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Determination of the effects of cure conditions on the photopolymerization of liquid crystalline monomers using differential photo-calorimetry

Robert T. Pogue[*], Jill S. Ullett, Richard P. Chartoff

Center for Basic and Applied Polymer Research, The University of Dayton, 300 College Park, Dayton, OH 45469-0130, USA

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Abstract

Photopolymerization of diacrylate liquid crystalline monomers has several advantages over thermal polymerization. Most notably, photopolymerization allows for the cure reaction to occur at a temperature where a mesophase exists. In this paper we discuss the effects of several cure conditions, including temperature, on the conversion and reaction rates of two liquid crystalline monomers. Each of these monomers exhibits a nematic mesophase at elevated temperatures. The data indicate that the presence of the mesophase has an impact on both reaction rates and conversion. Further studies concerning the effects of photoinitiator composition and concentration reveal that these parameters significantly influence the polymerization rate but do not affect the degree of conversion at extended irradiation times. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Liquid crystalline (LC) materials have recently gained considerable attention due to their interesting optical and mechanical properties. Liquid crystalline phases are often characterized as having orientational order with reduced or non-existent positional order [1]. A nematic phase, for example, contains orientational order without positional order, In this paper, we describe the photopolymerization of two diacrylate LC monomers, **1** and **2** (Fig. 1) which exhibit nematic phases at elevated temperatures [2]. LC monomers of this type have been used as molecular composites [3,4], to prepare anisotropic structural materials [5,6] and in polymer-dispersed liquid crystal films [7] to name just a few applications.

Photopolymerization offers a number of advantages over traditional thermal polymerization methods including spatial control of initiation, high polymerization rates, low energy requirements, and increased control over the properties of the resulting materials. While these advantages drive the use of photopolymerization for traditional monomers, the phase behavior of LC monomers makes it particularly useful for these types of systems [2,8–12] since photopolymerization has the additional advantage that it can be performed over a range of temperatures for most monomer/initiator systems. This allows for the preparation of highly crosslinked polymers from LC monomers while they are in an LC phase.

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[*] Corresponding author. Present address: Science Applications International Corporation, 4031 Colonel Glenn Hwy, Beavercreek, OH 45431, USA. Tel.: +1-937-431-2301; fax: +1-937-431-4343
E-mail address: poguer@saic.com (R.T. Pogue)

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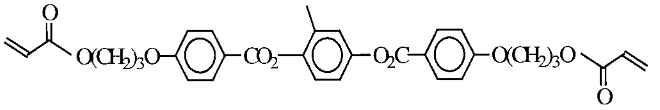
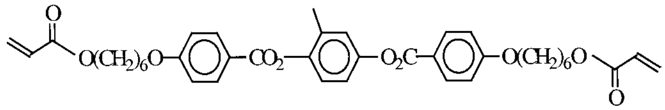


Monomer 1



Monomer 2

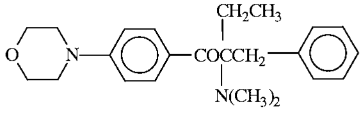
Fig. 1. Chemical structures of the LC monomers used in this study.

Broer and co-workers [10–12] have shown that cure temperature and LC phase have an important influence on the cure rate and final properties of polymers prepared by photopolymerization of LC monomers. Their findings indicate that both cure rate and degree of monomer conversion increase with temperature up to the nematic-to-isotropic transition due to molecular ordering and a higher vitrification point. Above the transition temperature both polymerization rate and conversion decrease.

