Novel Liquid Crystal Monomers for Stereolithography: Reaction Rates and Photopolymerization Conversion

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ABSTRACT

Liquid crystal (LC) monomers are a novel type of resin for stereolithography that result in polymers having unique physical and mechanical properties. These monomers consist of rigid central cores connected to acrylate functional groups by short aliphatic chains. Because of the rigid-rod structure of the monomer the cross-linked polymer networks formed have high glass transition temperatures (T_g). The high T_g's result in particularly high upper-use temperatures for stereolithography parts.

This paper reports on photopolymerization reaction rates and monomer conversion for two acrylate monomers measured using reflectance real-time infra-red spectroscopy (RRTIR). The RRTIR method measures the disappearance of reactive acrylate groups in the monomer as a function of time while the monomers are being exposed to UV light. For the two new resins, UV irradiation using an argon ion laser gives rapid photopolymerization with acrylate conversion as high as 95 %. Conversion and polymerization rates in these monomers are dependent upon photo-initiator selection and concentration. In addition, the results indicate that conversion increases with increased laser intensity and elevated temperatures.

INTRODUCTION

Previously, researchers at the University of Dayton introduced the technique of reflectance real-time infra-red (RRTIR) spectroscopy for evaluating resins used in stereolithography [1]. This method is an extension of a technique originally described by Decker and co-workers [2,3] which allowed the elucidation of reaction rates and monomer conversions for photopolymerization reactions completed within seconds of the initial irradiation. The original method involved a transmission infra-red spectrometer held at the wavelength of interest throughout the measurement. The reflectance technique uses a similar detection scheme, but expands on these capabilities by allowing precise control of the photopolymerization temperature [1]. Using RRTIR, Chartoff and Du investigated the effects of irradiation time, laser power, and temperature on the monomer conversion and polymerization rates for two diacrylate stereolithography resins [1]. In the current paper, we discuss the application of this technique to two liquid crystalline (LC) diacrylate monomers which are being evaluated for use in stereolithography. The RRTIR technique is particularly useful for such experiments since it requires very small samples (a few mg). This is an advantage in developing experimental resins where only small amount of the monomer are available.

LC monomers are a new category of stereolithography resins [4, 5]. Chemically, they consist of rod-like cores which are attached to reactive end-groups by aliphatic spacers. These monomers are of considerable interest because the high T_g's of the resulting crosslinked

polymers allow high upper use temperatures for the build object. In addition, the ability to cure LC monomers in an aligned state allows the user to impart anisotropic mechanical properties to stereolithography parts [5]. In order to determine the operating conditions needed to optimize the properties of any new monomer system it is necessary to fully understand the polymerization rates and conversions which occur under high intensity illumination. However, unlike commercially available stereolithography resins, the LC resins are crystalline at room temperature. For this reason instrumentation used to probe the curing reactions must be able to operate at elevated temperatures. RRTIR is ideally suited for this application.

In this paper, the effects of several operating parameters on both reaction rates and conversion are discussed for laser irradiation of thin LC films. The data indicate that both rate and conversions are related to laser intensity and reaction temperature. Moreover, the results reveal that polymerization rates are affected by both photoinitiator type and concentration. The final monomer conversion, however, does not vary significantly when only photoinitiator parameters are taken into account.

EXPERIMENTAL

Materials: The two LC monomers of interest are shown in Figure 1 and were first reported by Broer et al. [6-8]. Recently, Ullett, et al. described the use of these materials in rapid prototyping and discussed some of the processing conditions which are necessary for their use [5]. In this study, monomers **1** and **2** were formulated with two photoinitiators (shown in Figure 2), **3**, (Irgacure-369, Ciba-Geigy Corp.) and ,**4**, (Darocur-4265, Ciba-Geigy Corp.). Photo-resins were prepared by mixing the appropriate amounts of both monomer and photoinitiator in a methylene chloride solution under low-light conditions. The solutions were then vacuum dried for several hours. Samples were refrigerated until use. RRTIR measurements were conducted by placing a small amount of resin onto a pre-heated sample holder. The samples were allowed to melt into the LC phase and then covered with a NaCl window. Sample thickness was less than 10 μ in all cases.

