Medium Effects on the Polymerization Efficiency of a Cholesteryl-Bearing Methacrylate Monomer

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ABSTRACT: Photopolymerization of a cholesteryl-containing liquid crystalline methacrylate monomer with both a steady-state lamp and a pulsed laser has been followed by using a specially designed DSC exotherm unit. The polymerization kinetics are affected by changes in the medium occurring during the polymerization process. Photopolymerization of the liquid crystalline monomer in the hot stage of an optical microscope gives results which correlate with the photopolymerization in the DSC exotherm unit.

Introduction

Small molecules in the liquid crystalline state are characterized by enhanced order. One of the basic questions concerning polymerization of small-molecule liquid crystalline monomers deals with the influence of this enhanced ordering on the kinetics. It is anticipated that the liquid crystalline nature of the medium, which can change as a function of percent monomer conversion, may greatly alter the polymerization rate and efficiency. The status of polymerization in liquid crystalline systems has been reviewed in three comprehensive reports[1-3] which discuss in depth the evidence for monomer order and mobility effects on the polymerization rates. Some of the questions dealing with certain aspects of photoinitiated polymerization of liquid crystals raised in these three reviews have been addressed and answered in a recent series of papers by Broer et al.[4-8]

We having a continuing interest in the use of both steady-state and pulsed-light sources to initiate polymerization processes and during the past few years have conducted a comprehensive investigation of the photopolymerization of a variety of liquid crystalline monomers. This report on polymerization of acrylic liquid crystalline monomers describes results for monomers bearing nonaromatic mesogens. Our focus is on a kinetic investigation of the photopolymerization of a liquid crystalline methacrylate monomer (designated CMA-10) with a cholesteryl (C) group attached to the methacrylate (MA) unit via a long aliphatic (10 CH_2 chain) spacer group. The polymerization is followed by recording the rate of heat evolution (exotherm curve) from the polymerizing sample. This provides a unique opportunity to observe directly the polymerization from beginning to end. By varying the sample temperature, the polymerization kinetics can be measured under a variety of conditions. The results are interpreted by considering ordering, monomer mobility, and changes in the liquid crystalline medium on the polymerization rate. The analysis presented herein represents an extension of previous introductory notes dealing with the photopolymerization of CMA-10.[9,10]

Experimental Section

The synthesis of the CMA-10 monomer used in the present study has been described elsewhere and was repeated with minor changes.[11] The photopolymerization kinetics were followed on a modified Perkin-Elmer DSC-2B. The sample films (2.5 mg) containing 1% by weight of the photoinitiator α,α-dimethoxydeoxybenzoin (Irgacure 651, Ciba-Geigy) were cast by injecting a dichloroethane solution of monomer and photoinitiator into indented DSC pans. The solvent was allowed to evaporate, leaving behind a thin monomer film. A specially designed DSC photocalorimeter cell (with a quartz window to allow UV light penetration into the DSC pans) was used for the photopolymerization kinetic study. A medium-pressure mercury lamp (Canrad Hanovia) was used for the steady-state UV source. In cases where no band filters were used, the light intensity at the pans was 12.8×10^{-3} W/cm^2. All samples were purged with nitrogen for 5 min before exposure to the UV lamp. The heat evolved was recorded as an exotherm on a strip chart recorder (reported in millivolts, which is proportional to the reaction rate) attached to the DSC unit. For the phase behavior study, conducted with a polarizing microscope (Reichert Thermovar), monomer films containing 1% by weight photoinitiator (Irgacure 651) were cast onto glass slides. The photopolymerization was carried out at different temperatures by placing a hot stage containing the sample under the medium-pressure mercury lamp. The hot stage (Mettler FP 52) was then placed on the microscope, and the samples were viewed by the polarizing microscope.

A Questek Model 2460 excimer laser (XeF, λ_{ex} = 351 nm) was used for the laser-initiated polymerization studies. The samples of CMA-10 monomer (2.5 mg) containing 1% by weight of Irgacure 651 were prepared by casting films into indented DSC pans. All samples were purged with nitrogen for 5 min before exposure to the laser beam. The energy per pulse delivered to the sample pan, after passing through a combination of neutral-density filters of 1.0 and 0.5, was approximately 1.92×10^{-1} mJ cm^{-2} (measured at 40 Hz). At the wavelength employed, only the photoinitiator absorbed the light. In all cases the sample temperature remained constant during the polymerization process.

