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Theory of Dynamic Scattering from Copolymer Solutions Using the Random Phase Approximation

M. Benmouna,[‡] H. Benoit,[†] R. Borsali,[†] and M. Duval*[†]

Institut C. Sadron (CRM-EAHP), CNRS-ULP Strasbourg, F-67083 Strasbourg Cedex, France, and University of Tlemcen, Department of Physics, B.P. 119 Tlemcen, Algeria.
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ABSTRACT: The random phase approximation method is applied to study the dynamical behavior of copolymers in solution. The generalized expressions of the intermediate scattering functions and their relaxation modes are given in the Rouse model. Two different types of relaxation are identified. The first one Γ_I is characteristic of the copolymer nature of the chain. The second mode Γ_C represents the diffusion of the chain as a whole in the solution. Specific equations are given in the case of a diblock 50/50 copolymer. The influence of the scattering vector, the thermodynamical parameters of the solution, and the contrast factor is discussed. It is shown that experimental conditions can be found for which the two modes should be easily distinguished.

Introduction

The dynamic scattering function $S(q,t)$ for scattering from multimodal systems was formulated by Akcasu et al.[1] In recent papers we have first investigated the dynamics of bulk systems[2] made either from pure mixtures of homopolymers or pure copolymers and later generalized the same work to a solution of ternary mixtures[3] made of two homopolymers in a solvent. In the bulk problem, we have shown that the dynamics were characterized by a single relaxation process which was attributed to the relative motion of the two polymer species. In a solvent, two relaxation modes were identified: the first one is qualitatively identical with the process that appears in the bulk case; it was found to be x dependent where x is the fraction of polymer 1 in the system; the second mode has been called the cooperative diffusion mode. It is dependent on the total polymer concentration c and it is the only mode that appears when the two polymer species are identical. The extrapolation to the bulk limit shows that the cooperative mode disappears and one relaxation process is observed as described in ref 2.

In the present article, we would like to apply the same formalism to the case of a copolymer in solution in an attempt to characterize precisely the dynamics of such systems. In a first part, we present briefly the general formalism used to show the modification required by the copolymer nature of the chains. In a second part, we discuss some applications of this theory showing the conditions in which one can observe the two modes and the influence of the physical parameters on the dynamics of these systems.

General Formalism

a. Random Phase Approximation (RPA) Equations. In this section the RPA equations will be obtained by a straightforward generalization of the method described in ref 3 for a mixture of two homopolymers in a solvent. The fluctuations in concentration of the ith species $\partial\rho_i(q,s)$ are written as a response to an external potential applied to all species $\partial U_j(q,s)$, where q is the wave number related to the scattering angle θ and the wavelength λ of the incident radiation as $q = 4\pi/\lambda \sin(\theta/2)$ and s is the Laplace variable conjugate of time t. The Fourier–Laplace representation is chosen for reasons of convenience since the RPA equations can be written simply as

$$\partial\rho_i(q,s) = -\textstyle\sum_j \chi^0_{ij}(q,s)[U(q,s) + \partial U_j(q,s) + \sum_k v_{kj}\partial\rho_k(q,s)] \quad (1)$$

where $\chi^0_{ij}(q,s)$ is the Fourier–Laplace transform of the bare dynamical response function corresponding to a single copolymer chain made of species i and j and v_{ij} is the excluded volume parameter for pairs of monomers[4] i and j. The assumption of incompressibility allows one to eliminate U and to rearrange eq 1 in the form

$$\partial\rho_i(q,s) = -\textstyle\sum_j \chi_{ij}(q,s)\partial U_j(q,s) \quad (2)$$

which defines the response functions $\chi_{ij}(q,s)$ for the interacting systems.

