Photopolymerization of a Semifluorinated Difunctional Liquid Crystalline Monomer in a Smectic Phase

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ABSTRACT: The photoinitiated polymerization of a semifluorinated difunctional monomer, which can exist in both a smectic liquid crystalline phase and an isotropic phase, has been investigated as a function of temperature. Although the maximum rate attained for photoinitiated polymerization in the smectic phase is lower than for polymerization in the isotropic phase, the polymer chain kinetic lifetime is markedly longer in the smectic phase, presumably due to a relatively large decrease in termination rate compared to propagation. The results also suggest that both termination and propagation rate processes are diffusion controlled. By conducting polymerization at a temperature corresponding to the smectic phase of the monomer, it is possible to "lock-in" the order of the smectic phase in the cross-linked network generated.

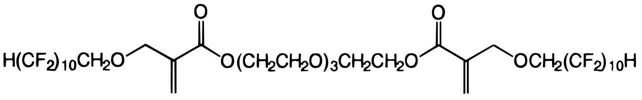
Introduction

There has been considerable interest during the past decade in producing polymers with varying degrees of cross-linking which maintain liquid crystalline type ordering via a variety of methods.[1−35] In many of these cases, photoinitiated polymerization of difunctional mesogenic monomers has been used to generate highly cross-linked networks which preserve to an extent the order characteristics of the monomer.[9−35] Over the years, investigations related to the kinetics of polymerization of both monofunctional and difunctional liquid crystals have been reported which address the effect of mesomorphoric ordering on such factors as polymerization rate, efficiency, and the molecular weights and stereoregularity of the polymers generated. Many of the results of these investigations have been summarized in reviews.[36−39]

It has been demonstrated that semifluorinated molecules characterized by hydrocarbon and perfluorinated $-[CF_2]-$ segments of sufficient length can exhibit structures[40−43] which have been identified as having smectic ordering over certain temperature ranges which depend on the exact nature of the segments.[40,41] The photoinitiated polymerization of such segmented semifluorinated molecules with polymerizable functional groups[42,43] has been reported. In one case, polymerization in the smectic phase of a monofunctional methacrylate was shown to exhibit unusually large polymerization rates compared to polymerization in the isotropic phase.[43] The rate increase was suggested to occur because of a decrease in the termination rate constant in the smectic phase.

In this paper, we extend previous work on the photoinitiated polymerization of semifluorinated monomers in the smectic phase. The goal of this report is twofold. First, we will demonstrate that it is possible to polymerize a difunctional semifluorinated liquid crystalline monomer and retain via a cross-linked network, at least under certain conditions, the smectic order originally exhibited by the monomer prior to polymerization. The second, and most important, goal is to investigate the polymerization kinetics of a sterically hindered monomer in the smectic phase. The semifluorinated difunctional monomer shown below with four ethylene oxide units and two fluorinated ether groups (designated DFLC for reference) has two reactive acrylic groups and is sterically hindered at the radical-forming carbon site. Steric hindrance, combined with the restrictions on mobility imposed by smectic phase organization, might be expected to result in reduction not only of the termination rate, but also of the propagation rate of a free-radical polymerization process.

Kinetic studies for polymerization in both the isotropic and smectic phases of DFLC are reported in this paper. The X-ray diffraction patterns and polarized optical micrographs of the monomer film prior to polymerization and of the cross-linked network resulting from the rapid photoinitiated polymerization process are presented in order to demonstrate the retention, to a certain degree, of mesomorphic-like order in the networks produced.



