

Novel Liquid Crystal Resins for Stereolithography: Mechanical and Physical Properties

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ABSTRACT

This paper considers photocurable liquid crystal (LC) monomers which are a new class of stereolithography resins. These resins form polymers with high upper-use temperatures. The rod-like molecules can be aligned by an external force. When cured in an aligned state, the aligned structure is "locked in" resulting in materials with anisotropic physical and mechanical properties. FTIR spectroscopy, thermo-mechanical analysis (TMA), dynamic mechanical analysis (DMA), and large strain mechanical tests were applied to liquid crystal photo-polymers, both in the green state and after postcure. These measurements showed that the photo-polymerization reaction locked in the molecular order. Elastic modulus in the glassy state, revealed approximately a factor of two difference between the directions parallel and perpendicular to the alignment. Thermal expansion measurements showed an anisotropic linear expansion that was very small, and sometimes negative in the alignment direction. Finally, these resins demonstrated high glass transition temperatures which could be advanced to as high as 150 °C by postcuring.

INTRODUCTION

To expand the applications of stereolithography, new resins must be developed that have better mechanical properties and higher use temperatures. Current stereolithography resins have softening temperatures well under 100 °C. As a result, they have limited usefulness in high temperature applications such as direct injection molding and under-the-hood automotive applications.

Liquid crystal (LC) monomers are a new class of stereolithography resins that can produce polymers with glass transition temperatures exceeding 100 °C and approaching 200 °C. These resins are typically made up of rigid, rod-shaped molecules. Unlike commercial resins, LC resins are often crystalline at room temperature and must be heated to exist in a liquid crystalline or isotropic liquid state. As a result, cure temperature becomes an important variable as it affects both processing parameters and green state properties. In addition, LC resins can be aligned unidirectionally using an external magnetic field. Curing the aligned monomer results in formation of an anisotropic network with a preferred direction, as shown in Figure 1. The resulting mechanical and physical properties of such a network are anisotropic. For example, the thermal expansion coefficient is much smaller in the direction parallel to alignment than perpendicular to the alignment. Thus parts can be directionally optimized for dimensional stability over broad temperature ranges. In addition, proper alignment allows optimization of

strength in a part. Finally, it may be possible to increase fracture toughness in these materials by varying the alignment from layer to layer.

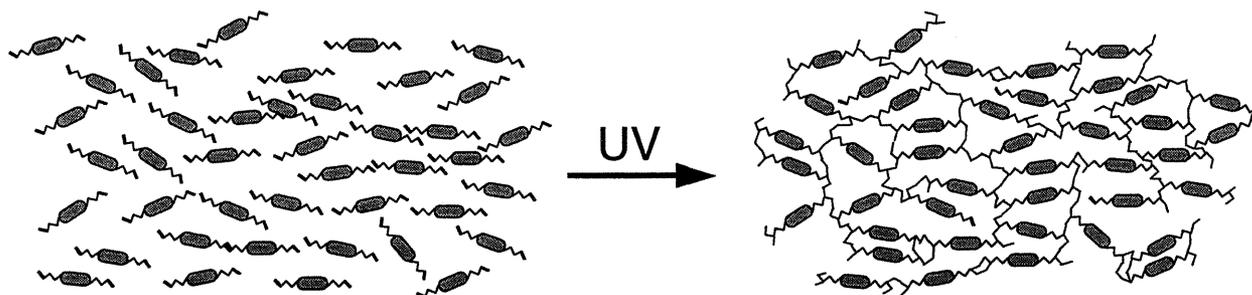


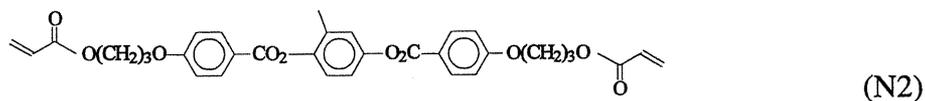
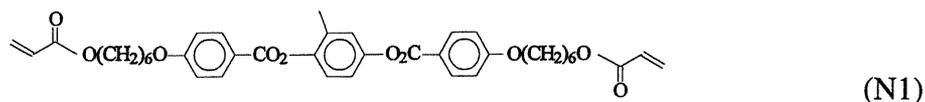
Figure 1. Schematic of aligned network of rigid rods formed by liquid crystal resins

In order to take advantage of these potentially useful properties, it is important to have a good understanding of the effects of polymerization conditions and postcure on the network formation and resulting anisotropic properties. A previous paper[1] considered some of the processing parameters of these resins, including orientation dynamics and working curve parameters. The present paper examines some of the anisotropic mechanical and physical properties of these new stereolithography resins. The focus of this paper is on the extent of anisotropy that can be achieved in the modulus and strength, and on the effect of different postcure conditions on the glass transition temperature. In addition, some linear thermal expansion data are also presented.

