

New polymer to enhance the permanent memory effect of polymer dispersed liquid crystal films

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ABSTRACT: Conventional polymer dispersed liquid crystals (PDLC) are devices with recognized applications. New PDLCs with permanent memory effect (PME) can be used as digital memory devices. The synthesis and characterization of a new monomer [pentaerythritoltetramethacrylate (PE4MA)] is here described. A PDLC was produced using the synthesized monomer (PE4MA) copolymerized with commercially available monomethacrylate oligomer poly(propyleneglycol) methacrylate (PPGMA) and 70% (w/w) liquid crystal (E7), showing 98% permanent memory effect, with 72% memory state contrast (MSC) and an electric field required to achieve 90% of the maximum transmittance (E_{90}) of $3 \text{ V } \mu\text{m}^{-1}$. The synthesized monomer (PE4MA) copolymerized with PPGMA seems to be a prospective material for preparation of PDLC with permanent memory effect with a view to application for digital memory devices based on write-read-erase cycles. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43482.

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INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films are dispersion of liquid crystal (LC) domains in a continuous polymer matrix. The principle functionality of PDLC films is the electrically controlled light scattering. Therefore, PDLCs can be switched from a highly scattering opaque state to a transparent one during the application of an electric field.¹ This transition of states is due to the mismatching and matching of the refractive index of the polymer and the ordinary refractive index of the liquid crystal. Despite, the potentialities of the PDLCs such as smart windows, optical sensors, and flexible display devices,² these electro-optical devices need a continuous supply of voltage to operate. For this reason, PDLCs would become more attractive if they keep the transparent state without spending energy. In other words, PDLC in an initial opaque state (OFF-state) with an application of an electric field change to a transparent state (ON-state) but this new state is kept even after the applied voltage has been switched off. For these PDLCs to return to opaque state, it is needed to reach the clarification temperature of the film.¹ This type of PDLCs has a permanent memory effect (PME) and it is low power consumer. For this reason, these PDLCs are the target of this investigation.

The electro-optical properties of PDLC including the permanent memory effect are dependent on a series of factors such as polymerization conditions, structure of polymerizable monomer, the microstructure of the polymer matrix, the type, and the concentration of liquid crystal,^{3–13} among other factors. Due to these large numbers of parameters involved, it is difficult to affirm which are implicating in permanent memory effect. However, our preliminary experiments showed that concentration of liquid crystal and the crosslink properties of the polymer¹⁴ greatly enhance the permanent memory effect. Crosslink properties of polymer matrix can affect the anchoring force between polymer and LC molecules through a change of surface to volume ratio (SVR)⁴ of PDLCs, through a modification of polymer surface roughness in contact with liquid crystal molecules. In a polymer ball morphology structure type, the decrease of surface roughness decreased the polymer surface in contact with LC molecules.⁴ Therefore, reduces the anchoring effect of polymer matrix on the LC molecules and consequently potentiate the permanent memory effect. Another parameter that could have influence on PME of PDLCs is the glass transition temperature (T_g) of polymeric matrix,¹⁵ being that T_g of polymer matrix lower than room temperature strengthen the PME. For this reason, the focus of this investigation is to consolidate the effects of the degree of crosslink properties of polymerizable

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monomers on surface to volume ratio/surface roughness and on the plasticity of polymer matrix. However, the relationship between these parameters and the permanent memory effect is also discussed in detail.

EXPERIMENTAL

Materials

The nematic liquid crystalline mixture E7, with the composition: 4-cyano-4'-pentyl-1,1'-biphenyl (51%), 4-n-heptyl-4'-cyanobiphenyl (25%), 4,4'-n-octyloxycyanobiphenyl (16%), and 4'-n-pentyl-4-cyanotriphenyl (8%) w/w,¹⁶ was supplied by Merck. The initiator for the thermal polymerization was 2,2'-azobis(isobutyronitrile) (AIBN) from Aldrich. The monomethacrylate oligomer was poly(propyleneglycol) methacrylate (PPGMA; purchased from Aldrich). The synthesis reagents pentaerythritol and methacrylic anhydride were purchased from Aldrich and used without further purification. The solvents used and triethylamine from Aldrich were purified before use. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz on a Bruker AMX-400 instrument in deuterated chloroform (CDCl_3) with chemical shift values (δ) reported in ppm downfield from tetramethylsilane (TMS). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on Perkin-Elmer Spectrum BX apparatus in KBr dispersions.

