

Dynamic Motion of Polyelectrolyte in a Composite Membrane : II. Molecular Study

Young Park* and Hwa A. Lim

Supercomputer Computations Research Institute,
The Florida State University, Tallahassee, FL 32306-4052 U. S. A.
(Received July 13, 1993, Accepted November 18, 1993)

막에서 전하고분자의 동적 현상 II. 미시적 연구

박영규* · 임화은

미국 플로리다주 텔라하시
플로리다 주립대학 슈퍼컴퓨터연구소 FL 32306-4052
(1993년 7월 13일 접수, 1993년 11월 18일 채택)

Abstract: Theoretical model for membrane transport of large polyelectrolyte is presented. When the electric field is applied, the molecular conformation quickly orients in the field direction showing overshooting orientation. The predicted dependence of overshoot time and orientation upon field intensity and molecular size aids to understand the dynamic motion of molecules in membrane transport. The dynamics of the overshoot is associated with self-trapping conformations of molecule. The understanding of these effects supports evidences for the electrophoretic filtration of polyelectrolyte in the polymeric membrane. This paper shows one example for molecular study in the theoretical review paper of membrane transport.

요 약 : 이 논문은 거대전하고분자의 막전달 현상을 위한 이론적 모델을 연구하는데 있다. 전기적 힘에 의한 전하고분자 물질의 형상은 빠르게 곧게 뻗으면서 진행되며, 곧게 뻗는 시간과 길이는 막 전달의 동적현상을 이해하는데 도움을 주고 있다. 빠르게 곧게 뻗을 때, 전하고분자의 두 끝이 전기력 방향으로 동시에 끌리는 현상이 일어난다. 이같은 현상의 이해는 거대전하고분자의 막분리를 이해하는데 도움을 주고 있다.

1. Introduction

The artificial membranes manufactured by polymer materials have pore diameter of about $\leq 10\text{nm}$.

The contour length of large polyelectrolyte like polymer colloids and nucleic acids is approximately 10 times the diameter of the average pore in the membrane matrix. Since a large polyelectrolyte is too

*To whom correspondence should be addressed

현주소 : 682-792 경남 울산시 동구 전하동 1번지, 현대중공업주 현대종합연구소 환경연구실

large to fit into a single pore, membrane transport using an electric field has been utilized to enhance permeation of membrane. Electrofiltrations of large polyelectrolyte using membrane transport have been developed in several applications. For example, blood plasma processing using electrofiltration [1] has been interested in the removal of trace plasma components without altering the functional or physicochemical properties. Electrofiltration [2] has been applied to dewater colloidal dispersions. Iontophoresis [3] has been investigated with the aim of enhancing hydrophilic drug permeation through hydrophobic membranes. Iontophoretic techniques have been developed recently in the field of transdermal delivery system. The electrophoretic transport of large polyelectrolyte in membranes also has an important application to wide range of separation and purification processes. Current interest has been focused on the purification of macromolecules, such as proteins and nucleic acids, for applications in biotechnology using membrane electrophoresis [4, 5]. In this paper, we suggest a molecular model which explains conformations of large polyelectrolyte in the presence of an electric field. The separations of large polyelectrolyte in membrane will be studied using overstretching length and time affecting molecular conformations.

The electrophoretic transport of large polyelectrolyte in a polymeric membrane leads to nonmonotonic relationship between the mobility and the molecular size. This nonmonotonic relationship is related to the anomalous mobility of polyelectrolytes, the shape of which has a compact conformations. This mechanism involved in the electrophoretic transport of polyelectrolyte is slowly being unraveled by advances in experimental and theoretical studies. Linear dichroism [6] and electric birefringence [7, 8] studies show that the initial orientation of molecular conformations involves a transient overshoot effect where the molecular orientation is larger, i. e., the molecule is more anisotropic, than even in the steady state. The overshoot effect is strongly dependent on molecular size of polyelectro-

lyte and electric field. The relationship between them aids to understand for the separation of large polyelectrolytes in the membrane. Therefore, the purpose of this paper is to study the orientational motion of polyelectrolyte chain as it advances through the pores of the polymeric membrane under the influence of an electric field.

