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Polymer molecular weight and chain transfer during the photopolymerization of an aliphatic monoacrylate in a smectic liquid crystal

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Abstract

Polymer/liquid crystal (LC) composites offer a unique opportunity to study polymerizations in ordered media, specifically the potential effect mesophase order can have on polymer properties including molecular weight. To develop successful polymer/LC composites for display applications, it is important to understand the effect of mesophase order on polymer molecular weight in order to optimize the electro-optic (EO) properties of the polymer/LC composite. Polymer molecular weight may be influenced in a LC by changes in polymerization rate as LC order is modulated and by chain transfer. This work focuses on the photopolymerization of an aliphatic monoacrylate monomer, decyl acrylate (DA), both in the ordered LC phases of 8CB as well as in isotropic solutions with LC and co-solvent.

When DA is polymerized using the LC as the solvent, enhanced polymerization rates and polymer molecular weights are observed in the highly ordered smectic phase compared to the less ordered nematic and isotropic phases. When conducted strictly in an isotropic environment using a co-solvent with increasing 8CB percentages, a dramatic decrease in the polymerization rate and a significant reduction of the polymer molecular weight is observed, implying degradative chain transfer to the LC. NMR results show that this chain transfer is a result of hydrogen abstraction from the liquid crystals, which leads to the reduction in the polymerization rate with increasing 8CB concentration. The most likely site of hydrogen abstraction is from the benzyl hydrogens of the alkyl chain of 8CB. This chain transfer also plays a role for polymerizations performed in the ordered phases of the LC. Chain transfer appears to be less significant when polymerizations are conducted in the smectic phase due to the anti-parallel association of the LC molecules. When polymerizations occur in the less ordered phases, chain transfer dominates leading to a large reduction in polymer molecular weight and polymerization rate.

Keywords: photopolymerization; Polymer/liquid crystal composites; chain transfer

1. Introduction

Polymer/liquid crystal (LC) composites have garnered a considerable amount of research interest over the past decade, fueled by their potential use in display applications [1–3]. The addition of a polymer network to a LC can potentially impact mechanical stability [4,5], modify electro-optic (EO) properties, or stabilize specific liquid crystalline textures [5,6]. If mechanical stabilization of an LC system is of primary interest, factors such as polymer organization, polymer molecular weight, as well as the impact of the polymer on LC order must be examined. The presence of the polymer, in fact, for the ideal polymer stabilized LC system would not significantly retard or even perhaps improve the EO properties of the LC [7–10]. A number of factors including polymer properties such as molecular weight and the order of the LC phase in which polymerization occurs may influence LC electro-optic properties.

Similar factors have also proven important for polymerization of mesogenic monomers. For mesogenic monomers polymerized in bulk, LC order has a significant impact on polymer molecular weight [11,12]. Previous research investigating the laser initiated polymerization of a cholesteryl monomer in both the smectic phase and the

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isotropic phase showed that higher molecular weight polymer is formed when the monomer is polymerized in the smectic phase. Furthermore, the authors also found when a phase change occurs during the course of polymerization, e.g. isotropic to smectic that a bimodal distribution of molecular weights develops with a lower molecular weight fraction from the polymerization in the less ordered phase and a higher molecular weight fraction from the polymerization occurring in the ordered phase [12].

Additional research has focused on the polymerization of a mesogenic semi-fluorinated liquid crystalline methacrylate monomer both in the smectic and isotropic phases [13]. Higher polymerization rates and molecular weights were observed for the fluorinated monomer when polymerizations were conducted in the ordered smectic phase versus the isotropic phase through ordering of the reactive methacrylate groups of the monomer. Polymerizations occurring in the more ordered smectic phase undergo a hindered termination process that leads to the significant increase in molecular weight in the smectic phase polymerizations [13].

While ample evidence demonstrating the influence of LC order on polymer molecular weight of neat mesogenic monomers is available, direct evidence indicating the effect of LC order on polymer molecular weight in polymer stabilized systems, in which the LC is the solvent, so far remains inconclusive. Initial studies by Amerik [14] involving the polymerization of *p*-methacryloxybenzoic acid in *p*-acetyloxybenozic acid yielded polymers with higher molecular weights when polymerization occurred in the smectic phase as compared to the isotropic phase; however, other studies have produced mixed results and little information is available for polymer stabilized systems [15]. While no conclusive relation between LC order and polymer molecular weight for PSLC systems has yet been developed, a considerable amount of research has recently been devoted to understanding the polymerization kinetics during the photopolymerization of mesogenic and non-mesogenic monomers within a ferroelectric liquid crystalline (FLC) solvent [16,17]. Monomer chemical structure and segregation behavior play a significant role in determining the polymerization behavior in these systems [18,19].

The polymerization kinetics of mesogenic and non-mesogenic monomers have been investigated specifically investigating the effect that LC order has on the apparent rate of polymer chain propagation and termination [16,17]. When certain monomers are polymerized in the increasingly ordered phases of an FLC, a corresponding increase in the apparent termination and propagation rates is observed which serves to increase the overall polymerization rate. When the kinetic rate parameters are considered for other monomers, an order of magnitude decrease in the apparent termination rate parameter is seen when the polymerizations are conducted in the more ordered smectic C^* phases while the apparent propagation constant does not appear to change.

