

# Effect of the ionic conductivity of a polymer matrix on the electrooptical properties of polymer-dispersed liquid crystal films

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## Summary

The influence of ionic conductivity on the electrooptical response was investigated. A new monomer of 2-(poly(ethylene glycol)oxycarbonyl)-bicyclo[2.2.1] hepta-2,5-diene (PEGOC-BCHD) was synthesized and polymerized. Polymer/liquid crystal composite films are composed of poly(PEGOC-BCHD), E8, and alkali metal salts. The ionic conductivities were measured as a function of the ratio of  $\text{LiClO}_4$ /ethylene oxide for various molecular weights of poly(ethylene glycol). The results indicate that the threshold field and response rise time can be reduced by increasing ionic conductivity of the matrix polymer. Liquid crystal droplets were observed in a continuous matrix phase in the form of 'Swiss cheese' morphology.

## Introduction

A new development in liquid crystal (LC) displays utilizes liquid crystalline droplets dispersed in a polymer matrix. These displays are becoming more important as electro-optic devices because of their broad applicability ranging from light modulators to large area displays (1-3). The composite films are electrically driven by sandwiching them between conducting electrodes. Each application has its own electrical constraints on such things as power consumption, driving voltage, maximum current, and frequency of operation. In spite of the inherent importance of the conductivity ( $\sigma$ ) and dielectric constant ( $\epsilon$ ) of the composite film in dictating these parameters, only a little work has been done to understand them. Typically, in the frequency range of interest for polymer/LC composition films operation, the strength of an ac electric field is modulated by the frequency of the imposed ac electric field. Since electronic and ionic polarization mechanisms are very far from their resonances which occur at or above infrared frequency region, only permanent dipole resonances resulting from molecular reorientation are related to the polymer-dispersed liquid crystal film (PDLC) operation. These resonances of the interfacial polarization occur in conjunction with changes in the dielectric constant and conductivity. It has been reported that the matrix polymer with greater magnitude of conductivity leads to enhancing the electrooptical response speed (4-5). Here, we prepared a new polymer/LC composite film employing an alkali metal salt and the matrix polymer with poly(ethylene glycol) (PEG) substituents. PEG exhibits high ionic conductivity when complexed with alkali metal salts. However, these systems have low glass transition temperatures and poor transparencies. In order to improve these properties, a new PEG-substituted monomer was introduced. It has a high glass transition temperature, optical transparency, and high conductivity. In this paper, we discuss the effect of the conductivity of the polymer matrix on the electrooptical properties of the PDLC.

## Experimental

**Materials:** Propiolic acid, poly(ethylene glycol) ( $M_n = 200, 400, 600$ ), p-toluenesulfonic acid, lithium perchlorate, and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Aldrich Chemical Company and used without further purification. Cyclopentadiene, dioxane, and tetrahydrofuran were distilled prior to use. E8 (mixture of nematic LCs with positive dielectric anisotropy,  $T_{NI} = 345$  °K,  $n_{||} = 1.774$ , and  $n_{\perp} = 1.527$ ) and micropearl-type spacer were used as supplied from Merck and Sekisui Fine Chemical Co. Ltd., respectively.

**Measurements:** Electro-optic measurements were carried out employing a He-Ne laser (wavelength = 633 nm, 5 mW) and a digital storage oscilloscope (Fluke M3380A). Morphology was observed using a scanning electron microscope (JEOL JSM-840A). Ionic conductivities were measured on a Dupont TA 2970 dielectric analyzer. Measurements were carried out at 25 °C. Proton NMR spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. Infrared spectra were obtained on a Bio-Rad FTS-165 spectrometer. Differential scanning calorimetry (DSC) data were obtained on a Dupont 2950 thermal analysis system. DSC measurements were made at a heating rate of 20 °C/min in nitrogen. Molecular weights of the polymers were determined in tetrahydrofuran at 40 °C using a Waters 510 HPLC pump and Waters 410 differential refractometer detector consisting of four  $\mu$ -styragel columns. The molecular weights were estimated relative to polystyrene standards.