DFLC

Experimental Section

A description of the synthesis of the difunctional liquid crystalline monomer[44] has been published. The transition temperature of the monomer (DFLC) was first checked by both DSC and an optical microscope equipped with a Mettler FP52 hot stage. DFLC was photopolymerized using a medium-pressure Hg lamp or an excimer laser (XeF) with a 351 nm output in a modified Perkin-Elmer DSC. The chamber of the DSC was purged with nitrogen, although some trace oxygen no doubt remained in the samples. The typical sample size was 2−3 mg with 1 wt % of photoinitiator [2,2-dimethoxy-2-phenylacetophenone (Iragacure 651, Ciba-Geigy)]. The sample was heated to its isotropic temperature and kept for 20 min with continuous nitrogen purging before cooling to the polymerization temperature to remove oxygen in the sample. The medium-pressure mercury (60 cycle ac power supply) lamp was equipped with an electric shutter to control the time of UV exposure. The exotherm of the sample from the DSC was recorded with a Perkin-Elmer chart recorder and simultaneously transformed to digital data by a microvoltmeter interfaced to a computer using an Assyst data collection program. In the pulsed laser initiated polymerization experiments, the laser firing was controlled by the computer with a program which determines the number and interval of laser pulses delivered to the sample. The digital data collected by

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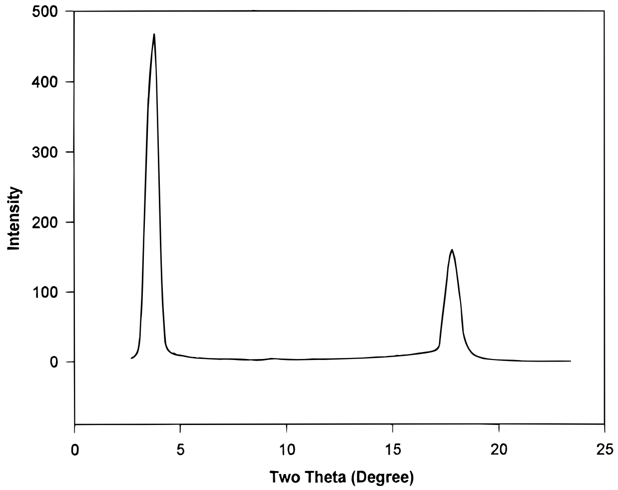

Figure 1. X-ray diffraction pattern of DFLC plotting scattering intensity versus the scattering angle 2θ.

the computer can be used to calculate the exotherm vs time plot, the percent conversion vs time plot, and the ratio of the termination to propagation rate constants, k_t/k_p.[45] X-ray diffraction experiments of the monomer and polymerized samples were performed on an XP 700p Siemens X-ray diffractometer.

Results and Discussion

In order to understand the polymerization kinetics of difunctional monomers which are capable of existing in mesophases, it is imperative that first the monomers be characterized with respect to the general phase type as a function of temperature. Hence, we will first present pertinent data for the difunctional DFLC monomer. We will then describe the polymerization exotherms recorded in response to photoinitiated polymerization using three light exposure systems: a continuous medium-pressure mercury lamp, a pulsed excimer laser (XeF, 350 nm), and a shuttered medium-pressure mercury lamp. Data from each type of experiment, together with observation of exposed and unexposed DFLC monomer via polarized optical light microscopy and X-ray diffraction, will be combined to provide a clear picture of the polymerization behavior in the smectic liquid crystalline phase at relatively low temperatures (below 42 °C).

DFLC Monomer Synthesis and Characterization. The DFLC monomer was synthesized by a method described in ref 44. From DSC heating and cooling scans, as well as direct observation via polarized optical microscopy, a smectic phase was observed at lower temperatures. During the second heating, DFLC was converted from a smectic to an isotropic phase at 52 °C. Upon cooling, the smectic phase was obtained at temperatures below 42 °C. The X-ray diffraction pattern of DFLC monomer at room temperature, where it exists in the liquid crystalline phase, showed strong peak maxima at 2θ scattering angles of 3.60 and 17.85°: these diffraction peaks correspond to 23.80 and 4.95 Å and represent interlayer and intermolecular spacings, respectively. (In some samples of DFLC, a very minor peak at a 2θ value of slightly greater than 9° was found, a hint of which is seen in Figure 1.) Although our characterization clearly shows X-ray diffraction patterns indicative of smectic layering with a relatively sharp intermolecular spacing, we do not speculate on the exact classification of the smectic structure. Certain semifluorinated molecules have been reported to adopt some type of hexagonal or pseudohexagonal packing.[40,41] We do note that the smectic phase of DFLC is quite viscous, thus providing the potential for altering termination, and perhaps even propagation, rates for polymerization of the sterically hindered DFLC monomer. Next, the polymerization results of DFLC will be presented for two temperatures, 40 and 55 °C, at which the monomer is in the smectic and isotropic phases, respectively. The first results presented are for the continuous mercury lamp initiated polymerization.

