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Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 3. Equation Describing the Relative Diffusion between Polymer Chain Ends

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ABSTRACT: An equation is derived from probability theories for the relative diffusion between ends of a Gaussian chain. Numerical solution of the derived equation gives the time-dependent end-to-end distance distribution function. As time approaches infinity, the time-dependent end-to-end distance distribution function approaches the Gaussian form regardless of the initial end-to-end distance of the Gaussian chain.

I. Introduction

The end-to-end distance of a polymer chain varies with time due to continuous changes in chain conformations. Variation of the relative separation distance between the end groups originally (at $t = 0$), R, with time is of both theoretical and experimental importance. In a previous paper in this series,[1] the root-mean-square end-to-end distances of end-labeled poly(methyl methacrylate) (PMMA) chains measured using the "Spectroscopic Ruler" technique in nonviscous solvents were found to be consistantly shorter than those determined from intrinsic viscosity measurements. It was suggested that the variations of the relative separation distances between the end groups during the fluorescence lifetime of the donor were partially responsible for the discrepancies.

Further, consider a chemical reaction between two ends of a polymer chain. If the variation in end-to-end distance is due to the relative diffusion between the chain ends and the reaction is diffusion-controlled, approach of the two end groups within an effective reaction radius, R_e, will result in instantaneous reaction. If the distribution function of the end-to-end distance, r, of such a chain is $S(r, R, t)$ at time t, the probability of reaction after time t for the end groups originally separated by $R > R_e$ at time t is

$$\rho(t,R) = \int_0^{R_e} S(r, R, t)\,\mathrm{d}r \tag{1}$$

Assuming that there are N molecules in the system and the end-to-end distance distribution function at time $t = 0$ is given by $P(R)$, the rate of reaction at time t is

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = N\int_{R_e}^{mx} P(R) \int_0^{R_e} \left(\frac{\mathrm{d}S(r, R, t)}{\mathrm{d}t}\right) \mathrm{d}t \tag{2}$$

Under Θ conditions, the equilibrium end-to-end distance distribution function of polymer chains can be described by the well-known Gaussian form.[2] The Gaussian probability function can then be related to a potential energy, as has been shown by Katchalski-Katzir et al.[3] The relative diffusion between the ends can now be described as the diffusion of particles in a potential field and is soluble by the Smoluchowski equation.[4]

In this paper, an approach to the derivation of the diffusion equation using pure probability theory is presented and compared to the approach using the Smoluchowski equation. The diffusion equation is solved numerically for chains starting with either $R < R_m$, $R = R_m$, or $R > R_m$, where R_m is the most probable end-to-end distance of the Gaussian chain at various times t. The statistical parameters for the chain are chosen on the basis of those PMMA samples described previously.[1]

II. Theory

The relative diffusion between chain ends can be pictured as many small jumps of distance δ occurring at very high frequency ψ. We are interested only in changes in the relative distances of chain ends. The coordinate system can be chosen in such a fashion that one end group is kept unchanged with time in the origin. The change in end-to-end distance, r, is depicted as solely caused by movement of the other end in space.

If spherical coordinates are used, the moving end can be pictured as making jumps from one sphere to another. The concentric spheres all have their centers at the origin. At time $t = 0$, the moving end is located at (R, θ_0, ϕ_0) and the end-to-end distance is R. At time t, the acceptor end group moves to position (r, θ, ϕ) and the end-to-end distance is then r. By making the next jump at time $(t + 1)/\psi$, the moving end group can be on any sphere with a radius ranging from $r - \delta$ to $r + \delta$, as shown in Figure 1. The probability for the moving end to be located on different spheres at time $(t + 1)/\psi$ is not the same for two reasons.

