Kinetic Analysis of Polymerization Rate Acceleration During the Formation of Polymer/Smectic Liquid Crystal Composites

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ABSTRACT: Polymerization and segregation behavior of *n*-decyl acrylate in a smectic liquid crystal were characterized. The polymerization rate increased dramatically as the temperature was decreased and the order of the liquid crystalline media increased. To ascertain the kinetic mechanisms behind this behavior, the kinetic constants of both the termination and propagation reactions were determined. The overall rate increase was driven by an increase in the propagation kinetic constant despite an increase in the termination kinetic constant. The segregation behavior of the monomer in the liquid crystal was also elucidated using polarized infrared spectroscopy and X-ray diffraction. The monomer segregated between the smectic layers, thereby concentrating the monomer double bonds in a much smaller volume. Using this type of segregation with the consequent layer spacing increase and assuming that diffusional limitations are negligible, a kinetic model was developed to explain the increases in polymerization rate as well as the increases observed in the kinetic constants. After analysis of both steady-state and unsteady-state conditions, increases in the polymerization rate and propagation and termination kinetic constants related to the increase in the layer spacing were predicted. These predictions agreed well with experimental results of polymerization rate and kinetic constants, indicating that this model is suitable in explaining the mechanisms driving the increases in both propagation and termination rates in this and other monomer/smectic liquid crystal systems.

Introduction

Liquid crystals (LCs), or anisotropic liquids, have been the subject of extensive research for many years. This inherent anisotropy makes these materials ideal for many applications including a wide array of display devices. Ordering in the LC may also change solute behavior, thereby creating a fascinating media in which to study chemical reactions.[1,2] Recently, radical polymerizations performed in the ordered environment of an LC have become prevalent as polymeric liquid crystals[3] and polymer/LC composites[4] have received increasing attention.

The formation of polymeric LCs via polymerization of ordered liquid crystalline monomers has been studied extensively.[5−16] Interestingly, many of these polymerizations show unique kinetic behavior when initiated in ordered LC phases. In fact, significant increases in polymerization rate have been observed in LC phases for a variety of different LC mono-[5] and diacrylates[6] with chemical structures including fluorinated[7] and cholesteryl[8] moieties as well as more common LC mesogenic groups.[9,10] These enhanced polymerization rates are remarkably dependent on the temperature and LC phase of polymerization.[11] Explanations for this accelerated rate behavior for LC monomers have included decreases in the termination rate[12,13] indicated by molecular weight measurements.[14] Direct evidence of decreased termination rates in ordered LC phases has also been shown[15] for polymerizations exhibiting this rate acceleration as well as for other LC monomer polymerizations in which no rate acceleration is observed.[16] These termination rate decreases have been attributed to decreased mobility of the polymer radical chains due to the anisotropy of the media.

Similar results in polymerization behavior have also been seen during the *in situ* polymerization of small percentages of dissolved monomer species in a low molar mass liquid crystalline solvent to form polymer/LC composites.[17] The temperature and the LC phase in which the polymerization is performed dramatically influences the polymerization behavior.[18] The rate of polymerization increases significantly for different systems as the temperature decreases and the order of the phase increases. Interestingly, the polymerization behavior is quite similar for different amorphous and mesogenic monomers with a wide range of physical and optical properties. Maximum polymerization rates in an ordered smectic phase are consistently 2−3 times those observed in the isotropic phase.

Although the accelerated polymerization rate behavior is similar for different monomers, the kinetic mechanisms behind these accelerated rates are not always the same. Two distinct kinetic behaviors have been observed. Polymerizations of certain monomer/LC mixtures exhibit a kinetic behavior similar to that in neat LC monomer polymerizations.[15] The termination rate decreases dramatically in the LC phases. Again, as noted for LC monomers, the growing polymer chains appear to be somewhat constrained and lose mobility in the ordered environment. Other monomer/LC mixtures, which do exhibit accelerated rates, do not show this decrease in termination, but instead show dramatic increases in both the propagation and termination rate. Obviously, the same diffusional limitations responsible for decreasing termination are not responsible for the changes observed when both propagation and termination are accelerated.

This altered polymerization behavior has been attributed to segregation of the monomer. Recently, models have been described which identify two specific modes of segregation within the LC.[19] One type is characterized by segregation of the monomer species between the LC smectic layers resulting in a layer spacing increase. The second type, on the other hand, is defined by segregation of the monomer within the smectic layers and alignment of the monomers with the

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LC molecules. Although these models do lend credence to the fact that segregation contributes to the accelerated polymerization rates, the two modes of segregation cannot be directly correlated to the two distinct types of kinetic behavior observed. Additionally, the two modes give little information to help explain the kinetic behavior in certain monomer/LC systems for which both termination and propagation rates increase. It is reasonable to suspect that this polymerization behavior is, in fact, related to the segregation and the templating effect that the liquid crystal induces. Unfortunately, it has been difficult to elucidate the precise effect that induces changes in the polymerization behavior.

