SPECIAL TOPIC — Physical research in liquid crystal

Effect of fluorine groups and different terminal chains on the electro-isomerization of azobenzene liquid crystals*

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A series of azobenzene liquid crystals with one or two terminal acrylate groups were synthesized and their polymers were fabricated. The azobenzene liquid crystals and their polymers achieved the photoisomerization from the liquid crystalline trans-isomer to the isotropic cis-isomer with UV irradiation. Then, the cis to trans isomerization induced by an electric field was studied, the time required for electro-isomerization was measured, the texture change and absorption variation from cis to trans form induced by the electric field were observed clearly, and the time required for electro-isomerization was much shorter than that for thermal relaxation. The influence of the polar group (fluorine), terminal acrylate group, and flexible alkyl chain on the time of electro-isomerization was studied. The results show that the compounds with polar fluorine group require shorter time for electro-isomerization and the polymerization of terminal acrylate group delays the electro-isomerization.

Keywords: electro-isomerization, azobenzene liquid crystals, fluorine

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1. Introduction

Since its discovery in the mid-1800s,[1] azobenzene and its derivatives have attracted much attention because of their excellent properties. Azobenzene was mainly used as an organic dye. In 1937, Hartley reported the identification of cis-azobenzene.[2] Since then, the azobenzene molecule has been deeply studied and successfully applied in many areas, such as high-density optical memory elements,[3] molecular devices,[4] surface-modified materials,[5–8] light-switchable liquid crystal materials,[9,10] and light-sensitive biomolecules.[11,12]

Azobenzene has two isomers: the rod-like trans-isomer and the bent-like cis-isomer.[13–16] Interconversion between these two isomers can be achieved using UV–visible light,[17,18] thermal induction,[19–21] mechanical stress,[22] and electric field stimulation.[23–25] The trans-isomer is more stable thermodynamically than the cis-isomer, and the cis-isomer can spontaneously slowly transfer back to the trans-isomer in the dark at room temperature. Among these isomerization methods, the photoisomerization is the most used and its mechanism has been deeply studied, four pathways (which are rotation, inversion, concerted inversion, and inversion-assisted rotation) have been proposed. However, many factors such as irradiation wavelength, molecular structure, temperature, pressure, and solvent properties influence the isomerization mechanism.

The process of transformation from cis-isomer to trans-isomer of azobenzene induced by an electric field is called electro-isomerization.[3,24] Fujishima *et al.* first reported the electrochemical process of the azobenzene electro-isomerization.[3] The process includes two steps: the cis form azobenzene formed by UV irradiation is reduced to hydrazobenzene firstly, then the hydrazobenzene is oxidized to the trans form azobenzene. Later, Enomoto *et al.* found that the cis-isomer azobenzene could return to the trans isomer via an electrostatic process without redox reaction.[26] After that, several discoveries about electric induced cis-trans isomerization were reported. For instance, reversible cis–trans isomerization of azobenzene molecules on a metal Au (111) surface was achieved by scanning tunneling microscopy (STM).[23,27] However, the threshold voltage demanded for the cis-tans isomerization was very high, in the range of 10^3 V/μm.

In 2008, Tong *et al.* reported the fast electro-isomerization from cis-isomer to trans-isomer of azobenzene induced by a low static electric field.[24] The possible reason is that some ions might exist in the materials of azobenzene-doped LCs, and were aggregated onto the indium-tin-oxide (ITO) surfaces when an electric field was applied, the aggregated ions developed a higher internal field at the azobenzene solution and the electrode interface. The most probable mechanism is that the cis-azobenzene was electrolyzed to a radical anion, which could transfer to trans-azobenzene radical anion, then the trans radical anion reduced another cis-azobenzene to cis radical anion, at the same time the trans radical anion was

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oxidized to trans-azobenzene.[28,29]

For application, the discovery of electro-isomerization gives an opportunity to use the combining effects of photo and electro-isomerization. However, there are few reports of new compounds designed and synthesized for electro-isomerization, and there is as yet no reported study of the electro-isomerization of liquid crystal polymer. In this paper, a series of azobenzene liquid crystals with terminal acrylate group were synthesized and their electro-isomerization properties were researched. The terminal acrylate groups were polymerized with UV irradiation. The time required for azobenzene liquid crystals and their polymers conversion from cis-isomer to trans-isomer under an electric field was measured. The influence of the polar group (fluorine), acrylate group, and flexible alkyl chain on the electro-isomerization time was studied.

