Effect of Repetition Rate on the Pulsed-Laser-Initiated Polymerization of a Liquid Crystalline Monomer

Charles E. Hoyle* and C. P. Chawla

Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, Mississippi 39406

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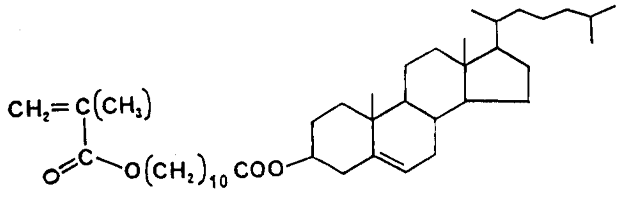
ABSTRACT: The use of high repetition rate laser pulses for the photoinitiated polymerization of a cholesteryl-bearing methacrylate liquid crystalline monomer has been investigated. In the case of polymerization in the isotropic phase, the molecular weight and yield of the polymer generated decreased with a decrease in time between firing of individual laser pulses. This phenomenon is in accordance with all previously reported results for isotropic monomers. However, polymerization in the smectic phase of the monomer was not affected by the laser repetition rate. It is postulated that for pulsed-laser-initiated polymerization in the smectic phase the rapid termination process of coupling of primary and short chain oligomeric radical terminator species with growing polymer radical chains, normally found for radical polymerization of isotropic monomers, is greatly reduced.

Introduction

During the past 2 decades there have been a number of reports describing polymerization of liquid crystalline monomers as well as polymerization of isotropic monomers in liquid crystalline media.[1−17] The literature in this area prior to 1985 has been aptly summarized in three excellent review papers.[1−3] Based upon these review papers and considering the results which have been reported subsequent to 1985 by several groups[4−8] including ours,[9−13,15−17] we can draw at least some conclusions with respect to free-radical polymerization of liquid crystalline monomers in mesogenic versus isotropic phases. First, polymerization of acrylate or methacrylate monomers with mesogenic groups decoupled from the reactive functionality by a methylene spacer does not involve any rate enhancement when polymerization is conducted in the nematic phase instead of the isotropic phase of the monomer species, except of course as a simple difference in temperature might dictate. The absence of a rate effect induced by nematic ordering was first demonstrated by Blumstein et al.[14] for a *N*-(*p*-cyanobenzylidene)-*p*-aminostyrene and subsequently confirmed by work in Broer's laboratory[4] for an acrylate monomer bearing a phenyl benzoate mesogen and most recently in our laboratory[15] for a cholesteric nematic phase formed by a styryloxy monomer with a cholesteryl group attached via a methylene spacer. The effect of smectic ordering can have marked consequences with respect to rate acceleration of monofunctional monomers. Indeed, we have found that the smectic A phase of the cholesteryl monomer depicted below, and designated CMA-10, has a significant effect on the polymerization rate, the rate being enhanced when polymerization is conducted in the smectic phase versus the isotropic phase of the neat monomer. In another case, Broer's laboratory[4] found that difunctional acrylates (methacrylates) with benzoate mesogenic units attached apparently show little, if any, rate enhancement in the smectic phase under the experimental conditions employed. Finally, polymerization of mesomorphic monomers which form smectic B type phases may experience either marked rate enhancement[13] or rate retardation[16] depending upon the exact nature of the medium and the monomer structure.



CMA-10

In a previous paper[17] we reported on the polymerization of the CMA-10 monomer in the smectic and isotropic phases and found that there is a marked rate enhancement when polymerization occurs in the smectic A phase at 45 °C. Importantly, polymerization of CMA-10 at 45 °C does not result in phase separation as the polymerization proceeds. This has been determined by monitoring during polymerization continuously the scattering of a HeNe laser (632.8 nm) beam which does not emit at a wavelength corresponding to an absorption band in either the monomer unit or the photoinitiator employed.[17] The origin of the rate enhancement in the smectic phase at 45 °C for CMA-10 is a decrease in the average polymer−polymer bimolecular termination rate constant by over 2 orders of magnitude compared to the isotropic phase.[17] Propagation is somewhat lower in the smectic phase, but only by a small factor, probably a simple result of the difference in temperature of the polymerization conducted in the isotropic and smectic phases at 80 and 45 °C, respectively. We concluded from our kinetic analysis that since termination involves the interaction of two growing polymer radical chains, which must combine after a translational/rotational diffusion process, it is quite reasonable that the smectic medium should exert a limitation on the termination process by inhibiting translational and/or rotational diffusion processes.