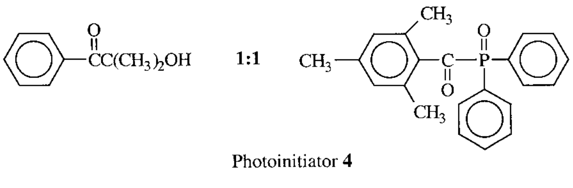
In order to make the most efficient use of the photopolymerization technique, it is necessary to investigate the reaction processes of the LC monomers. Optimization of resin cure characteristics can lead to higher conversions at the required temperatures and to higher polymerization rates. In addition, regulation of photoinitiator concentrations provides control over the penetration depth of the UV source, and the energy needed to initiate the polymerization reaction. In order to investigate the effects of several cure conditions on the photopolymerization reaction of two LC monomers, we employed differential photo-calorimetry (DPC). This technique is capable of providing kinetic data at elevated temperatures under low intensity radiation, and is well suited for comparative screening of resin formulations. It is also important to note here that heat flow obtained from the DPC experiment can be converted directly to polymerization rate for a given amount of monomer.

2. Experimental

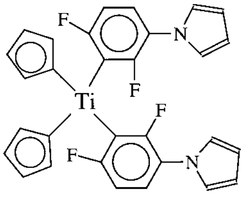
Materials: Monomers **1** and **2** (Fig. 1) were obtained from BDH LTD and used without further purification. 2-Benzyl-2-*N*,*N*-dimethylamino-1-(4-morpholinophenyl)-1-butanone, **3** (Irgacure-369, Ciba-Geigy) was used as a photoinitiator for **1** and **2** without purification in the concentrations described below. Also used as photoinitiators were **4** (Darocur-4265, Ciba-Geigy), a one-to-one mixture of 2-hydroxy-2-methyl-1-phenylpropan-1-one and 2,4,6-(trimethylbenzoyldiphenylphosphine) oxide and **5**(Irgacure-784, Ciba-Geigy), *bis*(eta 5-2,4-cyclopentadien-1-yl-*bis*[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl] titanium, a UV and visible photoinitiator recently made available by Ciba-Geigy structures of the photoinitiators are given in Figs. 2 and 3.



Photoinitiator **3**



Photoinitiator **4**



Photoinitiator **5**

Fig. 2. Structures of the photoinitiators used in this study.

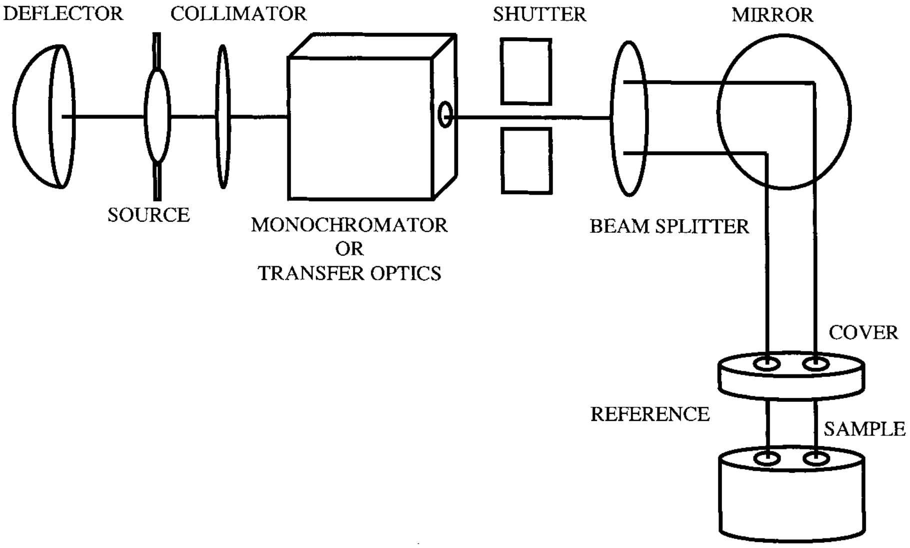


Fig. 3. Block diagram of a differential photo-calorimeter.