EXPERIMENT

Materials

The liquid crystal monomers used in this study, designated N1 and N2, are both diacrylate monomers with 'rigid rod' cores made of aromatic rings. The N1 monomer has 6-carbon aliphatic spacers on each side of the core while the N2 has shorter, 3-carbon spacers. N1 has been studied extensively by Broer et al.[2]. The molecular structures for the two monomers are,



The crystalline melting transitions for these monomers are 88 °C and 72 °C for N1 and N2 respectively. Above these temperatures, they are in a liquid crystalline phase. In the liquid crystal phase, the rigid cores of the molecules can be aligned towards a preferred direction. At higher temperatures (118 °C and 126 °C for N1 and N2 respectively) these resins undergo a second phase change into an isotropic liquid. In the isotropic phase, these resins lose their molecular order, so that their rigid cores are oriented randomly. For comparison purposes, commercially available resins also were considered. The commercial resins used were SL5149 and SL5170 (Ciba-Geigy).

Apparatus and Procedures

The samples were made in an experimental table-top stereolithography apparatus (TTSLA)[3]. The TTSLA includes a small heated aluminum vat and an external magnet with a field strength of approximately 0.32 Tesla. The magnet induces unidirectional alignment in the liquid crystal resin. The monomers were mixed with photoinitiator and photopolymerized in the liquid crystalline phase. To reduce warpage during cure, single layer samples were sandwiched between glass slides. UV curing was accomplished with an argon ion laser delivering approximately 33 mW of power. Both single and multi-layer parts were made. The single layer parts were scanned multiple times with narrow line spacings to insure a uniform cure. The multi-layer parts were made using a typical stereolithography process using supports.

Infrared dichroism was measured using Fourier transform infrared (FTIR) spectroscopy measurements made on a Nicolet 20DXB spectrometer. The transmittance of various polymer samples was measured both parallel and perpendicular to the alignment direction by inserting an infrared polarizer at different orientations into the optical path. To ensure sufficient signal strength, the sample thickness was kept below 15 microns.

Dynamic mechanical measurements were conducted on a Rheometrics solids analyzer (RSA II), using a thin film fixture. The measurements were made in tension at a frequency of 1 Hz, and a strain of approximately 0.05 percent. Sample dimensions were typically 22 mm long, 3 mm wide, and 0.17 mm thick. To ensure a uniform thermal history, the samples were heated above their glass transition temperatures and quickly cooled before testing.

For large strain testing, a Rheometrics Minimat tester was used in conjunction with a high resolution digital camera for accurate strain measurement. Specimens were dogbone shaped with gauge dimensions of approximately 25 mm length, 5 mm width, and 1 mm thickness. The testing procedures were done in accordance with ASTM D638M.

Linear expansion as a function of temperature was measured on a TA instruments TMA 2940 thermomechanical analyzer using a thin film fixture. The measurements were made with a linear temperature ramp of 2 °C/minute and with a load of 0.5 grams. Sample dimensions were typically 13 mm long, 4 mm wide, and 0.22 mm thick.

RESULTS

Molecular Order

To better understand the origin of the anisotropy in the various physical properties of these polymers, FTIR analysis was used to measure the degree of molecular order. To describe the amount of molecular order in the liquid crystal state, a generally accepted quantity is the molecular order parameter, S . The order parameter is defined so that for a completely ordered material, $S = 1$, and for an isotropic material (completely disordered), $S = 0$. In the FTIR technique, an infrared polarizer is used to measure the sample's absorbance as a function of orientation angle. To obtain order parameter from the absorbance data, the dichroic ratio is calculated, which is the ratio of absorbances parallel and perpendicular to the alignment direction. The molecular order parameter is then calculated from the dichroic ratio.

