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Electrostatic-field-induced chain alignment of liquid crystalline copolyether TPP thin films

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Abstract

A liquid crystalline (LC) copolyether has been synthesized from 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)propane with 1,7-dibromoheptane and 1,11-dibromoundecane with a 50/50 (both in %) equal composition of the 7- and 11-methylene monomers [coTPP-7/11(5/5)]. A mono-domain with a homeotropic alignment can be induced by a thin film surface in the LC phase. When an electrostatic field is applied to the surface-induced mono-domains parallel to the thin film surface normal, the molecular alignment undergoes a change from the homeotropic to uniaxial homogeneous arrangement. However, when the field is applied to a direction perpendicular to the thin film surface normal, the molecular alignment is about 10°-tilt with respect to the homeotropic alignment toward the a^*-axis. This is because the permanent dipole moment of the copolyether is not right vertical to the molecular direction. The calculation of molecular dipoles indicates that the permanent dipole moment of this copolyether is about 70° away from the molecular axis, which leads to a negative dielectric anisotropy. It is speculated that the 10°- rather than 20°-tilt is due to a balance between the alignment induced by the electrostatic field and the surface. In the electrostatic field, molecules are subjected to a torque τ, which is determined by the permanent dipole moment **P** and the electrostatic field **E**: $\tau = \mathbf{P} \times \mathbf{E}$. The molecular realignment in both parallel and perpendicular directions to the thin film surface normal is determined by satisfying the condition of $\tau = \mathbf{P} \times \mathbf{E} = 0$. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystal; Alignment; Electric field

1. Introduction

Alignment in response to an external field is a defining property of liquid crystals (LC), which have been extensively reported in applications of mechanical shearing, thin film surface-induced, and electric- and magnetic-field-induced alignments [1–3]. Surface-induced LC alignments can be in both homeotropic and homogeneous arrangements via specific chemical and physical modifications [4,5]. Electric-field-induced LC alignments are based on a dielectric anisotropy of LC molecules. This kind of alignment is enhanced because of a long-range orientation order along the molecular axis in the LC phase [6]. An efficiency of the electric-field-induced alignment in LC molecules is dependent upon the magnitude of dielectric anisotropy of the molecules, molecular mobility and the direction and voltage of the electric field applied [7]. In some cases, the electric field can also change arrangements of the chain alignment from originally aligned LC samples [8–10].

A series of main-chain LC polyethers and copolyethers have been synthesized from 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)propane with different α,ω-dibromoalkanes, abbreviated as TPP-*n* or coTPP-*n*/*m* (where *n* and *m* are the numbers of methylene units in α,ω-dibromoalkanes) [11]. Rich bulk phase structures and transition behaviors have been found in this series of LC TPP polyether and coTPP copolyether [12–15]. For instance, highly ordered smectic F and smectic G phases exist in the homopolyether TPP-7 and smectic F, smectic G and smectic H phases in the homopolyether TPP-11 [12]. In the case of the copolyether with equal molar compositions of coTPP-7/11(5/5), however, three LC phases have been observed, which are nematic (N), hexagonal columnar (Φ') and tilted hexagonal

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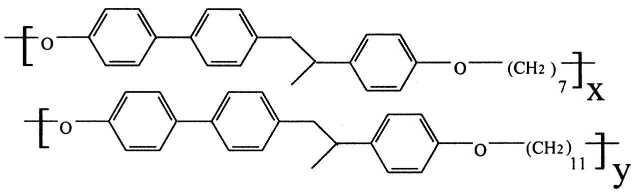
columnar (Φ_{TH}) phases in a sequence of cooling [15]. The Φ_{TH} phase is a tilted columnar phase with multiple tilt angles between the molecular axis and the normal of hexagonal lattice. However, the hexagonal lattice dimensions in the Φ_{TH} phase with various tilt angles are identical. The detailed structure of the Φ_{TH} phase has been described in a previous publication [15]. The columnar phase is formed in coTPP-7/11(5/5) because comonomers have different methylene unit lengths, which lead to an aperiodicity along the molecular chains [15]. In the thin films of this series of TPP, phase structures and transition behaviors are critically associated with the chemistry and physics of the surfaces on which the thin films are coated [16,17]. Highly ordered mono-domains with homeotropic alignment have been found in the homopolymer TPP thin films. The formation and ordering of mono-domains have been related to the structural symmetry and molecular mobility in different phases of the TPPs [16,17].

