Electro-Optical Properties of Polymer-Dispersed Liquid Crystal Prepared by Controlled Graft Living Radical Polymerization

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ABSTRACT: Living graft macromolecule has been prepared through reversible addition-fragmentation chain transfer (RAFT) living radical polymerization in one step. Then, it was used to make polymer-dispersed liquid crystal (PDLC) by controlling the mole ratio of styrene (St) to 1,6-hexanediol diacrylate (HDDA) and adjusting the content of prepared graft macromolecule. The results showed that electro-optical properties of PDLC have been optimized. Different concentration of living graft macromolecule and different mole ratio of St/HDDA led to substantial improvement of driving voltage (threshold voltage and saturation voltage) and memory effect of PDLC simultaneously. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2200–2208, 2012

Key words: electro-optical properties; films; liquid crystals; composites; graft copolymers

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) is one kind of novel materials that are made up of micro-sized nematic droplets dispersed in polymer matrix, and light scattering properties of PDLC can be controlled by electricity.[1] There are three different methods to prepare PDLC, i.e., solvent-induced phase separation (SIPS), thermally induced phase separation (TIPS), and polymerization-induced phase separation (PIPS).[2] Among them, PIPS is the most frequently used. During PIPS process, homogeneous mixture of liquid crystal (LC) and a prepolymer containing a certain amount of thermal initiator or photo initiator is introduced to the cells that consist of two pieces of indium tin oxide (ITO)-coated glass substrates.[3–5] When no voltage is applied on PDLC, [6,7] the thin film will display high optical heterogeneities; if certain voltage is applied to the PDLC cell, the film will turn to be transparent state. Electro-optical properties of PDLC relate to size and shape of the LC droplets, anchoring energy on the boundary surface, film thickness, LC concentration, and refractive index ratio of LC to polymer.[8] The structure and elasticity of polymer matrix are also important factors to affect electro-optical properties of PDLC such as driving voltage (threshold voltage and saturation voltage) and memory effect of PDLC.[9]

Recently, many researches have been done to improve the electro-optical properties of PDLC. Electron beam-cured tripropyleneglycoldiacrylate/E7 (E7 is a kind of nematic LC containing four cyanopara-phenylene derivatives) films investigated by Méchernène et al. exhibit sharp increase of transmission values as a function of voltage.[10] Formentín et al. have prepared PDLCs through combination of SIPS and TIPS to study the diameter of droplet of LC E7 with three different types of polymers as matrice.[11] It is also reported by Wu and Fuh that the size distribution of LC droplets forming in the array increases the electrical tunability of optical characteristics.[12]

During the past decades, controlled/living radical polymerization has displayed the most powerful techniques for polymer synthesis because of its advantages such as low polydispersity index and tolerance to a wide range of chemical function. Compared with the other living radical polymerization methods, reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the most successful living radical polymerization because of its applicability to a wide range of monomers.[13]

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Molecular weights, molecular weights distribution, and molecular architecture of polymeric materials prepared from a wide range of monomers have been controlled easily by RAFT.[14–16] Controlled graft polymers can also be synthesized by RAFT easily. Interests in macromolecules with graft structure is related to multiple graft chains and high concentration of functional terminal groups, along with architectural constraints, which can lead to significant changes of chemical and physical properties of highly grafted molecules when compared with their linear analogs. Highly grafted polymers generally exhibit much lower solution viscosities and melt viscosities compared to linear polymers of the same molecular weight.[17]

Our research group have researched on the electro-optical properties of PDLC based on living linear copolymer synthesized by RAFT radical polymerization, and the results suggested that controlled molecular weight of living linear polymer matrix has a great effect on the driving voltage of PDLC.[18] However, it was found that though reduced molecular weight of the linear polymer can cause the decrease in driving voltage, strong memory effect was induced by low molecular weight. It was necessary to investigate if driving voltage and memory effect can be decreased at the same time with the introduction of living graft copolymer. What's more, the influence mechanism of living graft copolymer on the electro-optical properties of PDLC has not been studied in detail. Graft copolymer shows apparent advantages on controlling structure and components of polymer matrix, which can further influence the physical properties of polymer matrix of PDLC. Also, few literatures have reported research on living graft copolymer as matrix of PDLC.

In this study, RAFT polymerization was used to synthesize a kind of living graft copolymer as matrix of PDLC. We controlled the content and monomers ratio of different kinds of living graft copolymer synthesized from 1,6-hexanediol diacrylate (HDDA) and Styrene (St) monomers. The electro-optical properties and morphologies of PDLC films were studied in detail.

EXPERIMENTAL

Materials

Commercially available nematic LC E7($T_{N\text{-}I}$ = 60°C, n_0 = 1.521, Δn = 0.22, $\varepsilon \parallel$ = 16, $\Delta\varepsilon$ = 5) was purchased from Shi Jia Zhuang Crown Display Material Co. Ltd. and photoinitiator (PI) 1104 from Changzhou Lan Ding Sci-Tech, Co. Ltd. A trithiocarbonate (TTC) was synthesized according to the reference.[19] Molecular structures of E7, PI, and TTC are presented in Figure 1. Reagent grade St, methyl acrylate (MA), and HDDA were passed through a silica gel column to remove inhibitors, and other reagents were used without further purification.

