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Polymer-dispersed liquid crystal films using poly(2-methyloxycarbonyl-bicyclo[2.2.1] hepta-2,5-diene-*co*-poly(ethylene glycol) methacrylate) as a matrix resin

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Summary

Dependence of the electrooptical response time of a polymer/liquid crystal (LC) composite film on the ionic conductivity and dielectric property of the matrix polymer has been investigated. Poly(2-methyloxycarbonyl-bicyclo[2.2.1]hepta-2,5-diene-co poly(ethyl -ene glycol) methacrylate) was synthesized by photo-polymerization. Ionic conductivity and relative dielectric constant were found to be greatly dependent on the content of poly(ethylene glycol) methacrylate in the copolymer. The results indicate that the matrix polymer with high conductivity and dielectric constant has led to the short response time.

Introduction

Polymer-dispersed liquid crystal (PDLC) films consisted of micron-sized droplets in a matrix polymer have received considerable attention, since they have a lot of advantages such as operation without polarizers and easy fabrication of large area display devices (1-4). The magnitude of the external electric field to the LC droplet is strongly dependent on the conductivity (σ) and dielectric constant (ε) of the matrix polymer in the polymer/LC composite film (5,6). The distribution of the external field can be imposed effectively to the LC phases when the polymer with large σ and ε is used. To improve these properties, we prepared a new polymer/LC composite film using a matrix polymer with poly(ethylene glycol) substituents and an alkali metal salt. In this paper, we discuss the effect of the conductivity and dielectric property of the polymer matrix on the electrooptical response of the PDLC.

Experimental

Materials

Methyl propiolate, poly(ethylene glycol) methacrylate (PEGMA) and 2,2-dimethoxy-2-phenylacetophenone (DMPAP) were purchased from Aldrich Chemical Co. and used without further purification. E8 (mixture of nematic LCs with 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. 2-Methyloxycarbonyl-bicyclo[2.2.1]hepta-2,5-diene (MOCBCHD) was prepared according to the literature (7).

Measurements
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. Electro-optic measurements were carried out employing a He-Ne laser (wavelength 633 nm, 5 mW) and a digital storage oscilloscope (Fluke M 3380 A). Morphology was observed using a scanning electron microscope (JEOL JSM-840A). DSC measurements were made at a heating rate of 10 °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 μ-styragel columns. The molecular weights were estimated relative to polystyrene standards.

Copolymerization of MOCBCHD with PEGAM
A mixture of MOCBCHD (0.6 g, 0.004 mol), PEGMA (0.36 g, 0.001 mol), and DMPAP (0.064 g, 5 mol %) in a quartz cuvette was exposed to UV irradiation from a 20 W high pressure mercury arc lamp, yielding intensity of about 10 mW/cm^2 at 365 nm. The polymer was isolated by precipitation in petroleum ether and dried in vacuo. ^{1}H-NMR ($CDCl_3$, ppm): δ 3.6 (s, 1H), 2.3-1.4 (m, 7H). IR (cm^{-1}): 3422 (OH), 2951 (aliphatic CH), 1719 (C=O).

Cell preparation of conductivity and dielectric constant
The ionic conductivity of the composite film was measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range of 20 Hz-10 MHz. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity could be obtained from the bulk resistance (R_b) found in the complex impedance diagram. The electrical impedance, Z^*, was converted to the complex dielectric permittivity using the equation.

$$\varepsilon^* = l\,(i\omega\varepsilon_0 A Z^*)^{-1} = \varepsilon' - i\varepsilon''$$

where ε_0 is the dielectric permittivity of free space, A is the surface area of the electrode, and I is the thickness of the composite film. In our study, the molar ratio of $LiClO_4$ and ethylene oxide unit in PEG in all the composite films was fixed to be 0.05.

Preparation of PDLC films
The mixture of MOCBCHD/PEGMA/DMPAP/$LiClO_4$/E8 was placed between the two indium/tin oxide coated glass plates separated by 10.5 μm thick micropearl-type spacer. A photo-polymerization induced phase separation process was conducted under UV light of 10 mW/cm^2 at 365 nm.

Results and discussion

Photo-polymerizations of MOCBCHD with PEGMA were carried out with various molar feed ratios in the presence of a photoinitiator, DMPAP, by UV exposure at 365 nm with 10 mW/cm^2 at room temperature and the results are summarized in Table 1. The PEGMA content of the copolymer was calculated by comparing the integral areas of the proton NMR as shown in Fig. 1.

