

Concentration Dependence of the First Cumulant for Partially Labeled Chains in Dilute Solutions

B. HAMMOUDA, *Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109*, A. Z. AKCASU,* *Center for Material Sciences, The National Bureau of Standards, Washington, DC 20234*, and M. BENMOUNA, *Département de Physique, Université de Tlemcen, BP 119 Tlemcen, Algeria*

Synopsis

We use Zimm's single-contact approximation to investigate the concentration dependence of the first cumulant for partially labeled chains in dilute solutions. This approximation allows us to express interchain properties (such as the interference part of the generalized mobility) in terms of static structure factors, which are then modeled using a Gaussian chain model. We present numerical results for three specific labeling sequences.

INTRODUCTION

The purpose of this paper is to use Zimm's single-contact approximation¹ (SCA) to study static as well as dynamic properties of partially labeled chains in dilute solution. Specifically, we calculate the concentration dependences of the static structure factor $S(q)$ and of the first cumulant $\Omega(q)$ for such chains. The concentration dependence of $S(q)$ has been thoroughly studied recently by Benmouna and Benoit² in the case of block copolymers, using the SCA. We briefly summarize some of their results for completeness. The SCA has been used earlier³ to study the concentration of $\Omega(q)$ for homopolymers. Here, we extend this approach to partially labeled chains and present numerical results for some labeling sequences (diblock DH, triblock DHD, and triblock HDH) to aid in the interpretation of dynamic scattering experiments, especially in the asymptotic q region.

CONCENTRATION DEPENDENCE OF THE STATIC STRUCTURE FACTOR

The static structure factor for elastic coherent scattering from an aggregate of monomers in solution can be written as

$$S(q) = (1/N) \langle \rho^*(\mathbf{q})\rho(\mathbf{q}) \rangle \quad (1)$$

where $\rho(\mathbf{q})$ is the density of monomers in Fourier space, viz.,

$$\rho(\mathbf{q}) = \sum_{\alpha=1}^{N_p} e^{i\mathbf{q}\cdot\mathbf{R}_\alpha} \rho_\alpha(\mathbf{q}) \quad (2a)$$

* Permanent address: Department of Nuclear Engineering, The University of Michigan, Ann Arbor, MI 48109.

with

$$\rho_\alpha(\mathbf{q}) = \sum_{j=1}^{N_\alpha} a_{\alpha j} e^{i\mathbf{q}\cdot\mathbf{S}_{\alpha j}} \quad (2b)$$

The quantity $\rho_\alpha(\mathbf{q})$ is the monomer density of the α th chain about its center of mass \mathbf{R}_α , and $a_{\alpha j}$ is the excess scattering length per monomer, i.e., the difference between its scattering length and the scattering length of the same volume of solvent (for incompressible solutions). $\mathbf{S}_{\alpha j}$ locates the positions of monomers about the center of mass and N_p is the number of chains in the system of volume V . The normalization factor \mathcal{N} is defined as

$$\mathcal{N} = \sum_{\alpha=1}^{N_p} \left(\sum_{i=1}^{N_\alpha} a_{\alpha i} \right)^2 \quad (3a)$$

When the chains are identical, i.e., $N_\alpha = N$ (the total number of monomers in each chain), as we henceforth assume, \mathcal{N} becomes

$$\mathcal{N} = N_p n^2 \quad (3b)$$

where

$$n = \sum_{i=1}^N a_{\alpha i} \quad (4)$$

can be interpreted as the number of labeled monomers in each chain if we assume $a_{\alpha i} = 1$ for labeled (deuterated) monomers and $a_{\alpha i} = 0$ for unlabeled (normal) ones. The normalization is chosen such that $S(\mathbf{q} = \mathbf{0}) = N_p$ in the case of identical chains.