Differential Scanning Calorimetry (DSC) measurements were carried using a DSC Q2000 from TA Instruments interfaced with a cooling accessory (Refrigerated Cooling System). Ice-water slurry as coolant and nitrogen purge (50 mL min^{-1}) was used. Sample masses of around 2 mg were weighted and encapsulated in a hermetically sealed aluminum pans. Measurements were carried out under nitrogen atmosphere with a flow rate of around $10^\circ\text{C min}^{-1}$.

The PDLC morphologies were studied using a scanning electron microscopy (SEM) equipped with a Hitachi S-2400 instrument with a Rontec standard energy dispersive X-ray spectroscopy (EDS) detector. PDLC cells for SEM analysis were open in order to separate the two conductive glasses exposing the dispersion of liquid crystal in a polymeric film. The liquid crystal was removed from the samples before microscopy by immersing the samples (open PDLC cells) in three Erlenmeyer flasks with fresh acetonitrile, all over 30 min and dried under vacuum overnight. The resulting samples were mounted on aluminum stubs carbon cement (D-400, Neubaer Chemikalien) and a several angstroms thick gold coating was deposited using a dual ion beam sputter coating apparatus.

Polarized optical microscopy (POM) experiments were conducted on an Olympus CX31P optical polarizing microscope connected to an Olympus SC-30 digital camera interfaced to a computer. The microphotographs of the dispersion of liquid crystal domains in PDLC films were obtained at a magnification of $100\times$ under crossed polarizers.

PDLC ITO glass cells (LC2-20) are commercially provided by (Boulder, CO80503, USA) with $20 \mu\text{m}$ of spacer between ITO substrates.

A handmade oven was used in thermal polymerizations, equipped with an auto-tune temperature controller provided by

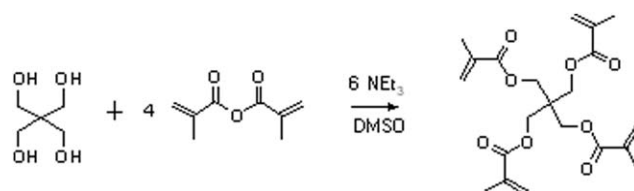


Figure 1. Scheme for the synthesis of pentaerythritoltetramethacrylate (PE4MA).

CAL Controls, model CAL 3300, and a resistance thermometer, Pt100/RTD-2, which can measure the temperature ranging from -200 to 400°C .

For the characterization of the electro-optical properties of the PDLC films, the transmittances were measured with increasing and decreasing voltage. The light transmittance studies were performed using a diode array Avantes spectrophotometer (AvaLight-DHS and AvaSpec 2048) with a halogen lamp and optical fiber connections. A 633 nm wavelength was selected. Spectrophotometer calibration was performed by using 0% and 100% transmittance. The electric pulse (1 kHz) was generated by a programmable waveform generator (Wavetek 20 MHz Synthesized Function Generator Model 90), producing an alternating current (AC) wave with a low amplitude (between 0 and 27 VRMS) for sample excitation. For the electro-optical measurements, an external electric field was applied across the PDLC film. The generator connected to a Vtrek TP-430 amplifier reaching a voltage of 47 VRMS was linked to a 220 V/9 V transformer inversely connected and it increased the applied voltage by a factor of 24. A resistance (1Ω) had the purpose of securing the amplifier from short-circuits and another resistance ($150 \text{ k}\Omega$) was used to standardize the voltage wave output. The amplifier was fed by a Kiotto KPS 1310 power supply. The output detector (AvaSpec-2048) was connected to a computer software data acquisition.

Synthesis and Characterization of Pentaerythritoltetramethacrylate (PE4MA)

The synthetic route for pentaerythritoltetramethacrylate (PE4MA) is shown in Figure 1. To prepare the pentaerythritoltetramethacrylate (PE4MA) monomer, 3.0 g of pentaerythritol (22 mmol), 18 mL of dimethyl sulfoxide (DMSO) under argon, and six equivalents of triethylamine (NEt_3) were added. This mixture was cooled to 0 – 5°C (ice bath) and four equivalent of methacrylic anhydride (88 mmol; 13.11 mL) was added slowly. The reactions were monitored by thin layer chromatography (TLC) and compounds were visualized by UV light (254 nm). The mixture was kept for 1 h at 60°C and then 24 h at room temperature. Then, the reaction mixture was diluted with dichloromethane (CH_2Cl_2) washed with HCl followed by distilled water until to obtain neutral pH and the organic phase was dried with sodium sulfate anhydrous, filtered and concentrated. The residue was purified by flash column chromatography with CHCl_3 to afford pentaerythritoltetramethacrylate as a white powder (4.12 g; 10 mmol; 45%). 1D(1H, 13C and DEPT) and 2D(COSY, HMQC) NMR and FTIR spectra are included in the supporting information.

