

BIREFRINGENCE THERMAL ANALYSIS OF LIQUID CRYSTALLINE MONOMERS AND THEIR PHOTOPOLYMERS

J. W. Schultz, R. T. Pogue, R. P. Chartoff and J. S. Ullett

The University of Dayton, Center for Basic and Applied Polymer Research, Dayton, Ohio 45469-0130, USA

Abstract

Birefringence analysis was used to measure thermal transitions in liquid crystal diacrylate monomers and their corresponding polymers. In this technique, linearly polarized light was used to probe the sample as the temperature increased via a linear ramp. Various phase transitions were observed in the liquid crystalline monomers. In addition, the monomers were isothermally photopolymerized in the liquid crystalline state and the resulting polymer networks retained their liquid crystalline order. Glass-to-rubber transitions as well as indications of further thermal polymerization and stress relaxation were detected. Results from birefringence experiments were compared to those of more traditional thermal analysis techniques including DSC and TMA.

Keywords: birefringence, liquid crystal, photopolymer, glass transition

Introduction

In recent years, there has been increasing interest in liquid crystalline polymers for both optical and structural applications. While traditional methods of thermal analysis are effective for characterizing these materials, they have a unique feature that provides an additional avenue for characterization. In particular, liquid crystals and liquid crystal polymers are birefringent.

Birefringence in liquid crystals results from their dielectric anisotropy. Nematic and smectic liquid crystals have cylindrically shaped molecules. In the liquid crystalline state, these molecules possess a certain degree of localized alignment, with their long axes oriented towards a preferred direction. Because of the directional polarizabilities and dipole moments of the individual molecules and because of their alignment, a net dielectric anisotropy exists. Equivalently, two different indices of refraction exist, which are in directions parallel and perpendicular to the material's optical axis. In this case, the material is called 'birefringent', and transforms plane polarized light into elliptically polarized light.

Like liquid crystals, solid crystals and crystalline polymers have molecular order, and therefore exhibit birefringence. Conversely, amorphous liquids and polymers do not usually exhibit birefringence because they do not have molecular order. They have a single index of refraction, which is a function of temperature. As a material goes through a phase transition, the index of refraction also changes. Some of

the earliest work, using index of refraction to study phase transitions in polymers, was done by Wiley [1]. His results indicate that the refractive index/temperature curve of poly(vinyl acetate) shows a sudden slope change at the glass transition. In subsequent work, Wiley and Brauer [2-5] studied many different polymers. They found good correlation between the refractive index method and traditional thermal analysis methods for determining glass/rubber transitions.

While amorphous polymers are not usually birefringent, a small degree of order can exist in glassy polymers. This order may be a result of placing the material under stress, or internal stresses caused by processing. Wiedemann *et al.* [6] discuss the method of 'thermo-optical analysis', in which the glass transition in amorphous polymers is detected not by refractive index, but by measuring the degree of birefringence. In this method, only the first heating curve is measured because the sample birefringence disappears by stress relaxation in the rubbery phase.

In the present work, birefringence analysis, or 'thermo-optical analysis', is used to study birefringence changes in some liquid crystalline monomers and their polymers as a function of temperature. The objective in this study is to evaluate the effectiveness of the birefringence method in determining transition phenomena in these liquid crystal monomers and polymers.

Experiment

The monomers used for this study, designated N1 and N2, are both diacrylate monomers with mesogenic cores made up of three aromatic rings linked by ester bridges, and with a methyl group on the central ring. The N1 has 6-carbon aliphatic spacers on each side of the core while the N2 has 3-carbon spacers. N1 has been studied extensively by Broer *et al.* [7].

The as-received monomer was mixed with 2% Irgacure 369 (Ciba-Geigy) photoinitiator. Each sample was mounted with a 20 micron wire spacer, between an untreated glass slide and cover slip. UV curing was carried out using an EFOS Ultracure 100 lamp. During the cure, samples were held at a temperature of 80°C and irradiated until fully UV cured (approximately 3 min).

