Application of Cascade Theory to Calculation of Quasielastic Scattering Functions. 2. Polydisperse Branched Molecules in Dilute Solutions

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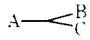
ABSTRACT: The decay constant $\Gamma(q)$ of the quasielastic scattering autocorrelation function (line width of the Rayleigh line) has been calculated on the basis of Bixon's theory for two systems of branched molecules. The formulas derived by means of the cascade theory cover the full region from quasielastic light to quasielastic neutron scattering. Hydrodynamic interaction between pairs of segments has been taken into account. The apparent diffusion constant $D_{\mathrm{app}}(q) = /q^2$ $(q = (4\pi/\lambda) \sin \theta/2)$ of the f-functional random polycondensate is found to be a unique function of the scattering vector q, and for large degrees of polymerization P_{w} this function is independent of the molecular weight and nearly independent of the functionality number f. For fairly large q values the function is well represented by the relationship $D_{\mathrm{app}} = (kT/\eta_0)0.053q$, in agreement with earlier calculations by Dubois-Violette and de Gennes for infinitly long linear chains. At very small q values (light scattering region) the function becomes independent of q and reduces to the z-average translatory diffusion constant D_{z}. D_{app} can for all functionalities be represented by $D_{\mathrm{app}} = D_{\mathrm{z}}P_{\mathrm{z}}^{-1/2}(q)$, where $P_{\mathrm{z}}(q)$ is the z average of the particle scattering factor of *elastically* scattered light. The second model considered consists of the restricted polycondensate of the  $\mathrm{A}{-}{<}^{\mathrm{B}}_{\mathrm{C}}$ type where group A can react with probability p with group C and probability $(1 - p)$ with group B, all other reactions are excluded. For branching probabilities $p > 0.1$ the apparent diffusion constant can in a wide range of q be approximated by $D_{\mathrm{app}} = D_{\mathrm{z}}P_{\mathrm{z}}^{-1/4}(q)$. The plot D_{app} vs. $P_{\mathrm{z}}^{-1/4}(q)$ shows, however, a weak upturn at very large q values (wide-angle neutron scattering). At $p < 0.05$ the plot shows a strong upturn, and the shape of the curve is governed by the number of branches per molecule.

In a preceding paper, part 1, cascade theory has been applied to the calculation of dynamic scattering functions of polydisperse linear chains.[1] Such calculations became possible through a recent paper by Akcasu and Gurol[2] who, on the basis of linear response theory,[3-5] derived equations for the quasielastic light and neutron scattering functions of monodisperse ideal linear chains.

The purpose of the present paper is to show that the framework of Bixon's theory[5] can likewise be employed for calculation of the dynamic coherent scattering functions of branched and polydisperse molecules. The formulas derived below by cascade theory are fairly simple and take account of the hydrodynamic interaction between segments of the branched molecules (Zimm–Rouse model). In the following, calculations are carried out for two types of branched molecules, i.e., (i) the f-functional random polycondensate and (ii) a trifunctional polycondensate where reaction between the three functional groups A, B, and C is restricted so that A can react with either of the groups B and C only. These two types were chosen as the resulting branched molecules differ significantly in the width of the molecular weight distribution.

Basic Equations

According to linear response theory the decay constant of the autocorrelation function (line width of a spectral line) is given by[1,2]

$$\Gamma = (\rho,L\rho)/(\rho,\rho) \tag{1}$$

where

$$(\rho,L\rho) = \int_0^\infty \rho(0)L\rho^*(0)\psi_0(\{\mathbf{R}\})\,\mathrm{d}\{\mathbf{R}\} \tag{2}$$

and

$$(\rho,\rho) = \int_0^\infty \rho(0)\rho^*(0)\psi_0(\{\mathbf{R}\})\,\mathrm{d}\{\mathbf{R}\} \tag{3}$$

In these equations L is a differential operator which is given in eq 8, and $\rho(t)$ is a time-dependent variable, specified below, which in general is a function of all internal coordinates $\{\mathbf{R}\}$ of a macromolecule, $\rho(0)$ is the same variable but at time $t = 0$, and $\rho^*(0)$ is the complex conjugate variable. $\rho(t)$ is generated by the action of the operator L by the formal equation

$$\rho(t) = [\exp(-tL)]\rho(0) \tag{4}$$

(The action of this operator equation becomes clear when expanding the exponential.) $\psi_0(\{\mathbf{R}\})$ is the equilibrium distribution function for the set of $3N$ coordinates of the N segments in a molecule or particle. As usual the distribution can be expressed by the partition function

$$\psi_0(\{\mathbf{R}\}) = z^{-1}\exp(-U(\{\mathbf{R}\})/kT) \tag{5}$$

$$z = \sum_{\text{all conformations}} \exp(-U(\{\mathbf{R}\})/kT) \tag{6}$$

The potential $U(\{\mathbf{R}\})$ is taken here as a purely intramolecular potential as only the limit of dilute solutions is considered. We confine the discussion to ideal flexible polymers where $U(\{\mathbf{R}\})$ depends on the position of the nearest neighbor only

$$U(\{\mathbf{R}\}) = \frac{3kT}{2b^2}\sum_{j=1}^{N}|\mathbf{R}_j - \mathbf{R}_{j-1}|^2 \tag{7}$$