Instrumental: RRTIR is a dispersive IR method. The RRTIR assembly (Figure 3) consists of a Nernst Glower and controller designed at the University of Dayton to maintain a constant signal output in the range from 0.5 to 25 μm. After reflecting off the polished brass sample holder, the IR light is directed through a chopper operated at 1 kHz. The beam then passes through a monochromator and into a mercury cadmium telluride IR detector cooled by liquid nitrogen. Using this instrumentation, IR absorption data were collected at a wavelength of 810 cm^{-1} corresponding to the C=C bending vibration of the acrylate double bond. Data were collected at regular intervals beginning 0.5 ms after initial laser exposure. The samples were irradiated for the appropriate time by an argon-ion laser operating at 363.8 nm. The laser power was 0.05 W/cm^2 unless otherwise noted. Sample temperature was regulated by heating the brass sample block using a variable transformer attached to a strip heater.

RESULTS

Relationship between laser power and monomer conversion: The intensity of the incident radiation is an important factor in the initiation step of the free-radical crosslinking reaction. Changes in laser power can be related directly to the number of photoinitiator molecules which undergo dissociation during the first step of initiation. Since this step is the rate determining step in the initiation sequence, it must be considered in the determination of the overall rate of polymerization. It follows then, that the overall rate of polymerization is related to the intensity

of the radiation source. Figure 4 illustrates the change in monomer conversion for three different laser power settings. The lowest power employed (0.05 W/cm^2) is the lowest setting at which photopolymerization is observed for this resin system. The figure reveals that the major portion of the total reaction is completed within the first second of irradiation. It is also evident from the data that both reaction rate and conversion increase with increasing intensity at low powers (<10 mW). At higher powers both conversion and rate increase asymptotically until increasing the laser power no longer has a significant effect. This apparent deviation from the expected relationship may be caused by self-termination of photoinitiator radicals due to their increased population in the illuminated region.

For comparison, samples of SL5149 (Ciba-Geigy) were analyzed with RRTIR at room temperature using the 0.05 W/cm^2 setting. This resin cured much more slowly than the resin comprised of monomer **1** and 0.5 % of **3** under the same laser irradiation. Furthermore, the commercial resin still exhibited significant cure advancement after 10 s of irradiation, and the final conversion (after 100 s exposure) was less than 0.6.

Effects of photoinitiator type and concentration: Two commercial photoinitiators were tested in the development of the LC resins. In order for the resins to be applicable to stereolithography, it is necessary that they cure rapidly enough to permit acceptable scan speeds, that conversion is great enough to impart sufficient green strength to the part, and that swelling of the solid polymer is negligible. In addition to these requirements, the photoinitiator variables must be carefully selected so that appropriate penetration depths can be reached. Ullett and co-workers [5] previously reported that monomer **2** containing 2 % of **3** yields a penetration depth of less than 80 μ (2.7 mils). Under the same conditions a sample of **2** containing 0.5 % of **3** gave penetration depths greater than 190 μ (7.3 mils). The RRTIR results for these two resins are shown in Figure 5. From the slopes of these conversion curves it is evident that polymerization rate increases when the initiator concentration increases. The increased rate found in samples having greater photoinitiator concentrations leads to faster film formation and reduced laser penetration in these samples. This result is consistent with those observed by Ullett et al. [5] and helps to explain the relationship that was observed between photoinitiator concentration and penetration depth in their stereolithography working curves. It is important to note that this difference in rate causes the conversions at short exposure times (< 2 s) to be widely different between the two resin formulations. At extended irradiation times (up to 100 s) the difference in conversion between the two is less than 5%.

Examples of monomer **1** containing two different photoinitiators are shown in Figure 6. Here **3** is shown to give much faster polymerization rates than observed when **4** is used as the photoinitiator. Again, the RRTIR data are consistent with working curve data which reveal that samples containing **4** yield deeper penetration depths than those containing **3** [9]. Again, it is important to note that at longer irradiation times (up to 100s) the difference in monomer conversion between the resins containing different photoinitiators is less than 5%.