2. Experiments

2.1. Material preparation

Five azobenzene liquid crystals (azo-LCs) with terminal acrylate group were synthesized, their chemical structures are shown in Fig. 1. The synthetic route of azo-LC C is shown in Fig. 2. The synthesis of other azo-LCs was similar. All of the compounds were confirmed by nuclear magnetic resonance (^{1}HNMR, ^{19}FNMR, Bruker AVANCE 400MHz) and high-resolution mass spectrometry (HRMS, Micromass GCTTM). The phase transition temperatures were measured by DSC (Perkin Elmer Diamond DSC) and polarized optical microscope (POM, Nikon ECIPSE LV100POL, crossed polarizers).

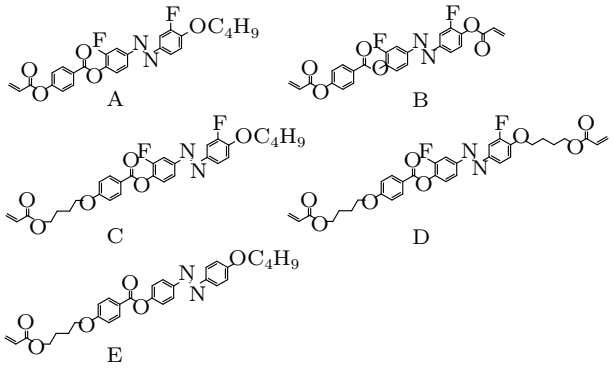


Fig. 1. Chemical structures of the synthesized azo-LCs A–E.

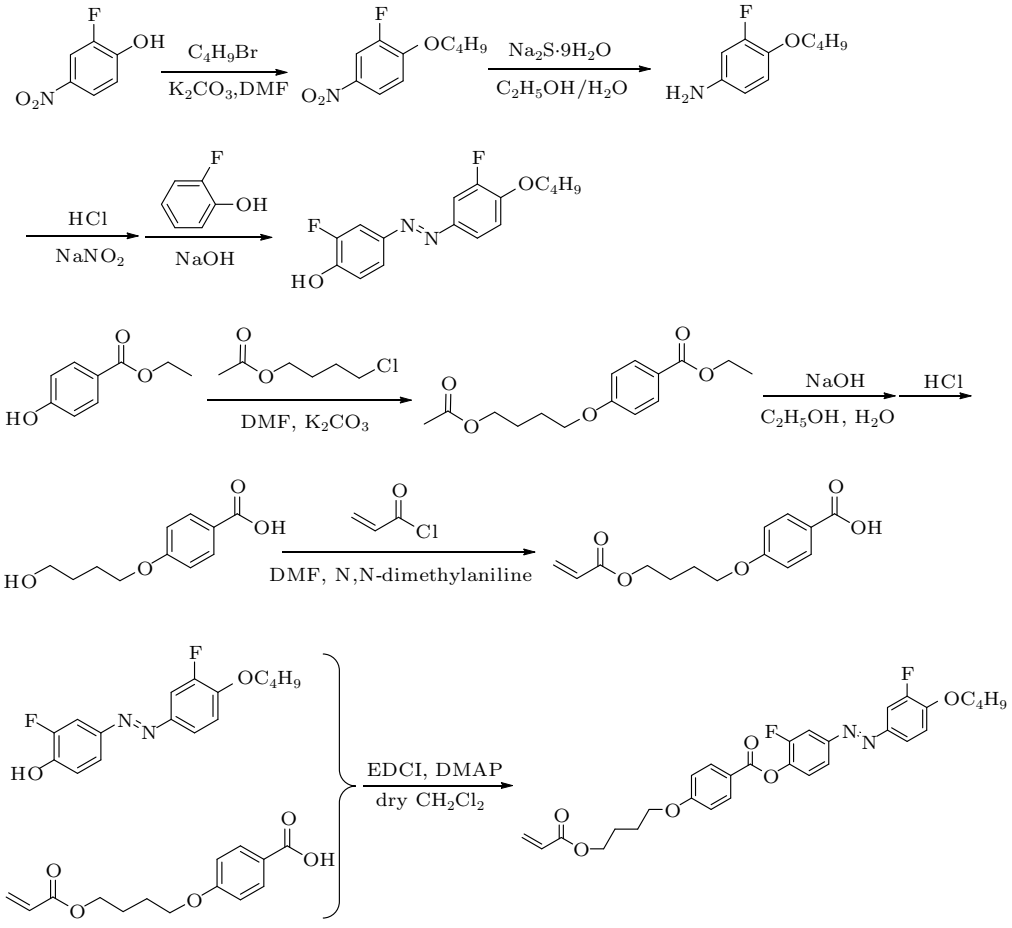


Fig. 2. The synthetic route of azo-LC C.

