Liquid Crystalline Behaviors of Polycholesterylmethacrylate and Poly(Cholesterylmethacrylate Co-1-hexene), Their Synthesis and Characterization

Samiul Hoque¹, Narendra Nath Dass¹, K. G. Bhattacharyya², and Neelotpal Sen Sarma¹
¹Physical Sciences Division, Polymer Section, IASST, Paschim Boragaon, Assam, India
²Department of Chemistry, Gauhati University, Guwahati, Assam, India

The synthesis of polycholesterylmethacrylate and poly(cholesterylmethacrylate-co-1-hexene) at different monomer feed ratios with their liquid crystalline behaviours have been reported in this article. Liquid crystalline phases of the polymer and copolymers have been detected under the hot stage microscope and also by differential scanning calorimetric and X-ray diffraction technique. The polymers are characterized by IR spectroscopy, proton NMR spectroscopy and GPC system. The reactivity ratios of cholesterylmethacrylate and 1-hexene are found to be \( r_1 = 2 \) and \( r_2 = 1.6 \), respectively. The number average molecular weight of the polymer is \( 1.01 \times 10^4 \) Daltons and that of the copolymers are much higher than the polymer.

Keywords Mesogens; Monomer feed; Polycholesterylmethacrylate; Polymer synthesis; Reactivity ratio

INTRODUCTION

The liquid crystalline state is the tendency of the molecules (mesogens) in a compound to point along a common axis, called the director at particular temperature range. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, the molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is in between the traditional solid and liquid phase. This is the origin of the term mesogenic state, used synonymously with liquid crystal state. Liquid crystalline polymers are a class of materials that combine the properties of polymers with those of liquid crystals. These “hybrids” show the same mesophases characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers[1].

A large number of liquid crystalline monomers have been synthesized and studied by different workers[2-6]. It is known that cholesteryl, cholestanyl, sitosteryl esters exhibit the liquid crystalline properties. Cholesterol has relatively small hydrophilic group (3β-OH) and a stereo chemically fused flat ring. Cholestanol is the dihydrocholesterol. Toth et al. in the year 1970 reported the liquid crystalline properties of cholestanol acrylate[7]. De Visser et al. in the year 1971 carried out thermal bulk polymerization of cholesterlylacyrlate to study the monomer ordering on polymerization rate and polymer properties[8]. Motoc et al. in the year 1979 reported the mesomorphic properties of sitosteryl esters[9]. Different types of copolymerization of mesogenic monomer were carried out by Hardy et al. in the year 1982[10]. Osada and his co-worker had synthesized the co-polymer of cholesteryl methacrylate with alkyl methacrylate and identified their liquid crystalline order[11]. Filip et al. also studied different liquid crystalline co-polymers using cholesteryl moiety as mesogenic group[12].

Singh et al. in the year 2001 synthesized the blends of two members of a group of side-chain cholesteric liquid crystalline silicones to study their phase behaviour by differential scanning calorimetry (DSC) and polarizing optical microscope[13]. The polymeric liquid crystals they synthesized were siloxane-based side-chain cyclic copolymers. These polymers differ only in the ratio of chiral (cholesterol derivative) to nonchiral mesogens (x: 1-x). As this ratio increases, the pitch of the polymer decreases. Srivastava in the year 2003 developed mesomorphic poly (methyl methacrylate) from methacrylate monomers by free radical polymerization using AIBN as initiator and studied their liquid crystalline behaviours using DSC result and X-ray studies[14]. Zhou et al. reviewed the current status of self-assembling liquid crystalline polymers comprising cholesterol[15]. They synthesized main chain liquid crystalline polymers and discussed about structure-property relationships and strategies to direct ordering and packing of meso- and nanostructures of cholesterol polymers in the neat- or melt state and in solution.

In the present work 1-hexene (achiral) has been chosen as the spacer group with chiral cholesterylmethacrylate
molecule and its properties were thoroughly studied keeping in the mind that incorporation of the spacer group (1-hexene) in the polymeric chain would change its liquid crystalline range and as such liquid crystalline phase transition temperature can be altered, whenever necessary changing 1-hexene ratio. Copolymerization involved in the process also improves the physiochemical property of the materials as found by Matariya et al. [16].

**EXPERIMENTAL**

**Materials**

Cholesterol (Merck), methacrylic acid (Merck), ethyl methyl ketone (Merck), chloroform (Ranbaxy), methanol (Ranbaxy), AIBN (Merck), benzene were used without further purification. The 1-hexene (Merck) was purified as reported in the literature [17].

