

Phase Transitions in Smectic Bent-Core Main-Chain Polymer Networks Detected by Dielectric and Ultrasonic Techniques

V. SAMULIONIS,^{1,*} Š. SVIRSKAS,¹ J. BANYS,¹
A. SÁNCHEZ-FERRER,² N. GIMENO,³ AND M. B. ROS³

¹Vilnius University, Physics Faculty, 10222 Vilnius, Lithuania

²ETH Zurich, Department of Health Sciences and Technology, 8092 Zurich, Switzerland

³University of Zaragoza, Materials Science Institute of Aragón (ICMA), 50009 Zaragoza, Spain

The dielectric and ultrasonic properties of a bent-core main-chain liquid-crystalline polymer network have been investigated. Dielectric measurements on this material showed two maxima in the real and imaginary components of the dielectric permittivity at 365 K and 450 K along with a temperature hysteresis showing the first order nature of the two phase transitions. Longitudinal ultrasonic attenuation and ultrasonic velocity measurements at 10 MHz frequency revealed some anomalies at the phase transition temperatures respect to the dielectric results. Above room temperature, a large ultrasonic attenuation was observed which can be related to the glass transition of this sample. Moreover, the piezoelectric sensitivity of this bent-core main-chain liquid-crystalline polymer network has also been studied.

Keywords Polymer network; bent-core; liquid crystals; phase transitions; ultrasonic properties; dielectric properties

Introduction

Ferroelectric liquid crystals are useful organic molecules as alternative to ferroelectric inorganic materials and ceramics in piezoelectric devices. In the past few years, bent-core liquid crystals (BCLC) have become a prime topic of research in the field of liquid crystals due to the singular properties of this type of materials [1–2]. BCLC are achiral molecules which contain aromatic rings disposed in a non-straight configuration, and are of interest because of their spontaneous segregation into chiral domains, showing ferro-[1], antiferro-[2] and piezoelectric [3] properties. Moreover, such molecules show nonlinear optical activity [4], optical biaxiality [5] or flexoelectric behavior [6], properties which are of high interest as potential new functional materials for the construction of electric or electro-optic devices. The combination of such bent-core based molecules with polymers results on macromolecular structures which keep the properties of both components, and

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*Corresponding author; E-mail: vytautas.samulionis@ff.vu.lt

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the chiral segregated domains contain the BCLC in a lamellar or columnar fashion. This combination enables to process the material and brings mechanical and thermal stability. Recently, the synthesis and characterization of linear BCLC main-chain polymers have been published, showing the “dark conglomerate” mesophase (DC) [7], which showed interesting dielectric and polarization switching properties under electric field. There are not so many ultrasonic measurements especially at high frequencies in polymeric materials [8]. It might also be of interest the detection of piezoelectric sensitivity in BCLC by ultrasonic method as for inorganic lamellar crystals of the CuInP_2S_6 family [9–11]. Herein, we report the ultrasonic and dielectric investigations on a BCLC main-chain polymer network synthesized via one-pot hydrosilylation reaction.

Experimental

The BCLC main-chain polymer network was obtained as a film of 200–300 μm thickness (details on the synthesis of the mesogen and hydrosilylation reaction can be found in reference [7]). The ultrasonic measurements were carried out by the pulse-echo method at 10 MHz frequency. The dynamic range of our ultrasonic system was higher than 70 dB, therefore large ultrasonic attenuation coefficients could be measured. Piezoelectric detection of the ultrasonic wave in this thin BCLC film was performed in the same pulse-echo ultrasonic setup in transmission mode of longitudinal ultrasonic waves when one ultrasonic lithium niobate transducer was exchanged by the BCLC plate (see reference [9] for more details about the setup). Silicone oil was used as an acoustic bond.

The complex dielectric permittivity of the BCLC main-chain polymer network was measured from 300 to 480 K temperature interval and from 1.2 kHz to 1 MHz frequency range. A HP4284A LCR-meter was used for measuring the capacitance and loss tangent. The dielectric permittivity was obtained according to the parallel plate capacitor model. The temperature rate during the experiment was $dT/dt = 1 \text{ K}\cdot\text{min}^{-1}$. The temperature was measured with Keithley Integra 2700 multimeter equipped with 100 Ohm platinum thermo resistor.

Results and Discussion

Measurements of the temperature dependences of ultrasonic properties were performed on a BCLC main-chain polymer network (Figure 1 and 2). Our ultrasonic setup allows for measuring the time-of-flight with changes smaller than 0.2 ns, therefore the relative ultrasonic velocity measurements on very thin samples of 200 to 400 μm thickness are accessible. In order to obtain better resolution, two pieces of 250 μm thickness were glued together. The longitudinal ultrasonic wave was excited by a LiNbO_3 transducer working at 10 MHz frequency.

