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Khushi Muhammad [a b], Ghulam Shabbir [a] & Shahid Hameed [b]
[a] Department of Chemistry, Government Post-Graduate Gordon College, Rawalpindi, Pakistan
[b] Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
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# Synthesis, Characterization, and Study of Thermal and Liquid Crystalline Properties of Poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic Acid)

KHUSHI MUHAMMAD,[1,2] GHULAM SHABBIR,[1] AND SHAHID HAMEED[2,*]

[1]Department of Chemistry, Government Post-Graduate Gordon College, Rawalpindi, Pakistan
[2]Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

*Poly(4-vinylphenol) was modified to poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid) for incorporating a flexible hexamethylene side chain with a terminal benzoic acid moiety to induce liquid crystallinity. The rigid core is generated through hydrogen bonding (H-bonding) between the pendant benzoic acid groups. The thermal stability of the modified polymer was determined by thermogravimetric analysis (TGA), whereas differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) were used to investigate the liquid crystalline behavior. The polymer exhibits mesomorphism over a wide temperature range.*

**Keywords** H-bonded core; liquid crystalline polymer; thermal properties



## Introduction

Polymers are modified to impart structural features, which endow specific properties for commercial applications. Another purpose of modification is the introduction of such groups that serve as reaction/binding sites. Small liquid crystal (LC) molecules are currently being employed in liquid crystal displays (LCDs); however, the manufacturing procedures with these low-molecular-mass materials are long, complicated, and costly. The LCD industry is looking for polymeric LC materials for simple and economical fabrication methods [1].

Side-chain liquid crystalline polymers (SCLCPs) are the materials being tested for use in flexible LCDs, which can be folded and rolled [2]. These polymers have been prepared by linking ligands to the base polymers either through covalent bonds or through noncovalent interactions [3]. The latter category is referred to as supramolecular SCLCPs [4]. Hydrogen bonding (H-bonding) is the most commonly employed interaction for the realization of such materials [5]. However, in either case, the approach of ligands to the polymer binding sites is a sterically hindered process.

To address the problem of restricted access, poly(4-vinylphenol) was modified to poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid). The synthesized polymer bears H-bonding sites separated from the main chain through hexamethylene units, which would

*Address correspondence to Shahid Hameed, Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan. Tel.: +92 51 9064 2133; Fax: +92 51 9064 2241. E-mail: shameed@qau.edu.pk, shahidhameed@daad-alumni.de

facilitate the approach of ligands. Polymers having such architecture also find applications in the metal ion-uptake processes [6].

The functionalized polymer was studied for its thermal, liquid crystalline, and metal ion-uptake properties. Thermogravimetric analysis (TGA) was performed to examine thermal stability. The LC temperature range was determined by differential scanning calorimetry (DSC) and the mesophase was identified using polarizing optical microscopy (POM). The metal ion-uptake by the polymer suspension in water and its tetrahydrofuran (THF) solution was determined for $Ca^{2+}$ and $Mg^{2+}$ ions at different temperatures.

## Experimental

### *Materials*

Poly(4-vinylphenol), 1,6-hexanediol, and *p*-toluenesulphonyl chloride were purchased from Aldrich Chemical Co. (Steinheim, Germany). Butanone and ethyl 4-hydroxybenzoate were purchased from Merck (Darmstadt, Germany). Butanone was dried over anhydrous $K_2CO_3$ and fractionally distilled. Diethyl ether and dichloromethane were supplied by Lab-scan. THF, pyridine, and conc. HCl were the products of Riedel-de-Haën (Seelze, Germany). Anhydrous $K_2CO_3$ and $MgSO_4$ were purchased from Fluka Chemical Co. (Buchs, Germany). Ethyl acetate and *n*-hexane were obtained from commercial source and distilled before use.

