Kinetics of Polymerization of Liquid Crystalline Monomers: An Exotherm and Light Scattering Analysis

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Received July 26, 1993; Revised Manuscript Received November 8, 1993®

ABSTRACT: An increase in the rate of polymerization of a cholesteryl-modified methacrylate functionality in a smectic liquid crystalline phase, compared to an isotropic medium, was attributed to a substantial decrease in the termination rate. Distinct changes in the medium composition and order when polymerization was initiated with the monomer initially in an isotropic phase resulted in rate acceleration processes. The rate acceleration process was again attributed to a decrease in the rate of termination. Polymerization of the methacrylate monomer at lower temperatures resulted in incomplete conversion due to a glassy matrix effect. Similar polymerization rate behavior was demonstrated for two other liquid crystalline monomers of similar structure.

Introduction

During the course of the last 2 decades, there have been a number of reports describing the kinetics of polymerization of liquid crystalline monomers and of isotropic monomers in liquid crystalline solvents. As a result of the consensus of three review articles detailing the literature published in the kinetics of polymerization of liquid crystalline monomers,[1-3] it must be concluded that a simple generalization of the effect of liquid crystalline media on such factors as polymerization rate and polymer molecular weight is difficult to make. This point is made most vividly by Blumstein.[3] Indeed, as suggested by Blumstein in ref 3 (and references therein), during the course of polymerization of a liquid crystalline monomer beginning either in one of its mesophases or in its isotropic phase, the polymerization kinetics may be influenced by a series of changes in the medium composition and phase behavior as a function of the conversion percentage. It is possible that for certain, or even all, compositions the polymer may not be totally miscible in the monomer from whence it is formed, resulting in phase separation into a polymer-rich phase and a monomer-rich phase. This of course can alter the polymerization kinetics.

Since free-radical polymerization is characterized by initiation, propagation, and termination rate processes, any attempt to define the effect of the medium must take into account the individual rate constants for propagation and termination as a function of the medium makeup and percent conversion. This necessitates measurement of initiation rates at the corresponding temperature and percent conversions for which the propagation and termination rate constants are desired. Direct calculation of initiation rates provides a means of taking into account variations in the amount of light absorbed by the photoinitiator due to light scattering by different medium textures. This is particularly important since variation in the amount of light absorbed by the photoinitiator due to scattering may hinder calculation of rate and/or quantum yield measurements for photoinitiated free-radical polymerization processes in mesomorphic media.

In this paper, we present polymerization exotherms for the photoinitiated polymerization of three monomers characterized by mesomorphic phases over a broad temperature range. In addition, results are presented for polymerization of the three monomers at temperatures for which the media are initially isotropic but which can change significantly during the course of polymerization. Sudden changes in the rate of polymerization occur at the same instant that changes in the medium take place. One of the monomers was chosen for a detailed kinetic analysis to illustrate the effect that liquid crystalline organization and phase behavior can have on propagation and termination rate constants.

Experimental Section

Syntheses of all monomers followed according to the basic procedures in ref 4. 1,1-Dimethoxy-1-phenylacetophenone (Irgacure 651; Ciba Geigy) was recrystallized from ethanol prior to use. 4-(2,2,6,6-Tetramethyl-1-piperidinyloxy) benzoate (TMPOBOA) was used as received from Aldrich Chemical Co. Samples of between 1.8 and 2.4 mg were cast from dichloromethane in indented DSC sample pans[5,6] with 1 wt % 1,1-dimethoxy-1-phenylacetophenone photoinitiator. A Perkin-Elmer DSC-2, modified as described in ref 5 and 6 to allow light penetration to the sample and reference pans, was employed for recording exotherms. For each exotherm measurement, the sample was heated to the isotropic phase and purged with nitrogen for 5 min. The sample temperature was then adjusted to the requisite temperature for exposure by the medium-pressure mercury lamp equipped with a 366-nm band-pass filter with a lamp intensity of 0.020–0.024 mW/cm^2 (except as specifically noted in Figure 2).

The phase behavior and phase diagrams were measured by polarization microscopy and differential scanning calorimetry on a DuPont 9900 DSC. The DSC/HeNe laser light scattering apparatus is described in the text.

Rate constants for k_t and k_p were measured according to the general procedure described in ref 7. The rate of formation of initiating radical species was determined at each percent conversion that k_i and k_p values were determined: A radical trap was used to quantitate the rate of production of radical initiating species by the photoinitiator under the photolysis conditions (lamp intensity) employed. The general procedure, as described in the text, utilized a Waters-based HPLC system to measure the rate loss of the radical trap. Although the steady-state polymerization rates were estimated for polymerization using a 60-cycle ac power supply, the rate constants determined were not measurably different from rate constants determined in a separate set of experiments using a xenon lamp system powered by a dc lamp source.

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® Abstract published in *Advance ACS Abstracts*, December 15, 1993.