The thermal average appearing in eq. (1) is taken with respect to the equilibrium distribution of a single chain in the presence of others. Therefore, it depends on polymer concentration $C_p = N_p/V$. This dependence can be made explicit by separating single-chain $S_s(q)$ and interference $S_I(q)$ parts in $S(q)$ as

$$S(q, C_p) = S_s(q) + C_p S_I(q) \quad (5)$$

where

$$S_s(q) = (1/n^2) \langle |\rho_1(\mathbf{q})|^2 \rangle_{\Psi_1(\mathbf{R}_1, \mathbf{S}_1)} \quad (6a)$$

$$S_I(q) = (V/n^2) \langle e^{i\mathbf{q}\cdot\mathbf{R}_{12}} \rho_1^*(\mathbf{q}) \rho_2(\mathbf{q}) \rangle_{\Psi_2(\mathbf{R}_1, \mathbf{S}_1, \mathbf{R}_2, \mathbf{S}_2)} \quad (6b)$$

It is to be noted that both $S_s(q)$ and $S_I(q)$ are concentration dependent in general. However, within the context of the SCA considered in this paper, $S_s(q)$ does not depend on concentration. Also $S_I(q)$ will be evaluated in the zero-concentration limit because it is already multiplied by concentration. In eqs. (6a) and (6b) the thermal averages are taken with respect to the one-chain $\Psi_1(\mathbf{R}_1, \mathbf{S}_1)$ and two-chain $\Psi_2(\mathbf{R}_1, \mathbf{S}_1, \mathbf{R}_2, \mathbf{S}_2)$ distribution functions, respectively. In Zimm's SCA only one pair of monomers that belong to two different chains is assumed to experience excluded-volume interaction at a time. Ψ_2 can therefore be expanded as follows:

$$\Psi_2(\mathbf{R}_1, \mathbf{S}_1, \mathbf{R}_2, \mathbf{S}_2) \simeq \Psi_1(\mathbf{R}_1, \mathbf{S}_1) \Psi_1(\mathbf{R}_2, \mathbf{S}_2) \left(1 - \chi \sum_{k,l} \delta(\mathbf{R}_{12} + \mathbf{S}_{1k2l}) \right) \quad (7)$$

where χ is the excluded volume per monomer. It is assumed, here, that χ is the

same for both labeled and unlabeled monomers. Using eq. (7), the interference term can be written as, for $q \neq 0$,

$$S_I(q) = -\chi N^2 S_R^2(q) \tag{8}$$

where

$$S_R(q) = \frac{1}{nN} \sum_{i,k} a_{1i} \langle e^{i\mathbf{q} \cdot \mathbf{S}_{1ik}} \rangle_{\Psi_1(\mathbf{R}_1, \mathbf{S}_1)} \tag{9}$$

is a partial form factor in which one of the summations is restricted to labeled monomers only. $S_R(q)$ becomes the familiar normalized single-chain static structure factor $S_s(q)$ in the case of totally labeled chains.

The concentration dependence of $S(q)$ is, therefore,

$$S(q, C_p) = S_s(q) [1 - k_s(q) C_p] \tag{10}$$

with

$$k_s(q) = \chi N^2 S_R^2(q) / S_s(q) \tag{11}$$

Expressions for both $S_s(q)$ and $S_R(q)$ are derived in Appendices A, B, and C for diblock DH, triblock DHD (label at both ends), and triblock HDH (label at the center) chains, respectively. A generalization to more complicated labeling sequences is straightforward.² We should note that in eq. (10), $S_s(q)$ is the single-chain static structure factor of the visible part only. It will be approximated in numerical calculations, ignoring the effect of the invisible part completely, by $S_s(q)$ for a chain identical to the labeled part.

CONCENTRATION DEPENDENCE OF THE FIRST CUMULANT

The first cumulant $\Omega(q)$ can be written in terms of the q -dependent mobility⁴ $\mu(q)$ as

$$\Omega(q) = q^2 k_B T \mu(q) / S(q) \tag{12}$$

with

$$\mu(q) = \frac{1}{N_p n^2} \sum_{\alpha, \alpha'} \sum_{j, j'} a_{\alpha j} a_{\alpha' j'} \left\langle \frac{\mathbf{q} \cdot \mathbf{D}(\mathbf{R}_{\alpha\alpha'} + \mathbf{S}_{\alpha j \alpha' j'}) \cdot \mathbf{q}}{q^2} e^{i\mathbf{q} \cdot (\mathbf{R}_{\alpha\alpha'} + \mathbf{S}_{\alpha j \alpha' j'})} \right\rangle \tag{13}$$

Here we use the conventional symbols for the diffusion tensor \mathbf{D} given by

$$\mathbf{D}(\mathbf{R}_{AB}) = (k_B T / \xi) [\mathbf{1} \delta_{AB} + \xi(1 - \delta_{AB}) \mathbf{T}(\mathbf{R}_{AB})] \tag{14}$$

the friction coefficient ξ and the Oseen tensor

$$\mathbf{T}(\mathbf{R}_{AB}) = \frac{1}{8\pi\eta\mathbf{R}_{AB}} \left(\mathbf{1} + \frac{\mathbf{R}_{AB}\mathbf{R}_{AB}}{\mathbf{R}_{AB}^2} \right) \tag{15}$$

We also choose the direction of \mathbf{q} along the z axis.

