Regular Block-Copolymeric Star Molecules. Static Structure Factor and First Cumulant of the Dynamic Structure Factor

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ABSTRACT: The static dynamic scattering behavior of regular heterogeneous star molecules is treated theoretically. In these stars the inner and outer sections of the rays have different refractive indices, and by the choice of a suitable solvent either the inner part or the outer part of the star molecule can be made invisible. If the outer sections are invisible, theory shows that the mean square radius of gyration $\langle S^2\rangle_{\mathrm{app}}$, the diffusion coefficient D^0_{app}, and the whole scattering behavior are that of a star which seems to have no outer ray sections. However, if the inner part is made invisible the apparent molecular quantities $\langle S^2\rangle_{\mathrm{app}}$ and D^0_{app} differ from those of a homogeneous star molecule, and the angular dependence of the particle scattering factor and of the first cumulant now more nearly resembles that of a hollow sphere. If the total refractive index increment is zero, $\langle S^2\rangle_{\mathrm{app}}$ goes to minus infinity while the apparent diffusion coefficient D^0_{app} goes to plus infinity. Preliminary measurements with an 18-arm star molecule composed of polyisoprene inner blocks and polystyrene outer blocks show good agreement with theory. For comparison the total time dependence of the dynamic structure factor for a heterogeneous Gaussian dumbbell is calculated.

Introduction

Recent refinement in the technique of anionic polymerization,[1,2] development of equipment,[3] and progress in theory[4-6] have made possible the synthesis and characterization of well-defined polymeric structures such as regular star and combmolecules. Here we present a theoretical treatment and preliminary measurements in dilute solution of regular star molecules in which the inner sections of the rays are polyisoprene (PI) blocks while the outer ray sections are polystyrene (PS) blocks. Such macromolecules are interesting not only in technical application but also for theoretical reasons.

We may ask how such chemically heterogeneous polymers behave dynamically, since PI is an example of a highly flexible chain while PS is more rigid, with a characteristic ratio twice as large as that of PI.[7] It will be informative for the overall properties of such stars to know the detailed dynamic behavior of the two blocks in the branched structure. It is possible to study the two joint blocks separately by light scattering or neutron scattering techniques, since the two blocks have sufficiently different refractive indices. Thus, either block can be made invisible by choosing a solvent that matches its refractive index. Static light scattering can give information on the position of the blocks in space and whether they show segregation or collapse. In dynamic light scattering (LS) on the other hand, the question arises what diffusion coefficient and which internal modes of motion are observed when the inner or the outer block is made invisible; will it be the diffusion coefficient of the visible block or will there also be some contribution from the invisible block?

In the following we assume Gaussian chain behavior for any subchain that connects two segments in the star molecule. We are aware that such a model cannot completely describe the real situation of such block copolymers in solution. As a first approximation, however, this idealized model can still give some insight into the behavior of copolymeric systems. The present treatment is confined to the regime of very dilute solutions where intermolecular interactions can be neglected. The calculations include, for $f = 1$ and $f = 2$, linear block copolymers of types AB and ABA, respectively.

Static and Dynamic Structure Factors of Copolymers

Static Light Scattering. Following the general theory of the scattering of light, one finds for the scattering intensity of monodisperse copolymers in dilute solution, i.e., with neglect of intramolecular interactions,[8-10]

$$R(q) = Kc\sum_j^x\sum_k^x \nu_j\nu_k M_{0j}M_{0k}\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle/(\nu^2M) \quad (1)$$

where

$$q = (4\pi/\lambda)\sin(\theta/2) \quad (2a)$$

and

$$M = \sum_j M_{0j} \quad (2b)$$

In this equation $R(q)$ is the Rayleigh ratio at an angle θ and K is an optical constant describing the contrast of the scattering intensity of the solution over that of the pure solvent. For vertically polarized light this constant is given by

$$K = 4\pi^2(\nu n_0)^2/\lambda_0{}^4N_{\mathrm{a}} \quad (3)$$

where $\nu = \mathrm{d}n/\mathrm{d}c$ is the refractive index increment of the copolymer which has a degree of polymerization x. The jth monomeric unit in the molecule has molecular weight M_{0j} and a refractive index increment $\partial n/\partial c_j$. Thus, each monomeric unit scatters light according to its mass and its $\mathrm{d}n/\mathrm{d}c$. The exponential functions in eq 1 describe the phase relations between the two waves emerging from elements j and k at the positions $\mathbf{R}_j$ and $\mathbf{R}_k$, respectively, where $R_{jk} = |\mathbf{R}_j - \mathbf{R}_k|$, and the angular brackets denote the ensemble average over the distance R_{jk}. The copolymer may be made of s different components; then the refractive index increment of the total polymer is related to those of the components by[9,10]

$$\nu = \sum_{j=1}^{s} w_j\nu_j \quad (4)$$

where w_j is the weight fraction of the jth component.

Equation 1 may be conveniently written as

$$R(q)/Kc = S(q)/M \quad (5)$$

where $S(q)$ is the static structure factor defined as

$$S(q) = \nu^{-2}\sum_j^x\sum_k^x \xi_j\xi_k\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \quad (6a)$$

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where for convenience we have set

$$\nu_j M_{0j} = \xi_j \qquad (6b)$$

In a homopolymer, all units have the same molecular weight M_0 and the same refractive index increment, and eq 5 then reduces to the familiar relationship

$$R(q)/Kc = MP(q) \qquad (7)$$

where

$$P(q) = S(q)/S(0) = x^{-2}\sum_j^x\sum_k^x \langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \qquad (8)$$

is the particle scattering factor which is normalized to unity at $q = 0$. Introducing the particle scattering factor into the general equation for copolymers, we may write

$$R(q)/Kc = M_{\text{app}}P(q) \qquad (9)$$

where

$$P(q) = \sum_j^x\sum_k^x \xi_j\xi_k\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \Big/ \sum_j^x\sum_k^x \xi_j\xi_k \qquad (10)$$

and

$$M_{\text{app}} = S(0)/M = (\nu^2 M)^{-1}\sum_j^x\sum_k^x \xi_j\xi_k \qquad (11)$$

In general the apparent molecular weight M_{app} is different from the true molecular weight M of the molecule,[8,9] but for molecules of identical composition one always has $M_{\text{app}} = M$.

The first coefficient in the series expansion of $P(q)$ in terms of q^2 yields the mean square radius of gyration

$$P(q) = 1 - (1/3)\langle S^2\rangle_{\text{app}}q^2 + ... \qquad (12)$$

where

$$\langle S^2\rangle_{\text{app}} = \sum_j^x\sum_k^x \xi_j\xi_k\langle R_{jk}^2\rangle \Big/ \Big(2\sum_j^x\sum_k^x \xi_j\xi_k\Big) \qquad (13)$$

This apparent mean square radius of gyration is different from the geometric true mean square radius of gyration, which is defined as

$$\langle S^2\rangle = \sum_j^x\sum_k^x \langle R_{jk}^2\rangle/2x^2 \qquad (14)$$

Dynamic Light Scattering. Here the time correlation function (TCF) of the intensity, $\langle i(0)i(t)\rangle$, is measured and in most cases is related to the electric field TCF, $g_1(t)$, by

$$\langle i(0)i(t)\rangle = A + B|g_1(t)|^2 \qquad (15)$$

where

$$g_1(t) = \frac{|\langle E(0)E^*(t)\rangle|}{\langle E(0)E^*(0)\rangle} = S(q,t)/S(q,0) \qquad (16)$$

In these TCF's the intensity (electric field) at time zero is multiplied by the corresponding quantity at a certain delay time t, where for typical experiments t is of the order of 10^{-7}–10^{-3} s. The dominator in $g_1(t)$ may be recognized as the static structure factor, and the numerator is called the dynamic structure factor. The dynamic structure factor is defined similarly to $S(q)$ as

$$S(q,t) = (\nu^{-2})\sum\sum \xi_j\xi_k\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk}(t))\rangle \qquad (17)$$

where

$$\mathbf{R}_{jk}(t) \equiv |\mathbf{R}_j(0) - \mathbf{R}_k(t)| \qquad (18)$$

The angular brackets denote here, however, an average over the space–time distance distribution, while in the static structure factor only the equilibrium space distribution is needed.

