

# LOW SHRINKAGE, HIGH $T_g$ LIQUID CRYSTAL RESINS FOR STEREOGRAPHY

J. S. Ullett, R. P. Chartoff, J. W. Schultz, J. C. Bhatt, M. Dotrong, and R. T. Pogue

The University of Dayton  
Center for Basic and Applied Polymer Research  
and  
Rapid Prototype Development Laboratory  
Dayton, OH 45469-0130, USA

## INTRODUCTION

The applications for stereolithography parts have grown from simple visualization of engineering designs to fabrication of functional end-use prototypes. With the growth of applications has come a need for higher performance resins. In particular, the upper-use temperature of cured resins needs to approach or exceed 200 °C for applications such as directly formed molds for injection molding, and under-the-hood automotive applications. Improved mechanical properties such as modulus and impact strength are also important for these applications. Dimensional accuracy has been a key issue for rapid building of functional parts. Dimensional accuracy is a function of resin shrinkage, draw style patterns, beam diameter compensation, galvanometer calibration, etc. While part accuracy has improved dramatically since the inception of stereolithography, further improvements are possible.

The University of Dayton in partnership with researchers at Case Western Reserve University is currently developing liquid crystal (LC) monomers for stereolithography applications. LC materials contain stiff rod-like mesogenic segments which can be aligned and upon cure may have glass transitions approaching 200 degrees Celsius because of their rigid rod segmental structures, orientation, and high degree of crosslinking. Curing in an aligned state "locks" in the anisotropic structure resulting in materials with anisotropic physical and mechanical properties. Also, because the reactive end groups are more tightly packed, cure in an aligned state should result in lower shrinkage than is obtained with conventional resins

The objective of this project is to produce LC diacrylate monomers that can be photopolymerized via stereolithography to produce parts having glass transition temperatures exceeding those possible with commercially available stereolithography resins, and having optimized mechanical properties. Parts with isotropic, anisotropic, or a combination (as a function of location in the part) of isotropic and anisotropic properties may be produced by varying the layer-to-layer alignment of the LC monomer or by varying the cure temperature (i.e., varying the mesogenic state). Realization of these goals will allow important new applications for stereolithography.

The research emphasis in the program has been on three areas: (1) synthesis of liquid crystal monomers suitable for use in stereolithography; (2) characterization of basic material properties and determination of processing parameters and

(3) stereolithography process optimization for LC monomers. The focus of this paper is on the last two areas.

## LIQUID CRYSTAL CHARACTERIZATION

Like crystalline solids, LC materials have some kind of long range molecular order, however, they lack the three-dimensional translational order found in truly crystalline materials. The simplest type of mesogenic phase is called nematic. In nematic phases, the molecular axes are on average parallel but lack any kind of translational order as indicated in Figure 1a. Smectic phases have both uniaxial molecular orientation and some degree of translational order as indicated in Figure 1b. Many different types of smectic phases have been identified. Some are more fluid in nature (e.g., smectic A) while others are more solid in nature (e.g., smectic D). At the clearing temperature, order disappears and the phase structure becomes isotropic as indicated in Figure 1c. Because the viscosity of nematics can be considerably lower than that of smectic phases, working in the nematic phase may be more ideal for stereolithography. Smectics, on the other hand, have a higher degree of order which may lead to less shrinkage and higher crosslink densities. As a result, both mesophase types are of interest. In the present work, the identification of phase type, and phase transition temperatures was done by polarized optical microscopy and differential scanning calorimetry.

### *Identification of Phases*

Liquid crystalline phases are birefringent, that is, the measured refractive index is directionally dependent. Particular phase structures can be identified by examining samples between crossed polarizers. A Nikon optical microscope fitted with polarizers and a Mettler FP-82 hot-stage was used to study the phase behavior of three LC reactive monomers. For example, Figure 2 is a photograph of a smectic A phase illuminated by polarized light.

Differential scanning calorimetry (DSC) is also used to measure phase transition temperatures and in addition measures the enthalpies of transitions. A TA Instruments model 2910 DSC was used to characterize the LC reactive monomers. The melting/crystallization behavior of the monomers was determined using multiple heating rates. The position of transitions depends on the heating rate and the (temperature) direction of the scan. Some mesogenic phases referred to as monotropic occur only upon cooling from the isotropic melt. The monomers were analyzed both with and without photo-initiators to establish the effect of photo-initiators on the breadth and position of the mesophases. Even small amounts of photoinitiator can have significant effects on the phase transitions. This information is needed to define the temperature range required for stereolithography operation.