(1) The linkage between the polymer ends makes completely random jumps improbable. Let us discuss the probability of making two jumps. One jump decreases the end-to-end distance by δ, and the other increases it by δ. At time $(t + 1)/\psi$, if the donor makes the first jump, the end-to-end distance will be $r - \delta$; otherwise, it will be $r + \delta$. The probability $\rho(r \rightarrow r - \delta)$ for the occurrence of an end-to-end distance of $r - \delta$ for a chain of n

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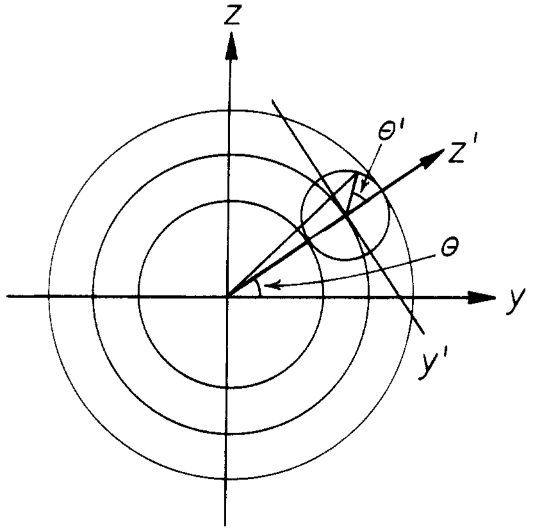

Figure 1. Cross-section of the coordinate system. At time $t = (t + 1)/\psi$, the other end can only jump to the surfaces of the sphere with radius δ and centered at (r, θ, ϕ).

repeat units is proportional to $P(r - \delta)$.

$$\rho(r \rightarrow h - \delta) \propto P(h - \delta) = 4\pi(h - \delta)^2\left(\frac{3}{2\pi R_n^{\,2}}\right)^{3/2} \exp\left[-\frac{3}{2}\left(\frac{h - \delta}{R_n}\right)^2\right] \quad (3)$$

if the chain is Guassian. R_n in eq 3 is the root-mean-square end-to-end distance for the chain and is equal to

$$R_n = (2n)^{1/2}\beta \quad (4)$$

where β is the statistical bond length. The probability for the other jump to occur is given by the same relation except that $h - \delta$ is replaced by $h + \delta$ in eq 3.

(2) At time $t = (t + 1)/\psi$, the moving end can only be at some point on the sphere with radius δ centered at (r, θ, ϕ). If we choose the radial direction of the (r, θ, ϕ) coordinate system as the z' axis of the spherical coordinate (δ, θ', ϕ') of the smaller sphere (Figure 1), the projection of the δ vector on the z' axis is the net change of the radius r due to a jump of distance δ. The projection of the δ on the z' axis is given by

$$z' = \delta_r(\theta') = \delta \cos \theta' \quad (5)$$

By making a jump of distance δ along the θ' direction, the end-to-end distance is changed from r to $r + \delta \cos \theta'$. Since θ' does not occur with equal probability, it is therefore expected that, by making a jump of distance δ, the end-to-end distance value $r + \delta \cos \theta'$ does not occur with equal probability.

The probability for the end-to-end distance of $r + \delta \cos \theta$ to occur is proportional to the product of two terms

$$\rho(r \rightarrow r + \delta \cos \theta') \propto P(\theta')\, P(r + \delta \cos \theta') \quad (6)$$

where $P(\theta')$ is the probability for the angle θ' to occur and $P(r + \delta \cos \theta')$ is the end-to-end distance distribution function for a Gaussian chain. We are interested in the relative change in the r values due to different jumps. We can, therefore, visualize the jump in 3D space as a 1D jump but with an average jump distance, δ_r, given by

$$\delta_r = \langle \delta_r^{\,2}(\theta') \rangle^{1/2} = \left[\frac{\int P(\theta')\, P(r + \delta \cos \theta')\delta_r^{\,2}(\theta)\, d\theta'}{\int P(\theta')\, P(r + \delta \cos \theta')\, d\theta'}\right]^{1/2} \quad (7)$$

Since the δ value is much smaller than R_n, we are justified in approximating $P(r + \delta \cos \theta')$ as a constant when calculating δ_r using eq 7. $P(\theta')$ is given by

$$P(\theta')\, d\theta' = \frac{2\pi\delta \sin \theta'\, \delta\, d\theta'}{4\pi\delta^2} = \frac{1}{2} \sin \theta'\, d\theta' \quad (8)$$

