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Radius of Gyration of Charged Reptating Chains in Electric Fields

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ABSTRACT: A new approach to calculate the average properties of long reptating polymer chains using a master equation is presented. As an example, the effect of electric fields on the radius of gyration and end-to-end distance of polymer chains having various distributions of electric charges on their end segments is obtained analytically. It is found that certain classes of charged polymers that share the same average end-to-end distance have different radii of gyration because the field induces different molecular conformations. Experiments and ways to synthesize these block ionomers are proposed and extensions of this calculation are discussed.

Introduction

Electric fields modify the dynamical properties of ionomers and polyelectrolytes and therefore offer a way to study these polymers using a tunable external parameter.[1,2] When the environment of the charged polymer chain offers uncharged obstacles, the electrophoretic migration is essentially through reptation;[3,4] i.e. the chain slides through openings like a thread through a series of pinholes. The effective electric force acting on a reptating charged polymer is then function of the instantaneous molecular conformation,[5] leading to interesting effects such as "self-trapping".[6] Recently, electrophoresis, which is a widely used technique in biology, was shown to be applicable to the study of synthetic polyelectrolytes, giving a more detailed molecular weight distribution than size exclusion chromatography.[7]

In the reptation model of polymer melt dynamics, the polymer chain has only two degrees of freedom:[4] (i) The chain moves in a tube formed by the topological constraints of the environment; net motion of the molecule can only happen along the tube axis since all transverse movements are rapidly stopped by obstacles. This one-dimensional Brownian motion can be biased when a field is present.[5,6,8,9] (ii) The head of the molecule, which finds its way through the obstacles to create new tube sections at each step, has the other degree of freedom (in fact, this represents two degrees of freedom as the segment has total angular freedom); this random end-segment motion can also be biased by fields.[8,9] In this paper, we study how electric forces acting on the ends of a reptating chain affect its radius of gyration and shape. We thus assume that there is no bias of the Brownian motion in the tube. In other words, we study the case where only the degree of freedom *(ii)* is biased by the field; this requires the use of long molecules having charges only on or near the ends.[2]

Our approach introduces a master equation describing the evolution of the orientation of the reptation tube with time; this allows us to calculate the shape of reptating molecules submitted to various nonuniform biases. The analytic results obtained for the special cases chosen here are discussed in terms of possible experiments, and the last section suggests ways to synthesize the relevant block ionomers. These experiments also represent interesting tests of the reptation theory.

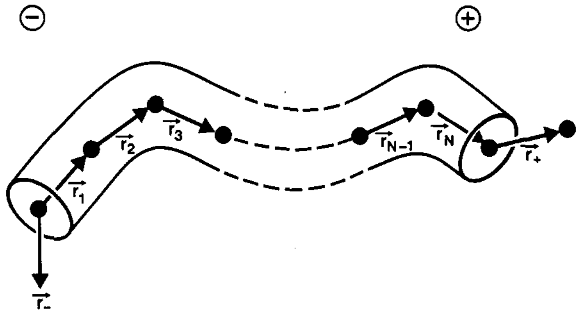

Figure 1. Schematic illustration of the polymer chain trapped in its "tube". The chain is made of $N + 1$ "beads" joined by N vector segments $\mathbf{r}_i$ ($1 \le i \le N$) pointing toward the "+" end of the tube. When the Brownian motion forces the $\mathbf{r}_N$ (or $\mathbf{r}_1$) segment to leave the original tube through the + (or −) end, a new tube section of orientation $\mathbf{r}_N = \mathbf{r}_+$ (or $\mathbf{r}_1 = -\mathbf{r}_-$) is created, and the $\mathbf{r}_1$ (or $\mathbf{r}_N$) section disappears at the − (or +) end of the tube.

The Reptation Model

The basic assumption of the model[3,4] is that the chain, modeled (see Figure 1) as a series of N vector segments $\mathbf{r}_i$ ($1 \le i \le N$), is forced to move in an effective tube formed by the obstacles restricting its transverse motion; these obstacles can be the fibers of a gel or other reptating molecules in a melt.

