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Synthesis, Characterization, and Properties of Thermotropic Novel Liquid Crystal Photosensitive Polymers Containing Mesogen and Photocrosslinkable Group

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A series of side chain liquid crystalline photosensitive polymers containing methyl methacrylate followed by the spacer and chalcone moiety were synthesized and characterized. Monomers, namely 4-[4{biphenyl oxy carbonyl phenyl oxy carbonyl} phenyl carbonyl ethylene phenyl] oxy butyl methacrylate (BOCPOCPCEPOBMA) and 4-[4{1-methoxy phenyl oxy carbonyl phenyl oxy carbonyl} phenyl carbonyl ethylene phenyl] oxy octyl methacrylate (MPOCPOCPCEPOOMA) was synthesized and subsequently polymerized using benzoyl peroxide as an initiator. The chemical structures and purity were characterized by FT-IR, ^{1}H- NMR, and ^{13}C-NMR analyses. The photocrosslinking studies of the polymers were investigated by UV spectroscopy. The rate of crosslinking increased with increase in the length of the methylene chain. The results of differential scanning calorimeter (DSC) analysis confirmed the formation of mesophase in the polymers. Hot stage optical polarized microscopy (HOPM) showed presence of nematic phase for poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA).

Keywords Nematic phase; side chain liquid crystalline polymer; thermal properties

Introduction

Liquid crystalline polymers [1,2] have been actively studied recently because of their technological potential and specific challenges [3–5]. Liquid crystalline polymers are regarded as materials with promising optical and electro optical properties for potential application in optical switching and image storage [6]. They are also used to transducer and amplify bimolecular events into optical outputs that are visible to the naked eye [7–9]. Polymers having a photo functional group that can be crosslinked by irradiation with ultraviolet (UV) light or electron beam have attracted much interest in microlithography [10], photo curable coatings [11], energy exchange materials [12], etc. The combination of unique optical properties of liquid crystals with photosensitivity provides a great possibility for the creation of a large variety of photochemical switches that can be used in optics and opto electronics [13–15]. A flexible photocrosslinkable main chain liquid crystalline polymer consists of mesogenic units separated by flexible alkyl spacers [16 and 17]. The

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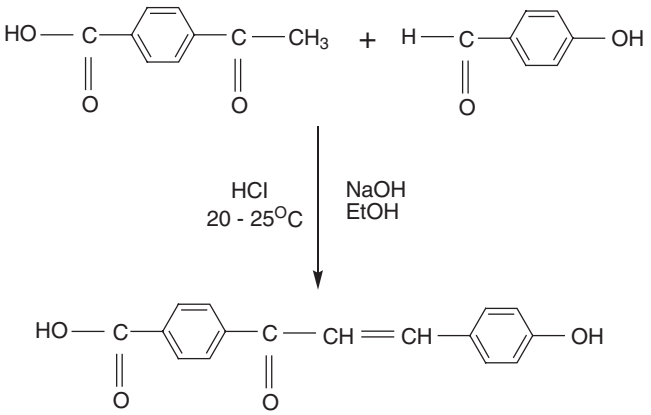
polymer backbones of side chain liquid crystalline polymers are primarily polyacrylates, polymethacrylate, however, because of polyacrylates and poly methacyrlates backbones their polymer show higher glass transition temperature and higher viscosity. In order to get a higher mobility of the liquid crystalline phase at moderate temperature to display mesomorphic properties at room temperature and the flexible spacer are chosen and used [18]. Thermotropic liquid crystalline polymers have unique combined properties of both liquid crystal and conventional thermoplastics as shown by their anisotropic mechanical properties, excellent thermal stability, and chemical resistance. The novel thermotropic liquid crystalline photoactive polymer may contain stiff mesogenic units containing three aromatic ring connected by suitable ester linkage [19]. Crosslinking is another effective approach for enhancing the glass transition and it is frequently assumed to high thermal stability of polymer system [20–22]. Since methylene spacers bonded to polymers were reported to contribute to liquid crystalline properties and feasibility of crosslinking chalcone moiety. We planned to synthesis the polymers possessing methylene spacer and chalcone moiety within built liquid crystals and photo resist characteristics. In this paper, we report the synthesis and characterization of polymers possessing both liquid crystalline and photosensitive properties by incorporating methylene spacers and pendant chalcone moiety of variable chain lengths. Their structures were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR techniques. The differential scanning calorimeter (DSC) analysis was used to verify the existence of liquid crystalline phase and to confirm the nature of the phase observed by the hot stage optical polarized microscopy (HOPM). Because of their methylene spacers, they showed excellent liquid crystalline property and with the pendant chalcone moiety they exhibit excellent photosensitivity.