The sum goes over all segments in the molecule, k is Boltzmann's constant, T is the absolute temperature, and b^2 is the mean square distance between two adjacent segments (or beads). Because of its similarity with the potential of a series of Hookian springs the model underlying eq 7 is called the spring-bead model.[6,7]

Obviously eq 3 is time independent and the static space correlation function which by the definition of a mean is the average of $|\rho(0)^2|$ may be written therefore as

$$(\rho,\rho) = \langle\rho(0)\rho^*(0)\rangle \tag{3'}$$

It can be calculated without principle difficulties if $\rho(0)$ is specified.[8,9]

The essential quantity in the calculation of Γ is the differential operator L. As long as dynamics deals with large particles immersed in a solvent which can be considered as a continuum L is the differential operator for Kirkwood's generalized diffusion equation[10] and is defined by[3,4,11]

$$L = \sum_j^N\sum_l^N [(kT)^{-1}\nabla_j\mathrm{U}\cdot\mathbf{D}_{jl}\cdot\nabla_l - \nabla_j\cdot\mathbf{D}_{jl}\cdot\nabla_l] \tag{8}$$

The quantities have the following meaning. The summation

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goes over all pairs of segments in a molecule, U is the potential given by eq 7, and ∇U is the entropic force that acts on the jth segment. $\mathbf{D}_{jl}$ is the diffusion tensor

$$\mathbf{D}_{jl} = kT[\mathbf{T}_{jl} + \zeta^{-1}\mathbf{1}\delta_{jl}] \quad (9)$$

with the Oseen tensor $\mathbf{T}_{jl}$

$$\mathbf{T}_{jl} = (8\pi\eta_0 R_{jl}^3)^{-1}[\mathbf{1}R_{jl}^2 + \mathbf{R}_{jl}\mathbf{R}_{jl}] \quad (10)$$

which describes the hydrodynamic interactions between segment pairs j and l.

Most recent theoretical treatments of chain dynamics start directly with the operator L in the form given by eq 8. This requires the calculation of $\nabla_j U$[4,5,12] and consequently the specification of a model at this point. No difficulties arise for ring polymers[5] and for large linear chains where the force acting on the chain-end segments can be neglected against the sum of forces acting on the central segments.[12] Such treatment is not possible for branched molecules with its numerous end groups, but consideration of the chain-end effects encumbers the problem with immense difficulties which up to date have been only solved for star molecules by Zimm and Kilb.[13]

However, the problem simplifies greatly when eq 8 is inserted into eq 2 and the integral is rearranged

$$(\rho,L\rho) = \int_0^\infty \Bigg[\rho(0) \sum_j^N \sum_l^N (kT)^{-1}\nabla_j U \cdot \mathbf{D}_{jl} \cdot \nabla_l \delta^*(0) - \rho(0) \sum_j^N \sum_l^N \nabla_j \cdot \mathbf{D}_{jl} \cdot \nabla_l \rho^*(0)\Bigg] \psi_0(\{\mathbf{R}\})\, \mathrm{d}\{\mathbf{R}\} \quad (11)$$

The second term vanishes identically since the divergence of the diffusion tensor is zero. From eq 5 we have

$$\nabla_j \psi_0 = -kT\psi_0 \nabla_j U \quad (12)$$

and thus

$$(\delta,L\delta) = -\sum_j^N \sum_l^N \int_0^\infty \rho(0)\nabla_j\psi_0 \cdot \mathbf{D}_{jl} \cdot \nabla_l \rho^*(0)\, \mathrm{d}\{\mathbf{R}\} \quad (13)$$

Integration by parts yields

$$(\rho,L\rho) = \sum_j^N \sum_l^N \int_0^\infty [\nabla_j \rho(0) \cdot \mathbf{D}_{jl} \cdot \nabla_l \rho^*(0)]\psi_0(\{\mathbf{R}\})\, \mathrm{d}\{\mathbf{R}\} \quad (14)$$

where again use is made of $\nabla_j \mathbf{D}_{jl} = 0$. The derivation of eq 14 is due to Bixon.[5] This equation has the remarkable property of containing no longer the intramolecular potential $U(\{\mathbf{R}\})$ explicitly and of being quite general. At no stage was specification to a special model, linear or branched, needed. All characteristics are absorbed in the static space variables $\rho(0)$ and the equilibrium distribution $\psi_0(\{\mathbf{R}\})$.

In coherent quasielastic scattering the relevant variables are[14]

$$\rho(0) = \sum_{j=1}^N \exp(i\mathbf{q} \cdot \mathbf{R}_j)$$

$$\rho^*(0) = \sum_l^N \exp(-i\mathbf{q} \cdot \mathbf{R}_l) \quad (15)$$

where $q = (4\pi/\lambda) \sin \theta/2$, λ is the wavelength in the medium, and θ is the scattering angle. The sum goes over all segments in a molecule. Performing the required gradient differentiation in eq 14 one obtains

$$(\rho,L\rho) = \sum_{j\neq}^N \sum_l^N \int_0^\infty [(\mathbf{q} \cdot \mathbf{D}_{jl} \cdot \mathbf{q}) \exp(-\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_l))]\psi_0(\{\mathbf{R}\})\, \mathrm{d}\{\mathbf{R}\} + \sum_{j=1}^N \int_0^\infty [(\mathbf{q} \cdot \mathbf{D}_{jj} \cdot \mathbf{q})]\psi_0(\{\mathbf{R}\})\, \mathrm{d}\{\mathbf{R}\} \quad (16)$$