In absence of a field, the chain undergoes thermal diffusion along its tube axis, with curvilinear diffusion coefficient D. The average distance between obstacles is denoted by $\langle |\mathbf{r}_i| \rangle = a$; this is the average pore size in a gel or the average entanglement spacing in a melt. The continuous one-dimensional diffusion of the chain in its tube is represented by random jumps of length a and time duration $\tau = a^2/2D$ along the tube axis. The equations of motion for these jumps are

$$\mathbf{r}_i(t + \tau) = {}^1/_2[1 + \eta(t)]\mathbf{r}_{i+1}(t) + {}^1/_2[1 - \eta(t)]\mathbf{r}_{i-1}(t) \qquad (1a)$$

where $\eta(t)$ is a stochastic variable taking the value $\eta(t) = +1$ for a forward (+) jump where the $\mathbf{r}_N$ end segment leaves the tube and $\eta(t) = -1$ for a backward (−) jump where the $\mathbf{r}_1$ end segment leaves the tube. These jumps are made randomly in the tube, i.e. the chain jumps toward either

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end of the tube with equal probability $p[\eta(t) = +1] \equiv p_+ = p[\eta(t) = -1] \equiv p_- = {}^1/_2$. When the chain jumps over a distance $\pm a$ in the tube, the end segment leaving the original tube to create a new tube section of length a can go in any direction until it meets the next obstacle. Its final orientation is denoted $\mathbf{r}_\pm$, and the boundary conditions of eq 1a thus are (see Figure 1) as follows:

$$\mathbf{r}_{N+1}(t) = \mathbf{r}_+(t) \qquad \mathbf{r}_0(t) = -\mathbf{r}_-(t) \tag{1b}$$

In absence of a field-induced bias, one has $\langle \mathbf{r}_\pm \rangle = 0$ and $\langle |\mathbf{r}_\pm| \rangle = a$. Note that both vectors $\mathbf{r}_\pm$ are chosen to point outside the tube for convenience.

If the chain is charged,[5] an electric field can change the probabilities $p_\pm$ and the time durations $\tau_\pm$ of the jumps, as well as the orientations $\mathbf{r}_\pm$. These effects have been shown to be very important in the case of DNA gel electrophoresis.[6,9]

If the charge $q_\pm$ of the two end segments are spread evenly along their length, a, an electric field $\mathbf{E} = E\mathbf{u}_x$ tends to orient the vectors $\mathbf{r}_\pm$ along the x axis with[2]

$$\langle \mathbf{r}_\pm \cdot \mathbf{u}_x \rangle / \mathrm{a} = \coth \Theta_\pm - 1/\Theta_\pm \approx {}^1/_3\Theta_\pm - {}^1/_{45}\Theta_\pm^3 + {}^2/_{945}\Theta_\pm^5 + \dots \tag{2a}$$

$$\langle (\mathbf{r}_\pm \cdot \mathbf{u}_x)^2 \rangle / a^2 = 1 - 2\langle \mathbf{r}_\pm \cdot \mathbf{u}_x \rangle / (a\Theta_\pm) \approx {}^1/_3[1 + {}^2/_{15}\Theta_\pm^2 - {}^4/_{315}\Theta_\pm^4 + \dots] \tag{2b}$$

where $\mathbf{u}_x$ is a unit vector along the field (x) axis, and

$$\Theta_\pm = q_\pm Ea/2k_\mathrm{B}T \tag{2c}$$

is a dimensionless measure of the field intensity. An electric field tends to align the end segments on the field axis when the latter create new tube sections; in reptation this effect accumulates as the Brownian motion slowly renews the entire effective tube through its ends, and the field thus leads to tube alignment in the field direction. In the transverse direction, one has

$$\langle \mathbf{r}_\pm \cdot \mathbf{u}_\perp \rangle = 0 \tag{2d}$$

$$\langle (\mathbf{r}_\pm \cdot \mathbf{u}_\perp)^2 \rangle / a^2 = 1 - \langle (\mathbf{r}_\pm \cdot \mathbf{u}_x)^2 \rangle / a^2 \approx {}^2/_3[1 - {}^1/_{15}\Theta_\pm^2 + {}^2/_{315}\Theta_\pm^4 \dots] \tag{2e}$$

Here, we assume that the electric forces do not change the probabilities $p_\pm$ and the time durations $\tau_\pm$, but only the orientations $\mathbf{r}_\pm$ as described above. Charges on the middle segments $\mathbf{r}_i$, with $1 < i < N$, do not contribute to the alignment of the end vectors $\mathbf{r}_\pm$; however, they can lead to field-induced chain drift, which is equivalent to biasing the probabilities $p_\pm$ and decreasing the jump times $\tau_\pm$ of the intratube curvilinear Brownian motion of the chain.[5] The easiest way to eliminate this drift is to put the charges only near the ends of the molecule (i.e. the charge is $q_i = 0$ for all $1 < i < N$). If the chain is charged only on one end, e.g. if $q_+ \neq 0$ and $q_- = 0$, an average electric force $\langle f_+ \rangle \approx q_+ \langle \mathbf{E} \cdot \mathbf{r}_+ \rangle / a$ pulls the chain in its tube toward the charged end with a velocity proportional to $\langle f_+ \rangle / N$, where the N comes from the fact that the curvilinear friction coefficient of the molecule scales like the molecular size N. This drift is negligible if $\langle f_+ \rangle a / 2k_\mathrm{B}T \ll 1$, which is equivalent to $(\Theta_+)^2 \ll 3$ from eq 2a; for these low field intensities, the Brownian motion dominates the small field induced drift. Therefore, we assume that the effective fields $\Theta_\pm$ are small here, and that the chain is charged only near its ends. Note that, in this case, $\langle \mathbf{r}_\pm \cdot \mathbf{u}_\perp \rangle = 0$ and $\langle (\mathbf{r}_\pm \cdot \mathbf{u}_\perp)^2 \rangle \approx {}^2/_3$ to first order in $\Theta_\pm$ according to eqs 2d and 2e, and the transverse dimensions of the tube are not changed appreciably;[2] we will thus focus on the properties of the tube conformations in the field direction.

