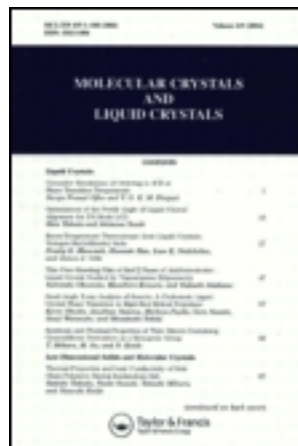


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Synthesis and Characterization of Novel Liquid Crystalline Photoactive Polymers with Pendant Chalcone Moiety

SIVAKUMAR JEYASHEELA AND KATHAVARAYAN
SUBRAMANIAN*

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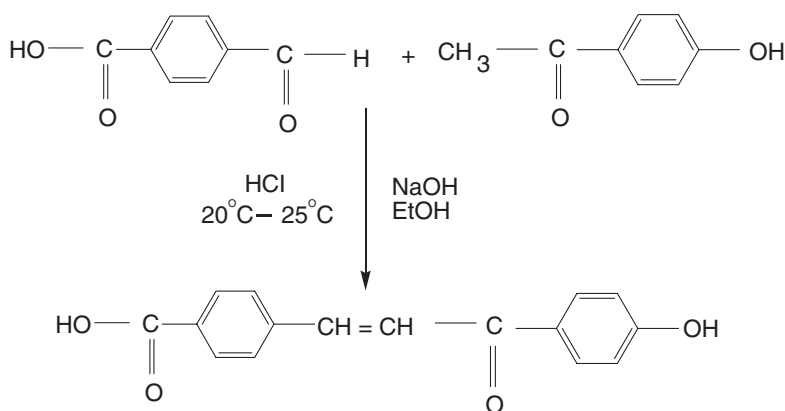
The side-chain liquid crystalline polymers containing terminally substituted biphenyl cinnamoyl esters were synthesized and characterized. The structures of the synthesized photosensitive liquid crystalline polymers have been characterized by spectral techniques such as IR, ^1H NMR and ^{13}C NMR, and UV visible spectrometer. The rates of photocrosslinking behavior and photoconversion of the polymers have been studied by UV visible spectroscopy. The UV study reveals that the polymer follows $(2\pi + 2\pi)$ cycloaddition reaction during their photocrosslinking. Polarizing optical microscopic and differential scanning calorimetry (DSC) studies confirm the formation of thermotropic mesophase upon heating. The above polymers exhibit nematic mesophase. The thermogravimetric analysis (TGA) and DSC studies prove that the nature of the terminal substituent has a significant effect on mesophase temperature as well as thermal stability of these liquid crystalline photoactive polymers.

Keywords NMR; photocrosslinking; thermal stability; UV irradiation

Introduction

In recent years, photocrosslinkable polymers have attracted considerable attention for the application in surface coatings, printing inks, printing plates, and photoresists due to their faster curing and higher thermal stability [1,2]. Anisotropic photocrosslinking reaction of a photosensitive moiety has long been known and has found its potential applications in lithography and in advanced electro-optic application [3–5]. The combination of unique optical properties of liquid crystals (LCs) with photosensitivity provides a great possibility for the creation of a large variety of photochemical switches, which can be used in optics and optoelectronics [6–8]. The polymers with pendant photofunctional groups, such as cinnamoyl esters of poly(vinyl alcohol) [9], poly(2-hydroxyethyl methacrylate) [10,11], poly(2-vinyl-4-methoxycinnamate) [12], poly(2-vinyl-4-ethoxycinnamate) [13], poly(vinyl-4-methoxycinnamate) [14], and many other groups [15–19], have been prepared and tested for their photosensitivity. The photochemistry involved in a number of photoresists and their technological applications have been reviewed [20–22]. Polymers containing α,β -unsaturated carbonyl groups such as cinnamoyl [23,24], benzylidene [25], and so on, undergo photodimerization ($2\pi + 2\pi$) upon irradiation with UV light. LCs occupy an important place

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Scheme 1.

in modern optical technology; π -conjugated polymers are promising candidates for thin-film transistors, light-emitting diodes, and organic lasers [26–28]. High photosensitivity, thermal stability, and good solubility are the required properties for a photocrosslinkable polymer. In the present investigation, we report the novel synthesis of side-chain liquid crystalline polymers with photoresponsive group containing methylene spacer and acetyl phenyl group and methyl phenyl group in the polymeric chain.

