Orientation Behavior of Polyelectrolyte in Solution under an External Electric Field. A Coarse Grain Molecular Dynamics Simulation Study

Kazuyoshi Ueda,* Nobu Iizumi, and Masaru Sakomura

Department of Material Science, Faculty of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

Received September 3, 2004; E-mail: k-ueda@ynu.ac.jp

A coarse grain molecular dynamics simulation method was applied to polystyrenesulfonate in aqueous solution to investigate the conformational and orientational behavior of flexible polyion under an external electric field. When the electric field was applied, the deviation of the counter-ion distribution and the rotational orientation of the polyion toward the direction of the electric field were observed. The orientation behavior of flexible polyelectrolytes depended on the field strength, and two typical orientational motions were detected. That is, at low electric field strength, elongation of the whole polyion chain conformation occurs at first stage and subsequently rotationally orients toward the field direction. On the other hand, segment orientation occurs at the high field because of the fast displacement of the counter ions on each polymer segment. The ionic polarization of the flexible polyion was evaluated by the component analysis of the counter-ion deviation. Results showed that the loosely-bound counter ions contribute largely to the ionic polarization.

Polyelectrolytes exhibit many complicated behaviors due to the interaction between dissociated polyions and counterions and the conformational changes of the macro-ions.[1–5] When the external electric field was applied to the polyion solution, it is well known that the polyions were oriented toward the electric field direction and the phenomena of the electric dichroism[6] and the electric birefringence[7–9] were observed. The origin of the orientation mechanism of the polyion is considered to be the induced dipole moment derived from the displacement of the counterion around the polyion by the external electric field. However, the details of this mechanism are still not known. In order to clarify the orientation mechanism more precisely, researches have often used rigid rod-like polyions both experimentally[9–11] and theoretically[12–14] to avoid the complexity that arises from the conformational flexibility of the polyions. One typical theoretical study was done by Yoshida et al.,[13] who performed the Monte Carlo simulation of the counter-ion distribution under an external electric field and evaluated the induced dipole moment by using a model of rod-like polyions.

However, polyions are usually long and flexible molecules. The effect of the flexibility should influence the orientation behavior and the signals of electric dichroism and birefringence. Actually, Kramer and Hoffmann[15] observed the anomalous birefringence signals which changed the sign of signals depending on the concentration of large flexible polystyrenesulfonate molecules. Our previous work also observed the electric birefringence signals of polystyrenesulfonate with large molecular weights, whose transient rise and decay signals largely depended on the electric field strengths.[7]

To investigate the above polyelectrolyte properties effectively, one should include both the flexibility and the counter-ion interaction in the analysis. For this purpose, molecular dynamics simulation would be one of the promising methods. However, the conventional atomic scale molecular dynamics simulation method is still difficult to apply, because one needs a tremendous number of atoms and prolonged calculation time to simulate such a system.[16] Stevens et al. performed a series of coarse-grain molecular dynamics simulations on the linear flexible polyion that successfully revealed the chain conformation in single and multi-chain systems.[17–19] Netz applied the coarse-grain molecular dynamics simulation method to the polyelectrolyte solution in the electric field, and discussed the scaling properties of the polyelectrolytes.[20]

In our work, we tried to apply the coarse-grain molecular dynamics simulation method to investigate the transient behavior of the orientation and polarization of polyelectrolyte under an external electric field. This will be a basis to understand the signals of the electric dichroism and birefringence observed in flexible polyions. The different orientation behavior patterns of flexible polyelectrolytes depended on the field strength. Although the conformational flexibility makes it difficult to quantitatively analyze the properties of the polyelectrolytes, component analysis along the principal axes of the counter-ion deviation could evaluate the ionic polarization.

