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Phase behaviour of mixtures of side-chain LC polyoxetanes with E7 and their field response

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We prepared and characterized a series of side-chain liquid crystalline (LC) homo- and copolyoxetanes containing varying fractions of the mesogenic 4-decyloxy-4'-cyanobiphenyl pendent and the non-mesogenic propoxy group. The miscibility of homo- and copolyoxetanes (Co-LCPs) with E7 also was studied. The LC properties of the Co-LCP/E7 mixtures were unique in that, although E7 is a nematic mixture, all the Co-LCP/E7 mixtures form layered smectic mesophases. Among the mixtures, the composition of 30 wt% of LCP bearing 16 mol.% of the mesogenic pendant, Co(16)-LCP, and 70 wt% of E7 formed the smectic phase over a broad range of temperature (−70 to 35°C), although the isotropization temperature of Co(16)-LCP itself was below room temperature. A flexible plastic display was constructed utilizing this mixture and its display characteristics were evaluated. For a device with a 10 μm thick active layer, the threshold voltage was about 30 V and exhibited a rising response time of 200 ms. The most remarkable observation made was that the blends revealed excellent memory behaviour.

1. Introduction

Flexible liquid crystal displays (LCDs) [1–4] based on plastic substrates and LCs are attracting a great deal of interest in academia as well as in industry because of their possible utilization in various display applications, including TVs and memory-type displays such as electronic papers and light shielding, for example, in smart windows.

A conventional approach to LCDs involving a polymeric matrix is the so-called polymer-dispersed LC display (PDLC) technology where phase separation between a crosslinked polymer matrix and small droplets of an LC compound dispersed in the continuous phase is utilized. A large number of papers [5–11] have been published on PDLC dealing with different factors controlling device performance.

Side-chain liquid crystalline polymers (SCLCPs) [12–35] have a structural feature combining the properties of low molar mass LCs and those of polymers, and, thus, exhibit field responsiveness as well as mechanical strength. Since many electro-optical applications require fast response time; polysiloxanes [16–27] and polyoxetanes [28–35] bearing pendant mesogenic groups have

been of particular interest due to the flexible nature of the main chains. Previously, we reported synthesis and characterization of new chiral SCLCPs exhibiting chiral smectic C (S_C^*) phases [34]. The main chains of the polymers were polyethers prepared by ring-opening polymerization [28–35] of oxetane monomers carrying a mesogenic substituent. Some of them revealed a fast response (0.3 ms) to an applied field with a spontaneous polarization of 20 nC cm^{−2}. Earlier, Coles and Simon [36] and Yamane *et al.* [24, 25] thoroughly studied switching behaviour of LCP/LC composites. The latter group found that polysiloxane SCLCP copolymers bearing *p*-cyanophenyl-*p'*-oxybenzoate mesogen pendants form the smectic A (S_A) phase but they are homogeneously miscible with E7 (Cr 263 N 333 I), a nematic mixture available from Merck. Moreover, some of the copolymer/E7 mixtures exhibited high-speed electro-optical switching (about 50 ms) and also a stable memory effect at room temperature. The miscibility between the smectic A matrix polymer and the nematic guest is rather unexpected, since, in the case of low molar mass LCs, it has been well established that miscibility is generally observed only between the isomorphic compounds or between compounds forming mesophases of the same or similar molecular orientation, as in nematic and cholesteric phases. This is often

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called the selective miscibility rule, which was originally proposed by Demus and Sackmann [37, 38]. Our previous studies [39, 40] also demonstrated that this rule satisfactorily applies to the mixing of main-chain LCs and dimeric LC compounds. In this investigation we studied the miscibility between a series of smectic SCLCPs, consisting of a polyoxetane main chain and *p*-cyanobiphenyl pendants, and E7. Preliminary studies on the electro-optical response of some of the mixtures are also reported. The *p*-cyanobiphenyloxydecyloxymethyl-substituted oxetane monomer was cationically copolymerized with a comonomer carrying the propoxy-methyl substituent.

2. Experimental

2.1. Monomer synthesis

The two monomers, **2** and **3**, were prepared following literature methods [28, 29, 33, 34], as shown in scheme 1.

2.1.1. 3-[(10-Bromodecoxy)methyl]-3-methyloxetane, **1**.

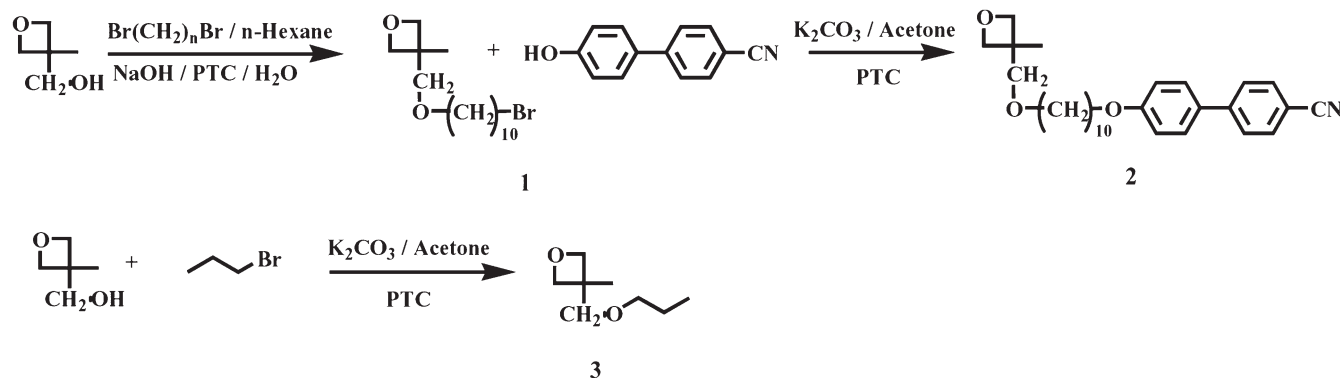
This compound was prepared following the literature method as described by Kawakami *et al.* [28, 29]. The crude product was purified by column chromatography (silica gel, eluent EA:hexane=1:15). The recovered yield was 78% (22.3 g). ¹H NMR (300 MHz, CDCl₃, ppm): 1.29 (s, CH₂CH₂CH₂), 1.31 (s, CH₃), 1.42 (m, CH₂CH₂CH₂Br), 1.67 (m, OCH₂CH₂), 1.85 (m, CH₂CH₂Br), 3.41 (t, CH₂Br), 3.45 (t, CH₂OCH₂CH₂), 3.47 (s, OCH₂O), 4.36 (d, oxetane CH₂), 4.49 (d, oxetane CH₂). FT-IR (KBr, cm⁻¹): 2928 and 2874 (aliphatic C–H stretchings), 1463 (–CH₂– stretchings) and 1262, 1243, and 1116 (C–O stretchings). Elemental analysis: calcd. for C₁₅H₂₉BrO₂, C 56.07, H 9.10, Br 24.87, O 9.96%; found C 55.96, H 9.05, O 10.05%.

