Therefore, $D_r/D_{t0\|} \sim c^{-2}L^{-9}$. By comparing Figures 8b and 7a, it is clear that $D_r/D_{t\|}$ is not proportional to c^{-2} at all. Therefore, for the concentrations studied, cooperative translational motions do not affect the rotational motion of the test rod while free translational motions are the dominant factor in determining the rotational motion, as shown in Figure 8b and eq 6 but not eq 40.

Conclusion

The time correlation function results indicate that the Edwards tube model is very useful in describing the motions of rods in solutions with concentrations on the order of $(dL^2)^{-1}$ (semiconcentrate region). Free translational motion persists in spite of the presence of other rods. Cooperative translational motion describes the effect of the presence of other rods and does have a strong concentration dependence. Rotational motion slows down with concentration. The concentration dependence of $D_{t\|}$ is not quite as expected even though polydispersity might be a contributing factor. It has been suggested that this is because the spacing of the gates within the tube is too approximate. On the other hand, the rotational diffusion coefficient does appear to follow the Doi and Edwards model for semidilute solution, suggesting that the rotation of a rod in semiconcentrate solution is dependent on the free translational motions of its neighboring rods (eq 6) and not on the cooperative translational motion (eq 40). In fact, we have observed

$$D_r \sim D_{t0\|}(c^2L^9)^{-1} \tag{41}$$

As we have demonstrated $D_r \propto c^{-2}$ in Figure 8b, $D_{t0\|}$ to be relatively independent of concentration in Figure 6a and $D_{t\|}$ to be concentration dependent in Figure 7a, we show $D_r/D_{t0\|} \propto c^{-2}$ while $D_r/D_{t\|} \not\propto c^{-2}$. It should be noted that the effect of rod thickness on rotation is independent of whether rotation is determined by cooperative translation or free translation. If rod thickness affects rotation, according to Doi,[26] $D_r \sim D_t(c^2L^9)^{-1}$ whereas if it does not $D_r \sim D_t(c^2L^8)^{-1}$. What we have observed is $D_t = D_{t0\|}$, demonstrating that the Edwards tube is still long in the concentration region of our investigation. From the values of D_r, $D_{t0\|}$, concentration, and rod length, we have estimated the L exponent to be 9 (as in eq 41) rather than 8 (as in eq 6). Therefore, although D_r depends on free diffusion, we cannot neglect the effects of rod thickness. In fact, rod thickness affects both translation and rotation, but cooperative translation does not affect rotation because of the length of the Edwards tube. It is interesting to note that Zero and Pecora[3] measured $D_r \propto L^{-9}$, yet they said they confirmed $D_r \propto L^{-8}$. Perhaps, they have confirmed Doi's original work instead of the Doi–Edwards model and showed the effects of rod thickness on rotation in semidilute solution.

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Dynamic Behavior of the Induced Polarization Arising from the Motion of Counterions Bound on a Rodlike Polyion

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ABSTRACT: To elucidate the dynamic behavior of counterions moving on a polymer frame where polyions are located, the transient induced polarization due to the sudden removal of an applied electric field is calculated for four cases: (i) free motion of counterions on polyions, (ii) strongly bound counterions in a harmonic potential, (iii) motion of counterions due to the chemical reaction site model, and (iv) diffusion of counterions on sites resulting from a cosine potential. It is shown that (i), (ii), and (iii) lead to single-exponential decaying polarizations, while (iv) gives polarization mainly characterized by two relaxation times. The former cases are treated analytically, whereas the latter case is considered by carrying out numerical computations.

I. Introduction

Without directly involving a dynamical treatment, Mandel[1] considered the motion of counterions on a polyion based on a site model and estimated the relaxation time for the electric polarization. To overcome this difficulty, Oosawa[2] calculated the electric polarization, assuming that the fluctuation of counterions forms a mean field, which results in introducing a convolution integral in the Smoluchowski equation for the distribution of the counterions. Since this approach is based on thermodynamical concepts and is therefore phenomenological, it seems necessary for us to use a more explicit model with direct appeal to the

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detailed dynamic behavior of the counterions. van Dijk, van der Touw, and Mandel[3] considered transport of counterions in the free phase to the bound phase on a rodlike polyion. They assumed that counterions in the bound phase move on the polyion without any specific preferred position and that exchange of counterions between the bound and free phases takes place along the radial direction of the polyion. They set up the Smoluchowski equation for the one-dimensional motion of the counterions, from which it follows that the influence due to the counterion exchange leads to the distribution function $w^* = w \exp(-Kt)$, where w is the distribution function for the free motion of counterions within the polyion chain without taking the counterion exchange into account, K is the exchange rate constant, and t is the time after the sudden removal of an external electric field at $t = 0$.