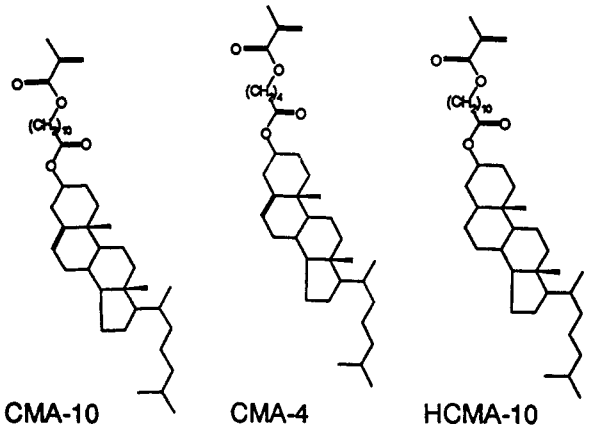
0024-9297/94/2227-3790$04.50/0

Table 1

monomer	transitions
CMA-4	heating: K 59 Ch 70 I cooling: I 67 Ch 28 S
CMA10	heating: K 52.3 S 54.8 Ch 64.4 cooling: I 62.7 Ch 51.5 S
HCMA-10	heating: K 43.6 Ch 48 I cooling: I 44.7 Ch 33.7 S

Results and Discussion

We have chosen to investigate three cholesteryl-type-bearing monomers characterized by differences in spacer length between a reactive methacrylate functionality and a cholesterol mesogenic group (CMA-10 versus CMA-4) or differences in the presence (CMA-10) or absence (HCMA-10) of a vinylic double bond in the steroid mesogen unit. We have previously investigated CMA-10.[5,6] Herein



we will expand results for CMA-10 and present initial results for CMA-4 and HCMA-10 for comparison of structural effects on polymerization kinetics. Transition temperatures obtained on the heating and cooling scans via DSC and cross-polarized optical microscopy are shown in Table 1 for the three monomers. In each case upon cooling, at least a 10 °C temperature range for the cholesteric nematic phase was obtained, followed by the formation of a smectic phase (in each case a smectic A phase) which was maintained to room temperature.

A. Basic CMA-10 Exotherm Curves. Initially, we will focus attention on the CMA-10 monomer polymerization and provide a detailed analysis of polymerization at selected temperatures in order to illustrate two effects: (1) The role of medium changes during polymerization in rate acceleration processes and (2) the severe suppression of termination rate constants for polymerization in the smectic phase at 45 °C, even at low conversions. Representative data for the photoinitiated polymerization of CMS-4 and HCMA-10 will then be presented to demonstrate that the same phenomena occur in these two systems and to highlight differences that spacer length (CMA-4) and unsaturation in the mesogen (HCMA-10) can play. Figure 1 shows a series of exotherm curves for CMA-10 with 1 wt % DMPA initiated with the 366-nm filtered output of a medium-pressure mercury light source. Only for the polymerization at the highest temperature (150 °C) does the exotherm curve display a continuous decrease in polymerization rate with photolysis time. At several temperatures up to and including 120 °C, the exotherm curves are characterized by a sudden increase in the polymerization rate. In past publications,[5,6] we have reported that abrupt rate increases in polymerization occur at the instance that changes in the polymerization medium birefringence and texture occur. In this paper we will

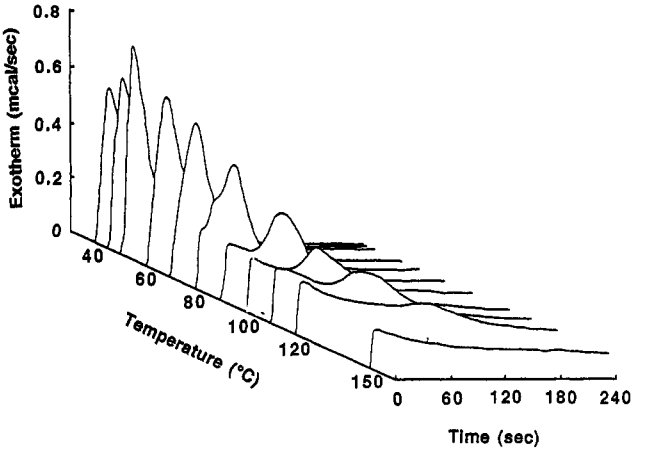


Figure 1. Polymerization exotherms of CMA-10 monomer with 1 wt % DMPA photoinitiator using a medium-pressure mercury lamp (366-nm filter) at several temperatures.