For a two monomer species the total dynamical response functions are given by

$$\chi_{11}(q,s) = \frac{\chi^0_{11}(q,s) + v_{22}\Delta\chi^0(q,s)}{D(q,s)} \quad (3)$$

and

$$\chi_{12}(q,s) = \chi_{21}(q,s) = \frac{\chi^0_{12}(q,s) - v_{12}\Delta\chi^0(q,s)}{D(q,s)} \quad (4)$$

$\chi_{22}(q,s)$ can be deduced from eq 3 simply by interchanging the indices 1 and 2. The denominator $D(q,s)$ is found by

$$D(q,s) = 1 + v_{11}\chi^0_{11}(q,s) + v_{22}\chi^0_{22}(q,s) + 2v_{12}\chi^0_{12}(q,s) + (v_{11}v_{22} - v_{12}^2)\Delta\chi^0(q,s) \quad (5)$$

and the quantity $\Delta\chi^0(q,s)$ is defined as

$$\Delta\chi^0(q,s) = \chi^0_{11}(q,s)\chi^0_{22}(q,s) - \chi^0_{12}{}^2(q,s) \quad (6)$$

The first observation to be made here is that by replacing in these equations $\chi(q,s)$ and $\chi^0(q,s)$ by the static structure factors $S(q)$ and $S^0(q)$, respectively, one obtains the corresponding static relationships between total $S_{ij}(q)$ and bare $S^0_{ij}(q)$ structure factors. In this respect it should be noted that

$$S_{ij}(q) = S^0_{ij}(q) + Q_{ij}(q) \qquad (i, j = 1, 2) \quad (7)$$

where $S^0_{ij}(q)$ is the intramolecular form factor of a copolymer chain and $Q_{ij}(q)$ the intermolecular contribution due to interferences between species i and j. In an earlier work,[4] we have determined $S_{ij}(q)$ in terms of $S^0_{ij}(q)$. It comes out from this study that the expressions of $S_{ij}(q)$ are given by

$$S_{11}(q) = \frac{S^0_{11}(q) + v_{22}\Delta S^0(q)}{D(q)} \quad (8)$$

$$S_{12}(q) = S_{21}(q) = \frac{S^0_{12}(q) - v_{12}\Delta S^0(q)}{D(q)} \quad (9)$$

where $\Delta S^0(q) = S^0_{11}(q)S^0_{22}(q) - S^0_{12}{}^2(q)$, and the denominator $D(q)$ is given by

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[†] Institut C. Sadron (CRM-EAHP).
[‡] University of Tlemcen.

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$$D(q) = 1 + v_{11}S^0{}_{11}(q) + v_{22}S^0{}_{22}(q) + 2v_{12}S^0{}_{12}(q) + (v_{11}v_{22} - v_{12}{}^2)\Delta S^0(q) \quad (10)$$

$S_{22}(q)$ is deduced from $S_{11}(q)$ by interchanging the indices. A second observation can be made concerning the limit of a mixture of two homopolymers in a solvent[3] which can be immediately deduced from the above formulas where, from the definition of the response function,[5] $\chi^0{}_{12}(q) = \chi^0{}_{21}(q) = 0$ and $S^0{}_{12}(q) = S^0{}_{21}(q) = 0$ since[6] $S^0{}_{12}(q) = kT\chi^0{}_{12}(q)$.

b. Intermediate Scattering Functions and Their Eigenmodes. The intermediate scattering functions $S_{ij}(q,t)$ are related to the dynamical response functions $\chi_{ij}(q,t)$ by the known relationship[2,3]

$$kT\chi_{ij}(q,t) = -(\partial/\partial t)S_{ij}(q,t) \qquad (i, j = 1, 2) \quad (11)$$

where T is the absolute temperature and k the Boltzmann constant. A relationship of this type is applied to both total and bare response functions in such a way that, when we combine them with eq 3 and 4, we obtain the time evolution of the intermediate scattering functions, knowing that of their bare counterparts $S^0{}_{ij}(q,t)$. In our earlier investigations on the dynamics of bulk systems and mixtures of homopolymers in solution, we have focused our attention on the first cumulant matrix and its eigenvalues $\Gamma_{\rm I}$ and $\Gamma_{\rm C}$ which we have shown to constitute the relaxation frequencies of the intermediate scattering functions. Using the same procedure as in ref 3 one can express the partial intermediate scattering functions $S_{ij}(q,t)$ simply in terms of two exponential decay modes

$$S_{11}(q,t) = a_{\rm I}e^{-\Gamma_{\rm I}t} + a_{\rm C}e^{-\Gamma_{\rm C}t} \quad (12)$$

$$S_{21}(q,t) = b_{\rm I}e^{-\Gamma_{\rm I}t} + b_{\rm C}e^{-\Gamma_{\rm C}t} \quad (13)$$