The above three papers are concerned with the translational motion of counterions. A case where this motion occurs on a rotating polymer frame has been studied by Tinoco and Yamaoka[4] and by Takezoe and Yu,[5] who used the following phenomenological equation with a single relaxation time τ_r for the polarizability $\alpha(t)$ in considering the transient buildup birefringence due to the slowly induced dipole moment:

$$\alpha(t) = \alpha(\infty)(1 - e^{-t/\tau_r}) \tag{1}$$

where $\alpha(\infty)$ is the polarizability in the limit of time $t \rightarrow \infty$. As explained in section IV, the phenomenon is far more complicated than they thought.

Fixman[6,7] considered the response of rigid polyelectrolyte molecules to an external electric field. Meyer and Vaughan[8] treated diffusion of counterions on the surface of a polyelectrolyte cylinder, approximately taking the Coulomb interaction into account. The main aim of the present study is to clarify the dynamic behavior of counterions moving on the polymer frame and physical conditions leading to a single-exponential decaying function after the sudden removal of an extremely low field that has been applied for a sufficiently long time. For this purpose, we consider the motion of positive counterions on a polyion under the influence of an applied electric field and calculate the induced polarization, assuming that negative ions are located on sites on a one-dimensional rigid rod; each site carries an equal charge $-q$, and the adjacent sites are equally spaced with a distance a. We therefore introduce a position-dependent potential for the counterions, whose exchange with the surroundings is, however, ignored. The calculation is carried out for the system where the field is applied parallel to the rod on the basis of two different approaches: (i) a diffusion model with a cosine potential and (ii) a chemical reaction site model, employing the reflecting boundary condition (that is, the counterions do not leak out from the ends of the rod but reflect back toward the center of the rod).

It is shown that the free motion of counterions on a polyion, strongly bound counterions in a harmonic potential, and the motion of counterions due to the chemical reaction site model lead to single-exponential decaying polarizations, whereas the diffusion model with a cosine potential gives polarization characterized mainly by two different relaxation times, i.e., one governing the short-time behavior due to the oscillatory motion in the potential minima and another characterizing the long-time behavior due to the length of time spent for counterions to escape from the potential.

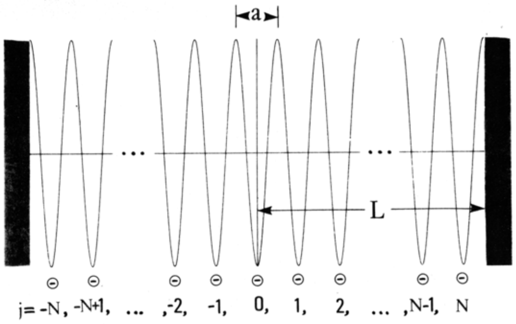

Figure 1. Cosine potential for the site model used for the motion of counterions on polyions.

II. Diffusion Model

We assume that $2N + 1$ positive counterions that do not interact with each other move on $2N + 1$ negative ions located with the same spacing a on a rodlike polymer of length $2L$. The regularly spacing of the negative ions forms potential minima for the mobile positive ions. This is schematically shown in Figure 1. The potential energy function $V(x)$, where x represents the position of a counterion, is then given by

$$V(x) = -V_0 \cos\left(\frac{2\pi}{a}x\right) \tag{2}$$

where $2V_0$ is the difference between the potential maxima and mimima. It is seen that

$$\frac{1}{a} = \left(N + \frac{1}{2}\right)\frac{1}{L} \tag{3}$$

The dynamical behavior of a counterion is assumed to be governed by the Smoluchowski equation, which takes into account the collisions between the counterions and the surrounding molecules and the motion due to the potential

$$\frac{\partial w(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial w}{\partial x} + \frac{2\pi}{a}\frac{V_0}{k_B T}\sin\left(\frac{2\pi}{a}x\right)w - \frac{qE}{k_B T}w\right] \tag{4}$$

where $w(x,t)$ is the distribution function, D is the diffusion constant, k_B is the Boltzmann constant, T is the absolute temperature, and E is an applied electric field. It is also assumed that the motion of the counterions is confined within the range of $-L \leq x \leq L$, thus imposing the reflecting boundary condition that the flux at $x = \pm L$ is zero; i.e.

