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Contribution of monomer functionality and additives to polymerization kinetics and liquid crystal phase separation in acrylate-based polymer-dispersed liquid crystals (PDLCs)

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Fundamental control of the polymerization behaviour of polymer-dispersed liquid crystals (PDLCs) is critical to the formation of high-performance devices by polymer-induced phase separation (PIPS). Previous PDLC research has shown that monomer functionality and additives such as surfactants or reactive diluents can impart significant changes to the electro-optical behaviour of a system, especially in acrylate-based materials. The influence of monomer functionality and additives on the polymerization kinetics and LC phase separation were examined in the formation of acrylate-based PDLCs. Real-time infrared (RTIR) spectroscopy was utilized to simultaneously monitor polymerization rate, double bond conversion and LC phase separation. In the formation of PDLCs by PIPS, increasing acrylate monomer functionality reduces the polymerization rate, overall double bond conversion and the extent of LC phase separation. Interestingly, the additives octanoic acid and *N*-vinylpyrrolidone (NVP) increase the polymerization rate but suppress LC phase separation. During PDLC formation, both octanoic acid and NVP enhance the solubility of the LC in the growing polymer matrix, reducing the rate of liquid–gel demixing and decreasing nematic fraction in PDLCs. As a non-reactive component, octanoic acid increases the polymerization rate by plasticizing the crosslinked polymerization. NVP, a reactive diluent added to decrease viscosity, increases polymerization rate through favourable copolymerization with acrylate monomer.

1. Introduction

Acrylate polymers have been extensively utilized in polymer/liquid crystal (LC) composites such as polymer-dispersed liquid crystals (PDLCs) and holographic polymer-dispersed liquid crystals (HPDLCs). These polymers are often chosen for PDLCs because of desirable polymerization behaviour including fast polymerization kinetics, early gelation and vitrification that correspondingly limits the size of the LC voids [1–5]. Acrylate polymer has been especially relevant in the formation of HPDLCs, in which nano-sized LC droplet domains are necessary to reduce deleterious light scattering that reduces diffraction efficiency [6–9].

Most often PDLCs are formed through polymer-induced phase separation (PIPS), a one-step process in which polymerization takes place in the LC [1–5, 10–14]. As the polymer forms, the polymer and LC demix by either liquid–liquid or liquid–gel demixing. Whereas

the formation of PDLCs by PIPS can be initiated thermally or photochemically (photopolymerization), photopolymerization is more common since it is temperature independent and enables facile control of the polymerization kinetics [5].

Other types of photopolymerizable systems that have served as polymer host for PDLCs include thiol–ene [13–18], epoxide [19–21] and methacrylate [22]. Much work has been devoted to systematic examination of a formulation containing the commercial thiol–ene mixture, NOA65, and the cyano-*n*-phenyl LC mixture, E7 [13, 14]. Recent research has examined the influence of thiol and ene monomer functionality on the polymerization kinetics and LC phase separation in thiol–ene-based PDLC formulations [23]. Mixing thiol and ene monomers with two to four functional groups per monomer can shift the polymer gel point from 33% to 71% monomer conversion in crosslinked systems. Shifting the gel point conversion dramatically alters the evolution of LC phase separation. Thiol–ene-based PDLCs have a maximum rate of phase separation at the

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gel point conversion of the polymer host. Ultimately, increasing monomer functionality in thiol-ene PDLCs reduces LC droplet size due to influences on polymerization kinetics and polymer gel point.

The effect of acrylate functionality on the morphology of PDLCs made from mixtures containing acrylate monomer, *N*-vinylpyrrolidone (NVP) and octanoic acid has also been studied [24]. Surprisingly, decreasing acrylate functionality does not significantly alter the LC domain size but does reduce the LC volume fraction in PDLC morphology. Previous research also has shown that decreasing effective monomer functionality by increasing the concentration of the monofunctional reactive diluent NVP reduces LC domain size [25]. However, adding monofunctional monomer to PDLCs can change solubility, glass transition temperature (T_g), polymerization kinetics and viscosity. Including surfactants in PDLC formulations can enhance performance. Surfactants such as octanoic acid reduce the anchoring energy of LC in PDLCs, thereby decreasing the voltage necessary to switch a device [26–29]. These additives also appear to decrease LC domain size in polymer/LC morphology that correspondingly improves optical performance in HPDLCs [25, 30, 31].

Previous work has shown that both monomer functionality and additives impart significant changes to polymer/LC morphology of acrylate-based PDLCs and HPDLCs. Systematically examining the contribution of acrylate functionality, octanoic acid and NVP to polymerization behaviour and LC phase separation of PDLCs will provide a more complete understanding of the contribution of performance-enhancing components and variables to the formation of PDLCs. In this work, polymerization behaviour was characterized with photo-differential scanning calorimetry (PDSC) and real-time infrared spectroscopy (RTIR). RTIR was utilized to simultaneously monitor the evolution of nematic LC (nematic fraction) as a function of polymer development. PDLC formulations containing acrylate monomers with functionality from two to five were examined in systems containing 30 wt % E7. Furthermore, the contribution of the additives octanoic acid and NVP to PDLC development was also studied. The influence of acrylate monomer functionality and additives on polymerization kinetics and nematic fraction was examined and correlated to changes in PDLC morphology as characterized by scanning electron microscopy (SEM). Examining the influence of monomer functionality and additives to PDLC formation will enable further understanding of the relationships between polymer gel point, polymerization rate and monomer/polymer/LC solubility on the

morphology and extent of LC phase separation in acrylate-based PDLCs.