Inserting eq 8 into eq 7, it can be shown that

$$\delta_r = (1/\sqrt{3})\delta \quad (9)$$

At time t, the end-to-end distance is r. By making the next jump, the other end moves to the sphere, either with the radius $r - \delta_r$ or $r + \delta_r$ according to the reduced 1D model. The probability for the end-group jump to $r - \delta_r$ and $r + \delta_r$ is

$$\rho(r \rightarrow r - \delta_r) = \frac{P(n, r - \delta_r)}{P(n, r - \delta_r) + P(n, r)} \quad (10)$$

$$\rho(r \rightarrow r + \delta_r) = \frac{P(n, r + \delta_r)}{P(n, r) + P(n, r + \delta_r)} \quad (11)$$

respectively. Using the Gaussian end-to-end distance distribution function, it can be shown that

$$\rho(r \rightarrow r - \delta_r) = \frac{1}{2} + \frac{\delta_r}{4R_n^{\,2}r}(3r^2 - 2R_n^{\,2}) + O(\delta_r^{\,2}) \quad (12)$$

$$\rho(r \rightarrow r + \delta_r) = \frac{1}{2} - \frac{\delta_r}{4R_n^{\,2}r}(3r^2 - 2R_n^{\,2}) - O(\delta_r^{\,2}) \quad (13)$$

where $O(\delta_r^2)$ denotes terms with δ_r^2 or higher order terms.

It is obvious that

$$\rho(r \rightarrow r - \delta_r) + \rho(r \rightarrow r + \delta_r) = 1 \quad (14)$$

$$\rho(r \rightarrow r + \delta_r) < \rho(r \rightarrow r - \delta_r) \quad \text{if } r > R_m \quad (15)$$

or

$$\rho(r \rightarrow r + \delta_r) > \rho(r \rightarrow r - \delta_r) \quad \text{if } r < R_m \quad (16)$$

where R_m, the most probable end-to-end distance, is given by

$$R_m = [2/3]^{1/2}R_n \quad (17)$$

In other words, eq 14 states that the chain end will certainly make a jump at every time interval of $1/\psi$, while eqs 15 and 16 show that if the end-to-end distance at time t is larger than the most probable value, it has a higher probability of making a jump in the direction to decrease the end-to-end distance and vice versa.

Consider the probability $S(r, (t + 1)/\psi)$ of finding the moving end to be r distance away from the origin at time $(t + 1)/\psi$. The difference equation for $S(r, (t + 1)/\psi)$ is[5]

$$S(r, (t + 1)/\psi) = \rho(r + \delta_r \rightarrow r)\, S(r + \delta_r, t) + \rho(r - \delta_r \rightarrow r)\, S(r - \delta, t) \quad (18)$$

where $\rho(r + \delta_r \rightarrow r)$ and $\rho(r - \delta_r \rightarrow r)$ can be shown to be

$$\rho(r + \delta_r \rightarrow r) = \rho(r \rightarrow r - \delta_r) + \frac{\delta_r^{\,2}}{4}\left(\frac{2}{r^2} + \frac{1}{R_n^{\,2}}\right) \quad (19)$$

and

$$\rho(r - \delta_r \rightarrow r) = \rho(r \rightarrow r + \delta_r) + \frac{\delta_r^{\,2}}{4}\left(\frac{2}{r^2} + \frac{1}{R_n^{\,2}}\right) \quad (20)$$

with higher order terms of δ_r omitted. Since $S(r, t)$ has continuous derivatives, we can expand the terms according to Taylor's theorem

$$S(r, (t+1)/\psi) = S(r,t) + \left(\frac{\partial S(r,t)}{\partial t}\right)\left(\frac{1}{\psi}\right) + O(1/\psi^2) \tag{21}$$

$$S(r+\delta_r, t) = S(r,t) + \left(\frac{\partial S(r,t)}{\partial r}\right)\delta_r + \left(\frac{1}{2}\right)\left(\frac{\partial^2 S(r,t)}{\partial r^2}\right)\delta_r^{\,2} + O(\delta_r^{\,3}) \tag{22}$$

$$S(r-\delta_r, t) = S(r,t) - \left(\frac{\partial S(r,t)}{\partial r}\right)\delta_r + \left(\frac{1}{2}\right)\left(\frac{\partial^2 S(r,t)}{\partial r^2}\right)\delta_r^{\,2} + O(\delta_r^{\,3}) \tag{23}$$

where $O(1/\psi^2)$ and $O(\delta_r^3)$ mean that terms containing $1/\psi^2$ and δ_r^3 or of higher order are truncated.