Quantum yields, intensity exponent, and percent conversions required for medium texture change were measured on the DSC exotherm unit. The lamp intensities employed in these studies depended on the filters used to isolate particular mercury lines and are indicated at the appropriate place in the text. Quantum yields are calculated based on the assumption of 50% reflectivity by sample pans and may reflect errors to ±20%. In addition, we note that quantum yields calculated for nonisotropic media do not take into account light scattering which can result in a reduction of the light intensity: thus quantum yields quoted for birefringent liquid crystalline media are lower limit values. (We note that absolute polymerization quantum yields may be subject to considerable error.)

The phase transitions of CMA-10 were determined by DSC at a heating rate of 1 °C/min and confirmed by polarized optical microscopy.

Results and Discussion

As demonstrated in a preliminary report, the pure CMA-10 monomer can exist in a crystalline state, a smectic mesophase, a cholesteric mesophase, and an isotropic phase, depending upon the temperature and thermal

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Table I
Transition Temperatures

	transition temp (°C)	transition type
first heating cycle	52.3	K–S
	54.8	S–Ch
	64.4	Ch–I
cooling cycle	62.7	I–Ch
	51.5	Ch–S
second heating cycle	54.5	S–Ch
	64	Ch–I

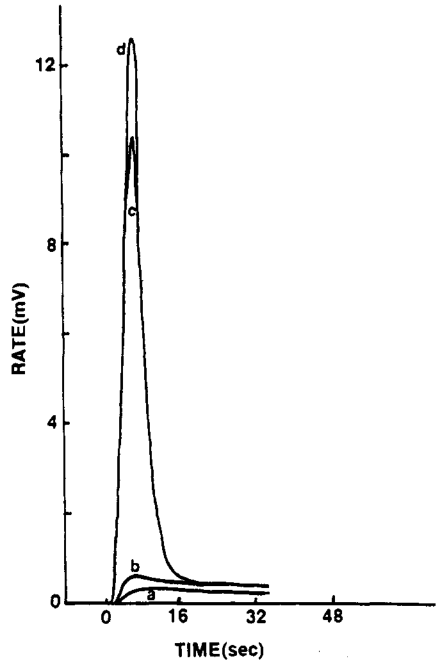

Figure 1. Polymerization exotherms of a cast CMA-10 exposed to the medium-pressure mercury lamp: (a) 32 °C; (b) 44 °C; (c) 52 °C; (d) 58 °C.

history of the sample. The liquid crystalline behavior of pure CMA-10 is summarized as follows: A room temperature solvent-cast (dichloroethane) film is crystalline with a transition to a smectic mesophase (K–S) at 52.3 °C followed by a smectic–cholesteric (S–Ch) transition at 54.8 °C. The monomer clears (Ch–I) to an isotropic melt at 64.4 °C. When the sample is cooled from 97 °C, the cooling curve shows an exothermic transition (I–Ch) to the cholesteric phase at 62.7 °C followed by a transition (Ch–S) at 51.5 °C to a smectic phase, which remains intact to room temperature as a supercooled smectic state (determined by polarized light microscopy). Liquid crystalline textural assignments (K, Ch, S) are in agreement with those made by Shannon.[11] Thus, depending on the temperature and thermal history, the CMA-10 monomer may exist in one of four states (thermal transitions summarized in Table I). We note that addition of low concentrations of photoinitiator lowers the transition temperatures slightly.

Photopolymerization with a Steady-State Lamp Source. Figure 1 shows photopolymerization exotherms (medium-pressure mercury lamp with pyrex filter) of the CMA-10 monomer (cast into a DSC pan) at four temperatures (curves a–d). The exotherm at the lowest temperature has a relatively low maximum rate of heat evolution (H_{max}), and the time required to reach H_{max} is quite large (>20 s). The parameter H_{max} has been shown[12] to be important in characterizing photopolymerization rates: in the present case, the relatively small H_{max} value indicates a low polymerization rate. Figure 2 shows a plot of H_{max} as a function of the polymerization temperature for several exotherms (similar to the ones in Figure 1).