The goal of this work, therefore, is to elucidate the mechanism of the polymerization rate acceleration for templated polymerization in which both termination and propagation rates increase. These answers will further the understanding of the evolution of the polymer structure within ordered LC media during the formation of polymer/LC composites. To accomplish this goal, the polymerization of a monomer exhibiting this polymerization behavior in ordered phases of an LC will be examined, and the influence of temperature and liquid crystalline phase on the polymerization rate and kinetic behavior will be determined. The segregation properties of the monomer in the LC will also be identified to determine what influence that the mode of segregation might impart to the polymerization characteristics. A theoretical model will then be developed to account for the segregation and its effect on initiation, propagation and termination. Polymerization rate and kinetic constants calculated from the model will be correlated with experimental data to determine the degree to which the polymerization behavior is accurately predicted. Through these experimental and theoretical studies, a greater knowledge and understanding of the complex processes involved in the polymerization of monomeric species in the ordered media of a liquid crystal will be attained.

Experimental Section

Materials and Procedure. The acrylate monomer chosen for study was *n*-decyl acrylate (Polysciences Inc., Warrington, PA). The liquid crystal used is composed of a 1:1 mixture of W82 and W7 (Displaytech, Longmont, CO). Photopolymerizations were initiated with Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone, Ciba Geigy, Hawthorne, NY). All materials were used without further purification. Chemical structure and pertinent properties of the monomer and liquid crystal components are shown in Figure 1. The monomer/LC mixtures were prepared with initiator concentrations approximately 5 wt % of the total monomer concentration.

Polymerization rate profiles were monitored with a differential scanning calorimeter equipped with a dual beam photocalorimetric accessory (DSC-DPA 7; Perkin-Elmer, Norwalk, CT). Polymerizations were initiated using monochromatic light of wavelength 365 nm with an intensity of 2 mW/cm^2. The DSC sample cell was also attached to a refrigerated circulating chiller (RTE-111; NESLAB, Newington, NH) to achieve isothermal reaction conditions. For monitored polymerizations approximately 12 mg of the monomer/LC mixture was placed in an aluminum DSC pan. Samples were also heated above the isotropic transition and then cooled to the appropriate polymerization temperature to insure uniform thickness and adequate thermal contact. The DSC sample cell was flushed with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition.[20]

Sample cells for infrared absorption measurement were prepared by introducing the sample between two rubbed nylon coated calcium fluoride substrates spaced 10 μm apart. To insure proper homogeneous alignment, samples were cooled at 0.05 °C/minute from the isotropic to the smectic C* phase. The alignment was then checked using polarizing microscopy. Polarized IR spectra (128 scans per spectrum) were obtained using an FTIR spectrometer (Magna IR 750; Nicolet, Madison, WI) equipped with a ZnSe wire grid polarizer at a resolution of 2 cm^{-1}. Smectic layer spacings were measured in a 1 mm quartz capillary (Charles Supper Co., Natick, MA) using an X-ray spectrometer (Rigaku RU-200) with a Cu Kα rotating anode source. Additionally, tilt angle measurements were performed using a polarizing optical microscope equipped with a rotating stage (Optiphot2-pol; Nikon, Melville, NY).

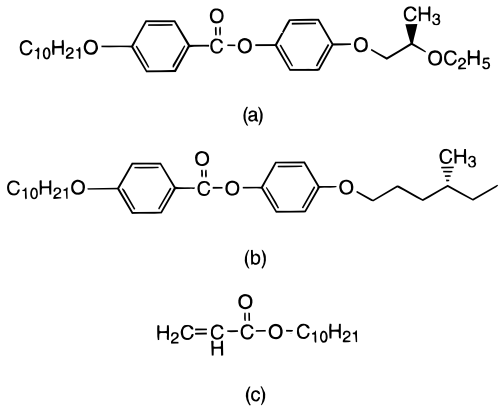

Figure 1. Chemical structures of the liquid crystals and acrylate monomer used in this study. Shown are (a) W7, (b) W82 (phase sequence for 1:1 W82,W7 mixture: isotropic → 58 °C → smectic A → 48 °C → smectic C* → 13 °C → more ordered smectic phase), and (c) *n*-decyl acrylate (DecA, bp 158 °C).

Analysis. Polymerization rate profiles and double bond conversions were determined from the heat flux measured by the DSC. For these studies the theoretical value of 20.6 kcal/mol was used as the heat evolved per acrylate double bond reacted.[21] To determine propagation and termination kinetic constants a series of experiments were performed. First, the lumped kinetic constant, $k_p/k_t^{1/2}$, was measured as a function of time from the polymerization rate profile. Then, by eliminating the initiation step at various stages in the polymerization (i.e., closing the shutter to the UV light source) and monitoring the "dark" reaction, the propagation and termination kinetic constants were uncoupled. The complete analysis method for the determination of polymerization rate, double bond conversion, and kinetic constants is described in detail elsewhere.[22]