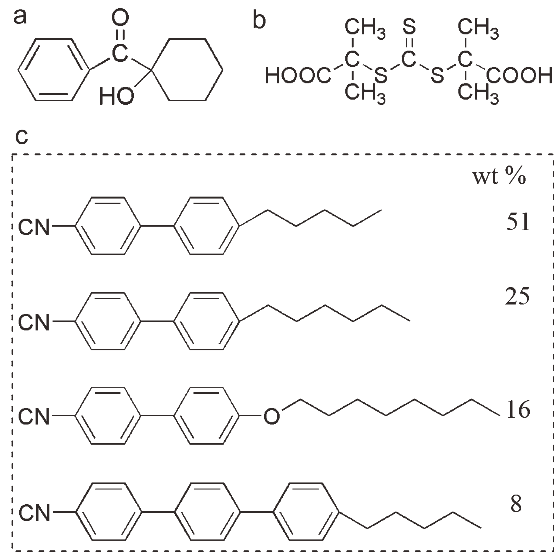

Figure 1 The structures of used compounds.

Preparation of living graft polystyrene (G-RAFT-PS)

G-RAFT-PS shown in Figure 2(a) was synthesized by RAFT as follows: A dried glass tube containing St (0.1 mol), TTC (0.3 mmol), HDDA (5 mmol), and 2,2′-azobisisobutyronitrile (0.1 mmol) sealed under vacuum. The tube was placed in a thermostated oil bath at 80°C. After 24 h polymerization, the reaction solution was diluted with tetrahydrofuran and poured into methanol. The precipitated G-RAFT-PS was separated out and dried under vacuum at 40°C to a constant weight.

Preparation of PDLC cells by photo-induced RAFT polymerization

A MA solution of G-RAFT-PS with different weight ratio of MA to G-RAFT-PS containing PI 1104 (PI : MA=1 : 1000, weight ratio) was placed between ITO-coated glass plates set to be 19 μm space with glass spheres. During the preparation of PDLC cells, dose of solution (G-RAFT-PS dissolved in MA) used is 0.05 g, which is mixed with the same amount of LC. Then, the mixture above was sandwiched into the ITO cells by capillary. The cell was irradiated under a 100 W UV lamp from a 20 cm distance at 25°C for 4 h, leading to the formation of a PDLC cell by PIPS. The structure of G-RAFT-PS-*co*-MA is shown in Figure 2(b). The thickness of the objective films of PDLC was 19 μm.

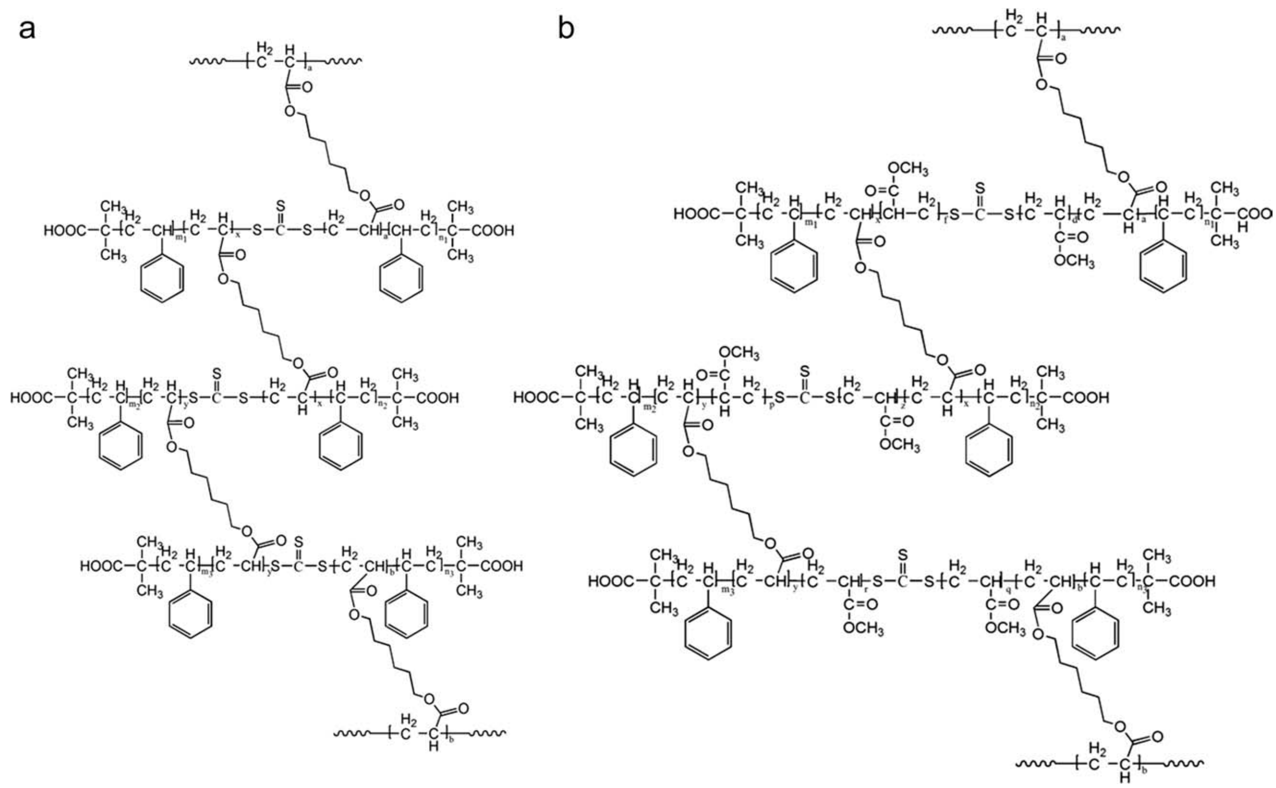

Figure 2 The structures of polymer synthesized (a) G-RAFT-PS and (b) G-RAFT-PS-*co*-MA.

