

$$\mathbf{S}^{-1}(q) = \begin{bmatrix} S_{0b}/\Delta S_0 + v_{aa} & -S_{0ab}/\Delta S_0 + v_{ab} \\ -S_{0ab}/\Delta S_0 + v_{ab} & S_{0a}/\Delta S_0 + v_{bb} \end{bmatrix} \quad (12)$$

$$\Delta S_0 \equiv S_{0a}S_{0b} - S_{0ab}{}^2 \quad (13)$$

Inverting this matrix yields the partial structure factors:

$$S_{aa} = [S_{0a} + v_{bb}\Delta S_0]/[1 + v_{aa}S_{0a} + v_{bb}S_{0b} + 2v_{ab}S_{0ab} + \Delta v\Delta S_0] \quad (14)$$

$$S_{ab} = [S_{0ab} = v_{ab}\Delta S_0]/[1 + v_{aa}S_{0a} + v_{bb}S_{0b} + 2v_{ab}S_{0ab} + \Delta v\Delta S_0] \quad (15)$$

$$\Delta v = v_{aa}v_{bb} - v_{ab}{}^2 \quad (16)$$

The structure factor S_{ba} is equal to S_{ab} for symetrical considerations, and S_{bb} can be deduced from S_{aa} by interchanging the indices a and b. The bare structure factors S_{0a}, S_{0b}, and S_{0ab} are defined in the presence of homopolymers by eq 6 and 7. Since there are no homopolymers in our systems and in order to keep the notations simple, we shall remove the subscripts h and c from the bare structure factors in the rest of this paper. This leads to:

$$S_{0a} = \varphi N f^2 P_a(q) \quad (17)$$

$$S_{0b} = \varphi N(1 - f)^2 P_b(q) \quad (18)$$

$$S_{0ab} = \varphi N f(1 - f) P_{ab}(q) \quad (19)$$

where φ represents the polymer volume fraction, N the degree of polymerization, and f the fraction of monomers A in the copolymer, namely, $\varphi = \varphi_a + \varphi_b$, $N = N_a + N_b$, and $f = N_a/N$. The form factors of the copolymers $P_a(q)$, $P_b(q)$ and $P_{ab}(q)$ depend upon their architecture and will be specified later for each of the three systems considered here. Combining eqs 13–19 yields

$$S_{aa}/[f^2\varphi N] = [P_a + v_{bb}(1 - f)^2\varphi N\Delta P]/\Lambda \quad (20)$$

$$S_{bb}/[(1 - f)^2\varphi N] = [P_b + v_{aa}f^2\varphi N\Delta P]/\Lambda \quad (21)$$

$$S_{ab}/[f(1 - f)\varphi N] = [P_{ab} - v_{ab}f(1 - f)\varphi N\Delta P]/\Lambda \quad (22)$$

$$\Lambda = 1 + v_{aa}f^2\varphi NP_a + v_{bb}(1 - f)^2\varphi NP_b + 2v_{ab}f(1 - f)\varphi NP_{ab} + \Delta v f^2(1 - f)^2\varphi^2N^2\Delta P \quad (23)$$

Having defined the partial structure factors, one is able to characterize completely the frequency matrix by using eqs 4 and 14–23. The results are

$$\Omega_{aa}/[D_{0a}q^2] = [P_b + v_{aa}f^2\varphi N\Delta P]/[f\Delta P] \quad (24)$$

$$\Omega_{bb}/[D_{0bq}{}^2] = [P_a + v_{bb}(1 - f)^2\varphi N\Delta P]/[(1 - f)\Delta P] \quad (25)$$

$$\Omega_{ab}/[D_{0a}q^2] = -[P_{ab} - v_{ab}f(1 - f)\varphi N\Delta P]/[(1 - f)\Delta P] \quad (26)$$

$$\Omega_{ba}/[D_{0b}q^2] = -[P_{ab} - v_{ab}f(1 - f)\varphi N\Delta P]/[f\Delta P] \quad (27)$$

where D_{0a} and D_{0b} are the diffusion coefficients in the Rouse limit:

$$D_{0a} = k_BT/(N_a\zeta_a) \qquad D_{0b} = k_BT/(N_b\zeta_b) \quad (28)$$

Note that for a nonsymmetric copolymer made of different monomer species, as in the present case, the dynamic structure matrix has four distinct elements in particular [$S_{ab}(q,t) \neq S_{ba}(q,t)$], as opposed to the off diagonal elements of the static matrix:

$$\mathbf{S}(q,t) = \begin{bmatrix} S_{aa}(q,t) & S_{ab}(q,t) \\ S_{ba}(q,t) & S_{bb}(q,t) \end{bmatrix} \quad (29)$$

