Chapter 3

Synthesis and characterization of side chain polyacrylate containing salicyladimine as a pendant group

3.1 Introduction

Side chain liquid crystalline polymers (SCLCPs) representing a combination of liquid crystalline behavior and polymeric properties have been the subject of intense research. The side chain liquid crystalline polymers have potential technological applications, such as optical data storage, nonlinear optics, and ferroelectrics devices [1,2]. Main chain and side chain polymeric arrangements of mesogenic units are the most common approach to obtain liquid crystalline polymers. The considerable attention has been paid to design of functionalized mesogenic monomers and their incorporation as side groups on different polymeric backbone [2], to produce anisotropic materials suitable for variety of advanced applications such as optical storage [3], nonlinear optics [4] or holographic imaging [5]. These possibilities of application can be extended by introducing different photochromic groups into the side chains of the polymers. Side chain liquid crystalline polymer containing photochromic groups were first described by Ringsdروf et al. [6]. In the past few years, a number of new liquid crystalline polymers with photochromic azobenzene, spiropyran, spironaphthoxazine
and flugimide - moieties in the side chains were synthesized and used for reversible optical data storage [7]. Paleos and Labes reported polyacrylate and polymethacrylate containing schiff base which, showed LC phases [8].

For side chain liquid crystalline polymers, the mesogenic units are usually attached to the polymeric backbone via a flexible spacer. The flexible spacer decouples the mesogenic side groups from the polymeric backbone and renders the mesogenic units to allign anisotropically. The liquid crystalline behavior is also detected when a rigid mesogenic unit is directly attached to the polymeric backbone. Poly(4-cyclohexylphenyl acrylate) [9], poly (4-biphenyl acrylate) [10], poly(4-biphenyloxycarbonylphenyl methacrylate) [11] etc. having no flexible spacer exhibit mesomorphic properties. Recently, a few groups reported the synthesis of liquid crystalline polymers containing salicyladimine as a pendant group which is able to co-ordinate with metal ions and used in different areas of material science [12-13]. In this chapter we will discuss the synthesis and characterization of a series of side chain polyacrylate containing salicylidimine as pendant group. The liquid crystalline behaviors of the polymers are detected with the help of polarized light microscope.

3.2. Experimental

3.2.1 Solvent and Chemicals

Acrylol chloride (AC) was purchased from E-Merck (Germany) and used as received. THF was refluxed with sodium metal and distilled under
reduced pressure. Benzaldehyde (E-Merck), 4-hydroxybenzaldehyde (E-Merck), 2,4-hydroxybenzaldehyde (Lancaster), KHCO$_3$ (BDH, India), p-anisidine (E-Merck), p-nitroaniline (BDH, India), Cu(II) acetate (BDH, India) and all other chemicals used are of analytical grade.

3.3 Synthesis of the Aza monomer M5 – M8

The synthetic approach for the preparation of the monomers M5 – M8 and other intermediates (M1-M4) compounds is shown in Scheme – 3.1.

a) Preparation of 4-hydroxybezylidene (M1)

In a 100 ml three necked round bottomed flask equipped with a dropping funnel and condenser. Methanolic solution of 4-hydroxybenzaldehyde (15.3 g, 0.125 mol) and aniline (0.126) were mixed and refluxed for 4h in a water bath. After 4h of reflux, the solution was chilled in ice water bath and the precipitate formed was collected by filtration. The crude product was recrystallized from methanol. Yield: 60%

FT-IR (KBr, v cm$^{-1}$): 3467.15 (Ar-OH), 1600 (-C=N-), 2800 (-CH-)

$^1$H- NMR (DMSO-d$_6$ / ppm): $\delta$ = 8.41 (1H, s, -CH=N-), 6.6 –8.3 (m, -Ar)

C$_{13}$H$_{11}$NO (197) Calcd: C 79.18 H 5.58, N 7.1 %

Found: C 78.77 H 5.57 N 7.79 %

b) Preparation (4'-hydroxybezylidene)- 4- methoxyaniline (M2)

