Efficient polymerization of a semi-fluorinated liquid crystalline methacrylate

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Polymerization of a liquid crystalline semi-fluorinated methacrylate monomer at a temperature which maintains a highly ordered smectic texture is extremely efficient. The efficiency in the isotropic phase is much lower. When polymerization is conducted in the isotropic phase at only a few degrees above its clearing temperature, a change to a low-order liquid crystal with smectic texture occurs during polymerization: the change is accompanied by an abrupt increase in the polymerization rate. At higher temperatures in the isotropic phase no change in texture occurs during polymerization, and the quantum efficiency of polymerization is two orders of magnitude lower than in the liquid crystalline medium. The polymerization efficiency for the semi-fluorinated methacrylate in the highly ordered smectic is greater than for the lower order of a cholesterol-bearing liquid crystalline methacrylate, or an isotropic trifunctional acrylate.

(Keywords: polymerization; methacrylate; liquid crystalline)

INTRODUCTION

During the past decade there have been a number of papers[1-9] which have highlighted the salient features of amphiphilic molecules composed of units of fluorocarbon and hydrocarbon segments. In a recent publication it has been clearly demonstrated[9] that such fluorocarbon/hydrocarbon molecules of the general formula $F(CH_2)_n(CH_2)_nH$ are characterized by tilted or modified smectic B phases, which are referred to as smectic G or J phases.

A paper by Höpken *et al.*[7] described the photopolymerization of gels composed of methacrylate functionalized semi-fluorinated moieties, as depicted by the generalized structure below.

$$F(CF_2)_n(CH_2)_m\text{-}OCO\text{-}(CH_3)C{=}CH_2$$

It was reported that polymerization of a 7.6 wt% semi-fluorinated methacrylate ($n=12$, $m=4$) solution in toluene resulted in the formation of the expected polymer. A similar monomer ($n=12$, $m=6$) yielded a polymer which retained the structure of the crystallite network characteristic of the monomer in toluene. Isolation of the polymer allowed analysis under a cross-polarized microscope: cooling the polymer ($n=12$, $m=6$) from the melt resulted in a birefringent film, presumably liquid crystalline.

Bearing this description of semi-fluorinated systems in mind, we turn to a brief discussion of polymerization of neat monomers which can assume liquid crystalline textures. Although Amerik[10] reported that polymerization of *p*-methacryloxybenzoic acid in the liquid crystalline medium generated by solvation in *p*-acetyloxybenzoic acid yielded polymers with molecular weights greater than those obtained by polymerization in isotropic media, subsequent reports produced mixed signals with respect to the effect of the liquid crystalline medium on polymerization rates and polymer molecular weight distributions. In fact, in their review article on the effect of liquid crystalline organization on polymerization, Barrall and Johnson[11] conclude that, due to media changes during polymerization of liquid crystalline monomers, the kinetics are very difficult to measure accurately and should be critically evaluated for each individual system. Other reports in the literature seem to echo this theme (see reviews in references 11 and 12 and the literature examples cited therein). Recent reports by Broer and coworkers[13-17] present examples of very careful polymerization studies of liquid crystalline monomers. We note that Broer used conventional mono- and difunctional methacrylates with phenyl benzoate type mesogenic units, which are characterized by high width-to-breadth ratios that impart liquid crystalline properties, i.e. lower-order smectic phases.

Herein we report the investigation of a highly ordered, viscous liquid crystalline monomer formed by groups composed of a semi-fluorinated mesogen. Our results will clearly demonstrate that such an ordered medium results in unusually large polymerization rates and high polymerization efficiency in comparison to other systems.

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EXPERIMENTAL

The cholesteric monomer synthesis has been described[18,19]. 1-Perfluorododecyl-ω-decanol was synthesized following the method reported by Höpken *et al.*[7]. The methacrylate was made by reacting the alcohol with methacryloyl chloride in THF at 50°C for 12 h. After recrystallization from ethanol and $CHCl_3$, the yield was 35%. ^1H n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.3 (broad s, 12 protons, $-CF_2-CH_2-CH_2-(C\underline{H}_2)_6-$); 1.53–1.7 (m, 4 protons, $-O-CH_2-C\underline{H}_2-$ and $-CF_2-CH_2-C\underline{H}_2-$); 1.95 (s, 3 protons, $CH_2{=}C(CO)-C\underline{H}_3$); 2.0 (m, 2 protons, $-CF_2-C\underline{H}_2-$); 4.15 (t, 2 protons, $-O-C\underline{H}_2-$); 5.53 (s, 1 proton, $HC\underline{H}{=}C(CH_3)$; 6.1 (s, 1 proton, $H\underline{C}\underline{H}{=}C(CH_3)$).

