Polymerization Behavior and Kinetics during the Formation of Polymer-Stabilized Ferroelectric Liquid Crystals

C. Allan Guymon and Christopher N. Bowman*

Department of Chemical Engineering, University of Colorado,
Boulder, Colorado 80309-0424

Received November 13, 1996; Revised Manuscript Received January 15, 1997⊗

ABSTRACT: The effects of photopolymerizing both mesogenic and nonmesogenic diacrylate monomers in ferroelectric liquid crystalline media were characterized. By using monomers with a variety of different physical and optical properties, the influence of the monomer as well as the ordered media was determined. Polymerization rate profiles and double-bond conversions were monitored at different temperatures and in different liquid crystalline phases. As the order of the media increased, the polymerization rates also increased dramatically for all of the monomers studied, despite large decreases in temperature. Solution polymerizations in the liquid crystal at temperatures for which the liquid crystal molecules are isotropically distributed and in an isotropic solvent were much slower and exhibited maximum rates less than one-third those observed in ordered phases. To elucidate the mechanisms behind this behavior, the kinetic constants of both the termination and propagation reactions were determined. For certain monomers, the rate increase was driven by a decrease in the termination kinetic constant causing an increase in the radical concentration. On the other hand, other monomer polymerizations in ordered phases exhibited an increase in both termination and propagation kinetic constants. The effects of increasing monomer concentration in the ferroelectric liquid crystal were also investigated.

Introduction

Liquid crystals form a fascinating media in which to study chemical reactions.[1,2] The inherent order present in liquid crystals (LCs) may alter solute behavior and ordering. Changes in diffusion, solubilities, and solute packing that occur as a result of the anisotropic environment may significantly affect the mechanism and kinetics of certain reactions.[3] Thermotropic LCs also provide a variety of different phases with different degrees of order and thus a wide range of different behaviors. Nematic and cholesteric phases afford unidirectional media, whereas smectic phases render a layered structure. Recently, a great deal of research has been dedicated to performing polymerizations within this ordered media as both polymeric liquid crystals and liquid crystals modified with polymers have increased in importance.

Liquid crystalline polymers can be formed in a variety of ways, including the polymerization of oriented LC monomers.[4,5] Although early work gave convincing evidence of altered kinetics during the polymerization of LC monomers,[6−8] the first research specifically examining the effect of the LC phase of polymerization was presented by Broer and co-workers,[9−12] in which they investigated the photopolymerization of oriented liquid crystalline mono- and diacrylates. The anisotropy exhibited in these systems substantially changed the polymerization rate in both monoacrylates[9] and diacrylates.[10,11] The polymer films formed during this photopolymerization also retain the order originally present in the LC monomer.[12] The reasons for these changes in polymerization behavior are attributed to a decrease in chain transfer processes normally occurring in acrylate polymerizations.[13,14] Other properties such as the birefringence and order parameters of these LC polymers are also changed when polymerized in ordered phases.[15]

Further implications of ordered polymerizations have been examined by Hoyle and co-workers.[16−25] The consequences of polymerizations in a variety of different LC phases are described for fluorinated,[16] cholesteryl,[17] and cross-linking[18] monomers. These reports also find accelerated polymerization rates in ordered phases for most polymerizations, but these enhanced rates depend strongly on the LC phase of polymerization.[19−21]

The reason behind this accelerated rate behavior was long attributed to a decrease in the termination rate because preliminary results showed that the molecular weight of the polymers produced in anisotropic media was larger than when samples were polymerized isotropically.[22,23] Further evidence was presented when the molecular weight distributions were examined for pulsed-laser-initiated polymerizations of LC monomers.[24] These results show that the molecular weight and yields of polymerizations initiated in ordered phases are not affected by the frequency of laser pulses, whereas both decrease significantly in isotropic polymerizations. This effect indicates that coupling of short chain oligomers and long chains occurs much less frequently in the anisotropic medium. Direct evidence of this decreased termination rate has recently been given.[25] Both the termination and propagation kinetic constants were determined for polymerizations exhibiting accelerated rates in a smectic phase. The propagation kinetic constant, k_p, decreases slightly in the ordered phase when compared to that found in the isotropic polymerization. Such a decrease would be expected as the temperature is lower in the smectic phase. The termination kinetic constant, k_t, however, decreases almost 2 orders of magnitude for the ordered polymerization. From this information, it was concluded that the enhanced polymerization rates arise from a dramatically decreased termination rate, as was previously anticipated.

LC polymers are not suitable for many applications as their response times are slow due to their extremely high viscosities. To take advantage of the faster response times of low molar mass liquid crystals and the inherent mechanical strength of polymers, polymer/