where the terms $j = l$ have been separated for obvious reasons. All terms in the square brackets depend on the interstitial coordinates of pairs only. Therefore, integration can be performed over all coordinates with the exception of the pair coordinates j and l. This gives the pair distance distribution

$$P(\mathbf{R}_{jl}) = \int_0^\infty \psi_0(\{\mathbf{R}\})\, \mathrm{d}\{\mathbf{R}\}/\mathrm{d}\mathbf{R}_{jl}$$

$$\mathbf{R}_{jl} = \mathbf{R}_j - \mathbf{R}_l \quad (17)$$

We thus arrive at the final relationship

$$(\rho,L\rho) = \sum_{j\neq}^N \sum_l^N \langle(\mathbf{q} \cdot \mathbf{D}_{jl} \cdot \mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_{jl})\rangle + \sum_j^N \langle \mathbf{q} \cdot \mathbf{D}_{jj} \cdot \mathbf{q}\rangle \quad (18)$$

and

$$(\rho,\rho) = \sum_j^N \sum_l^N \langle \exp(i\mathbf{q}\mathbf{R}_{jl})\rangle \quad (19)$$

The angle brackets now mean averages with respect to the segment pair distribution. Equation 18 was first derived by Akcasu and Gurol[2] under the restriction of linear chains. The derivation is repeated here in order to show that this equation is quite general and not restricted to linear chains or a special model.

Branched Molecules

Applying eq 18 and 19 to branched molecules we make the following approximations:

(1) The pair distance distribution $P(\mathbf{R}_{jl})$ is assumed to be Gaussian

$$P(\mathbf{R}_{jl}) = \left(\frac{3}{2\pi b^2|j-l|}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{\mathbf{R}_{jl}^2}{b^2|j-l|}\right) \quad (20)$$

where b is the effective bond length or step length in a random flight process.[7,15]

(2) A preaveraged diffusion tensor $\langle\mathbf{D}_{jl}\rangle$ is used, and the correct average in eq 18 is approximated by

$$\langle(\mathbf{q} \cdot \mathbf{D}_{jl} \cdot \mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_{jl})\rangle \sim \mathbf{q} \cdot \langle\mathbf{D}_{jl}\rangle \cdot \mathbf{q}\langle \exp(i\mathbf{q} \cdot \mathbf{R}_{jl})\rangle \quad (21)$$

The accuracy of the last approximation was tested by Akcasu and Gurol.[2] The deviations are found to be small for $q \cdot b < 0.5$ and do not exceed 25% if $q \cdot b = 1$. This region corresponds already to fairly wide angle neutron scattering. (If $\lambda = 1$ nm and $b = 1$ nm one has $\theta = 9.13$ angle degrees.) Thus the preaveraging approximation covers the full region of quasielastic light scattering and that of coherent small-angle neutron scattering.

With approximations (1) and (2) one obtains

$$(\rho_1 L\rho) = q^2\frac{kT}{\zeta}\left\{N + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b} \times \sum_{j\neq}^N \sum_l^N \int_0^\infty \exp(-(\beta^2 + q^2b^2/6)|j-l|)\, \mathrm{d}\beta\right\} \quad (22)$$

and

$$(\rho,\rho) = \sum_j^N \sum_l^N \exp(-(q^2b^2/6)|j-l|) = N^2P(q) \quad (23)$$

where $P(q)$ is the particle scattering factor and use has been made of the integral relationship[16,17]

$$|j-l|^{1/2} = \frac{2}{\pi^{1/2}} \int_0^\infty \exp(-\beta^2|j-l|)\, \mathrm{d}\beta \quad (24)$$

Polydisperse Systems

The decay constant of the quasielastic autocorrelation function of any polydisperse system was shown to be[1]

$$\overline{\Gamma}_{\mathrm{Qs}} = \frac{\sum w_N N^{-1}(\rho,L\rho)_N}{\sum w_N N^{-1}(\rho,\rho)_N} = \frac{\sum w_N N^{-1}(\rho,L\rho)_N}{P_{\mathrm{w}}P_{\mathrm{z}}(q)} \qquad (25)$$

In this equation w_N is the weight fraction of a polymer of degree of polymerization N, P_{w} is the weight-average degree of polymerization, and $P_{\mathrm{z}}(q)$ is the z average of the particle scattering factor. Collecting eq 22, 23, and 25 one obtains

$$\frac{\overline{\Gamma}_{\mathrm{Qs}}}{q^2(kT/\zeta)} = [P_{\mathrm{w}}P_{\mathrm{z}}(q)]^{-1}\left\{1 + \frac{2\zeta}{6^{1/2}\pi^2 b\eta_0} \times \int_0^\infty \sum_{N=1}^{\infty} w_{\mathrm{N}}\mathrm{N}^{-1} \sum_{j\neq}^{N}\sum_{l}^{N} \exp(-[\beta^2 + q^2b^2/6]|j-l|)\,\mathrm{d}\beta\right\} \qquad (26)$$

and

$$P_{\mathrm{w}}P_{\mathrm{z}}(q) = \sum_{n=1}^{\infty} w_N N^{-1} \sum_{j}^{N}\sum_{l}^{N} \exp(-(q^2b^2/6)|j-l|) \qquad (27)$$