The photopolymerization exotherm was recorded with a modified Perkin Elmer DSC-2. The solution of the monomer with 1 wt% photoinitiator (2,2-dimethoxy 2-phenylacetophenone) in 1,1,2-trichlorotrifluoroethane was injected into an indented d.s.c. pan, and then the solvent was evaporated overnight leaving the monomer-initiator film (2.5 mg, thickness ~200 μm). All samples were purged with nitrogen for 5 min before polymerization. The enthalpy of polymerization of F12H10MA was estimated as 15.5 kcal mol^{-1}, by assuming 95% conversion after exposure to 30 laser pulses, and then calculating the heat of conversion from the total area under the exotherm curve. The heat of polymerization of all other methacrylates and acrylates were taken as the standard values per functional group of 13.7 kcal mol^{-1} and 19.1 kcal, respectively.

A Questek model 2460 excimer laser (XeF, $\lambda = 351$ nm) was used for the laser-initiated polymerization studies. A medium-pressure mercury lamp (Canrad Hanovia) was used as the steady-state u.v. source. The thermal characterization was conducted with a DuPont DSC 910 and accompanying 9900 thermal analyser (scanning rate 10°C min^{-1}). A polarizing light microscope (Nikon Optiphot-Pol) equipped with a Mettler FP 52 hot stage was used for cross-polarized optical macroscopic measurements.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

Synthesis of the semi-fluorinated monomer (designated F12H10MA), which is the focus of this investigation, is essentially identical to that reported by Höpken *et al.*[7]. *Figure 1a* shows the d.s.c. (differential scanning calorimetry) scans of the first cooling and second heating of pure F12H10MA. The initial heating (not shown) of freshly cast F12H10MA shows a crystal–crystal transition which is not recovered upon cooling from the melt. The cooling curve in *Figure 1a* shows a relatively large transition at 88°C to what can be inferred from cross-polarized optical microscopy as a smectic liquid crystalline phase: the sample does flow below 88°C. Upon further cooling, the smectic phase is converted to a crystalline phase at 49°C which persists upon cooling to room temperature. The liquid crystalline phase below 88°C (shown in *Figure 3a*) is quite characteristic of a 'smectic B-like' phase having a mosaic texture with small lancets. The unusually large exotherm for the S→I transition is consistent with the results reported by Viney *et al.*[9] for perfluorodecyl decane and appears to be ubiquitous to semi-fluorinated liquid crystals. The second heating cycle shows a transition to a smectic phase at 60°C identical to that formed below 88°C on the first cooling cycle. Further heating results in clearing to the isotropic phase at 93°C. Although not shown, the second cooling results in a smectic phase at 88°C which persists to 49°C, whence crystallization occurs. The results from the d.s.c. and optical microscopy investigation of F12H10MA are shown in *Figure 1b* for quick reference. The transitions are similar to those reported in reference 7. The smectic phase is simply referred to by the letter S. The highly ordered smectic phase observed on heating and cooling are identical; probably the smectic B or one of the variants referred to previously[9]. We note that the transition temperatures are slightly lower for F12H10MA with 1 wt% photoinitiator. The interested reader is referred to reference 9 for a detailed discussion of the phase characterization of

