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Permanent memory effect in polymer dispersed liquid crystal (PDLC) films pre-
pared by thermal polymerization induced phase separation (PIPS) were studied. New
trimethylolpropane trimethacrylate (TMP3MA)/poly(propylene glycol) methacrylate
(PPGMA375)/E7/AIBN and pentaerythritol tetraacrylate (PE4A)/poly(propylene gly-
col) acrylate (PPGA475)/E7/AIBN PDLC films showed 86% permanent memory effect
with E90 = 6 V/µm and memory state contrast of 70% and full permanent memory effect
with E90 = 3 V/µm and total memory state contrast, respectively. These materials with
two stable states (opaque and transparent) seem to be promising for the development of
a new class of optical memories as they can be used for electrically write information,
optically read the written information and they can be thermally erased back to the
*initial scattered state.*

Keywords PDLC; anchorage force; polymeric network; permanent memory effect;
information storage

1. Introduction

A PDLC can be switched electrically from an opaque scattering state to a highly transparent
state when a film of liquid crystal (LC)-polymer mixture is sandwiched between two
conductive glass slides and the LC shows a positive dielectric anisotropy [1–2]. When
no electric field is applied the LC molecules would be oriented within each domain,
although this orientation is random from one domain to another and light propagation
normal to the film surface will probe a range of refractive indices between ordinary refractive
index (n_o) and extraordinary refractive index (n_e) of the liquid crystal. Since the optical
anisotropy of LC molecules used in PDLC is sufficiently large, the effective refractive
index is not generally matched with the refractive index of the polymer (n_p), light will
be scattered and the PDLC is opaque (OFF state). To maximize off-state scattering, the
birefringence ($\Delta n = n_e - n_o$) should be as large as possible [3]. On the other hand, when
an electric field with sufficient strength to overcome the interactions between polymer
matrix and liquid crystal molecules at interfaces of LC domains–polymer matrix is applied
across the film, liquid crystal directors within each domain become uniformly oriented
parallel to the direction of the electric field. If ordinary refractive index of the liquid crystal
matches the refractive index of the polymeric matrix (n_p) the film becomes transparent (ON
state). So, the transparency of the PDLC film can be tuned by applying an electric field.

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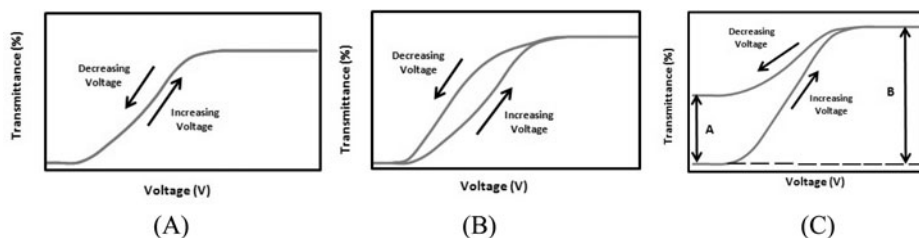
Figure 1. PDLC electro-optical study; (A) – No hysteresis; (B) – Hysteresis Effect and (C) –Permanent Memory Effect.

Usually the transmittance measured with increasing voltage is equal to the transmittance measured with decreasing voltage, as shown in Figure 1(A), although for some PDLC films a hysteresis can be seen, Figure 1(B). For particular films, hysteresis is too high and a transparent state is retained after the electric field is turned off, known as Permanent Memory Effect (PME), as shown in Figure 1(C). High PME must reflect a low driving force for bringing the LC molecules back to initial random distribution of LC domains in the polymer matrix, that means, low polymer-LC anchoring force.

The PME can be calculated through the following expression:

$$\text{PME} (\%) = \frac{A}{B} \times 100 \quad A = T_{OFF} - T_0; B = T_{ON} - T_0$$

where T_0 is the initial transmittance, T_{ON} the maximum transmittance when voltage is applied and T_{OFF} the transmittance when voltage is removed. The electric field (V/μm) required to achieve 90% of maximum transmittance, defined as E90, and memory state contrast (%C) as the difference $A = T_{OFF} - T_0$, are used to quantify the performance of PDLC films.