Model and the Simulation Method

In this study, sodium polystyrenesulfonate (NaPSS) in aqueous solution was used as the model polyion when investigating the solution behavior under an external electric field. In order to mimic the polyion, the freely joined bead-chain polymer model, which was precisely described by Stevens and Kremer,[17] was used in this simulation. The procedure of the simulation and the parameters for the NaPSS used in this work were all the same to those described by Stevens and Kremer.[17,21] In this model, a repeating unit of styrenesulfonate was represented as a sphere with a negative charge and the units were joined with bonds having length b. This length is equal to charge separation in this model. The FENE[21] potential was used as an attractive part and a purely repulsive Lennard-

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Jones potential was used as a repulsive part of the bond energy between the monomer units as follows:

$$U_{\mathrm{bond}} = U_{\mathrm{LJ}} + U_{\mathrm{FENE}} \tag{1}$$

$$U_{\mathrm{FENE}} = -\left(\frac{1}{2}\right) k R_0{}^2 \ln\left(1 - \frac{r^2}{R_0{}^2}\right) \tag{2}$$

$$U_{\mathrm{LJ}} = \begin{cases} 4\varepsilon_{\mathrm{LJ}}\left[\left(\dfrac{\sigma_{\mathrm{LJ}}}{r}\right)^{12} - \left(\dfrac{\sigma_{\mathrm{LJ}}}{r}\right)^{6} + \dfrac{1}{4}\right] & r \le r_{\mathrm{c}} \\ 0 & r > r_{\mathrm{c}} \end{cases} \tag{3}$$

with $r_{\mathrm{c}} = 2^{1/6}\sigma$.

The notations and the parameters that appear in the above equations are the same as those of Stevens et al.[17,21] Sodium ions were used as counter ions and the standard Lennard-Jones parameters were used. A polyion consisting of 200 monomer units and an equal number of positively charged counter ions were immersed in a cubic box having a length of 400 Å. The polyion concentration of the system is 5.2×10^{-3} M (1 M = 1 mol dm^{-3}). The time step of the simulation was set at 20 fs and the total length of the simulation time was 12 ns. The temperature of the system was kept at 300 K. The solvent molecules were not included explicitly and were treated as a continuous dielectric background with $\varepsilon = 80$. Instead, the effect of the solvent was included by the Langevin equation with dissipative and frictional forces.[22] The periodical condition was employed for the simulation box, and the electrostatic force was cut off at the half of the simulation box.

In the simulation with an external electric field, we modified the above procedures by adding the electric force term. That is, each particle was subjected to an electric force

$$F_{\mathrm{elec}} = -qeE_{\mathrm{elec}}, \tag{4}$$

where q is the charge of the particle, e is the elementary charge, and E_{elec} is the strength of the applied external electric field. Three different strengths of electric fields: 62 kV/cm, 125 kV/cm, and 250 kV/cm were employed in this study. The initial structure of the polyelectrolyte conformation and the distribution of the counter ions around the polyion were generated using random numbers. The obtained initial structure of the polyion with 200 monomer units is shown in Fig. 1(a).

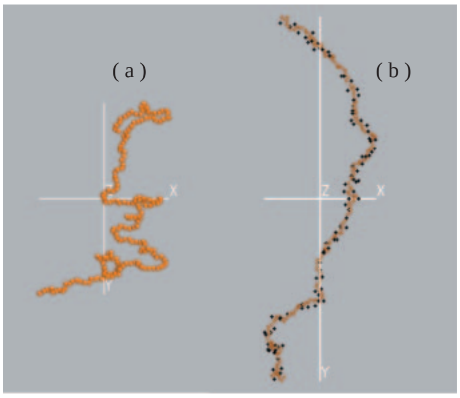

Fig. 1. Snapshots of NaPSS at initial (a) and at 12 ns (b) calculated for $E = 0$. Only the counter ions within 4.5 Å from the polyion are shown in (b).

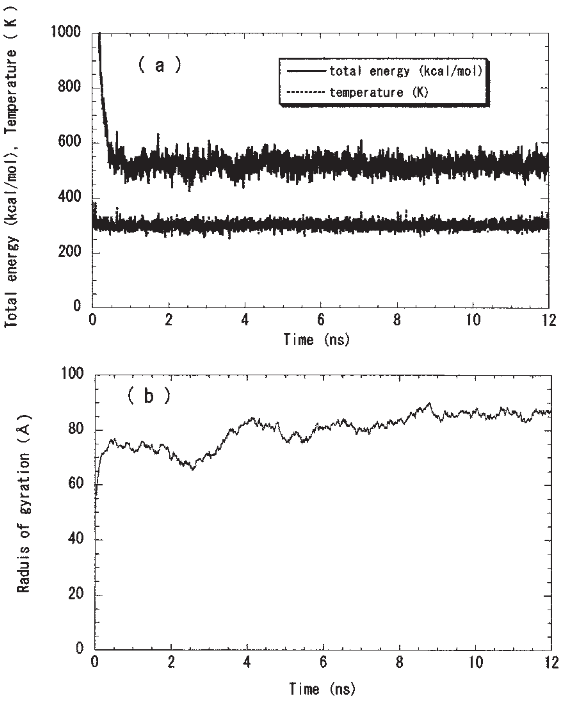

Fig. 2. Time courses of the total energy and the temperature (a), and the radius of gyration (b) of the NaPSS without an external electric field.