Figure 2 shows the order parameter as a function of cure temperature for polymer N1. In this plot, the order parameter from two different absorbance bands are shown. The 1605 cm^{-1}

band arises from an aromatic stretch, and therefore corresponds to the stiff central core of the monomer. The 2940 cm^{-1} band is due to an aliphatic stretch and corresponds to the flexible spacer. The order parameter of the aliphatic spacer is considerably lower than that of the rigid rod core. This is expected because of the increased flexibility of the spacer and because it must stretch and contort to accommodate the crosslinked network. The data in Figure 2 also show that there is little variation in the order parameter as a function of cure temperature (except for very near the liquid crystal to isotropic temperature). Thus when optimum cure conditions are being determined for these resins, the order parameter is not an important consideration, since it is only weakly dependent on cure temperature.

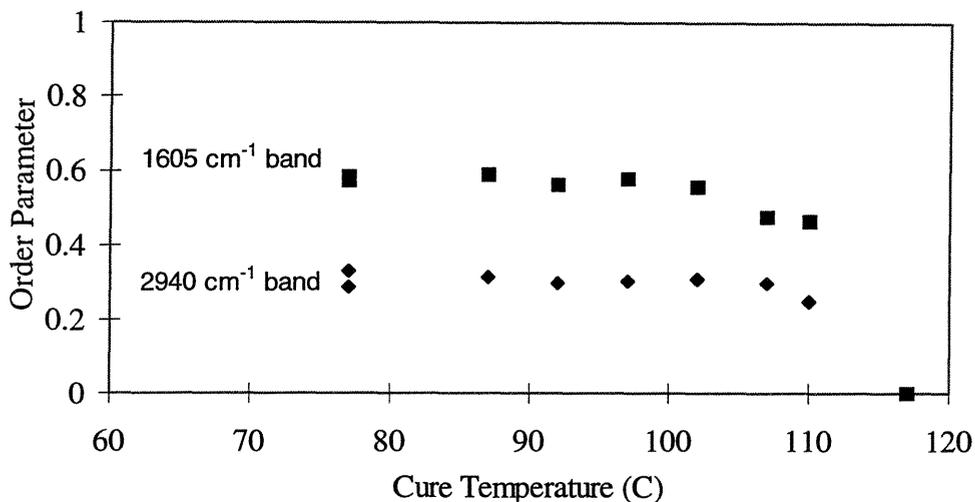


Figure 2. FTIR measured order parameter of N1 polymer as a function of cure temperature.

Mechanical Behavior

The DMA data show curves typical of network polymers with high crosslink densities. Because of the apparently high crosslink densities, the elastic modulus above T_g is too high to be called rubbery -- greater than 10^8 Pa. Figure 3 compares the elastic modulus of some commercial resins to the liquid crystal resins after they have been UV postcured. The LC resins show not only higher glass transition temperatures, but also the modulus above the glass transition is a factor of 5 to 15 higher than the commercial resins. Thus the usefulness of these liquid crystalline resins may extend well beyond their glass transition temperatures.

The data in Figure 3 also show that there is a significant difference in the modulus parallel and perpendicular to the alignment direction in these liquid crystal resins. This anisotropic modulus is shown in more detail in Figure 4. These data are for both single-layer and 2-layer parts made from resin N2. The modulus in the direction parallel to the alignment is 50 to 100% greater than in the perpendicular direction. In general the modulus of multi-layer parts is lower than that of the single layer films. This is expected, since multi-layer parts have a non-uniform cure. Other commercial resins have also shown similar differences in modulus when comparing multilayer parts to idealized single layer films[4].