The most successful kind of theory so far has made use of the concept of a "tube" [9] through which the chain passes. The model has been successfully applied to situations involving diffusion where nonexternal electric field is present. This theory can be extended to when a uniform external field is applied. The theoretical model accounts for the chain stretching out as the strength of the field increases. The reptational tube model cannot predict the transient overshoot because the length of tube is constant and the conformation of the tube is determined by the motion of the leading end. In this paper, we illustrate the process of a constitutive equation from kinetic theory [10] to account for this effect. The numerical simulation helps to clarify the mechanisms responsible for the molecular response to rapid changes in electric field conditions.

2. Theory

2.1. Theoretical Model

We consider the polyelectrolyte model shown in Figure 1, in which the polyelectrolyte is represented by an elastic dumbbell [10] consisting of N beads with equal friction coefficient ξ . The beads are connected by springs. The elastic dumbbell model with Brownian motion is an example of models consisting of N spherical "beads" joined by nonbendable "springs". The locations of the centers of beads are given by position vector \mathbf{r}_k with respect to the origin of a coordinate system, where $k=1, 2, \dots, N$ and the connector vectors are defined $\mathbf{R}_k = \mathbf{r}_{k+1} - \mathbf{r}_k$ as shown in Figure 1. The solution in the membrane is assumed to be sufficiently dilute that dumbbells do not interact with each other. It is assumed that

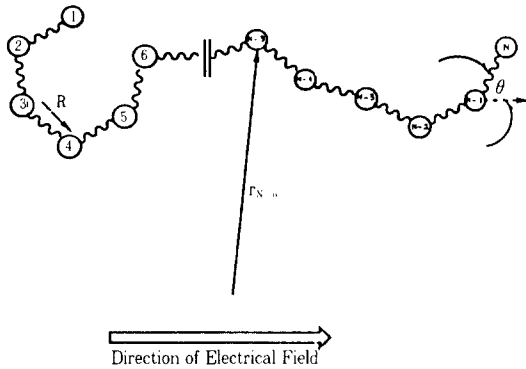


Fig. 1. Schematic picture of n beads-springs of a large polyelectrolyte in a membrane.

the dumbbells are so small that they experience “Brownian motion force”, the widely fluctuation random forces that are associated with thermal motion. The velocity field of the solvent is neglected and all of the springs are assumed to have the same force law.

The configurational distribution function, $\Psi(\mathbf{R}, t)$, which is defined such that $\Psi(\mathbf{R}, t) d\Psi$ is the probability that the dumbbell in the membrane has conformation in the range $d\mathbf{R}$ about \mathbf{R} at time t . We need to solve the following equation of continuity in the configuration space

$$\frac{\partial \Psi}{\partial t} = - \left(\frac{\partial}{\partial \mathbf{R}} \cdot \langle \mathbf{R} \rangle \Psi \right) \quad (1)$$

where $\langle \mathbf{R} \rangle$ is the velocity-space average of the time rate of change of the configuration vector \mathbf{R} . The expression of $\langle \mathbf{R} \rangle$ can be derived from a force balance on each of the beads. This leads to a balance of the forces for the internal motion acting on each bead as

$$-kT \frac{\partial}{\partial \mathbf{R}_i} \ln \Psi - \frac{\partial}{\partial \mathbf{R}_i} (\Phi_h + \Phi_e) + qE \langle \cos \theta \rangle = 0$$

for $i=1, 2, \dots, N$ (2)

The first term of equation (2) is a Brownian force when the Maxwellian velocity is used [10], the second term is the intramolecular force which includes mechanical force between beads and elect

rostatic forces due to the electric charge (q) in each bead, and the last term of equation (2) represents the external electric force term. The hydrodynamic drag force will not be considered in this paper. We model a polyelectrolyte with a chain of N beads connected by $N-1$ springs. For dilute solutions we assume that the configurational distribution function $\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N-1}; t)$ depends only on the connector vector and time. The diffusion equation is

$$\frac{\partial \Psi}{\partial t} = - \sum_{i=1}^N \frac{\partial}{\partial \mathbf{R}_i} \cdot \sum_{j=1}^N \mathbf{T}_{ij} \left\{ \frac{kT}{\xi} \frac{\partial}{\partial \mathbf{R}_i} \Psi - \frac{2}{\xi} \frac{\partial}{\partial \mathbf{R}_i} (\Phi_h + \Phi_e) \Psi + \frac{1}{\xi} qE \langle \cos \theta \rangle \Psi \right\} \quad (3)$$

where Φ_h is the interaction potential due to the spring forces between the beads and Φ_e is the electrical potential. The interaction potential can be written[11] as

