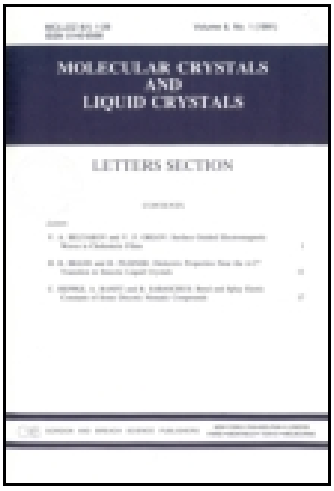

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Synthesis of Sulfonated Cholesterol Derivatives—Electrical, Thermal, and Optical Properties

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Synthesis of Sulfonated Cholesterol Derivatives—Electrical, Thermal, and Optical Properties

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Poly(cholesterylacrylatesulfone) (PCHAS) and poly(cholesterylacrylatesulfone-co-1-hexene)s (PCHASHs) at different ratios are synthesized from the monomer cholesteryl acrylate. The liquid crystalline phases are observed under a hot stage fitted with a polarizing optical microscope. The polysulfone and copolysulfones are characterized by FT-IR, ^{1}H-NMR, DSC, and TGA techniques. From SEM (EDX) the qualitative amounts of elemental sulfur found in PCHAS and PCHASH11 are 2.90 weights (%) and 4.39 weights (%), respectively. The GPC data using THF as the solvent shows that the number average molecular weight of the PCHAS is 5268 g/mol and the molecular weights of the PCHASHs are higher than the PCHAS.

Keywords Cholesterylacrylate; copolysulfone; hot stage; polarizing optical microscope; polysulfone

1. Introduction

It is well-known that cholesterol and its esters are fat-soluble that occur in nature. The main attraction of the researchers in the synthesis of liquid crystal is due to the rigidity and helical structure of cholesterol and its esters. The C_3-hydroxyl group of cholesterol allows the synthesis of various cholesteryl esters or ethers and also due to its rigid structure with eight chiral centers and the ease with which the structure can be derivatized, cholesterol has been incorporated extensively in side chain liquid crystalline polymers [1]. These materials are useful for the properties such as selective reflection of circularly polarized light, high optical rotary power, circular dichrosim, and electro-optic effect. Most of the ester of cholesterol shows thermotropic liquid crystalline phases in particular temperature region as reported by Cheng et al. [2].

Polymers which are able to form liquid crystalline phases readily are composed of mesogen-connected by flexible spacer either along the main chain or as side chain to a main

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chain. Zhou et al. have been prepared variety of side chain liquid crystalline homopolymer (SCLCPs) bearing cholesterol, by systemically varying (i) backbone (norbornene, acrylate, methacrylate, siloxane, and urethane) and also (ii) flexible spacers (methylene and siloxane). They have prepared first ester cholesterylmethacrylate (mesogen) and then finally polymerized methacrylate residue free radically using AIBN as initiator to poly (cholesterylmethacrylate), where the cholesteryl residue remains as side chain [3]. Poly (olefin sulfone)s have recently emerged as a new class of liquid crystalline polymer where the liquid crystallinity is inherent within the main chain [4].

Aromatic poly (ether sulfone)s are a family of amorphous thermoplastics that possess unique high-performance properties as engineering materials, proved by their continuous commercialization since 1965 [5]. From the chemical point of view, these polymers are characterized by aryl groups linked by sulfonyl (-SO_2-) and ether (O) groups. Also polysulfones has been widely used in last few years in the field of sensors. Polysulfones are used in the manufacture of medical equipment (nebulizers and dialysis components), appliances (coffeemakers, humidifiers, and microwave ovens), automobile parts (steering column lock switches, relay insulators, and pistons), and electronic equipment (television components and capacitor film) [6].

The function of a sensor is to provide information about the physical, chemical, and biological environment. The principle of a solid-state sensor device is based on the electrical response to the chemical environment and the electrical properties are influenced by the presence of gas phase or liquid phase species. This article will focus on the synthesis, liquid crystalline phase behavior and electrical conductivity of poly(cholesterylacrylatesulfone) (PCHAS) and poly(cholesterylacrylatesulfone-co-1-hexene)s (PCHASHs). These PCHAS and PCHASHs are synthesized to harness electric conductivity variation with temperature of suitable thick pellet of these materials.

2. Experimental Details

2.1. Materials

Cholesterol (Merck), acrylic acid (Merck), ethyl methyl ketone (Merck), chloroform (Ranbaxy), methanol (Ranbaxy), AIBN (Merck), and benzene were used without further purification. 1-hexene (Merck) was purified as reported in the literature [7].

2.2. Techniques

The IR spectra were recorded by the KBr method using Bruker Vector22 system in the range of 400–4000 cm^{-1}. The proton NMR spectrum was recorded by JMM-ECS 400 MHz NMR in $CDCl_3$ using tetra methylsilan as the reference. The molecular weights were measured in tetrahydrofuran (HPLC grade) with a three column GPC system (WATERS). 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 elemental analysis was carried out using SEM-EDX method (Leo 1430 VP). The DSC and TGA results were obtained from Perkin Elmer DSC 6000 and TGA 4000 by heating the samples at a heating rate of 5°C and 10°C per minute, respectively, in nitrogen atmosphere. The I-V characteristics were carried out by 2-probe method. The AC conductivity was calculated from bulk resistance, measured by HIOKI 3532-50 LCR HiTESTER.