To obtain the linear concentration dependence of $\mu(q)$, i.e.,

$$\mu(q, C_p) = \mu(q) [1 - k_\mu(q) C_p] \tag{16}$$

we follow the procedure used in ref. 3, but we restrict the summations to labeled monomers only; i.e., we separate eq. (13) into single-chain and interference parts.

The first part gives rise to the generalized mobility in the infinite-dilution limit:

$$\mu(q) = \frac{1}{N\xi} + \frac{1}{(2\pi)^3} \int d^3K \tilde{T}_{33}(\mathbf{K} - \mathbf{q}) \left(S_s(\mathbf{K}) - \frac{1}{n} \right) \quad (17)$$

and does not depend on the unlabeled portion of the chain explicitly. The second part is calculated using the SCA. Unlike the self part, the invisible portion of the chain enters explicitly because the labeled or unlabeled monomers in that portion can experience contacts with monomers of other chains. Therefore, the interference part contains the partial form factor $S_R(q)$ defined in eq. (9). Putting both parts together yields

$$\mu(q, C_p) = \mu(q) - C_p \frac{\chi N^2}{(2\pi)^3} \int d^3K \tilde{T}_{33}(\mathbf{K} - \mathbf{q}) \left(S_R(\mathbf{K}) - \frac{1}{N} \right)^2 \quad (18)$$

The concentration coefficient in eq. (16) can be obtained from eq. (18) as

$$k_\mu(q) = \chi N^2 I_2(q) / I_1(q) \quad (19)$$

where we have defined (neglecting the Rouse term)

$$I_1(q) = \int d^3K \tilde{T}_{33}(\mathbf{K} - \mathbf{q}) \left(S_s(\mathbf{K}) - \frac{1}{n} \right) \quad (20a)$$

$$I_2(q) = \int d^3K \tilde{T}_{33}(\mathbf{K} - \mathbf{q}) \left(S_R(\mathbf{K}) - \frac{1}{N} \right)^2 \quad (20b)$$

The angular integrations are performed analytically in ref. 3 yielding

$$I_1(q) = \frac{2\pi}{\eta} \int_0^\infty dK \left(\frac{K}{2q} \frac{K^2 + q^2}{q^2} \ln \frac{|K+q|}{|K-q|} - \frac{K^2}{q^2} \right) \left(S_s(\mathbf{K}) - \frac{1}{n} \right) \quad (21a)$$

$$I_2(q) = \frac{2\pi}{\eta} \int_0^\infty dK \left(\frac{K}{2q} \frac{K^2 + q^2}{q^2} \ln \frac{|K+q|}{|K-q|} - \frac{K^2}{q^2} \right) \left(S_R(\mathbf{K}) - \frac{1}{N} \right)^2 \quad (21b)$$

and the K integrations are done numerically for each of the cases considered in Appendices A-C.

The concentration dependence of the first cumulant

$$\Omega(q, C_p) = \Omega(q) [1 + k_\Omega(q) C_p] \quad (22)$$

follows from eq. (12) as

$$k_\Omega(q) \simeq k_s(q) - k_\mu(q) \quad (23a)$$

or

$$k_\Omega(q) \simeq \chi N^2 \left(\frac{S_R^2(q)}{S_s(q)} - \frac{I_2(q)}{I_1(q)} \right) \quad (23b)$$

which is the main result in this paper. Equation (23b) reproduces the homopolymer case³ if the chains are totally labeled [i.e., when $S_R(q) = S_s(q)$].