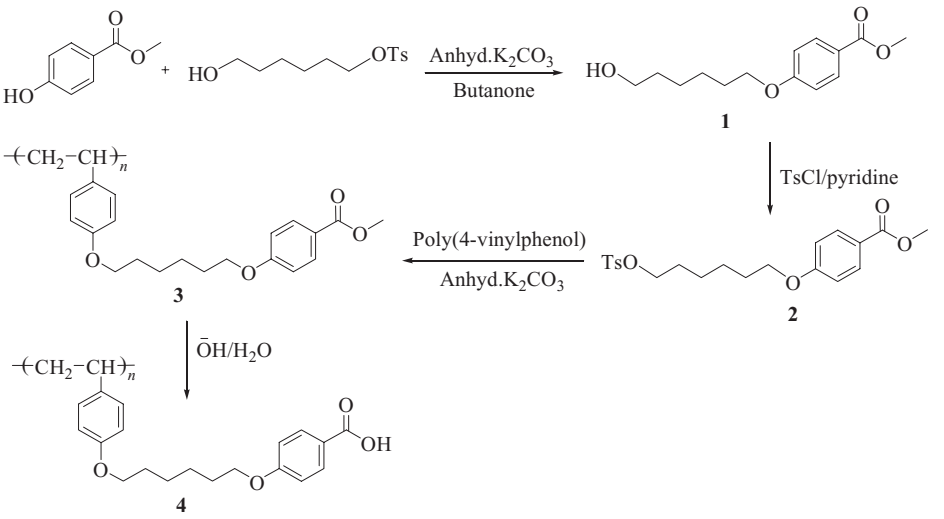
### *Characterization*

The melting points of the intermediates were determined by filling in open thin-walled capillary tubes using Gallenkamp melting point apparatus and are uncorrected. The infrared (IR) spectra were taken on Thermo Scientific Nicolet 6700 FT-IR spectrophotometer. The $^1H$ and $^{13}C$ NMR spectra were recorded on a BrukerAvance 300 MHz NMR spectrometer. TGA was performed using a Mettler Toledo TGA 851e, and the phase transition temperature was determined using DSC on a Mettler Toledo DSC 823e.The LC textures were observed using a polarizing optical microscope (Olympus BH-2) equipped with a Linkam hot-stage (LK-600PM). The $Ca^{+2}$ and $Mg^{+2}$ ions uptake capacity was determined by complexometric titrations [7].

### *Synthesis*

Poly(4-vinylphenol) was modified as outlined in Scheme 1. Methyl 4-(6-hydroxyhexyloxy)benzoate (**1**) was prepared [8] by the reaction of methyl 4-hydroxybenzoate and 6-hydroxyhexyl-4-methylbenzenesulphonate. The hydroxyl group was converted [9] into a good leaving tosyl group in (**2**). Substitution of tosyl by poly(4-vinylphenol) afforded [8] poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate) (**3**), which on hydrolysis [9] yielded the target poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid) (**4**).

*Synthesis of Methyl 4-(6-hydroxyhexyloxy)benzoate (**1**).* Methyl 4-hydroxybenzoate (1.52 g, 0.01 mol), 6-hydroxyhexyl tosylate (2.72 g, 0.01 mol), and anhydrous $K_2CO_3$ (1.38 g, 0.01 mol) were added to 40 mL dry butanone and the mixture refluxed for 8 h. The contents were transferred along with butanone washings to a separatory funnel, and butanone layer washed with 50 mL distilled water followed by 10% ice-cooled NaOH solution (2 × 50 mL). The organic layer was separated and the solvent removed under




**Scheme 1.** Reaction sequence for the synthesis of poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid) (**4**).

vacuum. The product obtained was pure enough to be used in the next step without further purification. Yield: 95%; mp: 54°C–56°C; IR ($\nu_{max}$, $cm^{-1}$): 3375, 3055, 2943, 2858, 1702, 1603, 1513, 1470, 1435, 1316, 1290, 1251, 1172, 1109, 1007, 912, 854, 771, 735, 697. $^1$H NMR ($CDCl_3$): $\delta$ 1.41–1.55 (5H, m), 1.63 (2H, quin, $J = 6.9$ Hz), 1.84 (2H, quin, $J = 6.3$ Hz), 3.68 (2H, t, $J = 6.6$ Hz), 3.40 (3H, s), 4.02 (2H, t, $J = 6.6$ Hz), 6.91 (2H, d, $J = 8.7$ Hz), 7.99 (2H, d, $J = 9.0$ Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.53, 25.85, 29.09, 32.64, 51.87, 62.86, 68.02, 114.04, 122.33, 131.58, 162.89, 166.95.

