Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 47 (2006) 2289–2298
polymer
www.elsevier.com/locate/polymer

The influence of *N*-vinyl-2-pyrrolidinone in polymerization of holographic polymer dispersed liquid crystals (HPDLCs)

Timothy J. White [a], William B. Liechty [a], Lalgudi V. Natarajan [b], Vincent P. Tondiglia [b], Timothy J. Bunning [c], C. Allan Guymon [a,*]

[a] *Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, IA 52242-1547, USA*
[b] *Science Applications International Corporation (SAIC), Dayton, OH 45433, USA*
[c] *Air Force Research Labarotory (AFRL), Materials and Manufacturing Directorate, Wright Patterson Air Force Base, OH 45433, USA*

Received 24 August 2005; received in revised form 9 January 2006; accepted 10 January 2006
Available online 28 February 2006

Abstract

Holographic polymer dispersed liquid crystals (HPDLCs) are targeted for application in a wide range of devices as dynamically switchable transmission or reflection diffraction gratings tunable through the visible spectra. The inclusion of *N*-vinyl pyrrolidinone (NVP) has been shown to reduce liquid crystal (LC) droplet size in HPDLC gratings and subsequently improve HPDLC performance. In this work, the influence of NVP on HPDLC polymer/LC morphology is examined and correlated to the influence of NVP on HPDLC photopolymerization kinetics and LC phase separation. As in other photopolymer systems, NVP significantly increases the rate of polymerization in HPDLC photopolymerization. In all the HPDLC formulations studied, NVP is completely incorporated into the polymer network while less than half of acrylate double bonds react. Furthermore, as the highly cross-linked polymer network forms, the small mono-vinyl NVP appears to react preferentially with acrylate double bonds, facilitating additional conversion of pendant double bonds otherwise trapped in the polymer network. NVP also induces a delay in the onset of reaction diffusion termination and extends the range of conversions for which reaction diffusion is observed. Interestingly, NVP also impacts polymer/LC morphology by delaying LC phase separation to higher double bond conversions. Together, the influence of NVP on the polymerization kinetics and LC phase separation alters HPDLC morphology by limiting LC droplet size, consequently resulting in improved HPDLC performance.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Holographic polymer dispersed liquid crystals (HPDLCs); Polymerization kinetics; *N*-vinyl pyrrolidinone (1-vinyl-2-pyrrolidinone, vinyl pyrrolidinone)

1. Introduction

Holographic polymer dispersed liquid crystals (HPDLCs) are a liquid crystal (LC) composite material targeted for application in photonic, telecommunication and display devices. In particular, HPDLCs offer the novel performance capability of dynamically switchable transmissive and reflective diffraction gratings. HPDLC gratings have already been demonstrated successfully in optically switchable Bragg reflectors [1], distributed feedback elements [2], active photonic bandgap materials [3] and display devices [4].

HPDLC prepolymer mixtures are typically based on a highly functional acrylate monomer, a eutectic mixture of either cyanobiphenyl or chloro-/fluoro-substituted LC molecules and inclusion of a solubilizer, typically *N*-vinyl-2-pyrrolidinone (NVP) [5]. Formation of HPDLCs is based on periodic photoinitiation of a prepolymer mixture that causes mass transport of reactive and non-reactive species [6]. Mass transport of monomer and liquid crystal (LC) results in classic HPDLC morphology—alternating lamellae of highly polymer and mostly LC regions. In acrylate-based HPDLCs, LC phase separation occurs via polymer-induced phase separation (PIPS) which is highly dependent on gelation, polymer vitrification and polymerization kinetics [7]. Understanding the contribution of components to polymerization kinetics, polymer composition and LC phase separation is paramount for optimization of HPDLC performance in devices, especially as HPDLCs are tailored to more specific and increasingly complex applications.

HPDLC research has primarily focused on improving performance parameters such as diffraction efficiency, switching voltage, and on/off state transmission. To optimize performance, numerous adjustments in the base formulation

---

* Corresponding author. Tel.: +1 319 335 5015; fax: +1 319 335 1415.
E-mail address: allan-guymon@uiowa.edu (C.A. Guymon).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.01.030

have been made. Reports have detailed the contribution of surfactant-like molecules, [8,9] NVP, [10,11] acrylate functionality, [12,13] and fluorinated monomers [14,15]. Most recently, enhanced HPDLC reflection gratings have been demonstrated in a thiol-ene system [16]. Changes in HPDLC performance often occur when a particular component influences polymer/LC morphology, most notably LC droplet size.

In addition to their use in HPDLC formulations, NVP and other *N*-vinyl amides are common additives in industrial polymerizations due to their reduction of oxygen inhibition [17,18]. Numerous reports detail the copolymerization of NVP with (meth)acrylate monomers [19]. Surprisingly, the reactivity of NVP with highly functional acrylates (>2), such as those used in HPDLCs, has not been well-characterized. NVP is a necessary component for the homogeneity of the six component HPDLC mixture and significantly changes LC droplet size and diffraction efficiency [10,11]. Despite this contribution, the precise reactivity and role of NVP in HPDLCs is not well understood.

Recently, the influence on polymerization behavior and phase separation of another additive in HPDLCs, octanoic acid, has been explored [20]. Adding octanoic acid to HPDLC formulations delays LC phase separation by extending the solubility of the LC in the polymer matrix thereby increasing the overall polymerization rate. Together, the contributions of octanoic acid to LC phase separation and polymerization kinetics result in reduced LC droplet size. It is highly possible that NVP may be acting similarly to octanoic acid in HPDLC formulations serving to extend LC solubility in the polymer matrix while increasing the polymerization rate. In addition to these contributions, any incorporation of NVP into the polymer matrix should shift the polymer gel point to higher conversions and delay the onset of LC phase separation. Examining the influence of NVP on the polymerization kinetics is, therefore, critical in determining the mechanism by which NVP influences HPDLC morphology and corresponding performance.

The goal of this work is to determine the mechanism by which NVP influences HPDLC performance through examination of the influence of NVP on the rate of polymerization and correlating any kinetic influence to subsequent changes in LC phase separation and polymer/LC morphology. Photo-DSC will be utilized to determine overall polymerization kinetics and the influence of reaction diffusion in these systems. RTIR spectroscopy will also be used to monitor the double bond conversions of both NVP and acrylate double bonds. The polymerization behavior of HPDLC formulations with increasing NVP concentration, without NVP, with the chemically similar but non-reactive analogue *N*-ethyl pyrrolidinone and with another common reactive diluent, hexyl acrylate will be examined. In addition, the evolution of phase separated LC during polymerization will be examined by monitoring the development of the nematic LC phase as a function of double bond conversion. Comparing the polymerization kinetics and phase separation of these systems will facilitate understanding of the role that NVP plays in the formation of HPDLC materials.