2.3. Synthesis of Compounds

2.3.1. Preparation of acryloyl chloride. The acryloyl chloride was prepared by distillation of acrylic 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 containing small amount of hydroquinone was kept inside an ice bath. Redistillation gave 68-72% of acryloyl chloride [8].

2.3.2. Preparation of cholesteryl acrylate (CHA). One mole of both cholesterol and acryloyl chloride were dissolved in ethyl methyl ketone (MEK) and then stirred for 5–6 hr inside a round bottom flask in 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 MEK. The viscous organic liquid on cooling gave cholesteryl acrylate. Cholesteryl acrylate was recrystallized and finally purified by column chromatography.

The yield of the product was 87.45% and its liquid crystalline phase range was 100–127°C.

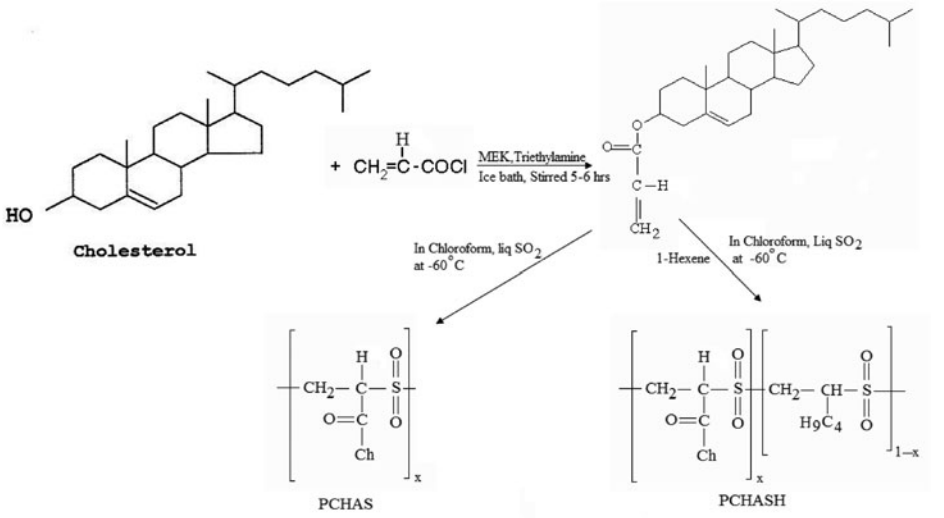
2.3.3. Preparation of the polysulfone (PCHAS). The ester cholesteryl acrylate (CHA) was dissolved in chloroform and transferred into a vacuum tube. A mixture of t-butylhydroperoxide with methanol (1:1 mole ratio) was then added to it. The vacuum tube was evacuated by high vacuum pump and after that the tube is kept inside a 1.5 L liquid N_2 canister at below –60°C. SO_2 gas was then passed in to the reaction tube and the tube was sealed. The sealed tube and the mixture were kept at that temperature for another 2–3 hr. When the reaction had completed, the reaction mixture was poured in acidified methanol. The dirty white color polysulfones, (PCHAS) was then recrystalized from hot methanol containing traces of chloroform. Finally, the product was washed several times with MEK.

2.3.4. Preparation of copolysulfones. The mesogenic ester CHA with 1-hexene at different mole ratios were dissolved in chloroform and the polymerization were done as before. The copolysulfones (PCHASHs) were isolated and recrystallized from hot methanol containing traces of chloroform. Finally the co-polymers were washed several times with MEK and dried over dessicator.

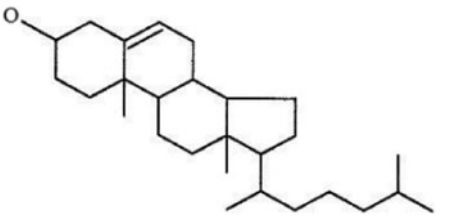
3. Results and Discussion

The polymerization of mesogenic monomer CHA with 1-hexene can be initiated by t-butyl hydroperoxide following free radical mechanism of polymerization and copolymerization. When SO_2 gas is passed to the reaction mixture in chloroform, free radical $HOSO_2$, and t-butyl-O-SO_2 are produced at low temperature and was reported by Dass in the synthesis of cholesteryl 4-pentenoate sulfone, its polymer and copolymer with cyclohexene [9]. The homopolymerization of CHA and copolymerization with 1-hexene initiated by t-butyl hydroperoxide in presence of liquid SO_2 below –60°C to give PCHAS and PCHASHs respectively are reported here.

The schematic reaction path of the formation of polysulfone and copolysulfone is given below:



Where the cholesteryl group (CH) is



The representative FT-IR curves of CHA, PCHAS, and PCHASH11 are shown in Fig. 1 to identify the changes to the structure. The CHA shows a C=O stretching vibration at 1720 cm^{-1} and C=C stretching vibration at 1639 cm^{-1}. The ester C−O stretching vibration can be characterized by the peak at 1203 cm^{-1}. When the monomer CHA was polymerized and copolymerized with 1-hexane in presence of liquid SO_2, the strong peak for C=C stretching vibration was almost disappeared while two new small peaks at 1315 cm^{-1} and 1126 cm^{-1} were observed for symmetric and asymmetric stretching vibration for sulfone groups of PCHAS and PCHASH11, respectively [10].