One critical aspect of polymerization in the smectic liquid crystalline phase of CMA-10 not explored in our previous work deals with the termination of growing polymer chains by primary and short chain oligomeric radicals. From a general survey of the literature[18−21] there is strong evidence that the rate of termination in free-radical polymerization is dependent upon the length of the growing polymer radical chain. For example, in

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an elegant set of experiments using an initiator radical identical in structure to the corresponding polymer radical chain end, Stickler[21] has clearly shown that the average rate constant for bimolecular reaction of such primary radicals with radical polymer chains can be as much as 50 times greater than that for bimolecular termination involving two "average" polymer radicals. In our previous work with CMA-10 we obtained bimolecular termination rate constants using classical kinetic assumptions. This analysis provides an estimation of an average value for k_t for bimolecular processes involving combinations of all size radicals. We found that the average termination rate constant for CMA-10 polymerization was about 2 orders of magnitude lower in the smectic A phase than in the isotropic phase. For termination involving coupling of high molecular weight polymer radicals and primary or low molecular weight oligomeric radicals, it is not at all clear whether there will be an appreciable effect by the medium ordering.

In this paper, we address the effect that the medium order has on the termination process operative in pulsed-laser-initiated polymerization when the delay time between firing of multiple pulses becomes quite short with respect to the lifetime of a growing polymer chain. Specifically, we ask the question of whether a smectic liquid crystalline phase affects termination of primary [and small-molecule radical oligomeric] radicals produced by a given laser pulse in a sequence of pulses with high molecular weight polymer radicals initiated by pulses previous to the given pulse. (This work has particular importance in cases which might require using high-intensity pulsed lasers with high repetition rates to initiate polymerization.) The answer to this question does not directly follow from the observation of a decrease in the bimolecular termination rate constant analysis previously conducted in our laboratory,[17] since only an average termination rate constant was determined in that investigation. The cumulative results from a number of laboratories[22-38] on pulsed-laser-initiated polymerization show that termination between high molecular weight polymers and low molecular weight radicals is operative in reducing the overall polymerization rate and product molecular weight for all isotropic monomers investigated to date, including free-radical homopolymerization of isotropic monofunctional monomers,[22-29,32-36] copolymerization of isotropic mixtures of monofunctional monomers,[30,31] and polymerization of multifunctional acrylated monomers[37,38] to give cross-linked networks. Only trifunctional monomers show some tendency for the polymerization rates to be independent of the laser repetition rate.[38] In all cases where linear, non-cross-linked polymers are formed, reduced molecular weight samples are produced at higher laser repetition rates (pulses spaced closer together in time). Herein, we clearly demonstrate that high molecular weight polymers can indeed be generated using high laser repetition rates provided that polymerization proceeds in an appropriate liquid crystalline smectic A phase.

Experimental Section

Synthesis of the cholesteryl methacrylate monomer designated CMA-10 was accomplished as described in ref 11. Thermal transitions for CMA-10 have been reported previously[11] as determined by DSC and optical microscopy.

Molecular weight distribution studies were conducted on a GPC system (35 °C) consisting of a Waters 6000A solvent delivery pump, a Model 7010 Rheodyne injector, a Waters 410 differential refractometer, and four Ultrastyragel (Waters) columns (100, 500, 10^4, and 10^4, and 10^6 Å) with a tetrahydrofuran mobile phase. Polymer Laboratories polystyrene standards were used as references. The flow rate was 1.0 mL/min, and the sample concentration used was 2.5 mg/0.3 mL of THF.

The photoinitiator, 1,1-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy), was recrystallized from methanol.

Polymerization exotherms[39] were recorded either on a modified Perkin-Elmer DSC-1B (Figures 7 and 8) or a DSC-2B (Figures 1−6). For photopolymerization studies, films containing 1 wt % photoinitiator were cast into Omnitherm DSC pans from dichloroethane solutions of the monomer to give either 3.3 mg (for Figures 7 and 8) or 2.5 mg (for Figures 1−6) of CMA-10 monomer. Typically, each sample was heated to the isotropic phase before cooling to the respective polymerization temperature while purging continuously with nitrogen for 10 min before polymerization. In this study, indented pans were not used, and hence samples were not distributed totally uniformly in the DSC pans, with higher monomer concentrations accumulating near the outer edges of the pans. This resulted in nonuniform light absorption by the samples.