The permanent memory effect seems to be exclusive of a kind of polymer matrix structure, when formed microsized polymer balls are merged together to form a network that is in contact with a continuous liquid crystal phase, the so-called polymer ball morphology [4]. Other polymer matrix structure, the most common one, can be seen when a droplet nucleation and growth occur and the isolated liquid crystal droplets or domains are formed, surrounded by polymer separation walls, the so-called droplet morphology. The polymer ball morphology implies a collective alignment of the LC molecules, related with a higher surface-to-volume ratio (SVR). In the case of isolated LC droplets, and after the reorientation of LC molecules in each droplet upon application of an electric field, with the removal of the field the LC molecules return to the initial configuration to minimize the elastic free energy. But with collective alignment as in polymer ball morphology, it shows a permanent memory effect as the LC molecules maintained the orientation even after the removal of electric field [4].

Various variables can influence the appearance of permanent memory effect in a PDLC film, being anchoring effect the most frequently explanation mentioned in literature. When the orientation of LC molecules is induced by electric field appliance, it opposes to the anchoring effect. If this orientation remains even after the applied voltage has been switched off, the liquid crystal does not relax back completely but remains aligned as it was when the electric field was on, and a high transparency state is displayed without any more energy consumption. Therefore, for this to happen there must be a weak force between LC
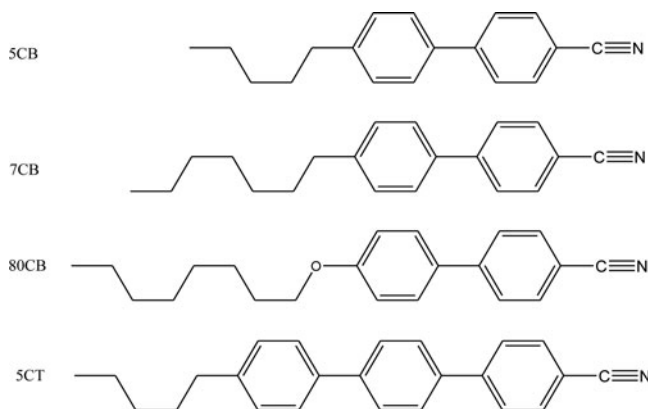
Figure 2. Molecular structure of the components of liquid crystal E7.

molecules and the polymer surface [5]. This low anchoring force should be more important in larger LC domains.

2. Experimental

2.1. Materials and Methods

Nematic liquid crystal E7 ($n_0 = 1.5217$, $\Delta n = 0.2255$, $T_{NI} = 58°C$, composition: (5CB) 4-cyano-4′-pentyl-1,1′-biphenyl (51wt%), (7CB) 4-n-heptyl-4′-cyanobiphenyl (25 wt%), (8OCB) 4,4′-n-octyloxycyanobiphenyl (16wt%) and (5CT) 4′-n-pentyl-4-cyanotriphenyl (8wt%)) was purchased from Merck® Co. Japan. The molecular structures of the different components of E7 are shown in Fig. 2 [6].

The initiator used for thermal polymerization was N,N-azobisisobutyronitrile (AIBN) from Aldrich. The liquid crystalline mixture and initiator were used as received without further purification.

The precursors of the polymeric matrix were trimethylolpropane trimethacrylate (TMP3MA), poly(propylene glycol) methacrylate (PPGMA375), poly(propylene glycol) acrylate (PPGA475) and pentaerythritol tetraacrylate (PE4A) and mixtures between the two acrylates and the two methacrylates. The chemical structures of the monomers and oligomers are shown in Fig. 3. Theses monomers and oligomers were previously passed through polystyrene divinylbenzene columns from Aldrich in order to eliminate the hydroquinone stabilizers.

2.2. Preparation of PDLC Films

For the preparation of PDLC films, monomer or oligomer and E7 were mixed together at room temperature until the mixture became homogeneous in different weight ratios.