2.1.2. 3-[(10-[(4-Cyanobiphenyl-4'-yl)oxy]decoxy)methyl]-3-methyloxetane, **2**.

4-Cyano-4'-hydroxybiphenyl (10 g, 51.2 mmol), potassium carbonate (6.15 g, 153.6 mmol) and tetrabutylammonium bromide (1.5 g, 5.1 mmol) were added to acetone (150 ml) solution of 3-[(10-bromodecoxy)methyl]-3-methyloxetane (**1**, 21.4 g, 66.7 mmol). After the mixture was allowed to react for 24 h at 60–70°C, insoluble precipitate was removed by filtration and solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel eluent EA:hexane=1:4). The recovered yield was 75% (16.7 g). ¹H NMR (300 MHz, CDCl₃, ppm): 1.30–1.57 (m, CH₃, CH₂CH₂CH₂), 1.80 (m, OCH₂CH₂CH₂), 3.46 (m, CCH₂O, OCH₂CH₂), 3.99 (t, ArOCH₂), 4.35 (d, oxetane CH₂), 4.49 (d, oxetane CH₂), 6.99 (d, Ar-H_a), 7.50 (d, Ar-H_b), 7.61, 7.66 (two d, Ar-H_c and Ar-H_d). FT-IR (KBr, cm⁻¹): 3040 (aromatic C–H stretching), 2939 and 2864 (aliphatic C–H stretchings), 2225 (C≡N stretching), 1604 and 1496 (aromatic C=C stretchings) and 1270, 1251, 1180 and 1106 (C–O stretchings). Elemental analysis: calcd. for C₂₈H₃₇NO₃, C 77.20, H 8.56, N 3.22, O 11.02%; found C 77.33, H 8.52, N 3.15%.

2.1.3. 3-[(3-Propoxy)methyl]-3-methyloxetane, **3**.

1-Bromopropane (4.0 g, 28 mmol), potassium carbonate (4.0 g, 30 mmol) and tetrabutylammonium bromide were added to an acetone (30 ml) solution of 3-(hydroxymethyl)-3-methyloxetane (1.4 g, 14 mmol) and then the mixture was reacted for 12 h at 60°C. Insoluble precipitates were removed by filtration and acetone was distilled off using a rotary evaporator. The crude product was purified by column chromatography (silica gel eluent EA:hexane=1:15). The recovered yield was 68% (2.7 g). ¹H NMR (300 MHz, CDCl₃, ppm): 0.92 (t, CH₂CH₃), 1.31 (s, CH₃), 1.61 (m, CH₂CH₂CH₃), 3.42 (t, OCH₂CH₂), 3.47 (s, CCH₂O), 4.34 (d, oxetane CH₂), 4.50 (d, oxetane CH₂). FT-IR (KBr, cm⁻¹): 2960, 2922 and 2874 (aliphatic C–H stretchings), 1462 and 1379 (–CH₂– stretchings), 1115



Scheme 1. Synthetic routes to the monomers.

(C–O stretching). Elemental analysis: calcd. for $C_8H_{16}O_2$, C 66.63, H 11.18, O 22.19%; found C 66.11, H 11.31, O 22.58%.

2.2. Polymerizations

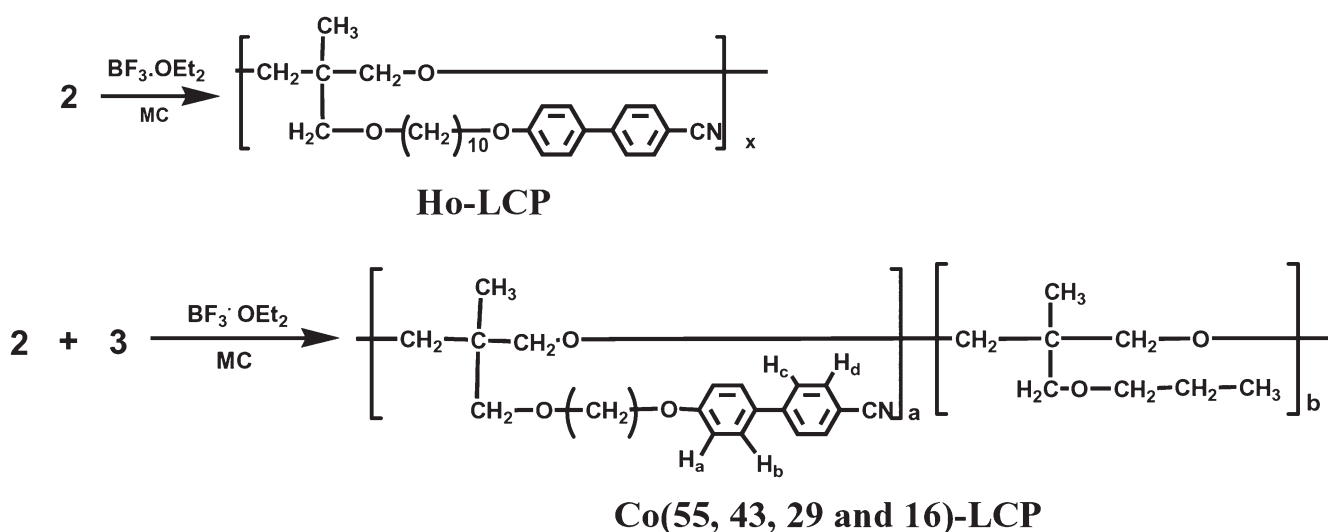
We conducted ring-opening polymerization (scheme 2) [28–35] of monomer mixtures of **2** and **3** in dichloromethane at -20°C using BF_3OEt_2 as cationic catalyst.

Dichloromethane was distilled over calcium hydride. The monomers were purified by column chromatography and then dried over magnesium sulfate. The solution of trifluoroborane etherate dissolved in dry dichloromethane was kept in a desiccator. All the glass wares were dried under reduced pressure at 120°C . Oligomers and catalyst residue in the product were removed by using a dialysis tube (M.W. cut-off: 12400, Aldrich). Detailed procedures are given below. The copolymer compositions were estimated by ^1H NMR and elemental analyses.