---

* Author to whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

S0024-9297(96)01677-4 CCC: $14.00

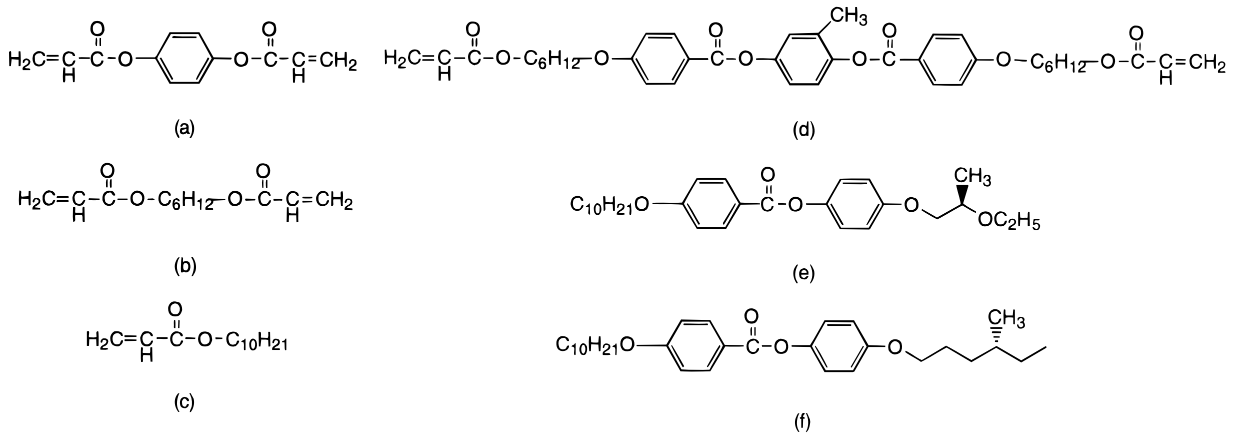

Figure 1. Chemical structures of the acrylate monomers used in this study. Shown are (a) *p*-phenylene diacrylate (PPDA, mp 89 °C), (b) 1,6-hexanediol diacrylate (HDDA, mp 5 °C, bp 316 °C), (c) *n*-decyl acrylate (DecA, bp 158 °C), and (d) C6M, a liquid crystalline diacrylate (phase sequence: isotropic → 116 °C → nematic → 86 °C → crystalline). Also shown are the ferroelectric liquid crystals (e) W7 and (f) W82 (phase sequence for 1:1 W82,W7 mixture: isotropic → 58 °C → smectic A → 48 °C → smectic C* → 13 °C → More ordered smectic phase).

liquid crystal composites have also been developed. Two types of these composites, namely, polymer-dispersed liquid crystals (PDLCs)[26−35] and polymer-stabilized liquid crystals (PSLCs),[36−42] have shown considerable promise in applications requiring resistance to mechanical shock.[37] Systems have been developed which incorporate both cholesteric and nematic LCs[26,27,29−32,41] as well as fast switching[43,44] ferroelectric LCs (FLCs).[28,31,33−40,42] PDLCs are characterized by a large amount of polymer (usually $>10\%$) dispersing the liquid crystal, usually into elliptical or spherical droplets. PSLCs, on the other hand, have relatively little polymer ($<5\%$) which is primarily used for mechanical or electro-optical stabilization. Another composite studied extensively by Hikmet *et al.*[15,45−51] uses liquid crystalline cross-linking monomers in a low molar mass liquid crystal. The phase behavior, electro-optic characteristics,[45−48] and optical properties[49,50] as well as the structure of the anisotropic network[15,51,52] in a variety of systems have been studied.

The polymer can have dramatic effects on the behavior of polymer/LC composites,[53] and thus, it would be desirable to understand the effect of polymerization conditions on the LC properties as well as on the polymerization itself. Some previous work has examined the effect of polymerization temperature and LC phase on certain electro-optic characteristics,[28] but very little is known about the polymerization and its implications during the formation of these composites. Such information would be quite helpful in optimizing electro-optic performance of polymer/LC systems through greater understanding of the interactions of the polymer and liquid crystal.

The goal of this work, therefore, is to characterize the photopolymerization behavior during the formation of polymer-stabilized ferroelectric liquid crystals and in so doing further understand the evolution of the polymer structure formed within the ordered LC media. To accomplish this goal, the polymerization of small amounts of monomer dissolved in a liquid crystal will be examined for a variety of different systems at different polymerization conditions. The influence of temperature and the liquid crystalline phase on the polymerization rate will first be investigated for various amorphous and liquid crystalline acrylate and diacrylate monomers. In these studies several host liquid crystals will be used. Polymerization of mixtures using an FLC with both smectic A and smectic C* phases will be characterized in detail. To determine whether the polymerization behavior is unique to the smectic C* phase of the FLC, photopolymerizations of monomers dissolved in another FLC possessing a nematic phase as well as a nonchiral LC with smectic A and nematic phases will be discussed. Further understanding of these polymerization mechanisms will be obtained by determining polymerization kinetic constants in both ordered and isotropic systems. Through these polymerization rate and kinetic constant studies, a greater understanding of the influence of the liquid crystal order on the formation of the polymer in polymer-stabilized liquid crystals will be achieved and knowledge about polymerizations and templating of reactions in ordered liquid crystalline media will be expanded.

Experimental Section

Materials and Procedure. The diacrylate monomers chosen for study were two commercially available monomers: *p*-phenylene diacrylate (PPDA) and 1,6-hexanediol diacrylate (HDDA) (Polysciences Inc., Warrington, PA). The monoacrylate also used was *n*-decyl acrylate (Polysciences), and the liquid crystalline diacrylate studied was C6M.[11] All monomers were used without further purification. Structures of these monomers as well as pertinent physical and LC properties are given in Figure 1. Two different ferroelectric liquid crystal (FLC) mixtures were used. The first consists of a 1:1 mixture of W82 and W7 (Displaytech, Longmont, CO), and the second is a commercial 10-component mixture (MX7425; Displaytech). Structures of W82 and W7 as well as phase behavior of the mixture are given in Figure 1. A single-component LC, 4-cyano-4′-octylbiphenyl (8CB; Merck) was also chosen for study. The isotropic solvent used was ethylene glycol diacetate (Aldrich, Milwaukee, WI). All photopolymerizations were initiated with Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone; Ciba Geigy, Hawthorne, NY).

Reaction profiles were monitored with a differential scanning calorimeter equipped with a dual beam photocalorimetric accessory (DSC-DPA 7; Perkin-Elmer, Norwalk, CT). The photocalorimetric accessory included a monochromator to produce light of a specific wavelength. For these studies, monochromatic light of wavelength 365 nm was selected. Polymerizations were initiated using a light intensity of 2.5 mW/cm^2. The DSC cell was also attached to a refrigerated circulating chiller (CFT-25; NESLAB, Newington, NH) to achieve isothermal reaction conditions.