Methanolic solution of 4-hydroxybenzaldehyde (15.3 g, 0.125 mol) and methoxy aniline (0.126 mol) were refluxed in 100 ml round bottomed flask for 4 hours. After reflux for 4h, the solution was chilled in ice water bath and the
precipitate formed was collected by filtration. The crude product was recrystallized from methanol. Yield: 55%

**FT-IR (KBr, v cm⁻¹):** 3407 (Ar-OH), 1610 (-C=N-), 2860 (-CH),

**¹H- NMR (DMSO-d₆, ppm):** δ = 8.44 (-CH=N-), 6.5-8 (Ar), 3.06(-CH₃)

C₁₄H₁₄NO₂ (227)

Calcd: C 74 H 5.72 N 6.1 %

Found: C 73.58 H 5.74 N 6.03 %

c) **Preparation of 4-methoxy- 4’ - (6-hydroxyhexyloxybenzylidine) (M3)**

A mixture of 4-hydorxybenzylidine - 4-methoxyaniline (1gm, 0.55 mmol), potassium hydroxide (1 mmol) and a small amount of potassium iodide were added to N,N-dimethylformamide (DMF) in a round bottomed flask. With stirring, 6-chloro-1-hexanol (0.55mmol) was added dropwise to the above solution at 120°C. The resulting mixture was refluxed for 24h. After the reaction mixture was poured into a large excess of water, the precipitate formed was collected and dried under vacuum. The crude product was recrystallized from ethyl acetate. Yield 70%.

**FT-IR (KBr, v cm⁻¹):** 3467.15 (Ar-OH), 1600 (-C=N-), 2800 (-CH- aliphatic)

**¹H- NMR (DMSO-d₆, ppm):** δ = 8.41 (-CH=N-), 6-8 (Ar , 3.6 (-OCH₃)

C₁₈H₂₆NO₃ (304)

Calcd: C 71.05 H 8.5 N 4.6 %

Found: C 70.58 H 7.74 N 4.03 %

d) **Preparation (6-hydroxyhexyloxybenzylidine) (M4)**

A mixture of M1 (0.75 gm, 0.57 mmol), potassium hydroxide (1 mmol) and a small amount of potassium iodide was added to 20ml N,N-dimethylformamide(DMF) solution in a 100ml of round bottomed flask. With
stirring, 6-chloro-1-hexanol (0.57mmol) was added dropwise to the above solution at 120°C. The resulting mixture was refluxed for 24h. After the reaction mixture was poured into a large excess of water, the precipitate formed was collected and dried under vacuum. The crude product was recrystallized from ethyl acetate. Yield 65%.

**FT-IR (KBr, v cm⁻¹):** 3467.15 (Ar-OH), 1600 (-C=N-), 2820 (-CH-, aliphatic)

**¹H- NMR (DMSO-d₆, ppm):** δ = 8.41 (-CH=N-), 6-8 (m, -Ar),

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₉H₂₃NO₂ (297)</td>
<td>C 76.76 H 7.74 N 4.71 %</td>
<td>C 75.58 H 6.74 N 5.03 %</td>
</tr>
</tbody>
</table>

**e) Preparation (4-acryloloxybenzylidine)-4-methoxyaniline (M7)**

4-methoxy-4'-(6-hydroxyhexyloxybenzylidine) (1mmol), triethylamine (2 ml, 1mmol), and a trace amount of hydroquinone were dissolved in tetrahydrofuran (THF), and the resulting mixture was cooled to 0°C. With stirring, acrylol chloride (1mmol) dissolved in 10ml THF was added dropwise to the solution, and the reaction mixture was stirred at the room temperature for 6h. The salt is separated by filtration. After that the solvent was removed by using rotatory evaporator. The crude product was purified by column chromatography on silica gel (eluent: CHCl₃) Yield: 50%.