^1H NMR (400 MHz, CDCl_3 , δ): 6.10 (s, 4H, $=\text{CH}_2$), 5.60 (s, 4H, $=\text{CH}_2$), 4.30 (s, 8H, CH_2), 1.94 (s, 12H, CH_3).

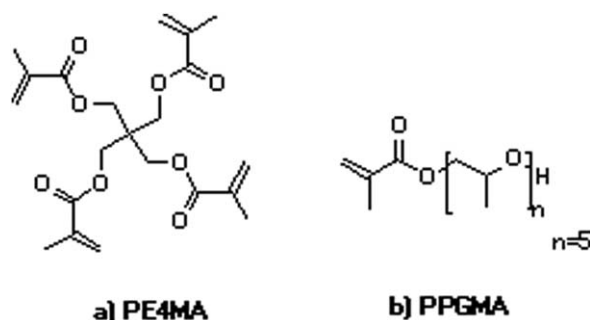


Figure 2. Chemical structures of the monomers used in the preparation of PDLC films.

^{13}C NMR (101 MHz, CDCl_3 , δ): 166.7 (C=O), 135.7 ($=\text{CH}_2-\text{CH}_3$), 126.4 ($=\text{CH}_2$), 62.9 (CH_2), 42.5 ($\text{C}(\text{CH}_2)_4$), 18.3 (CH_3).

FTIR (KBr, cm^{-1}): ν 2964.55 (CH_3), 1720.30 (OC=O), 1635.79 (C=C), 1167.57 (C-O).

Melting point: 70–71 °C.

ANAL. Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_8$: C, 61.75%, H, 6.91%. Found: C, 61.38, H, 6.82.

Preparation of PDLC Films

For the preparation of PDLC films, mixtures with different composition of the two monomers were prepared (Figure 2) and liquid crystal E7 with several weight ratios and AIBN 1% by weight with respect to the monomer mixture. The compositions of the composites from which the PDLC films were prepared are listed in Table I.

Then, the mixture was vigorously stirred and when required with mild heating until a homogeneous mixture had formed before they were filled into 20 μm ITO glass cell by capillary action. The cells filled with the mixture were kept isothermally at 74 °C for several minutes. PDLC cells were prepared by controlling the preparation conditions, such as the LC concentration, time of polymerization and copolymerization with different composition of the two monomers (Figure 2).

The permanent memory effect (%PME) can be calculated using eq. (1):

Table I. Composition of the Samples for the Preparation of PDLC Films

Samples	Monomers used	Weight ratio (%)	E7 (%)
A	PE4MA	30	70
B	PE4MA	40	60
C	PE4MA	20	80
D	PPGMA	30	70
E	PE4MA/PPGMA	75/25	70
F	PE4MA/PPGMA	50/50	70
G	PE4MA/PPGMA	25/75	70

All samples were prepared with AIBN 1% by weight with respect to the monomer mixture.

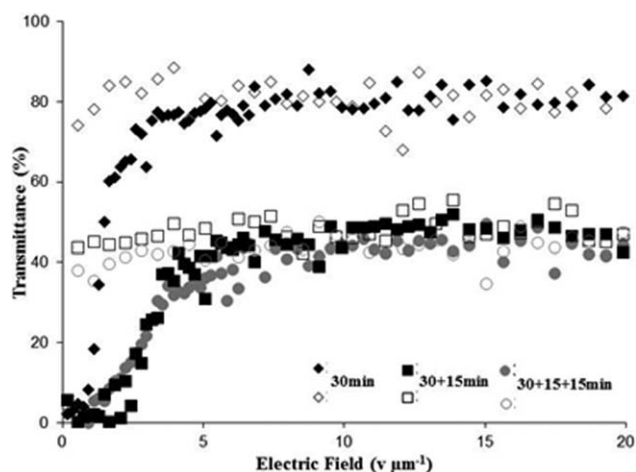


Figure 3. Electro-optical response of the PDLC films prepared from sample A (Table I) for 30, (30 + 15), and ((30 + 15) + 15) min of polymerization time. The sets of data represent a complete cycle of incrementing the applied field up (full symbols) to a maximum value followed by a decrease down to zero electric field (open symbols).

$$\%(\text{PME}) = \frac{T_{\text{OFF}} - T_0}{T_{\text{MAX}} - T_0} \times 100 \quad (1)$$

where T_0 is the transmittance for the initial opaque state (zero electric field), T_{MAX} is the maximum transmittance upon applying an electric field, and T_{OFF} is the transmittance after removing the applied electric field.⁴ One of the parameters