*Synthesis of Methyl 4-(6-(tosyloxy)hexyloxy)benzoate (**2**).* To an ice-cooled solution of methyl 4-(6-hydroxyhexyloxy)benzoate (2.52 g, 0.01 mol) in 30 mL pyridine was added an equimolar amount of *p*-toluenesulphonyl chloride (1.905 g) in small portions with stirring. The stirring was continued for 3 h when the reaction mixture was poured into separatory funnel containing 100 mL dichloromethane. The organic layer was washed with ice-cooled distilled water (2 × 100 mL) and subsequently with ice-cooled dil. HCl (100 mL, 10%). The organic layer was removed, dried over anhydrous $MgSO_4$, filtered, and the solvent evaporated on a rotary evaporator. The solid product was purified by crystallization from diethyl ether and dichloromethane solvent pair. Yield: 95%; mp: 71°C–72°C; IR ($\nu_{max}$, $cm^{-1}$): 2941, 2863, 1719, 1604, 1577, 1512, 1478, 1433, 1360, 1279, 1251, 1167, 1102, 1000, 953, 840, 814, 769. $^1$H NMR ($CDCl_3$): $\delta$ 1.39–1.45 (4H, m), 1.70 (2H, quin, $J = 6.6$ Hz), 1.77 (2H, quin, $J = 6.6$ Hz), 2.46 (3H, s), 3.90 (3H, s), 3.98 (2H, t, $J = 6.3$ Hz), 4.06 (2H, t, $J = 6.3$ Hz), 6.90 (2H, d, $J = 9.0$ Hz), 7.36 (2H, d, $J = 8.1$ Hz), 7.81 (2H, d, $J = 8.1$ Hz), 7.99 (2H, d, $J = 9.0$ Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 21.67, 25.17, 25.44, 28.75, 28.89, 51.88, 67.82, 70.46, 114.01, 122.40, 127.91, 129.84, 131.59, 133.09, 144.74, 162.79, 166.91.

*Synthesis of Poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate) (**3**).* Poly(4-vinylphenol) (3.6 g, 0.03 mol) was added in 50 mL dry butanone containing 4.14 g (0.03 mol) anhydrous $K_2CO_3$ and the mixture refluxed for 1 h. The reaction

mixture was cooled to room temperature and 12.18 g (0.03 mol) of methyl 4-(6-(tosyloxy)hexyloxy)benzoate was added. The reaction mixture was heated under reflux for another 36 h. The contents were poured into 500 mL distilled water accompanied by stirring with mechanical stirrer. The sticky solid was separated and purified by column chromatography using petroleum ether/ethyl acetate (90/10) as eluent. Yield: 84%; $^{1}$H NMR (THF): $\delta$ (ppm) 1.56 (5.7H, s), 1.81 (4.8H, s), 3.82 (2.8H, s), 3.85–4.05 (3.8H, m), 6.59 (4H, broad, s), 6.94 (1.95H, d, $J = 7.5$ Hz), 7.95 (1.97H, d, $J = 8.1$ Hz). $^{13}$C NMR (THF): $\delta$ (ppm) 25.92, 29.17, 29.49, 29.78, 39.62, 50.87, 67.33, 67.87, 113.87, 114.70, 122.44, 128.35, 131.21, 157.26, 162.96, 165.77.

*Hydrolysis of Poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate) (**4**).* Poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate) (5.19 g, 0.015 mol) was dissolved in a mixture of 40 mL THF and 10 mL water. To this solution 0.68 g (0.017 mol) of NaOH was added and the mixture refluxed for 12 h. After cooling to room temperature, the reaction mixture was acidified using 6 N HCl and poured into 500 mL distilled water with concomitant stirring. The pure product was filtered, washed with distilled water, and dried in vacuum desiccator at room temperature. Yield: 99.7%. IR ($\nu_{max}$, cm$^{-1}$): 3120–2580, 1678, 1604, 1511, 1472, 1426, 1287, 1240, 1166, 1107, 1009, 932, 846, 825, 772, 695, 642. $^{1}$H NMR (THF): $\delta$ 1.55 (5.7H, s), 1.80 (4.8H, s), 3.80–4.05 (3.8H, m), 6.59 (4H, broad s), 6.93 (1.95H, d, $J = 7.5$ Hz), 7.97 (1.97H, d, $J = 8.4$ Hz). $^{13}$C NMR (THF): $\delta$ 25.92, 29.18, 29.44, 39.62, 67.80, 113.71, 123.05, 128.21, 131.46, 157.12, 162.78, 166.50.