**FT-IR (KBr, v cm⁻¹):** 1710 (ester, -C=O-), 1630 (-CH₂=C-), 1605 (-C=N-), 3.2 (-OCH₃),

**¹H- NMR (DMSO-d₆, ppm):** δ = 8.11(-CH=N), 6.6-8.5 (m, -Ar), 5.4 (-CH₂=C-), 3.2 (-OCH₃),

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calcd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂₁H₂₆NO₅ (374)</td>
<td>C 67.4 H 7.74 N 3.14 %</td>
<td>C 65.58 H 6.04 N 3.03 %</td>
</tr>
</tbody>
</table>
Similarly M5, M6 and M8 were synthesized utilizing the similar procedure described for the M7.

3.4. Synthesis of the $-\text{NO}_2$ group containing salicyladimine intermediates and monomers

The synthetic approach for the preparation of the monomers (L3,L4 &L7,L8) and other intermediate (L1,L2 & L5, L6) are shown in Scheme – 3.2.

a) Preparation of salicyladimine intermediate L1

A three-necked round bottomed flask fitted with a dropping funnel, and a nitrogen inlet and outlet tubes was charged with a solution of 0.04 mol (4.88 g) p-hydroxybenzaldehyde in 20 ml DMF. To this solution 0.04 mol (5.52 g) p-nitroaniline dissolved in 15 ml DMF was added dropwise for a period of 10 min under nitrogen atmosphere. The stirring was continued throughout the reaction time. For the first 6 h reaction was carried out at room temperature and for next 6 h at 60°C. After the reaction was over, the one half of the solvent was removed by distillation under reduced pressure and then the contents of the flask were poured into crushed ice. The solid obtained was filtered, washed with hot water and dil. HCl repeatedly to remove unreacted compounds. The final purification was done by dissolving the solid in dil. NaOH followed by precipitation with dil. HCl unless complete neutralize. Thus the monomer obtained was dried in vacuum at 80 °C for 24 h. Yield was 52% (Scheme 3.2).
FT-IR (KBr, ν cm⁻¹): 3551 (Ar-OH), 1610 (-C=N), 2800 (-CH-), 1345 (-NO₂)

¹H- NMR (DMSO-d₆ / ppm): δ = 8.41 (1H, s, -CH=N-), 6.6 – 8.3 (m, Ar),

C₁₃H₁₀N₂O₃ (242)  Calcd:  C 64.46  H 4.13, N 11.5  %
Found:  C 65.12 H 4.57 N 10.86  %

Figure 3.1: FT-IR spectra of compound L₁

b) Synthesis of salicyladimine intermediate L₂

Similarly the other monomer L₂ has been synthesize using a similar procedure as described for the preparation of L₁ using 2,4-dihydroxy benzaldehyde instead of hydroxybenzaldehyde.

FT-IR (KBr, ν cm⁻¹): 3551 (Ar-OH), 1615 (-C=N), 2820 (-CH-), 1340 (-NO₂)

¹H- NMR (DMSO-d₆ / ppm): δ = 8.41 (1H, s, -CH=N-), 6.6 – 8.3 (m, Ar),
c) Synthesis of acrylate monomer L3

A mixture of L1 (1 mmol), triethylamine (2 ml, 1 mmol), and a trace amount of hydroquinone were dissolved in tetrahydrofuran (THF), and the resulting mixture was cooled to 0°C. With stirring, acrylol chloride (1 mmol) dissolved in 10 ml THF was added dropwise to the solution, and the reaction mixture was stirred at the room temperature for 6h. The salt was separated by filtration. After that the solvent was removed by using rotatory evaporator. The crude product was purified by column chromatography on silica gel (eluent: CHCl₃) Yield: 50%.

FT-IR (KBr, ν cm⁻¹): 1710 (ester, -C=O-), 1630 (-C=C-), 1601 (-C=N-), 2860 (-CH), 1348 (-NO₂)

¹H-NMR (DMSO-d₆, ppm): δ = 8.11(-CH=N-), 6.6-8.5 (Ar), 3.2 (-CH₂-),

Similarly L4 has been prepared by the same procedure described above.

d) Preparation of salicyladimine intermediate L5

A mixture of L2 (0.27 mmol), potassium hydroxide (1 mmol) and a small amount of potassium iodide was added to 20 ml N,N-dimethylformamide should (DMF) in a 100 ml of round bottomed flask. With stirring, 6-chloro-1-hexanol (0.27 mmol) was added dropwise to the above
solution at 120°C. The resulting mixture was refluxed for 24h. After the reaction mixture was poured into a large excess of water, the precipitate formed was collected and dried under vacuum. The crude product was recrystallized from ethyl acetate. Yield 65%.