2. Experimental section

2.1. Materials

The HPDLC formulation studied here is similar to that examined previously [5,8]. The primary monomers employed in this formulation are dipentaerythritol penta-/hexa-acrylate (DPPHA, Aldrich) and *N*-vinyl-2-pyrrolidinone (NVP, Aldrich). For comparison, the monomer hexyl acrylate (HA, Aldrich) and solvent/plasticizer *N*-ethyl-2-pyrrolidinone (NEP, Aldrich) were substituted for NVP in the HPDLC formulation. All photopolymerizations were initiated with 0.2 wt% of the ultra-violet (UV) photoinitiator mixture Darocur 4265 (DC-4265, Ciba). DC-4265 is a 50:50 weight mixture of 2-hydroxy-2-methyl-1-phenyl-propanone (HAP) and diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO). The remaining components in the HPDLC formulation are the surfactant-like molecule octanoic acid (Aldrich) and the liquid crystal E7 (EMD Chemical). The composition of E7 has been previously reported [21]. All chemicals were used as received. Chemical structures for NVP, NEP, hexyl acrylate, octanoic acid and DPPHA are shown in Fig. 1.

The base HPDLC formulation studied is given in Table 1. This formulation was adjusted to aide in the determination of the influence of NVP. Table 1 compares the base HPDLC formulation to two formulations in which the amount of NVP is replaced with NEP (HPDLC-B) and additional DPPHA (HPDLC-C). The viscosities of the HPDLC and HPDLC-B mixtures are approximately equal and somewhat lower than the viscosity of the HPDLC-C sample. Additionally, HPDLC formulations were studied as a function of NVP concentration. In these formulations, DC-4265, octanoic acid, and E7 concentrations were held constant while NVP and DPPHA concentration changed. It is important to note that the base formulation has a 5.8:1 molar ratio of acrylate to NVP double bonds.

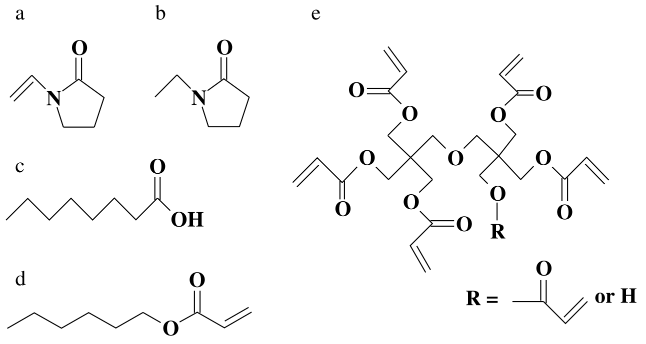

Fig. 1. Chemical structures of compounds included in the HPDLC formulations examined. Shown are: (a) *n*-vinyl-2-pyrrolidinone (NVP), (b) *n*-ethyl-2-pyrrolidinone (NEP), (c) octanoic acid, (d) hexyl acrylate and (e) dipentaerythritol penta-/hexa-acrylate (DPPHA).

Table 1
Composition of three HPDLC formulations used throughout this study

(wt %'s)	DC-4265	OA	NVP	NEP	E7	DPPHA
HPDLC	0.2	5	10	0	35	49.8
HPDLC-B	0.2	5	0	10	35	49.8
HPDLC-C	0.2	5	0	0	35	59.8

Initiator, surfactant and LC concentration are constant in all formulations.

2.2. Characterization

The photopolymerization kinetics was examined with the complementary techniques of photo-differential scanning calorimetry (PDSC) and real-time infrared spectroscopy (RTIR). The DSC used is a Perkin–Elmer diamond DSC. Photopolymerizations were initiated by a medium pressure Hg–Xe UV arc lamp (Ace Glass) using a 365 nm bandpass filter (Omega Optical). The light intensity for all PDSC experiments was 3.0 mW/cm^2. Samples were purged with ultrapure nitrogen for 6 min before polymerization to limit oxygen inhibition. A refrigerated chiller was used to maintain isothermal conditions at 30 °C. The rate of polymerization was calculated at each data point by Eq. (1):

$$R_\mathrm{p} = \frac{Q}{\Delta H_\mathrm{DPPHA} + \Delta H_\mathrm{NVP}},\ \Delta H = \frac{xmf\Delta H_\mathrm{rxn}}{M} \qquad (1)$$

where Q is the heat flow (J/s) measured by the calorimeter and ΔH is calculated for each monomer from the weight fraction (x), mass (m), functionality (f), reference values for ΔH_rxn (DPPHA—86,190.4 J/mol [22], NVP—53,900 J/mol [23]) and molecular weight (M). Double bond conversion can be calculated from the integration of the rate versus time curve. Determination of kinetic rate parameters for termination (k_t) and propagation (k_p) was accomplished through DSC after-effect experiments where the light was shuttered at different conversions, allowing values for k_t and k_p to be decoupled as described in detail elsewhere [24,25].

A Fourier transform infrared (FTIR) was adapted to allow real-time monitoring of photopolymerizations (RTIR). The FTIR employed is a Thermo Electron Nexus 670 with liquid nitrogen cooled MCT detector, purged with nitrogen to reduce noise from water vapor and carbon dioxide. A horizontal transmission accessory was fitted to the FTIR to allow examination of photopolymerization inside a sealed box purged with nitrogen, once again, to limit oxygen inhibition. Samples were sandwiched between two NaCl slides (International Crystal Labs) with approximately 10 μm spacing. In RTIR analysis, photopolymerization was initiated by a high-pressure Hg arc lamp (Exfo Acticure 4000) using 365 nm light with an intensity of 1.3 mW/cm^2. Data reported is the result of a series of single scans with 8 cm^{-1} resolution and 0.2 s data spacing. The percent double bond conversion was calculated by Eq. (2):

$$\text{Percent Conversion} = \frac{A_\mathrm{t} - A_0}{A_0} \times 100\% \qquad (2)$$

where at a specified wavenumber A_t is the IR peak height at time t and A_0 is the peak height before polymerization. An example of a series of IR spectra collected by RTIR is shown in Fig. 2 where the change in peak height for the acrylate peak at 1407 cm^{-1} and NVP double bond peak 1332 cm^{-1} can be monitored independently enabling the determination of distinct conversion profiles for both monomers. Additionally, the cyano absorbance at 2225 cm^{-1} was monitored to study LC ordering with RTIR. Upon phase separation, the initially isotropic LC molecules begin to exhibit the nematic mesophase. The absorption of the cyano moiety decreases as LC transitions from isotropic to nematic inducing a decrease in peak height at 2225 cm^{-1} [26,27]. The ultimate drop in the cyano absorbance from the value at time zero is indicative of the amount of nematic LC present in the system.

A scanning electron microscope (SEM, Hitachi S-9000, 2.5 keV) was used to directly examine the influence of formulation changes on polymer/LC morphology. Floodlit HPDLC formulations were polymerized, subjected to methanol extraction, vacuum dried overnight and freeze fractured with liquid nitrogen. Upon fracturing, samples were mounted on aluminum stubs via colloidal silver paint to enable analysis of the bulk morphology. After samples were mounted, a 2–5 nm coat of tungsten was applied by a K550 Emiteon Sputter Coater.