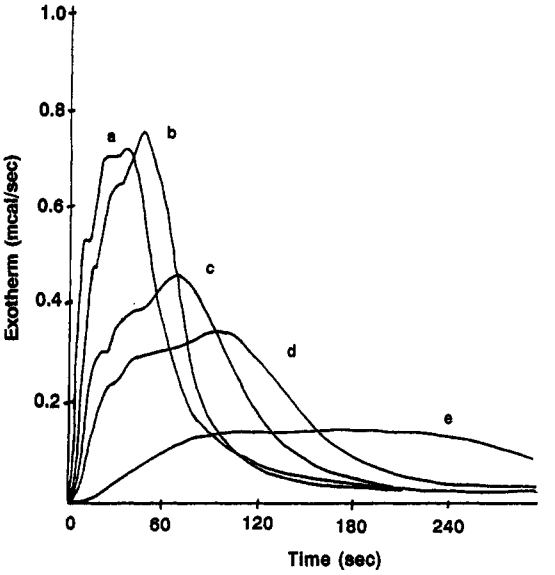


Figure 2. Polymerization exotherms of CMA-10 at 80 °C with 1 wt % photoinitiator using a medium-pressure mercury lamp (366-nm filter) for several light intensities: (a) 0.087 mJ cm^{-2} s^{-1}; (b) 0.044 mJ cm^{-2} s^{-1}; (c) 0.022 mJ cm^{-2} s^{-1}; (d) 0.014 mJ cm^{-2} s^{-1}; (e) 0.0044 mJ cm^{-2} s^{-1}.

provide data which correlate kinetic rates and phase changes in the medium in real time. This will allow us to determine the effect of medium organization and composition on individual rate processes for propagation and termination.

The feature which we focus on first from Figure 1 is the polymerization exotherm at 80 °C. It is characterized by a pronounced "2-fold" increase in the polymerization rate. A similar phenomenon occurs when other photoinitiators are used. These abrupt dual increases in the normal polymerization exotherm warrant additional consideration in the context of changes in the nature of the polymerization medium. First, we determined that the rate acceleration phenomenon is not dependent upon the intensity of the irradiating lamp source. This is clearly illustrated in Figure 2: Although the exact exotherm heat evolution rate response to photolysis time changed with the intensity of the photolysis lamp source, the presence of two rate accelerations at each light intensity is obvious. Plots of polymerization rate versus light intensity for the exotherms in Figure 2 show that the rate is dependent on the square root of the light intensity (at least approximately) up to about 70% conversion, indicating that the mode of termination (bimolecular) does not change

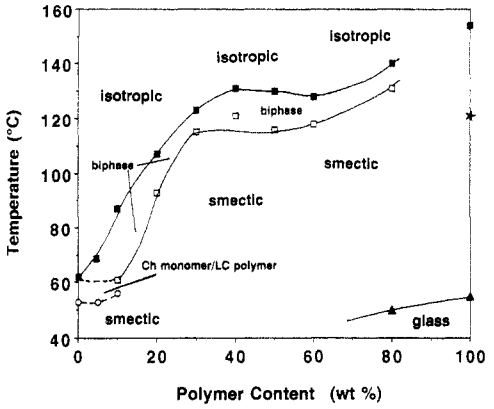


Figure 3. Phase diagram for CMA-10 monomer and CMA-10 polymer.

drastically when rate acceleration is operative. Furthermore, the percent conversions required to attain the first and second rate accelerations are approximately 7–8 and 20% for all of the light intensities employed.

B. CMA-10 Monomer/Polymer Phase Diagram and Polymerization Medium Changes. Figure 3 shows the phase diagram (obtained upon cooling) of CMA-10 and its corresponding polymer (made by polymerization of CMA-10 in solution) obtained by DSC and cross-polarized optical microscopy of mixtures independently prepared. The open squares and filled squares in Figure 3 represent respectively the onset and subsequent complete clearing to a homogeneous isotropic phase of a biphasic region comprised of an isotropic phase and a liquid crystalline phase (presumably dominated by the polymer) of unknown classification (via optical microscopic examination). We note that Shivaev[7] has identified a transition on heating (star on Figure 3) for the pure CMA-10 polymer at about 124 °C from a smectic phase to a second liquid crystalline phase which is apparently quite difficult to characterize. Since the primary attention in this paper is to polymerization at temperatures well below 100 °C, we simply indicate Shibaev's observation and refer the interested reader to ref 7 and additional references cited therein. A comment on the phase behavior between ~53 and ~61 °C at low polymer percentage (0–10%) is in order since this region was found to be particularly difficult to characterize. While mixtures above about 10–15% polymer are clearly in a smectic phase over this temperature range, lower polymer concentrations are tentatively assigned to a biphasic system comprised of a cholesteric monomer-rich and a second liquid crystalline (probably smectic) polymer-rich phase. We were not able to determine whether at very low polymer percentages a single phase was attained over this temperature range. At temperatures below those depicted by the open circles for the 0–10% polymer content range, the mixtures adopt a smectic homogeneous phase.

Concentrating on 45 and 80 °C for comparison, it is easily seen that at 45 °C the CMA-10 monomer/polymer mixture forms a smectic phase in all proportions. At 80 °C, media with low concentrations of the polymer are isotropic. From about 7% to 18–20% polymer, a birefringent region occurs which is, by optical microscopic examination, comprised of both polymer-rich and monomer-rich phases. Above ~20% polymer content, the mixture is clearly smectic only. Simple consideration of the phase diagram in Figure 3 would suggest that, at 45 °C, polymerization of CMA-10 should proceed in a smectic phase at all percentages of conversion. Of course, at higher percentages of conversion, we would expect the polymerization to stop short of complete conversion since the T_g of the pure polymer is around 55 °C. At 80 °C, while CMA-10 should be initially in an isotropic phase, we would expect from Figure 3 that polymerization might well lead to formation of an intermediate biphase and finally a smectic phase: Higher conversion should be possible at 80 °C since the pure polymer T_g is ~55 °C.