FT-IR (KBr, v cm⁻¹): 3467.15 (Ar-OH), 1600 (-C=N-), 2800 (-CH), 1440 (-NO₂)

¹H-NMR (DMSO-d₆, ppm): δ = 8.41 (-CH=N-), 6-8 (-Ar), 3.6 (-CH₂-)

C₁₉H₂₂N₂O₄ (342) Calcd C 66.66 H 6.43 N 8.18 %
                 Found   C 66.58 H 6.74 N 8.03 %

Similarly the L6 has synthesized according to the procedure described above for L5 with slight modification.

3.5. Polymer Synthesis

Synthesis of Polyacrylate (P1- P8)

All the polymerizations reactions were carried out in a 100ml three necked round bottomed flask fitted with a N₂ inlet and a condenser, using AIBN as free radical initiator (0.5% w/w with respect to monomer) in a dry THF solution. The reaction mixture was introduced in the round-bottomed flask, which was fitted with a nitrogen inlet and a stirrer. The polymerization reaction was carried at 70°C for 48h. The polymer was precipitated in methanol and the product was washed several times with methanol for the removal of the unreacted monomer. The crude product was dissolved in THF and reprecipitated twice with methanol and dried under vacuum at 40°C for 24h.
Scheme 3.1. Synthesis of monomer (M1-LM) & polymers (P1–P4)
Scheme 3.2. Synthesis of monomer (L1-L6) & polymers (P5–P8)
b) Synthesis of Cu (II) Containing polyacrylate P8(Cu)

0.5 g of polyacrylate dissolved in a mixture chloroform / ethanol (1:1 V/V) of copper (II) acetate solution in 15 ml of ethanol. A solid appeared and the mixture was stirred for 2 h under reflux condition. The solvent was partly removed under rotavapor and solid was filtered off. The Cu-complexed polymer was purified by the recrerpitation technique in dichloromethane.

3.6. Results and discussion

3.6.1 Synthesis and characterization of the monomer and polymer

The Scheme 3.1 & 3.2 which shows an outline of the synthetic approach used for the preparation of the intermediates, the acrylate monomers and polymers (P1 – P8) containing salicylidimine pendant groups. The aldehyde group was condensed with aromatic amine group. The flexible spacer for the liquid crystalline moiety was introduced by alkylation of the compound (M1, M2 & L1, L2) with 6-chloro-hexanol in the presence of potassium hydroxide as a base and catalycal amount of potassium iodide thereby produced the compounds (M3, M4 & L5, L6). Esterification of the hydroxylated compounds (M1 – M4 & L1,L2, L5, L6) with acryloyl chloride is carried out in the presence of acid acceptor triethylamine (TEA) producing the acrylic monomers (M5-M8 & L3,L4, L7,L8 ). All the acrylate monomers are obtained in good yield with satisfying purity. The intermediates, monomers and polymers are characterized by IR, 'H-NMR and UV- Vis spectra and the results are summarized in (Table 3.1 and 3.2).
Polyacrylates P1- P8 were prepared by free radical polymerization of the corresponding acrylate monomers using 2,2’ - azoisobutyronitrile (AIBN) as the initiator (0.5 % by weight). Polymerization yields ranged between 30 – 40%. Polymeric products were precipitated in methanol. All the polymers were purified through repeated washing with warm ethanol until no monomers could be detected by thin layer chromatography (TLC).