Neglecting the effect of memory functions, the general forms of amplitudes $a_{\rm C,I}$ and frequencies $\Gamma_{\rm C,I}$ can be expressed in terms of $S_{ij}(q)$ and Ω_{ij} only. Since these expressions are the same as in the mixture case we do not rewrite them here (see eq 19–24 of ref 3).

Furthermore, following the same arguments used in the case of mixtures of homopolymers in solution, we shall neglect the hydrodynamic interactions and use the Rouse model to calculate explicitly $a_{\rm C,I}$ and $\Gamma_{\rm C,I}$.

c. Rouse Model. Without loss of generality, we assume that the monomers of both species 1 and 2 are characterized by the same friction constant ζ. This leads to[3]

$$\Omega_{11} = q^2\frac{kT}{\zeta}\varphi_1\frac{S^0{}_{22} + v_{11}\Delta S^0}{\Delta S^0} \quad (14)$$

$$\Omega_{12} = -q^2\frac{kT}{\zeta}\varphi_1\frac{S^0{}_{12} - v_{12}\Delta S^0}{\Delta S^0} \quad (15)$$

where $\varphi_i = nN_i$ ($i = 1, 2$), n being the number of copolymer molecules per unit volume, and N_i is the number of monomers of type i per chain. Ω_{22} and Ω_{21} can be obtained from eq 14 and 15 by interchanging the indices 1 and 2.

By taking into account their expressions, it can be observed that $\Gamma_{\rm C,I}$ depend on both species 1 and 2 even in the case where $v_{12} = 0$. We recall that in the mixture problem, the two modes are decoupled in this limit as follows:[3]

$$\Gamma_{\rm I} = q^2\frac{kT}{\zeta}\varphi_1\frac{1 + v_{11}S^0{}_{11}}{S^0{}_{11}}$$

and

$$\Gamma_{\rm C} = q^2\frac{kT}{\zeta}\varphi_2\frac{1 + v_{22}S^0{}_{22}}{S^0{}_{22}}$$

Application to the Case of a 50/50 Diblock Copolymer

Obviously, the simplest case from a theoretical point of view when one considers a copolymer system is to assume that the chains are made of two blocks having the same radius of gyration. If it is assumed that they have also the same number of monomers N with the same volume one obtains[7]

$$S^0{}_{11}(q) = S^0{}_{22}(q) = \varphi(N/2)P_{1/2}(q) \quad (16)$$

$$S^0{}_{12}(q) = S^0{}_{21}(q) = \varphi(N/2)P_{12}(q) \quad (17)$$

$$P_{12}(q) = 2P_{\rm T}(q) - P_{1/2}(q) \quad (18)$$

where $\varphi = 2Nn$ is the volume fraction of polymer in the solution and $P_{1/2}(q)$, $P_{\rm T}(q)$, and $P_{12}(q)$ are the intramolecular form factors for a block and the total chain and the intramolecular interference factor between blocks 1 and 2, respectively. These form factors are normalized to unity for $q = 0$.

The substitution of eq 16–18 into eq 14 and 15 gives

$$\Omega_{11} = \Omega_{22} = q^2\frac{kT}{4N\zeta P_{\rm T}(P_{1/2} - P_{\rm T})}[P_{1/2} + 2v\varphi NP_{\rm T}(P_{1/2} - P_{\rm T})] \quad (19)$$

$$\Omega_{12} = \Omega_{21} = -q^2\frac{kT}{4N\zeta P_{\rm T}(P_{1/2} - P_{\rm T})}[P_{12} - 2(v + \chi)\varphi NP_{\rm T}(P_{1/2} - P_{\rm T})] \quad (20)$$

where we have let v_{11} and $v_{22} = v$ and $v_{12} = v + \chi$ with $\chi \ll v$. In these expressions the excluded volume parameters v_{ij} are normalized to the volume of a solvent molecule.

