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Synthesis of Novel Liquid Crystalline Polyesters of Cholesterol: Thermal, Electrical Conductivity and Dielectric Properties

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Novel liquid crystalline polyesters of cholesterol, Polycholesteryl-3,3-dimethylacrylate (PCHDMA) and Polycholesterylcrotonate (PCHC) are synthesized by free radical polymerization and characterized by FT-IR, ¹H-NMR, and GPC analysis. The thermal properties are studied by TGA and DSC techniques. The liquid crystalline phases are detected under hot stage optical microscope. Electronic conduction in the polymers is determined by Wagner polarization technique. There is about 5000 fold decrease in the impedance values of both PCHDMA and PCHC on increasing the frequencies from 40 Hz to 1 MHz at 30°C. Amperometric analysis of the polymers are also carried out at different temperatures and frequencies.

Keywords Conductivity; dielectric constant; hot stage microscope; liquid crystalline polymers; transport number

1. Introduction

Liquid crystalline polymers (LCPs) are prospective candidates for photonic materials to be used in integrated circuit as color switch. For fast electronic response, high frequency photonic switching becomes essential now. Since the transition temperature of liquid crystalline phase is composition specific, the thermo switch can also be visualized. Cholesteric LCPs have significant applications in optical electronics since they can selectively reflect different frequency ranges of incoming polarized light [1]. Thus they can exhibit different colors in the visible region and this property can be utilized in developing different electro-optical devices and paint technology [2–7]. Cholesteric LCPs also find applications in biotechnology because of their significant mechanical properties. Biodegradable cholesterol polyesters can be used as membranes in various biological applications [8–10]. Synthesis of various side chain cholesteric liquid crystal polymers have been reported recently [11–14]. Thermotropic liquid crystalline phases are shown by various esters of

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cholesterol in specific temperature range [15]. Liquid crystals also exhibit interesting viscoelastic properties which is useful for selection of suitable materials for display devices. Liquid crystals because of their anisotropic optical and dielectric properties are used in developing liquid crystal displays (LCDs) at low voltages. LCDs are the lowest electrical power consuming devices which are applied in the development of various devices like laptop computer screens, fax machines, calculators, screens for color TVs, portable compact disc players, [16] and so on.

Earlier, some sulfonated cholesteryl derivatives were successfully synthesized and characterized in our lab [17]. In the present study, we have synthesized and characterized some cholesteric liquid crystal polyesters from their mesogenic monomers Cholesteryl-3,3-dimethylacrylate and Cholesterylcrotonate. The thermal properties are studied with the help of DSC and TGA studies and their mesogenic phases are detected under a hot stage fitted with polarizing microscope. The main aim of this study is to determine the effect of different frequency and temperatures on the conductivity and dielectric properties of these liquid crystalline polyesters. Such study may be useful in selecting suitable application of these polymers as liquid crystal displays or in various other electronic and optical devices.

2. Experimental Details

2.1. Materials

Cholesterol (Merck), 3,3-dimethylacrylic acid (Merck), crotonic acid (Merck) Ethyl-methylketone (Merck), Chloroform (Ranbaxy), methanol (Ranbaxy), AIBN (Merck) were used without further purification.

2.2. Techniques

The FT-IR spectra was recorded using Bruker Vector 22 Spectrophotometer in the range of 400–4000 cm^{-1} . Samples for FT-IR measurements were prepared in the form of pellets by mixing about 20 mg of IR spectroscopic grade potassium bromide with about 2 mg of dried samples. The spectra were recorded in transmission mode over 64 scans. The proton NMR spectra were recorded using Varian 400 MHz FT-NMR in CDCl_3 . The molecular weight of the polymers was determined in THF by GPC system (WATERS 2414).

The Differential Scanning Calorimetric and Thermo Gravimetric Analysis of the compounds were carried out using Perkin Elmer DSC 6000 and TGA 4000, respectively, at heating rate 10°C per min with constant N_2 flow rate of 20 ml/min. The liquid crystalline range was detected by the phase change with the help of Mettler Toledo F90 Hot stage fitted with polarizing optical microscope and camera.

The bulk electrical conductivity of the compounds was evaluated from the complex impedance admittance plots recorded at different temperatures and frequencies using a HIOKI 3532-50 LCR HiTESTER. The plots were recorded in the frequency range of 42 Hz to 1 MHz at temperature range of 35°C to 70°C. I–V analysis of the polymers were carried out in the HIOKI 3532-50 LCR HiTESTER in the frequency ranges 10 kHz, 100 kHz, and 1 MHz and in the temperature range 40°C–70°C.