Since coTPPs possess a disturbed structure along the chain direction and high molecular mobility, the surface-induced lateral structural ordering in the coTPP thin films should be different from that in the homopolymers. In this work, one of the copolyethers, coTPP-7/11(5/5), is chosen for study of the surface- and electric-field-induced molecular alignment. We design an experiment by starting at the thin film which possesses the homeotropic alignment. After introducing an electrostatic field, it is observed that the homeotropic alignment changes with respect to the field orientation.

2. Experimental section

The LC copolyether with equal molar compositions of 1,7-dibromoheptane and 1,11-dibromoundecane, coTPP-7/11(5/5), was synthesized and the detailed synthetic routes were published in Ref. [11]. The molecular weight of this copolyether was around 30 kDa determined by gel permeation chromatography (GPC) based on polystyrene standards. The chemical structure of this copolyether is



The coTPP-7/11(5/5) thin films were cast from a 0.1% (w/w) solution in chloroform on an amorphous carbon coated surface. After the solvent evaporated at room temperature, the thin films were used for surface- and electrostatic-field-induced chain alignment experiments. The thickness of the films was around 50 nm.

In order to generate films having homeotropically aligned chain molecules, the surface-induced structural ordering experiment was carried out. The coTPP-7/11(5/5) thin films were first heated to above their melting temperatures and then cooled to the N or Φ' phases and annealed under nitrogen atmosphere for 10 h. They were subsequently cooled slowly to room temperature.

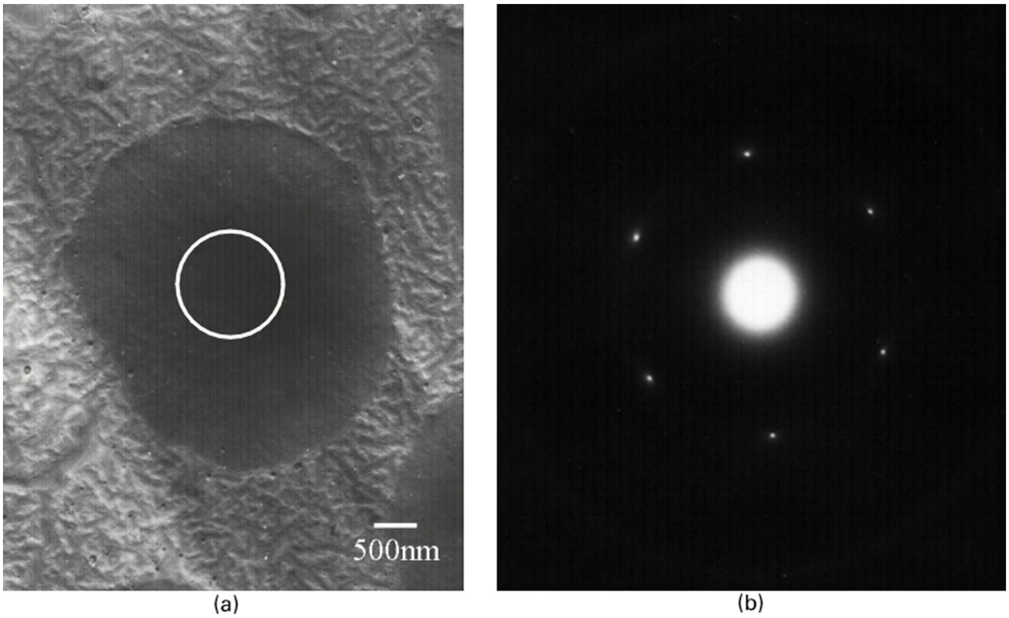
An electrostatic field was then applied to the films in which the chains were homeotropically aligned. The thin films were first placed at the bottom electrode surface with a heating stage. The instrument used was designed and built in our laboratory. Adjustable distances and voltages between the top and bottom electrodes could be controlled for changing the electrostatic field intensity. A hot stage was built under the bottom electrode and its temperature was controlled between 30 and 500°C with a temperature fluctuation of about ±0.5°C. The electrostatic field with an intensity of 5 kV/cm was applied onto the thin films for 2 h at a temperature in the N phase. In order to avoid the arc breakdown, experiments were carried out in vacuum (above 10^{-3} Pa). The thin films were then slowly cooled to room temperature as the electrostatic field was applied continuously. Both the perpendicular and parallel arrangements of the electrostatic field with respect to the thin film surface normal were adopted.