Instrumental: Conventional DSC was conducted using a TA Instruments DSC-2910. DPC measurements were carried out using a Perkin-Elmer DSC-7 equipped with a DPA-7 photo-calorimeter accessory depicted by a block diagram in Fig. 2. Samples of 2 mg(±5%) were placed in aluminum sampling pans and covered with 1 mm thick optical quartz discs (6 mm dia.) to ensure a reproducible illumination area and sample thickness. Samples, analyzed under He purge, were heated to the appropriate temperature at 10°C/min and allowed to equilibrate isothermally for 5 min prior to irradiation. Illumination wavelengths and isothermal photopolymerization temperatures are given with the appropriate text.

3. Results and discussion

3.1. Fractional conversion and heat flow

Some characteristic features of traditional acrylate photopolymerization are observed in the polymerization of LC acrylates as well. A plot of heat flow as a function of fractional conversion is given in Fig. 4 for monomer **1** containing 1% of **3**. The reaction quickly enters a region of autoacceleration. This autoacceleration is caused by a reduced termination rate resulting from restricted diffusion of the terminating radicals upon gelation. The fact that the reaction becomes autoaccelerating at very low conversion is an indication of the rigidity of the network which is enhanced by the mesogenic structure of the monomers. After the maximum rate is reached the reaction enters into a region of autodecelaration. At this point, the network begins to inhibit propagation and the reaction eventually stops.

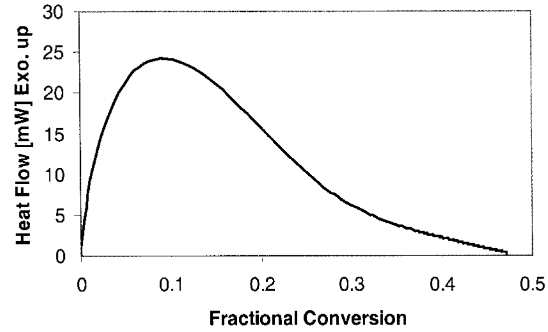


Fig. 4. Heat flow profile for monomer **1** containing 1% of photoinitiator **3**.

3.2. Dependence of reaction rate and conversion on reaction temperature

Upon heating, monomer **1** undergoes a crystalline-to-nematic (K–N) transition at 68°C and a nematic-to-isotropic (N–I) transition at 124°C. Monomer 2 undergoes a K–I transition at 85°C and an N–I transition at 117°C. The transition temperatures given here are in agreement with those given by the supplier. Upon cooling, monomer **1** undergoes an I–N transition 125°C but does not crystallize upon cooling to −70°C. Monomer **2**, on the other hand, undergoes the isotropic-to-liquid crystalline transition at 116°C and crystallizes at 25°C upon cooling.

As can be seen in Fig. 5, total heat flow for monomer **1** is strongly dependent on the temperature of the reaction. This is evident from the increase in heat flow as the temperature is raised over the 20°C range shown. The temperature range given in Fig. 5 was chosen such that the sample was within the nematic phase during curing. The trend described has been reported by Broer and co-workers in the investigation of both mono- [9] and di-acrylate [10–12] liquid crystals. In di-functional monomers, similar to those studied here, their data indicated an increase in polymerization rate as temperature was increased below the nematic-to-isotropic transition temperature and a rapid decrease in rate and conversion above this temperature. They attributed this phenomenon to several possible explanations including reduced molecular order at high temperatures, as well as gelation below the polymer glass transition temperature (T_g). Comparison is made in Fig. 6 between monomers **1** and **2** based upon their monomer conversion at various temperatures. Monomer **1** (Fig. 6A) undergoes a nematic-to-isotropic transition at 124°C. At this temperature there is an inflection point in the conversion vs. polymerization temperature curve. This effect is also observed in monomer 2 (Fig. 6B) where an inflection point is observed near its nematic-to-isotropic transition temperature.