## Results and Discussion

### *Synthesis*

The formation of methyl 4-(6-hydroxyhexyloxy)benzoate (**1**) was indicated in the IR spectrum by the presence of absorption peaks in the range of 2943–2858 cm$^{-1}$ due to aliphatic C–H stretching vibrations. In the $^{1}$H NMR spectrum, the appearance of two triplets at 3.68 and 4.02 ppm, two quintets at 1.63 and 1.84 ppm, and a multiplet integrating to five protons in the range of 1.42–1.55 ppm confirmed the formation of the product. In the $^{13}$C NMR spectrum, the appearance of six signals in the aliphatic region from 25.53 to 68.02 ppm provided further confirmation of the product.

The conversion of hydroxyl group into tosyloxy group was manifested in the IR spectrum by the presence of strong absorption bands at 953 and 814 cm$^{-1}$ due to S–O–C stretching vibrations, and disappearance of broadband at 3375 cm$^{-1}$ due to OH group in the reactant. The tosylation resulted in the change of integration of multiplet at 1.55–1.42 ppm from five protons in (**1**) to four protons (elimination of hydroxyl proton) at 1.45–1.41 ppm in the $^{1}$H NMR spectrum of (**2**). The triplet at 3.68 ppm for methylene attached to OH group in hydroxyhexyloxybenzoate (**1**) was shifted downfield to 3.98 ppm in tosyloxyhexyloxybenzoate (**2**). Another indication of the reaction was provided by the appearance of an additional singlet at 2.46 ppm for three protons of methyl group in tosyl part and two doublets, each integrating to two protons, at 7.81 and 7.36 ppm due to benzene ring protons of tosyl group. The structure of the compound was further confirmed in the $^{13}$C NMR spectrum by the appearance of eight peaks in the region of 162.79–114.01 ppm indicating the presence of two phenylene rings in the product.

The synthesis of poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate) (**3**) was manifested in the $^{1}$H NMR spectrum (Fig. 1) by the disappearance of sharp singlet for three protons of methyl group in tosyl moiety, and increase in integration of albeit three protons in the aliphatic region of 1.56–4.05 ppm corresponding to polyvinyl main chain of the

