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Laser-Initiated Polymerization of a Mesomorphic Monomer and the Resultant Molecular Weight Distribution

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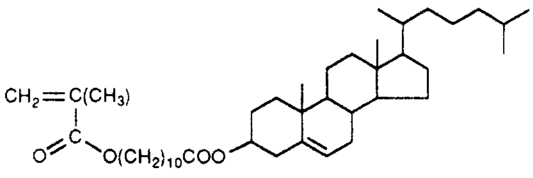
In a previous set of papers[1,2] we have shown that monomeric methacrylates bearing a mesogenic cholesteryl group separated via a methylene spacer linkage experience abrupt changes in the medium texture and order during polymerization. In comparing the effect of a smectic medium to that of an isotropic medium, the polymerization quantum efficiency is enhanced by a factor of between 2 and 5, depending upon such factors as the temperature of the liquid crystalline medium. For the cholesteryl monomer with a ten methylene chain spacer, assigned the acronym CMA-10 (see structure), we found that at temperatures just above the clearing temperature to temperatures well over 100 °C, polymerization initiated in the isotropic phase of the monomer proceeds to a birefringent liquid crystalline system. Higher temperatures above the clearing temperature require a greater percentage of polymer to be produced before the medium change occurs. Polymerization with the monomer initially in the cholesteric phase results in a rapid transition to a medium with a smectic texture after about only 1–2% polymer formation. In summarizing our results to date for CMA-10, we note that (a) polymerization quantum yields are higher in the smectic liquid crystalline medium than in the isotropic medium and (b) changes occur to yield a liquid crystalline system with a different texture (probably smectic by optical microscopy) during polymerization of the CMA-10 monomer which is initially in either the cholesteric or the isotropic phases.



CMA-10

In this brief note, we address one interesting question concerning polymerization in liquid crystalline media: What effect does polymerization in an anisotropic, mesomorphic medium have on the molecular weight distribution of the resultant polymers (see ref 4 for a critical analysis of the literature with respect to this and other questions dealing with various aspects of the polymerization of liquid crystalline systems)? We have elected to monitor the relative molecular weight distributions of polymers generated by exposure to single pulses (10-ns fwhm) from an excimer laser ($\lambda = 351$ nm) to answer this question.

To provide a framework for the results presented herein, we note that below the clearing temperature 63 °C (obtained upon cooling) but still above 52 °C, CMA-10 monomer is in a cholesteric phase, while below 52 °C to around room temperature (upon cooling) CMA-10 is in a smectic phase. [The smectic phase has been previously identified by Shannon.[3] We also note that transition temperatures for CMA-10 with 1 wt % photoinitiator are slightly lower than for the pure monomer, as expected.] Figure 1a shows the GPC chromatogram of the CMA-10 monomer (1–2% conversion) at 45 °C (temperature maintained constant throughout polymerization) after exposure to a single laser pulse (0.58 mJ cm^{-2} pulse^{-1}). By employing a photoinitiator (α,α-dimethoxydeoxybenzoin) at a concentration (1 wt %) which only absorbs a small fraction (approximately 26%) of the light, uniform sample exposure is ensured. The maximum of the refractive index versus time plot of the GPC data, by comparison to polystyrene standards, corresponds to a molecular weight of greater than 3 million. The GPC curve in Figure 1a reveals a relatively high molecular weight distribution resulting from polymerization in a smectic phase. The maintenance of a smectic texture at temperatures for which CMA-10 is initially smectic for polymerization to high conversion (above 80%) has been demonstrated in a previous paper.[1] Finally, we note that Shannon[5,6] reported cross-linking of CMA-10 at high conversion; however, at the low conversions in this report, while there may be some chain transfer to the allylic hydrogen on CMA-10, we detect no insoluble polymer.

In contrast to the results for polymerization at 45 °C, polymerization at 88 °C initiated by a single laser pulse takes place completely in an isotropic medium. At the low conversion (1–2%) of monomer to polymer produced by a single laser pulse ($\lambda = 351$ nm, power density = 2.36 mJ cm^{-2} pulse^{-1}), the GPC of the resultant polymer (Figure 1b) is characterized by a relatively broad molecular weight distribution with a peak maximum of the refractive index versus elution time plot corresponding to a polystyrene standard based molecular weight of 7.1×10^3. (At this point we note that the molecular weight distribution of a polymer sample generated by a single laser pulse has been described theoretically for methyl methacrylate, and the interested reader is referred to ref 7 for details.) The production of higher molecular weight species at 45 °C is in accord with higher quantum yield for polymerization in the smectic medium at 45 °C ($\Phi \approx 14\,900$) than in the isotropic phase at 88 °C ($\Phi \approx 3700$, lower limit value). (We note that absolute quantum yield measurements may be subject to considerable error.) One obvious explanation for the results in Figure 1a,b is a reduction in the termination rate processes when polymerization is conducted in the liquid crystalline state: such an explanation is suggested by work in refs 4b and 8. A decrease in the termination rate could result from a decrease in polymer radical center-of-mass diffusion, rotational relaxation restrictions on polymer chain ends, or both.