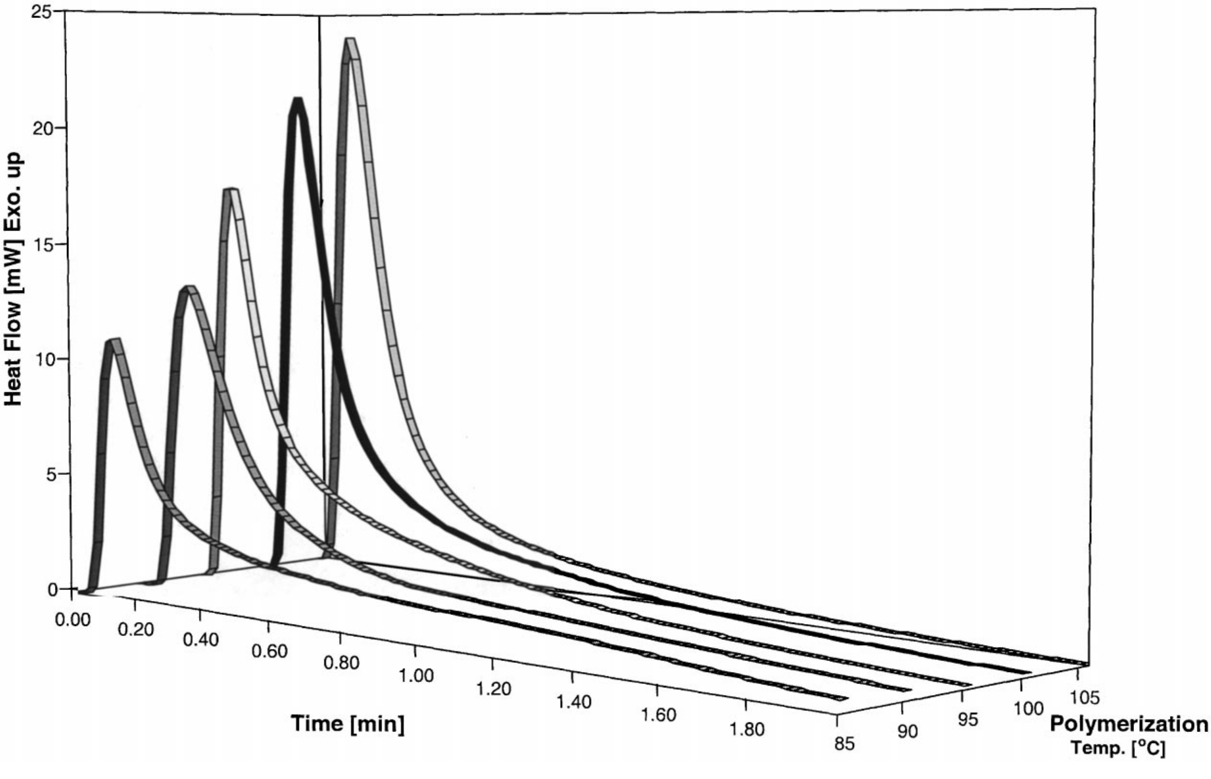


Fig. 5. Comparison of reaction rates obtained over a 20°C temperature range; monomer **1** containing 0.5% of **3**; 364 nm irradiation.

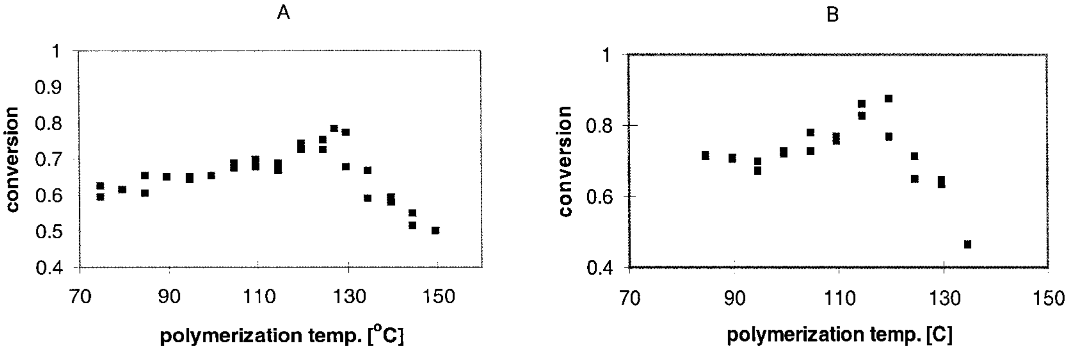


Fig. 6. Relationship between temperature and conversion for (A) monomer **1** and (B) monomer **2**, containing 0.5% of **3**, 10 min irradiation at 364 nm.