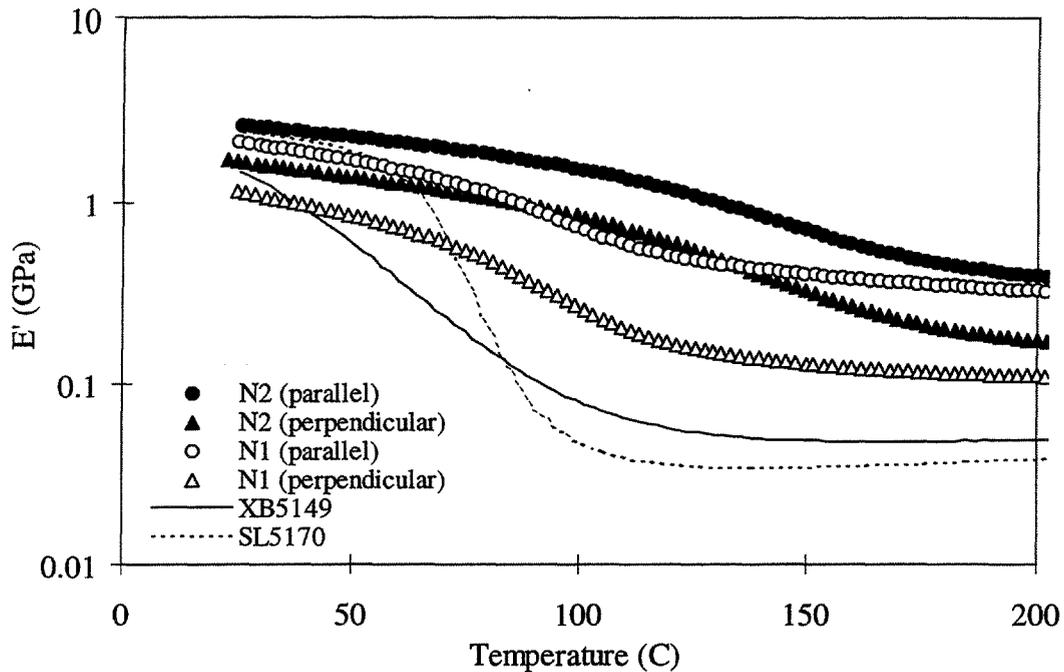


Figure 3. Comparison of elastic modulus of commercial resins and liquid crystal resins.

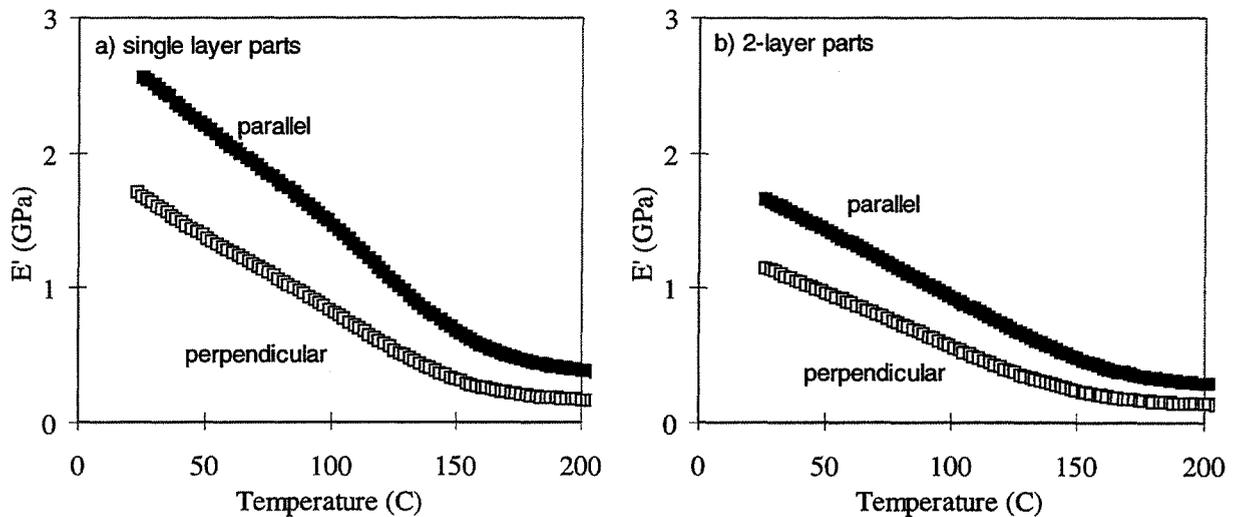


Figure 4. Anisotropic elastic modulus of N2 resins.

Since the linear elastic modulus is anisotropic, the tensile strength would be expected to behave similarly. This is indeed the case as shown for UV postcured samples of polymer N2 in Figure 5. While the strength is higher in the direction parallel to alignment, the strain at break is greater perpendicular to the alignment. N2 has tensile strengths of over 60 MPa parallel to alignment and 45 MPa perpendicular. Modulus values for N2 are about 3 GPa parallel to alignment and 2 GPa perpendicular. Because of the rotatable magnet, alignment can be varied on a layer to layer basis leading to composite-like structures. Thus mechanical modulus and strength can be directionally optimized in a part; though the amount of modulus anisotropy is still much less than in fiber reinforced composites.

