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Elastic Coherent Scattering from Multicomponent Systems. Applications to Homopolymer Mixtures and Copolymers

H. Benoit,[†] **W. Wu,***[‡] **M. Benmouna,**[§] **B. Mozer,**[‡] **B. Bauer,**[‡] **and A. Lapp**[†]

Centre de Recherches sur les Macromolécules (CNRS), 67083 Strasbourg Cedex, France, National Bureau of Standards, Center for Materials Science, National Measurement Laboratory, Washington, D.C. 20234, and Département de Physique, Université de Tlemcen, Tlemcen, Algeria.

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ABSTRACT: A general equation giving the scattering intensity of a solution of polymers and copolymers at any concentration and angle is derived. Its relation with thermodynamics and its application to polydisperse systems are discussed. Small-angle neutron scattering experiments on a diblock copolymer of deuterated polystyrene–poly(methyl methacrylate) (PS–PMMA) were performed in bulk and in solution near the Θ point. The results are consistent with the theoretical predictions.

In recent publications[1,2] a new method for the evaluation of the scattering intensity of a solution of two homopolymers as a function of the concentration was presented. The idea was to assume that the interactions between two polymer molecules can be evaluated by taking into account not only the direct contact but also linear chains of contacts.

The results are identical in the bulk limit with the formula obtained by de Gennes[3] using the "random phase approximation" RPA method. In solution, at zero scattering angle one finds the classical results of the theory of scattering by multicomponent systems.[4,5] This calculation which is made in the framework of a mean-field approximation is a poor approximation in the vicinity of the critical concentration c^* where the molecules begin to overlap but in concentrated solution it should be a reasonable approximation.

In this paper, we want first to generalize the method of ref 2 to the calculation of the scattering intensity of a solution containing an arbitrary number of polymers and copolymers, monodisperse and polydisperse.

This general formulation will be applied explicitly to the case of two or three constituents (one copolymer + one homopolymer of different natures and three homopolymers). The second part will describe experiments made by small-angle neutron scattering (SANS) on a diblock copolymer in bulk and in solution with a pure solvent. It will be shown how it is possible by applications of our theoretical results to interpret the data and to obtain from the measurements the values of the interaction parameters.

Theoretical Section

Mixture of Homopolymers. Let us assume that we have p species of polymers, each of them being characterized by its degree of polymerization n_i', its structure factor $P_i(q,c)$ which can depend on concentration, or the number of molecules per unit volume N_i. The intensity scattered by the unit volume of solution can be written if we neglect or subtract the compressibility effects as[6]

$$I(q) = \sum_{i=1}^{p} a_i^2 N_i n_i'^2 P_i(q) + \sum_{ij} a_i a_j Q_{ij}(q) \qquad (1)$$

$I(q)$ is the scattering intensity (neglecting a normalization factor which depends on the kind of radiation used (neutrons, X-rays, or light) as a function of the parameter $q = 4\pi \sin (\theta/2)/\lambda$ (λ is the wavelength of the incident beam and θ the scattering angle). The quantity a_i is the contrast factor corresponding to the species i in the solvent. For neutrons, it is the difference between the coherent scattering length of the monomeric unit i and the corresponding value for the solvent, after correction for the difference in specific volumes. Q_{ij} is the term due to interferences between waves scattered by molecules i and j.

In the classical single contact Zimm's approximation, it is given by the relation

$$Q_{ij} = -v_{ij} N_i n_i'^2 P_i(q) N_j n_j'^2 P_j(q) \qquad (2)$$

where v_{ij} is the excluded volume parameter for a contact between i and j molecules.

In the method developed in ref 1 and 2, one takes into account all the linear chains of contact between two molecules (Figure 1).

Let us call C_{nij} the contribution of a diagram such as Figure 1 to the interaction term Q_{ij}. If we define x_i by the relation

$$x_i = N_i n_i'^2 P_i(q)$$

we can write

$$C_{nij} = (-1)^{n+1} x_i^{n_1} \ldots x_k^{n_k} \ldots x_j^{n_j} v_{ik}^{n_{ik}} \ldots v_{kl}^{n_{kl}} \ldots v_{jm}^{n_{jm}} \qquad (3)$$

where $n_1, n_2, \ldots, n_j$ are the number of chains of each species. Since there are $n + 2$ chains in this diagram

$$\sum n_k = n + 2$$

remembering that the first chain in the series is of type i and the last one of type j. n_{ik} is the number of contacts between a chain of i species and a chain of k species such that

$$\sum n_{ij} = n + 1$$

[†] Centre de Recherches sur les Macromolécules.
[‡] National Bureau of Standards.
[§] Université de Tlemcen.

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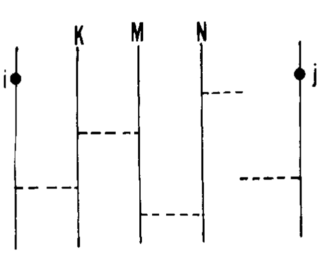

Figure 1. Vertical lines correspond to chain molecules, and dotted horizontal lines to single contacts with interaction parameter v_{mn} depending on the nature of the chain in a contact. Each chain contributes to the interaction through its form factor $n_i^2P_i(q)$.

Let q_{nij} be the sum of the contributions of all diagrams with $n + 2$ chains; we obtain Q_{ij} by summing over all possible values of n:

$$Q_{ij} = \sum_{n=0}^{\infty} q_{nij} \tag{4}$$

The problem now is to evaluate q_{nij}.

We shall establish a recurrence relation between q_{nij} and $q_{n+1,ij}$. In order to do so, we start from all the c_{nij} terms and we add one chain among the p species before the last one which has to be of j type. The multiplying factor will depend on the nature of the chain proceding the last. We therefore introduce the quantity q_{nikj}, which is the sum of all terms corresponding to a sequence of $n + 2$ chains beginning with an i chain and finishing with the sequence kj. If we introduce a chain m, we obtain a term for $q_{n+1,ikj}$ which is the product of the preceding term by $-x_m v_{km} v_{mj}/v_{kj}$. We can therefore write

$$q_{n+1,ikj} = -\sum_m q_{nimj} x_k v_{mk} v_{kj}/v_{mj} \tag{5}$$

This equation can be written in a matrix formulation

$$\mathbf{q}_{n+1,ij} = \mathbf{A}_{ij}\mathbf{q}_{nij} \tag{6}$$

where $\mathbf{q}_{nij}$ and $\mathbf{q}_{n+1,ij}$ are column vectors with components $q_{n,ikj}$ and $q_{n+1,ikj}$, respectively. $\mathbf{A}_{ij}$ is a $p \times p$ square matrix with elements $-x_k v_{km} v_{kj}/v_{mj}$. k and m are running indices going from 1 to p.