$$\Phi_h = \frac{kT}{2b} \sum_{i=2}^N (\mathbf{R}_i - \mathbf{R}_{i-1})^2$$

and the tensor in our case is written by $\mathbf{T}_{ij} = \mathbf{I} \delta_{ij}$ assuming hydrodynamic force can be neglected where \mathbf{I} is a unit tensor. The model equation (3) is a linear equation for \mathbf{R} . For an internal bead ($i=2, 3, \dots, N-1$), equation (3) can be rewritten, under an electric field, as

$$\xi \frac{\partial \mathbf{R}_i(t)}{\partial t} = F(\Delta \mathbf{R}_i) - F(\Delta \mathbf{R}_{i-1}) + f_{i,e}(t) + f_{i,b}(t) \quad (4)$$

$f_{i,e}(t)$ is an electric force term of $qE \cos \theta (i, t)$, which angle $\theta(t)$ is expressed by the angle between the bead-spring direction and electric field direction as seen in Figure 1. $f_{i,b}(i, t)$ is the curvilinear random force acting on internal bead i . The random force represents the sum of the forces due to the incessant collision of the fluid molecules with the Brownian particle. An important quantity characterizing the Brownian motion is the time correlation function. If the distribution of the Brownian random force is assumed to be Gaussian, the average is then taken with respect to $f(t)$ for the given distribution

two function as[11]

$$\langle f_b(t) \rangle = 0, \quad \langle f_b(t)f_b(t') \rangle = 2\xi kT\delta(t-t') \quad (5)$$

Assuming that at time t the segment has an orientation $\theta(t)$ ($0 < \theta < \pi$), then the probability density function [12] has the form

$$G(\theta) = \frac{\sin\theta}{2\Omega} \exp\left[\frac{qE \cos\theta}{2kT}\right] \quad (6)$$

where Ω is a normalizing factor obtained from the condition $\int_0^\pi G(\theta)d\theta = 1$. We find simply that Ω is equal to $\sinh \chi/\chi$ from normalizing equation (6) and $\chi = qE/2kT$. The form we assume for $G(\theta)$ is a simple extension, using a Boltzmann factor, of the ideas of the standard reptation theory. We can use $G(\theta)$ to calculate the average value of $\cos\theta$, i.e., the average value of $\cos\theta$ in the orientation :

$$\langle \cos\theta \rangle = \int_0^\pi G(\theta)\cos\theta d\theta = \coth\chi - \frac{1}{\chi} \equiv B(\chi) \quad (7)$$

The average represented by the angle brackets $\langle \rangle$ is a measure of average orientation over an infinite number of identical chains. $F(\Delta R_i)$ in equation (4) is the anharmonic entropic spring force [13] and is given by the elastic force of each spring in equilibrium with the electric force acting on it in the overshoot conformation. The motion of spring i between bead i and $i + 1$ has a length ΔR_i , and under this tension, the solution of equilibrium is

$$\frac{kT}{b} B^{-1}\left(\frac{a}{L}\right) + i\varepsilon = \frac{kT}{b} B^{-1}\left(\frac{\Delta R_i}{L}\right) \quad (8)$$

where B is the Langevin function defined in equation (7), "b" is the Kuhn length of the polymer, ΔR is the distance between two consecutive beads, i. e., $\Delta R \leq L$ and "a" is the average pore size in the membrane. The scaled effective force acting on each charge arm-bead using equation (8) is defined as $\langle \varepsilon \rangle = \varepsilon a / (2kT)$. We obtain $\langle \varepsilon \rangle = \chi \coth(\chi) - 1$.

2. 2. Stretching of the Polyelectrolyte Chain in a Composite Membrane

A sequence of polyelectrolyte stretchings is as-

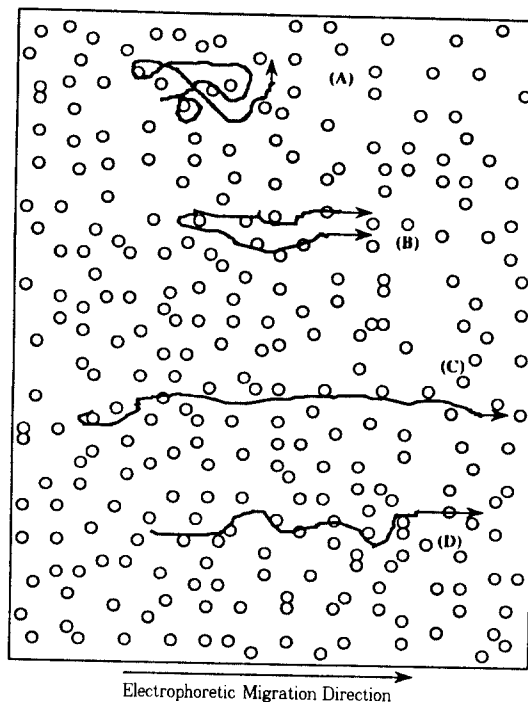


Fig. 2. Schematic picture of a polyelectrolyte stretching to the electric field. Circles mark indicates pores of polymeric membrane.