Given these results, it is reasonable to believe that a large difference in the molecular weight of polymers polymerized in ordered and less ordered LC phases should be observed. However, no conclusive evidence regarding the effect of the LC medium on polymer molecular weight has yet been given. The molecular weight of the polymer in PSLC systems could significantly alter the EO properties of the LC [20]. In addition, the molecular weight must be sufficient for the polymer to actually stabilize the liquid crystalline medium [21]. It is therefore important to more fully understand the effect that the LC solvent has on the resultant polymer molecular weight for non-mesogenic monomers in polymer stabilized systems. Additionally, understanding the effect of chain transfer, especially to the LC itself, on molecular weight is critical due to potential decreases in EO properties that would accompany such an event.

This work focuses on the polymerization of an aliphatic monoacrylate within a smectic liquid crystalline solvent. Polymerization rate and molecular weights are examined when polymerization occurs in various LC phases. To determine if chain transfer is occurring in the LC systems, isotropic solutions of monomer, smectic LC and co-solvent were polymerized. The polymerization rates and molecular weights were examined as a function of LC concentration. Structure elucidation of the resulting polymers from the isotropic solutions was performed using ^{1}H NMR. Through these studies, a greater understanding regarding the impact of chain transfer, polymerization conditions, and LC phase order on molecular weight and polymerization kinetics has been reached. This information will facilitate further development of not only polymer stabilized systems, but also has far reaching implications for other polymer/LC composites.

2. Experimental

2.1. Materials

The aliphatic monomer used in these studies was *n*-decyl acrylate (DA-Polysciences, Warrington, PA). The room temperature smectic A LC was 4-cyano-4′-*n*-octyl-biphenyl (8CB-Aldrich, St. Louis, MO). The co-solvent used for the isotropic system was ethylene glycol diacetate (EGDA-Aldrich, St. Louis, MO). EGDA was chosen because its low chain-transfer constant solubility of the various components. Chemical structures of the monomer, co-solvent, and LC as well as LC phase behavior are shown in Fig. 1. Photopolymerizations were initiated using Irgacure I-907 (Ciba Geigy, Hawthorne, NY). All materials were used as received without further purification. Monomer/LC and monomer/LC/co-solvent mixtures were prepared with initiator concentrations approximately 6 mol% of the total

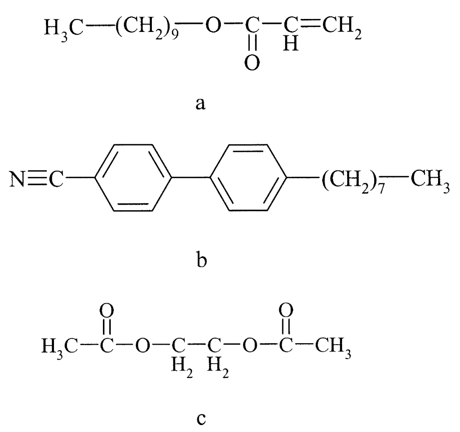

Fig. 1. Monomer, liquid crystal, and co-solvent structures of (a) decyl acrylate (DA); (b) 4-cyano-4′-*n*-octyl-biphenyl (8CB: phase sequence-isotropic → 40 °C → nematic → 32 °C → smectic (A); and (c) ethylene glycol diacetate (EGDA).

monomer double bond concentration. A typical monomer/LC mixture consisted of 0.2% initiator, 3.4% decyl acrylate (DA) and the rest 8CB by weight. The material compositions of the DA/8CB/EGDA solutions are presented in Section 3.

2.2. Procedure

All monomer/LC samples were prepared by dissolving the aliphatic monomer, LC, and photoinitiator in acetone and allowing the acetone to evaporate. The monomer/LC mixtures were polymerized after 10 min of nitrogen purge at a UV light intensity of 8.3 mW cm^{-2} in the appropriate LC phase. The isotropic solutions of monomer, LC, and co-solvent were prepared by dissolving the monomer, photoinitiator, and varying percentages of the LC in the co-solvent. These samples were polymerized in situ for 20 min at a UV light intensity of 8.3 mW cm^{-2} after 10 min of nitrogen purge. After polymerization of the isotropic DA/8CB/EGDA solutions the polymer was precipitated into methanol. The polymer was purified by dissolving the polymer into chloroform and reprecipitating into methanol to remove any residual LC, initiator, and unreacted monomer. This process was repeated five times before analysis.

2.3. Characterization

Polymerization rate profiles were monitored using a differential scanning calorimeter (DSC 7; Perkin–Elmer) modified with a medium pressure UV lamp. Polymerizations were initiated using 365 nm monochromatic light (unless otherwise noted) with an intensity of 1.5 mW cm^{-2}. The DSC sample cell was attached to a refrigerated circulating chiller to achieve isothermal conditions. For rate studies, approximately 10 mg of the monomer/LC mixture was placed in an aluminium DSC pan. The samples were heated above the isotropic transition temperature of the monomer/LC mixture and cooled to the appropriate polymerization temperature to ensure uniform thickness and sufficient thermal contact. The DSC sample cell was flushed with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition. The polymerization rate as calculated has units of 1 s^{-1} giving a normalized rate thereby facilitating comparison of different monomer concentrations [18].