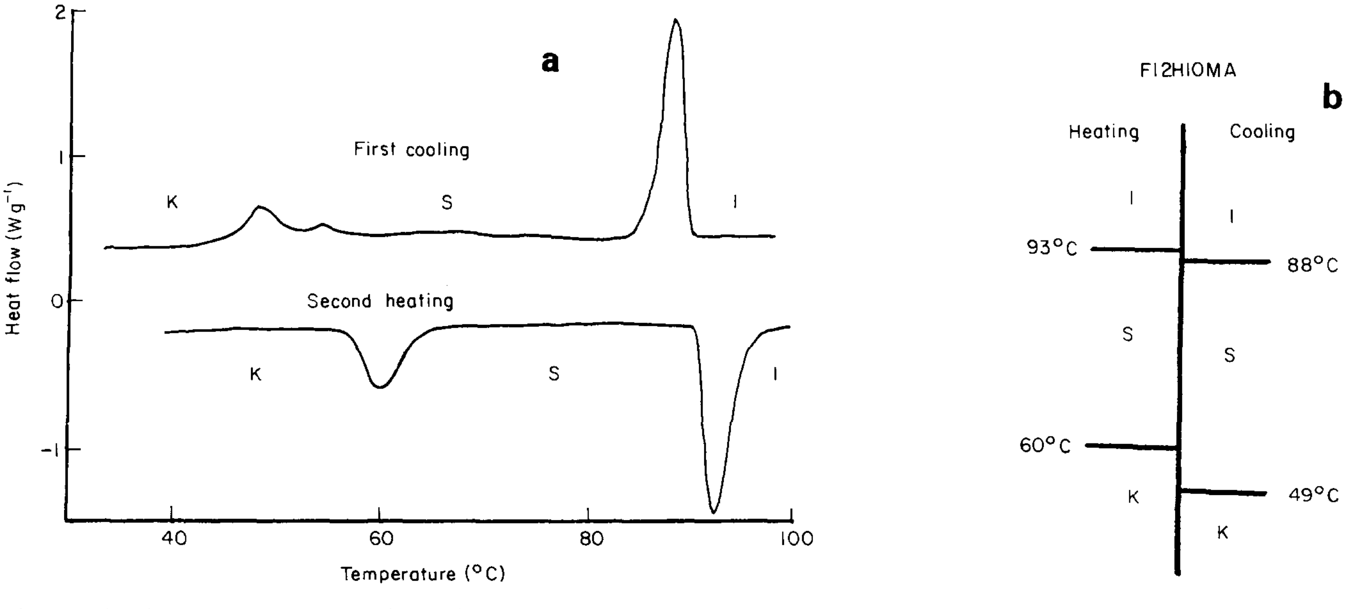


Figure 1 (a) First d.s.c. cooling cycle and second d.s.c. heating cycle for F12H10MA and (b) pictorial of d.s.c./optical microscopic examination of F12H10MA (K = crystalline; S = smectic; I = isotropic phase)

