

Phase Separation of Polymer Blends Induced by an External Static Electric Field

Qian Zhang and Xue-Hao He*

Department of Chemistry, School of Science, Tianjin University, Tianjin 300350, China

 Electronic Supplementary Information

Abstract The mechanism of the phase separation of polymer blends in the presence of a static electric field was investigated using the molecular dynamics with a modified coarse-grained polarizable model. Two electric field effects, *i.e.*, the promotion and hindrance of the phase separation, were found in the system of the upper critical solution temperature (UCST) by varying the dielectric properties of polymer components. Our simulation directly demonstrated that the electric field effects originate from the energy changes of intramolecular unit polarization, intermolecular van der Waals (VDW) and Coulomb interactions induced by the external electric field. The relationship of the energy change and the dielectric constant for the system under electric field is obtained. The interface orientation under electric field was found to happen even before the transition point of phase separation. By assuming that the relative order parameter of the phase separation undergoes the same fluctuations for a system with and without an electric field, the transition temperature under an electric field can be predicted, and quantitative consistency with simulations is obtained.

Keywords Phase separation; Electric field effects; Coarse-grained polarizable model; Order parameters

Citation: Zhang, Q.; He, X. H. Phase separation of polymer blends induced by an external static electric field. *Chinese J. Polym. Sci.* 2023, 41, 972–980.

INTRODUCTION

A polymer is a typical soft matter system and sensitive to stimulation by an imposed external field. An electric field modulates the phase transition and orientation of polymer mixtures.^[1,2] Responses to electric field have promising applications in the fabrication of organic capacitors, ultrahigh-density magnetic storage media and multiscale pattern templates.^[3–5] Understanding the mechanism by which an electric field affects a macromolecular system is crucial for exploiting its tailored regulation and extending its potential applications to nanoscale and smart materials.

Five decades ago, an electric field was discovered to change the phase separation temperature in small-molecule mixture systems such as nitrobenzene/2-2-4-trimethylpentane and cyclohexane/aniline.^[6–9] Such phenomena were also found in polymer solution systems, such as polystyrene/cyclohexane and polystyrene/ethylcarbitol.^[7] Similar results were further found in polymer blend systems, including polystyrene/poly(vinyl methyl ether), poly(vinylidene fluoride)/poly(1,4-butylene adipate) and poly(vinylidene fluoride)/poly(methyl methacrylate), as well as those including block copolymers such as polystyrene-

block-polyisoprene.^[10–14] These experiments showed that an external electric field could promote or inhibit phase separation regardless of the upper critical solution temperature (UCST) or lower critical solution temperature (LCST) behavior of these systems, with transition temperatures ranging from 0.015 K to 54 K.^[6–15] The underlying mechanism has attracted much attention. Debye *et al.* noted that the change in the phase separation temperature should depend on the square of the electric field and the second-order coefficient of the dielectric constant $\epsilon''(\partial^2\epsilon/\partial\phi^2)$.^[6,7,16–19] The work of Tsori *et al.* further focused on the effects of a non-uniform electric field on phase separation from experimental and theoretical perspectives.^[20] Due to the experimental difficulty in obtaining information on molecular polarization under an external electric field, there is a long-standing controversy regarding polymer phase separation induced by an electric field. Some experiments even gave conflicting results.^[10,11,21] How an electric field affects the phase transition of polymers is still puzzling, although various possible reasons for the discrepancies have been proposed, such as the electric field direction, experimental error in the heat conduction, the electrostriction effect, molecular specifications, the anisotropy of the material and influence of the first-order term of the dielectric constant.^[8,9,15,19,22,23]

In theoretical aspects, most studies employed the polymer self-consistent field theory to study the orientation and transition of the phase structure of block copolymer melts under

* Corresponding author, E-mail: xhhe@tju.edu.cn

Received August 13, 2022; Accepted September 22, 2022; Published online November 18, 2022

the electric field using the serious approximation to the mixed permittivity of the system.^[24–28] The molecular polarization and the corresponding change of the disorder-to-order phase transition under external electric field cannot be explored. Compared with experimental and theoretical methods, molecular simulation can provide detailed information of the thermodynamic and kinetics of molecules in physical and chemical processes. In polymer field, coarse-grained molecular dynamics (CGMD) is a powerful tool for exploring larger-scale phase separation in time and space. In the past, the conventional CG polymer model was mainly used to study the phase behaviors of the polymer melts in the absence of an external electric field. In order to study the electric effects, the polarizable CG polymer model based on the shell particle was proposed.^[29] In this work, we further develop a modified polarizable model based on the real particle Drude oscillator in CGMD to simulate the phase separation of polymer blends under an external electric field. Specifically, the present CG polarizable model can better describe the static and dynamic dielectric properties of polymers than the previous models.^[29] Using this model, we successfully reproduced the two electric field effects. The mechanism of phase separation induced by the external electric field is explored.

In the following section, the coarse-grained polarizable model used in this work is described in detail. The calculation method of the permittivity and Flory-Huggins parameters, the definition of the order parameter and the calculation method of the two-dimensional structure factor are introduced. In Section 3, two electric field effects (promotion and inhibition of phase separation) are found by varying the dielectric properties of the polymer blends. The mechanism of the phase separation of polymer blends in the presence of the electric field is analysed. The simulation is compared with the results of the mean field theory. We further proposed a simple way to predict the transition temperature of polymer blends under an external electric field. A good agreement with simulations is obtained. Finally, the current work and its potential applications are briefly summarized.

MODEL AND METHODS

Our simulations employ a modified coarse-grained polarizable model which is based on our previous work.^[29] In the present model, polymer chains are mapped as a series of connected CG units (see Fig. 1).^[30] One CG unit represents several tens of repeating units in a realistic polymer chain. Every CG polarizable unit consists of two beads with equal positive and negative charges. Different with previous CG polarizable model using shell particle, all beads used here are real and have the same mass. The two beads are connected by a harmonic potential with an equilibrium distance of zero, which acts as a Drude oscillator. CG units are then connected through the positively charged beads using the finitely extensible nonlinear elastic (FENE) potential to form a CG polymer chain. When there is no external electric field, the positive and negative beads can overlap and the model is close to the nonpolarizable CG model. When an external electric field is imposed, two overlapping beads with opposite charges can be separated to form a dipole. The dielectric constant of the polymer depends on the charge and elasticity of the dipole in the CG unit. The present modified

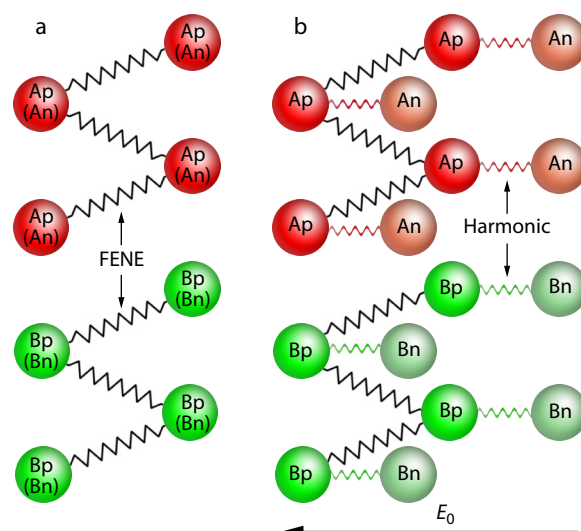


Fig. 1 Model diagram. A-type and B-type beads are represented in red and green, respectively. The black spring line represents the FENE potential, and the red and green spring lines represent the harmonic potential inside the A- and B-type CG polarizable units, respectively. (a) In the absence of an electric field, the positive (Ap or Bp) and negative (An or Bn) parts of the polarized units coincide. (b) The positive and negative parts of the polarized units are separated in the presence of an electric field. Bold black arrow indicates the direction of the electric field.