Applying the relation 6 n times gives

$$\mathbf{q}_{nij} = \mathbf{A}_{ij}^{\,n}\mathbf{q}_{0ij} \tag{7}$$

where $\mathbf{q}_{0ij}$ is a column vector with the only one nonzero term equal to $-v_{ij}x_i x_j$. Summing eq 7 over all possible values of n, one obtains

$$\mathbf{Q}_{ij} = [1/(\mathbf{I} - \mathbf{A}_{ij})]\cdot\mathbf{q}_{0ij} \tag{8}$$

assuming that the conditions of convengence are satisfied. Equation 8 allows for the calculation of Q_{ij}, which is the sum of all the terms of the column vector $\mathbf{Q}_{ij}$; therefore, our problem is formally solved.

Unfortunately, eq 8 is difficult to handle as soon as p becomes larger than 2. Therefore, the following more explicit formulation for Q_{ij} is suggested. Diagonalizing $\mathbf{A}_{ij}$ one obtains

$$\mathbf{A}_{ij} = \mathbf{P}\cdot\mathbf{D}\cdot\mathbf{P}^{-1} \tag{9}$$

where $\mathbf{D}$ is a diagonal matrix whose elements are the eigenvalues λ_i of the matrix $\mathbf{A}_{ij}$. These elements are obtained by solving the characteristic equation

$$F(\lambda) = (\lambda - \lambda_1)(\lambda - \lambda_2)...(\lambda - \lambda_p) = 0 \tag{10}$$

From the form of eq 8 it is evident that

$$q_{nikj} = \sum_{m=1}^{p} \alpha_{km}\lambda_m^{\,n} \tag{11}$$

where α_{km} are unknown coefficients which depend on the species i and j. Summing over all values of n and k one obtains

$$Q_{ij} = \sum_{n=0}^{\infty}\sum_{k=1}^{p}\sum_{m=1}^{p} \alpha_{km}\lambda_m^{\,n} = \sum_k\sum_m \frac{\alpha_{km}}{1 - \lambda_m} \tag{12}$$

If we let $\beta_m = \sum_k \alpha_{km}$, this equation becomes

$$Q_{ij} = \sum_{m=1}^{p} \frac{\beta_m}{1 - \lambda_m} \tag{12'}$$

The parameters β_m can be calculated if we know the quantities $q_{0ij}, q_{1ij}, ..., q_{pij}$ and use the definitions

$$q_{0ij} = \sum\beta_m$$

$$q_{1ij} = \sum\beta_m\lambda_m$$

$$q_{p-1,ij} = \sum\beta_m\lambda_m^{\,p-1} \tag{13}$$

We shall now show that one does not have to evaluate the eigen values of the matrix $\mathbf{A}_{ij}$ in order to obtain Q_{ij}. If we reduce eq 12′ to a common denominator, we obtain

$$Q_{ij} = \frac{\sum\beta_m(1 - \lambda_1)...(1 - \lambda_{m-1})(1 - \lambda_{m+1})...(1 - \lambda_p)}{(1 - \lambda_1)(1 - \lambda_2)...(1 - \lambda_p)} \tag{14}$$

The denominator is the value $F(1)$ of the characteristic equation (10) for $\lambda = 1$. Expanding $F(\lambda)$ as a function of λ gives

$$F(\lambda) = \lambda^p - S_1\lambda^{p-1} + S_2\lambda^{p-2} - ... + (-1)^p S_p \tag{15}$$

where

$$S_1 = \sum_i \lambda_i \qquad S_2 = \sum_{i \neq j} \lambda_i\lambda_j \qquad S_p = \lambda_1\lambda_2...\lambda_p$$

It is now easy to express the numerator of eq 14 as a function of the first q_{ij} and the S's. For instance, in the case of $p = 3$ one obtains

$$Q_{ij} = \frac{q_{0ij}(1 - S_1 + S_2) + q_{1ij}(1 - S_1) + q_{2ij}}{F(1)} \tag{16}$$

and in the general case, defining S_0 as unity, one obtains

$$Q_{ij} = \frac{1}{F(1)}\sum_{k=0}^{p-1}\sum_{l=0}^{p-k-1} (-1)^l S_l q_{kij} \tag{17}$$

Remark about $F(1)$. The results of eq 14–17 coupled with the definition of the matrix $\mathbf{A}_{ij}$ seem to show that the denominator of Q_{ij} depends on i and j. But this is difficult to accept. If we write $F(1) = 0$, we define the conditions for which the scattered light is infinite, i.e., the spinodal of the system which should be independent of the couple of components i and j. It is therefore useful to show that the equation $F(1) = 0$ is indeed independent of i and j. A close inspection of the matrix $\mathbf{A}_{ij}$ shows that it can be written as a product of three matrices

$$\mathbf{A}_{ij} = \mathbf{V}_i\cdot\mathbf{A}\cdot\mathbf{V}_i^{-1} \tag{18}$$

where $\mathbf{V}_i$ is a diagonal matrix with elements v_{ik}, V_i^{-1} is its inverse, and $\mathbf{A}$ is the matrix with general term $x_m v_{mn}$. It is well-known that, due to relation 18, $\mathbf{A}_{ij}$ and $\mathbf{A}$ have the same characteristic equation. It is therefore much simpler to use $\mathbf{A}$ instead of $\mathbf{A}_{ij}$ to obtain the quantity $F(1)$, which is now the determinant

$$F(1) = \begin{vmatrix} x_1v_{11} - 1 & x_2v_{12} & \cdots & x_1v_{1p} \\ x_2v_{21} & x_2v_{22} - 1 & \cdots & x_2v_{2p} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ x_pv_{p1} & x_pv_{p2} & \cdots & x_pv_{pp} - 1 \end{vmatrix} \tag{18'}$$

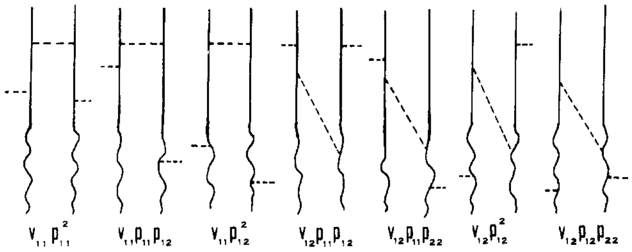

Figure 2. Some typical cases of contact between two copolymers. The quantities below the diagram indicate its contribution.

Application to Copolymers. Let us assume that the system contains not only homopolymers but copolymers as well. In order to simplify the expression but without loss of generality we shall assume that we have a copolymer made with monomer units 1 and 2. Our system will therefore be made of $p - 1$ different kinds of molecules. The species 1–2 will be the copolymer having N_{12} molecules per unit volume and respectively n_1' and n_2' monomeric units of each species. All other species from $i = 3$ to p are homopolymers.

As defined in eq 3

$$x_1' = N_{12}n_1'^2P_1(q)$$

$$x_2' = N_{12}n_2'^2P_2(q) \tag{19}$$

where P_1 and P_2 are the structure factors of parts 1 and 2 of the copolymer, respectively.

