

Mechanism of electric-field-induced segregation of additives in a liquid-crystal hostLu Lu,¹ Vassili Sergan,² and Philip J. Bos^{1,*}¹*Chemical Physics Interdisciplinary Program, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA*²*Department of Physics and Astronomy, California State University, Sacramento, 6000 J Street, Sacramento, California 95819, USA*

(Received 21 August 2012; revised manuscript received 3 October 2012; published 27 November 2012)

The mechanism for electric-field-induced segregation of additives, containing a polar group, in a host liquid crystal is proposed. It is shown that the polarity of an applied dc electric field, or the frequency of an ac electric field, strongly influences the segregation of reactive monomers containing an ester group. An explanation of this result is offered based on the association of dissolved ions with polar groups of the reactive monomers. This association is considered to cause these types of additives to drift to the cell surface in the presence of an external electric field. The described mechanism can be applied to the segregation of a broad range of additives in a liquid-crystal host.

DOI: [10.1103/PhysRevE.86.051706](https://doi.org/10.1103/PhysRevE.86.051706)

PACS number(s): 61.30.Gd, 61.30.Vx

I. INTRODUCTION

Segregation of additives, such as chiral molecules or reactive monomers could open new device fabrication techniques for liquid-crystal (LC) devices. For example, the effect of the dc electric field on the broadening of the reflection band has been observed [1,2] in polymer stabilized cholesteric liquid crystals; however, the segregation mechanism is not clear.

Causing a polymer layer to be localized on the surface has applications not only in new types of electro-optical devices, but also for information displays. In the polymer stabilized vertical alignment system [3], it has been pointed out that it is beneficial to polymerize monomers on a LC boundary [4–7] to achieve better electric-optic properties of the devices, such as response time, driving voltage, and viewing angles. However, those papers [4–7] did not make the mechanism of the electric-field effect on monomer segregation clear.

Several approaches have been given toward the goal of causing monomers to be polymerized on a surface instead of in LC bulk. One is spin-coating reactive monomers [8]. Another is using a phase separated film [9] formed by a joint effect of strong light absorption, slow polymerization, phase separation, and fast diffusion of small molecules. Another is selecting the wavelength of the polymerization inducing UV light [10], based on the UV absorption spectrum of the LC host, to cause the intensity of UV light to decrease as a strong function of distance from the illuminated surfaces. Another is utilizing an electric field. It has been suggested [11] that a precure process of applying an electric field *before* exposure to UV light could facilitate the segregation of reactive monomers to the surface and could provide an improved surface director alignment method. However, the mechanism of the effect of an electric field on monomer segregation has not been clarified.

In this paper, we focus on understanding the effect of an electric field on the segregation of guest molecules in a liquid-crystal host. An application of the segregation of reactive monomers to an improved surface alignment method is considered as verification of the proposed mechanism.

II. OBJECTIVE

It is the goal of this paper to understand how an applied voltage affects the segregation of guest molecules in a liquid-crystal host. Our hypothesis to explain this effect is as follows: Polar guest molecules that are associated with ions can be driven by an applied electric field to the surfaces of the cell. It is further assumed that the guest molecules driven to the cell surface tend to stay there as a phase separated layer. We aim to check predicted results based on this hypothesis. Predicted results are as follows: (1) When a dc field is applied, more guest molecules are deposited on one surface than on the other; and (2) when an ac field is applied, more guest molecules are transported to the surfaces while the electric-field frequency is lower.

III. EXPERIMENTAL METHODS

A UV illumination stage is set with a collimated UV light source (peak at 365 nm, light intensity at 3.5 mW/cm²). Two mirrors are arranged so that the UV light intensity illuminated on both sides of a LC cell is the same (Fig. 1). A two-step process is carried out: (1) An electric field is applied on the LC cell before turning on the UV light for assisting the monomer movement (precure process). (2) Then, the UV light is turned on while an electric field is applied on the sample at the same time (cure process). The voltage applied during the precure process is called precure voltage; voltage applied during the cure process is called cure voltage. To check our hypothesis about the effect of an ac (or dc) electric field on monomer transportation, the polymer layer thickness and LC pretilt angles on the “left substrate” and “right substrate” after this two-step process are measured.