2.2. Methodology

For the IR measurement, two CaF_2 glass substrates were combined to fabricate a cell with the cell gap of 9.0 μm. Azo-LC and photoinitiator (0.5 wt.%, Irgacure 184, BASF) were mixed at liquid crystal state, and then were filled into the cell. The sample was irradiated by 365 nm light (UV LED, 160 mW/cm^2) for 30 min to initiate the molecules to polymerize. The IR spectra (Bruker alpha) of the before-and-after exposure sample were measured to characterize whether the molecules in the cell were polymerized or not.

For the electro-isomerization study, two samples were prepared for each azo-LC compound. Sample I: the azo-LC was heated to liquid crystal state on a hot stage and filled into an intimate-tin-oxide (ITO) coated cell with a 9.5 μm gap. Sample II: the azo-LC and photoinitiator (0.5 wt.%) were mixed at liquid crystal state then filled into an ITO coated cell with a 9.5 μm gap. Then the cell was irradiated by 365 nm light (UV LED, 160 mW/cm^2) for 30 min to initiate the molecules to polymerize.

The samples were set on a precisely controlled hot stage (Instec HCS-302) and maintained the temperature of 10 °C above the melting temperature for 10 min. Then, the samples were exposed at this temperature to 365 nm light with an intensity of 10 mW/cm^2 for 300 s to stimulate the photoisomerization of the azo-LC. The absorption variations and texture changes were recorded by a spectrometer and a CCD camera, respectively, as shown in Fig. 3. By applying a DC voltage (5 V, 10 V, 15 V, 20 V, 30 V, 40 V respectively) to the sample, the absorption variations and the texture changes were recorded.

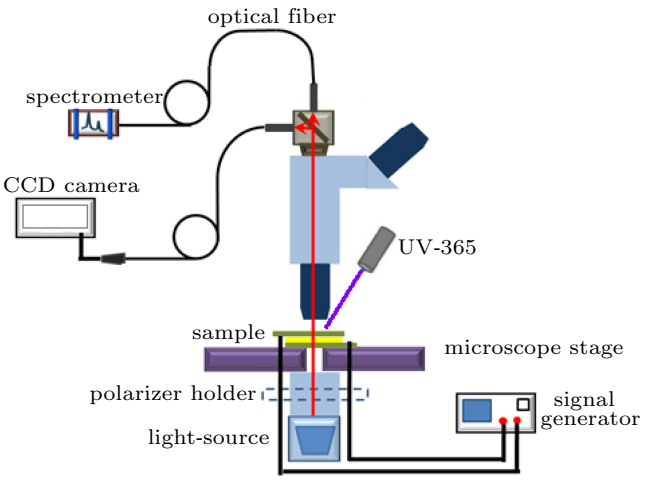


Fig. 3. (color online) The testing setup in the experiment. The sample was placed on a host stage. The backlight of the microscope was used as the white-light source. The electric field was applied through the signal generator. The UV light was applied through the UV LED. The backlight was split into two beams after transmitted through the sample, one was received by a spectrometer to record the absorption variations, and the other was detected by a CCD camera to monitor the texture changes.

3. Results and discussion

Firstly, the UV–visible absorption spectra of the azo-LCs were studied. The compounds were dissolved in dichloromethane with a low concentration (2.5×10^{-5} mol/L). The absorption spectra before and after UV irradiation were recorded. Figure 4 shows the absorption spectra of all the five azo-LCs. All of the azo-LCs show strong absorptions near 350 nm, which is correspond to the π–π^*. 365 nm UV–light was selected as the exposure source. Figure 5(a) shows the absorption spectra of azo-LC C under UV light irradiation (365 nm, 10 mW/cm^2, 10 s), quick drop of the peak around