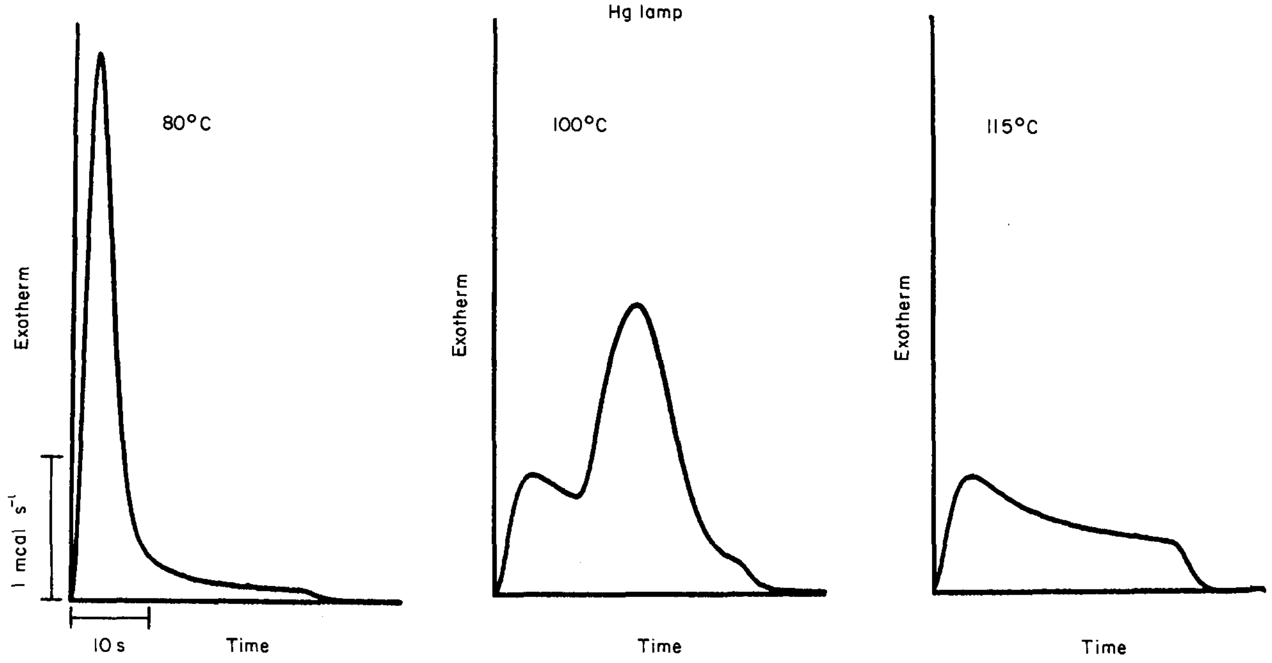


Figure 2 Exotherms of F12H10MA initiated with unfiltered medium-pressure mercury lamp at (a) 80°C, (b) 100°C and (c) 115°C

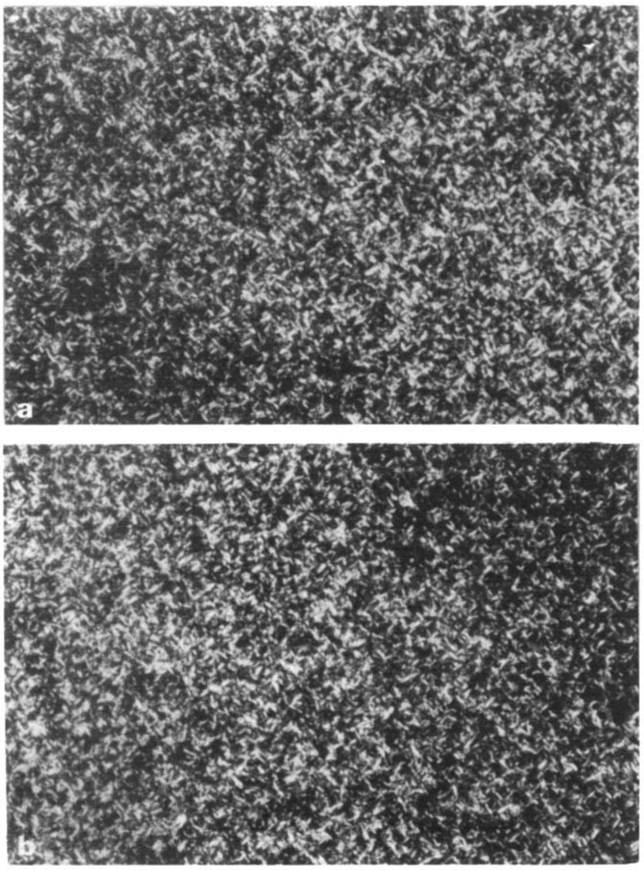


Figure 3 Micrographs of F12H10MA at 80°C (a) before and (b) after polymerization by exposure to the output of a medium-pressure mercury lamp

a similar semi-fluorinated species. For our purposes, we assume that the smectic phase of F12H10MA is a highly ordered modified 'smectic B-type' phase. We then ask the question of how such a highly ordered medium effects the polymerization of the methacrylate functionality attached to the semi-fluorinated mesogen.

Photopolymerization of F12H10MA

Figure 2 shows representative exotherms for the photoinitiated polymerization (mercury lamp at 10.19 mJ s^{-1} cm^{-2}) of F12H10MA (1 wt% α, α-dimethoxy 2-phenylacetophenone) at 80°C (monomer smectic), 100°C (monomer isotropic), and 115°C (monomer isotropic). The exotherm curves, which were recorded on a modified DSC-2B, are quite different depending on the temperature of the polymerization process. At 80°C the exotherm rate, which is linearly related to the polymerization rate, reaches a large maximum (*Figure 2a*) at a relatively short exposure time. *Figure 3* shows that the cross-polarized optical micrograph of F12H10MA at 80°C is identical prior to (*Figure 3a*) and after (*Figure 3b*) exposure to the unfiltered output of a medium-pressure mercury lamp for 15 s to ensure high conversion of F12H10MA to polymer. It is apparent that the exotherm in *Figure 2a* represents polymerization of F12H10MA in a medium in which the highly ordered texture (as determined by polarized microscopy) is maintained throughout the polymerization. At this time we cannot rule out the possibility of microphase separation at 80°C on a scale not observable by our current analysis technique. A cross-polarized optical micrograph of F12H10MA at 100°C (*Figure 4*) reveals the presence of a birefringent sandy-like medium which is formed only after exposure of the monomer to the mercury lamp: the medium generated at 100°C is probably not as ordered (grainy structure by optical microscopy – most likely phase separated) as at 80°C. The results of the optical micrograph in *Figure 4* parallel the abrupt increase in the polymerization exotherm at 100°C (*Figure 2b*). We have shown in previous investigations of other liquid crystalline monomers that an increase in the polymerization rate occurs when the medium converts from a purely isotropic to a liquid crystalline medium during the course of polymerization. The results at 100°C can be contrasted to those in *Figure 2c*, which depicts a very low exotherm curve at 115°C with no abrupt changes