Each one of the four elements decays following a double exponential function representing two different modes of relaxation. The general forms of these modes is useful for these systems as well as for other polymer systems made of two monomers, A and B. These modes are defined through the various partial dynamic scattering functions:

$$S_{aa}(q,t) = A_{aaf}e^{-\Gamma}\mathrm{f}^t + A_{aas}e^{-\Gamma}\mathrm{s}^t \quad (30)$$

$$S_{ab}(q,t) = A_{abf}e^{-\Gamma}\mathrm{f}^t + A_{abs}e^{-\Gamma}\mathrm{s}^t \quad (31)$$

The frequencies Γ_f and Γ_s are the eigenvalues of $\mathbf{\Omega}(q)$:

$$\Gamma_f = \Omega_{av} + \{\Omega_{av}{}^2 - \Delta\Omega\}^{1/2} \quad (32)$$

$$\Gamma_s = \Omega_{av} - \{\Omega_{av}{}^2 - \Delta\Omega\}^{1/2} \quad (33)$$

$$\Omega_{av} = (\Omega_{aa} + \Omega_{bb})/2 \qquad \Delta\Omega = \Omega_{aa}\Omega_{bb} - \Omega_{ab}\Omega_{ba} \quad (34)$$

The amplitudes of $S_{aa}(q,t)$ are

$$A_{\mathrm{aaf}} = \{S_{\mathrm{aa}}[\Omega_{\mathrm{bb}} - \Gamma_{\mathrm{f}}] - S_{\mathrm{ab}}\Omega_{\mathrm{ab}}\}/\{\Gamma_{\mathrm{s}} - \Gamma_{\mathrm{f}}\} \quad (35)$$

$$A_{\mathrm{aas}} = \{S_{\mathrm{aa}}[\Omega_{\mathrm{bb}} - \Gamma_{\mathrm{s}}] - S_{\mathrm{ab}}\Omega_{\mathrm{ab}}\}/\{\Gamma_{\mathrm{f}} - \Gamma_{\mathrm{s}}\} = S_{\mathrm{aa}} - A_{\mathrm{aaf}} \quad (36)$$

Likewise, the amplitudes of $S_{\mathrm{ab}}(q,t)$ are:

$$A_{\mathrm{abf}} = \{-S_{\mathrm{ab}}[\Omega_{\mathrm{bb}} - \Gamma_{\mathrm{f}}] + S_{\mathrm{bb}}\Omega_{\mathrm{ab}}\}/\{\Gamma_{\mathrm{f}} - \Gamma_{\mathrm{s}}\} \quad (37)$$

$$A_{\mathrm{abs}} = \{S_{\mathrm{ab}}[\Omega_{\mathrm{bb}} - \Gamma_{\mathrm{s}}] - S_{\mathrm{bb}}\Omega_{\mathrm{ab}}\}/\{\Gamma_{\mathrm{f}} - \Gamma_{\mathrm{s}}\} = S_{\mathrm{ab}} - A_{\mathrm{abf}} \quad (38)$$

$S_{\mathrm{bb}}(q,t)$ and $S_{\mathrm{ba}}(q,t)$ can be obtained from eqs 30−38 by interchanging the subscripts a and b. In the discussions below, we shall focus our attention on the time evolution of $S_{\mathrm{aa}}(q,t)$ only since this is the quantity which is investigated by Amis et al.[9] using quasi-elastic light scattering. Theoretical predictions including the other dynamic partial scattering functions are given above in the case where other polymer systems made of A and B monomers are considered. Another useful quantity would be the first cumulant of $S_{\mathrm{aa}}(q,t)$ denoted $\langle\Gamma\rangle$:

$$\langle\Gamma\rangle = -\frac{\partial}{\mathrm{d}t} \log S_{\mathrm{aa}}(q,t)|_{t=0} \quad (39)$$