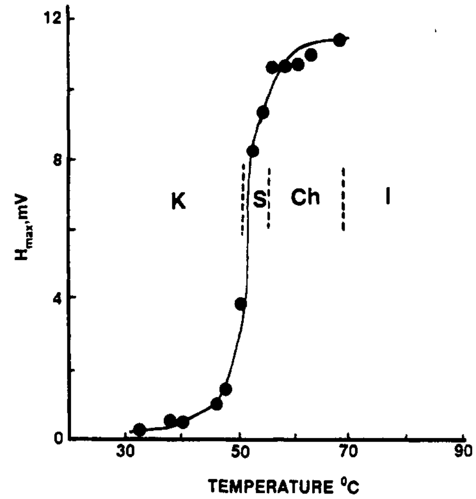

Figure 2. H_{max} vs temperature plot of CMA-10 for medium-pressure mercury lamp polymerization. Phase states of the monomer prior to polymerization are indicated directly on the figure.

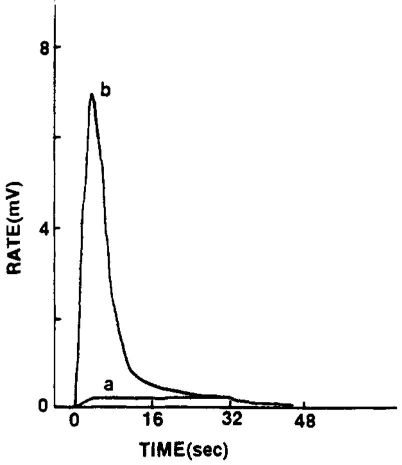

Figure 3. Mercury lamp initiated polymerization exotherms of CMA-10 at 32 °C in (a) crystalline and (b) smectic media.

The onset of the liquid crystalline transition, which begins at about 50 °C, results in enhanced polymerization rates reflected by the dramatic increase in H_{max}. Apparently, the relative monomer mobility afforded by the liquid crystalline medium compared to the crystal provides for faster polymerization rates. This is illustrated directly by comparison of the exotherm curves in Figure 3 for photopolymerization of CMA-10 where the monomer is in the crystalline (as-cast) state at 32 °C and the smectic state (obtained by cooling from the isotropic melt) at 32 °C. Thus, even though the crystal at 32 °C may have more order, apparently the monomer mobility allowed in the mesophase results in a relatively higher polymerization rate.

The results in Figures 1 and 3, while meaningful from a polymerization rate standpoint, provide no detailed information regarding changes in the medium which may occur during the polymerization process. In addition, results for polymerization at temperatures above the clearing temperature have not been presented. Both of these points will be reconciled in the ensuing discussion. Figure 4 depicts polymerization exotherms for the photopolymerization of CMA-10 at temperatures ranging from 50 to 125 °C. The exotherm curves a, b, and c are quite large, reach a maximum value (H_{max}) at relatively short times, and are reasonably symmetrical. The striking similarity of exotherm curves a, b, and c results from the

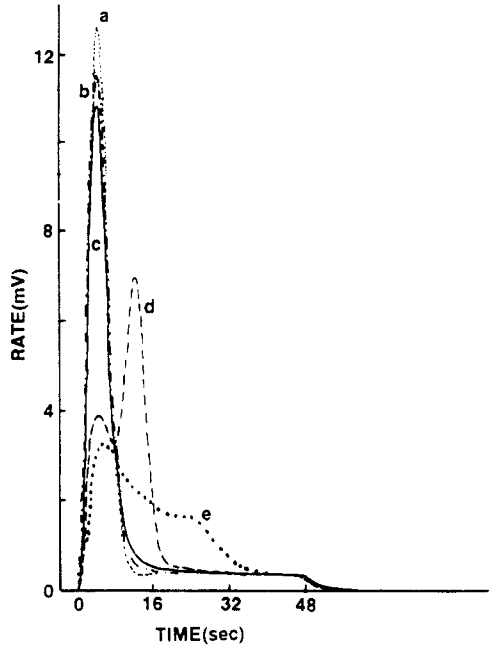

Figure 4. Mercury lamp initiated polymerization exotherms of CMA-10 at (a) 50, (b) 58, (c) 75, (d) 97, and (e) 125 °C.