Two types of light sources were used: (1) a medium-pressure mercury lamp (Canrad Hanovia) with a 366-nm filter; (2) a pulsed excimer laser (Lumonics; HE-440, XeF, λ_{ex} = 350 nm). The intensity of the laser could be modified by insertion of neutral density filters. The total number of pulses delivered from the laser, as well as its repetition rate, was controlled by an external computer. The light intensity measurements were made either with an ILC radiometer/photodiode (calibrated) or by absorption of black-body pans placed in the DSC sample holder. Where values are given in W cm^{-2}, the measurement was made with the ILC radiometer. Otherwise, where values are quoted in mJ/pulse, the measurements were made in the DSC with a black-body pan and have a greater error than the values determined with the ILC radiometer.

Results and Discussion

We have previously shown[11] that CMA-10 can exhibit either a cholesteric nematic phase (62.7−51.5 °C) or a smectic A phase (below 51.5 °C) upon cooling from the isotropic melt (above 62.7 °C). (Use of low photoinitiator concentrations lower transition temperatures slightly.) In this paper, although we are focusing on the pulsed-laser-initiated polymerization of CMA-10 in smectic A and isotropic phases, it is necessary to first consider steady-state GPC results and the general effect of phase structure on the molecular weight distribution of the polymers generated.

Steady-State Polymerization of CMA-10. In order to build a framework for the laser repetition rate study, as well as to illustrate the basic differences in the polymer samples produced by polymerization of CMA-10 (with 1 wt % 1,1-dimethoxy-2-phenylacetophenone) in the smectic A phase (45 °C) and in the isotropic phase (88 °C) to low conversions (less than 15−20%), we first show GPC traces (Figure 1) for samples (10-s exposure) generated by a mercury lamp (366-nm filter; intensity = 8.4×10^{-5} W cm^{-2}). In all figures which display GPC traces, elution volumes of polystyrene standards are indicated directly with vertical lines. It is quite obvious