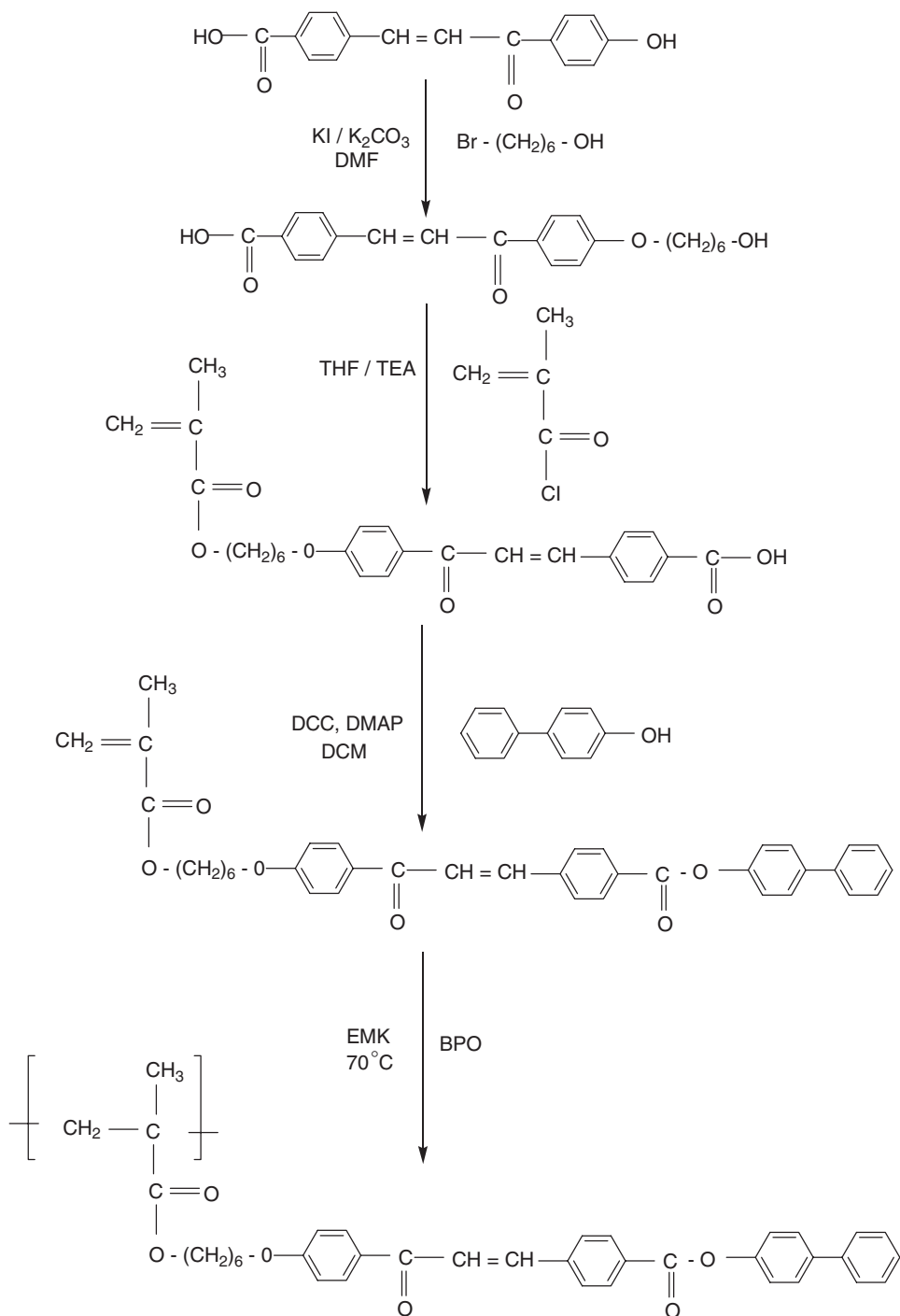
Experiment

Material

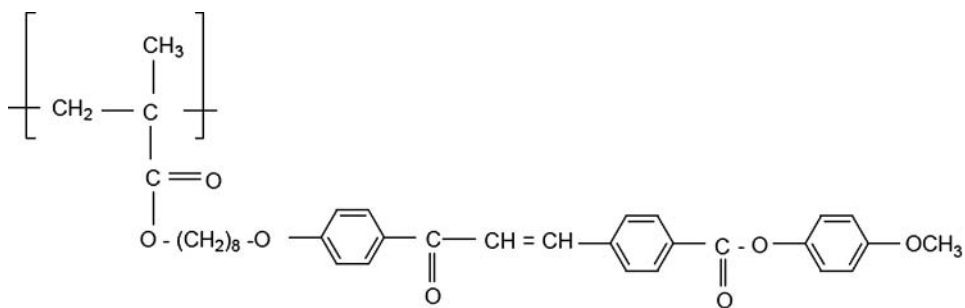
4-phenyl phenols, 6-bromobutanol, and 8-bromohexanol (Aldrich) were used as received. 4-formyl benzoic acids, 4-hydroxyacetophenone, and 4-methoxy phenol were purchased from Spectrochem chemicals. Triethylamine, N,N' -dicyclohexyl carbodiimide, and 4-dimethylamino pyridine were purchased from Lancaster. Dichloromethane, ethanol, methanol, tetrahydrofuran (THF), and ethyl methyl ketone (EMK; SRL) were purified by the usual procedure and dried before use. Anhydrous potassium carbonate (Merk) and benzoyl peroxide (BPO) were freshly recrystallized from a chloroform/methanol (1:1) mixture. All other chemicals and solvent were analytical grade samples used as received.

Synthesis of Precursors

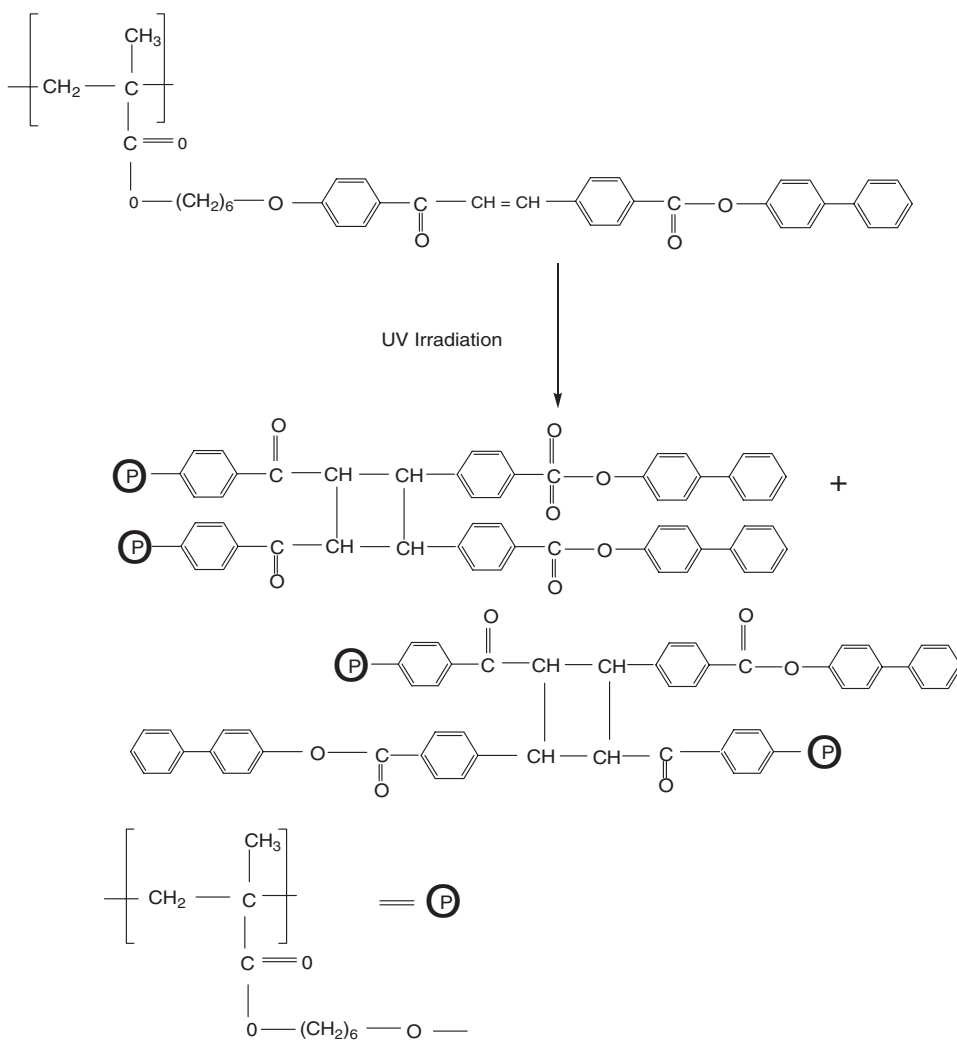
Synthesis of 4-Carboxy Styryl 4'-Hydroxy Phenyl Ketone (CSHPK). Synthesis of 4-carboxy styryl 4'-hydroxy phenyl ketone (CSHPK) was carried out following the reported procedure (Scheme 1) [29]. 4-hydroxyacetophenone (0.05 mol, 6.8 g) was dissolved in ethanol (80 ml) in a 500 ml round bottom flask. 4-formyl benzoic acid (0.05 mol, 7.5 g) was dissolved in ethanol (80 ml) and was added dropwise to the flask and while stirring, NaOH (7%) solution was simultaneously added into the reaction mixture. The stirring was continued for 48 hr and then the reaction mixture was poured into ice-cold 1:1 HCl for neutralization to get yellow-colored solid, which is then filtered and washed with distilled water. The crude product thus obtained was recrystallized from methanol to get a pure compound CSHPK. The structure of CSHPK was confirmed by IR, ^1H NMR, and ^{13}C NMR spectra, which is in good agreement with the assigned structure.



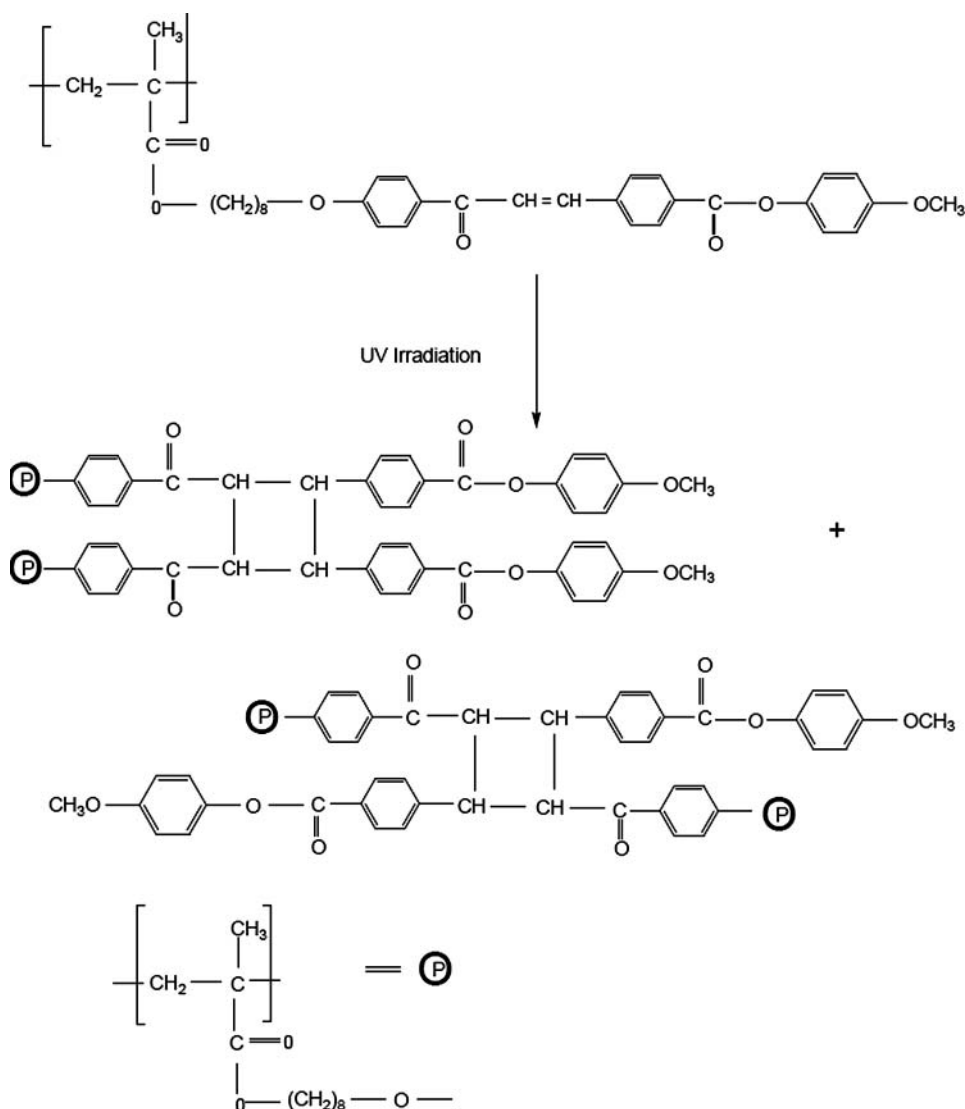
Scheme 2. Synthesis of polymer BOCCPOHMA (polymer 1a).