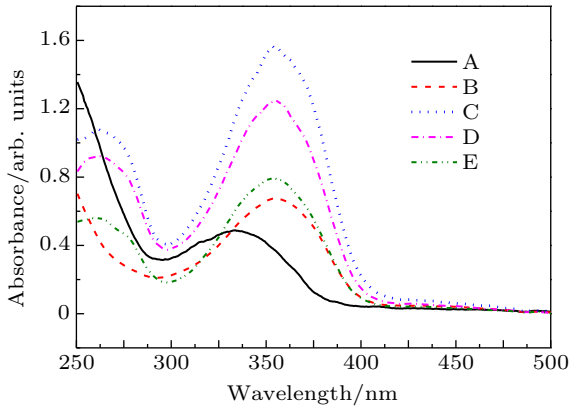


Fig. 4. (color online) UV–vis absorption spectra of azo-LCs.

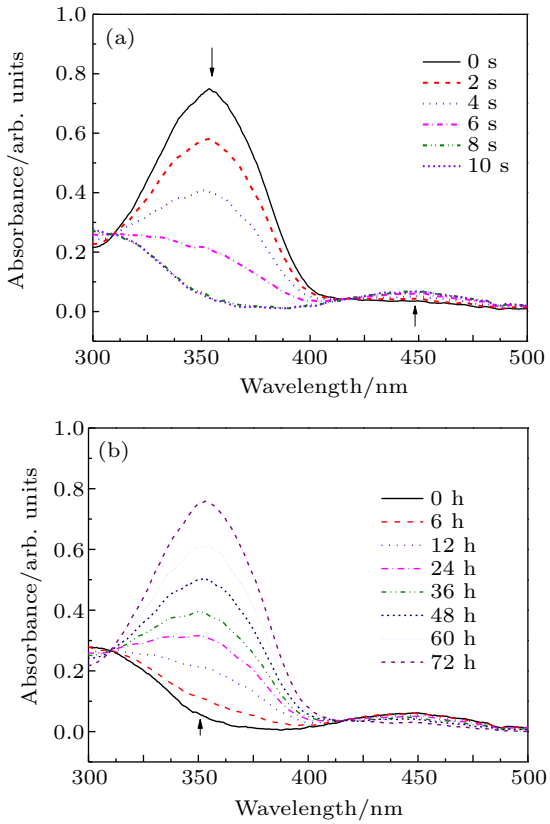


Fig. 5. (color online) UV–vis absorption spectra of azo-LC C: (a) under UV irradiation, (b) thermal relaxation in dark.

350 nm and slight rise of the peak around 450 nm due to efficient tans to cis photoisomerization are observed. Figure 5(b) shows the absorption spectra of the recovery in the dark, the recovery process is very slow (more than 2 days), which is due to the very slow thermal conversion of the cis-isomer azo-LC back to the trans form.

The isomerization of the azobenzene compound is very difficult when the compound is at a crystal state, so the azobenzene compound is usually dissolved or doped in fluid material for study and application. If the azobenzene molecule has a liquid crystalline property, at the liquid crystal phase, then the molecular isomerization is much easy due to the fluidity. The molecular shape in this paper was designed as the rod-like shape which is benefit to the liquid crystal phase. The polar fluorine substituents increase the molecular polarity and decrease the viscosity and clearing temperature. The liquid crystalline properties of the synthesized compounds were studied. As expected, all five compounds have liquid crystalline phase, N phase with typical texture was observed (Fig. 7). As the compounds have terminal acrylate groups which can be polymerized by UV irradiation, the polymer can be formed at liquid crystal phase to obtain the ordered molecular arrangement. Fortunately, the obtained polymers are also liquid crystals. The melting and clearing temperatures of the polymers are lower than those of their monomers. The data are shown in Table 1. The IR spectra were used to verify the polymerization of azo-LCs. Figure 6 shows the IR spectra of azo-LC C before-after UV exposure. Comparing the two spectra, the characteristic peaks at 1633.1 cm^{-1} and 985.2 cm^{-1} for the terminal acrylate group are decreased obviously after UV exposure, indicating the polymerization of the acrylate groups. Figures 7 and 8 show the micrographs of azo-LC C and its polymer.