From the ^{1}H-NMR spectra of CHA, PCHAS, and PCHASH11 it is revealed that the protons Ia, Ib, and II are absent but found in the monomer, CHA [11]. The two new signals are found for the protons I' and II' of main chain containing sulfone group of the PCHAS and PCHASH11 indicating the formation of polysulfone (PCHAS) and copolysulfones (PCHASH11).

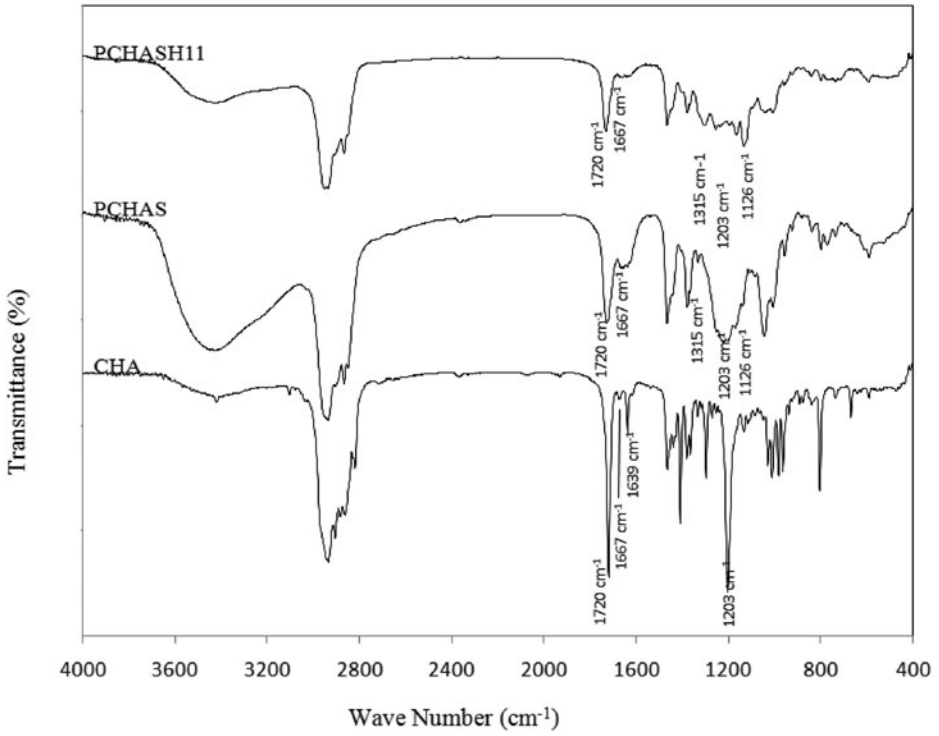
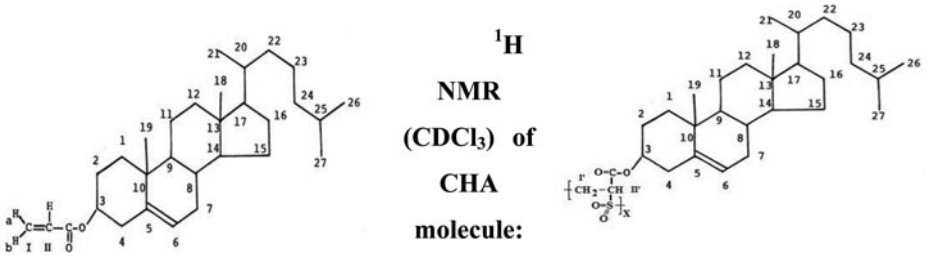


Figure 1. FT-IR Spectra of CHA, PCHAS, and PCHASH11.

CHA molecule: PCHAS molecule



^{1}H NMR (CDCl$_3$) of CHA molecule: δ (ppm) = 6.36(dd, I_a),6.10(t,$_{II}$), 5.81(dd, I_b), 5.38 (t, H_6), 4.70 (m, H_3), 2.35 (d, H_4), 2.25-0.1.1 (m, H_1, H_2, H_7, H_8, H_9, H_{10}, H_{11}, H_{12}, H_{14}, H_{15}, H_{16}, H_{17}, H_{20}, H_{22}, H_{23}, H_{24}, H_{25}), 0.99 (s, H_{19}), 0.89 (d, H_{21}), 0.85 (dd, H_{26}, H_{27}), and 0.65 (s, H_{18}).

^{1}H NMR (CDCl$_3$) of PCHAS molecule: δ (ppm) = 5.38 (t, H_6), 4.70 (m, H_3), 4.05 (t, $H_{I'}$), 3.68(d, $H_{II'}$), 2.35 (d, H_4), 2.25-0.1.1 (m, H_1, H_2, H_7, H_8, H_9, H_{10}, H_{11}, H_{12}, H_{14}, H_{15}, H_{16}, H_{17}, H_{20}, H_{22}, H_{23}, H_{24}, H_{25}), 0.99 (s, H_{19}), 0.89 (d, H_{21}), 0.85 (dd, H_{26}, H_{27}), and 0.65 (s, H_{18}).