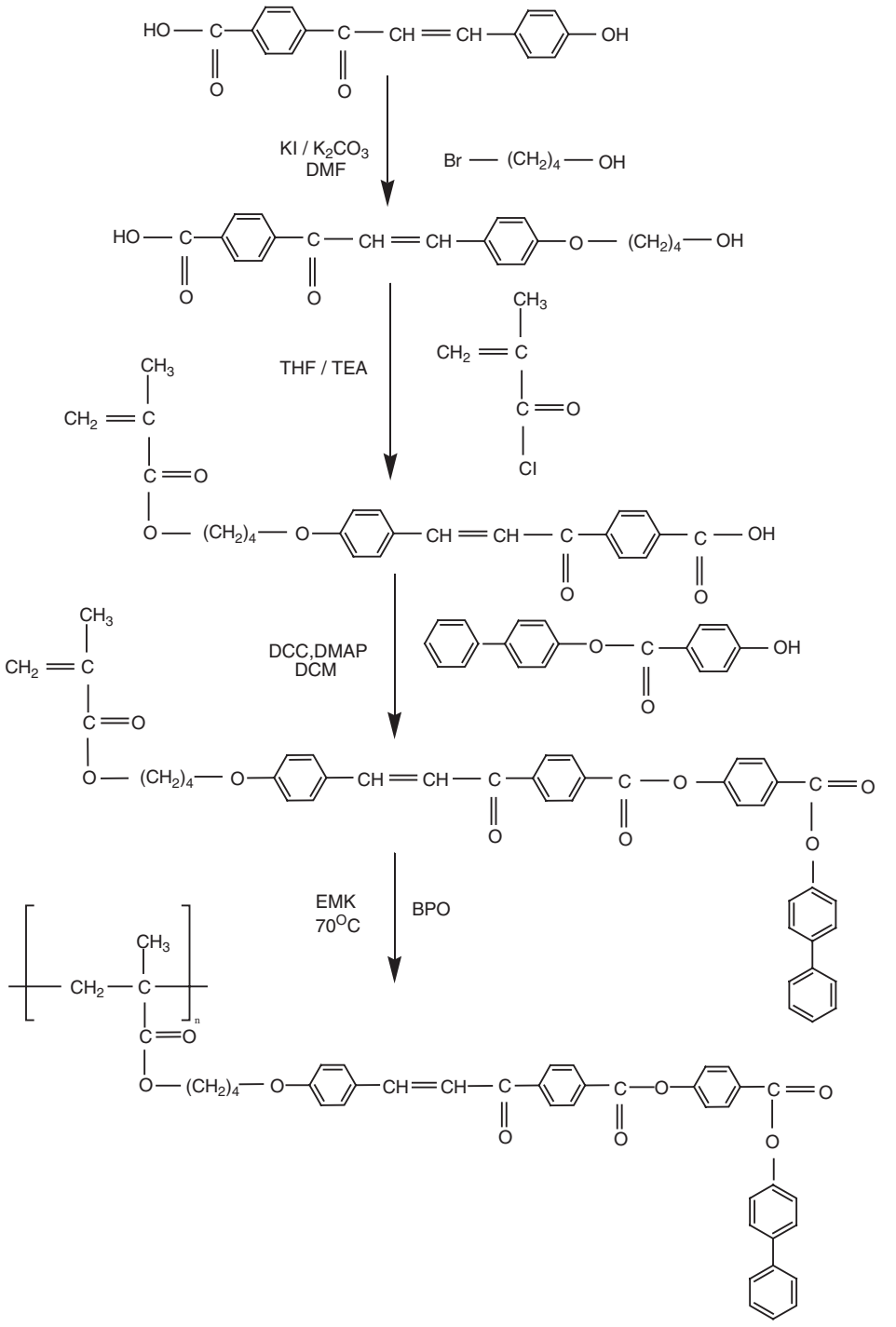


Scheme 1. Synthesis of chalcone.