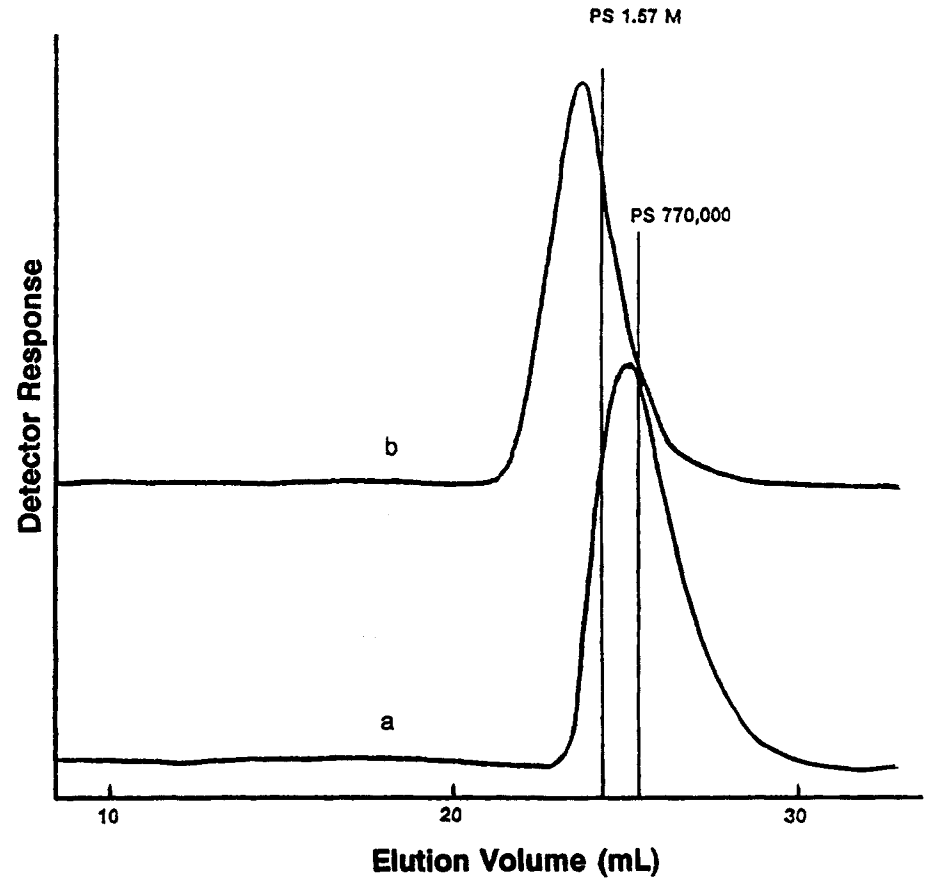

Figure 1. GPC traces for CMA-10 exposed to the mercury lamp (366-nm filter, light intensity = 8.4 × 10^{-5} W cm^{-2}) for 10 s: (a) at 88 °C, isotropic; (b) at 45 °C, smectic.

from the results in Figure 1 that polymerization in the smectic phase at 45 °C produces polymer with much higher molecular weight than polymerization in the isotropic phase at 88 °C. [We note that for the results in Figure 1, as well as those to be presented in Figures 3 and 4, the GPC curves at low elution volumes (short retention times) may not be totally accurate due to the inability of the GPC column set employed to totally resolve the high molecular weight polymers.] The GPC detector response sensitivity and the amount of sample injected onto the GPC columns were different for the two chromatograms in Figure 1. In separate experiments we have determined that at low conversions the overall yield of polymer at 45 °C (smectic) is actually higher than that at 88 °C (isotropic) for a given photolysis time, i.e., the ratio of the quantum yield at 45 °C ($\Phi_{45\ °C}$) to the quantum yield at 88 °C ($\Phi_{88\ °C}$) is approximately 3. The results in Figure 1 are in complete agreement with a detailed kinetic analysis[17] which shows that the average termination rate constant is decreased by over 2 orders of magnitude in the smectic phase at 45 °C.

To be complete, results for higher conversion are also presented. Polymerization at 88 °C, from the isotropic phase initially, to higher extents of polymerization produces a biphasic medium characterized by contribution from a polymer-rich liquid crystalline phase at conversions above about 19%.[17] The exotherm curve in Figure 2 illustrates the rate acceleration for CMA-10 polymerization at 88 °C which occurs after about a 32-s exposure to the 366-nm filtered output of the medium-pressure mercury lamp (intensity = 8.4 × 10^{-5} W cm^{-2}). We have shown that the rate acceleration for CMA-10 is caused by a decrease in the termination rate constant which accompanies the abrupt change in medium ordering occurring after a conversion of about 19% is attained.[17] Figure 3 shows GPC traces for polymer samples produced by exposure to the same light source used to generate the exotherm curves in Figure 2, but for varying periods of total exposure. For the results in Figures 3–5, care was taken to ensure that the detector sensitivity and sample amount were identical for each GPC run. The most striking feature of the set of GPC curves in Figure 3 is the increase in higher molecular weight species (short retention times) at higher conversions. The high molecular weight contribution to the total GPC curve increases as the exposure time increases, i.e., as polymerization takes place in the biphasic medium formed after about 19% conversion.

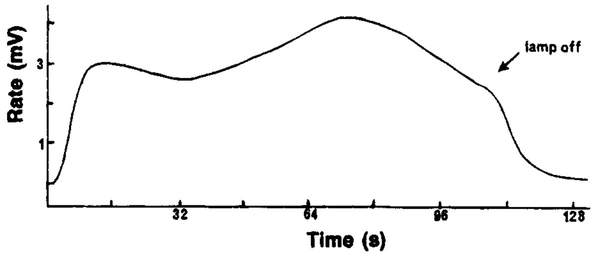

Figure 2. Polymerization exotherm for CMA-10 exposed to the mercury lamp (366-nm filter, light intensity = 8.4 × 10^{-5} W cm^{-2} at 88 °C).