Scheme 3. Polymer MPOCCPOOMA (polymer 1b).



Scheme 4. Photocrosslinking studies on polymer BOCCPOHMA.



Scheme 5. Photocrosslinking of polymer MPOCCPOOMA.

IR (KBr, cm^{-1}): 3510 (phenolic-OH), 1600 (ethylene $-\text{CH}=\text{CH}-$), 1750 (ester $>\text{C}=\text{O}$), 1500 (aromatic ring breathing). ^1H NMR (CDCl_3 , δ in ppm): 7.32 (m, 5H, aromatic pendant phenyl), 8.22 (s, aromatic carbon, $-\text{OCO}-$ attached), 6.3 (d, 2H, $-\text{CH}=\text{CH}-$). ^{13}C NMR (CDCl_3 , δ in ppm): 160–180 (carbonyl), 120–140 (aromatic carbon), 60–10 (aliphatic carbon).

Synthesis of 4-Carboxy Styryl (m-Hydroxy Alkyloxy) Phenyl Ketone (m = 6, 8). Synthesis of 4-carboxy styryl (m-hydroxy alkyloxy) phenyl ketone ($m = 6, 8$) was carried out as reported previously (Schemes 2 and 3) [30]. A typical procedure for the synthesis of 4-carboxy styryl (6-hydroxy hexyloxy) phenyl ketone (CSHHPOK) is as follows. The pendant chalcone CSHPK (0.01149 mol, 3 g) was dissolved in dry dimethylformamide

(DMF; 20 ml). Anhydrous potassium carbonate (K_2CO_3 ; 0.0111 mol, 2.76 g) and a pinch of KI were added to it. The reaction mixture was continuously heated to $90^\circ C$ with constant stirring. 6-bromo-1-butanol (0.011 mol, 1.66 g) was added dropwise to the reaction mixture and stirred for 48 hr. Then, the reaction mixture was cooled to room temperature and poured into ice-cold dilute HCl. The precipitated product was filtered, washed, and dried in vacuum (yield 85%, mp $78^\circ C$ – $80^\circ C$). Synthesis of 4-carboxy styryl (8-hydroxy octyloxy) phenyl ketone (CSHOOPK) was carried out by adopting the similar procedure (yield 77%, mp $70^\circ C$ – $75^\circ C$). The structure of the compound CSHHPOK was identified by the spectroscopic techniques (IR, 1H NMR, and ^{13}C NMR).

IR (KBr, cm^{-1}): 1265 (C–O stretch), 1640 (olefinic $-CH=CH-$), 1640 (C=C stretching), 1540 (aromatic, C=C), 2230 (aliphatic $-CH_2$), 1743 (ester C=O), 1255 (Ar–O– CH_2). 1H NMR ($CDCl_3$, δ in ppm): 9.00 (O–H), 7.23 (m, 5H, aromatic pendant phenyl), 8.15 (s, aromatic carbon, $-OCO-$ attached), 6.5 (d, 2H, $-CH=CH-$), 7.5 (m, biphenyl oxy group). ^{13}C NMR ($CDCl_3$, δ in ppm): 169–175 (carbonyl), 120–140 (aromatic carbon), 60–10 (aliphatic carbon).

Synthesis of 4[4-Carbonyl Styryl Carbonyl-4-Phenyl Oxy-6-Hexylene] Methacrylate (CSCPOHMA). The compound CSHHPOK (0.008 mol, 2.5 g) was dissolved in THF (50 ml), triethylamine (0.008 mol, 2 ml) was added to the reaction mixture, and then the reaction mixture was cooled to $0^\circ C$ – $5^\circ C$. Chlorocarbonyl phenyl methacrylate (0.008 mol, 1.8 g) was added to the reaction mixture and continuously stirred for 5 hr. The precipitated triethylamine hydrochloride was filtered and the filtrate was evaporated under reduced pressure by keeping the bath temperature below $40^\circ C$. The residue obtained was treated with petroleum ether to remove unreacted chloro carbonyl phenyl methacrylate. The precipitate thus obtained was recrystallized using methanol (yield 71%, mp $90^\circ C$ – $93^\circ C$). Another compound 4[4-carbonyl styryl carbonyl-4-phenyloxy-8-octylene] methacrylate (CSCPOOMA) was synthesized by adopting the same procedure (yield 77%, mp $70^\circ C$ – $75^\circ C$). The structure of the compound CSCPOHMA was identified by the IR, NMR, and ^{13}C NMR spectra.

IR (KBr, cm^{-1}): 1748 (C=O), 3024 ($-CH_3$), 2915 (methylene chain), 1693 ($-C=O$), 1655 ($-C=CH_2$), 1611 ($-C=C-CH_3$). NMR ($CDCl_3$, δ in ppm): 7.59 (d, 1, Ar, aromatic pendant phenyl), 8.15 (s, aromatic carbon, $-OCO-$ attached), 6.5 (d, 2H, $-CH=CH-$). ^{13}C NMR ($CDCl_3$, δ in ppm): 170 (carbonyl), 120–140 (aromatic carbon), 60 (aliphatic carbon), 68 (O– CH_2).

Synthesis of Monomers

Synthesis of 4[4{1-Biphenyl Oxy Carbonyl} Cinnamoyl Phenyl Oxy Hexyl] Methacrylate (BOCCPOHMA) (M1). The compound CSCPOHMA (0.004 mol, 2 g), 4-phenyl phenol (0.004 mol, 0.6 g), N,N'-dimethylaminopyridine (DMAP) (0.004 mol, 0.488 g), and N,N'-dicyclohexylcarbodiimide (DCC; 0.004 mol, 0.82 g) were suspended into 100 ml of dry methylene chloride and stirred at room temperature overnight. The precipitated urea was removed by filtration and the solution was washed with 5% acetic acid followed by saturated brine solution. Organic layer was dried over anhydrous sodium sulfate and removed under vacuum distillation. The residue thus obtained was purified by column chromatography using 10% methanol in chloroform as an eluent (yield 85%, mp $75^\circ C$ – $80^\circ C$). Another monomer 4-[4-(1-methoxy phenyl oxy carbonyl) cinnamoyl phenyl oxy octyl] methacrylate. (MPOCCPOOMA) (M2) was synthesized by following the similar procedure (yield 77%, mp $70^\circ C$ – $75^\circ C$). The structure of the compound was identified by the spectroscopic techniques (IR, 1H NMR, and ^{13}C NMR).

The structure of the monomer M1 was identified by the spectral techniques.