The total ionic transport number, t_{ion} was evaluated by the standard Wagner polarization technique [11]. The cell SS/(PCHDMA/PCHC)/SS (SS stands for Stainless Steel) was polarized by a step potential (about 1V) and the resulting potentiostatic current was monitored as a function of time. The stainless steel acts as blocking electrodes for the above

cell. The t_{ion} was evaluated using the formula:

$$t_{\text{ion}} = (i_T - i_e)/i_T$$

where i_T and i_e are total and residual current, respectively.

2.3. Synthesis

2.3.1. Preparation of Acid Chlorides. The acid chlorides were prepared by distillation of 3,3-dimethylacrylic acid/crotonic acid and benzoyl chloride (in 1:2 mole ratios) with 0.05 g of hydroquinone at its boiling point in a 25 cm long distillation column. The receiver contains hydroquinone and it was kept inside an ice bath. Redistillation gave 65%–72% of 3,3-dimethylacryloyl chloride/crotonyl chloride [18].

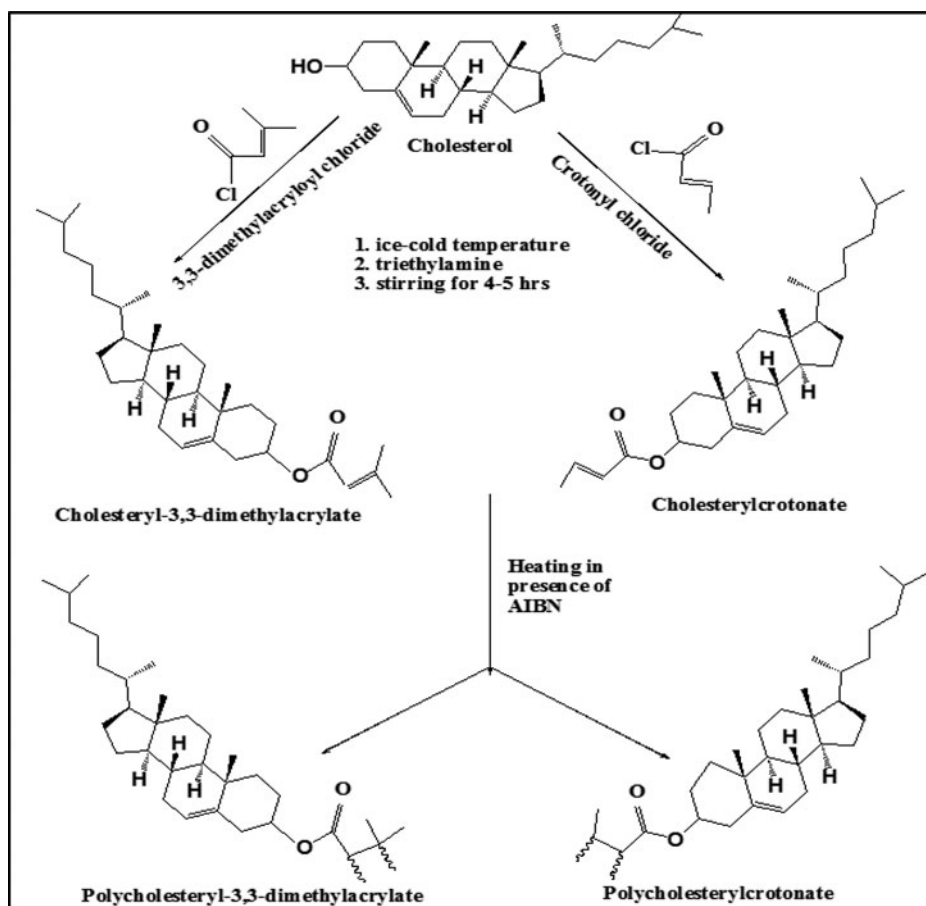
2.3.2. Preparation of Monomers (CHDMA/CHC). One mole of both cholesterol and 3,3-dimethylacryloyl chloride/crotonyl chloride were dissolved in ethyl methyl ketone (MEK) and then stirred for 5–6 hrs inside a round bottom flask in the presence of triethyl amine and small amount of hydroquinone in an ice bath. The reaction mixture was then filtered and washed several time with distilled water. The organic layer was separated and distilled to remove ethyl methyl ketone (MEK). The viscous organic liquid on cooling gave cholesteryl-3,3-dimethylacrylate/cholesteryl crotonate which was recrystallized and finally purified by column chromatography. The product yields were found to be 85.45% and 86%.