2. Experimental

2.1. Materials

All PDLC formulations contain 0.2 wt % of the UV photoinitiator Darocur 4265 (DC-4265, Ciba) and 30 wt % E7 (EMD Chemical). Acrylate monomers used in this study include diethylene glycol diacrylate (diacrylate, Sartomer), trimethylolpropane triacrylate (triacrylate, Sartomer), di(trimethylol)propane tetraacrylate (tetraacrylate, Sartomer) and dipentaerythritol pentaacrylate (pentaacrylate, Sartomer). PDLC additives octanoic acid (Aldrich) and *N*-vinylpyrrolidone (NVP, Aldrich) were also utilized. Chemical structures of the acrylate monomers, octanoic acid and NVP are shown in figure 1.

2.2. Characterization

2.2.1. Polymerization kinetics. Polymerization behaviour was examined with the complementary techniques of PDSC and RTIR spectroscopy. The PDSC used was a Perkin Elmer Diamond DSC purged with nitrogen to prevent oxygen inhibition during photopolymerization. The light source for the DSC was a high-pressure mercury-xenon arc lamp (Ace Glass) which was filtered to 365 nm (Omega Optics) at an intensity 2.0 mW cm^{-2} . Approximately $2.0 \pm 0.3 \text{ mg}$ samples were used for PDSC examination. The rate of polymerization was calculated directly from the heat evolution profile associated with the photopolymerization, as described elsewhere [31].

RTIR was used to determine the conversion of acrylate and NVP double bonds in the photopolymerization of PDLCs. A Thermo-Electron Nexus 670 FTIR was adapted with a horizontal transmission accessory. Polymerization was initiated with a high pressure mercury lamp (Exfo Acticure 4000) filtered to 365 nm at an intensity of 2.0 mW cm^{-2} . Double bond conversion and polymerization rate of acrylate was examined using the C=C peak at 3105 cm^{-1} , whereas NVP conversion was monitored in examination of the C=C peak at 1335 cm^{-1} . Double bond conversion was calculated from the change in peak height absorbance as double bonds convert into polymer. The polymerization rate, as determined by RTIR, is the time derivative of the fractional conversion of a given monomer. Calculation of the rate of polymerization and double bond conversion has been described in further detail elsewhere [31].

2.2.2. LC phase separation. The formation of PDLCs imparts changes to the RTIR spectra that can be simultaneously monitored with the polymerization

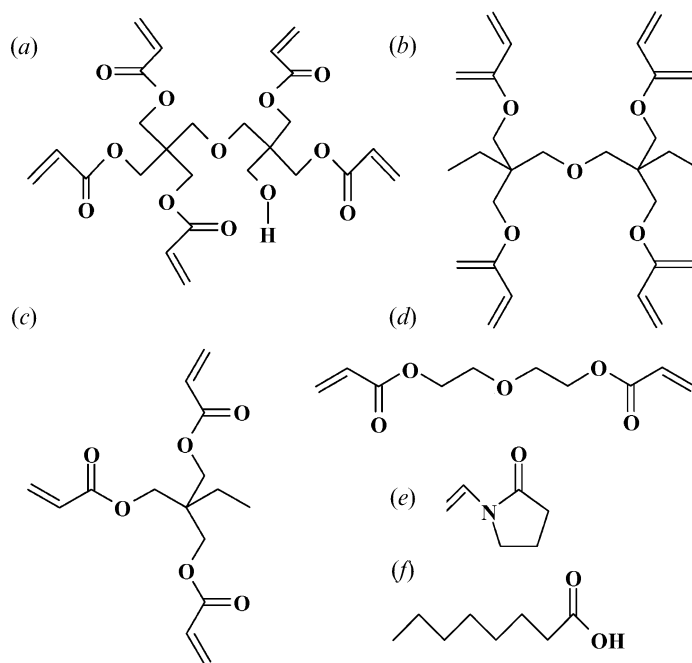


Figure 1. Chemical structures of compounds used in this investigation: (a) dipentaerythritol pentaacrylate; (b) di(trimethylol)propane tetraacrylate; (c) trimethylolpropane triacrylate; (d) diethylene glycol diacrylate; (e) *N*-vinylpyrrolidone; (f) octanoic acid.

behaviour to give information regarding the influence of polymer development on the polymerization-induced phase separation (PIPS) process. In this study, the mesophase-dependent absorbance of the cyano moiety at 2225 cm^{-1} was used as a means to quantify the amount of LC that is in the nematic phase, which is directly related to the degree of LC phase separation [13, 14]. The change in absorbance at 2225 cm^{-1} is used to calculate the nematic fraction, which is indicative of the extent of LC in a PDLC that is phase separated LC in the nematic phase. The calculation of nematic fraction from RTIR examination has been more thoroughly described elsewhere [23, 31].

2.2.3. Morphology. Scanning electron microscopy (SEM) was used to image polymer/LC morphology in acrylate-based PDLCs. The SEM used is a Hitachi S-4000, with an accelerating voltage of 5 keV. Samples were prepared between glass slides with $15\text{ }\mu\text{m}$ spacers. Upon fabrication, samples were subjected to methanol extraction, freeze fractured and mounted on aluminium samples stubs for examination of the internal morphology.

3. Results and discussion

3.1. Acrylate functionality

The molecular weight evolution, gel point and vitrification of polymer are known to be critical to the

formation and corresponding performance of PDLCs [4]. A number of acrylate monomers with different functionality and chemical structure are readily available that form PDLCs with different polymerization behaviour and thermo-mechanical properties. The contribution of acrylate monomer functionality to polymerization kinetics and LC phase separation in PDLC systems has not yet been examined. Altering polymerization rate and the amount of phase separated LC can significantly change polymer/LC morphology and ultimately, electro-optical performance of a PDLC.