After insertion of eqs 19–23 and some simplification, eq 18 becomes

$$\frac{\partial S(r,t)}{\partial t} = D\left[\frac{\partial^2 S(r,t)}{\partial r^2} + \left(\frac{3r}{R_n^{\,2}} - \frac{2}{r}\right)\frac{\partial S(r,t)}{\partial r} + \left(\frac{2}{r^2} + \frac{3}{R_n^{\,2}}\right)S(r,t)\right] \tag{24}$$

where, according to Bueche[6]

$$D = \frac{1}{2}\phi\delta_r^{\,2} = \frac{1}{6}\phi\delta^2 \tag{25}$$

Equation 24 can also be derived from the Smoluchowski equation[4] originally used to describe the coagulation of colloidal particles in their respective electric fields. When the potential field between particles A and B is denoted as $U(r)$, the probability of finding the two particles separated by a distance between r and $r + dr$ at time t is $4\pi r^2 R(r, t)$, where $R(r, t)$ is defined by

$$\frac{\partial R(r,t)}{\partial t} = D \operatorname{div}\{\operatorname{grad} R(r,t) + \operatorname{grad} U(r)\, R(r,t)/kT\} \tag{26}$$

where div and grad denote divergence and gradient, respectively, and kT is the thermal energy. In eq 26 $R(r, t)$ is related to $S(r, t)$ by

$$S(r,t) = 4\pi r^2 R(r,t) \tag{27}$$

The gradient of the radial potential field, $U(r)$, between the end groups of a Gaussian chain has been implicitly derived by Katachalski-Katzir et al.[3] to be

$$\frac{\partial U(r)}{\partial r} = -kT\left(\frac{\partial \ln R_0(r)}{\partial r}\right) = kT\left(\frac{3r}{\mathbf{R}_n^{\,2}}\right) \tag{28}$$

where $R_0(r)$ is the equilibrium radial distribution function of a Gaussian chain. Inserting eq 28 into eq 26 and remembering that the radial divergence of a vector **j** in spherical coordinates is given by

$$\operatorname{div}\mathbf{j} = \frac{1}{r^2}\left(\frac{\partial(r^2\mathbf{j})}{\partial r}\right) \tag{29}$$

one obtains

$$\frac{\partial R(r,t)}{\partial t} = D\left[\frac{\partial^2 R(r,t)}{\partial r^2} + \left(\frac{3r}{R_n^{\,2}} + \frac{2}{r}\right)\frac{\partial R(r,t)}{\partial r} + \left(\frac{9}{R_n^{\,2}}\right)R(r,t)\right] \tag{30}$$

Inserting eq 27 and performing variable change from $R(r, t)$ into $S(r, t)$, one obtains

$$\frac{\partial S(r,t)}{\partial t} = D\left[\frac{\partial^2 S(r,t)}{\partial r^2} + \left(\frac{3r}{R_n^{\,2}} - \frac{2}{r}\right)\frac{\partial S(r,t)}{\partial r} + \left(\frac{2}{r^2} + \frac{3}{R_n^{\,2}}\right)S(r,t)\right] \tag{31}$$

Equations 24 and 31 are exactly the same and sufficient for most applications. In certain cases, however, eq 24 breaks down due to truncation errors in calculating $\rho(r \rightarrow r - \delta_r)$, $\rho(r \rightarrow r + \delta_r)$, $\rho(r + \delta_r \rightarrow r)$, and $\rho(r - \delta_r \rightarrow r)$. The terms containing δ_r in eqs 12 and 13, for example, yield absolute values much greater than $^1/_2$ if r is smaller than δ_r used in a numerical solution. The strong advantage of using the more general expression for the diffusion equation 18 is demonstrated elsewhere.[7]

Analytical solution of eq 24 is difficult; therefore, we propose a numerical solution. Before proceeding with the numerical solution, it is easier to reduce the variables to nondimensional ones.[8] In doing this, we define new variables

$$\Theta = Dt/R_n^{\,2} \tag{32}$$

and

$$h = r/R_n \tag{33}$$

In terms of the new variables, eq 24 is rewritten as

$$\frac{\partial S(h,\Theta)}{\partial \Theta} = \frac{\partial^2 S(h,\Theta)}{\partial h^2} + [3h - (2/h)]\frac{\partial S(h,\Theta)}{\partial \Theta} + [3 + (2/h^2)]S(h,\Theta) \tag{34}$$

where h takes values between 0 and m_x/R_n with m_x being the contour length and R_n the root-mean-square end-to-end distance of the polymer chain.