model is a real particle CG polarizable model (RPPM) and can better describe the static and dynamic dielectric properties for polymers than previous model (S2 in the electronic supplementary information, ESI).^[30]

In the simulation of UCST-type polymer blends, two kinds of homopolymers (A-type and B-type polymers) are used. The reduced unit is used in our simulation. The polymer chains have the same length $N=20$. The spatial size of the system is $20\sigma \times 20\sigma \times 20\sigma$, and the system contains 1.6×10^4 beads, corresponding to 400 polymer chains. The simulation employs the velocity Langevin dynamics. All beads in each CG unit have the same mass $m=0.5$. The time step is $\delta t=0.001$, and the friction constant is set to $\gamma=2.0$. The reduced temperature in the system is T^* . The harmonic potential parameter of the CG polarizable unit is $k_H=500$. The elastic coefficient and bond length in the FENE potential of the polymer chain are set to $k_{FENE}=30$ and $b_{FENE}=1.5$. The Lennard-Jones (LJ) potential is used for the van der Waals (VDW) interaction between CG beads. The standard strength and length of the LJ potential are set to $\kappa_0=1.0$ and $\sigma=1.0$, respectively. Detailed parameters are in S1 in ESI.^[28] Our system includes 10 kinds of VDW interactions. Among them, six parameters (κ_{Ap-Ap} , κ_{An-An} , κ_{Ap-An} , κ_{Bp-Bp} , κ_{Bn-Bn} and κ_{Bp-Bn}) describe the interactions between the similar CG units, and 4 parameters (κ_{Ap-Bp} , κ_{Ap-Bn} , κ_{An-Bp} and κ_{An-Bn}) describe the interactions between the dissimilar CG units. Here, Ap and An represent two beads with positive and negative charges in each CG polarizable unit of an A-type polymer chain. Similarly, Bp and Bn are two beads in each CG polarizable unit of a B-type polymer chain. For simplicity, six parameters are set to the same value, $\kappa_1=0.25$, and four parameters are set to $\kappa_2=0.175$. The simulation proceeds in the NVT ensemble. Replica exchange molecular dynamics (REMD)

is used to obtain the phase separation transition temperature.^[31] In REMD, 24 copies are used, the temperature interval is 0.03~0.04, the exchange frequency is 2000 δt , and the average exchange probability measured is $P=0.2\sim 0.3$.^[30] Simulations were carried out using the molecular dynamics software GROMACS.^[32]

In the present work, the dielectric constant of a system is calculated using the dipole moment fluctuation equation without an external electric field:^[33]

$$\epsilon_r = 1 + \frac{\overline{M^2} - \overline{M}^2}{3\epsilon_0 VT^*} \quad (1)$$

Note that the dielectric constant can also be calculated using the polarization equation under an external electric field:^[34]

$$\epsilon_r = 1 + \frac{\overline{M}}{\epsilon_0 VE_0} \quad (2)$$

where ϵ_r is the relative dielectric constant. M is the total dipole moment and $\overline{M^2} - \overline{M}^2$ represents the fluctuation of M . ϵ_0 is the vacuum dielectric constant. V and T^* represent the volume and temperature respectively. E_0 is the external electric field.^[30] For the present real particle CG polarizable model (RPPM), these two methods for the calculation of dielectric constant are consistent (Fig. 2). The dielectric properties of the model are discussed in S2 in ESI.^[30]

The Flory-Huggins parameters of the polymer blends in our simulation are determined using the method proposed by Groot *et al.*^[35,36] At first, a system with the box size of $80\sigma \times 20\sigma \times 20\sigma$ is constructed. A-type polymer chains are put into the left part of the system and B-type polymer chains are put into the right part. The periodic boundary condition is still used. Then, the simulation proceeds at proper temperature for 5×10^7 time steps till equilibrium. Finally, the concentrations of A-type and B-type beads along X direction of the system is like the profile shown in Fig. 3.

The concentration ϕ_A of A-type beads in the middle region ($X/\sigma \approx 60$) of A phase is measured using statistic average after the system reaches the equilibrium. The Flory-Huggins para-

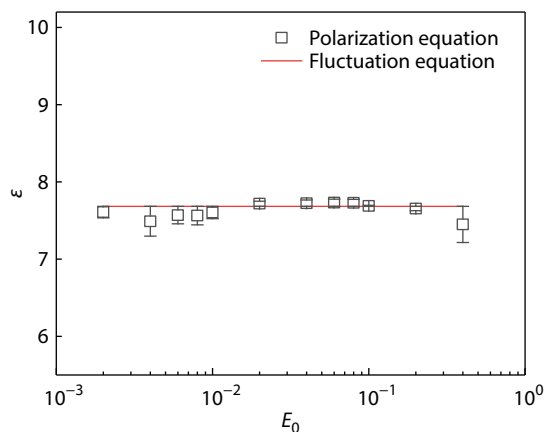


Fig. 2 Comparison of two methods for the calculation of dielectric constant. The red line is the reference value calculated using the dipole moment fluctuation equation without electric field. Black squares indicate the results calculated using the polarization equation with an electric field. This system containing only A-type components ($N=20$), where $q_A=0.94$, $T^*=1.8$.

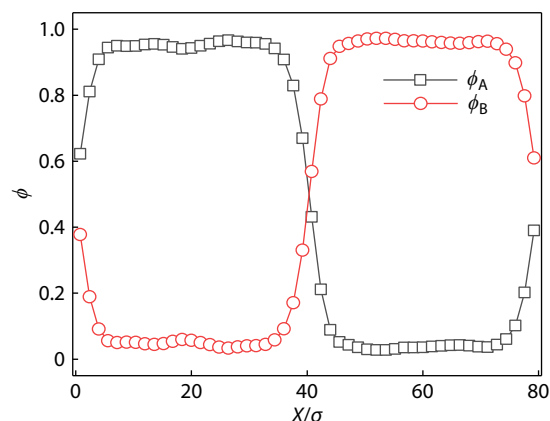


Fig. 3 The concentrations of A-type and B-type beads along X direction. Other parameters are $N=20$, $\kappa_2=0.175$ and $T^*=3.3$.

meter can be obtained:

$$\chi N = \frac{\ln[(1 - \phi_A)/\phi_A]}{1 - 2\phi_A} \quad (3)$$

The dependence of Flory-Huggins parameters on temperature, chain length, interaction strength and charge amount can be found in S3 in ESI.^[30]

Usually, the heat capacity C_V is used to determine the phase transition point of a system under varying temperature. The peak position of C_V curve should be the phase separation temperature. Instead of this method, we apply the order parameter to determine the transition point more exactly due to the largely statistical error of C_V . Using the difference between the local component density and average component density in the system, we define an order parameter:

$$SS = \frac{1}{n} \sum_{i=1}^n \left| \frac{n_A^{\text{local}}(r_i) - n_B^{\text{local}}(r_i)}{n_A^{\text{local}}(r_i) + n_B^{\text{local}}(r_i)} - \frac{|n_A - n_B|}{n_A + n_B} \right| \quad (4)$$

where $n^{\text{local}}(r_i)$ is the number of A-type (or B-type) beads in a spherical space of radius 2.5σ around the i^{th} bead at position r_i . n_A , n_B and n are the numbers of A-type, B-type and total beads in the whole system, respectively. The transition temperature is determined by taking the derivative of the statistical average $\overline{SS}$ with respect to temperature (Fig. 4).