This quantity is simply the average of Γ_{f} and Γ_{s} weighted with respect to the amplitudes of $S_{\mathrm{aa}}(q,t)$:

$$\langle\Gamma\rangle = [A_{\mathrm{aaf}}\Gamma_{\mathrm{f}} + A_{\mathrm{aas}}\Gamma_{\mathrm{s}}]/[A_{\mathrm{aaf}} + A_{\mathrm{aas}}] \quad (40)$$

In the next section, we apply these equations to the following systems: (a) the linear triblock BAB, (b) the linear diblock BBA, and (c) the cyclic diblock BBA, where B ≡ stands for the block B or PDMS and A ≡ stands for the block A or PS (see Figure 1a−c of ref 11). In referring to the diblocks, the symbol B is repeated twice to underline the fact that the total block B is made of the adjunction of the two ends in the triblock copolymer. The application of the above formalism to our systems is implemented here by specifying the chain architectures through the form factors $P_{\mathrm{a}}(q)$, $P_{\mathrm{b}}(q)$, and $P_{\mathrm{ab}}(q)$. This is the subject of the application in the next section.

3. Application

These expressions of the form factors are greatly simplified if one introduces the following notations. The Debye function represents the form factor of a Gaussian unperturbed chain. It will be denoted $D(x)$ hereafter:

$$D(x) = 2[\mathrm{e}^{-x} + x - 1]/x^2 \quad (41)$$

Another function which appears frequently in the form factors of Gaussian block copolymers is:

$$H(x) = [1 - \mathrm{e}^{-x}]/x \quad (42)$$

In dealing with cyclic polymers, one also encounters the Dawson integral or related functions such as the error function with a complex argument.[18] Here, we introduced another related function, $C(x,v)$:

$$C(x,v) = (2/\sqrt{x})e^{-x/4}\int_v^{x^{1/2}/2} \mathrm{d}t\, e^{t^2} \quad (43)$$

As an example of this function, one notes that the form factor of a cyclic homopolymer can be written as[19]

$$C(u,v=0) = C(u) = (2/\sqrt{u})e^{-u/4}\int_0^{u^{1/2}/2} \mathrm{d}t\, e^{t^2} \quad (44)$$

where $u = q^2R_{\mathrm{g}}^2$ and $R_{\mathrm{g}} = \sigma\sqrt{(N/6)}$ is the radius of gyration of a linear Gaussian chain having a degree of polymerization N and a monomer length σ. Besides these definitions, we shall use the quantities u_{a} and u_{b} which are related to u and f as:

$$u_{\mathrm{a}} = fu \qquad u_{\mathrm{b}} = (1 - f)u/2 \quad (45)$$

With these notations, one could write the form factors for the three copolymers described earlier with the simple expressions given below.

The Linear Triblock BAB.

$$P_{\mathrm{a}}(q) = D(u_{\mathrm{a}}) \quad (46)$$

$$P_{\mathrm{b}}(q) = [D(u_{\mathrm{b}}) + e^{-u_{\mathrm{a}}}H(u_{\mathrm{b}})^2]/2 \quad (47)$$

$$P_{\mathrm{ab}} = H(u_{\mathrm{a}})\, H(u_{\mathrm{b}}) \quad (48)$$

The Linear Diblock BBA. The fact that the block B in this copolymer is twice as large as the one in the triblock appears clearly through a factor of 2 in front of u_{b} in the equations below:

$$P_{\mathrm{a}}(q) = D(u_{\mathrm{a}}) \quad (49)$$

$$P_{\mathrm{b}}(q) = D(2u_{\mathrm{b}}) \quad (50)$$

$$P_{\mathrm{ab}} = H(u_{\mathrm{a}})\, H(2u_{\mathrm{b}}) \quad (51)$$

The Cyclic Diblock BBA. The form factors for the cyclic diblock copolymer are quite different from the preceeding ones and involve the integral defined in eq 43, which has to be evaluated numerically. One finds

$$P_{\mathrm{a}}(q) = [(f - 1/2)/f^2]C[u,(1/2 - f)\sqrt{u}] + (1 - f)H[uf(1 - f)]/f \quad (52)$$

$$P_{\mathrm{b}}(q) = [(1/2 - f)/(1 - f)^2]C[u,(f - 1/2)\sqrt{u}] + f\mathrm{H}[uf(1 - f)]/(1 - f) \quad (53)$$

$$P_{\mathrm{ab}}(q) = [C(u) - f^2P_{\mathrm{a}}(q) - (1 - f)^2P_{\mathrm{b}}(q)]/[2f(1 - f)] \quad (54)$$