In this paper, we used the BL006 nematic mixture (from EMD Chemicals) (the nematic or isotropic phase transition temperature is 113 °C; birefringence is $\Delta n = 0.286$, dielectric anisotropy is $\Delta\epsilon = 17.3$ at 25 °C). We added 1.2% of RM 257 (from EMD Chemicals) and about 0.12 wt % of Irgacure 651 photoinitiator sensitive to UVA and UVB (from Sigma-Aldrich). In the following experiments (Secs. III A–III C), a fresh mixture was heated to the isotropic phase and was vortex mixed for 3 min before being filled into glass cells.

*pbos@kent.edu

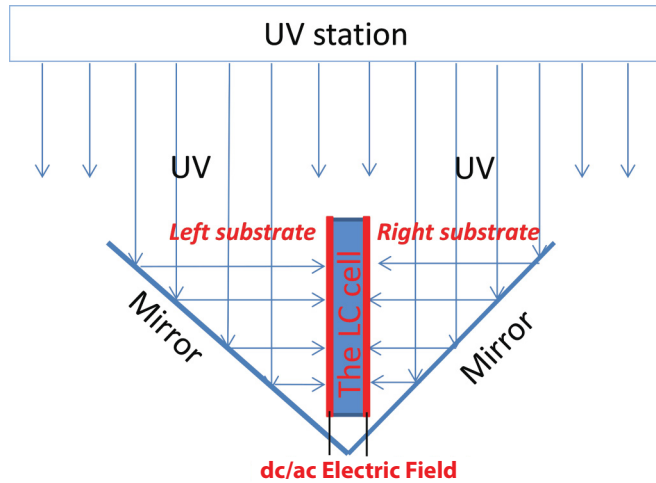


FIG. 1. (Color online) A V-shaped UV station is used for making samples. A dc or ac electric field is applied to the LC cell before (preure process) and during (cure process) the polymerization.

For different fabrication conditions (an ac or dc electric field), several cells are fabricated.

A. Scanning electron microscope characterization

A scanning electron microscope (SEM) is used to check the thickness and the morphology of the polymer layer on the cell surface. However, the resolution of the Hitachi S-2600N SEM for polymer samples is only about 100 nm. Therefore, thick cells (around $65 \mu\text{m}$) are made to form a thicker polymer layer on each substrate. Here, cells are made by using nonconductive tape as a spacer between the substrates that are held together with clips. With the removal of the clips, the cell is easily disassembled, and the substrates are then immersed in a mixture of *n*-hexane: methanol = 4:1 (volume ratio) for a few minutes to extract the liquid crystal. A sharp razor blade is utilized to form an edge of the polymer layer on the substrate. Then, a thin gold layer is sputtering on the cell surface, as the conductive layer, for the SEM study performed with the substrates tilted at 60° to see the cross section of the polymer layer.

B. Atomic force microscopy characterization

An atomic force microscope (AFM) (Digital Instruments, Nanoscope III Multimode Scanning Probe Microscope) was used in a noncontact mode for improved measurement resolution of the layer thickness. For each sample, the section analysis method of the AFM is used to determine the height of the polymer layer thickness of each location (d_i). For each tested sample, the layer thickness (d_i) is measured at 20 different locations, and then the averaged value of the layer thickness (\bar{d}), the standard deviation (σ), and the 95% confidence intervals are calculated. For an ac electric field, two samples are cured at different frequencies. The “ac cells” are precured (no UV light applied) with 120 V 6000 and 60 Hz ac for 20 min and are cured (with UV light applied) with 120 V 6000 and 60 Hz ac for 10 min. “dc Cell2” is precured with a 180 V dc field for 10 min and is cured with a 180 V dc field for 5 min. “dc Cell3” is precured at a 180 V dc field for 40 min and is cured at a 180 V dc field for 5 min. UV light intensity, when the cure voltage was applied, was $3.5 \text{ mW}/\text{cm}^2$.

C. Pretilt angle measurement

Samples for the pretilt measurement are prepared following this procedure: Top and bottom substrates are coated with the polyimide PI2555, which is rubbed in the opposite direction on the two surfaces. Nonconductive tape is applied along the edge of the bottom indium tin oxide (ITO) glass substrate to set the cell gap. Another piece of ITO glass is placed on top and is held in place with binder clips to form the cell. A fresh mixture of 1.2% RM257 in BL006 is filled into the cells. A defined voltage is applied during the precure process (no UV light) and the cure process (with UV light). After curing, the cell is disassembled by removing the clips, and each substrate is cut in half. Then, the halves are reassembled into two new cells whose substrates are both from the same substrate of the original cell. For different fabrication conditions (an ac or dc electric field), several cells are fabricated.