sumed to take place when an electric field is suddenly applied to the membrane. These models have been studied using the reptation model of polymer [14]. We suggest a simple analytical model which explains the available experimental data [15] on transient overshoot.

Figure 2 shows how a reptating molecule behaves as the molecule assumes new molecular conformations during its migration. This result can be observed using fluorescence microscope. The instantaneous mobility is proportional to the instantaneous distance between the ends of that molecule in the x -direction, the direction of the electric field[16]. For a polyelectrolyte that migrates without stretching (Fig. 2A), the two ends of polyelectrolyte are first pulled down through the obstacles and two arms are growing out of the initial globular random-walk conformation. The two arms of the polyelectrolyte chain become aware of each other when the arms reach the maximum extension permitted by the

equilibrium between the external electric forces and the internal entropic (or elastic) forces (Fig. 2B). In this case, the molecular chains do not migrate in response to the applied electric field. The initial molecular conformation, which is preserved during this process, contains fewer beads and acts more and less as a random-walk molecule. This compact conformation is called a "self-trapping effect". When equilibrium between the electric and elastic forces is reached, the longer arm starts pulling on the shorter arm and keeps growing at the expense of the shorter arm until the chain is totally disengaged from the obstacle of polymeric membrane. And an overstretched conformation is reached (Fig. 2c). After relaxation of the intramolecular stress with a reduction of the end-to-end distance, the molecule reptates through the membrane head first for its steady-state electrophoretic migration, with large length fluctuation[17, 18]. During migration, the head hesitations and collisions with the gel obstacles allow the other parts of the molecule, which simply follow the path previously chosen by the head, to catch up. Thus, the leading end is compressed near the head of the migrating, that is, partially stretched conformation(Fig. 2d).

The maximum spring overstretching is clearly obtained in a self-trapping conformation. Total contour length of the molecules seems to be maximum when the internal elastic forces reach their maximum value. Since a stretched spring means that the polyelectrolyte are aligned between the two beads it joins, the chain orientation overshoot should occur when the arms of the self-trapping conformation in Figure 2(b), which point in the field direction, assume a maximum total contour length, i. e., when we have the "overshoot conformation". The calculations for the properties of overstretching aid to understand membrane transport of large polyelectrolyte and they will be explained in the next section.

2. 3. Drift and Overstretching of the Polyelectrolyte Chain

The position of the center of mass, $\mathbf{R}_{cm} = \frac{1}{N} \sum_{i=1}^N \mathbf{R}(t)$.

The total contour length of the springs is $L_t = \sum_{i=1}^N \mathbf{R}(t)$.

When a given chain moves forward, we have $\mathbf{R}_i \rightarrow \mathbf{R}_{i+1}$, and the r_N segment leaves the original tube. We denote by N_0 the number of beads trapped inside the obstacle of polymeric membrane when self-trapping conformation is reached, and we assume that the two arms then possess each $(N-N_0)/2$ beads. We further assume the maximum arm length is L_{Max} , then the total time T_M need to reach the overshoot conformation from the unstretched conformation, i. e., the time needed for the arms to grow to the length L_{Max} . The total arm length at this time is thus

$$L_{Max} = \sum_{i=2}^{(N-N_0)/2} \Delta \mathbf{R} \approx \int_1^{(N-N_0)/2} \Delta \mathbf{R} di \quad (9)$$