If polymerization of CMA-10 is carried out at 75 °C with the monomer initially in the isotropic phase, but where conversion to a liquid crystal state (postulated to be smectic) occurs at about 1–2% conversion (estimated from photopolymerization using a very low intensity continuous output source), one might expect to see a bimodal distribution in the GPC chromatogram with peak maxima corresponding to polymerization in (a) an isotropic phase for those polymers which terminate by combination processes prior to attaining the percent polymer required to induce the phase change and (b) a liquid crystalline system for those polymer chains which are still "living" at the instance of the phase change process. Figure 1c confirms this expectation and is noteworthy since it not only suggests that the polymerization proceeds to higher molecular weight for the anisotropic liquid crystalline system but also seems to indicate that the change from an isotropic to a liquid crystalline medium occurs, at least locally, within the time frame of polymerization of a single

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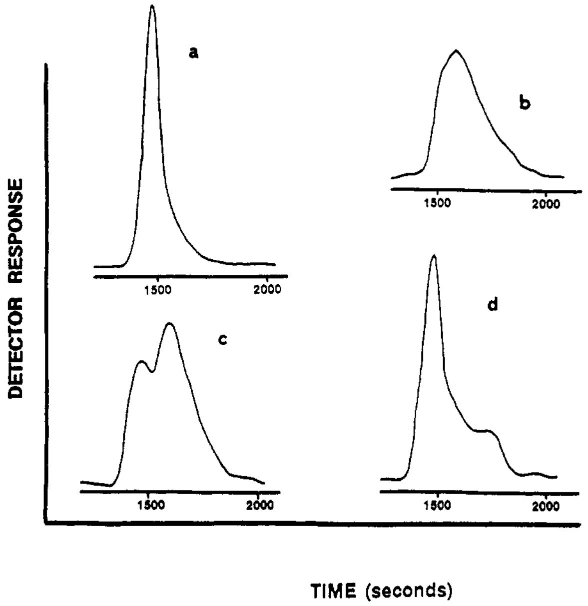

Figure 1. GPC of polymer generated by exposure of CMA-10 (1 wt % photoinitiator) in a DSC pan to a single laser pulse (λ = 351 nm): (a) 0.58 mJ cm^{-2} $pulse^{-1}$, 45 °C; (b) 2.56 mJ cm^{-2} $pulse^{-1}$, 88 °C; (c) 0.58 mJ cm^{-2} $pulse^{-1}$, 75 °C; (d) 0.58 mJ cm^{-2} $pulse^{-1}$, 58 °C.

polymer chain—remember that all chains were initiated by the laser at exactly the same time. Our results suggest that a single given high molecular weight polymer chain propagates with two sets of rate constants corresponding to polymerization in an isotropic medium, prior to the change, and a liquid crystalline medium, after the change.

The GPC of the polymer produced upon polymerization at 58 °C (monomer initially cholesteric) in Figure 1d shows significant contribution from a high molecular weight portion produced after the medium change (probably cholesteric to smectic) and a much smaller contribution from low molecular weight species produced prior to the medium change. Apparently, the change at 58 °C occurs at a somewhat lower percent conversion than for polymerization at 75 °C, accounting for the rather large contribution of the higher molecular weight fraction in the GPC results of Figure 1d.

In summary, results of the laser-initiated polymerization of CMA-10 clearly illustrate the important point that the molecular weight of the sample generated is high when polymerization occurs entirely in a liquid crystalline medium with a uniform smectic texture maintained. If a change from an isotropic (or a cholesteric) phase occurs during polymerization of a set of polymer radicals, the molecular weight distribution is bimodal with the lower molecular weight fraction representing polymers which experience termination while the sample is in an isotropic medium. Additional results from an investigation of other monomers will be forthcoming. In addition, a detailed molecular weight distribution analysis will be conducted with additional columns which can accurately separate very high molecular weight samples: a more precise polydispersity of the polymers produced will thus be obtained. We are currently developing methods to check for medium inhomogeneity or limits on monomer/polymer miscibility during polymerization of liquid crystalline monomers and will present our results in a future report.

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References and Notes

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Registry No. CMA-10 (homopolymer), 53880-96-9.