To analyse the phase structure, the two-dimensional static structure factors of the system is calculated:^[37]

$$S(\mathbf{q}) = \frac{1}{n^2} \sum_j \sum_k^n \langle e^{i\mathbf{q}\cdot\mathbf{r}} [\rho_j \rho_k] \rangle \quad (5)$$

where n is the total number of beads in system and $\mathbf{q} = (q_x, q_y, q_z)$ is the scattering wave vector, and $\mathbf{r} = (r_x, r_y, r_z)$ is the position vector. At $\mathbf{r}$, if occupied by A-type particle, the density is denoted here as $\rho_A=1.0$, $\rho_B=0.0$; If occupied by B-type particle, denote $\rho_A=0.0$, $\rho_B=1.0$. According to this method, the particle density difference $\rho_j = \rho_A - \rho_B$ at any position $\mathbf{r}$ can be obtained. ρ is the average density of the system. The final two-dimensional static structure factor is calculated statistically using all frames. Meanwhile 8 samples for each frame with rotation around the Z axis is employed.

RESULTS AND DISCUSSION

When the bead charges are set to $|q_{Ap/A\eta}| = 0.94$ and

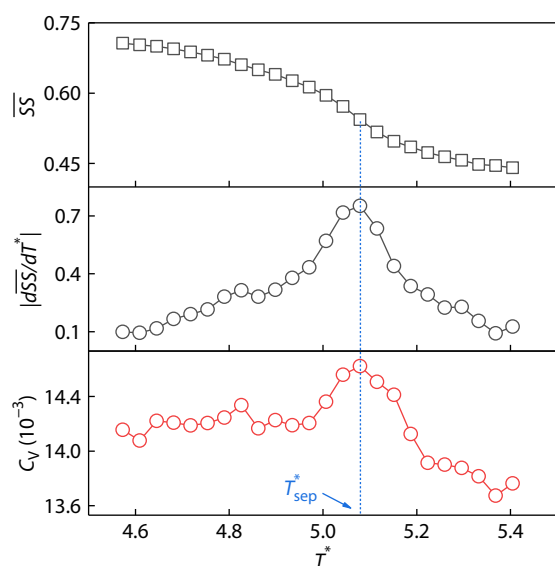


Fig. 4 Comparison between C_V and $|d\overline{SS}/dT^*|$. The black square and circle represent $\overline{SS}$ and $|d\overline{SS}/dT^*|$, respectively. The red circle represents C_V . The blue dotted line marks the position of the phase separation temperature T_{sep}^* , which is determined by the maximum value of $|d\overline{SS}/dT^*|$ or C_V . The data is obtained from the polymer blends system with $N=20$, $\phi_A=0.2$ and $E_0=0.5$. Here, the dielectric constants of A and B polymer are $\epsilon_A=6.0$ and $\epsilon_B=2.5$, respectively.

$|q_{Bp/Bn}| = 0.68$, the dielectric constants of A- and B-type polymers are equal to $\epsilon_A=6.0\pm0.25$ and $\epsilon_B=2.5\pm0.09$ at $T^*=5.0$, respectively. The phase separation temperature increases when an external electric field is imposed. The electric field promotes phase separation, as shown in Fig. 5(a). However, when the dielectric constants are the same ($\epsilon_A=\epsilon_B=6.0\pm0.25$), with $|q_{Ap/An}| = |q_{Bp/Bn}| = 0.94$, the phase separation temperature decreases, and the electric field inhibits phase separation, as shown in Fig. 5(b). The simulations clearly show that an external electric field can change the phase separation temperature.

Fig. 6 shows the phase structure changes with decreasing temperature when the volume fraction ϕ_A of the A-type polymer in the system equals 0.1 and the volume fraction of the B-type polymer is $\phi_B = 1 - \phi_A$. When the electric field is absent, spherical aggregation occurs after phase separation. However, when the electric field is imposed, the phase structure shows an orientation along the electric field direction, and cylinder aggregation occurs. Similar behaviour has been found in experiments and simulations.^[24,26] The static structure factor clearly shows changes in the phase structure. The scattering intensities in all directions are the same in the case of no external electric field. As the temperature decreases, the peak position shifts to a smaller scattered wave vector. This indicates that larger aggregates form. However, when the external electric field is applied, the two-dimensional scattering intensity is not circularly symmetric. The phase domain remains oriented along the electric field direction. Noted that such anisotropy occurs even before the phase separation point, i.e., orientation of the concentration fluctuation occurs once the electric field is imposed. According to Maxwell electric field equation $\nabla \cdot (\epsilon E) = 0$, $\nabla \epsilon \cdot E + \epsilon(\nabla \cdot E) = 0$ is given. The direction of the electric field is perpendicular to the gradient

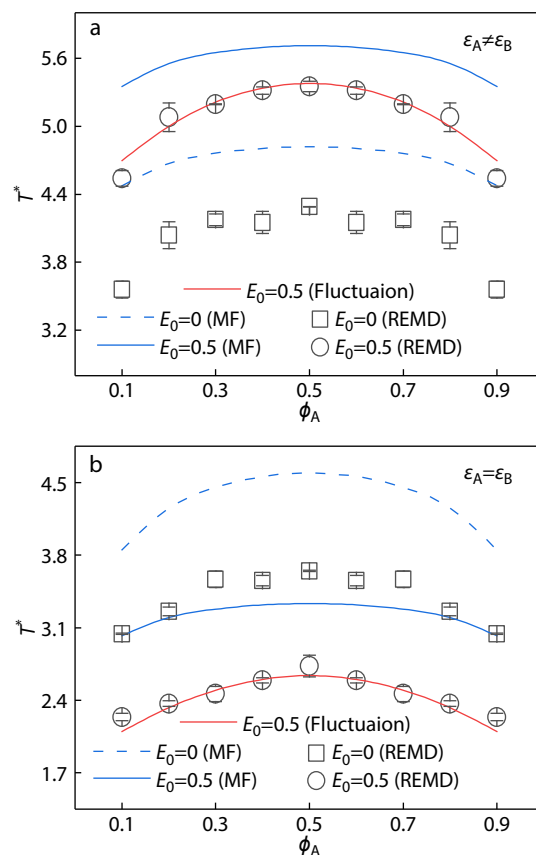


Fig. 5 Influences of an electric field on the phase diagram. The data for $\phi_A=0.6\sim0.9$ are obtained from symmetry with those of $\phi_A=0.4\sim0.1$. Black represents the REMD results, blue represents the mean-field results, and red represents the prediction with the fluctuation effect. (a) $\epsilon_A \neq \epsilon_B$, (b) $\epsilon_A = \epsilon_B$. The order parameter variation for each system can be found in S4 in ESI.^[30]