**Preparation of Methacryloylchloride**

The methacryloyl chloride was prepared by distillation of methacrylic acid and benzoyl chloride in 1:2 mole ratios with 0.05 g of hydroquinone at its boiling point in a 25 cm long distilling column. The receiver contains hydroquinone kept inside an ice bath. Redistillation gave pure methacryloyl chloride.

**Preparation of Cholesterylmethacrylate (CHMA)**

One mole of both cholesterol and methacryloyl chloride each was dissolved in ethyl methyl ketone (MEK) and then stirred for 5–6 h in 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 times with distilled water. The organic layer was separated and distilled to remove ethyl methyl ketone (MEK). The viscous organic liquid on cooling gave CHMA. CHMA was recrystallized and finally purified by column chromatography. The yield of the product: 75.76%. Liquid crystalline phase transition temperature is 85°C–115°C.

**Preparation of Polycholesterylmethacrylate (PCHMA)**

One mole of the mesogenic ester, CHMA and 1 mol% of AIBN was dissolved in chloroform in a flask. The reaction flask was evacuated by vacuum pump and then heated for 24 h at 70°C. When the reaction was completed, the reaction mixture was poured in acidified methanol. The white color polymer (PCHMA) was then precipitated from hot methanol containing traces of chloroform. Finally the residue was washed several times with MEK and dried over dessicator.

**Preparation of Polycholesteryl methacrylate Co-1-hexene (PCHMAH)**

The mesogenic ester CHMA with 1-hexene at different mole ratios were dissolved in chloroform in presence of AIBN initiator and the polymerization was done as before. The copolymers (PCHMAH) were precipitated from hot methanol containing traces of chloroform. Finally the co-polymers were washed several times with MEK and dried over dessicator.

The IR spectra were recorded using Bruker Vector 22 Spectrophotometer in the range 400–4000 cm⁻¹. The proton NMR (¹H-NMR) spectra were recorded by Varian 400 MHz FT NMR in chloroform D. The molecular weights were measured in THF with a three column GPC system (WATERS). The liquid crystalline phase transition temperature was detected by the phase change with the help of Mettler Toledo F90 hot stage fitted with polarizing optical microscope and camera. The DSC results were obtained from Perkin Elmer DSC6000 by heating the samples at heating rate 5°C per minute in nitrogen atmosphere. X-ray diffraction (XRD) studies were carried out by XRD D8 ADVANCE BRUKER instrument at scan rate 2 sec per step.

**RESULTS AND DISCUSSION**

The polymerization of mesogenic monomer CHMA with 1-hexene can be initiated by AIBN by free radical mechanism of polymerization and co-polymerization. The mesogenic monomer CHMA is selected to see the effect of methyl group in the side chain. The reactivity ratio in the copolymerization reaction of CHMA and 1-hexene are \( r_1 = 2.0 \) and \( r_2 = 1.6 \) respectively. Therefore, the block copolymers will have a long sequence of monomer CHMA followed by a long sequence of monomer 1-hexene alternately.

The schematic synthetic path of monomer and polymer (see Scheme 1) are shown below:

The FT-IR spectra were recorded for different functional groups from the transparent pellet of sample and potassium bromide (KBr) by mixing at mortar in the ratio 1:10. The IR spectra of CHMA show the strong bands at 1720 cm⁻¹ and 1179 cm⁻¹ for symmetric stretching frequency of C=O and C-O of ester group (Fig. 1). A strong band for C=C is observed at 1639 cm⁻¹. The ester C=O

![SCH. 1. Schematic synthetic path of CHMA, PCHMA, and PCHMAH.](image-url)
symmetric stretching band for polymer molecule appears at the same position at 1720 cm\(^{-1}\) as we found in its ester molecule but the band for C–C is absent because of the conversion of π bond to π\(^{1}\) [18].

The typical \(^{1}\)H-NMR spectra for methacrylic residue of ester CHMA is shown in Figure 2(a). The peak for CH\(_3\) proton appears at a chemical shift of δ 3.1 ppm and the H\(_2\)C– protons give two different signals for the two protons, one is at higher chemical shift at δ 6.1 ppm and the other at δ 5.5 ppm due to the different orientation of the two protons. The OC–H proton gives a signal at chemical shift of δ 4.8 ppm and corresponding to signal at 4.6 ppm as reported by Casper et al.[19] for 1-Ethoxycarbonyl -1-[5-(Cholesterlyoxyxcarbonyl)pentoxycarbonyl] -2- vinyloxy- cyclopropane. The \(^{1}\)H-NMR signal for =CH protons of cholesteric residue appears at a chemical shift of δ 5.4 ppm.