$$\frac{\partial w}{\partial x} + \frac{2\pi}{a}\frac{V_0}{k_B T}\sin\left(\frac{2\pi}{a}x\right)w - \frac{qE}{k_B T}w = 0, \quad \text{at } x = \pm L \tag{5}$$

We find after substituting eq 2 in eq 4 and writing it in the dimensionless form by putting

$$\tau = \left(\frac{\pi}{L}\right)^2 Dt$$

$$\xi = \frac{\pi}{L}x$$

$$v_0 = \frac{V_0}{k_B T}$$

and

$$\epsilon = \frac{qLE}{\pi k_B T}$$

that

$$\frac{\partial w}{\partial \tau} = \frac{\partial}{\partial \xi}\left\{\frac{\partial w}{\partial \xi} + (2N + 1)v_0 \sin\left[(2N + 1)\xi\right]w - \epsilon w\right\} \tag{6}$$

In order to calculate the induced dipole from eq 6, it is convenient to define the function $\Psi_m(\tau)$:

$$\Psi_m(\tau) = \frac{1}{R}\int_{-\pi}^{\pi}\sin\left(\frac{2m-1}{2}\xi\right)w(\xi,\tau)\,\mathrm{d}\xi \qquad (7)$$

from which we immediately find that

$$w(\xi,\tau) = \frac{R}{\pi}\sum_{m=1}^{\infty}\Psi_m(\tau)\sin\left(\frac{2m-1}{2}\xi\right) \qquad (8)$$

where

$$R = \int_{-\pi}^{\pi}w(\xi,\tau)\,\mathrm{d}\xi$$

It should be noted from eq 7 that

$$\Psi_{-m}(\tau) = -\Psi_{m+1}(\tau)$$

Equations 5 and 6 lead to

$$\mathrm{d}R/\mathrm{d}\tau = 0$$

$$\frac{\mathrm{d}\Psi_m(\tau)}{\mathrm{d}\tau} = -\left(\frac{2m-1}{2}\right)^2\Psi_m(\tau) - \left(\frac{2m-1}{2}\right)\left(\frac{2N+1}{2}\right)v_0[\Psi_{(2N+1)+m} + \Psi_{(2N+1)-(m-1)}] \qquad (9)$$

The first equation accounts for the conservation of the number of counterions within the polymer frame. The polarization is defined by

$$P(t) = q(2N+1)\langle x\rangle = q(2N+1)\frac{\int_{-L}^{L}xw(x,t)\,\mathrm{d}x}{\int_{-L}^{L}w(x,t)\,\mathrm{d}x} = q(2N+1)\frac{8L}{\pi^2}\sum_{m=1}^{\infty}\frac{(-1)^{m-1}}{(2m-1)^2}\Psi_m(\tau) \qquad (10)$$

where the angular brackets represent the ensemble average. We are interested in calculating the decay polarization $P(t)$ after the sudden removal of an electric field E at $t = 0$, because the linear-response theory provides us with the relation between $P(t)$ and the buildup polarization $P_b(t)$ obtained by switching E on suddenly at $t = 0$ through the equation

$$P_r(t) = P(0) - P(t)$$

provided the condition of $\epsilon \ll 1$ prevails. Thus we impose the following initial condition for $w(x,0)$:

$$w(x,0) = C(1 + \epsilon\xi)\exp[v_0\cos(2N+1)\xi] \qquad (11)$$

where C is a constant. In view of eq 7, this leads to

$$\Psi_m(0) = \epsilon\frac{\int_0^{\pi}\xi\sin\left(\frac{2m-1}{2}\xi\right)\exp[v_0\cos(2N+1)\xi]\,\mathrm{d}\xi}{\int_0^{\pi}\exp[v_0\cos(2N+1)\xi]\,\mathrm{d}\xi} \qquad (12)$$

It is seen that since ϵ is independent of m and τ; $\Psi_m(\tau)/\epsilon$ also satisfies eq 10. The normalized polarization $P^*(\tau)$ is therefore given by

$$P^*(\tau) = \frac{P(\tau)}{P(0)} = \frac{\sum_{m=1}^{\infty}\frac{(-1)^{m-1}}{(2m-1)^2}\left[\frac{\Psi_m(\tau)}{\epsilon}\right]}{\sum_{m=1}^{\infty}\frac{(-1)^{m-1}}{(2m-1)^2}\left[\frac{\Psi_m(0)}{\epsilon}\right]} \qquad (13)$$

In this paper, $P^*(\tau)$ is calculated numerically from eq 9 and 10 together with the initial condition in eq 12. The result will be discussed in section IV.

