Methacrylate based side chain liquid crystalline polymers with pendant cholesterol group: Preparation and investigation of electrical conductivity mechanism

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ABSTRACT: Methacrylate based side-chain liquid crystalline polymers (SCLCP) bearing cholesterol pendant moieties with various lengths of aliphatic spacer were synthesized and their electrical conductivity mechanism was studied for their possible applications in elastic microelectronic devices. All the polymers exhibited liquid crystalline behavior of broken focal-conic fan texture of smectic phase. The dielectric properties of polymers were investigated by impedance spectroscopic technique in the frequency range of 100 Hz to 15 MHz at room temperature. Alternating current (AC) conductivity ($\sigma_{AC}$) of the liquid crystalline polymeric films was observed to vary with angular frequency, $\omega$ as $\omega^s$ with $s < 2$. Detailed conductivity analysis revealed that the conductivity of the polymeric films follows quantum mechanical tunneling and correlated barrier hoping conductivity mechanisms at low frequency regime, whereas it obeys super linear power law and direct current conductivity mechanisms at high frequency region. The investigation of the SCLC polymeric films helped to propose a model system for their possible potential applications. In the light of this study, the SCLC polymers will be employed as the gate insulator for organic field effect transistor applications, such as large area flexible arrays or as other advanced microelectronic devices that have superior performance. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2017, 134, 45207.

KEYWORDS: cholesterol; conductivity; dielectric constant; liquid crystalline; methyl methacrylate

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INTRODUCTION

Liquid crystal polymers (LCPs) are unique materials which combine the features of liquid crystals and polymers. In order to exhibit liquid crystal characteristics for polymers, mesogenic groups (rod-like or disk-like units) must be attached to polymer on main or side chain. If they are the part of main chain of polymer, the polymer is called main chain liquid crystal polymer (MCLCP). Otherwise, side chain liquid crystal polymer (SCLCP) is formed when mesogens are incorporated into polymer as side groups. MCLCPs cannot show mesogenic property in large temperature ranges, whereas mesogenic behavior of SCLCPs is in a large range.1–3 SCLCPs can be varied by altering their components, such as polymer backbone, mesogenic group, and flexible spacer between polymer backbone and mesogen.4–7 The literature suggests that SCLCPs can be synthesized mostly with chiral compounds, such as cholesterol (Chol), isosorbide, and menthol.8–11 Chol which plays a crucial role in the field of self-organizing organic systems is a rigid component of many natural lipid bilayers.12 In Chol containing polymers, Chol groups produce mesomorphic structures.13 LCP with pendant Chol side groups have significant utility due to their optical properties.14 They form chiral nematic and smectic phases and can be usually employed in electro- and thermo-optical applications.15 By changing the polymer backbone (i.e., acrylate, methacrylate, and siloxane) and flexible spacers (i.e., methylene and siloxane), Chol containing SCLCPs have been prepared.16–20 The synthesis of block copolymers [[poly(methyl methacrylatecholesterol-b-styrene)] and poly(cholesterylmethacrylate-b-2-hydroxyethyl methacrylate)] have been also reported.20,21 In semiconductor industry, liquid crystals are one of the most promising materials especially for microelectronic devices.22–25 In the last decades, OFETs attract a great deal of attention as an important type of electronic devices for their use in lightweight, elastic, and low-cost electronic instruments.26–29 They can be
implemented in wide range of applications such as flat-panel displays, electronic paper, and chemical sensors. It is observed that OFETs, prepared with LC-gate insulator, are very sensitive low level gas quantity. Because of the strong dipole effect of LC molecules, drain currents on the channel layer is enhanced. Potentially, SCLCPs could be used as a key component in the field of organic microelectronics.

Poly(methyl methacrylate) (PMMA) is one of the well-known polymers as dielectric materials. It is a hard, hydrophobic, less-polar, brittle, and easily prepared material. An advance property of PMMA relies on its high resistance and nontracking characteristics in high voltage applications. Its dielectric constant ranges from about 3.5 (at 5 kHz) to 2.6 (at 1 MHz) and can be used as a gate dielectric layer in OFETs.

In this study, methyl methacrylate-based SCLC homopolymers and copolymers containing Chol pendant groups with various lengths of aliphatic spacer (n = 3, 7, and 10 methylene units) were first synthesized and characterized (Schemes 1 and 2). The chemical structures of the polymers and intermediates at various stages were confirmed by the means of 1H NMR and FTIR analysis techniques and mesomorphic properties were investigated by using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD).

To exploit their possible applications for flexible OFET and
organic photovoltaic (OPV) assemblies, dielectric properties and conductivity mechanisms of the polymers were then studied in details. Dielectric properties and conductivity mechanisms of the polymer films were estimated using parallel plate impedance spectroscopic technique.