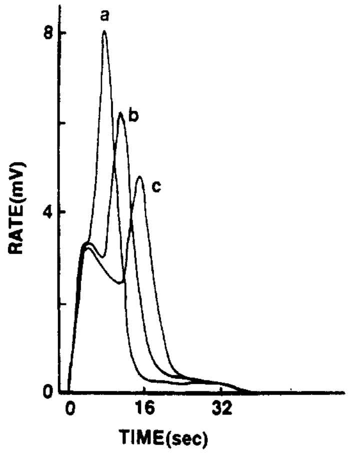

Figure 5. Mercury lamp initiated polymerization exotherms of CMA-10 at (a) 88, (b) 97, and (c) 106 °C.

rapid change of the cholesteric (58 °C) and isotropic systems (75 °C) to a medium with a grainy texture (when viewed by cross-polarized optical microscopy) at very low percentages (approximately 2–3%): initial analysis indicates that the medium texture (after 2–3% conversion) is smectic at 58 and 75 °C. The exotherm curve for polymerization at 97 °C, however, is characterized by two distinct maxima. Such behavior can readily be attributed to an abrupt change in the medium texture during polymerization. At 125 °C, the exotherm curve once again is characterized by a single peak maximum; however, the maximum is significantly lower and there is a substantial tail indicating a slower overall polymerization rate. When polymerization exotherms were recorded from 65 to 150 °C, it was found that single exotherm peaks were clearly discernible only from 65 to 75 °C and above 125 °C. Figure 5 shows representative exotherm curves obtained at 88, 97, and 106 °C. In each case, two exotherm peaks are observed, with the second peak occurring at later times and being reduced in magnitude with increasing temperature. We note that under the conditions (light intensity) employed changes in the inital polymerization exotherm curves at 75 and 58 °C at less than 2–3% conversion cannot be resolved due to the instrumental time response of the DSC. A careful analysis of exotherms produced with the isolated 366-nm line of the mercury lamp (output a sample pan was 9.05×10^{-5} J s^{-1} cm^{-2}) showed the medium changes to occur approximately at 22% conversion for 88 °C and 28% conversion for 97 °C. The conversion required at 106 °C was calculated to be about 49%.

To provide a more complete representation of the polymerization of CMA-10, polarized optical micrographs in Figure 6 were obtained before and after initiating polymerization at five different temperatures, i.e., 50 (S), 58 (Ch), 75 (I), 88 (I), and 125 °C (I) (the initial monomer phases are shown in parentheses). As expected, at 50 °C the optical micrographs before and after polymerization (Figures 6a,b) are essentially identical; i.e., a uniform well-defined smectic texture (probably smectic A) is maintained throughout the polymerization. At 58 °C, however, after only a brief exposure to the full output of the mercury lamp source the polymerization medium is characterized by a totally different sandy texture (Figure 6d) which is formed over the entire exposed area. It is obvious that this new ordering (probably smectic A) is quite different from the initial cholesteric texture (Figure 6c) of the monomer. Figure 6e shows the birefringent phase produced immediately upon exposure of the isotropic CMA-10 monomer at 75 °C to the medium-pressure mercury lamp. It is clearly identical with the texture of the liquid crystalline medium formed upon polymerization at 58 °C. Thus, photopolymerization at either 58 or 75 °C with the monomer initially in the cholesteric or isotropic phase results in a rapid conversion to a common birefringent medium with a concomitant increase in the polymerization rate characterized by rapid achievement of a single-peak exotherm maximum, similar to that obtained at 50 °C, where no discernible change in the smectic liquid crystalline texture occurred. We should note that the early conversion of the medium texture at 58 and 75 °C prohibits us from discerning the rate acceleration which accompanies the textural change: a laser-initiated polymerization method, however, clearly identifies the early rate acceleration process. Details are relegated to a future publication. From laser-initiated polymerization results, we know that the percent conversion required for the medium changes at 58 and 75 °C is about 2–3%.