^{1}H NMR (CDCl$_3$) of PCHASH11 molecule: δ (ppm) = 5.38 (t, H_6), 4.70 (m, H_3), 4.05 (t, $H_{I'}$), 3.68(d, $H_{II'}$), 2.35 (d, H_4), 2.25-0.1.1 (m, H_1, H_2, H_7, H_8, H_9, H_{10}, H_{11}, H_{12}, H_{14}, H_{15}, H_{16}, H_{17}, H_{20}, H_{22}, H_{23}, H_{24}, H_{25}), 0.99 (s, H_{19}), 0.89 (d, H_{21}), 0.85 (dd, H_{26}, H_{27}), and 0.65 (s, H_{18}).

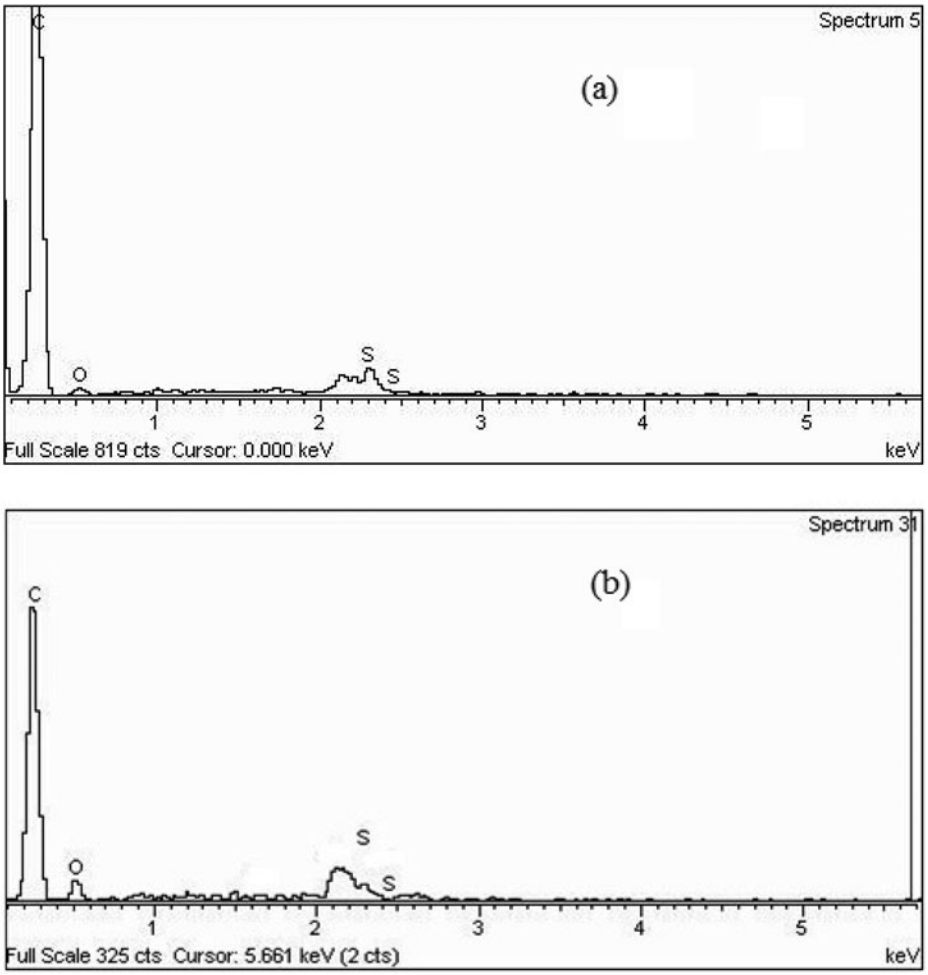


Figure 2. (a) SEM (EDX) spectrum of PCHAS and (b) SEM (EDX) spectrum of PCHASH11.

The elemental analysis by SEM (EDX) method shows the presence of sulfur (Fig. 2) in the PCHAS and PCHASH11 confirming the introduction of SO_2 molecules and the formation of PCHAS and PCHASH11. The qualitative amounts of elemental sulfur found in PCHAS and PCHASH11 are 2.90 weights (%) and 4.39 weights (%), respectively. The percentage of elemental C, O, and S found from EDX are shown in supplemental material.

The molecular weights of the PCHAS and PCHASHs were determined by GPC method using HPLC grade THF as the solvent and polystyrene as the standard. All together three standards were used for the measurement with molecular weight 0.27×10^4, 0.64×10^4, and 480×10^4 g/mol. The number average molecular weight (M_n), weight average molecular weight (M_w), M_w/M_n, phase transition temperatures and ΔH for isotropic phase transition are shown in Table 1. The M_n and M_w value of the PCHAS are found as 5268 g/mol and 5706 g/mol, respectively, with an M_w/M_n value of 1.083. The M_n and M_w value of PCHASHs are found higher than that of PCHAS. This may be due to the inclusion of spacer 1-hexene in PCHASHs at different mole ratios. Since the M_w/M_n values for PCHAS and all PCHASHs are less than 1.5 indicating that they are all monodispersed by fractionation

Table 1. Number average molecular weight (M_n), Weight average molecular weight (M_w), polydispersity (M_w/M_n), liquid crystalline phase, and ΔH value for isotropic phase transition of PCHAS and PCHASHs

Polymer	Monomer feed ratio	M_n (Deltons)	M_w (Deltons)	M_w/M_n	T_g (°C)	LC phase (°C)	Delta H value for isotropic phase transition (J/g)
PCHAS	—	5268	5706	1.08	105	120–144	1.85
PCHASH21	2:1	5639	6889	1.22	104	119–161	17.39
PCHASH11	1:1	7060	9605	1.36	75	84–136	1.44
PCHASH12	1:2	7535	12305	1.63	130	149–192	1.28
PCHASH23	2:3	5951	6721	1.14	82	93.5–135.5	5.78

as found by Tanka et al. in the LC polymer of various molecular weights and spacer lengths [12].