The expression for $\partial S(h, \Theta)/\partial\Theta$ is derived from eq 19 by replacing the $1/\psi$ value with $\delta\Theta$

$$\frac{\partial S(h,\Theta)}{\partial \Theta} = \frac{S(h, \Theta + \delta\Theta) - S(h,\Theta)}{\delta\Theta} + O(\delta\Theta^2) \tag{35}$$

Adding eqs 20 and 21, one obtains

$$\frac{\partial^2 S(h,\Theta)}{\partial h^2} = \frac{S(h+\delta h, \Theta) - 2S(h,\Theta) + S(h-\delta h,\Theta)}{(\delta h)^2} \tag{36}$$

Inserting eq 36 into eqs 20 or 21 yields

$$\frac{\partial S(h,\Theta)}{\partial h} = \frac{S(h+\delta h,\Theta) - S(h-\delta h,\Theta)}{2\delta h} \tag{37}$$

Finally, on substituting $[\partial S(h, \Theta)]/\partial\Theta$, $[\partial^2 S(h, \Theta)]/\partial h^2$, and $[\partial S(h, \Theta)]/\partial h$ in eq 34 with eqs 35–37, one has

$$S(h, \Theta + \delta\Theta) = \{1 + [3 + (2/h^2)]\delta\Theta\}S(h,\Theta) + [3h - (2/h)]\left(\frac{S(h+\delta h,\Theta) - S(h-\delta h,\Theta)}{2\delta h/\delta\Theta}\right) + \frac{S(h+\delta h,\Theta) - 2S(h,\Theta) + S(h-\delta h,\Theta)}{(\delta h)^2/\delta\Theta} \tag{38}$$

The numerical solution of the differential equation is stable only if $\delta\Theta/(\delta h)^2 \leq 1/2$. Using the value of 0.02 for δh, the maximum value for $\delta\Theta$ is 0.0002. We used a $\delta\Theta$ value of 0.000 18 for all calculations. It is obvious from eq 38 that any values of $S(h, \Theta + \delta\Theta)$ can be determined from the S values at time Θ.

Suppose that at time $\Theta = 0$, the moving end group is at $h = 0.50$. The probability of finding the particle at h

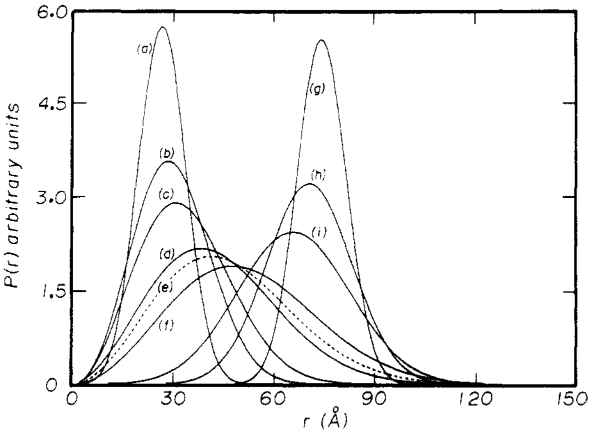

Figure 2. Evolution of the end-to-end distance distribution function for a chain started at an end-to-end distance of $R_n/2$ (curves a–d) and $1.5R_n$ (curves f–i) at $t = 0$. (a) $\Theta = 60\ d\Theta$, (b) $\Theta = 200\ d\Theta$, (c) $\Theta = 400\ d\Theta$, (d) $\Theta = 1600\ d\Theta$, (e) Gaussian, (f) $\Theta = 1600\ d\Theta$, (g) $\Theta = 60\ d\Theta$, (h) $\Theta = 200\ d\Theta$, (i) $\Theta = 400\ d\Theta$.