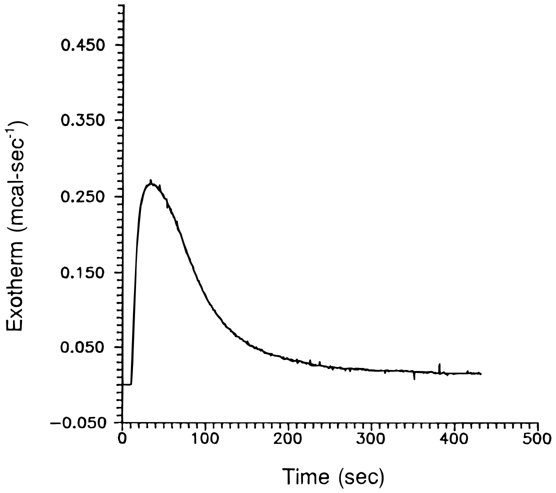

Figure 2. DSC exotherm of DFLC at 40 °C initiated with a medium-pressure mercury lamp (0.24 mcal cm^{-2} s^{-1}).

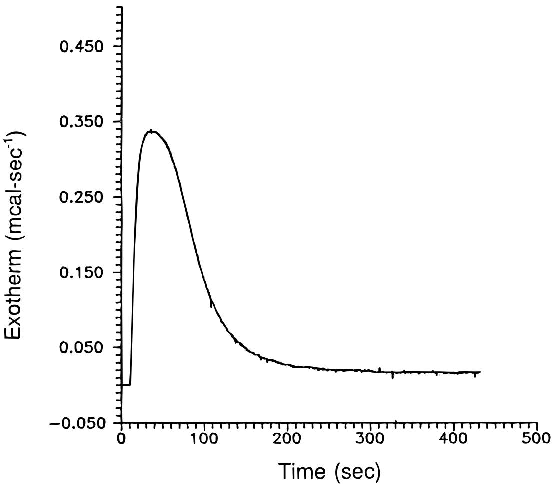

Figure 3. DSC exotherm of DFLC at 55 °C initiated with a medium-pressure mercury lamp (0.24 mcal cm^{-2} s^{-1}).

Photopolymerization of DFLC with a Medium-Pressure Mercury Lamp Source. Figures 2 and 3 show the exotherms recorded for the photoinitiated polymerization of DFLC at 40 and 55 °C with 1% 2,2-dimethoxy-2-phenylacetophenone photoinitiator. The polymerization maximum is attained very early during the conversion process at both temperatures. The maximum rate of polymerization was apparently greater for polymerization at 55 °C than at 40 °C. The DFLC polymerization can best be represented by percent conversion versus exposure time plots in Figures 4 and 5. At 40 °C, the polymerization rate (as reflected by the slope of the percent conversion−time plots) was slower than for polymerization at 55 °C, even though at 40 °C the monomer phase is smectic. These results are different from our previous observations for other smectic monomers which exhibited rate enhancement

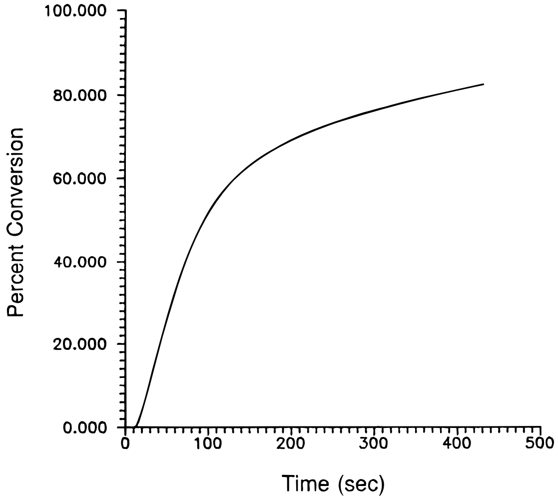

Figure 4. Percent conversion versus time plot of exotherm data in Figure 2.