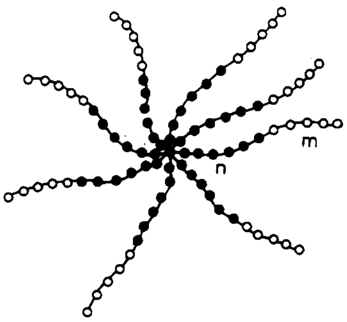

Figure 1. Sketch of a heterogeneous star molecule. The filled circles represent the n monomeric units of a polyisoprene block and the open circles the m monomeric units of a polystyrene block.

The dynamic structure factor is a decaying function of time, which in most cases is not a single exponential.[11-13] Still, the *initial* part of $S(q,t)$ can in every case be represented by a decay coefficient, Γ, that is called the first cumulant[14,15] of the TCF. From eq 16,

$$\Gamma = [-\partial \ln (S(q,t))/\partial t]_{t=0} = [-\partial \ln (g_1(t))/\partial t]_{t=0} \qquad (19)$$

For further calculations an equation of motion is needed which for polymers in solution must take into account the hydrodynamic interaction (HI) between segments. From Kirkwood's equation,[16] the first cumulant can be calculated[4] with the aid of a method due to Fixman,[17] Bixon,[18] and Zwanzig.[19] The result for the copolymer case is

$$\Gamma = S(q)^{-1}\sum_j^x\sum_k^x \xi_j\xi_k(\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q})\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \qquad (20)$$

where now the angular brackets denote the spatial *equilibrium* average, and $\mathbf{D}_{jk}$ is the diffusion tensor[16,20,21] which describes the HI:

$$\beta D_{jk} = \delta_{jk}/\zeta_j + (1 - \delta_{jk})(8\pi\eta_0 R_{jk})^{-1}(1 + \mathbf{R}_{jk}\cdot\mathbf{R}_{jk}/R_{jk}^2) \qquad (21)$$

where $\beta = 1/kT$.

In the limit of $q^2 \rightarrow 0$ the first cumulant is related to the translational diffusion coefficient as

$$\Gamma = D^0_{\text{app}}q^2 = S(0)^{-1}\sum\sum \xi_j\xi_k\langle(\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q})\rangle, \qquad (q \rightarrow 0) \qquad (22)$$

This diffusion coefficient is an apparent one[22] and reduces to the actual diffusion coefficient only when $\xi_j = \xi_k$ for all j and k.

The relationships given so far for the static and dynamic scattering and for the diffusion coefficient are valid for any type of molecule structure and for any equilibrium distribution of the distances R_{jk}. Precautions have to be taken, however, for rigid particles, where constraints have to be introduced in order to cut the contributions to the cumulant resulting from very fast motions which are not detected by the autocorrelators available at present.[23,24] To proceed further, the distribution function and the molecular model have to be specified.

Model

The model considered here is sketched in Figure 1. The star molecule has f rays, each consisting of an inner block with n monomeric units and an outer block with m monomeric units. Comparison of eq 6, 20, and 22 reveals that in all cases a double sum has to be evaluated over a function ϕ_{jk} that depends on the path length between a unit j and a unit k in the molecule. Evaluation of the double sum is facilitated by labeling the type of path by superscripts (i) and (o) and the length and composition of the path by subscripts; for instance ${}^{(i)}\phi^{(o)}{}_{s+n+l}$ denotes

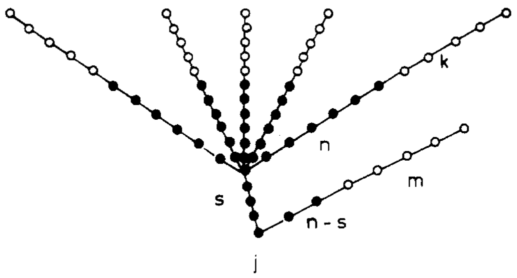

Figure 2. Heterogeneous star molecule with 6 rays represented as a rooted tree. A path from unit j (the root) to a unit k consists in this case of s units from the inner block of the one ray, n units from the inner block of another ray, and l units from the outer block, leading to element k.

a path which starts at a unit from the inner block and ends at a unit from the outer block (see Figure 2). The subchain contains in this case s units from the inner block of the one ray, n units from the inner block of another ray, and l units from the outer block of the same ray. With this nomenclature, eq 20 leads [25,26] to

$$\Gamma = f(T_\mathrm{i} + T_\mathrm{o})/S(q) \tag{23}$$

with

$$T_\mathrm{i} = \xi_\mathrm{i}^2[n + 2\sum_s^n\sum_k^{s-1} {}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_k] + \xi_\mathrm{i}\xi_\mathrm{o}\sum_s^n\sum_l^m {}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n-s+l} + (f-1)[\xi_\mathrm{i}^2\sum_s^n\sum_k^n {}^{(\mathrm{i})}\phi^{(\mathrm{i})}{}_{s+k} + \xi_\mathrm{i}\xi_\mathrm{o}\sum_s^n\sum_l^m {}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n+s+l}] \tag{24a}$$

$$T_\mathrm{o} = \xi_\mathrm{o}^2[m + 2\sum_t^m\sum_l^{t-1} {}^{(\mathrm{o})}\phi^{(\mathrm{o})}{}_l] + \xi_\mathrm{i}\xi_\mathrm{o}\sum_t^m\sum_k^n {}^{(\mathrm{o})}\phi^{(\mathrm{i})}{}_{t-1+k} + (f-1)[\xi_\mathrm{i}\xi_\mathrm{o}\sum_l^m\sum_k^n {}^{(\mathrm{o})}\phi^{(\mathrm{i})}{}_{t-1+n+1+k} + \xi_\mathrm{o}^2\sum_t^m\sum_l^m {}^{(\mathrm{o})}\phi^{(\mathrm{o})}{}_{t-1+2n+1+l}] \tag{24b}$$

The equation for the static structure factor is obtaine when $\langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle$ is set at unity in eq 20, and the equation for the apparent translational diffusion coefficient is obtained when $\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle = 1$. Explicit relationships can be derived from eq 24 when Gaussian statistics are assumed for the configurations of the subchains.

Static Structure Factor. In this case the function ϕ_{jk} is defined as

$$\phi_{jk} = \exp(i\mathbf{q}\cdot\mathbf{R}_{jk}) \tag{25}$$

where the angular brackets denote the equilibrium average. As an example we consider a subchain that has $n - s$ units from the inner block, with an effective bond length b_i, and l units from the outer block of the same ray, with effective bond length b_o. The end-to-end distance distribution for such a Gaussian subchain is then given by

$$W(R_{jk}) = (3/2\pi)^{3/2}[b_\mathrm{i}^2(n-s) + b_\mathrm{o}^2 l]^{-3/2} \exp(-3R_{jk}^2/[2(b_\mathrm{i}^2(n-s) + b_\mathrm{o}^2 l)]) \tag{26}$$

The average procedure yields for this case

$$\phi_{jk} = {}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n-s+l} = \phi_\mathrm{i}^{n-s}\phi_\mathrm{o}^{l} \tag{27}$$

with

$$\phi_\mathrm{i} = \exp(-b_\mathrm{i}^2 q^2/6) \equiv \exp(-y_\mathrm{i}^2) \tag{28a}$$

$$\phi_\mathrm{o} = \exp(-b_\mathrm{o}^2 q^2/6) \equiv \exp(-y_\mathrm{o}^2) \tag{28b}$$