The methacrylate solutions were prepared through mixtures of monomethacrylate (PPGMA375) with cross-linker trimethacrylate (TMP3MA) in the weight ratios 100:0, 75:25, 50:50, 25:75 and 0:100. All mixtures contain AIBN and E7 in the proportion of 1 and 70%wt, respectively, with respect to the monomer mixture.
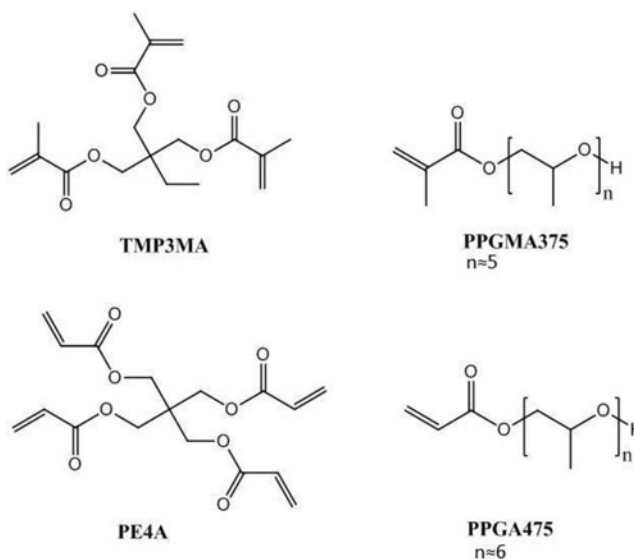
Figure 3. The chemical structures of monomers and oligomers used in the polimeric matrix.

The acrylate solutions were prepared through mixtures of monoacrylate (PPGA475) with cross-linker tetraacrylate (PE4A) in the weight ratios 100:0, 75:25, 50:50, 25:75 and 0:100. All mixtures contain AIBN and E7 in the proportion of 1 and 60%wt, respectively, with respect to the monomer mixture.

Samples were prepared by introducing the mixtures by capillarity into a 20 μm ITO glass cell with polyimide anti-parallel rubbing alignment layer with a pretilt angle of 3°, provided by Instec Inc. Polymerization reactions occur directly within ITO cell. The thermal polymerizations were carried out in a handmade oven. The cells filled with the mixture were cured isothermally for several minutes at 74°C.

2.3. *Morphology of Polymer Network in the PDLC Films*

Scanning Electronic Microscopy (SEM) provided images of the morphology of the polymeric matrix in the PDLC. Cells containing cured methacrylate PDLCs were fractured to obtain an interface representative of the bulk morphology. Samples of acrylate for SEM analysis were obtained with different preparation: thermal polymerizations of mixtures were performed in a support of Teflon. In order to extract E7 of the PDLC films, all the samples (fractured cells and polymeric films) were immersed in acetonitrile three times and dried under vacuum overnight. The resulting polymeric matrix films were mounted on aluminium stubs carbon cement (D-400, Neubaeur Chemikalien) and a thick gold coating was deposited using a dual ion beam sputter coating apparatus. The measurements were obtained on a microscope Hitachi S-2400 instrument with a Rontec standard energy dispersive x-ray spectroscopy (EDS) detector.

2.4. *Electro-Optical Measurements*

An optical system was used to characterize the electro-optical properties of the PDLC films. The transmitted light intensity through the sample was measured by means of a Avantes
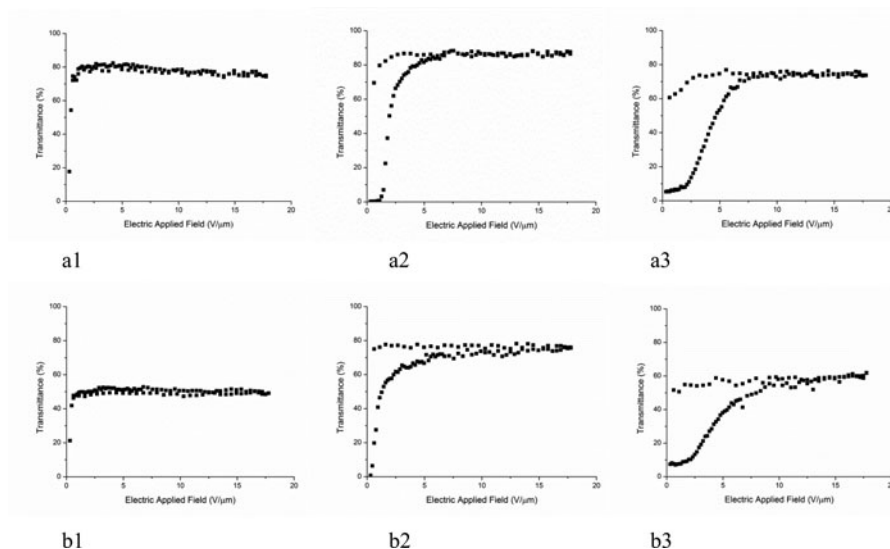
Figure 4. The electro-optical response for PDLC films 40 minutes polymerized at 74°C for different monomer/co-monomer ratios: A) PPGMA-co-TMP3MA (a1) 100–0 wt%, (a2) 50–50 wt%, (a3) 0–100 wt% for 30/70 monomer/E7 ratio and B) PPGA-*co*-PE4A (b1) 100–0 wt%, (b2) 50–50 wt%, (b3) 0–100 wt% for 40/60 monomer/E7 ratio.