In formation of PDLCs through PIPS, the LC acts as a solvent for the polymerization. To understand if the presence of LC influences the polymerization behaviour of acrylate monomer, the polymerization of diethylene glycol diacrylate (diacrylate) and dipentaerythritol pentaacrylate (pentaacrylate) was examined with PDSC for systems containing monomer and initiator (neat) and PDLC formulations (with 30 wt % E7). Interestingly, in both diacrylate and pentaacrylate polymerization, adding LC increases polymerization rate. The maximum polymerization rate of diacrylate (figure 2a) in LC is 60% higher than the neat diacrylate polymerization. The influence of adding LC is slightly greater in the pentaacrylate system (figure 2b), as the maximum polymerization rate of pentaacrylate in LC is 80% faster than the neat polymerization of pentaacrylate. Also notable is the impact of LC to double bond conversion. In figure 2a, diacrylate double bond

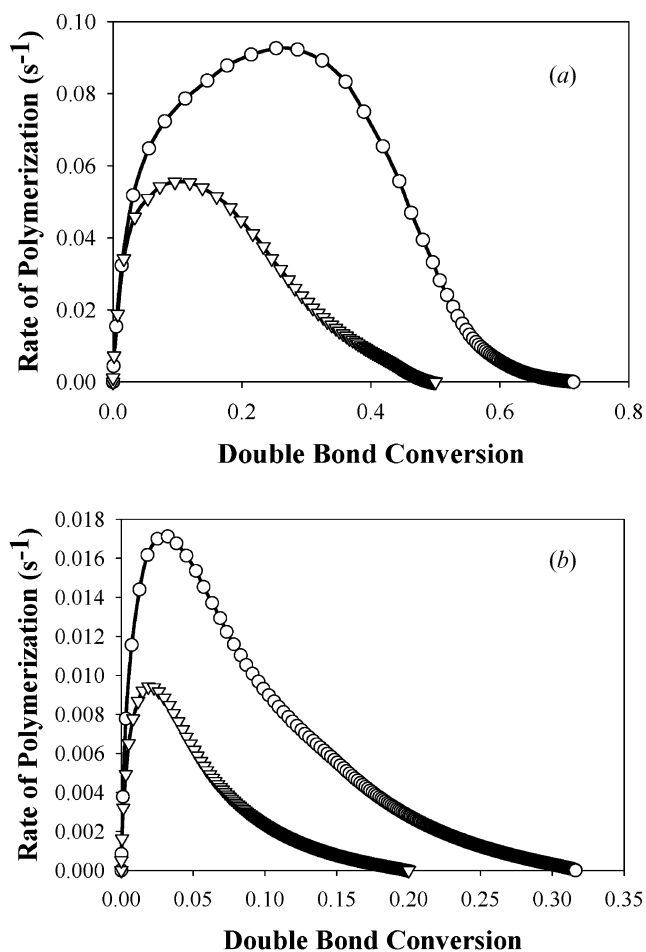


Figure 2. Rate of polymerization versus double bond conversion as determined by PDSC for (a) diacrylate and (b) pentaacrylate systems in PDLC polymerization with 30 wt % E7 (\circ) and bulk polymerization (∇).

conversion is increased from 50% to 70% with the addition of 30 wt % E7. For the pentaacrylate-based polymerizations examined in figure 2b, double bond conversion increases from 20% to 30%. Polymerization of diacrylate and pentaacrylate monomer forms cross-linked networks of infinite molecular weight (i.e. gelled polymer) at very low conversion [32]. Monomer mobility in the polymer network is extremely limited due to the constraints of the highly crosslinked, gelled polymer. Low molecular weight solvents (plasticizers) can significantly improve monomer mobility in these conditions. As such, LC acts as a plasticizer that reduces diffusional constraints in crosslinked polymerization in PDLCs subsequently causing increased polymerization rate and increased overall double bond conversion.

The polymerization rate of the diacrylate PDLC is significantly greater than that of the pentaacrylate PDLC. To understand how acrylate monomer

functionality alters polymerization behaviour in PDLCs, figures 3a and 3b shows RTIR examination of double bond conversion and polymerization rate for PDLCs based on diacrylate, triacrylate, tetraacrylate and pentaacrylate in 30 wt % E7. Figure 3a is a plot of acrylate double bond conversion versus time. As monomer functionality increases, double bond conversion decreases from nearly 85% in diacrylate PDLCs to approximately 45% in pentaacrylate PDLCs. Such a dependence has been previously seen in neat systems [33]. Interestingly, the evolutions of double bond conversion with time for triacrylate and tetraacrylate PDLCs are nearly identical.

Monomer functionality is also influential on the rate of polymerization. Figure 3b compares the polymerization rate, also determined by RTIR, for the same PDLC