Observations of the morphology for the thin film samples were carried out using a JEOL 2010 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The thin films were floated on the surface of water and then recovered with copper grids. The thin films were shadowed using Pt for morphology observations. In order to determine the lateral structural order and chain alignment direction, electron diffraction (ED) experiments were carried out in TEM. A tilting stage was used. The Au was used to calibrate the ED spacing.

3. Results and discussion

3.1. Surface-induced homeotropic alignment

Following the previous work [16,17], Fig. 1a shows a mono-domain of coTPP-7/11(5/5) formed when the thin film was cast on an amorphous carbon substrate and annealed isothermally at 153°C in the Φ' phase. The circular shape of the mono-domain indicates that the growth of the mono-domain is isotropic, which is dominated by the structural symmetry of the hexagonal packing. The ED pattern of the [001] zone in Fig. 1b illustrates the existence of lateral hexagonal packing and homeotropic chain alignment in the mono-domains formed in the Φ' phase. Note that this homeotropic alignment can also be achieved when the thin films are annealed in the N phase temperature region. These thin films having homeotropic alignment are used as starting samples for the study of molecular realignments under the electrostatic field.



(a)

(b)

Fig. 1. TEM micrograph and ED patterns of coTPP-7/11(5/5) thin films annealed at the Φ' phase. The ED pattern originates from the circled area of the mono-domains.

3.2. Molecular structure and dipole moment

It is known that LC molecular alignments depend on their molecular dielectric anisotropy. Two principle dielectric constants, $\varepsilon_{\|}$ for parallel and $\varepsilon_{\perp}$ for perpendicular to the molecular axis, can be recognized. The dielectric constant difference, $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$, represents the dielectric anisotropy of LC molecules. These dielectric constants are determined by the detailed chemical structure of LC molecules in which each polar chemical bond possesses a dipole [6]. When the molecules are uniaxially oriented, the vector summation of all the dipoles attributed to each chemical bond becomes a permanent dipole moment, which has a fixed relationship with respect to the molecular axis. If there is a permanent dipole moment parallel or nearly parallel to the long molecular axis, the dipole can be oriented efficiently by an electric field along the chain axis. But an electric field normal to the chain axis has only a weak effect on the dipole [6]. Thus, in this case, $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp} > 0$ and molecules favor an alignment parallel to the electrostatic field. If a molecule has a permanent dipole moment that is more or less perpendicular to the molecular axis, the molecules then favor an alignment perpendicular to the direction of an electrostatic field since $\Delta\varepsilon < 0$. The dielectric realignment under electrostatic field in both the cases is schematically shown in Fig. 2.

The dipole moments and repeat unit conformation of coTPP-7/11(5/5) are calculated using a software of Mopac 6.0, which is a semi-empirical molecular orbital package. The summation dipole moment of one comonomer TPP-7 evaluated from the point charge and hybrid is 2.480 Debye. The corresponding components of the dipole moments with respect to the x, y, and z directions shown in Fig. 3 are -0.90, 2.22, and 0.63 Debye, respectively. The dipole moment of another comonomer TPP-11 is calculated to be 2.484 Debye with components of -0.83, 2.28, and 0.53 Debye in the x, y, and z directions, respectively. Since the coTPP-7/11(5/5) is a random copolymer having