The length of random-walk conformation $(N-1) \times a$ contains N_0 beads under the tension applied by the two last free beads ($i=(N-N_0)/2$) on each arm, with

$$N_0 = \frac{(N-1)a}{\Delta \mathbf{R}_{(N-N_0)/2}} \quad (10)$$

The value of N_0 is not an integer in general; we thus use the integral form of equation (L_{Max}) to obtain "smooth" quantitative results. In order to have large overstretching, one needs to have $L \gg a \gg b$, i. e., a large amount of "stored" polyelectrolyte in the absence of electric field. In this case, we can use $B^{-1}(a/L) \approx 3(a/L)$ in equation (8) to replace the force acting on the end beads of the reptating chain by $3(kT/a)$ (the springs are then nearly harmonic in thermal equilibrium); Equations (9) and (10) then become

$$\begin{aligned} L_{Max} &= L \times \sum_{i=1}^{(N-N_0)/2} B\left(\frac{2i\langle \epsilon \rangle + 3}{m}\right) \\ &\approx L \int_1^{(N-N_0)/2} \left[\coth\left(\frac{2i\langle \epsilon \rangle + 3}{m}\right) \right] - \left(\frac{2i\langle \epsilon \rangle + 3}{m}\right)^{-1} di \end{aligned}$$

$$\begin{aligned}
 &= \frac{Lm}{2\langle \epsilon \rangle} \cdot \ln \left[\frac{\sinh \left\{ \frac{[(N-N_0)\langle \epsilon \rangle + 3]}{m} \right\}}{\frac{[(N-N_0)\langle \epsilon \rangle + 3]}{m}} \right] \\
 &\quad \frac{2\langle \epsilon \rangle + 3}{\frac{m}{\sinh \left[\frac{2\langle \epsilon \rangle + 3}{m} \right]}} \quad (11)
 \end{aligned}$$

and

$$N_0 = \frac{\frac{N}{m}}{B \left\{ \frac{[(N-N_0)\langle \epsilon \rangle + 3]}{m} \right\}} \quad (12)$$

where $m=L/a=a/b$ is the maximum number of pores a single spring can occupy, such that $N_0=N/m$ for a completely stretched chain.

When bead i leaves the self-trapping conformation, the total force pulling on the growing arm is $i \times \epsilon$. Because half of the chain is involved in the growth of this arm, the total frictional force opposing this motion is $(N/2)\xi$, where ξ is the friction coefficient due to one bead. The time between the fall of the beads i and $i+1$ from the self-trapping conformation is thus, with our assumptions :

$$\tau(i) \approx \frac{\Delta R(i)}{2i\epsilon} N\xi \quad (13)$$

By definition, it is when the bead number $(N-N_0)/2$ leaves the self-trapping conformation that the arm has its maximum extension (overstretching); this occurs at a time

$$\begin{aligned}
 T_M &= \sum_{i=1}^{(N-N_0)/2} \tau(i) \approx \int_1^{(N-N_0)/2} \tau(i) di \\
 &= \frac{N\xi}{2\epsilon} \int_1^{(N-N_0)/2} \left[\frac{\Delta R(i)}{i} \right] di \\
 &= \tau_m \times \left(\frac{Nm}{2\langle \epsilon \rangle} \right) \int_1^{(N-N_0)/2} \left\{ \frac{B \left[\frac{2\langle \epsilon \rangle + 3}{m} \right]}{i} \right\} di \quad (14)
 \end{aligned}$$

where $\tau_m = \xi a^2 / 2(kT)$ is the natural unit of time. For large fields we can use the approximations $N_0 = N/m$ and $\Delta R(i) = L$ to obtain from equation (14),

the asymptotic behavior of T_M :

$$\begin{aligned}
 T_M &\approx \tau_m \times \left[\frac{Nm}{2\langle \epsilon \rangle} \right] \ln \left[\frac{2}{1} \left(1 - \frac{1}{m} \right) N \right] \\
 &\text{for } \langle \epsilon \rangle \gg 1 \quad (15)
 \end{aligned}$$

3. Results and Discussion

The arm length L_{\max} is plotted as a function of the scaled electric field χ in Figure 3. Both the asymptotic limit (N large) and the small stretching regime (N small) are clearly present, with the asymptotic limit being reached for smaller molecular sizes at higher electric fields. At high electric field, maximum arm lengths are independent on electric field. The scaled overstretched time is plotted as a function of the molecular size N in Figure 4. The overstretched time as a function of the electric field is inversely proportional to the molecular size. Higher electric field makes the overstretch time short and are independent of high molecular size. When the electric field is weak, overstretching time is negligible. The overstretched time in a larger polyelectrolyte becomes larger and this makes transport rate of polyelectrolyte slower.