2.3.3. Preparation of Polymers (PCHDMA/PCHC). One mole of the mesogenic ester, CHDMA/CHC and 1 mole% of AIBN were dissolved in chloroform in a flask. The reaction flask was evacuated by vacuum pump and then heated for 24 hrs at 70°C. When the reaction was completed, the reaction mixture was poured in to an acidified methanol solution. The polymers were then recrystallized from hot methanol containing traces of chloroform. Finally the residue was washed several times with MEK and dried over dessicator. The above reactions are represented schematically in Scheme 1.

3. Results and Discussions

3.1. FT-IR Analysis

The IR spectra of CHDMA as shown in Fig. 1A indicates strong peaks at 1720 cm^{-1} and 1179 cm^{-1} for symmetric stretching frequency of C=O and C–O of ester group. The cholesteryl C=C bond is present at 1662 cm^{-1} both in the monomer and in the polymer. The ester C=O and C–O symmetric stretching band for polymer molecule appears at the same position at 1720 cm^{-1} and 1179 cm^{-1} as is observed in the monomer but the peak for 3,3-dimethylacrylate C=C present at 1622 cm^{-1} in the monomer is absent in the polymer which is the indicative of complete polymerization of the monomer. A comparative study of the FT-IR spectra of CHDMA and PCHDMA is shown in Fig. 1B. Similarly, the major peaks observed in CHC are 1727 cm^{-1} , 1662 cm^{-1} , 1625 cm^{-1} , and 1154 cm^{-1} among which the crotonate C=C bond at 1625 cm^{-1} is absent in the polymer assuring complete polymerization [19].



Scheme 1. Schematic representation of all the reactions involved.

3.2. $^1\text{H-NMR}$ Analysis

More strong evidence of formation of the polymers is obtained from $^1\text{H-NMR}$ spectroscopy at 500 MHz in CDCl_3 . The $^1\text{H-NMR}$ spectra, as shown in Fig. 1B, of CHDMA gives two sharp signals at 5.4 ppm and 5.5 ppm due to $=\text{CH}$ of the cholesteryl $\text{C}=\text{C}$ and the ester $\text{C}=\text{C}$ bond. There are two signals at 2.4 ppm and 2.5 ppm due to the two terminal- CH_3 groups, respectively of ester residue. The peak at 5.5 ppm due to the $\text{C}=\text{C}$ bond of the ester group is absent in the PCHDMA which indicates complete polymerization of the monomer [20].

The $^1\text{H-NMR}$ spectra of CHC gives sharp signals at 5.4 ppm and at 6.1 ppm due to $=\text{CH}$ of the cholesteryl $\text{C}=\text{C}$ and the ester $\text{C}=\text{C}-\text{HCOO}$ bond. The terminal- CH_3 group of the crotonate group gives a sharp signal at 1.7 ppm. The $\text{CH}=\text{proton}$ of the $\text{Me}-\text{CH}=\text{C}$ group gives a sharp signal at 6.5 ppm. In the polymer PCHC, the signals at 6.5 ppm and 6.1 ppm disappears indicating complete polymerization of the monomer. The signal due to the cholesteryl $\text{C}=\text{C}$ at 5.4 ppm remains as it is in both the polymers indicating that the cholesteryl double bond remains unaffected during polymerization.