One needs to introduce a new quantity x_{12}' defined as

$$x_{12}' = N_{12}n_1'n_2'P_{12}(q) \tag{19'}$$

where P_{12} is the cross term corresponding to intramolecular interferences between waves scattered by monomer 1 and 2. It obeys the relation

$$(n_1' + n_2')^2P_T = n_1'^2P_1 + n_2'^2P_2 + 2n_1'n_2'P_{12} \tag{20}$$

where P_T is the structure factor of the whole molecule. These quantities have been precisely defined and calculated in ref 7 for various copolymers. The definition of the Q_{ij} is not modified even if i and j are 1 or 2. With these notations, eq 1 is replaced by

$$I(q) = \sum a_i^2x_i' + 2a_1a_2x_{12}' + \sum a_ia_jQ_{ij} \tag{21}$$

Using the same procedure as before one notes that when a copolymer is in a chain of contacts one has to take into account four types of contacts seen in the diagram of Figure 2. Taking this into account one can reproduce exactly the same calculations as before. Here we give only the result. In the case where a copolymer 1–2 is present in the mixture, the matrix **A** of eq 18 is modified as follows:

$$\mathrm{A}' = \begin{bmatrix} x_1'v_{11} + x_{12}'v_{12} & x_1'v_{12} + x_{12}'v_{22} & \cdots & x_1'v_{1p} + x_{12}'v_{2p} \\ x_2'v_{12} + x_{12}'v_{11} & x_2'v_{22} + x_{12}'v_{12} & \cdots & x_2'v_{2p} + x_{12}'v_{1p} \\ x_3v_{31} & x_3v_{32} & \cdots & x_3v_{3p} \\ \cdots & \cdots & \cdots & \cdots \\ x_pv_{p1} & x_pv_{p2} & \cdots & x_pv_{pp} \end{bmatrix} \tag{22}$$

This structure is easily generalized to the case of more than one copolymer or to copolymers of more then two types of units. Knowing the matrix **A**′, one writes its characteristic equation $F(\lambda)$ and deduces the quantities S_i defined in eq 15. As in the preceding case one evaluates the first quantities q_{ijn} and using eq 17 one obtains Q_{ij} and hence $I(q)$.

Effect of Polydispersity. Until now we have assumed that all the molecules of the same species were identical. Because of the model used here, the structure of the polymer of species i appears only through the quantities x_i for a homopolymer and x_i', x_j', and x_{ij}' for a copolymer. It is therefore clear that in the case of a polydisperse system, it is sufficient to replace these quantities by their average values. This means, for instance, that we have to write[8]

$$x_i = \sum_k N_{ik}n_{ik}'^2P_{ik}(q) \tag{23}$$

where N_{ik} is the number of molecules of species i with degree of polymerization n_{ik} and structure factor $P_{ik}(q)$. For the copolymer 1-2 we have

$$x_{12}' = \sum_i\sum_j N_{12ij}n_{1i}'n_{2j}'P_{12ij}(q)$$

$$x_1' = \sum_i N_{12i}n_{1i}'^2P_{1i}(q) \tag{23'}$$

where N_{12ij} is the number of copolymers having n_{1i}' monomers of type 1 and n_{2j}' monomers of type 2, and $N_{12i} = \sum_j N_{12ij}$.

As already suggested one can replace a polydisperse copolymer by a mixture of homopolymers.[8a] This immediately transforms the matrix (22) into the matrix **A** of eq 18 showing the consistency of both results. The equations established previously are therefore valid, of course, in the framework of our model in the case of polydisperse mixtures of homopolymers and copolymers.

As an example let us evaluate x_a', x_b', and x_{ab}' for a diblock copolymer made by anionic polymerization. In this case, it is possible to assume that the polydispersities of the sequences have no correlations. We shall use the well-known Zimm–Schultz distribution[9]

$$f(n') = [y^k/\Gamma(k)]n'^{k-1}\exp(-yn')$$

$f(n')$ is a normalized weight distribution, $k/(k - 1) = n_w'/n_n'$, n_w' and n_n' are the weight- and number-average degrees of polymerization, y is the quantity k/n_w', and $\Gamma(k)$ is the gamma function. Assuming that the chains are Gaussian, one writes

$$P(q) = (2/z^2)(z - 1 + \exp(-z))$$

where $z = q^2R^2 = q^2b^2n'/6$, R is the radius of gyration, and b is the statistical length. If we use these relations, a straightforward calculation gives[10]

$$x_1' = Nn_1'^2\left[\frac{2}{z_1} - \frac{2}{z_1^2} + \frac{2}{z_1^2}\left(\frac{1}{1 + \dfrac{z_1}{k_1 - 1}}\right)^{k_1-1}\right]$$

$$x_{12}' = Nn_1'n_2'\frac{1}{z_1z_2}\left[1 - \left(\frac{1}{1 + \dfrac{z_1}{k_1 - 1}}\right)^{k_1-1}\right] \times \left[1 - \left(\frac{1}{1 + \dfrac{z^2}{k_2 - 1}}\right)^{k_2-1}\right]$$

k_1 and k_2 characterize the polydispersities of the sequences

1 and 2, respectively; $z_1 = q^2b^2n_1/6$ and $z_2 = q^2b^2n_2/6$.

Relations with Thermodynamics. In our final eq 17 and 18, the thermodynamic variables are the excluded volume parameters v_{ij} which are functions of concentration. In dilute solution they are related to the quadratic terms as a function of the concentrations of the different species, but in some cases, especially if one wants to extrapolate these results to the bulk, it would be useful to determine the v_{ij} from thermodynamic quantities. The quantities used in this paper are volume fractions. If the number of solvent molecules per unit volume is called N_s, one can define the volume fraction, ϕ_i, of the species i in a mixture of homopolymers by the relation

$$\phi_i = \frac{N_in_i'}{N_s + \sum_i N_in_i'} = \frac{N_in_i'}{N}$$

n_i' is therefore the ratio of the volume occupied by one molecule of species i to the volume v_s of one solvent molecule which is called the unit cell. N is the total number of unit cells per unit volume (i.e., $Nv_s = 1$). We can define the free enthalpy per unit cell, G_c (the volume v_s of a unit cell being the volume of a solvent molecule) as

$$G_c = G/(N_s + \sum N_in_i') \tag{24}$$

where G_c is an intensive quantity and can be expressed as a function of the ϕ_i alone. We can eliminate the volume fraction of the solvent ϕ_s since $\phi_s + \sum\phi_i = 1$. If we assume that for $q = 0$ we have to reproduce the thermodynamic results obtained from the theory of multicomponent systems, one easily obtains[4]

$$v_{ij} = \frac{v_s}{kT}\frac{\partial^2 G_c}{\partial\phi_i\partial\phi_j} \tag{25}$$

$$v_{ii} = \frac{v_s}{kT}\left(\frac{\partial^2 G}{\partial\phi_i^2} - \frac{1}{\phi_in_i'}\right) \tag{25$'$}$$

If we assume that the Flory–Huggins theory is valid for these systems, we can write G_c for a mixture of homopolymers as[11]

$$G_c = kT[\phi_s \ln \phi_s + \sum\phi_i \ln \phi_i + \phi_s \sum\chi_{is}\phi_i + \sum_{ij}\chi_{ij}\phi_i\phi_j] \tag{26}$$

where χ_{ij} is the interaction parameter. The substitution of eq 26 into eq 25 gives

$$v_{ii} = v_s(1/\phi_s - 2\chi_{is}) \tag{27}$$

$$v_{ij} = v_s(1/\phi_s - \chi_{is} - \chi_{js} + \chi_{ij}) \tag{27$'$}$$

and this result is also valid for copolymers.