III. Chemical Reaction Approach

Instead of representing the motion of counterions by the Smoluchowski equation as in the previous section, we assume that a counterion takes one of the states represented by $A_1, A_2, ..., A_n$ and its motion is governed by the following chemical reaction scheme:

$$A_1 \underset{k'}{\overset{k}{\rightleftarrows}} A_2 \underset{k'}{\overset{k}{\rightleftarrows}} \cdots \underset{k'}{\overset{k}{\rightleftarrows}} A_n \qquad (14)$$

where the rate constants for the forward and reverse reactions are designated by k and k', respectively. The rate equations are given by

$$\begin{aligned}
\mathrm{d}a_1(t)/\mathrm{d}t &= -ka_1(t) + k'a_2(t)\\
&\cdots\\
\mathrm{d}a_j(t)/\mathrm{d}t &= -(k + k')a_j(t) + ka_{j-1}(t) + k'a_{j+1}(t) \quad (j = 2, 3, ..., n-1)\\
&\cdots\\
\mathrm{d}a_n(t)/\mathrm{d}t &= -k'a_n(t) + ka_{n-1}(t) \qquad (15)
\end{aligned}$$

where $a_j(t)$ represents the concentration of A_j at time t. Although the solutions for these differential equations have been obtained exactly with arbitrary initial conditions by Morita,[9] we use a more convenient method to calculate the induced polarization $P(t)$, which is given by

$$P(t) = q(2N+1)a\sum_{j=1}^{2N+1}(j - N - 1)a_j(t) = q(2N+1)a\left[\sum_{j=1}^{2N+1}ja_j(t) - (N+1)\sum_{j=1}^{2N+1}a_j(0)\right] \qquad (16)$$

We have used the condition of conservation of counterions; i.e.

$$\sum_{j=1}^{2N+1}a_j(t) = \sum_{j=1}^{2N+1}a_j(0)$$

which follows immediately from eq 15. On multiplying both sides of eq 15 by $y, y^j, ..., y^n$ from the top to bottom equations, respectively, and adding together, we find that

$$\partial\sigma(y,t)/\partial t = [-(k + k') + ky + k'y^{-1}]\sigma(y,t) + k'(y-1)a_1(t) - ky^n(y-1)a_n(t) \qquad (17)$$

where $\sigma(y,t)$ is a generating function for $a_j(t)$ and defined by the equation

$$\sigma(y,t) = \sum_{j=1}^{n}y^ja_j(t) \qquad (18)$$

It is evident that if we put $z = y^{-1}$ in eq 18, $\sigma(z,t)$ can be regarded as the z transform for $a_j(t)$. It is noted that the first term on the right of eq 16

$$M(t) = \sum_{j=1}^{2N+1}ja_j(t) \qquad (19)$$

is related to $\sigma(y,t)$ by the equation

$$M(t) = \left.\frac{\partial\sigma(y,t)}{\partial y}\right|_{y=1} \qquad (20)$$

After carrying out the partial differentiation of both sides of eq 17 with respect to y and putting $y = 1$, we find that $M(t)$ satisfies

$$\mathrm{d}M(t)/\mathrm{d}t = (k - k')\sum_{j=1}^{2N+1}a_j(0) + k'a_1(t) - ka_n(t) \qquad (21)$$

which immediately can be integrated to lead to

$$M(t) = M(0) + (k - k')t\sum_{j=1}^{2N+1}a_j(0) + k'\int_0^t a_1(t')\,\mathrm{d}t' - k\int_0^t a_n(t')\,\mathrm{d}t' \qquad (22)$$

Therefore it is seen that in calculating $P(t)$ from eq 16, we only need to know the time dependence of $a_1(t)$ and $a_n(t)$, which are the concentrations at the ends of the potential sites. Since the procedure for calculating $a_1(t)$ and $a_n(t)$ with the arbitrary initial condition $a_j(0)$ is published elsewhere,[9] we just write here the final result for $M(t)$

$$M(t) = M(0) + \sum_{m=1}^{2N} \frac{1 - e^{\alpha_m t}}{{\alpha_m}^2}(kC_{m,n} - k'C_{m,1}) \qquad (23)$$

where

$$\alpha_m = -k - k' + 2(kk')^{1/2} \cos \phi_m$$

$$\phi_m = m\pi/n$$

$$n = 2N + 1$$

$$C_{m,n} = 2k'(-1)^{m+1}\frac{\sin \phi_m}{n}\{-a_n(0) \sin (n-1)\phi_m + \sum_{j=1}^{n-1} a_j(0)[{K_e}^{(n-j+1)/2} \sin (j\phi_m) - {K_e}^{(n-j)/2} \sin (j-1)\phi_m]\}$$