3. Results and discussion

The inclusion of *N*-vinyl-2-pyrrolidinone (NVP) in HPDLC formulations results in morphology with smaller liquid crystal (LC) droplets but less LC phase separation [10,11]. This influence of NVP on HPDLC morphology indicates a possible role in HPDLC polymer formation either as a plasticizer/solubilizer or as a reactive diluent. Quantifying the

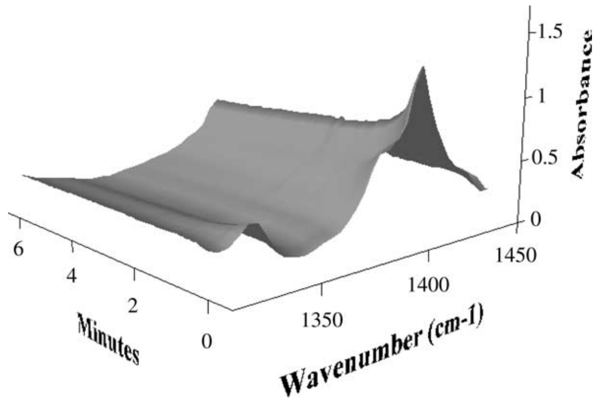

Fig. 2. RTIR series spectra in the region of 1315–1450 cm^{-1}. The small peak at 1330 cm^{-1} is a vinyl absorption for NVP. The peak at 1407 cm^{-1} is due to acrylate absorption for DPPHA.

contribution of NVP to the photopolymerization kinetics in HPDLC formulations should serve to determine the role NVP plays in influencing polymer formation in HPDLCs. The incorporation of NVP into the crosslinked polymer matrix or any contribution to the polymerization kinetics could delay liquid crystal phase separation and ultimately be the source of altered HPDLC morphology. Understanding the influence of NVP on kinetics, phase separation and polymer/LC morphology will facilitate development of a complete picture regarding the role of NVP in HPDLC formation.

In order to determine the relative impact of NVP on HPDLC development, the polymerization of the base HPDLC formulation containing NVP (Table 1) was studied alongside other analogous formulations by photo-DSC (PDSC). Plotted in Fig. 3 are the polymerization rate profiles of the base HPDLC formulation with NVP, the HPDLC-B (Table 1) formulation with NEP, the HPDLC-C (Table 1) formulation without NVP and the neat polymerization of NVP and DPPHA. The homopolymerization of DPPHA is typical for a crosslinked acrylate, exhibiting a rapid rise to a maximum rate of polymerization that occurs prior to 5% double bond conversion. Ultimately, the highly crosslinked nature of the polymerization limits DPPHA double bond conversion to slightly over 20%. The homopolymerization of NVP, much different than DPPHA, exhibits a slow but steady rate of polymerization up to about 30% double bond conversion. At this point autoacceleration occurs, causing a dramatic rise in the rate of polymerization to a maximum at 60% conversion. These results provide a foundation for understanding the polymerization of the three HPDLC formulations studied in Fig. 3. The lowest rate for the LC containing systems is that of the HPDLC-C formulation without NVP. The maximum rate of polymerization for the HPDLC-C formulation is 10% greater than that of the homopolymerization of DPPHA. This sample then can be compared to the HPDLC-B formulation once again without NVP, but with the chemically similar (but non-reactive) analogue *N*-ethyl-2-pyrrolidinone (NEP). The rate of polymerization for this HPDLC-B formulation containing NEP is more than 50% higher than that of the homopolymerization of DPPHA and also faster than the HPDLC-C formulation without NVP. The base HPDLC formulation, containing 10 wt% NVP, exhibits the highest maximum rate of polymerization with an overall double bond conversion of about 40%.

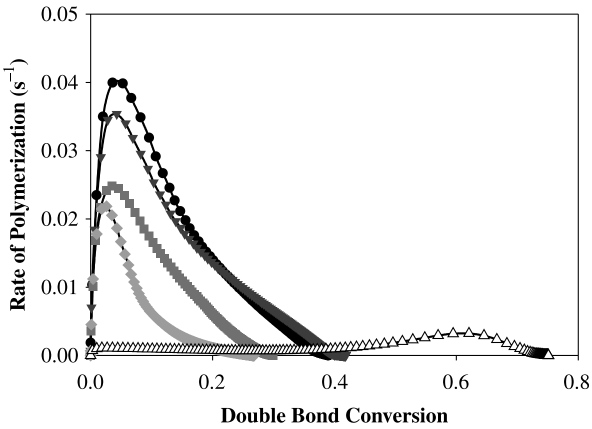

Fig. 3. Rate of polymerization as a function of double bond conversion as determined by PDSC for HPDLC formulations containing 10 wt% NVP (●), 10 wt% NEP (HPDLC-B) (▾) and without NVP (HPDLC-C) (■). Also shown are polymerization rates of neat DPPHA (◆) and NVP (△).

Comparing the rate profiles for the homopolymerization of DPPHA and NVP to the three HPDLC formulations leads to a number of conclusions. First, when examining the polymerization of HPDLC formulations without NVP it is quite evident in the case of the HPDLC-C and HPDLC-B formulations that plasticization by the non-reactive components including LC, surfactant and when added, NEP is quite influential on the polymerization rate. These HPDLC formulations are based on the homopolymerization of DPPHA that is initially fast but severely hindered by its highly functional character. Adding components such as LC, surfactant and NEP increase the non-reactive free volume in the polymer matrix, especially before LC phase separation. Notably, when NVP is included in the HPDLC formulation, the rate of polymerization is 15% faster than the rate for the HPDLC-B formulation with NEP substituted for NVP. The comparison of the NVP (HPDLC-A) and NEP (HPDLC-B) containing samples indicates that the difference in the two formulations, the double bond and consequent reactivity of NVP, is the source of the increase in the rate of polymerization upon addition of NVP. Thus, the rise in the rate of polymerization with the inclusion of NVP indirectly indicates the reactivity of NVP in the formation of the HPDLC polymer matrix.

The indirect evidence of NVP incorporation from PDSC study can be confirmed by real-time IR (RTIR) spectroscopy. RTIR spectroscopy [28] directly measures conversion and has been a useful tool to independently monitor the conversion of distinct functional groups both in free radical copolymerizations of acrylates with other vinyl compounds [29] along with systems such as thiol-enes [30]. Fig. 4(a) is a plot of the double bond conversion of NVP and DPPHA versus time for the base HPDLC formulation containing 10% NVP. In the polymerization of the base HPDLC formulation, the conversion of NVP occurs very rapidly with complete consumption of the vinyl moiety in approximately 100 s. Acrylate conversion is approximately 50% in this photopolymerization, much less than that of NVP. Very little additional reaction of DPPHA occurs after NVP is completely converted, indicating that the conversion of DPPHA may be coupled to that of NVP.