The sum in both equations is directly obtained from the derivative of a path weighted generating function $U_1'(1,\phi) \equiv (\mathrm{d}U_0(s,\phi)/\mathrm{d}s)_{s=1}$ for the branched molecules which has been derived for several branching models previously.[18,19] ϕ is a special statistical weighting function which defines the desired average. As shown in part 1[1] one has

$$P_{\mathrm{w}}P_{\mathrm{z}}(q) = U_0'(1,Z(q)) \qquad (28)$$

and

$$\int_0^\infty \sum_{N=1}^{\infty} w_N N^{-1} \sum_{l\neq}^{N}\sum_{j}^{N} \exp(-[\beta^2 + q^2b^2/6]|j-l|)\,\mathrm{d}\beta = \int_0^\infty U_0'(1,Z(q)\exp(-\beta^2))\,\mathrm{d}\beta \qquad (29)$$

where the abbreviation is used

$$Z(q) = \exp(-q^2b^2/6) \qquad (30)$$

We apply these relationships to the models of f-functional random polycondensates[18] and of a trifunctional polycondensate[19] formed under the restriction that group A had reacted with either of the two groups B and C only.[20]

f-Functional Random Polycondensates

The derivative of the path weighted generating function was derived by Kajiwara et al.[18]

$$U_0'(1,\phi) = \phi_0 + \frac{\alpha f\phi}{1-(f-1)\alpha\phi} \qquad (31)$$

where α is the link probability, i.e., the extent of reaction for the functional groups. The factor ϕ_0 is added to take into account the statistical weight for the path length zero, i.e., $\mathbf{R}_{jl} = 0$. In most cases ϕ_0 is zero but not for the particle scattering factor where

$$\phi_0 = \exp(-q^2\langle \mathbf{R}_{jl}^2\rangle) = 1 \quad \text{if } \langle \mathbf{R}_{jl}^2\rangle = 0 \qquad (32)$$

With the specification for ϕ given by eq 28 and 29 one finds

$$P_{\mathrm{w}}P_{\mathrm{z}}(q) = \frac{1+\alpha Z(q)}{1-\alpha(f-1)Z(q)} \qquad (33)$$

$$\frac{\overline{\Gamma}_{\mathrm{Qs}}}{q^2(kT/\zeta)} = [P_{\mathrm{w}}P_{\mathrm{z}}(q)]^{-1} \times \left\{1 + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b}\int_0^\infty \frac{\alpha f Z(q)\exp(-\beta^2)}{1-\alpha(f-1)Z(q)\exp(-\beta^2)}\,\mathrm{d}\beta\right\} \qquad (34)$$

with $Z(q)$ given by eq 30.

Integrals of the form in eq 34 can be approximated within 0.1% by

$$\int_0^\infty \left[\frac{\exp(-\beta^2)}{1-c\exp(-\beta^2)}\right]^n \mathrm{d}\beta \sim \frac{1.57/n}{(1-c)^{n-1/2}} - 1.1 \qquad (35)$$

if

$$0.875 \le c < 1; \quad n = 1, 2 \qquad (36)$$

The region of validity corresponds to $P_{\mathrm{w}} > 30$ if $qb = 1$ and $P_{\mathrm{w}} > 10$ if $qb = 0.2$. Hence,

$$\frac{\overline{\Gamma}_{\mathrm{Qs}}}{q^2(kT/\zeta)} = [P_{\mathrm{w}}P_{\mathrm{z}}(q)]^{-1} \times \left\{1 + \frac{2\zeta\alpha f Z(q)}{6^{1/2}\pi\eta_0 b}\left[\frac{1.57}{(1-\alpha(f-1)Z(q))^{1/2}} - 1.1\right]\right\} \qquad (37)$$

The z-average diffusion constant results from eq 37 in the limit of $q \to 0$

$$D_{\mathrm{z}} = \frac{(kT/\zeta)}{P_{\mathrm{w}}}\left[1 + \frac{2\zeta\alpha f}{6^{1/2}\pi^2\eta_0 b}\left(\frac{1.57P_{\mathrm{w}}^{1/2}}{(1+\alpha)^{1/2}} - 1.1\right)\right] \qquad (38)$$

With the use of eq 38 the angular distribution of the decay constant can be written

$$\frac{\overline{\Gamma}_{\mathrm{Qs}}}{q^2} \equiv D_{\mathrm{app}}(q) = (D_{\mathrm{z}}/P_{\mathrm{z}}(q)) \frac{1+ (2\zeta\alpha f Z(q)/6^{1/2}\pi^2\eta_0 b)(1.57/(1-\alpha(f-1)Z(q))^{1/2} - 1.1)}{1 + (2\zeta\alpha f/6^{1/2}\pi^2\eta_0 b)[1.57/(1-\alpha(f-1))^{1/2} - 1.1]} \qquad (39)$$

The link probability α can be expressed either by the weight-average degree of polymerization or the z-average mean square radius of gyration[18]

$$P_{\mathrm{w}} = \frac{1+\alpha}{1-\alpha(f-1)} \qquad (40)$$

$$\langle S^2\rangle_{\mathrm{z}} = b^2\frac{\alpha f}{2(1+\alpha)[1-\alpha(f-1)]} \qquad (41)$$