Results and Discussion

Equilibrium Conformation and Counter-Ion Distribution around Polyion with No Electric Field. Time courses of the total energy and the temperature were monitored to check the achievement of the equilibrium state, the results are shown in Fig. 2(a). The total energy converged to the steady value after 1ns simulation run. The temperature of the system also kept at 300 K. The conformational change during the simulation was monitored with the radius of gyration, and the result is shown in Fig. 2(b). The figure shows that the conformation expanded from the initial structure at the beginning stage, and then approached to the steady state value after 4 ns. From these results, it can be considered that the system attained the equilibrium state after 4 ns.

A snapshot comparing the initial conformation with the polyion conformation at the end of the simulation with no electric field is shown in Fig. 1(b). The polyion assumed an elongated worm-like conformation at the end of the simulation. In this figure, it was also observed that several counter ions condensed in the vicinity of the polyion moiety. This phenomenon is widely known in the experiments as "counter-ion condensation".[23] Manning predicted that some of the counter ions are strongly attracted in the vicinity of the polyion domain by the Coulomb interaction and called them "condensed counter ions".[24] The remaining counter ions are weakly bound or existed freely in the region outside the condensed region. Manning showed that the counter-ion condensation occurs when the charge density parameter ξ is larger than unity. In his theory, the ratio of the condensed counter ions ϕ in the system without any added salt is expressed by the following equation.[24]

$$\xi = \frac{e^2}{\varepsilon k_b T b}, \quad \phi = 1 - \frac{1}{\xi}. \tag{5}$$

From these equations, ϕ calculated for NaPSS in aqueous solution is 0.64. Manning's theory was examined by calculating the ratio of the condensed counter ions around the flexible polyion in our simulation. To obtain the ratio of the condensed counter ions, the number of counter ions within the radius r from the polyion, N_r, was calculated at each time step of the simulation. The time-averaged value of N_r was normalized by the total number of counter ions N_{tot}; then, the ratios of N_r/N_{tot} were plotted versus the distance r in Fig. 3(a). It shows that the counter ions rapidly increased at the vicinity of the polyion up to a distance of approximately 4–8 Å. However, the rate of increment suddenly decreased above that distance. Although the value of N_r/N_{tot} changed continuously, it was considered that the region in which the counter ions exist was roughly divided into two areas as the Manning theory predicted. Since the ratio of the condensed counter ion from Manning's theory is 0.64, Fig. 3(a) indicates that the theoretically predicted threshold distance between the condensed and other regions should exist at $r = 7.5$ Å. We can see that this value reasonably falls in the inflection region of our plot shown in Fig. 3(a).

Counter-Ion Distribution around Polyion under the External Electric Field. Next we applied the external electric field to this system along the uniaxial direction of the solution (this direction was defined as the x-axis in this study). That is, three different electric field strengths were applied to the same polyion conformation of Fig. 1(b), which was a equilibrated structure without any electric field. The ratios of the condensed counter ions around the polyion under the external electric field were investigated and the results are shown in Fig. 3(b). At a field strength of 62 kV/cm, the number of the counter ions within the radius r from the polyion was the same as that in the case without any electric field. On the other hand, the number of the counter ions within the same radius r decreased at higher electric fields of 125 kV/cm and 250 kV/cm. Compared to the case without any electric field, the rate of the condensed counter ion decreased by 8% in average at each distance r at 125 kV/cm, and decreased by 20% on average at 250 kV/cm. This indicates that a part of the condensed counter ions stripped out from the vicinity of the polyion as the electric field strength increased.