= 0.48, 0.50, and 0.52 at time $\Theta = 0.000\,18$ is calculated from eq 38 to be 0.437 73, 0.101 98, and 0.460 287 7, respectively. The sum of the $S(h, 0.0018)$ is 0.999 998, slightly smaller than 1.000 000 due to the approximation of the differential equation using definite difference equations. The S value at $h = 0.50$ is in error due to the discontinuing distribution of S and therefore the infinitely large derivatives at $h = 0.50$ at time $\Theta = 0$. It is, however, a fortunate property of the diffusion equation that the numerical solution quickly approaches the analytical solution, and its accuracy is probably acceptable after a few time steps.[8] Since we are concerned with Θ values much larger than 0.000 18, it is not necessary to secure the accuracy in the neighborhood of singularity either by developing an analytical or a series solution applicable for small Θ or by transforming the variables so that the singularity is removed.

III. Results and Discussion

Numerical solution of eq 38 was achieved on an Apollo computer. The relative diffusion of the end groups for a hypothetical chain consisting of 80 repeat units was simulated. Each repeat unit of the hypothetical chain is assumed to contain two C–C bonds and the statistical bond length, β, is assumed to be 4.0 Å.

Curves a–d in Figure 2 show the evolution of the end-to-end distance distribution function of the hypothetical chain starting with an end-to-end distance of $R_n/2$ at time $\Theta = 0$ with the nondimensional time Θ. R_n, the root-mean-square end-to-end distance, is calculated using

$$R_n = (2 \times 80)^{1/2}(4.0) \tag{39}$$

to be 50.6 Å. The nondimensional time interval $d\Theta$ was 1.8×10^{-4}. At time $\Theta = 0$, the other end of the polymer chain is located at a distance $R_n/2$ away from the end located at the origin. The end-to-end distance distribution function is then a δ function

$$S(r) = \delta(r - R_n/2) \tag{40}$$

At time $\Theta = 60\ d\Theta$, the distribution is given by curve a. At subsequent times $\Theta = 200$, 400, and 1600 $d\Theta$, the end-to-end distance distribution functions are given by curves b–d. Curve e is the equilibrium Gaussian end-to-end distance distribution function. As expected, as time progresses, the end-to-end distance distribution functions approaches the Gaussian form.

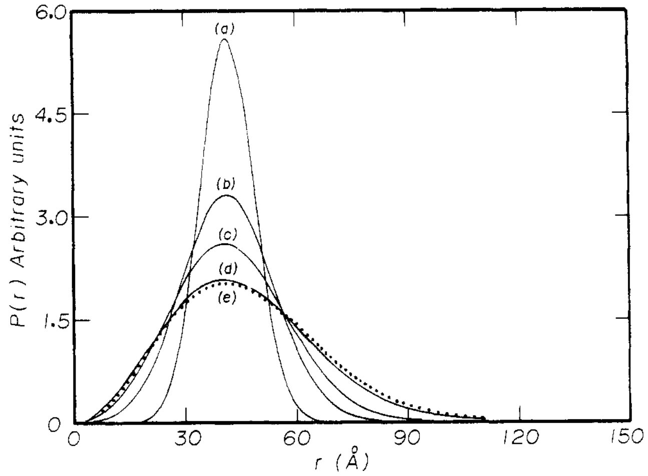

Figure 3. Evolution of the end-to-end distance distribution function for a chain started at an end-to-end distance of R_m at $t = 0$: (a) $\Theta = 60\ d\Theta$, (b) $\Theta = 200\ d\Theta$, (c) $\Theta = 400\ d\Theta$, (d) $\Theta = 1600\ d\Theta$, (e) Gaussian.

With the hypothetical chain, the root-mean-square end-to-end distance is 50.6 Å. The $d\Theta$ value of 1.8×10^{-4} corresponds to a $D\ dt$ value of

$$D\ dt = R_n^2\ d\Theta = 0.4609\ (\text{Å}^2) \tag{41}$$

If we assume that the coefficient of relative diffusion between the chain ends is 1.0×10^{-6} cm^2/s, the corresponding time delays for the curves are 2.77, 9.22, 18.4, and 73.7 ns, respectively.

The changes in end-to-end distance distribution functions with Θ are also shown in Figure 2 (curves g, h, i, and f) and in Figure 3 (curves a–d) for Gaussian chains started with end-to-end distance $^3/_2R_n$ and $(2/3)^{1/2}R_n$, the most probable end-to-end distance, respectively. Again, as Θ increases, the distribution approaches Gaussian, regardless of the starting end-to-end distance separations.