The monomer/FLC mixtures were prepared with initiator approximately 10 mol % of the total double bonds in each sample. For monitored photopolymerizations approximately

10 mg of sample was weighed in aluminum DSC pans, and samples were left uncovered during polymerization. Samples were also heated above the isotropic transition and then brought to the appropriate polymerization temperature to insure uniform thickness and adequate thermal contact. The DSC cell with the sample in it was flushed with nitrogen for 10 min prior to polymerization to prevent oxygen inhibition.[54]

Analysis. The rate of polymerization was determined from the heat flux measured by the DSC as follows

$$\text{rate} = \frac{(Q/s)M}{n\Delta H_{\text{pol}}\text{mass}} \tag{1}$$

where Q/s is heat flow per second, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule, ΔH_{pol} is the heat released per mole of double bonds reacted, and the mass is the mass of monomer in the sample. The polymerization rate in eq 1 is the polymerization rate divided by the initial monomer concentration, thus having units of 1/s. This normalized rate allows for a more facile comparison of systems with different concentrations and types of monomer. The theoretical value of 20.6 kcal/mol was used as the heat evolved per acrylate bond[54] for these calculations. Double-bond conversion was thereafter calculated by integration of the polymerization rate as a function of time. To determine the propagation and termination kinetic constants, a series of experiments were performed. First, the lumped kinetic constant, $k_p/k_t^{1/2}$, was determined as a function of time from the rate of polymerization profile using the pseudosteady state assumption[55] as such

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[\text{M}](\phi I_o \epsilon[\text{A}])^{1/2}} \tag{2}$$

where R_p is the rate of polymerization, [M] is the molar concentration of monomer double bonds, ϕ is the initiator quantum yield, I_o is the incident light intensity, ϵ is the molar extinction coefficient of the initiator, and [A] is the initiator concentration. For these studies ϕ was not measured directly and is assumed to be unity throughout the reaction for all temperatures. This is most likely not the case, however, and this term is lumped together with the reported values of k_p and k_t.

After the polymerization was allowed to proceed, the shutter which exposes the sample to UV light was closed at various stages during the polymerization, therefore eliminating the initiation step. The ensuing 'dark' reaction rates were monitored, allowing uncoupling of the termination and propagation kinetic constants[56] as follows

$$\left.\frac{1}{R_p}\right|_{t=t_1} = \frac{2k_t(t_1 - t_0)}{k_p[\text{M}]} + \left.\frac{1}{R_p}\right|_{t=t_0} \tag{3}$$

where t_0 is the time at which the shutter is closed and t_1 is some time later in the dark reaction. Thus, a plot of $1/R_p$ versus the time elapsed is linear with a slope of $2k_t/k_p/[\text{M}]$. The individual values of k_p and k_t were then determined.

Results and Discussion

Polymerization behavior during the formation of a polymer network in an FLC may be significantly altered as compared to that exhibited in a bulk or solution polymerization. In an earlier work it was reported that the normalized photopolymerization rate in the anisotropic environment increases with increasing concentration[40] as would be expected in solution polymerization. At very low concentrations the rate curves manifest delayed and gradual autoacceleration. Autodeceleration is also gradual, and thus, the reaction is relatively slow as would also be observed in low-concentration solution polymerizations. As the concentration of monomer increases in the FLC environment, however, autoacceleration is more pronounced, dramatically increasing the rate and decreasing the time for reaction. Interestingly, these polymerizations in the ordered media are considerably faster than would be expected in a solution polymerization of comparable concentration.

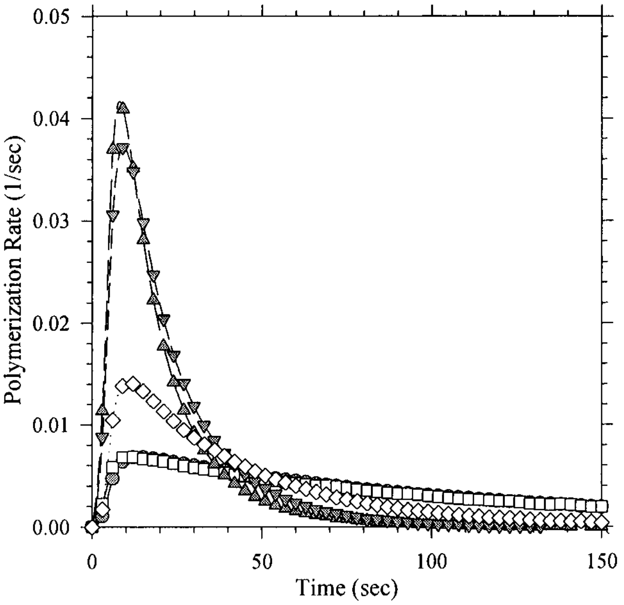

Figure 2. Polymerization rate as a function of time for 2% HDDA in ethylene glycol diacetate polymerizing at 35 °C (●) and 70 °C (□) and for 2% HDDA in W82,W7 polymerizing in smectic C* at 35 °C (▲) and 45 °C (▼) and in the isotropic phase at 70 °C (◇).

To investigate the effects of the FLC phase on these rate differences, the polymerization rate was determined for a variety of diacrylate monomers in both anisotropic FLCs and isotropic solvents. Figure 2 shows the normalized photopolymerization rate plotted versus time for 2% hexanediol diacrylate (HDDA) in W82,W7 and in ethylene glycol diacetate at different temperatures. The higher temperature corresponds to an isotropic phase in the FLC, and the lower two temperatures correspond to the ordered smectic C* phase. The polymerization rate in the solvent changes very little with a 35 °C increase in temperature. In fact, as is evident in Figure 2, the curves are almost indistinguishable. For all of these polymerizations, the reaction proceeds slowly with little pronounced autodeceleration and achieves a maximum conversion of 70%. The rate in the isotropic phase of the FLC is somewhat larger than that in the ethylene glycol diacetate, indicating that these two solvents affect the polymerization differently. In spite of these rate differences, the two polymerizations exhibit quite similar behavior. In contrast, the two polymerizations in the ordered smectic C* phase are significantly accelerated. The maximum rate observed in these reactions is 3 times that observed in the isotropic FLC media and almost 6 times that seen in the isotropic solvent. The maximum double-bond conversions are also considerably larger. As the temperature of polymerization increases, and thus the order of the FLC/monomer system decreases, the polymerization rate decreases. This behavior is consistent with that observed by Hoyle[16-25] and Broer[9-12] for bulk polymerizations of certain liquid crystalline monomers.