The magnetic null method [12] with capacitive detection is used to measure the pretilt angle. The measuring voltage on test cells was 100 mV. For cells fabricated with the same

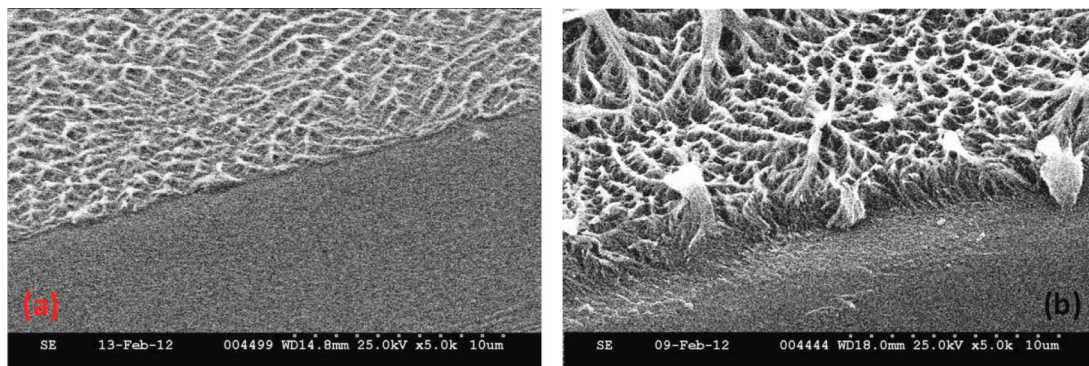


FIG. 2. (Color online) SEM images of cells cured under the dc field. (a) Substrate connected to the positive side of the dc voltage source and (b) substrate connected to the negative side.

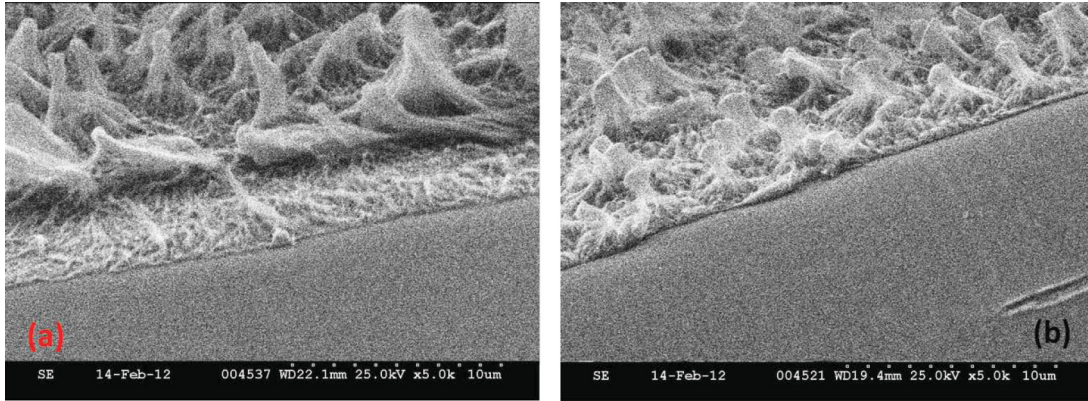


FIG. 3. (Color online) SEM images of cells cured under the ac field. (a) Left side substrate and (b) right side substrate.

conditions, the averaged value of the pretilt angle is recorded in the Results section.

D. Retardation measurements of regions of localized polymer segregation

A single polymerized stripe is made by inserting a photomask with a single 800 μm slit between the UV light source and the cell. A fresh mixture of 1.2% RM257 in BL006 was mixed by sonication at 70 °C for 10 min and was filled into a 22 μm thick ITO coated glass substrate cell, with rubbed polyimide PI2555 for the alignment layer, at room temperature. The frequency of the applied field during the precure process (no UV) and cure process (with UV) is varied. The UV light intensity for the cure process is 3.5 mW/cm². After the cure, a polarized light microscope with a green light color filter (λ = 543 nm) is used to observe the phase retardation difference (Δδ) between the cured area and the noncured area. A larger phase retardation difference represents a larger pretilt angle in the cured area and provides a simple and very direct approach to reveal the effect of the electric field on monomer segregation.

