Electronic Supplementary Information

A PIEZOELECTRIC THERMOPLASTIC ELASTOMER CONTAINING A BENT CORE LIQUID CRYSTAL

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1. Sample Preparation

The bent-core LC 4-chloro-1,3-phenylene bis(4-(4-(decyloxy)benzoyloxy)benzoate) (BLC) was synthesized following to the procedure described for its unsaturated analogue [1]. Linear SIBSTAR (073T) was used as received from Kaneka Corporation (M_n = 66,700 g/mol; M_w/M_n = 1.24; 31 wt% PS). LC/Polymer composite films were prepared by solution casting of 7 wt% solutions of the corresponding amounts of BLC and SIBSTAR in tetrachloroethylene (Aldrich, ACS reagent, used as received). The solution was stirred at 40°C until homogeneous after which it was poured into open Teflon dishes approximately 1 cm deep and 2.5 cm in diameter. The solution was allowed to dry at room temperature overnight. Additional vacuum drying was carried out for 24 h at room temperature. After the solvent had evaporated the films were removed and cut into smaller pieces. The samples were then compression molded in a temperature controlled Carver® hydraulic press shown in *Figure 1(a)*. The mold containing the material was placed in the hydraulic press and heated to 150°C for 20 min at a pressure of 200 psi. The pressure was then increased to approximately 700 psi (~50 atm) and kept at constant

pressure and constant temperature. After 2 min the sample was cooled at 1.4°C/min, while maintaining the high pressure. The sample was removed when the temperature reached 65°C (±1°C). Stainless steels molds were used to produce samples of 2 cm by 2 cm lateral dimensions and 1 mm thickness (*Figure 1(b)*).

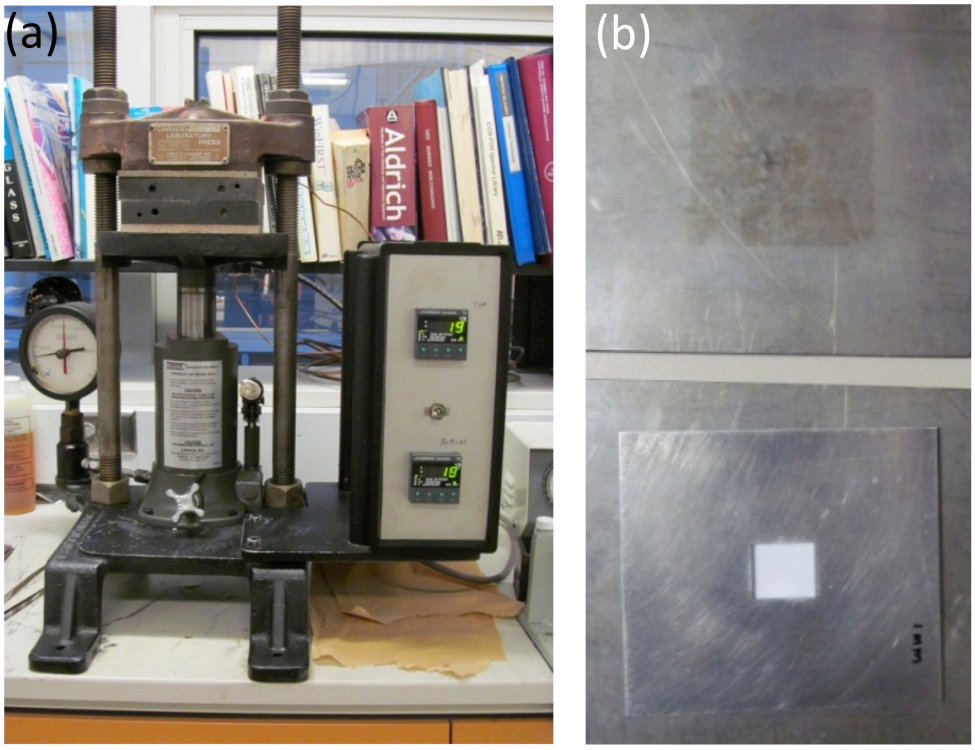

Figure 1: Compression molding device and sample images of various concentrations of the liquid crystal BLC. (a) Hydraulic press; (b) Mold. Top: top plate, Bottom: bottom plate and middle plate with sample.

2. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were performed with a TA Instruments Q2000 series DSC using heating and cooling rates of 10°C/min, between 25°C and 120°C. Tzero Aluminum pans were used. DSC spectra of the composite material (solid line) containing 50 wt% was compared to that of the pure BLC (dashed line) in *Figure 2*. The heating cycle of the pure BLC shows a transition at 63°C between two different crystalline phases. The transition at 88°C corresponds to the melting from the crystalline to the nematic. A small peak at around

91°C corresponds to the transition from the nematic to the isotropic phase. In cooling, BLC shows the nematic phase from 91°C down to approximately 64°C where it transitions to an optically isotropic phase (called X phase) [2] followed by the crystalline phase at 49°C. In the LC/polymer composite material in 10°C/min heating there is only one peak at 89.6°C with a small shoulder at 84°C. In cooling no peak showing the isotropic to nematic transition appears, although polarizing microscopy studies clearly shows a transition to a nematic phase at 91°C.

