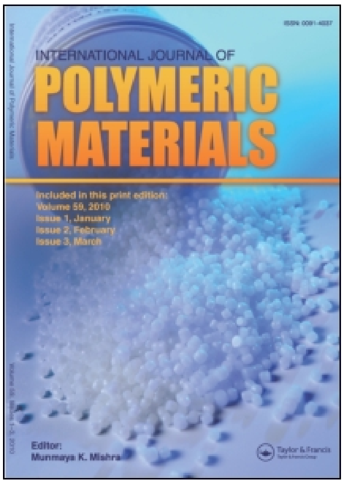

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AC Impedance of Liquid Crystalline Copolyesters in the Solid Phase*

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This work deals with the effect of composition on the ac impedance of liquid crystalline copolyester of 4-Hydroxybenzoic Acid (HBA) and 2-Hydroxy 6-Naphthoic Acid (HNA) in the solid phase. The results show that the ac conductivity increases with increasing the content of HBA residues. The Cole–Cole plot yields good semi-circles for liquid crystalline copolyesters specimens. The intensity of the observed relaxation in the plot of the imaginary component of the ac impedance *versus* frequency increases with the content of HNA residues. This was interpreted to be due to a rotational motion of the identical ester linkages.

Keywords: Impedance; Relaxation; Cole–Cole; Conductivity

1. INTRODUCTION

The dynamic mechanical and dielectric properties has been studied for different compositions of liquid crystalline copolymers in the solid phase. The studies emphasized the relaxation transitions [1–6] and structure [7, 8]. In common with most conventional polymers, the liquid crystalline copolymers show three relaxations α, β, and γ, in the solid phase . The α relaxation is associated with the main chain motion with an activation energy in the order of 200 Kcal/mole, β is associated with a local mode motion of HNA residues with an activation energy in the order of 35 Kcal./mole [1, 2], and the γ relaxation is assigned to a

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* Dedicated to Professor S. Fakirov on the occasion of his 65th birthday.
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localized motion of HBA residues. Concerning the structure of liquid crystalline copolyesters in the solid phase, three models were proposed [7,8]. An ordered glass held together by small homo-polymer units, a paracrystalline model in which the entire sample is treated as a perturbed crystal of the dominant homo-polymer component, and the model based on sequence matching where similar monomer combinations find themselves in the solid state and form a series of small crystals of varying compositions.

In this paper we report the results of ac impedance for three samples of liquid crystalline copolyesters of 4-Hydroxy Benzoic Acid (HBA) and 2-Hydroxy-6 Naphthoic Acid (HNA) with 30/70, 58/42 and 75/25 molar ratio of HBA/HNA.

In order to study the effect of composition on ac impedance the contact area are fixed for the three samples and the values of ac impedance were reported in units of ohm/cm.

2. EXPERIMENTAL

2.1. Materials

Isotropic samples of nematic random HBA/HNA copolyesters in the solid phase were manufactured by Hoechst-Celanese, USA in the form of molded rods of 6 mm in diameter. Samples in the form of discs with thickness of 2 mm were machined carefully using a microtome.

2.2. AC Measurements

The ac measurements were carried out at room temperature in the frequency range 1 Hz. To 10^6 Hz, using a Solarton (Schlumberger instrument). The apparatus is controlled by software packages that maximize the performance and data handling of the system. Carefully applied graphite electrodes were added onto each surface of the disc specimen, this is fully sandwiched between two copper parallel plates. The sample set-up was then kept in a shielded cavity to improve low frequency measurements. Best signal generator and dc bias were selected after performing a series of amplitude and dc bias sweeping tests.

3. RESULTS AND DISCUSSION

The electrical and mechanical properties of liquid crystalline copolymers (LCP) can be modified by careful control of structure and composition. This phenomenon is exploited in the production of high performance materials with special characteristics such as mechanical strength and electrical insulation [9–12]. However, the measurements of ac impedance give an indication of fundamental electrical characteristics *i.e.*, conductance and impedance. AC impedance and phase angle were measured at room temperature in the frequency range 1 Hz to 10^6 Hz. The real (Z') and the imaginary (Z'') components of the measured ac impedance were calculated from the relations $Z' = Z^* \cos\theta$ and $Z'' = Z^* \sin\theta$, where Z^* is the complex ac impedance and θ is the phase angle.