The gel permeation chromatography used was carried out at 25 °C in tetrahydrofuran (THF) using a Thermo Separation Products refractive index detector and a binary liquid chromatography pump from Perkin–Elmer. The DA/LC samples were dissolved in THF and characterized. The aliphatic polymers from the DA/8CB/EGDA solutions were first purified as described above, dissolved in THF and characterized. The ^{1}H NMR solution spectra were obtained using a Bruker AC-200 instrument and $CDCl_3$ as solvent after the aforementioned purification of the polymer.

3. Results and discussion

One of the most interesting features regarding polymerizations conducted in liquid crystalline solvents is the ordering effect of the LC on the monomer [16–18]. The LC phase can have a significant impact on the polymerization rate, due to order imposed on the reacting system. LC ordering often directs the formation of higher polymer molecular weights for mesogenic monomers when polymerizations are conducted in ordered LC phases [12,13]. The impact that the LC medium has on the molecular weight of non-mesogenic monomers polymerized in LC solvents, however, is not yet understood. To understand how the effect of the LC solvent on polymer molecular weight in polymer stabilized systems is critical due to potential effects on final LC electro-optic properties. In addition, for mechanical stabilization purposes, an optimum molecular weight and/or crosslink density may be necessary in order to achieve a desired degree of stabilization.

To shed light on any possible changes in molecular weight, it is desirable to first understand the polymerization kinetics and the influence of the LC phase on polymerization rate. Fig. 2 shows the maximum polymerization rate as a function of polymerization temperature for DA in the various LC phases of 8CB. As the order of the LC solvent increases, a significant increase in the polymerization rate is observed despite a substantial decrease in the polymerization temperature. A slight increase in the polymerization rate is observed when the polymerization temperature is decreased to the nematic phases from the isotropic phase. The polymerization rate more than doubles when polymerization is conducted in the smectic phase compared to the nematic phase. The differences in DA polymerization rate demonstrate the significant impact that the LC phase has on monomer polymerization. It is important to note that each monomer/LC sample was checked using polarized light microscopy to ensure that phase continuity was maintained

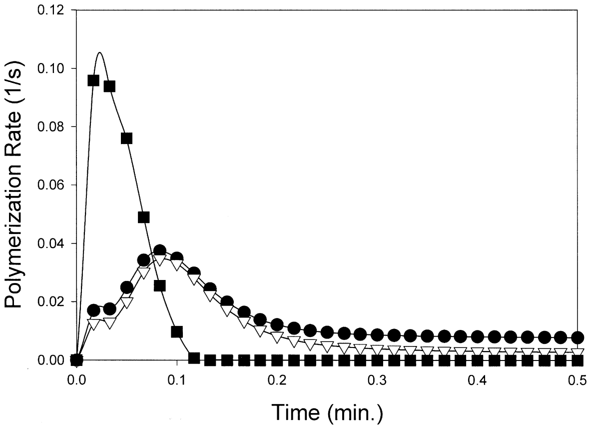

Fig. 2. Polymerization rate profiles of 3.4% decyl acrylate polymerized in the smectic (■), nematic (●) and isotropic (▽) phases of 8CB.

through the course of the polymerization. The rate increase observed in the ordered smectic phase is due to the ordering of the monomer between the smectic layers of the LC [16, 17]. The ordering of the monomer increases the local double bond concentration and may also decrease the growing radical mobility, which consequently serves to enhance the polymerization rate. The local ordering of the monomer between the smectic layers of the LC could potentially lead to changes in the polymer molecular weight when polymerizations are conducted in different LC phases.

To determine if any changes in molecular weight are observed as LC phase ordered is modulated, DA was polymerized in the various LC phases of 8CB and the polymer molecular weight examined. Table 1 shows the number average (M_n) and weight average (M_w) molecular weight for 5% DA polymerized in the smectic, nematic, and isotropic phases of 8CB. A substantial increase in the molecular weight of the polymer is observed as the order of the LC phase is increased. The M_n increases by more than 2000 g mol^{-1} in nematic phase polymerizations versus isotropic phase polymerizations. When polymerization occurs in the more ordered smectic phase, an even more dramatic increase of almost 7000 g mol^{-1} is seen over polymers formed in the isotropic phase. Similar significant increases in M_w are evident when polymerizations are conducted in the smectic phase compared to the isotropic phase. The M_w for the polymers resulting from smectic phase polymerization is almost double that of polymers resulting from isotropic polymerization.

Since M_w is a weighted average, this value indicates of the relative number of high molecular weight polymer chains. The observation of a larger increase in M_w than in M_n for DA polymerizations implies that a greater number of high molecular weight polymer chains are formed when the polymerization is conducted in the smectic phase compared to the other less ordered phases. Longer polymer chains might be expected in the ordered smectic phase due to the increase in local double concentration and the possible decrease in polymer chain termination. Decreases in the polydispersity index (PDI) are also seen as the order of the LC decreases. The lower PDIs in the less ordered phases may be due to the occurrence of a more homogeneous polymerization in these phases. The higher PDI value of 1.78 from the smectic phase polymerization may be due to the formation of polymer fractions both before and after the phase separation that occurs during polymerization [18].