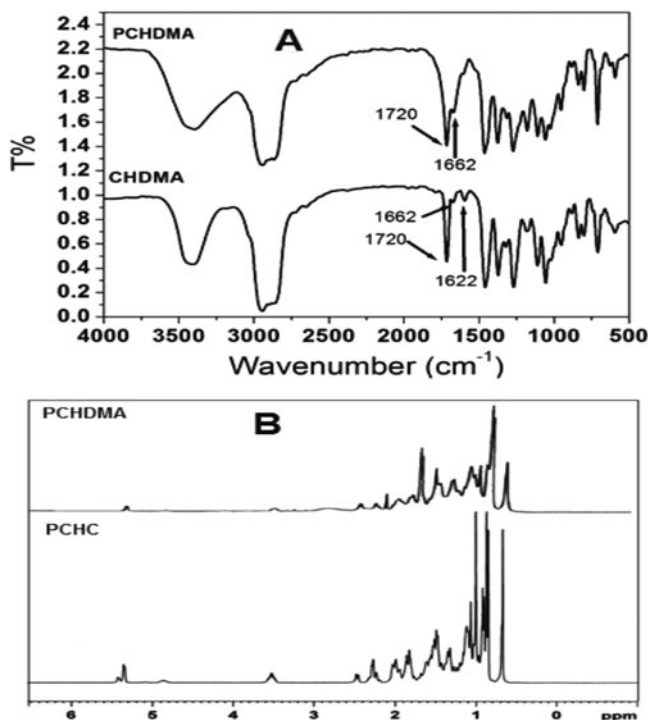


Figure 1. (A) IR spectra of CHDMA and PCHDMA (B) ^1H -NMR spectra of CHDMA and PCHDMA.

3.3. Molecular Weight Determination by GPC

The number average molecular weight (M_n), Weight average molecular weight (M_w) and the Polydispersity of the polymers is measured by Waters GPC using HPLC grade THF as the solvent and polystyrene as the standard. All together three standards are used for the measurement with molecular weight 0.27×10^4 , 0.64×10^4 , and 480×10^4 g/mol. From the experimental data, it is found that both the polymers have very high molecular weights with uniform chain length as the polydispersity is almost 1 in both the cases [21].

For PCHDMA: $M_n \approx 57,400$ Daltons, $M_w \approx 69,300$ Daltons and $\text{PDI} = 1.206$

For PCHC: $M_n \approx 68,800$ Daltons, $M_w \approx 84,000$ Daltons and $\text{PDI} = 1.215$

3.4. Thermal Studies by DSC and TGA Thermograms

The DSC plots (Fig. 2A and 2B) seem to consist of two distinct phase transitions. The glass transition temperature (T_g) for the PCHDMA is at 105°C and that of PCHC is 96°C . The low values of transition enthalpies further confirm the formation of LC order in both the polymers. The mesophase for the PCHDMA is $105\text{--}130^\circ\text{C}$ and that for PCHC is at $96\text{--}125^\circ\text{C}$ is observed at a lower temperature for the polymer as compared to the monomer. The phase transition at the higher temperature in the DSC curve is for the isotropic melt, as observed under the polarizing microscope. The thermal stability of the polyesters are determined with the help of thermogravimetric analysis. The TGA thermograms in Fig. 2C show that PCHDMA and PCHC are thermally stable up to about 300°C with a weight loss

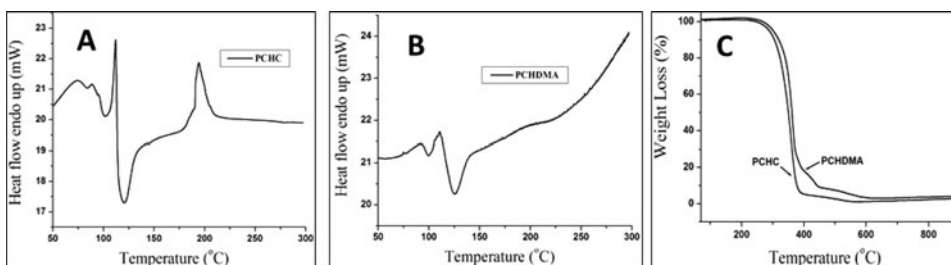


Figure 2. (A) DSC plot of PCHC (B) DSC plot of PCHDMA (C) TGA thermograms.

of 5% and 9%, respectively. Complete degradation of PCHDMA occurs at about 600°C and that of PCHC occurs at about 570°C.

The phase transition temperatures from anisotropy to isotropy of the polyesters PCHDMA and PCHC are observed under the hot stage optical microscope and photographed with the camera attached. Small amount of sample is heated under the microscope for this purpose. The phase transitions shown by the DSC curves for these compounds correlate with those observed under the hot stage microscope. The liquid crystalline phases of the polyesters PCHDMA and PCHC under the hot stage optical microscope are shown in Fig. 3. Both PCHDMA and PCHC do not exhibit colors other than green on increasing the temperature, probably due to the temperature ranges of the chiral nematic phase being narrow as observed by Pandey et al. in mesogen based on cholesterol derivatives [22].