Pulsed-Laser-Initiated Polymerization of CMA-10. Returning to a consideration of CMA-10 photopolymerization at 45 and 88 °C to low conversions (this avoids the region where the medium change/rate acceleration occurs), we first consider the difference in lifetimes of the polymer radical chains at 45 and 88 °C at low conversion. From decay of exotherm curves (not shown) obtained upon the abrupt removal of the poly-

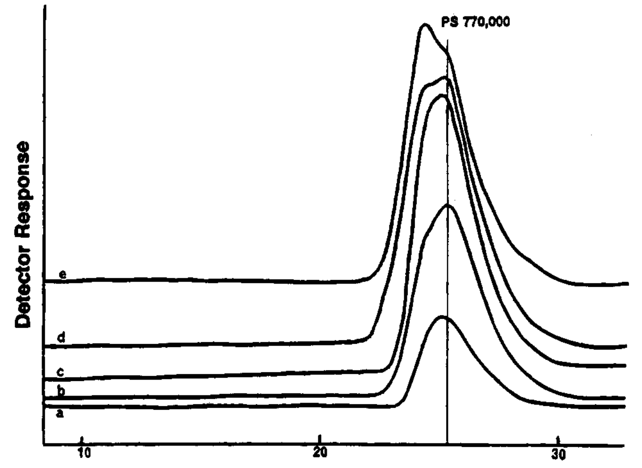

Figure 3. GPC traces for CMA-10 exposed to the mercury lamp (366-nm filter, light intensity = 8.4 × 10^{-5} W cm^{-2}) at 88 °C for (a) 10, (b) 32, (c) 42, (d) 52, and (e) 92 s.

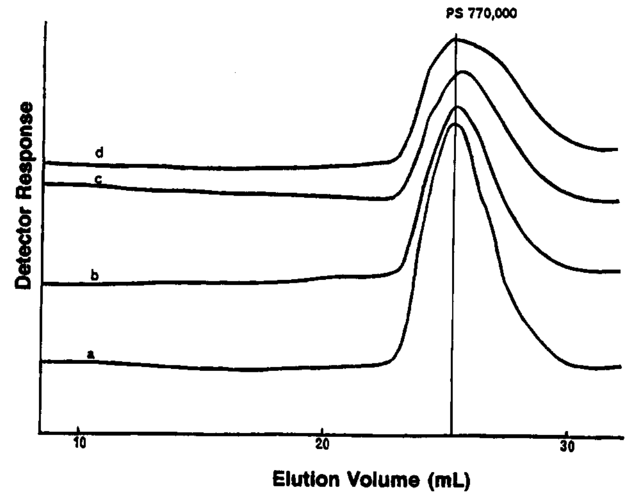

Figure 4. GPC traces for the laser-initiated polymerization of CMA-10 at 88 °C in the isotropic phase at different laser repetition rates (power per pulse = 5.9 × 10^{-3} mJ delivered to the sample pan): (a) 5, (b) 10, (c) 20, and (d) 40 Hz.

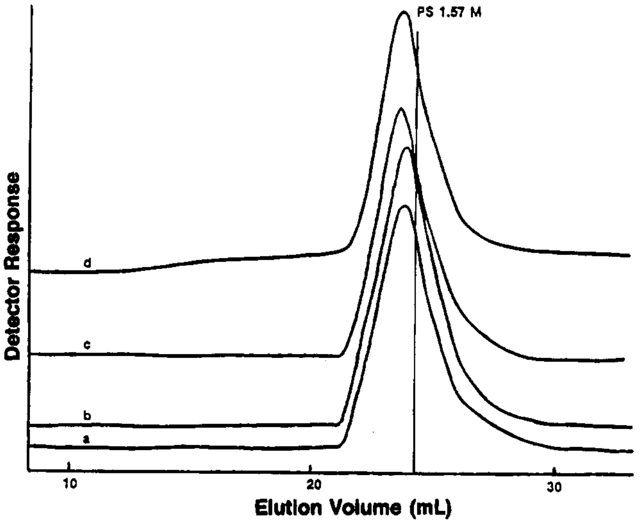

Figure 5. GPC traces for the laser-initiated polymerization of CMA-10 at 45 °C in the smectic phase at different laser repetition rates (power per pulse = 5.9 × 10^{-3} mJ delivered to the sample pan): (a) 5, (b) 10, (c) 20, and (d) 40 Hz.