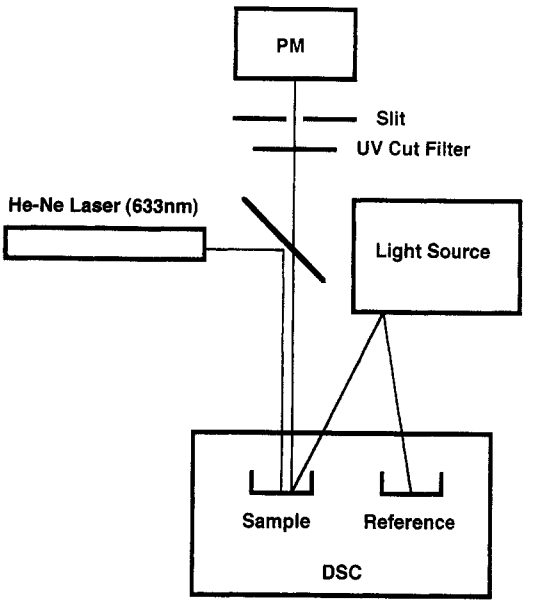


Figure 4. General experimental setup for simultaneous exotherm/light scattering measurement.

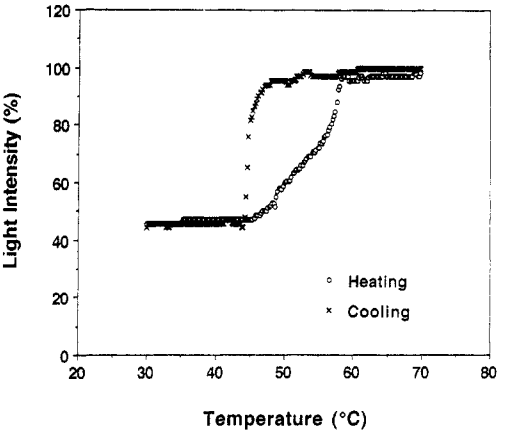


Figure 5. Reflected light intensity versus temperature for CMA-10 in the DSC apparatus depicted in Figure 4.

In order to shed light on actual changes in the medium during the course of the polymerization process and thereby provide comparison between the results in the phase diagram in Figure 3 and the polymerization exotherms in Figure 1 (in particular the double rate acceleration phenomenon), we designed the continuous laser-light scattering unit in Figure 4. This experimental setup allows us to monitor medium changes occurring during the polymerization process which result in enhanced light scattering. Any increases in medium light scattering results in a decrease in the intensity of light reaching the photodiode since scattering from the medium decreases the intensity of the reflected light from the aluminum DSC plan. In order to provide a reference for the extent and relative amount of light scattered from various mesophases, Figure 5 shows a plot of reflected light intensity (reaching the photodiode upon reflection) versus temperature for a sample of CMA-10. Upon cooling from the isotropic phase, the cholesteric phase tends to adopt a planar texture, and the smectic phase exhibits homeo-

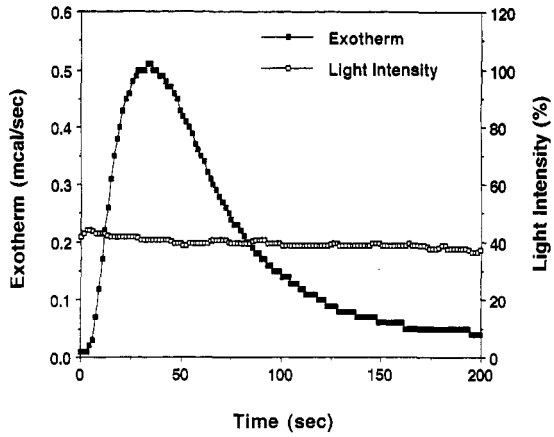


Figure 6. Polymerization exotherms and simultaneous HeNe reflected light intensity for the CMA-10 sample in DSC at 45 °C with 1 wt % DMPA photoinitiator using the 366-nm (filtered) output of a medium-pressure mercury lamp.