TABLE I. Results summary of polymer layer thickness by AFM.

ac cells	60 Hz ac cell (nm)	6000 Hz ac cell (nm)
Averaged value	135	37
Standard deviation	37.6	7.7
95% confidence interval	[118,151]	[34,41]
dc Cell2	(+) side (nm)	(-) side (nm)
Averaged value	48	171
Standard deviation	6	56
95% confidence interval	[46,51]	[146,196]
dc Cell3	(+) side (nm)	(-) side (nm)
Averaged value	64	400
Standard deviation	19	203
95% confidence interval	[56,73]	[312,490]
dc Cell4	(+) side (nm)	(-) side (nm)
Averaged value	54	485
Standard deviation	11	65
95% confidence interval	[49,59]	[457,514]

IV. RESULTS

A. Morphology of a segregated polymer on surfaces as a function of a dc or an ac electric field

For these measurements, cells were used that had a precure voltage of 180 V dc (or ac) field applied for 20 min and then were cured at a 180 V dc (or ac) field for 10 min. For each type of fabrication condition, several cells were made. SEM images of each type of cell were recorded.

The polarity of the dc field is observed to have a strong effect on the polymer layer (Fig. 2). By using the dc field during the precure and cure processes, the polymer layer formed on each substrate has a very different layer thickness and morphology. A thicker polymer layer is formed on the negative side charged glass substrate, which implies more monomers moved to that side [Fig. 2(b)].

By using a 60 Hz ac field during the precure and cure processes, both substrates form the same thickness polymer layer with similar morphology (Fig. 3). It infers that, under an ac field, monomers are equivalently moved to both substrates.

B. Polymer thickness on a surface as a function of the polarity of a dc electric field or the frequency of an ac electric field

With the above procedure in Sec. III B, the layer thickness information on each substrate has been calculated and has been summarized in Table I. The frequency of an ac electric field has a strong influence on the formed layer thickness. A thicker polymer layer was formed when using a lower frequency ac field. Comparing the positive side and negative side charged substrate in each dc-field cured samples, the polarity of a dc electric field is important.

TABLE II. dc-field cured cells have different pretilt values on the left and right substrates, which depend on the polarity of the dc field.

Fabrication conditions	Pretilt angles
1) Precure at 180 V dc, 20 min	θ ₊ = 40°
Cure at 180 V dc, 5 min	θ ₋ = 85°
2) Precure at 180 V dc, 40 min	θ ₊ = 45°
Cure at 180 V dc, 5 min	θ ₋ = 85°

TABLE III. ac-field cured cells have similar pretilt values on the left and right substrates. A lower frequency ac field generates a bigger pretilt value.

Fabrication conditions	Pretilt angles
1) Precure at 120 V, 6000 Hz ac, for 20 min Cure at 120 V, 6000 Hz ac, for 10 min	$\theta_L = 40^\circ$ $\theta_R = 42^\circ$
2) Precure at 120 V, 60 Hz ac, for 20 min Cure at 120 V, 60 Hz ac, for 10 min	$\theta_L = 85^\circ$ $\theta_R = 85^\circ$

C. Comparisons between the effect of dc and ac electric fields on pretilt angles

When the dc electric field is used for the precure and cure processes, the left and right substrates of the cell have very different pretilt angles, which is a direct indication of a difference in the polymer layers. In Table II, θ_+ (or θ_-) is the pretilt angle of the cell assembled with the substrate, which is connected with the positive (or negative) side of the dc power supply during the precure and cure processes.

In comparison, when the ac field is used for the precure and cure processes, pretilt angles on the left (θ_L) and right (θ_R) substrates do not have a big difference (Table III). However, the frequency of the ac field has a strong function on the magnitude of the pretilt angles. A low frequency (e.g., 60 Hz) ac field is able to induce larger pretilt angles than a high frequency ac field (e.g., 6000 Hz).

D. Effect of the ac electric-field frequency before and during the polymerization process

The effect of the ac-field frequency before the UV initiated polymerization process (precure voltage) is studied. In this comparison, only the frequency of the precure voltage is varied; all other experimental conditions are kept the same. As shown in Table IV, when the precure voltage is 60 Hz, the cured area gives the largest pretilt angle with these conditions.

Next, without a precure process, the effect of the ac-field frequency during the polymerization process (cure voltage) is investigated. In this comparison, only the frequency of the cure voltage is varied. Samples cured at a 6000 Hz ac field show the minimum pretilt angles in the cured area (Table V). Therefore, a low frequency ac field at the cure process correlates achieving large pretilt angles, which is consistent with a greater effect from the surface polymer layer.

