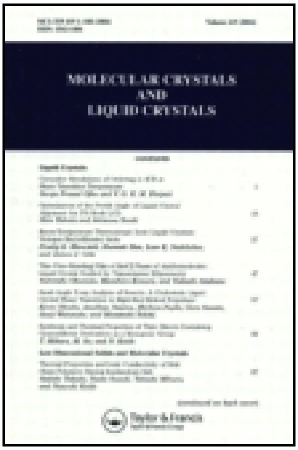

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Photopolymerization of a Liquid Crystalline Monomer

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PHOTOPOLYMERIZATION OF A LIQUID CRYSTALLINE MONOMER

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Abstract Photopolymerization of a liquid crystalline methacrylate monomer containing a cholesteryl moiety was conducted in different phase states of the monomer. The polymerization rate, followed with a modified differential scanning calorimeter, was highest in the cholesteric (Ch) phase and least in the crystalline (K) state. Apparently the polymerization rate depends both on the ordering and the mobility of the monomer.

INTRODUCTION

The vast majority of polymerization studies reported in the literature have been conducted on either neat amorphous monomer liquids or on non-mesomorphic monomers in isotropic solvents. There are notable exceptions dealing with the polymerization of mesomorphic monomers or with non-mesomorphic monomers in mesomorphic media. Several excellent reviews have been written which summarize the reported studies on free radical polymerization kinetics of liquid crystalline monomers and non-mesomorphic monomers in liquid crystalline media to which the reader is referred.[1-3] An examination of previous studies of polymerization in liquid crystalline media leads to the conclusion that two basic properties of liquid crystalline materials may contribute to polymerization kinetics of liquid crystalline monomers. First, and probably the most readily addressable, is the ordering effect in liquid crystalline media. This might provide a unique alignment of polymerizable monomers which could alter the polymerization kinetics, affecting both propagation and termination processes. Second, liquid crystalline systems by their very nature have anisotropic mobility and diffusion. This could well lead to significant changes in the propagation and termination kinetics which, subject to the particular controlling factors in the polymerization process, might be critically dependent on the specific nature of the mesophase. For example, as pointed out by Barrall and Johnson,[2] the nematic and cholesteric mesophases allow two degrees of translational motion compared to only one for smectic phases. A recent study[4] of siloxane side chain liquid crystalline polymers has again emphasized the anisotropic nature of diffusion processes parallel and perpendicular to the nematic director in such systems. Thus, while mesomorphic monomers might be expected to provide some favorable alignment for enhancement of polymerization rates, their anisotropic mobility (one component greater than the isotropic; the other component less than the isotropic analogue) must also be taken into account. Perhaps it is these competing factors (ordering of monomers versus restriction or enhancement of monomer mobility) which prohibits a general statement on the effect of liquid crystalline order on free radical polymerization kinetics and accounts for the variance in results presented in the literature.

This paper reports our initial results for the photopolymerization of a methacrylate monomer with a cholesteryl moiety attached via a decoupling spacer group. Depending upon the detailed thermal treatment of the monomer, the polymerization can be studied in either the crystalline, smectic, cholesteric, or isotropic phase. This allows the presentation of kinetic results for photopolymerization of a single monomer in a variety of phases and thus provides direct information on the ordering and mobility factors as they relate to the polymerization rate.

EXPERIMENTAL

Materials

Ethanol-free chloroform was prepared by washing reagent grade chloroform 3 to 4 times with distilled water, drying over anhydrous $CaCl_2$ and then distilling. Cholesterol was recrystallized from ethyl acetate. The acid chloride, 11-bromoundecanoyl chloride, was purchased from Alfa and used as received. Potassium methacrylate was prepared as described by Shannon.[5]

Synthesis

Synthesis of the monomer has been described by Shannon[5] and was repeated here with minor changes.

DSC Analysis of Monomer Transitions

Thermal transitions were recorded on a DuPont 9900 (910 DSC) thermal analyzer, K53.2S54.8Ch64.4I. Due to the question of enantiotropic smectogenicity in this compound, DSC scans were obtained at a 0.5°/min. heating rate. This unusually slow rate permits observation of the enantiotropic smectic phase which is not clearly evident at commonly employed heating rates such as 10°/minute.