DISCUSSIONS

Zimm's SCA was used to estimate static as well as dynamic properties of partially labeled chains in dilute solutions. This approximation enables one to express the intermolecular structure factor $S_I(q)$ in terms of an intramolecular

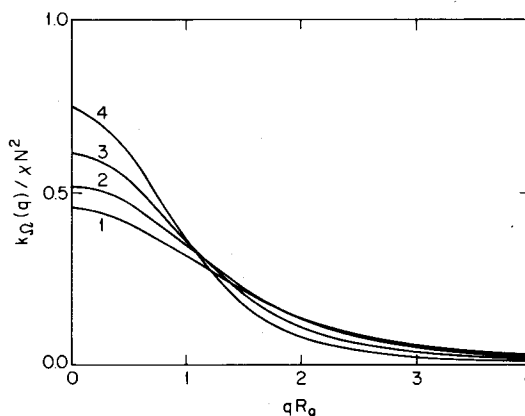


Fig. 1. Variation of $k_{\Omega}(q)/\chi N^2$ vs. $qR_g(N)$ in the diblock DH case for the following labeled fractions: 1, $3/4$, $1/2$, and $1/4$ (in curves 1, 2, 3, and 4, respectively). Debye functions have been used for the different static structure factors.

one $S_R(q)$. Another way of estimating $S_I(q)$ would be to use an explicit form for the pair distribution function $g(R)$ as a function of the intermolecular distance R , as was presented earlier⁵ for homopolymers. In ref. 5, $g(R)$ obtained from Monte Carlo simulation⁶ of chain interactions was used. The SCA approach used here does not rely on such $g(R)$ data. It is based on the knowledge of the static structure factor $S(K)$ over the whole range of momentum transfer K only.

The ratio $k_{\Omega}(q)/\chi N^2$ is plotted in Figures 1, 2, and 3 for diblock DH, triblock DHD, and triblock HDH chains, respectively. We consider four different labeled fractions $n/N = 1, 3/4, 1/2$, and $1/4$ in each case, and use the Gaussian-chain model [the completely swollen-chain model^{7,8} (with $\nu = 3/5$) could also be used instead] for the static structure factors $S_s(q)$. As we see in the appendices, the partial structure factor $S_R(q)$ can be expressed in terms of $S_s(q)$ for labeled and unlabeled portions and for the whole chain. The Gaussian-chain assumption requires a large number of statistical units; if the labeled sequence becomes too small, this model becomes questionable and we must resort to direct summations [as in Eq. (6a)].

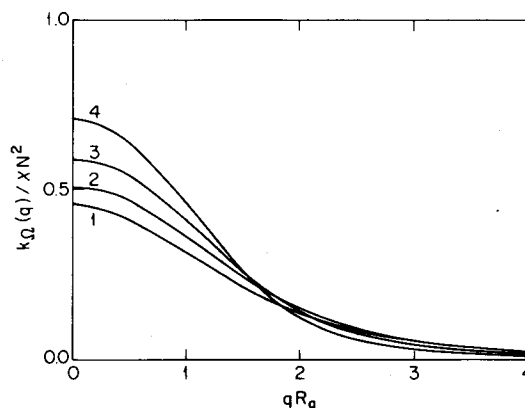


Fig. 2. As in Fig. 1 for triblock DHD.

UNA

the infinite-dilution

$$S_R(\mathbf{K}) - \frac{1}{n} \quad (17)$$

explicitly. The second portion of the invisible portion of labeled monomers in that chains. Therefore, the $S_R(q)$ defined in eq. (9).

$$S_R(\mathbf{K}) - \frac{1}{N} \quad (18)$$

obtained from eq. (18) as

$$(19)$$

$$S_R(\mathbf{K}) - \frac{1}{n} \quad (20a)$$

$$S_R(\mathbf{K}) - \frac{1}{N} \quad (20b)$$

locally in ref. 3 yielding

$$S_R(\mathbf{K}) - \frac{1}{n} \quad (21a)$$

$$S_R(\mathbf{K}) - \frac{1}{N} \quad (21b)$$

for each of the cases considered in

cumulant

$$C_p(q) \quad (22)$$

$$C_p(q) \quad (23a)$$

$$\frac{I_2(q)}{I_1(q)} \quad (23b)$$

Equation (23b) reproduces the homopolymer case [i.e., when $S_R(q) = S_s(q)$].

NS

as well as dynamic properties of the system. This approximation enables one to express $S_I(q)$ in terms of an intramolecular

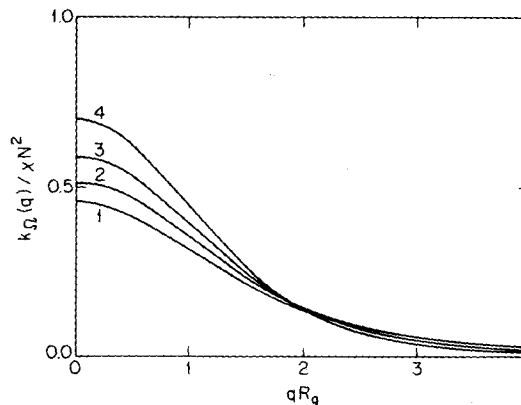


Fig. 3. As in Fig. 1 for triblock HDH.