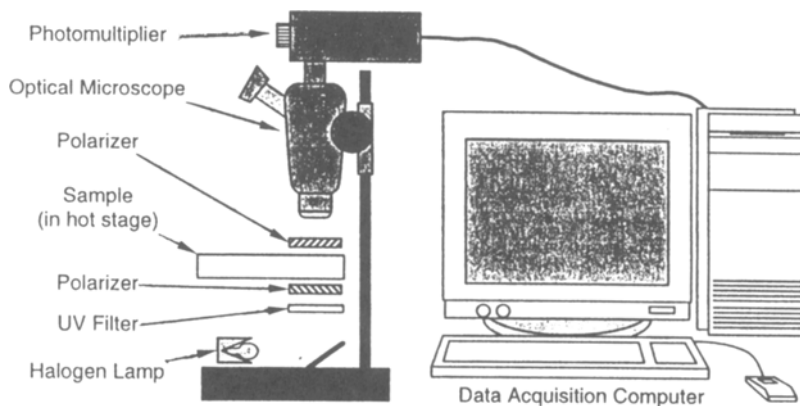


Fig. 1 Experimental apparatus for measuring optical birefringence

The experimental apparatus for measuring birefringence is shown in Fig. 1. Samples were placed in a Mettler FP82 hot stage for temperature control. For most experiments, a linear ramp of $5^{\circ}\text{C min}^{-1}$ was used. The hot stage was positioned between crossed polarizers and viewed with a microscope using broad band illumination from a halogen lamp. An UV cutoff filter was used on the lamp to avoid pre-polymerization of the sample. A photomultiplier tube was used to measure the intensity of light transmitted through the sample. Data were acquired in real time by a digital multimeter and downloaded to a computer.

Besides birefringence experiments, samples were also analyzed with a TA Instruments 2910 differential scanning calorimeter (DSC) and a 2940 thermo-mechanical analyzer (TMA). As in the birefringence experiments, a linear ramp of $5^{\circ}\text{C min}^{-1}$ was used for all experiments. In the TMA experiments, a linear expansion probe was used to measure linear thermal expansion of the polymer films. Film thickness for the TMA data shown was 0.4 mm.

Discussion

Liquid crystalline phase transitions are easily detected using the birefringence method, as shown in the lower curve of Fig. 2. In this figure, the birefringence data from the pure N1 monomer (without photoinitiator), is compared to the corresponding DSC data. In both curves, the N1 is heated from a crystalline state. Both curves clearly show the transitions from crystalline to nematic states, and from nematic to isotropic states. In the isotropic state, the N1 is no longer birefringent, and the transmitted intensity is essentially zero. The transition temperatures measured by both techniques match quite well and are very reproducible. Though not shown, the N2 monomer behaves similarly.

Both the birefringence and DSC techniques detect phase changes quite well for the monomer, however, the same cannot be said for the polymer. In particular, the photopolymers from these monomers formed highly crosslinked networks with

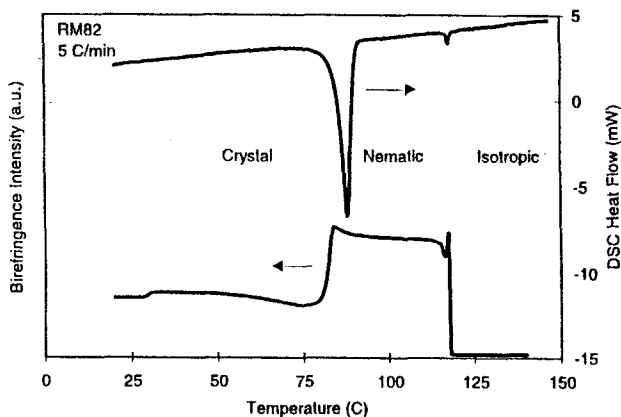


Fig. 2 Phase transition behavior of N1 monomer measured by both birefringence and DSC

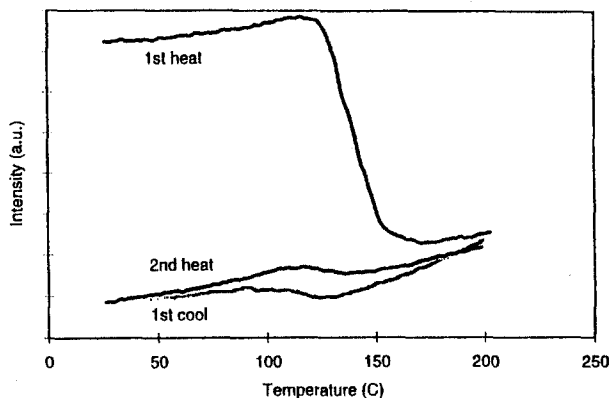


Fig. 3 Birefringence data for the photopolymer of N1, cured at 80°C (in the nematic phase)

weak, broad glass transitions, and DSC analysis was unable to detect this transition. As shown in Fig. 3, however, the birefringence is still sensitive to the glass transition, even in these highly crosslinked systems.