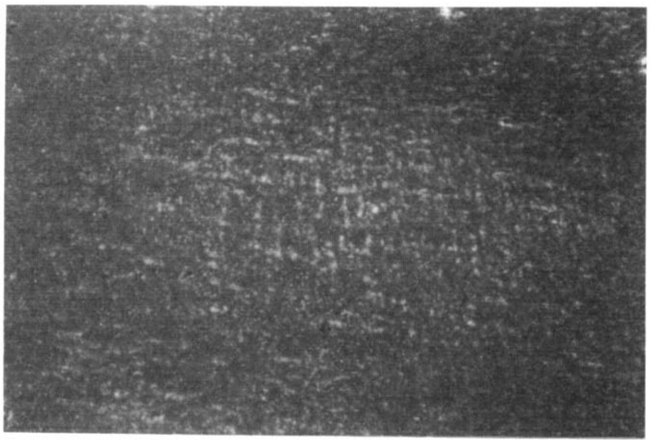


Figure 4 Micrograph of F12H10MA at 100°C after polymerization by exposure to a medium-pressure mercury lamp

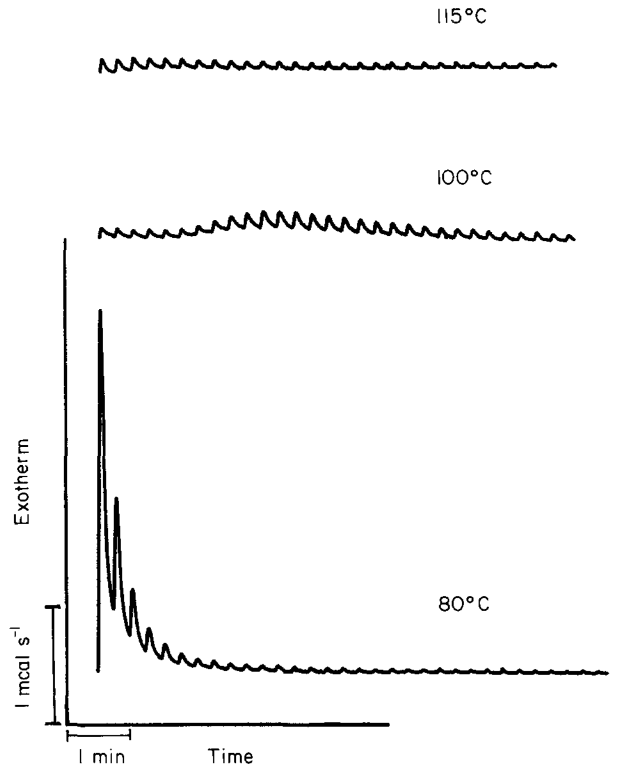


Figure 5 Single-pulse exotherms of F12H10MA at (a) 80°C, (b) 100°C, and (c) 115°C initiated with pulsed excimer laser ($\lambda_{ex}=351$ nm; pulses 15 s apart; 4.17 mJ cm^{-2} pulse^{-1})

in the polymerization rate and no corresponding change in the order of the isotropic medium during polymerization (at least to the degree of polymerization attained).