$$C_{m,1} = 2k(-1)^{m+1} \frac{\sin \phi_m}{n}\{-a_1(0) \sin (n-1)\phi_m + \sum_{j=2}^{n} a_j(0)[{K_e}^{-j/2} \sin (n-j+1)\phi_m - {K_e}^{-(j-1)/2} \sin (n-j)\phi_m]\}$$

$$K_e = k/k'$$

In determining $a_j(0)$, we suppose that because of the application of E for $t < 0$

$$K_e = \exp\left(\frac{qaE}{k_BT}\right) = 1 + \frac{qaE}{k_BT} + ... \qquad (24)$$

It is obvious that no field for $t > 0$ leads to $K_e = 1$, i.e., $k = k'$. The equilibrium value of A_j obtained from eq 15 by putting $[\mathrm{d}a_j(t)/\mathrm{d}t] = 0$ is used for $a_j(0)$, which is

$$a_j(0) = \frac{{K_e}^{j-1}(K_e - 1)}{{K_e}^n - 1} \sum_{j=1}^{n} a_j(0) \qquad (25)$$

It should be noted that the normalized polarization $P^*(t)$ is independent of the total concentration

$$\sum_{j=1}^{2N+1} a_j(t) = \sum_{j=1}^{2N+1} a_j(0)$$

$P^*(t)$ is thus calculated by putting $k = k'$ in eq 23 and using the initial condition in eq 25, whose result will be shown in section IV.

IV. Discussion

For free-moving counterions, we find by putting $v_0 = 0$ in eq 9 that

$$\Psi_m(\tau) = \Psi_m(0) \exp\left[-\left(\frac{2m-1}{2}\right)^2 \tau\right] \qquad (26)$$

In view of eq 12, it follows that

$$\Psi_m(0) = \epsilon\frac{4}{\pi} \frac{(-1)^{m-1}}{(2m-1)^2} \qquad (27)$$

which leads to

$$P^*(\tau) = 6\left(\frac{2}{\pi}\right)^4 \sum_{m=1}^{\infty} \frac{1}{(2m-1)^4} \exp\left[-\left(\frac{2m-1}{2}\right)^2 \tau\right] \qquad (28)$$

where the relation

$$\sum_{m=1}^{\infty} \frac{1}{(2m-1)^4} = \frac{1}{6}\left(\frac{\pi}{2}\right)^4 \qquad (29)$$

has been used. It should be noted that at least 98.55% contribution to the sum on the right-hand side of eq 28 comes from the first term where $m = 1$. Therefore, we can approximately put

$$P^*(\tau) \simeq \exp\left(-\frac{\tau}{4}\right) = \exp\left[-\left(\frac{\pi}{2L}\right)^2 Dt\right]$$

The relaxation time in this special case is seen to be proportional to L^2 and D^{-1}. $P(t)$ is proportional to $P(0)$, which is seen to be $(2N + 1)q^2L^2E/3k_BT$. This agrees with the results of Mandel.[1]

Perhaps it is worth mentioning that the Laplace transforms of $w(\xi,\tau)$ and $P^*(\tau)$ with respect to τ in the case of $v_0 = 0$ can be obtained exactly without expanding the Fourier series in the following closed form:

$$\mathcal{L}[w(\xi,\tau)] = \int_0^\infty w(\xi,\tau)e^{-s\tau}\, \mathrm{d}\tau = C\left[\frac{1}{s} + \frac{\epsilon\xi}{s} - \frac{\epsilon}{s^{3/2}} \frac{\sinh (\xi s^{1/2})}{\cosh (\pi s^{1/2})}\right]$$

$$\mathcal{L}[P^*(\tau)] = \frac{1}{s} + \frac{3}{\pi^2 s^2}\left[\frac{1}{\pi s^{1/2}} \tanh (\pi s^{1/2}) - 1\right] \qquad (30)$$

On using the relations

$$\frac{1}{s^{1/2}} \tanh (\pi s^{1/2}) = \frac{2}{\pi}\sum_{m=1}^{\infty}\left[s + \left(\frac{2m-1}{2}\right)^2\right]^{-1}$$

$$\sum_{m=1}^{\infty} (m-1)^{-2} = \frac{\pi^2}{8}$$

and eq 29 and taking the inverse Laplace transform of the right-hand side of eq 30, we find the same expression for $P^*(\tau)$ in eq 28.