### *Cure Analysis*

The UV absorbance of purified monomer samples was measured using a Hewlett-Packard model 8452A diode array spectrophotometer. The UV absorbance spectra were used to determine the most appropriate laser wavelength for cure. Monomers with various photo-initiators were analyzed with a Perkin-Elmer photo-DSC-7. Photo-differential scanning calorimetry (PDSC) is a useful method for the rapid and comprehensive development of appropriate cure conditions for the monomers of interest.

With PDSC it is possible to determine cure information based on photo-initiator and sensitizer concentrations as well as cure temperature and irradiation wavelength. PDSC investigations of photoinitiator type and concentration have led to optimal cure rates and have been useful in improving the glass transition temperatures of photo-polymerized samples. The cure rates observed are comparable to those of commercial acrylate stereolithography resins.

#### *Glass Transition Temperature*

The glass transition temperature of cured samples has been measured by a variety of techniques including DSC, dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA). Thus far, the results are encouraging in that the LC monomers under study form high  $T_g$  polymers upon cure. Figure 3 shows data from thermal mechanical analysis using a penetration probe for a sample photocured at 45 °C and thermally postcured by heating to 300 °C. The measured softening point for the sample was 210 °C. For materials cured with a scanning laser, the initial glass transition temperature is a function of the monomer temperature in the vat. Thermal postcures may be used to advance the glass transition temperature of photocured parts. We are currently studying the effects of UV postcure on  $T_g$  values

The birefringence technique developed to follow phase transitions in the monomers was also found to be useful in studying transitions in the polymers. Curves from the birefringence technique clearly showed where glass transitions occurred, even when DSC could not. They also indicated that additional polymerization continued after heating past the initial photocure temperatures. Comparisons of polymer films were made between randomly aligned and externally aligned polymers. These experiments showed evidence of additional relaxation effects at the glass transition presumably associated with the regions between liquid crystalline domains in the randomly aligned samples.

## **CREATING AND MEASURING ALIGNMENT**

An important aspect of this project is an investigation of ways to align the liquid crystal monomers and ways to measure the alignment. Photopolymerization of the LC monomer in the aligned state may lead to stereolithography parts with superior mechanical properties and minimal cure shrinkage. In addition, it will be possible to build parts having anisotropic properties. This flexibility will allow a part's physical and mechanical properties to be optimized for particular applications. There are a number of ways to align a mesogen such as by application of: electric field, magnetic field, shear, rubbed films, and combinations of the aforementioned. Electric field alignment is used in most liquid crystal display (LCD) applications [1]. Alignment of an LC monomer in a stereolithography vat presents challenges not encountered in other LC applications because we are proposing to align the LC domains over large areas (e.g., 254 mm x 254 mm). A magnetic field is the method selected for alignment for this application.

#### *Alignment Measurement and Alignment Kinetics*

**X-ray.** The inter-molecular spatial relationships in a LC material are measured most accurately using X-ray diffraction. LC structures result in specific diffraction phenomena.

As described by Samulski in [2], the azimuthal intensity distribution,  $I(\chi)$ , comes from the superposition of scattering from many mesogens having a continuous orientation distribution of  $\mathbf{l}$  about the director  $\mathbf{n}$  symbolized as  $W(\beta)$  where  $\beta$  is the angle between  $\mathbf{l}$  and  $\mathbf{n}$ . The measurable distribution  $I(\chi)$  is related to  $W(\beta)$  and  $I(\omega)$ , where  $I(\omega)$  is the scattering intensity from a single prolate mesogen, by an integral equation as shown below [2].

$$I(\chi) \approx \int W(\beta) \cdot I(\omega) \sin \omega \, d\omega \quad (1)$$

The average orientation of  $\mathbf{l}$  relative to  $\mathbf{n}$  is the nematic order parameter  $S$  which is defined in terms of  $W(\beta)$  as shown below.

$$S \equiv \int_0^{\pi/2} P_2(\cos \beta) \cdot W(\beta) \sin \beta \, d\beta \quad (2)$$

Typically, nematic LC materials, which have directional order but not positional order, create X-ray diffraction patterns having diffuse outer rings and sometimes diffuse inner rings [3]. Smectic LC materials consist of layers of directionally ordered molecules. In addition to having a diffuse outer ring, the large scale periodicity of the smectic layers causes small angle scattering, which appears as a sharp inner ring [3].

Although X-ray diffraction is probably the best method to determine the molecular orientation, other techniques can be used to calculate the order parameter or to measure changes in alignment. A sampling of these techniques include: NMR [4-6], SANS [7], FTIR [8], Raman spectroscopy [9-12], Mossbauer Effect spectroscopy [13], dielectric [14,15] and refractive index [16-18].