At this stage, it is sufficient to substitute these results into the general expressions of $S_{ij}(q)$ and $\Omega_{ij}(q)$ and deduce the amplitudes and the frequencies of the eigenmodes of $S_{\mathrm{aa}}(q,t)$. The results are presented below and their implications are discussed taking into consideration the recent quasi-elastic light scattering data published by Amis et al.[9,10]

4. Results and Discussions

In order to get some insight into the effects of chain architecture on the dynamic scattering function $S_{\mathrm{aa}}(q,t)$, it is necessary to cover a wide range of q values which goes beyond the rather narrow range accessible by light scattering. For this reason, we investigate the variations of the amplitudes and frequencies of the eigenmodes covering a range of u between 0 and 10. This includes the region of high q's accessible by the neutron spin-echo technique. In the figures below, the following conventions are used to designate the results for the three copolymers under consideration: The dotted lines

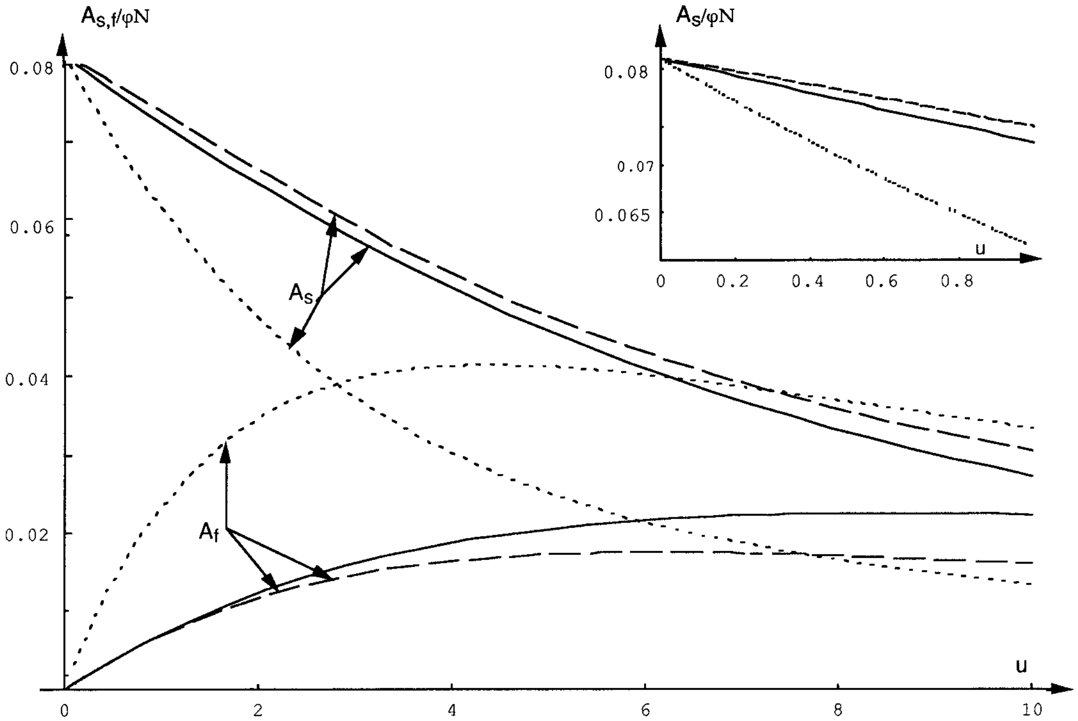

Figure 1. The variations of the normalized amplitudes of the fast and slow modes $A_{aaf}/\varphi N$ and $A_{aas}/\varphi N$, respectively, as a function of u. The dotted lines correspond to the linear diblock, the dashed lines correspond to the linear triblock, and the continuous lines to the cyclic diblock copolymer. These plots are made with $f = {}^1/_3$, $A_0 = 2A_{2a}Mc = (c/c^*) = 0.1$, $\alpha = A_{2b}/A_{2a} = 5$ and $\beta = A_{2ab}/A_{2a} = 3.1$. The insert represents a detailed view of the slow mode amplitude in the range $0 < u < 1$ accessible by light scattering.