Although evidence for the significant effect of the smectic B texture on the polymerization of F12H10MA is shown in *Figure 2*, a true sense of the magnitude of the effect at 80°C can best be illustrated by resorting to measurement of exotherms initiated by single laser pulses (~10 ns fwhm) spaced 15 s apart. *Figure 5* then shows exotherms produced by 30 consecutive excimer laser pulses ($\lambda_{ex}=351$ nm) for F12H10MA (1 wt% photoinitiator) at 80°C, 100°C, and 115°C. The differences in the first three to five laser pulses are considerable, especially if one keeps in mind that the same light intensity (and thus an identical number of photons) is injected into each sample. The percentage conversion on the first pulse alone is over 40% at 80°C compared to less than 1% at 100°C or 115°C! (We note that at this time we cannot rule out the possibility that the polymerization efficiency at 80°C may be altered somewhat by a change in the initiation rate in the mesophase.)

Figure 6 is a plot of the cumulative percentage conversion *versus* time for the exotherm pulses in *Figure 5*. From both the results in *Figures 5* and *6* it is apparent that polymerization at 80°C results in a rapid buildup in percentage conversion at short times (a few pulses) followed by only relatively small changes in conversion with additional pulses. At 115°C, the polymerization rate is very low and results in only a very small percentage conversion of monomer to polymer. At least for the number of pulses injected into the sample (30 total pulses), no significant change in the medium (by cross-polarized optical microscopy) occurs at 115°C. In contrast, at 100°C, instead of levelling off as at 115°C, a marked increase in efficiency occurs at about 8–10% conversion. This 'S'-type cumulative conversion *versus* time plot at 100°C is characteristic of rate acceleration accompanying abrupt changes in the polymerization medium. We have shown in *Figure 4* that at 100°C, F12H10MA monomer converts to a birefringent liquid crystalline medium upon polymerization. Thus, there is a correlation between the increase in the cumulative plot in *Figure 6* and the change from an isotropic to a liquid crystalline medium. This is also seen from the steady-state (continuous output mercury lamp) exotherm curves in *Figure 5b*, as discussed previously.

A quantitative comparison of the efficiency of polymerization at 80°C and 100°C can be made by calculating polymerization quantum yields at low conversion (less than 5% in both cases) upon exposure to a filtered medium (366 nm) medium-pressure mercury lamp which is shuttered to allow a limited total photon

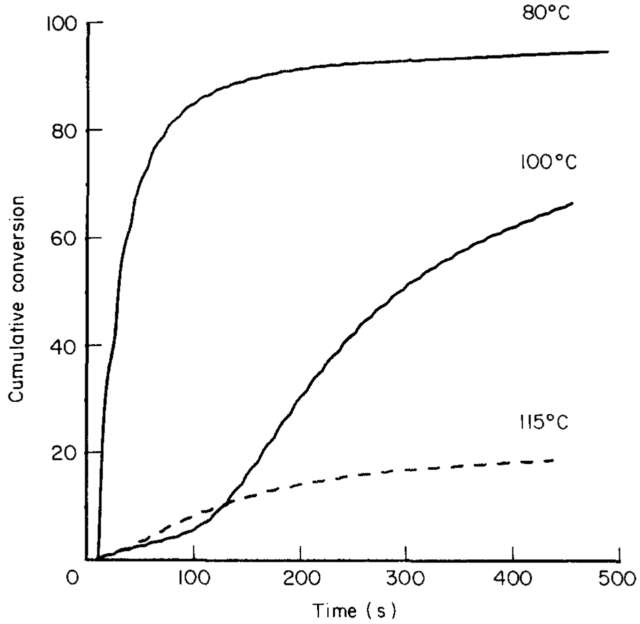


Figure 6 Cumulative percentage conversion *versus* time for single-pulse exotherms in *Figure 5*