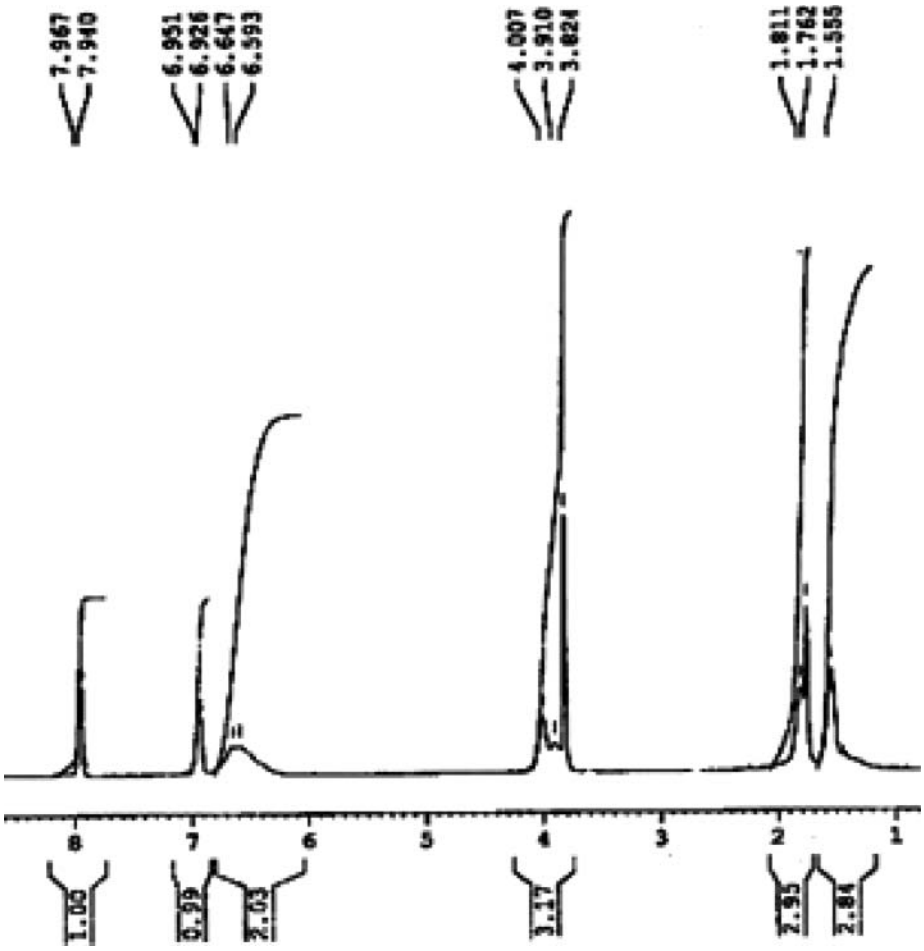



**Figure 1.** $^{1}$H NMR spectrum of poly(methyl 4-(6-(4-vinylphenoxy)hexyloxy)benzoate).

polymer. The extent of substitution was 97.5%, as calculated from integration of the signal for aromatic protons at 6.94 ppm.

The hydrolysis of polymer (**3**) into the target poly(4-(6-(4-vinylphenoxy) hexyloxy)benzoic acid) (**4**) was indicated in the IR spectrum by the presence of a broad-band in the range of 3120–2580 $cm^{-1}$ due to carboxyl O–H stretching vibrations and a sharp absorption peak of medium intensity at 932 $cm^{-1}$ due to O–H out-of-plane bending vibrations. In the $^{1}$H NMR spectrum, the appearance of a broad signal for carboxyl proton at 11.02 ppm and disappearance of ester methyl singlet at 3.82 ppm provided further confirmation of hydrolysis (Fig. 2). The degree of substitution remained unaffected by hydrolysis, as shown by integration of H-signal at 6.93 ppm.

### *Thermal Stability*

Thermal stability of poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid) was determined by TGA. The polymer was found thermally stable up to 447°C and 56.16% decomposition occurred at 447.5°C, whereas 84.57% degradation was observed at 507.2°C (Fig. 3).