Thermogravimetric analysis (TGA) thermograms were obtained by heating the samples of about 5–6 mg inside the sample chamber in nitrogen atmosphere at a heating rate of 10°C per minute are shown in Fig. 3. From the TGA thermograms of PCHAS and PCHASHs it

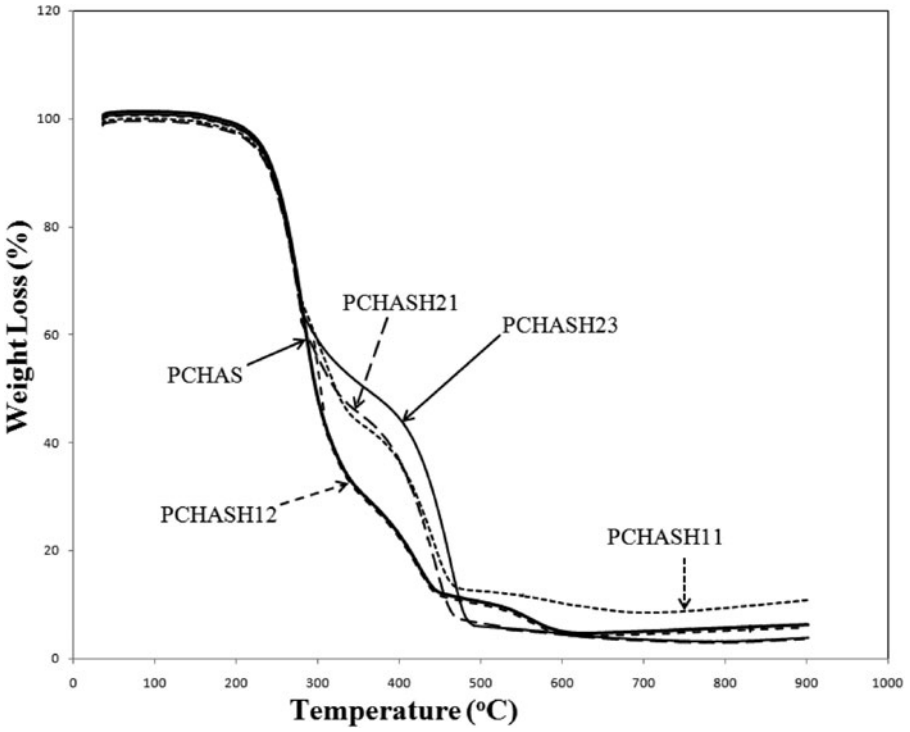


Figure 3. TGA thermograms of PCHAS and PCHASHs.

Table 2. Variation of current (mA) against voltage (V) of 25-μm-thick pellet for PCHAS and PCHASH11

PCHAS	Current (mA)			PCHASH11	Current (mA)		
Voltage (DC)	30°C	60°C	120°C	Voltage (DC)	30°C	60°C	90°C
0.00	0.0	0.00	0.00	0.00	1.0	0.00	0.00
1.00	0.40	0.50	0.25	1.00	0.19	0.21	1.15
2.00	1.46	1.62	2.84	2.11	0.42	0.75	3.34
3.09	3.22	3.55	4.85	3.03	0.68	2.53	3.34
4.01	6.14	6.25	8.88	4.19	0.92	3.78	4.17
5.00	9.11	9.25	12.25	5.09	1.48	6.42	7.82
6.00	26.00	32.50	34.00	6.00	2.20	15.00	43.75
7.08	40.75	47.00	49.00	8.04	4.20	59.5	75.00
8.10	58.75	63.50	65.00	11.19	71.13	76.00	125.50
9.00	74.75	77.75	80.00	13.02	74.75	77.75	80.00
10.00	84.31	88.56	89.00	24.02	223.00	230.00	238.75
12.02	106.00	107.00	112.00				
14.00	120.25	123.75	127.20				
24.60	212.75	214.00	224.00				

is evident that they are all stable up to about 195°C after which degradation starts and are decomposed completely at around 495°C.

4. Electrical Properties

The current (I) versus DC voltage (V) measurements were carried out by 2-probe method in ambient temperature and under a relative humidity of 50%. A good electrical performance is observed as shown in Table 2 supported by the similar observation by Mcculloch et al. for LC semiconducting polymers [13]. I-V characteristics of 25-μm-thick pellet reveals that the breakdown voltage is very close to 5 volt for PCHAS (Fig. 4(a)) and slightly greater than 7 volt for PCHASH11 at 30°C (Fig. 4(b)) where, when the voltage is raised further caused a sudden rise of about 50 mA current. Breakdown voltage decreases with the rise of temperature for both PCHAS and PCHASH11. Both the PCHAS and PCHASH11 show ohmic behavior before and after the breaking voltage. Observation shows that PCHASH11 is more stable than PCHAS at 30°C.