Effects of temperature on kinetic results: Comparison of conversion profiles for monomer **2** is given in Figure 7 at two temperatures. The final conversion (after 100 s irradiation) increases from approximately 84 % at 85 °C to greater than 95 % at 100 °C. Two factors may be contributing to the high conversions which are observed. First, it has been demonstrated with differential photo-calorimetry that in monomer **1** [10] and others [7, 11] both polymerization rate and conversion increase with polymerization temperature up to the point where the monomer undergoes a transition from a nematic liquid crystal to isotropic liquid. In addition, Ullett et al. have reported that the glass transition temperature (T_g) of the polymer resulting from the laser photopolymerization of **2** ranged from 75 to 94 °C following postcure [5]. During RRTIR

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analysis of the reaction at 100 °C the reaction temperature is higher than the highest observed T_g. Therefore, the growing network remains in the rubbery state and the mobility of the chain radicals is not restricted by network vitrification.

Figure 8 reveals the relationship between temperature and polymerization rate for monomer **1** containing 2 % of **3** at six different fractional conversions. From this figure, several trends are evident. First, the polymerization rates increase with temperature up to 95 °C. Above this temperature the rates plateau at lower conversions and decrease slightly at higher conversions. Second, the polymerization rate is highest at a fractional conversion of 0.2 for all temperatures. Finally, the change in polymerization rate with temperature is much greater at higher conversions than at lower conversions. At 60 % conversion the rate undergoes a three order-of-magnitude change over the observed temperature range. In contrast, at 10 % conversion there is less than one order of magnitude change in the rate.

CONCLUSIONS

The effects of operating parameters on polymerization rates and monomer conversion for two experimental liquid crystalline monomers have been investigated using reflectance real-time infra-red spectroscopy. This technique is well suited for investigating monomers of this type since it ideal for documenting rapid reaction, uses only small samples, and operates conveniently at elevated temperatures. The results indicate that both conversion and rate increase asymptotically with temperature as well as laser power. Furthermore, changes in photoinitiator type and concentrations can alter the polymerization rates significantly. It is interesting to note that changing the photoinitiator type or concentration do not change the overall conversion. Using RRTIR it is possible to investigate the effects of operating parameters on small amounts of developmental resins prior to scale-up for testing in the stereolithography apparatus.

ACKNOWLEDGEMENTS

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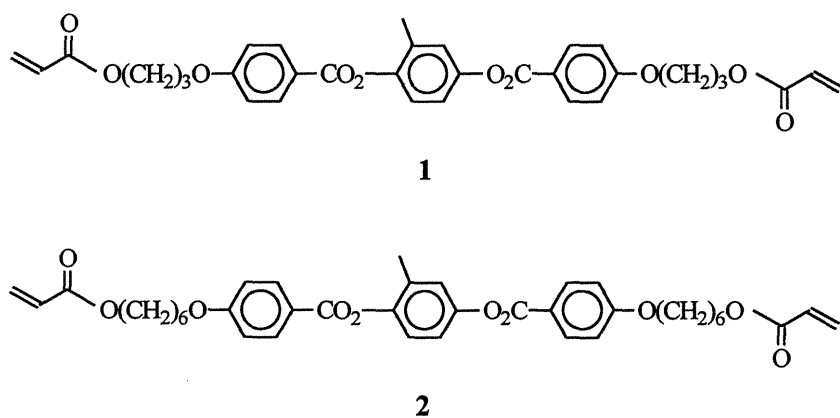11.   Broer, D. J., G. N. Mol, and G. Challa, Makromol. Chem. **1991**, 192, 59-74.

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Figure 1. Chemical structures of the LC monomers