It has been suggested, as described above, that changes in the relationship between conversion and cure temperature at the inflection point are related to the ordering of the monomers. Schultz and Chartoff [5] have shown that the molecular order (i.e. the estimated order parameter) decreases slightly in each of these monomers as the temperature is raised within the nematic phase in agreement with the well-known Maier–Saupe theory [13]. As the phase transition temperature is reached, the molecular order drops to zero and the molecules are randomly aligned with respect to one another. If rate was only affected by molecular ordering it would be expected that the rate would decrease slightly throughout the nematic range and drop dramatically at the transition temperature. Such a relationship is observed in the photopolymerization of acrylates in polymer-stabilized liquid crystals [7]. It is clear then that additional drivers must be contributing to the temperature-related behavior. It can be assumed that as the temperature is increased throughout the nematic region, the viscosity of the uncured monomer decreases allowing greater mobility of the propagating radicals which may lead to increased polymerization rates. Furthermore, previous data [6] has indicated that the photopolymer resulting from monomer **2** has a broad T_g of approximately 83°C (based upon E" values obtained from DMA) whereas monomer **1** has a T_g of approximately 119°C following photopolymerization. The T_g of the photopolymer prepared from monomer **2** is below the temperature range in which the material may be cured. For this reason, vitrification is not expected to be a factor in determining the propagation rate and conversion for this sample. In monomer **1**, however, the K–N transition occurs well below the observed the T_g of the resulting photopolymer. At cure temperatures between the K–N transition and the ultimate T_g, vitrification can inhibit polymerization leading to reduced conversions. Although such speculation may be helpful it is clear that more work in this area needs to be done to determine the role of temperature on the polymerization of LC monomers.

3.3. Heat flow and conversion changes related to photoinitiator type

Fig. 7 illustrates the effect of changing photoinitiators on the photopolymerization of monomer **2**. Photoinitiators **3** and **4** (Fig. 2) are both known to dissociate via alpha cleavage reactions known as Norrish type I reactions [14]. Photoinitiator **5** is a titanocene initiator that is believed to dissociate via a two-step reaction leading to a ketene acetal radical [14]. Fig. 7 reveals that changing photoinitiator type can have a dramatic effect on the photopolymerization of LC monomers. Although photoinitiators **4** and **5** react by very different mechanisms, they have almost indistinguishable reaction rates and conversion profiles. Initiator **3**, on the other hand, reacts more quickly and reaches final conversion more quickly than the other two for this monomer. Although it is difficult to determine reaction onset times for these systems using DPC, it is interesting to note that the reaction begins much sooner when **3** is employed compared to both **4** and **5**which have similar induction times. The results can be partially explained on the basis of Beer's law. For

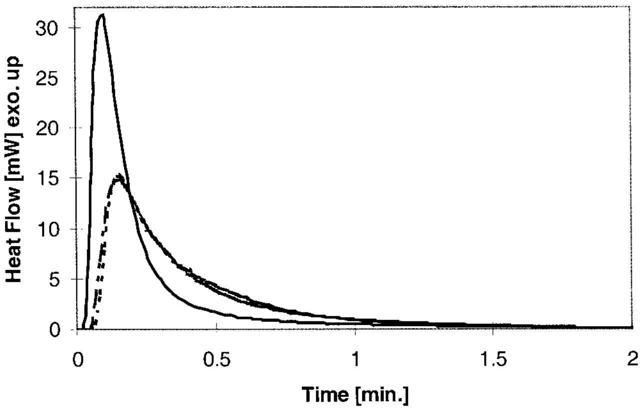


Fig. 7. Comparison of reaction rates for monomer **2** containing 1% of photoinitiator **3** (—) photoinitiator **4** (-·-·-·), and photoinitiator **5**, (······); 85°C, 364 nm.