2.2.1. Poly[3-{{10-[(4-cyanobiphenyl-4'-yl)oxy]decoxy-methyl}-3-methyloxetane}], Ho-LCP. Trifluoroborane etherate (0.016 g, 0.14 mmol) in dry dichloromethane (1.0 ml) was added slowly to a solution of 3-{{10-[(4-cyanobiphenyl-4'-yl)oxy]decoxy} methyl}-3-methyloxetane (**2**, 3 g, 6.88 mmol) in 15 ml of dry dichloromethane under an argon atmosphere. After the mixture was stirred at -20°C for 24 h, the absence of the monomer in the reaction mixture was checked by thin-layer column chromatography (TLC). The mixture then was warmed to room temperature and stirred for an additional 1 h. Dichloromethane in the mixture was removed under a reduced pressure at 60°C . The crude product, dissolved in 2 ml of dichloromethane, was

transferred into a dialysis tube. The tube was placed in 250 ml of methanol, which was stirred for 2 h followed by replacement with fresh methanol. This procedure was repeated six times. The recovered yield was 74% (2.2 g). ^1H NMR (300 MHz, CDCl_3 , ppm): 0.87 (br, CH_3), 1.26–1.80 (br m, OCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.21–3.38 (br m, $\text{CH}_2\text{CCH}_2\text{O}$ main chain), 3.48 (m, CCH_2OCH_2), 3.99 (t, Ar- OCH_2), 6.97 (br, Ar- H_a), 7.51 (br Ar- H_b), 7.52, 7.59 (br, Ar- H_c and Ar- H_d). FT-IR (KBr, cm^{-1}): 3040 (aromatic C–H stretching), 2930 and 2853 (aliphatic C–H stretchings), 2226 ($\text{C}\equiv\text{N}$ stretching), 1604 and 1495 (aromatic C=C stretchings), and 1270, 1251 and 1106 (C–O stretchings). Elemental analysis: calcd. for $C_{28}H_{37}NO_3$, C 77.20, H 8.56, N 3.22, O 11.02%; found, C 77.12, H 8.66, N 3.26%.

2.2.2. Poly[3-{{10-[(4-cyanobiphenyl-4'-yl)oxy]decoxy-methyl}-3-methyloxetane]-co-(3-propoxy-3-methyloxetane)], Co(55)-LCP. Trifluoroborane etherate (0.020 g, 0.18 mmol) dissolved in dry dichloromethane (1.0 ml) was added slowly to a solution of 3-{{10-[(4-cyanobiphenyl-4'-yl)oxy]decoxy}methyl}-3-methyloxetane (**2**, 2.00 g, 4.60 mmol) and 3-{{3-propoxy}methyl}-3-methyloxetane (**3**, 0.65 g, 4.60 mmol) in 15 ml of dry dichloromethane under an argon atmosphere. After the mixture was stirred at -20°C for 24 h, it was warmed to room temperature and was stirred for one more hour. The polymer obtained was then purified as above described. The recovered yield was 73% (1.93 g). ^1H NMR (300 MHz, CDCl_3 , ppm): 0.89 (br s, CH_3), 1.30–1.58 (br m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.80 (br, OCH_2CH_2), 3.20 (br s, $\text{CH}_2\text{CCH}_2\text{O}$ main chain), 3.24 (br s, CCH_2OCH_2), 3.34 (br, $\text{CH}_2\text{OCH}_2\text{CH}_2$), 4.00 (br, Ar- OCH_2), 7.00 (br d, Ar- H_a), 7.53 (br d, Ar- H_b), 7.53, 7.62 (br m, Ar- H_c and



Scheme 2. Synthetic routes to the polymers.

Ar-H_d). FT-IR (KBr, cm⁻¹): 3040 (aromatic C–H stretching), 2930 and 2860 (aliphatic C–H stretchings), 2226 (C≡N stretching), 1605 and 1496 (aromatic C=C stretchings), 1270, 1251, and 1105 (C–O stretchings). Elemental analysis: calcd. for C₁₈H_{26.5}N_{0.5}O_{2.5}, C 74.56, H 9.23, N 2.42, O 13.80%; found, C 74.89, H 9.39, N 2.65%.

2.2.3. Co(43)-LCP. This polymer was prepared by the same manner as described above for the preparation of Co(55)-LCP. 3-([10-[(4-Cyanobiphenyl-4'-yl)oxy]decoxy]methyl)-3-methyloxetane (**2**, 3.00 g, 6.88 mmol) and 3-[(3-propoxy)methyl]-3-methyloxetane (**3**, 1.49 g, 10.3 mmol) were utilized for polymerization in the presence of trifluoroborane etherate (0.038 g, 0.34 mmol). The recovered yield was 65% (2.9 g). ¹H NMR (300 MHz, CDCl₃, ppm): 0.91 (br s, CH₃), 1.30–1.61 (br m, CH₂CH₂CH₂), 1.79 (br, OCH₂CH₂), 3.20 (br s, CH₂CCH₂O main chain), 3.24 (br m, CCH₂O), δ 3.34 (m, OCH₂CH₂), 3.98 (br, ArOCH₂), 6.96 (br d, Ar-H_a), 7.50 (br d, Ar-H_b), 7.63, 7.66 (br m, Ar-H_c and Ar-H_d). FT-IR (KBr, cm⁻¹): 3040 (aromatic C–H stretching), 2930 and 2855 (aliphatic C–H stretchings), 2227 (C≡N stretching), 1605 and 1496 (aromatic C=C stretchings), 1251, 1270 and 1105 (C–O stretchings). Elemental analysis: calcd. for C₁₆H_{24.4}N_{0.4}O_{2.4}, C 73.68, H 9.45, N 2.15, O 14.72%; found, C 73.95, H 9.62, N 2.29%.

2.2.4. Co(29)-LCP. This polymer was prepared by the same manner as described above for the preparation of Co(55)-LCP. 3-([10-[(4-Cyanobiphenyl-4'-yl)oxy]decoxy]methyl)-3-methyloxetane (**2**, 2.00 g, 4.60 mmol) and 3-[(3-propoxy)methyl]-3-methyloxetane (**3**, 1.98 g, 13.7 mmol) were polymerized in the presence of trifluoroborane etherate (0.042 g, 0.37 mmol). The recovered yield was 68% (2.7 g). ¹H NMR (300 MHz, CDCl₃, ppm): 0.91 (m, CH₃), 1.31 (br m, CH₂CH₂CH₂), 1.54 (m, CH₂CH₂CH₂), 1.81 (m, OCH₂CH₂), 3.21 (br s, CH₂CCH₂O main chain), 3.24 (s, CCH₂O), 3.35 (m, CH₂OCH₂CH₂), 4.00 (br, ArOCH₂), 6.96 (br d, Ar-H_a), 7.50 (br d, Ar-H_b), 7.63, 7.66 (br m, Ar-H_c and Ar-H_d). FT-IR (KBr, cm⁻¹): 3040 (aromatic C–H stretching), 2924 and 2855 (aliphatic C–H stretchings), 2227 (C≡N stretching), 1605 and 1496 (aromatic C=C stretchings), 1251, 1270 and 1104 (C–O stretchings). Elemental analysis: calcd. for C_{13.4}H_{21.7}N_{0.27}O_{2.5}, C 72.19, H 9.82, N 1.70, O 16.29%; found, C 71.31, H 10.20, N 1.78%.