IR (KBr, cm^{-1}): 1748 (C=O), 3024 ($-\text{CH}_3$), 2915 (methylene chain), 1693 ($-\text{C}=\text{O}$), 1655 ($-\text{C}=\text{CH}_2$), 1611 ($-\text{C}=\text{C}-\text{CH}_3$). NMR (CDCl_3 , δ in ppm): 7.59 (d, 1, Ar, aromatic pendant phenyl), 8.15 (s, aromatic carbon, $-\text{OCO}-$ attached), 6.5 (d, 2H, $-\text{CH}=\text{CH}-$). ^{13}C NMR (CDCl_3 , δ in ppm): 170 (carbonyl), 120–140 (aromatic carbon), 60 (aliphatic carbon), 68 ($\text{O}-\text{CH}_2$).

The structure of the monomer M2 was identified by the spectral techniques.

IR (KBr, cm^{-1}): 1718 (C=O), 3014 ($-\text{CH}_3$), 2905 (methylene chain), 1653 ($-\text{C}=\text{O}$), 1645 ($-\text{C}=\text{CH}_2$), 1611 ($-\text{C}=\text{C}-\text{CH}_3$). NMR (CDCl_3 , δ in ppm): 7.6 (s, 1H, Ar- $\text{CH}=\text{C}$), 7.59 (d, 1, Ar, aromatic pendant phenyl), 8.15 (s, aromatic carbon, $-\text{OCO}-$ attached), 6.5 (d, 2H, $-\text{CH}=\text{CH}-$), 7.5 (m, biphenyloxy group). ^{13}C NMR (CDCl_3 , δ in ppm): 170 (carbonyl), 120–140 (aromatic carbon), 60 (aliphatic carbon), 68 ($\text{O}-\text{CH}_2$).

Polymerization

Both polymers were prepared by the free radical solution polymerization method at 70°C using BPO as initiator. They were polymerized as 1 M solution in dry THF using benzoyl peroxide as initiator at 70°C. Appropriate quantities of monomer, the initiator (0.5 wt%), and solvent were taken in a polymerization tube and the mixture was purged with dry nitrogen gas for 10 min. Then the tube was closed and kept in the thermostat at 70°C for 24 hr. After that the contents were cooled and poured into excess methanol to precipitate the polymers. The above polymers were purified by reprecipitation by methanol, filtered, washed, and dried under vacuum at 50°C (yield 60%).

Measurements

The FT-IR spectra of polymers were recorded on a Perkin Elmer FT-IR spectrometer RXI. The specimen was prepared using KBr pellets. ^1H NMR spectroscopic measurement was recorded using a Bruker MSC 300 spectrometer. Thermal stability of polymers was investigated by thermogravimetric analysis (TGA) using NETZSCH STA 409 C/CD. The number average and weight average molecular weight of the polymers were determined by PL-GPC 650. Glass transition temperatures of polymer were measured by differential scanning calorimeter (DSC) NETZSCH.DSC.204. The photolysis studies were carried out by using a Perkin Elmer Lambda 35 UV visible spectrometer. The four fluorescence spectra of the polymers were recorded in FluroMax 2.0. The textures of the prepared polymer sample were studied by a Euromax polarizing microscope equipped with a Linken HFS91 heating stage. The samples were prepared by a small quantity of the material being melted between two thin glass coverslips to get a uniform film and anisotropic behavior observed by heating and cooling with Kodak film.

Result and Discussion

Synthesis

The polymers 1a and 1b were prepared by free radical polymerization method at 70°C using BPO as initiator. Table 1 shows the molecular weight data of poly (BOCCPOHMA) and poly (MPOCCPOOMA).

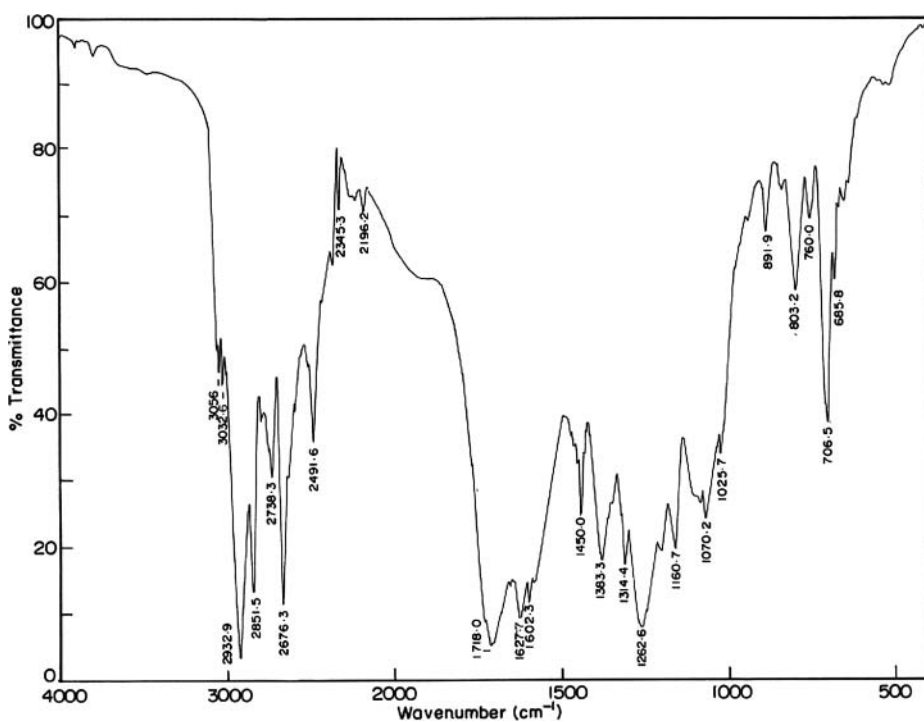
Table 1. TGA and molecular weight data of polymers BOCCPOHMA and MPOCCPOOMA

Polymers	\overline{M}_n	PDI	IDT	Temperature (°C) at weight loss (%)				
				10	30	50	60	70
BOCCPOHMA	3.92	1.78	150	190	248	255	270	280
MPOCCPOOMA	3.61	1.76	140	78	225	240	260	276

Note: IDT, initial decomposition temperature (°C); PDI, polydispersity index; \overline{M}_n and \overline{M}_w are the number and average molecular weight of polymer.

Characterization of Polymers

IR Spectroscopy of Polymers. *IR Spectra of Polymer 1a.* The olefinic CH stretching vibration occurs at 3067 cm^{-1} . The corresponding C=C stretching vibration occurs at 1627 cm^{-1} . The CH₂ symmetric and asymmetric stretching vibrations are at 850 and 2920 cm^{-1} respectively. The C=O stretching occurs at 1727 cm^{-1} . The aromatic ring breathing vibrations occur at 603 , 1514 , and 1449 cm^{-1} . The CH₂ bending modes are at 1361 and 1449 cm^{-1} . The ester COO vibration gives a broad band at 1274 cm^{-1} . The C–O vibrations give a group of peaks at 1112 , 1068 , and 1024 cm^{-1} and the para-substituted aromatic ring gives its CH bending vibration at 840 cm^{-1} . The free phenyl in biphenyl shows its CH bending vibrations at 713 and 769 cm^{-1} . Hence, the IR spectra establish the structure of the polymer as shown in Fig. 1. The phenolic C–O vibration also occurs close to it. The

