# Properties of a High Temperature Liquid Crystal Stereolithography Resin

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## Abstract

A liquid crystal monomer has been developed that contains both acrylate and acetylene reactive groups. The curing behavior and mechanical properties of the polymers formed from this monomer have been characterized in this study. Complete cure can be carried out in two separate steps, combining both photo and thermal polymerization. The initial photo- polymerization to form a robust "green" polymer involves crosslinking through the acrylate groups and the subsequent thermal polymerization to increase the crosslink density is accomplished by reaction of the acetylene groups. After the thermal postcure the polymer has an unusually high glass transition, in excess of 300°C. In addition, the monomer exhibits an ordered liquid crystalline (LC) phase. Photopolymerization while in the LC phase locks in the molecular ordering. Mechanical property data and additional information on curing in both the isotropic and LC phases are reviewed in the following presentation.

## Introduction

In order to expand the usefulness of stereolithography, new resins must be developed that have better functional mechanical properties at high temperatures. Current stereolithography resins have softening temperatures well under 100°C. As a result, they have limited value as high temperature structural materials. By increasing their high temperature mechanical stiffness and strength, stereolithography resins will find new and expanded applications in areas such as direct injection molding, wind tunnel testing, and under-the-hood automotive applications.

One way to increase the high temperature mechanical capability of a resin is to modify its molecular structure. Liquid crystal monomers represent a new class of stereolithography resins that incorporate rigid, rod-shaped molecular segments. The rigid molecular segment lends itself to two important properties: high glass transition temperature ($T_g$), and the possibility of liquid crystalline order. Rigid-rod monomers can produce polymer networks with glass transition temperatures exceeding 100°C. In addition, their anisotropic molecular shape provides the possibility of liquid crystalline phase behavior, which can result in anisotropic physical and mechanical properties. At the University of Dayton, we have recently investigated a variety of rigid-rod photo-reactive resins. Four of these resins had liquid crystal phases. Some of the resins were cured with UV light, and some were cured with visible light. Table 1 summarizes $T_g$ and elastic modulus data for these materials. The anisotropic physical and mechanical property characteristics of these materials are the subject of several previous papers [1- 4 ].

**Table 1 Summary of rigid-rod resin characteristics**

| Resin | LC Phase | Cure Wavelength | $T_g$ (°C) (with postcure) | E' (GPa) (modulus at room temperature) |
|---|---|---|---|---|
| N1 | Yes | 364 nm | 103 | 1 GPa |
| N2 | Yes | 364 nm | 150 | 2 GPa |
| S1 | Yes | Broadband, visible | 150 | 2 GPa |
| S2 | Yes | Broadband, visible | >350 | 2.2 GPa |
| I1 | No | Broadband, visible | 130 | 1.9 GPa |
| I2 | No | Broadband, visible | 158 | 1.75 GPa |

In order to take advantage of such potentially useful properties, it is important to have a good understanding of the effects of monomer properties, polymerization conditions and postcure on the croslink network formation and glass transition of these new materials. In this paper we consider resin S2, one that develops a particularly high apparent glass transition temperature, in excess of 300°C. This resin consists of a monomer that is both liquid crystalline and has two reactive acetylene groups. In addition to the acetylene groups, the monomer contains terminal acrylate groups that give it a "dual" curing capability. The network formation can proceed by first photo-curing through the acrylate groups, and then thermally postcuring the acetylene groups. This dual-curing capability allows increased flexibility in the processing of these materials for various applications.

## Experimental

### Material Preparation

Shown in Figure 1 is the monomer of interest, S2, which is a diacrylate with a rigid, rod-shaped core. The rigid core consists of a biphenyl moiety surrounded by acetylene bonds. On either side of the core are 3-carbon aliphatic spacers that connect to the reactive acrylate end groups.

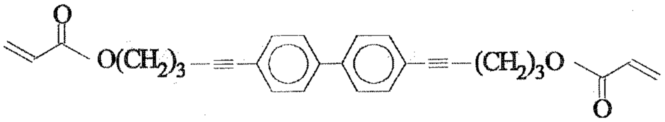

Figure 1 Chemical structure of monomer S2 showing two sets of reactive groups: acrylate and acetylene.