In this study dielectric and birefringence measurements have been used to detect changes in alignment of the LC materials with the application of a magnetic field. These techniques can also be used to follow relaxation of order after the aligning field has been removed.

**Dielectric Analysis.** Dielectric analysis techniques can be used as a means to calculate the molecular order parameter. Unfortunately, the relative convenience of measuring the dielectric permittivity of a liquid crystal under different orientations comes at the cost of a relatively complicated theory relating permittivity to the order parameter.

On the other hand, if the mesogens have little or no dipole moment, then the theory relating order parameter to permittivity anisotropy simplifies greatly. However, because the electric polarizabilities of the molecules cannot be measured in practice, an extrapolation method based on the nematic to isotropic transition temperature must be used to estimate them. In the case of a crosslinked polymer network, no transition to the isotropic state exists, so there is nothing on which to base the extrapolation. Hence only measurement of the monomers can provide quantitative estimates of the order parameter in this technique.

Preliminary experiments have been conducted with a Hewlett Packard 4192A impedance analyzer, with a frequency range of 10 Hz to 13 MHz. The samples were

placed between parallel plate electrodes with a spacing of approximately 300 microns. Alignment was created in the nematic state using a permanent magnet. For the monomers measured so far, there is little dipole moment, so the dielectric anisotropy is due solely to anisotropy in the polarizability. This results in dielectric permittivity differences of about 0.8 between parallel and perpendicular orientations of the magnet. Temperature studies are planned so that the extrapolation method can be extended to estimate order parameter as a function of temperature.

**Birefringence.** One of the simplest (and least expensive) ways to determine if a material is liquid crystalline, is to place it between crossed polarizers in a microscope and look for 'birefringence'. Unlike an isotropic fluid, the index of refraction in a liquid crystalline material is not constant. For the case of uniaxial nematics and smectics, the birefringence,  $\Delta n$ , is defined as the difference between the indices of refraction parallel to and perpendicular to the director,

$$\Delta n = n_{\parallel} - n_{\perp}. \quad (3)$$

This equation relates three quantities, so two separate measurements are needed to completely characterize the index of refraction of a liquid crystal: one to measure  $\Delta n$  and another to measure one of the components of  $n$ .

As in the dielectric method for estimating order parameter, an extrapolation based on the nematic to isotropic transition temperature must be used. This limits the usefulness of the method to the monomers. In the photopolymers, the multifunctional network locks in the liquid crystalline order, so no transition to the isotropic state occurs.

## PROCESS MODIFICATIONS

Currently a modified version of the table-top SLA (TTSLA) device built at The University of Dayton and described in [19] is being used for experimentation with LC monomers. The principal modification to conventional stereolithography apparatus is the addition of a magnet outside the vat in order to align the monomer before cure. Figure 4 is a schematic of the TTSLA apparatus. The magnet is positioned on a rotatable platform so that alignment can be established at any angle relative to the galvanometer axes. A second requirement is to have temperature control of the vat over a wide range. This is desirable so that it is possible to work with all LC phases: smectic, nematic and isotropic. The third modification envisioned is a means to measure molecular alignment in-situ. An ellipsometry technique is being considered for this purpose, but is not yet fully operational. Ellipsometry is analogous to birefringence except that reflectance measurements are used instead of transmitted light.

Initial experiments in the TTSLA have focused on determining the effect of cure temperature, phase, and laser draw speed on cure depth and width (working curves). Strands and simple single-layer parts have been made with monomers in the nematic and isotropic states. In the nematic state, the curing laser beam is scattered much as it is in the two-phase resin SOMOS 2100 [20]. This effect results in cured strand widths being greater than the laser beam diameter. Future experiments will characterize scattering effects as a function of alignment direction relative to the draw direction. By the time of

presentation at the SFF Symposium we expect to have additional data based on the experiments cited above and from processing studies on multiple layer parts.

## SUMMARY

Liquid crystalline reactive monomers are being studied for stereolithography applications. Various characterization techniques were used to determine the types of LC phases present and their temperature ranges. UV spectroscopy and photo-DSC were used to find applicable photoinitiators for the resins investigated. High glass transition temperatures, approaching 200 °C, have been measured for photo-polymerized resins that have been thermally post-cured.