**Preparation of poly(ethylene glycol) propiolate (PEGP):** A mixture of propiolic acid 2.80 g (0.04 mol), poly(ethylene glycol) ( $M_n = 200$ ) 16 g (0.08 mol), benzene 90 ml, and p-toluenesulfonic acid (0.03 g) was refluxed in a Dean-Stark apparatus for 5 h at 90 °C. The mixture was washed several times with 0.5 N sodium bicarbonate, dried over magnesium sulfate, and concentrated. The product was obtained in a yield of 13.7 g (73%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  3.9-3.7 (q, 4H), 3.6 (s, 1H), 2.1 (s, 1H). IR ( $\text{cm}^{-1}$ ): 3392 (OH), 2946 (aliphatic CH), 2116 (C=C), 1715 (C=O).

**Preparation of 2-(poly(ethylene glycol) oxycarbonyl)-bicyclo[2.2.1]hepta 2,5-diene (PEGOC-BCHD):** Into an 1.8 liter stainless steel autoclave was charged 4.98 g (0.03 mol) of poly(ethylene glycol) propiolate, freshly distilled cyclopentadiene 4.76 g (0.036 mol), and 40 ml of anhydrous tetrahydrofuran. The autoclave was purged two times with nitrogen at room temperature and then heated to 180 °C for 5 h. After the Diels-Alder reaction was completed, the reaction mixture was cooled to room temperature. The mixture was concentrated and then unreacted cyclopentadiene was removed under reduced pressure. The desired fractions were combined and dried in vacuo to yield 6.24 g (64.1%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  7.5 (s, 1H), 6.6-6.8 (m, 2H), 4.1 (q, 2H), 3.9-3.7 (q, 4H), 3.6 (s, 1H), 2.0 (m, 2H). IR ( $\text{cm}^{-1}$ ): 3324 (OH), 2874 (aliphatic CH), 1738 (C=O), 1649 (vinyl).

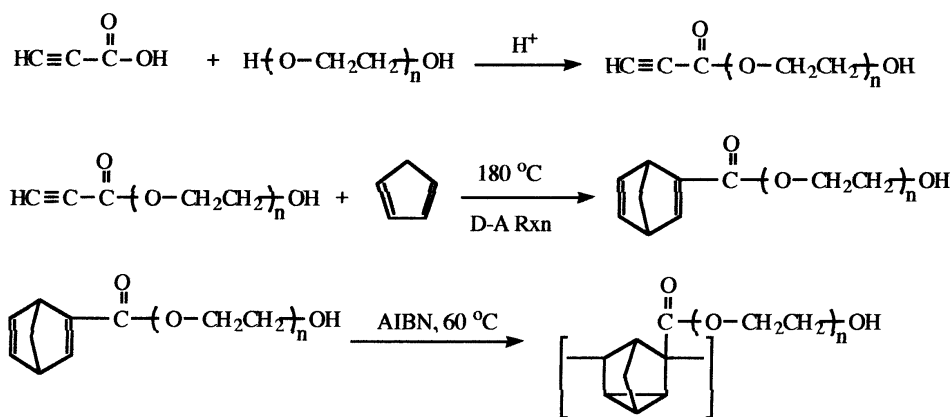
**Free radical polymerization of PEGOC-BCHD:** A solution of PEGOC-BCHD in dioxane that contained AIBN was heated at 60 °C under vacuum in a sealed ampoule. The polymer was isolated by precipitation in methanol and dried in vacuo to yield 73.2%.  $T_g$  190 °C,  $M_n = 2.3 \times 10^4$ ,  $n = 1.498$ . IR ( $\text{cm}^{-1}$ ): 3324 (OH), 3070 (aliphatic CH), 1738 (C=O), 1649 (vinyl).

**Preparation of PDLC film:** The mixture of poly(PEGOC-BCHD),  $\text{LiClO}_4$ , and E8 was dissolved in tetrahydrofuran at room temperature. The solution was placed between the two indium/tin oxide coated glass plates separated by 10.5  $\mu\text{m}$  thick micropearl spacer. A solvent induced phase separation (SIPS) process was employed to prepare PDLC films (6). The PDLC film was dried in a vacuum oven for 5 h at room temperature to remove residual solvent.