merization light source, we know that at low conversions the lifetime of the polymer radical chain at 45 °C in the smectic phase is much greater than that at 88 °C. If premature termination were based on the lifetime of the polymer radical chain only, we would certainly expect that polymer radical chains in the smectic phase (45 °C) would be more susceptible than their counterparts in isotropic media (88 °C) to reaction with low molecular weight small-molecule radicals produced by a pulsed laser operating in a multiple pulse, high repetition rate mode. As discussed in the Introduction, such termination processes have been obtained in a number of laboratories for a variety of isotropic systems[22-38] where the polymer radical chain lifetimes are, in general, much shorter. The high repetition rate, multiple pulse laser-initiated polymerization experiment used in the present study involves exposing the CMA-10 monomer sample (with 1 wt % photoinitiator) to a series of laser pulses at varying time delays between individual laser pulses. The repetition rate, which dictates the time interval between laser pulses, is varied while keeping the total number of pulses delivered to each sample constant (in the present case a total of 25 consecutive pulses). It is expected for the isotropic case that, as the laser pulses are spaced at smaller time intervals, the reaction of polymer chains initiated by a given laser pulse and the radical species produced by subsequent pulses will result in a lower amount of polymer produced and a concomitant reduction in the contribution of high molecular weight polymers to the sample. A complete description of the polymerization dependence on laser repetition rate, first introduced by Aleksandrov in ref 22, and the theory behind the phenomenon are laid out in great detail in refs 23–25. The reader is referred to these excellent papers for an introduction to the subject. In Figure 4, GPC results for a pulsed-laser-initiated polymerization experiment conducted at 88 °C (25 pulses total) for repetition rates of 5 Hz (1 pulse every 0.2 s) to 40 Hz (1 pulse every 0.025 s) are shown. (In all cases, the percent conversion was less than 5% as estimated via DSC exotherm analysis.) The most obvious result in Figure 4 is a marked increase in contribution from lower molecular weight polymer species (at longer retention times) as the laser repetition rate increases. (The amount of polymer produced, as judged by the area of the GPC peaks, decreases with increasing repetition rate.) As noted previously, the marked increase in low molecular weight species at the expense of high molecular weight species is characteristic of pulsed-laser-initiated polymerization results for isotropic monomers.

In contrast to the results at 88 °C, Figure 5 shows that the molecular weight distribution of the polymer generated at 45 °C (smectic) by 25 laser pulses is independent of the laser repetition rate. Moreover, there appears to be little difference in the areas (estimated via DSC to be about 10–13% in each case) under the GPC curves in Figure 5. Apparently, the polymer radicals generated by a given laser pulse do not react efficiently with the small-molecule radical species produced by subsequent pulses. This behavior is unique, since all of the pulsed-laser-initiated polymerization investigations to date for monofunctional isotropic systems exhibit a pronounced effect, resulting in substantially lower molecular weight species being generated. The results in Figure 5 are particularly important since they show that the pulsed-laser-initiated polymerization of this particular liquid crystalline monomer in the smectic phase yields high molecular weight polymer in good yield even if the laser is operated at

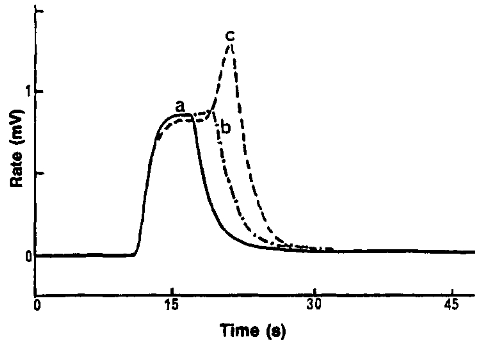

Figure 6. Polymerization exotherms for the laser-initiated polymerization of CMA-10 at 88 °C for different numbers of laser pulses at a laser repetition rate of 5 Hz: (a) 30 pulses (13.1% conversion); (b) 40 pulses (18.9% conversion); (c) 50 pulses (25.0% conversion).