Table 1
Molecular weight of decyl acrylate formed in liquid crystalline phases of 8CB

Liquid crystal phase	M_n	M_w	Polydispersity (PDI)
Smectic (20 °C)	20,457	36,446	1.78
Nematic (31 °C)	16,062	27,223	1.70
Isotropic (45 °C)	13,931	19,114	1.37

These results are direct evidence of the impact that the liquid crystalline solvent can have on the polymerization of non-mesogenic monomers within a liquid crystalline solvent. A number of questions remain regarding the polymerization of non-mesogenic monomers in liquid crystalline solvents. The most fundamental of these deals with the mechanism that serves to drive the increase in polymer molecular weight as LC order increases. Ample evidence regarding changes in termination [16,17] and segregation [18] has been previously presented that should serve the increase the molecular weight. Whether or not this is the only mechanism, or if chain transfer contributes as well is still an issue.

Chain transfer is simply the transfer of the radical on a growing polymer chain to another species including initiator, monomer, and solvent. This process typically results in decrease in the polymer molecular weight [22]. The effect of chain transfer on the polymerization rate and polymer molecular weight depends on the rate of reinitiation. If the new radical species is comparable in reactivity to the original propagating radical reinitiation is fairly rapid and no change in the polymerization rate is seen, even though the molecular weight may decrease dramatically. However, when a large decrease in the polymerization rate as well as the molecular weight occurs the new radial species is less reactive than the original polymer chain, which leads to retardation or degradative chain transfer. The presence of chain transfer in polymer stabilized systems has the potential to significantly affect polymer molecular weight and consequently the mechanical and EO properties as well.

Depending on the mode of chain transfer, the event may be suppressed in smectic phase polymerizations which may be a significant driving force resulting in the observed higher molecular weight polymer. Understanding the advent of chain transfer is paramount because of the prevalence of cyano biphenyl LCs in virtually all display applications. Chain transfer in these systems could potentially alter crosslink density in polymer dispersed systems, molecular weight in polymer stabilized systems, and even remove LC through incorporation on the polymer chain and lead to degradation of LC electro-optic properties. In an effort to determine the extent of chain transfer to the liquid crystalline solvent, isotropic solutions of 8CB, DA, and ethylene glycol diacetate (EGDA) were polymerized while monitoring polymerization rate and polymer molecular weight.

Fig. 3 shows the maximum polymerization rate of 10% DA in isotropic solutions of 8CB and EGDA with increasing weight percent of 8CB. It is important to note that the isotropic solutions do not exhibit LC phase behavior due to the addition of the non-mesogenic diluent, EGDA. Interestingly, a monotonic decrease in the polymerization rate is observed as the weight percentage of 8CB increases. When the 8CB concentration is increased to 20%, the polymerization rate of DA is almost half that of the 0% 8CB polymerization. Decreases in polymerization rate continue with increasing 8CB concentration until the polymerization rate is nearly zero at 8CB concentrations above 60%. In fact, when the polymerization rate at 0 and 80% 8CB are compared, the drastic seven-fold decrease in polymerization rate is even more striking. The observed decrease in polymerization rate with increasing 8CB concentration is an indication that chain transfer to the LC is occurring during DA polymerization.

Further understanding of the effects of increasing 8CB concentration in the isotropic solutions can be gained though examination of the polymer conversion as a function of 8CB weight percent. Fig. 4 is a plot of the polymerization rate profiles of 10% DA in isotropic solutions of 8CB/EGDA as a function percent conversion of double bonds. Increased 8CB concentration leads to a considerable decrease in the polymer conversion. In fact, the conversion decreases by almost 50% when the 8CB weight percent is increased from 20 to 80%. The conversion is significantly reduced as the 8CB weight percent increases, but most notably at 8CB concentrations above 60%. The decrease in conversion tracks well with the polymerization rate data and is further evidence chain transfer to 8CB is occurring during the course of polymerization.

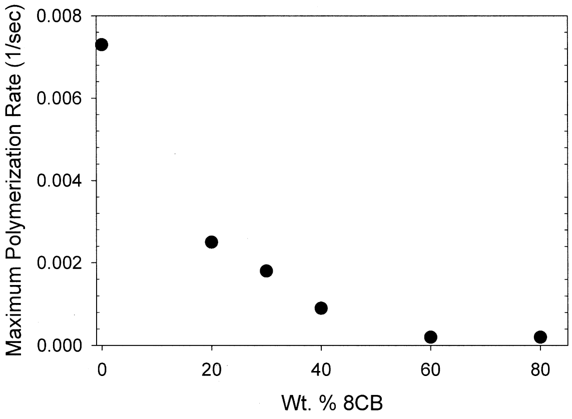

Fig. 3. Maximum polymerization rate of isotopic solutions of DA/8CB/EGDA with increasing 8CB concentrations.

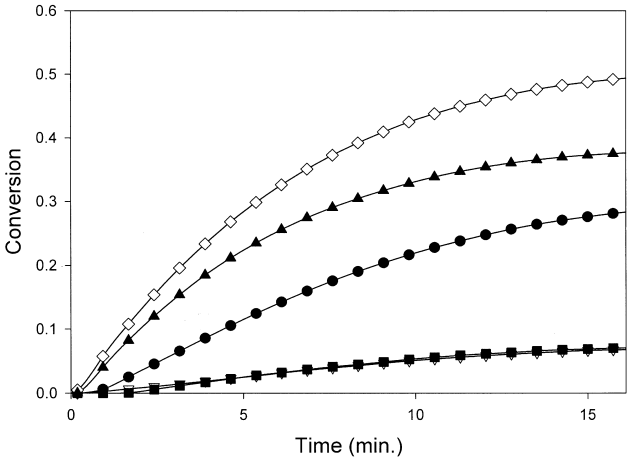

Fig. 4. Double bond conversion of 10% DA as the polymerization proceeds at 20% (◇), 30% (▲),40% (●), 60% (■), 80% (▽) 8CB in isotropic solutions of DA/8CB/EDGA.