Spinodal. As we have already mentioned, if $F(1) = 0$ is satisfied, the scattered intensity diverges and one reaches the spinodal if this happens at $q = 0$.

Therefore, our equation of the spinodal coincides with the characteristic equation of the matrix **A** (eq 18 or 22) for $q = 0$. **A** is a $p \times p$ matrix and not the classical $(p + 1) \times (p + 1)$ matrix obtained when one starts from the second derivative of G. This can, in some cases, simplify the calculations.

It can happen that $F(1) = 0$ for $q \neq 0$. This has been predicted for pure block copolymers[12] but, following the structure of eq 18, this can be quite general. If there are such transitions, they can be interesting to identify since they cannot be detected by classical thermodynamics. This point is worthy of discussion and we shall come back to it in the Experimental Section.

Case of a Copolymer in Solution. The general equation we have given in the first part can be solved exactly for any system. Since we are interested in a copolymer in solution, we shall give the results now and leave for the Appendix the case of one copolymer with a different homopolymer.

In the case of a diblock copolymer AB, the matrix **A** becomes

$$\begin{bmatrix} x_a'v_a + x_{ab}'v_{ab} & x_a'v_{ab} + x_{ab}'v_b \\ x_b'v_{ab} + x_{ab}'v_a & x_b'v_b + x_{ab}'v_{ab} \end{bmatrix} \tag{28}$$

Its characteristic equation is

$$F(\lambda) = \lambda^2 + \lambda(x_a'v_a + x_b'v_b + 2x_{ab}'v_{ab}) + (x_a'x_b' - x_{ab}'^2)(v_av_b - v_{ab}^2)$$

giving immediately the denominator $F(1)$ and the sums S_1 and S_2. The direct calculation of Q_{0AA}, Q_{0AB}, Q_{1AA}, and Q_{1AB} is straightforward, leading to the following result:

$$Q_{0AA} = v_ax_a'^2 + v_bx_{ab}'^2 + 2v_{ab}x_a'x_{ab}' \tag{29a}$$

$$Q_{0AB} = v_ax_a'x_{ab}' + v_bx_b'x_{ab}' + v_{ab}(x_a'x_b' + x_{ab}'^2) \tag{29b}$$

$$Q_{1AA} = x_a'^3v_a^3 + 2x_{ab}'^3v_{ab}v_b + x_a'x_{ab}'^2(2v_av_b + 3v_{ab}^2) + 4x_a'^2x_{ab}'v_av_{ab} + x_a'^2x_b'(v_{ab}^2 + v_b^2) + 2x_a'x_b'x_{ab}'v_{ab}v_b \tag{29c}$$

$$Q_{1AB} = x_a'^2x_{ab}'v_a^2 + x_{ab}'x_b'^2v_b^2 + (x_{ab}'^3 + 3x_a'x_b'x_{ab}')v_{ab}^2 + v_av_{ab}(3x_a'x_{ab}'^2 + x_a'^2x_b') + v_av_bx_a'x_b'x_{ab}' + v_av_b(x_a'x_{ab}'^2 + x_{ab}'^3) + v_bv_{ab}(2x_b'x_{ab}'^2 + x_a'x_b'^2) \tag{29d}$$

Putting these results into eq 21 leads to the general formula

$$I(q) = \{a^2x_a' + b^2x_b' + 2_{ab}x_{ab}' - (x_a'x_b' - x_{ab}'^2) \times (a^2v_b + b^2v_a - 2_{ab}v_{ab})\}/\{1 + x_a'v_a + x_bv_b + 2v_{ab}x_{ab}' + (x_a'x_b' - x_{ab}'^2)(v_av_b - v_{ab}^2)\} \tag{30}$$

which reduces to known results in special cases. For example, in a monodisperse system at $q = 0$ or for a statistical copolymer $x_a'x_b' - x_{ab}'^2 = 0$. Equation 30 reduces to the simple form characterizing a homopolymer if one defines

$$(n_a + n_b)\bar{a} = an_a + bn_b$$

$$(n_a + n_b)^2\bar{v} = n_a^2v_a + n_b^2v_b + 2n_an_bv_{ab} \tag{31}$$

It is well-known that in the bulk the radiation scattered by a copolymer exhibits a peak for a given value of q.[12] This peak increases with the interaction parameter χ. It becomes infinite for a given value of χ depending on the structure. This leads us to say that we cross a generalized spinodal at this value of the interaction parameter. It is interesting to see if such a peak can be obtained for a copolymer in solution. This requires that the denominator of eq 30 vanish for finite q. In order to show that this is possible, let us assume that the two parts A and B are identical, i.e., $x_a' = x_b'$, and write

$$v_a = v + \epsilon$$

$$v_b = v - \epsilon$$

$$v_{ab} = v + w$$

Hence, the denominator of eq 30 becomes

$$F(1,q) = 1 + 2Nn'^2[2vP_T(q) + wP_{ab}(q)] - 4N^2n'^4\chi(q)[\epsilon^2 + w(2v + w)] \tag{32}$$

where $\chi(q) = P_T(P_a - P_T)$. The intramolecular form factors $P_a(q)$, $P_T(q)$, and $P_{ab}(q)$ are normalized to unity at $q = 0$. Therefore, $\chi(0) = 0$ but $\chi(q)$ has a maximum for qR of the order of unity. The spinodal is defined by

$$F(1,0) = 1 + 2Nn^2[2v + w] = 0 \qquad (33)$$

Above the spinodal, the quantity $2v + w$ is slightly negative and if the factor $\epsilon^2 + w(2v + w)$ is positive, then one subtracts from the first two terms a quantity which has a maximum, and therefore, one may reach a zero value for $F(q)$. This includes a phase separation without any anomaly at $q = 0$. This argument is purely qualitative. It is based on the fact that v_a and v_b are different. The same behavior can be observed for $v_a = v_b$ but $n_a' \neq n_b'$. It was interesting to check whether or not this behavior could be observed experimentally and this point will be discussed later in the Experimental Section.