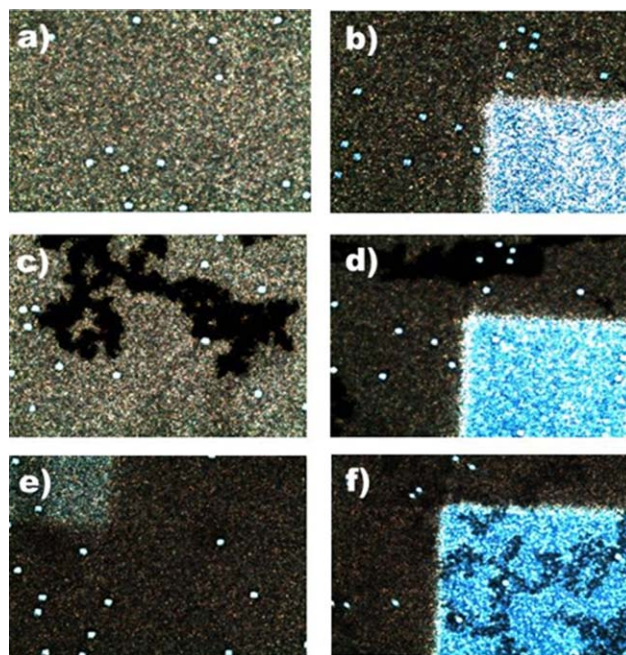


Figure 4. Polarized optical micrographs with crossed polarizers of PDLC films prepared with sample A (Table I) thermal polymerized at different exposure time: (a,b) 30 min before and after applied electric field, respectively; (c,d) 30 + 15 min before and after applied electric field, respectively; and (e,f) 30 + 15 + 15 min before and after applied electric field, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

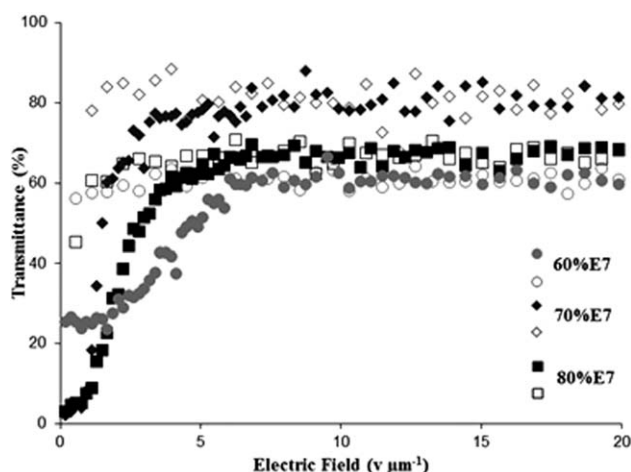


Figure 5. The electro-optical response of PDLC films prepared from different percentages of E7: 60%, 70%, and 80% (w/w) (Table I). The sets of data represent a complete cycle of incrementing the applied field up (full symbols) to a maximum value followed by a decrease down to zero electric field (open symbols).

used to evaluate the PDLC electro optical response efficiency is the electric field required to achieve 90% of the maximum transmittance and is designated as E_{90} . The memory state contrast (%MSC) is defined as the difference between T_{OFF} and T_0 .

RESULTS AND DISCUSSION

In order to determine the optimal PDLC polymerization time to monitor the permanent memory effect, we prepared PDLC films from sample A (Table I) with 30 min, (30 + 15) min, and [(30 + 15) + 15] min of polymerization time. For less than 30 min, there was no polymerization degree enough to produce phase separation. For the first 30 min of polymerization, the sample was kept isothermally at 74 °C. After the electro-optical study, the sample was kept isothermally for more 15 min and after this time, another electro-optical response was determined. Finally, after another 15 min of polymerization, a last electro-optical response was recorded. These electro-optical responses are depicted in Figure 3 and electro-optical properties are summarized in supporting information (Table S1).

It is clear from Figure 3 that the optimal time for PDLC polymerization is 30 min. In these conditions, a 92% PME with 72% MSC and E_{90} of $6 \text{ V } \mu\text{m}^{-1}$ were observed.

The decreased of electro-optical response with increased polymerization time can be related with the heterogeneity of the dispersion of LC domains in polymer matrix. This possibility is supported by polarized optical microscopy (POM) under crossed polarizers. POM micrographs explicitly show the formation of no-birefringent areas for PDLC polymerized for more than 30 min [Figure 4(c,d,f)].