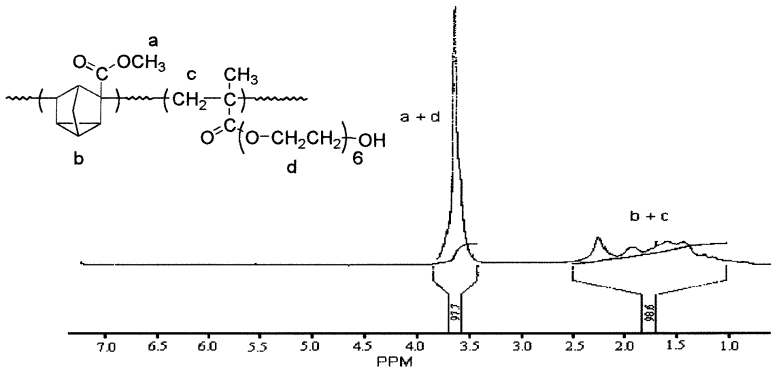

Fig.1. ^{1}H-NMR spectrum of poly(MOCBCHD-co-PEGMA).

Table 1. Copolymerization of MOCBCHD with PEGMA

Monomer feed ratio[a]			Content of PEGMA (mol %)	M_w[b] (10^4)	T_g[c] (℃)
MOCBCHD	PEGMA	Photoinitiator (mol %)			
4	1	5	17	2.8	107
10	1	5	9	5.4	131
20	1	5	3	6.5	158

[a] Polymerizations were carried out in MOCBCHD/PEGMA molar feed ratios.

[b] Molecular weights were measured by GPC in tetrahydrofuran and estimated relative to the polystyrene standards.

[c] T_g was measured with a Perkin-Elmer TA 7 system at a heating rate 10℃/min.

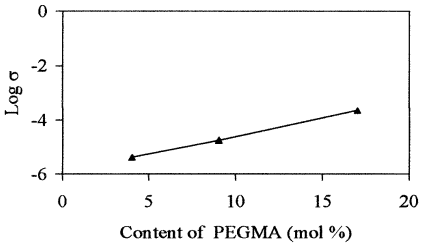

Fig.2. Ionic conductivity of poly (MOCBCHD-co-PEGMA)/$LiClO_4$ as a function of PEGMA content at 25℃.

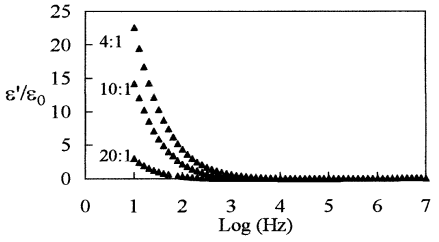

Fig.3. Frequency dependence of the relative dielectric constant for poly(MOCBCHD-co-PEGMA)/$LiClO_4$ as a function of PEGMA content at 25℃.

Ionic conductivities of the poly(MOCBCHD-co-PEGMA)/$LiClO_4$ for various content of PEGMA are given in Fig.2. The ionic conductivity of the system increased with the increase of content of PEGMA. The conductivities at room temperature are measured to be in the range of 3.8 x 10^{-4} to 7.2 x 10^{-6} S/cm. To investigate relationship between dielectric property and light switching behavior on the composite film, the dielectric relaxation studies of the poly(MOCBCHD-co-PEGMA)/$LiClO_4$ system were carried out. The relative dielectric constant ($\varepsilon'/\varepsilon_0$) vs. frequency plots are illustrated in Fig.3. The $\varepsilon'/\varepsilon_0$

was increased with increasing content of PEGMA.
Fig.4 illustrates the influence of transmittance as a function of electric field for various PEGMA contents and frequencies. The transmittance shifted to the higher values with the increase of the content of PEGMA and the frequency.