In order to discuss the behavior of the curves in Figures 1-3 near the origin we consider the zero- q limit of $k_{\Omega}(q)$ in eq. (23b). Since $\Omega(q)/q^2$ approaches the short-time diffusion coefficient $D(C_p)$ in this limit, eq. (22) can be written as

$$D(C_p) = D(0)(1 + k_D C_p) \quad (24)$$

where $k_D \equiv k_{\Omega}(0)$ and denotes the concentration coefficient of the short-time diffusion coefficient for partially labeled chains. It is given by

$$k_D = \chi N^2 [1 - I_2(0)/I_1(0)] \quad (25)$$

The expressions of $I_1(0)$ and $I_2(0)$ follow from eqs. (21) as

$$I_1(0) = \frac{8\pi}{3\eta} \int_0^{\infty} dK \left(S_s(K) - \frac{1}{n} \right) \quad (26a)$$

and

$$I_2(0) = \frac{8\pi}{3\eta} \int_0^{\infty} dK \left(S_R(K) - \frac{1}{N} \right)^2 \quad (26b)$$

For homopolymers for which $n = N$, eq. (25) can be cast into the form

$$k_D^v = 8X^3 \left[1 - \frac{2}{\pi} \frac{R_H}{R_G} \int_0^{\infty} dy \left(S_s(y, N) - \frac{1}{N} \right)^2 \right] \quad (27)$$

if the number concentration C_p in eq. (24) is expressed as a volume fraction C_V using $C_V = v_H C_p$, where $v_H = \frac{4}{3}\pi R_H^3$, and denotes the hydrodynamic volume. The factor χN^2 in eq. (25) is replaced by $8v_H X^3$, where $X = \bar{S}/R_H$. In the latter, \bar{S} denotes the effective radius of excluded volume per molecule, and is defined as the radius of hard spheres with the same second virial coefficient as the actual polymers. The numerical value of the integral in eq. (27) is 1.247 when $S_s(y, N)$ is taken to be the Debye function for a chain of length N , and 1.425 when it is calculated using the fully swollen Gaussian-chain model (Peterlin's model⁷) with $\nu = 0.6$. The ratio R_H/R_G varies from 0.665 at the theta point to 0.537 in the good-solvent limit. The latter value is also calculated using the fully swollen Gaussian-chain model. With these numerical values one obtains $k_D^v = 4.6X^3$ and $3.7X^3$ using the Debye function and $R_H/R_G = 0.537$ and 0.665, respectively,

when Peterlin's model is used one finds $k_D^v = 4.1X^3$ and $3.1X^3$ for the same two values of R_H/R_G ratio. Other theoretical estimates^{8,10} of k_D^v for homopolymers cluster around 2 when $X = 1$, which is a value closer to the experimental results than those predicted from the above formulas. It is concluded that eq. (27), which is based on the single-contact approximation, predicts too large a concentration dependence for the short-time diffusion coefficient in the case of homopolymers.

In order to discuss the predictions of eq. (25) in the case of partially labeled chains, we consider 50% deuterated chains and calculate first the ratio D^{DHD}/D^{HDH} . Here, D^{DHD} denotes the short-time diffusion coefficient in the zero-concentration limit of the center of mass of the deuterated portions of length $1/4 N$ each at the two ends (DHD sequence), and D^{HDH} denotes the same in the case of an HDH sequence. Ignoring the Rouse term we obtain from eq. (17)

$$D^{DHD}/D^{HDH} = I_1^{DHD}(0)/I_1^{HDH}(0) \tag{28}$$

With the results presented in Appendices B and C one finds

$$I_1^{DHD}(0) = \int_0^\infty dK \left(4S_s(K, N) + S_s(K, 1/2N) - 1/2S_s(K, 3/4N) + 1/2S_s(K, 1/4N) - \frac{1}{N} \right)$$

and

$$I_1^{HDH}(0) = \int_0^\infty dK \left(S_s(k, 1/2N) - \frac{1}{N} \right)$$

These integrals can be reduced to a single integral of the Debye function if $S_s(K, m) - 1/N$ is taken to be the normalized Debye function $S_s(y)$, where $y = KR_G(m)$. In the latter $R_G(m)$ denotes the radius of gyration of a chain of length m including swelling. The result is