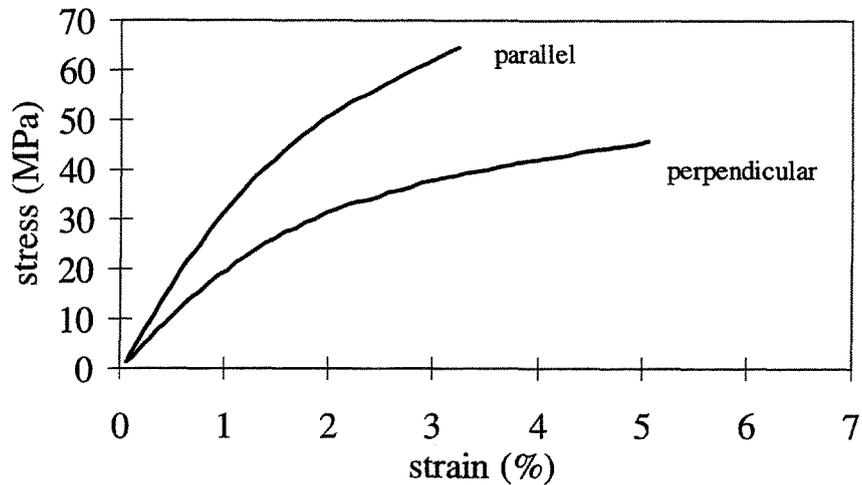


Figure 5. Typical tensile stress-strain curves for polymer N2 after UV postcure

Postcure Effects

While the glass transition temperature of the green polymer is already higher than current commercial resins, considerable advancement of the glass transition temperature is possible by postcuring. Two approaches to postcure have been studied: UV postcure at lower temperature and dark postcure at higher temperature. Figure 6a shows the effect of UV postcure on polymer N2. For these samples, a 100 W mercury vapor lamp was used to postcure with the temperature held at 150 °C. The data show that as postcure advances, the glass transition temperature shifts upward towards an ultimate T_g of approximately 120 °C as measured by the peak in the loss modulus at 1 Hz. In addition the intensity of the glass transition loss peak decreases as shown by the $\tan \delta$ data. This decreasing intensity of the glass transition is an indication of the increasing crosslink density which results in an even stiffer network above the glass transition.

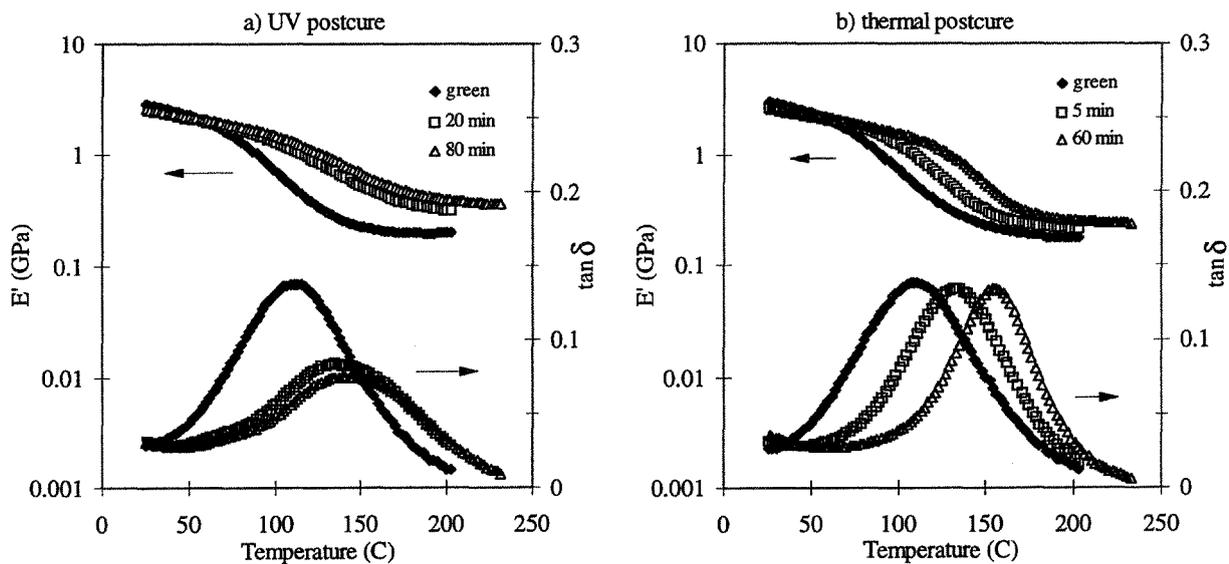


Figure 6. Postcure effects on N2 resin.