Photopolymerization at 88 °C is characterized by an isotropic polymerization medium which converts to a birefringent (by cross-polarized optical microscopy) system after mercury lamp exposures (unfiltered) of greater than 3 s. Unlike the phase change observed at 58 and 75 °C, the initial transition from an isotropic to a birefringent medium is characterized by what appears initially to be (by polarized optical microscopy) a sandy texture which is not fully developed over the exposed area. Only at exposure times of about 6 s or greater does the system appear to have a uniform sandy appearance (probably smectic). Finally, when the polymerization is conducted at 125 °C, the system remains isotropic for exposure times greater than 10 s: only after very long exposure times does the medium display a weak birefringence.

The polarized optical micrograph results provide an explanation for the exotherm curves in Figures 4 and 5. Polymerizations at 50, 58, and 75 °C are distinguished (Figure 4, curves a–c) by a large sharp exothermic maximum characteristic of polymerization in a liquid crystalline medium. At temperatures above 80–85 °C (Figure 4, curve d, and Figure 5, curves a–c), the polymerization proceeds to relatively high conversions in an isotropic medium until ample polymer is present to induce creation of a birefringent liquid crystalline medium,

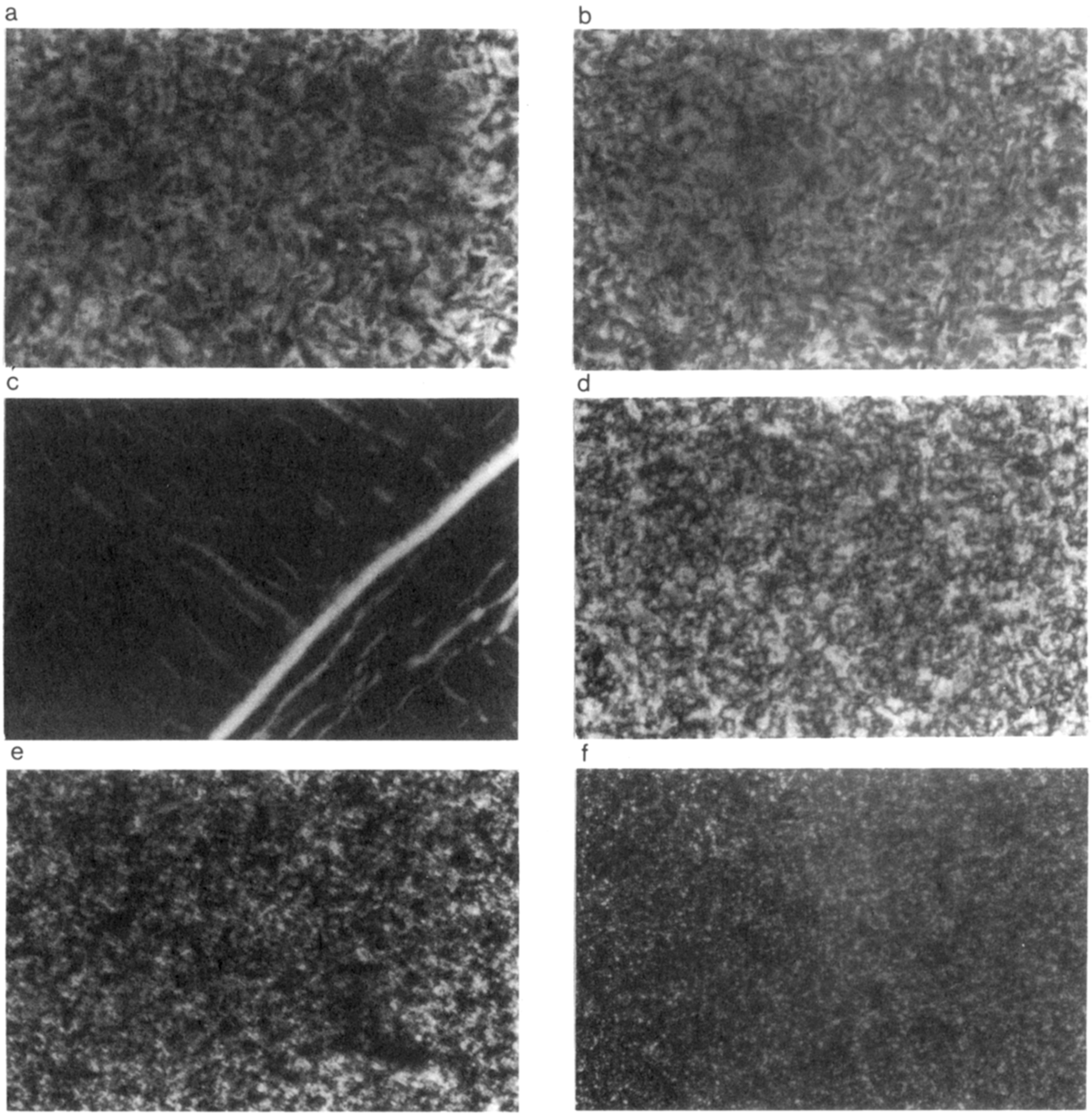

Figure 6. Optical micrographs of CMA-10: (a) in the smectic phase at 50 °C before photopolymerization; (b) after 20-s exposure to the medium-pressure mercury lamp; (c) in the cholesteric phase at 58 °C before photopolymerization; (d) after ~1-s exposure to the lamp; (e) after ~1-s exposure at 75 °C to the lamp; (f) after ~6-s exposure at 88 °C to the lamp.

whereupon a rate acceleration in the polymerization occurs. The medium changes and rate acceleration require longer exposure times (more polymer) as the temperature of polymerization increases.