2.2.5. Co(16)-LCP. This polymer was prepared by the same manner as described above for the preparation of Co(55)-LCP. 3-([10-[(4-Cyanobiphenyl-4'-yl)oxy]decoxy]methyl)-3-methyloxetane (**2**, 1.00 g, 2.30 mmol)

and 3-[(3-propoxy)methyl]-3-methyloxetane (**3**, 1.98 g, 13.8 mmol) were polymerized in the presence of trifluoroborane etherate (0.036 g, 0.32 mmol). The recovered yield was 65% (1.9 g). ¹H NMR (300 MHz, CDCl₃, ppm): 0.91 (br m, CH₃), 1.30 (br, CH₂CH₂CH₂), 1.56 (br, CH₂CH₂CH₂), 1.80 (m, OCH₂CH₂), 3.20 (s, CH₂CCH₂O main chain), 3.24 (s, CCH₂O), 3.35 (t, CH₂OCH₂CH₂), 3.98 (br, ArOCH₂), 6.97 (d, Ar-H_a), 7.51 (d, Ar-H_b), 7.65, 7.67 (m, Ar-H_c and Ar-H_d). FT-IR (KBr, cm⁻¹): 3040 (aromatic C–H stretching), 2963, 2930 and 2855 (aliphatic C–H stretchings), 2227 (C≡N stretching), 1605 and 1496 (aromatic C=C stretchings), 1251, 1270 and 1105 (C–O stretchings). Elemental analysis: calcd. for C_{10.8}H_{18.9}N_{0.14}O_{2.1}, C 70.22, H 10.36, N 1.06, O 18.36%; found, C 69.98, H 10.42, N 1.19%.

2.3. Identification and characterization

The FT-IR and ¹H NMR spectra of the compounds and polymers were recorded, respectively, on a Bomen MB FT-IR (Quebec, Canada) spectrophotometer using solid KBr pellets or liquid films and on a Bruker AM 300 Spectrometer (Palo Alto, CA) with TMS as internal standard. Elemental analyses were performed by the Korea Basic Science Institute, Seoul, Korea, with a Flash EA 1112 series elemental analyzer (Milan, Italy). The molecular weights of the polymers were determined by gel permeation chromatography (GPC 410, Santa Barbara, CA) equipped with RI 2410 detector and Styragel HR52 column using polystyrene as standard. THF was employed as an eluent.

The thermal transition temperatures were determined under N₂ atmosphere using a Mettler Toledo DSC 821e (Greifensen, Germany) differential scanning calorimeter. The heating and cooling rates were kept at 5°C min⁻¹. Indium was utilized as reference for calibration of temperature and enthalpy. The peak maximum or minimum points on DSC thermograms were taken as transition temperatures. The thermal properties and optical textures of the compound mesophases were observed on a polarizing microscope (Olympus BH-2, Japan) equipped with an automatically controlled (FP-90, Greifensen, Germany) hot stage (FP-82HT, Greifensen, Germany). X-ray diffractograms were obtained at varying temperatures using a synchrotron radiation (1.542 Å) of the 3C2 beam line at Pohang Synchrotron Laboratory, Pohang, Korea.

2.4. Measurement of the electro-optical properties of the mixtures

The plastic substrate (polyester) was coated with ITO and no further surface treatment was performed. The

cell (10 μm thick) constructed with two ITO-coated polyester sheets was filled with the Co-LCPs/E7 mixtures at 100°C by the capillary method in vacuum. A linearly polarized He–Ne laser was used as a light source without any polarizer either at the front or at the back side of the cell. The light that passed through the cell was detected by a photodiode and was recorded in a computer. The temperature was regulated up to $\pm 0.01^\circ\text{C}$ with a temperature regulator (TMS94, Linkam). The operating modes [28, 29, 41] of the Co-LCPs/E7 mixtures depend on the frequency of the applied field of ac 50 V. The dynamic mode [28, 29, 41] was achieved when the system was subjected to 0.1 Hz or 1 kHz frequency of ac electric field without interruption. When a low-frequency (0.1 Hz) electric field is applied, the system functions in the scattering state. With the high-frequency (1 kHz) electric field applied, the systems become transparent. When the applied field is removed, the sample maintains its modes regardless of whether it is in the scattering or transparent state. So in the memory mode [28, 29, 42] operation, the memory state is achieved by just turning off the selected field applied. The electro-optical response times, τ_R and τ_D , are measured as the elapsing time for the transmittance to change from 10% to 90% when the sample changes from scattering state to transparent state, and that from 90% to 10% when the sample changes from transparent to scattering state, respectively.

3. Results and discussion

3.1. Synthesis of monomers and polymers

The LC monomer **2** and the comonomer **3** were prepared by literature methods [28, 29, 33–35] via known intermediates. The synthetic route to monomers **2** and comonomer **3** is shown in scheme 1. All the intermediates were purified as required and their structures were confirmed spectroscopically and also by elemental analysis.

Polymerization of **2** and copolymerization of the mixtures of **2** and **3** were conducted cationically at -20°C in dichloromethane. The boron trifluoride/ether complex was utilized as an initiator. The polymers

formed were dialyzed using a dialysis tube with the nominal molar mass cut-off at 12 400 in order to remove low molar mass oligomers and polymers. Probably, that is why the polydispersity indices of the present polymers are comparatively low, i.e. less than 2 with the exception of Ho-LCP (see table 1). The molecular weights of polymers obtained are higher than 13 000 and degree of polymerization greater than 43. The copolymer compositions determined by NMR are the same as feed compositions, although those determined by element analysis are slightly different from the feeds.