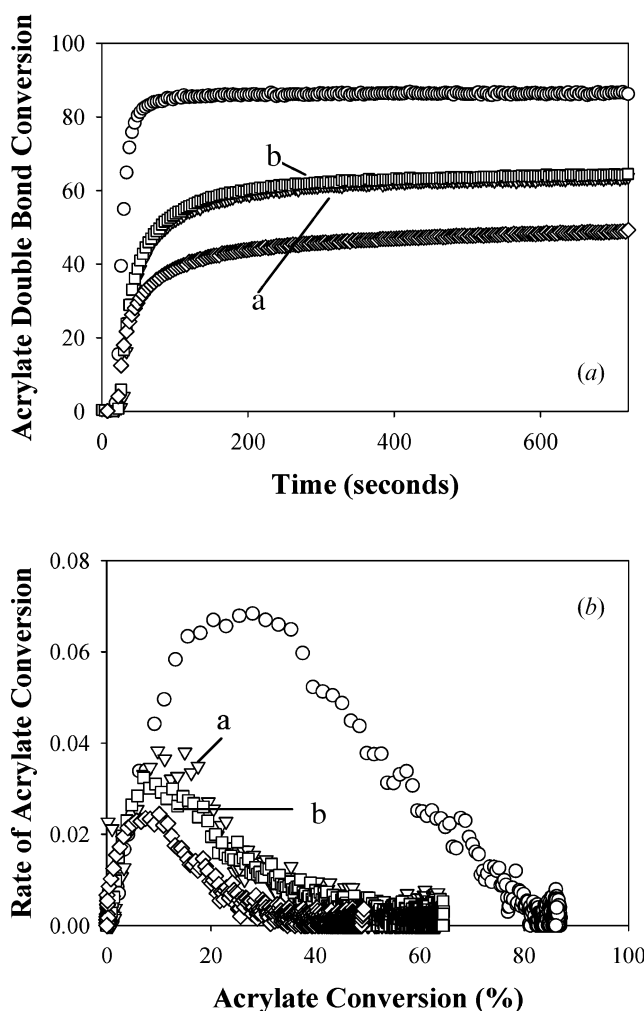


Figure 3. RTIR examination of (a) acrylate double bond conversion versus time and (b) rate of acrylate conversion versus acrylate double bond conversion for PDLC polymerization of diacrylate (\circ), triacrylate (∇ , 'a'), tetraacrylate (\square , 'b') and pentaacrylate (\diamond).

formulations. As monomer functionality is increased, the maximum rate of polymerization decreases from greater than 0.07 s^{-1} in the diacrylate PDLC to 0.025 s^{-1} in the pentaacrylate PDLC. Again, the polymerization behaviour of the triacrylate and tetraacrylate are similar. As monomer functionality is increased, the diffusional constraints associated with increased crosslink density reduce monomer mobility, thereby reducing polymerization rate.

Increasing acrylate monomer functionality can also change polymer gel point and vitrification (i.e. T_g) in PDLCs. Previous examination of PIPS in acrylate-based PDLCs has shown that both the onset of gelation and vitrification affect the onset and evolution of LC phase separation [10–12]. Recently, RTIR has been used to monitor the evolution of nematic fraction in thiol-ene PDLCs during photopolymerization as means to indirectly monitor LC phase separation [13, 14, 34]. RTIR examination of LC phase separation in PDLCs takes advantage of the mesophase-dependent absorbance of the cyano group at 2225 cm^{-1} [13, 14, 35]. Upon PIPS, the LC undergoes an isotropic to nematic transition. From monitoring the absorbance at 2225 cm^{-1} the nematic fraction can be determined as a function of time or double bond conversion. The nematic fraction is directly related to LC phase separation since only phase-separated LC should exhibit the nematic LC phase. In addition to examining the extent of LC phase separation in PDLCs, RTIR can give information regarding the rate of LC phase separation in these systems. Interestingly, in the examination of thiol-ene PDLCs, the maximum rate of LC phase separation occurs at the approximate gel point of the thiol-ene polymer utilized, indicating that liquid-liquid demixing is more favourable than liquid-gel demixing. The gel point conversion of thiol-ene polymers can be as high as 71% in crosslinked systems. With high gel point conversion, LC phase separation in thiol-ene-based PDLCs predominately occurs via liquid-liquid demixing [34]. On the other hand, acrylate polymers have gel point conversion as low as 2% and LC phase separation occurs via liquid-gel demixing [10–12].

Figure 4 plots the nematic fraction as a function of acrylate double bond conversion for PDLCs based on diacrylate, triacrylate, tetraacrylate and pentaacrylate. In general, as monomer functionality increases, the nematic fraction decreases. Regardless of acrylate monomer functionality, the appearance of nematic order begins instantaneously upon photopolymerization implying that phase separation does as well. In the immediate stages of photopolymerization, LC phase separation is associated with both liquid-liquid and liquid-gel demixing, as acrylate polymerization forms

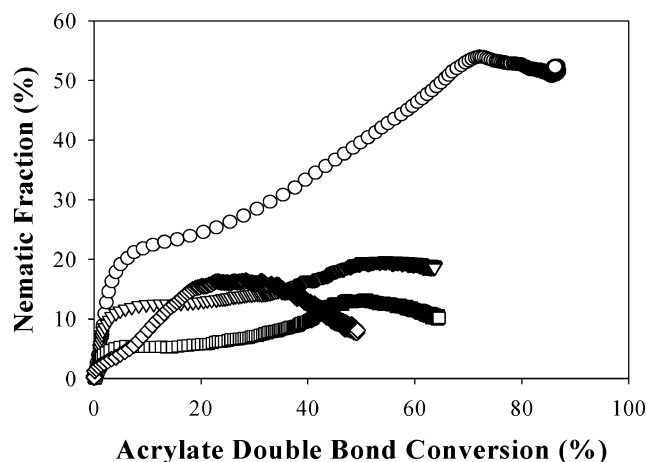


Figure 4. RTIR determination of nematic fraction (%) versus acrylate double bond conversion in PDLC polymerization of diacrylate (○), triacrylate (▽), tetraacrylate (□) and pentaacrylate (◇).