These areas seem to appear due to higher crosslinked network formation with the increased polymerization time, which means polymer network

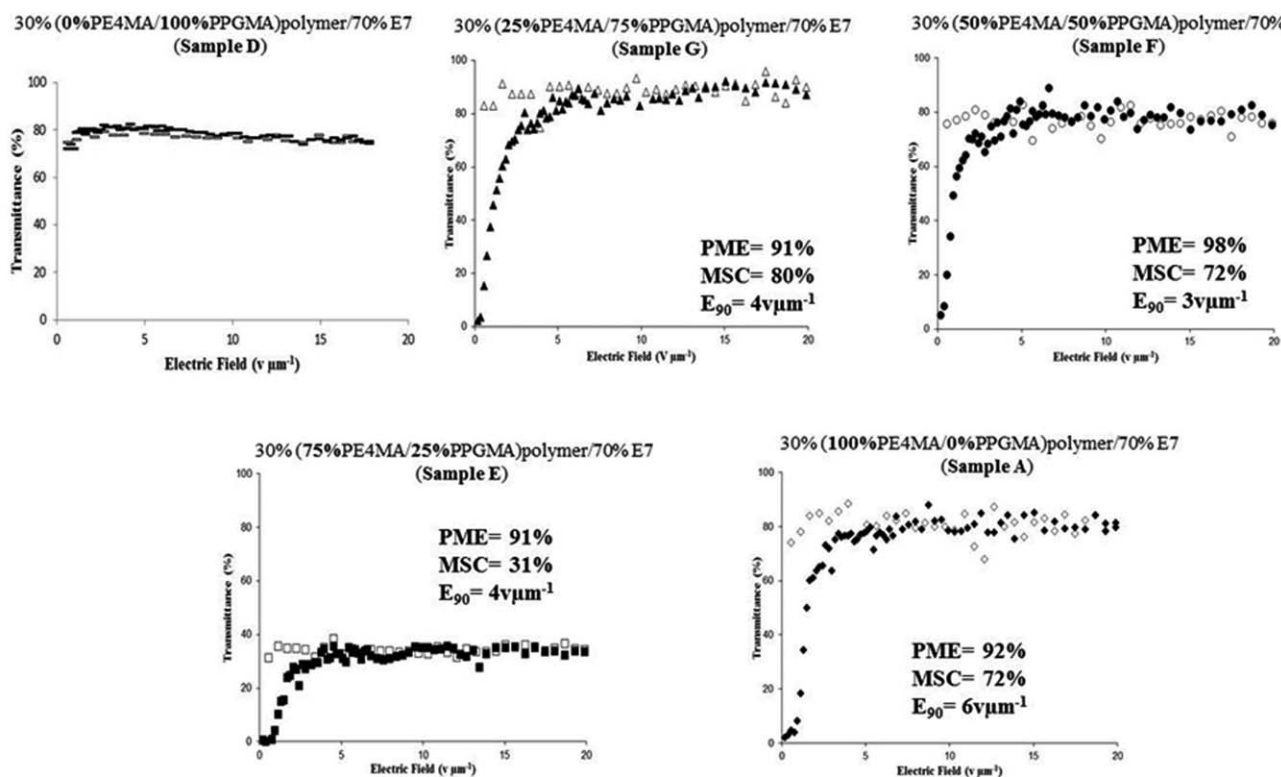


Figure 6. The electro-optical response for PDLC films prepared with different composition (Table I) of two monomers (PE4MA and PPGMA). The sets of data represent a complete cycle of incrementing the applied field up (full symbols) to a maximum value followed by a decrease down to zero electric field (open symbols). The PME is the permanent memory effect, MSC is the memory state contrast, and the E_{90} the electric field required to achieve 90% of the maximum transmittance.