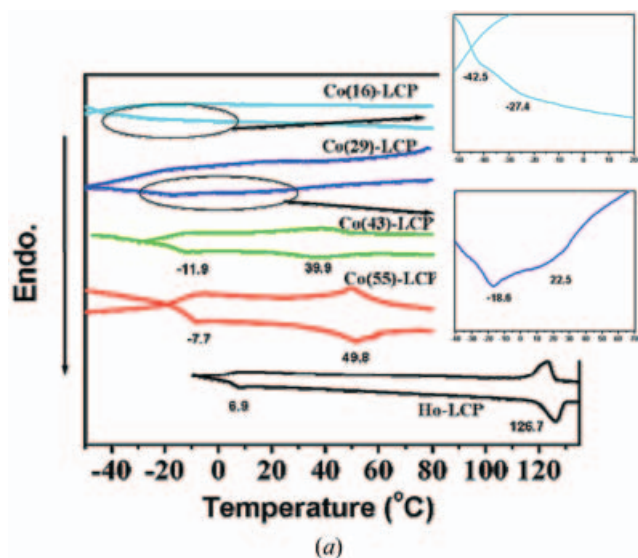
3.2. LC properties of polymers

The glass transition temperature, T_g , determined by differential scanning calorimetry (DSC; figure 1 a), of the polymers decreases from 7.0°C for Ho-LCP to -42.5°C for Co(16)-LCP with increasing content of the comonomer unit (see table 1 and figure 1 b).

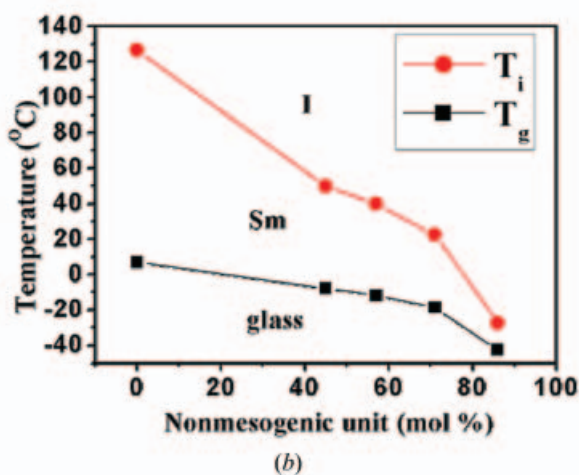
All the present polymers were found to be thermotropic. X-ray diffractograms of the polymers Ho-LCP, Co(55)-LCP and Co(43)-LCP taken at room temperature show not only a sharp diffraction peak in the small-angle region ($2\theta=1.55\text{--}1.98$; long spacing= $44.6\text{--}57.0\text{ \AA}$), but also a broad peak at $2\theta=19.2\text{--}20.0$ (short spacing= $4.1\text{--}4.6\text{ \AA}$). The polymers are in the mesophase at room temperature, because their T_g values are lower than room temperature. The second broad peak corresponds to an inter-chain distance or short spacing of $4.4\text{--}4.6\text{ \AA}$. The fact that we observe the appearance of two X-ray diffraction peaks (one sharp peak in the small-angle region and the second broad peak in the wide-angle region) implies that the mesophase formed by the polymers is a fluid smectic phase. Since Co(29)-LCP and Co(16)-LCP are in the isotropic phase at room temperature, their X-ray diffractograms, shown in figure 2 a, do not show any small-angle diffraction peak. The optical texture of the polymers (figure 3) observed on a cross-polarizing microscope exhibits fan textures, typical to the smectic A (S_A) phase. All the DSC thermograms given in figure 1 a each clearly show two transitions: glass transition at a lower temperature and isotropization, i.e. LC–isotropic phase transition at

Table 1. Average molar weight and unit mole ratio of polymers (solvent: THF; reference: polystyrene).

	Repeating unit ratio (<i>a/b</i>)			Average molecular weights				Transition temperatures/ $^\circ\text{C}$	
	feed	by NMR	by EA	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$	\overline{DP}	T_g	T_i
LCP	–	–	–	43 600	125 500	2.9	100	7.0	127.0
Co(55)-LCP	50/50	50/50	55/45	13 500	20 600	1.5	44	-7.7	50.0
Co(43)-LCP	40/60	40/60	43/57	15 200	23 800	1.6	52	-12.0	40.0
Co(29)-LCP	27/73	27/73	29/71	18 800	26 200	1.4	82	-18.5	22.5
Co(16)-LCP	14/86	16/84	16/84	52 900	95 600	1.8	277	-42.5	-27.5



(a)



(b)

Figure 1. (a) DSC thermograms of polymers and (b) the dependence of T_g and T_i of the polymers on the mole fraction of the non-mesogenic unit.

a higher temperature. However, Co(29)-LCP and Co(16)-LCP did not exhibit clear-cut optical textures when they were observed through the polarizing microscope between their T_g and T_i values, although they were birefringent. Therefore, at the present moment the nature of the mesophase of the two polymers is not definitive, although, as will be discussed later, their mixtures with E7 formed smectic structures according to X-ray analysis. This is taken as a strong implication they may also be smectic LCs.

Table 2 lists the spacings obtained from the diffraction data together with the values estimated from a molecular model: the long spacings coincide with the layer thickness of the S_A organization and the short spacings correspond to inter-chain distance. The long

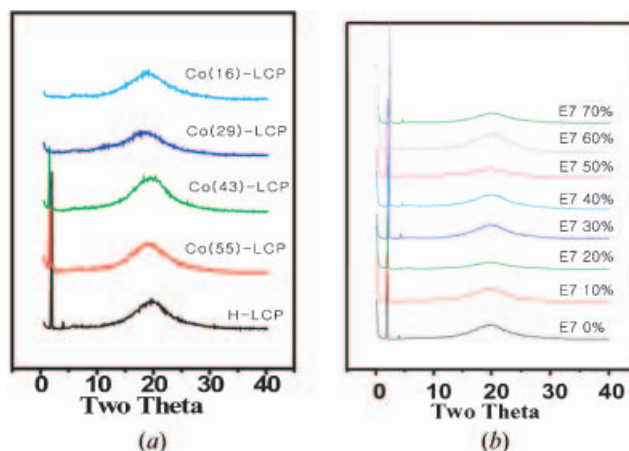


Figure 2. Wide-angle X-ray diffractograms of (a) Ho- and Co-LCPs and (b) Co(55)-LCP/E7 mixtures at 25°C.

spacing values tabulated in table 2 reveal two interesting phenomena. The long spacing value increases from 44.6 Å for the homopolymer, Ho-LCP, to 57 Å for the copolymer Co(43)-LCP and it diminishes as the content of E7 in the mixtures increases. For example, the long spacing value of Co(55)-LCP is 54.9 Å. The value steadily decreases to 40.8 Å for the 30/70 Co(55)-LCP/E7 mixture. The molecular models shown in figure 4 were designed to match the long spacing values of Ho-LCP, Co(43)-LCP and Co(55)-LCP, respectively. According to the molecular models, Ho-LCP exhibits the greatest overlap between the two mesogens of the partner chains, whereas Co(43)-LCP forms the dimeric structure resulted from dipolar interaction between the two nitrile groups. The degree of overlap between the counterpart mesogens of Co(55)-LCP chains lies in between. Although the models match very well the experimentally determined long spacings, we are not yet able to explain why the presence of the non-mesogenic comonomer units causes such changes.