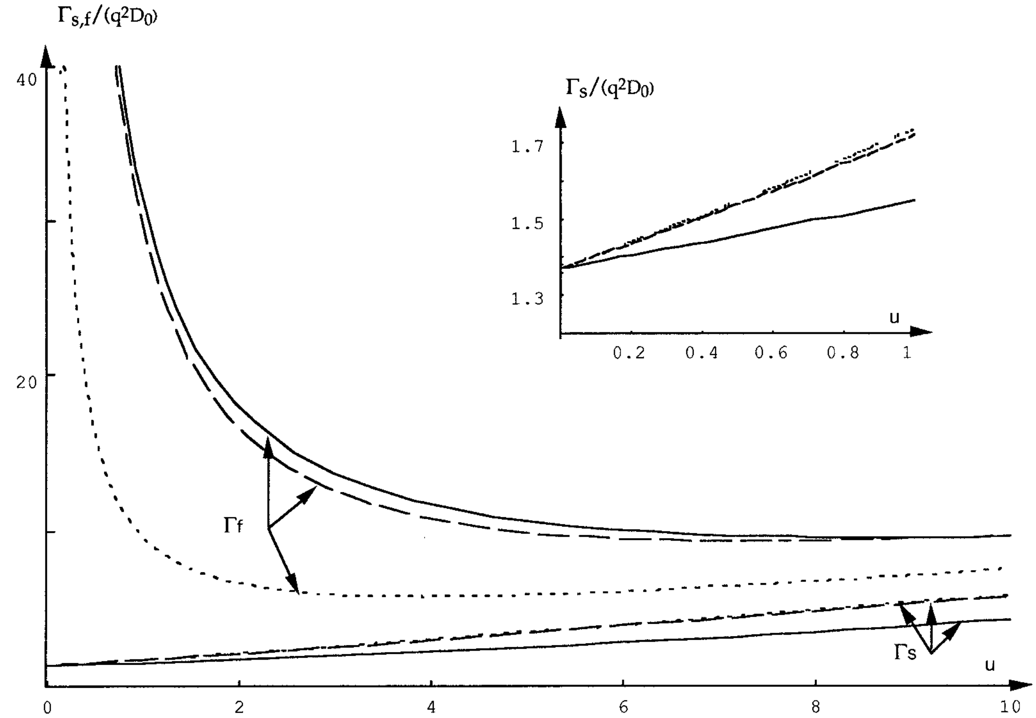

Figure 2. The variations of the normalized frequencies of the fast and slow modes, Γ_f/D_0q^2, $\Gamma_s/D_{0q}{}^2$, respectively, as a function of u. The insert represents a detailed view of the slow mode frequency in the range $0 < u < 1$ accessible by light scattering. The symbols and the numerical values are the same as in Figure 1.

represent the results of the linear diblock copolymer, and the dashed lines correspond to those of the linear triblock, whereas the continuous lines refer to the cyclic diblock copolymer. Figure 1 gives the variations of the normalized amplitudes $A_{aas}/\varphi N$ and $A_{aaf}/\varphi N$ as a function of u for the slow and fast modes, respectively. The upper curves represent the amplitude of the slow mode, $A_{aas}/\varphi N$, and the lower ones represent those of the fast mode, $A_{aaf}/\varphi N$. Likewise, in Figure 2, we display the variations of the normalized frequencies of the eigenmodes as a function of u. The upper and lower curves correspond to Γ_f/q^2D_0 and Γ_s/q^2D_0 for the fast and slow modes, respectively. Here, D_0 represents the diffusion coefficient of the total chain assuming that the friction coefficient (ζ) represents some averaged value of ζ_a and ζ_b:

$$D_0 = k_B T/(N\zeta)$$

In all the plots, the concentration and the interaction parameters are chosen in such a way that