These results demonstrate the strong dependence of the frequency of the electric field on controlling the pretilt angles and, therefore, the surface polymer layer thickness.

TABLE IV. Effect of precure conditions on pretilt angles: Cells are precured with 100 V (60 or 6000 Hz) for 15 min and are cured with a 100 V 6000 Hz electric field for 5 min under UV light.

Precure condition	Pretilt angle
No precure	38°
Precured at 60 Hz	52°
Precured at 6000 Hz	38°

TABLE V. Effect of cure condition on pretilt angles: All samples are cured at 100 V with different frequencies for 5 min without a precure process.

Cure condition	Pretilt angle
Cure at 1 Hz	58°
Cure at 10 Hz	58°
Cure at 60 Hz	61°
Cure at 6000 Hz	38°

V. DISCUSSION

As shown in the above results, the polarity of a dc electric field and the frequency of an ac electric field have a strong effect on both the polymer layer thickness and the pretilt angles. In this section, a possible mechanism for this effect is discussed.

A. Possibility of ionic association with reactive monomers

The strong dc-field effect on the polymer layer thickness and surface pretilt angles can be explained by the ion association ability of RM257. Ions in a liquid-crystal host have the potential to associate with the reactive monomer RM257 because of its polar groups.

It has been previously made clear that both the ester group and the cyano group have strong interactions with positive ions [13]. The infrared spectrum of the host liquid-crystal BL006 [14] shows the existence of cyano groups in the BL006 mixture but no ester groups. The reactive monomer RM257 has four ester groups, which implies RM257 has a strong potential for ion association. Additional evidence in the literature of the strong ion association power of RM257 has been given [15] by a comparison with RM84 (which has two ester groups) of the measured residual dc voltage.

Visualizing the partial charge of the atoms in a molecule is a good approach for understanding potential interactions with ions, therefore, the partial charge of RM257 was calculated using Chem3D. In Fig. 4, atoms with large partial charges are indicated, and it is seen that oxygen atoms of the ester groups have a large negative partial charge and have the potential to associate with positive ions.

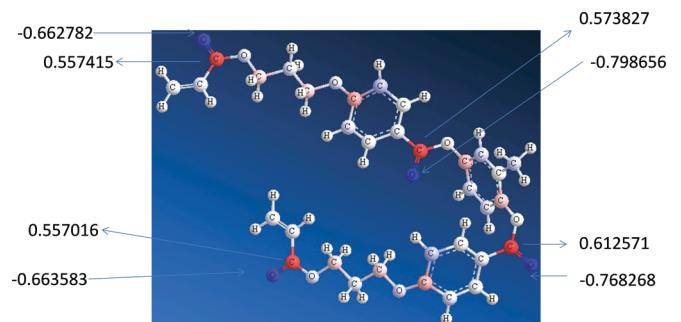


FIG. 4. (Color online) Partial charges for RM257.

TABLE VI. Mobility of ions and ion drift time.

Ion size (nm)	Mobility ($\text{m}^2 \text{v}^{-1} \text{s}^{-1}$)	Ion transit time (ms)
0.5	9.56×10^{-10}	5
1	4.78×10^{-11}	10
5	9.56×10^{-11}	50

B. Motion of reactive monomers with associated ions in an electric field

The effect of the ac-field frequency can be explained by the motion of reactive monomers that are associated with ions. Due to the large combined size of the ions and associated reactive monomers, the mobility of them is relatively small. The mobility (μ) of ions in liquid crystals with different sizes (r) has been calculated by Sawada *et al.* [16] using $\mu\eta = q/6\pi r$, where q is the charge that we assume is $q = 4 \times 1.602 \times 10^{-19} \text{ C}$ because of the existence of four ester groups in RM257 (that we assume are each associated with an ion). Because of the relatively high viscosity ($\eta = 71 \text{ cP}$ at 20°C) of the LC BL006, the mobility (μ) of ions in the LC BL006 is estimated to be on the order of 10^{-10} – $10^{-11} \text{ m}^2 \text{v}^{-1} \text{s}^{-1}$. Accordingly, the mobility in this range corresponds to a transit time (t) of 5–50 ms between electrodes $22 \mu\text{m}$ apart under an applied voltage of 100 V as shown in Table VI. [The calculation process of the ion transit time (t): $t = d/V_d$; d is the cell gap; V_d is the drift velocity, $V_d = \mu E$; E is the electric field $E = V/d$. So, the response time is $t = d/(\mu E)$.]