Measurements

The measurements of electro-optical properties were carried out at 550 nm at ambient temperature (25°C) with the UV 1810 PC spectrometer.[18–21] The refractive index of the polymer matrix of PDLC was measured using an Abbe refractometer at 25°C. The morphology of PDLC films was observed on a polarized optical microscope (POM) at 25°C. According to literature,[21] threshold voltage (V_{th}) and saturation voltage (V_{sat}) were defined as the electric voltage required for the optical response to reach 10% and 90% of ΔT ($\Delta T = T_{ON} - T_{OFF}$, where T represents transmittance of PDLC films), respectively. ON-State transmittance (T_{ON}) is defined as the transmittance of PDLC upon application of voltage (ON-State), whereas OFF-State is the transmittance (T_{OFF}) of PDLC under the voltage of 0 V. Memory effect of PDLC films could be estimated by the difference of transmittance between two opaque states $\Delta T_{OFF} = T_{OFF} - T'_{OFF}$ (T_{OFF} is the transmittance of initial opaque state, and T'_{OFF} is the transmittance on removal of the applied field).

RESULTS AND DISCUSSION

H-NMR spectrum (Fig. 3) of precursor polymer G-RAFT-PS contains distinct signals for both Styrene and HDDA units. Signals at 7.48–6.24 ppm are due to aromatic protons, and those at 4.21–4.02 ppm are assignable to the $-\underline{CH_2}-O-$ protons of the moiety of the HDDA unit. The $-C\underline{H}-S-$ and the methyne (CH) proton of the styrene is characterized by resonance signals at 3.89–3.35 ppm. The resonance signals at 2.02–1.48 ppm are assignable to the methylene ($-CH_2-$) protons of both monomeric units. The structure of polymer matrix G-RAFT-PS-*co*-MA is based on the structure of G-RAFT-PS, and G-RAFT-PS-*co*-MA is synthesized through the RAFT living radical copolymerization mechanism.

After the living graft copolymer were obtained, PDLC films were made accordingly. The different compositions of PDLC samples with G-RAFT-PS and the refractive index of matrix of PDLC are presented

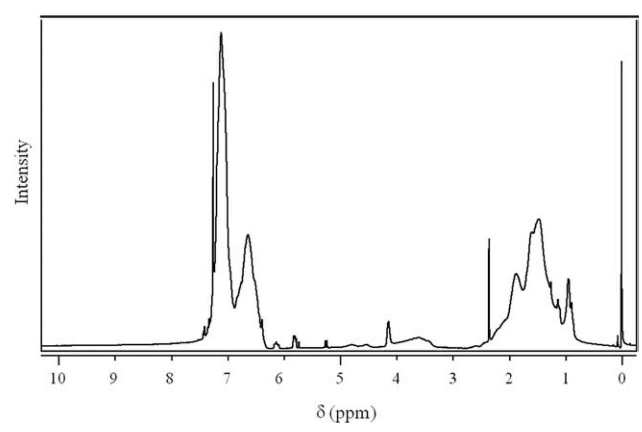

Figure 3 H-NMR spectrum of G-RAFT-PS.

TABLE I
The MATRIX Copolymers of PDLC Formed in the Photo-Induced RAFT Process[a]

Matrix[b]	St/HDDA (mole ratio)	G-RAFT-PS /MA (weight ratio)	Refractive index	Matrix[b]	St/HDDA (mole ratio)	G-RAFT-PS/MA (weight ratio)	Refractive index
1	10 : 1	15 : 85	1.535	7	20 : 1	5 : 95	1.521
2	20 : 1	15 : 85	1.533	8	20 : 1	10 : 90	1.530
3	30 : 1	15 : 85	1.529	9	20 : 1	15 : 85	1.533
4	40 : 1	15 : 85	1.527	10	20 : 1	20 : 80	1.535
5	50 : 1	15 : 85	1.527	11	20 : 1	25 : 75	1.537
6	100 : 0	–	1.592	12	–	0 : 100	1.479

[a] The reaction conditions are given in Experimental.
[b] LC(E7) : polymer matrix = 50 : 50 (weight ratio).

in Table I and plotted in Figure 6 and Figure 11, respectively. According to Figure 6, the refractive index of polymer matrix decreased from 1.535 to 1.527 as the mole ratio of St/HDDA (when weight ratio of G-RAFT-PS/MA was fixed to 15 : 85) increased from 10 : 1 to 50 : 1. The refractive index of polymer matrix increased from 1.521 to 1.537 as the weight ratio of G-RAFT-PS/MA (when the mole ratio of St/HDDA was fixed to 20 : 1) varied from 5 : 95 to 25 : 75 in Figure 11. This is caused by the changed density and content of graft chains[22]; the more content and density of G-RAFT-PS in the PDLC, the higher the refractive index of polymer matrix will be.