$$A_0 = c/c^* = 0.1 \qquad c^* = [2A_{2a}M]^{-1}$$

$$\alpha = A_{2b}/A_{2a} = 5 \qquad \beta = A_{2ab}/A_{2a} = 3.1$$

If one assumes that the second virial coefficient of PS in cyclohexane is roughly $A_{2a} \approx 10^{-4}$ g^{-2} cm^3, considering the total molecular weight $M = 4 \times 10^4$ g/mol, one could introduce a critical concentration $c^* = [2A_{2a}M]^{-1}$, which is comparable with the overlap concentration. For the numerical values given above, one finds $c^* \approx 0.125$ g/cm^3, which is approximately 4 times the highest concentration used by Amis et al.[9,10] In the quasi-elastic light scattering measurements, Amis et al. covered the range of concentration 3.59 mg/mL < c < 29.8 mg/mL, and in the static measurements, they covered the range 0.05 mg/mL < c < 30 mg/mL. In terms of the parameter $A_0 \equiv (c/c^*)$, the highest experimental concentration would be roughly $A_{0\max} \approx 0.25$. The plots in Figures 1 and 2 are made using an intermediate value of $A_0 = 0.1$, which would correspond to the concentration c = 12.5 mg/mL. With regards to the other interaction parameters used in these plots, the quantity $\alpha = (A_{2b}/A_{2a})$ is taken equal to 5, meaning that cyclohexane dissolves roughly 5 times better PDMS than PS. The quantity $\beta = A_{2ab}/A_{2a}$ is calculated by using

$$A_{2ab} = A_0^*(1/\varphi_s - \chi_{as} - \chi_{bs} + \chi_{ab}) = [A_{2a} + A_{2b}]/2 + \chi_{ab}A_0^*$$

$$\beta = A_{2ab}/A_{2a} = 1/2 + \alpha/2 + \chi_{ab}A_0^*$$

Letting $\alpha = 5$ and $\chi_{ab}A_0^* = 0.1$, one finds $\beta = 3.1$. These values are chosen throughout the rest of this paper together with $f = {}^1/_3$ according to the systems considered by Amis et al. Furthermore, considering the wavelength and the scattering angles used in refs 9 and 10 (λ = 5145 Å, 30° < θ < 145°) and using a radius of gyration R_g = 130 Å, one finds that the maximum value of $u = q^2R_g^2$ reached in these experiments corresponds to $u_{\max} \approx 0.15$. The inserts in Figures 1 and 2 show detailed views of the variations of the amplitudes and the frequencies in the range $0 < u < 1$ corresponding to the experimental conditions of the quasi-elastic light scattering measurements. Figures 1 and 2 indicate that, in this range of u, both amplitudes and the frequency of the fast mode show strong differences between the linear diblock, on the one hand, and the triblock and the cyclic diblock, on the other hand. The frequency of the slow mode seems to be comparable for the linear copolymers. Furthermore, in the low q range, where the light scattering measurements were made, the amplitudes of the fast mode are zero at $q = 0$ and represent less than 2% of the total amplitude up to u = 0.5. Considering the same range of q, one observes that the normalized frequency of the fast mode Γ_f/q^2 is very high. It tends to infinity as q^{-2} when q goes to zero, which implies that Γ_f is finite at $q = 0$. This is a nondiffusive process which is characteristic of the structural properties of block copolymers. It has been predicted theoretically for linear copolymers in bulk[1] and in solutions[2] and has been first observed by light[4] and neutron scattering experiments[5,6] on various linear copolymers. However, so far, it has not been reported for cyclic copolymers. With regards to the systems investigated by Amis et al., because of the low q's and the long time windows available in these experiments, the structural mode is too fast to be observed. It could be detected for this system only if one had access to higher q's and to lower time windows, which are accessible only by neutron spin-echo technique. Figure 1 shows that, for the linear diblock, the amplitudes of both modes cross each other at $u \approx 3$, whereas for the triblock and the ring copolymers, the amplitudes of the slow modes remain higher than those of their counterparts for the fast mode in the entire range of u used in the calculations. This result shows that the favorable region of u where one could observe simultaneously the two modes at this concentration for the triblock and the ring is $u \approx 3-8$. In this region, the amplitudes of the fast mode is more than 25% of the total amplitude, and its relaxation frequency is much larger than that of the slow mode. For the linear diblock, this region seems to be shifted to lower q, corresponding to $u \approx 1-3$, where the amplitudes are comparable but the frequencies are widely different. The amplitude of the fast mode clearly reflects the architecture of the block copolymer and shows the usual variation of the scattered intensity as a function of q. It is zero at $q = 0$ and shows a maximum at a finite $q = q_m$. This peak is most obvious in the case of the linear diblock and is located at $u_m \approx 4$ or, equivalently, $q_m \approx 2/R_g$. In spite of the fact that the total radius of gyration is the same for the two linear copolymers, one finds that, for the linear triblock, the maximum is less sharp and its position is displaced to a higher u between $u_m \approx 5$ and 6. For the ring copolymer, the maximum is also broad and shifted to a higher u. If one admits that $q_m \approx 2/R_{gc}$, recalling that the radius of gyration of a cyclic polymer, R_{gc}, is smaller by a factor $1/\sqrt{2}$ than its linear counterpart (i.e., $R_{gc} \approx R_g/\sqrt{2}$), one indeed finds that q_m for the cyclic copolymer should increase by a factor $\sqrt{2}$, which is consistent with the trend observed above.