Results and Discussion

Polymerization and Segregation Behavior. The polymerization characteristics during the formation of a polymer in an LC environment may be altered significantly when the polymerization occurs in ordered liquid crystalline phases. One characteristic, namely the polymerization rate, is dramatically enhanced in the smectic C* phase in certain monomer/LC mixtures.[18] This particular feature also appears to be prevalent in the polymerization of *n*-decyl acrylate (DecA) in the smectic C* phase of W82,W7 as shown in Figure 2. Here, the polymerization rate of 9% DecA in W82,W7 is plotted as a function of double bond conversion for two different polymerization temperatures. It is important to note that the phase behavior of the W82,W7 system is altered considerably by the addition of the monomer. The phase transitions are lowered somewhat, but the polymerization temperatures are chosen so that the LC phase remains the same throughout the polymerization and is the same as would be observed at the same temperature in the neat LC. The lower temperature (23 °C) corresponds to the ordered smectic

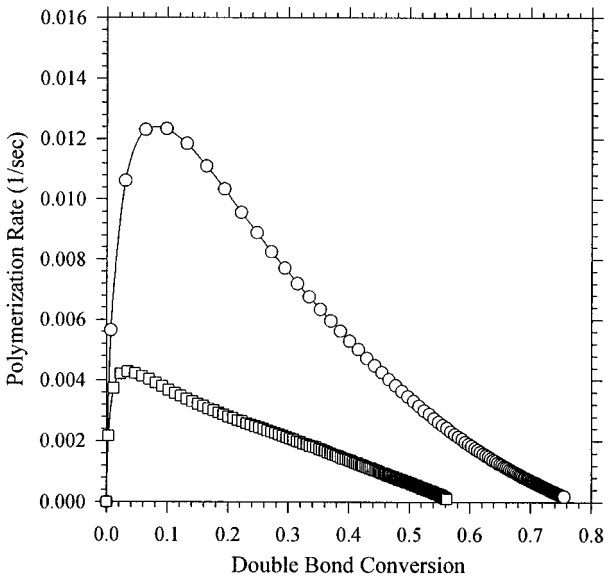

Figure 2. Polymerization rate as a function of double bond conversion for DecA polymerizing in W82,W7. Shown are polymerizations of 9% DecA in Smectic C* at 23 °C (○) and in the isotropic phase at 65 °C (□).

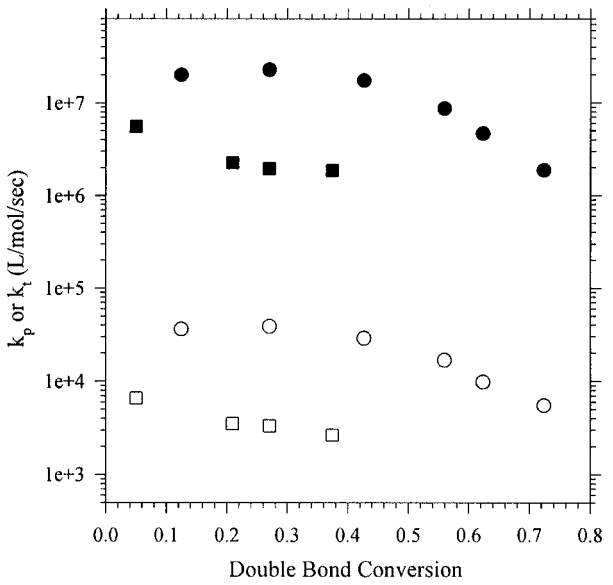

Figure 3. Polymerization kinetic constants, k_p, at 23 °C, smectic C* (○), and 65 °C, isotropic (□), and k_t at 23 °C, Smectic C* (●), and 65 °C, isotropic (■), for polymerization of 9% DecA in W82,W7.

C* phase, whereas the higher temperature (65 °C) corresponds to the isotropic phase in which all of the LC molecules are randomly oriented. Polymerization in the smectic C* phase is significantly faster and exhibits a maximum rate over 3 times that observed in the isotropic LC media. It also appears that the double bond conversion is higher in the ordered media polymerization. This behavior may be due in part to the fact that, at higher conversions for the isotropic polymerization, the heat released is quite small and is difficult to separate from the baseline. Differences in the rate of initiation for the two polymerization temperatures might be partially responsible for the observed changes, but in order for such a change to be the primary mechanism behind the overall rate acceleration, the initiation rate would have to increase almost an order of magnitude in the ordered phase polymerization. This behavior is highly unlikely and contrary to previous results.[18]