Effect of St/HDDA on the electro-optical properties of PDLC

The variation of morphologies of PDLC films with different ratio of St/HDDA are presented in Figure 4. It is clear that the radius of droplets of LC increases with the increase of ratio, and the distribution of droplets become less uniform. High content of HDDA results in high molecular weight of polymer matrix, which is beneficial to the fast formation and phase separation of LC droplet from polymer matrix. On the contrary, low molecular weight can lead to slow formation and phase separation of droplet.[23] As a result, PDLC films formed the morphologies in Figure 4.

The curve of relation between ON-State transmittance of PDLC with different ratio of St/HDDA and voltage applied from 0 to 30 V was shown in Figure 5. According to Figure 5, the transmittance of samples increases with the increase of voltage applied except samples with ratio 10 : 1, which is caused by its strong anchoring energy between LC and polymer matrix. As a result, the LC in the samples cannot align with the direction of the applied field, and the transmittance is low. On the other hand, transmittance of PDLC depends on whether the refractive index (n_o) of LC droplet and that (n_p) of polymer matrix match well with each other.[24] The refractive index of polymer matrix in Figure 6 decreases from 1.535 to 1.527, which is very near n_o (1.521) of LC E7. Therefore, n_o 1.521 of LC droplet and n_p 1.527 of polymer matrix show the least difference and match much better than those with a lower mole ratio of St/HDDA, resulting in high transmittance of PDLC cells with the mole ratio of St/HDDA 50 : 1.

Figure 7 describes the relation between V_{th} of PDLC and mole ratio of St/HDDA, and it shows that the V_{th} of PDLC also declined with the increase of St/HDDA. According to eq. (1), where V_{th}, d, R, k, and $\Delta\varepsilon$ represent the threshold voltage of PDLC, PDLC film thickness, radius of the droplet of LC, elastic constant, and dielectric anisotropy of LC, respectively, V_{th} of PDLC shows reciprocal proportion to the radius of LC droplet of PDLC.[25–27] The radius of LC droplet increases with the increase of St/HDDA in Figure 4, so the V_{th} decreases with the radius.

$$V_{th} \cong \frac{d}{R}\sqrt{\frac{k}{\Delta\varepsilon}} \tag{1}$$

Figure 7 depicts the relation between V_{sat} of PDLC and mole ratio of St/HDDA. As seen from Figure 7, the V_{sat} of PDLC decreases with the increase of St/HDDA. V_{sat} can be affected by anchoring energy of droplet of LC on the surface of polymer matrix and large anchoring energy can lead to high V_{sat}. According to the morphology of droplet in Figure 4, radius of LC droplet increases, which results in low anchoring energy of LC on the surface of polymer matrix. Therefore, the V_{sat} decreases with the increase of the ratio St/HDDA.

Figure 8 is the relation of memory effect of PDLC verse different ratio of St/HDDA. Memory effect decreases from 4.7 to 1.8 with increase of ratio from 10 : 1 to 50 : 1. With the decrease of HDDA in the chain of G-RAFT-PS, LC droplet is wrapped by less and less complicated polymer chains, and the force exerted on LC droplet comes from only several directions, which are less than that on LC droplet with