Figure 5 shows how the total contour length of polyelectrolyte chain's stretch after an electric field is applied. Main result indicates that the initial orientation goes through the maximum point because both chain ends first move in the field direction independently from each other, which leads to a self-trapping conformation, in agreement with the experimental observations mentioned previously [19]. Figure 6 shows a series of conformations obtained from the computer simulations. The initial conformation is a random walk as shown in Figure 6 (a). When electric field goes to zero, $\langle \cos\theta \rangle$ decreases gradually toward zero. Polyelectrolyte in the membrane has the field-free Brownian motion modeled by a random force. Brownian motion would simply destroy any orientation driven by the electric field and the leading segment is biased toward the electric field direction. The two arms of

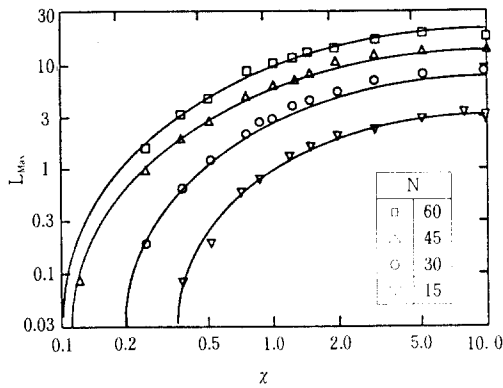


Fig. 3. Log-log plot of the scaled arm length as a functions of molecular size(N) and the electric field.

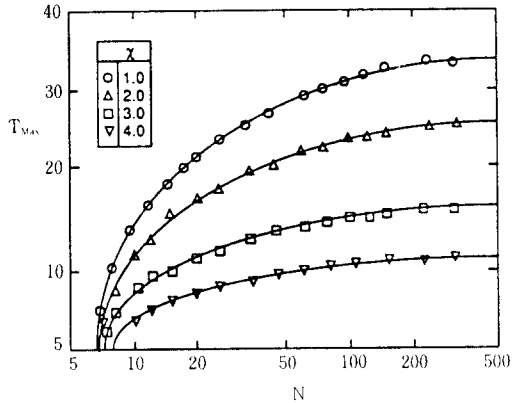


Fig. 4. Log-log plot of the scaled overstretching time vs. molecular size for $m=4$ and four different values of the scaled field χ .

the polyelectrolyte are growing in (b) of Figure 6, but the initial random walk is still present. At $t\tau = T_m$, the two arms reach their maximum extension in Figure 6(d). The two ends of a chain both advance in the same direction while the middle is hung up on polymeric pores. The polyelectrolyte chain assumes compact conformation as seen in Figure 6(d) where the electric forces acting on the polyelectrolyte cancel. In this case, the main velocity overshoot is thus due to the simultaneous effect of internal relaxation and final chain engagement. The springs near the head of the arm are quickly stretched by the electric pull of the stretched arm and the molecular chains

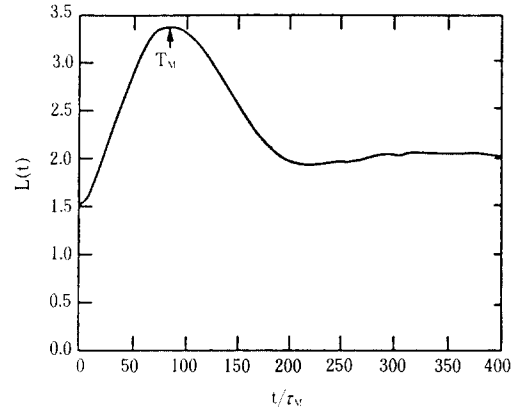


Fig. 5. Conformation results about the contour length of the polyelectrolyte as a function of the dimensionless time at $N=30$, with $m=4.0$ and $\chi=2.0$.

do not migrate in response to the applied electric field, but only diffuse by slow Brownian motion. This self-trapping effect is responsible for the anomalous membrane transport of polyelectrolyte. This self-trapping results in the chain unravelling in the direction of the field, forming a U-shape conformation about the entanglement. For $t > T_m$, the longer arm is growing at the expense of the smaller one (e) of Figure 6. The chain eventually disengages completely from its initial random-walk tube, having passed by the state of maximum velocity, but it is still very stretched in (f) of Figure 6. The extent of orientation of the polyelectrolyte is related to electric field. Large polyelectrolyte is strongly field dependent. This observation supports the evidence that electric field forces the polyelectrolyte into a stretched conformation which can move more rapidly through the polymeric membrane. Electric field enhances the permeation of large polyelectrolyte through the membrane. The membrane transport in the presence of electric field can be greatly changed by molecular sizes. The conformational analysis of polyelectrolytes driven by electric field has been generated by computer simulation. As the chain elongates, the tension builds in the chain which results in the long end of the chain growing at the expense of the short end. The longer