Interesting results can also be seen when looking at polymerization of different concentrations of monomer. Figure 3 shows the normalized polymerization rate versus the double-bond conversion for both 5% and 10%

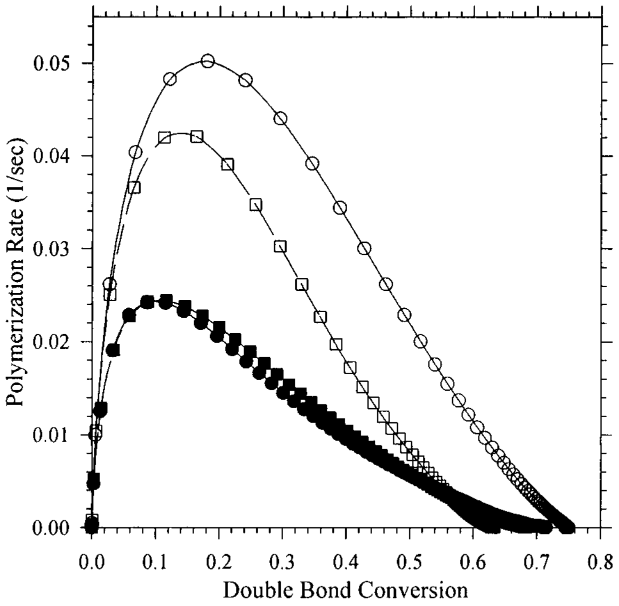

Figure 3. Polymerization rate as a function of double-bond conversion for HDDA polymerizing in W82,W7. Shown are polymerizations of 5% HDDA in smectic C* at 23 °C (○) and in the isotropic phase at 65 °C (●) as well as 10% HDDA in smectic C* at 23 °C (□) and in the isotropic phase at 65 °C (■).

HDDA in W82,W7 at two different temperatures. The rate for the 10% polymerization in the ordered phase is actually lower than that observed for the 5% sample. For the isotropic polymerizations, on the other hand, no real change is seen. These results support the supposition that the polymerization is more rapid in the ordered phases. For HDDA the saturation concentration in W82,W7 is approximately 5% as observed by optical microscopy. For 10% HDDA two regions exist at 23 °C: one which is liquid crystalline and saturated with HDDA and another that is isotropic and rich in monomer. As noted earlier, the polymerization is slower in the isotropic regions. The rate of polymerization for the 10% sample is then a combination of the polymerization in the ordered and isotropic regions. The polymerization rate is therefore lower than that observed for polymerization in an ordered media and higher than that in an isotropic media.

To elucidate if this polymerization rate effect is limited to monomers similar to HDDA, a solid monomer, *p*-phenylene diacrylate (PPDA), and a liquid crystalline monomer (C6M), as well as a liquid monoacrylate, *n*-decyl acrylate (DecA), were polymerized in W82,W7 at temperatures corresponding to the two LC phases, smectic A and smectic C*, as well as in the isotropic phase. The polymerization rate for C6M is plotted versus double-bond conversion for two different temperatures in Figure 4. Here, the higher temperature corresponds to the isotropic phase and the lower temperature to a smectic C* phase. As observed earlier for HDDA systems, the rate increases as the order of the LC phase increases. The maximum rate of the polymerization in the isotropic phase is nearly one-half of that observed in the smectic C* phase despite a 42 °C increase in temperature. Similar overall behavior is observed in the polymerizations of the solid diacrylate PPDA and the liquid monoacrylate DecA in the various LC phases.

The effect of polymerizing in the ordered media of an FLC is clearly seen in Figure 5. Here, the maximum rate is plotted versus the polymerization temperature

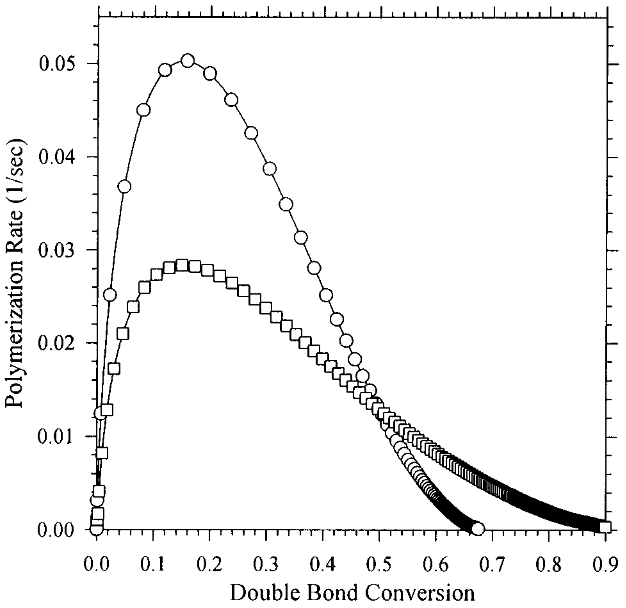

Figure 4. Polymerization rate as a function of double-bond conversion for 10% C6M in W82,W7 polymerizing in smectic C* at 23 °C (○) and in the isotropic phase at 70 °C (□).