In absence of a field, an N segment tube of length Na has a random-walk conformation for which it is well known that[10]

$$\langle h^2 \rangle = 6\langle R_\mathrm{g}^2 \rangle = Na^2 \tag{3}$$

where h and R_g are the end-to-end distance and radius of gyration of the molecule (or tube), respectively. With a field, the tube is not a random walk and these values are changed. It is the goal of this paper to suggest a technique to calculate these new values and to suggest experiments on the relevant block ionomers.

A New Theorem on Reptation

Since new tube sections are created only when the $\mathbf{r}_1$ and $\mathbf{r}_N$ end segments leave the original tube, all orientations $\mathbf{r}_i$ ($1 \leq i \leq N$; see Figure 1) of the N tube segments have been chosen in the past by one of the two end segments (we neglect here tube leakage or any other degree of freedom not included in the ideal reptation model). Because the chain is continuous, the n_+ segments that owe their present orientation to a past $\mathbf{r}_N \rightarrow \mathbf{r}_+$ jump are consecutive, starting from the end segment r_N. Similarly, the $n_- = N - n_+$ segments oriented in the past by $\mathbf{r}_1 \rightarrow -\mathbf{r}_-$ jumps are consecutive, starting from $\mathbf{r}_1$. If $g(n_+,t)$ is the probability that n_+ segments of the chain owe their orientation at time t to past $\mathbf{r}_+$ jumps, the relevant master equation is

$$g(n_+;t+\tau) = p_+(t)g(n_+-1;t) + p_-(t)g(n_++1;t) \tag{4}$$

with the boundary conditions

$$g(N;\mathrm{t}+\tau) = p_+(t)[g(N;t) + g(N-1;t)] \tag{5a}$$

$$g(0;t+\tau) = p_-(t)[g(0;t) + g(1;t)] \tag{5b}$$

In this paper, we study the steady-state regime $g(n_+,t+\tau) = g(n_+,t) \equiv g(n_+)$, or $\partial g(n_+)/\partial t = 0$, of the case where the motion inside the tube stays random in the presence of the electric field ($p_+ = p_- = {}^1/_2$ and $\tau_\pm = \tau = a^2/2D$). The normalized ($\sum_0{}^N g(n_+) = 1$) solution of these equations is then

$$g(n_+) = 1/(N+1)^{-1} \qquad 0 \leq n_+ \leq N \tag{6}$$

In the steady state therefore, all the tube segments (including $\mathbf{r}_1$ and $\mathbf{r}_N$) have equal probability of having been oriented by either end of the tube. This surprising result is due to the fact that eqs 4–5 also apply for a long random walk between two close reflecting walls; in this case, the probability distribution for the final position of the particle is indeed uniform between the walls. Equations 4–5 can also be used with other conditions; for example, one can study relaxation with $\partial g(n_+)/\partial t \neq 0$ or the effect of a simple biased diffusion with $p_\pm = {}^1/_2[1 \pm \delta]$. In the latter case, eq 4 would reduce to a differential equation with a drift term proportional to the bias δ.

Finally, from eq 6, we obtain the following useful averages:

$$\langle n_+ \rangle = {}^1/_2N \qquad \langle n_+^3 \rangle = {}^1/_4N^2(N+1)$$
$$\langle n_+^2 \rangle = {}^1/_6N(2N+1)$$
$$\langle n_+^4 \rangle = {}^1/_{30}N(2N+1)(3N^2+3N-1) \tag{7}$$

from which $\langle (n_+ - \langle n_+ \rangle)^2 \rangle = N(N+2)/12 \approx {}^1/_3\langle n_+ \rangle^2$.