**Figure 1.** FT-IR spectrum of polymer BOCCPOHMA.

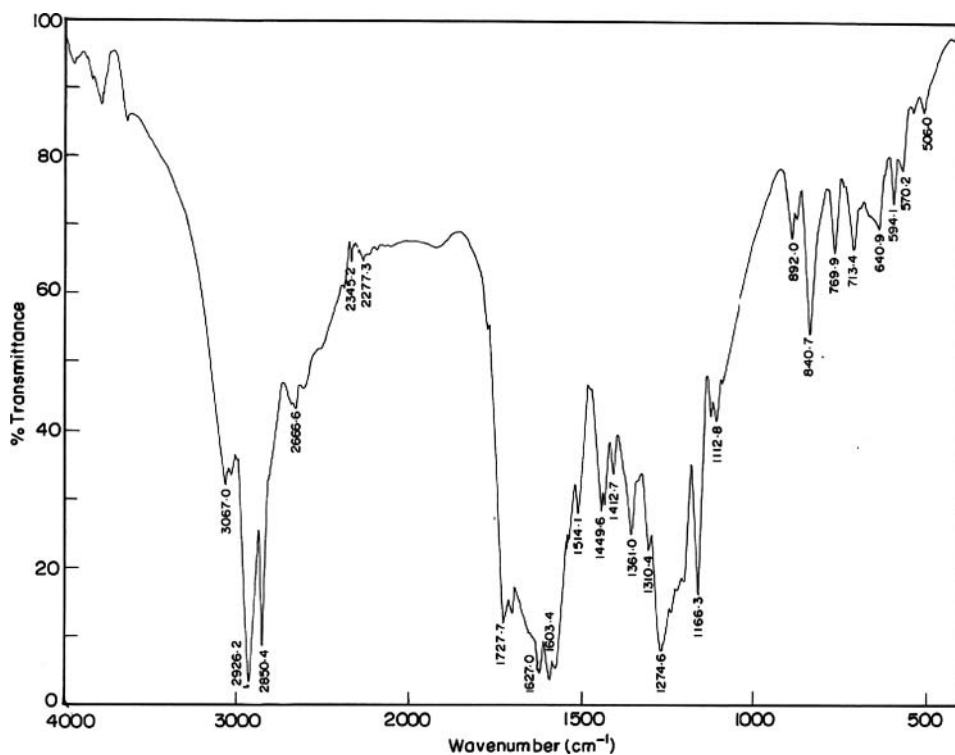


Figure 2. FT-IR spectrum of polymer MPOCCPOOMA.

peaks at 962 and 1310 cm^{-1} illustrate trans position, which occurs for the C=C bond substituents.

IR Spectra of Polymer 1b. The olefinic CH stretching vibration produces its peak at 3056 cm^{-1} . The corresponding C=C stretching vibration occurs at 1627 cm^{-1} . The CH₂ symmetric and asymmetric stretching vibrations occur at 2851 and 2932 cm^{-1} respectively. The C=O stretching occurs at 1718 cm^{-1} . The aromatic ring breathing vibrations occur at 1602 and 1450 cm^{-1} . The CH₂ bending modes are observed at 1450 and 1383 cm^{-1} . The ester COO vibration gives a broad band at 1262 cm^{-1} . The C—O vibrations give a group of peaks at 1160, 1070, and 1025 cm^{-1} and the para-substituted aromatic ring gives its CH bending vibration at 891 cm^{-1} . Hence, the IR spectrum establishes the structure of the polymer as shown in Fig. 2. The peak at 1261 cm^{-1} is also common to Ar—O stretching vibration.

¹H NMR Spectra of Polymers. *¹H NMR Spectra of Polymer 1a.* The ¹H NMR spectrum of poly (BOCCPOHMA) is shown in Fig. 3. The aromatic protons give a group of multiplets between 7.75 ppm and 6.95 ppm. The olefinic protons of the pendant chalcone moiety give their characteristic signal at 6.4 ppm. The backbone methylene (—CH₂) groups show their peak at 2.3 ppm. The resonance signals at 3.4 ppm is due to alkoxy methylene protons and the peak at 1.7 ppm is due to the methyl protons.

¹H NMR Spectra of Polymer 1b. The ¹H NMR spectrum of polymer MPOCCPOOMA is shown in Fig. 4. The aromatic protons show multiplets between 6.5 ppm and 7.9 ppm. The signal due to olefinic protons of the pendant chalcone moiety is located at 6.1 ppm.

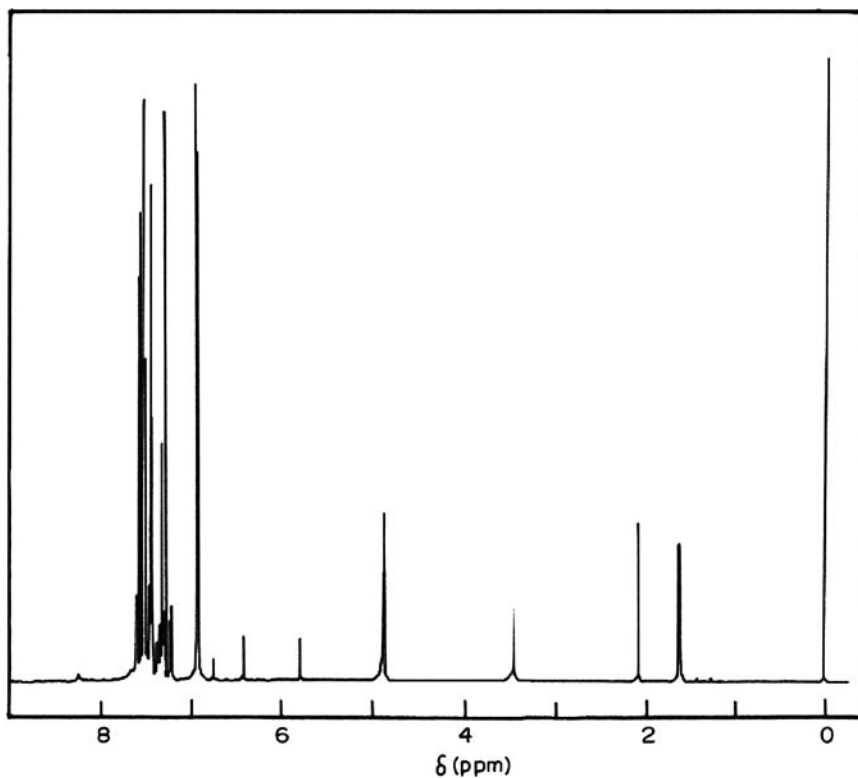


Figure 3. ^1H NMR spectrum of polymer BOCCPOHMA.

The signal due to the backbone methylene oxy ($-\text{OCH}_2$) groups is observed at 3.5 ppm. The methoxy protons show their signal at 3.1 ppm. The methyl proton signal occurs at 1.2 ppm.

^{13}C NMR Spectra of Polymers. ^{13}C NMR Spectra of Polymers 1a and 1b. The proton decoupled ^{13}C NMR spectrum of polymers 1a and 1b is presented in Fig. 5. ^{13}C NMR chemical shift assignment was made from the off-resonance decoupled spectra of the polymer. The resonance signals appear at 179 and 177 ppm, which correspond to ester carbonyl carbon. The ketone carbon signal is observed at 192 and 191 ppm. The signals at 105 ppm are due to $>\text{CH}=\text{CH}<$ (olefinic) carbon connected to the benzene ring. The aromatic carbon gives signals at 120–140 ppm and the aliphatic carbon gives signals at 14, 15, 16, 18, 23, and 25 ppm. The signal observed at 40–50 ppm is assignable to the backbone carbon ($-\text{C}-$) of the polymer BOCCPOHMA and MPOCCPOOMA units.

Molecular Weight. The number and weight average molecular weight of polymers BOCCPOHMA and MPOCCPOOMA were determined by gel permeation chromatography presented in Table 1. The polydispersity indexes of polymers BOCCPOHMA and MPOCCPOOMA are 1.78 and 1.76, respectively; the theoretical values of M_w/M_n for polymers produced via radical combination and disproportionation are 1.5 and 2.0, respectively [31,32]. The weight (M_w) and number average molecular weight (M_n) and the polydispersity index of polymers BOCCPOHMA and MPOCCPOOMA determined by the gel