The coupled reactivity of NVP and DPPHA is isolated in Fig. 4(b), where the conversion profiles of NVP and DPPHA in the base HPDLC formulation are normalized by their final conversion value. The normalized conversion data enable a clear comparison of the relative rates of conversion for NVP and DPPHA in the base HPDLC formulation. The overlap of the normalized conversion of NVP and DPPHA in the HPDLC formulation is striking and indicates that DPPHA conversion has a dramatic dependence on NVP. The slope of the normalized conversion of NVP and DPPHA is identical up to nearly 90% NVP conversion. The equivalent slopes of the

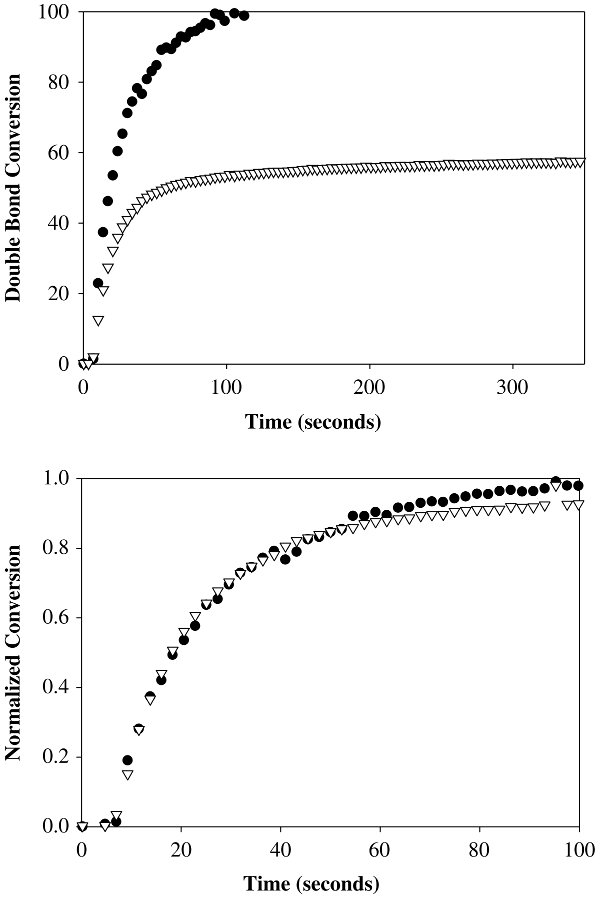

Fig. 4. (a) RTIR examination of double bond conversion for NVP (●) and DPPHA (▽) and (b) normalized conversion for NVP (●) and DPPHA (▽) in the standard HPDLC formulation containing 10 wt% NVP.

normalized conversion of DPPHA and NVP in the base HPDLC formulation suggest that the double bonds of each monomer appear to be consumed at rates proportional to each other, implying that the reaction of acrylate and NVP double bonds are integrally related. This behavior certainly shows that NVP is not only becoming incorporated in the acrylate polymer network, but is, in fact, also facilitating the acrylate polymerization.

To further understand the dependence of HPDLC polymerization kinetics on NVP, the influence of NVP concentration on the rate of polymerization has also been examined using PDSC. Fig. 5(a) shows a plot of the rate of polymerization versus double bond conversion for HPDLC formulations containing increasing concentrations of NVP. For each increase of 5 wt% NVP in the HPDLC formulation, the rate of polymerization subsequently increases by 15–20%. This rate increase is significant for such small changes in concentration [31] and indicates that NVP has a substantial impact on the kinetics of polymer formation of HPDLCs.

For comparison, the polymerization of DPPHA with increasing NVP concentration was studied and is plotted in Fig. 5(b). This simple DPPHA/NVP system, containing only reactive species, could help elucidate whether the HPDLC rate enhancement is a function of the polymerization reaction or based on some other phenomena present in the HPDLC formulation. Fig. 5(b) plots the rate of polymerization against double bond conversion for polymerization of neat DPPHA and DPPHA with increasing NVP concentration. Similar to the study of NVP concentration in the HPDLC formulation, a general trend of increasing rate with increasing NVP concentration is evident. Interestingly, adding only 5 wt% NVP to DPPHA decreases the rate of polymerization in comparison to the homopolymerization of DPPHA. However, the rate of polymerization for HPDLC formulations containing 10 and 15 wt% NVP is greater than the neat polymerization of DPPHA. Also notable is that the sample containing 15 wt% NVP shows a markedly pronounced increase in the rate of polymerization in comparison to the other polymerizations. These results clearly show that the increased rate with NVP concentration in the HPDLC formulation is due to synergistic effects in the NVP and DPPHA copolymerization.

HPDLC formulations have long included NVP as it is an effective solubilizer and exhibits a desirable refractive index. However, to determine whether the influence of NVP on the rate of polymerization seen in Fig. 5(a) and (b) is simply an effect of only NVP or rather an influence of adding a monovinyl monomer, HPDLC formulations containing hexyl acrylate were examined by PDSC. Just like NVP, adding hexyl

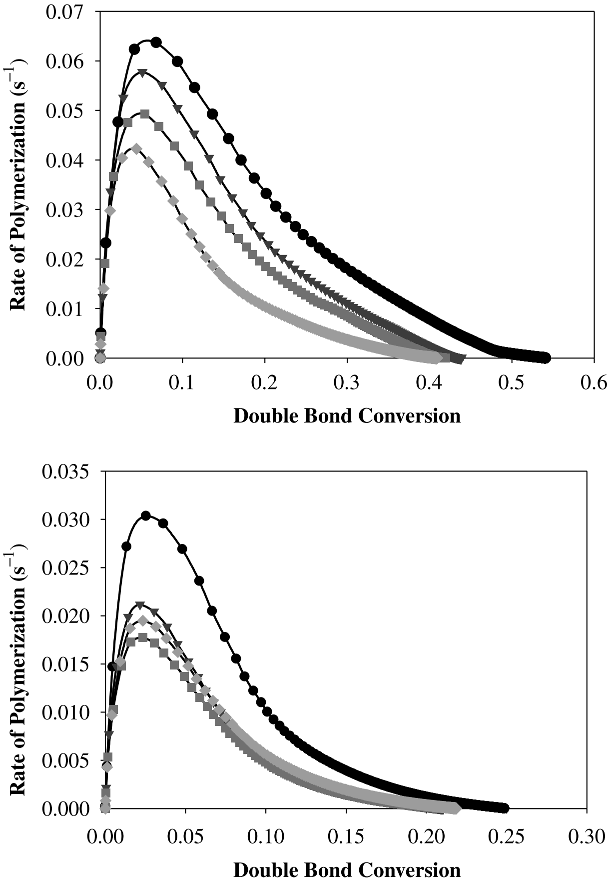

Fig. 5. Rate of polymerization versus double bond conversion for (a) HPDLC formulations with 0 (◆), 5 (■), 10 (▼) and 15 (●) wt% NVP and (b) DPPHA:NVP formulations with 0 (◆), 5 (■), 10 (▼) and 15 (●) wt% NVP.

acrylate reduces viscosity, lowers average functionality and can act as a solubilizer. Additionally, the double bond in hexyl acrylate should be the same reactivity as the acrylate double bonds in DPPHA. Plotted in Fig. 6 are the HPDLC formulations as in Fig. 5(a) but with hexyl acrylate substituted for NVP. Similar to Fig. 5(a), hexyl acrylate increases the rate of polymerization with increasing concentration. Notably, when comparing Fig. 6 to Fig. 5(a), the rate increases due to increased hexyl acrylate concentration are not as significant as that of NVP. Such behavior has been previously documented [18].