diode array spectrophotometer (AvaLight-DHS and AvaSpec 2048) at $\lambda = 633$ nm and room temperature. The measurement system was controlled by a data acquisition computer and the films were oriented normally to the incident light beam. Starting from an electrical off-state, a signal generator (Wavetek 20 MHz Synthesized Function Generator Model 90) created a 1 kHz sinusoidal wave with amplitude varying between 1mV and 10 V which was then amplified 40X by a Vtrek TP-430 amplifier, up to a maximum voltage of 400 V. The 1 kHz pulse was applied to the sample for 200 ms, followed by 1000 ms to allow relaxation to off-state. Transmittance was measured with increasing and decreasing voltage and 210 experimental points at 180 ms after the beginning of the pulse were collected.

2.5. *Differential Scanning Calorimetry Measurements*

Differential Scanning Calorimetry measurements were carried using a DSC Q2000 from TA Instruments interfaced with a cooling accessory (RCS). An ice-water slurry as coolant and nitrogen purge (50 mL.min^{-1}) were used. Sample masses of around 2 mg were weighted and encapsulated in a hermetically sealed aluminium pans. Identical heating and cooling rated were applied in the temperature ranged from -80°C to 180°C. Data analysis has been carried out on the first and second heating ramp.

The monomer and polymer glass transition temperatures were determined from the midpoint of the transition range of the thermographs.

3. Results and Discussion

Representative examples of permanent memory state transmittance in PDLC films thermally polymerized for 40 minutes at 74°C for PPGMA-co-TMP3MA and PPGA-*co*-PE4A, at different ratios of monomer/co-monomer, are shown in Fig. 4.

Table 1. Electro-optical results for 40%(PPGA-co-PE4A)/60%E7 and 30%(PPGMA-co-TMP3MA)/70%E7 PDLC films with different monomer/co-monomer ratios

%wt monomer/co-monomer	PPGA-co-PE4A			PPGMA-co-TMP3MA		
	PME (%)	E90 (V/μm)	C (%)	PME (%)	E90 (V/μm)	C (%)
100/0		n.a.			n.a.	
75/25	83	4	79	17	8	10
50/50	96	5	77	86	6	70
25/75	100	3	70	82	9	54
0/100	86	9	52	73	12	55

From the electro-optical response studies, the permanent memory effect (%PME), the electric field required to achieve 90% of maximum transmittance, defined as E90, and the memory state contrast (%C) can be calculated. All results for monomer/co-monomer ratios for both 40%(PPGA-co-PE4A)/60%E7 and 30%(PPGMA-co-TMP3MA)/70%E7 are presented in Table 1.