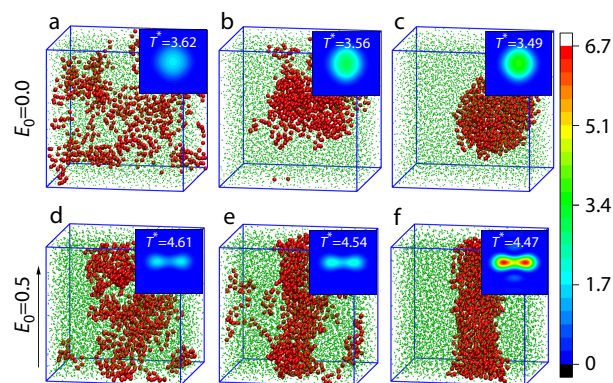


Fig. 6 Snapshots of typical phase structures at different temperatures in the blend system with $\phi_A=0.1$ and $\epsilon_A \neq \epsilon_B$ ($\epsilon_A=6.0$ and $\epsilon_B=2.5$). The two-dimensional structure factor is shown in the top right corner in each picture. The red spheres represent A-type particles, and the green dots represent B-type particles. (a–c) $E_0=0.0$; (d–f) $E_0=0.5$.

direction of the dielectric constant, i.e., $\nabla \epsilon \cdot E = 0$. The interface parallel to the direction of electric field results in lower energy.^[38] In the presence of an electric field, the spherical domain transforms into an oriented columnar domain at low

ϕ_A . As ϕ_A increases, an oriented lamellar domain can be found.

The permittivity, energy and dielectric work of the system are functions not only of the composition, but also of temperature, and they are all calculated at a specific temperature where the system is in a homogeneous mixed state. To determine how an external electric field affects the phase separation, the system energy is analysed. The system energy per unit volume includes four parts, $U_E = U_{\text{Polar},E} + U_{\text{FENE},E} + U_{\text{VDW},E} + U_{\text{Coulomb},E}$, where the four terms on the right correspond to the polarization energy of CG units, the bonding potential energy of chains, the VDW interaction energy among CG units and the Coulomb inter-action energy, respectively. These terms strongly depend on the component concentration except for $U_{\text{FENE},E}$. $U_{\text{Polar},E}$ shows the form: $U_{\text{Polar},E} = U_{\text{Polar},0} + c_{\text{Polar}}E_0^2$, where E_0 represents the external electric field and $U_{\text{Polar},0}$ represents the polarization energy in the absence of an electric field. Figs. 7(a) and 7(b) show that c_{Polar} is a quadratic function of the concentration: $c_{\text{Polar}}(\phi_A) = c_{\text{Polar}}(1)\phi_A + c_{\text{Polar}}(0)\phi_B - c''_{\text{Polar}}\phi_A\phi_B$, $c''_{\text{Polar}} = \partial^2 c_{\text{Polar}} / \partial \phi_A^2$. Fig. 7(c) shows that the difference in the potential energies with and without an electric field, $U_{\text{Polar},E} - U_{\text{Polar},0}$, is proportional to the square

of the strength of the external electric field E_0^2 . Additionally, $U_{\text{VDW},E}$ and $U_{\text{Coulomb},E}$ have similar forms. So, the total system energy under electric field has the form:

$$U_E = U_0 + c_{\text{Total}}E_0^2 \quad (6)$$

where $c_{\text{Total}} = c_{\text{Polar}} + c_{\text{VDW}} + c_{\text{Coulomb}}$ is given after neglecting the influence of FENE potential. To understand the relationship between the dielectric constant and the energy change, the dielectric work per unit volume from the external electric field is needed $W = -E_0 M_E / (2V)$, where M_E is the total electric dipole moment in the presence of external electric field E_0 (S6 in ESI).^[30,39] Through the relation of the dielectric constant and the total dipole moment $\epsilon_r = 1 + M_E / (\epsilon_0 V E_0)$, where ϵ_0 represents the vacuum dielectric constant, the dielectric work can be expressed in terms of the dielectric constant:^[33]

$$W = -(\epsilon_r - 1)\epsilon_0 E_0^2 / 2 \quad (7)$$

The dielectric work includes two parts corresponding to the changes of internal energy and entropy respectively. In Fig. 8(a), we compare the potential energy change with the dielectric work under different electric field strengths, and Fig. 8(b) shows the dependence of the dielectric constant on temperature. Considering the statistical error caused by the