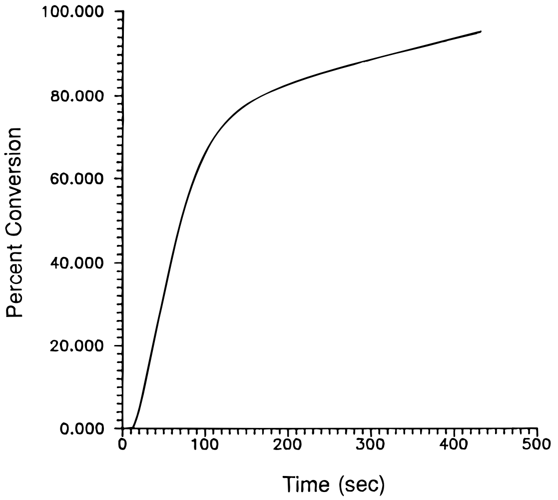

Figure 5. Percent conversion versus time plot of exotherm data in Figure 3.

in smectic phases.[43,46−48] At both temperatures, relatively high conversions were attained.

We next focus on the texture of the network films produced by the photoinitiated polymerization of DFLC at 40 and 55 °C. At 40 °C, the initial texture of the monomer observed by cross-polarized optical microscopy was maintained in the cross-linked polymer network produced by photopolymerization. Furthermore, two X-ray diffraction peaks were found for the network film produced by polymerization at 40 °C at angles corresponding to an intermolecular spacing of ~4.5 Å and an interlayer spacing of 24.5 Å. On the other hand, polymerization conducted at 55 °C from the monomer isotropic phase gave a network that was nonbirefringent (not ordered) by cross-polarized optical microscopy. Hence, we conclude that it is indeed possible to produce a cross-linked network of a semifluorinated difunctional monomer in the smectic mesophase with retention of the basic order present in the monomer mesophase. Moreover, for polymerization conducted from the monomer isotropic phase, no change in medium organization at the temperature employed was found to occur during the course of the polymerization process. That is, polymerization did not generate an ordered network from the isotropic monomer melt.

We next discuss the effect of the cross-linking process on retention of the smectic-like texture of the network observed immediately upon polymerization. The network films, characterized by sharp interlayers spacings of 24.5 Å, were heated to 130 °C, where they remained birefringent. Upon subsequent cooling from 130 °C to room temperature, despite having never reached a clear order−disorder network transition upon heating, the X-ray diffraction pattern was distinctly broader, lower in intensity, and had a peak corresponding to a value of 27.5 Å. The broadening and decrease in intensity of the X-ray diffraction pattern and the shift to a larger nominal interlayer spacing suggest that disordering occurred during the heating/cooling cycle even though no discernible transition was observed. We conclude that the cross-linking is only partially effective in maintaining order upon heating.

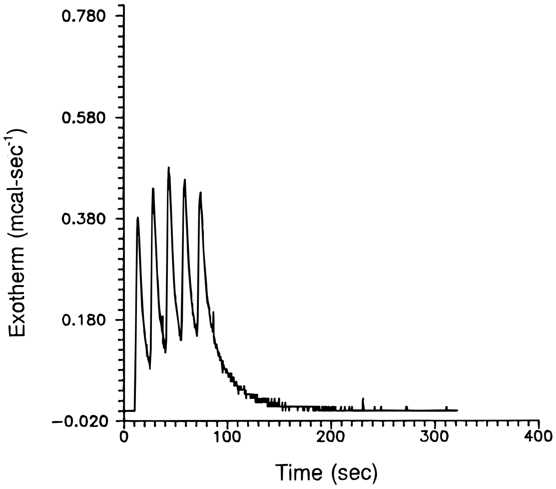

Figure 6. Exotherm curves of DFLC at 40 °C initiated with an excimer laser at 350 nm (0.145 mcal cm^{-2} pulse^{-1}).