It is useful to consider the limit of large P_{w} where $\alpha(f-1) \sim 1$[20]

$$\langle S^2\rangle_2 \to b^2\frac{f-1}{2f}P_{\mathrm{w}} \qquad (42)$$

$$D_{\mathrm{z}} \to kT\frac{1.57}{3^{1/2}\pi^2\eta_0}\langle S^2\rangle_2^{1/2} = 0.0918(kT/\eta_0)\langle S^2\rangle_{\mathrm{z}}^{-1/2} \qquad (43)$$

Furthermore, if $qb \ll 1$ the term 1 in the numerator of eq 39 can also be neglected yielding

$$D_{\mathrm{app}}(q) \to (D_{\mathrm{z}}/P_{\mathrm{z}}(q))\left(\frac{1+\alpha}{1+\alpha Z(q)}\right)^{1/2} Z(q) \qquad (44)$$

and in the limit of small q^2

$$D_{\mathrm{app}}(q) = D_{\mathrm{z}}(1 + (1/6)\langle S^2\rangle_{\mathrm{z}}q^2 + \ldots) \qquad (45)$$

Trifunctional Polycondensate Formed Under Constraints

Let α be the extent of reaction of functional group A and β and γ the extents of reaction of the functional groups B and C. The constraint to which the three functional groups are submitted, i.e., that A can react with B or C only, is represented then analytically by

$$\alpha = \beta + \gamma = \alpha(1-p) + \alpha p \qquad (46)$$

The probability p has the meaning of a branching density while $(1-p)$ gives the probability for the formation of a linear chain. The statistics of this model were treated in previous papers,[19,20] and the derivative of the path weighted generating function was found to be

$$U_0^1(1,\phi) = \phi_0 + \frac{2\alpha\phi}{1-\alpha\phi} + \frac{2\alpha^2 p(1-p)\phi^2}{(1-\alpha\phi)^2} \qquad (47)$$

Using the specification of eq 28 and 29 one obtains

$$P_wP_z(q) = 1 + \frac{2\alpha Z(q)}{1-\alpha Z(q)} + 2p(1-p)\left(\frac{\alpha Z(q)}{1-\alpha Z(q)}\right)^2 \quad (48)$$

and

$$\frac{\overline{\Gamma}_{Qs}}{q^2(kT/\zeta)} = (P_wP_z(q))^{-1}\left\{1 + \frac{2\zeta}{6^{1/2}\pi^2\eta_0 b} \times\left[\int_0^\infty \frac{2\alpha Z(q)\exp(-\beta^2)}{1-\alpha Z(q)\exp(-\beta^2)}\,\mathrm{d}\beta + \int_0^\infty 2p(1-p)\left(\frac{\alpha Z(q)\exp(-\beta^2)}{1-\alpha Z(q)\exp(-\beta^2)}\right)^2\mathrm{d}\beta\right]\right\} \quad (49)$$

where $Z(q)$ is given by eq 30. With the approximation of eq 35 for the two integrals in eq 49 one finds

$$\frac{\overline{\Gamma}_{Qs}}{q^2(kT/\zeta)} = (P_wP_z(q))^{-1}\left\{1 + \frac{2\zeta}{6^{1/2}\pi^2\nu_0 b} \times\left[2\alpha Z(q)\left(\frac{1.57}{(1-\alpha Z(q))^{1/2}} - 1.1\right) + 2p(1-p)\alpha^2 Z(q)^2\left(\frac{0.775}{(1-\alpha Z(q))^{3/2}} - 1.1\right)\right]\right\} \quad (50)$$

and

$$D_z = \frac{kT}{P_w}\left\{\zeta^{-1} + \frac{4\alpha}{6^{1/2}\pi^2\eta_0 b}\left[\left(\frac{1.57}{(1-\alpha)^{1/2}} - 1.7\right) + \alpha p(1-p)\left(\frac{0.775}{(1-\alpha)^{3/2}} - 1.1\right)\right]\right\} \quad (51)$$

As in the case of the random f-functional polycondensates the link probability α can be replaced by P_w or by $\langle S^2\rangle_z$[19,20]

$$P_w = \frac{1-\alpha^2[1-2p(1-p)]}{(1-\alpha)^2} \quad (52)$$

$$\langle S^2\rangle_z = b^2\frac{\alpha - \alpha^2(1-p)^2 - \alpha^2p^2}{[1-\alpha^2(1-p)^2-\alpha^2p^2](1-\alpha)} \quad (53)$$

Asymptotic Behavior

For large degrees of polymerization $P_w \gg 1$ one has $\alpha Z \sim 1$, hence

$$\frac{\overline{\Gamma}_{Qs}}{q^2} \equiv D_{app}(q) = (D_Z/P_z(q))\left[\frac{1-\alpha}{1-\alpha Z(q)}\right]^{3/2} \times\frac{(1-\alpha Z(q))\alpha Z(g) + (p(1-p)/2)(\alpha Z(q))^2}{(1-\alpha)\alpha + (p(1-p)/2)\alpha^2} \quad (54)$$

and

$$D_z = \frac{kT}{P_w}\frac{3.14}{6^{1/2}\pi^2\eta_0 b}\frac{\alpha^2(1-p)p + 2\alpha(1-\alpha)}{(1-\alpha)^{3/2}} \quad (55)$$