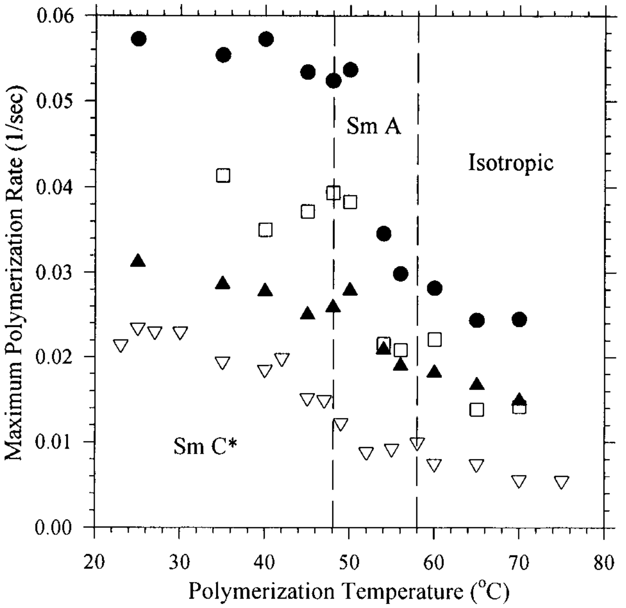

Figure 5. Maximum polymerization rate as a function of polymerization temperature for 6.2% C6M (●), 2% HDDA (□), 2% PPDA (△), and 4% DecA (▽) in W82,W7. Phase transitions are indicated by dashed lines.

for all four monomers studied. The transition temperatures for the neat FLC and the phases are also noted. These data give strong evidence for the enhancement of the reaction in ordered media. For each monomer the maximum rate changes dramatically from one phase to the next, with the smectic C* polymerizations having rates up to 3 times that seen in the isotropic phase. It is also important to note that these changes are similar for four different monomers with such a wide range of physical properties and functionalities.

Similar behavior is also seen in Figure 6 when the maximum rate is plotted for polymerizations of 3% HDDA in MX7425 which exhibits a nematic phase in addition to the smectic A and C* phases seen in W82, W7. These polymerizations are much slower than those in W82,W7 and thus exhibit much lower maximum rates. Because of this, the sensitivity is reduced and

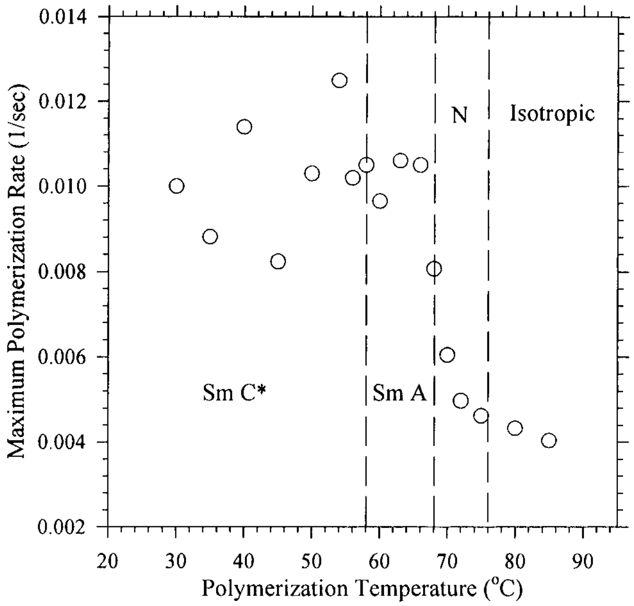

Figure 6. Maximum polymerization rate as a function of polymerization temperature for 3% HDDA in MX7425. The dashed lines indicate phase transition temperatures.

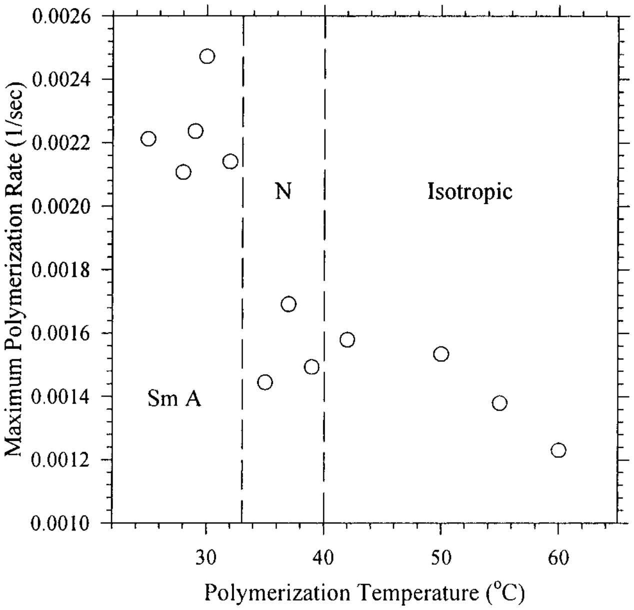

Figure 7. Maximum polymerization rate as a function of polymerization temperature for 2% HDDA in 8CB. The dashed lines indicate phase transition temperatures.

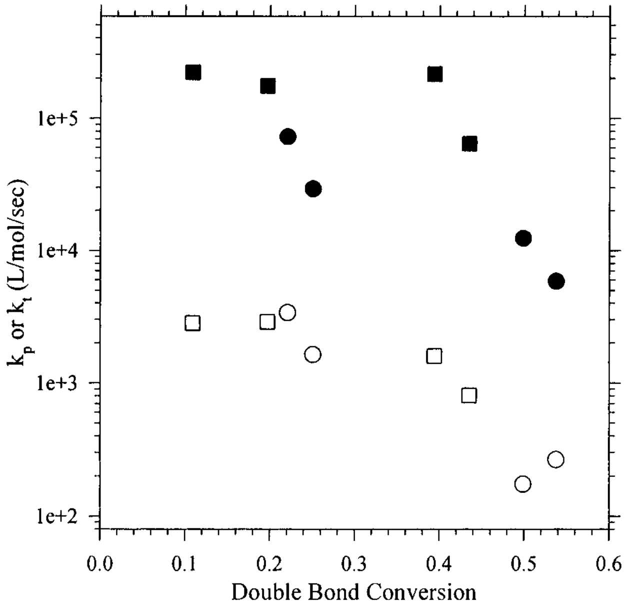

Figure 8. Polymerization kinetic constants k_p at 23 °C (smectic C*, ○) and 65 °C (isotropic, □) and k_t at 23 °C (smectic C*, ●) and 65 °C (isotropic, ■) for polymerization of 5% HDDA in W82,W7.