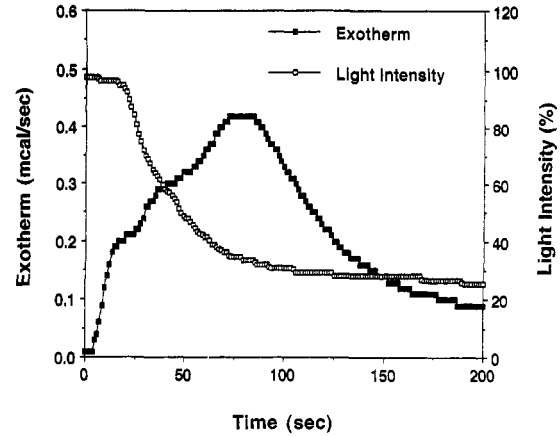


Figure 7. Polymerization exotherm and simultaneous HeNe reflected light intensity for the CMA-10 sample in DSC at 80 °C with 1 wt % DMPA photoinitiator using the 366-nm (filtered) output of a medium-pressure mercury lamp.

tropic alignment in the DSC pan, thereby limiting the extent of light scattering. This results in only a minor decrease in the measured reflected light intensity to about 45 °C whereupon a large decrease occurs. Upon heating in the DSC pan, the smectic and cholesteric phases adopt fanlike textures, resulting in enhanced light scattering (decreased transmitted light) compared to the isotropic phase. If polymerization of CMA-10 is conducted at 45 °C, the resultant plot of reflected light intensity versus time throughout the polymerization process can be obtained. Figure 6 shows the reflected light intensity results at 45 °C superimposed on the same time scale as the exotherm curve, which is shown for direct comparison. It is obvious that polymerization in the smectic phase of CMA-10 at 45 °C involves essentially no change in the amount of light scattered by the medium. Accordingly, the exotherm curve shows no sudden increases in the polymerization rate: The rate is, however, very fast even in the very early stages of conversion. If the polymerization is followed continuously by cross-polarized optical microscopy, no evidence for any large change in the medium is discernable: It remains smectic. This is certainly in agreement with the equilibrium phase behavior at 45 °C depicted in Figure 3. (Of course, we cannot totally rule out some small degree of microphase separation during polymerization at a level not detected by optical microscopy or light scattering.) One final point concerning polymerization at 45 °C is that the ultimate conversion attainable is only about 75% conversion. This may be attributed to the T_g of the pure polymer which is about 55 °C, approximately 10 °C higher than the polymerization temperature. At high conversions, when the T_g of the polymer exceeds the polymerization temperature at 45 °C, polymerization ceases. At 80 °C, in stark contrast to the results at 45 °C, there is an abrupt decrease in the reflected light intensity (Figure 7) which occurs at exactly the same time that the increase in the polymerization rate occurs. The decrease in reflected light intensity continues until the maximum rate of polymerization is obtained; thereafter, little additional decrease in the reflected light intensity occurs for the rest of the polymerization process. The decrease in light intensity and its correlation with the rate increases in polymerization at 80 °C for CMA-10, suggest that a medium change, or series of changes, is responsible for the acceleration in the polymerization kinetics. Interestingly, an optical microscopic investigation of the polymerization process reveals that a change in the medium texture occurs from totally dark under cross-polarizers (nonbirefringent isotropic medium) to a biphasic medium apparently comprised of a liquid crystalline polymer-rich phase and an isotropic phase. The result is a rate acceleration (the first one that occurs in Figure 7). There is a second change in the optical texture to a system which appears to be predominately smectic: This second change correlates with the second rate acceleration.

Interestingly, a DSC scan of a sample polymerized to a conversion well above that required for rate acceleration suggests that a single homogeneous smectic phase, which according to Figure 3 is the thermodynamic equilibrium state, may not be formed completely during polymerization, i.e., the system may not be totally a single phase. This is under continued investigation.

C. CMA-10 Kinetic Analysis. In order to establish the kinetic origin of the results in Figures 6 and 7 at 45 and 80 °C, we employed the method first described by Tryson and Shultz[8] for evaluation of individual propagation, k_p, and termination, k_t, rate constants using a DSC to evaluate steady-state and non-steady rates as a function of time. This method requires the assumption of approximate attainment of a steady-state radical concentration upon light irradiation and a decay to the base line (upon abruptly ending the light exposure) of the polymerization rate which occurs on a time scale longer than the instrument response function of the DSC. Since the polymerization rate at both 45 and 80 °C is approximately dependent upon the square root of the exciting light intensity over the conversion range being considered (at least up to about 50 % conversion), we work from the premise that, at least for our calculations, the steady-state assumption during irradiation is valid (or at least approached) for CMA-10. Except for very low conversions at 80 °C in the isotropic shape of CMA-10 where the decay of the polymerization exotherm upon removal of the excitation light source is very close to the response time for the DSC, the exotherm decays at both 45 and 80 °C are substantially longer than the DSC response function. The steady-state polymerization is evaluated by eq 1 to give the ratio of $k_p/k_t^{1/2}$, while the exotherm decay is evaluated by eq 2 to give k_t/k_p from the slope of a plot of the reciprocal exotherm rate versus time.

$$\text{polymerization rate} = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \frac{k_p}{k_t^{1/2}}[\mathrm{M}][(\Phi(I_{ABS})]^{1/2} = \frac{k_p}{k_t^{1/2}}[\mathrm{M}]R_i^{1/2} \quad (1)$$

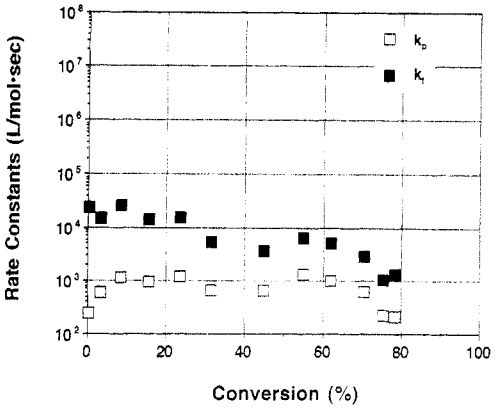


Figure 8. Plots of k_t and k_p versus percent conversion for polymerization of CMA-10 at 45 °C.