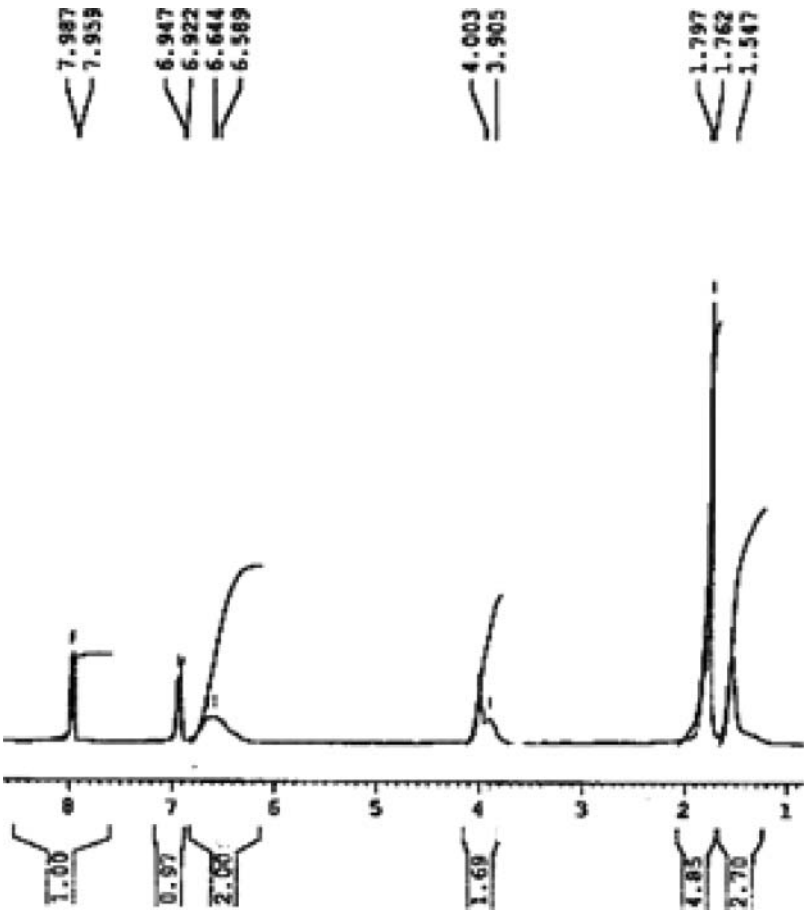



**Figure 2.** A part of $^{1}$H NMR spectrum of poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid).

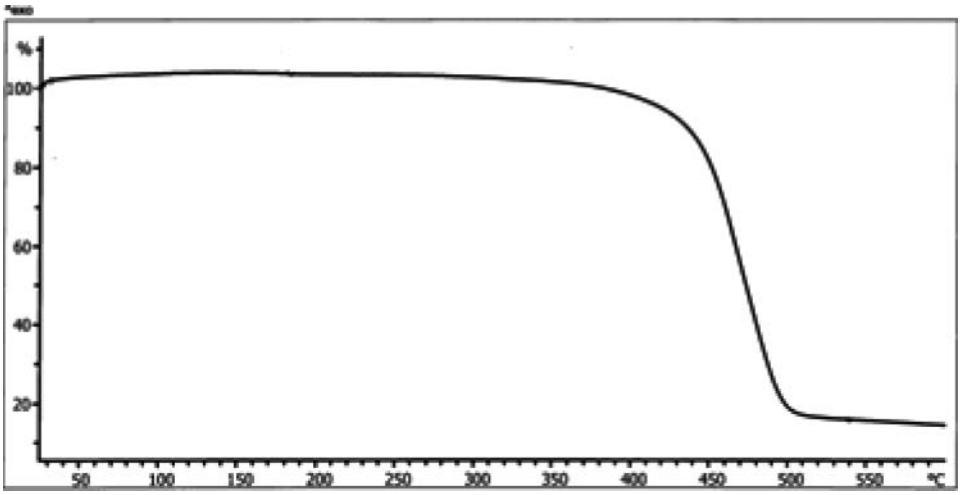



**Figure 3.** Thermogram of poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid).

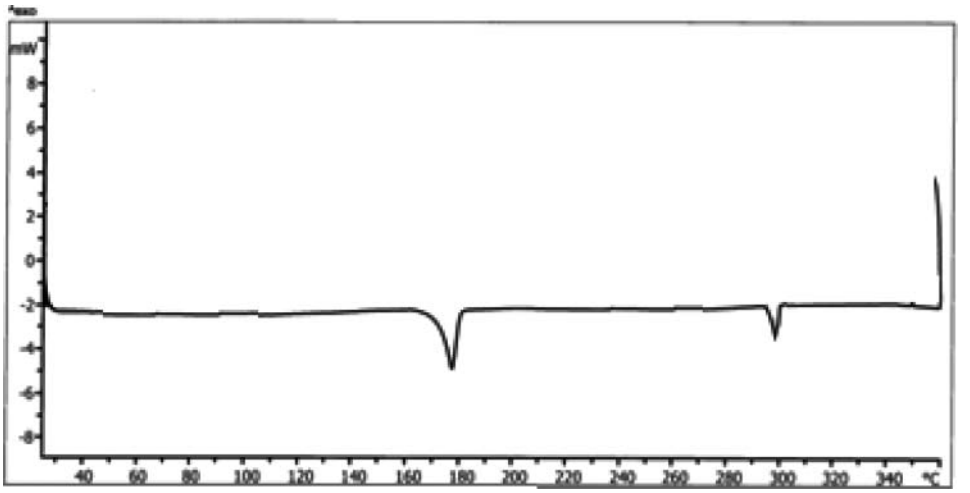



**Figure 4.** DSC thermogram (first heating) of poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid).



### *Liquid Crystalline Property*

The polymer exhibits mesomorphism in the temperature range of 170°C–300°C. The onset of liquid crystallinity was indicated in DSC thermogram by a large absorption peak at 170°C, and the clearing temperature was manifested by a small endothermic peak at 300°C as shown in Fig. 4.

A characteristic texture for the polymer nematic phase was observed over the entire temperature range under polarizing optical microscope with crossed polarizer analyzer arrangement and is shown in Fig. 5.