$$D^{DHD}/D^{HDH} = 1 + R_G(1/2N)[4R_G^{-1}(N) + 1/2R_G^{-1}(1/4N) - 1/2R_G^{-1}(3/4N)] \tag{29}$$

In the asymptotic power-law limits $R_G(m)/R_G(n) = (m/n)^\nu$ where $\nu = 0.5$ and 0.6 in the theta and good-solvent limits, respectively. Hence

$$D^{DHD}/D^{HDH} = 0.861 \quad (\text{theta}) \\ = 0.869 \quad (\text{good solvent}) \tag{30}$$

A simple physical interpretation of these results can be given when the length of the deuterated portion n is much smaller than the total length of the chain N . In this case the hydrodynamic interaction between the two halves of the labeled sections at the two chain ends in DHD sequence can be ignored (free draining). Then D^{DHD} becomes equal to one-half of the diffusion coefficient of a chain of length $1/2n$. Since D^{HDH} is the diffusion coefficient of a chain of length n , we find

$$D^{DHD}/D^{HDH} = 2^{\nu-1}$$

which yields 0.707 and 0.758 in the theta and good-solvent limits, respectively. These numerical values represent lower bounds for the ratio D^{DHD}/D^{HDH} , and are indeed smaller than those obtained in eq. (30) for 50% deuterated chains.

Equation (29) can also be used to calculate $D^{\text{DHD}}/D^{\text{HDH}}$ for intermediate solvents in terms of radii of gyration at a given solution temperature.

Since the numerical values in eq. (30) are universal numbers for 50% deuterated chains they can be tested experimentally by dynamic scattering. However, one must remember that the diffusion coefficients considered in the above discussion are all short-time diffusion coefficients.^{13,14} The long-time translational diffusion coefficient of a chain of length N is unique regardless of the length and arrangement of its experimentally visible portions. Is it then possible to measure the short-time diffusion coefficients in a dynamic scattering experiment? The initial decay of the normalized dynamic scattering function $S(q,t)$ is given by $\exp[-q^2 D^{\text{HDH}}(n)t]$, for example, in the case of an HDH sequence. The observation time interval in which $S(q,t)$ decays by a factor $\exp(-\alpha)$ is given by $q^2 D^{\text{HDH}}(n)t = \alpha$. On the other hand, long-time diffusion sets in crudely after the center of mass of the full chain diffuses across the size of the molecule, i.e., after $t_1 = R_G^2(N)/6D(N)$, which is an estimate of the longest Zimm relaxation time. Hence

$$\frac{t}{t_1} = \frac{6\alpha}{q^2 R_G^2(N)} \left(\frac{n}{N}\right)^\nu$$

In order to observe the short-time diffusion coefficient of the labeled portion, $t/t_1 \ll 1$ must hold. This implies

$$\alpha \ll \frac{1}{6}(N/n)^\nu q^2 R_G^2(N)$$

Since customarily $qR_G(N)$ is chosen to be sufficiently smaller than unity in diffusion experiments, an upper bound of α can be taken as $\frac{1}{24}(N/n)^\nu$ with $qR_G(N) = 0.5$. For a 50% deuterated chain with $\nu = 0.5$ this corresponds to only 6% decay of $S(q,t)$. It appears that the measurement of D^{DHD} by dynamic scattering is at least difficult if not impossible unless the ratio n/N is sufficiently small. We note, however, that the first cumulant $\Omega(q)/q^2$ is a measure of the short-time diffusion coefficient of a chain section with an end-to-end distance proportional to $1/q$, insofar as it is an internal motion of the chain and thus accessible without labeling by increasing q .

Figures 2 and 3 show that the magnitude and shape of the concentration coefficient $k_\Omega(q)$ as function of q are very similar for HDH and DHD sequences. This is somewhat expected because $k_\Omega(q)$ involves hydrodynamic interaction not only between the labeled monomers but among all monomers, visible or not, and consequently it is not sensitive to the sequence of the labeled monomers, at least for 50% deuteration.