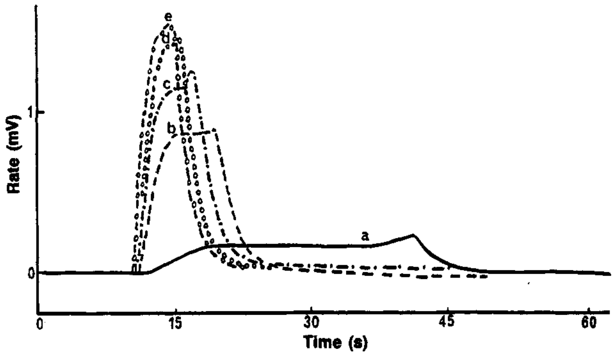

Figure 7. Polymerization exotherms for the laser-initiated polymerization of CMA-10 at 88 °C for different laser repetition rates: (a) 1 Hz (30); (b) 5 Hz (40); (c) 10 Hz (60); (d) 20 Hz (90); (e) 40 Hz (160). The numbers in parentheses indicate the number of laser pulses required for phase separation.

very high repetition rates. This is especially interesting in view of the longer lived polymer radical chains in the smectic phase at 45 °C compared to the isotropic phase. One final point should be noted. Since our GPC columns cannot differentiate species with extremely high molecular weights, there may be some amount of relatively slow termination which does take place between growing polymer radicals and the small-molecule radicals, but if it occurs it is a relatively minor process resulting in only a small reduction in polymer molecular weight.

One direct consequence of the operation of the laser at high repetition rate at 88 °C is the variation in the total number of photons (delivered to the sample) required to induce the rate acceleration phenomenon which results from the change in the medium organization. Figure 6 shows polymerization exotherms obtained for CMA-10 initiated by operation of the laser at 5 Hz. The total number of laser pulses was varied in order to determine the exact number required for the rate acceleration to begin. The exotherm in Figure 6 produced by delivery of a total of 30 pulses at 5 Hz resulted in 13.1% conversion and hence no rate acceleration. After delivery of 50 pulses (trace C), rate acceleration has clearly started. For the exotherm produced by delivery of 40 pulses at 5 Hz (trace C), the phase change-induced acceleration is just beginning at a conversion of about 18.9%. It was decided to determine the number of pulses required to attain the onset of the medium change-induced rate acceleration at several additional laser repetition rates. Figure 7 shows polymerization exotherms of CMA-10 at 88 °C for laser repetition rates ranging from 5 to 40 Hz. In each case the number of pulses delivered to the sample was just enough to induce the rate acceleration. [The exact number of pulses required to induce the medium change-induced rate acceleration was determined in a separate set of experiments at each repetition rate wherein the onset of rate acceleration was bracketed]. From the exotherms in Figure 7, we readily deduce that the total number of laser pulses required to cause the onset of rate acceleration increases as the repetition rate increases; i.e., at 10 Hz a total incident dose of about 11.4 mJ delivered to the sample pan (60 pulses) is required, while at 40 Hz a total dose of approximately 30.4 mJ delivered to the sample pan (160 pulses) is needed to realize the onset of rate acceleration. (We note that under the experimental conditions employed the incident dose is not absorbed uniformly by the sample due to variation in sample thickness in the pan as described in the Experimental Section.) As discussed before, because of significant primary radical termination at higher repetition rates a greater number of pulses (larger total dose) is required to attain the same percent conversion.

Conclusions

In this paper we have shown the consequences that the rapid polymerization rate and high quantum efficiency of polymerization in a smectic A phase can have on the molecular weight distribution of the polymers generated via both a medium-pressure mercury lamp and a pulsed laser source. Initially, we showed that when the mercury lamp is used, polymerization at 45 °C in the smectic phase results in polymer with very high molecular weight compared to that produced at low conversion in the isotropic phase at 88 °C prior to the change in medium order. Higher molecular weight polymer is produced for conversions greater than about 19% at 88 °C corresponding to polymerization in a biphasic medium with enhanced order. We then showed that operation of the laser at a high repetition rate in the smectic phase at 45 °C does not lead to reduction in the molecular weight of the polymer produced, while higher repetition rates in the isotropic phase at 88 °C leads to enhanced termination. This important result, which is the key focus of the paper, clearly demonstrates that primary [and low molecular weight oligomeric] radicals do not combine effectively with polymer radical chains in the smectic A phase, an important observation that to date is unique to polymerization in an ordered liquid crystalline phase. Finally we note that the total dose required to attain a medium change-induced rate acceleration at 88 °C increases as the laser repetition rate increases.

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