S2 has a smectic LC phase with a crystalline to smectic melting transition at 49°C and a smectic to isotropic transition at 64°C. These transition temperatures were measured by differential scanning calorimetry at a 10°C/min heating rate. To enable photopolymerization, the monomer was mixed with a photoinitiator, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone (Irgacure 369,Ciba-Geigy), at 0.5 % concentration (by weight). Photopolymerization was carried out with a 100 Watt, broadband mercury lamp. Thermal post-curing was carried out without any additional initiator. Samples of polymer also were prepared from the monomer by thermal polymerization, either in its pure form or with a thermal initiator, dicumyl peroxide, at a concentration of 0.5 % (by weight).

### Characterization Methods

Differential scanning calorimetry (DSC) was used to identify phase transitions and to determine thermal cure temperature ranges for S2. The DSC instrument was a TA Instruments 2910 DSC, operated at a heating rate of 10°C/min. Thermo-gravimetric analysis (TGA) was used to identify thermal degradation of the polymer. The TGA instrument was a TA Instruments 2950 TGA, operated at a heating rate of 5°C/min.

Infrared spectra were measured in the transmission mode with a Nicolet 20DXB Fourier transform infrared (FTIR) spectrometer. To ensure sufficient signal from the instrument, the samples were kept very thin – approximately 10 microns. These thin-film samples were manufactured by sandwiching a small amount of LC monomer between glass slides. After photopolymerization, the films were carefully separated from the glass slides and were mounted, free standing in the FTIR spectrometer.

Linear viscoelastic characterization by dynamic mechanical analysis (DMA) was conducted with a Rheometrics RSA II instrument, using a thin film fixture. The measurements were made in the tension mode. All the samples were heated to 150°C and uniformly cooled immediately before testing to ensure a common thermal history and to minimize internal stresses caused by cure shrinkage.

### Results and Discussion

Network formation of S2 can occur via free-radical polymerization of the acrylate groups, the acetylene groups, or both. Without an initiator, thermal polymerization of the pure monomer occurs at a temperature of approximately 240°C. Addition of a free radical thermal initiator can substantially lower the polymerization temperature. This is shown in Figure 2, which plots the heat flow as a function of temperature for both pure monomer and monomer that is mixed with dicumyl peroxide. These data show that at room temperature, the monomer is in crystalline form. As the monomer is heated to a temperature of 49°C, it melts from a solid crystalline phase to a liquid crystalline (smectic) phase as shown by the first endothermic peak in Figure 2. At 69°C, the monomer undergoes a second melting transition from liquid crystalline to isotropic liquid as indicated by the second endothermic peak in Figure 2. For the pure monomer, the large exothermic peak at 240°C indicates the main polymerization reaction. This polymerization reaction is centered at 167°C for the monomer mixed with dicumyl peroxide. There is also a much smaller but repeatable exothermic peak at 175°C in the pure monomer sample. It is possible that this exotherm results from impurities, however the exact origin of this reaction peak is unclear.

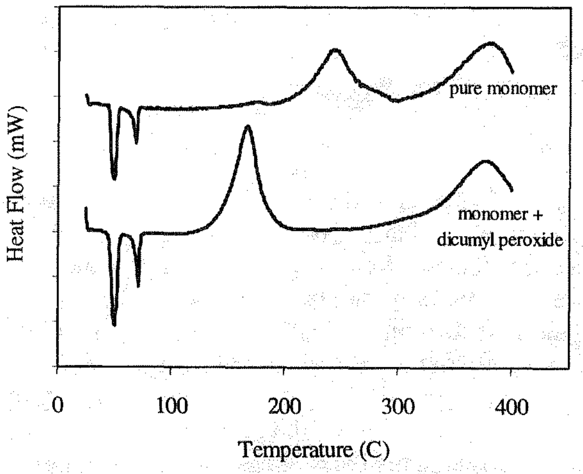

Figure 2 Differential scanning calorimetry data of monomer S2 in pure form and mixed with peroxide

At a temperature of 380°C, there is another large exothermic peak that occurs for both samples. This peak is caused by thermal degradation of the polymer. Confirmation that the 380°C peak is caused by degradation of the polymer is given by the thermo-gravimetric data of Figure 3. These data show the weight of monomer S2 as a function of temperature in an inert atmosphere. The temperature in this experiment was ramped at a linear rate of 5°C/min except at 250°C, where the temperature was held constant for 120 minutes before continuing the linear temperature ramp. The hold at 250°C allowed time for more complete network formation via thermal polymerization.