The mesomorphic behavior may be the result of the linking of pendant benzoic acid moieties through H-bonding as depicted in Fig. 6. The tricyclic structure constitutes the rigid core, while hexamethylene chains on both sides serve as flexible parts, thus fulfilling the requirement for liquid crystallinity [10]. At higher temperature, H-bonding breaks

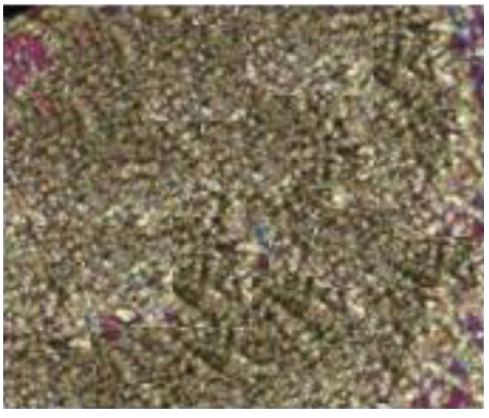


**Figure 5.** POM microphotograph of the polymer at 185°C.

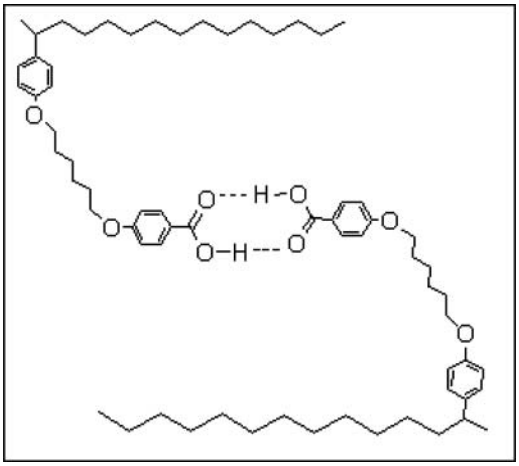


**Figure 6.** Linking of pendant benzoic acid moieties through H-bonding.

and the rigid core is destroyed with concomitant loss of mesomorphism. On cooling, H-bonding is re-established with the formation of tricyclic rigid core and regeneration of liquid crystallinity. Such dynamic materials constitute an important type of self-organized systems [11].

### *Ion-uptake Properties*

*Determination of $Ca^{+2}$ and $Mg^{+2}$ Ions Uptake Capacity.* For the determination of $Ca^{2+}$ and $Mg^{2+}$ cations uptake capacity, 0.1 g of the polymer was suspended in 100 mL distilled water. To 10 mL of this suspension was added 10 mL of tap water (with permanent hardness of 480 ppm) and titrated against standard EDTA solution, using Eriochrome Black-T as an indicator. An increase in the ion-uptake capacity was observed with increase in temperature (Table 1). This increase in uptake capacity is attributed to increase in solubility of the polymer in water with rise in temperature. This observation is further supported by a higher ion-uptake when the polymer dissolved in THF was used for these studies. For this purpose, a clear solution of the polymer was prepared by dissolving 0.1 g of the polymer in 10 mL of THF. To 1.0 mL of this solution was added 10 mL of tap water and the concentration of residual $Ca^{2+}$ and $Mg^{2+}$ ions found to be only 80 ppm with uptake of 40%. Here no effect of temperature was observed.

**Table 1.** Effect of temperature on ion-uptake capacity of polymer (**4**)

| S. no. | Temp. (°C) | Volume (mL) of EDTA solution used | Conc. (ppm) of residual $Ca^{2+}$ and $Mg^{2+}$ ions | Ion-uptake capacity (%) |
|---|---|---|---|---|
| 1 | 20 | 1.2 | 240 | 24 |
| 2 | 40 | 1.0 | 200 | 28 |
| 3 | 60 | 0.9 | 180 | 30 |
| 4 | 100 | 0.8 | 160 | 32 |

*Determination of $Ca^{2+}$ Ions Uptake Capacity.* The $Ca^{2+}$ ion content of the hard water was found to be 280 ppm using muroxide as an indicator. The residual concentration of $Ca^{2+}$ was determined as 110 ppm after adding 10 mg of the polymer (dissolved in 1 mL THF) in 10 mL of hard water. Thus, the $Ca^{2+}$ uptake capacity was found to be 17%.

## Conclusion

Poly(4-vinylphenol) was modified to poly(4-(6-(4-vinylphenoxy)hexyloxy)benzoic acid) in quantitative yields. The polymer showed high thermal stability with 56.16% decomposition at 447°C. The nematic LC phase was observed in the temperature range of 170°C–300°C. The $Ca^{2+}$ and $Mg^{2+}$ uptake by the polymer suspension in water varied with temperature with a maximum of 32% at 100°C. The cations uptake capacity of THF solution of the polymer was found to be 40% with little effect of temperature. The polymer may be used as high temperature LC and ion-exchange material.

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