In a recent investigation of the scattering peak for multiblock linear and cyclic copolymers, Benoit et al.[20] observed that when the number of blocks is sufficiently large, the ring and the linear multiblock copolymers show the same scattering peak. If one reduces the number of blocks, the scattering curves shift in opposite directions, depending on whether one deals with the linear or the cyclic chain. For the linear copolymers, the curves shift upward when the number of blocks decreases, whereas for the cyclic copolymer they shift downward. An important consequence of this behavior is that the driving force toward microphase separation would be enhanced for the linear chain as the number of blocks is reduced, whereas for the cyclic copolymer, this driving force is reduced. Although Figure 1 displays separately two different parts of the scattering intensity, the fact that the amplitude of the fast mode for the linear diblock is higher than that for the triblock is consistent with the above observations. Had we considered the case of a triblock cyclic copolymer, we would have expected the curves of the corresponding amplitude to shift downward with respect to the amplitude of the cyclic diblock.

The amplitude of the slow mode decays with increasing q and reflects essentially the behavior one would obtain from a solution of homopolymers under good solvent conditions. Likewise, its frequency, Γ_s, seems to follow the variation

$$\Gamma_s/q^2 \approx D_s[1 + \text{const}\cdot q^2]$$

where the constant, independent of q, is rather small, as one can see from the slopes of the bottom lines in Figure 2. D_s is the slow mode diffusion coefficient; it is a function of the polymer concentration and coincides with D_0 in the infinite dilute limit, i.e., $D_s(c=0) = D_0$. For $u \leq 1$, Γ_s is proportional to q^2, indicating that it is a diffusive process. As u increases, one finds that $\Gamma_s \approx q^4$, which is a signature of the Rouse dynamics. The same behavior is shown for the three copolymers, except that the slope of the cyclic chain is slightly lower, indicating a smaller value for the constant introduced in the above equation. This model does not allow us to distinguish between the diffusion coefficient of the three copolymers, since Γ_s is normalized with the single chain diffusion coefficient and the extrapolation of Γ_s/D_0q^2 to $q = 0$ is the same regardless of the system. To make this distinction, one needs to address specifically the calculation of the single chain diffusion coefficient and investigate its dependence upon chain architecture. Such a calculation would be useful but lies beyond the scope of the present paper.

It is worthwhile to note that the slow mode in the present model bears similar properties with the fast mode observed by Amis et al. and certainly has nothing to do with their slow mode. The latter is rather due to aggregates which form as the temperature is lowered below a certain critical value. This critical temperature seems to be 20 °C for the triblock copolymer and probably below 12 °C for the cyclic chain. Such a phase transition is not accounted for within the simple model calculations presented by relying on mean field arguments.

It was observed earlier that the first cumulant of $S_{aa}(q,t)$ coincides with the mean value of Γ_f and Γ_s weighted with respect to the amplitudes A_{aaf} and A_{aas}. Combining eqs 32−40 and 20, one finds this frequency as

$$\langle\Gamma\rangle = q^2 k_B T M_{aa}(q)/S_{aa}(q) \tag{55}$$

In the Rouse model, the mobility is independent of q and given by $M_{aa} = \varphi_a/\zeta_a$, with $\varphi_a = f\varphi$ and $\zeta_a = \zeta$. Substituting this into eq 55 and using equation 20 yields

$$\langle\Gamma\rangle/[q^2 D_0] = \{1 + A_0 f^2 P_a + A_0\alpha(1-f)^2 P_b + 2A_0\beta f(1-f)P_{ab} + [A_0 f(1-f)]^2(\alpha-\beta^2)\Delta P\}/\{[P_a + A_0\alpha(1-f)^2\Delta P]\} \tag{56}$$