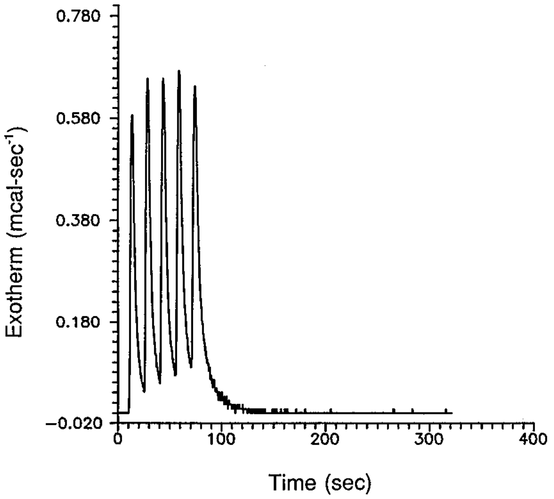

Figure 7. Exotherm curves of DFLC at 55 °C initiated with an excimer laser at 350 nm (0.145 mcal cm^{-2} pulse^{-1}).

Photopolymerization of DFLC with a Pulsed Excimer Laser (λ_{ex} = 351 nm). Figures 6 and 7 show the polymerization exotherms produced as a result of exposure of monomer samples of DFLC (1 wt % photointiator) to 5 pulses from the excimer laser (each pulse approximately 10−15 ns fwhm; pulses spaced 15 s apart; λ_{ex} = 351 nm). At 40 °C, where polymerization occurred in the smectic phase, two observations can be made. First, each pulse at 40 °C (Figure 6) led to attainment of a lower maximum heat evolution rate than at 55 °C (Figure 7). Second, there was still a substantial exotherm from each pulse (after the first pulse) at 40 °C prior to firing of the next pulse. This is

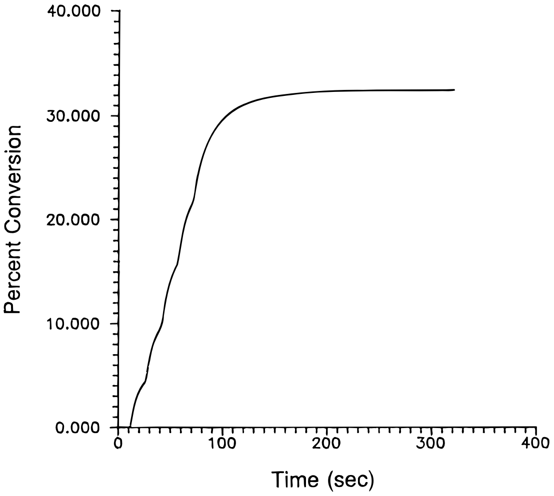

Figure 8. Percent conversion versus time plot of exotherm data in Figure 6.

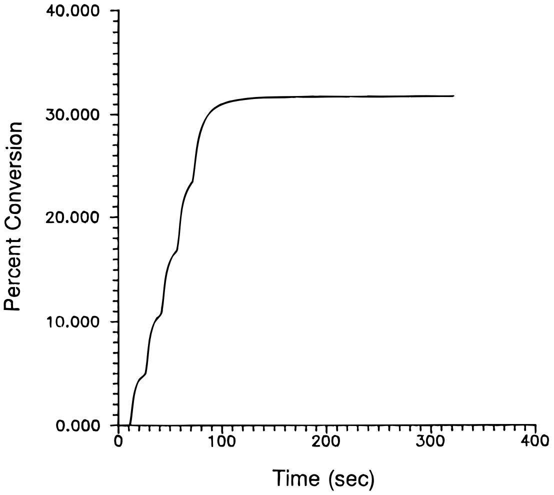

Figure 9. Percent conversion versus time plot of exotherm data in Figure 7.

apparently a result of a reduced termination to propagation rate constant ratio (k_t/k_p) at 40 °C (compared to 55 °C), which results in a longer lived polymerization process. Figures 8 and 9 display the resultant percent conversion versus time plots derived from the integrated data in Figures 6 and 7. As seen in Figure 8, at 40 °C the polymerization continued for well over 1 min after pulse 5 was delivered. At 55 °C, the polymerization exotherm diminished rapidly (Figure 9) after the last laser pulse was delivered to the sample (this is also seen by direct comparison of the exotherm curves in Figures 6 and 7). Additional analysis of the long-lived polymerization of DFLC at 40 °C is provided by the exotherm decay kinetics in the next section.