3.6.2. FT-IR Analysis

In all the compounds M1 – M7 & L1 – L4 shows characteristics band around 1600 cm⁻¹ for -CH=N- group which confirms reaction of amine group with aldehyde group. A band at 1680 cm⁻¹ was not observed which indicates the absence of an aldehyde group in the intermediates as well as in the monomers. This also confirms the formation of – CH=N-. Band around 3400 cm⁻¹ appears which is assigned for hydroxyl groups and another bands around 1380 cm⁻¹ appears which is assigned for the bending vibration of the – OH. Absorption at 800 – 1100 cm⁻¹ is assigned for aromatic rings. In the FT-IR spectra of the monomer (M4 - M7 & L1 –L4) shows characteristics absorption for vinyl group at 1600 – 1680 cm⁻¹. In the FT-IR spectra of L1 – L8 shows characteristics absorption around 1340 for – NO₂.

The FT-IR spectra of the polyacrylate showed expected absorptions typical for groups (– CH₂ -) at 2910, 2870 cm⁻¹, for (>CHCOOAr) at 1750 cm⁻¹ and for the ester group at 1734 cm⁻¹. A characteristics absorption peak around 1600 cm⁻¹ is observed which is due to the (-C=N-) stretching of the
### Table 3.1: UV and IR data of polymer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV(nm)</th>
<th>IR (KBr) $\nu$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar$^b$</td>
<td>-CH=N$^c$</td>
</tr>
<tr>
<td>P1</td>
<td>345</td>
<td>292</td>
</tr>
<tr>
<td>P2</td>
<td>345</td>
<td>290</td>
</tr>
<tr>
<td>P3</td>
<td>343</td>
<td>291</td>
</tr>
<tr>
<td>P4</td>
<td>335</td>
<td>280</td>
</tr>
<tr>
<td>P5</td>
<td>324</td>
<td>278</td>
</tr>
<tr>
<td>P6</td>
<td>350</td>
<td>365</td>
</tr>
<tr>
<td>P7</td>
<td>345</td>
<td>360</td>
</tr>
<tr>
<td>P8</td>
<td>340</td>
<td>375</td>
</tr>
</tbody>
</table>

$^a$In chloroform as a solvent  
$^b$UV absorption due to the aromatic rings  
$^c$UV absorption due to the $\pi \rightarrow \pi^*$ transition of the CH=N bond
azomethynic group. (Table 3.1). In the polyacrylate P6 and P8 stretching at 3400 cm\(^{-1}\) is observed which in due to the \(-\text{OH}\) group in the ortho position.

3.6.3. \(^1\text{H}-\text{NMR analysis}\)

In all the compounds M1 – M7, \(^1\text{H}-\text{NMR}\) characteristics peaks observed at \(\delta = 6 - 8\) for the aromatic protons and at \(\delta = 8.1 - 8.4\) for the protons of \(-\text{CH=N}\). An addition peak at around 8 ppm is observed for the \(-\text{OH}\) group in L2, L4, L6, L8.

The \(^1\text{H}-\text{NMR}\) spectra of the polymer P2 peaks at \(\delta = 1.6 - 2.8\) appeared for the protons of \(-\text{CH}_2\) and \(>\text{CHCOO}\). A multiplet is observed in the range \(\delta = 6-8\) ppm for the protons of aromatic protons of the polymer and peak at \(\delta = 8.4\) is observed for the protons of \(-\text{CH=N}\) group.

3.6.4. UV – Visible Analysis

In all the polyacrylates exhibit a UV absorption band between 341 and 345 nm due to the \(\pi \rightarrow \pi^*\) transition of the -CH=N bond in the pendant aza group and a UV absorption band around 263 nm is due to the absorption of the aromatic rings in chloroform (Table 3.1).
3.6.5. Molecular weight and Solubility of the Polyacrylates