microgels, i.e. small pockets of gelled polymer, even at very low conversion. As acrylate conversion increases, the evolution of the nematic phase slows at a point evident in each of the nematic fraction profiles. The double bond conversion at which this transition occurs increases with reduced monomer functionality from 1–2% in pentaacrylate-based PDLC to 10–12% in diacrylate-based PDLC. The delay of these transitions to higher double bond conversion with increasing acrylate monomer functionality is likely associated with the onset of macrogelation in these polymers, which shift to higher conversion as monomer functionality is reduced. As evident in previous examination of thiol-ene PDLCs, liquid-liquid demixing occurs at a faster rate than liquid-gel demixing, leading to increased nematic fraction in PDLCs with high gel point conversion [34]. Delaying the onset of macrogelation to later double bond conversion by reducing acrylate monomer functionality extends the regime that LC phase separation can occur via liquid-liquid demixing, leading to more overall LC phase separation. After macrogelation, it is apparent that the liquid-gel demixing process is significant in each of the PDLCs. The rate of liquid-gel demixing (i.e. the slope of the nematic fraction) in the diacrylate PDLC is the fastest, rising to a maximum percent nematic fraction of greater than 50% at 75% acrylate conversion. The evolution of liquid-gel demixing in both the triacrylate and tetraacrylate are once again, similar. Liquid-gel demixing in these PDLC systems occurs more slowly than for the diacrylate PDLC. Interestingly, liquid-gel demixing in the pentaacrylate PDLC rapidly increases to a maximum nematic fraction of approximately 15% with 25%

acrylate conversion. At the later stages of the polymerization, the nematic fraction actually decreases with further double bond conversion for each of the acrylate-based PDLCs. This effect could be associated with polymer shrinkage or contamination of the LC domains with unreacted monomer and is most pronounced in the pentaacrylate PDLC, for which the nematic fraction is reduced from 15% to 8%.

Changes in polymerization behaviour or LC phase separation can alter the morphology of the PDLCs and, consequently, impart significant differences to electro-optical performance. The polymer/LC morphology of PDLCs was characterized with SEM. Figure 5 compares the morphology of PDLC systems as acrylate monomer functionality is increased. In general, these acrylate-based PDLCs exhibit a polymer ball morphology. The interconnected void space (black areas) in each of the images in figure 5 marks the morphology of the LC before extraction. Evident in the micrograph of the diacrylate PDLC (figure 5a), is a morphology containing polymer balls of approximately 100–150 nm in size. Comparing this micrograph to figures 5b–5d, the size of the polymer balls in the polymer/LC morphology decreases with increasing acrylate functionality. Increasing acrylate monomer functionality also reduces the amount of void space (black) in the polymer/LC morphology, indicating less LC phase separation. The SEM observations in figures 5a–5d are consistent with the examination of the nematic fraction which also indicates that LC phase separation is reduced as acrylate monomer functionality is increased.

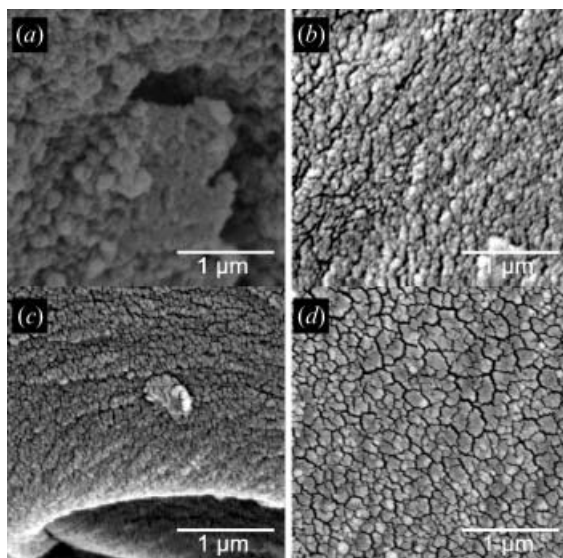


Figure 5. SEM micrographs of PDLCs made from (a) diacrylate, (b) triacrylate, (c) tetraacrylate and (d) pentaacrylate.

3.2. Additives

Previous research on both acrylate-based PDLCs and HPDLCs has shown that adding surfactants such as octanoic acid reduces switching voltage [26–28]. To determine the effect of octanoic acid on polymerization behaviour, the polymerization rate as a function of octanoic acid concentration was determined with PDSC. Figure 6 plots the rate of polymerization versus double bond conversion for PDLC formulations containing 0–9 wt % octanoic acid, 10 wt % NVP, 35 wt % E7 and pentaacrylate. Interestingly, increasing the octanoic acid concentration increases the polymerization rate of the pentaacrylate PDLC by 15%. As with the addition of LC, octanoic acid may improve monomer mobility through plasticizing the polymer to enable faster polymerization rate [29].

Reactive diluents have also been added to PDLC and HPDLC formulations to increase the solubility of the mixture and reduce viscosity, in efforts to increase sample consistency and device reproducibility. Figure 7 examines the influence of a common reactive diluent, NVP, on the polymerization kinetics in PDLC formulations containing approximately 0–15 wt % NVP, 30 wt % E7, 5 wt % octanoic acid and pentaacrylate. As observed with both LC and octanoic acid, increasing NVP concentration significantly increases the polymerization rate in PDLCs. Samples without NVP attain a maximum rate of 0.04 s^{-1} , as measured by PDSC. Increasing NVP concentration by 5 wt % increases polymerization rate by 15–30%, with PDLC formulations containing 15 wt % NVP attaining a maximum polymerization rate of 0.065 s^{-1} . The polymerization rate enhancement associated with NVP is due to

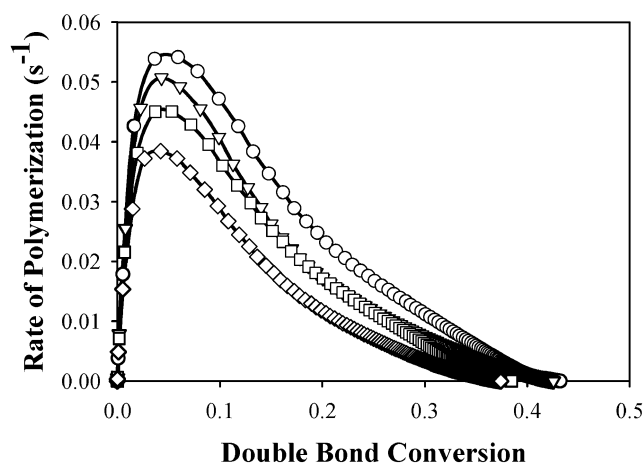


Figure 6. Rate of polymerization versus double bond conversion for a pentaacrylate/10 wt % NVP based PDLC containing 9 wt % (\circ), 6 wt % (∇), 3 wt % (\square) and 0 wt % (\diamond) octanoic acid as determined by PDSC.