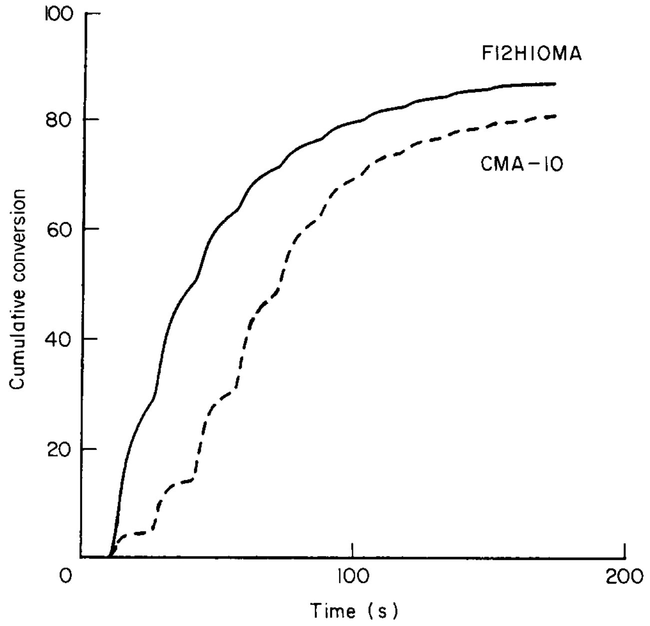


Figure 7 Cumulative percentage conversion *versus* time plots for F12H10MA and CMA-10 (λ_{ex} = 351 nm; pulses 15 s apart; 1.19 mJ cm^{-2} pulse^{-1}) generated with pulsed excimer laser

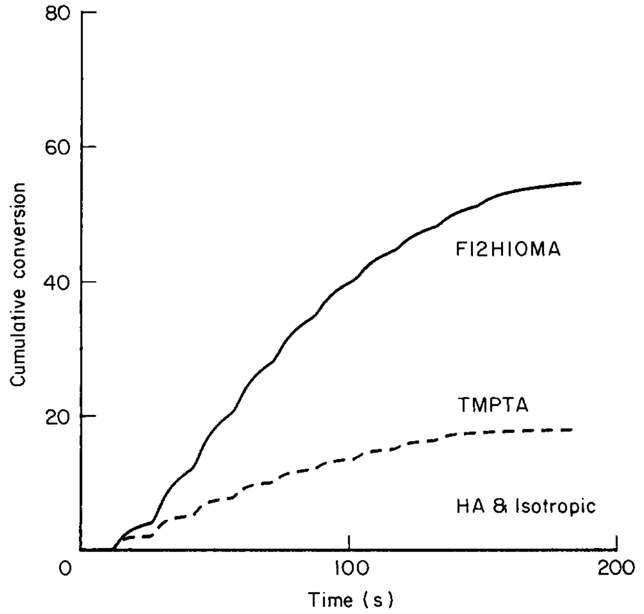


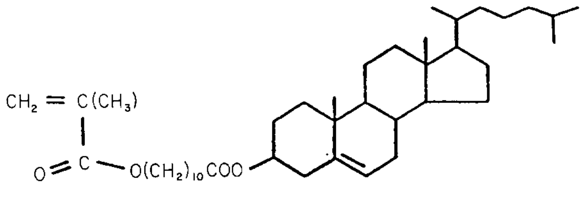
Figure 8 Cumulative percentage conversion *versus* time plots for F12H10MA at 80°C and 100°C, TMPTA, and HA (λ_{ex} = 351 nm; pulses 15 s apart; 0.11 mJ cm^{-2} pulse^{-1}) generated with pulsed excimer laser

dose to fall on the sample. The exotherms generated by the calibrated dose of photons have been analysed to determine the moles of F12H10MA monomer converted to polymer. By knowing the number of moles of monomer converted and the moles of photons actually absorbed by the photo-initiator in the sample (sample has an area of 0.126 cm^2 and is approximately 200 μm thick as defined by the dimensions of the indented sample pan) the quantum efficiencies of the photopolymerization at each temperature were estimated as about 200 (100°C) and 19 000 (80°C). We note that the error at 80°C is largest since, among other things, we were not able to take into account quantitatively light scattering which may occur.

As expected from our previous discussion of the steady-state (*Figure 2*) and pulsed laser exotherms (*Figure 5*), the quantum efficiency for polymerization at 80°C is about a hundred times higher than at 100°C. This is a result of the severe limitation on the termination process upon polymerization in the liquid crystalline system at 80°C.

Finally, we should note that the polymers formed by polymerization of F12H10MA appear to have severely limited solubility in organic solvents, even fluorocarbon solvents. This prohibits molecular weight measurements. However, we can speculate that the polymer formed at 80°C has high molecular weight and relatively low crosslink density (the monomer is monofunctional) since it readily flows above its clearing temperature at 125°C.