IV. Conclusions

We have derived the time-dependent differential equation for the end-to-end distance distribution function of Gaussian chains from probability theory. Numerical methods were used for the solution of the differential equation. Numerical simulations have shown that the end-to-end distance distribution function approaches the stationary distribution function, Gaussian distribution function, at long times regardless of the initial end-to-end separation distance at time $t = 0$.

The results support our previous assumption that diffusion of polymer chain ends during donor fluorescence lifetime contributes to energy-transfer efficiencies, as were observed in an energy-transfer experiment using polymer samples end-labeled with donor and acceptor groups.[1] In previous experiments,[1] a typical value of R_0, the critical energy-transfer distance, is around 17 Å. For a donor and acceptor pair separated by 50 Å, approximately the root-mean-square end-to-end distance, the probability of energy transfer is negligible in the absence of end-group diffusion. However, in cases of significant diffusion of the end groups, there is a finite probability that the two groups will move within 17 Å and undergo energy transfer during the fluorescence lifetime of the donor group. Diffusion of polymer end groups increases energy-transfer efficiencies.

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Application of the "Spectroscopic Ruler" to Studies of the Dimensions of Flexible Macromolecules. 4. Theoretical Discussion of the Effect of End-Group Diffusion

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ABSTRACT: The relative diffusion between polymer chain ends during donor excitation lifetimes has been shown to increase the energy-transfer efficiencies experimentally observed between energy donor and acceptor groups attached at the ends of polymer chains. The relative diffusion of the end groups has also been shown to alter both donor and acceptor fluorescence decay curves. The feasibility of using these techniques for experimental measurement of relative diffusion coefficients of polymer chain ends is discussed.

I. Introduction

In previous papers in this series[1] it was shown that the root-mean-square end-to-end distances for end-labeled PMMA samples measured by the "spectroscopic ruler" technique in nonviscous solvents are shorter than those measured by other techniques, e.g., viscometry. The diffusion of the end groups during the donor fluorescence lifetime is thought to be responsible for these discrepancies. In this paper a model is developed that takes the diffusion of the end groups into account and allows one to formulate the energy-transfer efficiency between donor and acceptor groups measured in nonviscous media. Under favorable experimental conditions, this model will enable one to evaluate the coefficient of relative diffusion between the end groups.

Extensive experimental results concerning energy transfer between small molecules have shown that diffusion of donor and acceptor groups during donor fluorescence lifetimes enhances energy-transfer efficiency.[2,3] Birks and Leite,[4] for example, studied energy transfer between naphthalene and 9,10-diphenylanthracene in fluid solution. When Förster's theory was used, the critical transfer distance was calculated to be 24 Å. Due to diffusional motion, the experimentally observed effective critical energy-transfer distance was found to be 65 Å, almost 3 times as large.

Knowledge of the diffusion coefficients of polymer chain ends is of both theoretical and experimental importance. Theoretically, the diffusion coefficient of a segment is related to the diffusion coefficient of the center of mass of the polymer chain.[5,6] The diffusion coefficient of the center of mass can be measured by techniques such as photon correlation spectroscopy,[7] sedimentation,[8] and NMR pulse-gradient spin–echo experiments.[9] In contrast to extensive documentation of diffusion coefficients of polymer samples, experimental results on diffusion coefficients of polymer segments are rare. This makes the verification of theoretical computations difficult.

Measurement of the diffusion coefficients of polymer chain ends should help provide a better understanding of the kinetics of intramolecular cyclization reactions[10] and also the kinetics of termination processes in free-radical polymerization reactions.[6] For diffusion-controlled intramolecular cyclization reactions, knowledge of the coefficients of relative diffusion between polymer end groups enables the immediate estimation of the rate constant of cyclization using the Smoluchowski equation[11] and therefore the quantum yield of the cyclization product. In free-radical polymerization reactions, two end radicals react and terminate the polymerization. This mechanism of termination requires two cooperative diffusional processes: (a) the translational diffusion of the center of mass of polymer molecules and (b) the relative translational and rotational diffusion of those segments bearing active chain ends. It was experimentally inferred that the segmental diffusion process of the chain end is the rate-determining process in the case of alkyl methacrylates.[12,13] Knowledge of the coefficients of the relative diffusion between chain ends will there-

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