End-to-End Distances

The average end-to-end distance $\langle (h_x)^2\rangle$ is defined as

$$\langle (h_x)^2\rangle = \langle (\mathbf{h}\cdot\mathbf{u}_x)^2\rangle = \langle (\sum_{i=0}^{n_-}(\mathbf{r}_i\cdot\mathbf{u}_x) + \sum_{i=[n_-+1]}^{N}(\mathbf{r}_i\cdot\mathbf{u}_x))^2\rangle \quad (8)$$

where we have divided the chain in two groups of segments $\mathbf{r}_i$ according to which end segment the $\mathbf{r}_i$'s vectors owe their present orientation. The first n_- segments have been oriented in the past by a backward (−) jump, while the $n_+ = N - n_-$ others have been oriented by forward (+) jumps. The $\langle ... \rangle$ averages have to be performed according to eq 2 for the average projections $\langle (\mathbf{r}_\pm\cdot\mathbf{u}_x)^k\rangle \equiv \langle x_\pm{}^k\rangle$, with k = 1,2, and according to eq 6 for the averages over the numbers $n_\pm$. The result is

$$\langle (h_x)^2\rangle/a^2 = {}^1/_2 N[\langle x_+^2\rangle + \langle x_-^2\rangle] + {}^1/_3 N(N-1)[\langle x_+\rangle^2 - \langle x_+\rangle\langle x_-\rangle + \langle x_-\rangle^2] \quad (9)$$

Using series expansions of eq 2, we can calculate the end-to-end distance for the four possible[1,2] classes of chains (see Figure 2):

$$\langle (h_x)^2\rangle = {}^1/_3 Na^2 \quad \text{for } q_\pm = 0 \quad (10a)$$

$$\langle (h_x)^2\rangle \approx {}^1/_3 Na^2[1 + {}^1/_9\Theta_+^2(N - {}^2/_5) - {}^2/_{135}\Theta_+^4(N - {}^4/_7) + ...] \quad \text{for } q_+ \neq 0 \text{ and } q_- = 0 \quad (10b)$$

$$\langle (h_x)^2\rangle \approx {}^1/_3 Na^2[1 + {}^1/_3\Theta_+^2(N - {}^3/_5) - {}^2/_{45}\Theta_+^4(N - {}^5/_7) + ...] \quad \text{for } q_+ = -q_- \quad (10c)$$

$$\langle (h_x)^2\rangle \approx {}^1/_3 Na^2[1 + {}^1/_9\Theta_+^2(N - {}^1/_5) - {}^2/_{135}\Theta_+^4(N - {}^1/_7) + ...] \quad \text{for } q_+ = q_- \quad (10d)$$

Of course, one can also have $|q_+| \neq |q_-|$ in cases c and d above; for simplicity, we study only the case where the two charges are of same magnitude in this paper.

Two remarks can be made here. First, the end-to-end distance is maximum when the ends have opposite charges: this is expected[2] since the two end segments then point in opposite directions (see Figure 2c). Second, the end-to-end distance is coincidentally the same in b and d above (for $\Theta^2 \ll 3$); in b, a part of the chain is oriented in the field direction when the $\mathbf{r}_N$ segment leaves the tube to take direction $\mathbf{r}_+$, while the other part of the chain retains a random-walk conformation (see Figure 2b) due to the random nature of the $\mathbf{r}_-$ vector; in d, the two end segments point in the same direction, giving a J- (or U-) shaped conformation (see Figure 2d). In the next section, we will see that the radius of gyration is very different for these two cases, showing that very different conformations lead to eqs 10b and 10d.

Finally, it should be noted that eq 9 is general and that it can be used for any distribution of charges near the ends of the chain where eq 2 may not apply (for example, a case where a single charge would be on the last monomer of the chain).

Radii of Gyration

The radius of gyration is the average distance squared between the different parts of the object and its center of mass. It describes the distribution of matter around the center of mass and therefore gives information on the average shape that the end-to-end distance does not give. It can be measured by various scattering techniques in the case of polymers.[11]