The observation of such a large decrease in polymerization rate and conversion with increasing 8CB concentration indicates the radical created via the chain transfer step does not reinitiate polymerization as quickly as the propagating polymer chain radical if at all. In order to understand the nature of chain transfer in the isotropic solutions i.e. degradation, retardation, etc., it is important to examine polymer molecular weight as function of 8CB concentration in the isotropic solutions. Fig. 5 is shows the number average and weight average molecular weights as a function of 8CB concentration. A large decrease in M_n and M_w is observed as the weight percent of 8CB is increased. A particularly large decrease, almost half, in M_n is observed from 0% 8CB to 20% 8CB with a steady decrease thereafter to 80% 8CB. When M_w is examined, the same trend is observed with decreases in molecular weight with increasing 8CB concentration. The M_w and M_n data indicates that a larger percentage of high molecular weight polymer chains are being formed at lower 8CB concentrations while a larger percentage of lower molecular weight polymer chains are

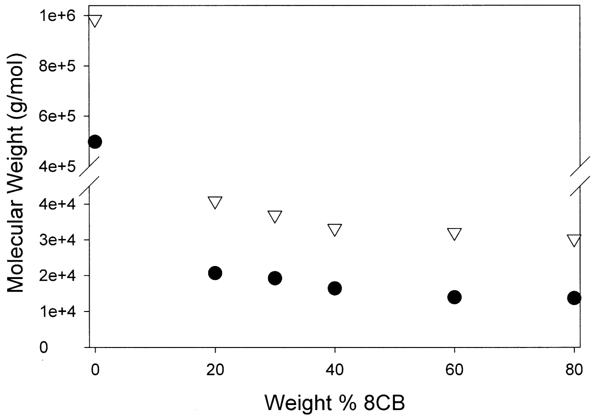

Fig. 5. Number average (●) and weight average (▽) molecular weight of 10% DA polymerized in DA/8CB/EDGA solutions as a function of 8CB concentration.

formed at higher 8CB concentrations. In particular, the large value of M_w for the DA solution polymerization (0% 8CB) indicates that termination occurs through polymer chain coupling and not chain transfer. When 8CB is added to the system, it appears that polymer chain coupling is suppressed and chain transfer predominates, limiting polymer chain length as well as rate and conversion. Interestingly, when the PDIs are considered, an increase in PDI is observed as 8CB concentration increases. This observed increase in PDI with increasing 8CB concentration might be due to the increased prevalence of chain transfer to the LC.

Based on these results which show a large decrease in polymerization rate and polymer molecular weight, the chain transfer to 8CB appears to be degradative in nature. In order to fully understand the exact mechanism of chain transfer, examination of the aliphatic polymer structure produced in the isotropic 8CB solutions could yield important information. This information could be especially useful if moieties characteristic of 8CB are found on the polymer. Solution ^{1}H was used to directly determine if chain transfer to 8CB is occurring by examining the DA polymer structure produced from 8CB/EGDA/DA solutions. The spectra of 8CB, polyDA, and the polyDA produced during polymerization in isotropic solutions of 8CB/EGDA have been examined. Fig. 6 shows the ^{1}H spectra of the pure LC. The primary peaks of interest in the proton spectra are the aromatic proton multiplet between 7 and 8 ppm and the methylene envelope between 0.8 and 1.8 ppm. Fig. 7 shows the ^{1}H spectra of DA polymerized in EGDA only. In the spectra the protons off the aliphatic tail exhibit broad peaks between 0.5 and 2 ppm. The protons of the methyl carbons along the polymer backbone are observed between 2 and 3 ppm.

The spectra of the neat 8CB and the DA polymer are as would be expected for these materials. Direct evidence regarding chain transfer to 8CB would be provided if crossover between the spectra for both materials were observed. To determine is such crossover can be seen the ^{1}H spectra of DA polymer resulting from 10% DA polymerized in an isotropic solution of 70% 8CB and 20% EGDA is shown in Fig. 8. The polymer from this polymerization was dissolved in chloroform and reprecipitated into methanol five times to remove any residual LC, un-reacted monomer, and initiator. The spectra of this polymer looks quite similar to that of the pure DA polymer, but with one noticeable difference. When the ^{1}H spectra is examined, a multiplet is observed between 7 and 8 ppm. These protons correspond to the aromatic biphenyls of 8CB. The intensity of the proton peaks is small, but the peaks are clear, especially when magnified. These results clearly indicate that LC is incorporated onto the DA polymer chain.