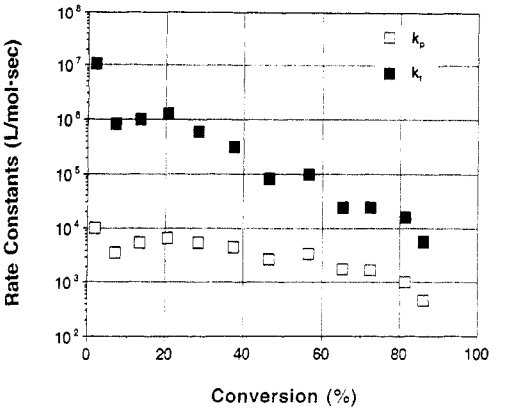


Figure 9. Plots of k_t and k_p versus percent conversion for photopolymerization of CMA-10 at 80 °C.

$$\frac{[M]/-d[M]}{dt} = \frac{[M]_0}{(R_p)_s} + \frac{k_t}{k_p}t \qquad (2)$$

where Φ = quantum yield of initiating radical formation, I_{ABS} = intensity of light absorbed, $(R_p)_s$ = steady-state polymerization rate at the conversion when the light source is terminated, $[M]_0$ = the monomer concentration when the light source is terminated, and R_i = rate of initiation.

Results for $k_t/k_p^{1/2}$ and k_t/k_p are used to obtain individual rate constants for k_t and k_p at several percentages of conversion. Incidentally, the initiation rates, R_i, used to calculate the ratio $k_t/k_p^{1/2}$ were obtained by measuring the rate of reaction of primary initiation radicals with a radical scavenger, 4-(2,2,6,6-tetramethyl-1-piperidinyloxy) benzoate (TMPO-BOA), at a series of conversions. This allowed us to calculate the initiation rate as a function of percent conversion. The initial initiation rate was approximated by measuring the loss of TMPO-BOA initially present in the CMA-10 sample by HPLC analysis as a function of photolysis time. The rate of consumption of TMPO-BOA was equated to the initiation rate. At higher percentages of conversion, the polymerization was temporarily interrupted by terminating the light source, followed by injection of a small amount TMPO-BOA into the sample. After waiting for mixing and equilibration of the system, the loss of TMPO-BOA was measured by HPLC as a function of photolysis time. Again, the initiation rate was equated to the rate of loss of TMPO-BOA. While this method introduces some error into the estimation of the initiation rate, it allows for individual rate constants for propagation and termination to be approximated. Because of the errors introduced when attempting to estimate initiation rates by any method and since use of the ac 60-cycle mercury lamp source allows us to only estimate steady-state polymerization rates, the rate constants quoted for k_p and k_t must be viewed only as approximations. We also note that there are errors in the calculation of k_p and k_t values due to incomplete purging of oxygen from samples in the extotherm unit using our nitrogen degassing procedure. In addition, there is also error due to incomplete purging of oxygen from samples in the exotherm unit via our nitrogen degassing procedure. The results for k_p and k_t are shown in Figures 8 and 9 for polymerization of CMA-10 at 45 (smectic) and 80 °C (initially isotropic). What kind of information can we obtain from a comparison of k_p and k_t values at 45 and 80 °C? Concentrating our discussion first on low conversion (less than 8%), it is quite obvious that, at 45 °C in the smectic phase, k_t is substantially lower (3 orders of magnitude) than that at 80 °C: This is not simply due to a temperature change, since temperature changes of 30 °C would only at most result in an approximate doubling or tripling of the rate constant (depending on the activation energy). In the smectic phase (45 °C) the calculated propagation rate constant is a factor of about 4 less than that in the isotropic phase. (We should point out that there is significant error in the k_t and k_p values obtained for CMA-10 at 80 °C at low conversion due to the high value of k_t/k_p.) The rapid decay of the exotherm rate at 80 °C makes it very difficult to calculate the ratio of k_t/k_p accurately: Our experience indicates that, for the first values at low conversion, k_t is probably a lower limit estimate, while the value for k_p is probably an upper limit value and is probably closer to the value for k_p obtained at ~8% conversion where the decay curve for the k_t/k_p calculation is not so fast and the polymer lifetimes are longer. From the results at low conversions at 45 °C (smectic phase) and 80 °C (isotropic phase), we can conclude that polymerization in the highly viscous smectic phase has a profound effect in lowering k_t. Such a result was anticipated by both Blumstein[3] and Broer.[9] It is the magnitude of the decrease in k_t in the smectic medium at 45 °C that is so profound and responsible for the resultant rapid rate of polymerization (at low conversions) and the increased quantum efficiency (reported in ref 5) in the smectic phase compared to the isotropic phase. Considering the origin of the large decrease in the rate in the smectic phase at low conversion, we can attribute it to either a decrease in the chain translational mobility, a decrease in the chain end rotational mobility, or a decrease in both translational and rotational mobility in the viscous medium.