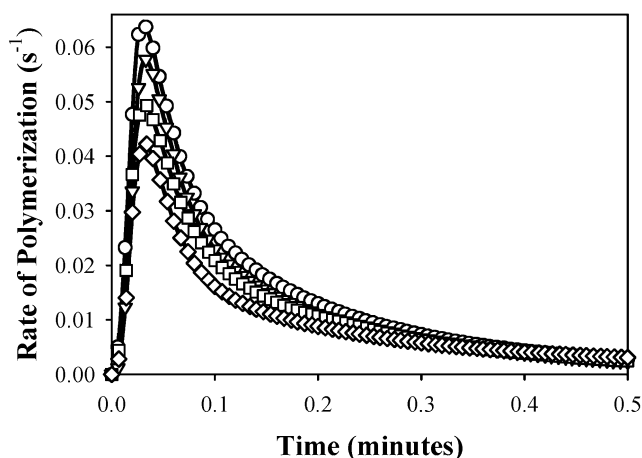


Figure 7. Rate of polymerization versus time for a pentaacrylate/5 wt % octanoic acid based PDLC containing 15 wt % (○), 10 wt % (▽), 5 wt % (□) and 0 wt % (◇) NVP as determined by PDSC.

plasticization and the copolymerization behaviour of NVP and acrylate monomer, as detailed elsewhere [31, 36].

In addition to increasing polymerization rate, both NVP and octanoic acid also influence the evolution of double bond conversion in PDLCs. Figure 8a compares the acrylate conversion of pentaacrylate PDLC formulations as measured by RTIR. The PDLC formulation with both octanoic acid and NVP has the highest acrylate conversion of nearly 60%. Removing either octanoic acid or NVP decreases acrylate conversion to 55% and 45%, respectively. Figure 8b plots NVP conversion against time for the polymerization of pentaacrylate PDLC formulations. Interestingly, adding octanoic acid is also influential on the conversion of NVP monomer in PDLC systems. As previously documented, NVP reaches complete conversion in pentaacrylate-based PDLC systems [31]. In samples containing octanoic acid, NVP reaches complete conversion in just over 50 s. Removing octanoic acid from the pentaacrylate-based PDLC formulation increases the amount of time necessary for NVP to be completely converted by over 100 s. The increase in conversion rate of NVP is likely also related to the plasticization effect of octanoic acid.

Additives such as octanoic acid and NVP significantly alter the mixing characteristics of PDLC systems. In the case of a pentaacrylate-based PDLC, adding NVP and octanoic acid reduces viscosity and enables greater photoinitiator concentrations to be utilized. Figure 9 examines the evolution of the nematic fraction of NVP and octanoic acid samples by RTIR. PDLCs that contain both octanoic acid and NVP have an ultimate nematic fraction of only 20%. As indicated by

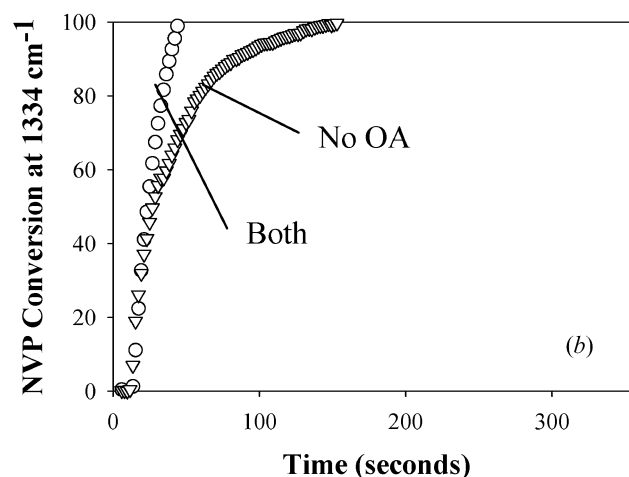
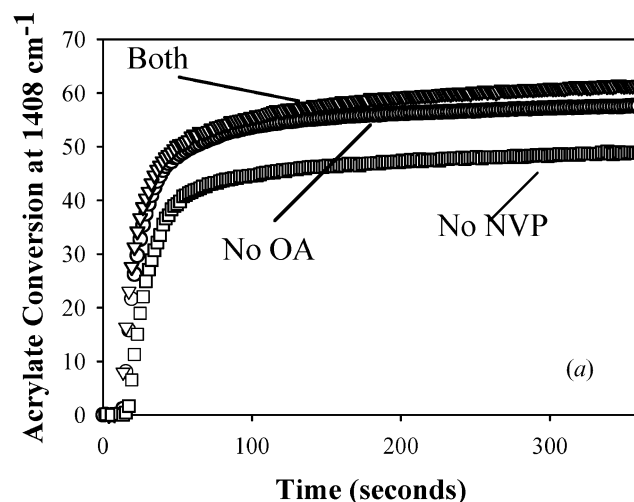


Figure 8. (a) Acrylate double bond conversion versus time for pentaacrylate-based PDLCs with 10 wt % NVP/5 wt % octanoic acid (▽), 10 wt % NVP/0 wt % octanoic acid (○) and 0 wt % NVP/5 wt % octanoic acid (□). (b) NVP double bond conversion versus time for pentaacrylate-based PDLCs containing 10 wt % NVP and either 5 wt % octanoic acid (○) or 0 wt % octanoic acid (▽).

the slope of the nematic fraction, the rate of LC phase separation is increased when octanoic acid is removed, indicating that octanoic acid increases the solubility of the LC in the polymer. Removing NVP increases both the extent of nematic fraction and the LC phase separation kinetics. PDLC samples without NVP have a nematic fraction over 30%. As indicated by the slope of the nematic fraction, samples without NVP exhibit the fastest rate of liquid-gel demixing. NVP and octanoic acid, by increasing LC solubility, suppress the rate at which LC phase separation occurs consequently limiting nematic fraction.