A possible mechanism by which 8CB could become

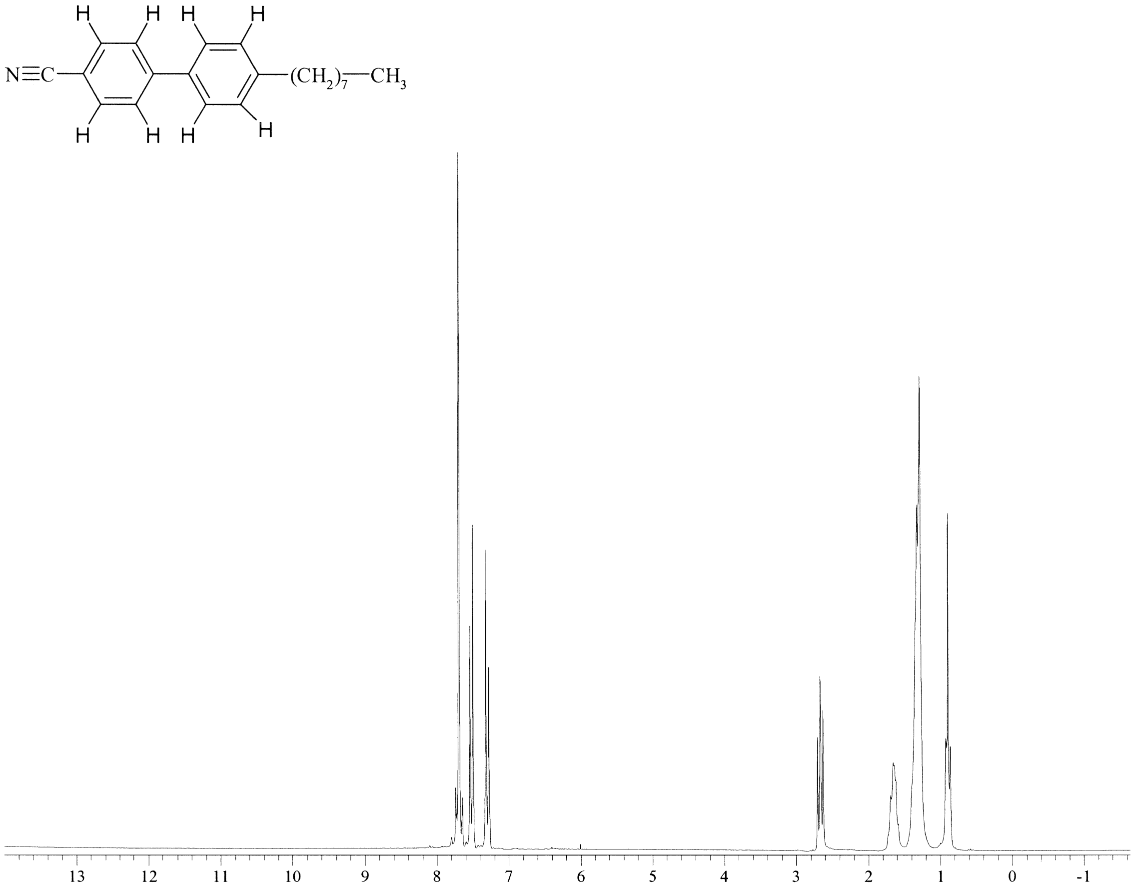

Fig. 6. ^{1}H spectra of the pure liquid crystal in chloroform.

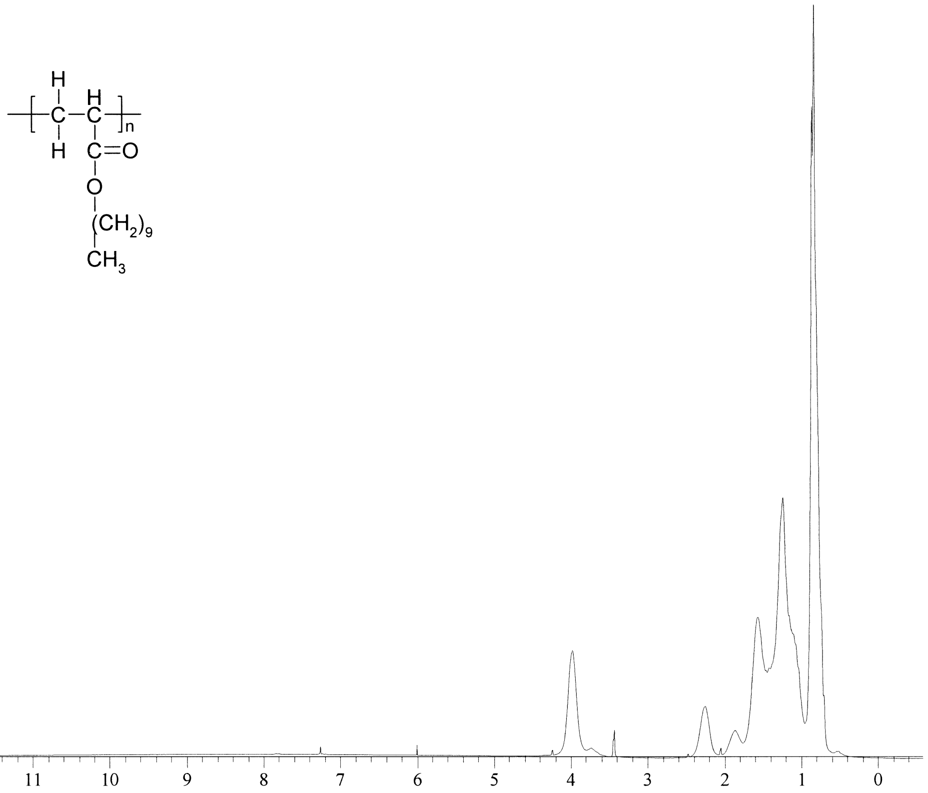

Fig. 7. ^{1}H spectra of decyl acrylate polymer formed during polymerization in EGDA only. The solution from which the polymer was extracted was 10% DA in EGDA.