In another limiting case where v_0 is so large that a counterion is trapped in the potential minimum and undergoing Brownian motion so that the counterion cannot escape from it even by the application of an electric field, the potential energy $V_j(x)$ for the jth counterion where $j = 0, 1, 2, ..., N$ is given by

$$V_j(x) = \tfrac{1}{2}k_s{u_j}^2 \qquad (31)$$

where k_s is the spring constant and $u_j = x - ja$. Since the counterion is moving only in the restricted range of $|u_j| << a$, the motion of the jth counterion is assumed not to influence that of other counterions. Then u_j is regarded as an independent variable. We use the following Langevin equation, for which inertial effects are neglected

$$\beta \frac{\mathrm{d}u_j}{\mathrm{d}t} = A(t) - \frac{k_s}{m}u_j \qquad (32)$$

where $m\beta$ is the friction constant, which is related to the diffusion constant D by the Einstein relation, i.e., $m\beta = k_BT/D$, and $A(t)$ is the random acceleration whose average is zero. This equation immediately gives rise to

$$\langle u_j(t)\rangle = \langle u_j(0)\rangle \exp\left(-\frac{Dk_s}{k_BT}t\right)$$

In view of eq 10, since

$$P(t) = (2N+1)\langle x\rangle = \sum_{j=-N}^{N} \langle u_j(t)\rangle = [\sum_{j=-N}^{N} \langle u_j(0)\rangle] \exp\left(-\frac{Dk_s}{k_BT}t\right) \qquad (33)$$

we find that

$$P^*(t) = \exp\left(-\frac{Dk_s}{k_BT}t\right)$$

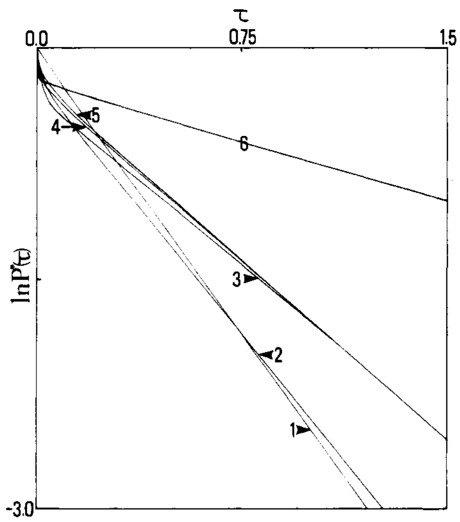

Figure 2. Plots of ln $P^*(\tau)$ obtained from the diffusion model with the cosine potential vs. τ: (1) $\upsilon_0 = 0$ (the free motion); (2) $\upsilon_0 = 0.5, N = 2$; (3) $\upsilon_0 = 1, N = 1$; (4) $\upsilon_0 = 1, N = 2$; (5) $\upsilon_0 = 1, N = 3$; (6) $\upsilon_0 = 2, N = 2$.

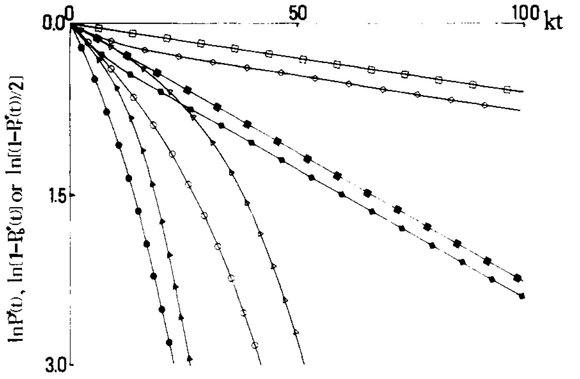

Figure 3. Plots of ln $P^*(t)$ obtained for $n = 21$ ((♦) $K_e = 1.01$; (■) $K_e = 5.0$) and $n = 41$ ((◊) $K_e = 1.01$; (□) $K_e = 5.0$) vs. kt together with those of ln $[1 - P_b^*(t)]$ for $n = 21$ ((♦) $K_e = 1.01$; (●) $K_e = 5.0$) and $n = 41$ ((◊) $K_e = 1.01$; (○) $K_e = 5.0$) and ln $[(1 - P_r^*(t))/2]$ for $n = 21$ ((♦) $K_e = 1.01$; (▲) $K_e = 5.0$) and $n = 41$ ((◊) $K_e = 1.01$; (△) $K_e = 5.0$).