Figure 6b shows the effect of high temperature (250 °C), dark postcure on polymer N2 after various lengths of time. As in the UV postcure, the glass transition shifts upward, however the T_g 's obtained from thermal postcure can be considerably higher. Instead of the 120 °C ultimate T_g from the UV postcure, thermal postcure can result in T_g 's as high as 150 °C for polymer N2 and 105 °C for polymer N1. However, while the glass transition becomes weaker and broader during UV postcure (i.e. the $\tan \delta$ peak), the thermal postcure results in glass transitions that are just as intense as in the green part. This indicates that with a high temperature thermal postcure, the increase in T_g may arise from a different chemical reaction than occurs in the UV postcure.

Linear Expansion

Just as the aligned polymer samples have anisotropic mechanical modulus and strength, they also have anisotropic thermal expansion. Figure 9 compares the linear expansion of polymer N2 with the commercial resin, SL5170. In the direction perpendicular to the alignment (i.e. in the y direction), the linear expansion of N2 looks much like the commercial polymer, with the linear thermal expansion coefficient going from approximately 110 $\text{mm}/\text{m}^\circ\text{C}$ below T_g to 220 $\text{mm}/\text{m}^\circ\text{C}$ above T_g . In the direction parallel to alignment, the liquid crystal polymer has a very small positive coefficient of expansion below T_g which changes to a negative coefficient of expansion above the glass transition region. This type of response has been cited in the literature for other LC thermosetting systems[5]. Thus, molecular alignment results in anisotropic thermal expansion, and by varying the layer to layer alignment, composite like structures can be manufactured to directionally optimize the linear expansion properties.

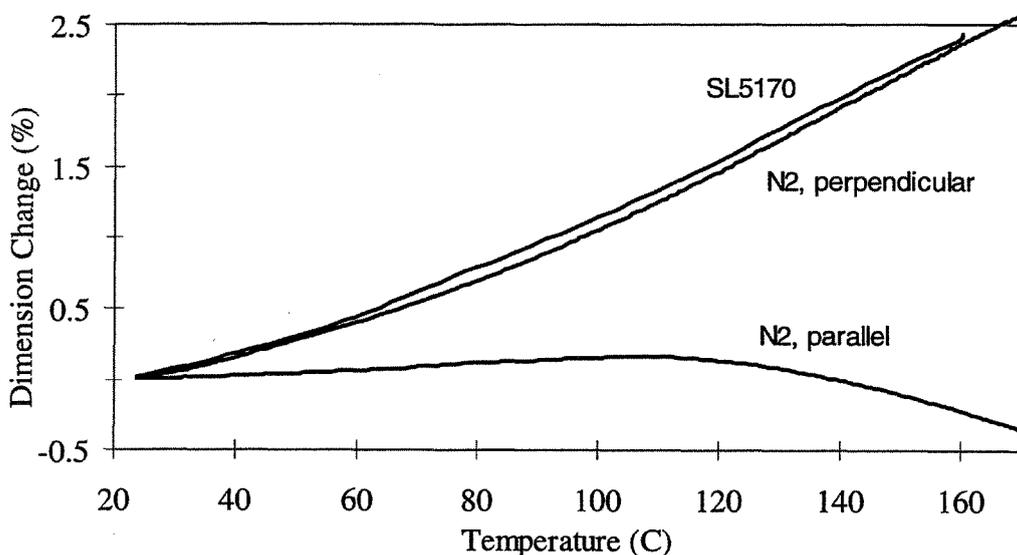


Figure 7. Linear expansion of N2 liquid crystal resin and XB5170 commercial resin.

CONCLUSIONS

Two liquid crystal monomers were processed in a table-top stereolithography apparatus. A magnet placed outside the vat aligned the monomer before photopolymerization. FTIR spectroscopy showed that the alignment was locked in by the photopolymerization, and that the amount of order in the polymer was relatively independent of polymerization temperature.

The aligned polymer specimens show anisotropic mechanical and physical properties. Glassy state elastic moduli of samples tested parallel and perpendicular to the alignment direction differ by a factor of two. The tensile strength shows a similar anisotropy. Linear expansion is similar to that of the commercial SLA resins in the direction perpendicular to alignment, while in the direction parallel to alignment, the expansion coefficient is very small and even becomes negative at temperatures above the glass transition.

In addition to the anisotropic properties, these new stereolithography resins show high glass transition temperatures. Green specimen T_g s ranged from 50 to 82 °C while postcured specimens had T_g s ranging up to 150 °C.

ACKNOWLEDGMENTS

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