attached to a polymer chain is via abstraction of a hydrogen from the LC during chain transfer. A probable hydrogen abstraction site is the benzyl hydrogen located on the first carbon of the aliphatic tail of 8CB attached to the biphenyl ring. The abstraction of a benzyl hydrogen would leave a stable radical. This benzyl radical could go on to reinitiate polymerization albeit to a smaller degree than the DA propagating radical or may participate in chain termination, which might account for the observation of the aromatic protons in the DA polymer generated in isotropic 8CB/EGDA solutions. Given this evidence of chain transfer, it is easier to understand the observed decreases in polymerization rate and molecular weight for DA polymerizations when the LC is the solvent.

The research reported here has demonstrated that the polymerization rate of DA is accelerated in the more ordered LC phases due to monomer segregation effects. A substantial increase in polymer molecular weight when polymerization occurs in the smectic phases compared to nematic and isotropic phases is also observed. A fundamental question is whether the polymer molecular weight is higher solely due to changes in polymerization kinetics, or does chain transfer simply increase in the less ordered LC phases. The evidence presented here points to a combination of the two effects. When polymerization occurs in the smectic phase the benzyl hydrogen abstraction may be suppressed since the LC molecules exist in an anti-parallel arrangement [23] anchored by the highly polar cyano groups. The monomer is sequestered between the smectic layers of the LC and so the benzyl hydrogens are not as readily available for abstraction. Also, the polymerization rate is significantly accelerated in the smectic phase and chain termination is decreased, which also serves to generate higher molecular weight polymer. When polymerizations occur in the less ordered nematic and isotropic phases, the polymer chain radical has significantly more access to the hydrogens leading to significantly reduced polymer molecular weight due the predominance of chain transfer to 8CB. The chain transfer to 8CB and its possible incorporation into the polymer backbone itself has interesting implications on the properties of an LC device. In a crosslinked polymer system, chain transfer can lead to reduced crosslink density, while in a linear polymer systems molecular weight may be limited. In both cases a reduction in mechanical stability and more importantly in the stability of the system, as a whole would be seen. Consequently, the EO properties of an LC device may also be affected. Incorporation of the LC into the polymer chain would remove LC from the LC matrix and thus have detrimental effects on EO properties.

4. Conclusions

This work examines the polymerization rate and molecular weight of DA in a smectic LC and in isotropic