The polymers are soluble in common organic solvents such as tetrahydrofuran (THF), dichloromethane and chloroform. The inherent viscosity of the polyacrylates are found between 0.61 – 0.42 dL.g\(^{-1}\) and the number average molecular weights are in the range between 15,000 – 21,000 gm / mol (Table 3.2). The polydispersity index is in the range 1.42 – 1.5. It has well been established that in the free radical polymerization of acrylate monomers, the polydispersity index values obtained polymers depend on the chain termination mechanism, and the theoretical values \(M_w/M_n\) for polymers produced via radical disproportion are 1.5 and 2.0 respectively [14]. Therefore, the obtained polymers were mainly found via free radical recombination.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\eta_{inh}(\text{dLg}^{-1}))</th>
<th>(M_w)</th>
<th>(M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.61</td>
<td>21764</td>
<td>14469</td>
</tr>
<tr>
<td>P2</td>
<td>0.50</td>
<td>20071</td>
<td>11490</td>
</tr>
<tr>
<td>P3</td>
<td>0.44</td>
<td>17001</td>
<td>14000</td>
</tr>
<tr>
<td>P4</td>
<td>0.53</td>
<td>15600</td>
<td>13000</td>
</tr>
<tr>
<td>P5</td>
<td>0.56</td>
<td>17009</td>
<td>13500</td>
</tr>
<tr>
<td>P6</td>
<td>0.45</td>
<td>16500</td>
<td>12002</td>
</tr>
<tr>
<td>P7</td>
<td>0.51</td>
<td>18000</td>
<td>15600</td>
</tr>
<tr>
<td>P8</td>
<td>0.42</td>
<td>14500</td>
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</tr>
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</table>
3.7 Thermal properties and LC phase behavior of polymer

3.7.1. Mesomorphic behavior of polymer P1 – P4

The thermal properties and phase behavior of the polymers were studied by a combination of DSC and polarized light microscopy (PLM) with hot stage. The DSC thermograms of the polymer P2 is given in Figure 3.2. Polymer P2 shows a crystal to mesophase transition temperature at 120 °C (nematic mesophase) and the mesophase to isotropic transition at 280 °C. The polymer P2 exhibits a characteristics birefringence typical for nematic mesophase at 120 °C, which is detected by polarized light microscope (Figure 3.3). The polymer P2 started degradation at 300 °C. The mesophase transition of the polymer P3 in which the mesogen is attached to the acrylate backbone by a hexamethylene spacer, is observed at 100 °C with an isotropization transition at 270 °C. On heating the polymer started melting and displayed nematic mesophase at 100 °C, which is detected by polarized light microscope (Figure 3.4). But polymer P1 and P4 did not show any characteristics mesophase texture. This may be due to the absence of any electron donating group such as –OCH₃ group in the tail of the mesogen of the polymer. Polymer P2 shows liquid crystalline property without having flexible spacer in between the polymer backbone and mesogen. This may be due to the flexible characteristics of the polymer backbone. The introduction of flexible spacer in P3 brings down the mesophasic transition temperature (Table 3.3 & 3.4).
3.7.2. Thermal & mesomorphic behavior of polymer P5 – P8

The thermal properties and phase behaviors of the polymers are summarized in Table 3.3. The acrylate monomers did not show any mesomorphic behavior. The polymer P5 and P6 showed only glass transition. They did not exhibit any mesomorphic behavior when studied by DSC as well as PLM. The polymers P7 and P8 showed mesomorphic behavior. Polymer P7 shows a crystal to nematic mesophase transition temperature $T_{K-N}$ at 70 °C and the mesophase to isotropic transition at 150 °C. The polymer P7 exhibits a characteristics birefringence typical for nematic mesophase at 80 - 145 °C, when observed under polarized light microscope.
Figure 3.3: PLM photograph of polymer P2 during heating at 120 $^\circ$C

Figure 3.4: PLM photograph of polymer P3 during heating at 100$^\circ$C
The polymer P7 started degradation at 280 °C. The polymer P8 shows crystal to mesophase transition at 95 °C and mesophase to isotropic at around 165 °C (Figure 3.5). When this polymer is observed under polarizing microscopy a smectic mesophase has been observed which is characterized by the focal conic fan and homeotropic textures (Figure 3.6) [15]. The nematic mesophase of the polymer P7 is show in Figure 3.7.