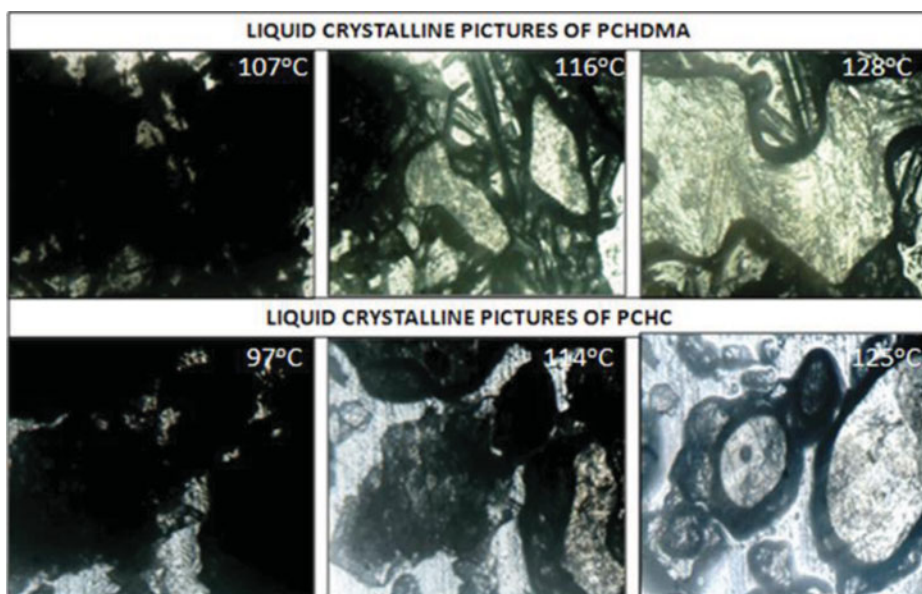


Figure 3. Liquid crystalline phases of the compounds under Hot stage microscope.

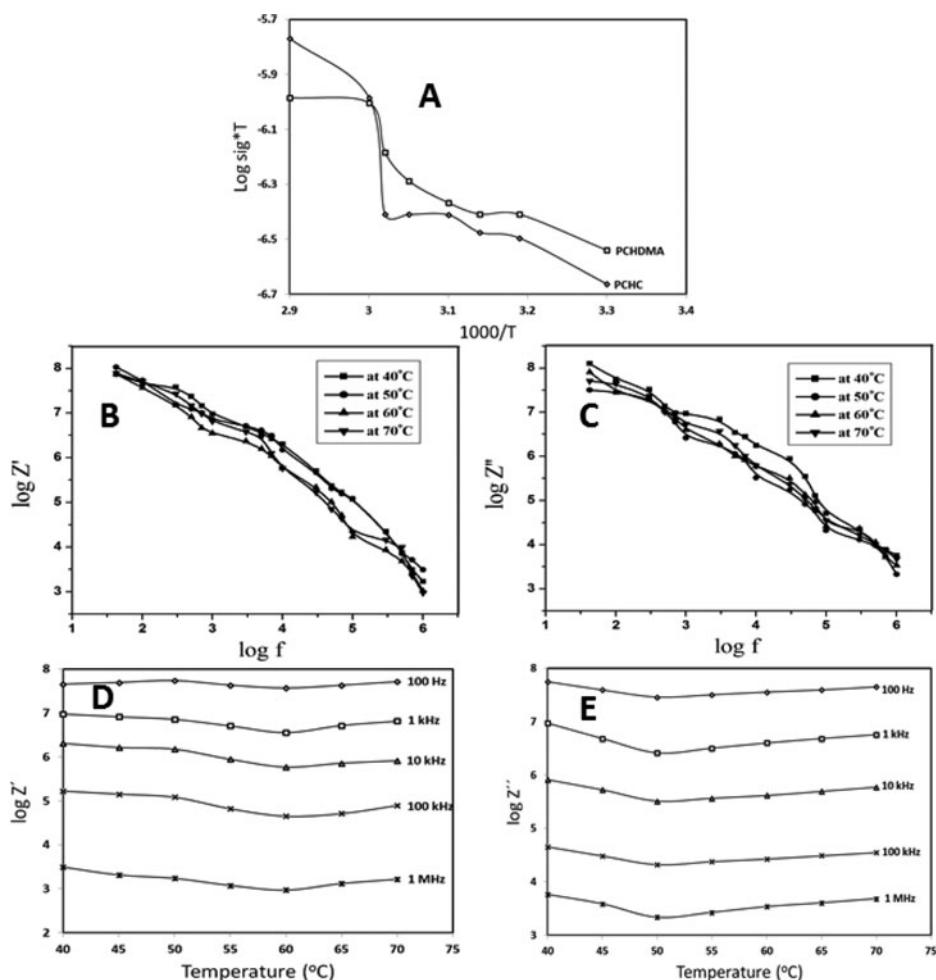


Figure 4. (A) Arrhenius plots of the polymers showing semiconducting behavior, (B) $\log Z'$ vs. $\log f$, (C) $\log Z''$ vs. $\log f$, (D) $\log Z'$ vs. T , (E) $\log Z''$ vs. T of PCHDMA.