The bulk resistance of CHA, PCHAS, and PCHASH11 were evaluated by the complex impedance-admittance plots recorded from 35°C (308 K) to 105°C using a HIOKI 3532-50 LCR HiTESTER frequency response analyzer. The plots were recorded in the frequency range from 40 Hz to 30 kHz keeping the signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity is SS | 25-μm-thick polymer pellet | SS, where SS plate (SS stands for Stainless Steel) was used as electrode. The electrical conductivities of CHA, PCHAS, and PCHASH11 were calculated form bulk resistance as Chetri et al. determined for poly(2-vinyl pyridinium) salts in solid state [14] following the equation, $\sigma = (d/A) \times R$, where d = thickness of the pellet, A is the area of the pellet, and R = Bulk resistance. The calculated conductivities values of CHA, PCHAS, and PCHASH11 are shown in Table 3. It is observed that the conductivity of CHA is almost constant with the rise of temperature

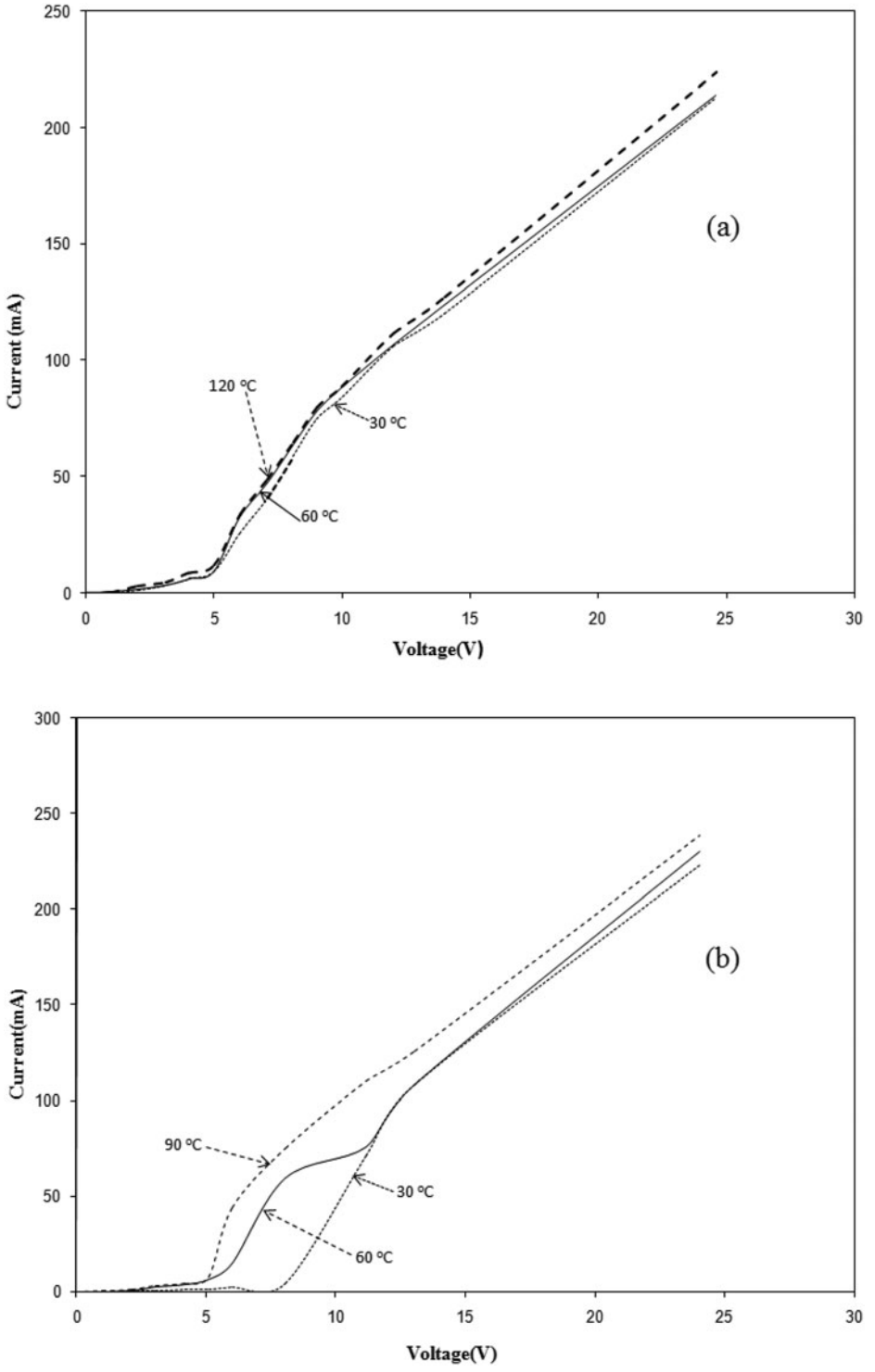


Figure 4. I-V characteristics of (a) PCHAS and (b) PCHASH11 at different temperatures.