The sums in eq 24 now reduce to finite geometric series which can be evaluated analytically. The result is

$$S(q) = (f/\nu^2)\{\xi_\mathrm{i}^2[P_{2\mathrm{i}} + (f-1)P_{1\mathrm{i}}^2] + \xi_\mathrm{o}^2[P_{2\mathrm{o}} + (f-1)\phi_\mathrm{i}^{2n}P_{1\mathrm{o}}^2] + 2\xi_\mathrm{i}\xi_\mathrm{o}[1 + (f-1)\phi_\mathrm{i}^{n}]P_{1\mathrm{i}}P_{1\mathrm{o}}\} \tag{29}$$

with

$$P_{1\mathrm{i}} = y_\mathrm{i}^{-2}(1 - \phi_\mathrm{i}^{n}); \qquad y_\mathrm{i}^2 = b_\mathrm{i}^2q^2/6$$
$$P_{2\mathrm{i}} = 2y_\mathrm{i}^{-4}(ny_\mathrm{i}^2 - (1 - \phi_\mathrm{i}^{n}))$$
$$P_{1\mathrm{o}} = y_\mathrm{o}^{-2}(1 - \phi_\mathrm{o}^{m}); \qquad y_\mathrm{o}^2 = b_\mathrm{o}^2q^2/6$$
$$P_{2\mathrm{o}} = 2y_\mathrm{o}^{-4}(my_\mathrm{o}^2 - (1 - \phi_\mathrm{o}^{m})) \tag{30}$$

From the definition of ν given by eq 4 it can be verified that $S(0) = M^2$. Thus the particle scattering factor is

$$P(q) = S(q)/S(0) = S(q)/M^2 \tag{31}$$

Expansion of $P(q)$ in terms of q^2 yields the apparent mean square radius of gyration

$$\langle S^2\rangle_\mathrm{app} = f^2/(M\nu)^2[(\xi_\mathrm{i}n)^2\langle S^2\rangle_\mathrm{i} + (\xi_\mathrm{o}m)^2\langle S^2\rangle_\mathrm{o} + (\xi_\mathrm{i}n)(\xi_\mathrm{o}m)\langle S^2\rangle_\mathrm{io}] \tag{32}$$

with

$$\langle S^2\rangle_\mathrm{i} = nb_\mathrm{i}^2(3f-2)/6f$$
$$\langle S^2\rangle_\mathrm{o} = mb_\mathrm{o}^2(3f-2)/6f + nb_\mathrm{i}^2(f-1)/f$$
$$\langle S^2\rangle_\mathrm{io} = nb_\mathrm{i}^2(3f-2)/2f + mb_\mathrm{o}^2/2 \tag{33}$$

Apparent Diffusion Coefficient. Here the average

$$\phi_{jk} = \langle 1\cdot\mathbf{D}_{jk}\cdot 1\rangle \tag{34}$$

has to be calculated. As an example we again consider a subchain with $n - s$ units from the inner block and l units from the outer block of the same ray. For Gaussian subchains we then obtain

$${}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n-s+l} = kT[\delta(n-s)/\zeta_\mathrm{i} + \delta(l)/\zeta_\mathrm{o}] + (1-\delta(n-s)) \times (1-\delta(l))A'[b_\mathrm{i}^2(n-s) + b_\mathrm{o}^2 l]^{-1/2} = \mathrm{FD} + \mathrm{ND} \tag{35}$$

The first term represents the free draining part (FD) and the second term the nondraining (ND) contribution that results from the hydrodynamic interaction. Making use of the well-known integral

$$(2/\pi^{1/2})\int_0^\infty \exp(-ax^2)\,\mathrm{d}x = a^{-1/2} \tag{36}$$

the ND term may be written as

$$\mathrm{ND} = (2A'/\pi^{1/2})\int_0^\infty \exp(-[b_\mathrm{i}^2(n-s)/6 + b_\mathrm{o}^2 l/6]q^2)\,\mathrm{d}q = (2A'/\pi^{1/2})\int_0^\infty \phi_i^{n-s}(y_\mathrm{i}^2)\phi_\mathrm{o}^{l}(y_\mathrm{o}^2)\,\mathrm{d}q \tag{37}$$

where

$$A' = kT/(6\pi^{3/2}\eta_\mathrm{o}) \tag{38}$$

Thus the translational diffusion coefficient can be obtained from the static structure factor $S(q^2)$ by integration over the complete q space:

$$D = D_\mathrm{FD} + D_\mathrm{ND}$$

with

$$D_\mathrm{FD} = \frac{kTf}{M^2}\left(\frac{n\xi_\mathrm{i}^2}{\zeta_\mathrm{i}} + \frac{m\xi_\mathrm{o}^2}{\zeta_\mathrm{o}}\right) \tag{39a}$$

$$D_\mathrm{ND} = (2A'/\pi^{1/2}M^2)\int_0^\infty [S(q^2) - 1/x]\,\mathrm{d}q \tag{39b}$$

where $S(q^2)$ is given by eq 29 and 30. Now $S(q^2)$ has three contributions which can be integrated separately, so that the ND part of the diffusion coefficient may be written as

$$D_{\mathrm{ND}} = f^2/(M\nu)^2[\xi_{\mathrm{i}}^2n^2D_{\mathrm{i}} + \xi_{\mathrm{o}}^2m^2D_{\mathrm{o}} + \xi_{\mathrm{i}}n\xi_{\mathrm{o}}mD_{\mathrm{io}}] \quad (40)$$

with

$$D_{\mathrm{i}} = (8/3f)(A'/B_{\mathrm{i}})(1 + (2^{1/2} - 1)(f - 1)) \quad (41\mathrm{a})$$

$$D_{\mathrm{o}} = (8/3f)(A'/B_{\mathrm{o}})\{1 + (2^{1/2} - 1)(f - 1)[(B_{\mathrm{i}}/B_{\mathrm{o}})^3 + (1 + B_{\mathrm{i}}^2/B_{\mathrm{o}}^2)^{3/2}] - (f - 1)(1 + 2B_{\mathrm{i}}^2/B_{\mathrm{o}}^2)^{3/2}\} \quad (41\mathrm{b})$$

$$D_{\mathrm{io}} = (8/3f)(A'/(B_{\mathrm{i}}B_{\mathrm{o}})^2)[(f - 1) \times (B_{\mathrm{o}}^2 + 2B_{\mathrm{i}}^2)^{2/3} - (f - 1)B_{\mathrm{i}}^3 - B_{\mathrm{o}}^3 - (f - 2)(B_{\mathrm{i}}^2 + B_{\mathrm{o}}^2)^{3/2}] \quad (41\mathrm{c})$$

where

$$B_{\mathrm{i}}^2 = nb_{\mathrm{i}}^2/6; \qquad B_{\mathrm{o}}^2 = mb_{\mathrm{o}}^2/6 \quad (42)$$

Angular Dependence of the First Cumulant. The angular dependence of the first cumulant is given by eq 20. Here a pair function of the kind

$$\phi_{jk} = \langle(\mathbf{1}\cdot\mathbf{D}_{jk}\cdot\mathbf{1}) \exp(i\mathbf{q}\cdot\mathbf{R}_{jk})\rangle \quad (43)$$

occurs. This average was calculated first by Akcasu and Gurol,[4] and their result can be extended to heterogeneous subchains where for instance $n - s$ units belong to the outer block and l units to the other. The result is

$${}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n-s+l} = kT[\delta(n - s)/\zeta_{\mathrm{i}} + \delta(l)/\zeta_{\mathrm{o}} + [1 - \delta(n - s)] \times (1 - \delta(l))](A'q/X)(3/4)H(X) \quad (44)$$

where

$$H(X) = (2X^{-1} + X^{-3})\mathcal{D}(X) - X^{-2} \quad (45\mathrm{a})$$

$$\mathcal{D}(X) = \exp(-X^2)\int_0^x \exp(t^2)\,\mathrm{d}t \quad (45\mathrm{b})$$

$$X^2 = Kq^2 \quad (45\mathrm{c})$$

$$K = (n - s)b_{\mathrm{i}}^2/6 + lb_{\mathrm{o}}^2/6 \quad (45\mathrm{d})$$

In the following we confine the discussion to the ND term. The occurrence of the Dawson integral in eq 45b introduces practical difficulties with the summations in eq 24a and 24b. Exact analytic relationships can be obtained for the two limiting regions of small and very large q values. For the intermediate region an approximation can be applied which consists of the hydrodynamic preaverage approximation plus a correction term[6]

$$\phi_{jk} = \phi_{jk,\mathrm{pre}} + \Delta\phi_{jk} \quad (46\mathrm{a})$$

$$\phi_{jk,\mathrm{pre}} = (A'q/X)\exp(-X^2) \quad (46\mathrm{b})$$

$$\Delta\phi_{jk} = (A'qX/5)\exp(-0.72X^2) \quad (46\mathrm{c})$$

This approximation agrees with eq 44 exactly up to powers of X^4, and it yields for the asymptote at large q value that differs only by 1% from the exact solution.[6]