The fact that the long spacing values decrease with increasing the content of E7 in LCP/E7 mixtures, regardless the composition of LCPs, can be ascribed to the gradual destruction by E7 of dimeric structure depicted in the models shown in figure 4. It should be noted that, as shown in figure 5, all the components of E7 are either alkyl or alkoxyaromatic nitriles that are the same or similar to the chemical structure of the mesogen of the present LCPs. The low molar mass aryl nitriles of the E7 mixtures are expected to be involved in the same type of molecular interactions, pictorially depicted in figure 4, with the mesogenic units of the present polymer. This would reduce the long spacing as we observe in the present cases. Another important observation is that even non-LC polymers

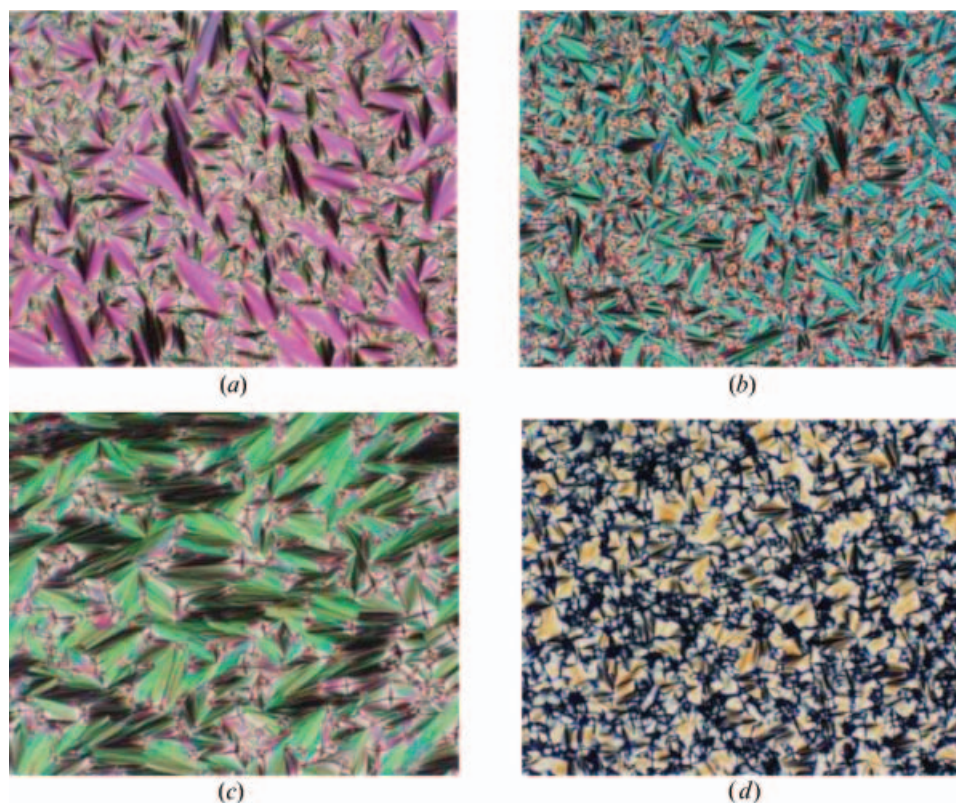


Figure 3. Optical textures of (a) Co(55)-LCP taken at 28.0°C on cooling, (b) Co(55)-LCP/E7 (50/50 wt%) taken at 30.2°C on cooling, (c) Co(43)-LCP/E7 (70/30 wt%) taken at 28.4°C on cooling, (d) Co(43)-LCP/E7 (50/50 wt%) taken at 35.0°C on cooling (magnification 200 \times).

at room temperature, such as Co(29)-LCP and Co(16)-LCP, when mixed with E7, they were able to form layered morphology, whose long spacing values can again be found in table 2.

All the polymers underwent the $S_A \rightarrow$ isotropic phase transition, or isotropization, which could be detected by both DSC analysis and visual observation of optical texture on a hot (cold) stage attached to the polarizing microscope. As shown in table 1 and figure 1 b, the isotropization temperature, T_i , of the polymers drops rapidly as the content of the non-mesogenic comonomer unit increases: the T_i of the homopolymer (Ho-LCP) is 127°C and those of Co(50)-LCP and Co(25)-LCP are 50 and 40°C, respectively. The T_i value of Co(16)-LCP is much lower (-27.5°C) than room temperature. Since the

lowering by the non-mesogenic comonomer unit of the T_g value of the copolymers is not so severe and, thus, the mesophase temperature range (i.e. $T_i - T_g$) of the polymers narrows rapidly with increasing content of the comonomer unit (see figure 1 b).

3.3. Miscibility of polymers and E7

We studied the miscibility between the present polymers and E7 and found that all of them are miscible in all proportions. It is rather surprising to note that the present polymers are smectic and E7 is nematic, but they form homogeneous mixtures. It is a general rule for LC compounds that miscibility is achieved only when the compounds are of the same mesophase. This is

Table 2. Variation of layer (in Å) calculated from small-angle X-ray diffractograms of Ho-LCP, Co-LCPs and mixtures at 25°C.

E7/% wt. (feed ratio)	0	10	20	30	40	50	60	70
Ho-LCP	44.6	42.7	41.7	40.1	39.8	39.8		
Co(55)-LCP	54.9	51.1	49.7	46.3	44.2	42.1	41.5	40.8
Co(43)-LCP	57.0	56.3	55.3	50.5	46.5	44.0	42.6	41.1
Co(29)-LCP	–	59.0	57.0	55.9	53.6	51.4	49.4	47.2
Co(16)-LCP	–	–	–	64.1	63.1	62.2	60.8	59.9