The ultrasonic attenuation experiments showed anomalies which correspond to the following phase transition sequence: the highly order smectic-to-smectic phase transition at 370 K, and the smectic-to-isotropic phase transition at 453 K (Figure 1). The anomalous absorption observed in the smectic phase near 453 K might be due to two additive contributions: i) the critical attenuation related to order parameter fluctuations, and ii) the attenuation due to the relaxation of the order parameter itself [12], *i.e.* the Landau-Khalatnikov process [13]. To the best of our knowledge, the anomalous ultrasonic behavior near the highly order smectic phase can be interpreted by the same Landau-Khalatnikov relaxation mechanism implying a different order parameter. The temperature dependence of the ultrasonic velocity shows that the relaxation time of the order parameter near both

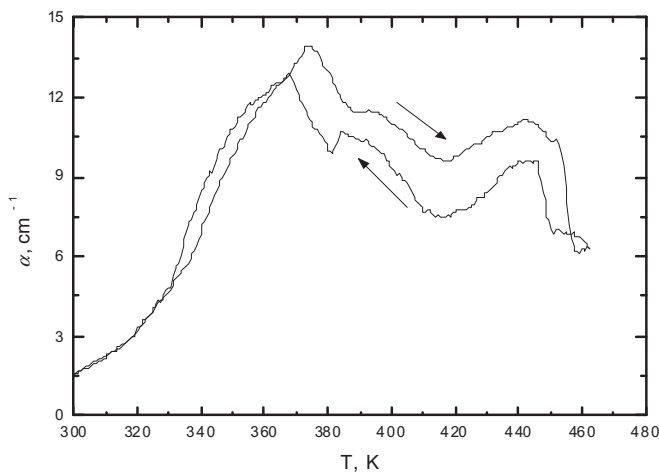


Figure 1. Temperature dependence of the ultrasonic attenuation for the BCLC main-chain polymer network. The arrows show the direction of the temperature variation.

phase transitions is comparatively long (Figure 2), and the velocity dip at the phase transition temperature vanishes as observed for ferroelectric phase transitions in DDSP [14]. The increase in velocity below the transition temperature can be related to the contribution of the order parameter-strain interaction of fourth order [14], and the temperature hysteresis could be related to the first order smectic-to-isotropic phase transition.

The ultrasonic anomalies at the phase transitions are difficult to describe quantitatively because of the additional large attenuation peak and decrease of velocity close to the highly order smectic-to-smectic phase transition temperature. This large broad attenuation peak in the vicinity of 375 K can be attributed to the effects induced by the glass transition. Such ultrasonic relaxation process is similar to what we have observed in poly-urea elastomers [9].

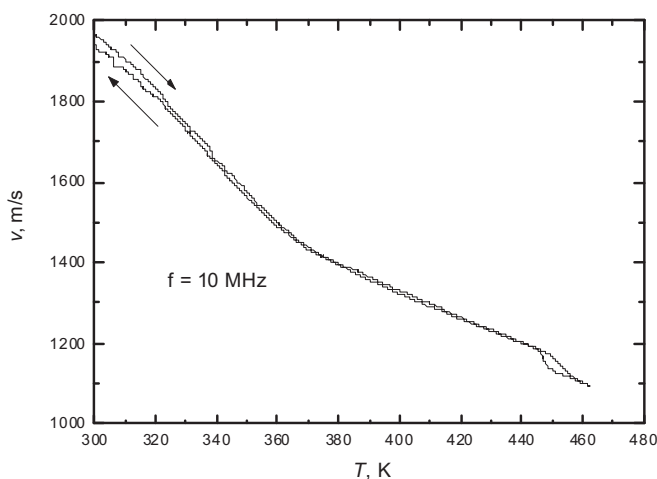


Figure 2. Temperature dependence of the ultrasonic velocity for the BCLC main-chain polymer network. The arrows show the direction of the temperature variation.

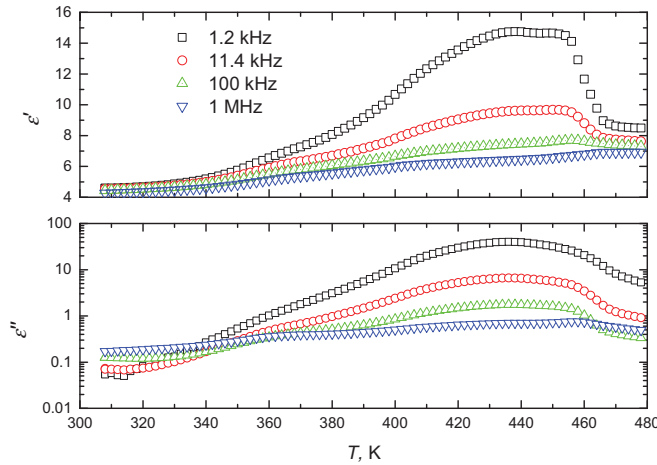


Figure 3. Temperature dependence of the complex dielectric permittivity for the BCLC main-chain polymer network.