more scatter of the points is observed. It is evident, however, that the same basic trends are present in this mixture as seen earlier. As the medium increases in order (i.e., the temperature is lowered), the polymerization rate also increases. For reasons not totally apparent, the rates for both smectic phases are nearly the same, in strident contrast to the dramatic increase from smectic A to C* in the W82,W7 system. There is, however, a significant drop in the maximum rates for nematic phase polymerizations and an even further drop for polymerization in the isotropic phase. The same trends are thus evident in both FLC systems, and the relationship between the order of the phase and the consequent polymerization rate enhancement is clear. As the order of the polymerization media increases, a concomitant increase in polymerization rate is observed.

Comparable results are also observed for photopolymerizations of HDDA in the single-component LC 8CB, as shown in Figure 7. 8CB does not exhibit a chiral smectic C phase but does exhibit both nematic and smectic A phases in which the polymerization is studied. As observed for polymerizations in MX7425, the polymerization rate does not increase significantly as the temperature is decreased from the isotropic phase to the nematic phase. As the temperature is lowered below the transition to the more ordered smectic A phase, the polymerization rate increases dramatically, similar to that observed for the two other LC systems studied.

From these results it is logical to conclude that somehow the monomer is segregating within the FLC, thus effectively increasing the local concentration of double bonds and enhancing the polymerization rate. It is still not obvious what manner of segregation occurs or what mechanisms drive the rate acceleration. To understand more fully this phenomenon, it is important to determine the kinetic parameters of polymerization in these systems. So, the rate constant for the propagation reaction, k_p, and the rate constant for the termination reaction, k_t, were determined for the diacrylate polymerizations in the FLC medium at different temperatures and at different conversions.

The kinetic constants for polymerizations of 10% HDDA in W82,W7 are presented in Figure 8. The higher temperature corresponds to the isotropic phase and the lower temperature to the smectic C* phase. The propagation constant, k_p, decreases with increasing conversion at both polymerization temperatures. Furthermore, the values of k_p for both temperatures do not deviate considerably from one another. If a change in propagation kinetics were driving the rate increase, these values should be significantly different indicating that the monomer reactivity was enhanced. This behavior is not observed, however, implying that the driving mechanism must come from termination. The values for the termination kinetic constant, k_t, are almost 1 order of magnitude lower in the ordered phase at lower conversions and appear to remain so throughout the reaction. In these systems, decreased termination leads to higher radical concentrations and thus higher rates.

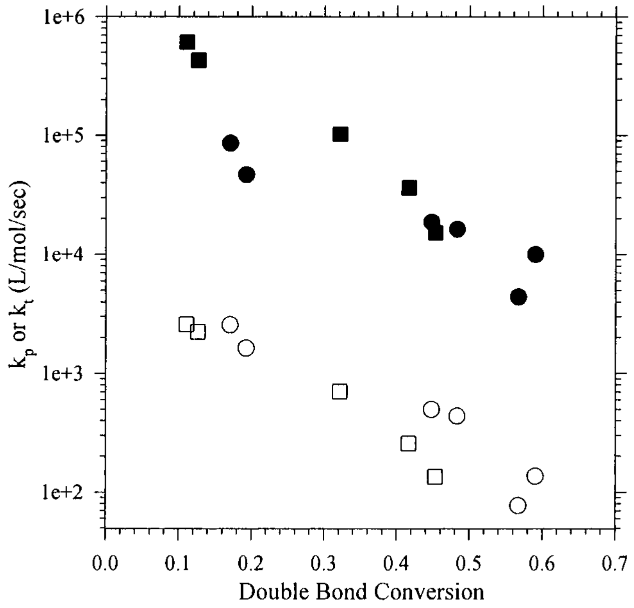

Figure 9. Polymerization kinetic constants k_p at 23 °C (smectic C*, ○) and 65 °C (isotropic, □) and k_t at 23 °C (smectic C*, ●) and 65 °C (isotropic, ■) for polymerization of 5% PPDA in W82,W7.

The differences in k_t and similarities in k_p are particularly evident at conversions close to the rate maximum which occurs between 10% and 20% conversion. As the conversion increases, however, the trends are not as obvious and may not even be the same at higher conversions, but this feature is as might be expected after examination of the rate data. The largest difference in polymerization rate between isotropic and ordered polymerizations occurs near the rate maximum. As the reaction proceeds, the rate decreases for both isotropic and ordered polymerizations, and at higher conversions when most of the reaction has taken place, the rates are quite similar. These results imply that the kinetic constant trends may not be the same for all conversions and could be significantly different at higher conversions when compared to low conversions near the rate maximum.

Similar results are obtained when these constants are examined at different conversions for polymerization of 5% PPDA in W82,W7 as shown in Figure 9. For both polymerizations, k_p is comparable, particularly at lower conversions. This constant is higher for the ordered phase toward the end of the polymerization, but this is long after the major rate enhancement has taken place. Again, it appears as if the termination mechanism drives the rate increase. The termination kinetic constant is considerably lower in the ordered phase at low conversions. At higher conversions the value converges somewhat, but again this convergence takes place at conversions after most of the reaction has already taken place. Thus, as we increase the order of the polymerization media, particularly at lower conversions, propagation does not change a great deal but termination decreases considerably, driving the faster polymerizations and higher polymerization rates. These reaction characteristics imply that the reactivity of the monomer is comparable in both ordered and nonordered systems, but the ability of two radical species to come together and react is reduced in the ordered systems. This effect occurs because mobility of the radical chains is diminished. Similar results demonstrating a near constant k_p and decreasing k_t have also been reported for bulk polymerizations of LC diacrylates.[25]