At this juncture, we should comment on the molecular weight distributions of the polymers produced at each polymerization temperature. Although molecular weight data will be presented in a separate paper, a general observation extracted from that work shows that the molecular weights (by GPC) of the polymers produced at 50, 58, and 75 °C are quite high. At 88 °C in the isotropic system at low conversion, the molecular weight (by GPC) of the polymer produced is much lower. In short, our experience shows that polymerization in the liquid crystalline medium results in polymers with much higher molecular weights.

A direct comparison between polymerization at several temperatures was accomplished by first polymerizing the monomer to a given percent conversion. Then a specific number of photons were delivered to each sample by placing a time shutter (5 s) between the filtered medium-pressure mercury lamp (output at sample pan was 2.16 × 19^{-5} J s^{-1} at 366 nm) and the DSC pan containing the prepolymerized sample. Table II summarizes the results. The entry in the second column is the percent conversion obtained prior to delivery of the shuttered pulse to the sample. The moles of photons absorbed by the sample, the resultant moles of monomer polymerized (measured by the area under the exotherm curve), and the resultant polymerization quantum yields are given in the next three columns (see Experimental Section for caution in interpretation of quantum yields). Several observations can be made. First, the quantum yield for polymerization in the birefringent liquid crystalline medium at 88 °C is about 75% larger than for polymerization in the isotropic state at the same temperature. Additionally, the quantum yield

Table II
Quantum Yields

sample yield ref	% conv prior to measurement^b	mol of photons^a absorbed (X)	mol of monomer polymerized (Y)	quantum yield (Y/X^c)
88 °C (before medium charge)	5	1.48×10^{-11}	5.51×10^{-8}	3700
88 °C (after medium charge)	27	1.48×10^{-11}	9.58×10^{-8}	6500
75 °C (after medium charge)	12	1.48×10^{-11}	1.43×10^{-7}	9700
58 °C (after medium charge)	10	1.48×10^{-11}	1.86×10^{-7}	12600
45 °C	11	1.48×10^{-11}	2.20×10^{-7}	14900

[a] Assumes 50% reflectivity by sample pans. [b] Errors up to 10% possible. [c] Errors up to 20% possible in absolute quantum yield. Values in media having liquid crystalline textures are lower limit values since light scattering by medium at excitation wavelength could not explicitly be accounted for.