In the limit $q = 0$, all the P's are normalized to 1, leading to the simple result

$$\langle\Gamma\rangle/[q^2 D_0]_{q=0} = 1 + (c/c^*)[f^2 + \alpha(1-f)^2 + 2\beta f(1-f)] \tag{57}$$

where the definition $A_0 = (c/c^*)$ has been used. Equation 56 does not depend upon the type of copolymer, except perhaps via the interaction parameters A_{2a}, α, and β. It shows that $\langle\Gamma\rangle/[D_{0a}q^2]|_{q=0}$ varies linearly with the concentration following the equations:

$$\langle\Gamma\rangle/[D_0 q^2]|_{q=0} = 1 + 2A_{2\text{app}}Mc \tag{58}$$

$$A_{2\text{app}} = A_{2a}[f^2 + \alpha(1-f)^2 + 2\beta f(1-f)] \tag{59}$$

Choosing $A_{2a} = 10^{-4}$ g^{-2} cm^3, $\alpha = 5$, $\beta = 3.1$, and $f = 1/3$, one finds $A_{2\text{app}} = 3.71 \times 10^{-4}$ g^{-2} cm^3, which coincides with the apparent second virial obtained experimentally for the cyclic copolymer. This agreement suggests that the theoretical predictions together with these numerical values, in particular for the interaction parameters, correspond to reasonable choices.

It is worthwhile to note that in the limit of $q = 0$, the amplitude of the fast mode is zero and the relaxation of $S_{aa}(q=0,t)$ is entirely due to the slow mode. In this case, the first cumulant $\langle\Gamma\rangle$ coincides with the frequency of the slow mode. This can be seen from the intercept with the vertical axis in Figure 2, which is ca. 1.37, consistent with the prediction of eq 59.

5. Concluding Remarks

This paper gives a theoretical framework for a comparative study of the dynamic scattering properties of cyclic and linear copolymers in solution. It predicts two relaxation modes for the dynamic scattering function. The amplitudes and frequencies of these modes are analyzed as a function of the scattering wavevector and the polymer concentration. This investigation has been prompted by the recent static and dynamic light scattering experiments reported by Amis and co-workers on linear and cyclic copolymer made of PDMS and PS blocks in cyclohexane. These experiments were a guide in the investigations particularly for the selection of the theoretical parameters. It is true that, given the conditions of these experiments, a much easier theoretical argument based upon a perturbation method would be sufficient to analyze the results. If one recognizes that the fast experimental motion corresponds to the slow theoretical mode, then the problem becomes almost trivial and not much different from the standard diffusion problem in binary homopolymer solutions. However, our purpose in the present investigation was to point out some of the interesting properties of cyclic and linear block copolymers and stress the fact that certain aspects such as the structural mode can be observed only in an extended range of wavevectors and time scales which are beyond the ranges accessible by the light scattering apparatus used by Amis et al.

Furthermore, the transitions observed both in the static and the dynamic scattering from the triblock copolymer are probably due to aggregation or micelle formation, as pointed out by Amis et al. This issue of phase transition is not addressed within our theoretical formalism and would be implemented through an additional third mode, a sort of ultraslow process as already observed in the work of Duval et al.[21]

One of the main assumptions made here is inherent in eq 1 which not only neglects memory effects but also assumes that all the relevent information is contained in the first cumulant matrix $\mathbf{\Omega}(q)$. There are other possible models for the study of the dynamics of multicomponent polymer mixtures. One of them is a straightforward extension of the RPA (random phase approximation) argument as first suggested by Jannink and de Gennes[22] and later applied to neutron scattering data by Csiba et al.[23] Using this procedure, one can improve substantially the dynamical description of the system by incorporating all the possible effects that can govern single chain motion and in particular the effects of memory and long range hydrodynamic interaction. This method is different from the one adopted here and is quite attractive, perhaps mostly because it enables one to have a better understanding of the physical meaning of the modes. Especially, with regard to the structural or fast mode, which strongly depends upon the single chain dynamics, one can control better the phenomena that govern the fast mode and indicate which part of the relaxation spectrum contributes to build up its relaxation frequency, Γ_f. However, this method requires heavy numerical work which can be made only with a limited accuracy at the expense of simplicity. Perhaps more seriously, such mathematical complications would overshadow the goals which we seek here of distinguishing those effects that are due to the presence of cyclic chains in homopolymer and copolymer mixtures as compared to their counterpart systems made of linear chains exclusively.

With regard to the physical interpretation of the modes of relaxation for multicomponent mixtures of homopolymers and/or copolymers predicted by theories similar to the one presented here, one can find useful discussions in several papers by Akcasu and co-workers.[3,24,25]

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