The combination of these equations with the definitions of $\Gamma_{\rm C,I}$ gives

$$\Gamma_{\rm C} = \frac{q^2kT}{2N\zeta P_{\rm T}}(1 + 2v\varphi NP_{\rm T}) \quad (21)$$

and

$$\Gamma_{\rm I} = \frac{q^2kT}{2N\zeta(P_{1/2} - P_{\rm T})}[1 - \chi\varphi N(P_{1/2} - P_{\rm T})] \quad (22)$$

Introducing a generalized q-dependent Flory parameter as

$$\chi_{\rm C}(q) = [N\varphi(P_{1/2} - P_{\rm T})]^{-1}$$

One can write $\Gamma_{\rm I}$ as follows

$$\Gamma_{\rm I} = \frac{q^2kT}{2N\zeta(P_{1/2} - P_{\rm T})}[1 - \chi/\chi_{\rm C}(q)] \quad (23)$$

which becomes identical with the bulk result[2] if we let $\varphi = 1$. Finally it is useful to recall the expressions of amplitudes $a_{\rm C,I}$ in this case of a 50/50 diblock copolymer:

$$a_{\rm C} = \frac{nN^2P_{\rm T}[1 - \chi/\chi_{\rm C}(q)]}{D} \quad (24)$$

$$a_{\rm I} = \frac{nN^2(P_{1/2} - P_{\rm T})(1 + 2v\varphi NP_{\rm T})}{D} \quad (25)$$

where

$$D = 1 + 2v\varphi NP_{\rm T}[1 - \chi/\chi_{\rm C}(q)] + \chi\varphi N(2P_{\rm T} - P_{1/2}) \quad (26)$$

These quantities (i.e., $\Gamma_{\rm C,I}$ and $a_{\rm C,I}$) characterize completely the scattering function if one chooses a solvent which masks one block of the copolymer. In this case the intermediate scattering function coincides with $S_{11}(q,t)$ which is given by eq 12. Moreover it can be noted that the expressions of $\Gamma_{C,I}$ and $a_{C,I}$ become identical with those obtained in the single chain copolymer study[8] if we let $\varphi \rightarrow 0$. The following limits of Γ_I in various q regions can be discussed:

(i) In the small q region, expanding the form factor as a function of q and assuming that the chains are Gaussian, one shows that Γ_I is independent of q:

$$\Gamma_I \rightarrow 3kT/N\zeta R_{gT}^2 \tag{27}$$

where R_{gT} is the radius of gyration of the total chain.

(ii) In the intermediate q region, using the asymptotic development for the Debye function $[P(q) \approx (qR_{gT})^{-2}]$ one obtains the familiar q^4 behavior:

$$\Gamma_I \rightarrow \frac{1}{12}\frac{kT}{\zeta a^2}(qa)^4 \tag{28}$$

where a is the statistical unit length. These limits were also found in the bulk state[2] and for a single copolymer chain.[8]

It is also interesting to see what happens for high values of χ or negative values of v in which case a phase separation can occur.

Discussion

a. Behavior in the Vicinity of a Phase Separation. The theoretical treatment presented in the preceding section shows that the diffusion of a copolymer in solution can be decomposed into relaxation processes characterized by two relaxation frequencies which were called Γ_C and Γ_I. Equations 21 and 22 show that the influence of thermodynamic interactions on their values is entirely different. Γ_C depends principally on the excluded volume between monomers and solvent (it was assumed that it was the same for both monomers building the copolymer). Γ_I depends only on χ, the interaction parameter between the two kinds of monomers. This shows that the physical interpretation of these two relaxations must be quite different.