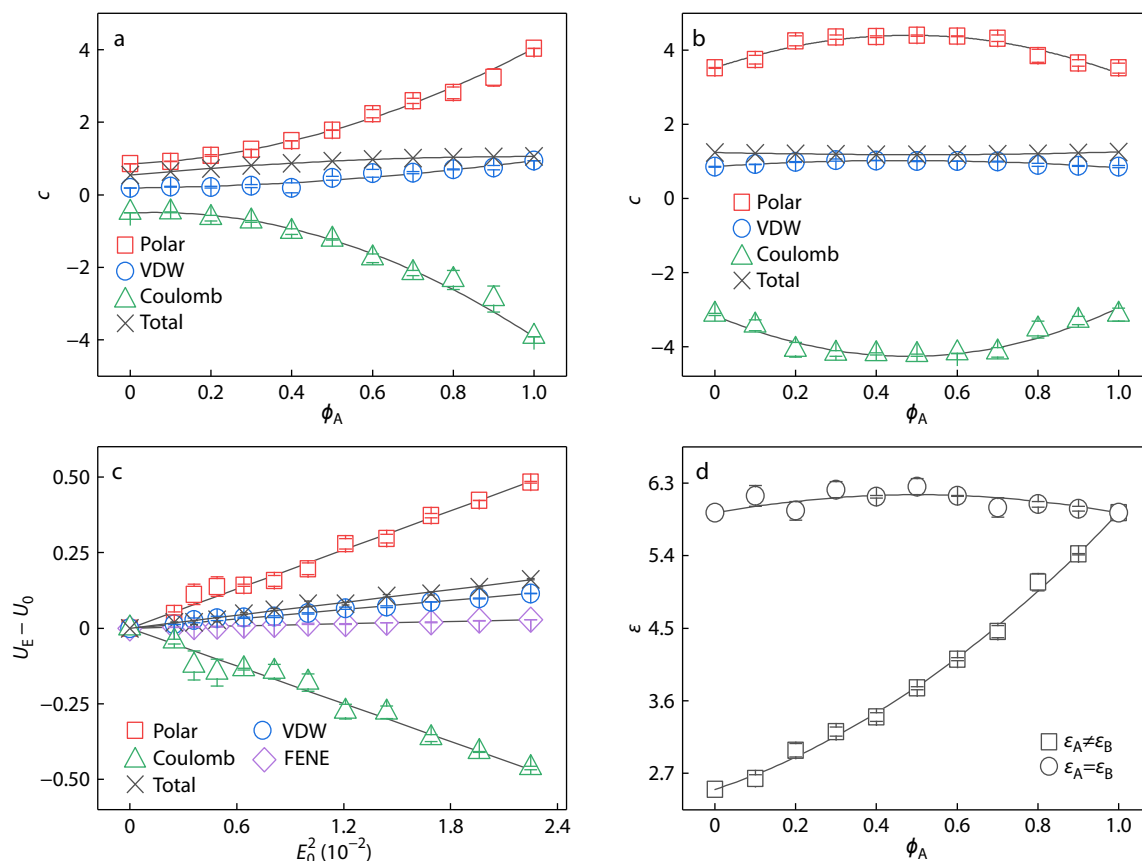


Fig. 7 (a) $\epsilon_A \neq \epsilon_B$: $c''_{\text{Polar}} = 2.69$, $c''_{\text{VDW}} = 0.65$, $c''_{\text{Coulomb}} = -3.84$ and $c''_{\text{Total}} = -0.5$. (b) $\epsilon_A = \epsilon_B$: $c''_{\text{Polar}} = -3.81$, $c''_{\text{VDW}} = -0.70$, $c''_{\text{Coulomb}} = 4.78$ and $c''_{\text{Total}} = 0.27$. In (a) and (b), c was calculated from the system at four electric field strengths (0.0, 0.05, 0.10 and 0.15). (c) $U_E - U_0$, changes in the polarization (red squares), VDW (blue circles), Coulomb (green triangles), FENE (purple diamonds) and total (black crosses) potentials under an external electric field at $\phi_A = 1.0$, $\epsilon_A = 6.0$ and $T^* = 5.0$, where U_E and U_0 represent the potential energy with and without an electric field, respectively. (d) Dependence of the dielectric constant ϵ_r on the component concentration. The values after fitting are $\epsilon'' = 1.75$ ($\epsilon_A \neq \epsilon_B$, black squares) and $\epsilon'' = -0.9$ ($\epsilon_A = \epsilon_B$, black circles). Dependence of energy coefficient and component concentration at $T^* = 5.0$.

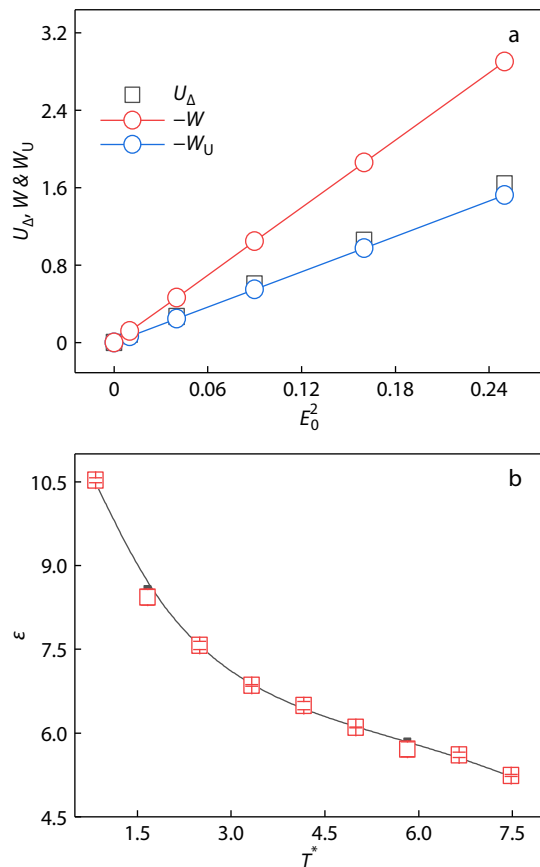


Fig. 8 (a) Comparison of the change in potential energy of a system with the dielectric work at $T^* = 5.0$ ($\epsilon_A = 6.0$ and $\phi_A = 1.0$). Black squares represent potential energy changes, $U_\Delta = U_E - U_0$. The red line represents the dielectric work, $-W$. The blue line represents the dielectric work without entropy effects, $-W_U$. (b) The dependence of dielectric constant on temperature. Here $\partial\epsilon_r/\partial T^*|_{T^*=5.0} = -0.42$, and $S_\Delta|_{E_0=0.5} = -0.28$.

fluctuation of dielectric constant and potential energy, the relationship $U = U_E - U_0 = -W_U$ is proved since the energy change and dielectric constant of the system can be calculated in the present work. Here, U_0 is the system energy without the external electric field, and $W_U = W - T^*S$. $S_\Delta = (\partial\epsilon_r/\partial T^*)\epsilon_0 E_0^2/2$ is the entropy effect.^[39] Finally, the relation is obtained:

$$c_{\text{Total}} = [\epsilon_r - 1 + T^*(\partial\epsilon_r/\partial T^*)]\epsilon_0/2 \quad (8)$$

For polymer blends, the dielectric constant of the blend system has the similar form $\epsilon_r(\phi_A) = \epsilon_A\phi_A + \epsilon_B\phi_B - \epsilon''\phi_A\phi_B$, and the values are shown in Fig. 7(d). Here, ϵ_A and ϵ_B are the dielectric constants of the two pure components. The mixing dielectric work from the electric field is $\Delta W\phi_A = W(\phi_A - \phi_A W(1) - \phi_B W(0) = \epsilon''\epsilon_0\phi_A\phi_BE_0^2/2$. At the same time, the change in the mixing energy caused by the electric field is

$$U_{AB,E}(\phi_A) = U_{AB,0}(\phi_A) - W_U(\phi_A) \quad (9)$$

where $W_U(\phi) = c''_{\text{Total}}\phi_A\phi_BE_0^2$, $c''_{\text{Total}} = c''_{\text{Polar}} + c''_{\text{VDW}} + c''_{\text{Coulomb}}$ and $U_{AB,0}(\phi)$ represents the mixing energy without an electric field. Therefore, $c''_{\text{Total}} = (\epsilon'' + T^*\partial\epsilon''/\partial T^*)\epsilon_0/2$ is obtained. To describe the free energy minimization of the system evolution under an electric field, the free energy $\tilde{F}_E$ of the system is defined as

$\tilde{F}_E = F_0 + W$. Notably, the sign of the free energy change under electric field depends on its reference selection.^[40]

So, the mixing free energy of the blend system is:

$$\Delta\tilde{F}_{AB,E}(\phi_A) = \Delta F_{AB,0}(\phi_A) + \Delta W(\phi_A) \quad (10)$$

where $\Delta\tilde{F}_{AB,E}(\phi_A)$ and $\Delta F_{AB,0}(\phi_A)$ represent the mixing free energies with and without an electric field respectively. Here, $\Delta F_{AB,0}(\phi_A) = \Delta U_{AB,0}(\phi_A) - T\Delta S$. In the classic polymer mean-field theory, the mixing free energy under an external electric field is obtained:^[41,42]

$$\Delta\tilde{F}_{AB,E}(\phi_A)/T^* = [\chi_{AB} + \epsilon''\epsilon_0 E_0^2/(2T^*)]\phi_A\phi_B - \Delta S \quad (11)$$

Here, χ_{AB} is the Flory-Huggins parameter without an electric field, and $S = -(\phi_A \ln \phi_A + \phi_B \ln \phi_B)/N$. Let $(\chi_{AB}N)_E = \chi_{AB}N + N\epsilon''\epsilon_0 E_0^2/(2T^*)$, which is calculated with mapping technology.^[35] The Flory-Huggins parameter has the empirical form:^[43]

$$(\chi_{AB}N)_E = a_E + b_E/T^* \quad (12)$$

where the parameters a_E and b_E are obtained by linear fit-ting, as shown in Figs. 9(a) and 9(b). According to Eq. (12) and the condition $(\Delta F_E)' = 0$, the mean-field transition temperatures corresponding to the binodal lines without and with an electric field can be predicted: $T_{\text{sep},0}^{\text{MF}} = b_0(\Theta - a_0)$ and $T_{\text{sep},E}^{\text{MF}} = b_E(\Theta -$