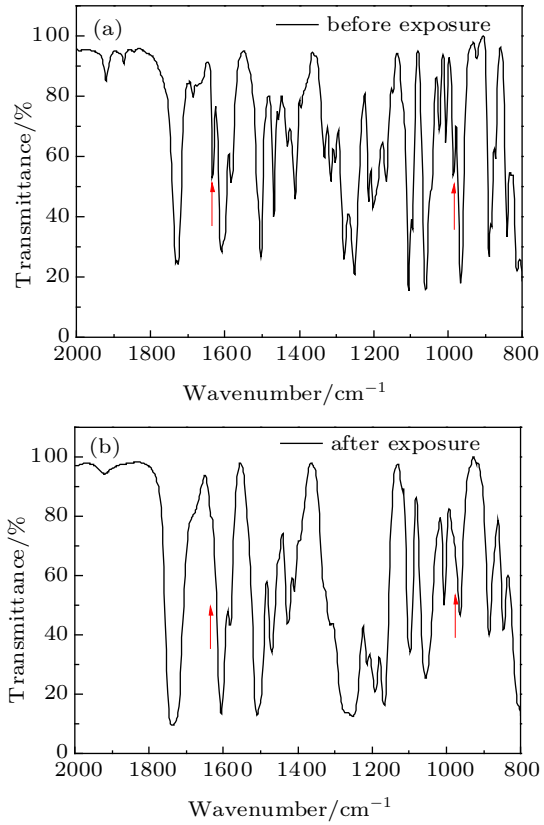


Fig. 6. (color online) The IR spectra of azo-LC C (a) before and (b) after UV exposure.

Table 1. The phase transition temperatures of azo-LCs and their polymers.

Sample	Material	Phase transition temperature/°C	
		Cr-N	N-Iso
S1	A	143	235
S2	A'polymer	133	220
S3	B	155	223
S4	B'polymer	137	198
S5	C	77	174
S6	C'polymer	67	164
S7	D	83	186
S8	D'polymer	63	172
S9	E	95	205
S10	E'polymer	73	198

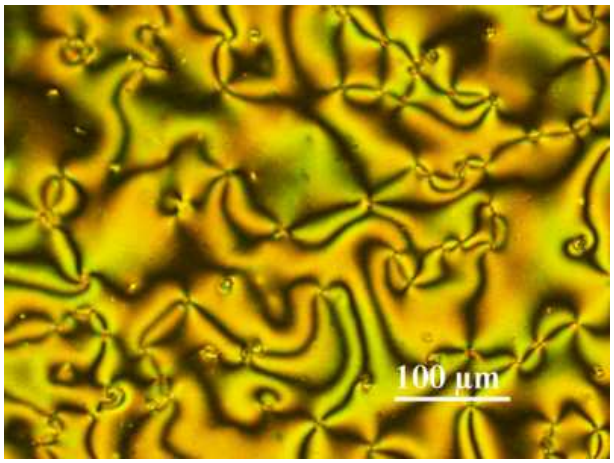


Fig. 7. (color online) Micrograph of azo-LC C (N phase at 120 °C, crossed polarizers).

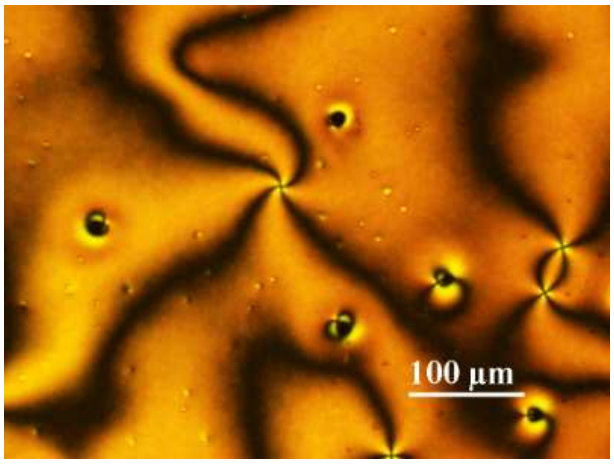


Fig. 8. (color online) Micrograph of azo-LC C's polymer (N phase at 158 °C, crossed polarizers).

The time required for electro-induced cis to trans isomerization of each azo-LC and their polymers was measured. The samples were heated to nematic phase at the hot stage, a UV light was utilized to achieve the photoisomerization from trans to cis-isomer, then an electric field (5 V) was applied to the cell (the cell gap is 9.5 μm). The texture change was observed by the CCD camera and the absorption variation was monitored by the spectrometer. Figure 9 shows the absorption variations of azo-LC C around 450 nm. Before UV irradiation, the absorbance at 450 nm was weak owing to the dominant of trans-isomer. Then, the peak rose when the sample was irradiated by UV light because of the efficient photoisomerization, as shown in Fig. 9(a). Later, with the applying of an electric field, the peak became weak gradually, finally, the peak coincided with the absorb peak before UV irradiation, as shown in Fig. 9(b).