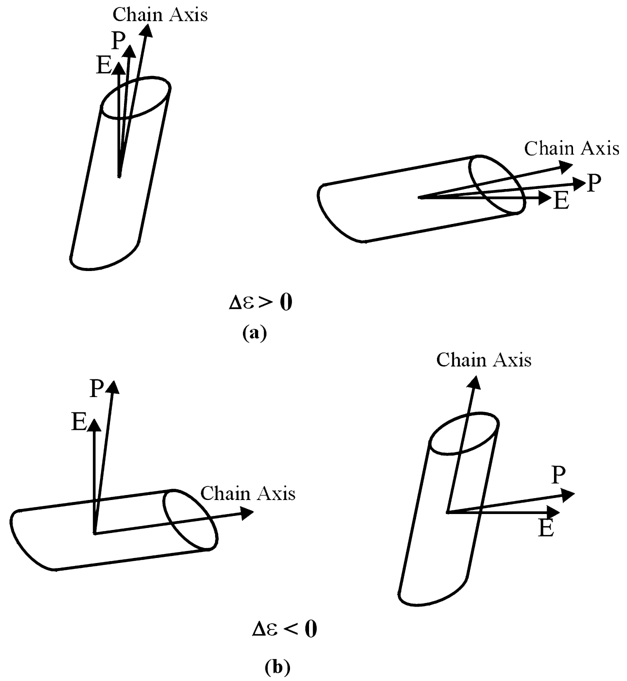


Fig. 2. Schematics of relationships among dipole moment direction, electrostatic field direction and chain molecular axis after the dielectric realignment. **P** is the permanent dipole moment and **E** is the electric field.

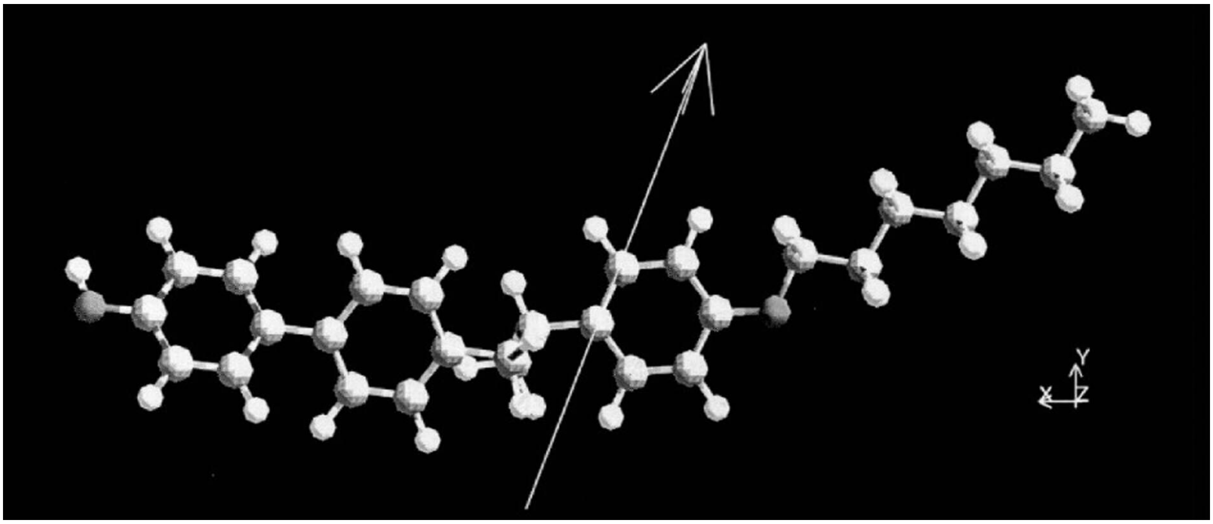


Fig. 3. Molecular geometry and permanent dipole moment direction of a TPP-7 repeat unit with a fully extended conformation.

equal molar compositions of TPP-7 and TPP-11, its permanent dipole moment should be a statistical average over the vector summation of the contributions of the TPP-7 and TPP-11. The calculated dipole moment of coTPP-7/11(5/5) is thus 2.481 Debye. The angle between the dipole moment and molecular axis can be determined from the permanent dipole moment and its x component since the x component is along the molecular axis. For coTPP-7/11(5/5) the angle is calculated to be 69.6°. This indicates that the permanent dipole moment is more or less perpendicular to the molecular axis. Therefore, a negative dielectric anisotropy ($\varepsilon_{\parallel} < \varepsilon_{\perp}$) for coTPP-7/11(5/5) can be recognized. In this case the molecular realignment induced by an electrostatic field should be more or less perpendicular to the direction of the electrostatic field for this copolyether (Fig. 2b).