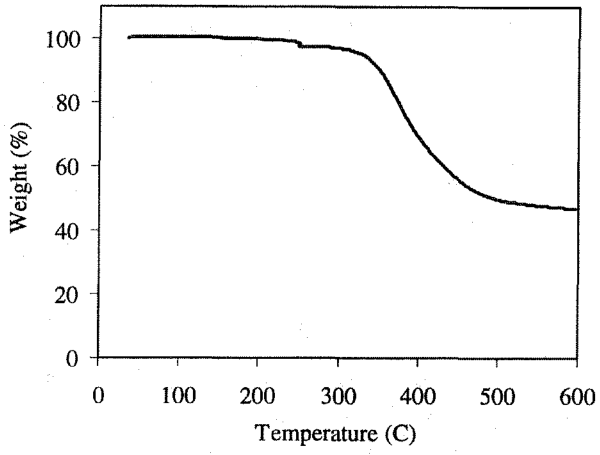

Figure 3 Thermo-gravimetric data for monomer S2 at 5°C/min in Argon atmosphere

The DSC data of Figure 2 show single polymerization peaks, which imply that when thermally polymerized, both sets of reactive groups (i.e. the acrylate and acetylene groups) undergo crosslinking simultaneously. However, this monomer is interesting because network formation can also occur by two separate cure steps: 1) UV photo-cure and 2) subsequent thermal postcure. Furthermore, the UV cure step is apparently dominated by acrylate crosslinking and the thermal postcure is then dominated by acetylene crosslinking. This last assertion is supported by FTIR spectra of the material at different stages during the cure.

The infrared spectrum of the pure monomer has IR absorption peaks centered at wavenumbers of 2230 cm$^{-1}$ and 1638 cm$^{-1}$. The 2230 cm$^{-1}$ peak is relatively weak. It can be attributed to absorption by the $C \equiv C$ (acetylene) stretch, while the 1638 cm$^{-1}$ absorption is most likely due to a $C = C$ stretch in the acrylate moiety [5]. This is supported by the fact that the 1638 cm$^{-1}$ band disappears after photopolymerization.

The infrared spectra of polymerized films are shown in Figure 4. This Figure compares the infrared spectra of a film sample of S2 after photopolymerization at a temperature of 80°C (before thermal postcure), and after subsequent thermal treatment at 250°C (after thermal postcure). As in the monomer spectra, the UV cured sample shows a weak absorption at 2230 cm$^{-1}$, which can be attributed to the acetylene moiety. This band is shown more clearly in Figure 4b. In addition, the 1638 cm$^{-1}$ band associated with the acrylate group in the monomer is almost non-existent in the UV cured sample. Thus UV photopolymerization results in crosslinking through the acrylate groups while leaving the acetylene groups intact. After thermal postcure at 250°C, the acetylene absorption disappears. Furthermore, a new band at 1605 cm$^{-1}$ becomes apparent. This band likely can be attributed to a $C = C$ olefin stretch. Hence the IR spectra indicate that upon thermal postcure, there is a disappearance of the acetylene moiety and an appearance of a new carbon-carbon double bond. Such double bonds may be expected as a result of the acetylene reaction [6,7].