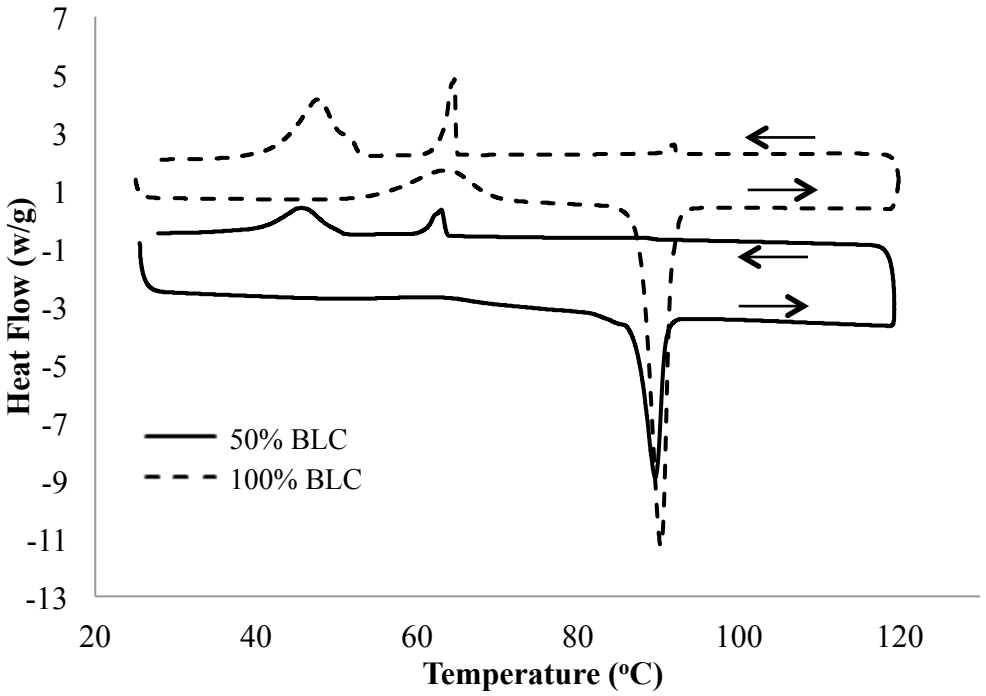

Figure 2: DSC spectra of the pure bent-core LC BLC (dotted line) and LC/ SIBSTAR polymer composite 50% LC (solid line).

The temperature dependences of the heat flow in cooling at 10ºC/min rate are shown in *Figure 3*.

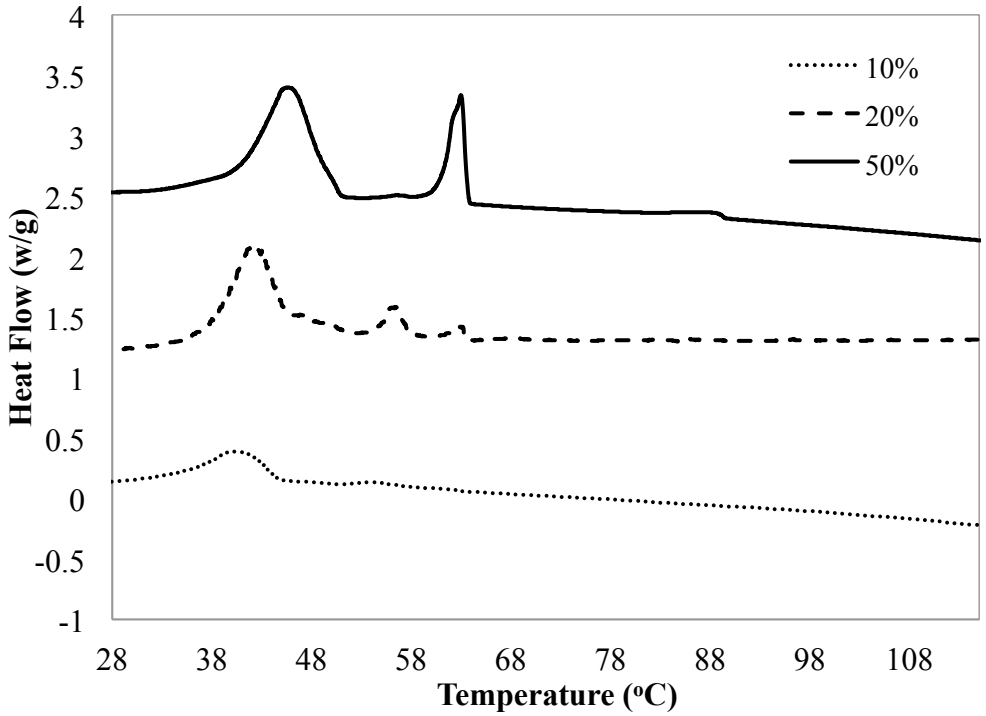

Figure 3: DSC spectra of the BLC/SIBSTAR composites at 10, 20 and 50 wt% BLC concentrations in cooling at 10°C/min.