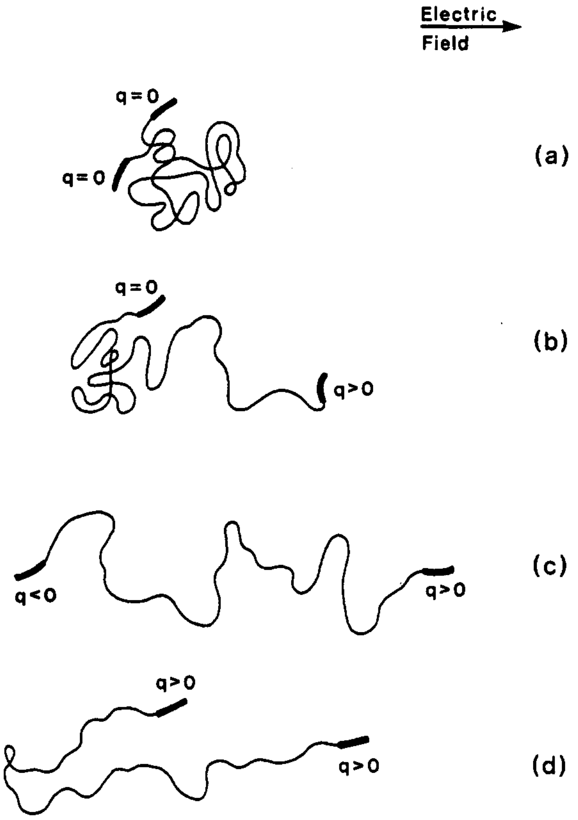

Figure 2. Schematic molecular conformations in the four classes of polymers described in the text: (a) random-walk conformation of an uncharged chain; (b) P-shaped conformation of a reptating chain having a charge q_+ on one end only; (c) I-shaped conformation of a reptating chain having charges of opposite signs on its ends; and (d) J-shaped conformation of a reptating chain having identical charges on both ends. The average transverse size is approximately the same in all cases at low field. In the field direction, the average end-to-end distance is equal in b and d, but all radii of gyration are very different.

Here, we use the Lagrange formula[12] for the radius of gyration R_g:

$$R_g^2 = \langle \sum_{0\le i<j\le N} s_{ij}^2\rangle/(N+1)^2 \quad (11)$$

where s_{ij} is the distance between the ith and jth part of the chain, and the average is made over all possible conformations. The $N + 1$ parts of the chain are the $N + 1$ "beads" connected by the N vectors $\mathbf{r}_i$, where $\mathbf{r}_i$ joins beads $i - 1$ and i (see Figure 1). We calculate the radius of gyration in a given direction $\mathbf{u}_w$ ($w = x, y, z$). If n_- segments have been oriented in the past by the $\mathbf{r}_1$ segment, thus getting an average orientation $-\langle \mathbf{r}_-\rangle$, while $n_+ = N - n_-$ have been oriented by the $\mathbf{r}_N$ segment, with an average orientation $\langle \mathbf{r}_+\rangle$, we can rewrite the radius of gyration R_{gw} in the $\mathbf{u}_w$ direction as

$$(N+1)^2 R_{gw}^2 = \langle \sum_{0\le i<j\le n_-} w_{ij}^2 + \sum_{n_-\le i<j\le N} w_{ij}^2 + \sum_{0\le i<n_-}\ \sum_{n_-<j\le N} w_{ij}^2\rangle \quad (12)$$

where w_{ij} is the distance between the ith and jth beads of the chain in the $\mathbf{u}_w$ direction (with $[x_{ij}]^2 + [y_{ij}]^2 + [z_{ij}]^2 = [s_{ij}]^2$). The averages have to be done over the various conformations, i.e. over the values of w_{ij} and n_-, with w_{ij}

given by

$$w_{ij} = \sum_{k=i+1}^{j} (\mathbf{r}_i \cdot \mathbf{u}_w) \tag{13}$$

Using eq 13 for the distance w_{ij}, writing $\langle (\mathbf{r}_i \cdot \mathbf{u}_w)^k \rangle \equiv \langle (w_\pm)^k \rangle$ for the average projections of the $\mathbf{r}_i$ vectors on each of the three w axis (according to which part of the chain the $\mathbf{r}_i$ vector belongs), and using eq 7 to average over the n_-'s, we get

$$\begin{aligned} 60N^{-1}(N+1)^2 R_{gw}^2 = {} & 5(N+1)(N+2)[\langle w_+^2 \rangle + \langle w_-^2 \rangle] - \\ & (N-1)(N^2+5N+1)\langle w_+ \rangle \langle w_- \rangle + \\ & (N-1)(N+2)(2N+1)[\langle w_+ \rangle^2 + \langle w_- \rangle^2] \end{aligned} \tag{14}$$

Since $\langle y_\pm \rangle = \langle z_\pm \rangle = 0$, the last two terms cancel in the transverse directions y and z, and the radius of gyration in these directions is given by (in the limit $N \gg 1$)

$$\begin{aligned} R_{gy}^2 = R_{gz}^2 = {}^1/_{24} N[2a^2 - \langle x_+^2 \rangle - \langle x_-^2 \rangle] \approx \\ Na^2/18[1 - {}^1/_{30}[\Theta_+^2 + \Theta_-^2] + ...] \end{aligned} \tag{15}$$

The transverse radii of gyration are thus modified only to order Θ^2, as expected.