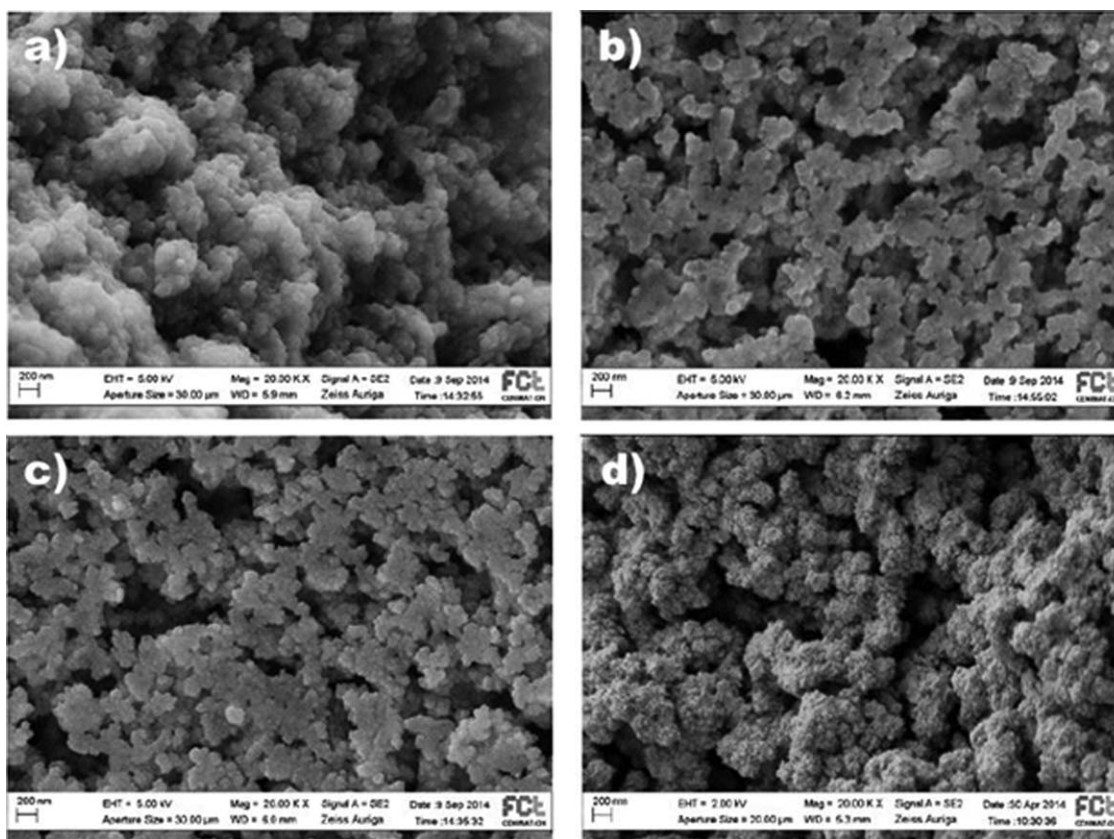


Figure 7. SEM micrograph for the microstructure of the polymer matrix of PDLC films prepared with different composition in two monomers (PE4MA and PPGMA): (a) 25% PE4MA-75% PPGMA (Table I, sample G); (b) 50% PE4MA-50% PPGMA (Table I, sample F); (c) 75% PE4MA-25% PPGMA (Table I, sample E); and (d) 100% PE4MA-0% PPGMA (Table I, sample A).

regions that do not incorporate liquid crystal domains. Therefore, it is possible that phase separation occurs during polymerization before the completion of the polymerization reaction.

In Figure 4(b,d,f), it is also evident that even after electric field was removed LC molecules remain align (region where electric field was applied is more bright under crossed polarizers) proving permanent memory effect.

In order to evaluate the outcome of LC concentration in permanent memory effect, for monomer PE4MA and polymerization temperature at 74 °C during 30 min, different E7 concentrations were used: 70%, 60%, and 80% (w/w) (Table I, samples A, B, and C, respectively). From Figure 5, it is evident that LC concentration affects the permanent memory effect. As expected, an optimal E7 concentration range was needed to optimize the permanent memory effect and electro-optical properties are summarized in supporting information (Table S2).

PDLC films prepared with 60% of E7 looks slightly transparent at zero electric field ($T_0 = 26\%$) because the LC concentration is too small for efficient visible light scattering. In contrast, higher LC concentrations (70 and 80%) seem to be enough to produce PDLCs totally opaque at zero electric field. However, 80% of LC is a higher concentration to enable the formation of polymer network with an efficient dispersion of the LC domains but with lower permanent memory effect (66%) and memory state contrast (42%). Therefore, for the optimal E7 concentration of 70%, 92% PME, $6 \text{ V } \mu\text{m}^{-1}$ for E_{90} , and 78% of MSC were observed.

In order to control the higher crosslinked network formation regions, co-polymerization with one commercial monomethacrylate monomer (PPGMA) was tested. For this purpose, PPGMA was incorporated in the preparation of PDLCs as opposed to crosslinker synthesized tetramethacrylate (PE4MA). All PDLC cell were prepared at 74 °C during 30 min of polymerization time. The electro-optical responses are presented in Figure 6 and electro-optical properties are summarized in supporting information (Table S3).

It is evident from Figure 6 that the methacrylate solution prepared through mixtures of crosslinker tetramethacrylate and monomethacrylate in proportion of 50% PE4MA–50% PPGMA (w/w) (Table I, sample F) used in preparation of PDLC enhance the permanent memory effect. With these proportions the PDLC showed 98% PME, 72% MSC, and E_{90} of $3 \text{ V } \mu\text{m}^{-1}$.