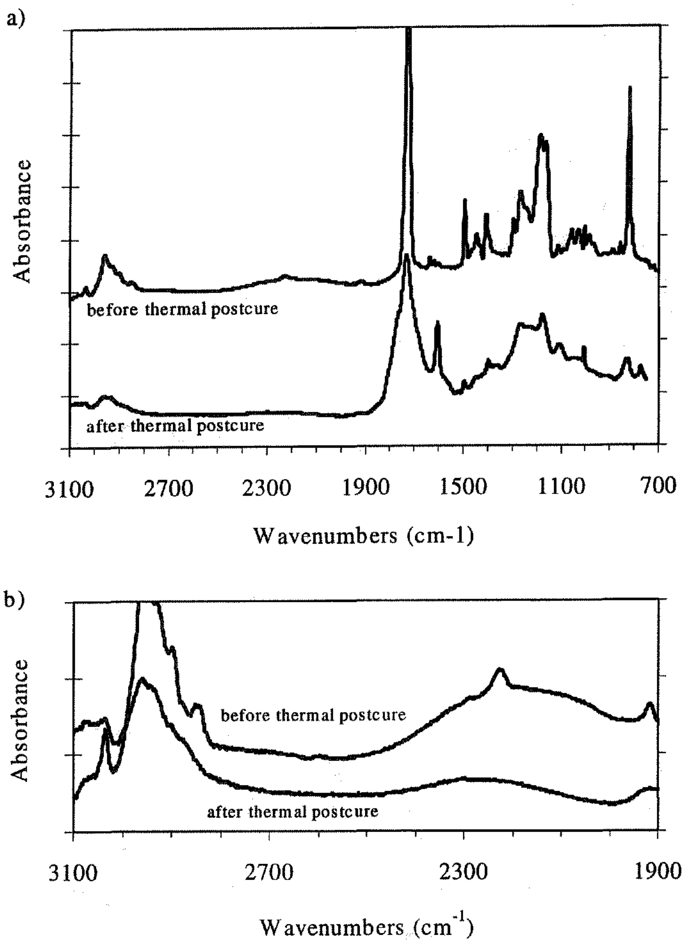

Figure 4 Fourier transform infrared spectra of networks formed from S2 i) after UV photopolymerization and ii) after subsequent thermal postcure at 250°C for 3 hours. Figure 4b shows the same spectra with an expanded scale.

Thus, the use of both photopolymerization and thermal postcuring allows the network formation to occur in two steps. This enables flexibility over the initial polymerization temperature so that the network can be formed by photo-curing the monomer in either the isotropic liquid state or liquid crystalline state. When the initial cure temperature is above the liquid crystalline to isotropic melting temperature of 69°C, the resulting polymer network shows no birefringence (when observed between crossed optical polarizers) and is, therefore, also isotropic. Conversely, when the initial cure temperature is below the 69°C melting temperature, the resulting network shows a birefringent texture, retaining the local ordering and liquid crystalline morphology of the monomer.

### Viscoelastic Behavior

When viewed with polarized optical microscopy, polymers cured while in different phases can have drastically different appearances. Thus it is interesting to see what effect an ordered network has on the viscoelastic properties. If, for example, a polymer is cured in a non-aligned liquid crystalline state, then it has molecular order on a local level but no macroscopic alignment. A polymer cured from a liquid crystalline state might be expected to have different mechanical properties from a polymer cured from an isotropic state, where there is no local molecular order. Such a comparison is made in Figures 5 and 6.

Figure 5 compares the dynamic mechanical behavior of S2 after UV cure in the isotropic state and in the non-aligned liquid crystal state. The isotropic sample was cured for 30 minutes under a 100-watt UV lamp while being held at a temperature of 80°C. The liquid crystal sample was cured at room temperature under a UV lamp for 3 days. The networks that resulted from cure in the two different phases (and at two different temperatures) have considerably different characteristics. Based solely on the positions of the loss modulus peaks, the isotropic sample appears to have a lower glass transition temperature than the liquid crystal sample. The glass transition temperature, $T_g$, is often used as an empirical measure of the crosslink density [8, 9]. However, because of the influence of the network structure on the characteristics of the glass transition, $T_g$ is not necessarily a reliable measure in highly crosslinked networks. The differences in network structure between the isotropic and liquid crystalline samples are reflected in the shapes of the loss modulus curves of Figure 5, where the loss modulus peak is broad for the isotropic polymer and narrow for the liquid crystal polymer. A possible explanation for these dramatically different shapes is that the *distribution* of molecular weights between crosslinks is much narrower in the liquid crystal network than in the isotropic network.

As shown by the FTIR data, monomer S2 has two different sets of reactive groups, which can be reacted separately. While the free-radical reaction initiated by UV exposure causes the acrylate end-groups to polymerize, there are acetylene groups in each monomer unit which crosslink only after heating to higher temperatures. This acetylene crosslinking is also illustrated in the modulus data of Figure 5. As described previously, these two samples were UV cured at relatively low temperatures. Figure 5 shows that as they are heated above 150 °C, the plateau modulus values begin to rise again indicating additional crosslinking. Thus by heating to high temperatures and holding there, these polymers can be thermally postcured to an even greater extent of polymerization.