Figure 3.5: DSC traces of polymer P8
Figure 3.6. Smectic mesophase of polymer P8 at 145 °C

Figure 3.7: Nematic mesophase of polymer P7 at 130 °C
Table 3.3. Thermal properties of polyacrylate P1 – P8 & P8 (Cu)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Spacer</th>
<th>Mesogenic Unit</th>
<th>$T_{meso}$ ($^\circ$C)</th>
<th>$T_{iso}$ ($^\circ$C)</th>
<th>LC Phase</th>
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<td>P2</td>
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<td>Nematic</td>
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<tr>
<td>P3</td>
<td>(CH$_2$)$_6$-</td>
<td><img src="image" alt="Chemistry Image" /></td>
<td>100</td>
<td>270</td>
<td>Nematic</td>
</tr>
<tr>
<td>P4</td>
<td>(CH$_2$)$_6$-</td>
<td><img src="image" alt="Chemistry Image" /></td>
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</tr>
<tr>
<td>P6</td>
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<td><img src="image" alt="Chemistry Image" /></td>
<td>-</td>
<td>-</td>
<td>No mesophase</td>
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<tr>
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<td>(CH$_2$)$_6$-</td>
<td><img src="image" alt="Chemistry Image" /></td>
<td>70</td>
<td>150</td>
<td>Nematic</td>
</tr>
<tr>
<td>P8</td>
<td>(CH$_2$)$_6$-</td>
<td><img src="image" alt="Chemistry Image" /></td>
<td>95</td>
<td>165</td>
<td>Smectic</td>
</tr>
<tr>
<td>P8(Cu)</td>
<td>(CH$_2$)$_6$-</td>
<td><img src="image" alt="Chemistry Image" /></td>
<td>115</td>
<td>183</td>
<td>Smectic</td>
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Table 3.4: Phase transition of the polyacrylates on heating and cooling

<table>
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<th>Polymer</th>
<th>Phase transition (°C)</th>
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<td>Heating</td>
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<tr>
<td></td>
<td>Cooling</td>
</tr>
<tr>
<td>P2</td>
<td>110 K 120 N 280</td>
</tr>
<tr>
<td></td>
<td>109 N 118 K</td>
</tr>
<tr>
<td>P3</td>
<td>90 K 100 N 260</td>
</tr>
<tr>
<td></td>
<td>89.5 N 99.8 K</td>
</tr>
</tbody>
</table>

*a K, solid; N nematic, I, isotropic

3.7.3. Influence of –OH group on the mesomorphic properties

Very interesting results have been observed in this case of polymer P8. The polymer P7 that did not contain any –OH group in the ortho position of the salicyladimine group shows only nematic mesophase where introduction of hydroxy functionalization resulted in formation of smectic mesophase. The –OH group in ortho position has played a significant role in the mesophase stability and in induction of the smectic mesophase. The introduction of ortho hydroxy functional group in bezylidine moiety manifesting intramolecular H-bonding which enhances the mesophase stability and responsible for the induction of smectic mesophase.
Scheme 3.3: Intramolecular H – Bonding in salicylaldimine group

3.8. Synthesis of Cu(II) containing polyacrylate

The hydroxyl groups in the ortho position of the salicylaldimine group forms H-bonds thereby making a strong chelation rings with the N-atom of the salicylaldimine group. The chelation rings afford an exceptionally good position to introduce transition metal. This idea motivated us to prepare the complex compound of Cu(II) with P8. The synthesis of the metal complexed polyacrylate was done by a method described elsewhere. 0.5 g of polyacrylate dissolve in a mixture chloroform / ethanol (1:1 V/V) of copper (II) acetate solution in 15 ml of ethanol. A solid appeared and the mixture was stirred for 2 h under reflux condition. The solvent was partly removed under rotavapor and solid was filtered off. The Cu-complexed polymer was purified by the recrprception technique in dichloromethane.
The complexation can easily be observed by change of the colour of the parent polyacrylate. The colour of the polymer solution has changed from light yellow to greenish when Cu(II) ions has inserted. The insertion of the copper atom has also been proved by the FT-IR spectroscopy. In the FT-IR spectra of parent polyacrylate P8, a shift of the stretching frequency of the $\nu_{\text{C=N}}$ from 1615 cm$^{-1}$ to 1600 cm$^{-1}$ observed which is mainly due to the metal complexation. The metal complexed polyacrylate was washed with methanol in order to remove any unbound copper (II) ions.
3.9. **Mesomorphic properties of Cu (II) polymer**