It has been shown[3] that, in the case of a mixture of two polymers in a solvent, one has also two relaxation processes. The first one corresponds to the fluctuations of the total polymer concentration which has been called the cooperative relaxation. The other corresponds to the relative fluctuations of the concentration of each polymer species with respect to the other and is called the interdiffusion mode. They were identified on the basis of different types of phase separation occurring in the mixture. If the polymers are incompatible two phases will appear, one being rich in polymer 1 and the other in polymer 2. If the two polymers are compatible and if the quality of the solvent is the same for both polymers, in the case of a bad solvent one phase will be rich in polymer and the second will be practically pure solvent. At the onset of separation between the two polymers (first process) Γ_I goes to zero. In the phase separation between polymers and solvent (second process) Γ_C goes to zero.[3] This type of analysis can apply also to the problem of copolymers. In this case at $q = 0$

$$\Gamma_C = 0 \quad \text{if} \quad 1 + 2v\varphi N = 0 \tag{29}$$

This is the equation for reaching the spinodal in a polymer–solvent mixture. Therefore Γ_C corresponds to the concentration fluctuations of the polymer and would be the same for a homopolymer. We refer to previous work[3] for further discussion of this point. The quantity Γ_I is more interesting. In the case of a 50/50 diblock copolymer, from eq 22, Γ_I goes to zero for

$$1 = \chi\varphi N[P_{1/2}(q) - P_T(q)] \tag{30}$$

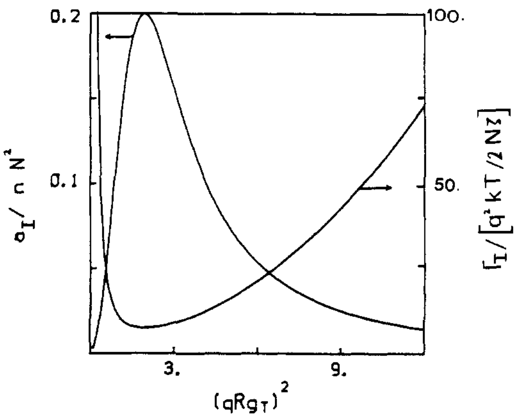

Figure 1. Variation of the amplitude (a_I/nN^2) and the frequency $[\Gamma_I/(q^2kT/2N\zeta)]$ of the "copolymer" relaxation process as a function of $(qR_{gT})^2$ (see eq 23 and 25) for $v\varphi N = 0.5$ and $\chi/v = 5 \times 10^{-2}$.

This can never be the case for $q = 0$ since by definition the quantities $P_{1/2}$ and P_T are equal to 1. The influence of the scattering vector q has to be taken into account. The quantity $[P_{1/2}(q) - P_T(q)]$ reaches a maximum value of $m \simeq 0.19$ for $(qR_{gT})^* \simeq 1.41$. At this maximum $\Gamma_I = 0$ if

$$1 - m\chi\varphi N = 0 \tag{31}$$

It can be shown[9,10] that this condition is, with a good approximation, the condition for the appearance of mesophases even in the presence of solvent. This means that when Γ_I, given by eq 22, becomes negative, the two species are incompatible and form domains with lamellae or cylindrical or spherical structures.

One deduces from this that Γ_I is characteristic of the motions of one part of the copolymer with respect to the other. It is an internal mode in solution and it is also the only mode in the bulk.

Since it is obvious from the preceding discussion that Γ_I is strongly q dependent, it was interesting to plot Γ_I and a_I, the corresponding amplitude, as a function of $(qR_{gT})^2$. This has been done in Figure 1 where we have plotted, in arbitrary units, Γ_I and a_I for a given concentration ($v\varphi N = 0.5$) and assuming $\chi = (5 \times 10^{-2})v$. It appears that a_I goes through a maximum as expected since at zero angle or large distance, the relative fluctuations between the monomers 1 and 2 are not seen. In contrast, Γ_I presents a strong minimum for practically the same value of qR_{gT} where a_I is maximum. This is also qualitatively justified since in the neighborhood of $(qR_{gT})^*$ where a phase transition can occur, the relaxation processes are slower. Moreover these quantities depend very little on the concentration which is also evident since it is an internal mode.