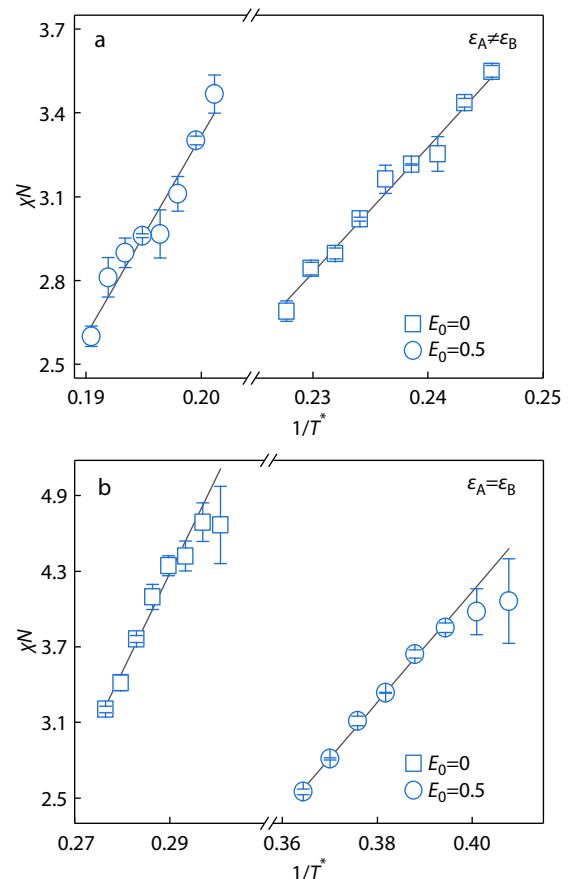


Fig. 9 Flory-Huggins relationship: $\chi N = a_0 + b_0/T^*$ and $\chi N = a_E + b_E/T^*$. Blue squares indicate the absence of an electric field, blue circles indicate the presence of an electric field, and black lines are fitting results. Only the high-temperature data are used for linear fitting. (a) $\epsilon_A \neq \epsilon_B$, $a_0 = a_E = -9.1$, $b_0 = 51.25$, $b_E = 64.13$; (b) $\epsilon_A = \epsilon_B$, $a_0 = a_E = -12.0$, $b_0 = 55.77$, $b_E = 40.0$.

a_E), respectively, in which $\Theta = \ln[(1 - \phi_A)/\phi_A]/(1 - 2\phi_A)$. Furthermore, $a_E = a_0$ and $b_E = b_0 + 0.5N\epsilon''\epsilon_0 E_0^2$ are found, and the transition temperatures without and with an electric field have a relation:

$$T_{\text{sep},E}^{\text{MF}}/T_{\text{sep},0}^{\text{MF}} = b_E/b_0 \quad (13)$$

When ϵ'' is positive ($\epsilon'' = 1.75$ at $T^* = 5.0$), the electric field makes the binodal line move to higher temperatures and promotes phase separation, as shown in Fig. 5(a). In contrast, when ϵ'' is negative ($\epsilon'' = -0.9$ at $T^* = 5.0$), the electric field pushes the binodal line to lower temperatures and inhibits the phase separation, as shown in Fig. 5(b). The trend of the prediction is consistent with that of the simulations, but the deviation in the quantities is large because the above results are based on the mean-field approximation, i.e., the blend system is regarded as being in the homogeneous state. The deviation critically results from the negligence of the composition and phase fluctuations, which is an intractable problem in mean-field theory.^[44] Orzechowski *et al.* derived the electrostatic energy under electric field by expanding the effective electric field.^[23] They found that the dielectric contrast, i.e., the first derivative term of dielectric constant plays the impor-

tant mixing effects on the system. In the system of nitrobenzene+octane mixture, a perfect agreement of theory and experiment was achieved. This term is also used to explain the discrepancy of Debye's experiment with theory.

Here, it is worthy to note that our system is special because the periodic boundary condition (PBC) is employed to simulate the infinite space. In such system, the effective electric field E is equal to the external electric field E_0 due to the particularity of PBC. Laplace equation, i.e., Maxwell electric field equation, does not need to be solved in our work. The electrostatic energy, i.e., dielectric work is only the function of dielectric constant under the external electric field E_0 (see Eq. 7). As a result, the second-order coefficient ϵ'' of the dielectric constant is only involved (see Eq. 11).

Since the deviation of $T_{\text{sep},0}^{\text{MF}}$ and $T_{\text{sep},E}^{\text{MF}}$ of the mean field theory from the simulation is from the negligence of the fluctuations, how to solve it becomes critical. At first, we check the fluctuation at the phase transition point. Using the weighted histogram analysis method (WHAM), the distribution of the order parameter at the phase separation temperature is obtained, as shown in Fig. 10(a) (S5 in ESI).^[30,45,46] The distribution is wide and has two peaks corresponding to the phase