Figures 1(a and b) show the variation of Z^* and the phase angle for three different compositions as a function of frequency. The general

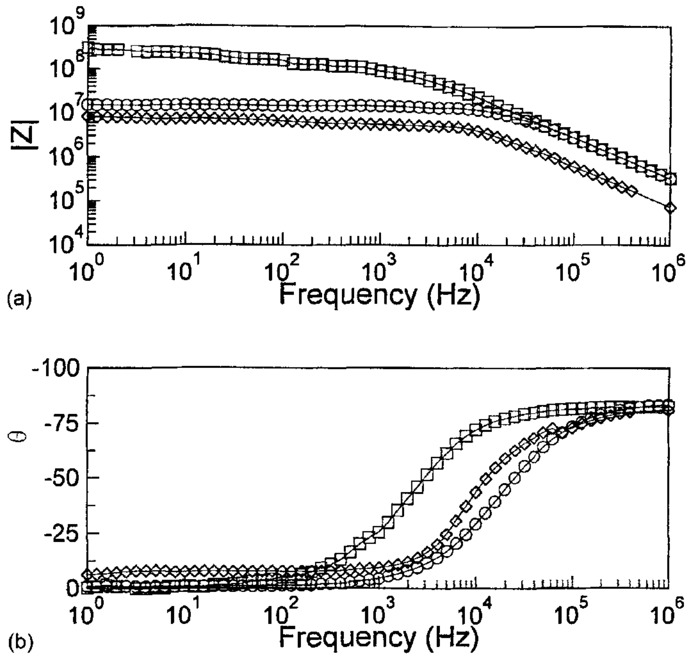

FIGURE 1 (a) ac impedance *versus* frequency and (b) Phase angle (θ) for HBA/HNA liquid crystalline copolyesters in the solid phase. □ 30/70, o 58/42 and ◇ 75/25.

feature of the plot of Z^* and θ *versus* frequency is similar to that observed for RC network in parallel, where the ac impedance is independent of frequency at low frequency range and becomes proportional to the inverse of frequency in the high frequency range. This indicates that interfacial polarization does not contribute to the cell impedance in the low frequency range. Therefore, the frequency dependence of liquid crystalline copolyester specimen and the cell is equivalent to RC network in parallel where the phase angle increases from $-90°$ to $-5°$ in the measured frequency range. Table I gives the equivalent bulk resistance and capacitance for three liquid crystalline copolyester specimens.

The ac impedance for each composition is nearly constant in the frequency range 1 Hz to 5×10^3 Hz and then drops dramatically with increasing frequency. The high impedance value at low frequency may be due to space charge polarization in the bulk materials, structure defects and electrodes effects. The impedance in the plateau region in the plot of Z^* *versus* frequency decreases with increasing the content of HBA residues. However, the ac conductivity increases with increasing HBA content from 1.7×10^{-8} (ohm-cm)$^{-1}$ to 5.1×10^{-7} by changing the content oh HBA residues from 30% to 75%. The increase in ac conductivity of LCP with increased content of HBA residues may be due to increase in the degree of crystallinity and/or lower flexibility of the polymer chains. This indicates that increased content of HBA units seems to cause some type of ordering *i.e.*, para-crystalline regions. This may cause an increase in the ac conductivity in the plateau region where the conduction mechanism is dominated by ohmic conduction.

The plot of Z'' *versus* Z' for three compositions, as shown in Figure 2, yield semi-circles with some distortion. The semi-circles indicate that a certain polarization mechanism of single relaxation

TABLE I Equivalent resistance (R) and equivalent capacitance (C) for isotropic HBA/HNA liquid crystalline copolyesters

HBA/HNA	*R (ohm)*	*C (F)*
30/70	1.1×10^8	7.2×10^{-13}
58/42	1.45×10^6	6.2×10^{-12}
75/25	5.30×10^6	2.98×10^{-12}