Photopolymerization of DFLC with a Shuttered Mercury Lamp Source. In order to provide a more detailed observation of the difference between polymerization at 40 and 55 °C, shuttered light from a medium-pressure mercury lamp can be used to generate exotherm decay curves. Analysis of the resultant non-steady-state exotherm can yield direct information about the relationship of the termination and propagation rate constants. In this set of experiments, samples in the DSC were exposed to the shuttered output of a medium-pressure mercury lamp for approximately 1.2 s. The subsequent "decay" of the exotherm to the baseline was utilized to deduce relative rate constants.

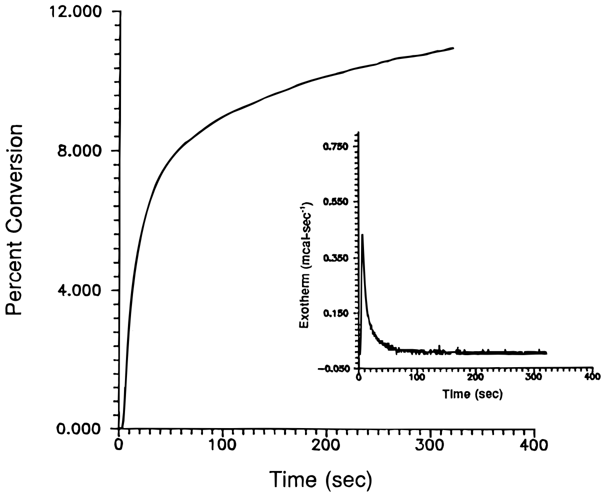

Figure 10. Percent conversion versus time plot of DFLC at 40 °C initiated with a shuttered (1.21 s) mercury lamp (0.345 mcal cm^{-2}); exotherm curves are shown in the inset.

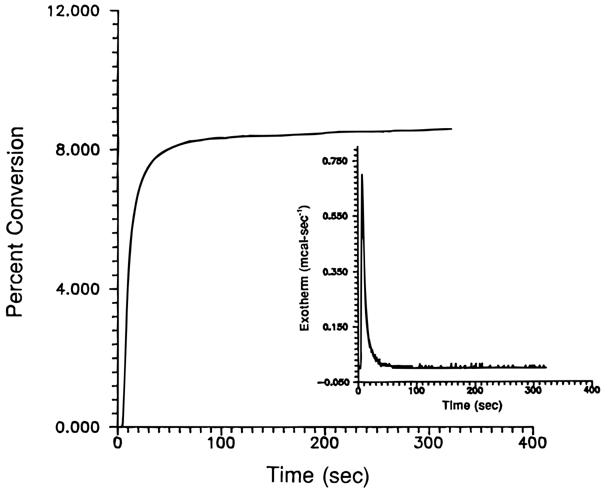

Figure 11. Percent conversion versus time plot of DFLC at 55 °C initiated with a shuttered (1.23 s) mercury lamp (0.345 mcal cm^{-2}); exotherm curves are shown in the inset.

Figures 10 and 11 show the percent conversion versus time plots at 40 and 55 °C, respectively. The actual exotherms recorded are shown in the insets in Figures 10 and 11. The first item to note is the very rapid decay of the sample polymerized at 55 °C in the isotropic phase as exemplified by the large slope of the percent conversion versus time plot in Figure 11. A conversion of approximately 8.5% was attained rapidly, essentially within the time response of the instrument. In contrast to the results at 55 °C, the exotherm decay at 40 °C in Figure 10 shows that the polymerization continued for a long period (up to at least 300 s) after the lamp shutter was closed.