Figure 10 shows the texture changes during the process. In the nematic phase (Fig. 10(a)), the dominated trans-isomer has a rode-like geometry formation which is beneficial to liquid crystal. The disappearance of nematic phase in Fig. 10(b) corresponds to the photoisomerization. It is well known that the bent cis-isomer has no liquid crystalline phase. The dark state in Fig. 10(c) means that the liquid crystalline phase disappeared, which indicates that the photoisomerization was completed, and the rod-like trans-isomers were converted to bent cis-isomers completely. The colourful platelets appeared again in Figs. 10(d) and 10(e) after the electric field was applied. After applying the electric field for 5 min, the DC voltage was taken off, the texture returned to the initial state, as shown in Fig. 10(f).

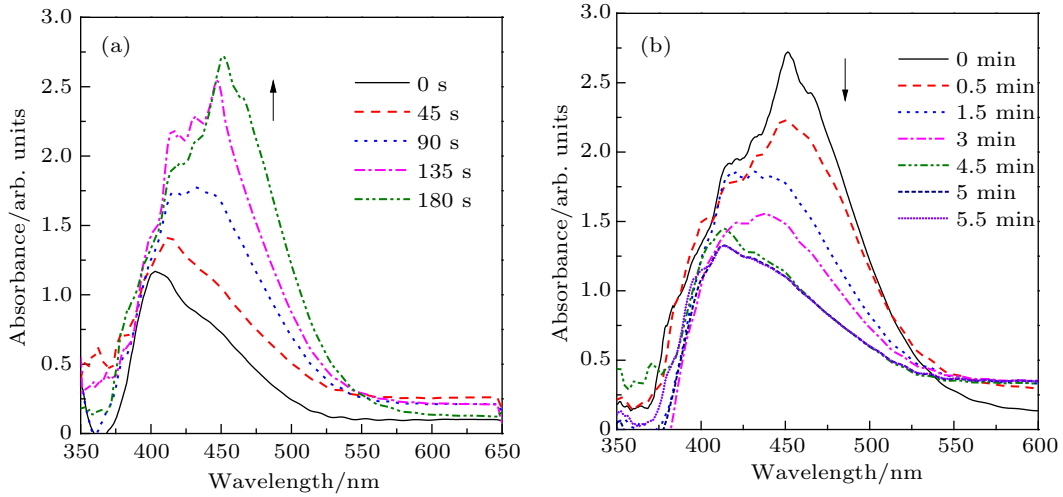


Fig. 9. (color online) The absorption variations of azo-LC C around 450 nm: (a) under UV irradiation (10 mW/cm^2), (b) with an electric field (5 V) applied.