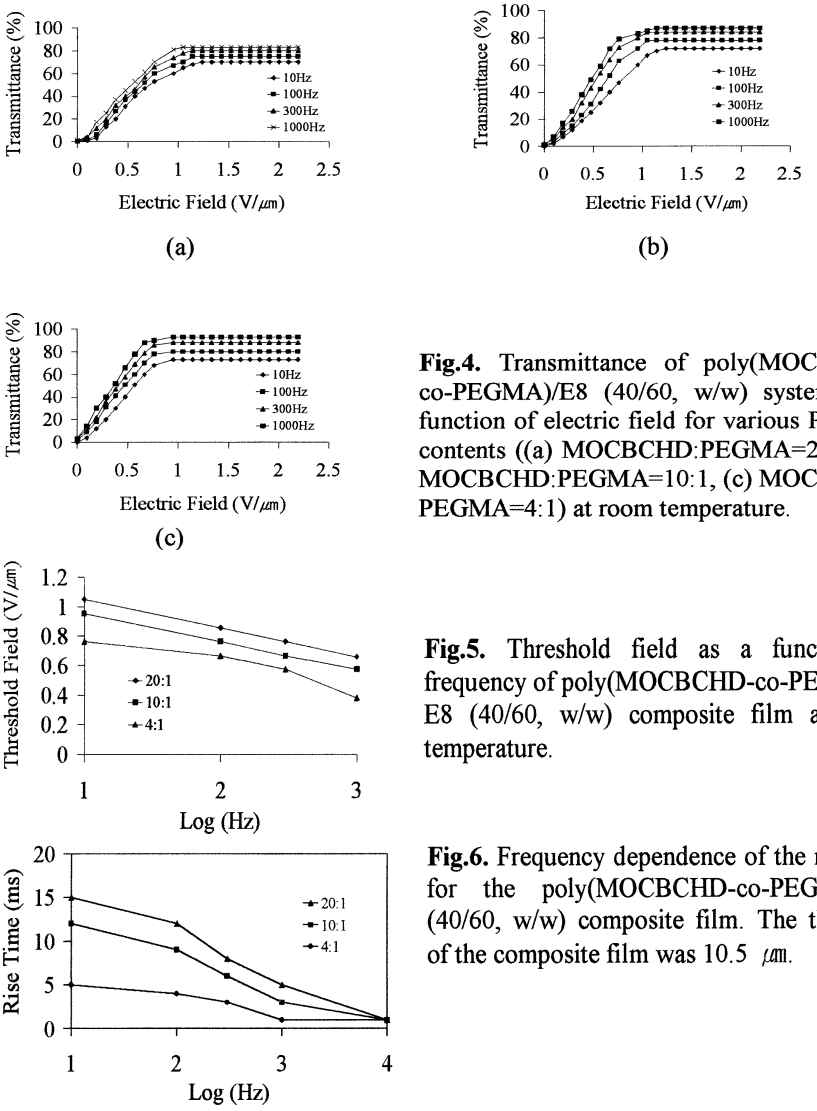

Fig.4. Transmittance of poly(MOCBCHD-co-PEGMA)/E8 (40/60, w/w) system as a function of electric field for various PEGMA contents ((a) MOCBCHD:PEGMA=20:1, (b) MOCBCHD:PEGMA=10:1, (c) MOCBCHD:PEGMA=4:1) at room temperature.

Fig.5. Threshold field as a function of frequency of poly(MOCBCHD-co-PEGMA)/E8 (40/60, w/w) composite film at room temperature.

Fig.6. Frequency dependence of the rise time for the poly(MOCBCHD-co-PEGMA)/E8 (40/60, w/w) composite film. The thickness of the composite film was 10.5 μm.

Threshold field which is defined as the electric field required to achieve 90% of maximum transmittance is shown in Fig.5. Threshold field decreases with an increase of the PEGMA content and the frequency. This result is related to the fact that the increased conductivity of the matrix polymer leads to a decrease of the threshold field. The frequency dependence of the rise time for the composite film is presented in Fig.6. The response rise time for the matrix polymer with low content of PEGMA (MOCBCHD:PEGMA = 20:1) sharply decreases from 15 to 1 ms with an increase in

frequency. However, in the case of the composite film with high content of PEGMA (MOCBCHD:PEGMA = 4:1), the rise time decreases from 5 to 1 ms in the same frequency range. The results show that the matrix polymer with large conductivity and dielectric constant has led to a considerable improvement of the electrooptical response speed. In order to examine the durability of the electrooptical response, the change of transmittance and threshold field with standing time was measured. As shown in Table 2, the driving voltage does not change with standing time. The results show that the alkali metal salt in the PDLC film did not affect the stability of the electrooptical properties. Fig.7 shows the scanning electron micrograph of the composite film after removal of LC by extraction with methanol. LC droplets were observed in a continuous matrix phase in the form of 'Swiss cheese' morphology (8). The average diameter of LC droplets is 3 μm.

Table 2. Change of transmittance and threshold field for the poly(MOCBCHD-co-PEGMA)/E8 (40/60, w/w) composite film with standing time at room temperature and 1 kHz.

Standing time (hr) \ PEGMA content		4:1	10:1	20:1
0	Transmittance[a] (%)	93	87	83
	Threshold field[b]	0.38	0.57	0.66
6	Transmittance[a] (%)	93	87	83
	Threshold field[b]	0.38	0.57	0.66

[a] Maximum transmittance
[b] Threshold field at 90% of maximum transmittance

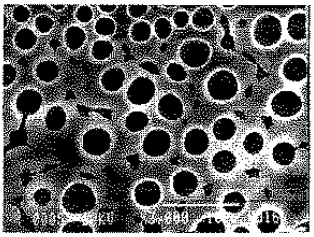

Fig.7. The scanning electron micrograph of poly(MOCBCHD-co-PEGMA)/E8 composite film (40/60, w/w).

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