It is useful to consider the case $1-\alpha \ll p(1-p)$. One readily verifies

$$P_w \to \frac{2p(1-p)}{(1-\alpha)^2} \quad (56)$$

$$\langle S^2\rangle_z \to \frac{b^2}{1-\alpha}\left(1 - \frac{1-\alpha}{2p(1-p)}\right) \to \frac{b^2}{1-\alpha}[1-(2p(1-p)P_w)^{-1/2}] \quad (57)$$

$$D_z \to \frac{kT}{\eta_0 b}\frac{1.57}{6^{1/2}\pi^2}\left(\frac{2p(1-p)}{P_w}\right)^{1/4}[1+4(2p(1-p)P_w)^{-1/2}] \quad (58)$$

or

$$D_z \to \frac{kT}{\eta_0}\frac{1.57}{6^{1/2}\pi^2}\langle S^2\rangle_z^{-1/2}[1+2(2p(1-p)P_w)^{-1/2}] \quad (59)$$

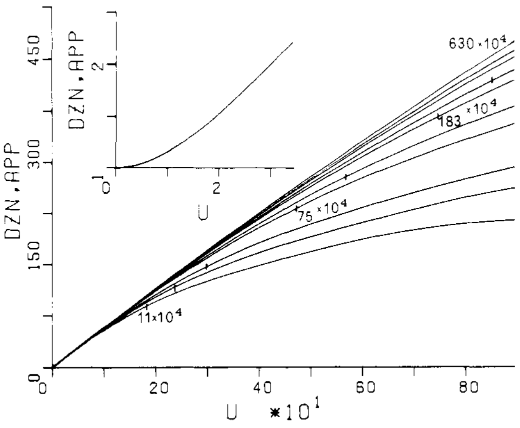

Figure 1. Plot of D_{app}/D_z (= DZN, APP) against $u = q\langle S^2\rangle_z^{1/2}$ for f-functional random polycondensates of various degrees of polymerization P_w. The bars indicate the limit of $qb = 1$. The set of curves is nearly independent of the functionality number f. Insert: behavior at small u values (light-scattering region).

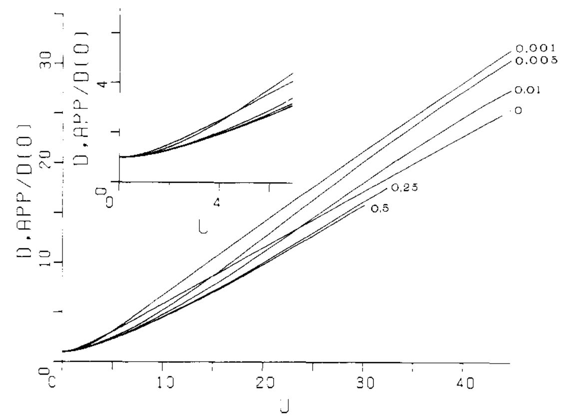

Figure 2. Plot of D_{app}/D_z against u for the trifunctional $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polycondensates. The numbers indicate values of the branching probability p, $P_w = 10^8$. Insert: behavior at small u.

and

$$D_{app} = D_zP_z^{-1/4}(q)Q(p,q) \quad (60)$$

with

$$Q(p,g) = \left(\frac{1-\alpha^2[1-2p(1-p)]}{1-\alpha^2Z^2(q)[1-2p(1-p)]}\right)^{3/2} \times\frac{Z(q) + 2[(1-\alpha Z(g))/p(1-\mathrm{p})]}{1+2[(1-\alpha)/p(1-p)]}Z(q) \quad (61)$$

$P_z(q)$ is given by eq 48. For comparatively small values of q (light scattering region) the function $Q(p,q) \sim 1$. Expansion in terms of q^2 gives, if $1-\alpha \ll p(1-p)$

$$D_{app} = D_z(1 + (1/12)\langle S^2\rangle_z q^2 + \ldots) \quad (62)$$

For $p = 0$ on the other hand all the equations for a linear chain with a most probable length distribution are retained, i.e., $f = 2$ in random polycondensates. In this limit the coefficient of the term $\langle S^2\rangle_z q^2$ in eq 62 is 1/6. We did not succeed in deriving simple approximate equations for very small branching probabilities p. The relationships depend in a rather complicated manner on both the branching probability and the degree of polymerization.

Computations and Discussion

Angular Dependence of $D_{app}(q)$. The angular dependence of the apparent diffusion constant, defined as $\overline{\Gamma}_{QS}/q^2$ by eq 39 and 52, respectively, has been computed. The result is plotted in various ways in Figures 1 to 4. Since for the f-

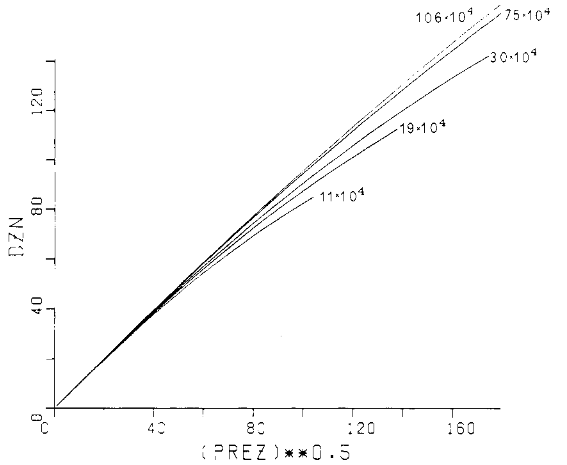

Figure 3. Plot of D_{app}/D_z against $P_z^{-1/2}(q)$ for the *f*-functional polycondensates of different *P*. $P_z(q)$ is the particle scattering factor of the *elastically* scattered light. PREZ = $P_z^{-1}(q)$.