Schultz and Tryson[45] have analyzed exotherm decay processes according to eq 1,

$$\frac{[\mathrm{M}]}{-\mathrm{d}[\mathrm{M}]/\mathrm{d}t} = \frac{k_t}{k_p}t + \frac{[\mathrm{M}]_0}{(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_0} \tag{1}$$

where $[\mathrm{M}]_0$ is the monomer concentration at the instant that the light is abruptly terminated (via a shutter), $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t$ is the rate loss of monomer at time "t" after the shutter is closed, $(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)_0$ is the rate loss of monomer at the time that the shutter is closed, and k_t/k_p is the ratio of the termination and propagation rate constants for the free-radical polymerization process. From plots of [M]/(−d[M]/d*t*) vs time, a value of 37 for the ratio of k_t/k_p at 40 °C can readily be obtained from the slope for a conversion of 10−12%, while a lower limit value for k_t/k_p of ∼400 is obtained at 55 °C (isotropic phase) for a conversion of ∼9−11%.

Our previous results for polymerization of a cholesterol-bearing methacrylate monofunctional monomer in a smectic phase (classified as an A phase) showed that a decrease in the k_t/k_p ratio was accompanied by faster, not slower, polymerization rates[43,46−48] as observed by DFLC. By kinetic analysis of the polymerization process of the monofunctional cholesteric methacrylate monomers in the smectic phase, the increase in the rate of polymerization was shown to result from an over two order magnitude decrease in k_t. The smectic phase had no measurable effect on k_p.[48] In the case of DFLC, the low value of k_t/k_p ratio for polymerization in the smectic phase (40 °C) at low conversions is similar to that found for the monomeric cholesteric methacrylate in the smectic phase.[48] Now we must address the critical question: Why do we observe a slower polymerization rate in the smectic phase of DFLC? [A similar drop in the polymerization rate in the smectic phase of a monofunctional semifluorinated analog of DFLC at room temperature has been observed.] We suggest the possibility that diffusion-controlled propagation and termination processes occur for DFLC in the smectic phase at 40 °C even at low conversions, with a concomitant decrease in the propagation rate and hence lower overall polymerization rate. This would require that both k_t and k_p decrease in the smectic phase in such proportion that the overall polymerization rate decreases. Such is clearly not the case for nonsterically hindered acrylate and methacrylate liquid crystalline monomers investigated in our laboratory previously[43,46−48] which exhibit rate acceleration, not a decrease in rate, in smectic phases. In the present case, not only is diffusion no doubt greatly reduced in the smectic phase, but also DFLC is highly hindered at the radical-forming site. This structural effect might well contribute to the decrease in the propagation process. Finally, at this time, while we do not have evidence for reaction diffusion, which couples the termination and propagation processes in the photointiated polymerization of isotropic difunctional monomers,[49,50] there is no reason to believe that such a process would not be operative in polymerization of difunctional liquid crystalline monomers.

Conclusions

In this paper, the photoinitiated polymerization of a difunctional semifluorinated liquid crystalline monomer was investigated via exotherm measurements in both isotropic and smectic phases. In answering questions dealing with retention of mesophase ordering upon generation of cross-linked networks from liquid crystalline phases and the alteration of polymerization kinetics, two distinct observations were made.

1. It is indeed possible to generate cross-linked networks which retain the smectic ordering of the difunctional monomer precursor.

2. The kinetics of polymerization in the smectic phase of the difunctional monomer were characterized by a long-lived polymer radical chain at low conversion as well as a concomitant lower overall maximum polymerization rate.

We speculate that for the DFLC difunctional monomer, which is the focus of this study, the termination and propagation rate constants may both be diffusion controlled in the smectic phase, resulting in the dual lowering of k_t and k_p. The smectic phase is more viscous than the isotropic phase and, combined with the steric hindrance at the carbon radical propagation center, might be expected to contribute to establishment of a diffusion-controlled propagation process. Results for the monofunctional analog of DFLC will be presented in a future paper.

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