A further understanding of this altered polymerization behavior can be achieved when the kinetic constants of polymerization are determined experimentally in both the ordered smectic C* phase and in the isotropic phase. Figure 3 shows propagation kinetic constants, k_p, and termination kinetic constants, k_t, for polymerizations of 9% DecA in W82,W7 at the same temperatures examined previously. After evaluation of only k_t, one may expect an actual decrease in the polymerization rate instead of the increase observed. The values for this kinetic constant in the smectic C* phase are almost 1 order of magnitude higher than those in the isotropic phase which, in and of itself, would produce a decrease in the polymerization rate. To be able to understand this phenomenon fully, it as also important to ascertain the changes in k_p. Here, the propagation kinetic constant also shows increases in the ordered phase quite similar to those for the termination constant. The combination of these two effects will lead to the rate acceleration detected previously. The polymerization rate is dependent on $k_p/k_t^{1/2}$, and therefore, a concomitant increase in both constants will lead to an increase in the rate. Interestingly, the values for both constants at both temperatures do not change tremendously from the initial values at low conversions, indicating that

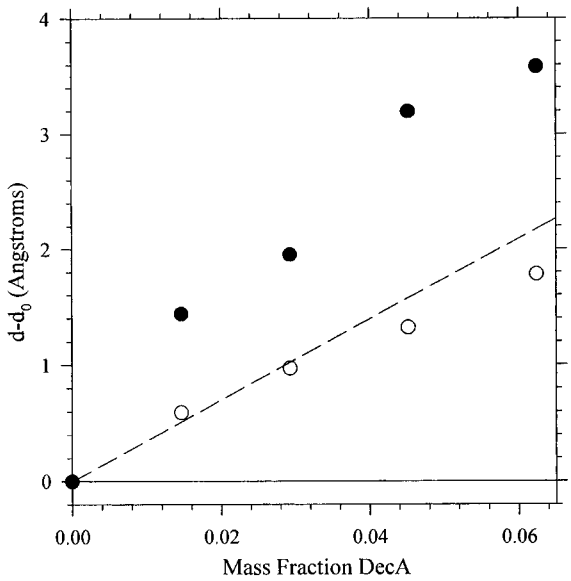

Figure 4. Smectic layer spacing increase ($d - d_0$) for DecA in W82,W7 at 23 °C as a function of concentration. Shown are the increase in layer spacing for each concentration as compared to the layer spacing of neat W82,W7 (●) and the increase when corrected for the tilt angle (θ) at each concentration of DecA (○). The dashed line corresponds to the layer spacing increase if all of the molecules segregated between the smectic layers, whereas the solid line corresponds to the increase if the monomer segregates into the smectic layers.

diffusional limitations in both propagation and termination do not play an important role until later in the reaction. At higher conversions in the ordered polymerization, values do begin to decrease, but this is long after the majority of the polymerization has occurred.

These results seem to indicate that somehow the monomer or the monomer double bonds are segregating within the liquid crystal, thus effectively increasing the local concentration of double bonds. Although the kinetic results give some credence to this hypothesis, it is also of great import to obtain direct measurements of any segregation of the monomer molecules in the LC environment. Other studies[19] have shown that molecules similar in structure to DecA segregate between

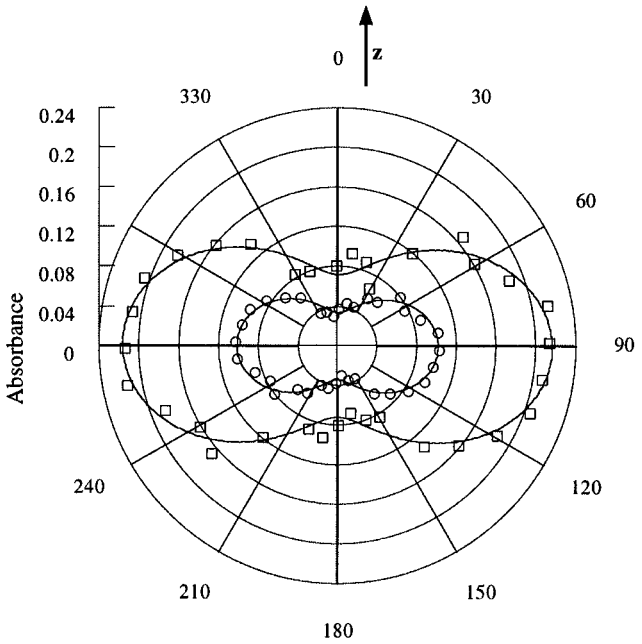

Figure 5. Polar plot of the absorbance $A(\Psi)$ of the IR bands for the acrylate C═C stretch at 1635 cm^{-1} (○) and for the acrylate C—H wag at 1408 cm^{-1} (□) for 5% DecA in W82,W7.

Table 1. Smectic C* Tilt Angle for DecA/W82,W7 systems

wt % DecA in W82,W7	tilt angle (θ) at 23 °C	wt % DecA in W82,W7	tilt angle (θ) at 23 °C
0	27.5	4.52	22.3
1.47	25.3	6.24	20.2
2.93	23.8		

the smectic layers and thereby contribute to a layer spacing increase. To ascertain if an increase is observed in these mixtures, the layer spacings were determined using X-ray diffraction. Figure 4 shows the increase in the smectic layer spacing ($d - d_0$) for DecA/W82,W7 mixtures as the monomer concentration is increased. In this figure the dotted line is the increase calculated under the assumption that all of the monomer molecules segregate between the smectic layers and contribute their volume to a layer spacing increase. The solid line corresponds to the increase if the monomers are segregating into the smectic layers and therefore adding nothing to the layer spacing. As seen in Figure 4, the layer spacing increases dramatically as the concentration increases, and, in fact, the increase is significantly underpredicted by the theoretical increase for complete interlayer segregation.