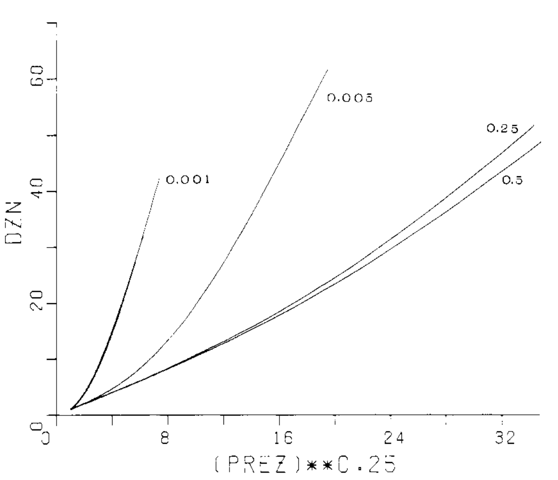

Figure 4. Plot of D_{app}/D_z against $P_z^{-1/4}(q)$ for the $A\!-\!\!<^{B}_{C}$ polycondensates. The numbers indicate the branching probability. $P_w = 10^8$.

functional random polycondensates D_{app} behaves asymptotically like $P_z^{-1/2}(q)$ and since the reciprocal particle scattering factor can be well represented by[18,20]

$$P_z(q)^{-1} = 1 + 1/3\langle S^2\rangle_z q^2$$

one finds with eq 44 the asymptotic behavior

$$D_{app}(q) \to D_z(1 + 1/3\langle S^2\rangle_z q^2)^{1/2} \to D_z\langle S^2\rangle_z^{1/2} q/3^{1/2} \tag{63}$$

and with the use of eq 43 the simple relationship

$$D_{app}(q) \to 0.053(kT/\eta_0)q \tag{64}$$

The last relationship is independent of the functionality number *f* and therefore valid for $f = 2$ too, which is the case of linear chains which obey the most probable length distribution, i.e., $P_w/P_n = 2$.[1] Dubois-Violette and de Gennes[21] and recently Akcasu and Gurol[2] found for monodisperse linear chains the somewhat larger value of

$$D_{app}(q) \to 0.055(kT/\eta_0)q \tag{65}$$

Computations indeed yield a common curve for D_{app}/D_z as a function of *q* which holds for all numbers of functionalities and different degrees of polymerization. A spread of curves, independent of the functionality, is obtained, however, for various P_w if D_{app}/D_z is plotted against $u = q\langle S^2\rangle_z^{1/2}$. This plot exhibits an almost rectilinear behavior in a wide range of *u*. The curves are, however, not strictly linear, and the constant of eq 64 represents the maximum slope at fairly small *q* values. Empirically the somewhat lower value of 0.050 is obtained when averaging over the slightly bent curve by a straight line. At very small *q* values, the light scattering region, the curve is not linear but becomes gradually independent of *q* as could be expected from eq 63 (see insert in Figure 1).

The curves bend down at very large *q* values, the wide-angle neutron scattering region, and finally a constant value is approached. The appearance of this plateau cannot be assigned a physical meaning, because in that region the variable *qb* is already much larger than 1; the validity of the present model calculations is, however, confined to values of $qb < 1$. In fact, besides the mathematical limit of validity, the effect of chain stiffness starts to play an important role. Also, it remains doubtful whether the neglect of the memory term, defined in part 1,[1] is still justified. Finally local modes of motion will now govern the dynamic behavior, which by no means can properly be described by the spring-bead model with its somewhat artificial segment concept.[22] The same arguments apply to the plateau found by Akcasu and Gurol[2] for monodisperse linear chains. Since $u = q\langle S^2\rangle_z^{1/2}$ and $\langle S^2\rangle_z \propto P_w$ the deviations from the almost rectilinear line occur at lower *u* values for samples with lower molecular weight.

In contrast to the random *f*-functional polycondensates the linear section in a plot of D_{app}/D_z against *u* is short, if it exists at all, for the trifunctional polycondensate formed under constraints. See Figure 2. This behavior could be anticipated from eq 59. The curves in Figure 2 lie close together as long as the branching probability *p* is larger than 0.05; for values $p < 0.05$ a strong variation in shape results for the curves which are now determined by the number of branches per molecule, i.e., by values of pP_w. An almost linear graph is obtained for values of $D_{app}/D_z < 10$ if this function is plotted against $P_z^{-1/4}(q)$. Figure 4 demonstrates the validity of this approximation with values of the branching probability of p = 0.5–0.05. At larger value of D_{app}/D_z a small upturn is obtained. This upturn becomes very pronounced for small branching probabilities and depends on the magnitude of pP_w.

A well-defined linear graph within a wide range of *q* is also found for the *f*-functional random polycondensate, but now a plot against $P_z^{-1/2}(q)$ is applied, see Figure 3. At large *q* values a molecular weight dependent downturn occurs similar to that shown in Figure 1. The essential difference in behavior of the random polycondensate with its $P_z^{-(1/2)}(q)$ dependence and the non-randomly formed trifunctional polycondensate of the $A\!-\!\!<^{B}_{C}$ type with its $P_z^{-1/4}(q)$ dependence may help differentiating experimentally between randomly and non-randomly formed branched polymers, but it requires measurements of both the elastic and quasielastic scattering functions of the same sample. However, the full angular dependence of $P_z(q)$ is not necessarily required; the initial part will suffice as may be seen from Figure 5, where D_{app}/D_z is plotted against $u^2 = q^2\langle S^2\rangle_z$. The slope for the linear chain, i.e., $p = 0$ or $f = 2$, respectively, is $1/6$; it decreases then as the branching probability is increased and reaches a value of $1/12$ if $p > 0.05$.