A last observation is that $k_\Omega(q)/\chi N^2$ increases when the labeled fraction of the chain is decreased. This is due to the fact that $k_\Omega(q)$ represents the change in $\Omega(q, C_p)$ with concentration relative to $\Omega(q, 0)$, which increases when n/N is decreased. Had the concentration coefficient been defined as $\Omega(q, C_p) = \Omega(q) + K_\Omega(q)C_p$, $K_\Omega(q)$ would probably have decreased when the visible part was shortened.

The formalism used here can be applied to star and comblike branched chains as well. Burchard et al.⁹ have recently studied $S(q)$ as well as $\Omega(q)$ for block copolymeric star molecules in the infinite-dilution limit. The SCA has been extensively tested in the case of $S(q)$ and is being routinely used to extract the radius of gyration and the second virial coefficient from static scattering data.

as in the diblock case, and

$$S_R^{\text{HDH}}(q) = \frac{1}{nN} \sum_{i,j=(N-n)/2+1}^{(N+n)/2} \langle e^{i(\mathbf{q} \cdot \mathbf{S}_{1ij})} \rangle + \frac{2}{nN} \sum_{i=1}^{(N-n)/2} \sum_{j=(N-n)/2+1}^{(N+n)/2} \langle e^{i(\mathbf{q} \cdot \mathbf{S}_{1ij})} \rangle \quad (\text{C2})$$

Here also, using

$$2 \sum_{i=1}^{(N-n)/2} \sum_{j=(N-n)/2+1}^{(N+n)/2} \langle e^{i(\mathbf{q} \cdot \mathbf{S}_{1ij})} \rangle = \left(\frac{N+n}{2}\right)^2 S_s \left(q, \frac{N+n}{2}\right) - n^2 S_s(q, n) - \left(\frac{N-n}{2}\right)^2 S_s \left(q, \frac{N-n}{2}\right)$$

eq. (C2) becomes

$$S_R^{\text{HDH}}(q) = \frac{1}{nN} \left(\frac{N+n}{2}\right)^2 S_s \left(q, \frac{N+n}{2}\right) - \frac{1}{nN} \left(\frac{N-n}{2}\right)^2 S_s \left(q, \frac{N-n}{2}\right) \quad (\text{C3})$$

The different static structure factors introduced in these appendices are modeled by Debye functions

$$S_s(q, m) = (2/x^2)(e^{-x} + x - 1)$$

where $x = q^2 R_G^2(m)$ [$R_G(m)$ being the swollen radius of gyration for a chain of length m]; in the case of the fully swollen Gaussian-chain model^{7,8} the following equation could have been used instead:

$$S_s(q, m) = \frac{1}{\nu x^{1/2\nu}} \left[F \left(\frac{1}{2\nu}, x \right) - \frac{1}{x^{1/2\nu}} F \left(\frac{1}{\nu}, x \right) \right]$$

where $x = \frac{1}{6} q^2 a^2 m^{2\nu}$ ($\nu = 3/5$ for good solvents) and the function

$$F(b, x) = \gamma(b, x) - \gamma(b, x/m^{2\nu})$$

is given in terms of the incomplete gamma function

$$\gamma(b, x) = \int_0^x dt e^{-t} t^{b-1}$$

References

1. B. Zimm, *J. Chem. Phys.*, **14**, 164 (1946); **16**, 1093 (1948).
2. M. Benmouna and H. Benoit, *Polymer*, to appear.
3. B. Hammouda and A. Z. Akcasu, *Macromolecules*, **16**, 1852 (1983).
4. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University, Ithaca, NY, 1979.
5. A. Z. Akcasu and B. Hammouda, *Macromolecules*, **16**, 951 (1983).
6. O. F. Olaj, N. Lantschbauer, and K. H. Pelinka, *Macromolecules*, **13**, 299 (1980).
7. A. Peterlin, *J. Chem. Phys.*, **23**, 2462 (1955).
8. A. Z. Akcasu and M. Benmouna, *Macromolecules*, **11**, 1193 (1978).
9. W. Burchard, K. Kajiwara, D. Neger, and W. H. Stockmayer, *Macromolecules*, to appear.
10. A. Z. Akcasu, *Polymer*, **22**, 1169 (1981).
11. C. C. Han and A. Z. Akcasu, *Polymer*, **22**, 1165 (1981).
12. H. Van den Berg and A. M. Jamieson, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2311 (1983).
13. M. Fixman, *Macromolecules*, **14**, 1706 (1981).
14. A. Z. Akcasu, *Macromolecules*, **15**, 1321 (1982).

Received May 27, 1983

Accepted November 4, 1983