It would be interesting to observe the effect of a copolymer AB when it is added to a mixture of homopolymers A and B, by writing down the corresponding form of the denominator in eq 30, i.e.

$$1 + v_a(x_a + x_a') + v_b(x_b + x_b') + 2v_{ab}x_{ab}' + (v_av_b - v_{ab}^2)[(x_a + x_a')(x_b + x_b') - x_{ab}'^2]$$

where we have used primes for the quantities characterizing the copolymer. In the usual case of a repulsive interaction between A and B monomers such that $v_av_b - v_{ab}^2$ is negative, and in the limit of $q = 0$, this expression enables one to study the enhancement of solubility due to the presence of the copolymer. One also observes that the system shows mesomorphic phases only if this expression goes to zero at a finite value of q (i.e., $q \neq 0$).

Extrapolation to the Bulk. In order to obtain an equation valid in the bulk we shall use the Flory–Huggins value for v_{ij} given by eq 27 and 27′ and let ϕ_s go to zero. This gives

$$I(q) = (a - b)^2 \frac{x_a'x_b' - x_{ab}'^2}{x_a' + x_b' + 2x_{ab}' - (2\chi_{ab}/N)(x_a'x_b' - x_{ab}'^2)} \qquad (34)$$

which has been previously obtained by Leibler.[12] In the case of a mixture of homopolymer, $x_{ab}' = 0$ and we have

$$I^{-1}(q)(a - b)^2 = 1/x_a' + 1/x_b' - 2\chi_{ab}/N \qquad (35)$$

which is the formula obtained by de Gennes.[3] This result is not surprising since it is known that the RPA and the linear chain model used here are equivalent.[14]

Experimental Section

In order to check the validity of our results we investigated the case of a diblock copolymer by the small-angle neutron scattering technique. This allows study of the scattering intensity in a convenient range of q values where the maxima which are expected from the theory should be observable.

It was decided to use a copolymer which does not have a large incompatibility in order to be able to reach high enough concentrations. Therefore, we used a polystyrene–poly(methyl methacrylate) (PS–PMMA) copolymer which was prepared by anionic polymerization.

The monomers, deuterated styrene (PSD) and methyl methacrylate, were distilled over sodium before polymerization. The polymerization was carried out under argon by using tetrahydrofuran as solvent. The polymerization of styrene came first using potassium 1-phenylethyl as initiator at −75 °C. After completion of the reaction the terminal carbanion is replaced by addition of a few drops of 1,2-diphenyethylene to reduce the reactivity and avoid side reactions. The methacrylate was polymerized at −90 °C. The polymer was terminated by methanol and recovered by precipitation in excess methanol. It was fractionated afterward by using benzene as solvent and chlorobenzene as precipitant in order to eliminate any homopolystyrene. The composition was measured by elementary analysis, UV absorption, and dn/dc measurements. It was found to be 43% PSD and 57% PMMA.

Molecular weight was measured by light scattering, and polydispersity by GPC on the final product and the polystyrene precursor. A value of n_w'/n_n' of 1.25 was estimated for each block. The following values were used for our copolymer:

$$M_{n1}'(\text{PS}) = 83000, \qquad n_1' = 741$$

$$M_{n2}'(\text{PMMA}) = 110000, \qquad n_2' = 1100$$

$$M_{w1}/M_{n1} = M_{w2}/M_{n2} = 1.25$$

The scattering curve in the bulk was examined first. This should allow testing if, from eq 34, a value for the interaction parameter χ_{ab} can be obtained.

A second experiment was suggested at the end of the Theoretical Section. The question was raised on how the peak, which is characteristic of a block copolymer, does change in the vicinity of the spinodal. For such experiments, cyclohexanol, which is known to be a solvent for PS, PMMA, and their copolymer, was used. The Θ temperatures for both polymers are fairly close.[13] Accordingly, the interaction parameters between this solvent and these two polymers are very close and they were assumed equal in the calculations.

Preparation of Samples. Bulk. A bulk sample of PSD–PMMA was prepared for the SANS measurement in a brass vacuum mold. The sample dimensions are 2 cm in diameter and 1 mm in thickness. Dried polymer powder of 0.4 g was first evacuated in the brass mold to a vacuum of 10^{-1} mmHg and was maintained throughout the molding process. Thereafter the mold was heated and kept at 150 °C for 30 min and then quenched in ice water. This molding process resulted in bulk samples free of any gas bubbles. A polystyrene homopolymer specimen prepared in the process was examined with a small-angle X-ray scattering unit. Over the q region between 5×10^{-3} and 5×10^{-1} Å^{-1}, no significant scattered intensities were observed, indicating absence of air bubbles.

Solution. A solution was prepared of 20% by weight polymer in cyclohexanol; a large concentration was used in order to increase the signal-to-noise ratio and the magnitude of the last term in the denominator of eq 30. For the background subtraction a mixture of low molecular weight compounds was prepared with the same ratio of atoms as in the 20% solution, assuming 43% PSD content. It contained weight fractions 0.700 of cyclohexanol, 0.185 of acetone, 0.086 of benzene-d_6, and 0.029 of benzene.

The solvent and polymer were heated in an oven at 100 °C to form a solution and injected into a heated cell, forming a clear solution. The cell was rapidly cooled in ice water to solidify the contents. When reheated, the solution re-formed giving a clear, single-phase solution.

The cells containing the solution and liquid mixture were quartz containers with flat sides 1 mm apart. The solid was placed between two quartz disks. Each of the cells was placed in a cell holder equipped with resistive heaters. Temperature was measured by a thermocouple and a proportional voltage source was used to maintain temperature control of ±0.1 °C in the holder giving ±1 °C in the sample.

The precipitation point of the 20% solution was determined by placing the sample in the cell holder and maintaining a temperature that dissolved the polymer. A laser beam was directed through the sample and scattered intensity was measured at an angle of about 15°. As the temperature was slowly lowered, the scattered intensity increased sharply at the precipitation point. The lowest temperature neutron scattering run was at 76 °C, just slightly above the precipitation point. The sample was examined visually before and after the neutron scattering experiment and showed no signs of cloudiness.