The comparison of HPDLC formulations with hexyl acrylate and NVP highlights the unique behavior of NVP. In particular, comparing polymerization rates in formulations containing these two common reactive diluents show that the influence of NVP is not rooted in viscosity reduction or an influence on crosslink density, but rather some inherent difference between the two monomers. The polymerization rate increases associated with NVP suggest synergy in the copolymerization of NVP and DPPHA. Interestingly, moderate rate enhancement with NVP concentration is even evident in the linear copolymerization of hexyl acrylate and NVP at similar molar concentrations [32] indicating that cross-propagation between radical species and the two different double bonds is kinetically favorable and the source of at least some of the increase in polymerization rate.

While the rate enhancement associated with NVP is in part due to kinetically favorable cross-propagation, greater understanding regarding the synergy in the copolymerization of NVP and DPPHA in HPDLC formulations could be achieved by closer examination of the influence of NVP on acrylate conversion. To study the influence of NVP on acrylate reactivity, a series of HPDLC formulations containing increasing concentration of NVP were examined by RTIR. Fig. 7 plots the conversion of acrylate monomer, measured at 1407 cm^{-1}, versus time. As NVP concentration is increased, the overall acrylate conversion is markedly increased. The polymerization of the HPDLC formulation containing 15 wt% NVP achieves 40% acrylate conversion in just a few seconds in comparison to the HPDLC formulation without NVP which reaches 40% conversion in approximately 3 min. This analysis reveals that NVP increases the rate of polymerization in HPDLCs through a significant increase in the rate of acrylate conversion. Further, NVP concentration dramatically increases DPPHA conversion from 45% to greater than 60% conversion. Increasing the acrylate conversion in the actual formation of HPDLCs could reduce the routes for degradation of these materials over time [33].

Previous study of neat and solvent polymerizations of DPPHA [32] have shown that polymerizations based on this pentafunctional monomer exhibit what has been termed reaction diffusion termination [34–36]. Generally, reaction diffusion termination is prevalent in polymerizations when segmental and diffusional termination processes are impossible such that the only route for bimolecular termination is through propagation via local, unreacted double bonds. It is highly possible that the polymerization of HPDLCs, based on this monomer, could also exhibit reaction diffusion termination. Intuitively, NVP could delay the onset of the diffusion limitations that bring about the reaction diffusion mechanism since it reduces viscosity and crosslink density.

The study of the reaction diffusion mechanism can be examined through two quantities: $k_t/(k_p[M])$ and $R_p^2/[M]$, where once again, k_t and k_p are the kinetic rate parameters for termination and propagation, $[M]$ is the double bond concentration and R_p is the rate of polymerization. When the value of $k_t/(k_p[M])$ is constant over a range of double bond conversion this coupling of the propagation and termination kinetic parameters indicates reaction diffusion. Further, the quantity $R_p^2/[M]$ indicates reaction diffusion termination when the change in this parameter is proportional to k_p [34,35].

To determine if reaction diffusion is prevalent in HPDLC systems, both $k_t/(k_p[M])$ and $R_p^2/[M]$ were determined for the base HPDLC formulation and are plotted in Fig. 8(a). For this polymerization, the quantity $k_t/(k_p[M])$ initially starts out at a relatively high value then decreases to a constant value of around 40 L/mol between 5 and 30% double bond conversion. Additionally, the change in $R_p^2/[M]$ is proportional to the

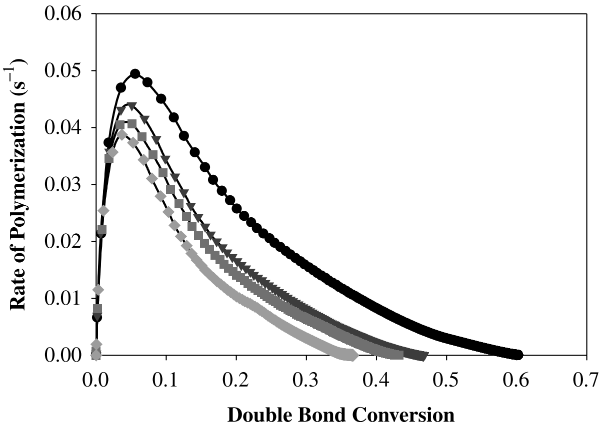

Fig. 6. Rate of polymerization versus double bond conversion for HPDLC formulations (no NVP) with 0 (◆), 5 (■), 10 (▼) and 15 (●) wt% hexyl acrylate.

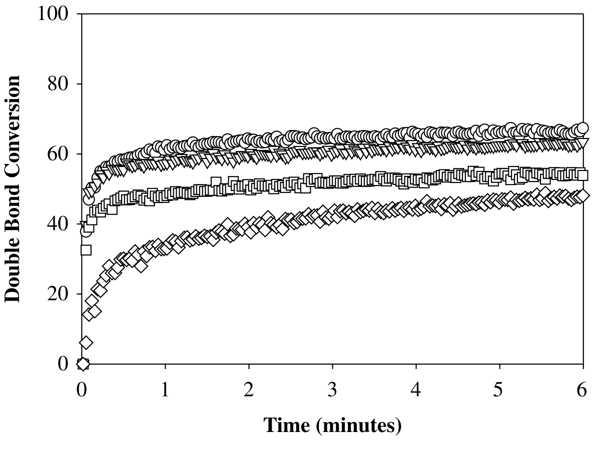

Fig. 7. RTIR determination of acrylate conversion at 1407 cm^{-1} for samples containing 0 (◇), 5 (□), 10 (▽) and 15 (○) wt% NVP.

change in k_p between 5 and 30% double bond conversion. As expected, both $k_t/(k_p[M])$ and $R_p^2/[M]$ indicate the reaction diffusion termination mechanism is prevalent in HPDLC formation from 5 to 30% double bond conversion. It should be noted that the k_p and k_t values are average values representative of the copolymerization of NVP and DPPHA in this base HPDLC formulation.

The synergistic influence of NVP on the rate of polymerization in HPDLCs along with the codependence between NVP and DPPHA copolymerization may both be tied to an influence on reaction diffusion. Formulations with increasing concentration of NVP were studied in a similar manner to Fig. 8(a). Fig. 8(b) is a plot of $R_p^2/[M]$ versus double bond conversion for HPDLC formulations with increasing amounts of NVP. It is evident from Fig. 8(b) that the onset of reaction diffusion, indicated by the maximum of the $R_p^2/[M]$, is delayed with increasing NVP content. Therefore, as expected, NVP incorporation as a function of concentration delays the diffusional limitations that trigger the reaction diffusion termination mechanism. This delay in diffusion limitations may be partially responsible for the dramatic increase in polymerization rate with NVP concentration. NVP not only delays the onset of reaction diffusion but is also significant at later stages of the reaction. The proportionality of $R_p^2/[M]$ to k_p (k_p for base HPDLC formulation is plotted in Fig. 8(a)) is extended with increasing NVP concentration as the predominance of the reaction diffusion termination mechanism is shifted from 25% double bond conversion (0% NVP) to greater than 40% double bond conversion with 15% NVP. Such behavior indicates that NVP is facilitating greater reactivity for the unreacted DPPHA double bonds mostly contained in the polymer matrix.