Figure 3 also shows that there was an irreversible relaxation that occurred the first time the polymer was heated past its glass transition temperature. Subsequent thermal cycling results in fairly reproducible curves that show little or no change at the glass transition. In birefringence analysis of amorphous polymers, Wiedemann *et al.* [6] saw a similar effect, caused by relaxation of internal stresses created during initial polymer processing. This may explain the results obtained in the liquid crystal polymers. However, in these materials, birefringence is an intrinsic property and does not disappear upon heating past T_g . Another possible explanation may be index of refraction changes due to thermal advancement of the cure.

The polymer cured from the N2 behaved similarly to the N1. It also had a large decrease in birefringence upon heating past T_g for the first time; and, subsequent heats showed little or no change in birefringence. Comparing the first heating curve

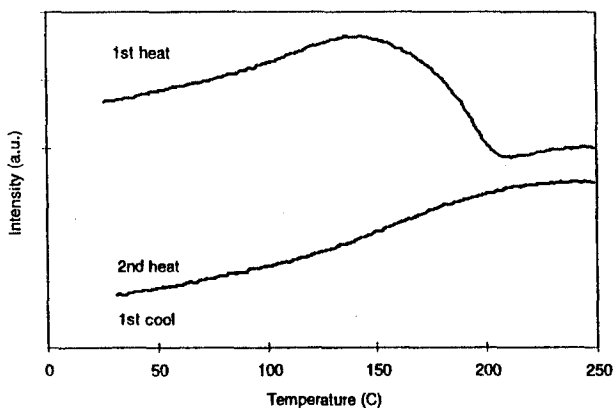


Fig. 4 Birefringence data for the photopolymer of N2, cured at 80°C (in the nematic phase)

of the N1 polymer (Fig. 3) with that of the N2 (Fig. 4) shows that the N2 polymer has a somewhat higher T_g . This is expected since the N2 has fewer flexible carbons and is a stiffer molecule. Broer *et al.* [7] measured T_g of the N1 using the loss tangent from dynamic mechanical analysis. They found that the transition region was very broad with a peak at approximately 90°C. It is not completely clear where T_g should be assigned in the birefringence data of Figs 3 and 4, however the peak of the curve for N1 (Fig. 3) occurs at approximately 115°C. This is higher than the value quoted by Broer *et al.* The discrepancy may be due to differences in the cure conditions or photoinitiator chemistry.

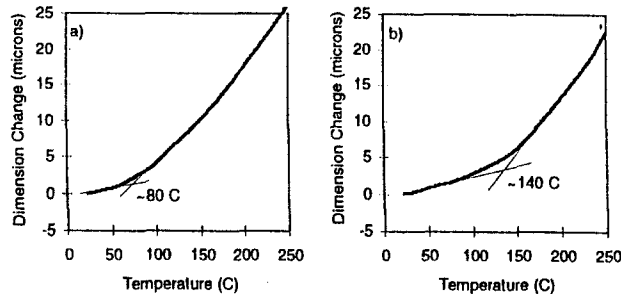


Fig. 5 TMA data for the photopolymer of N2, cured at 80°C. Curve a) shows the initial scan with a T_g corresponding to the cure temperature. Curve b) shows a subsequent scan, with an 'ultimate' T_g of 140°C

For the N2 polymer shown in Fig. 4, the peak of the first heating curve occurs near 140°C. This matches the glass transition temperature measured by TMA as shown in Fig. 5b. The data of Fig. 5b were measured after thermal cycling of the sample, while Fig. 5a shows the first thermal scan of the sample (immediately after photopolymerization and before thermal cycling). All these data show that the initial T_g of the N2 polymer corresponds to the cure temperature, 80°C, and that after thermal cycling to 250°C, an ultimate T_g of 140°C is obtained. The birefringence data of Fig. 4 show that this ultimate T_g is obtained rather quickly during the first heating cycle of the sample.

Conclusions

A birefringence analysis method was used successfully to measure phase transitions and glass transitions of two liquid crystal monomers and their corresponding photopolymers. This method was easy to implement and provided valuable data on the thermal characteristics of the monomers and polymers. In the case of the glass transition, it proved to be considerably more sensitive than DSC analysis.

An irreversible change in the polymers occurred upon heating past the glass transition temperature. This can be explained by either stress relaxation, or index of refraction changes associated with the advancement of the cure during thermal cycling. Comparisons were made between the birefringence method and other tech-

niques including DSC and TMA. Transition temperatures, measured by birefringence, agreed with the corresponding DSC and TMA measurements.

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