Table 3. Variation of conductivity with Temperature of CHA, PCHAS, and PCHASHs

	Conductivity, σ (S/cm)					
Temperature T (K)	CHA	PCHAS	PCHASH21	PCHASH11	PCHASH12	PCHASH23
308	4.83×10^{-8}	2.48×10^{-10}	1.43×10^{-8}	2.23×10^{-10}	5.21×10^{-8}	7.54×10^{-8}
318	5.79×10^{-8}	3.29×10^{-10}	3.48×10^{-8}	2.40×10^{-10}	5.38×10^{-8}	7.83×10^{-8}
328	7.24×10^{-8}	2.41×10^{-10}	7.10×10^{-6}	2.63×10^{-10}	6.44×10^{-8}	1.59×10^{-7}
338	6.44×10^{-8}	3.48×10^{-9}	3.99×10^{-8}	3.05×10^{-10}	7.43×10^{-8}	3.15×10^{-3}
348	6.44×10^{-8}	4.50×10^{-9}	1.19×10^{-6}	2.41×10^{-8}	3.00×10^{-7}	3.27×10^{-9}
358	6.58×10^{-8}	5.46×10^{-9}	1.28×10^{-5}	2.90×10^{-8}	1.05×10^{-6}	3.54×10^{-3}
368	4.53×10^{-8}	7.08×10^{-9}	1.22×10^{-5}	5.79×10^{-5}	2.26×10^{-6}	8.42×10^{-4}
378	4.83×10^{-8}	7.65×10^{-9}		4.14×10^{-4}		

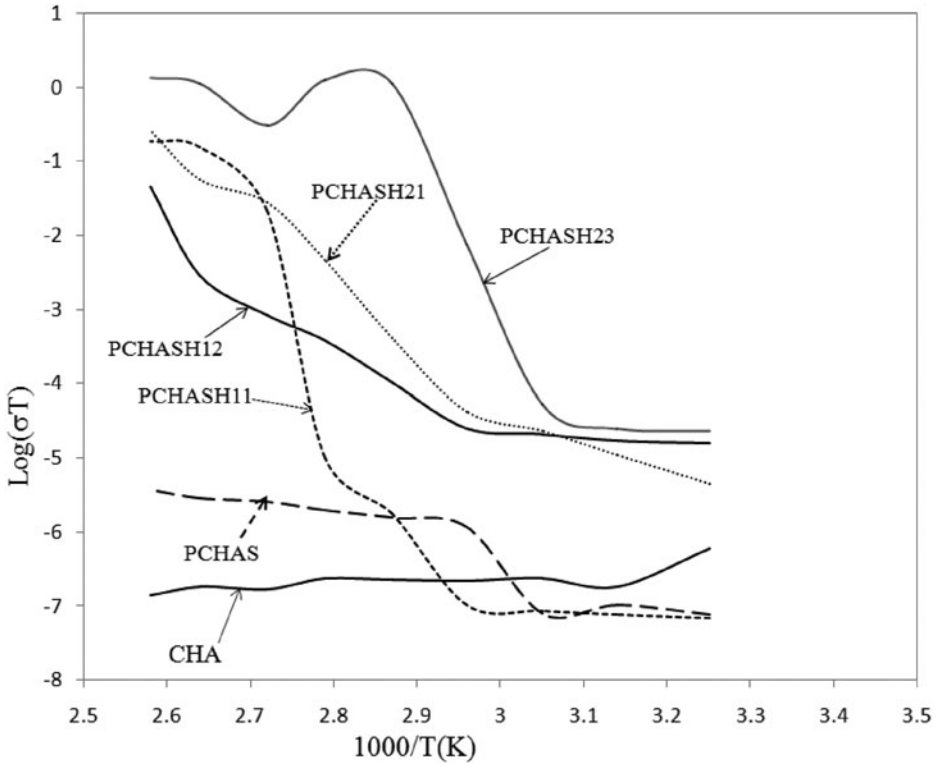


Figure 5. Plot of 1000/temperature (TK) versus Log (σT) of polysulfone and copolysulfones.

(Fig. 5). The conductivities of PCHAS and all PCHASHs except PCHASH23 are increased gradually with the rise of temperature. The conductivity increases due to the mobility of lone pair electron of sulfur in the sulfonyl group of PCHAS and PCHASHs with the rise of temperature.

5. Optical Properties

The phase transition temperatures from isotropy to cholesteric of the PCHAS and PCHASHs were observed by heating very small amount of samples under the hot stage microscope and photographed with the camera attached are shown in Fig. 6(a), 6(b), 6(c), and 6(d). The DSC heating curves of PCHAS and PCHASHs (Fig. 7) display phase transitions which are quite similar with the results found from hot stage on heating and are shown in Table 1. The polysulfone, PCHAS exhibited characteristics, cholesteric oily green color focal-conic texture at 140°C under polarizing optical microscope in heating cycle. It is well known that selective reflection of light occurs when its wavelength is equal to the pitch of the helical structure in the chiral nematic phase. Both PCHAS and all PCHASHs 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 [15]. The low value of ΔH at peaks 144°C and 136°C for PCHAS and PCHASH11, respectively, indicate the transition from LC phase to isotropic phase (Table 1). Thus the polysulfone, PCHAS and also copolysulfones, PCHASHs displayed