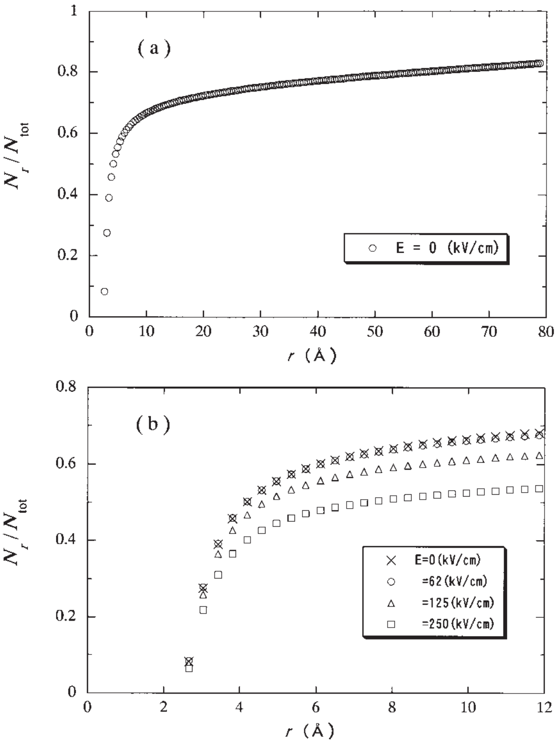

Fig. 3. The ratios, N_r/N_{tot}, are plotted against the distance r from the polyion. The results for $E = 0$ are shown for wide range of distance r in (a). The results with applied electric fields are shown in (b) in comparison with the data for $E = 0$.

To investigate the effect of the external electric field more precisely, we examined the distribution of the counter ions along the electric field. In this analysis, the polymer chain was divided into three equal length domains along the direction of the electric field. These regions are denoted as [+], middle, and [−] regions from the high electric potential side. The ratio of the counter ions, N_r/N_{tot}, was obtained for each domain, and the results are shown in Fig. 4. As the number of monomer units in each domain depended on the conformation of the polyion at each time step, N_{tot} was taken as the number of monomer units included in each domain in this analysis. Figure 4(a) shows that the ratio of the counter ions around the polyion is different along the direction of the field even at the lowest strength of 62 kV/cm. At this field strength, the ratio of the condensed counter ions for the whole polyion did not change, as indicated in Fig. 3(b). These results indicate that the counter ions are strongly bound around the vicinity of the polyion; however, they can easily move toward the direction of the electric field along the polyion chain.

The deviation of the counter-ion distribution along the direction of the field increased as the external electric field increased, as shown in Fig. 4. Additionally, the total number of counter ions also decreased with an increment of the field strength for high field, as shown in Fig. 3(b). These results may indicate that the counter ions that migrated toward [−] region due to the high electric field could not remain in that region because it was already saturated with the condensed ions. Therefore, some of the migrated counter ions stripped out from the moiety of the polyion at such a high field.

Evaluation of the Ionic Polarization of Flexible Polyion. The deviation of the counter-ion distribution along the polyion chain causes the ionic polarization. In the calculation of Yoshida et al.,[13] the model polyelectrolyte was assumed to be a rod-like molecule with its molecular axis is in accordance with the direction of the electric field. Thus, the displacement of the counter ions can be assumed to be directly proportional to the induced dipole moment. However, in our simulation, the polyion chain is flexible and the conformation may deform in the field orientation process. Therefore, the principal axes of the bulk conformation were first calculated at each time step. Then, the time-averaged displacements of the counter ions for each principal axis from the center of gravity were calculated as the induced dipole moments along the longitudinal (m_{long}) and transverse (m_{tr1}, m_{tr2}) directions, respectively. Finally, the anisotropy of the induced dipole moment was