The \(^{1}\)H-NMR signals for protons =CH and OC–H of mesogenic residue in the polymer molecule appear at chemical shift δ 5.4 ppm and δ 4.7 ppm respectively (Fig. 2(b)). The other signals found for the ester are absent indicating the formation of the polymer of CHMA. The peak at δ 2.3 ppm in PCHMAH accounts for CH proton as reported[20]. Further, the new signal appearing at δ 2.45 ppm confirms the formation of the copolymer (Fig. 2(c)). The composition of the copolymers can be determined from \(^{1}\)H-NMR spectra and their reactivity ratios are calculated using Finemann and Ross method (Fig. 3). The reactivity ratios of monomer CHMA and 1-hexene are found as r\(_1\) = 2.0 and r\(_2\) = 1.6, respectively.

The molecular weights of the polymers were determined using THF as solvent and polystyrene as the standard. All together three standards were used and are \(0.27 \times 10^4\), \(0.64 \times 10^4\), \(480 \times 10^4\) Daltons. The number average molecular weight (M\(_n\)) of the polymer PCHMA is \(1.01 \times 10^6\) Daltons and weight average molecular weight (M\(_w\)) is \(1.30 \times 10^4\) Daltons with polydispersity 1.29 (Fig. 4(a)), but the molecular weight of the copolymers (Fig. 4(b)) are found higher than the PCHMA. The M\(_n\), M\(_w\) and intrinsic viscosities of the polymer and copolymers are given in Table 1. The ‘K’ and ‘a’ values are determined from intrinsic viscosities using Mark-Houwink-Sakurada equation for the copolymer. The values are found to be \(1.50 \times 10^{-4}\) dl/g and 0.85, respectively, for benzene used as solvent.

The phase transition temperatures from anisotropy to isotropy of the polymers can be observed under the hot stage microscope and photographed with the camera attached. It is seen that the phase transition temperature
changes with the monomer feed in the copolymers. The liquid crystalline phase transition temperatures for the polymers and the copolymers are indicated in Table 2.

The DSC heating curve of polymer and copolymers (Fig. 5) in nitrogen gas atmosphere display phase transitions which are quite similar with the results found from hot stage on heating and also transition enthalpies for that polymers and copolymers are shown in Table 2. The DSC plots seem to consist of two distinct phase transitions. The phase transition at the higher temperature is for the isotropic melt, as observed under the polarizing microscope (Figs. 6a and b). Moreover, a slow increase of the specific heat is observed just before the phase transition at lower temperature for the polymer and copolymers. It seems possible that this increase results from the occurrence of a glass transition as reported[21].

The low values of transition enthalpies in all polymers (Table 2) further confirmed the formation of LC order in polymer and copolymers[22]. XRD studies are carried out to obtain more detailed information on the mesogenic phase structure. In general, a broad peak associated with lateral packing is observed in wide-angle X-ray diffraction (WAXD) curves for the mesophase phase of the polymer and copolymers are shown in the Figure 7 as referred by Zheng et al.[23]

We also synthesized and characterized liquid crystalline polycholesteryl acrylate (PCHMA) and copolymers of cholesteryl acrylate with 1-hexene (PCHAH) and reported earlier[24]. The liquid crystalline phase transition temperatures of PCHMA and PCHMAHs are compared with

<table>
<thead>
<tr>
<th>Polymer/co-polymers</th>
<th>Molar ratio in</th>
<th>Weight average molecular weight ((M_w)) Daltons \times 10^{-4}</th>
<th>Polydispersity</th>
<th>Intrinsic viscosities (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCHMA</td>
<td>1.01</td>
<td>1.30</td>
<td>0.38</td>
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<tr>
<td>PCHMAH21</td>
<td>2:1</td>
<td>1.29</td>
<td>0.41</td>
<td></td>
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<tr>
<td>PCHMAH11</td>
<td>1:1</td>
<td>1.28</td>
<td>0.55</td>
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<tr>
<td>PCHMAH12</td>
<td>1:2</td>
<td>1.79</td>
<td>0.64</td>
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<tr>
<td>PCHMAH23</td>
<td>2:3</td>
<td>1.80</td>
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<tr>
<td></td>
<td></td>
<td>1.88</td>
<td>1.33</td>
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TABLE 1
Molecular weights, polydispersity and intrinsic viscosity of the polymer and co-polymers

It is found that LC phase transition temperature of PCHMA and PCHMAHs are higher than that of PCHA and PCHAHs. This is due to the presence of methyl group in the side chain of CHMA both in polymer and in copolymer.