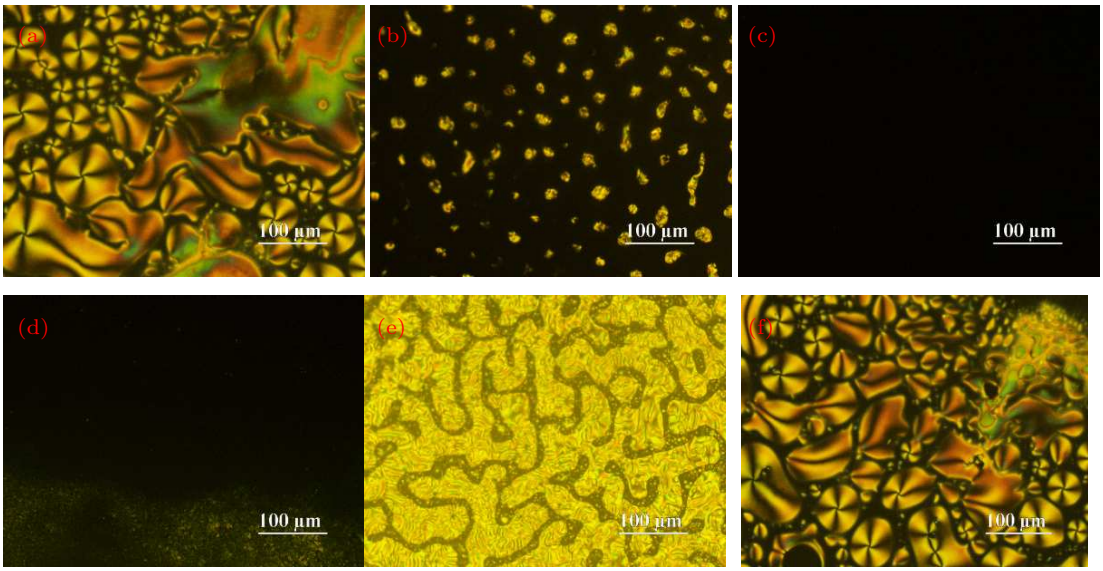


Fig. 10. (color online) Micrographs of azo-LC C during the photo and electro-isomerization: (a) before UV irradiation; (b) UV irradiation for 1.5 min; (c) UV irradiation for 3 min; (d) DC voltage on 30 s; (e) DC voltage on 3 min; (f) DC voltage off after applying the electric field for 5 min.

The time for isomerization of each compound from cis to trans form with or without electric field was measured. Tables 2, 3 and Figure 11 give the results. From the tables and figure, we can find that the time required for cis-trans electro-isomerizarion is much shorter than that without electric field. For the thermal relaxation without electric field, the isomerization time is more than 45 min. However, the electro-isomerization time required for all samples is in the range of 1–20 min, the effect of the electric field is significant. The time required for the polymers is more than that for their monomers because the networks in the polymers confine the structure change of the molecules.

Table 2. The time required for electron-isomerization of azo-LCs and their polymers.

Sample	Material	Temperature/°C	Time required for electro-isomerization/min					
			5 V	10 V	15 V	20 V	30 V	40 V
S1	A	153	9.0	7.0	5.0	4.5	3.0	2.5
S2	A'polymer	153	10.0	8.5	6.5	5.0	3.5	3.0
S3	B	165	15.0	13.5	9.5	7.5	4.5	2.0
S4	B'polymer	165	17.5	15.5	12.5	9.0	6.5	4.0
S5	C	86	5.0	4.0	3.5	3.0	2.0	1.0
S6	C'polymer	86	6.5	5.0	4.5	3.5	2.0	1.5
S7	D	93	16.5	14.0	11.5	9.0	6.5	3.0
S8	D'polymer	93	19.0	17.0	14.0	11.0	9.0	6.0
S9	E	110	10.0	8.5	7.0	5.5	3.0	2.0
S10	E'polymer	110	12.0	10.5	8.5	7.0	5.0	3.5

Table 3. The time required for thermal relaxation of azo-LCs and their polymers.

Sample	Material	Temperature/°C	Time required for thermal relaxation/min
S1	A	153	50
S2	A'polymer	153	70
S3	B	165	85
S4	B'polymer	165	110
S5	C	86	45
S6	C'polymer	86	60
S7	D	93	90
S8	D'polymer	93	120
S9	E	110	60
S10	E'polymer	110	75

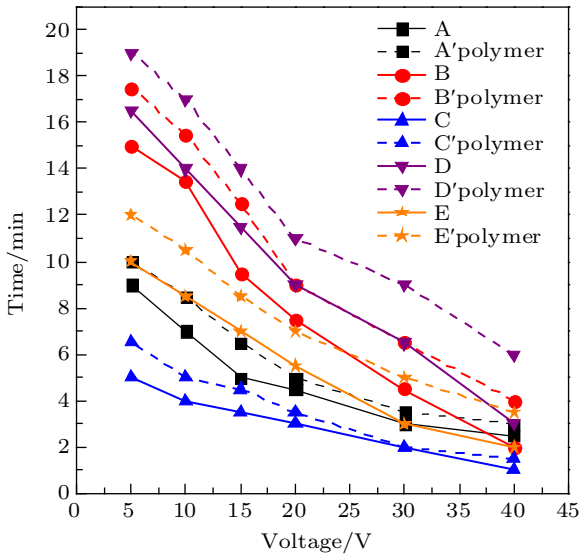


Fig. 11. (color online) The time required for electro-isomerization of azo-LCs and their polymers.