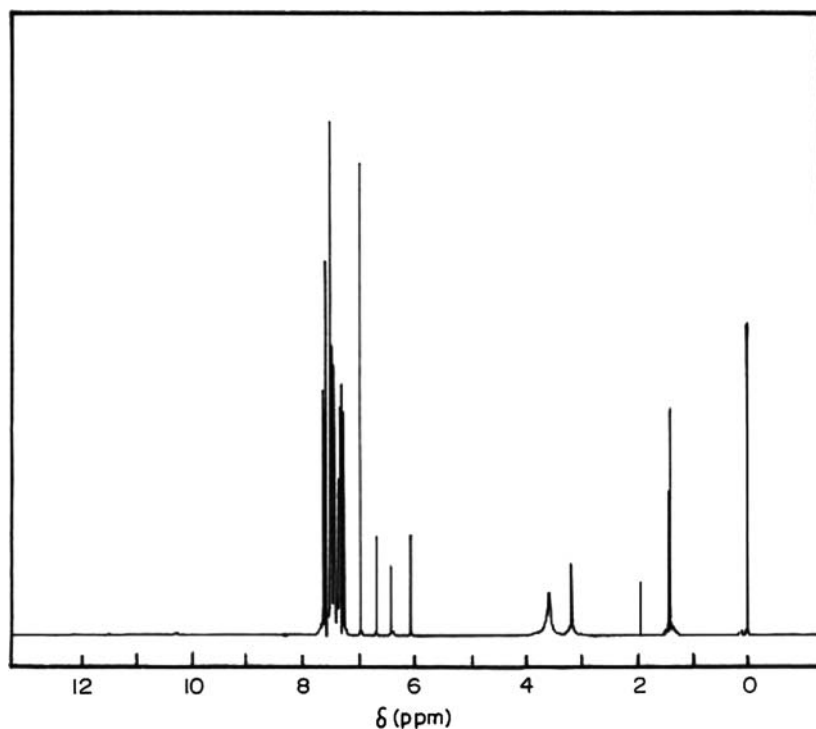


Figure 4. ^1H NMR spectrum of polymer MPOCCPOOMA.

permeation chromatography are as follows.

$$\begin{aligned} \overline{M}_w \times 10^{-4} &= 3.92; \quad \overline{M}_n \times 10^{-4} = 2.20; \quad \overline{M}_w/\overline{M}_n = 1.78, \\ \overline{M}_w \times 10^{-4} &= 3.61; \quad \overline{M}_n \times 10^{-4} = 2.05; \quad \overline{M}_w/\overline{M}_n = 1.76. \end{aligned}$$

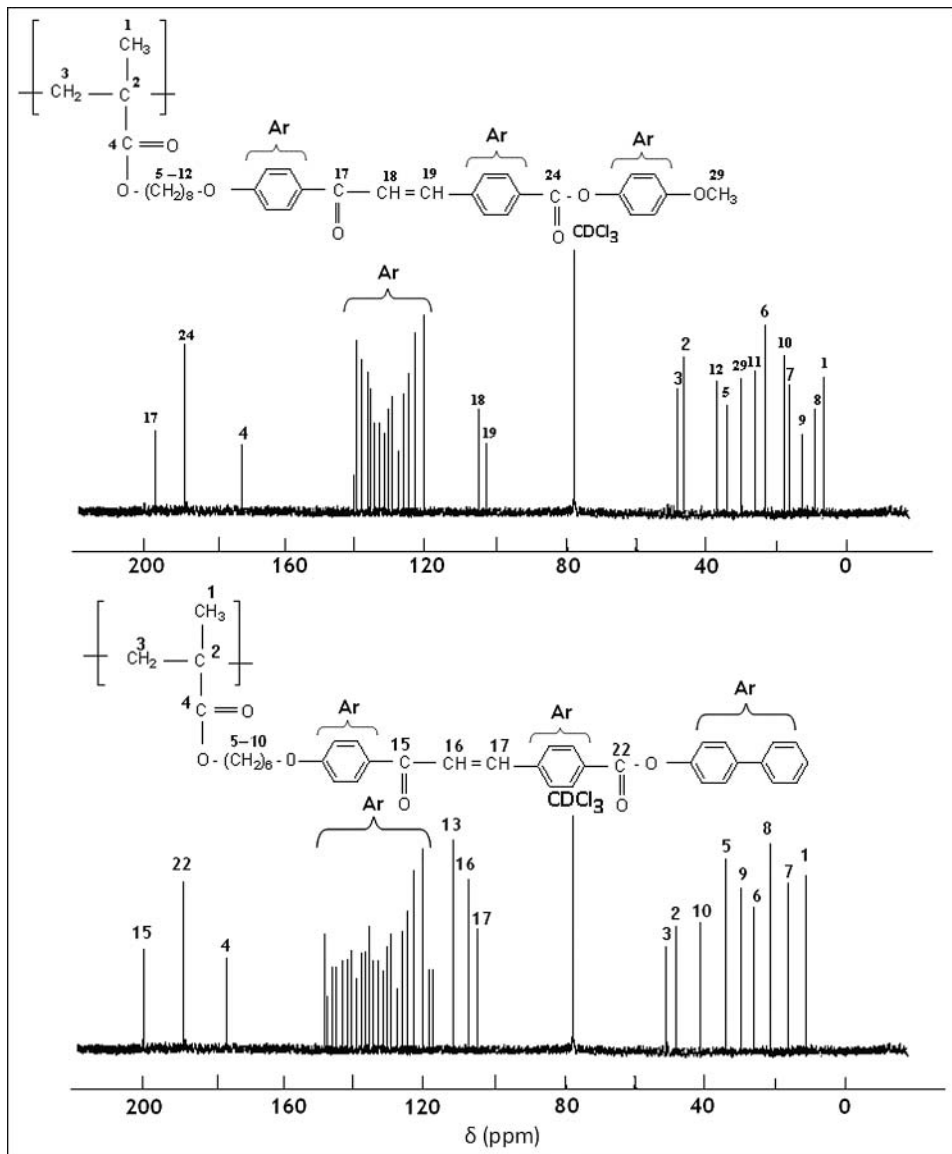
Usually the polydispersity index M_w/M_n of poly(meth)acrylates prepared by free radical polymerization of the monomer depends, among other factors, on the chain termination mechanism. The polydispersity index value of polymers BOCCPOHMA and MPOCCPOOMA suggests that the tendency for chain termination by disproportionation is more than that for dimerisation.

Thermal Studies. DSC Analysis of Polymers. DSC analysis investigated the mesogenic transition of the polymers 1a and 1b. The DSC thermograms of the polymers were measured at a heating rate of 10 c/min and representative thermograms of polymers are shown in Figs. 6 and 7. The phase transition temperatures of all the polymers are summarized in Table 2. The two DSC thermograms show two endothermic peaks, which reveals that the mesogenic transition values decrease with an increase in methylene group. The polymer 1a shows higher mesogenic transition temperature as compared with polymer 1b, which is due to the effect of substituent of benzene ring on the thermal properties of the polymer.

TGA of Polymers. The TGA traces of the polymers are shown in Figs. 8 and 9 and the data are given in Table 1. The thermal stability of all polymers was investigated at various temperatures and the weight loss (%) was observed. TGA revealed that polymer 1a was stable up to 210°C–270°C and was found to be more stable than that of

Table 2. DSC data of polymers BOCCPOHMA and MPOCCPOOMA

Polymers	DSC			
	T_m (°C)	T_i	ΔT	T_g
BOCCPOHMA	110	138	28	78
MPOCCPOOMA	98	36	38	65

**Figure 5.** ^{13}C NMR spectrum of polymers BOCCPOHMA and MPOCCPOOMA.

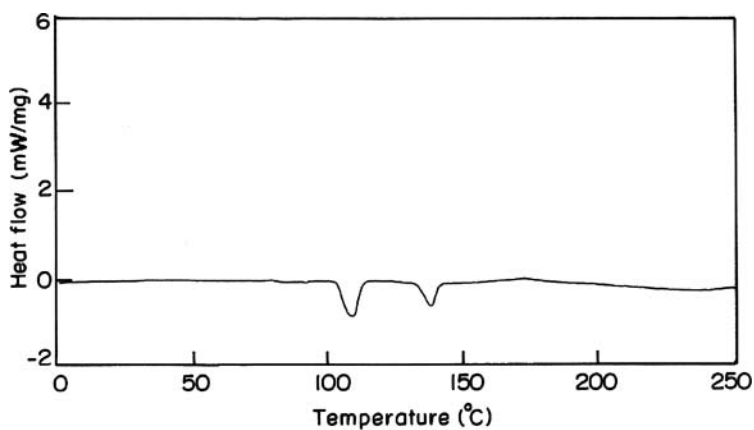


Figure 6. DSC trace of polymer BOCCPOHMA.