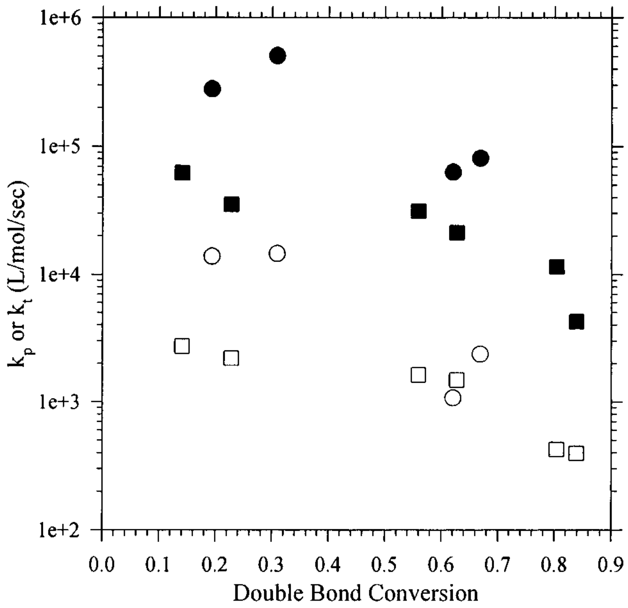

Figure 10. Polymerization kinetic constants k_p at 23 °C (smectic C*, ○) and 65 °C (isotropic, □) and k_t at 23 °C (smectic C*, ●) and 65 °C (isotropic, ■) for polymerization of 10% C6M in W82,W7.

As noted earlier, polymerizations of the LC diacrylate in this study, C6M, in an FLC behave much like those of other nonliquid crystalline amorphous monomers. The reaction rate increases as the order of the polymerization media increases. To determine if the kinetics behind this behavior are also comparable, the kinetic constants for this system were determined and are shown in Figure 10. Dramatic differences are seen in these values when compared with the earlier results. Previously, for HDDA and PPDA, k_t decreased approximately 1 order of magnitude in ordered phases; however, for C6M k_t increases in the ordered phases by about 1 order of magnitude at low conversions. Similar to results for polymerizations of HDDA and PPDA, these trends change at higher conversions, but again this change occurs at higher conversions after the bulk of the polymerization is complete.

In polymerizing the LC monomer, termination actually increases, and therefore we may expect a decrease in the polymerization rate. A decrease is not observed, however, and upon examination of k_p the rate increases for C6M may be explained. In this case the propagation kinetic constant also shows increases similar to those for the termination kinetic constant. As the polymerization rate is dependent on k_p to the first power and only dependent on k_t to the negative one-half power (see eq 2), a similar increase in both constants will result in an increase in the rate. C6M has many of the structural properties of the FLC, and thus, it would be reasonable to suspect that the C6M molecules transverse the smectic layers with the reactive double bonds simply concentrating between the smectic layers instead of the whole molecule. It is suspected that this behavior is somehow responsible for the observed changes in k_p and k_t.

Due to the nature and speed of these polymerizations and the method by which the kinetic parameters are determined, it is extremely difficult to obtain values at identical conversions. Therefore, errors in these measurements cannot be directly ascertained. Upon examination of kinetic parameters at similar conversions, however, it is evident that these values are typically within 50% of each other. Variations in the kinetic constants for polymerizations in the various LC phases are much greater than this 50%, indicating that the differences observed are significant.

Conclusions

The photopolymerization behavior and kinetics in a ferroelectric liquid crystalline media at different temperatures and in different LC phases are described examining both mesogenic and nonmesogenic diacrylate monomers. It was found that the temperature and LC phase of polymerization have a dramatic effect on the nature of polymerization. The rate of polymerization increases dramatically as the order of the LC phase increases and the temperature decreases. Maximum rates observed in smectic C* are 2−3 times that seen in the isotropic phase and up to 6 times that seen in isotropic solvent polymerizations. Rates are also higher for smectic A polymerizations. These rate increases are comparable for a number of different acrylate monomers. Similar results are also obtained for other LC systems exhibiting a nematic phase as well as smectic phases.

Interestingly, the kinetics behind this behavior is surprisingly different. For one type of monomer, the termination kinetic constant, k_t, decreases in ordered phases whereas the propagation kinetic constant, k_p, remains the same for both ordered and isotropic polymerizations. These results indicate that an increase in the local radical concentration takes place in the ordered phases causing an increase in the polymerization rate. In contrast, for a second type of monomer this accelerated rate is driven by both an increase in k_t and k_p.

Acknowledgment. The authors would like to thank the Department of Defense for its support of this work through a fellowship to C.A.G. and Dr. Dirk Broer for generously providing the C6M monomer. The financial support of the National Science Foundation through a grant (MRG Grant DMR-9224168) and DuPont is also gratefully acknowledged.