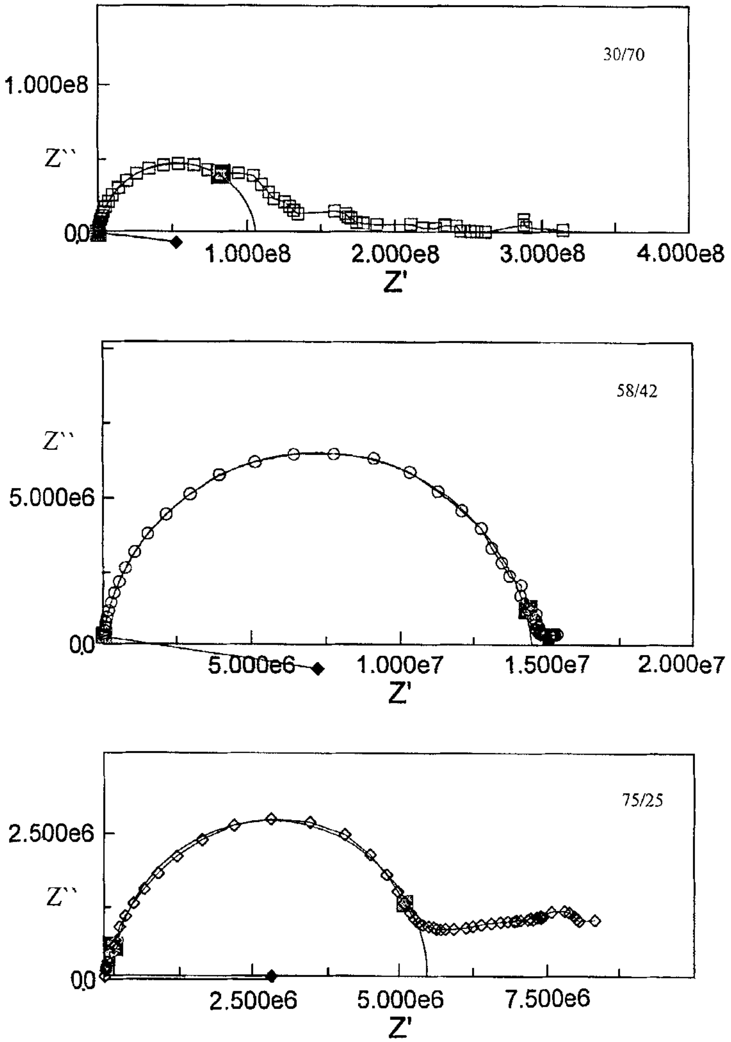

FIGURE 2 Cole–Cole plot for HBA/HNA liquid crystalline copolyesters in the solid phase.

time is taking place. However, the semi-circle plots give different maximum frequency, therefore the relaxation time τ can be calculated from the relation

$$\omega\tau = 1$$

where, ω is the angular frequency at which Z'' is at maximum. The relaxation time for the three compositions varied because of the change in composition as given in Table II.

Comparing the three compositions as shown in Figure 3 that represents the plot of Z'' *versus* frequency, it is readily apparent that the relaxation is more intense in the sample with greater HNA units. This confirms the association of the relaxation process with the motion of HNA units [14, 15]. It is believed that this relaxation is due to

TABLE II Maximum angular frequency (ω) and relaxation time (τ) for isotropic HBA/HNA liquid crystalline copolyesters

HBA/HNA	ω	τ (*ms*)
30/70	6.33×10^4	1.58×10^{-2}
58/42	1.1×10^4	9.4×10^{-3}
75/25	1.29×10^4	7.75×10^{-3}

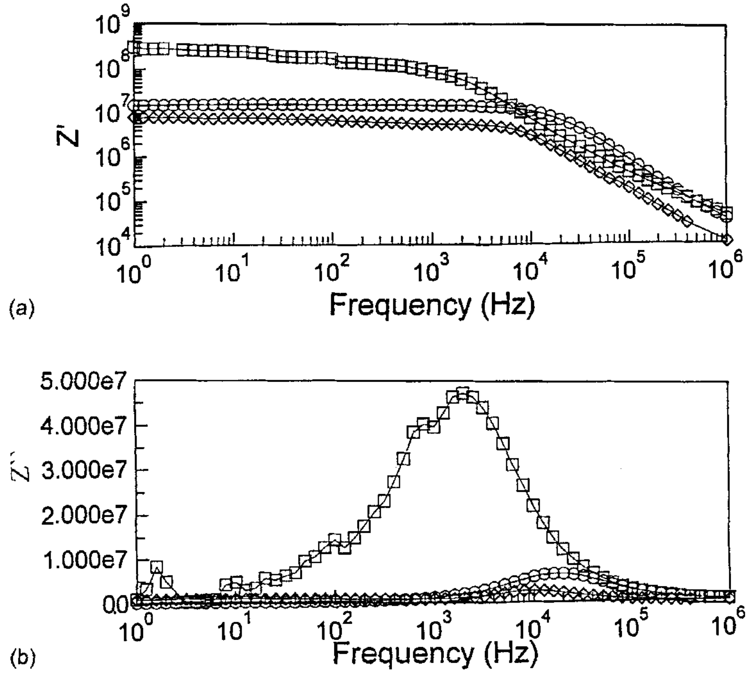

FIGURE 3 Imaginary components (Z'') and (b) real component of ac impedance (Z') *versus* frequency for HBA/HNA liquid crystalline copolyesters. □ 30/70, o 58/42 and ◇ 75/25.

certain motion of the ester linkages between the aromatic rings that are free to rotate independently of the aromatic rings. If this is the case, then we might expect a single mode process arising from their motion, since all ester linkage are identical. It should be noted, though, that the intensity of the relaxation process in the sample contains 70% of HNA residue is the highest. This may indicate that in the samples contains less HNA residues, a significant fraction of dipoles are held immobile in the ordered region. If this is the case then we expect that the large portion of the dipoles that are held immobile in the crystalline regions is the major reason for the decreased intensity of the observed relaxation. On the other hand, the broad peak in the plot of Z'' spectrum and the extension of the semi-circles at low frequency region indicate that the relaxation can be assigned to localized motion of HNA and to contribution of structural boundaries between the ordered regions similar to the effects of grain boundaries in polycrystalline materials [16, 17].

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