In order to determine if co-polymerization influence in PME is associated with the change of the morphology of the polymer matrix, scanning electron microscopy (SEM) was used, Figure 7. Regardless of permanent memory change, according to the percentage of co-polymerization, the morphology of all samples can be assigned as polymer ball morphology type. Therefore, permanent memory effect is not related with different morphologies. From Figure 7, it is particularly interesting to observe that the degree of surface to volume ratio (SVR) changed according to the percentage of co-polymerization. In other words, with the increase of the percentage of crosslinker

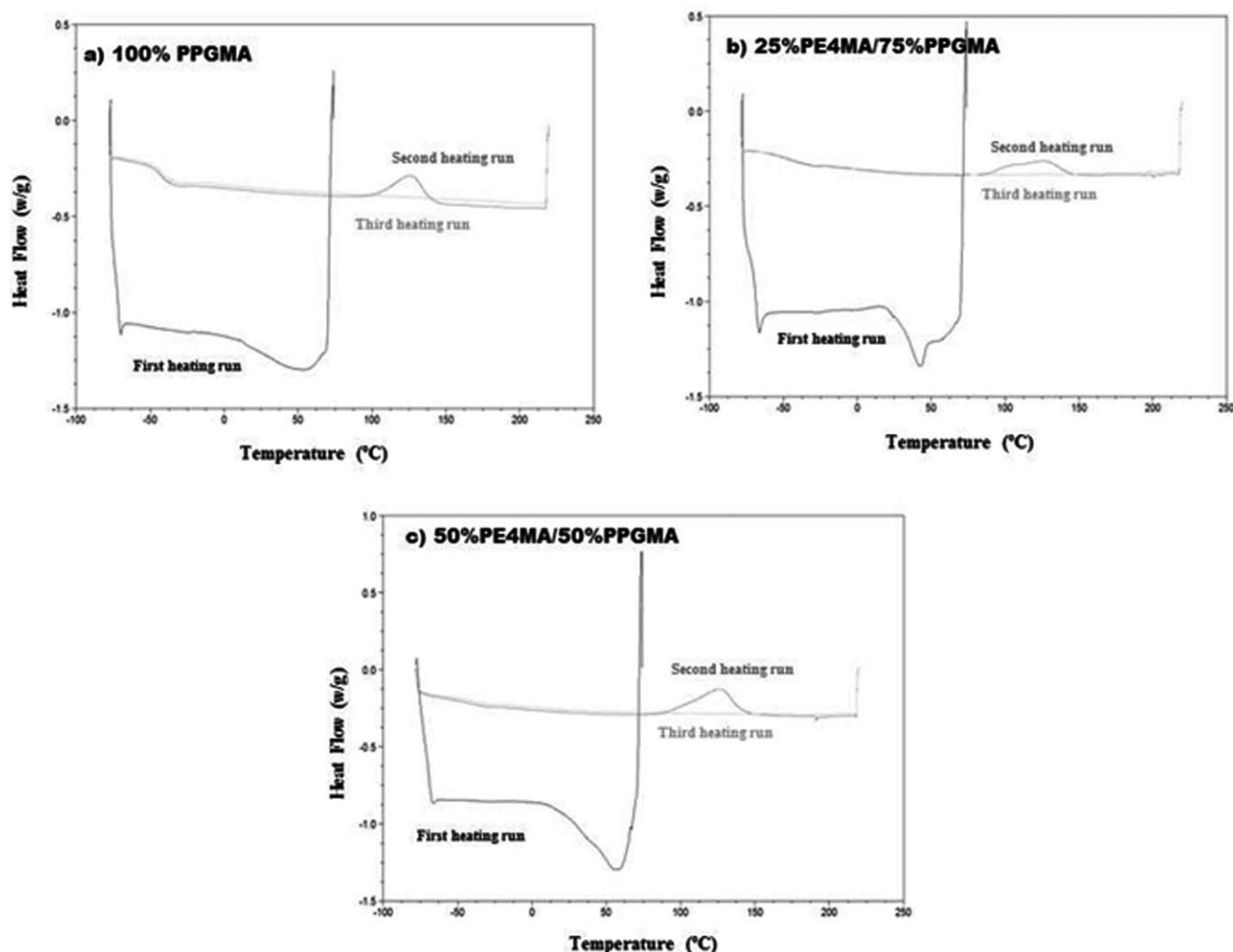


Figure 8. DSC measurements obtained for mixtures of: (a) 0% PE4MA-100% PPGMA (Table I, sample D); (b) 25% PE4MA-75% PPGMA (Table I, sample G); and (c) 50% PE4MA-50% PPGMA (Table I, sample F) during the first, second, and third heating run. (All samples were prepared with AIBN 1% by weight with respect to the monomer mixture).