(i) Γ/q^2 at Small q^2. Expansion of the Dawson integral, as well as expansion of eq 43 to eq 45 yields at small arguments[6]

$$\phi_{jk} = A'q/X - (4/5)qX + \ldots \quad (47)$$

where $X^2 = Kq^2$. For the various paths occurring in eq 24a and 24b, K is given by

$$K = b_{\mathrm{i}}^2k/6 \qquad \text{for path function } {}^{(\mathrm{i})}\phi^{(\mathrm{i})}{}_k$$

$$K = b_{\mathrm{o}}^2l/6 \qquad \text{for path function } {}^{(\mathrm{o})}\phi^{(\mathrm{o})}{}_l$$

$$K = (n - s)b_{\mathrm{i}}^2/6 + lb_{\mathrm{o}}^2/6 \qquad \text{for path function } {}^{(\mathrm{i})}\phi^{(\mathrm{o})}{}_{n-s+l} \quad (48)$$

and similar expressions for the other paths. With eq 36 the relationships for ϕ_{jk} may be also written as

$$\phi_{jk} = (2A'/\pi^{1/2})\left\{6^{1/2}\int_0^\infty \exp(-Kq^2)\,\mathrm{d}q - (4/5)q^2\left(6^{1/2}\int_0^\infty [\mathrm{d}\,(\exp(-Kq^2))/\mathrm{d}q^2]\,\mathrm{d}q\right)\right\} \quad (49)$$

Introducing this integral representation into eq 24, one finds for the q-dependent first cumulant at small q^2

$$\Gamma/q^2 = [2A'/(\pi^{1/2}(1 - 1/3\langle S^2\rangle_{\mathrm{app}}q^2))] \times \left\{\int_0^\infty S(q^2)\,\mathrm{d}q - (4/5)q^2\int_0^\infty [\mathrm{d}S(q^2)/\mathrm{d}q^2]\,\mathrm{d}q\right\} \quad (50)$$

Or

$$\Gamma/(q^2D^0{}_{\mathrm{app}}) = 1 + C\langle S^2\rangle_{\mathrm{app}}q^2 - \ldots \quad (51)$$

where

$$C = 1/3 - (4/5)(\langle S^2\rangle_{\mathrm{app}}D^0{}_{\mathrm{app}})^{-1}\int_0^\infty [\mathrm{d}S(q^2)/\mathrm{d}q^2]\,\mathrm{d}q \quad (52)$$

Again the integrals can be solved, resulting in

$$C = 1/3 - (4/5)(\langle S^2\rangle_{\mathrm{app}}D^0{}_{\mathrm{app}})^{-1}[(f/M\nu)^2(\xi_{\mathrm{i}}^2n^2A_{\mathrm{i}} + \xi_{\mathrm{o}}^2m^2A_{\mathrm{o}} + \xi_{\mathrm{i}}n\xi_{\mathrm{o}}mA_{\mathrm{io}})] \quad (53)$$

where

$$A_{\mathrm{i}} = (8/3f)A'B_{\mathrm{i}}[1 + (2(2^{1/2}) - 1)(f - 1)]$$

$$A_{\mathrm{o}} = (8/3f)A'B_{\mathrm{o}}[1 + (f - 1)/2((2B_{\mathrm{i}}^2/B_{\mathrm{o}}^2)^{5/2} + (1 + B_{\mathrm{i}}^2/B_{\mathrm{o}}^2)^{5/2}) - (1 + 2B_{\mathrm{i}}^2/B_{\mathrm{o}}^2)^{5/2}]$$

$$A_{\mathrm{io}} = (8/3f)A'(B_{\mathrm{i}}B_{\mathrm{o}})^{-2}[(f - 2)B_{\mathrm{i}}^5 - B_{\mathrm{o}}^5 - (f - 2) \times (B_{\mathrm{i}}^2 + B_{\mathrm{o}}^2)^{5/2} - (f - 1)((2B_{\mathrm{i}}^2)^{5/2} - (2B_{\mathrm{i}}^2 + B_{\mathrm{o}}^2)^{5/2})] \quad (54)$$

(ii) Asymptote of the First Cumulant. Applying arguments given in a previous paper[6] we find in the limit of large q the same result as for homopolymers:

$$\Gamma/q^2 \rightarrow qkT/(16\eta_0) \quad (55)$$

whatever the copolymer structure composition.

(iii) Intermediate Region. We note that eq 46b and 46c can be written in the alternative form[27]

$$\phi_{jk,\mathrm{pre}} = (2A'/\pi^{1/2})\int_0^\infty \exp(-Kq^2 - K\beta^2)\,\mathrm{d}\beta \quad (56\mathrm{a})$$

$$\Delta\phi_{jk} = (A'/5\pi^{1/2})q^2\int_0^\infty \beta^{-2}[\exp(-0.72Kq^2) - \exp(-0.72Kq^2 - K\beta^2)]\,\mathrm{d}\beta \quad (56\mathrm{b})$$

where we have made use of $X = qK^{1/2}$ and of the identity

$$K^{-1/2} = (2/\pi^{1/2})\int_0^\infty \exp(-K\beta^2)\,\mathrm{d}\beta \quad (57\mathrm{a})$$

$$K^{1/2} = -1/2\int_0^K K^{-1/2}\,\mathrm{d}K = -(1/\pi^{1/2})\int_0^\infty\int_0^K \exp(-K\beta^2)\,\mathrm{d}\beta\,\mathrm{d}K = -(1/\pi^{1/2})\int_0^\infty \beta^{-2}(1 - \exp(K\beta^2))\,\mathrm{d}\beta \quad (57\mathrm{b})$$

Introducing these relationships into eq 24a and 24b and performing the summation prior to integration, one obtains

$$\Gamma/q^2 = A'/(S(0)\pi^{1/2})\left\{2\int_0^\infty S(q^2 + \beta^2)\,\mathrm{d}\beta - 0.2q^2\int_0^\infty \beta^{-2}[S(0.72q^2) - S(0.72q^2 + \beta^2)]\,\mathrm{d}\beta\right\} \quad (58)$$

or when using the value of Γ_0/q^2 in the limit of $q^2 \rightarrow 0$

$$\Gamma/\Gamma_0 = \left[2P(q)\int_0^\infty S(q^2)\,\mathrm{d}q\right]^{-1}\left\{2\int_0^\infty S(q^2 + \beta^2)\,\mathrm{d}\beta - 0.2q^2\int_0^\infty \beta^{-2}[S(0.72q^2) - S(0.72q^2 + \beta^2)]\,\mathrm{d}\beta\right\} \quad (59)$$

where $S(q^2)$ is the static structure factor given by eq 29, $P(q)$ the particle scattering factor, and $S(0.72q^2 + \beta^2)$ means a structure factor in which the argument q^2 is replaced by $0.72q^2 + \beta^2$. In principle the integrals can be solved analytically, but we have preferred numerical integration by Simpson's rule.

Results and Discussion

As was mentioned in the Introduction, solvents can be chosen such that either the outer or the inner blocks of the star molecule can be made invisible. A third possibility consists in the choice of a solvent where the *total* refractive index increment of the polymer is zero. Under the latter conditions no light is scattered at zero angle, but this does *not* mean that no light is scattered at finite angles, as will be shown below. We take up now the question posed in the introduction: what diffusion coefficient, what mean square radius of gyration, and which angular dependence of the static and dynamic light scattering is measured? These questions will be answered in four steps depending on the refractive index of the solvent n_s in comparison to those of the two blocks and the total copolymer, respectively.