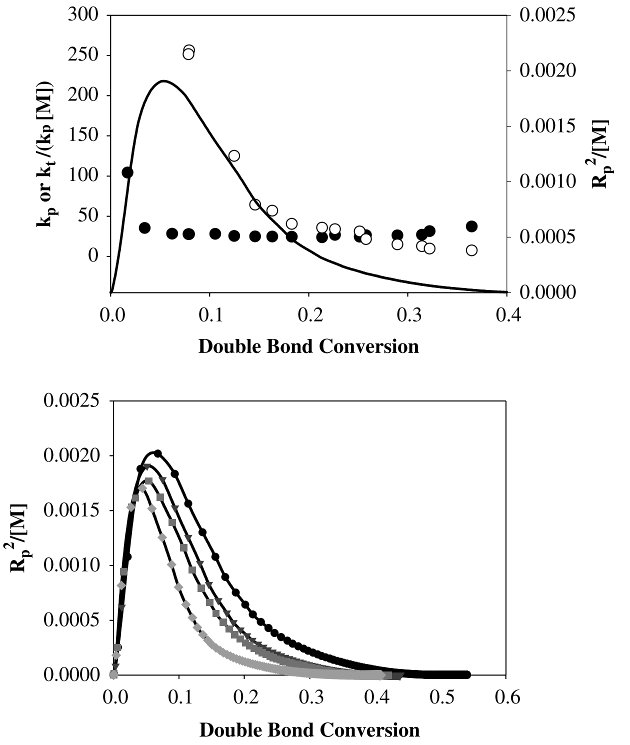

Fig. 8. (a) $R_p^2/[M]$ (—), k_p (●) and $k_t/(k_p[M])$ (○) versus double bond conversion for the base HPDLC formulation containing 10 wt% NVP. (b) $R_p^2/[M]$ versus double bond conversion for HPDLC formulations containing 0 (◆), 5 (■), 10 (▼) and 15 (●) wt% NVP.

The codependence of NVP and DPPHA conversion as shown in Fig. 4 and the reaction diffusion results appear to be related. The reactivity ratios, r_1 and r_2, for NVP (monomer 1) and acrylate (monomer 2) are reported to be 0.02 and 0.8, respectively [19]. These values indicate that a growing NVP polymer radical should react more readily with an acrylate over an NVP double bond, while an acrylate polymer radical should react similarly to both acrylate and NVP double bonds. Therefore, as the polymer network formed from the pentaacrylate becomes vitrified and essentially immobile, both the polymer radical and numerous pendant double bonds become trapped within the network, making further reaction very difficult. The more mobile monovinyl NVP can diffuse to the trapped radicals and propagate, thereby extending the length of the radical chain. This extension then allows the radical to react with other trapped acrylate pendant double bonds. The NVP essentially acts to enhance reaction diffusion by allowing the trapped radicals to grow through propagation. Such behavior also helps explain the results in Fig. 4 that show equal rates of consumption for both NVP and acrylate double bonds. Once reaction diffusion becomes predominant, the acrylate radicals cannot further react because of their low mobility. As the majority of acrylate monomer has at least one double bond incorporated into the network, other pendant acrylate double bonds are trapped and, therefore, not available for polymerization. When NVP diffuses to the active site, the radical readily propagates across the NVP double bond.

From the polymerization kinetic results, it is evident that NVP has a distinct influence on HPDLC polymer formation by increasing the rate of polymerization and increasing acrylate conversion. Similar influences on the polymerization of related polymer/LC composite materials have been shown to be significant in altering the LC phase separation process which is highly dependent on gelation, vitrification and polymerization kinetics [37]. Recently, real-time infrared spectroscopy (RTIR) has been used to examine polymer/LC systems by simultaneously collecting data that indicates the onset of phase separation along with determination of functional group conversion [26,27]. RTIR has the additional capability to record the isotropic to nematic transition of cyano-containing LC as it shifts from solvated, isotropic LC into phase separated nematic droplets bound by polymer. The use of RTIR to determine the influence of NVP on phase separation, LC ordering and polymerization kinetics will give further insight into the impact of NVP on the formation of HPDLC materials.

These previous reports clearly show that increased light intensity and adding monofunctional monomer can delay the onset of LC phase separation (in respect to double bond conversion) by increasing the photopolymerization rate [37–39]. Study of phase separation in the formation of

PDLCs based on moderately crosslinked polymerizations has often taken advantage of the significant change in transmission upon LC phase separation. Such transmission changes can be detected in a number of ways and monitored as a function of double bond conversion (PDSC, RTIR) or time (light scattering). Unfortunately the nanosized LC droplets in this highly crosslinked system impart insignificant turbidity changes to be detected by our RTIR instrumentation. However, phase separation can be indirectly studied by the examination of the appearance of the nematic mesophase in the polymerization of HPDLC formulations.

RTIR examination of the isotropic to nematic mesophase transition is based on the order-dependent absorbency of the cyano moiety at 2225 cm^{-1}. The absorbance of the cyano-containing LC is greatest when these molecules are in an isotropic state. Upon phase separation and transition to the nematic phase, the cyano absorbance decreases. RTIR examinations of polymerizations of HPDLC formulations show a clear, sudden decrease in the cyano absorbance at 2225 cm^{-1} that can be monitored in time or as a function of double bond conversion. Such determination of isotropic to nematic transition is plotted in Fig. 9, where the normalized absorbance at 2225 cm^{-1} is plotted against total double bond conversion for systems with various concentrations of NVP and NEP. The normalized absorbance is the absorbance at 2225 cm^{-1} at a time during polymerization divided by the absorbance at 2225 cm^{-1} before polymerization. Acrylate double bond conversion was chosen as the independent variable because it highlights the dominance of NVP on the appearance of the nematic phase.

From Fig. 9, the mixture containing no NVP exhibits the most dramatic increase in nematic phase (reflected as a decrease in the normalized peak height at 2225 cm^{-1}) as a function of acrylate double bond conversion. The HPDLC formulation with 5 wt% NVP exhibits the second greatest rate of nematic phase appearance. The other HPDLC formulations containing NVP (10 and 15%) exhibit a slower, nearly identical increase in nematic phase as a function of acrylate double bond conversion. Comparatively, an HPDLC formulation containing 10 wt% NEP exhibits a similar rate of nematic phase appearance to the 10 and 15 wt% NVP HPDLC formulations. The respective change from the initial normalized cyano absorbance value of 1.0 indicates the relative amount of LC in the nematic phase in each of the formed PDLCs. The NEP-containing formulation, which exhibits a slow appearance of nematic phase, also possesses the least degree of order. Interestingly, the samples containing increasing NVP concentration exhibit similar amounts of nematic LC in flood-lit HPDLC samples with normalized values all nearly 0.96. The sample without NVP (or NEP) exhibits the greatest degree of LC in the nematic phase.