## Results and discussion

A new PEG-substituted monomer, PEGOC-BCHD, was prepared by Diels-Alder reaction and polymerized in the presence of a radical initiator, AIBN, as shown in Scheme 1.

< Scheme 1 >



The ionic conductivities of the poly(PEGOC-BCHD)/ $\text{LiClO}_4$  for various molecular weights of PEGs are given as a function of Li/EO ratio (molar ratio of Li and ethylene oxide unit in PEG) in Figure 1. In the tested Li/EO ratio range, the ionic conductivity of the system increased with the increase of Li/EO ratio and the increase of the chain length of the PEG substituent because of the increase in the number of charge carriers. When the Li/EO ratio is 1.0, the ionic conductivity of the system reaches the value of  $10^{-2}$  S/cm.

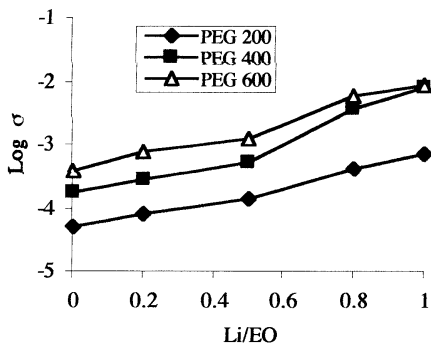


Figure 1. Ionic conductivities of poly(PEGOC-BCHD)/LiClO<sub>4</sub> system as a function of Li/EO ratio at 25 °C.

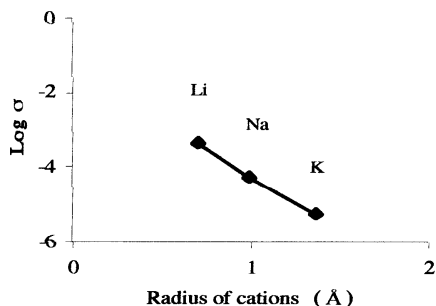


Figure 2. The relationship between the ionic conductivity and the radius of the cation at 25 °C.

Figure 2 shows the influence of different cations on the ionic conductivities of the poly(PEGOC-BCHD)/MClO<sub>4</sub> systems, where the molecular weight of PEG is 200, M is an alkali metal ion, and M/EO ratio is 1.0. The order of the ionic conductivity values of the system is  $\sigma_{\text{LiClO}_4} > \sigma_{\text{NaClO}_4} > \sigma_{\text{KClO}_4}$ . Comparing the radii of the related cations,  $r_{\text{Li}^+} = 0.70 \text{ \AA}$ ,  $r_{\text{Na}^+} = 0.99 \text{ \AA}$ , and  $r_{\text{K}^+} = 1.37 \text{ \AA}$ , it can be seen that the ionic conductivity of the system increases with a decrease in the radius of the cation.

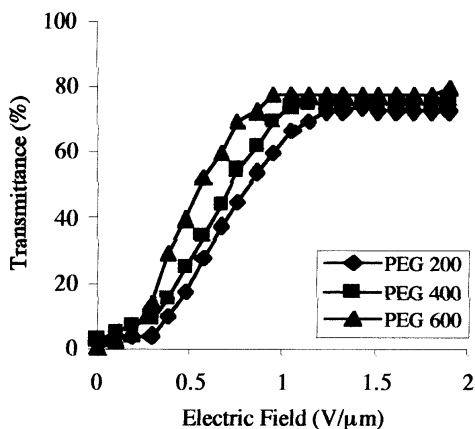


Figure 3. Transmittance as a function of electric field for the poly(PEGOC-BCHD)/E8 (40/60, w/w) composite film at 25 °C and 1 kHz.