The temperature dependence of the complex dielectric permittivity at different frequencies is depicted in Figure 3 during the heating cycle. The BCLC main-chain polymer network shows a very interesting temperature dependence profile of the dielectric permittivity. There is a frequency independent region at the lowest temperature region, *i.e.* $T < 340$ K. The imaginary part indicates that the dielectric loss increases when the probing frequency is increased, which is characteristic for dipolar relaxation processes. Moreover, at room temperature, no conductivity effects are observed.

When the temperature is further increased from $340 < T < 450$ K, the conductivity starts to emerge: the dielectric losses increase more rapidly at the lowest frequencies – relative to high frequencies (Figure 3). The real part of the dielectric permittivity exhibits an anomaly which might be also related to the phase transition. The jump is also observable in the dielectric loss at 1 MHz frequency, where at lower frequencies it is masked by the above-mentioned conductivity. The increase of dielectric losses might be one of the reasons for the decrease in the detected piezoelectric signal (Figure 4), and reaches a minimum around 370 K. It is obvious that above 370 K the dielectric loss is weakly dependant on the temperature. Another reason for this local minimum in the piezoelectric sensitivity is the above-mentioned broad peak in the ultrasonic attenuation near 370 K. The increase of the piezoelectric coefficient when approaching the ferroelectric phase transition is another safe assumption and would explain the increase in the amplitude of the detected piezoelectric signal upon increasing temperature (Figure 4). The drop of the piezoelectric sensitivity above the first order phase transition shows that piezoelectric effect vanishes in the centrosymmetric isotropic phase of BCLCs.

At the highest temperature region $T > 450$ K, the dielectric measurements show a dramatic decrease in both the real and imaginary part of the dielectric permittivity (Figure 3). This observation is also related to the phase transition already observed by the ultrasonic techniques. This phase transition is manifested by the huge drop in conductivity. Further decrease of the loss factor at the lowest frequencies is observed as well, and at higher temperature it is expected to drop down even more than the loss factor at 1 MHz, if no other conductivity mechanism is triggered. This means

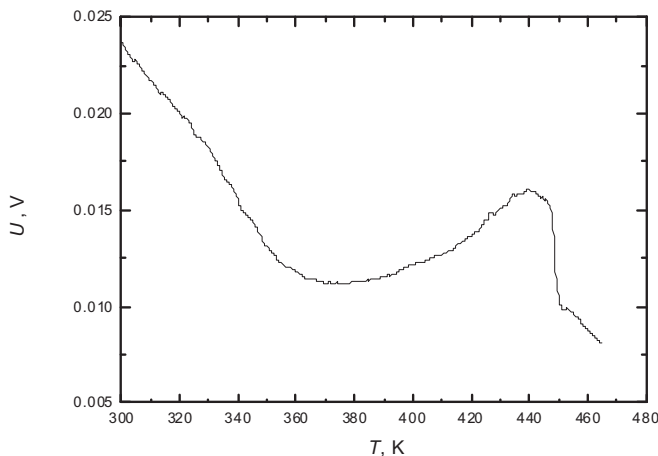


Figure 4. Temperature dependence of the ultrasonically detected piezoelectric signal for the BCLC main-chain polymer network.

that the dielectric properties in this phase are determined by dipolar relaxation processes.

Conclusions

The temperature dependences of the piezoelectric response, longitudinal ultrasonic velocity and ultrasonic attenuation in a new bent-core main-chain liquid-crystalline polymer network were measured. In the ultrasonic attenuation experiments, velocity anomalies appeared at the phase transitions located at 370 K (highly order smectic-to-smectic) and at 453 K (smectic-to-isotropic). In addition, the large ultrasonic attenuation peak related to the glass transition has been observed above room temperature, and the piezoelectric sensitivity was observed for such liquid-crystalline network. The temperature dependence of the complex dielectric permittivity shows the same anomalies as observed in ultrasonic experiments, although the anomaly related to the glass transition is less pronounced. The dielectric properties are determined by dipolar relaxation processes at the lowest and highest temperature, while in the middle temperature range from 340 to 450 K conductivity appears to be significant.

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