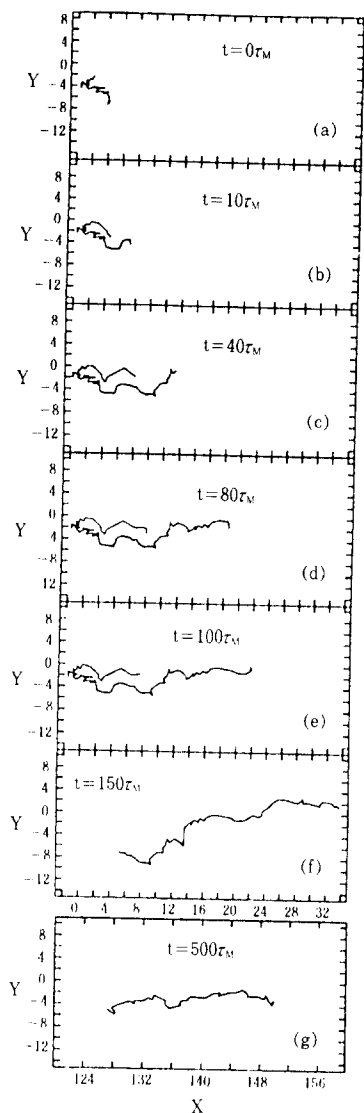


Fig. 6. Stretching conformations of polyelectrolyte as a function of the dimensionless time at $N = 30$, with $m = 4.0$ and $\chi = 2.0$.

- (a) initial random-walk conformation.
- (b), (c) growths of two-arm out of random-walk conformation.
- (d) self-trapping conformation having maximum length at $t = T_M$.
- (e) growing of longer arm.
- (f) the chain is almost stretched to electric field.
- (g) the internal stress has relaxed and the steady-state is reached.

arm then grows so quickly that it more than compensates for the backward motion of the shorter arm in Figure 6(g). As the chain unravels the leading chain segments begin to slide round the entanglements again and a shorter arm is replaced by very stretched spring that feed the growth of the longer arm. Therefore, the front head of the arm is found to be more densely packed.

The qualitative predictions of the analytical model regard the shift of the self-trapping effect to higher molecular weights as a result of field-dependent conformational changes. And no overshoot are found for the small size molecules when the electric field is first applied. And for large molecular size and higher electric field, the globular shape deforms. Higher fields may eliminate the effects of self-trapping. Figure 5 shows how the contour length reaches a maximum before they assume their steady-state values.

The maximum arm length of the large polyelectrolyte is quickly stretched in the field direction. The overstretching phenomenon has a number of other effects on the polyelectrolyte. The large polyelectrolyte is stretched in the field direction, leading to a movement that depends only on the electric field. The molecular stretching increases with molecular size as shown in Figure 3. The diffusion constant of polyelectrolyte in membrane transport is much larger in the presence of the electric field, a phenomenon due to the alignment of the polyelectrolyte in the field direction. With stronger field the self-trapping effects are formed faster. The time to reach the peak increases as the electric field decreases. Electrophoretic filtration of polyelectrolyte in the membrane becomes more efficient in higher electric field. But the extremely large polyelectrolytes orient in the field direction without being affected by the thermal fluctuation. In this case, the self-trapping occur irrespective of electric field. This effect implies that bands tend to broaden more in high fields, it is impossible to separate large molecules even in large fields. This result for electrofiltration in the membrane affects design

of polyelectrolyte-to-pore ratio.

The velocity and broadening rate of polyelectrolyte have been understood. When the polyelectrolytes are in the self-trapping conformation, the two arms of the self-trapping shape are not exactly of the same length. The fact that both arms of the chain move in the field direction during the arm growth phase explains why the velocity of the chain reaches a small maximum for $t < T_M$ as seen in Figure 5. The combined effect of internal redistribution of stress and final bead-spring disengagement leads to an overshoot in the velocity for $t < T_M$. Since it has been suggested that T_M might be related to the overshoot time, it is very important to understand the electrophoretic transport of polyelectrolyte in the polymeric membrane. Our analytical results are different from a computer simulation of a Rouse chain trapped inside a tube and the available quantitative experimental results. We predicted that T_M is proportional to $M \log(M)$ in the high molecular size limit, while available experimental result of Holzwarth et al. [19] seems to indicate that T_M is proportional to M . Longer overstretching time of large polyelectrolyte makes the movement of polyelectrolyte slower in the membrane. In a similar study, Norden et al. [20] found approximately that T_M is proportional to $E^{-(1.1-1.23)}$, while Holzwarth et al.[19] also obtained that T_M is proportional to $E^{-(1.1-1.15)}$. The results are in fair agreement with our asymptotic regime where both our analytical and numerical results give that T_M is proportional to $ME^{-1} \log(M)$.