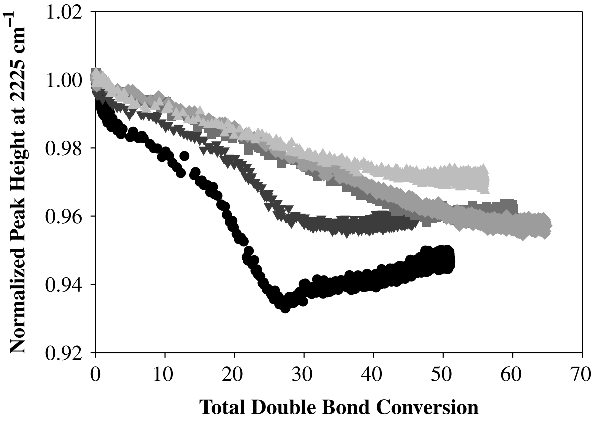

Fig. 9. Normalized peak height of the cyano moiety at 2225 cm^{-1} versus total double bond conversion for HPDLC formulations containing 0 (■), 5 (◆), 10 (▼) and 15 (●) wt% NVP and 10 wt% NEP (◇).

From these results it is apparent that adding NVP and NEP delays the appearance of the nematic phase in the polymerization of HPDLC formulations. Such delays may arise from the homogenizing impact of NVP (or NEP), which likely also delays LC phase separation. Any delay in phase separation should also manifest itself in a delay in the appearance of the nematic phase. If NVP has little influence on LC phase separation, it would be expected that the appearance of the nematic phase for all HPDLC formulations in respect to acrylate double bond conversion would be nearly identical.

Previously, SEM examination of HPDLC morphology as a function of NVP concentration has shown reduced LC phase separation with increased NVP concentration [10,11]. Fig. 5(a) clearly shows the significant increase in polymerization rate with NVP. This increased rate of polymerization coupled with the homogenizing influence of NVP may be the source of the reduction in the amount of LC phase separation. Intuitively, if NVP concentration delays phase separation but also increases the photopolymerization kinetics there is a greater likelihood that isotropic LC will be trapped in the polymer matrix, reducing the amount of LC phase separation. This decrease in the amount of phase separation would also result in less nematic LC when NVP is included.

The influence of NVP on the polymerization kinetics and phase separation can markedly impact polymer/LC morphology and subsequently alter HPDLC performance. The examination of the influence of NVP on HPDLC formulations can be understood further by examining the morphology of the base HPDLC formulation in comparison to an HPDLC formulation with NEP substituted for NVP (HPDLC-B, Table 1). The comparison of the polymer/LC morphology resulting from these two formulations with drastically different polymerization kinetics should highlight how the kinetic influence and incorporation of NVP dictates morphology. Fig. 10 presents the representative SEM micrographs of a flood-lit HPDLC formulation with NVP (top) and NEP (bottom). Since the LC was extracted prior to imaging, the LC droplets are indicated by the dark voids present in the polymer morphology. Comparing the two images clearly shows that the sample with NVP has smaller LC domains than the HPDLC formulation with NEP. It is also evident from Fig. 10 that the polymer domains in the NVP containing sample are smaller in size. The great

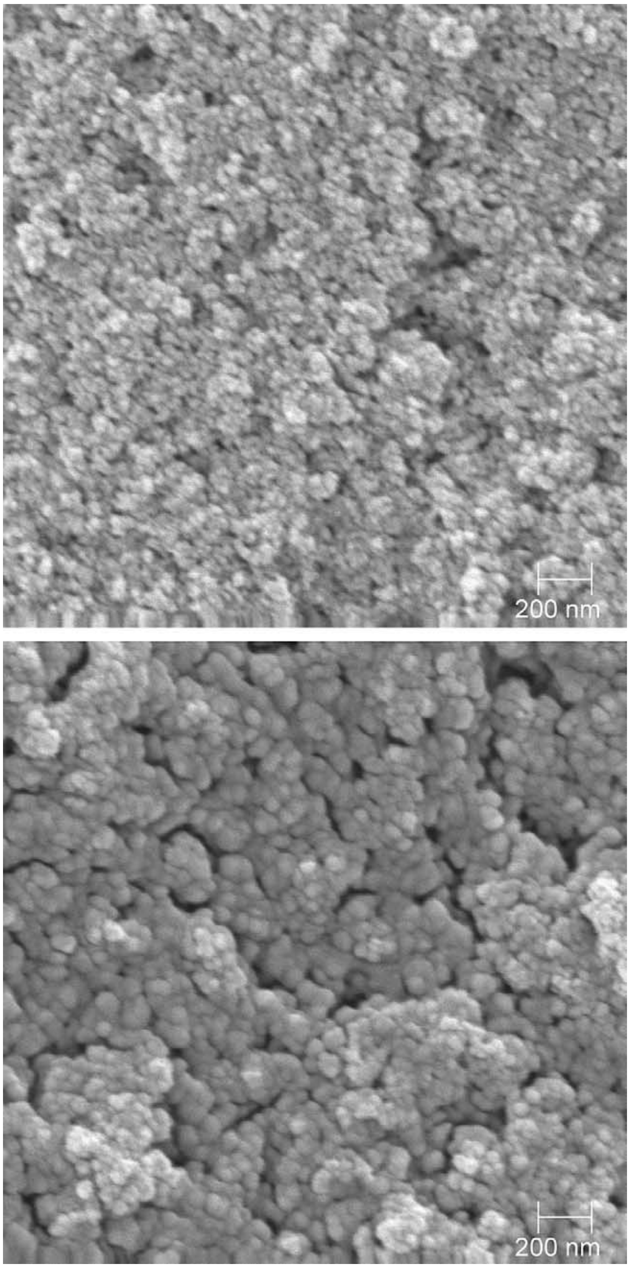

Fig. 10. SEM micrographs of flood-lit HPDLC formulations containing (top) 10 wt% NVP and (bottom) 10 wt% NEP.

discrepancy in the kinetics in the polymerization of these two formulations is likely the source of the different morphologies. In the case of the NEP-containing HPDLC formulation, the slower rate of polymerization and the corresponding increase in time between LC phase separation and morphology vitrification allows greater LC droplet nucleation and coalescence, resulting in larger droplets. Samples containing NVP have a greater rate of polymerization that limits the time gap between LC phase separation and vitrification, subsequently limiting droplet size. In all, through influencing the rate of polymerization, NVP dictates polymer/LC morphology with smaller LC droplets that in the end result in HPDLC gratings with higher diffraction efficiency.