**EXPERIMENTAL**

**Materials**

Methyl methacrylate (MMA, Alfa Aesar, 99%) were passed through a column of alumina to remove the inhibitor and were then stored under argon. Triethylamine (TEA, ≥99.5%) was obtained from Fluka, dried over CaH₂ and stored over 3 Å molecular sieves. Tetrahydrofuran (THF, Merck, 99.8%) was freshly dried by refluxing over Na-K alloy and then distilled in a dry argon atmosphere. Dimethylformamide (DMF, Merck, 99.8%) was both dried and stored over activated 4 Å sieves. Methacrylic acid (MAA, Fluka, 99%), hydroquinone (HQ, Alfa Aesar, 99%), cholesterol (Chol, C_{27}H_{46}O, Sigma, 94%), 4-bromobutyryl chloride (C_6H_5BrClO, Alfa Aesar, 97%), 8-bromooctanoic acid [Br(CH₂)₈COOH, Alfdrich, 97%], 11-bromoundecanoic acid [Br(CH₂)₁₀COOH, Aldrich, 99%], ethyl 2-bromoisobutyrate (EBIB, Aldrich, 98%), N,N,N’,N”-pentamethylene diamine (PMDETA, Aldrich, 99%), copper(I) bromide (CuBr, Sigma-Aldrich, 98%), potassium hydrogen carbonate (KHCO₃, Sigma-Aldrich, ≥99.5%), N,N’-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-(dimethylamino)pyridine (DMAP, Fluka, ≥99.0%), hydroquinone (HQ, Alfa Aesar, 99%), anisole (CH₃OC₆H₅, Fluka, ≥99.0%) were used as purchased without further purification.

**Measurements**

¹H NMR spectra was recorded in CDCl₃ solutions on a Varian UNITY INOVA 500 MHz spectrometer using tetramethylsilane (TMS) as an internal reference at 25 °C. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with Perkin-Elmer Spectrum 100 spectrometer using the attenuated total reflectance (ATR) method. Average molecular and molecular weight distributions of the polymers were determined on an Agilent GPC Instrument (Model 1100) consisting of a pump, a refractive index detector, and two Waters Styragel columns (HR 5E), using THF as the eluent at a flow rate of 0.5 mL/min at 23 °C. DSC analysis was performed on a DSC 4000 (Perkin Elmer) under a protective nitrogen atmosphere from 25 to 200 °C at a heating/cooling rate of 10 °C/min to determine the melting points and crystallization temperatures of the polymers. Thermogravimetric analysis (TGA) was performed on a TGA/SDTA 851 (Mettler Toledo) thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 700 °C under a nitrogen atmosphere. The phase transition behavior of the polymers was observed by means of POM (Leitz Wetzlar Orthoplan-pol.) equipped with a hot stage (Linkam TMS 93) and a temperature controller (Linkam LNP). XRD patterns of thermally treated polymeric films were obtained at room temperature on a Rigaku SmartLab X-ray diffractometer using Cu-Kα radiation with a wavelength of 1.54 Å over a 2θ range from 0° to 30° at speed of 0.1° min⁻¹. The voltage and current were set to 40 kV and 30 mA, respectively. Electrical properties of the polymers were analyzed using parallel plate impedance spectroscopic technique. Parallel plate type structures were developed on glass substrates as shown in Scheme 3. The fabrication of the structures was started with cleaning indium tin oxide (ITO) coated glass substrates using acetone, methanol, ethanol, and isopropyl alcohol in an ultrasonic bath in turn. Drying of the substrates was carried out using argon blow and thermal oven. The solutions of the polymers were prepared in toluene by the process of magnetic stirring for 24 h at room temperature. The polymeric films were coated on cleaned ITO-coated glass substrates by spin coating at 2000 rpm using the filtered polymer solutions. The size of the filter was 0.45 µm. Then the samples were kept in the nitrogen environment for 12 h to evaporate solvent. Finally, 50 nm thick top contact was made by evaporating aluminum on the polymeric films through the shadow mask using Leybold Univex 450, vacuum evaporator at 1 × 10⁻⁵ mbar pressure. The thicknesses of the polymeric films were measured using DEKTAK-8 profilor. Impedance Analyzer, HP-4194 A was used to determine the electrical and dielectric properties of the polymers in the frequency range of 100 Hz to 15 MHz. A signal of 1 V peak to peak was applied to the samples during the measurements. All the tests and measurements were performed in the ambient conditions.

**Synthesis of Side-Chain Liquid Crystalline Polymers (SCLCPs)**

Synthesis of methacrylate-based side-chain liquid crystalline polymers bearing cholesterol mesogen with aliphatic spacer 3 (n = 3) was given as the representative example for other aliphatic spacers (n = 7, 10) (see the Supporting Information for the experimental and characterization details of other SCLCPs).