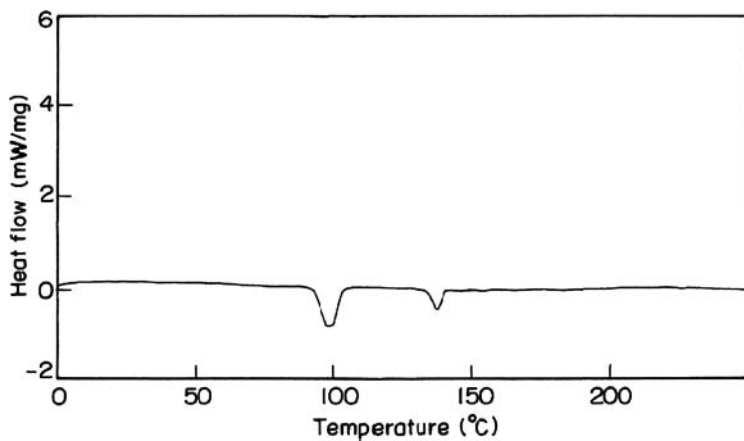


Figure 7. DSC trace of polymer MPOCCPOOMA.

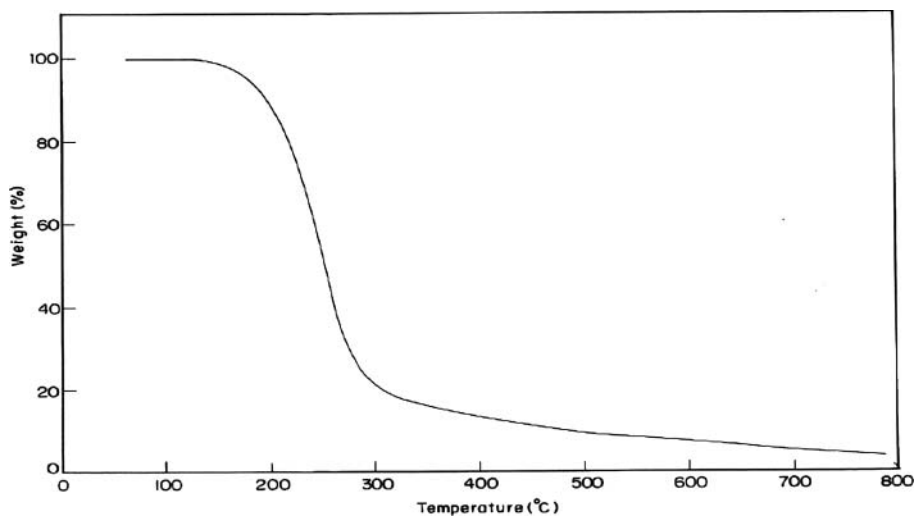


Figure 8. TGA thermogram of polymer BOCCPOHMA.

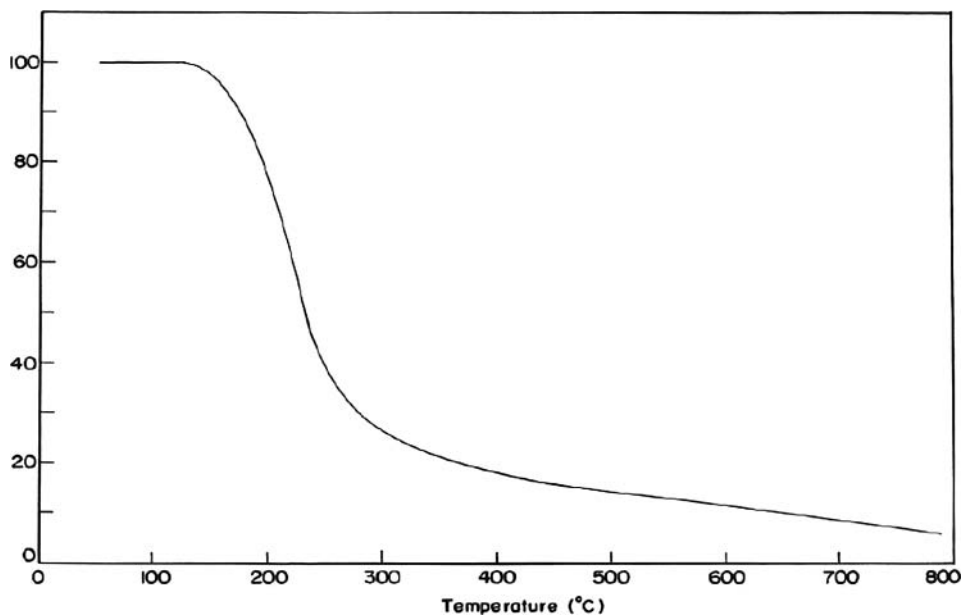


Figure 9. TGA thermogram of polymer MPOCCPOOMA.

polymer 1b. Thermal stability of the polymer usually decreases with an increase in methylene spacer in pendant chains. The polymer MPOCCPOOMA is less stable than the polymer BOCCPOHMA. Thermal stability of the polymer BOCCPOHMA was higher than that of polymer MPOCCPOOMA, which is due to the increased aromaticity of the polymer backbone. The thermal stability of the polymer MPOCCPOOMA decreases with an increase in the methylene spacer.>

Photocrosslinking Behavior Studies. The polymers containing the mesogenic chalcone pendant unit undergo photo crosslinking by UV irradiation and the structural changes were monitored by UV spectroscopy. The photosensitivity of polymers BOCCPOHMA and MPOCCPOOMA was measured by irradiation with a high-pressure mercury lamp (schemes 4 and 5) [29]. The pendant chalcone moiety ($>C=C<$) of the polymers shows a UV absorption band at 290 and 320 nm due to the $\pi-\pi^*$ transition. The irradiation of polymer solutions, poly (BOCCPOHMA) and poly (MPOCCPOOMA) chloroform, was carried out using a light of 290 and 320 nm at room temperature and the results are illustrated in Figs 10 and 11. In poly (BOCCPOHMA) the absorption band around 290nm corresponds to $\pi-\pi^*$ transition of the olefinic double bond of the mesogenic unit in the polymer backbone. During irradiation with UV light a decrease in intensity of the absorption was observed due to formation of cyclo butane ring through $2\pi + 2\pi$ cyclo addition of carbon-carbon double bond chalcone unit. The plots of conversion versus irradiation time of the poly (BOCCPOHMA) and poly (MPOCCPOOMA) are shown in Figs. 12 and 13.

Polarized Optical Microscopy Analysis. The DSC trace of the polymers shows two endothermic peaks, corresponding to the melting (T_m) and isotropic (T_i) transition temperatures. Generally, the melting transition temperature decreases with an increase in aliphatic spacers as expected. The two polymers exhibited liquid crystalline nature with nematic textures on heating. The polymer BOCCPOHMA was heated to 135°C to exhibit a nematic texture as shown in Fig. 14. The optical texture is always stable throughout the whole

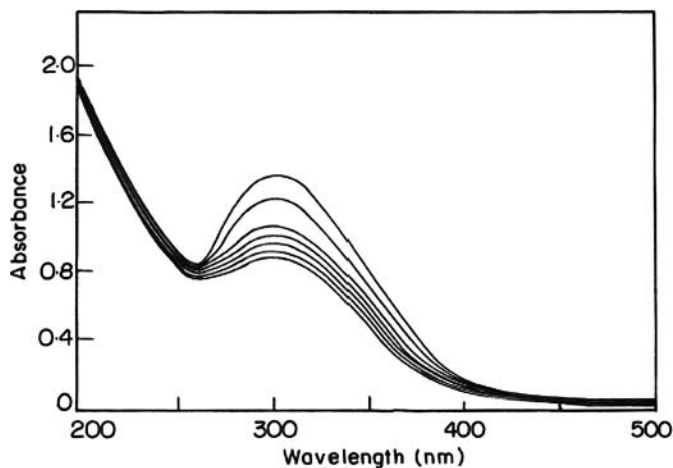


Figure 10. Change in UV spectral characteristics, during the photolysis of polymer BOCCPOHMA.