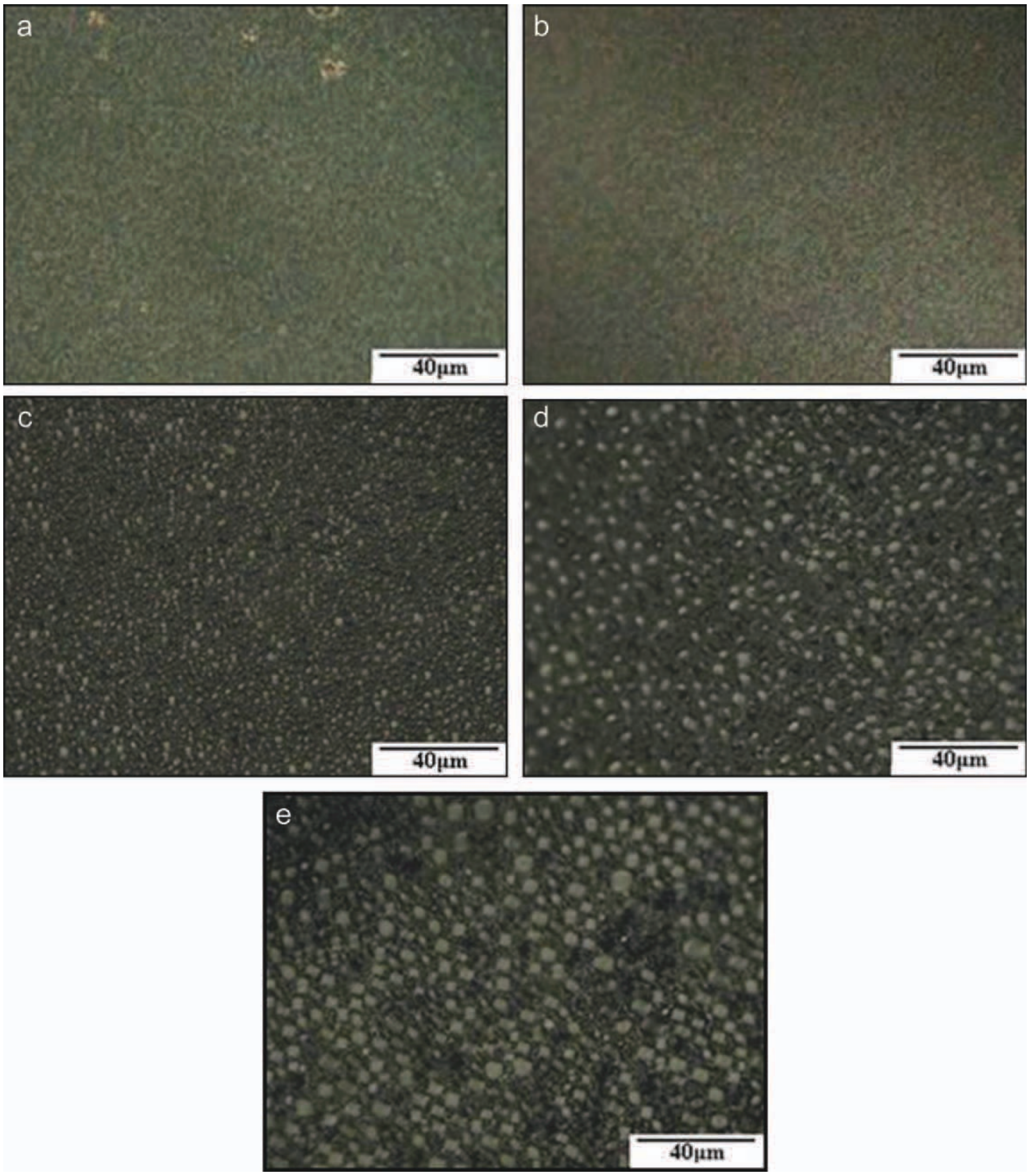

Figure 4 Polarized optical micrographs of PDLC films with different mole ratio of St/HDDA (a) 10 : 1; (b) 20 : 1; (c) 30 : 1; (d) 40 : 1; (e) 50 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more HDDA in the chain. Therefore, LC droplet can revert to its original state rapidly after electric field was removed. On the contrary, PDLC film containing more HDDA cannot revert to its original state easily. So far from the results above, it was novel that V_{th}, V_{sat} and memory effect can be controlled simultaneously by living graft copolymer G-RAFT-PS.

G-RFAT-PS on the electro-optical properties of PDLC

Figure 9 is the morphologies variation of PDLC films with contents of G-RAFT-PS varying from 5 to 25 wt %. The radius of LC droplets gradually increase with the increase of G-RAFT-PS contents, while the distribution of droplets gets more uniform. High content of G-RAFT-PS makes the polymerization rate slow and low molecular weight of polymer matrix, which brings the formation and separation of LC droplet much slow and homogeneous.

Figure 10 displays the relation of transmittance of PDLC with different contents of G-RAFT-PS and voltage applied varying from 0 to 30 V. The ON-State transmittance of PDLC increases with the increase of living G-RAFT-PS content. In Figure 11, the refractive index of polymer matrix of PDLC

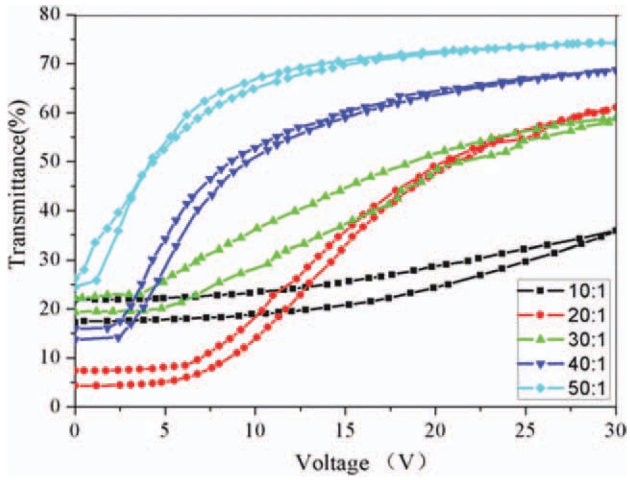

Figure 5 The electro-optical curves of PDLC films with different mole ratio of St/HDDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases from 1.521 to 1.537 when the content of G-RAFT-PS varies from 5 to 25 wt %. Consequently, the refractive index n_o of LC droplet and refractive index n_p of polymer matrix can get well match and the transmittance of PDLC increase gradually.