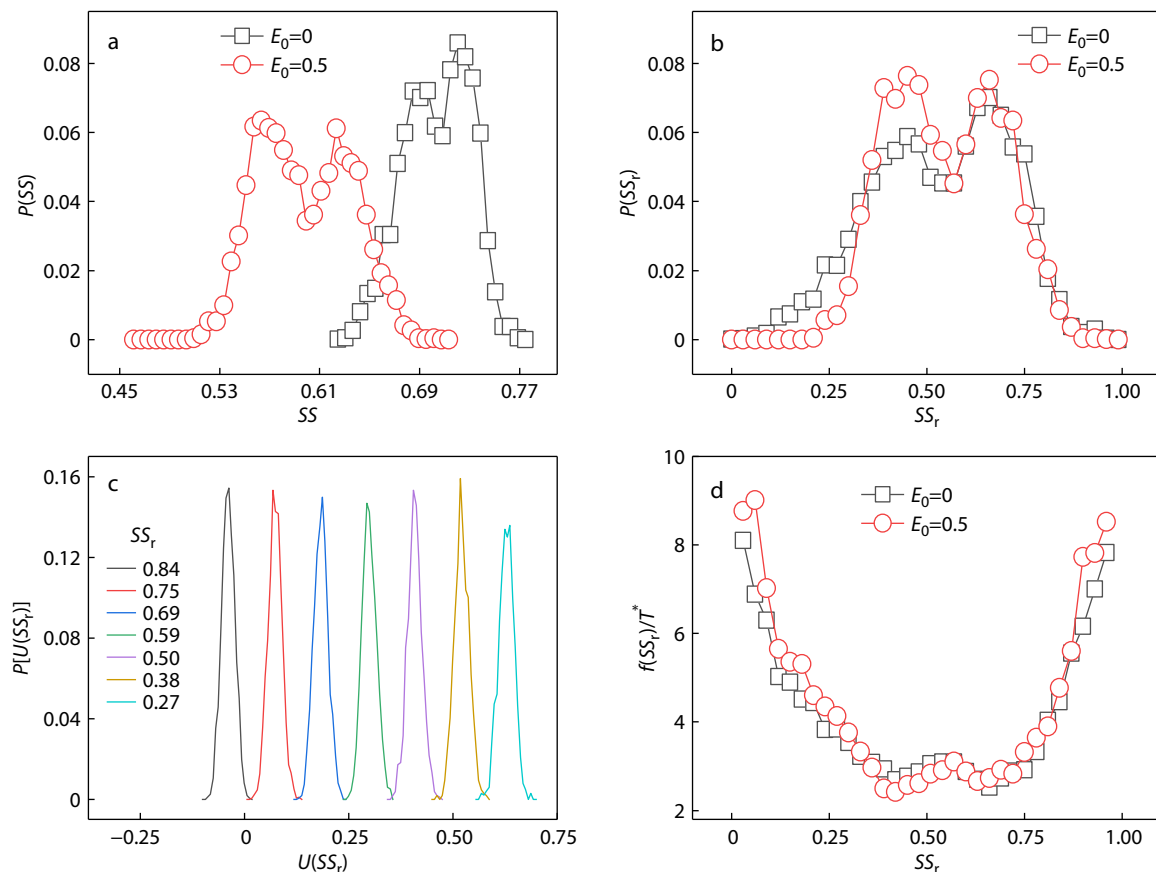


Fig. 10 Distribution of the order parameter, SS , and its related properties calculated by the WHAM for the blend system ($\epsilon_A = \epsilon_B$, $\phi_A = 0.2$). (a) Probability distribution of SS at temperature $T_0^* \pm \Delta T^*$ (black squares without an electric field) and $T_E^* \pm \Delta T^*$ (red circles with an electric field). Here, $T_0^* = 3.26$, $T_E^* = 2.4$ and $\Delta T^* = 0.3$. ΔT^* is used to control the range of samples in the REMD results. The order parameter SS in (a) is transformed into a relative order parameter SS_r , and the probability distribution of SS_r is given in (b). (c) Each relative order parameter SS_r corresponds to an energy state $U(SS_r)$, which has a narrow probability distribution. SS_r has a width range of $SS_r \pm 0.03$ without an electric field. (d) The ratio of the free energy corresponding to relative order parameter SS_r to the corresponding temperature, $f(SS_r)/T^*$, is the same with or without an electric field.

structures with low and high SS.

The curve profiles without and with the external electric field are very similar. Based on the principle of physical universality, two fluctuation distributions can be merged into one curve when the relative order parameter is used, as shown in Fig. 10(b). The relative order parameter is defined as $SS_r = (\overline{SS} - \overline{SS}_{T_{sep}^* + \Delta T^*}) / (\overline{SS}_{T_{sep}^* - \Delta T^*} - \overline{SS}_{T_{sep}^* + \Delta T^*})$, where T_{sep}^* is the phase separation temperature and $T^* = 0.5$ is selected as sufficiently large. This indicates that the external electric field does not change the phase structure fluctuation at the transition point with an appropriate order parameter.

Fig. 10(c) shows that each relative order parameter, SS_r , corresponds to an energy state $U(SS_r)$. The energy distribution of the phase structure with the SS_r is narrow. Therefore, a free energy function $f(SS_r)$ can be used to describe the phase structure distribution, as shown in Fig. 10(d). According to the above evidence, an assumption of identical fluctuation at the transition point can be made. It yields the equality of the SS_r distribution:

$$\exp[-f_E(SS_r)/T_{sep,E}^{\text{Fluct}}] = \exp[-f_0(SS_r)/T_{sep,0}^{\text{Fluct}}] \quad (14)$$

where $f_E(SS_r)$ represents the mixing free energy of the system with relative order parameter SS_r at phase separation temperature $T_{sep,E}^{\text{Fluct}}$ with an electric field E_0 , and $f_0(SS_r)$ is that for the system at $T_{sep,0}^{\text{Fluct}}$ without an electric field. From Eq. (14), we obtain $f_E(0)/f_0(0) = T_{sep,E}^{\text{Fluct}}/T_{sep,0}^{\text{Fluct}}$. Here, $f_E(0)$ is the mixing free energy of $SS_r=0$ corresponding to the homogenous phase state. It is simply ΔF_E in Eq. (11). Finally, the transition temperature with an electric field is obtained by combining Eqs. (11), (12) and (14):

$$T_{sep,E}^{\text{Fluct}} = b_E T_{sep,0}^{\text{Fluct}} / b_0 \quad (15)$$

Although the form of Eq. (15) is the same as that of Eq. (13), the physical concept behind it is essentially different. The transition temperature in Eq. (15) refers to that with consideration of the phase fluctuation in a realistic system. The new predictions agree well with the simulations, as shown in Fig. 5. This method avoids calculation of the phase fluctuation and takes advantage of the transition temperature of the fluctuating system without an electric field under the identical fluctuation assumption (S7 in ESI).^[30]

CONCLUSIONS

In summary, we have proposed a modified polarizable CG model to reveal the mechanism of an external electric field affecting phase separation. The present model succeeds in reproducing the effects of promotion and suppression of phase separation under an external electric field. The simulations directly show how changes in the molecular polarization energy, VDW interaction and Coulomb interaction induced by an external electric field affect the phase separation strength, which in turn leads to changes in the transition temperature. Orientation of the concentration fluctuation occurs once the electric field is imposed, even before the phase separation point. The external electric field does not affect the distribution state at the phase separation temperature. Accordingly, a simple method is proposed to quantitatively predict the change in the phase separation temperature with an electric field by utilizing

the phase separation temperature without an electric field. Perfect agreement is achieved. The present simulation method and theory can be applied to other systems such as the phase transition of polymer solutions or block polymers under an electric field.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2877-z>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 91127046).

REFERENCES

- Ruppel, M.; Pester, C. W.; Langner, K. M.; Sevink, G. J. A.; Schoberth, H. G.; Schmidt, K.; Urban, V. S.; Mays, J. W.; Böker, A. Electric field induced selective disordering in lamellar block copolymers. *ACS Nano* **2013**, 7, 3854–3867.
- Amundson, K.; Helfand, E.; Davis, D. D.; Quan, X.; Patel, S. S.; Smith, S. D. Effect of an electric field on block copolymer microstructure. *Macromolecules* **1991**, 24, 6546–6548.
- Thurn-Albrecht, T.; Schotter, J.; Kästle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates. *Science* **2000**, 290, 2126–2129.
- Chu, B.; Zhou, X.; Ren, K.; Neese, B.; Lin, M.; Wang, Q.; Bauer, F.; Zhang, Q. M. A dielectric polymer with high electric energy density and fast discharge speed. *Science* **2006**, 313, 334–336.
- Roy, P.; Gooh Pattader, P. S. Electrohydrodynamic instability: effect of rheological characteristics on the morphological evolution of liquid crystal-polymer interface. *Bull. Mater. Sci.* **2020**, 43, 169.
- Debye, P. Spectral width of the critical opalescence due to concentration fluctuations. *Phys. Rev. Lett.* **1965**, 14, 783–784.
- Wirtz, D.; Fuller, G. G. Phase transitions induced by electric fields in near-critical polymer solutions. *Phys. Rev. Lett.* **1993**, 71, 2236–2239.
- Orzechowski, K. Electric field effect on the upper critical solution temperature. *Chem. Phys.* **1999**, 240, 275–281.
- Beaglehole, D. A critical binary liquid in an electric field. *J. Chem. Phys.* **1981**, 74, 5251–5255.
- Reich, S.; Gordon, J. M. Electric field dependence of lower critical phase separation behavior in polymer-polymer mixtures. *J. Polym. Sci., Part B: Polym. Phys.* **1979**, 17, 371–378.
- Kriisa, A.; Roth, C. B. Electric fields enhance miscibility of polystyrene/poly(vinyl methyl ether) blends. *J. Chem. Phys.* **2014**, 141, 134908.
- Lee, J. S.; Prabu, A. A.; Kim, K. J.; Park, C. Phase separation and crystallization behavior of poly(vinylidene fluoride)/poly(1,4-butylene adipate) blends under an electric field. *Macromolecules* **2008**, 41, 3598–3604.