This explicitly shows that a counterion strongly bound to a polyion leads to a single-exponential decaying polarization whose relaxation time is k_BT/Dk_s, where the spring constant, k_s, represents the binding strength between the counterion and polyion.

In Figure 2, the result from the diffusion model in section II is shown. Curves 3, 4, and 5 are obtained for $n = 1, 2$, and 3, fixing $\upsilon_0 = 1$. It is seen that an increase in the number of sites influences the short-time behavior slightly, leading to the long relaxation time due to the increased resistance for counterion motion, whereas an increase in the potential barrier υ_0 (see curves 2, 4, and 6 for $\upsilon_0 = 0.5$, 1, and 2 for $n = 2$, respectively) influences the dynamic process more significantly. These curves suggest that the short-time behavior is governed by the oscillatory motion around the potential minima, resulting in the short relaxation time for large υ_0, and the long-time behavior is influenced by the time spent for the counterions to escape from the potential maxima, requiring a longer relaxation time for a higher potential barrier.

Table I
Values of Q_1^* for Various Values of n and K_e

	K_e			
n	1.01	1.5	2.0	5.0
11	0.987	0.968	0.946	0.903
21	0.986	0.935	0.902	0.864
31	0.986	0.909	0.878	0.848
41	0.985	0.891	0.864	0.839
51	0.985	0.878	0.854	0.834

The chemical reaction model in section III is treated with the full consideration of the dynamic processes whereas Mandel[1] estimated the relaxation time and the polarization from time-independent treatments based on a model similar to the one in section III. Plots of ln $P^*(t)$ from the chemical reaction model vs. kt are shown in Figure 3, for $n = 21$ ((♦) $K_e = 1.01$; (■) $K_e = 5.0$) and $n = 41$ ((◊) $K_e = 1.01$; (□) $K_e = 5.0$). It is seen that for values of K_e close to 1, which is the case for $qaE/k_BT << 1$ in view of eq 23, $P^*(t)$ may be approximated by a single-exponential decaying function. To show this result, we write $M(t)$ responsible for the present transient decay case where $K_e = 1$ for $t > 0$ and

$$M(0) = \frac{nK_e^n(K_e - 1) - K_e^n + 1}{(K_e - 1)(K_e^n - 1)}\sum_{j=1}^{n} a_j(0) \tag{34}$$

in the form

$$M(t) = M(0) + \sum_{m=1}^{2N} \frac{k(1 - e^{\alpha_m t})}{{\alpha_m}^2}(C_{m,n} - C_{m,1}) \tag{35}$$

where

$$\alpha_m = -4k \sin^2 (\phi_m/2) \tag{36}$$

$$C_{m,n} - C_{m,1} = 2k(-1)^{m+1}[1 + (-1)^{m+1}]\frac{\sin \phi_m}{n}\sum_{j=1}^{n} a_j(0) \times [\sin (j\phi_m) - \sin (j - 1)\phi_m] \tag{37}$$

The summation over j in eq 37 can be carried out by using eq 25, leading to the result

$$Q_m = \frac{k}{{\alpha_m}^2}(C_{m,n} - C_{m,1}) = -[\sum_{j=1}^{n} a_j(0)]\frac{K_e^n + 1}{K_e^n - 1} \times \frac{(K_e - 1)^2}{n}\left[\frac{1}{1 - 2K_e \cos \phi_m + K_e^2}\,\frac{1 + \cos \phi_m}{1 - \cos \phi_m}\right] \tag{38}$$

It is seen from eq 37 that $m = 2, 4, 6, ..., 2N$ lead to $Q_m = 0$. Also, it is evident that

$$P^*(t) = \frac{\sum_{m=1}^{2N} Q_m e^{\alpha_m t}}{\frac{n + 1}{2}\sum_{j=1}^{n} a_j(0) - M(0)}$$

On defining the maximum contribution from all the relaxation modes to $P^*(t)$ by

$$M_{\text{total}} = \sum_{m=1}^{2N} Q_m = \sum_{r=1}^{n-2} Q_{2r-1} = \frac{n + 1}{2}\sum_{j=1}^{n} a_j(0) - M(0)$$

we find that the minumum contribution of the term corresponding to $m = 1$ to $P^*(t)$ is given by

$$Q_1^* = Q_1/M_{\text{total}}$$

Of course, the larger t becomes, the more significant the contribution of the first term is. Q_1^* for various values of n and K_e are collected in Table I. The relaxation time for the Q_1 mode is given by