This underprediction can be explained after examination of the tilt angle in the DecA/W82,W7 systems. As mentioned previously, the addition of DecA to the LC does decrease the phase transitions. This change, in turn, also changes the tilt angle at room temperature as shown in Table 1. In smectic C* liquid crystals such as W82,W7, the tilt angle decreases as the temperature in the smectic C* phase increases.[24] Therefore, as DecA is added to the LC and the phase transitions decrease, a decrease in the tilt angle will also be observed. This tilt angle decrease will consequently increase the smectic layer spacing. The layer spacing increase, adjusted to neglect the increase due to the tilt angle decrease and thereby reflect only the increase caused by the DecA molecules swelling the layers, is also shown in Figure 4. As is evident from the figure, the data agree well with what would be expected if the monomers are completely segregating between the smectic layers. This trend continues at higher concentrations of monomer and the increase in layer spacing is approximately what would be expected given the previous discussion. At these higher monomer concentrations, however, it becomes difficult to determine the tilt angle in the smectic C* phase due to changes in the optical properties and profligation of optical defects induced by the large percentage of nonmesogenic molecules in the mixture. Because of this uncertainty in tilt angle, results at larger monomer concentrations for the smectic layer spacing are not included in the figure, although it is reasonable to believe that the same type of segregation behavior is present prior to polymerization.

Further evidence of this segregation is seen from results using polarized infrared spectroscopy to obtain orientations of specific bonds.[23] In DecA/W82,W7 mixtures two bands, one at 1635 cm^{-1} (C═C stretch) and another at 1408 cm^{-1} (C—H wag), unique to the acrylic C═C groups of the DecA can be isolated in the infrared spectrum. Figure 5 shows polar plots for these two bands in a 5% DecA/W82,W7 mixture. If the monomer double bonds were randomly distributed in the LC, the absorbance for all different polarization angles would be the same. This is obviously not the case for either band. The maximum absorbance for the DecA acrylic bands both exhibit a maximum at 90°, corresponding to light polarized perpendicular to the normal (**z**) director, or parallel to the smectic layers. In fact, this maximum for the 1635 cm^{-1} band is approximately almost 3.5 times the minimum absorbance observed for light polarized perpendicular to the smectic layers. This ratio is only slightly less (2.5) for the 1408 cm^{-1} band. These data indicate that the DecA double bonds are oriented primarily parallel to these layers and the orientation appears to be substantial as indicated by the relatively large dichroic ratios. Comparable results are also observed for mixtures in the smectic C* phase with higher concentrations of DecA.

This segregation behavior is quite similar to that observed previously for hexanediol diacrylate.[19] Hexanediol diacrylate (HDDA) polymerizations also show rate increases in the ordered smectic LC phases similar to DecA. The polymerization kinetics, however, are significantly different. For HDDA polymerizations the accelerated rate is driven by decreases in the termination rate, much different from the increases in termination and propagation rates observed for DecA. The segregation of both monomers definitely plays an important role in the accelerated polymerizations, but the mode of segregation is obviously not the only determining factor.

Model Development. To understand this phenomenon further, consider the polymerizing system shown in Figure 6. The monomer is segregated between the LC smectic layers, thereby increasing the local concentration of double bonds. Let the ratio of the volume in which the monomer has partitioned to the total volume be represented by α, i.e. $\alpha = \delta/L$. Additionally, let all bulk averaged (or isotropic) concentrations and rates be represented by an asterisk and all local (segregated) concentrations and rates within the monomer layer, be represented by a slanted prime. For the analysis we also assume that diffusional limitations are not significant in either the propagation or termination reactions for both segregated and isotropic polymerizations. This assumption implies that the "real" values of k_p and k_t

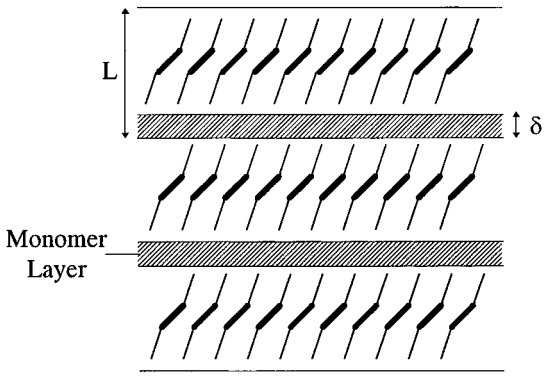

Figure 6. Segregation model for DecA/W82,W7 and other similar mixtures in the smectic C* phase. δ corresponds to the layer spacing increase induced by the segregation of monomer, and L is the total smectic layer spacing.