PCHA and respective PCHAHs as shown in Table 3. It is found that LC phase transition temperature of PCHMA and PCHMAHs are higher than that of PCHA and PCHAHs. This is due to the presence of methyl group in the side chain of CHMA both in polymer and in copolymer.

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**TABLE 2**

<table>
<thead>
<tr>
<th>Polymer and co-polymers</th>
<th>No. of moles of CHMA (M1)</th>
<th>No. of moles of 1-hexene (M2)</th>
<th>M = (M1) / (M2)</th>
<th>X1 (X1)</th>
<th>X2 (X2)</th>
<th>M-M</th>
<th>PM 2</th>
<th>Phase transition temperature (°C)</th>
<th>Enthalpy change (D_Hm) for mesomorphic transformation (J·g(^{-1}))</th>
<th>Enthalpy change (D_Hi) for isotropic change (J·g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCHMA</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PCHMAH21</td>
<td>0.02</td>
<td>0.01</td>
<td>2</td>
<td>2.53</td>
<td>0.529</td>
<td>0.11</td>
<td>0.11</td>
<td>17.33</td>
<td>5.25</td>
<td>—</td>
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<tr>
<td>PCHMAH11</td>
<td>0.01</td>
<td>0.01</td>
<td>1</td>
<td>2.471</td>
<td>0.571</td>
<td>0.11</td>
<td>0.11</td>
<td>13.89</td>
<td>5.06</td>
<td>—</td>
</tr>
<tr>
<td>PCHMAH12</td>
<td>0.01</td>
<td>0.02</td>
<td>0.5</td>
<td>1.637</td>
<td>0.33</td>
<td>0.67</td>
<td>0.67</td>
<td>69.53</td>
<td>14.62</td>
<td>—</td>
</tr>
<tr>
<td>PCHMAH12</td>
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<td>0.03</td>
<td>0.67</td>
<td>1.233</td>
<td>0.408</td>
<td>0.592</td>
<td>0.592</td>
<td>67.69</td>
<td>12.44</td>
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</table>

FIG. 5. DSC of the polymer and copolymers in nitrogen gas atmosphere.

FIG. 6a. Image of PCHMAH11 under hotstage microscope at 170.4°C, magnification @ 40X, total field of view 1000μm; b. Image of PCHMAH12 under hotstage microscope at 306°C, magnification @ 40X, total field of view 1000μm.
copolymers
Polymers and 1-hexene are found as r1 group. The reactivity ratios of monomer CHMA and can be altered, whenever necessary using suitable spacer as such liquid crystalline phase transition temperature polymeric chain changes their liquid crystalline range and range. Incorporation of a spacer group (1-hexene) in the good liquid crystalline behaviour at their LC temperature range. 

CONCLUSION

The polymer PCHMA and copolymer PCHMAH show good liquid crystalline behaviour at their LC temperature range. Incorporation of a spacer group (1-hexene) in the polymeric chain changes their liquid crystalline range and as such liquid crystalline phase transition temperature can be altered, whenever necessary using suitable spacer group. The reactivity ratios of monomer CHMA and 1-hexene are found as r1 = 2.0 and r2 = 1.6, respectively. DSC result of PCHMA and PCHMAHs correlate with hot stage data. Comparison with PCHA and PCHAHs shows that LC phase transition temperatures are more for PCHMA and PCHMAHs.

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REFERENCES


FIG. 7. XRD pattern of the polymer and copolymers at their liquid crystalline phase.

TABLE 3

Comparison of liquid crystalline range of the polymers and copolymers

<table>
<thead>
<tr>
<th>Polymers and copolymers</th>
<th>Mole ratio in monomer feed</th>
<th>Liquid crystalline range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCHMA</td>
<td>—</td>
<td>181–285</td>
</tr>
<tr>
<td>PCHA</td>
<td>—</td>
<td>116–157</td>
</tr>
<tr>
<td>PCHMAH21</td>
<td>2:1</td>
<td>172–269</td>
</tr>
<tr>
<td>PCHAH21</td>
<td>2:1</td>
<td>134–171</td>
</tr>
<tr>
<td>PCHMAH11</td>
<td>1:1</td>
<td>154–254</td>
</tr>
<tr>
<td>PCHAH11</td>
<td>1:1</td>
<td>95–132</td>
</tr>
<tr>
<td>PCHMAH12</td>
<td>1:2</td>
<td>179–319</td>
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<td>PCHAH12</td>
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<tr>
<td>PCHMAH23</td>
<td>2:3</td>
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<tr>
<td>PCHAH23</td>
<td>2:3</td>
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