Neutron Experiment. Small-angle neutron scattering (SANS) measurements of the block copolymer samples were taken on the National Bureau of Standards SANS spectrometer.[15] The spectrometer was used with focused collimation having 15″ of arc or less on the sample and at an incoming neutron wavelength of 7.5 Å determined by a velocity selector having 25% wavelength resolution. The spectrometer's area detector was positioned 3.6 m from the sample for all our measurements. Resolution of the scattered beam was controlled by the dimension of the sample area perpendicular to the beam. The area was a 1.5-cm circle. This leads to a divergence of 15″ of arc at the detector. Samples

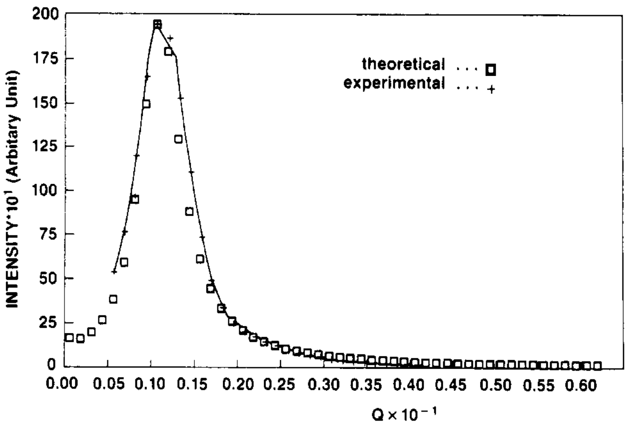

Figure 3. Scattered intensity by a diblock copolymer PSD-PMMA at 160 °C as function of q.

of the block copolymer were contained in quartz sample holders if liquid and stacked in equivalent-thickness quartz plates for the solid. These sample holders in turn were positioned in a specially designed sample-changing fixture of the spectrometer, but only one position of the fixture was used to ensure that our samples were precisely positioned for each measurement. The shape of the incoming beam was determined by using a beam attenuator. Next, the beam stop was precisely positioned in front of the detector by using a standard aluminum scatterer. Data were then taken on PSD–PMMA in cyclohexanol, the background liquid prepared to yield equivalent density scattering, and the solid PSD–PMMA. Three different temperatures were used for the polymer in solution and for the solid. These temperatures were 76 °C, near the transition, 82 and 110 °C for the liquid mixture, and 20, 110, and 160 °C for the solid. After these measurements were made, a measurement of the background was obtained. Finally, a beam attenuator was inserted into the incoming beam and the beam stop removed so that transmission measurements of the samples could be made. To get the corrected data I_{cor}, we used the relation

$$(I_{\mathrm{S}} - I_{\mathrm{B}}) - (T_{\mathrm{S}}/T_{\mathrm{M}})(I_{\mathrm{M}} - I_{\mathrm{B}}) = I_{\text{cor}} \qquad (36)$$

where I_{S}, I_{M}, and I_{B} are the monitor-normalized intensities for the sample, monomer, and background measurements for each elements of the detector. T_{S} and T_{M} are the transmission of the sample and background liquid. The data were not normalized to an absolute cross section. The transmission of the PSD–PMMA cyclohexanol was 0.552 ± 0.003 while that for background liquid was 0.558 ± 0.003. These are equivalent within one standard deviation. No resolution or multiple scattering corrections were applied to the data.

Results and Discussion

Bulk. A conspicuous peak was observed in the SANS result of the bulk samples (Figure 3). Only the result of 160 °C is shown. The curve for the solid at the other temperatures does not change its shape with temperature but only shows slight intensity changes. Since the shape of the peak depends strongly on χ_{12} and since χ_{12} is supposed to be a function of temperature, different results at different temperatures were expected. This is the reason that runs at 160 and 110 °C and room temperature were made. Unfortunately, there was no significant change in $I(q)$. This observation suggests either that χ_{12} does not depend on temperature significantly or, more likely, that equilibrium was not reached at 110 °C and room temperature.

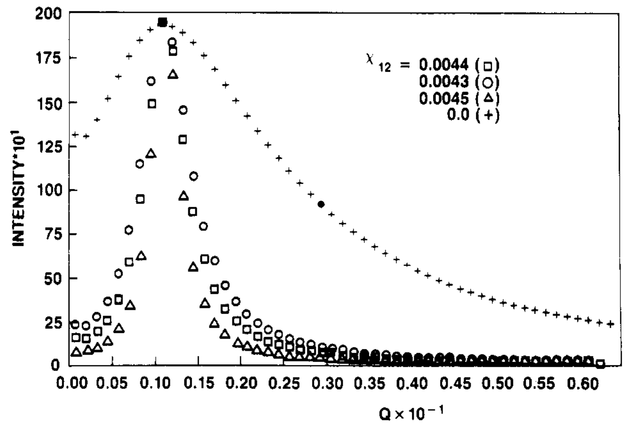

Figure 4. Theoretical values of the scattered intensity for different values of the interaction parameter χ reduced to the same height of the maximum.

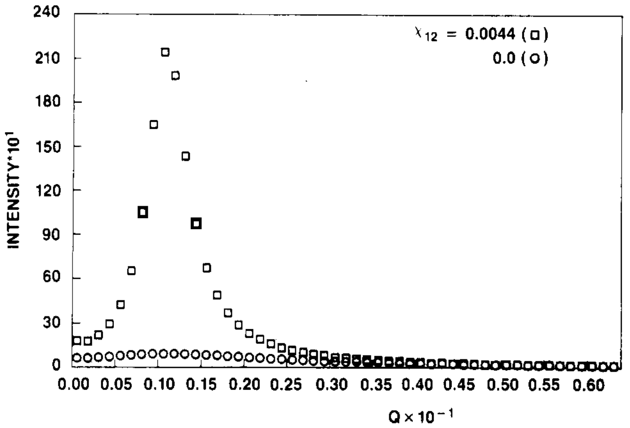

Figure 5. Comparison between the scattered intensity of the sample ($\chi = 4.4 \times 10^{-3}$) and of a sample without interaction parameter ($\chi = 0$), using the same units.

Estimates of the resolution corrections for both the angular and wavelength spread were so as to assess their effect on the broadening of the main peak. These corrections amount to a small fraction of the observed width in both the liquid and solid samples. The intensity of the scattering maximum was so large compared with the background and the incoherent intensities that no data subtraction was undertaken. The peak occurred at the q value of 0.0115 Å^{-1} and its half-width is much narrower than the peak observed for a copolymer made of one deuterated and one hydrogenated polystyrene block.[16] The fact that only one maximum is present strongly suggests that the diblock polymer used herein does not segregate to a layer structure. Otherwise, one expects to observe several higher order scattering maxima in Figure 3. Strictly speaking, other experimental evidence is needed to ensure that the bulk specimens are in a homogeneous state so that the equations derived in a mean-field approach are applicable. Since there was no absolute calibration, it was not possible to compare the values of the scattering intensity with the theoretical predictions. Therefore, the theoretical and experimental curves were set equal at the maximum. Increasing χ_{12} narrows the theoretical peak very fast and the best fit with the data is obtained for $\chi_{12} = 0.0044$ (note that χ is defined as the interaction parameter per monomeric unit). The theoretical curves have been calculated by taking into account the polydispersity of the samples using in eq 34 the values of x_{a} and x_{b} evaluated from eq 23′. In fact, in order to obtain the best fit $n_{\mathrm{w}}/n_{\mathrm{n}} = 1.33$ had to be used instead of 1.25, which was obtained by GPC (cf. Figure 3). If the system is really at equilibrium, this kind of experiment is perhaps the most precise method for determining χ_{12} (recalling that it can be used only when the polymers are compatible enough to avoid phase separation).

Figure 4 shows how sensitive the scattering intensity is and how a change of 2% in the parameter χ could change the shape of the scattering curve.