3

4
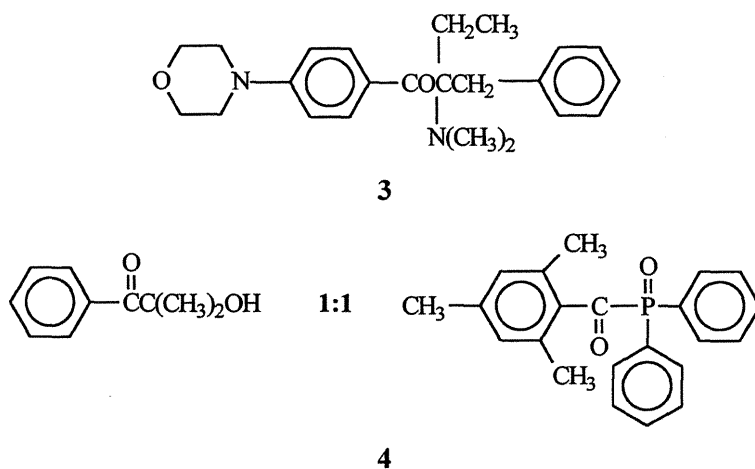
Figure 2. Chemical structures of the photoinitiators
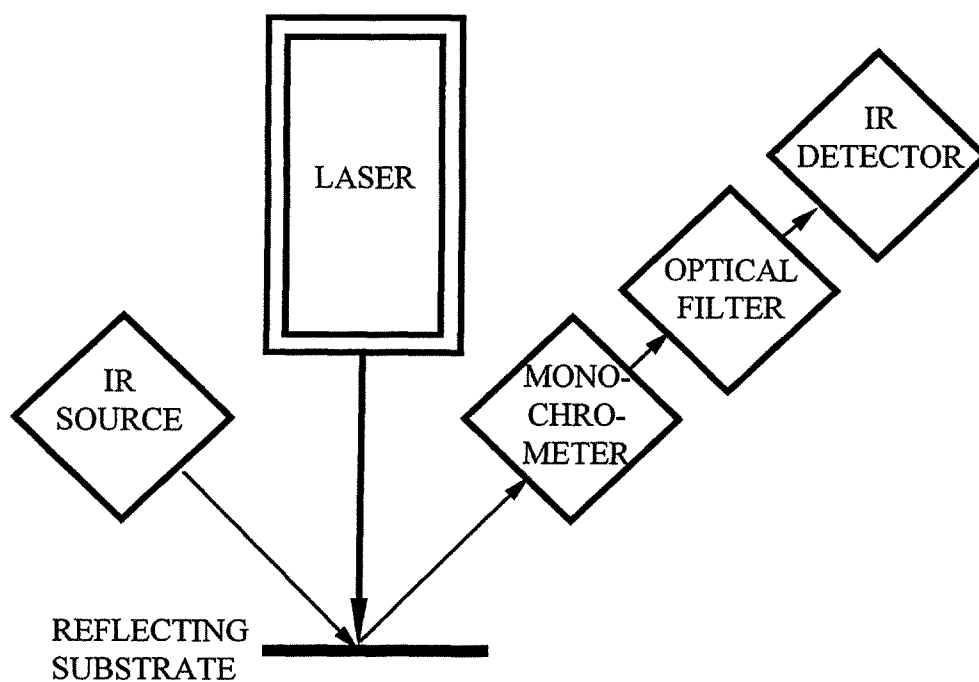
Figure 3. Block Diagram of RRTIR apparatus showing major components.
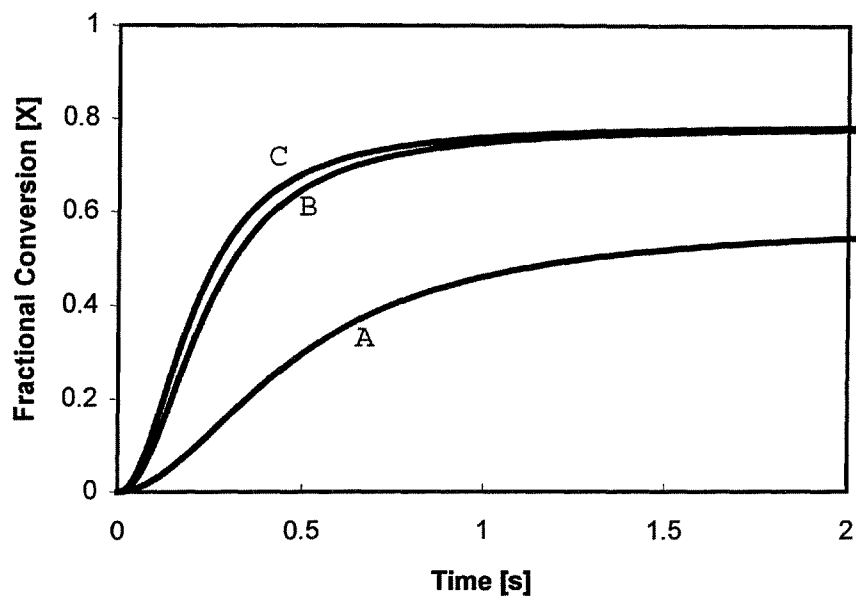
Figure 4. RRTIR Conversion profiles for monomer 1 containing 0.5 % 3 at (A) 0.05 