Transmittance of poly(PEGOC-BCHD)/E8 for various chain lengths of PEGs as a function of electric field is given in Figure 3. The transmittance increases with electric field up to 1.0-1.2 V/μm, beyond which it is almost independent on the applied electric field, indicating that the director orientation is almost completed at that electric field and the

transmittance reaches its maximum. Figure 4 illustrates the influence of transmittance as a function of electric field for various Li/EO ratios and the molecular weights of PEGs. In comparing the four sets of data, the transmittance shifted to the higher values with the increase of the lithium salt concentration because the ordinary refractive index of the liquid crystal matches more closely with that of the polymer. The refractive indices of the polymer matrixes were 1.498, 1.512, and 1.528 when the Li/EO ratios were 0, 0.2, and 1.0, respectively.

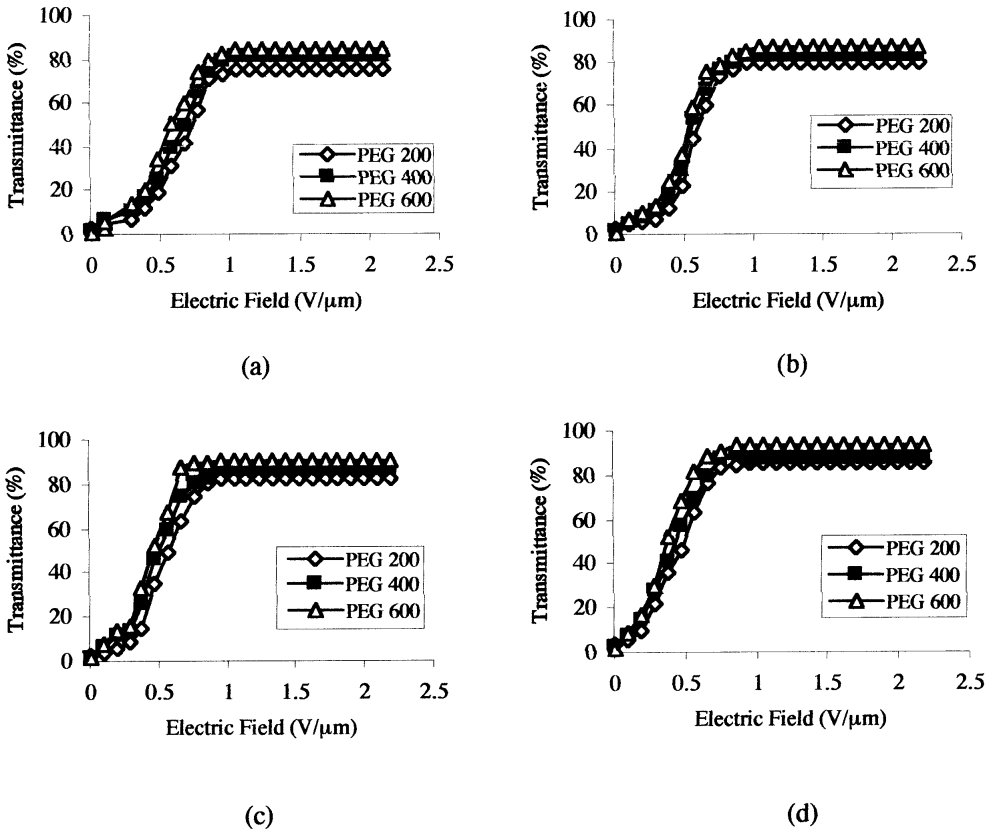


Figure 4. Comparison of transmittance curves of poly(PEGOC-BCHD)-LiClO<sub>4</sub>/E8 (40/60, w/w) system as a function of electric field for various Li/EO ratios (a) 0.2, (b) 0.5, (c) 0.8 (d), 1.0) at 25 °C and 1 kHz.

