



Temperature dependency of impedance spectroscopy behaviors in side-chain liquid crystalline polymer

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ARTICLE INFO

Article history:

Received 15 November 2008

Received in revised form 29 June 2009

Available online 21 October 2009

PACS:

77.84.Nh

Keywords:

Conductivity

Dielectric properties, relaxation,

electric modulus

Polymers and organics

ABSTRACT

In this paper, the electrical properties of side-chain liquid crystalline polymer (SLCP) are investigated by impedance spectroscopy technique. We report the measurement of dielectric and conductivity for SLCP from 1 kHz to 10 MHz within the temperature range from 300 to 370 K. The DC conductivity obeys Arrhenius law and it gives a small deviation at 315 K. The activation energies are equal to 0.20 eV and 0.75 eV for high and low temperatures, respectively. The frequency dependence of conductivity satisfies the power law, $\sigma_{AC} = Aw^s$, with $s = 0.50$ – 0.57 . The evaluated power law exponent s exhibits nearly linear decreasing behavior with temperature. This suggests that the Correlated Barrier Hopping (CBH) model is the operating mechanism.

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1. Introduction

During the last 40 years, lots of researches have been reported on AC measurements of disordered solid-like ionic conducting glasses, amorphous and poly crystalline semiconductors, electron and ion conducting polymers, metal cluster compounds, transition metal oxides, etc. Experimental data were usually reported in terms of both frequency and temperature dependence of either the complex dielectric constant $\epsilon^*(w) = \epsilon'(w) - i\epsilon''(w)$ [1].

Most of the technological applications utilize materials in thin film form. Recently, there has been growing interest in the dielectric-like behaviors in polymer films. Dielectric spectroscopy (DS) has been widely used to investigate the phase transitions in polymers. This technique also provides some relevant dielectric/electrical information that may be important in specific applications [2].

Liquid crystals (LC) are non-linear optical materials, and several of their properties investigated so far have revealed the promising characters of these materials. Employing nematic LC between transparent electrodes is the fundamental technique for producing spatial light modulators that are widely used and are important in various adaptive optics and image/signal processing systems [3]. Director-axis reorientation based effects have also been extensively

studied so far [3–11]. This phenomenon has potential applications such as holographic data storage. In technology, LC is commonly preferred to be used in their doped forms so that the considered effects would be dominant. Actually polymer-dispersed LC is among one of these categories in related research on highly efficient orientational photorefractive effects [12–18]. Electrical properties of a side-chain liquid crystalline polymer (SLCP) composite were investigated for laser-induced circumstances [19]. Actually temperature dependency of phase transitions on SLCP doped LCs were investigated in detail in our previous work [20].

In the scope of this current work, we have carried out complex impedance studies on SLCP to investigate its electrical properties and the temperature dependency of these properties in AC and DC regime.

2. Experimental

ITO (indium–tin-oxide) coated glass based cells, whose thicknesses are 8 µm and the dimensions of the electrodes were 10 × 10 mm², were used in the measurements. These cells were made up of two conductive glass plates (ITO) with planar alignment. Sample cell was filled with a mixture of E7/SLCP 10% (w/w) via capillary action at the room temperature. Actually E7 is the mixture of four nematicogens (51% K15, 25% K21, 16% M24, and 8% T15) and it was purchased from Merck. Poly (methyl

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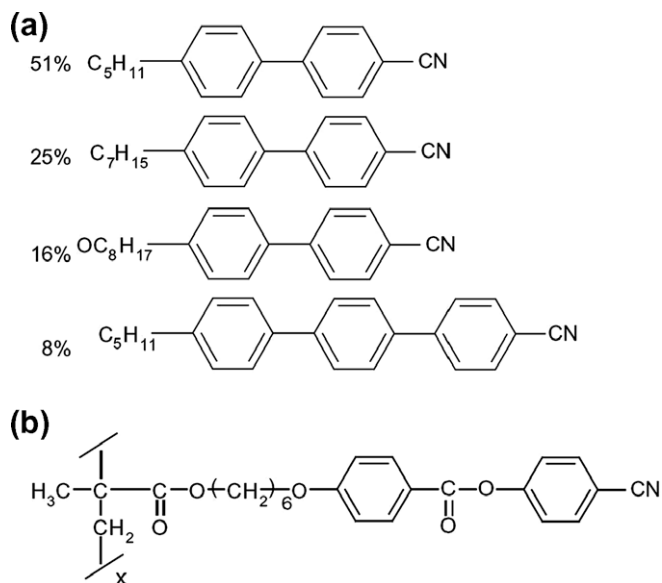


Fig. 1. Chemical formulas of: (a) nematic host, E7, (b) side-chain liquid crystalline polymer (SLCP).

methacrylate) comprising a 4-cyanophenyl benzoate side group was synthesized by means of radical polymerization and used as our SLCP. Chemical formulas of the SLCP and nematic host are depicted in Fig. 1.