A polymeric matrix without cross-linker showed low viscosity, very large LC domains and a structure not rigid enough to support them. Phase separation occurs and LC molecules and polymer regions agglomerate in large domains. For films made with only PPGA or PPGMA as monomer, the initial transmittance was usually high and the film produced was not very opaque and homogeneous. Increasing the amount of cross-linker, a more rigid polymeric structure was obtained, the LC domains would be reduced in dimension and it is clear from Table 1 that an optimum ratio between monomer and cross-linker can be obtained to gave rise a extremely high permanent memory effect in the PDLC films. As shown in Fig. 5, PME showed a dependence on the monomer/co-monomer ratio. The LC
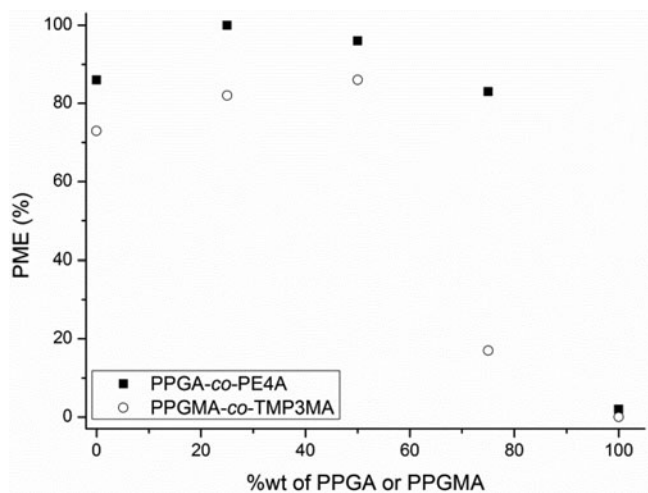
Figure 5. Permanent memory effect dependence on monoacrylate or monomethacrylate composition for PPGA-co-PE4A and PPGMA-co-TMP3MA PDLC films with E7.
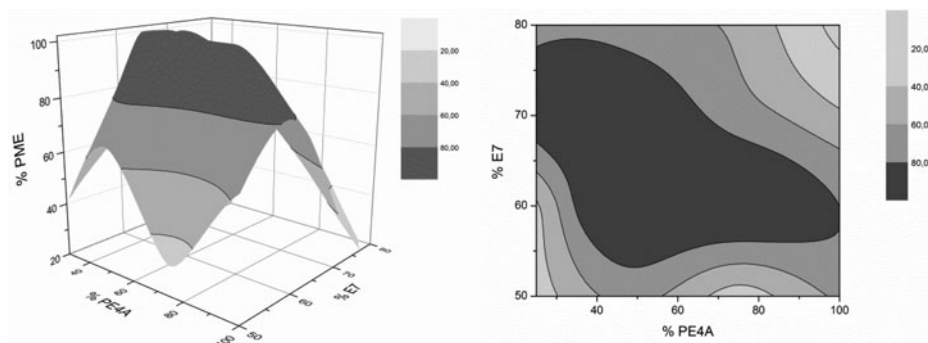
Figure 6. Permanent memory effect dependence on E7 and PPGA/PE4A composition for (PPGA-co-PE4A)/E7 films 40 minutes polymerized at 74°C.

rich regions dimension is very important in PME. Increasing the cross-linker concentration in the matrix the surface volume ratio (SVR) increases because the size of polymer balls would decrease. On the other side, too much cross-linker can turn the LC rich regions too small and implies a too high SVR, which reduce PME due to a stronger anchoring strength between liquid crystal and the polymer surface.

In order to develop a PDLC film with maximum PME, the PPGA-co-PE4A system was chosen and several compositions of E7/PPGA/PE4A were studied. Those films showed very high PME with a more narrow dependence on E7, in the range 60–75wt%, being the remained ratio less dependent on monomer/cross-linker proportion, where %PE4A can be in the range 40–80 wt%, as shown in Fig. 6. Preferred studies were made with 40%(PPGA-co-PE4A)/60%E7.

All these polymeric matrices have shown polymer ball morphology type, with polymer ball diameter around 50 nm, agglomerated in larger units with 2 μm in diameter, Fig. 7. A larger proportion of PE4A in the polymeric blend of the matrix makes the edges of polymer ball sharper and the morphology better detailed.