Investigations of the alignment of LC materials have determined that alignment by a magnetic field is feasible. Initial experiments using newly synthesized LC monomers show that alignment over significant distances (3-10 cm) can be achieved. Experiments using a table-top SLA (TTSLA) device have shown that considerable scattering of the curing laser beam occurs when the monomer is in the unaligned nematic state. Work is underway to determine the effects of monomer temperature, alignment, laser power, and draw speed on working curve characteristics and final part properties.

## ACKNOWLEDGMENTS

The authors thank Mary Galaska, John Murphy and Katy Weaver of The University of Dayton for their help in conducting the experiments discussed in this paper. This research was sponsored by the National Science Foundation under NSF Grant No. DMR-9420357.

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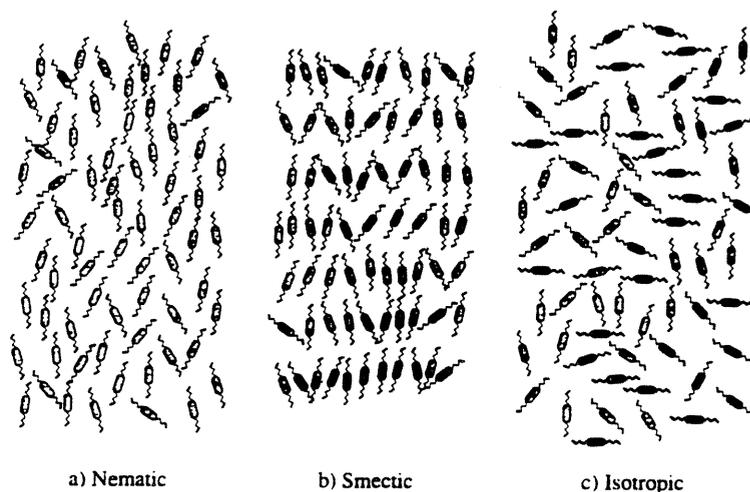


Figure 1. Schematic illustration of monomer molecules in a) nematic phase, b) smectic phase and c) isotropic phase

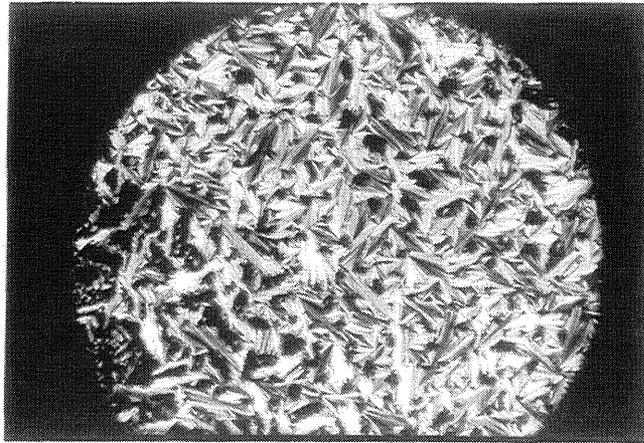


Figure 2. Photomicrograph taken using polarized light of a LC monomer in the smectic A phase.