W/cm^2, (B) 0.27 W/cm^2, and (C) 0.5 W/cm^2 laser power; 363.8 nm irradiation with argon-ion laser at 85 ^{o}C.
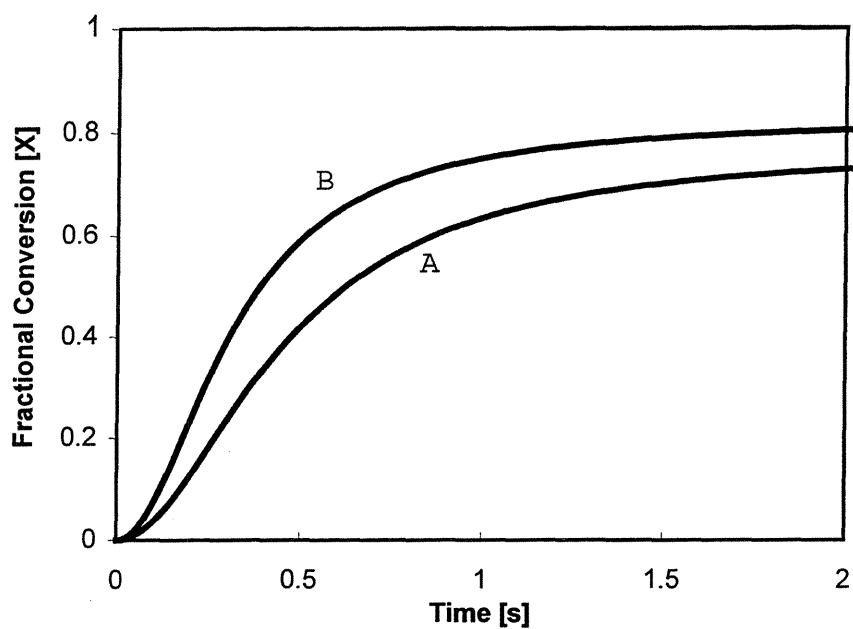
Figure 5. RRTIR conversion profiles for monomer **2** containing (A) 0.5 % and (B) 2 % of **3**; 363.8 nm irradiation at 85 °C, 0.05 W/cm^2.
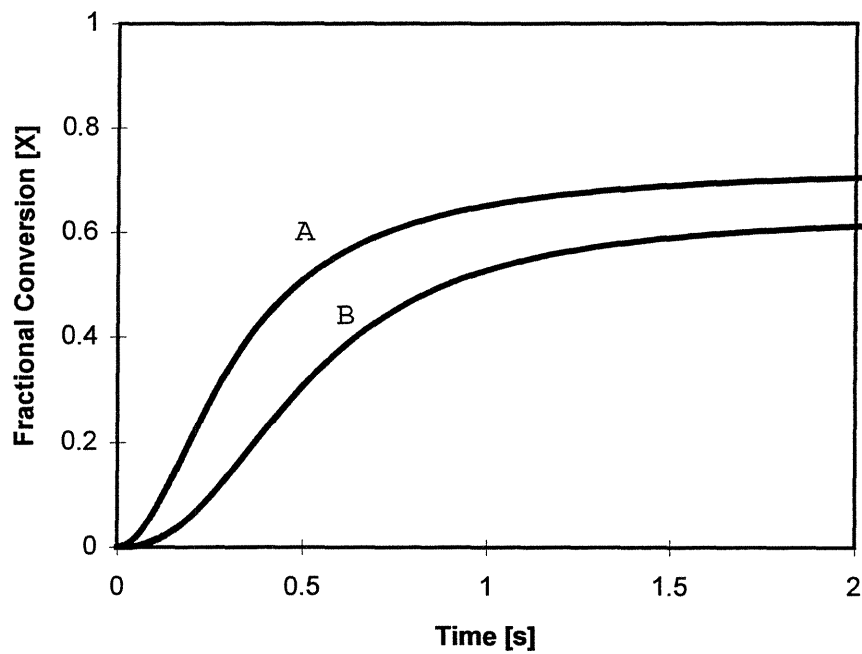