**Synthesis of Cholesteryl 4-Bromobutyrte (Chol-3-Br)**

Chol-3-Br was synthesized according to the literature method with the minor modifications. Chol (10.0 g, 25.86 mmol) was dissolved in anhydrous THF (50 mL) in a two-necked flask equipped with a magnetic stirrer and a rubber septum under inert argon atmosphere. TEA (6.80 g, 67.25 mmol) was added then the reaction vessel was cooled to −15°C by using ice-salt mixture. 4-Bromobutyryl chloride (6.24 g, 33.62 mmol) was dissolved in THF (10 mL) and added dropwise to the mixture in 20 min. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with DCM (100 mL) and washed with 1N HCl solution (2 × 50 mL). After
the organic layers were combined and dried with MgSO₄, the solvent was concentrated to about 5 mL by rotary evaporator and the bromide end-functional Chol was isolated by precipitating in cold methanol. The recovered product was dried under reduced pressure at ambient temperature until a constant weight.

Yield: 10.96 g (79%). M.P.: 64–67 °C. FTIR (ATR, cm⁻¹): 2940 and 2865 (C–H); 1724 (C=O); 1470 (C–H); 1235 [(C=O)–O]; 1045 (C–O–C). ¹H NMR (500 MHz, CDCl₃, d, ppm): 0.50–2.05 (overlapping multiplets, 43 H); 2.17 [2 H, O(–CO–CH₂CH₂Br)]; 2.47 [1 H, t, (O–CO–CH₂CH₂Br)]; 2.55–3.00 (4 H, 2CH₂CH₂); 3.46 [2 H, O(–CO–CH₂CH₂Br)]; 4.61 (1 H, CH–O in Chol); 5.36 (s, 1 H, ≡CH in Chol).

Synthesis of Cholesteryl 4-Methacryloxybutyrate (Chol-3-MMA)

Chol-3-MMA was synthesized according to the literature method with the minor modifications. 37–39 Methacrylic acid (1.81 g, 21.00 mmol) was added cholesteryl 4-bromobutyrate (7.50 g, 14.00 mmol), potassium carbonate (KHCO₃) (2.10 g, 21.00 mmol) at room temperature for 8 h. The reaction mixture was stirred with potassium hydrogen carbonate (100 mL), and the reaction mixture was stirred at 100 °C overnight. On cooling, DCM (100 mL) and water (300 mL) were added to the reaction mixture and stirred. The organic layer was washed with water, 5% aqueous sodium hydroxide and water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed. The product was purified by column chromatography (silica gel, DCM) and recrystallized twice from ethanol.

Yield: 1.63 g (65%). FTIR (cm⁻¹): 2938 and 2867 (C–H); 1729 (C=O). ¹H NMR (500 MHz, CDCl₃, d, ppm): 0.50–2.05 (overlapping multiplets, 43 H); 2.25 (2 H, m, –CH₃CH₂CH₂–COO–); 3.91 (2 H, t, –OOCCH₂CH₂CH₂); 4.54 (1 H, m, COOC–CH₂); 5.29 (1 H, m, >C=CH–).

Synthesis of Poly(Chol-3-MMA-Co-MMA)
The reaction was carried out in the round bottom flask in calculated amount of Chol-3-MMA (2.05 g, 3.79 mmol) and MMA (0.38 g, 3.79 mmol) in anisole (2.5 mL), and EBB (6.16 mg, 0.032 mmol) was added as initiator, followed by PMDETA (10.95 mg, 0.063 mmol), copper (I) bromide (4.53 mg, 0.032 mmol), respectively. The reaction mixture was deoxygenated by purging gently with oxygen-free argon for 10 min. Then, the flask was tightly sealed and immersed in a thermostated oil bath at 90 °C to initiate polymerization. At this point, the mixture was stirred for 12 h. The solvent was then evaporated, and the residue was dissolved in a minimum amount of DCM. The polymer was then precipitated into a large amount of cold methanol. The crude product was collected as follows: Soxhlet extracted overnight (using methanol, to remove unreacted monomer), extracted with DCM, concentrated and reprecipitated into methanol. Next, the precipitate was isolated by filtration and dried at room temperature in vacuo until a constant weight was obtained.

Yield: 1.41 g (58%). FTIR (cm⁻¹): 2943 and 2867 (C–H); 1728 (C=O). ¹H NMR (500 MHz, CDCl₃, d, ppm): 0.60–2.10 (overlapping multiplets, 49 H); 2.31 (2 H, m, –CH₂CH₂CH₂COO–); 3.59 (3 H, s, –COOCH₃); 3.97 (2 H, t, –OOCCH₂CH₂CH₂); 4.61 (1 H, m, COOC–CH₂); 5.37 (1 H, m, >C=CH–).