The situation is different, however, in the field direction ($w = x$). Using eqs 2 and 14, we obtain, for our four classes of charged chains (in the limit $N \gg 1$):

$$R_{gx}^2 = R_{gy}^2 = R_{gz}^2 = {}^1/_{18} Na^2 \qquad \text{for } q_\pm = 0 \tag{16a}$$

$$\begin{aligned} R_{gx}^2 = \frac{N}{12}\left[\frac{a^2}{3} + \langle x_+^2 \rangle\right] + \frac{1}{30}[N\langle x_+ \rangle]^2 \approx \\ \frac{Na^2}{18}\left[1 + \frac{1}{15}N\Theta_+^2 + ...\right] \qquad \text{for } q_+ \neq 0;\ q_- = 0 \end{aligned} \tag{16b}$$

$$\begin{aligned} R_{gx}^2 = \frac{N}{6}\langle x_+^2 \rangle + \frac{1}{12}[N\langle x_+ \rangle]^2 \approx \\ \frac{Na^2}{18}\left[1 + \frac{1}{6}N\Theta_+^2 + ...\right] \qquad \text{for } q_+ = -q_- \end{aligned} \tag{16c}$$

$$\begin{aligned} R_{gx}^2 = \frac{N}{6}\langle x_+^2 \rangle + \frac{1}{20}[N\langle x_+ \rangle]^2 \approx \\ \frac{Na^2}{18}\left[1 + \frac{1}{10}N\Theta_+^2 + ...\right] \qquad \text{for } q_+ = q_- \end{aligned} \tag{16d}$$

These results show that the radius of gyration is changed to order $N\Theta^2$ in the field direction, which can be very large for long ($N \gg 1$) charged molecules even though only the ends of the chain are charged (this is because the reptative motion makes the tube alignment cumulative).

One can write these radii of gyration as the sum of (i) a random-walk term $(R_{gw})^2 \approx Na^2/18 + 0(\Theta^4)$ for each direction (x, y, and z), plus (ii) the radius of gyration $(R_{gx})^2 = (L_x)^2/12$ of an equivalent rod^2 of length L_x. The latter is the length of a rod having the radius of gyration given by the N^2 terms in the eq 16. One can see the various charged chains as behaving more and more as rods as they orient in the field direction to take an average conformation which is increasingly elongated in this direction.

In classes b and d, the lengths of these equivalent rods are $L_x = ({}^{12}/_{30})^{1/2} N\langle x_+ \rangle$ and $L_x = ({}^{12}/_{20})^{1/2} N\langle x_+ \rangle$, respectively. Therefore, although these chains have the same end-to-end distances (see eqs 10b and 10d), the fact that the average conformations have different shapes (Figure 1) leads to different sizes L_x in the field direction. The d molecules, with equal charges on both ends, orient more in the field direction and therefore take more extended conformations having a larger radius of gyration R_{gx} but not larger end-to-end distance $\langle (h_x)^2 \rangle$ because they have U- and not an I-shaped conformations. In c, the length of the equivalent rod is $L_x = N\langle x_+ \rangle$, as is expected for a molecule whose two ends are going in opposite directions: all N segments then have projections $+\langle x_+ \rangle$ on the field axis, giving an end-to-end distance $\langle (h_x)^2 \rangle \approx (L_x)^2$.

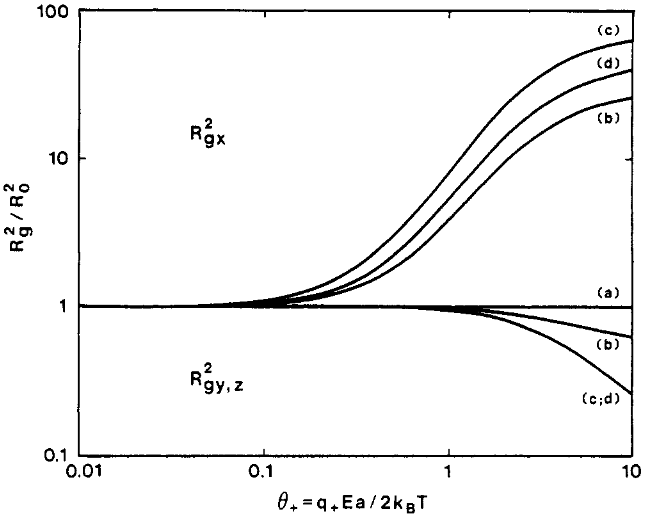

Figure 3. Reduced radius of gyration as a function of the scaled electric field Θ_+ for a chain of length $N = 50$; $(R_g)^2$ is scaled by $R_0{}^2 = Na^2/18$, the radius of gyration of an uncharged (a) molecule in each of the three space directions. The lower curves correspond to the transverse radii of gyration $R_{gy,z}$, and the upper curves are for the parallel field radii of gyration R_{gx}. The charged chains have as in Figure 2: (b) a charge on only one end segment; (c) charges of opposite signs on the two ends; and (d) identical charges on both ends of the molecule.