example, compound **3** had a molar extinction coefficient of 4555 l mol^{-1} cm^{-1} at 363 nm whereas initiator **5** has a molar extinction coefficient of less than 900 l mol^{-1} cm^{-1} at that wavelength [15]. These values indicate that compound **3** has five times greater absorption at 363 nm. It would therefore be expected that the sample containing **3** is slightly faster than that containing **5**. Since rate is proportional to the square root of $(1 - e^{-2.3A})$ where A is absorbance, the maximum rate of polymerization for the sample containing compound **5** should be slightly less than 95% of that observed for the sample containing **3** based upon molar absorptivity and concentration (for a primer on these calculations see [16]). Looking at Fig. 7 it is obvious that this is not the case and therefore other factors including reaction efficiency and dissociation rates must also contribute to the observed results.

It is important to remember, however, that by controlling rate and conversion through the careful selection of reaction conditions allows for optimization based upon the application where the final material is to be used. For example, Ullett and co-workers have indicated how altering the resin formulation for monomers of this type allows greater control of part thickness for rapid prototyping applications [6]. Finally, experiments conducted using real-time infra-red spectroscopy have indicated that for laser exposure at extended times (up to 100 s) there is no significant difference in the extent of cure for samples containing different photoinitiators when they were polymerized at the same temperature [17].

3.4. *Reaction rate as a function of photoinitiator concentration*

To illustrate the effect of varying the photoinitiator concentration on the photopolymerization rate, we have selected four concentrations of **3** in monomer **1**. The results of this study are given in Fig. 8 for 0.5%, 1%, and 2% photoinitiator. The sample containing 4% photoinitiator cured only at the surface and gave less than 10% conversion. As expected, the maximum reaction rate increases as photoinitiator concentration is increased. Results obtained indicate, as described above, that while varying the concentration greatly affects the rate at which the sample is polymerized, there is no real change in extent of cure for equivalent exposure at long exposure times [17]. Due to the

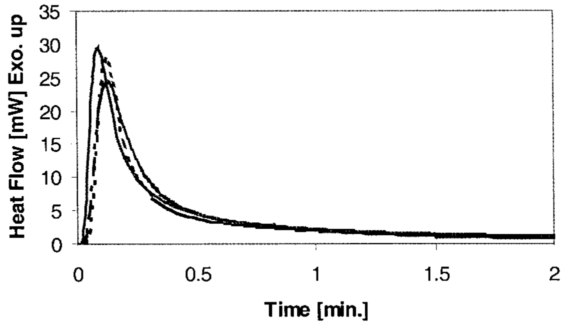


Fig. 8. DPC comparison of results obtained for monomer **1** containing (—) 2%, (-·-·-·) 1% and (······) 0.5% of photoinitiator **3**; 85°C, 364 nm.

response time of the DPC it is difficult to determine exact induction times for the photopolymerization of these acrylate monomers. In every case, however, the reaction appears to have reached 10% of its maximum rate in less than 3 s and the apparent induction time decreases as photoinitiator concentration is increased.

4. Conclusions

This work demonstrates the effectiveness of DPC measurements in determining the effects of photoinitiator concentration, temperature, and wavelength on the photoinitiated reaction of liquid crystalline diacrylate monomers. The results indicate that the polymerization conversion and reaction rate increase as the reaction temperature increases within the nematic temperature range. Polymerization rate and the time required to reach maximum rate are also related to the type and concentration of photoinitiator present in the resin.

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