RESULTS AND DISCUSSION

Characterization of Methacrylate-Based SCLCPs

The methacrylate monomers containing cholesteryl pendant moiety (Chol-n-MMA) were prepared in a two-step reaction sequence. Firstly, cholesteryl ω-bromoalkyl esters were prepared by esterification reaction of Chol with ω-bromoalkyl carboxylic acid. Then, synthesis of the monomers, which have a cholesteryl moiety connected to a flexible methylene chain, were achieved via the displacement reaction between bromide ion of ω-bromoalkyl esters and potassium methacrylate salt (Scheme 1). The homopolymers of Chol-n-MMA and its random copolymers with MMA were prepared by ATRP and their conductivity mechanisms were investigated for their possible applications in elastic microelectronic devices.

¹H NMR and FTIR spectroscopic methods were employed to characterize the structures of the cholesterol containing methacrylate-based monomers and polymers. The FTIR spectra of Chol-3-Br, Chol-3-MMA, and the polymers are shown in Figure 1. After the reaction of Chol bearing OH functional group with 4-bromobutyl chloride, the disappearance of the hydroxyl signal in the FTIR spectrum of the resulting compound (Chol-3-Br) in Figure 1(b) indicates that the hydroxyl functionality of cholesterol [Figure 1(a)] were successfully converted into bromide via the esterification reaction. The detection of the peak at 1639 cm⁻¹ in the FTIR spectrum of Chol-3-MMA [Figure 1(c)] designates the presence alkene functional
groups after the displacement reaction between Chol-3-Br and potassium methacrylate salt. The disappearance of the alkene signal at 1639 cm$^{-1}$ was a clear indication of the successful homopolymerization [Figure 1(d)] and copolymerization of Chol-3-MMA with MMA [Figure 1(e)].

Regarding the $^1$H NMR analysis, the proton signals of Chol were observed at 5.36 (Ha), 4.61 (Hb) and 0.5–2.05 (overlapping multiplets) (He) ppm in the $^1$H NMR spectrum of Chol-3-Br [Figure 2(a)]. After esterification reaction, some new peaks related to the methylene protons of the terminal 4-bromobutyryl moiety (Hc, Hd, and He) appeared at 2.47, 2.17, and 3.46 ppm, respectively. In addition, the integral ratios between the proton signal of the methylene group adjacent to the bromide and those of the methine groups in the cholesterol are very close to the theoretical values. $^1$H NMR spectrum of Chol-3-MMA is shown in Figure 2(b). The comparison of $^1$H NMR spectra of Chol-3-Br [Figure 2(a)] to that of Chol-3-MMA [Figure 2(b)] proves the successful esterification reaction of cholesterol with 4-bromobutyryl chloride. After the attachment of the methacryloyl group, the proton signals of the double bond appeared at 6.03 and 5.49 ppm and the signal of the methylene group previously bearing bromine shifted from 3.46 to 4.11 ppm. Furthermore, the experimental and theoretical integral ratios among the proton signal of the methine groups in the cholesterol, the proton signals of the double bond of the methacryloyl group, and those of the methylene group adjacent to the ester group are 0.99:1.00:1.02:2.11 (Hf:Hg:He:He), which are very close to the theoretical values. (1:1:1:1:2). After ATRP of Chol-3-MMA, the proton signals (5.49 and 6.03 ppm) of the double bond of the monomer precursor disappeared in the $^1$H NMR spectra [Figure 3(a,b)]. The copolymers, poly(Chol-n-MMA-co-MMA), were synthesized at the feed ratio of [Chol-n-MMA]/[MMA] = 1. $^1$H NMR spectrum of poly(Chol-3-MMA-co-MMA) is shown in Figure 3(b), where the signal of methyl protons of the ester group in MMA were also observed in the $^1$H NMR spectrum. The composition of copolymers was calculated by comparing the integral peak areas of the methyl protons COOC$_3$H$_7$, $^1$H NMR analysis (Figures 2 and 3) clearly showed the successful synthesis of the polymers.

Average molecular weights of the polymers and their molecular weight distributions were estimated by GPC and related data are given in Table I. The polymers showed symmetrical and unimodal elution peaks with polydispersity values in the range of 1.12 to 1.49.

### Thermal Properties of the Polymers

Thermal properties of the polymers were investigated by determining the weight loss upon linearly increasing the temperature by conventional TGA under nitrogen flow with a heating rate of 10°C min$^{-1}$ from room temperature to 700°C. $T_{onset}$, $T_{max}$, and the percent char yield data are given in Table II and the percent weight loss against temperature curves of the polymers are plotted in Figure 4. $T_{onset}$ and $T_{max}$ values of the homopolymers and copolymers generally increased with increasing flexible spacer. Additionally, the char yield percent of all the polymers were found to be close to each other.