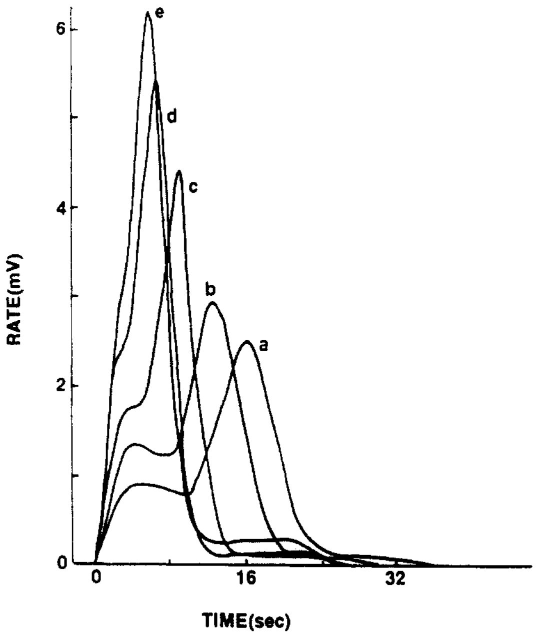

Figure 7. Laser (XeF, λ_{ex} = 351 nm) initiated polymerization exotherms of CMA-10 monomer at 88 °C as a function of laser repetition rate: (a) 5, (b) 10, (c) 20, (d) 40, and (e) 80 Hz.

at ~12% conversion at 75 °C is almost 3 times larger than in the isotropic state at 88 °C, reflecting the effect of the liquid crystalline system at 75 °C on the polymerization efficiency. The fact that the increase in the quantum yield at 88 °C after the medium change is rather modest may be due to a decreased ordering compared to the ordering generated in the medium at 75 °C, as confirmed qualitatively by a polarized optical microscopic examination of the sample at 88 °C. Finally, there is a rather marked decrease in the quantum yield obtained as the temperature is raised from 45 to 75 °C. This may well be due to a decrease in the orientational ordering with increasing temperature. We plan to obtain X-ray diffraction measurements to determine the exact ordering of the liquid crystalline medium as a function of temperature and thereby confirm this presumption.

We have also measured the dependence of the polymerization rate on the light intensity at 45 and 88 °C (before and after the texture change) using a medium-pressure mercury lamp. In each case, the polymerization rate depends on the light intensity to about the 0.6 power. Within experimental error the exponent is constant and reflects a uniform mode of termination.

Finally, we speculate that the origin of the rate acceleration in the liquid crystalline media and the resultant high quantum yields compared to the isotropic phase is a result of a reduced termination rate. Such a reduction in termination rate is expected in a medium in which translation (center of mass) and/or rotational (chain ends) is restricted. A reduced mobility of termination polymer radicals has indeed been suggested as a possibility for liquid crystalline systems previously.[2,5]

Laser-Initiated Polymerization. Having established the origin of the rate acceleration above 80 °C, the laser-initiated polymerization (λ_{ec} = 351 nm, pulsed xenon fluoride excimer laser) of the CMA-10 monomer was investigated as a function of the repetition rate of the laser at 88 °C (Figure 7, curves a–e). Since the power per pulse of the laser does not vary significantly with laser repetition rates above 5 Hz, several conclusions can be deduced. First, H_{max} for the second peak on each curve increases with laser repetition rate. Second, the time required for acceleration to occur is significantly diminished as the repetition rate increases. Finally, it should be noted that even at the highest repetition rates used in the study (to 80 Hz), the rate acceleration is still evident; i.e., there is a shoulder on exotherm curve e in Figure 7 at short times. This observation underscores the remarkable sensitivity of the photocalorimetric technique in detection of rate changes of isotropic monomers which undergo changes in the order of the medium during the polymerization process.

Conclusions

The photopolymerization of a liquid crystalline monomer has been successfully followed by exotherm calorimetric measurements. When exotherm curve analysis is combined with a cross-polarized optical micrograph analysis of the polymerization medium, a clearer account of the polymerization process is presented. It can be concluded that exotherm analysis is a powerful and quite sensitive tool for examination of the onset of rate acceleration of photopolymerization of liquid crystalline monomers.

It must be stressed that the exact origin of the rate accelerations reported in this paper for CMA-10, as well as other monomers we have investigated, is difficult to define. Future publications will deal with more exacting descriptions of the polymerization media and the cause of the rate acceleration, which according to ref 2, may result from any of several factors. We are currently initiating a comprehensive investigation to determine the exact nature of the phases formed during the polymerization at different temperatures with respect to compositional purity and order. In addition, methods to evaluate initiation efficiency, termination and propagation rate constants, and any medium inhomogeneity or limited monomer/polymer miscibility as a function of percent conversion for CMA-10 as well as other liquid crystalline systems are under development.

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