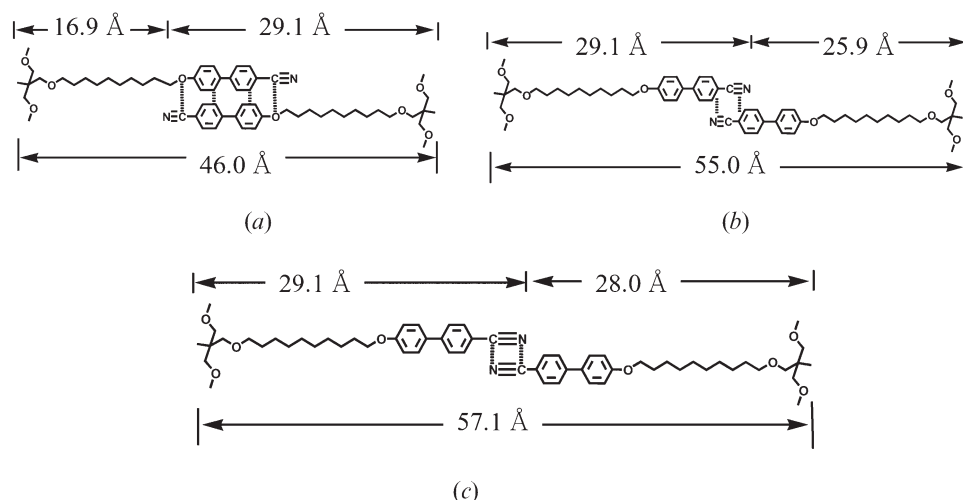


Figure 4. Schematic representations of the possible packing of Ho-LCP, Co(55)-LCP and Co(43)-LCP in the LC (smectic) phase. (a) CN-O and π - π , (b) π -CN and (c) CN-CN interactions.

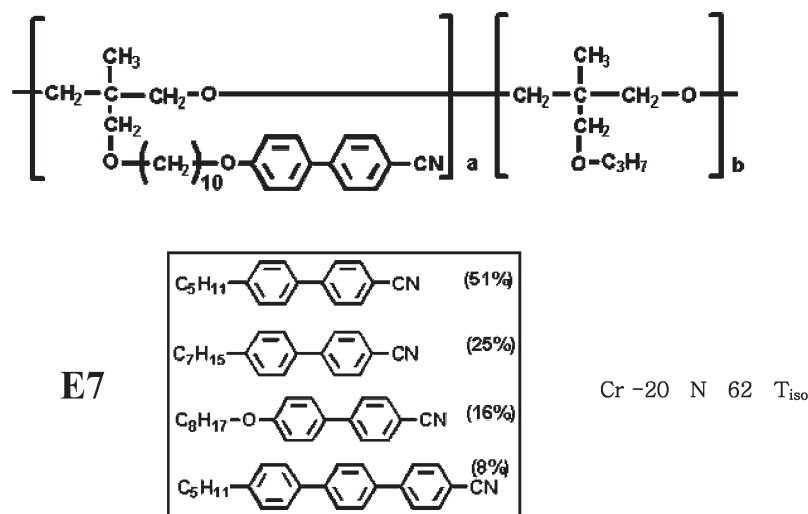


Figure 5. Structure of low molecular weight liquid crystal (E7) and poly[3-[[10-[(4-cyanobiphenyl-4'-yl)oxy]decoxy]-methyl]-3-methyloxetane]-*co*-(3-propyloxy-3-methyloxetane)] (Co(55, 43, 29 and 16)-LCP).

called the selective miscibility rule, as proposed by Demus and Sackmann [37, 38].

Figure 6a presents a collection of DSC thermograms obtained for the mixtures of Co(27)-LCP/E7 and figure 6b shows the dependence of T_g and T_i values on the composition of the polymer/E7 mixtures.

The latter clearly demonstrates that the T_g and T_i values smoothly change with the content of E7 in the mixture and that the mesophase temperature range, i.e. $T_i - T_g$, of the polymer/E7 mixtures widens with increasing the amount of E7 in the mixtures, because E7 tends to increase the T_i value while lowering the T_g value. It also is noted that the T_i values of the mixtures increases with increasing content of E7 because the T_i value (62°C) of E7 is higher than the T_i values of the

copolymers. Ho-LCP is the only polymer with a T_i value (127°C) higher than that of E7. Therefore, the Ho-LCP/E7 mixtures exhibit diminishing T_i values with increasing the level of E7.

One important point to be noted in the dependence of T_i of the mixtures on composition (figure 6b) is that all of the mixtures reveal the close-to-ideal behaviour with only a slight positive deviation [39, 40]. This strongly implies that there exists an excellent miscibility between the LC copolymers and E7 mixture. Earlier, Kajiyama *et al.* [24, 25] reported a thorough study on the miscibility between a series of smectic polysiloxane side-group copolymeric LCPs and nematic E7 and their bistable electro-optical switching behaviour. In this study, they demonstrated that, although LCPs and E7 each form

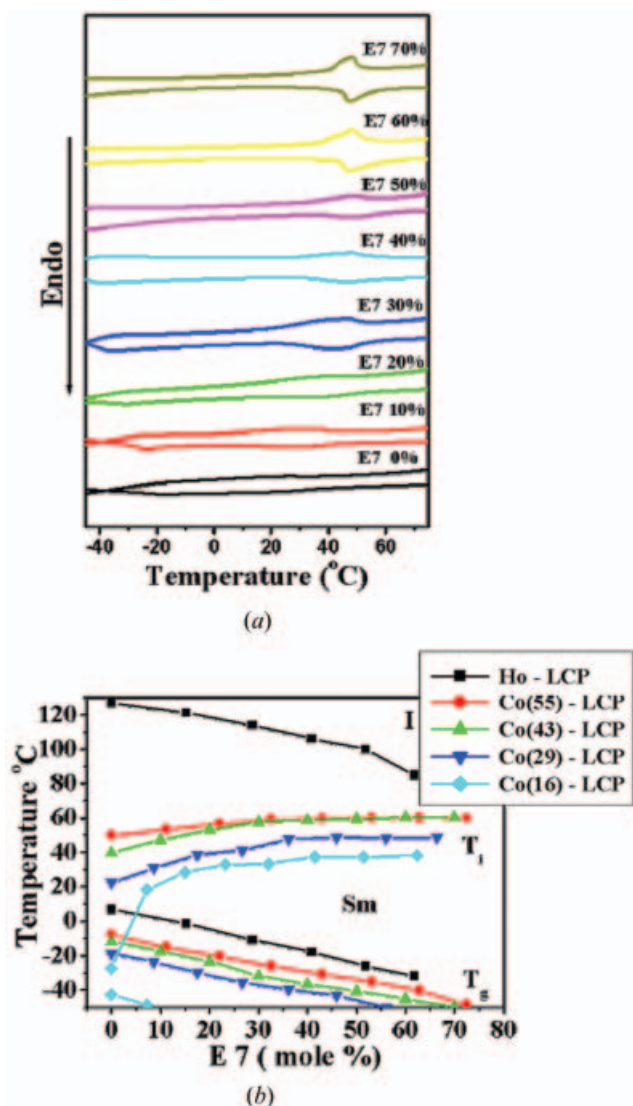


Figure 6. (a) DSC thermograms of Co(29)-LCP/E7 mixtures and (b) the dependence of T_g and T_i of the mixtures on the mole fraction of E7 (heating and cooling rates 5°C min^{-1}).

different mesophases, they were homogeneously miscible forming smectic phases. They also showed that some of the copolymers reveal biphasic phases over narrow temperature ranges.