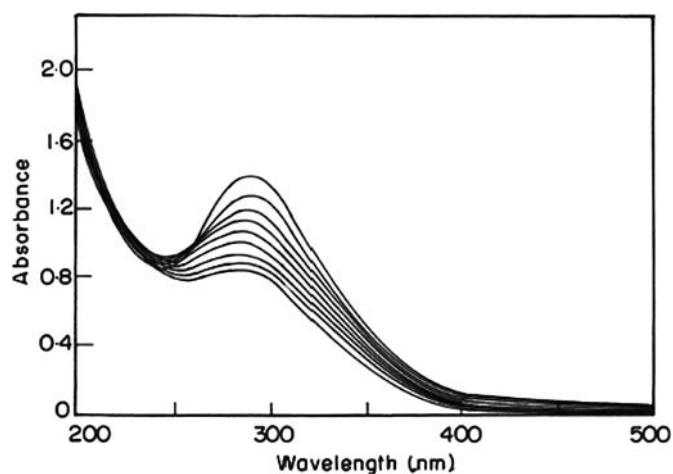


Figure 11. Change in UV spectral characteristics, during the photolysis of polymer MPOC-CPOOMA.

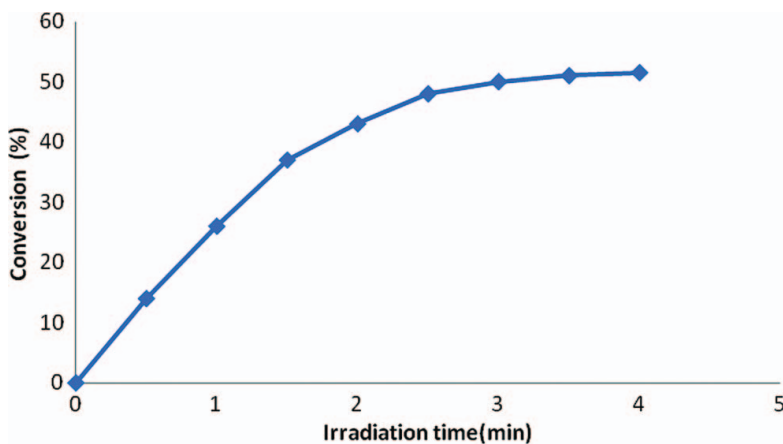


Figure 12. Dependence of the photocrosslinking rate on irradiation time of polymer BOCCPOHMA.

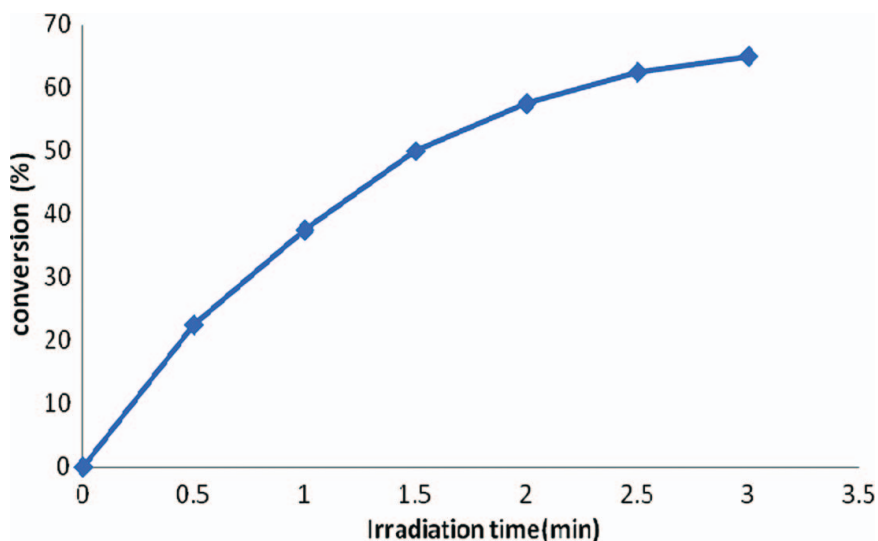


Figure 13. Dependence of the photocrosslinking rate on irradiation time of polymer MPOC-CPOOMA.

mesogenic range. On cooling the polymer from isotropic melt (T_i), the reproducibility of the phase was satisfactory. The polymer MPOCCPOOMA was heated to 130°C to exhibit a grainy texture as shown in Fig. 15. The rigidity of the mesogenic core with the flexible spacer length and terminal units highly influences the melting temperature, mesophase temperature, and even molecular arrangement. Highly polar, hindered pendant groups revealed to have high interaction leading to the formation of liquid crystalline phase.

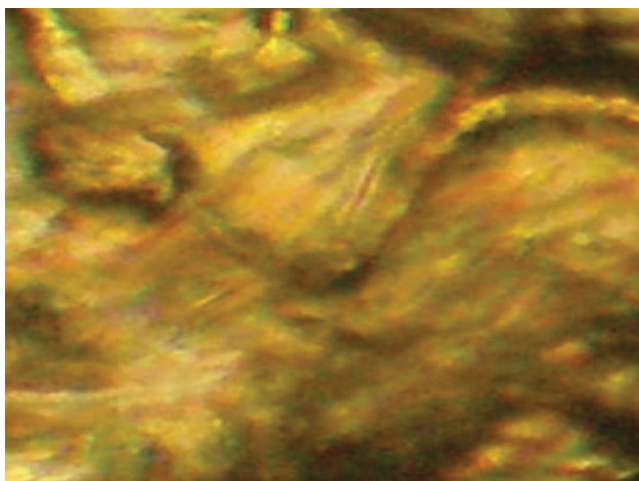


Figure 14. HOPM photograph of polymer BOCCPOHMA.

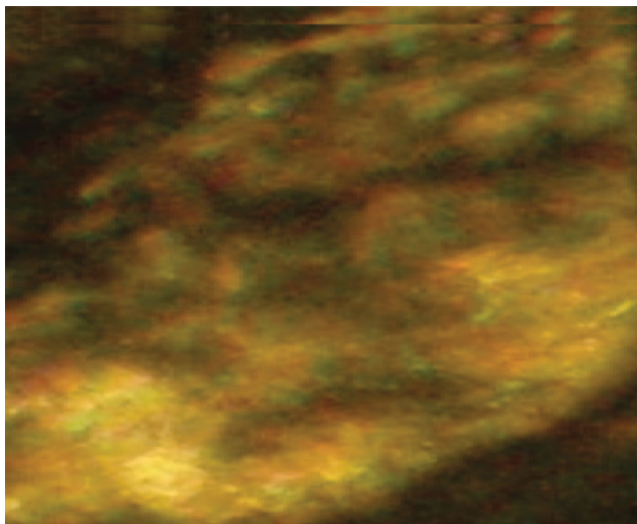


Figure 15. HOPM photograph of polymer MPOCCPOOMA.

Conclusions

The polymers BOCCPOHMA and MPOCCPOOMA were synthesized by free radical polymerization in solution using benzoyl peroxide as initiator. The synthesized polymers were characterized by the IR, ^1H NMR, ^{13}C NMR spectral techniques. The photocrosslinkable liquid crystalline polymers containing cinnamoyl moiety with various terminally substituted phenyl groups in the side chains, which act as mesogen, were synthesized and characterized spectroscopically. The intrinsic viscosity of the polymer data reveals that these polymers have reasonable molecular weight. Thermal stability of the polymer 1a was higher than the polymer 1b due to the increased aromaticity of the polymer backbone in the former. The thermal stability decreases with an increase in the methylene spacer. The T_m and T_i of the polymers decrease with an increase in even number of methylene spacer. The HOPM (Hot stage polarized microscopy) study indicates that the two prepared polymers exhibit LC properties with nematic texture. The photocrosslinking properties of two polymers were examined by UV spectroscopy, and the photocrosslinking polymers proceed through $(2\pi + 2\pi)$ cycloaddition reaction of the olefinic group present in the mesogen of the polymer. The two polymers showed photocrosslinking behavior under UV radiation and the photolysis reaction completed within 5–7 min. The photolysis studies of various methylene-spacer-containing polymers reveal that the rate of photocrosslinking depends on the length of methylene chain and it follows via octamethylene > hexamethylene. Finally, it may be concluded that these polymers can be suitably exploited for developing photoresists, printing plate integrated circuit technology, photofabrication, surface coating, energy exchange materials, etc.

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