$$[4k \sin^2 (\pi/2n)]^{-1}$$

which indicates that for large n, the relaxation time is proportional to $n^2 = 4L^2/a^2$ and to k^{-1}. This result is similar to that for the free motion of counterions. Equation 23 not only gives the decay polarization $P^*(t)$ but also the polarizations $P_b^*(t)$ and $P_r^*(t)$ for the buildup and the rapidly reversing fields, respectively, in which cases the initial values for $a_j(0)$ are

$$a_j(0) = \frac{1}{n}\sum_{j=1}^{n} a_j(0)$$

and

$$a_j(0) = K_e^{-(j-1)}(K_e^{-1} - 1)/(K_e^{-n} - 1)$$

We have calculated $P_b^*(t)$ and $P_r^*(t)$ and to compare them conveniently with the normalized decay polarization $P^*(t)$, we have also plotted ln $[1 - P_b^*(t)]$ and ln $[(1 - P_r^*(t))/2]$ vs. kt for $K_e = 5.0$ in Figure 3 ((●) $n = 21$ and (○) $n = 41$ for the buildup field; (▲) $n = 21$ and (△) $n = 41$ for the rapidly reversing field from $-E$ to $+E$). As expected from the linear-response theory, we have actually found that ln $P^*(t)$, ln $[1 - P_b^*(t)]$, and ln $[(1 - P_r^*(t))/2]$ for $K_e = 1.01$ gave the same values. However, it is seen from Figure 3 that when the contribution from nonlinear terms with respect to E is large, corresponding to large values of K_e, the polarizations cannot be expressed simply by a single mode of the relaxation processes. This is particularly significant when we consider the relaxation processes caused by an external electric field such as a stepup field or a rapidly reversing field, which is commonly used in electrooptical measurements, because the external field directly drives the charge transport together with the molecular collisions, making the relaxation processes more complex than in the case of field-free motion. It is evident that if we consider field-induced dynamic processes caused by the external field, we cannot expect a linear response whose relaxation times are independent of the field strength.

The reflecting boundary condition employed in eq 5 is similar to that of van Dijk et al.,[3] who considered the counterion exchange between the free and bound phases. The chemical reaction model in section III also takes into account the condition that the number of counterions within the rod be conserved and counterions at both ends of the rod may stay there or reflect back to the neighboring sites. Fixman[6,7] and Meyer and Vaughan[8] used more elaborate boundary conditions.

The repulsive interaction of counterions is neglected as in most of the existing work, even though it is important for investigating the dynamic behavior of counterions.

Since the present treatment is concerned with the induced dipole moment where the rod is fixed in space (no rotation) and the field is applied parallel to the rod, we cannot use the present results directly for the Kerr effect relaxation at a low applied electric field where counterions move along a polymer frame that is rotating at the same time. When the time rate of the translational motion of counterions is comparable to that of the rotational motion of the polyion rod, we should consider the slowly induced dipole. This arises from the interaction between counterions and negative ions. The stronger the interaction is, the more slowly the dipole is induced. The limiting strong case corresponds to rigidly bound counterions. Representing the angle that the rod makes with the direction of the applied field by θ, we should take into account the fact that the direction of the flow of counterions becomes suddenly opposite as soon as the polymer rod crosses over past $\theta = 90°$, and the field strength acting on the counterionds depends upon θ. The previous studies[4,5] have not taken these points into account, leading to serious difficulties, not to mention[5] the introduction of an apparent permanent dipole influenced by an external electric field. The former factor is important not for high field but for low field, because for high field the torque due to the external field surpasses that due to the molecular collisions. In this case, however, nonlinear effects are significant instead. In treating this problem properly, we should have to solve the problem of the coupling of the translational motion of counterions to the rotational motion of the rod, which is left for future work. It is hoped that the present simple treatment will serve as a starting point for attacking such a problem.

Takezoe and Yu[5] investigated the electric birefringence for dilute aqueous suspensions of bovine disk membrane vesicles, observing a characteristic rise and dip for the buildup and reversing fields, respectively. This was ascribed by them to the slowly induced dipole moment caused by field-induced displacement of the photopigment distribution on the vesicular surface. In connection with the experimental study of the slowly induced dipole moment, Itoh, Ookubo, and Hayakawa[10] recently measured dielectric dispersions of sodium salts of poly(styrenesulfonic acid) and carboxycellulose.

We summarize the assumptions used for deriving the results of this paper: (A) limiting low electric field, (B) neglect of the interaction of counterions, (C) equal spacing of negative ions firmly attached to the rigid polyion rod, (D) bound counterions whose motion is confined within the rod, and (E) neglect of rotational motion.

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