Threshold field ( $E_{th}$ ) which is defined as the electric field required to achieve 90% of maximum transmittance is shown in Figure 5.  $E_{th}$  decreases with an increase of the chain length of PEG and the Li/EO ratio. This result is related to the fact that the increased conductivity of the matrix polymer leads to a decrease of threshold voltage. The dependence of the rise time,  $\tau_r$ , on the ratio of Li/EO for the PDLC films is given in Figure 6.  $\tau_r$  is defined as the time period required for a change of transmittance from 10% to 90% upon switching the film on (7).  $\tau_r$  decreases with increasing the ratio of Li/EO in the composite film.  $E_{th}$  and  $\tau_r$  were remarkably improved with the increase of conductivity of the matrix

polymer. The magnitude of the electric field in the LC phase is strongly dependent on the conductivity of the matrix polymer. The distribution of the external electric field can be imposed effectively to the LC phases when the polymer with large conductivity is used. Thus the matrix polymer with larger conductivity led to improvement of  $E_{th}$  and  $\tau_r$ .

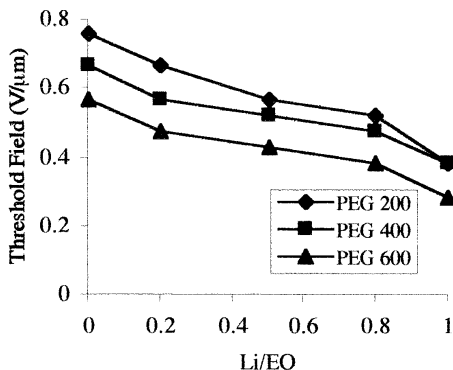


Figure 5. Threshold field as a function of Li/EO ratio of poly(PEGOC-BCHD)/E8 (40/60, w/w) at 25 °C and 1 kHz.

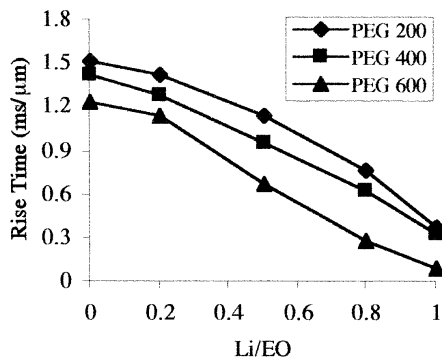


Figure 6. Influence of rise time as a function of Li/EO ratio of poly(PEGOC-BCHD)/E8 (40/60, w/w) at 25 °C and 1 kHz.

Figure 7 shows scanning electron micrographs of polymer/LC composite films after removal of LC by extraction with methanol. The degree of light scattering in the absence of an external electric field strongly depends on the aggregation state of the composite film, which is controlled by the type of polymer and LC, film composition, solvent, and film preparation condition (8). LC droplets were observed in a continuous matrix phase in the form of ‘Swiss cheese’ morphology. The average diameters of LC domains are (a) 3.1 μm, (b) 1.2 μm, and (c) 0.7 μm, respectively. The LC domain size is larger in E8-rich composite films.

Further studies are needed to determine the dielectric property relationship of polymer/LC composite films and their influence on electrooptical properties will be published.

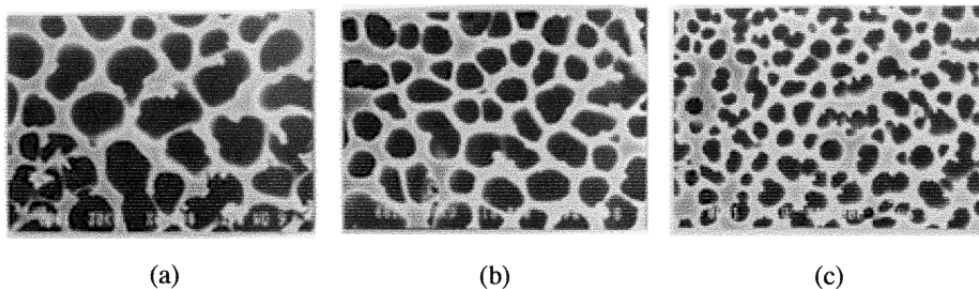


Figure 7. Scanning electron micrographs of poly(PEGOC-BCHD)/E8 composite films for various LC ratios. (a) poly(PEGOC-BCHD)/E8 (20/80, w/w), (b) poly(PEGOC-BCHD)/E8 (40/60, w/w), and (c) poly(PEGOC-BCHD)/E8 (60/40, w/w).

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