Based on the molecular structure of RM257 in Fig. 4, its molecular size is estimated to be 5 nm by Chem3D. So, the corresponding ion transit time is predicted to be 50 ms.

Accordingly, when an ac-field frequency of 6000 Hz is applied and the potential is only constant for 0.16 ms, there is not significant segregation of the reactive monomers. However, a low frequency electric field does cause reactive monomers with ester groups to be transported to the surface and to be localized there.

VI. SUMMARY

The effect of an electric field on facilitating the localization of reactive monomers at the surface of a liquid-crystal cell has been confirmed by pretilt angle measurements, SEM, and AFM characterizations. When an ac field is applied, monomers are evenly deposited on two substrates of the cell with a greater thickness for a low frequency electric field as compared to when a high frequency field is applied. When a dc field is applied, monomers are deposited on one surface more than on the other. A possible mechanism for this effect is that ions are associated with the reactive monomers and cause them to drift to the cell surface due to the electrostatic force. The proposed mechanism fits very well with the ion solvation power [14,15] of the considered monomer and the drift rate estimation [16]. With the knowledge of the electric-field effect on controlling segregations of additives that contain polar groups, a broad range of applications for optical and biological [17] devices is opened.

ACKNOWLEDGMENTS

Thanks to L. Qiu for her great assistance with the SEM and AFM characterizations, and thanks to Pixel Optics for their support for this project.

-
- [1] V. T. Tondiglia, L. V. Natarajan, C. A. Bailey, M. M. Duning, R. L. Sutherland, D. Ke-Yang, A. Voevodin, T. J. White, and T. J. Bunning, *J. Appl. Phys.* **110**, 053109 (2011).
 - [2] W. Hu, H. Y. Zhao, L. Song, Z. Yang, H. Cao, Z. H. Cheng, Q. Liu, and H. Yang, *Adv. Mater.* **22**, 468 (2010).
 - [3] R. Penterman, S. L. Klink, H. de Koning, G. Nisato, and D. J. Broer, *Nature (London)* **417**, 81 (2002).
 - [4] C. H. Pai, T. Y. Cho, S. C. Tsai, C. Y. Chiu, T. S. Chen, H. C. Lin, J. J. Su, and A. Lien, *J. Soc. Inf. Disp.* **18**, 960 (2010).
 - [5] S. G. Kim, S. M. Kim, Y. S. Kim, H. K. Lee, S. H. Lee, G. D. Lee, J. J. Lyu, and K. H. Kim, *Appl. Phys. Lett.* **90**, 261910 (2007).
 - [6] K. Maruyama, T. Houryu, and Y. Iimura, *Jpn. J. Appl. Phys., Part 1* **46**, 726 (2007).
 - [7] Y. Kizu, R. Hasegawa, I. Amemiya, S. Uchikoga, and H. Wakemoto, *J. Soc. Inf. Disp.* **17**, 647 (2009).
 - [8] R. A. M. Hikmet and C. de Witz, *J. Appl. Phys.* **70**, 1265 (1991).
 - [9] T. Qian, J.-H. Kim, S. Kumar, and P. L. Taylor, *Phys. Rev. E* **61**, 4007 (2000).
 - [10] S. W. Kang, S. Sprunt, and L. C. Chien, *Macromolecules* **35**, 9372 (2002).
 - [11] V. V. Sergan, T. A. Sergan, and P. J. Bos, *Chem. Phys. Lett.* **486**, 123 (2010).
 - [12] T. J. Scheffer and J. Nehring, *J. Appl. Phys.* **48**, 1783 (1977).
 - [13] M. Bremer, S. Naemura, and K. Tarumi, *Jpn. J. Appl. Phys., Part 2* **37**, L88 (1998).
 - [14] Y. Zhao, Y. Chenard, and N. Paiement, *Macromolecules* **33**, 1049 (2000).
 - [15] Y. Nakanishi, K. Hanaoka, M. Shibasaki, and K. Okamoto, *Jpn. J. Appl. Phys.* **50**, 051702 (2011).
 - [16] A. Sawada, K. Tarumi, and S. Naemura, *Jpn. J. Appl. Phys., Part 1* **38**, 1423 (1999).
 - [17] I. H. Lin, D. S. Miller, P. J. Bertics, C. J. Murphy, J. J. de Pablo, and N. L. Abbott, *Science* **332**, 1297 (2011).