In order to assess the efficiency for polymerization of the semi-fluorinated monomer we ask the question, how do the polymerization exotherms for F12H10MA compare to those of other systems? Three monomeric acrylates/methacrylates were chosen for investigation. Results in *Figure 7* compare the cumulative percentage conversion *versus* time plots for another liquid crystalline monomer. This liquid crystalline monomer, designated CMA-10 and shown pictorially below, has a cholesteryl group attached to a methacrylate functionality via a methylene spacer group and has been described previously[18].



CMA-10

The results in *Figure 7* generated using the laser output at 351 nm (1.19 mJ cm^{-2} pulse^{-1}) clearly demonstrate the efficiency of polymerization of F12H10MA in the highly ordered smectic phase at 80°C compared to polymerization of CMA-10 at 45°C (obtained upon cooling) which has been shown is smectic upon cooling from the melt[20]. CMA-10 was chosen for comparison with F12H10MA since it apparently maintains a lower-order smectic-type texture (probably A) throughout the polymerization process at 45°C.

The results in *Figure 8* are perhaps even more revealing since they provide a direct comparison between the efficiency for polymerization of F12H10MA and of two isotropic monomers – hexyl acrylate (HA) and trimethylolpropane triacrylate (TMPTA). The exotherms for F12H10MA at 80°C are larger than for TMPTA at 50°C, which is trifunctional, an acrylate, and thus exhibits an unusually rapid, efficient polymerization process due to extensive crosslinking at low conversions. Under the conditions employed, i.e. the low laser pulse intensity, the percentage conversions attained by HA, or F12H10MA at 100°C in the isotropic phase, are so low that they do not even appear as a distinct curve on the scale used in *Figure 8*. Thus, as seen in *Figure 8*, a highly ordered smectic medium provides for efficient, rapid polymerization of F12H10MA. We project that the efficient polymerization in these liquid crystalline systems is due in large part to a reduction in the termination rate process: this will be considered further in future work.

CONCLUSION

In this report the role of a highly ordered (smectic B type) mesophase in the polymerization of a semi-fluorinated methacrylate (F12H10MA) has been explored. Unlike other liquid crystalline monomers this monomer has no 'classical' mesogenic moieties such as cholesteryl, phenylbenzoate, or stilbene which possess high width-to-breadth ratios. Nonetheless, it affords a unique medium for rapid and efficient polymerization. Compared to other systems investigated in our lab where an increase in efficiency by (at most) a factor of only 4 or 5 is observed, the smectic B-type organization has a drastic effect on the efficiency. Specific results from this investigation are summarized below:

1. Polymerization of F12H10MA at 80°C in the smectic medium results in rapid production of a high molecular weight polymer.
2. Polymerization of F12H10MA at 100°C in an isotropic medium is relatively inefficient. A change occurs at 100°C to a liquid crystalline medium with some moderate rate enhancement.
3. Polymerization of F12H10MA at 115°C in the isotropic phase is inefficient.
4. Polymerization of F12H10MA is more efficient than another lower-order smectic monofunctional liquid crystalline monomer and two typical isotropic monomers (one monofunctional and the other trifunctional).

In general, we speculate that liquid crystalline media can exert a particularly marked influence on the termination rate process, i.e. termination in a liquid crystalline medium is decreased as has been previously suggested[14,21]. One could, upon first thought, argue that the propagation in a liquid crystalline system might be increased via ordering. However, there is a decrease in diffusion rate which accompanies the order in liquid crystalline media, and thus it may well be that the propagation rate in a liquid crystalline medium experiences little or no increase in comparison to an isotropic medium. It is likely that propagation is even reduced, possibly significantly, in an ordered liquid crystalline system. While at this point we cannot present a definite argument separating the effect of propagation and termination processes, we favour the explanation of a severely hindered termination process as being responsible for the reported enhancement in efficiency.

Future work will involve exploration of other critical issues involving photo-initiated polymerization of various liquid crystalline monomers, including tacticity, structural effects of monomer on efficiency and rate, and the effect of ordering of monomers via electrical and magnetic fields on the polymerization rate. We are also currently attempting to calculate propagation and termination rate constants as well as initiation rates during polymerization of several liquid crystalline systems. In addition, quantitation of changes in phase composition, ordering, and possible microphase separation, and the subsequent consequences of such changes are being explored to provide a clearer description of polymerization rates observed for several liquid crystalline systems, including CMA-10 and F12H10MA.

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