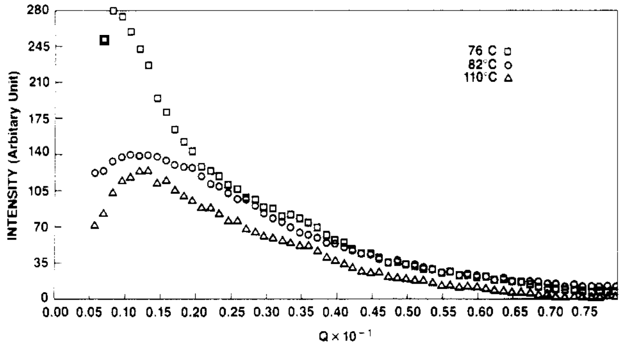

Figure 6. Experimental results on the scattered intensity by a 20% copolymer solution in cyclohexanol at different temperatures.

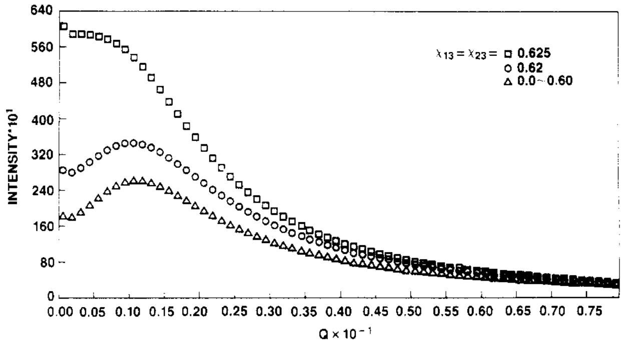

Figure 7. Theoretical curves for the intensity scattered by the same diblock copolymer for $\chi_{12} = 4.4 \times 10^{-3}$ and different values of $\chi_{13} = \chi_{23}$.

In Figure 5 the actual observed peak is compared to the one which can be obtained from a copolymer made of two identical blocks differing only by their coherent scattering lengths. One observes a striking difference.

Solution. The SANS results of a 20% solution at three different temperatures are presented in Figure 6. No measurement was made below 76 °C because at this temperature the solution becomes cloudy, which is consistent with the Θ point of these copolymers.[13]

The interesting fact which is also predicted by the theory is that the peak height increases considerably when the temperature decreases as obtained by Roe et al.[17] using small-angle X-ray diffraction on styrene–butadiene block copolymers. In our case, we hoped that if a temperature low enough could be reached, there would be divergency for $q \neq 0$.

A quantitative comparison between theoretical and experimental values was attempted. This is not easy since even with accurate knowledge of the molecular characteristics of the sample there are three parameters to adjust χ_{12}, χ_{13}, and χ_{23}. One can use the value of χ_{12} obtained from the experiment in bulk, but this quantity was measured at high temperature and we know nothing about its temperature dependence. Moreover, it is not clear whether or not one can use the same χ value in bulk and in solution.

Having these difficulties in mind, we tried however to evaluate the theoretical values of $I(q)$ (on an arbitrary scale) using $\chi_{12} = 0.0044$ and different values for $\chi_{13} = \chi_{23}$ (see Figure 7). If this last parameter is increased a little further, the maximum is lost and it is restored only if χ_{12} is increased. One observes that the three curves of Figure 7 are very similar to the experimental curves of Figure 6.

Until now, the peak position has not been discussed. Equation 30 and 34 show that this position coincides with the maximum of the quantity $x_a x_b - x_{ab}$, and should therefore be the same in bulk and in solution if the molecular dimensions are the same. This should be the case since the solvent is near the Θ conditions. The q value of the peak $q = 0.0115$ Å^{-1} corresponds to the predicted value using Θ dimensions of PS and PMMA from the literature.[18] This has been observed within the experimental accuracy.

Conclusion

In the framework of a mean-field approximation expressions have been given for the scattered intensity of a multicomponent system containing copolymers, at any angle and any concentration. These expressions should be valid in concentrated solutions where monomers are expected to be randomly distributed. An important feature of these results is that they show that the scattering intensity diverges either at zero angle characterizing the spinodal or at a finite angle giving what we have called the "generalized spinodal".

The results are not expected to be valid when the interactions are strong, leading to large fluctuations in the composition. For instance, it is probable that the formation of micelles cannot be predicted by this formalism. Nevertheless, it has been shown that it can be applied to block copolymers in the vicinity of phase separation, thereby giving a new tool for studying such systems.

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Appendix

Consider a solution containing in addition to the solvent a mixture of one copolymer A–B characterized by the already defined quantities x_a', x_b', and x_{ab}' and one homopolymer of type c. There are six excluded volume parameters υ_a, υ_b, υ_c, υ_{ab}, υ_{ac}, and υ_{bc}. The matrix corresponding to this system is easily obtained from the matrix (22) and its characteristic equation reads

$$F(\lambda) = \lambda^3 - S_1\lambda^2 + S_2\lambda - S_3 \qquad \text{(A.1)}$$

where S_1, S_2, and S_3 are given by

$$S_1 = -(\upsilon_a x_a' + \upsilon_b x_b' + \upsilon_c x_v + 2\upsilon_{ab} x_{ab}')$$

$$S_2 = (\upsilon_a\upsilon_b - \upsilon_{ab}^2)x_a'x_b' + (\upsilon_a\upsilon_c - \upsilon_{ac})x_a'x_c + (\upsilon_b\upsilon_c - \upsilon_{bc})x_b'x_c - (\upsilon_a\upsilon_b - \upsilon_{ab}^2)x_{ab}'^2 + 2(\upsilon_c\upsilon_{ab} - \upsilon_{ac}\upsilon_{bc})x_{ab}'x_c$$

$$S_3 = -(\upsilon_a\upsilon_b\upsilon_c + 2\upsilon_{ab}\upsilon_{ac}\upsilon_{bc} - \upsilon_a\upsilon_{bc}^2 - \upsilon_b\upsilon_{ac}^2 - \upsilon_c\upsilon_{ab}^2)x_c(x_a'x_b' - x_{ab}'^2) \qquad \text{(A.2)}$$

This gives the following expression for the denominator Δ of all the quantities Q_{ij}:

$$\Delta \equiv F(\lambda = 1,q) = 1 + \upsilon_a x_a' + \upsilon_b x_b' + \upsilon_c x_c + 2\upsilon_{ab}x_{ab}' + (\upsilon_a\upsilon_b - \upsilon_{ab}^2)(x_a'x_b' - x_{ab}'^2) + (\upsilon_a\upsilon_c - \upsilon_{ac}^2)x_a'x_c + (\upsilon_b\upsilon_c - \upsilon_{bc}^2)x_b'x_c + 2(\upsilon_c\upsilon_{ab} - \upsilon_{ac}\upsilon_{bc})x_{ab}'x_c + (\upsilon_a\upsilon_b\upsilon_c + 2\upsilon_{ab}\upsilon_{ac}\upsilon_{bc} - \upsilon_a\upsilon_{bc}^2 - \upsilon_b\upsilon_{ac}^2 - \upsilon_c\upsilon_{ab}^2) \times x_c(x_a'x_b' - x_{ab}'^2) \qquad \text{(A.3)}$$