Figure 12 describes the relationship of V_{th} and G-RAFT-PS with concentration, V_{th} increases gradually with the increase of contents of G-RAFT-PS from 5 to 15 wt %, and then decrease with the concentration from 15 to 25 wt %. POM image of the PDLC film with different content of G-RAFT-PS is given in Figure 9, which indicates that the form of LC changes from free continuous flow to separate droplet with the increase of content of G-RAFT-PS. Anchoring

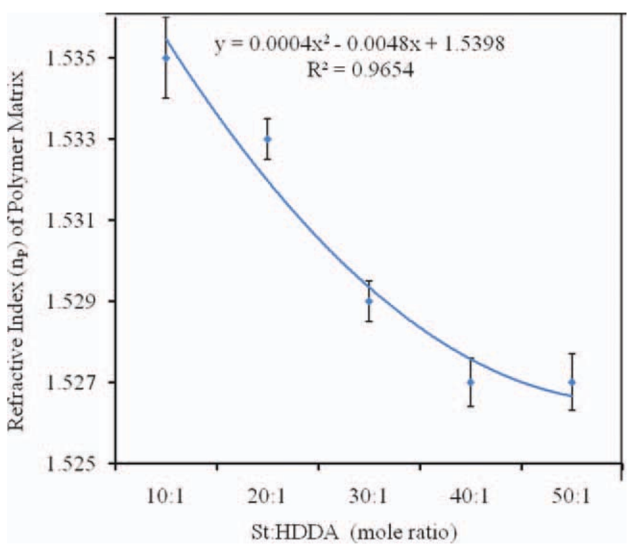

Figure 6 Refractive index of polymer matrix of PDLC with different mole ratio of St/HDDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

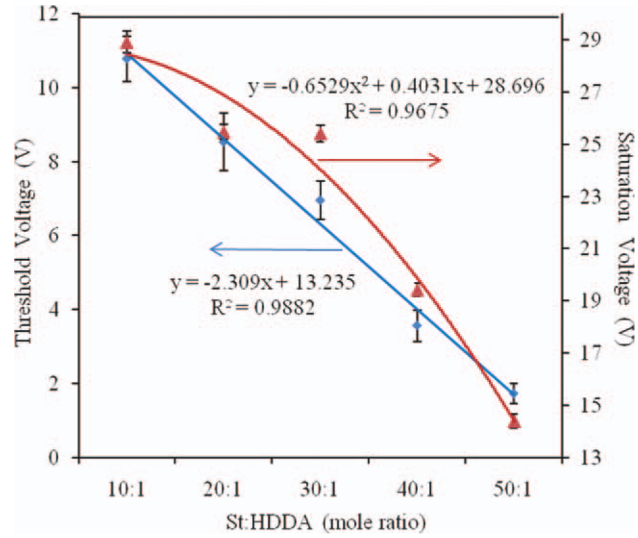

Figure 7 Threshold voltage and saturation voltage of PDLC with different mole ratio of St/HDDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

energy plays a key role in determination of V_{th} of PDLC from content 5 to 15 wt % of G-RAFT-PS. However, when the content of G-RAFT-PS changes from 15 to 25 wt %, the radius of LC droplet increases and anchoring energy decreases, which caused the decrease in V_{th} of PDLCs according to eq. (1). The radius of LC droplet is the most important factor to determine V_{th} at this stage.

The correlation between V_{sat} and contents of G-RAFT-PS is exhibited in Figure 12; it is clear that V_{sat} decreases with the contents of G-RAFT-PS. The form of LC changes from free continuous flow to separate droplet from content 5 to 25 wt % of G-RAFT-PS. The reason is not clear; it was estimated that it is difficult to drive free continuous LC to flow

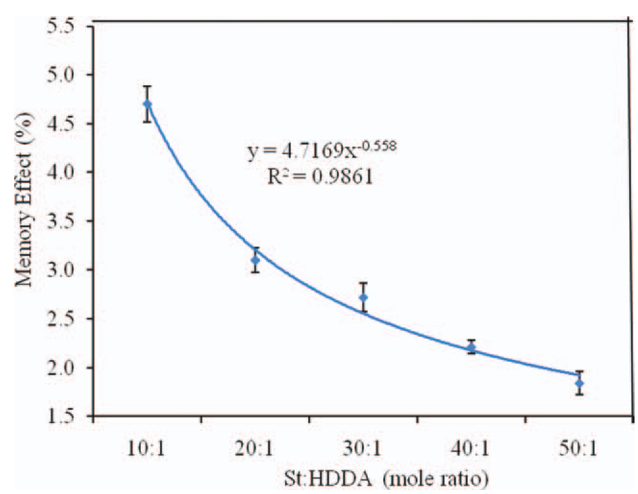

Figure 8 Memory effect of PDLC with different mole ratio of St/HDDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