D_z as a Function of P_w. The formulas for the z-average diffusion constant are by-products of the calculating of the autocorrelation decay constant as a function of the scattering angle. The relationships result from the equations for $D_{app}(q)$ at $q = 0$. For the random *f*-functional polycondensate one finds in the limit of large P_w.

$$D_z = \frac{kT}{\eta_0} b 0.1299 \left(\frac{f}{f-1}\right)^{1/2} P_w^{-1/2} \tag{66}$$

This result agrees with calculations by Kajiwara.[17] In contrast to this square-root dependence on the degree of polymerization P_w the trifunctional restricted polycondensate of

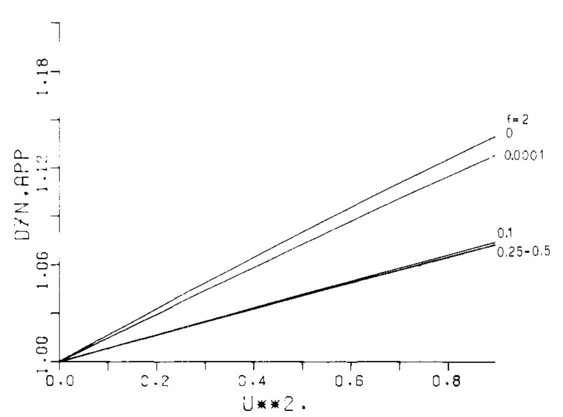

Figure 5. D_{app}/D_z as a function of u^2. The numbers give the values of the branching probability. Note: $p = 0$ represents the linear chain with most probable length distribution and corresponds to the case $f = 2$ of the random f-functional polycondensates.

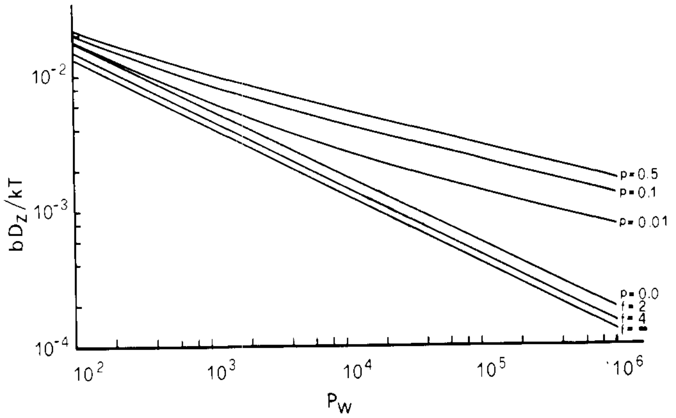

Figure 6. Molecular weight dependence of the z-average diffusion constant D_z for the $A\!-\!\!<^{B}_{C}$ type polycondensates, upper four curves, and for the f-functional polycondensates, lower three curves.

the $A\!-\!\!<^{B}_{C}$ type shows behavior that varies between a $P_w^{-1/2}$, at small P_w and low branching density, and a $P_w^{-1/4}$ dependence, at large P_w, see eq 56. The corresponding curves are shown in Figure 6 and are compared with those of the random f-functional polycondensates. The case $p = 0$ in the one model and $f = 2$ in the other represents linear chains with most probable length distribution and consequently the two straight lines for both models coincide.

Concluding Remarks

The pioneering work by Pecora aroused expectations that the lowest modes of the internal vibrations in the spring-bead model could be determined by quasielastic light scattering or neutron small-angle scattering. This expectation has its root in the approximate solution of the mathematical problem by means of a series expansion. The results obtained by Pecora turn out now to be a consequence of the truncation of the series expansion. Büldt[23] who succeeded recently in solving Pecora's power series without any truncation showed, however, that the higher terms must not be neglected. He found that the autocorrelation decay constant is a smooth function of the scattering vector q, and in the Rouse limit of no hydrodynamic interaction the decay constant is solely determined by the reciprocal particle scattering factor of the elastically scattered light and the z-average translatory diffusion constant. The same behavior is found in the present paper from eq 37 when the second term in the brackets is small compared with 1.

Certainly the case of hydrodynamic interaction is more realistic and plays the predominant role at large degrees of polymerization. Also in this case the angular dependence of the decay constant is widely determined by the particle scattering factor, but the functional dependence of $P_z(q)$ depends now on the type of branching.

In the discussion on quasielastic neutron scattering[24] the expectation has been expressed that vibrational modes of the branching points may cause significant deviations from the behavior of linear chain sections which are mainly observed in neutron scattering. For randomly branched polymers such expectation is not justified. The large distribution of isomeric structures inevitably causes a broad spectrum of relaxation times that overlap the relaxation spectrum of the linear chain sections, and in scattering experiments it is not possible to filter out a fairly narrow region of relaxation modes. A possibility of detecting vibrational modes from branching points may arise in branched block copolymers where spherical nuclei formed by the one component are the branching points which are connected by linear chains of uniform length. In such polymers the relaxation spectra of the branching points and of the linear sections may be separated widely enough.

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