Photopolymerization

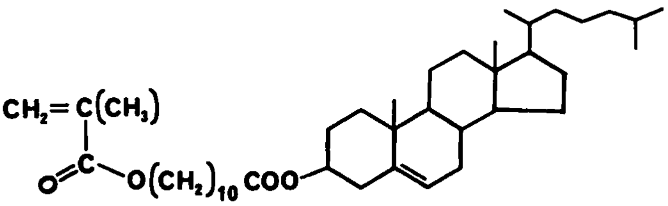
For the purpose of photopolymerization, the monomer and the photoinitiator were dissolved in ethylene dichloride. The photoinitiator, α,α-dimethoxydeoxybenzoin (Irgacure 651--Ciba-Geigy), was 1% by weight of each sample. The monomer films (2.5 mg) were cast by injecting the solution into degreased DSC pans (Omnitherm) and then allowing the solvent to evaporate.

The exotherm studies were conducted on a modified Perkin-Elmer DSC-1B.[6,7] A pyrex window was used to screen the deep UV output of a medium pressure Mercury lamp (Canrad Hanovia) projection system designed in our laboratory. The sample (2.5 mg) was maintained at a constant temperature by the DSC, and the exotherm output was recorded on a strip-chart recorder. The sample chamber was thoroughly purged with nitrogen for 2 minutes before exposure to the mercury lamp. The nitrogen purge was continued during the polymerization process.

RESULTS AND DISCUSSION

Although we have investigated the photopolymerization kinetics of a number of liquid crystalline monomers, this introductory report will concentrate on the methacrylate monomer (CMA-10) shown below since it has both smectic and cholesteric mesophases in temperature regimes which are easily studied by our exotherm instrument.

When the CMA-10 monomer is cast (24 °C) from a dilute ethylene dichloride solution, a crystalline film results. The DSC scan (0.5 °C/min.) of the pure monomer (Figure 1) is characterized by endotherms with maxima at 53.2 °C for the crystal-smectic transition; 54.8 °C for the smectic-



CMA-10 monomer

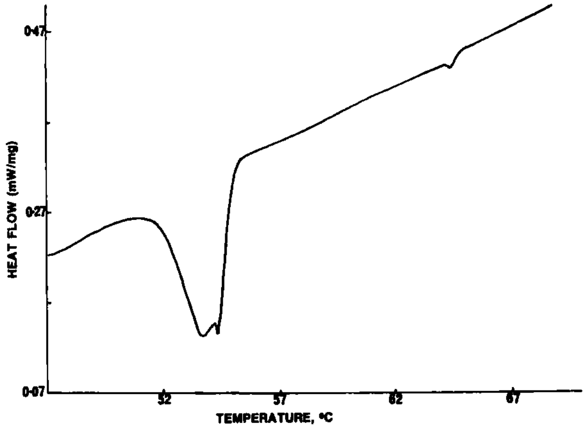


FIGURE 1. DSC heating scan of the monomer CMA-10 at 0.5 °C/min.

cholesteric transition; and 64.4 °C for the cholesteric-isotropic transition.

Figure 2 shows exotherms for the photopolymerization of CMA-10 [1% by weight of Irgacure 651 photoinitiator] with a medium pressure mercury lamp (pyrex cutoff filter). The power of the lamp at the sample pan is 8.66×10^{-3} W/cm^2. It has been clearly demonstrated[6,7] that two aspects of polymerization exotherms are particularly important in characterizing the polymerization rate, the maximum rate of

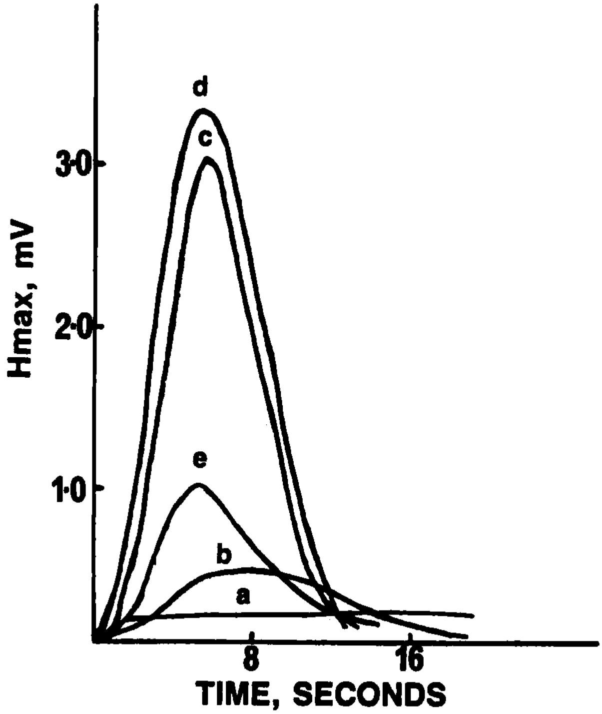


FIGURE 2. Photopolymerization exotherms of CMA-10 at different temperatures.