Through influencing polymerization kinetics and LC phase separation, both octanoic acid and NVP alter

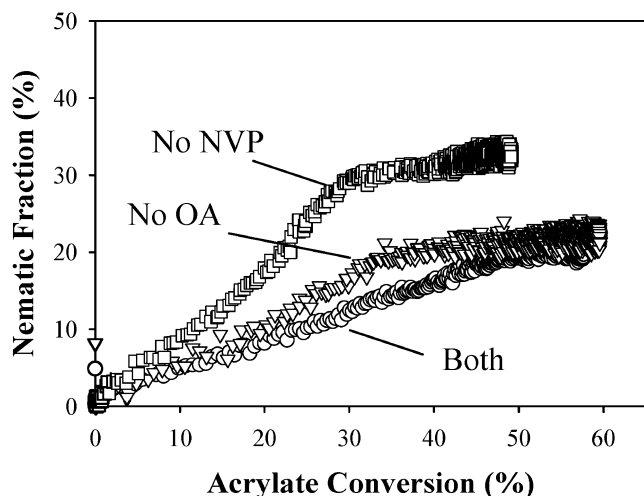


Figure 9. Nematic fraction (%) versus acrylate conversion (%) for pentaacrylate-based PDLCs with 10 wt % NVP/5 wt % octanoic acid (○), 10 wt % NVP/0 wt % octanoic acid (▽) and 0 wt % NVP/5 wt % octanoic acid (□).

polymer/LC morphology. Shown in figure 10 are SEM micrographs of pentaacrylate-based PDLCs that contain both NVP and octanoic acid (figure 10a), without octanoic acid (figure 10b) and without NVP (figure 10c). In general, all samples exhibit polymer ball morphology with interconnected LC voids (black regions). The size of the polymer ball morphology is dependent on the kinetics of the samples, with the smallest polymer balls evident in figure 10a in the sample containing both NVP and octanoic acid. The void space evident in figure 10, a direct measure of LC phase separation, increases with the removal of either NVP or octanoic acid. SEM, like RTIR determination of nematic fraction, indicates that octanoic acid and

NVP reduce LC phase separation in PDLC formulations that contain both NVP and octanoic acid. Decreasing LC domain size can improve the performance of materials such as nano-PDLCs and HPDLCs.

4. Conclusion

The polymerization kinetics and LC phase separation in acrylate-based PDLCs were examined to determine the effect of monomer functionality and components including LC, octanoic acid and NVP on the formation of these materials. The LC acts as a plasticizer that increases the maximum polymerization rate by 60–80% in comparison to neat systems (i.e. just monomer and initiator). Increasing acrylate functionality decreases polymerization rate and double bond conversion in PDLCs. Increasing acrylate monomer functionality also reduces the nematic fraction in PDLCs by limiting the extent of liquid–liquid demixing. Adding octanoic acid to PDLCs increases polymerization rate through plasticization that allows improved monomer mobility. Octanoic acid also reduces the extent of LC phase separation, as measured by the nematic fraction. As with octanoic acid, NVP increases polymerization rate but reduces LC phase separation. Both octanoic acid and NVP increase the solubility of the LC in the polymer, limiting the rate of LC demixing and correspondingly, nematic fraction in PDLCs.

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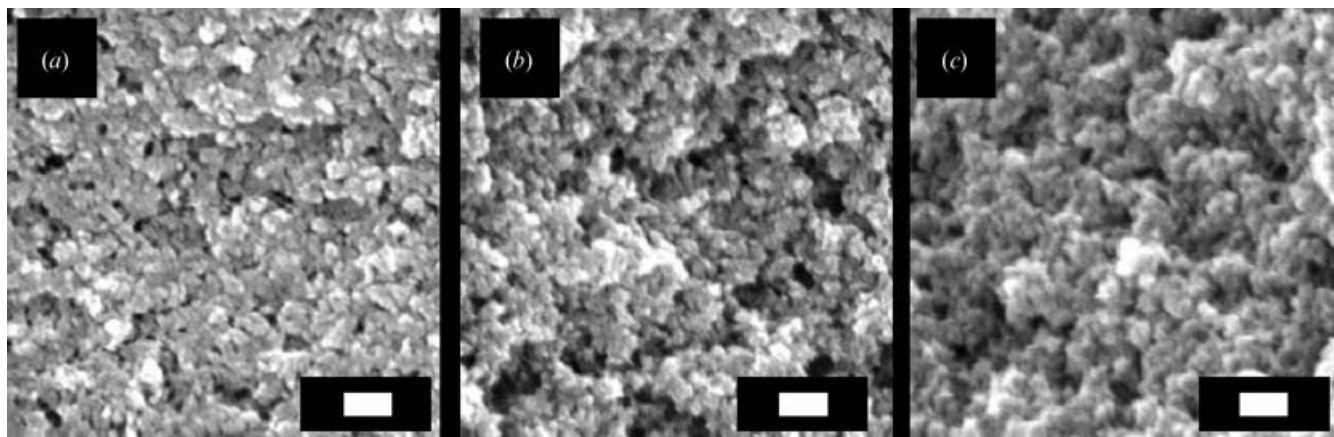


Figure 10. SEM micrographs of pentaacrylate-based PDLCs with (a) 10 wt % NVP/5 wt % octanoic acid, (b) 10 wt % NVP/0 wt % octanoic acid and (c) 0 wt % NVP/5 wt % octanoic acid. Scale bars are 100 nm.