Mesomorphic behavior of the Cu (II) containing polymer was studied by DSC and PLM. The Cu (II) containing polymer P8 (Cu) showed a crystal to mesophase transition at 115 °C and mesophase to isotropic transition at around 185 °C. When the sample was observed under polarizing microscopy it shows a smectic mesophase in 110 – 180 °C. From this we may say that introduction of Cu(II) ions results in increase the mesomorphic to isotropic transition temperature. Introduction of the Cu(II) ions induces a larger mesomorphic range as compared to parent polyacrylate (Table 3.4).

**Table 3.4. Comparison of mesophase transition temperature of polymer P7 – P8**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_{K-N} ) (°C)</th>
<th>( T_{N-I} ) (°C)</th>
<th>Mesophase</th>
</tr>
</thead>
<tbody>
<tr>
<td>P7</td>
<td>70</td>
<td>150</td>
<td>Nematic</td>
</tr>
<tr>
<td>P8</td>
<td>95</td>
<td>165</td>
<td>Smectic</td>
</tr>
<tr>
<td>P8(Cu)</td>
<td>115</td>
<td>183</td>
<td>Smectic</td>
</tr>
</tbody>
</table>
3.10. EPR measurements of the P8(Cu)

Electron paramagnetic resonance (EPR) signals recorded on a Bruker EMX spectrometer operating in the X-band, utilizing a 100kHz field modulation and microwave power of 1 mW. The EPR signal measured at room temperature (Figure 3.9) shows a very broad, asymmetric feature centered at $g_{\text{eff}} \sim 2.05$. The signal can be interpreted as being due to Cu$^{2+}$ centers in a square planner environment.

**Figure 3.8.** Sketch of geometry of copper complexed polymer

**Figure 3.9.** X-band EPR spectra of polymer P8(Cu)
3.11. X-Ray Analysis

The X-ray diffractogram obtained for polymer P2 is represented in (Figure 3.10). This shows only a broad reflections at wide angles \(2\theta = 20^0\) (associated with the lateral packing), indicating the formation of crystalline phase [16].

![X-ray diffractogram of polymer P2](image)

\(2\theta\)

Figure 3.10. X-ray diffractogram of polymer P2

3.12. Conclusion

A series of polyacrylate containing salicyladimine pendant group have been synthesized and characterized. The mesophase behavior of the polymers are investigated along with analogous polymer. The polyacrylates containing salicyladimine group having electronic donating group in tail of the mesogenic pendant group shows mesomorphic behavior. Liquid crystalline property for such polyacrylate is also detected, even mesogen attached to the polymer backbone without having flexible spacer. It is found that the mesophasic transition temperature is reduced on introduction of flexible spacer in the acrylate monomer.
In another series where electron accepting –NO₂ groups has used in the tail of the salicyladimine pendant group. The polymer without any flexible group shows only glass transition temperature. The polymer where the salicyldaimine group is spaced from the polymer backbone by a hexamethylene alkane spacer shows mesomorphic behavior. The polymer (P7) shows nematic and the polymer P8 shows a smectic mesophase when studied by DSC and hot stage polarizing microscopy. The polymer P8 containing a –OH group ortho to the salicyldaimine group contributes to the induction of the smectic mesophase presumably due to the intramolecular H-bonding thereby making a strong chelation rings with the N-atom of the salicyladaimine group. The polymer P8 forms complex with Cu(II) ions through the ortho hydroxyl bonding and showed smectic mesomorphosim and coordination increase the larger mesomorphic range.
References:


