Photoinitiated polymerization of a liquid crystalline monomer: order and mobility effects

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The photopolymerization of a cholesterol-containing monotropic liquid crystalline (LC) acrylate monomer has been followed with polarized light microscopy and a modified differential scanning calorimeter. Polymerization in the cholesteric phase is accompanied by a phase change of the initial LC state. The acrylate LC monomer can exist in two distinct crystalline states having different degrees of order. The photopolymerization in two crystalline phases, LC phase and isotropic phase, reveals the importance of ordering and mobility in the polymerization process.

(Keywords: liquid crystal; photoinitiation; polymerization; mobility)

INTRODUCTION

Liquid crystalline (LC) organization of reactive monomers presents a unique opportunity to investigate the effects of alignment and mobility on polymerization processes. Thus it is not surprising that the literature records a number of studies dealing with polymerization in liquid crystalline media. As summarized in three reviews dealing with polymerization in organized, anisotropic media, one of the critical requirements for reliable kinetic studies is accurate characterization of the state of the monomer before the polymerization process[1-3]. A second factor which must at least be considered, if not totally reconciled, is the nature of any phase changes or phase separation which may take place during the course of polymerization, keeping in mind that a final goal of polymerization studies of liquid crystalline, or for that matter crystalline, monomers is to discover the consequences of ordering and mobility on the polymerization rate. To that end, we describe results in the present paper for the photo-initiated polymerization of a reactive acrylate monomer with a pendant cholesterol group. This monomer is particularly interesting since, as will be shown, it may exist in a cholesteric liquid crystalline phase, two distinct crystalline states, and an isotropic state. The optimum polymerization rate, as indicated by differential scanning calorimetry (d.s.c.) exotherm analysis, is attained for polymerization in which the initial phase of the monomer is liquid crystalline.

EXPERIMENTAL

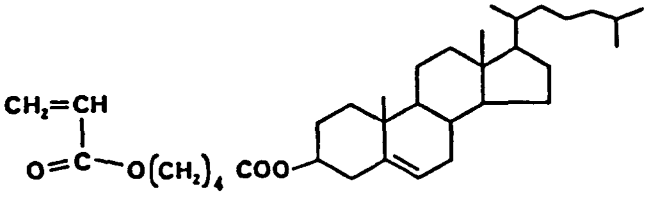
Materials

The monomer used in this study (CA-4; see next section) was prepared according to the method of Shannon[4]. The chloroform used as the reaction medium was washed three times to remove ethanol, dried over anhydrous $CaCl_2$, and then distilled. Thermal transitions of CA-4 were recorded on a DuPont 910 differential scanning calorimeter attached to a 9900 thermal analyzer. Polarizing light microscopy studies were carried out on a Reichert Thermovar optical microscope and a Mettler FP52 hot-stage. For the photopolymerization investigation, a solution of CA-4 monomer containing 1 wt% of the photoinitiator α,α-dimethoxy deoxybenzoin (Irgacure 651 from Ciba Geigy) was prepared in ethylene dichloride. The monomer/photoinitiator films (2.5 mg) were cast by injecting the ethylene dichloride solution into d.s.c. pans (Omnitherm) followed by solvent evaporation. A modified Perkin–Elmer DSC-1B was used for the exotherm measurements. The d.s.c. cell has a pyrex window to allow ultraviolet light penetration from a specially designed medium pressure mercury lamp (Canrad Hanovia) projection system into the sample and reference d.s.c. pans. The rate of heat evolution was recorded as a function of time on a strip chart recorder. For studying phase changes during photopolymerization, monomer films containing 1 wt% of the photoinitiator were cast from dichloroethane solution onto microscope slides. The photopolymerization was conducted by placing the hot stage under the medium pressure mercury lamp. The samples were then examined for phase change under the microscope.

RESULTS AND DISCUSSION

Monomer characterization

CA-4 consists of a reactive acrylate attached to cholesterol via a hydrocarbon spacer group as shown below:



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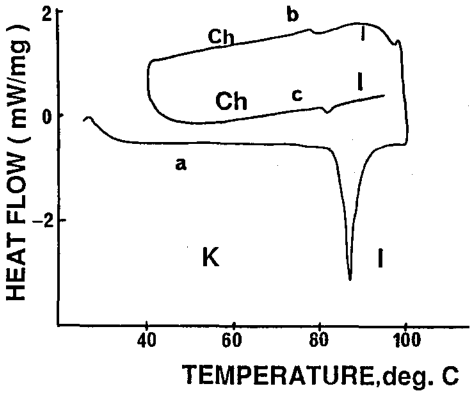

Figure 1 D.s.c. scans of CA-4 monomer: (a) first heating; (b) cooling; (c) second heating (10°C min^{-1})

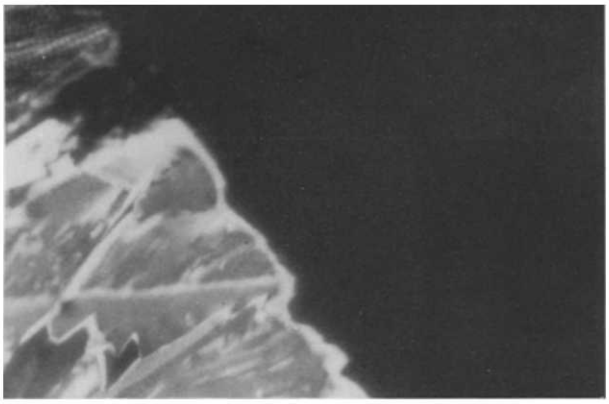

Figure 2 Optical micrograph of CA-4 monomer at 35°C

It has been reported that CA-4 is a monotropic liquid crystalline monomer with the following transitions: K87I and I79Ch (Reference 4). The initial heating/cooling d.s.c. trace for CA-4 in *Figure 1* confirms this assignment with transitions at 87°C (heating cycle – melting transition K87I) and 79°C (cooling cycle – I79Ch) corresponding to crystalline(K)/isotropic(I) and isotropic(I)/cholesteric(Ch) transitions. If the temperature of the cooled CA-4 monomer is kept above ≈40°C, it remains in the cholesteric phase (determined by polarized optical microscopy) until heated to the cholesteric/isotropic transition at 82°C (see second heating cycle in *Figure 1*). By contrast, cooling from the isotropic melt (10°C min^{-1}) to 20°C results in the formation of two distinct crystalline phases (designated as K_1 and K_2 for purposes of discussion) from the cholesteric phase, one of which is believed to possess a higher degree of ordering. The polarized optical micrograph in *Figure 2* shows the two crystalline phases in the presence of the cholesteric state at 35°C. Further cooling to 20°C results in loss of the cholesteric phase accompanied by crystallization to give the two crystalline states exclusively. The d.s.c. trace for the second heating cycle for CA-4 from 20°C (K_1 and K_2 only present) to well above the isotropic transition in *Figure 3* shows endotherm peaks at 56 and 87°C. The transition at 56°C involves the transformation of only the solid crystalline phase K_2 to the cholesteric phase as determined by polarized optical microscopy. Slowly heating the sample above 58°C results in a transition of the cholesteric state to the crystalline K_1 state, indicating that the cholesteric state, at least in the presence of K_1, is metastable above 58°C. Finally, at 87°C the crystalline state K_1 melts. The results from the d.s.c. analysis seem to suggest that K_2 and the cholesteric state have less order than K_1. The consequences of structural order for K_1 and K_2 are manifested in the polymerization rates of the monomer, as will be illustrated in the next section.

Photopolymerization of CA-4 monomer

Having characterized the initial monomer phases, photopolymerization of CA-4 was conducted in each of its four states. *Figure 4* shows d.s.c. exotherms for the photoinitiated polymerization (mercury lamp through pyrex filter with 1% photoinitiator in sample) of CA-4 initially in the cholesteric (50 and 78°C) and isotropic states (97°C). A 28°C temperature increase in the polymerization temperature from 50 to 78°C results in little or no change in the exotherm curve (curves a and b in *Figure 4*), while an increase in the polymerization temperature from 78 to 97°C (curve c) results in a marked decrease in the maximum polymerization rate attained and a much slower overall polymerization process. It is obvious that when the polymerization is conducted in the liquid crystalline phase, the polymerization rate is much faster. This effect is underscored in *Figure 5*, which shows a plot of the maximum rate of polymerization

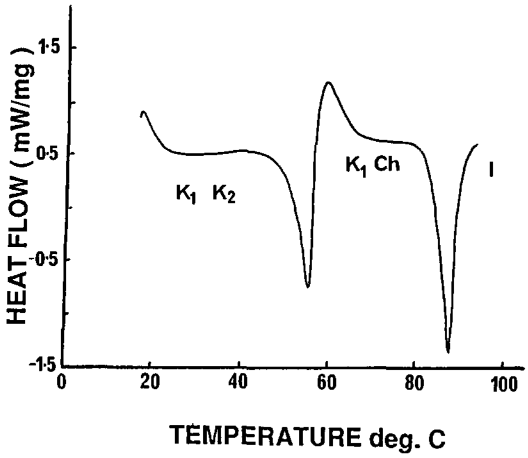

Figure 3 D.s.c. scan (second heating cycle) of CA-4 monomer at 10°C min^{-1}

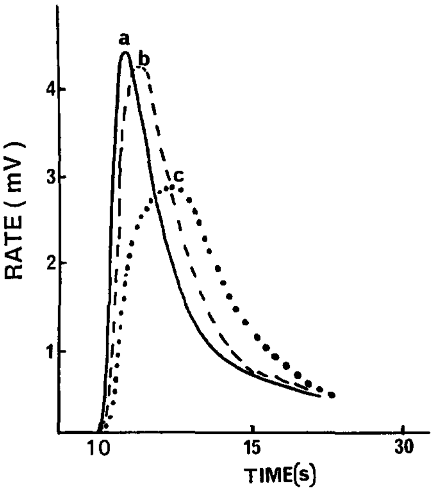

Figure 4 Photopolymerization exotherms of CA-4 monomer cooled from the isotropic phase at: (a) 50°C, cholesteric; (b) 78°C, cholesteric; (c) 97°C, isotropic phase

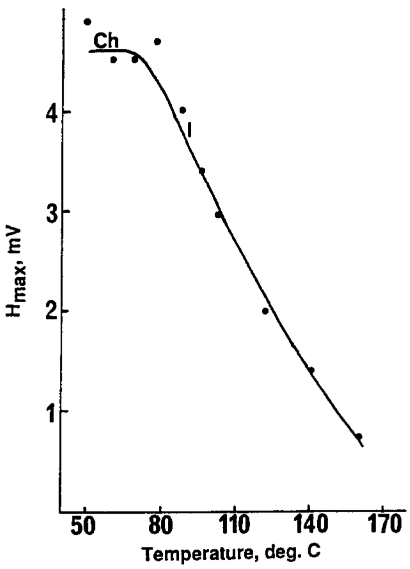

Figure 5 H_{max} *versus* temperature for photopolymerization of CA-4 monomer

(H_{max}) recorded for a series of exotherms at different temperatures. From the results in *Figure 5* it is seen, as was previously pointed out, that the polymerization rate is fastest in the liquid crystalline phase. But perhaps of some surprise is the decrease in H_{max} (and for that matter in the total integrated area under the exotherm) with increasing temperature. Further investigation shows that above approximately 160°C the polymerization is negligible, indicating the presence of a ceiling temperature.

One particularly interesting aspect of the polymerization process between 65 and 87°C is the resultant phase change which occurs in the very early stages of polymerization. *Figure 6* shows polarized optical micrographs of CA-4 between pyrex cover slips at 75°C before and after exposure to the shuttered ($\approx$1 second) output of a medium pressure mercury lamp through a pyrex filter (1 wt% photoinitiator). Conversion to a smectic texture is immediately observed. Further exposure of the sample results in no additional phase change. These results are consistent with the rapid polymerization and lack of detection of phase separation by the d.s.c. exotherms in *Figure 4*. Apparently the polymerization at 75°C, although initiated in the cholesteric phase, takes place primarily (at least after 1 s) in a smectic phase, as there is no evidence for the blue cholesteric phase initially exhibited by the monomer under crossed polarizers once the polymerization is initiated. At temperatures between 45 and 65°C the phase remains cholesteric during polymerization.

It is interesting to note how the results of the phase change shown in *Figure 6* impact upon the conclusions previously reached to explain the results in *Figure 4*. Clearly, there is a significant rate enhancement when the polymerization is conducted in the liquid crystalline phase, which we now see to be a smectic phase, i.e. the monomer is in the smectic phase during most of the polymerization process. This is certainly not what would be predicted if one only observed the distinct cholesteric state of the monomer before polymerization.

In reviewing the results presented so far, the order of the liquid crystalline phase is important in causing a high polymerization rate even though there is restricted monomer mobility. Polymerization in the crystalline state(s) of CA-4, which have a very high degree of order, may occur at lower rates due to restriction of monomer mobility. In addition, differences may be found between crystalline states K_1 and K_2 since, as indicated before, K_2 probably has a lower degree of ordering than K_1.

In practice, it is possible to obtain either K_1 or K_2 exclusively by the proper heat treatment. K_1 is obtained by slowly cooling CA-4 from the melt followed by annealing for 30 min at 50°C. Rapidly lowering the temperature from the melt at 90 to 0°C results in complete conversion to K_2 with no evidence for any contamination by K_1. (This provides further indirect evidence for the reduced order of K_2 compared with K_1, with K_1 being the thermodynamically more stable state.) *Figure 7* shows photopolymerization exotherms at 32°C for CA-4 in both the K_1 (curve a) and K_2 (curve b) state. Both exotherms are much lower than the exotherm for polymerization in the liquid crystalline or isotropic state, which is most likely to be due to the restricted mobility of the monomer

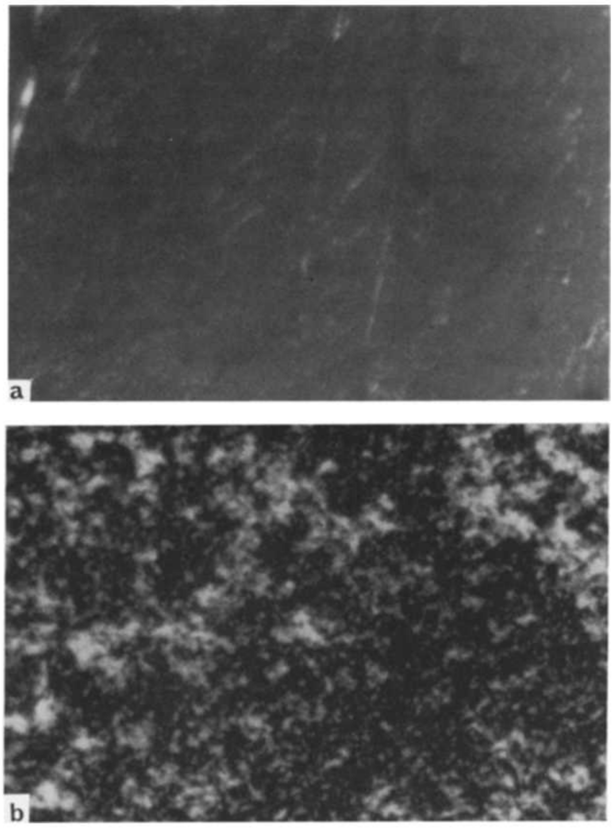

Figure 6 Optical micrographs of CA-4 monomer: (a) cooled from isotropic to cholesteric phase at 75°C before photopolymerization; (b) after 1 s exposure of the cholesteric monomer to the medium pressure mercury lamp

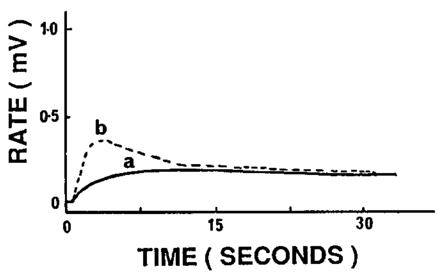

Figure 7 Photopolymerization exotherms of CA-4 at 32°C in (a) K_1 crystalline state and (b) K_2 crystalline state

in the crystalline state. Of particular interest is the higher polymerization rate for CA-4 in the K_2 crystalline state. This is most likely to be attributable to the lower degree of ordering for K_2 proposed in our earlier discussion of K_1 and K_2. Certainly, a lower degree of ordering would allow for increased monomer mobility.

CONCLUSIONS

A thermal and optical investigation of the photopolymerization of a liquid crystalline monomer before and after exposure to ultraviolet light has been presented with emphasis on the correlation of phase influence on polymerization rates. The acrylate cholesterol-containing monomer CA-4 can exist in four states, an isotropic state (I), a cholesteric state (Ch), and two crystalline states (K_1 and K_2), which can be exclusively isolated under the proper conditions. Even though the crystalline states K_1 and K_2 would be expected to have a relatively high degree of order associated with their crystalline structures, their overall polymerization rates, as measured by a d.s.c. photocalorimeter, are low compared with rates in the liquid crystalline and isotropic phases. Polymerization in the liquid crystalline phase, which incidentally occurs primarily in a smectic phase generated from the cholesteric phase during the initial stages of polymerization, occurs much faster than in the isotropic phase. One can conclude that the liquid crystalline phase offers a combination of both order and mobility which allows the photoinitiated polymerization of CA-4 to proceed at a maximum rate.

We are currently in the process of conducting detailed studies of the laser-initiated polymerization of CA-4 and similar acrylate and methacrylate monomers. In this context, we are initiating a concerted effort to study the molecular weight distributions and tacticity of polymers produced upon exposure of liquid crystalline monomer/photoinitiator systems to pulsed laser sources.

ACKNOWLEDGEMENT

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