3.5. Conductivity and Dielectric Studies

The variation of conductivity with increase in temperature of the polymers is investigated within the temperature range of 35°C–70°C and a frequency range of 42 Hz to 1 MHz at a step temperature of 5°C. From the plots, it is observed that the conductivity of the compounds increases nonlinearly with the increase in temperature. The polymers show small rise in conductivity with the rise in temperature from 1.9×10^{-9} to 3.75×10^{-9} Scm⁻¹ for PCHDMA and 1.08×10^{-9} to 3.93×10^{-9} Scm⁻¹ for PCHC at a temperature range of 35–70°C.

3.5.1. Effect of Temperature and Frequency on Impedance Values of PCHDMA and PCHC.

Impedance measurement is also performed on the polymers as a variance of frequency and that of temperature as shown in Fig. 4. Figure 4B and 4C show the variance of $\log Z$ with $\log f$ at different temperatures (40°C, 50°C, 60°C, 70°C) of PCHDMA and it is observed

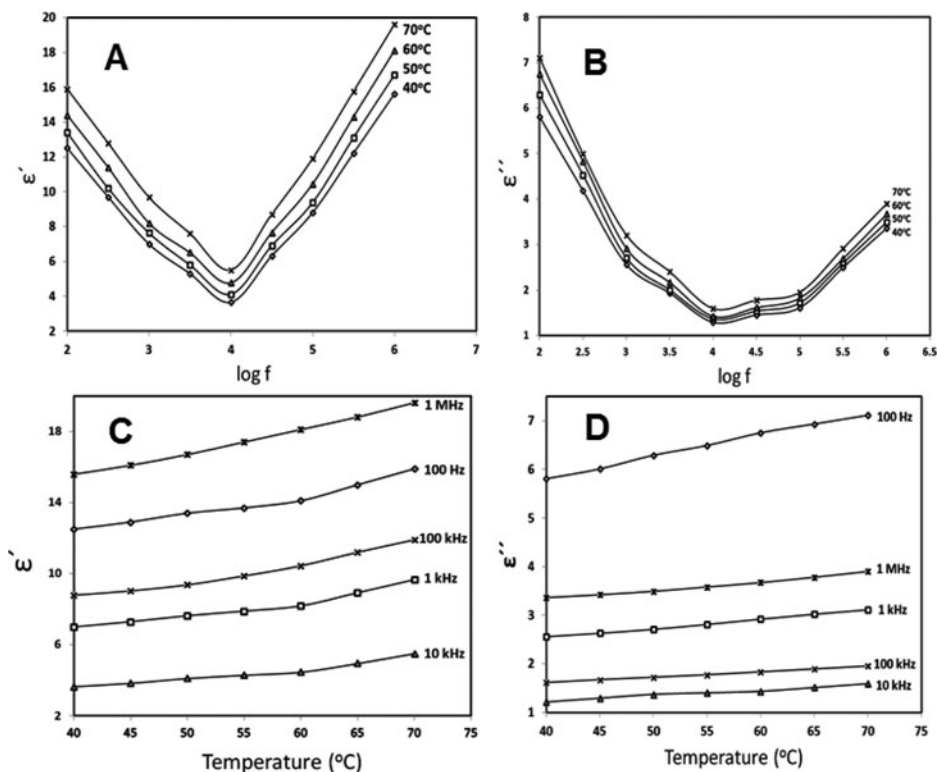


Figure 5. (A) ϵ' vs. $\log f$, (B) ϵ'' vs. $\log f$, (C) ϵ' vs. T, and (D) ϵ'' vs. T.

that impedance values decrease with the increase in frequency. Figure 3D and 3E show the variance of real and imaginary parts of $\log Z$ with different temperatures at different frequency ranges (100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz) for PCHDMA and it is seen that impedance values decrease sharply with the increase in frequency. There is about 4910 and 5100 fold decrease in the impedance values of PCHDMA and PCHC on increasing the frequencies from 40 Hz to 1 MHz at 30°C. This shows that there is a huge rise in conductivity of the compounds with rise in frequency.