The results at low conversion at 45 and 80 °C are in agreement with the results reported in previous publications for CMA-10.[4,5] Specifically, for polymerization at low conversion at 45 and 88 °C (results are similar for 80 °C), we had previously reported that the polymer samples generated had much higher molecular weights and higher formation quantum yields when polymerization was conducted at 45 °C in the smectic phase of CMA-10. These results are certainly consistent with the low initial value of k_t at 45 °C compared to 80 °C reported herein.

Up to this point, our discussion has focused on the polymerization kinetics for CMA-10 at low conversion at 45 and 80 °C. While k_p and k_t change relatively little at higher conversion for polymerization of CMA-10 at 45 °C in the smectic phase (Figure 8), there is a dramatic decrease in k_t at 80 °C at higher conversions, while k_p decreases very little (but some) up to about 60–70% conversion. An analysis of the decrease in k_t experienced at 80 °C at higher conversions is very informative when evaluated in the context of the maximum changes during polymerization. Judging from the small decrease in k_t with conversion for

CMA-10 at 45 °C, which is in a medium with much higher viscosity than at 80 °C, we project that changes in k_t at 80 °C will result from specific medium changes such as conversion to a liquid crystalline medium. With this in mind, we note that the initial drop in k_t from about 10^7 to about 10^5 L mol^{-1} s^{-1} coincides with the medium phase change/separation and concomitant decrease in reflected light intensity (which begins to be noticeable at percentages of conversion of about 5–8%). The medium from about 8 to ~20% conversion is characterized by a significant contribution from a liquid crystalline phase containing a high polymer content and an isotropic phase containing primarily monomer. Hence, one is tempted to assign the drop in k_t to a change in order alone and the accompanying decrease in medium mobility. As a result, we project that the lower k_t value at 80 °C from ~8–20% conversion, compared to k_t at low conversions less than 8%, is a result in large part to the presence of the liquid crystalline phase and no doubt an overall reduction in translational and/or rotational diffusion rates of polymer chains. The additional drop at conversions greater than about 20% correlates with the continued decrease in the reflected light intensity (Figure 7) and the change to a medium which has a more fully developed (but still probably exhibiting some degree of phase separation as discussed earlier) smectic texture. The drop in k_t from approximately 10^6 to 2×10^4 L mol^{-1} s^{-1} on going from 20 to 60% conversion is due in large part to the reduction in diffusional mobility of the reaction medium. The final decrease in k_t above 70% conversion is most likely due to an additional increase in the system viscosity attained at high conversion: The reason for the decrease in k_t at 80 °C above 70% conversion is probably similar to that for the decrease at 45 °C at higher conversions.

One final observation concerning polymerization for CMA-10 at other temperatures is important. At 50 °C, with the monomer initially smectic but probably of lower order than at 45 °C, since it is closer to the transition to the cholesteric nematic phase, the polymerization is characterized by an almost immediate decrease in reflected light intensity and rapid polymerization. In addition, at higher conversions for 50 °C, as determined by a DSC scanning analysis of a sample polymerized to about 70% conversion, the medium is characterized by at least some degree of polymer/monomer phase separation; i.e., the equilibrium phase mixture predicted by Figure 3 for a miscible monomer/polymer system is not attained during the polymerization process. This "phase separation" is probably dictated by kinetic inability to attain complete thermodynamic miscibility. At temperatures corresponding to the case where the CMA-10 monomer is initially in a cholesteric phase, an increase in light scattering and a concomitant increase in rate also occur as the transition to a medium which, although characterized by some phase separation between monomer and polymer, is largely smectic as inferred by optical microscopy. Hence, the rate increase occurs as the mobility of the medium (controlled by the smectic phase) is reduced.

D. HCMA-10 and CMA-4 Exotherm Curves. In order to illustrate that the double acceleration phenomenon described in detail for CMA-10 is operative for other systems with slight structural modifications, exotherm curves for photopolymerization of HCMA-10 and CMA-4 are presented in Figures 10 and 11. At 100 °C for CMA-4 and 60 °C for HCMA-10, the double rate acceleration phenomenon is prominent. In both cases, for CMA-4 at 100 °C and HCMA-10 at 60 °C, polymerization involving double rate acceleration occurs well above the clearing temperatures (see Table 1) in the isotropic phase. Without

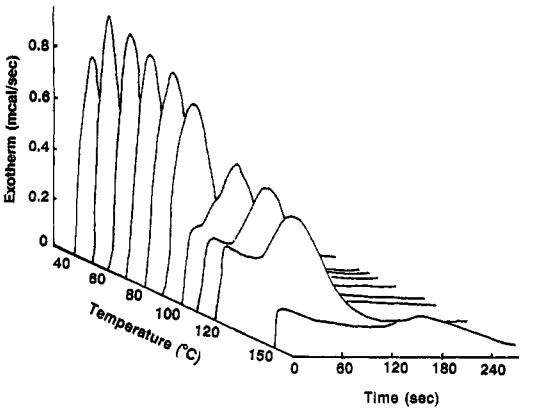


Figure 10. Polymerization exotherms of CMA-4 with 1 wt % DMPA photoinitiator using a medium-pressure mercury lamp (366-nm filter) at several temperatures.