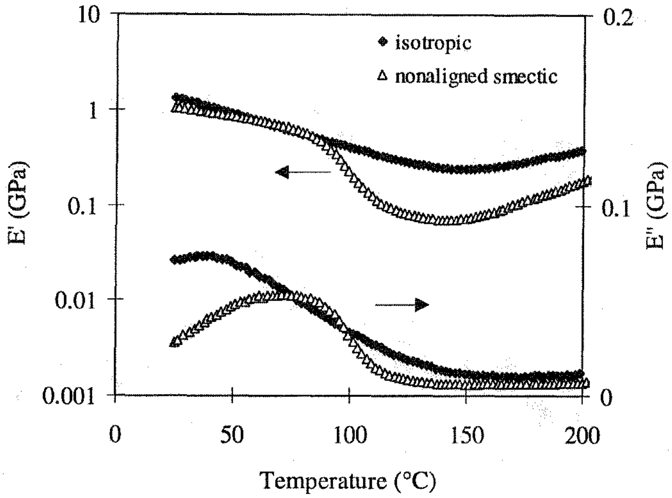

Figure 5 Comparison of storage and loss moduli at 1 Hz of polymer films formed from S2 after photo-cure but before thermal postcure.

Figure 6 shows the storage moduli of isotropic and liquid crystalline polymer samples after they have undergone thermal postcuring. Both samples were postcured at 250 °C for three hours. Figure 6 shows that from a practical standpoint, there is only a modest difference between the modulus of the sample cured in the isotropic state and that of the sample cured in a non-aligned liquid crystal state. The isotropic polymer modulus is approximately 23% higher than the modulus of the liquid crystalline polymer. Comparisons of the loss modulus data also show only minor differences in the glassy state. The apparent transition (loss modulus peak) at 375°C in Figure 6 corresponds to high temperature degradation of the polymer, which was verified by the thermo-gravimetric data of Figure 3. Thus, the glass transition behavior can not be measured in the postcured polymers because they are highly crosslinked enough so that thermal degradation occurs first.

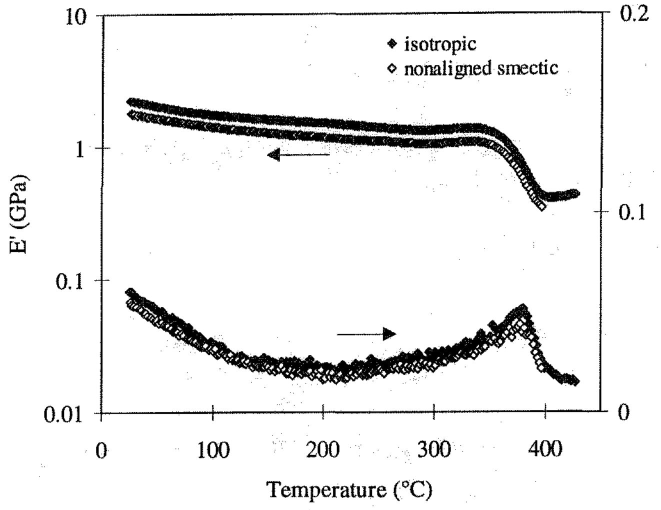

Figure 6 Comparison of storage and loss moduli at 1 Hz of polymer films formed from S2 after thermal postcure.

## Conclusions

The crosslink network formation of a rigid-rod shaped, liquid crystalline monomer was studied using various methods. The monomer contained two sets of reactive groups, acrylate and acetylene, and exhibited a dual-curing capability. In particular, the monomer was initially photopolymerized and subsequently thermally postcured. DSC and FTIR spectroscopy showed that the photopolymerization step was dominated by reaction of the acrylate groups while the subsequent thermal postcure caused additional crosslinking through the acetylene groups. Because of this dual curing capability, the monomer could be polymerized from either the liquid crystalline phase or the isotropic phase. Birefringence microscopy showed that the molecular order of the monomer when cured in the LC state was locked into the network of the formed polymer. The postcured polymer has a high crosslink density resulting in an apparent Tg in excess of 350°C

Dynamic mechanical analysis was used to study the viscoelastic behavior of networks formed from either isotropic or liquid crystalline monomers. The storage modulus(E') and loss modulus(E") indicated that the liquid crystalline-cured polymer appeared to have a lower crosslink density and a narrower distribution of molecular weights between crosslinks, while the isotropic-cured polymer had a higher crosslink density and a broader distribution (more heterogeneous network). After postcure both isotropic and liquid crystalline networks thermally degraded before reaching their ultimate glass transitions. The only observable viscoelastic difference between the postcured networks was that the isotropic network showed a 23% higher glassy state modulus than the liquid crystalline network.

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