are the same for both types of polymerization systems and that any differences in observed kinetic behavior arise because of the segregation alone. Given these definitions and assumptions, one can write

$$R_p' = k_p[M]'[R^\bullet]' \tag{1}$$

where R_p' is the local polymerization rate, k_p is the kinetic constant for propagation, $[M]'$ is the local monomer concentration, and $[R^\bullet]'$ is the local polymer radical concentration. The observed bulk rate can then be written as

$$R_{p,obs} = \alpha R_p' + (1-\alpha)R_{p,LC}' = \alpha R_p' = \alpha k_p[M]'[R^\bullet]' \tag{2}$$

since all of the polymerization is occurring only in the segregated monomer layer. The local monomer concentration is simply found from

$$[M]' = \frac{1}{\alpha}[M]^* \tag{3}$$

To determine the radical concentration, one must consider what happens to the initiator. One possible scenario is that all of the initiator is able to initiate polymerization, and the initiation rate is consequently unchanged by the monomer segregation. Such behavior would occur if the initiator itself segregates between the smectic layers or if the initiator can readily diffuse to the interstitial region. In this type of system the rate of initiation in the segregated volume is given by

$$R_i' = \frac{1}{\alpha}R_i^* \tag{4}$$

where R_i represents the rate of initiation. Therefore, using the pseudo steady-state assumption[25] and again assuming that diffusion limitations of the growing polymer radicals in the segregated region do not influence the polymerization significantly, the balance on radicals becomes

$$\frac{\partial[R^\bullet]'}{\partial t} \approx 0 = \frac{1}{\alpha}R_i^* - 2k_t[R^\bullet]'^2 \tag{5}$$

thus,

$$[R^\bullet]' = \left(\frac{R_i^*}{2k_t}\right)^{1/2}\left(\frac{1}{\alpha}\right)^{1/2} = [R^\bullet]^*\left(\frac{1}{\alpha}\right)^{1/2} \tag{6}$$

The observed polymerization rate can then be rewritten as

$$R_{p,obs} = \alpha k_p[M]'[R^\bullet]' = k_p[M]^*[R^\bullet]^*\left(\frac{1}{\alpha}\right)^{1/2} \tag{7}$$

but, for an isotropic system the bulk polymerization rate is

$$R_p^* = k_p[M]^*[R^\bullet]^* \tag{8}$$

Consequently, an increase in the rate caused by the monomer segregation relative to an isotropic polymerization is predicted as such

$$\frac{R_{p,obs}}{R_p^*} = \left(\frac{1}{\alpha}\right)^{1/2} \tag{9}$$

Therefore, if the monomer segregates into a smaller volume, the polymerization rate increase is directly related to this volume reduction. After examination of the traditional rate expression,[18] an expression relating the lumped kinetic parameters for the ordered and isotropic polymerizations can be obtained as follows

$$\frac{(k_p/k_t^{1/2})_{obs}}{(k_p/k_t^{1/2})^*} = \left(\frac{1}{\alpha}\right)^{1/2} \tag{10}$$

This model, therefore, predicts an increase in the observed polymerization rate and the observed lumped kinetic constant, $k_p/k_t^{1/2}$, proportional to the square root of $1/\alpha$ if all primary radicals can initiate polymerization.

Further information can be obtained when the relationship between the segregation volume and the individual kinetic constants is identified. Consider the unsteady state reaction after the light is extinguished, thereby eliminating the initiation of radicals. After analysis of the radical balance, one obtains

$$\frac{1}{[R^\bullet]'} - \frac{1}{[R^\bullet]_0'} = 2k_t t \tag{11}$$

where $[R^\bullet]_0'$ is the local radical concentration when initiation is stopped ($t = 0$). Then, by substituting the relationship between the radical concentration and the rate of polymerization, eq 11 becomes

$$\frac{1}{R_p'} - \frac{1}{R_{p0}'} = \frac{2k_t}{k_p[M]'}t \tag{12}$$

Then, after substitution of eqs 2 and 3, one obtains

$$\frac{1}{R_p^*} - \frac{1}{R_{p0}^*} = \frac{2k_t}{k_p[M]^*}t \tag{13}$$

which is identical to the expression that would be obtained if the monomer were homogeneously distributed throughout the system. Consequently, the comparison of kinetic constant ratios that would be observed experimentally as compared to those in an isotropic system becomes

$$\frac{(k_t/k_p)_{obs}}{(k_t/k_p)^*} = 1 \tag{14}$$

Therefore, the ratio of the kinetic constants found by experimental observation is the same as would be

observed simply in the segregated volume. This allows the effect of segregation on each kinetic constant to be determined by combination with eq 10. The observed values for the kinetic constants as compared to the values for an isotropic polymerization can then be obtained as such

$$\frac{k_{t,obs}}{k_t^*} = \frac{1}{\alpha} \tag{15}$$

$$\frac{k_{p,obs}}{k_p^*} = \frac{1}{\alpha} \tag{16}$$

Therefore, if all primary radicals can initiate polymerization, an increase in both k_t and k_p proportional to $1/\alpha$ will be observed experimentally because of the monomer segregation. The rate constants determined in systems with these characteristics will therefore be different than the "real" kinetic constants. This difference is related to the volume reduction of the polymerizing system which can be directly determined experimentally. Additionally, the observed polymerization rate will also increase because of the segregation by the square root of $1/\alpha$. In other words, if the primary radicals are mobile and can diffuse to the monomer layer or are already segregated in the monomer layer and diffusional limitations are not significant, then an increase in the overall polymerization rate as well as increases in propagation and termination should be observed experimentally.