In Figure 2, Γ_I is plotted as a function of $(qR_{gT})^2$ for different values of $\chi\varphi N$. If $\chi\varphi N$ is too large (for instance if the molecular weight of the copolymer is too large), Γ_I becomes negative in a given interval of q. This means that the system cannot exist for these values of χ, N, and φ as a single phase.

It is evident that in order to check this theory, it would be quite interesting to be able to observe simultaneously the two relaxation modes. This is possible if A_I and A_C, which are the amplitudes of the two modes in the expression of the total intermediate scattering function $S(q,t)$, are of the same order of magnitude and for experimental convenience Γ_I and Γ_C very different. In order to do so one has to adjust the contrast between the solvent (s) and the two components (b_1, b_2) of the copolymer (s and $b_{1,2}$ are the refractive indices in light scattering or the scattering lengths in neutron scattering).

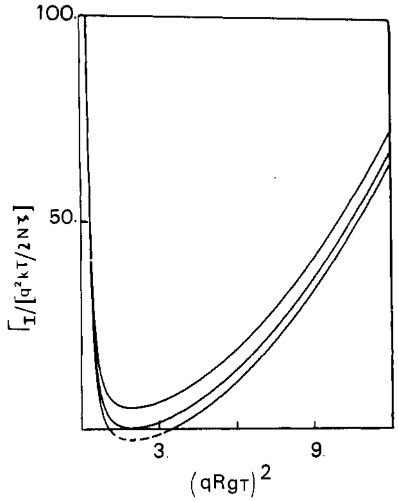

Figure 2. Variation of $\Gamma_I/(q^2kT/2N\zeta)$ as a function of $(qR_{gT})^2$ at different $\chi\varphi N$ values; from top to bottom $\chi\varphi N = 2.5 \times 10^{-2}$, 5, and 8.

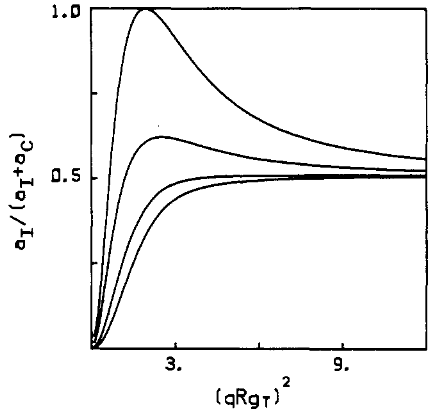

Figure 3. Relative contribution of the "copolymer" mode to the amplitude of the total intermediate scattering function $S(q,t)$ (one block is masked by the solvent) as a function of $(qR_{gT})^2$. From top to bottom $\chi\varphi N$ = 5, 2.5, 0.5, and 0.

If one of the sequences of the copolymer is not "seen" in the solvent (for instance $b_2 = s$), $S(q,t)$ reduces to $S_{11}(q,t)$. In this case $A_I = a_I$ and $A_C = a_C$. In Figure 3 we have plotted the ratio $a_I/(a_I + a_C)$ as a function of $(qR_{gT})^2$. It comes out that at small q values, $a_I \simeq 0$; while in the intermediate q range, a_I is predominant. At large q values $a_I \simeq a_C$. If we increase the polymer concentration the contribution of the internal fluctuations increases especially in the range $qR_{gT} \simeq 1$ as it should be according to our model.

In fact there is a very interesting case where the "copolymer" relaxation mode has a major contribution to the total intermediate scattering function $S(q,t)$. Indeed in a solvent such that $s = (b_1 + b_2)/2$ there is no scattered light by a 50/50 diblock copolymer at zero angle. It corresponds to the case where the concentration fluctuations of the copolymer as a whole are not visible. Therefore at any q values the amplitude A_C must be zero, as appears to be the case from theoretical equations.