3.3. Molecular realignment under electrostatic field

After a thin film with the homeotropic chain alignment shown in Fig. 1 is achieved, an electrostatic field parallel to the thin film surface normal with an intensity of 5 kV/cm is applied to this thin film. The sample is heated to the N phase temperature range. Fig. 4 shows a series of ED obtained after the thin film is annealed at 170°C for 2 h. The pattern is very similar to the uniaxial wide angle X-ray diffraction (WAXD) fiber pattern of this sample obtained in an oriented sample [15]. In Fig. 4, multiple ED spots are almost aligned on a pair of ‘lines’ nearly parallel to each other and they exhibit a symmetric pattern with respect to the line which passes the center of the ED (meridian direction in a WAXD fiber pattern). It has been reported previously that based on the WAXD results, this kind of pattern represents the tilted hexagonal columnar phase Φ_{TH} with different tilting β angles [15]. No reflections can be found in (001) because of the aperiodic structure along the chain direction in this columnar phase due to the nature of this random copolyether.

This ED pattern thus reveals that the electrostatic field parallel to the thin film surface normal has realigned the chain molecules from the originally homeotropic alignment shown in Fig. 1 to a uniaxially oriented homogeneous alignment. The driving force behind this realignment is the interaction of the electrostatic field with the permanent dipole moment in this coTPP-7/11(5/5), which has a negative dielectric anisotropy. In the electrostatic field, each permanent dipole is subject to a torque τ, depending upon the angle between the dipole moment $\mathbf{P}$ and the electrostatic field $\mathbf{E}$: $\tau = \mathbf{P} \times \mathbf{E}$. This torque is the cause of realignment of the molecules until the dipole moment is parallel to the electrostatic field, namely, $\tau = \mathbf{P} \times \mathbf{E} = 0$. For coTPP-7/11(5/5) with the dipole moment nearly 70° away from the molecular axis, the electrostatic field parallel to the thin film surface normal should induce a molecular alignment that is more or less perpendicular to this field. Therefore, this leads to a uniaxial homogeneous alignment in the thin film. Strictly speaking, the alignment direction should lead to an angle of ±20° between the molecule axis and thin film surface. However, the stability requirement of the molecules has to let the chains lie down perpendicular to the thin film surface normal.

After the electrostatic field is applied perpendicular to the thin film surface normal, an ED pattern shown in Fig. 5a can be obtained. From this figure, only a pair of (200) ED reflections can be observed, indicating that chains are aligned with a tilted homeotropic alignment. This result is supported by tilted ED experiments. A [001] zone ED pattern in Fig. 5b can be obtained after the sample is tilted about 10° along the a^*-axis in both the clockwise and anti-clockwise directions. This reveals that the chains tilt 10° from the homeotropic alignment. Based on the anisotropic dielectric analysis of coTPP-7/11(5/5), the permanent dipole moment