monomer (PE4MA) the polymer balls are progressively weakly merged increasing the surface roughness, then the size of the polymer balls change from 200 nm for the case with 25% of PE4MA [Figure 7(a)] to 10 nm for the case of 100% of PE4MA [Figure 7(d)]. This last case enhances the formation of a struc-

ture with higher polymer surface in contact with the LC molecules. According to the authors,⁴ as the SVR increased, permanent memory effect must increase. However, this study showed opposite results, as our previously paper.¹⁴ It seems that the decrease of surface roughness, reduced the anchoring force

Table II. Glass Transition Temperature of Mixture (PE4MA/PPGMA) with AIBN 1% by Weight with Respect to the Monomer Mixture Obtained by DSC during Different Heating Runs

Composition in the two monomers by weight (PE4MA/PPGMA)	Glass transition temperature (°C)		
	First heating run	Second heating run	Third heating run
(100% PE4MA/0% PPGMA)	-	-	-
(0% PE4MA/100% PPGMA)	-69.36	-42.73	-42.07
(25% PE4MA/75% PPGMA)	-65.67	-47.81	-42.11
(50% PE4MA/50% PPGMA)	-65.97	-42.55	-43.82
(75% PE4MA/25% PPGMA)	-	-	-

The first, second, and third heating run can be assigned to thermal properties of: monomer, polymer obtained after 30 min of polymerization time at 74 °C, and polymer obtained after a heating run up to 220 °C, respectively.

between polymer matrix and liquid crystal molecules increasing the PME from 91% to 98% (for our best result) for PDLCs prepared with 100% PE4MA (Table I, sample A) and 50% PE4MA-50% PPGMA (Table I, sample F), respectively.

The glass transition temperature (T_g) of the polymeric matrix is believed to have influence in permanent memory effect. Thermal properties of PPGMA, PE4MA, and co-polymerization of PPGMA-co-PE4MA were studied by differential scanning calorimetry (DSC). In a first heating run, the monomer mixture was heating between -80°C up to 74°C and stayed at this final temperature during 30 min (first heating run) in order to polymerize with the same polymerization time that during the preparation of PDLC films. After this first heating run, samples were cooled down to -80°C . In order to determine the thermal properties of the material obtained after 30 min of polymerization time at 74°C the cooled sample were submitted at a heating run up to 220°C (second heating run). Finally, to verified the thermal properties of completed polymerized material, after cool down the sample to -80°C , a third heating run were imposed up to 220°C . Figure 8 present the DSC thermograms collected on the three heating runs. The glass transition temperatures were taken at the inflection point of the specific heat capacity variation in the transition and are summarized in Table II.

For 100% of PE4MA and 75% of PE4MA-co-25% PPGMA polymers, it was not possible to determine the glass transition temperatures by DSC studies due to the high crosslinker degree of the polymers.¹⁷ The relationship between the permanent memory effect and glass transition temperature was referred by other authors.¹⁵ The T_g of polymer matrix is lower than room temperature provided that LC molecules when reoriented along to the electric field tend to force the polymer chain to form a new conformation. If this new configuration is stable, LC molecules tend to keep the alignment and do not return to a random configuration when electric field is switched off and a high transparency state is preserved (permanent memory effect). In the present study, the T_g of polymer matrix it is always lower than room temperature, range between -42°C and -48°C . These lower T_g values are in accordance with the higher permanent memory effect between 91% and 98%. Therefore, the plasticity of polymer matrix as the surface to volume ratio/surface roughness decrease enhances the permanent memory effect.

CONCLUSION

In this work the synthesis of a new monomer (pentaerythritol tetramethacrylate (PE4MA)) was reported, which demonstrated potential application on preparation of PDLC film with permanent memory effect. PDLC films have been prepared using mixture with different composition of two monomers: the synthesized PE4MA monomer and one commercially available monomethacrylate monomer (poly(propyleneglycol) methacrylate (PPGMA)). With this copolymerization, it was possible to understand that the permanent memory effect depends strongly on the surface roughness of the polymer ball morphology. The introduction of PPGMA in PE4MA polymeric matrix smooth the surface roughness and permanent memory effect increased. The adjusting from a low surface roughness of the polymer ball morphology and the plasticity of the polymer matrix enhance the permanent memory effect. It was found that these are the major factors for

permanent memory effect that can be controlled by the different composition of the two monomers. Therefore, the synthesized monomer (PE4MA) copolymerized with PPGMA seems to be a prospective material for preparation of PDLC with permanent memory effect with our best result of 98% for this effect, 72% of memory state contrast and $3\text{ V }\mu\text{m}^{-1}$ of electric field to achieve 90% of the maximum transmittance.

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