The optimal range of cross-linker monomer concentration in the matrix, in Fig. 7 between 50%wt and 100%wt, determine the anchoring strength that permit the alignment of LC molecules with a relatively low driving voltage and the permanency of this alignment even when electric field is removed. This anchoring strength can be correlated with the morphology of polymeric matrix.
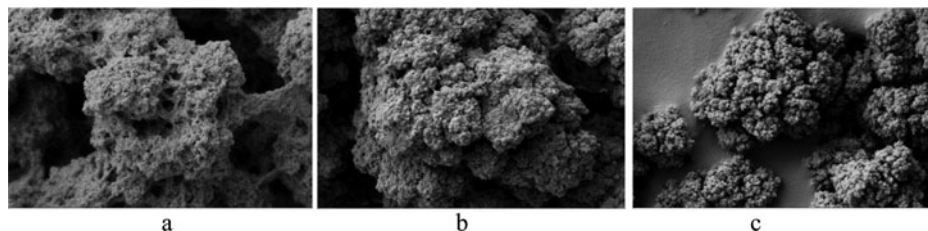
Figure 7. SEM images of polymeric matrix of 40%(PPGA-co-PE4A)/60%E7 PDLC films for different monomer/co-monomer ratios: a) 50–50 wt%, b) 25–75 wt%, c) 0–100 wt% (all with 20000× magnification).
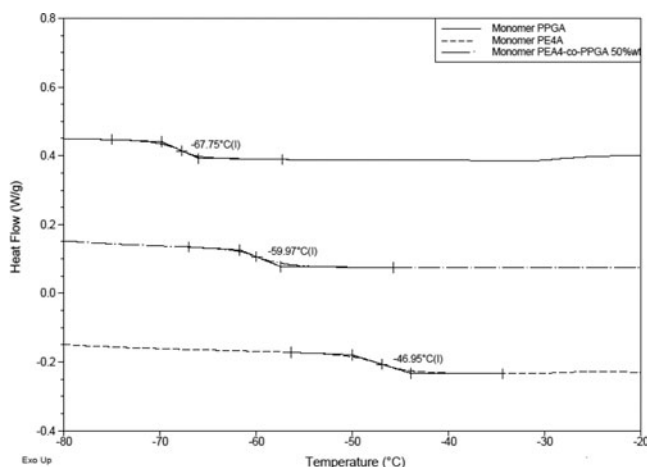
Figure 8. DSC plot of 40%(PPGA-co-PE4A)/60%E7 PDLC films for different monomer-co-monomer ratios: PPGA-co-PE4A 100–0 wt%, 0–100 wt% and 50–50 wt%.

Differential Scanning Calorimetry measurements showed monomers glass transition temperatures for PPGA, PE4A and 50%wt mixture of the two at 205.40 K, 226.20 K and 213.18 K, respectively, clearly following the Fox equation, Fig. 8. Nevertheless, it was not possible to determine the glass transition temperatures of polymeric matrices due to the high cross-linker degree [7].

These PDLC films that permit to access interchangeably two stable states (opaque and transparent) seem to be promising for the development of a new class of materials to be used as optical memories as they can electrically write information in a digitally way, 0 and 1, optically read the written information as transmittance and they can be thermally erased back to the initial scattered state by applying temperature above PDLC clarification temperature, in these cases around 68°C.

4. Conclusions

In summary it is observed that permanent memory effect of PDLC is greatly influenced by the percentage of cross-linker monomers used as precursors of polymeric matrix. The optimal range of percentage of this monomer it is between 40 and 80%wt for both studied systems, when compared with total monomer-co-monomer weight. With these percentages it is possible to produce PDLC with very high PME between 80 and 100%.

It is hypothesized that the optimal range of percentage of cross-linker monomer determine the anchoring strength that permit the alignment of LC molecules with a relatively low driving voltage and the permanency of this alignment even when electric field is removed. This anchoring strength can be related with the morphology of polymeric matrix. The polymer matrices microstructure can be all assigned to polymer ball morphology. However, with the decrease of cross-linker monomer the surface volume ratio (SVR) decreases because the size of polymer balls increase. PDLC with low SVR (low polymer surface in contact with LC molecules) exhibit a weak anchoring strength between liquid crystal and the polymer molecules that increase the PME.

Another factor that can explain the higher values of PME is the low glass transition temperature of polymeric matrix [8]. Co-polymerizations can result in an elastomer polymer

with lower T_g than room temperature (211K for PPGA-co-PE4A 50%wt with 40min of polymerization at 74°C but impossible to measure for higher PE4A concentration). For this reason when the LC molecules reoriented along to the electric field may drag polymer chains to form a new stable conformation and so the LC molecules do not tend to return to a random configuration when electric field is switched off. Therefore, the PDLCs would not go back to its initial opaque state and a high transparency state is preserved.

Funding

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