It is also of interest to examine another case in which a fraction of initiator molecules equal to α initiate polymerization. This implies that the local rate of initiation in the segregated layer is identical to the bulk averaged rate. Therefore, after solving for the radical concentration from the balance on the radical species, it is readily apparent and intuitively obvious that the segregated local radical concentration is identical to the bulk averaged concentration. Then, by substituting this concentration and eq 3 into the rate expression given in eq 2, it becomes evident that no rate acceleration and consequently, no change in the termination or propagation rate would be observed. An increase in polymerization rate for the DecA/W82,W7 system is observed, however, and therefore, this scenario, in which only a small fraction of the initiator could actually initiate polymerization, does not seem to be the dominant mechanism.

Model Predictions. In light of these results, it appears logical to conclude that the DecA/W82,W7 system shows behavior that might be expected if the monomer is segregating between the smectic layers and that all primary radicals can initiate polymerizations. The segregation pattern is consistent with the IR and XRD results showing preferential orientation of the double bonds parallel to the smectic layers and increased layer spacings very close to those predicted if all of the DecA molecules segregate between these layers. The necessary assumption that diffusional limitations in the ordered phase are not significant appears to be consistent with the kinetic constant data since the isotropic values for k_p and k_t do not significantly decrease until conversions greater than 40% are attained. Additionally, the model seems to fit the experimental results quite well qualitatively, but this model not only predicts an increase in polymerization rate and kinetic constants, but also gives quantitative predictions for these increases.

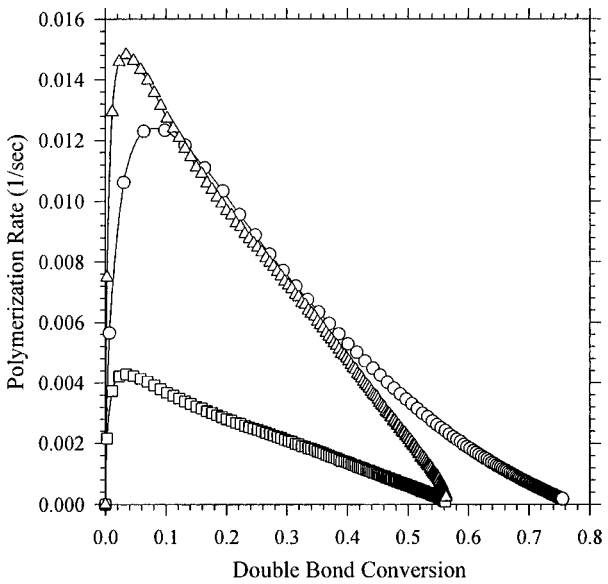

Figure 7. Polymerization rate as a function of double bond conversion for 9% DecA in W82,W7 in smectic C* at 23 °C (○) and in the isotropic phase at 65 °C (□) as given in Figure 2. Also shown is the predicted rate profile for 9% DecA in the smectic C* phase (△).

To verify the model, it is therefore important to determine if these predictions agree with the polymerization kinetic data from the DecA/W82,W7 systems. Figure 7 shows the polymerization rate as a function of double bond conversion for 9% DecA in W82,W7 at temperatures corresponding to the smectic C* phase (23 °C) and to the isotropic phase (65 °C) as plotted previously in Figure 2. Additionally, however, the rate predicted from the model for the polymerization in the smectic C* phase is also shown. To calculate this rate, α was determined from the theoretical layer spacing increase calculated if all DecA molecules contribute to the increase. The rate in the isotropic phase at each conversion is then multiplied by the factor $(1/\alpha)^{1/2}$ (3.3 for this data). As can be seen from the figure, the model predicts the rate behavior very well, particularly at intermediate conversions.

At low conversions, however, the calculated rate is higher than the experimental data. This behavior likely arises from the fact that the DSC does exhibit a certain lag time after the polymerization is initiated. Often, after the onset of reaction, the large change in the rate of heat release prevents the calorimeter from accurately measuring the heat release rate. This lag time is exacerbated as the initial heat release is increased. Consequently, the lag time for the smectic C* polymerization would be greater and therefore, the actual rate may be somewhat higher than that measured. Additionally, polymerization is an activated process and the isotropic polymerization at 65 °C would be somewhat higher than what would observed in the same media at 23 °C if it were completely isotropic.