References

- [1] L. Bouteiller, P. Le Barny. *Liq. Cryst.*, **21**, 157 (1996).
- [2] D. Coates. *J. Mater. Chem.*, **5**, 2063 (1995).
- [3] D.A. Higgins. *Adv. Mater.*, **12**, 251 (2000).
- [4] M. Mucha. *Prog. Polym. Sci.*, **28**, 837 (2003).
- [5] P. Drzaic. *Liquid Crystal Dispersions*. World Scientific, Singapore (1995).
- [6] T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, R.L. Sutherland. *Annu. Rev. Mater. Sci.*, **30**, 83 (2000).
- [7] G.P. Crawford. *Opt. Photonics News*, **14**, 54 (2003).
- [8] R.T. Pogue, R.L. Sutherland, M.G. Schmitt, L.V. Natarajan, S.A. Siwecki, V.P. Tondiglia, T.J. Bunning. *Appl. Spectrosc.*, **54**, 12A (2000).
- [9] R.L. Sutherland, L.V. Natarajan, T.J. Bunning, V.P. Tondiglia. *Switchable Holographic Polymer-Dispersed Liquid Crystals*. Academic Press, San Diego, CA (2001).
- [10] H.M.J. Boots, J.G. Kloosterboer, C. Serbutoviez, F.J. Touwslager. *Macromolecules*, **29**, 7683 (1996).
- [11] J.G. Kloosterboer, C. Serbutoviez, F.J. Touwslager. *Polymer*, **37**, 5937 (1996).
- [12] C. Serbutoviez, J.G. Kloosterboer, H.M.J. Boots, F.J. Touwslager. *Macromolecules*, **29**, 7690 (1996).
- [13] R. Bhargava, S.Q. Wang, J.L. Koenig. *Macromolecules*, **32**, 8982 (1999).
- [14] R. Bhargava, S.Q. Wang, J.L. Koenig. *Macromolecules*, **32**, 8989 (1999).
- [15] A.J. Lovinger, K.R. Amundson, D.D. Davis. *Chem. Mater.*, **6**, 1726 (1994).
- [16] G.W. Smith. *Phys. Rev. Lett.*, **70**, 198 (1993).
- [17] G.W. Smith. *Mol. Cryst. liq. Cryst.*, **239**, 63 (1994).
- [18] N.A. Vaz, G.W. Smith, G.P. Montgomery Jr. *Mol. Cryst. liq. Cryst.*, **146**, 1 (1987).
- [19] N.A. Vaz, G.W. Smith, G.P. Montgomery Jr. *Mol. Cryst. liq. Cryst.*, **146**, 17 (1987).
- [20] F. Simoni, G. Cipparrone, C. Umeton, G. Arabia, G. Chidichimo. *Appl. Phys. Lett.*, **54**, 896 (1989).
- [21] J.W. Doane, N.A. Vaz, B.G. Wu, S. Zumer. *Appl. Phys. Lett.*, **48**, 269 (1986).
- [22] J.L. West. *Mol. Cryst. liq. Cryst.*, **157**, 427 (1988).
- [23] T. White, L.V. Natarajan, V.P. Tondiglia, T.J. Bunning, C.A. Guymon. *Macromolecules*, **40**, 1112 (2007).
- [24] R.T. Pogue, L.V. Natarajan, S.A. Siwecki, V.P. Tondiglia, R.L. Sutherland, T.J. Bunning. *Polymer*, **41**, 733 (2000).
- [25] T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, G. Dougherty, R.L. Sutherland. *J. Polym. Sci. B*, **35**, 2825 (1997).
- [26] V.P. Tondiglia, L.V. Natarajan, R.M. Neal, R.L. Sutherland, T.J. Bunning. *MRS Proc.*, **479**, 235 (1997).
- [27] L.V. Natarajan, R.L. Sutherland, V.P. Tondiglia, T.J. Bunning. *J. nonlinear opt. Mater.*, **5**, 89 (1996).
- [28] C.C. Bowley, S.D. Kossyrev, J. Colegrove, J. Kelly, T. Fiske, H. Yuan, G.P. Crawford. *Mol. Cryst. liq. Cryst.*, **359**, 327 (2001).
- [29] J. Klosterman, L.V. Natarajan, V.P. Tondiglia, R.L. Sutherland, T.J. White, C.A. Guymon, T.J. Bunning. *Polymer*, **45**, 7213 (2004).
- [30] T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, R.L. Sutherland, R. Haaga, W.W. Adams. *SPIE Proc.*, **2651**, 44 (1996).
- [31] T.J. White, W.B. Liechty, L.V. Natarajan, V.P. Tondiglia, T.J. Bunning, C.A. Guymon. *Polymer*, **47**, 2289 (2006).
- [32] K.S. Anseth, C.M. Wang, C.N. Bowman. *Macromolecules*, **27**, 650 (1994).
- [33] E. Andrzejewska. *Prog. Polym. Sci.*, **26**, 605 (2001).
- [34] T.J. White, L.V. Natarajan, V.P. Tondiglia, P.F. Lloyd, T.J. Bunning, C.A. Guymon. *Macromolecules*, **40**, 1112 (2007).
- [35] L.M. Babkov, I.I. Gnatyuk, S.V. Trukhachev. *J. mol. Struct.*, **744-747**, 425 (2005).
- [36] T.J. White, W.B. Liechty, C.A. Guymon. *Radtech 2006 Technical Proceedings* (2006).