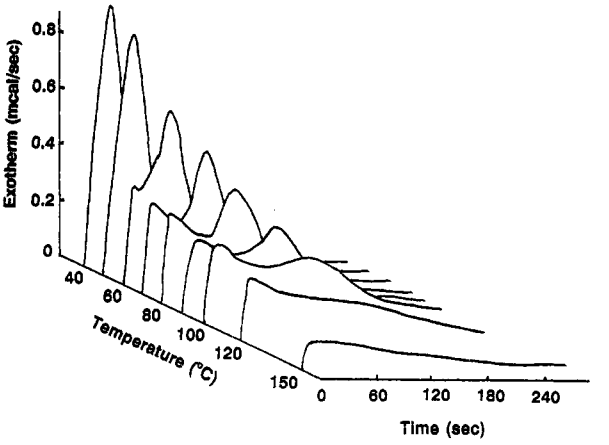


Figure 11. Polymerization exotherms of HCMA-10 with 1 wt % DMPA photoinitiator using a medium-pressure mercury lamp (366-nm filter) at several temperatures.

presenting a detailed kinetic analysis of each monomer at different temperatures, we simply note that the double acceleration phenomenon is very prominent at about 15–30 °C above the clearing temperature of the respective monomer. The exact temperature at which the double rate acceleration phenomenon for CMA-10, CMA-4, HCMA-10 takes place will be dictated by the relative viscosity of the polymerization phase(s) and the resultant effect of the ordering on the change in k_t.

The results for HCMA-10 in Figure 11 are particularly interesting for comparison since the rate accelerations occur at relatively lower temperatures than for CMA-10: Presumably this reflects a more flexible mesogenic group. The results for CMA-4 illustrate that when the spacer is shortened, the dual rate acceleration, presumably via the same mechanism as operative for CMA-10, occurs at much higher temperatures: The shorter methylene chain in CMA-4 allows coupling of the mesogenic groups to the backbone of the polymer generated. These preliminary results for CMA-4 and HCMA-10 are presented herein simply to illustrate the universality of such dual rate accelerations and their sensitivity to the side-chain length and the chemical nature of the mesogenic group in these closely related cholesteric liquid crystalline monomer types.

Conclusions

In this paper, we describe detailed kinetics for the photoinitiated polymerization of a cholesteryl-bearing methacrylate (CMA-10). By selecting temperatures at which the polymerization was conducted (a) completely

in a smectic phase and (b) initially in an isotropic phase followed by conversion to a biphasic medium, the effect of liquid crystalline phases on polymerization kinetics was evaluated. The following conclusions are drawn from the results in this study of CMA-10.

1. The values for k_t are much lower in the smectic phase at 45 °C than in the isotropic phase at 80 °C.
2. The modest decrease in k_p at 45 °C (compared to 80 °C) is due in large part to a simple decrease in temperature.
3. During the course of polymerization of CMA-10 initially in an isotropic phase at 80 °C, two rate acceleration processes occur corresponding to distinct changes in the medium composition and order: A dramatic decrease in the termination rate process accounts for these results.
4. Polymerization of CMA-10 at 80 °C leads to almost 100% conversion, while polymerization at 45 °C, which is below the glass transition of the pure polymer (55 °C), proceeds only to about 86% conversion.

Finally, we also noted that two other structurally similar monomers display essentially the same rate acceleration phenomenon as CMA-10, but at different temperatures.

Our results are in accord with the supposition that polymerization in media which are ordered by liquid crystalline alignment can have profound effects on individual kinetic rate constants. In the present case, termination rate constants are dramatically lowered in the smectic liquid crystalline phases, while propagation rate constants are only marginally lower (due in large part to a temperature effect). Although not presented in this paper, we have found systems in which the rate can actually decrease in a liquid crystalline medium. In the present case for CMA-10, the large drop in k_t compared to k_p results in a relative enhancement. In other systems we have worked with, in particular some semifluorinated methacrylates and acrylates, an even greater rate enhancement occurs. The kinetics of these systems are currently being investigated.

Acknowledgment. We thank D. Kang for numerous preliminary experiments and the establishment of certain experimental techniques used in this study. We acknowledge both the National Science Foundation [Grant No. DMR-8917485 (Polymers Program)] and JSR Corp. (T.W.) for support of this work.

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