Case 1: $|\boldsymbol{n}_i - \boldsymbol{n}_o| \ll |\boldsymbol{n}_i - \boldsymbol{n}_s|$. Under these conditions $\xi_i \simeq \xi_o \simeq \nu M/X$. Thus the different ξ_j cancel in all equations, and the quantities are very close the true values of $\langle S^2\rangle$, $P(q)$, D, and Γ/Γ_0.

Case 2: $\boldsymbol{n}_s = \boldsymbol{n}_o$. Here $\xi_o = 0$, and the outer blocks scatter no light. Equation 4 becomes

$$\nu^2 = (\xi_i n/M)^2$$

and eq 29, 32, and 59 reduce to

$$P(q) = (fn^2)^{-1}[P_{2i} - (f-1)P_{1i}^2] - (2/fV_i^2)[1 - (1 - \exp(-V_i)) + (f-1)/2(1 - \exp(-V_i))^2] \tag{60a}$$

where

$$V_i = b_i^2 n q^2/6$$

$$\langle S^2\rangle_{app} = \langle S^2\rangle_i = nb_i^2(3f-2)/6f \tag{60b}$$

$$D^0{}_{app} = D_i = (8A'/3n^{1/2}f)(1 + (2^{1/2} - 1)(f-1)) \tag{60c}$$

where

$$A' = kT/(6^{1/2}\pi^{3/2}b_i\eta_0)$$

$$\Gamma/\Gamma_0 = 1 + C_i\langle S^2\rangle_i q^2$$

with

$$C_i = 1/3 - \frac{4f(1 + (2^{3/2} - 1)(f-1))}{25(3f-2)(1 - (2^{1/2} - 1)(f-1))} \tag{60d}$$

These are exactly the equations for a star that seems to consist of only the inner blocks of the rays. The outer blocks, though existent, do not contribute to the initial time derivative. However, the same is not true when the inner blocks are made invisible.

Case 3: $\boldsymbol{n}_s = \boldsymbol{n}_i$. Now $\xi_1 = 0$ and $\nu^2 = (f\xi_o/M)^2$. Equations 29, 32, 40, and 59 reduce to

$$P(q) = (fm^2)^{-1}[P_{2o} - (f-1)\phi_i^{2n}P_{1i}^2] = (2/fV_o)\{1 - (1 - \exp(-V_o) + (f-1))/2[\exp(-V_i) - \exp(-V_i - V_o)]^2\} \tag{61a}$$

$$\langle S^2\rangle_{app} = \langle S^2\rangle_o = mb_o^2(3f-2)/6f + nb_i^2(f-1)/f \tag{61b}$$

$$D^0{}_{app} = D_o = (8A/3m^{1/2}f)\{1 + (2^{1/2} - 1)(f - 1)[(B_i^2/B_o^2)^3/^2 + (1 + B_i^2/B_o^2)^{3/2} - (1 + 2B_i^2/B_o^2)^{3/2}]\} \tag{61c}$$

$$\Gamma/q^2D^0{}_{app} = 1 + C_o\langle S^2\rangle_{app}q^2; \quad C_o = 1/3 - (3/5)A'/(D_o\langle S^2\rangle_o) \tag{61d}$$

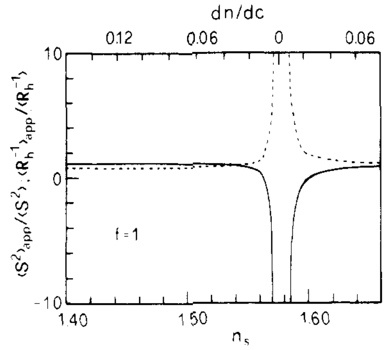

Figure 3. Variation of the apparent mean square radius of gyration $\langle S^2\rangle_{app}$ and the apparent reciprocal hydrodynamic radius $\langle R_h^{-1}\rangle_{app}$ as a function of the solvent refractive index n_s for a linear AB-block copolymer; i.e., $f = 1$: block B, polyisoprene, $M = 230000$; block A, polystyrene, $M = 150000$.

These quantities deviate from those of a homopolymeric star by additional terms; e.g., the mean square radius of gyration is enlarged by the term $nb_i^2(f-1)/f$ which is $(f-1)/f$ times the mean square end-to-end distance from the junction point of the outer to the inner block of the one ray to the corresponding junction point of another ray. The diffusion coefficient is altered in a similar manner. In other words, although the inner part of the star molecule is not seen, the measurable quantities depend on how the outer blocks are connected through the invisible inner links.

Case 4: $\nu = 0$ **or** $\boldsymbol{nM}_i\nu_i \simeq -\boldsymbol{mM}_o\nu_o$. In such cases we have positive contributions from the inner and outer blocks but a negative from the cross term X_{io}, which contains the negative prefactor $n\xi_i m\xi_o$. The total behavior near $\nu = 0$ now becomes rather complex.

We consider first the case where $n\xi_i$ is very close to $m\xi_o$ but not exactly equal in magnitude, so that $1/\nu$ remains finite. The prefactors which contain the refractive index increments can then be extracted, and the behavior of $\langle S^2\rangle_{app}$, $D^0{}_{app}$, and C_{app} is determined by

$$\langle X\rangle_{app} = (\nu_i/\nu)^2 w_i^2 \Delta X = (\xi_i/M_i\nu)^2 w_i^2 \Delta X \tag{62}$$

with

$$\Delta X = X_i + X_o - X_{io} \tag{63}$$

where X may be $\langle S^2\rangle$, D, or C, and w_i is the weight fraction of the inner block. Since $\nu_i^2 w_i^2 \neq 0$, we notice that the apparent quantities tend to infinity as ν goes to zero. Second, the apparent quantities can become *negative* if ΔX becomes negative. It turns out that for $D^0{}_{app}$ and C_{app} the difference ΔX remains positive, but for $\langle S^2\rangle_{app}$ one obtains *negative* values. Thus near $\nu = 0$ the apparent mean square radius of gyration tends to minus infinity. This result is in agreement with the general theory of linear copolymers.[8,9]

For sufficiently large values of ν one has, of course, to take into account the different prefactors to $\langle S^2\rangle_i$, $\langle S^2\rangle_o$, and $\langle S^2\rangle_{io}$, and eventually positive values are obtained, which approach the true mean square radius of gyration (compare case 1). The curve of $\langle S^2\rangle_{app}$ as a function of ν^2 is not symmetric around $\nu = 0$, and the extent of asymmetry depends on the number of rays attached to the star center. This is shown in Figures 3–5. For $f = 1$, the linear AB-block copolymer, one finds a continuous decrease of $\langle S^2\rangle_{app}$ to minus infinity when $\nu = 0$ is approached, and a gradual return to $\langle S^2\rangle$ as one proceeds further to negative ν. For $f = 2$, the linear ABA-block copolymer, one obtains at first a slight increase and then the approach to minus infinity. The initial increase of $\langle S^2\rangle_{app}$ becomes more pronounced with the number of attached chains, and for

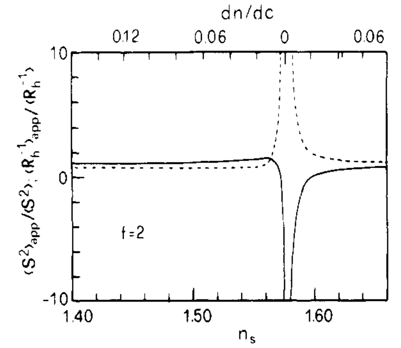

Figure 4. The same plot as in Figure 3 but for $f = 2$, the linear ABA-triblock copolymer.