6. Conclusion

The separation of large polyelectrolytes in the membrane is related to their conformations driven by electric field. Fast movement can be enhanced by increase of electric field, but the movement in much larger polyelectrolyte is almost found to be independent on electric field. This result is closely related to self-trapping conformation of polyelec-

trolyte. The theoretical result gives that the overshoot time is proportional to the $M \log(M)$. The overshoot time by molecular size aids to understand the electrophoretic filtration of large polyelectrolyte in the membrane. Therefore, the findings of this paper are useful in guiding the design of electrophoretic membrane process in the presence of electric field.

Nomenclatures

a	Pore size
b	Kuhn Length
B	Langevin function in equation(7)
E	Electric strength
k	Boltzmann constant
L	Maximum length of bead-spring
L_{Max}	Overshoot length
L_i	Contour length
m	a/b of equation(12)
N	Number of bead-spring
N_0	Number of beads trapped
p	Probability in equation(9)
r	Position vector
q	Electric charge
Q	Total electric charge
R	Interbead vector
t	time
T	Absolute temperature
T	Tensor in equation(3)
T_M	Overshoot time

Greek Letters

Φ	Potential energy
χ	Scaled intensity in equation(5)
θ	Angle defined in equation(2)
ϵ	Total electric force
τ	Dimensionless time defined in equation(14)
τ_m	Natural time unit defined in equation (15)
Ψ	configuration distribution function
ξ	Friction coefficient
Ω	Normalizing factor

Superscripts

- M Maximum
X x-direction

References

1. W. C. McGregor, Membrane Separations in Biotechnology, Marcel Dekker, Inc New York (1986).
2. L. E. Bromberg, *Journal of Membrane Science*, **62**, 145(1991).
3. J. M. Anderson and S. W. Kim, Advances in Drug Delivery System, E, Elsevier, Amsterdam (1988).
4. P. E. Grimshaw and A. J. Grodzinsky, *Chemical Engineering Science*, **45**, 2917 (1990).
5. W. C. Olson, C. K. Colton, and M. L. Yarmush, *Journal of Membrane Science*, **56**, 247(1991).
6. C. B. Holzwarth, C. B. McKee, and G. Carter, *Nucleic Acids Res.*, **15**, 10031(1987).
7. J. Sturm and G. Weill, *Phys. Rev. Lett.*, **62**, 1484 (1989).
8. M. Jonsson, B. Akerman, and B. Norden, *Biopolymers*, **27**, 381(1988).
9. P. G. de Gennes, *Journal of Chemical Physics*, **55**, 572(1971).
10. R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, Dynamics of Polymeric Liquid, John Wiley & Sons, New York(1977).
11. M. Doi and S. F. Edwards, The Theory of Polymer Dynamics, Clarendon, Oxford(1986).
12. B. Zimm, *Phys. Rev. Lett.*, **61**, 2965(1988.).
13. R. I. Tanner, Engineering Rheology, Oxford University, Oxford(1985).
14. M. Doi and S. F. Edwards, *J. C. S. Faraday II*, **74**, 1802(1978).
15. B. Akerman, M. Jonsson, B. Norden, and M. Lalande, *Biopolymer*, **28**, 1541(1989).
16. O. J. lumpkin, P. Dejardin, and B. Zimm, *Biopolymer*, **24**, 1573(1985).
17. M. Doi and S. F. Edwards, *J. C. S. Faraday II*, **74**, 1789(1978).
18. J. L. Viovy, *Phys. Rev. Lett.*, **62**, 855(1988).
19. G. Holzwarth, K. J. Platt, C. B. McKee, R. W. Whitcomb, and G. D. Crater, *Biopolymer*, **28**, 1043(1989).
20. B. Akerman, M. Jonsson, B. Norden, and M. Lalande, *Biopolymer*, **28**, 1541(1989).