References and Notes

(1) Percec, V.; Jonsson, H.; Tomazos, D. In *Polymerization in Organized Media*; Paleos, C. M., Ed.; Gordon and Breach: Philadelphia, 1992; p 1.
(2) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413.
(3) Leigh, W. J. In *Liquid Crystals: Applications and Uses*; Bahadur, B., Ed.; World Scientific: London, 1991; Vol. 2, p 357.
(4) Blumstein, A. *Midland Macromol. Monogr.* **1977**, *3*, 133.
(5) Barrall, E. M.; Johnson, J. F. *J. Macromol. Sci.- Rev. Macromol. Chem.* **1979**, *C17*, 137.
(6) Blumstein, A.; Blumstein, R. B.; Hsu, E. C. *Macromolecules* **1975**, *8*, 73.
(7) Perplies, E.; Ringsdorf, H.; Wendorff, J. H. *Makromol. Chem.* **1974**, *175*, 553.
(8) Perplies, E.; Ringsdorf, H.; Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 243.
(9) Broer, D. J.; Mol, B. N. *Makromol. Chem.* **1989**, *190*, 19.
(10) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.
(11) Broer, D. J.; Hikmet, R. A. M.; Challa, G. *Makromol. Chem.* **1989**, *190*, 3201.
(12) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.
(13) Broer, D. J.; Mol, G. N.; Challa, G. *Polymer* **1991**, *32*, 690.
(14) Hikmet, R. A. M.; Lub, J.; Tol, A. J. W. *Macromolecules* **1995**, *28*, 3313.
(15) Hikmet, R. A. M.; Lub, J.; Maassen vd Brink, P. *Macromolecules* **1992**, *25*, 4194.
(16) Hoyle, C. E.; Kang, D.; Jariwala, C.; Griffin, A. C. *Polymer* **1993**, *34*, 3070.
(17) Hoyle, C. E.; Chawla, C. P.; Griffin, A. C. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 639.
(18) Hoyle, C. E.; Watanabe, T.; Whitehead, J. B. *Macromolecules* **1994**, *27*, 6581.
(19) Hoyle, C. E.; Chawla, C. P.; Griffin, A. C. *Polymer* **1989**, *60*, 1909.
(20) Hoyle, C. E.; Kang, D.; Chawla, C. P.; Griffin, A. C. *Polym. Eng. Sci.* **1992**, *32*, 1490.
(21) Hoyle, C. E.; Griffin, A. C.; Kang, D.; Chawla, C. P. In *Irradiation of Polymeric Materials*; Reichmanis, E., O'Donnell, J. H., Frank, C. W., Eds.; American Chemical Society: Washington, DC, 1993; Vol. 527, p 118.
(22) Hoyle, C. E.; Chawla, C. P.; Kang, D.; Griffin, A. C. *Macromolecules* **1993**, *26*, 758.
(23) Hoyle, C. E.; Kang, D. *Macromolecules* **1993**, *26*, 844.
(24) Hoyle, C. E.; Chawla, C. P. *Macromolecules* **1995**, *28*, 1946.
(25) Hoyle, C. E.; Watanabe, T. *Macromolecules* **1994**, *27*, 3790.
(26) Doane, J. W.; Golemme, A.; West, J. L.; Whitehead, J. B.; Wu, B.-G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.
(27) Doane, J. W. In *Liquid Crystals: Applications and Uses*; Bahadur, B., Ed.; World Scientific: London, 1991; Vol. 1, p 361.
(28) Molsen, H.; Kitzerow, H.-S. *J. Appl. Phys.* **1994**, *75*, 710.
(29) Braun, D.; Frick, G.; Grell, M.; Klines, M.; Wendorff, J. H. *Liq. Cryst.* **1992**, *11*, 929.
(30) Yamaguchi, R.; Sato, S. *Liq. Cryst.* **1993**, *14*, 929.
(31) Kitzerow, H.-S. *Liq. Cryst.* **1994**, *16*, 1.
(32) Drzaic, P. S. *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995.
(33) Kitzerow, H.-S.; Molsen, H.; Heppke, G. *Appl. Phys. Lett.* **1992**, *60*, 3093.
(34) Zyryanov, V. Y.; Smorgon, S. L.; Shabanov, V. F. **1993**, *143*, 271.
(35) Lee, K.; Suh, S.-W.; Lee, S.-D. *Appl. Phys. Lett.* **1994**, *64*, 718.
(36) Dumon, M.; Nguyen, H. T. *Polym. Adv. Tech.* **1992**, *3*, 197.
(37) Lester, G.; Coles, H.; Murayama, A.; Ishikawa, M. *Ferroelectrics* **1993**, *148*, 389.
(38) Hikmet, R. A. M.; Michielsen, M. *Adv. Mater.* **1995**, *7*, 300.
(39) Hikmet, R. A. M.; Boots, H. M. J.; Michielsen, M. *Liq. Cryst.* **1995**, *19*, 65.
(40) Guymon, C. A.; Hoggan, E. N.; Walba, D. M.; Clark, N. A.; Bowman, C. N. *Liq. Cryst.* **1995**, *19*, 719.
(41) Yang, D.-K.; Chien, L.-C.; Fung, Y. K. In *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks*; Crawford, G. P., Zumer, S., Ed.; Taylor & Francis: London, 1996; p 103.
(42) Guymon, C. A.; Hoggan, E. N.; Rieker, T. P.; Clark, N. A.; Walba, D. M.; Bowman, C. N. *Science* **1997**, *275*, 57.
(43) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899.
(44) Walba, D. M. *Science* **1995**, *270*, 250.
(45) Hikmet, R. A. M. *J. Appl. Phys.* **1990**, *68*, 4406.
(46) Hikmet, R. A. M.; Zwerver, B. H. *Liq. Cryst.* **1991**, *10*, 835.
(47) Hikmet, R. A. M. *Liq. Cryst.* **1991**, *9*, 405.
(48) Hikmet, R. A. M.; Zwerver, B. H.; Lub, J. *Macromolecules* **1994**, 27, 6722.
(49) Hikmet, R. A. M.; Zwerver, B. H. *Liq. Cryst.* **1992**, *12*, 319.
(50) Hikmet, R. A. M.; Zwerver, B. H. *Liq. Cryst.* **1993**, 561.
(51) Hikmet, R. A. M.; Boots, H. M. J. *Phys. Rev. E* **1995**, *51*, 5824.
(52) Heynderickx, I.; Broer, D. J.; Van Den Boom, H.; Teesselink, W. J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 215.
(53) Guymon, C. A.; Dougan, L. A.; Hoggan, E. N.; Bowman, C. N. *Chem. Mater.*, in preparation.
(54) Anseth, K. A.; Kline, L. M.; Walker, T. A.; Anderson, K. J.; Bowman, C. N. *Macromolecules* **1995**, *28*, 2491.
(55) Odian, G. *Principles of Polymerization*; John Wiley & Sons: New York, 1991; p 207.
(56) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650.

MA9616773