Figure 3 shows how the radii of gyration vary with the scaled field Θ_+ for the four classes of chains and the three directions for a molecule of size $N = 50$. The charged chains have radii of gyration R_{gx} that increase with the field, and the numerical values are all different even though class b and d chains have the same end-to-end distances $\langle (h_x)^2 \rangle$ (see eqs 10b and 10d). In the transverse directions, however, the radii of gyration are decreasing very slowly; for example, at $\Theta_+ = 1$, $(R_{gx})^2$ is already 5–10 times larger than at zero field, while $(R_{gy,z})^2$ are just a few percent smaller. Note that class c and d chains have the same transverse radii of gyration because they differ only by a hairpin bend of negligible transverse dimensions. At very high fields, there is a saturation since we then have $\langle x_+ \rangle = \langle (x_+)^2 \rangle = 1$, i.e. we then have a rod of length Na (and negligible width) aligned in the field direction.

Discussion

The concept of biased reptation of charged polymers in neutral environments has proven to be useful in explaining the results of continuous field DNA gel electrophoresis,[6,9] especially the band inversion effect which results from a phenomenon called "self-trapping".[6] In fact, biased reptation can be invoked for polymers having any charge distribution, as long as reptation remains the leading mode of diffusion (for long molecules, dense and uncharged obstacles, low concentration of charged polymers, and the persistence length of the polymer of the same order of magnitude than the average distance between obstacles).

In this paper, we have studied the case where the reptating molecule wears charges only near its ends. The motion of the molecule is then essentially a one-dimensional random walk in a tube that tends to be oriented in the field direction when new tube sections are created by the charged end segment(s). The small electric forces align the end segments, but otherwise leave the reptative motion intact.

Such polymers can be seen as ABC ionic block copolymers, where B is a long uncharged (neutral) polymer, and A and C are sections of length $\approx a$ (the average distance between obstacles, i.e. the average pore size of the supporting gel, or the average entanglement spacing if the copolymer is in a melt of long neutral polymers) of a polymer chosen according to the class of block copolymers under investigation. Class a chains are BBB, or a homogeneous neutral polymer. Class b and d polymers are ABB and ABA chains, respectively, where A is a short ionomeric block. Finally, class c polymers are asymmetrical ABC block copolymers where the A and C sections are ionomers of opposite polarity. For practical reasons, b and d polymers are preferable since they would not tend to aggregate. The next section discusses the possible strategies to synthesize these block ionomers.

For these polymers, we have to relax the normal reptation rule[4,10] of the randomness of the new tube orientations ($\langle \mathbf{r}_\pm \rangle = 0$). In order to calculate the properties of a chain that create dissimilar tube sections with its two end segments during reptative motion, we introduced a new theorem on tube properties and a new theoretical approach.

In this new approach, a master equation is written for the number of tube sections created by each end of the chain. In general, this equation can include external fields, space- and time-dependent terms, and special boundary conditions. For example, by writing $p_\pm = {}^1/_2[1 \pm \delta]$, one can study the effect of a field or density gradient induced drift of the molecule in its tube, such as the one responsible for electrophoretic migration of DNA in agarose gels.[5,8] One can also study uncharged block copolymers at interfaces, or the average shape of AB block copolymers when the two end segments have different $\mathbf{r}_\pm$ properties (e.g. due to differences in persistence length, or stiffness, of the A and B parts). Nonequilibrium and relaxation processes (for example, the relaxation that follows initial stretching by an external tensile force) can also be studied using this approach.

When applied to unbiased reptation ($p_+ = p_- = {}^1/_2$), this approach leads to a new theorem on reptation: in equilibrium, every tube section $\mathbf{r}_i$ ($1 \le i \le N$) has equal probability of having been oriented by either end segment of the chain ($\mathbf{r}_1$ and $\mathbf{r}_N$) in the past. This is a new definition of tube equilibrium.

Here, as an example of the usefulness of this new concept, we have calculated the average steady-state properties of block copolymers that create tube sections of different average orientations with their two end segments. We found that the properties of the chains in the field direction are very much dependent upon the applied electric field and the distribution of charges on the ends of the molecule. The various conformations, shown schematically on Figure 2, can be probed by scattering techniques that can measure the radius of gyration directly.[11]

In simple terms, the tube tends to orient in the field direction, and a rod-like contribution is added to the random walk like radius of gyration $(R_{gx})^2 = Na^2/18$. The length of the effective rod is however different for the three possible charge distributions studied here. The most interesting cases are class b and d molecules, i.e. AB and ABA ionic block copolymers. These molecules are predicted to have the same average end-to-end distance in the presence of an electric field (see eq 10), although one expects different conformations (see Figure 2). However, their radii of gyration (in the field direction) are predicted to be different.