4. Conclusion

NVP is known to be a critical component in improving acrylate-based HPDLC grating diffraction efficiency by reducing LC droplet size. As is the case in many acrylate systems, NVP causes an increase in the rate of polymerization with increasing concentration in HPDLC formulations. This increase in the rate of polymerization occurs through the incorporation of NVP into the HPDLC polymer matrix. HPDLC formulations containing up to 15 wt% NVP demonstrate complete NVP conversion. Examination of double bond conversion evolution in HPDLC formulations reveal that NVP and DPPHA conversion are codependent at relatively low double bond conversions. This dependence results from the reaction of NVP double bonds with trapped acrylate radical species. The NVP radicals can then react with other trapped pendant acrylate double bonds. Therefore, significant rate increases and increased acrylate conversion result with NVP addition. The preferential reactivity of NVP with acrylate also serves to delay the onset of the reaction diffusion termination mechanism while also extending its predominance into higher double bond conversion.

NVP is also a major influence on LC phase separation in the formation of HPDLCs and ultimate polymer morphology. Study of the appearance of the nematic phase, an indirect examination of phase separation, shows that samples containing NVP or the chemically similar but non-reactive molecule NEP, exhibit a slower appearance of the nematic phase when compared to an HPDLC formulation without NVP (or NEP). In general, increasing NVP concentration extends the homogeneity of the polymer/LC mixture into higher double bond conversions—slowing the LC phase separation process and the appearance of the nematic phase. Further, the kinetic influence of NVP coupled with its solubilizing capability reduces the amount of LC phase separation, which subsequently reduces the overall amount of nematic LC. These effects are also evident in the polymer/LC morphology. With NVP incorporation droplet size is much smaller than that observed when incorporating the non-reactive analogue NEP. The rate of polymerization for the HPDLC formulation containing NVP is much greater than that containing NEP. This behavior, in turn, is the cause of the significant reduction in LC droplet size and improved HPDLC performance with NVP inclusion.

Acknowledgements

Support of this work by the Air Force Research Labs Materials and Manufacturing Directorate is gratefully acknowledged.

References

[1] Urbas A, Klosterman J, Tondiglia V, Natarajan L, Sutherland R, Tsutsumi O, et al. Adv Mater 2004;16(16):1453.

[2] He GS, Lin T-C, Hsiao VKS, Cartwright AN, Prasad PN, Natarajan LV, et al. Appl Phys Lett 2003;83(14):2733.

[3] Jakubiak R, Bunning TJ, Vaia RA, Natarajan LV, Tondiglia VP. Adv Mater 2003;15(3):241.
[4] Sutherland RL, Natarajan LV, Tondiglia VP, Bunning TJ. SPIE Proc 2003;34.
[5] Sutherland RL, Natarajan LV, Tondiglia VP, Bunning TJ. Chem Mater 1993;5(10):1533.
[6] Bunning TJ, Natarajan LV, Tondiglia VP, Sutherland RL. Annu Rev Mater Sci 2000;30:83.
[7] Drzaic PS. Liquid crystal dispersions. Singapore: World Scientific Publishing; 1995.
[8] Natarajan LV, Sutherland RL, Tondiglia VP, Bunning TJ. J Nonlinear Opt Phys Mater 1996;5(1):89.
[9] Bowley CC, Kossyrev SD, Colegrove J, Kelly J, Fiske T, Yuan H, et al. Mol Cryst Liq Cryst 2001;359:327.
[10] Bunning TJ, Natarajan LV, Tondiglia VP, Sutherland RL, Haaga R, Adams WW. SPIE Proc 1996;44.
[11] Bunning TJ, Natarajan LV, Tondiglia VP, Dougherty G, Sutherland RL. J Polym Sci, B 1997;35(17):2825.
[12] Pogue RT, Natarajan LV, Siwecki SA, Tondiglia VP, Sutherland RL, Bunning TJ. Polymer 2000;41(2):733.
[13] De Sarkar M, Gill NL, Whitehead JB, Crawford GP. Macromolecules 2003;36:630.
[14] De Sarkar M, Qi J, Crawford GP. Polymer 2002;43:7335.
[15] Schulte MD, Clarson SJ, Natarajan LV, Tomlin DW, Bunning TJ. Liq Cryst 2000;27(4):467.
[16] Natarajan LV, Shepherd CK, Brelik DM, Sutherland RL, Chandra S, Tondiglia VP, et al. Chem Mater 2003;15(12):2477.
[17] Miller CW, Jonsson S, Hoyle CE, Yang D, Kuang WF, Kess R, et al. Radtech 2000; Proc 2000:754.
[18] Miller CW, Hoyle CE, Jonsson S, Nason C, Lee TY, Kuang WF, et al. ACS Symp Ser 2003;847.
[19] Al-Issa MA, Davis TP, Huglin MB, Yip DCF. Polymer 1985;26:1829.
[20] Klosterman J, Natarajan LV, Tondiglia VP, Sutherland RL, White TJ, Guymon CA, et al. Polymer 2004;45(21):7213.
[21] Lovinger AJ, Amundson KR, Davis DD. Chem Mater 1994;6:1726.
[22] Guymon CA, Dougan LA, Martens PJ, Clark NA, Walba DM, Bowman CN. Chem Mater 1998;10:2378.
[23] BASF published value.
[24] Andrzejewska E. Prog Polym Sci 2001;26:605.
[25] Lester CL, Colson CD, Guymon CA. Macromolecules 2001;34(13):4430.
[26] Bhargava R, Wang SQ, Koenig JL. Macromolecules 1999;32:8982.
[27] Bhargava R, Wang SQ, Koenig JL. Macromolecules 1999;32:8989.
[28] Decker C, Moussa K. Makromol Chem 1988;189(10):2381.
[29] Lee TY, Kuang W, Jonsson S, Lowery K, Guymon CA, Hoyle CE. J Polym Sci, A 2004;42(17):4424.
[30] Lee TY, Roper TM, Jonsson S, Guymon CA, Hoyle CE. Macromolecules 2004;37(10):3606.
[31] A control examination of the polymerization of DPPHA with 5 wt% incremental increases in solvent (ethylene glycol diacetate) show minor increases (3–5%) in the rate of polymerization in comparison to the large trends of this study.
[32] White TJ, Hammond CT, Guymon CA. Unpublished results.
[33] Klosterman AM, Pogue RT, Schmitt MG, Natarajan LV, Tondiglia VP, Tomlin D, et al. MRS Proc 1999;129.
[34] Anseth KS, Wang CM, Bowman CN. Macromolecules 1994;27:650.
[35] Anseth KS, Kline LN, Walker TA, Anderson KJ, Bowman CN. Macromolecules 1995;28:2491.
[36] Anseth KS, Decker C, Bowman CN. Macromolecules 1995;28:4040.
[37] Kloosterboer JG, Serbutoviez C, Touwslager FJ. Polymer 1996;37:5937.
[38] Boots HMJ, Kloosterboer JG, Serbutoviez C, Touwslager FJ. Macromolecules 1996;29:7683.
[39] Serbutoviez C, Kloosterboer JG, Boots HMJ, Touwslager FJ. Macromolecules 1996;29:7690.