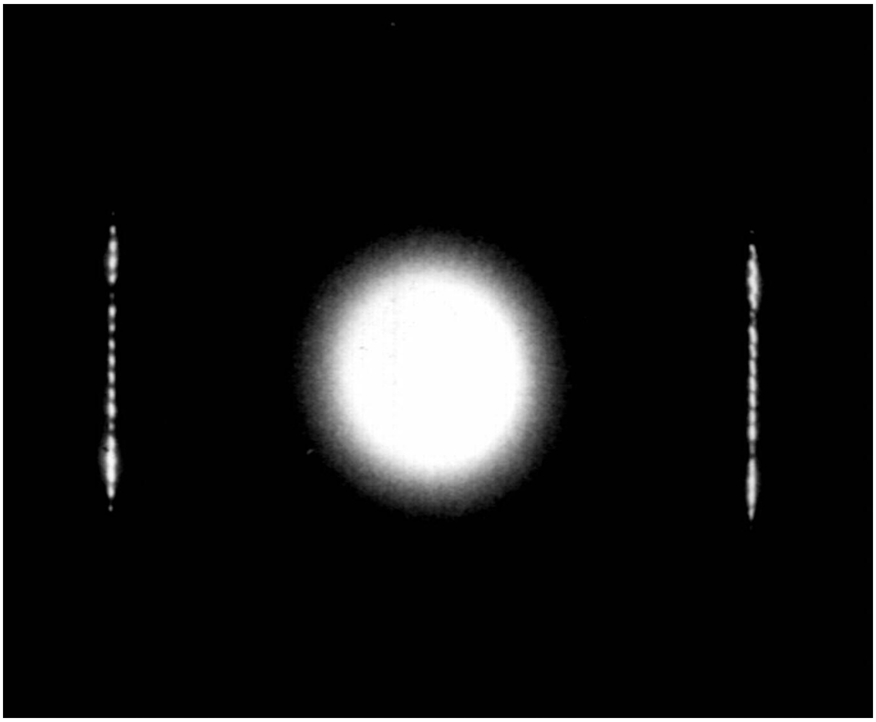


Fig. 4. ED patterns of the coTPP-7/11(5/5) thin films after being heated to 170°C and annealed for 2 h under the electrostatic field having an intensity of 5 kV/cm. The electrostatic field is parallel to the surface normal of the thin film.

is not exactly normal to the chain axis. In order to satisfy $\tau = \mathbf{P} \times \mathbf{E} = 0$, the chain alignment in the electrostatic field perpendicular to the thin film normal should be tilted about 20° away from the homeotropic arrangement. The observed tilted angle of 10 rather than 20° may arise from a competition between surface-induced and electrostatic-field-induced alignments. Note that the surface-induced chain orientation always takes the homeotropic alignment. If this speculation is held, it suggests that the surface effect still plays a role in this chain realignment experiment. This may reveal that thermodynamically, the balance of the free energies in both surface and electrostatic field effects may stabilize the 10°-tilted chain realignment experimentally observed.

4. Conclusions

The surface-induced homeotropic chain alignment in the coTPP-7/11(5/5) thin films can be realigned after an electrostatic field is applied. When the electrostatic field is parallel to the thin film surface normal, the chain molecules in the thin films are realigned to a uniaxially homogeneous alignment, similar to the oriented fibers. However, a 10°-tilted chain realignment can be observed when the electrostatic field is applied perpendicular to the thin film surface normal. It is recognized that the chain realignment under an electrostatic field depends upon the direction of the electrostatic field with respect to the molecular permanent dipole moment of the coTPP-7/11(5/5). The experimental

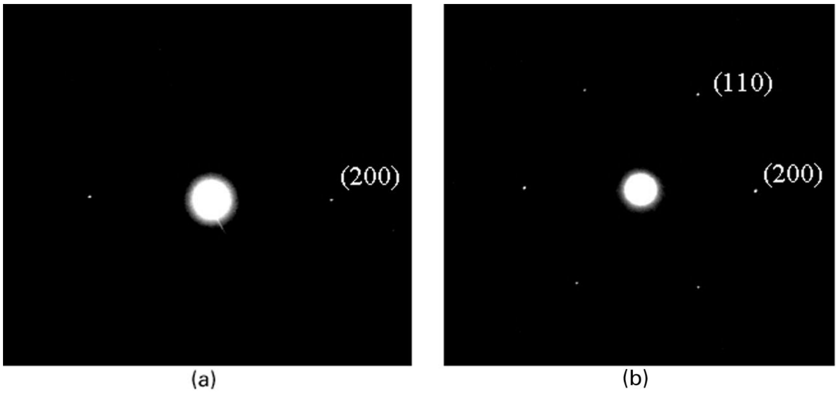


Fig. 5. ED patterns without (a) and with (b) a 10°-tilting with respect to the a^*-axis of the coTPP-7/11(5/5) thin films after treatment in an electrostatic field having an intensity of 5 kV/cm. The electrostatic field is perpendicular to the thin film normal.

observations can be explained by the negative dielectric anisotropy in coTPP-7/11(5/5), $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$, and therefore, the chain molecular axis of the coTPP-7/11(5/5) prefers to be aligned in a direction perpendicular to the electrostatic field. Both the surface and the electrostatic field effects can affect the chain realignment process.

Acknowledgements

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