3. Polarizing Optical Microscopy (POM)

The POM images were observed using an Olympus BX60 polarizing optical microscope. The samples were placed in a computer-controlled Instec Hot Stage to regulate the temperature. The images were captured using a Sony CCD camera under transmitted light between crossed polarizers. Unless otherwise noted, the images of pure LC samples were taken in standard test cells with 5μm gap and planar alignment oriented at 45° to the polarizer. Images of the polymer composite were taken on a standard glass microscope slide.

4. Small Angle X-Ray Scattering (SAXS)

The small angle X-ray scattering (SAXS) measurements were taken at the X6B beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The samples were mounted into a custom-built aluminum cassette that allowed X-ray detection with ±13.5° angular range. The cassette fits into a standard hot stage (Instec model HCS402) that allowed temperature control with ±0.1°C precision. Two-dimensional SAXS images were recorded on a Princeton Instruments 2084 × 2084 pixel array CCD detector. The beamline was

configured for a collimated beam (0.2mm x 0.3 mm) at energy 16 keV (0.775 Å). Periodicity was calculated using $d=2\pi/q$, and correlation lengths were calculated using $\xi=2\pi/\Delta q$, where Δq is the full width at half maximum (FWHM) of the scattering peak.

5. Interferometric Microscopy

To measure the converse piezoelectric effect, measurements were carried out with a Leitz Mirau Interferometer mounted on an Olympus BH2 microscope. A cell was made by placing the polymer film containing the bent-core LC between two indium-tin-oxide (ITO) coated glass substrates functioning as electrodes. The bottom substrate was fixed to the microscope's table, only the top substrate could move freely. The principle of the measurement is illustrated in *Figure 4*.

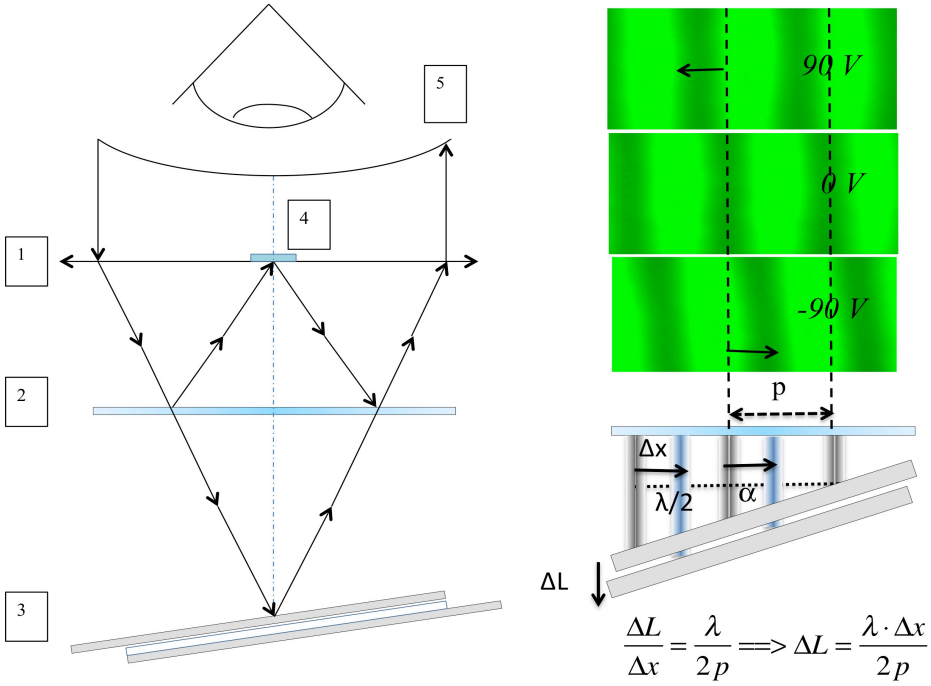

Figure 4: Principle of the Mirau interferometric system to measure Electric field – induced change of the film thickness. The angle a between the beamplitter and the top substrate of the film is exaggerated to show the principle better. 1: Reference surface; 2: Beamsplitter mirror; 3: Cover plate of the film; 4: Reference mirror; 5: Microscope objective.

Light was reflected off the top of the cell in order to produce the interference pattern. When the film surface is not exactly parallel to the Beamsplitter mirror, one sees stripes separated by a

distance p. When a voltage is applied between the electrodes, a contraction or expansion of the film occurs due to the piezoelectric effect causing movement of the top substrate of the cover plate position by ΔL. This leads to a sidewise shift of the stripes by a distance Δx. Measuring this shift, one can calculate the thickness change ΔL as shown in the equation in the bottom right corner of *Figure 4*.

6. References

[1] K. Fodor-Csorba, A. Vajda, G. Galli, A. Jákli, D. Demus, S. Holly, E. Gács-Baitz, *Macromolecular Chemistry and Physics* **2002**, *203*, 1556–1563.