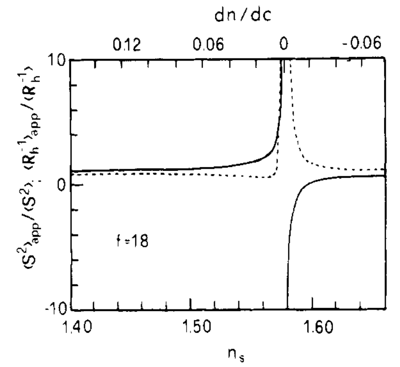

Figure 5. The same plot as in Figure 3 but for the heterogeneous star molecule $(AB)_f$ with $f = 18$.

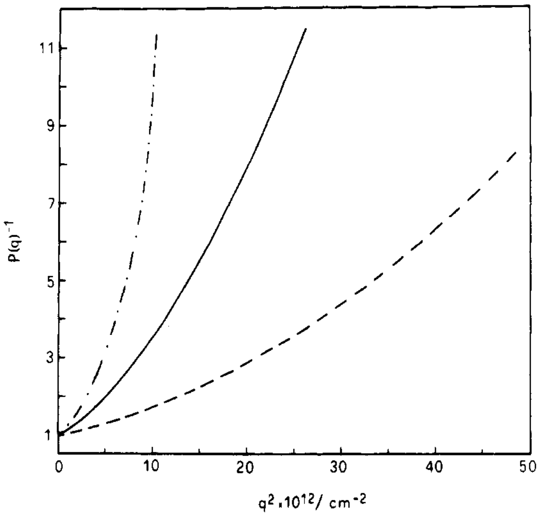

Figure 6. Plot of the reciprocal particle scattering factor $P(q)^{-1}$ against $q^2 = (4\pi/\lambda)^2 \sin^2 \theta/2$ calculated for a polyisoprene/polystyrene star molecule with $f = 18$. Total molecular weight $M = 6.84 \times 10^6$, inner block; $M_{PI} = 150000$, outer block, $M_{PS} = 230000$. The solid line represents the case $\nu_i \equiv \nu_o$, the dotted line $\nu_o = 0$ (outer ray sections matched), and the dash-point curve $\nu_i = 0$ (inner ray sections matched).

the 18-star molecule the increase is very pronounced and the turn back to minus infinity occurs only in close vicinity of $\nu = 0$.

Figures 3–5 show for comparison also the curves for the apparent reciprocal hydrodynamic radii which are defined by the diffusion coefficients through the Stokes–Einstein relationship

$$D^0_{app} = \frac{kT}{6\pi\eta_0}\left\langle\frac{1}{R_h}\right\rangle_{app} \tag{64}$$

Again the curves are asymmetric around $\nu = 0$, but under no conditions are negative values obtained for $\langle R_h^{-1}\rangle_{app}$ as was already mentioned above.

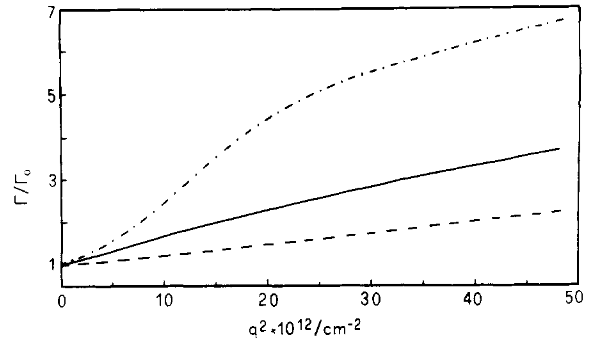

Figure 7. Plot of the reduced and normalized first cumulant Γ/Γ_0 for the same cases as described in Figure 6. Γ_0 is the first cumulant at $q^2 \to 0$.

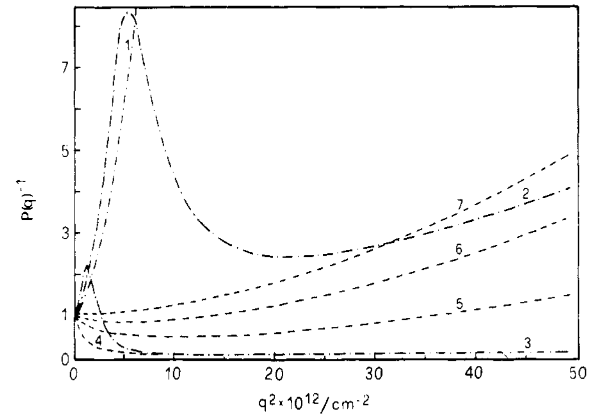

Figure 8. Plot of the reciprocal particle scattering factor as a function of q^2 for various values of ν ($M_{oi} = 68$, $M_{oo} = 104$): 1, 0.0105; 2, 0.0065; 3, 0.0017; 4, −0.0023; 5, −0.0067; 6, −0.0117; 7, −0.0161; 8, −0.0284.

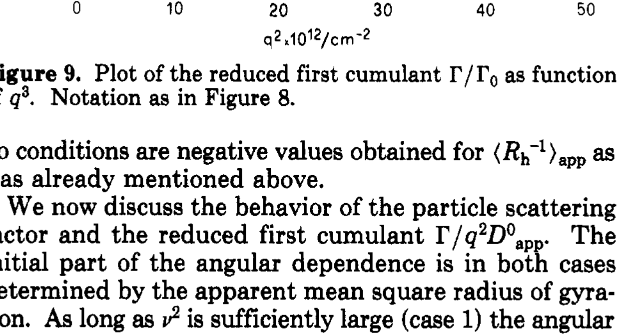

Figure 9. Plot of the reduced first cumulant Γ/Γ_0 as function of q^3. Notation as in Figure 8.

We now discuss the behavior of the particle scattering factor and the reduced first cumulant $\Gamma/q^2D^0_{app}$. The initial part of the angular dependence is in both cases determined by the apparent mean square radius of gyration. As long as ν^2 is sufficiently large (case 1) the angular dependence of $P(q)^{-1}$ and of $\Gamma/q^2D^0_{app}$ shows no drastic changes in shape. Figures 6 and 7 show the curves for $\nu_i = \nu_o$ (case 1), $\nu_i = 0$ (case 2), and $\nu_o = 0$ (case 3). In all three cases we have only positive terms which contribute to the scattering intensity.

Near $\nu = 0$, however, $P(q)^{-1}$ and $\Gamma/q^2D^0_{app}$ can decrease for small q^2 when $\langle S^2\rangle_{app}$ is negative, but it also can increase at first and then pass through a maximum. Figures 8 and 9 give some examples. The reason for this strange behavior becomes clear when the three contributions ar-

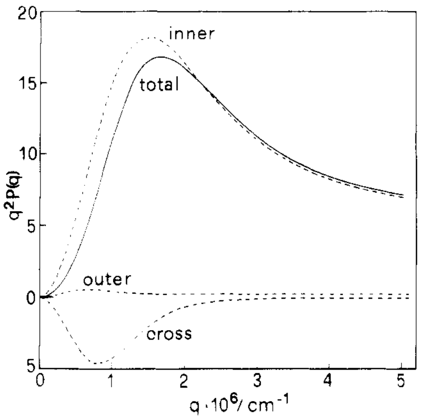

Figure 10. Kratky plot ($q^2P(q)$ vs. q) for a heterogeneous star molecule with $\nu = 0.015$. The curves labeled inner, outer, cross, and total represent the contributions to the scattering intensities from the inner, outer, and cross terms and from the sum of these three contributions. The composition of the star is the same as given in Figure 8.

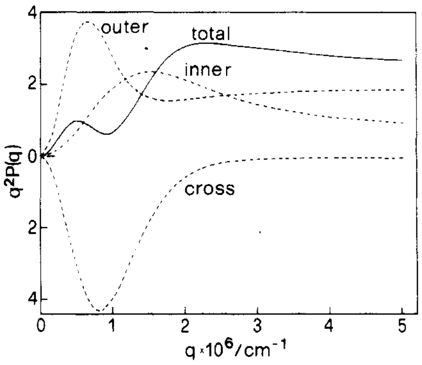

Figure 11. The same plot as in Figure 10 but for $\nu = -0.0117$.

ising from the individual blocks and from the cross term are plotted separately. This is done in Figures 10 and 11 for the two cases where dn/dc is slightly positive and slightly negative, respectively. The Kratky plot has been used in these cases. One realizes now that the strange behavior is caused by the relative magnitude of the negative cross-term contribution.