### Mesomorphic Properties

The mesomorphic properties of SCLCPs were investigated by DSC, POM, and XRD techniques. DSC was used to examine the thermal behaviors of the polymers. Normalized DSC graphics are given in Figure 5.

Table III reveals that all the polymers exhibit a clearing point (Tc = smectic – isotropic transition) in the range 99 to 181°C and show different thermal ranges. For example, the DSC heating scan for poly(Chol-3-MMA) shown in Figure 5 shows a peak at 181°C corresponding to the highest Tc. With increasing

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**Figure 1.** FTIR spectra of (a) cholesterol, (b) Chol-3-Br, (c) Chol-3-MMA, (d) poly(Chol-3-MMA), and (e) poly(Chol-3-MMA-co-MMA). [Color figure can be viewed at wileyonlinelibrary.com]

**Figure 2.** $^1$H NMR spectra of (a) Chol-3-Br and (b) Chol-3-MMA.
the flexible spacer, the Tcl values become lower up to 10 and in poly(Chol-n-MMA-co-MMA) series, an elastic and viscous state may prevail.\textsuperscript{40,41} Despite of the effect of internal plasticization, Tcl is higher in poly(Chol-n-co-MMA) (n > 7).\textsuperscript{42}

**Optical Textures**

Poly(Chol-n-MMA) and poly(Chol-n-MMA-co-MMA) series exhibited 90 to 130°C melting transition range when heated and cooled as a thin film between two glass plates.

POM characterization results revealed that poly(Chol-3-MMA) and poly(Chol-3-MMA-co-MMA) showed a crystalline to isotropic transition at 120 to 130°C. The types of phases are considered as a broken focal-conic fan texture of smectic phase from POM images in Figure 6.\textsuperscript{41} Also, the same phase transitions and liquid crystal textures were observed for the other homopolymers and copolymers. The observations under POM showed that all poly(Chol-n-MMA) and poly(Chol-n-MMA-co-MMA) series have liquid crystallinity properties.

XRD analysis was also employed to obtain more information about liquid crystallinity. Mostly, a strong and sharp peak, which shows the arrangement of the molecules in regularly spaced layers and the distance between first and second layers

![Figure 3. 1H NMR spectra of (a) poly(Chol-3-MMA), and (b) poly(Chol-3-MMA-co-MMA).](image)

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$m_{\text{Chol-3-MMA}}$</th>
<th>$m_{\text{Chol-3-MMA}}$</th>
<th>$M_w$/GPC</th>
<th>$M_w/M_n$</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(Chol-3-MMA)</td>
<td></td>
<td></td>
<td>28,100</td>
<td>1.36</td>
<td>65</td>
</tr>
<tr>
<td>Poly(Chol-3-MMA-co-MMA)</td>
<td>0.50</td>
<td>0.67</td>
<td>24,800</td>
<td>1.36</td>
<td>58</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA)</td>
<td></td>
<td></td>
<td>19,700</td>
<td>1.38</td>
<td>61</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA-co-MMA)</td>
<td>0.50</td>
<td>0.54</td>
<td>35,000</td>
<td>1.49</td>
<td>54</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA)</td>
<td></td>
<td></td>
<td>37,100</td>
<td>1.24</td>
<td>71</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA-co-MMA)</td>
<td>0.50</td>
<td>0.71</td>
<td>18,700</td>
<td>1.12</td>
<td>64</td>
</tr>
</tbody>
</table>

$^a$ $m_{\text{Chol-3-MMA}}$ and $m_{\text{Chol-3-MMA}}$ are the mole fraction of Chol-3-MMA in the feed and copolymer, respectively.

$^b$ $M_w$/GPC and $M_w/M_n$ were determined by GPC analysis with PMMA standards. THF was used as the eluent (RI detector).

$^c$ Determined gravimetrically.
(d1 value), is seen at small-angle X-ray scattering (SAXS) region (0.2° < 2θ < 4°) for smectic phase. The SAXS region was examined for the polymers at room temperature in order to get knowledge about the organization of layers. Therefore, thermally heated and then cooled film samples were prepared for XRD analysis. At SAXS region a strong peak was observed for all the polymers at their 2θ. XRD curves of the polymers seen in Figure 7 indicates the liquid crystallinity.