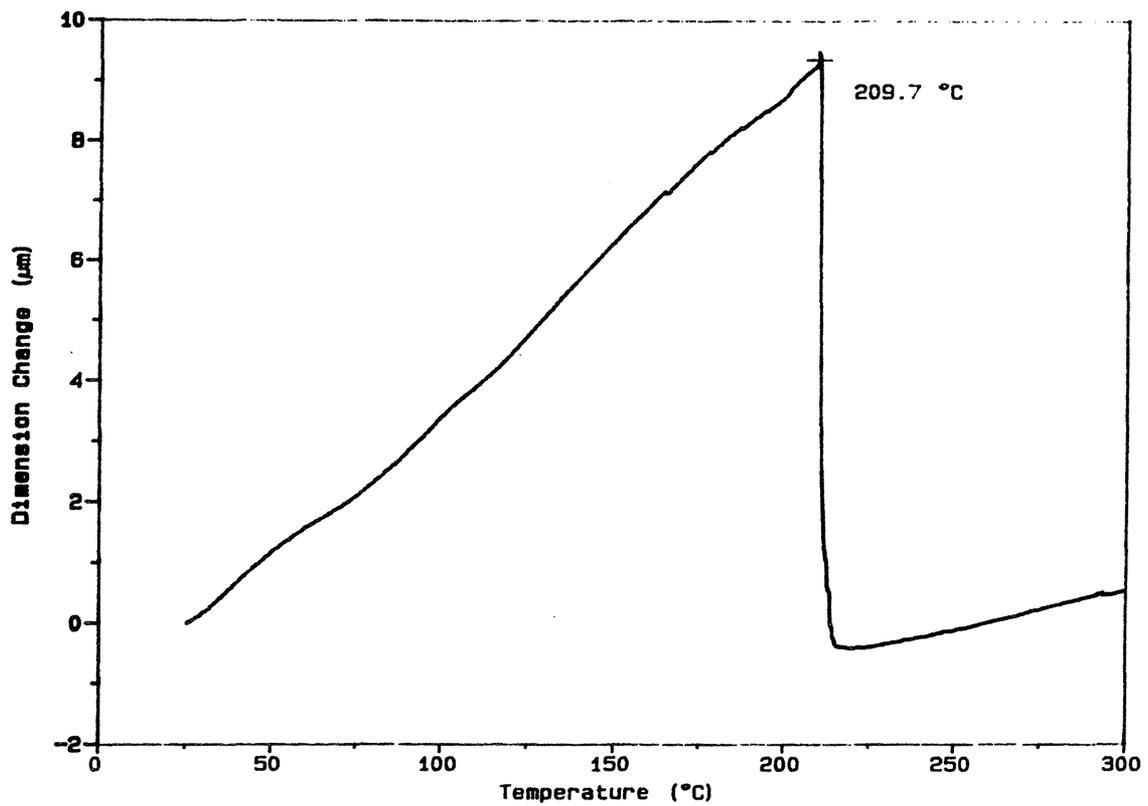


Figure 3. Example TMA data using penetration probe of LC material photocured using a wide-band UV source and thermally postcured by heating to 300 °C. Indicated glass transition temperature is 210 °C.

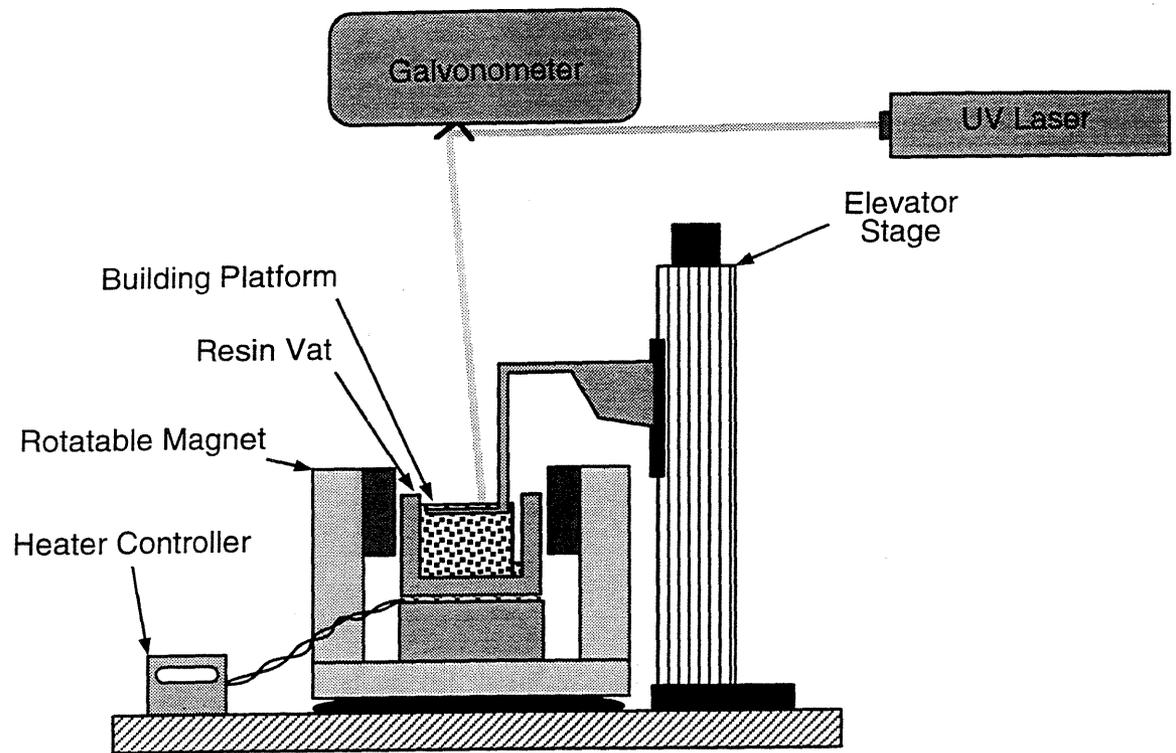


Figure 4. Schematic of modified stereolithography apparatus for use with liquid crystal monomers.