Figure 6. RRTIR conversion profiles for monomer **1** containing (A) 1 % of **3**, and (B) 1 % of **4**; 363.8 nm irradiation at 85 °C, 0.05 W/cm^2.
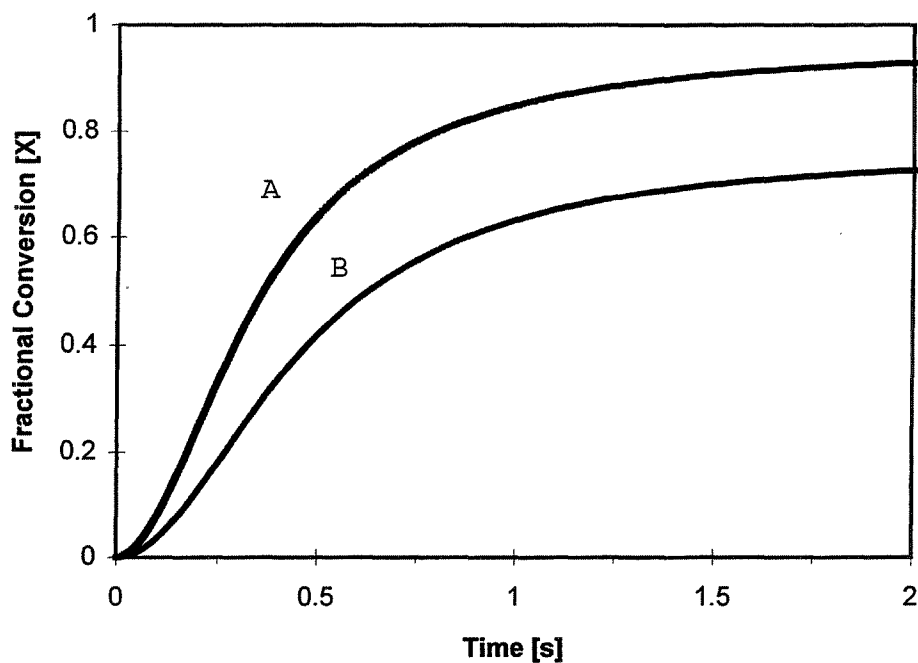
Figure 7. RRTIR conversion profiles for **2** containing 0.5 % of **3** at (A) 100 °C and (B) 85 °C; 363.8 nm irradiation with argon-ion laser at 0.05 W/cm^2.
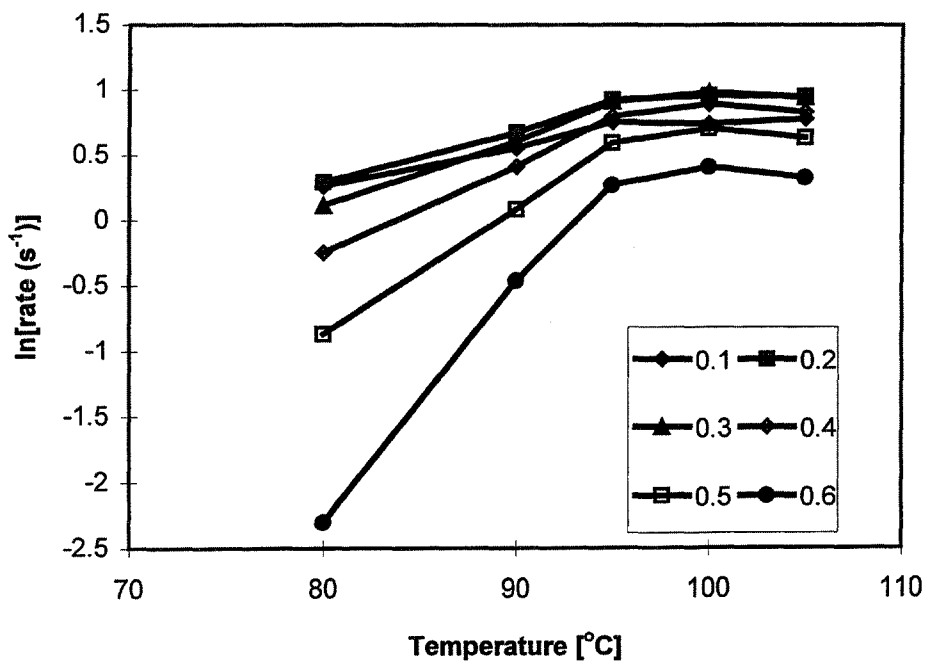

Figure 8. Relationship of reaction rate with temperature for six fractional conversion values for monomer **1** containing 2 % of **3** (wt/wt.); 363.8 nm irradiation with argon-ion laser at 0.05 W/cm^2.