**AC Conductivity Mechanism of SCLCPs**

The real ε′(ω) and the imaginary ε′′(ω) parts of the complex dielectric constant are described as ε*=ε′(ω) − iε′′(ω). Figure 8 shows the frequency dependence of the real ε′(ω) parts of the complex dielectric constant on a semi-log scale at room temperatures in the parallel plate device under test for PMMA (Chol-n-MMA), and PMMA(Chol-n-MMA-co-MMA). As seen in Figure 8, all the polymers have shown almost constant value of ε′(ω) at low frequencies up to 10 kHz, indicating a stable dielectric response over a wide frequency band (100 Hz–10 kHz). In higher frequencies, especially after 10 kHz nearly all polymers show dielectric relaxation. Among the investigated polymers, the polymers with n = 3 [in Figure 8(a)] have shown the highest dielectric values whereas the polymers with n = 7 [in Figure 8(b)] have demonstrated the lowest values of dielectric constants. Real dielectric constant values of the polymers are given in Table IV. Results revealed that dielectric constants of the polymers vary as a function of chain lengths. In accordance with recent investigation, the polymers with lowest spacer lengths i.e., poly(chol-3-MMA-co-MMA) and poly(chol-3-MMA) showed higher values of dielectric constants. Likewise, Wang et al. investigated OFET using two different azaborine compounds with varying lengths of alkyl side chains and obtained higher field effect mobility values and performance for the case of devices realized using compounds with lower length of side chain similar to our findings. Lower dielectric constants values for polymers having longer chains may be attributed due to deteriorated charge transport, considerable bimolecular recombination, unfavorable intermolecular interaction and packing, which consequently lead to poor dielectric performance. Dielectric constants values of polymers with spacer length of 10 are higher than polymers with chain length of 7 which seems contrary to above statement that dielectric performance decreases with increase in the length of spacer. However, lowest dielectric constant values for the case of polymers having spacer lengths of 7 are due to its higher polydispersity values (Table I) as known that high polydispersity value negatively impacts on the materials performance.

**Table II. Thermal Properties of the Polymers**

<table>
<thead>
<tr>
<th>Polymers</th>
<th>T_{onset}^a (°C)</th>
<th>T_{max}^b (°C)</th>
<th>Char yield (%)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(Chol-3-MMA)</td>
<td>303.13 (±2.5)</td>
<td>345.78 (±2.3)</td>
<td>0.11 (±0.04)</td>
</tr>
<tr>
<td>Poly(Chol-3-MMA-co-MMA)</td>
<td>328.95 (±1.8)</td>
<td>355.62 (±1.7)</td>
<td>0.54 (±0.03)</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA)</td>
<td>299.33 (±1.7)</td>
<td>357.53 (±1.8)</td>
<td>0.32 (±0.06)</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA-co-MMA)</td>
<td>337.79 (±1.9)</td>
<td>375.02 (±2.1)</td>
<td>0.45 (±0.05)</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA)</td>
<td>346.16 (±2.1)</td>
<td>376.20 (±1.9)</td>
<td>0.46 (±0.05)</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA-co-MMA)</td>
<td>345.65 (±2.0)</td>
<td>380.87 (±2.2)</td>
<td>0.32 (±0.07)</td>
</tr>
</tbody>
</table>

^a T_{onset} is the onset decomposition temperature of the polymers.

^b T_{max} is the temperature corresponding to the maximum rate of weight loss.

^c The percent of char yield at 600°C.

**Figure 4.** TGA curves of the polymers. [Color figure can be viewed at wileyonlinelibrary.com]

**Figure 5.** DSC curves of the polymers in the second heating ramp. [Color figure can be viewed at wileyonlinelibrary.com]
The real $\varepsilon'(\omega)$ part of the dielectric constant is described as:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_1 - \varepsilon_\infty) \frac{1 + (\omega \tau_0)^{1-\alpha} \sin \frac{\alpha \pi}{2} \sin \frac{(\omega \tau_0)^{2(1-\alpha)}}{2}}{1 + 2(\omega \tau_0)^{1-\alpha} \sin \frac{\alpha \pi}{2} \sin \frac{(\omega \tau_0)^{2(1-\alpha)}}{2}}$$

(1)

Here, $\varepsilon_1$ and $\varepsilon_\infty$ are low and high angular frequency dielectric constant, $\omega = 2\pi$ times frequency, $\tau_0$ is a generalized relaxation time, and $\alpha$ is the shape parameter. The shape parameter $\alpha$ changes from 0 to 1 ($0 < \alpha \leq 1$). If $\alpha = 0$, it corresponds to standard Debye type relation, nearly-Debye type when $\alpha$ value is close to zero and non-Debye type for $0 < \alpha \leq 1$ regions. We have calculated $\tau_0$ relaxation time and $\alpha$ shape parameter from eq. (1) and fitted by the results given in Figure 8(a–c). The calculated values of $\tau_0$ and $\alpha$ are given in Table IV. The values of parameter $\alpha$ are higher than 0 which indicates a non-Debye type relation.