The calculation of Q_{ij} is done by using the definition

$$Q_{ij} = Q_{0ij}(1 - S_1 + S_2) + Q_{1ij}(1 - S_1) + Q_{2ij}$$

where Q_{0ij}, Q_{1ij}, and Q_{2ij} are obtained by straightforward but tedious calculations. We just give the final results:

$$\Delta\cdot Q_{aa} = \upsilon_a x_a'^2 + \upsilon_b x_{ab}'^2 + 2\upsilon_{ab}x_a'x_{ab}' + (\upsilon_a\upsilon_b - \upsilon_{ab}^2)(x_a'x_b' - x_{ab}'^2)x_a' + (\upsilon_a\upsilon_c - \upsilon_{ac}^2)x_a'^2x_c + (\upsilon_b\upsilon_c - \upsilon_{bc}^2)x_{ab}'^2x_c + 2(\upsilon_c\upsilon_{ab} - \upsilon_{ac}\upsilon_{bc})x_a'x_{ab}'x_c + (\upsilon_a\upsilon_b\upsilon_c + 2\upsilon_{ab}\upsilon_{ac}\upsilon_{bc} - \upsilon_a\upsilon_{bc}^2 - \upsilon_b\upsilon_{ac}^2 - \upsilon_c\upsilon_{ab}^2) \times (x_a'x_b' - x_{ab}'^2)x_a x_c \qquad \text{(A.4)}$$

Q_{bb} is obtained from this equation by exchanging a and b.

$$\Delta\cdot Q_{cc} = x_c^2 v_c + (v_a v_c - v_{ac}^2)x_a' + (v_b v_c - v_{bc}^2)x_b' + 2(v_c v_{ab} - v_{ac}v_{bc})x_{ab}' + (v_a v_b v_c + 2v_{ab}v_{ac}v_{bc} - v_a v_{bc}^2 - v_b v_{ac}^2 - v_c v_{ab}^2)(x_a' x_b' - x_{ab}'^2) \quad (A.5)$$

$$\Delta\cdot Q_{ab} = v_a x_a' x_{ab}' + v_b' x_b' x_{ab}' + v_{ab}(x_a' x_b' + x_{ab}'^2) + (v_a v_b - v_{ab}^2)(x_a' x_b' - x_{ab}'^2)x_{ab}' + (v_a v_c - v_{ac}^2)x_a' x_{ab}' x_c + (v_b v_c - v_{bc}^2)x_b' x_{ab}' x_c + (v_c v_{ab} - v_{ac}v_{bc})(x_{ab}' + x_a' x_b')x_c + (v_a v_b v_c + 2v_{ab}v_{ac}v_{bc} - v_a v_{bc}^2 - v_b v_{ac}^2 - v_c v_{ab}^2)(x_a' x_b' - x_{ab}'^2)x_{ab}' x_c \quad (A.6)$$

$$\Delta\cdot Q_{ac} = x_a' x_c v_{ac} + (v_b v_{ac} - v_{ab}v_{bc})x_b' + (v_{ab}v_{ac} - v_a v_{bc})x_{ab}' + x_{ab}' x_c v_{bc} + (v_a v_{bc} - v_{ab}v_{ac})x_a' + (v_{ab}v_{bc} - v_b v_{ac})x_{ab}' \quad (A.7)$$

Q_{bc} is obtained from this last equation simply by changing a to b. As already mentioned, this formulation is also valid for a mixture of three homopolymers A–C, and a copolymer AB changing only the definition of x_a', x_b', and x_{ab}'. In the absence of the copolymer, the system is reduced to three homopolymers and the corresponding values of Q_{ij} are immediately obtained by letting $x_{ab}' = 0$ and $x_a' = x_a$, $x_b' = x_b$.

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Rayleigh–Brillouin Spectra of Poly[(phenylmethyl)siloxane] under High Pressures

George Fytas,*,† Gerd Meier,‡ and Thomas Dorfmüller

Faculty of Chemistry, University of Bielefeld, D-4800 Bielefeld 1, West Germany.

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ABSTRACT: We report polarized Rayleigh–Brillouin spectra of bulk poly[(phenylmethyl)siloxane] (PPMS) with a molecular weight of about 2500 in the temperature range 20–150 °C and in the pressure range 1–950 bar. The frequency of the hypersonic waves, f_B, and the temperature T_{max}, at which the Brillouin line width has its maximum value, are both increasing functions of the hydrostatic pressure P. On the other hand, the relaxation strength, R, is virtually independent of the hydrostatic pressure. The plane (P,T_{max}) consists of an isokinetic curve, which is in agreement with previous high-pressure photon correlation measurements. It appears that the two light scattering techniques monitor the same physical process.

Introduction

Brillouin scattering (BS) and photon correlation spectroscopy (CS) have been applied to study relaxation processes in bulk polymers.[1-4] Above the glass transition temperature, the so-called local primary glass–rubber relaxation dominates the highly nonexponential photon correlation functions of the scattered light from density fluctuations. The corresponding mean relaxation time, $\bar{\tau}$ (1 to 10^{-6} s), exhibits a strong temperature and pressure dependence.[5] On the other hand, the same structural relaxation process affects, in principle, the high-frequency (and hence high temperature) Brillouin spectra via the stress correlation function.[6] The frequency shift, f_B, and the line width, $2\Gamma_B$, of the Brillouin doublet exhibit a dispersion with respect to temperature. The calculation of the relaxation time τ ($=1/2\pi f_{max}$, where f_{max} is the frequency shift at temperature T_{max} at which $2\Gamma_B$ has its maximum value) involves the simplest type of analysis.[3] An alternative approach to analyze the Brillouin spectra[4,6] leads to the temperature dependence of τ, which requires knowledge of the adiabatic ultrasonic frequency f_0. The extent of the information which can be extracted by studying hypersonic dispersion has recently been examined by taking into account the temperature dependence of the Brillouin spectra.[7] In this paper, we performed high-pressure Brillouin scattering measurements on bulk polymers using Fabry–Perot interferometry. The objective is to investigate the pressure effect on f_B and $2\Gamma_B$ of the Brillouin doublet. We have chosen poly[(phenylmethyl)siloxane] (PPMS) for this study on account of the convenient temperature range and the existence of photon correlation high-pressure measurements.[8] Thus, the characteristic times for the structural relaxation process obtained by the two light scattering techniques can be compared in terms of their pressure dependence.

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† Permanent address: Department of Chemistry, University of Crete, Iraklion, Greece.

‡ Present address: Institute of Physical Chemistry, University of Mainz, D-6500 Mainz, West Germany.

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