An electric field represents a tunable parameter by which the properties of reptating charged molecules can be changed. Increased end-to-end distances and orientations have been predicted[8,9,13] and observed[14-17] in the case of DNA gel electrophoresis. Acting directly on the conformations of DNA by using pulsed electric field[18,19] and various field configurations[20-23] was shown to increase the usefulness and range of applicability of gel electrophoresis of nucleic acids.

We suggest that studying other charged polymers, such as the synthetic ionic block copolymers proposed in this paper, is a good way to probe the details of the reptative motion. On a more applied side, since electric fields can modify the end-to-end distance of charged molecules, these phenomena can be used to advantage in techniques where orientation and extension is looked for, or where the two ends of the molecule should either react together (cyclization) or avoid doing so. Clearly a chain with opposite charges on its two ends might cyclize in the gel, greatly reducing its mobility. These interactions would be reduced at high ionic strengths, however, because of screening by the ionic medium.

Synthesis of Partially Charged Block Ionomers

Many types of ionomeric block copolymers can be produced by well-known techniques.[24-26] Several illustrative examples will be given of the synthesis of the various types of polymers. A discussion of some aspects of this problem has been given by Selb and Gallot.[27]

A. Neutral Midblock and Cationic Endblocks, ABA Type. This structure can be achieved, for example, by a sodium naphthalene initiated polymerization of styrene followed by the addition of any of the vinyl pyridines (2-vinyl-4-vinyl or 2-methyl-5-vinyl are most common). The living polymer is terminated with methanol and recovered by precipitation into a nonsolvent such as methanol or ether (depending on the length of the VP segments) and subsequent drying. Quaternization can be accomplished by immersing the powder into a solution of an alkyl iodide (e.g. methyl iodide) in any suitable solvent, e.g. an alcohol, toluene, etc. The quaternized polymer is soluble in dimethylformamide; because of its amphiphilic character it is not soluble in much else. If one wishes to produce a completely water-soluble polymer, one would have to utilize ethylene oxide as the midblock; it should be noted, however, that the addition of vinylpyridine to a growing ethylene oxide chain has not been attempted, to our knowledge.

B. Neutral Block and Cationic Block, AB Type. Butyllithium initiation can be used here to initiate the styrene, and, once a PS block length of sufficient size has been achieved, the vinyl pyridine is added. The isolation procedure is identical. Again, water-soluble species can be achieved by use of ethylene oxide as the neutral species, with the same cautionary note as mentioned before.

C. Neutral Midblock and Anionic End Block, ABA Type. Again sodium naphthalene is used as the initiator for the polystyrene midblock except that now *tert*-butyl methacrylate is used for the A block. That monomer hydrolyzes very easily because of the large size of the *tert*-butyl group. Hydrolysis, however leads to species which become insoluble as the reaction proceeds. Polar or water-soluble midblocks might circumvent this difficulty.

D. Ionic Midblock and Neutral Endblocks, ABA Type. This structure could be prepared by the polymerization of a *tert*-butyl methacrylate midblock followed by the addition of hexyl methacrylate or any other anionically polymerizable monomer which is initiated by the *tert*-butyl methacrylate anion but which does not hydrolyze as easily. Such an approach was taken to the synthesis of AB blocks by McGrath et al.[28]

E. Anionic/Cationic Diblocks. These have been prepared by Stille et al.,[29] but we know of no examples of anionic/neutral/cationic ABC type triblocks.

In addition to the techniques discussed above, postpolymerization modification should also be considered. Thus, a diblock of polyisobutylene/polystyrene could be hydrogenated, which would affect only the isobutylene sequences, and subsequently sulfonated, which would affect only the styrene. Clearly many other techniques can be suggested. It is to be noted that very few techniques have actually been tried, in this context, so that the number of different ionic block copolymers is quite small.

Some cautionary comments need to be made. In this paper we hypothesize a compatible four component system—buffer, gel, A block, and B block. Most of the target compounds however will not satisfy the compatibility criteria. First, many of the proposed neutral blocks are hydrophobic and may adsorb strongly to the gel matrix. Second, many of these materials are likely to be insoluble in water, or will form micellar structures. Another approach is to perform electrophoresis in a nonaqueous environment, thus suppressing many of the undesirable interactions. Alternatively, one might use synthetic polypeptides, which are known to be inert under conventional electrophoresis conditions. Recent work[30] on the orientation and relaxation of protein–sodium dodecyl sulfate complexes during pulsed intermittent field polyacrylamide gel electrophoresis has shown evidence for reptation in these systems.

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