The dielectric strength $\Delta \varepsilon$ is the difference between the dielectric values at low and high frequencies. In the dielectric spectroscopy technique, the dielectric strength $\Delta \varepsilon$ is expressed as given in eq. (2):

$$\Delta \varepsilon = \varepsilon_1 - \varepsilon_\infty$$

(2)

where $\varepsilon_1$ and $\varepsilon_\infty$ are the low and high frequencies components of the real part of dielectric constant. $\Delta \varepsilon$ values are well accordance with $\varepsilon_1$ values, while the $\varepsilon_\infty$ values are almost same. As it is seen in Table IV, the change in polarity of the samples have nearly the same variation with the results of static dielectric constants.

Table IV also presents the values of parameters $\varepsilon_1$, $\varepsilon_\infty$, and $\Delta \varepsilon$ which were estimated from Figure 8. In this figure, it is seen that poly(Chol-7-MMA-co-MMA) has the lowest dielectric strength depending on AC frequency while the highest $\Delta \varepsilon$ is obtained by poly(Chol-3-MMA). These parameters change due to flexible spacer. Equivalent dielectric constants vary according to the flexible spacer for both homopolymers and copolymers.

Figure 9 depicts the frequency dependence of the imaginary $\varepsilon''(\omega)$ parts of the complex dielectric constant on a semi-log scale at room temperatures in the parallel plate device under test. Critical frequency values of all the investigated polymers were determined from Figure 9 indeed. These frequency values correspond to the maximum peak frequency of imaginary dielectric constant. Significant variation in the critical frequency of the samples was observed, which is in agreement with the variation of other parameters. Table IV also presents the values of parameters $\varepsilon''_{\text{max}}$, and $f_c$ which were estimated from Figure 9.
Cole–Cole plots of the polymers are shown in Figure 10. These Cole–Cole plots were obtained from the imaginary versus real values of dielectric constants ($\varepsilon''-\varepsilon'$). Equivalent circuit model analysis of the Cole–Cole plots shows parallel resistance-capacitance (RC) and series resistance regimes for the investigated samples.

Plots have shown non-Debye and nearly-Debye type relaxation phenomena. The non-Debye type plots are most suitable for the description of the interface molecular relaxation mechanisms. $\varepsilon''-\varepsilon'$ curves (Cole–Cole plots) of the polymers indicate the depressed semicircles. Origins of poly(Chol-3-MMA) and poly(Chol-7-MMA-co-MMA) polymers' arcs are close to x-axis as they are exhibited nearly-Debye type properties and the others are non-Debye type.

Angular frequency evolution of the AC conductivity ($\sigma'$) of the polymers is shown in Figure 11. In order to understand the conductivity mechanism of the samples, In $\sigma'$ – In $\omega$ graphs of the polymers were drawn and investigated. Some of these polymers show frequency linear regions on their plots as indicated in Figure 12. The AC conductivity dependency of the angular frequency can be expressed by the following relation, which is known as the empirical Jonscher’s universal law.$^{51}$

![Figure 8. Frequency evolution of the real ($\varepsilon'$) part of the dielectric constants for: (a) poly(Chol-3-MMA) and poly(Chol-3-MMA-co-MMA), (b) poly (Chol-7-MMA) and poly(Chol-7-MMA-co-MMA), (c) poly(Chol-10-MMA), and poly(Chol-10-MMA-co-MMA), (d) poly(Chol-$n$-MMA-co-MMA). [Color figure can be viewed at wileyonlinelibrary.com]](image)

Table IV. Shape Parameter ($\alpha$), Relaxation Time ($\tau_0$), Dielectric Parameters ($\varepsilon_\infty$, $\varepsilon''_{\max}$ and $\Delta\varepsilon$) and Critical Frequencies ($f_c$) of Poly(Chol-$n$-MMA) and Poly(Chol-$n$-MMA-co-MMA) ($n = 3, 7,$ and $10$)