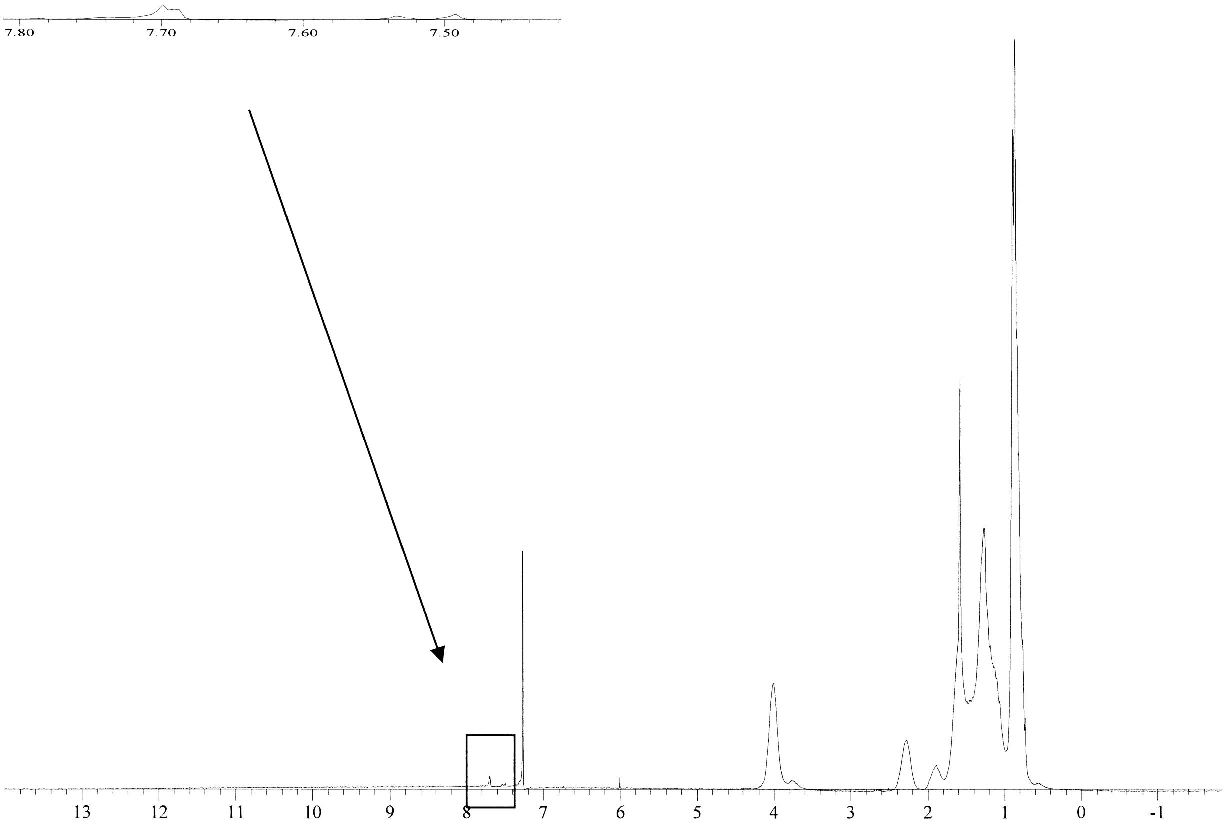

Fig. 8. ^{1}H spectra of decyl acrylate polymer formed during polymerization in DA/8CB/EDGA solutions. The solution from which the polymer was extracted was 10% DA in 70% 8CB and 20% EGDA.

solutions incorporating the same smectic LC at different levels. When polymerizations are conducted using 8CB as the solvent, an almost three fold increase in the polymerization rate is observed when polymerization occurs in the smectic phase as compared to the unordered isotropic phase. This increase in rate could be due to an increase in the local double bond concentration between the smectic layers of the LC and decreases in termination due to limited mobility of the growing polymer chain. In addition, higher molecular weight polymer is formed when DA is polymerized in the smectic phase versus the nematic and isotropic phases. The higher molecular weight polymer formed in the more ordered LC phases is direct evidence of the impact that LC order has on monomer polymerization in polymer stabilized liquid crystalline systems.

Other effects are observed in isotropic solutions incorporating the LC. In fact, as the weight percent of 8CB is increased in isotropic solutions of monomer with EGDA, a significant decrease in the polymerization rate of DA in these solutions is observed. This behavior implies that chain transfer is occurring to the LC. Further evidence of chain transfer is observed when the molecular weight of the DA polymer from the isotropic solutions is examined. Large decreases in the molecular weight are observed as the 8CB concentration increases, implying that degradative chain transfer occurs to the LC. NMR results show that the most probable mechanism of chain transfer is polymer radical hydrogen abstraction of the benzyl hydrogens from 8CB. When polymerizations are conducted using the LC as the solvent, chain transfer is depressed in smectic phase polymerizations due to the segregation of the monomer between the smectic layers of the LC and the anti-parallel association of the LC molecules which limits benzyl hydrogen accessibility. When polymerizations occur in the nematic and isotropic phases, the benzyl hydrogens are more accessible leading to more hydrogen abstraction and lower polymer molecular weights.

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References

[1] Hikmet RAM, Michielsen M. Adv Mater 1995;7:300.
[2] Gu DF, Jamieson AM, Chien LC. Technical Reports on ALCOM Symposium; 1994, p 101.
[3] Rajaram CV, Hudson SD, Chien LC. Chem Mater 1996;8:2451.
[4] Dierking I, Kosbar LL, Lowe C, Held GA. Liq Cryst 1998;24:387.

[5] Britten M, Mitchel GR. Mol Cryst Liq Cryst Sci Technol Sect A 1999; 329:757.
[6] Hikmet RAM. Liq Cryst 1991;9:405.
[7] Hikmet RAM. Mol Cryst 1991;198:357.
[8] Hikmet RAM, Higgins JA. Liq Cryst 1992;12:831.
[9] Hikmet RAM. J Appl Phys 1990;68:4406.
[10] Chen LC, Sprunt S, Lee SN. Liq Cryst 2001;28:637.
[11] Hoyle CE, Watanabe T. Macromolecules 1994;27:3790.
[12] Hoyle CE, Chawla CP, Griffin CA. Mol Cryst Liq Cryst Incorp Nonlinear Opt 1988;157:639.
[13] Hoyle CE, Kang D, Chawla CP, Griffin AC. Polym Engng Sci 1992; 32:1490.
[14] Amerik YB, Konstantivov II, Krentsel VA. Vysokomol Soedin 1967; 9:2236.
[15] Barrall EM, Johnson JF. J Macromol Sci, Rev Macromol Chem 1979; 17:137.
[16] Guymon CA, Bowman CN. Macromolecules 1997;30:1594.
[17] Guymon CA, Bowman CN. Macromolecules 1997;30:5271.
[18] McCormick DT, Chavers R, Guymon CA. Macromolecules 2001;34: 6929.
[19] McCormick DT, Fordham ZW, Guymon CA, Liquid Crystals 2003;30:49.
[20] Bai Y, Chen X, Wan X, Zhou Q, Liu HL, Zhang B, Gong Q. Appl Phys Lett 2001;80:10.
[21] Kim BK, Ok YS, Choi CH. J Polym Sci, Part B Polym Phys 1995;33: 707.
[22] Odian G. Principles of Polymerization, 3rd Ed. New York: Wiley; 1991.
[23] Collings PJ, Hird M. Introduction to liquid crystals: chemistry and physics. Philadelphia: Taylor & Francis; 1997.