heat evolution (H_{max}) and the time (T_{max}) required to reach H_{max}. Bearing these two definitions in mind, it is readily seen that the prominent features of the polymerization exotherm of the crystalline (Figure 2, curve a) monomer (31.6 °C) are the relatively low value (0.19 mV) for the maximum rate of polymerization (H_{max}) and the long time (> 20 s) required to reach H_{max}. When the temperature of polymerization is increased to 43.7 °C the value for H_{max} (Figure 2, curve b) increases modestly from 0.19 mV (31.6 °C) to 0.44 mV (43.7 °C) while T_{max} decreases to 7.6 s. At 52.1 °C, the CMA-10 monomer is melting to a smectic phase. The increase in mobility afforded to the monomer while concomitantly retaining registry in two dimensions results in a dramatic increase in H_{max} accompanied by a decrease in T_{max} (Figure 2, curve c). At 57.8 °C the monomer is in the cholesteric liquid crystalline phase and H_{max} again increases while T_{max} decreases (Figure 2, curve d); however, the change is not as dramatic (16.5% increase in H_{max} from 52.1 °C to 57.8 °C) as the enhancement from 43.7 °C to 52.1 °C (a 550% increase in H_{max}). Apparently, at 52.1 °C the mobility required for polymerization rate enhancement has been attained. Results in the cholesteric mesophase illustrate the critical balance between orientation and monomer mobility in determining the rate of polymerization of CMA-10. Apparently, enhanced monomer mobility parallel to the director in the cholesteric phase, is extremely important in facilitating the necessary association of vinyl moieties resulting in an increase in polymerization rate over that in the more ordered smectic phase. It should be noted that the greater order parameter in smectic phases over that in cholesterics would argue for increased alignment of vinyl groups underscoring again the importance of monomer mobility on the polymerization rate. Finally, the exotherm (curve e, Figure 2) for the photopolymerization of the CMA-10 monomer in the isotropic phase at 125 °C shows a dramatic decrease in H_{max}, accompanied by an increase in T_{max}. Apparently in the isotropic phase both random diffusion processes and loss of monomer orientation result in a lower polymerization rate. The results from Figure 2 are summarized in Table I for ready reference.

TABLE I Summary of thermal and rate parameters

T(°C)	Monomer Phase	Monomer Thermal History	H_{max}(mV)	T_{max}(s)
31.6	Crystalline	Cast Film	0.19	> 20
43.7	Crystalline	Cast Film	0.44	7.6
52.1	Smectic	Cast Film	2.85	5.8
57.8	Cholesteric	Cast Film	3.32	5.5.
125.0	Isotropic	Cast Film	0.99	5.8
31.6	Smectic	Heat Cycled Film	2.00	5.4
57.8	Cholesteric	Heat Cycled Film	3.51	5.5
125.0	Isotropic	Heat Cycled Film	0.99	5.8

In order to further investigate the effect of phase type and temperature, undercooling of the S to K transition was employed to permit easy examination of the effect of smectic structure on polymerization rates over a wide temperature range (although not reported here, photopolymerization has been examined at a variety of temperatures in the smectic phase using this undercooling technique, heat cycling). A solvent cast film of CMA-10 monomer was heated to the isotropic state at 97 °C and slowly cooled (10 °C/min) to 31.6 °C. At 31.6 °C the CMA-10 monomer is (by polarized light microscopy) in a smectic liquid crystalline phase which is characterized by the DSC curve shown in Figure 3 wherein the supercooled smectic phase is heated from approximately 30 °C through the S-Ch transition and finally through the clearing (Ch-I transtion. Figure 4 (curve a) shows the DSC exotherm for the photopolymerization of CMA-10 in the smectic phase at 31.6 °C. Comparison of this result with the polymerization exotherm of CMA-10 in the crystalline phase at 31.6 °C (Figure 1, curve a) is quite revealing. The value for H_{max} in the smectic phase (Figure 4, curve a) is almost 14 times greater than that obtained for photopolymerization of the cast crystalline monomer (Figure 2, curve a) quite