<table>
<thead>
<tr>
<th>Polymers (Adj. $R^2$ 0.99)</th>
<th>$\alpha$</th>
<th>$\tau_0$ (s)</th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon''_{\max}$</th>
<th>$\Delta\varepsilon$</th>
<th>$f_c$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(Chol-3-MMA)</td>
<td>0.06</td>
<td>$5.22 \times 10^{-8}$</td>
<td>4.02</td>
<td>$-0.301$</td>
<td>2.36</td>
<td>$4.321 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-3-MMA-co-MMA)</td>
<td>0.39</td>
<td>$7.07 \times 10^{-8}$</td>
<td>3.82</td>
<td>$-0.102$</td>
<td>1.96</td>
<td>$3.902 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA)</td>
<td>0.28</td>
<td>$6.64 \times 10^{-8}$</td>
<td>2.66</td>
<td>$-0.100$</td>
<td>1.3</td>
<td>$2.76 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-7-MMA-co-MMA)</td>
<td>0.04</td>
<td>$5.80 \times 10^{-8}$</td>
<td>2.39</td>
<td>$-0.135$</td>
<td>1.43</td>
<td>$2.425 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA)</td>
<td>0.74</td>
<td>$8.01 \times 10^{-8}$</td>
<td>2.85</td>
<td>0.029</td>
<td>1.3</td>
<td>$2.821 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-10-MMA-co-MMA)</td>
<td>0.27</td>
<td>$6.86 \times 10^{-8}$</td>
<td>3.25</td>
<td>$-0.117$</td>
<td>1.66</td>
<td>$3.367 \times 10^6$</td>
</tr>
<tr>
<td>Poly(Chol-$n$-MMA-co-MMA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where $A$ is a constant, $\omega$ is the angular frequency, and $s$ is the frequency exponent parameter which determines AC conduction mechanisms.

The values of parameter $s$ (angular frequency exponent) were calculated from the slopes of Figure 12. Linear increase in the Figure 12 with frequency is fitted and AC conductivity is acquired from this fit. During the fit slope, we use linear equation, $y = a + b \times x$, expressing $b = \ln \sigma/\ln \omega$ with $R^2 \approx 0.99$.

The variations of $\ln \sigma_{AC}$ with angular frequency is given in Figure 12 for poly(Chol-$n$-MMA) and poly(Chol-$n$-MMA-co-MMA). As the angular frequency exponent, $s$, is used to determine the electrical conductivity mechanism for poly(Chol-$n$-MMA) and poly(Chol-$n$-MMA-co-MMA), its values were calculated from the slopes of Figure 12 for the low and high frequency regions. The $s$ parameter values can be interpreted by conductivity mechanisms for frequency dependent conductivity given by $s < 1$ (Ref. 54) for super linear power law (SLPL) high frequency regions are given inset table in Figure 12.

The polymers contain four conductivity mechanisms in the low and high frequency regions. These mechanisms are QMT and CBH conductivity mechanisms at low frequency regime and SLPL and DC conductivity mechanisms at high frequency region. As can be seen, the values of exponent “$s$” are varying from $\sim 0.029$ to $\sim 1.81$ ($\pm 0.004$). Generally, all the polymers demonstrate conduction mechanism at high or low frequencies. At low and high frequencies, all the polymers showed QMT and SLPL conduction mechanism respectively, except poly(Chol-7-MMA-co-MMA) which indicated CBH mechanism at low frequencies. Furthermore, angular frequency dependent measurement of poly(Chol-10-MMA) showed three different conductivity mechanisms. The significance of this polymer is that it reaches saturation at high frequencies with no slope and parameter $s$ value near to 0, which indicates DC conductivity like the behavior of the polymer at higher frequencies.

The performance of an OFET is function of the properties of its gate dielectric films. Peng et al.\textsuperscript{55} have realized all organic field effect transistors using a variety of polymer dielectrics and correlated change in the field effect mobility values of the devices with varying dielectric constants values of dielectric films. Dielectric constants and other promising dielectric properties of the investigated SCLCPs suggest their suitability for the development of high frequency flexible OFETs for large area sensing and other advanced applications.

**CONCLUSIONS**

We reported the synthesis and characterization of a series of methacrylate based SCLC homopolymers [poly(Chol-$n$-MMA)] and copolymers [poly(Chol-$n$-MMA-co-MMA)] with flexible methylene spacer ($n = 3, 7, \text{and} 10$) between the poly(methyl methacrylate) backbone and cholesteryl mesogen. These spacers are known to permit a decrease in the steric hindrances provided by the backbone chains and provide sufficient flexibility.
for the arrangement of mesogens in polymeric LC phases. All the polymers exhibited the liquid crystalline behavior of broken focal-conic fan texture of smectic phase. Real and imaginary dielectric constants, shape parameter, relaxation time, dielectric strength, and critical frequency values of the polymers were determined using parallel plate impedance spectroscopic technique. The dielectric constant values of the polymers were found to increase with decreasing aliphatic methylene spacer length. Lowest dielectric constant values for the case of polymers having spacer lengths of 7 are due to its higher polydispersity values as known that high polydispersity value effect negatively on the dielectrics performance.

Homopolymer with \( n = 10 \) showed the saturation or DC conductivity behavior at higher frequencies which represents its suitability for the development of high frequency regions organic photovoltaic devices.

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REFERENCES