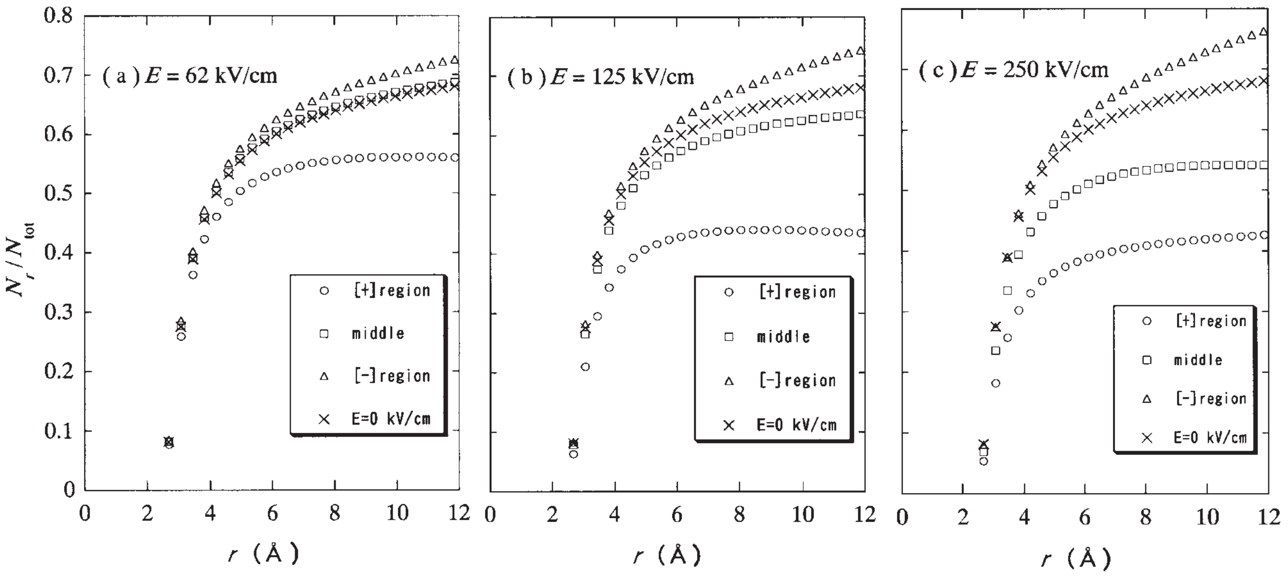

Fig. 4. The ratios, N_r/N_{tot}, calculated at [+] (○), middle (□), and [−] (△) regions. The electric field strengths were 62 kV/cm (a), 125 kV/cm (b), and 250 kV/cm (c), respectively.

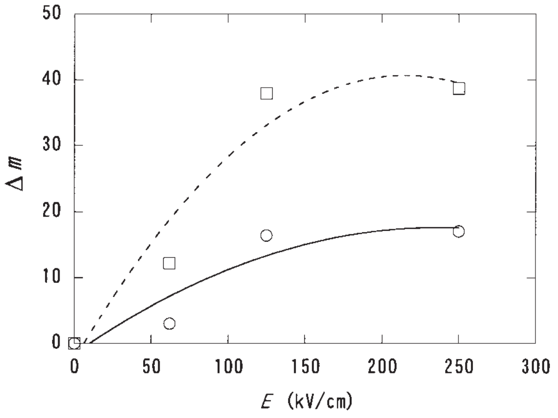

Fig. 5. Plots of Δm versus E. The values of Δm were calculated for the counter ions within $r = 7.5$ Å (○) and above 7.5 Å (□), respectively.

calculated using the following equation:[14]

$$\Delta m = m_{\text{long}} - (m_{\text{tr1}} + m_{\text{tr2}})/2. \tag{6}$$

As the counter ions around the polyion were divided into two regions at a threshold distance of 7.5 Å, the values of Δm were calculated for these two regions separately. The values of Δm were averaged for the trajectory from 6 ns to 9 ns. The results are plotted versus the external electric field strength in Fig. 5. It can be seen that the induced dipole moments increased with the increment in the external electric field in both cases. At high field strength, the tendency to saturate was also observed. It is important to note that the dipole moment produced from the loosely-bound counter ions was larger than that of the condensed counter ions. This result is similar to that obtained by Yoshida et al.[13] for the rod-like polyions irrespective of the difference of the polyion conformation, one is rods and the other is flexible chains, from the qualitative point of view. The quantitative analysis of the induced dipole moment of the flexible polyion, such as the dependence of the molecular length, will be investigated in the next study.

Transient Behavior of the Electric Field Orientation of Polyion. Polyelectrolytes orient toward the direction of the external electric field by the interaction between the electric field and the induced dipole moment. In order to observe the orientation behavior of the flexible polyion, we took snapshots of the conformation at different time steps during the orientation process after the application of electric field; these are shown in Fig. 6. The simulation profiles shown in Figs. 6(a) and (b) were both started from the same polyion conformation, which was the snapshot at the end of the simulation with no electric field. At the field strength of 125 kV/cm, the polyion first elongated to resemble a linear conformation within 6 ns, and then it rotated and oriented its long axis toward the direction of the field. At the end of the simulation (12 ns), the distribution of the tightly bound counter ions can be observed to deviate toward the high electric potential direction (left side in the figure).