3.5.2. Effect of Temperature and Frequency on Dielectric Constant of PCHDMA and PCHC. The effect of temperature on Dielectric constant of the polymer PCHDMA is observed by plotting dielectric constant at different temperatures (40°C, 50°C, 60°C, 70°C) against \log of different frequency values (100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz) as shown in Fig. 5A and 5B. The frequency is changed at a particular temperature in equal intervals and the values of C_p (static capacitance in parallel equivalent circuit mode), D ($\tan\delta$), and G (conductance) are observed. The real part, ϵ' , and the imaginary part, ϵ'' of permittivity are calculated from the equations:

$$\epsilon' = (C_p d) / (\epsilon_o A) \quad (1)$$

and

$$\epsilon'' = \epsilon' \tan \delta \quad (2)$$

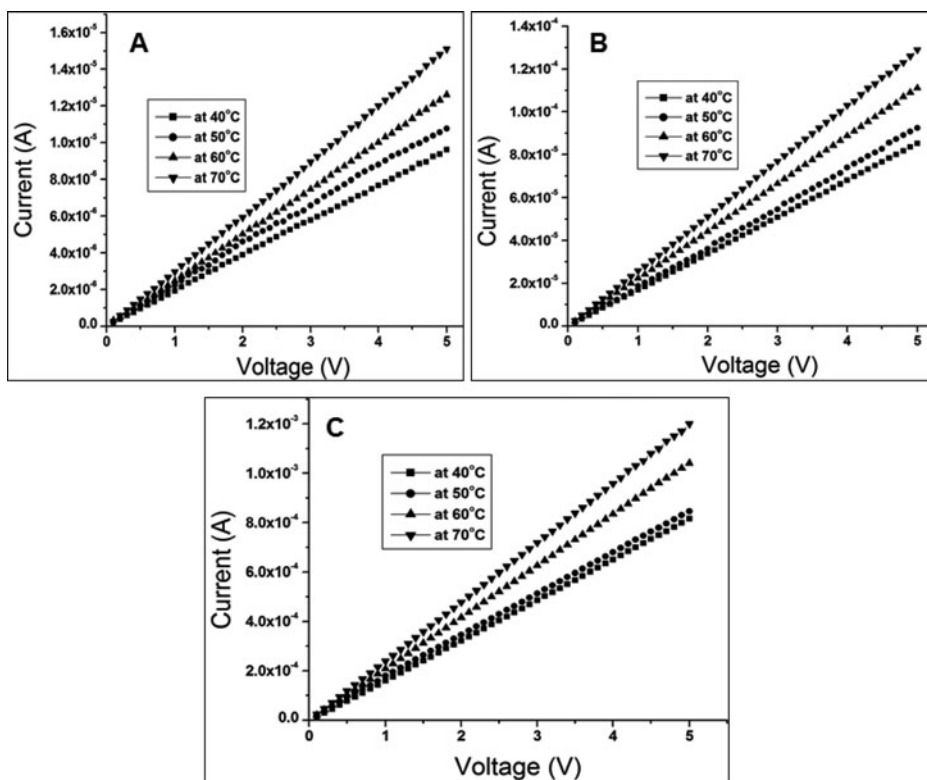


Figure 6. I–V studies of the polymers at frequency ranges (A) 10 kHz (B) 100 kHz, and (C) 1 MHz.

Where d is the thickness of the sample; $\epsilon_0 = 8.854 \times 10^{-12}$ F/m and A (effective area) $= \pi r^2$ (m²)

Figure 5A shows the change of real part of permittivity with change in frequency while in Fig. 5B the change of imaginary part of permittivity is observed with increase in frequency. It is observed that the values of dielectric constant sharply decrease with increasing frequencies from 100 Hz to 10 kHz while it again increase sharply with the increase in frequency from 10 kHz to 1 MHz. The nature of all the curves in different temperatures is similar in nature.

The effect of frequency on dielectric constant is observed by plotting dielectric constant of the sample at different temperatures (40°C, 50°C, 60°C, and 70°C) as shown in Fig. 5C and 5D. It is clearly observed that with increase in temperature, the dielectric constant increases for the compounds in different frequency ranges. This can be explained by the fact that with increase in temperature, polarization increases which leads to the observed increase in permittivity.