Figure 4 shows the evolution of Γ_C and Γ_I as a function of $(qR_{gT})^2$ for $v\varphi N = 0.5$ and $\chi/v = 5 \times 10^{-2}$. At higher values of $v\varphi N$, Γ_I becomes negative. As has been already discussed, this corresponds to a phase separation.

In order to be complete we should have introduced a discussion on the effect of polydispersity. This can be done by a generalization of what has been done for a monodisperse system but would need long developments. The only thing that can be said qualitatively is that as soon as polydispersity in composition appears, Γ_I will not go to infinity and a_I to zero for $q = 0$. The maximum of a_I as a function of q will become less and less pronounced and disappears completely if each block has a polydispersity larger than $M_w/M_n = 2$.

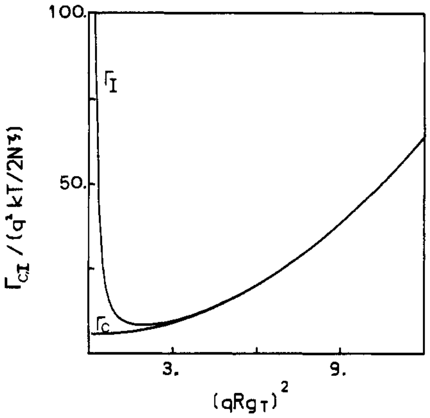

Figure 4. Variation of $\Gamma_{C,I}/(q^2kT/2N\zeta)$ as a function of $(qR_{gT})^2$; $v\varphi N = 0.5$ and $\chi/v = 5 \times 10^{-2}$.

b. Influence of the Structure of the Block Copolymer. This discussion has been limited to a two-block copolymer with blocks of equal length. It could be interesting to extend the results to polymers with another architecture. This is difficult and will not bring very different results in general but is particularly simple for a multiblock copolymer $(A-B)_r$ made of r successive identical blocks A and B (one can think, for instance, of a copolymer made by polycondensation of hard and soft segments). This kind of polymer has exactly the same symmetry as the two-block copolymer and therefore the results can be applied after modification of the meaning of $P_{1/2}(q)$ which becomes $P'_{1/2}(q)$, the form factor of all blocks of one species, and replacement of N by Nr. Furthermore Benoit and Hadziioannou[11] have shown that the quantity $X'(q) = r[P'_{1/2}(q) - P_r(q)]$ is practically independent of r for $r \geq 10$ and, by examining the expressions

$$\Gamma_C = \frac{q^2kT}{2Nr\zeta P_T(q)}[1 + 2v\varphi NrP_T(q)] \tag{32}$$

and

$$\Gamma_I = \frac{q^2kT}{2N\zeta X'(q)}[1 - \chi\varphi NX'(q)] \tag{33}$$

one observes that the two modes behave quite differently. While Γ_C remains the same regardless of the copolymer structure, Γ_I is found to be independent of the number of diblocks r and therefore independent of the length of the chain. This shows that Γ_C characterizes the diffusion of the polymer as a whole, since it depends on the total length Nr, whereas Γ_I is independent of the number of blocks and has to be attributed to the relative motion of one species of blocks with respect to the other since it depends only on their size N. This is another way of justifying the notion of an internal mode. These observations suggest the use of a multiblock copolymer for establishing the existence of the two modes. With Γ_C proportional to $1/r$, the ratio Γ_I/Γ_C becomes proportional to r at a given, concentration which makes the distinction of these two modes easier.

Conclusion

In this paper we have tried to give a systematic analysis of the intermediate scattering function $S(q,t)$, as it can be measured on a copolymer in solution. The main feature which appears in this study is the possibility of having two relaxation mechanisms. The first relaxation mode is characteristic of the motion of the copolymer as a whole. The second mode is due to the internal concentration fluctuations. We have shown that it is possible from an experimental point of view to detect these motions in one experiment. We hope to be able in the near future to see if there is agreement between these theoretical results and experiments.

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References and Notes

(1) Akcasu, Z. A.; Hammouda, B.; Lodge, T. P.; Han, C. C. *Macromolecules* **1984**, *17*, 759.