- 13 Lee, J. S.; Prabu, A. A.; Kim, K. J. UCST-type phase separation and crystallization behavior in poly(vinylidene fluoride)/poly(methyl methacrylate) blends under an external electric field. *Macromolecules* **2009**, *42*, 5660–5669.
- 14 Schobert, H. G.; Schmidt, K.; Schindler, K. A.; Böker, A. Shifting the order-disorder transition temperature of block copolymer systems with electric fields. *Macromolecules* **2009**, *42*, 3433–3436.
- 15 Early, M. D. Dielectric constant measurements near the critical point of cyclohexane-aniline. *J. Chem. Phys.* **1992**, *96*, 641–647.
- 16 Onuki, A.; Doi, M. Electric birefringence and dichroism in critical binary mixtures. *EPL* **1992**, *17*, 63–68.
- 17 Onuki, A. Electric-field effects in fluids near the critical point. *EPL* **1995**, *29*, 611–616.
- 18 Debye, P.; Gravatt, C. C.; Ieda, M. Electric field effect on the critical opalescence. II. Relaxation times of concentration fluctuations. *J. Chem. Phys.* **1967**, *46*, 2352–2356.
- 19 Martin, J. M.; Delaney, K. T.; Fredrickson, G. H. Effect of an electric field on the stability of binary dielectric fluid mixtures. *J. Chem. Phys.* **2020**, *152*, 234901.
- 20 Tsoi, Y.; Tournilhac, F.; Leibler, L. Demixing in simple fluids induced by electric field gradients. *Nature* **2004**, *430*, 544–547.
- 21 Reich, S.; Cohen, Y. Phase separation of polymer blends in thin films. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1255–1267.
- 22 Katsir, Y.; Tsoi, Y. Recent advances in liquid mixtures in electric fields. *J. Phys.: Condens. Matter* **2016**, *29*, 063002.
- 23 Orzechowski, K.; Adamczyk, M.; Wolny, A.; Tsoi, Y. Shift of the critical mixing temperature in strong electric fields. theory and experiment. *J. Phys. Chem. B* **2014**, *118*, 7187–7194.
- 24 Xu, T.; Zvelindovsky, A. V.; Sevink, G. J. A.; Gang, O.; Ocko, B.; Zhu, Y.; Gido, S. P.; Russell, T. P. Electric field induced sphere-to-cylinder transition in diblock copolymer thin films. *Macromolecules* **2004**, *37*, 6980–6984.
- 25 Lyakhova, K. S.; Zvelindovsky, A. V.; Sevink, G. J. A. Kinetic pathways of order-to-order phase transitions in block copolymer films under an electric field. *Macromolecules* **2006**, *39*, 3024–3037.
- 26 Tsoi, Y.; Tournilhac, F.; Andelman, D.; Leibler, L. Structural changes in block copolymers: coupling of electric field and mobile ions. *Phys. Rev. Lett.* **2003**, *90*, 145504.
- 27 Lin, C.-Y.; Schick, M.; Andelman, D. Structural changes of diblock copolymer melts due to an external electric field: a self-consistent-field theory study. *Macromolecules* **2005**, *38*, 5766–5773.
- 28 Martin, J. M.; Li, W.; Delaney, K. T.; Fredrickson, G. H. SCFT study of diblock copolymer melts in electric fields: selective stabilization of orthorhombic Fddd network phase. *Macromolecules* **2018**, *51*, 3369–3378.
- 29 Zhang, Q.; Xu, R.; Kan, D.; He, X. Molecular dynamics simulation of electric-field-induced self-assembly of diblock copolymers. *J. Chem. Phys.* **2016**, *144*, 234901.
- 30 See Supplemental Material for further simulation details and theoretical derivation.
- 31 Sugita, Y.; Okamoto, Y. Replica-exchange molecular dynamics method for protein folding. *Chem. Phys. Lett.* **1999**, *314*, 141–151.
- 32 Bauer, P.; Hess, B.; Lindahl, E. *GROMACS 2022.2*. Zenodo: **2022**.
- 33 Neumann, M. Dipole moment fluctuation formulas in computer simulations of polar systems. *Mol. Phys.* **1983**, *50*, 841–858.
- 34 Neumann, M.; Steinhauser, O. Computer simulation and the dielectric constant of polarizable polar systems. *Chem. Phys. Lett.* **1984**, *106*, 563–569.
- 35 Groot, R. D.; Warren, P. B. Dissipative particle dynamics: bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.* **1997**, *107*, 4423–4435.
- 36 Horsch, M. A.; Zhang, Z.; Iacovella, C. R.; Glotzer, S. C. Hydrodynamics and microphase ordering in block copolymers: are hydrodynamics required for ordered phases with periodicity in more than one dimension. *J. Chem. Phys.* **2004**, *121*, 11455–11462.
- 37 Marro, J.; Bortz, A. B.; Kalos, M. H.; Lebowitz, J. L. Time evolution of a quenched binary alloy. II. Computer simulation of a three-dimensional model system. *Phys. Rev. B* **1975**, *12*, 2000–2011.
- 38 Tsoi, Y. Colloquium: phase transitions in polymers and liquids in electric fields. *Rev. Mod. Phys.* **2009**, *81*, 1471–1494.
- 39 Bottcher, C. J. F. *Theory of Electric Polarization*. Elsevier Scientific Publishing Company: AMSTERDAM, **1973**, Vol. 1.
- 40 Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*. Pergamon: Amsterdam, **1984**, Vol. 8.
- 41 Huggins, M. L. Solutions of long chain compounds. *J. Chem. Phys.* **1941**, *9*, 440–440.
- 42 Flory, P. J. Thermodynamics of high polymer solutions. *J. Chem. Phys.* **1941**, *9*, 660–660.
- 43 Bates Frank, S. Polymer-polymer phase behavior. *Science* **1991**, *251*, 898–905.
- 44 Fredrickson, G. H.; Helfand, E. Fluctuation effects in the theory of microphase separation in block copolymers. *J. Chem. Phys.* **1987**, *87*, 697–705.
- 45 Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. The weighted histogram analysis method for free-energy calculations on biomolecules. I. The method. *J. Comput. Chem.* **1992**, *13*, 1011–1021.
- 46 Gallicchio, E.; Andrec, M.; Felts, A. K.; Levy, R. M. Temperature weighted histogram analysis method, replica exchange, and transition paths. *J. Phys. Chem. B* **2005**, *109*, 6722–6731.