Deviations from the calculated and actual rates are also observed at higher conversions. This divergence may be caused by the onset of diffusional limitations in the ordered phase, particularly for the termination reaction. As the conversion increases, the mobility of the growing polymer chains will decrease. In the ordered media this decrease may be augmented by further diffusional limitations. Therefore, the radical lifetime may increase, allowing the polymerization to proceed to higher conversions. This suppression of the

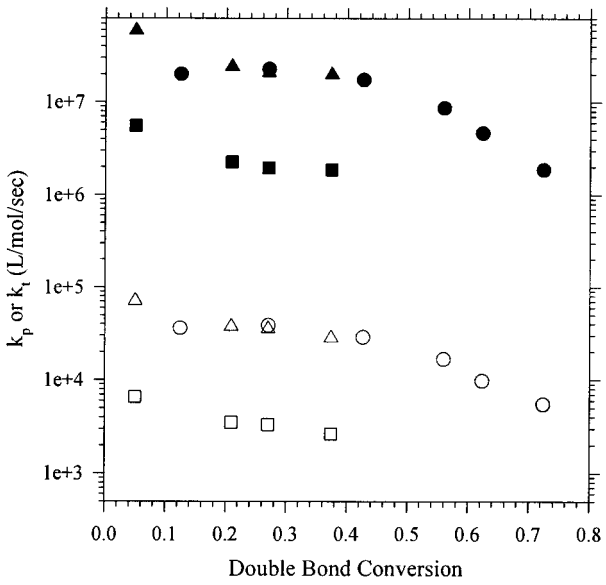

Figure 8. Polymerization kinetic constants, k_p, at 23 °C, smectic C* (○), and 65 °C, isotropic (□), and k_t at 23 °C, smectic C* (●), and 65 °C, isotropic (□), for polymerization of 9% DecA in W82,W7 as shown previously in Figure 3. Additionally, the predicted rate constants, k_p (△) and k_t (▲), for polymerization of 9% DecA in the smectic C* phase is given.

termination reaction is consistent with what has been observed in other polymerizations in and of liquid crystals.[15,20] All in all, however, the rate is predicted quite proficiently by the model.

Further agreement is observed when the predicted values for k_p and k_t are compared with the experimental data as seen in Figure 8. The kinetic constant data from Figure 3 is plotted along with the predicted values calculated by multiplying k_p and k_t by $1/\alpha$ (approximately 10.7). Interestingly, excellent agreement between the calculated and experimental values is observed. Especially at intermediate conversions for both k_p and k_t, there is very little difference between the two sets of values. Again, some deviations are observed at low conversions and at high conversions the heat release is not significant enough to measure accurately the kinetic constants, but the kinetic behavior appears to follow well the predictions made by the model.

Additionally, this model could prove valuable in another sense. Other types of monomer/LC systems exhibit the same type of kinetic behavior. The model could help predict some of the reasons for altered polymerization behavior in systems in which the monomer does not segregate between the smectic layers. Accelerated polymerization rates have been reported for an LC monomer polymerized in a low molar mass smectic LC.[18] This accelerated rate is driven by a kinetic mechanism very similar to that reported here; i.e., both termination and propagation kinetic constants increase significantly in the ordered phase. Segregation of the monomer is evident, but instead of segregating between the layers as for the DecA system, this monomer spans the smectic layers, concentrating the reactive double bonds, but not the entire monomer. Therefore, by examining the increase in the overall polymerization rate and in the propagation and termination rates, this model would be able to give a measure of how much the monomer double bonds are concentrating. This knowledge is important in understanding the formation of the polymer and its consequent effects on the overall performance of polymer/LC composites.

Conclusions

This work presents the photopolymerization behavior and kinetics of a monoacrylate in a liquid crystalline media. Additionally, a model describing this behavior is derived and compared with experimental results. The photopolymerization rate shows a dramatic increase when the monomer is polymerized in the ordered smectic C* phase of the liquid crystal. This rate acceleration is driven by an increase in the propagation rate despite an increase in the termination rate. Segregation of the monomer appears to be responsible for this behavior to some extent as the monomer segregates between the smectic layers of the liquid crystal.

A model describing this behavior in the absence of any diffusion limited reactions has also been developed. The reaction system is characterized by segregation of the polymerization system, thereby increasing the local concentration of reactive species. By analyzing the polymerization reaction for this system in which the monomer segregates between the smectic layers and that all of the initiator can initiate polymerization, the rate will show acceleration relative to an isotropic system equal to the square root of the inverse of the reduced volume, i.e. $(1/\alpha)^{1/2}$. Information about the termination and kinetic constants can also be obtained after analysis of the unsteady state reaction. Thereafter, an increase by the factor $1/\alpha$ in the termination and propagation kinetic constants is also predicted. These predictions show excellent agreement with experimental observations for the polymerization rate and kinetic constants exhibited in the polymerization of the monoacrylate/smectic LC mixtures. In summary, this model accurately predicts the polymerization behavior for certain monomer/LC systems in which the reactive double bonds and initiator segregate into a smaller volume.

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