(2) Akcasu, Z. A.; Benmouna, M.; Benoit, H. *Polymer* **1986**, *27*, 1935.

(3) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. A. *Macromolecules* **1987**, *20*, 1107.

(4) Benoit, H.; Wu, W.; Benmouna, M.; Mozer, M.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986. (In fact, v_{ij} are excluded volume parameters times kT as opposed to the v_{ij} that multiply the structure factors. We have kept the same symbol to ease the notation hoping this will not cause any confusion.)

(5) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(6) De Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1970**, *31*, 235.

(7) Benmouna, M.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227.

(8) Benmouna, M.; Duval, M.; Borsali, R. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

(9) Benoit, H., unpublished result.

(10) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.

(11) Benoit, H.; Hadziioannou, G., manuscript in preparation.

Statistical Chemical Heterogeneity of Copolymers. Modification of the Stockmayer Distribution Function of Chemical Composition

Jaroslav Stejskal* and Pavel Kratochvil

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia. *Received February 5, 1987*

ABSTRACT: The distribution function of chemical composition describing the statistical chemical heterogeneity of statistical copolymers derived by Stockmayer is adapted to cover the case of (a) copolymers with any Schulz–Zimm distribution of degrees of polymerization and (b) copolymers with monomeric units of different molecular weights. The variance of the molar chemical composition is independent of the width of distribution of degrees of polymerization. The derived expressions can be applied to graft copolymers prepared by statistical copolymerization of an ordinary monomer with a macromonomer. In this case, the chemical composition distributions are asymmetrical and much broader than those of common statistical copolymers with identical average composition.

Introduction

The statistical chemical heterogeneity of copolymers prepared by statistical copolymerization of two monomers, A and B, which can be described in terms of the simple scheme with two monomer reactivity ratios, r_A and r_B, has been analyzed by Stockmayer in his classical paper.[1] The two-dimensional differential weight distribution[2] of degrees of polymerization P and of deviations $y = F - \bar{F}$ of the chemical composition of the individual chains, F, from the average copolymer composition, $\bar{F}$, was derived as

$$W(P,y) = \left[\frac{P}{P_n^{\,2}}\exp\left(-\frac{P}{P_n}\right)\right]\left[\frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{y^2}{2\sigma^2}\right)\right] \qquad (1)$$

on assumption that the termination is by disproportionation. A similar equation has also been derived[1] for a case when recombination of radicals is involved. P_n is the number-average degree of polymerization and the parameter σ^2 is defined by

$$\sigma^2 = \frac{\bar{F}(1-\bar{F})k}{P} \qquad (2)$$

where

$$k = [1 + 4\bar{F}(1-\bar{F})(r_Ar_B - 1)]^{1/2} \qquad (3)$$

The compositions F and $\bar{F}$ are expressed in mole fractions of component A.

The distribution function (eq 1) describes the statistical (also called instantaneous or natural) chemical heterogeneity of statistical copolymers. It does not cover the effect of chemical heterogeneity caused by a drift in the composition of the monomer mixture with conversion during copolymerization.[3] Function 1 formally consists of two factors. The first one is immediately recognized as the weight distribution of degrees of polymerization for a polymer prepared by a polymerization where termination of growing chains occurs entirely by disproportionation, i.e., as the most probable distribution,

$$W(P) = \frac{P}{P_n^{\,2}}\exp\left(-\frac{P}{P_n}\right) \qquad (4)$$

The second factor represents a normal (Gaussian) distribution,

$$W(y|P) = \frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{y^2}{2\sigma^2}\right) \qquad (5)$$

and states that the compositions of chains of a given degree of polymerization, P, are normally distributed about the mean value with standard deviation σ. Function 5 is denoted here as a conditional distribution function, $W(y|P)$, i.e., as the distribution of deviations y on condition, that the degree of polymerization has a value of P.

By integration of the two-dimensional function 1 over all degrees of polymerization, P, Stockmayer derived also

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