Finally we present in Figure 12 some preliminary measurements on an 18-ray star molecule where the inner PI blocks have a molecular weight of $M_{\rm PI} = 230\,000$ and for the outer PS blocks $M_{\rm PS} = 150\,000$. A normalized graph is shown, where $q^2\langle S^2\rangle$ is ploted on the abscissa. In such a plot all particle scattering factors show the same initial part with a slope of $^1/_3$. One realizes that in THF, where both blocks scatter light strongly, and in bromoform, where only the inner region is visible, $P(q)^{-1}$ has essentially the same shape. When, however, the inner region is made invisible the particle scattering factor deviates considerably from that of a star molecule and resembles more nearly that of a hollow sphere, as was pointed out earlier by one of the present authors.[28]

Heterogeneous Gaussian Dumbbell. In the preceding sections analytic expressions have been derived for the first cumulant and the apparent diffusion coefficient of heterogeneous regular star molecules. The first cumulant represents, by definition, the dynamic scattering in the limit of $t \to 0$. Physically, in this limit the internal modes of motion of the macromolecule are not relaxed, and this is the reason that the apparent translational diffusion coefficient differs from the true steady-state value which would be measured by classical, long-time diffusion techniques. At sufficiently long times, the quasi-elastic light scattering method must also yield the true diffusion coefficient. This state is now illustrated simply for an optically heterogeneous free-draining Gaussian dumbbell.

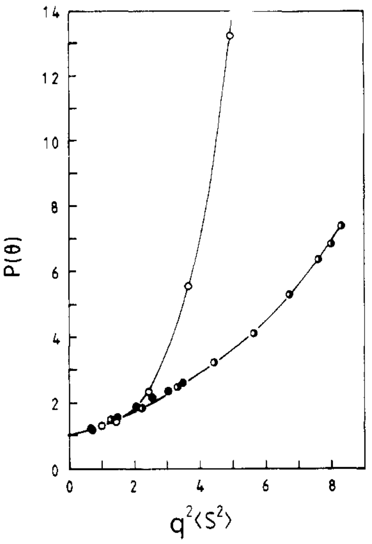

Figure 12. Static light scattering measurements from a polyisoprene/polystyrene 18-ray star: (◑) $\nu = 0.145$, in THF; (○) $\nu = 0.021$, in C_6H_5Cl; (●) $\nu = -0.43$, in $CHBr_3$.

Let the refractivity increments for the two beads of the dumbbell be ν_1 and ν_2. For simplicity, we treat the hydrodynamically symmetric case for which both beads have the same friction coefficient ζ. We then find (cf. Appendix) the correlation function

$$g_1(t) = e^{-q^2Dt}[(\nu_1 + \nu_2)^2 \cosh (ue^{-t/\tau}) + (\nu_1 + \nu_2)^2 \sinh (ue^{-t/\tau})]/[(\nu_1 + \nu_2)^2 \cosh (u) + (\nu_1 - \nu_2)^2 \sinh (u)] \quad (65)$$

where

$$u = q^2b^2/12 \quad (66a)$$

$$D = kT/2\zeta \quad (66b)$$

$$\tau = b^2\zeta/6kT = b^2/12D \quad (66c)$$

Here D is the translational diffusion coefficient of the dumbbell, τ is the relaxation time for the internal motion, and b^2 is the mean square distance between the two beads. For the reduced first cumulant we then obtain

$$\Gamma/q^2 = 2D(\nu_1^2 + \nu_2^2)/(\nu_1^2 + \nu_2^2 + 2\nu_1\nu_2e^{-2u}) \quad (67)$$

which for small u may be written

$$\Gamma/q^2 = D^0_{\rm app}[1 + Cq^2\langle S^2\rangle_{\rm app} + ...] \quad (68)$$

with

$$D^0_{\rm app} = 2D(\nu_1^2 + \nu_2^2)/(\nu_1 + \nu_2)^2 \quad (69)$$

$$\langle S^2\rangle_{\rm app} = b^2\nu_1\nu_2/(\nu_1 + \nu_2)^2 \quad (70)$$

and $C = {}^1/_3$. The last equation is consistent with the apparent particle scattering factor

$$P(q) = (\nu_1^2 + \nu_2^2 + 2\nu_1\nu_2e^{-2u})/(\nu_1 + \nu_2)^2 \quad (71)$$

Although the calculated first cumulant of the dumbbell varies greatly with ν_1 and ν_2, it is seen from eq 65 that when the internal motion has relaxed ($t \gg \tau$) the correlation function becomes

$$g_1(t) = \exp(-q^2Dt)(\nu_1 + \nu_2)^2/[(\nu_1 + \nu_2)^2 \cosh (u) + (\nu_1 - \nu_2)^2 \sinh (u)], \qquad t \gg \tau \quad (72)$$

which now decays exponentially according to the true translational diffusion coefficient D whatever the values of ν_1 and ν_2.

We can now discuss various special cases. If $\nu_1 = \nu_2$, we have an homogeneous Gaussian dumbbell, with

$$g_1(t) = \exp(-q^2Dt) \text{ sech } (u) \cosh (ue^{-t/\tau}) \qquad (73a)$$

$$\Gamma/q^2 = D(1 + \tanh (u)), \qquad D^0{}_{\text{app}} = D \qquad (73b)$$

If, on the other hand, $\nu_1 = 0$ or $\nu_2 = 0$, we get $D^0{}_{\text{app}} = 2D$ and $\langle S^2\rangle_{\text{app}} = 0$; i.e., there is no angular dependence of the first cumulant or of the integrated light scattering. At longer times, however, an angular dependence emerges, as the correlation function in this case is

$$g_1(t) = \exp(-q^2Dt) \exp(ue^{-t/\tau} - u) \qquad (74)$$

Finally, if $\nu_1 = \nu_2$, we obtain

$$\Gamma/q^2 = D(1 + \coth (u)) \qquad (75)$$

which gives $D^0{}_{\text{app}} \rightarrow \infty$ and $\langle S^2\rangle_{\text{app}} \rightarrow -\infty$, as for a heterogeneous star molecule. Thus in this case measurements cannot meaningfully be extrapolated to zero angle.

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Appendix

Here we derive the dynamic structure factor for an optically heterogeneous Gaussian dumbbell. Let the beads have position vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ and refractivities ν_1 and ν_2. Then, defining

$$\rho(0) = \nu_1 \exp(i\mathbf{q}\cdot\mathbf{R}_1) + \nu_2 \exp(i\mathbf{q}\cdot\mathbf{R}_2) \qquad (A1)$$

we have

$$\rho(0)\rho^*(0) = \nu_1{}^2 + \nu_2{}^2 + 2\nu_1\nu_2 \cos (\mathbf{q}\cdot\mathbf{R}) \qquad (A2)$$

where the interparticle distance is $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$. If the equilibrium distribution of $\mathbf{R}$ is Gaussian, with a mean square value $\langle R^2\rangle = b^2$, the structure factor, $S(q) = \langle\rho(0)\rho^*(0)\rangle$, is readily evaluated, and the equilibrium particle scattering factor is found to be

$$P(q) = S(q)/S(0) = (\nu_1{}^2 + \nu_2{}^2 + 2\nu_1\nu_2e^{-2u})/(\nu_1 + \nu_2)^2 \qquad (A3)$$

with

$$u \equiv b^2q^2/12 \qquad (A4)$$

This result is given as eq 71 of the text.