AC conductivity and dielectric properties were analyzed from the capacitance and the conductance values at different temperatures at different frequencies. HP 4194A impedance analyzer was utilized during these measurements. Dielectric response was considered between 1 kHz and 10 MHz and *rms* amplitude of the device is ~ 495 mV. Keithley 2400 Source Meter and Function Generator DC conductivity was measured at 10 kHz frequency. The temperature was controlled by using a PT 100 resistor, which is in direct thermal contact with the sample. It could be monitored between 25 and 100 °C with accuracy better than 0.1 °C by using NOVOTHERM Temperature Control System.

3. Results and discussion

3.1. The temperature dependence of the dielectric constant

Actually the variation of the real part of dielectric constant with temperature is described by the Curie–Weiss relation;

$$\varepsilon = \frac{C}{T - T_0} \quad (1)$$

where C is the Curie–Weiss constant and T_0 is the Curie–Weiss temperature. In (2), the dielectric constant is characterized as $\varepsilon \rightarrow \infty$ when T_0 is approached from zero. The order of the phase transition can be determined by this equation indeed. If T_0 is equal to the phase transition temperature, T_c , the phase transition is of second order. When $T_0 \neq T_c$, it is of first order type. It is clear from Fig. 2 that the phase transition is first order. The Curie–Weiss constants and temperatures were obtained from the slope and intercept of $1/\varepsilon$ versus temperature plots ($C = 2 \times 10^4$ K). The obtained values suggest that phase is of the first order. A more-or-less random intersection of the thermodynamic functions in such a phase transitions is responsible for the properties of the crystal to how close it is to phase transition point. Basic information about phase transitions is this kind is contained in the Clausius–Clapeyron equation, which relates the slope of the phase equilibrium curve to jumps in the vol-

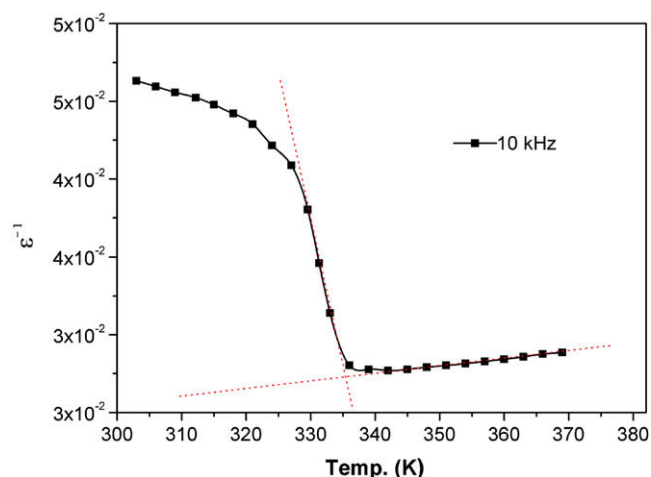


Fig. 2. Temperature dependence of inverse dielectric constant at 10 kHz.

ume and entropy upon transition from one to another [21]. So, the phase transition requires a latent heat.

3.2. Temperature dependence of the DC conductivity

DC conductivity, which is estimated from the bulk response of the material, has been observed to be a function of temperature as demonstrated in Fig. 3. Conductivity versus temperature response is linear at higher temperatures and this can be explained by a thermally activated transport process. It was also found that the conductivity character obeys the Arrhenius law;

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \quad (2)$$

where σ_0 the pre-exponential factor, E_a is the activation energy of the mobile charge carriers, and k_B is the Boltzmann's constant. The activation energies are estimated from the slope of $\ln \sigma - 1000/T$ curves. At lower temperatures, a slight deviation from the linear behavior of conductivity has been noticed. The activation energy of the material has been estimated to be 0.20 and 0.75 eV at high temperatures (315–380 K), and at low temperatures (300–315 K), respectively. It is well known that, at least two transport mechanisms are considered when a change is observed in the slope of the DC conductivity, (see Fig. 3). One of these mechanisms is a transport, which is by carriers excited beyond a mobility edge into

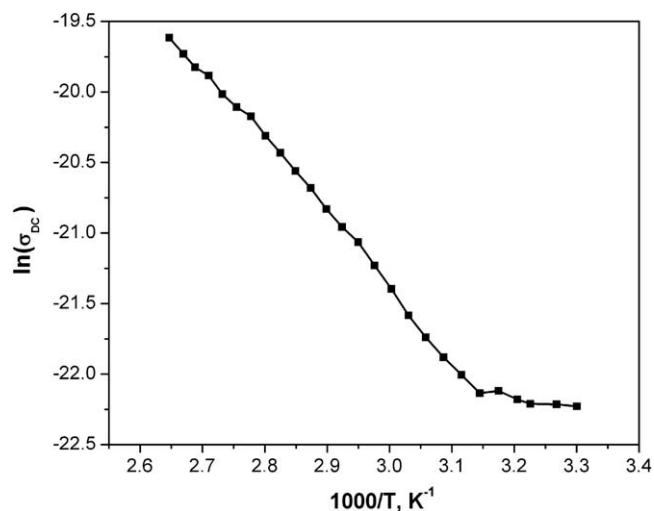


Fig. 3. Temperature dependence of the DC conductivity.

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