3.6. Amperometric Analysis

The influence of applied voltage on the conductivity at different temperatures and frequency ranges are studied by amperometric analysis. In Fig. 6A–6C, the current passing through PCHDMA at different temperatures (40°C, 50°C, 60°C, and 70°C) is studied in frequency ranges (A) 10 kHz, (B) 100 kHz, and in (C) 1 MHz. The linear increase of conductivity

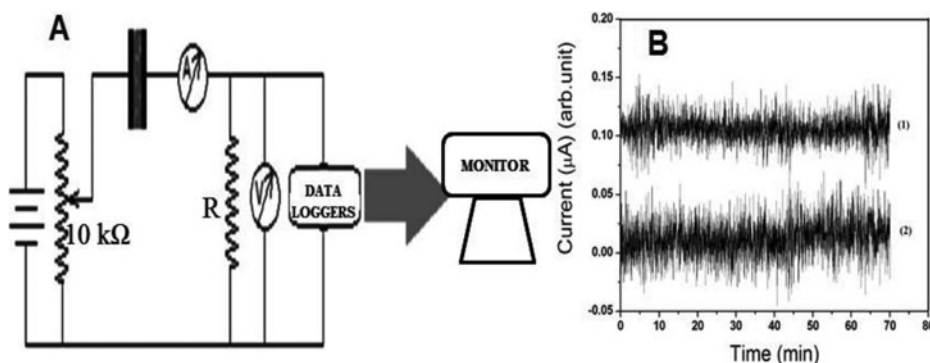


Figure 7. (A) Schematic representation of the cell circuit used to determine the transport number (B) Polarized current Vs time plot of 1.PCHDMA and 2.PCHC.

with rise in temperature is verified by Ohm's law ($V = IR$). When the applied potential is increased from 0 V to 5 V, the current passing through PCHDMA is different in different frequencies. It is clearly observed that with increase in frequency, the current passing through the samples also increases. At a frequency of 1 MHz, the current passing through the samples is in the range of mA. This again verifies that the compounds show much better electrical properties at higher frequencies. The plots (as shown in Fig. 6) are found to be continuous and no breakdown voltage is apparent for both the compounds within this observed range.

3.7. Transport Number Determination by Wagner Polarization Method

The total ionic and electronic contribution to the conductivity is determined by standard Wagner polarization technique, generally used to determine ionic transport number. Accordingly, on application of voltage to the cell, ionic migration occurs until steady state is reached. At the steady state, the cell is polarized and any residual current flows because of electron migration across the sample and interfaces. For ionic samples, the currents passing through an ion-blocking electrode falls rapidly with time. A cell is prepared to observe electronic conductivity, keeping the sample (in pellet form) in between two stainless steel anvils. A step potential of about 1V is then applied and resulting potentiostatic current is monitored as a function of time using a data loggers and software. The stainless steel anvils acts as ion blocking electrodes for the above cell. The circuit diagram of the cell is shown in Fig. 7A.

For the experimental polymers the current vs time plot, Fig. 7B shows no initial decrease in total current with respect to time mostly observed in an ionic conduction. This observation shows that the polymers are nonpolar/ nonionic in nature. The plots obtained from Wagner polarization technique show that there is no ionic contribution for the conduction and the small amount of conductivity showed by the polymers is purely electronic in nature.

4. Conclusion

In the present study, we have synthesized high molecular weight liquid crystalline polyesters of Cholesterol by thermal polymerization technique. The phase transitions are studied under a hot stage optical polarizing microscope which correlates with that shown in the DSC

thermograms. The compounds show good thermal stability up to about 300°C as observed from their thermogravimetric analysis. The electrical studies were also carried out which includes ac conductivity, impedance studies, dielectric studies, current-voltage and transport number measurements. The observed increase in conductivity with rise of temperature is due to the semiconducting behavior of the materials and the conduction is purely electronic in nature as is shown by the transport number measurements. There is about 5000 fold decrease in impedance values with increase in frequency from 42 Hz to 5 MHz, which simultaneously shows the huge increase in ac conductivity of the compounds with rise in frequency. The dielectric properties also show significant variations with change in temperature and frequency. The current-voltage studies show that the increase in temperature and frequencies leads to significant rise in the current passing through the samples. Such cholesteric liquid crystal polymers may be useful in various future applications as well as in the development of different opto-electronic devices.

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