To evaluate the dynamic structure factor we require

$$S(q,t) = \langle\rho^*(0)\rho(t)\rangle = \langle e^{iq\cdot(\mathbf{r}_t-\mathbf{r}_0)}\{\nu_1{}^2e^{i\mathbf{q}\cdot(\mathbf{R}_t-\mathbf{R}_0)/2} + \nu_2{}^2e^{i\mathbf{q}\cdot(\mathbf{R}_t-\mathbf{R}_0)/2} + \nu_1\nu_2e^{i\mathbf{q}\cdot(\mathbf{R}_t+\mathbf{R}_0)/2} + \nu_1\nu_2e^{-i\mathbf{q}\cdot(\mathbf{R}_t+\mathbf{R}_0)/2}\}\rangle \qquad (A5)$$

where

$$\mathbf{r} \equiv (\mathbf{R}_1 + \mathbf{R}_2)/2 \qquad (A6)$$

and the subscripts denote values at time t and 0. To perform the average indicated we require the dynamic distribution function $\Psi(\mathbf{r},\mathbf{R},t)$ which is a solution of the diffusion equation for the free-draining dumbbell

$$\beta\zeta(\partial\Psi/\partial t) = \nabla_1\cdot(\nabla_1\Psi + \Psi\beta\nabla_1U) + \nabla_2\cdot(\nabla_2\Psi + \Psi\beta\nabla_2U) \qquad (A7)$$

where $\beta = 1/kT$, and where, for the Gaussian dumbbell,

$$U = 3kTR^2/2b^2 \qquad (A8)$$

Equation A7 is separable in the variables $\mathbf{R}$ and $\mathbf{r}$ previously defined and is further separable into cartesian components. The point-source solution for both translational and internal diffusional motions are well-known[29] and may be written

$$\Psi(\mathbf{r},\mathbf{R},t) = G(\mathbf{r}_t,t|\mathbf{r}_0)G(\mathbf{R}_t,t|\mathbf{R}_0) \qquad (A9)$$

with

$$G(\mathbf{R}_t,t|\mathbf{r}_0) = (4\pi Dt)^{-3/2} \exp[-(\mathbf{r}_t - \mathbf{r}_0)^2/4Dt] \qquad (A10)$$

and

$$G(\mathbf{R}_t,t|\mathbf{R}_0) = (\alpha^2/\pi)^{3/2} \exp[-\alpha^2(\mathbf{R}_t - \mathbf{R}_0e^{-t/\tau})^2] \qquad (A11)$$

where

$$\alpha^2 = (3/2b^2)(1 - e^{-2t/\tau})^{-1} \qquad (A12)$$

Finally, we recall that $\mathbf{R}_0$ has a Gaussian distribution with variance b. The averaging process can now be carried through in eq A5 and after some tediens yields the result

$$\langle\rho^*(0)\rho(t)\rangle = S(q,t) = \exp(-Dq^2t) \exp(-u)[(\nu_1{}^2 + \nu_2{}^2) \exp(ue^{-t/\tau}) + 2\nu_1\nu_2 \exp(-ue^{-t/\tau})] \qquad (A13)$$

After normalization through division by $S(q,0)$, we obtain the correlation function $g_1(t)$ given as eq 65 of the text.

Registry No. (Isoprene)·(styrene) (copolymer), 25038-32-8.

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(31) The first cumulant $\Gamma(q)/q^2$ can be expressed quite generally as[30]

$$\frac{\Gamma(q)}{q^2} = \frac{k_BT}{\xi}\frac{1}{S(q)}\left\{1 + \frac{\xi}{(2\pi)^3}\int d^3k\ \bar{T}_{33}(\mathbf{q}-\mathbf{k})[S(k) - 1/x]\right\}$$

where $\bar{T}_{33}(k) = (1-\mu^2)/\eta k^2$ and $S(k) = \sum_{j,m}\nu_j\nu_m \exp(i\mathbf{k}\cdot\mathbf{R}_{jm})/\sum_j\nu_j^2$; $\mu = \mathbf{k}\cdot\hat{\mathbf{q}}$. This form is not restricted to unperturbed Gaussian chains or any particular choice for the Oseen tensor, chain structure, etc. The apparent diffusion coefficient follows from it as

$$D_{\text{app}} = (k_BT/\xi)(\textstyle\sum\nu_j^2/(\sum\nu_j)^2)\left\{1 + (\xi/3\pi^2\eta)\int_0^\infty dq\ [S(q) - 1/x]\right\}$$

Local Structures in Ionomer Multiplets. A Vibrational Spectroscopic Analysis

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ABSTRACT: The results obtained from a systematic Fourier transform infrared study of the alkali metal, alkaline earth, and zinc salts of an ethylene–methacrylic acid copolymer are presented. The infrared spectra of samples, acquired at elevated temperatures, show spectral features characteristic of local ordered ionic structures commonly referred to as multiplets. From a consideration of the known coordinating tendencies of the different cations, together with a symmetry analysis of the most probable structures, we show that the experimental infrared results of the different ionomers are entirely consistent with the presence of specific local structures.

Introduction

The vibrational spectrum of most polymeric systems can be interpreted in terms of the normal modes of a theoretically isolated chain. The influence of interchain interactions is apparent in only one or two systems, principally because most interchain forces are relatively small and their effect upon the spectrum can be treated as a perturbation. Consequently, infrared and Raman spectroscopy are (for the most part) only sensitive to three-dimensional order in materials where specific strong interactions can be identified. One such class of polymeric materials is ionomers, where the arrangement of charged species should have a major affect on specific normal modes because of the strong electrostatic forces involved.

A number of infrared spectroscopic studies of ionomers have been reported.[1-7] The far-infrared work of Risen and co-workers[3-5] demonstrated the sensitivity of low-frequency vibrations to the nature of the anions and cations involved and the degree of cluster formation. Research in this laboratory[6,7] has concentrated on the bands due to the antisymmetric stretching vibration of carboxylate anions in the spectra of sodium and calcium ionomers of ethylene–methacrylic acid copolymers. These bands coalesce into a single broad entity upon annealing at room temperature for extended periods of time. We previously rationalized such observations in terms of the cluster model of Eisenberg.[8] More recently, we have been forced to reevaluate this interpretation as a result of a study of the effect of water on the carboxylate modes. This work, however, will be presented at another time. Here we will be concerned with results that, at least from a spectroscopic point of view, are more intriguing. In the spectra of melt-quenched and annealed samples a collection of carboxylate modes near 1550 cm^{-1} that are sensitive to thermal history and hence structure can be observed.

In our previous work we interpreted a doublet in the spectrum of calcium ionomers in terms of a splitting due to interactions between pairs of carboxylate groups. The sodium ionomers also gave a collection of bands, but we assigned these modes to multiplet and ion pairs isolated by the quencing process. From the high ground attained by further experimental observations, we can now look back and see that these interpretations were not only naive but more than likely just plain wrong. In fact, one of the referees of our original paper[6] suggested that the collection of bands observed in the spectrum of the sodium ionomer could also be interpreted in terms of a splitting due to interactions between carboxylate groups. At the time we casually dismissed this argument, but in the present paper we will concede that it is indeed correct.

Essentially, the work presented here largely concerns the local arrangement of carboxyl groups in structures termed multiplets by Eisenberg.[8] (Such local structures are probably also found in clusters, but we will address this point separately when we consider the origin of the band broadening previously observed upon annealing.[6]) Our investigation follows two lines. The first is purely experimental. We have obtained the spectra of the ionomers of different cations, principally those of the group 1 and group 2 elements of the periodic table. As we will demonstrate, these results force a major reassessment of our original interpretation. Our second line of arguments is built on questions that arise from theoretical considerations. Based on the coordinating tendencies of specific cations what type of local structures within multiplets would be anticipated? Furthermore, based on the symmetry of such structures what bands or pattern of bands would we predict in the vibrational spectrum? We will show that the spectroscopic predictions of this theoretical approach dovetail neatly with the experimental observations.

Experimental Section

The ethylene–methacrylic acid copolymer used in this study was obtained from E. I. du Pont de Nemours and Company (Surlyn 1650) and was reported to contain 4.1 mol % methacrylic acid. The metal salts were prepared as described in our previous papers by using the pertinent hydroxides.[6,7] To prepare films for infrared analysis each sample was pressed at 40 000 psi and at

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