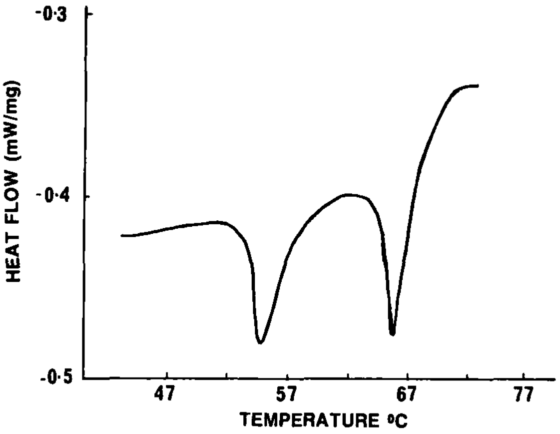


FIGURE 3. DSC heating scan of CMA-10 from 42 °C in smectic phase on heat cycled sample.

similar to the results discussed previously for the heating run (Figure 2, curve c). Apparently, some degree of mobility, as afforded by the smectic state even at this lower temperature, is required in order to obtain a rapid photopolymerization rate. Figure 4 also shows polymerization exotherms for the heat cycled CMA-10 monomer in the cholesteric (57.8 °C) and isotropic (curve c, 125 °C) phases. A brief comparison of the exotherms in the smectic (curve a) and the cholesteric phases (curve b) in Figure 4 reveals an increase in H_{max} for photopolymerization in the

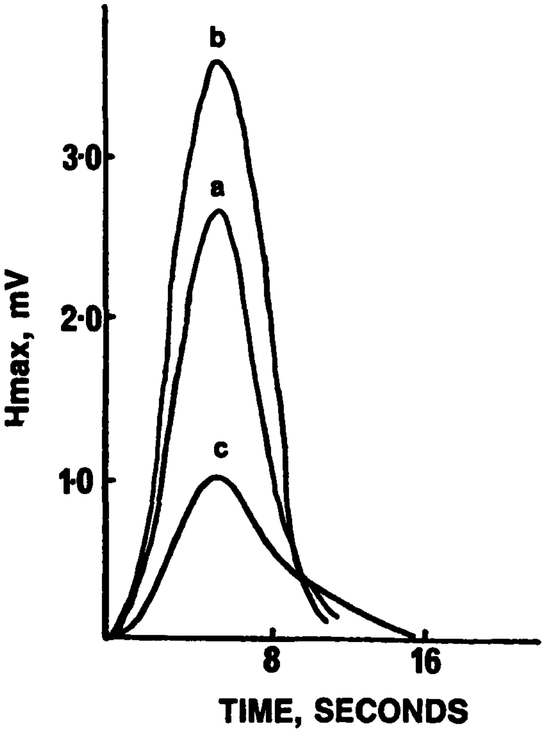


FIGURE 4. Photopolymerization exotherms of heat cycled CMA-10 at different temperatures.

cholesteric phase. The results from Figure 4 (summarized in Table I) are particularly important since they illustrate an increased polymerization rate in the cholesteric phase, which as noted before, is somewhat less ordered than the smectic phase although it allows a more rapid translation of the molecular species along the director leading to faster polymerization. Although the effect is by no means dramatic (the values for H_{max} are only 0.5-0.6 mV higher in the cholesteric phase), it nonetheless underscores the requirement for balance between orientation and diffusion in the photopolymerization of CMA-10. In contrast to the relatively high polymerization rate maxima (H_{max} values) in the smectic and cholesteric phases, polymerization in the non-ordered isotropic phase (curve c) results in a dramatic decrease in the polymerization rate. For both the original film and the heat cycled film, the ordering afforded by the liquid crystalline mesophase is important in increasing the polymerization rate and the isotropic nature of diffusion processes in the amorphous liquid impedes the proper alignment of the vinyl moieties required for photopolymerization.

Finally it should be noted that there is the possibility of phase separation of the polymer during polymerization which might have an effect on the observed polymerization kinetics. Work is currently underway to assess, the role, if any, of phase separation on the polymerization process.

CONCLUSIONS

It has been shown that the rate of polymerization of a liquid crystalline methacrylate monomer is influenced by the phase of the monomer. Polymerization in both the cholesteric and smectic mesophases is very rapid in comparison to the rate in the crystalline and isotropic phases. In addition, the rate in the cholesteric phase is somewhat higher than in the smectic phase presumably due to rapid translational diffusion parallel to the local director in the cholesteric phase. The cholesteric phase seems to provide the optimum balance between monomer order and translational mobility resulting in a maximum polymerization rate.

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