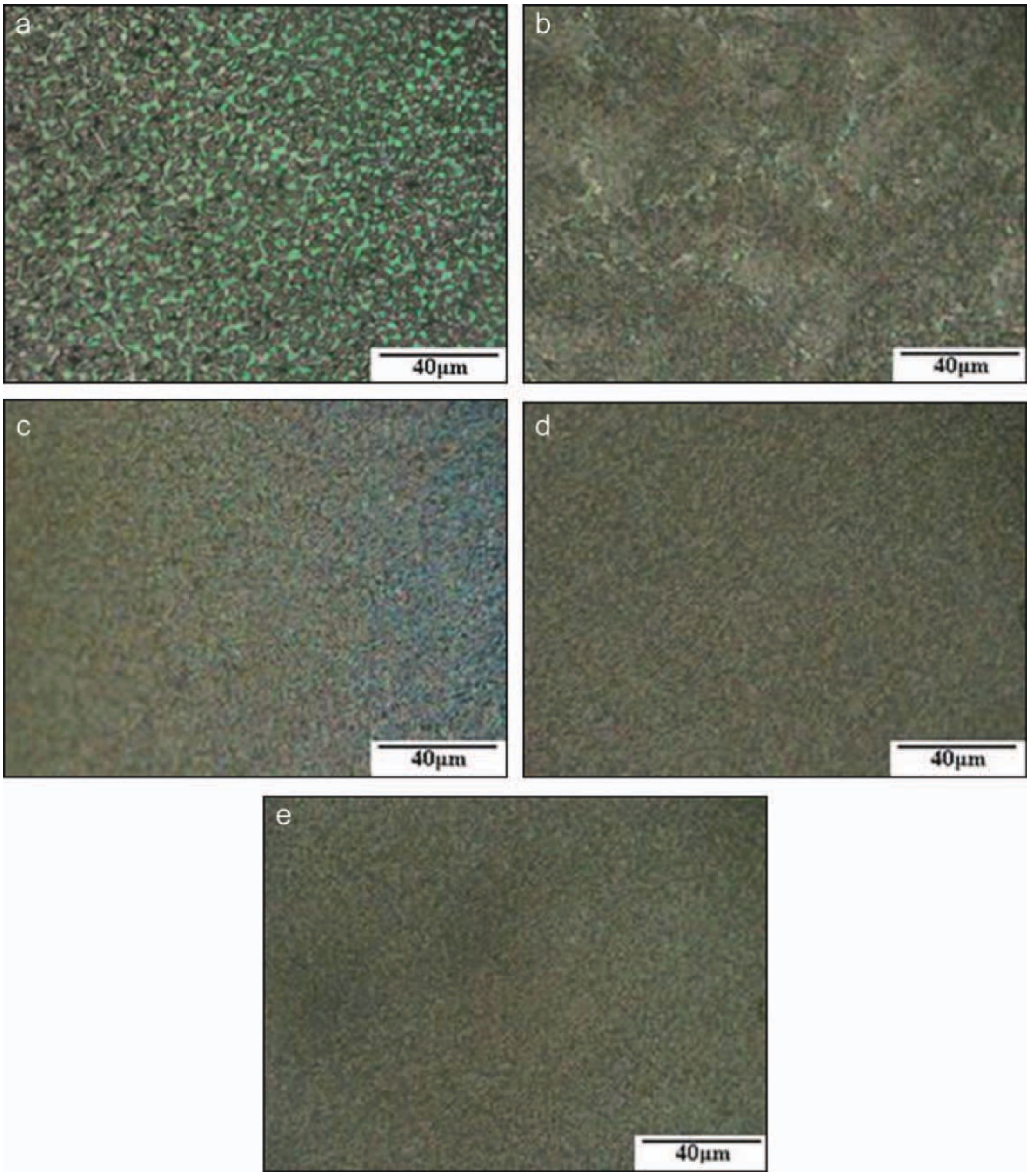

Figure 9 POM of PDLC films with different content of G-RAFT-PS (St/HDDA = 20 : 1 mole ratio) (a) 5%, (b) 10%, (c) 15%, (d) 20%, and (e) 25%.(weight ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the large anchoring energy. Therefore, the V_{sat} of PDLC is large when the content of G-RAFT-PS is 5 wt %. Then, LC droplet begins to form and the radius increase gradually, which leads to the decrease of V_{sat} of PDLC.

Figure 13 shows the relation between memory effect of PDLC and different content of G-RAFT-PS. What can be drawn from this graph is that memory effect increases from 0.7 to 4.2 when the contents increase from 5 to 25 wt %. The LC droplet cannot easily revert to its original state because molecular weight of graft copolymer matrix becomes lower as content of G-RAFT-PS increases. Lower molecular weight induced less entanglements between chains, which made lower anchoring energy between LC droplets and polymer matrix. Lower anchoring energy can lead to strong memory effect.[28] As a result, the memory effect of PDLC increases with content of G-RAFT-PS varying from 5 to 25 wt %.

By comparing the electro-properties of PDLC samples prepared with different St/HDDA ratio with the electro-properties of those prepared with different content of G-RAFT-PS, we can find that the transmittance of PDLC prepared with the latter method is much higher; the threshold voltage, saturation voltage, and memory effect are much lower than those

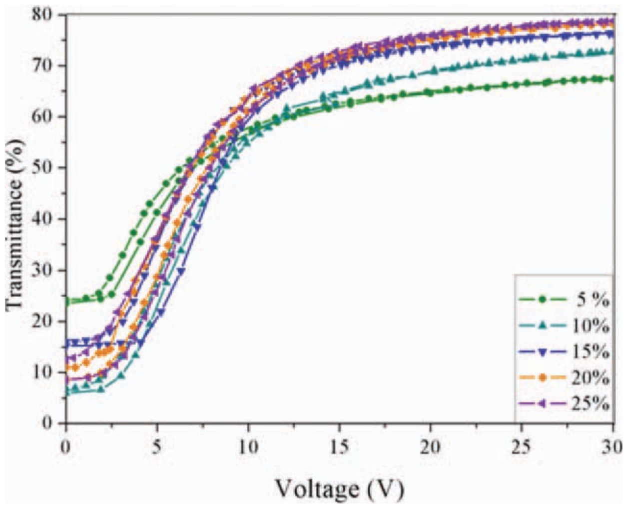

Figure 10 The electro-optical curves of PDLC films with different content of G-RAFT-PS (St/HDDA = 20 : 1 mole ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