For application, the polymers are more useful than their monomers because of their better stability. The fastest electro-isomerization for C'polymer in our study required 1.5 min (40 V, cell gap 9.5 μm); when the DC voltage was decreased to 10 V, 5 min was needed, which is much shorter than those of the thermal relaxation.

In the five azo-LCs that we synthesized, four azo-LCs contain fluorine on phenyl ring except for azo-LC E. Azo-LCs B and D contain two terminal acrylate groups, and azo-LCs A, C, and E contain one. Azo-LCs C, D, and E contain flexible alkyl chain between the rigid core and the acrylate group. For investigating the effect of the polar fluorine group, terminal acrylate group, and flexible alkyl chain on the electro-induced cis to trans isomerization of azo-LCs, the electro-isomerization experiments were carried out at the same temperature. Considering the Cr-N transition temperature of azo-LC B is 155 °C and the N-iso transition temperature of C' polymer is 164 °C, 160 °C was chosen as the test temperature. Table 4 and figure 12 show the results.

The best result is obtained for compound C, and its polymer is also a good one among the polymers. Compound C and C'polymer have the polar fluorine groups, flexible alkyloxy terminal chains, and alkyl chains between the rigid cores and the acrylate groups. Such molecular structure leads to the fast electro-isomerization from cis form to trans form. As the electro-isomerization is supposed to an electrochemical process, larger polarity of the molecules with F group is benefit to electro-isomerization, the compounds B'polymer and D'polymer have the worst result because the molecules are polymerized at two terminals, and the strong networks prevent the molecular structure change.

Table 4. The time required for electro-isomerization of azo-LCs and their polymers at 160 °C.

Sample	Material	Temperature/°C	Time required for electro-isomerization/min					
			5 V	10 V	15 V	20 V	30 V	40 V
S1	A	160	7.5	6.5	5.0	4.0	2.5	2.0
S2	A'polymer	160	9.5	8.0	6.5	5.0	3.5	3.0
S3	B	160	14.5	12.5	9.0	7.0	4.5	2.0
S4	B'polymer	160	16.0	13.5	11.0	9.0	6.5	3.5
S5	C	160	4.5	4.0	3.0	2.5	1.0	0.5
S6	C'polymer	160	5.0	4.5	4.0	3.0	2.0	1.0
S7	D	160	14.0	11.0	9.0	6.5	3.5	1.5
S8	D'polymer	160	16.5	14.0	12.5	9.5	7.0	4.0
S9	E	160	7.0	5.5	5.0	4.0	2.0	1.5
S10	E'polymer	160	10.5	9.0	8.0	6.0	4.5	3.0

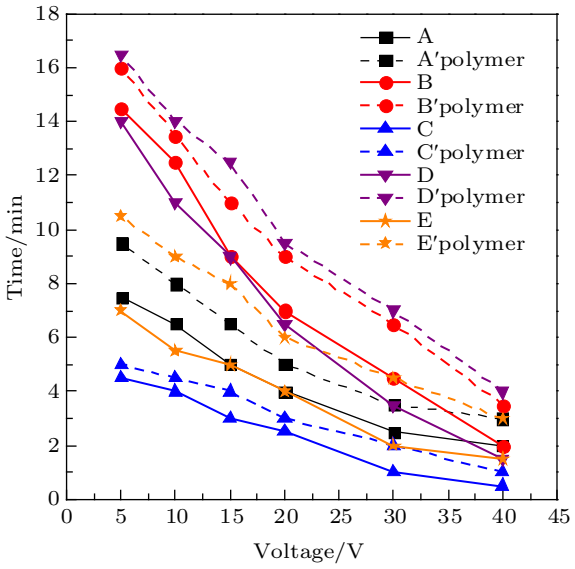


Fig. 12. (color online) The time required for electro-isomerization of azo-LCs and their polymers at 160 °C.

4. Conclusion

Five azobenzene liquid crystals were synthesized and their polymers were fabricated. Their liquid crystalline properties were investigated. It was found that polymerization can decrease the phase transition temperatures of the azobenzene liquid crystals. The time required for electro-induced cis to trans isomerization was measured. The influence of the polar group (fluorine), acrylate group, and flexible alkyl chain on the electro-isomerization was also studied. The results revealed that the fluorine group can accelerate the electro-isomerization. Polymerization of the terminal acrylate group delays the electro-isomerization. And the flexible alkyl chains are favorable for electro-isomerization of azobenzene liquid crystal polymer.

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