3.4. Electro-optical properties of Co-LCP/E7 mixtures

We have conducted a preliminary study on the electro-optical properties of Co-LCP/E7 mixtures. We found that the electro-optical behaviour can be satisfactorily studied both in the dynamic scattering mode [28, 29, 41] and also in the transmittance memory mode [28, 29, 42].

Figure 7 shows the electro-optical response of a Co(43)-LCP/E7 (50/50 wt%) mixture in the two different modes at room temperature. Although the rise time

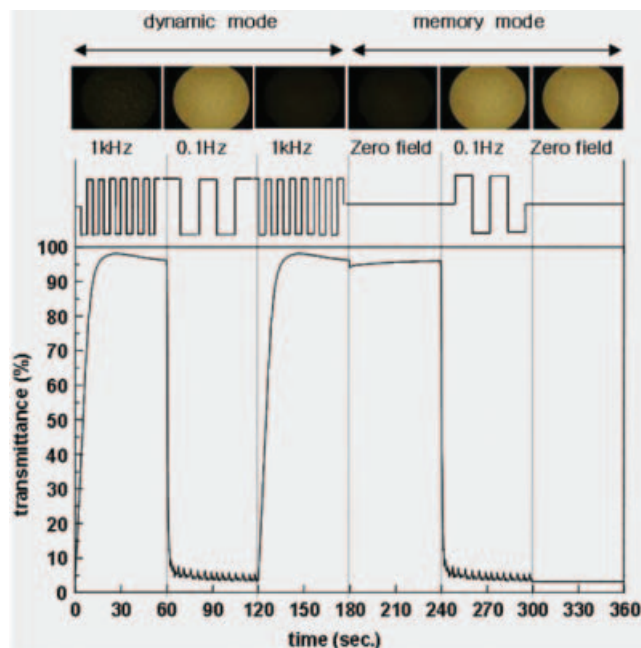


Figure 7. Schematic illustration of the scattering and transmittance mode for the Co(43)-LCP/E7 (50/50 wt%) mixture under the application of an ac electric field with different frequencies.

in the dynamic mode between two (1 kHz and 0.1 Hz) ac frequencies is not very fast, we observe that this mixture reveals a reproducible response. The same mixture exhibits a very stable memory-type display capacity at room temperature.

Figure 8a shows a simplified operation of the device we fabricated. Needless to say, the rise and decay times of the mixture are very strongly dependent both on the composition of a LC copolymer and the content of E7 in a mixture. For example, figure 8b depicts a strong dependence of the rise and decay time of the Co(16)-LCP/E7 mixtures in the scattering mode on the content of E7; when the content of E7 is 30 wt%, the rise and decay times were greater than 100 s, but they decreased to less than 1 s at an E7 content of 70%.

Moreover, we found that the flexible plastic memory type display fabricated with the Co(16)-LCP/E7 (30/70 wt%) mixture displayed an excellent stability throughout repeated bending of the device 20 times without refreshing pulse. When the refreshing field was occasionally applied, the sample could stably maintain its state (figure 9). A detailed report on the display behaviour of the mixtures will follow soon.

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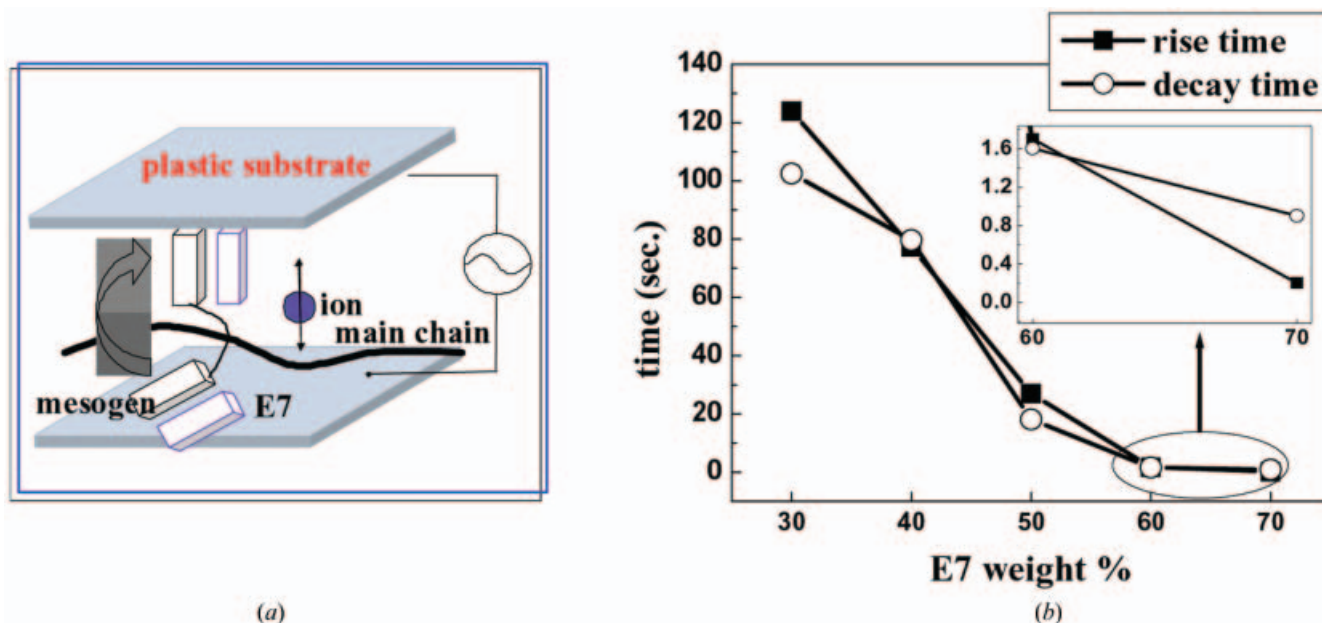


Figure 8. (a) Schematic illustration of device operation. (b) The rise and decay time of Co(16)-LCP/E7.



Figure 9. (a) Photograph of the memory state at 0V, (b) curved shape like a paper for the Co(16)-LCP/E7 (30/70 wt%).

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