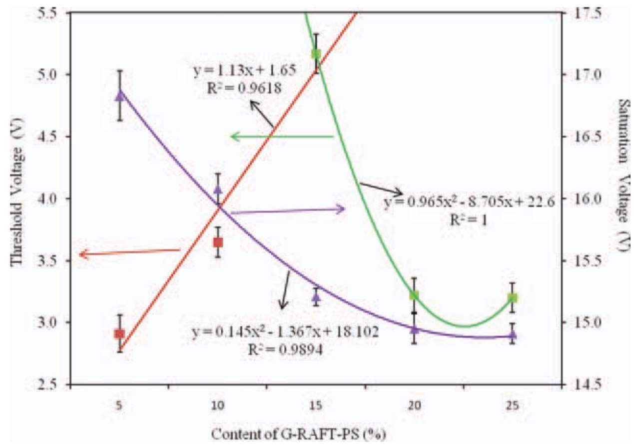

Figure 12 Threshold voltage and saturation voltage of PDLC with different content of G-RAFT-PS (St/HDDA = 20 : 1 mole ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

made with the former method. Therefore, adjusting the content of G-RAFT-PS is an effective way to prepare PDLC with desired electro-optical properties. The threshold voltage and saturation voltage of PDLC films in this research work is less than 6 V and 20 V, respectively. However, these PDLC films show nearly the same ON-State transmittance value as the research results based on RAFT living radical polymerization in literatures[18,20] in which the threshold voltage and saturation voltage were much higher, and the memory effect was much stronger than the values of our current samples.

CONCLUSIONS

Living graft copolymer matrix of PDLC has been prepared through RAFT living radical polymerization in one step. Electro-optical properties of PDLC has been optimized by controlling the mole ratio of St to HDDA and adjusting the content of prepared graft macromolecule. The results indicate that low content of HDDA leads to low threshold voltage, low saturation, high transmittance, and weak memory effect. What's more, when the mole ratio of St to HDDA was controlled at 20 : 1 and the content of prepared G-RAFT-PS changed from 5 to 25 wt %, driving voltage and transmittance of PDLC, especially the saturation voltage, have been improved greatly. The results from the research work done in

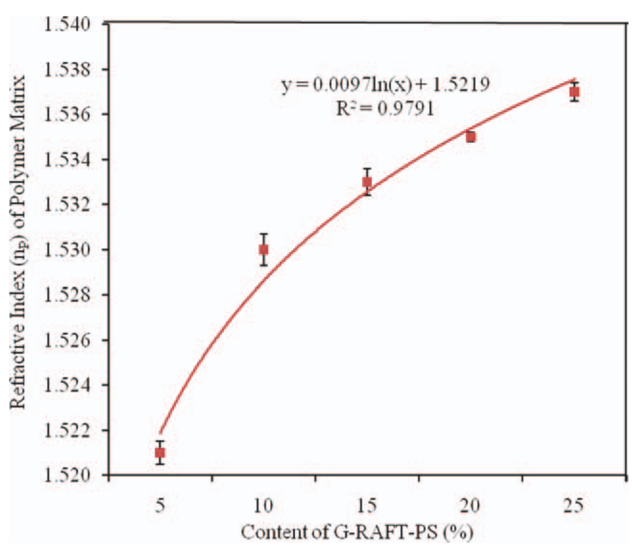

Figure 11 Refractive index of polymer matrix of PDLC with different content of G-RAFT-PS (St/HDDA = 20 : 1 mole ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

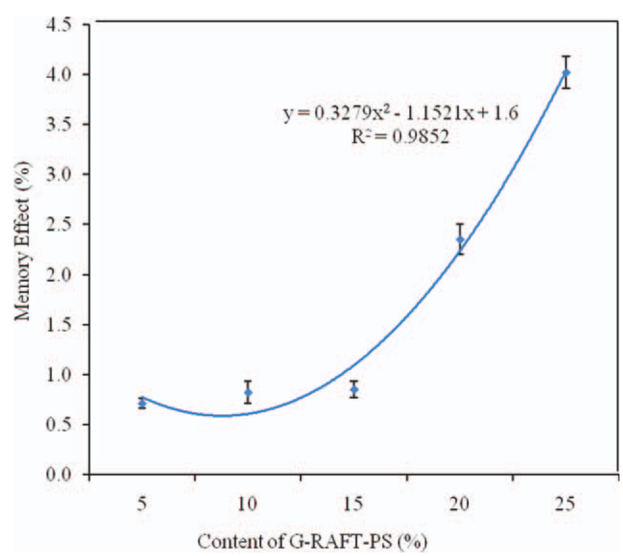

Figure 13 Memory effect of PDLC with different content of G-RAFT-PS (St/HDDA = 20 : 1 mole ratio). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this article show some apparent advantages that the transmittance, threshold voltage, saturation voltage, and memory effect of PDLC can be controlled simultaneously, which cannot be achieved in other already published research work.

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