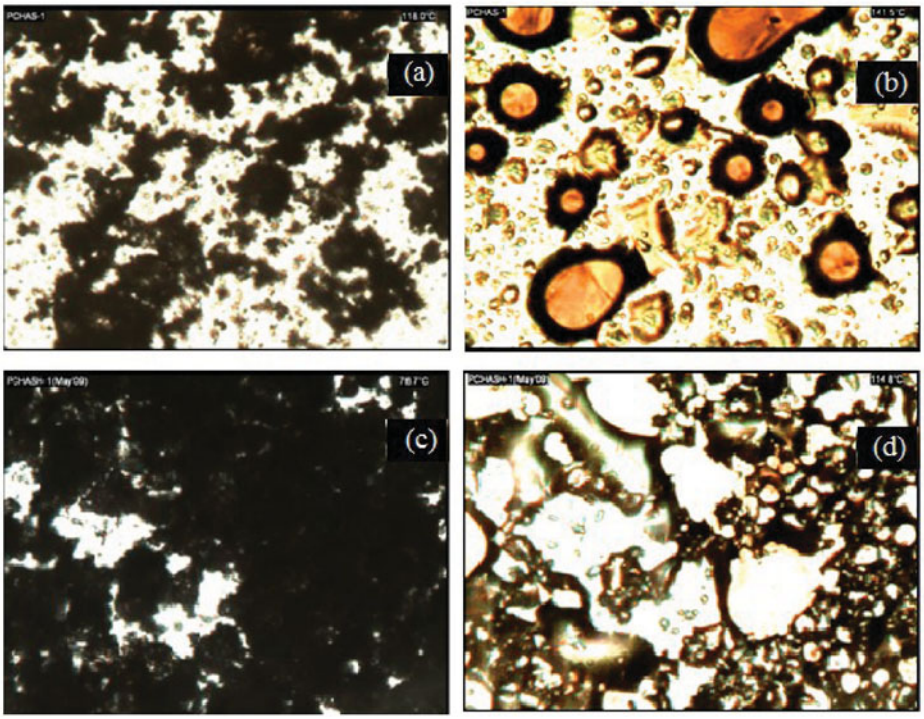


Figure 6. Picture under hot stage microscope of PCHAS at (a) 118°C and (b) 140.5°C, of PCHASH11 at (c) 78.7°C and (d) 114.8°C.

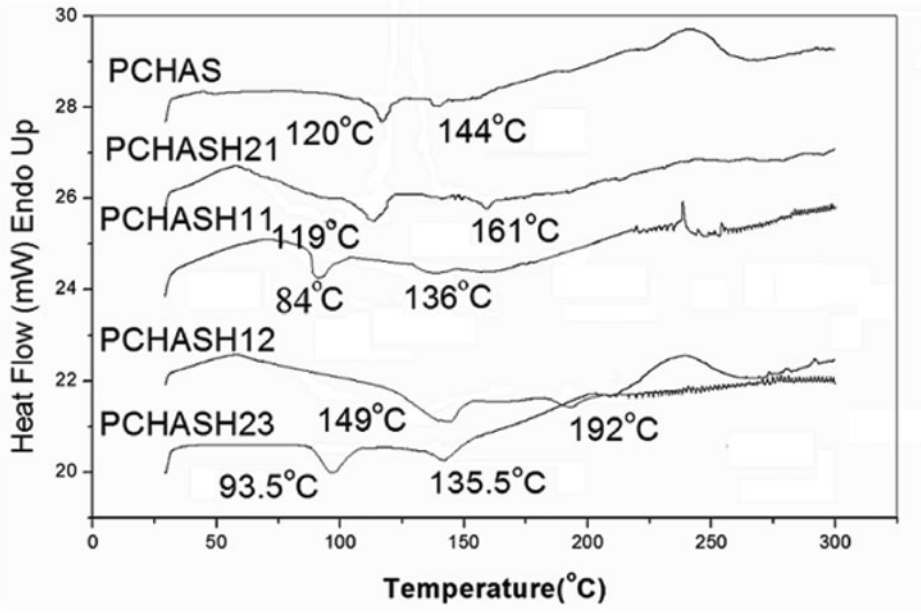


Figure 7. DSC results of PCHAS and PCHASHs.

oily green color focal-conic texture of nematic phase only in heating cycle so they are monotropic.

The liquid crystaline properties of the synthesized PCHAS and PCHASHs were also determined by DSC analysis. The results were obtained by heating 2–5 mg of the samples inside the sample chamber in nitrogen atmosphere at a heating rate of 5°C per minute and the data are presented in Table 1. Two distinct phase transitions are observed in the DSC heating curves of polysulfone and copolysulfones (Fig. 7). The phase transition at the higher temperature (T_{cl}) is for the isotropic melt and is further confirmed by the hot-stage and the polarizing microscope fitted with it. In this study, it is found that the LC phase transition temperature ranges of PCHASHs are more than the PCHAS. The phase transitions, particularly melting and LC transitions are strongly molecular weight dependent up to a certain molecular weight, for both main chain and side chain liquid crystalline polymers and also for LC copolymers as observed by Filip et al. [16]. Although in our study, it is found that the LC phase transitions of PCHASHs are independent of M_n, the T_{cl} of PCHASHs increase with the increase in composition of 1-hexene in the copolysulfones. The value is highest in case of copolysulfone PCHASH12.

LC polymers having identical main chains can show very different T_g values depending on their mesogenic groups and the spacer length as reported by Srivastava [17]. We also observed similar data with PCHASHs (Table 1).

5. Conclusions

It was observed that both PCHAS and PCHASHs exhibited good thermotropic liquid crystalline phases in certain temperature regions on heating phase only, therefore they are monotropic. In our study, it was found that the LC phase transition temperature ranges of PCHASHs were more than the PCHAS. Since the DC breakdown voltage of PCHASH11 was higher than PCHAS, it is more stable than PCHAS at 30°C. The conductivities of PCHAS and all PCHASHs except PCHASH23 were increased gradually with the rise of temperature.

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