For the electric field strength of 250 kV/cm, however, the segment orientation of the polyion appeared in the early stage. This is because of the rapid movement of the counter ions under the high electric field. In each segment, we observe a deviation of the counter ion distribution toward the high electric potential region. Following the segment orientation, the orientation of whole molecular chain was observed to be toward the direction of the electric field due to the "reptation" motion.[25] The cases shown in Fig. 6 may represent the typical orientation processes of the flexible chain molecule that depend on the strength of the electric field.

Conclusion

The behavior of the flexible polyelectrolyte in the external electric field is generally complicated. This is because of the combined effects of the changes of counter-ion distribution and of the conformation of the polyion. In this work, the coarse grain molecular dynamics simulation method was applied to sodium polystyrenesulfonate in aqueous solution and the be-

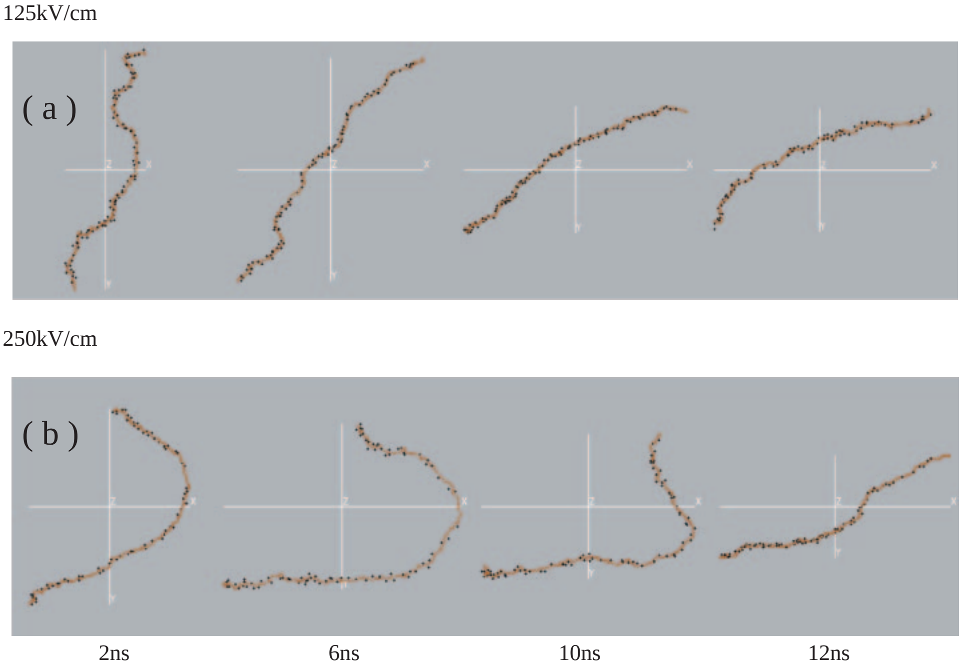

Fig. 6. Snapshots of the orientation behavior of polyion under the external electric field of 125 kV/cm (a) and 250 kV/cm (b). Initial structure ($t = 0$) for both cases (a) and (b) are the same as was shown in Fig. 1(b). The counter ions existing within a range of 4.2 Å from the polyion are shown by dots.

havior of the flexible polyions under the external electric field was analyzed. One of the interesting features found in this work is the orientation behavior of the flexible polymer under the electric field. That is, at low electric field strength, elongation of the polyion conformation occurred at first, and then, the polyion rotationally oriented toward the electric field direction. On the other hand, segment orientations occurred at the high field because of the fast displacement of the counter ions on each polymer segment.

The other point was the ionic polarization which was induced by the displacement of the counter ions toward the direction of the electric field. Although the displacement of the counter ion depends on both the conformational deformation and the strength of the electric field, the component analysis of the counter-ion deviation showed that the loosely-bound counter ions contribute largely to the ionic polarization. The orientation and polarization found in this work would be represented in the transient signals of electric birefringence and dichroism. The simulation of such signals will be studied in our future work.

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