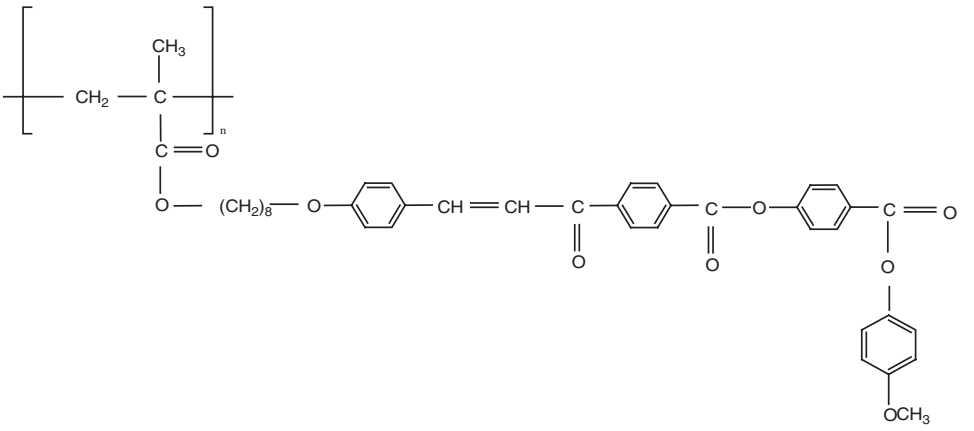
Experimental

Materials and Methods

4-carboxy acetophenone, 4-hydroxy benzaldehyde, 4-hydroxy benzoic acid, 4-phenyl phenol, 4-methoxy phenol, 4-bromobutanol, 8-bromooctanol, triethylamine, and N,N′-dicylohexyl carbodimide (DCC) were purchased from a cross chemical Co. from Lancaster chemical Co. All organic solvents were purchased from Sigma-Aldrich Co. LLC (St. Louis, MO). Solvents, like dichloromethane, ethanol methanol, tetrahydrofuran (THF), and ethyl



Scheme 2. Synthesis of poly 4-[4{1-biphenyl oxy carbonyl}-phenyl oxy carbonyl phenyl carbonyl ethylene phenyl] oxy butyl methacrylate (BOCPOCPCEPOBMA).



Scheme 3. Poly 4-[4{1-methoxy phenyl oxy carbonyl}-phenyl oxy carbonyl phenyl carbonyl ethylene phenyl] oxy octyl methacrylate (MPOCPOCPCEPOOMA).

methyl ketone (EMK), were purified by the usual procedure [23]. Methacryloyl chloride was synthesized according to the method of stempel et al. [24]. Anhydrous sodium sulphate was used to dry all organic extracts. Benzoyl peroxide (BPO) was freshly recrystallized from 1:1 methanol and chloroform.

Synthesis of Precursors

Synthesis of 4-hydroxy styryl-4′ carboxy phenyl ketone (HSCPK). The chalcone was synthesized according to the literature procedure [25]. 4-Carboxy acetophenone (0.07 mol) was dissolved in ethanol (80 ml) in a 500 ml round bottomed flask and kept under stirring. 4-Hydroxyl benzaldehyde (0.07 mol) dissolved in ethanol (80 ml) was slowly adder to it and the temperature was brought down to 5°C. To the mixture NaOH (5%) solution in ethanol was added dropwise and the stirring continued for 48 hr. The reaction mixture was then poured to ice cold water and then neutralized with 3 ml HCl. The precipitated product was filtered, washed with distilled water, and dried in vacuum (m.p. 105°C−108°C). The crude product was recrystallized with methanol (Scheme 1). The structure of the compound 4-Hydroxy styryl-4′ carboxy phenyl ketone was confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR spectra.

IR (KBr cm^{-1}): 3500 (Phenolic-OH), 1610(ethylene −CH=CH−), 1710 (ester >c=o), 1550 (aromatic ring breathing).

^{1}H-NMR ($CDCl_3$. δ in ppm): 7.3 (m, 4H, aromatic ring bonded to OH), 8.05 (s, 4H aromatic ring bonded to COOH), 6.01 (m 2H; −CH=CH−), 10.8 ppm (S, COOH).

^{13}C- NMR ($CDCl_3$), δ in ppm) 170 (−COOH), 125–140 (aromatic rings), 115 (−CH=CH−).

Synthesis of 4-carboxy (m-hydroxy alkoxy styryl) phenyl ketone (m = 4 and 8). 4-Carboxy (4-hydroxy butyl oxy styryl) phenyl ketone was synthesized by following Williamson aryl ether synthesis method in these precursors was synthesized [26]. The typical procedure of synthesis was follows: A solution of potassium carbonate (0.09 mol) and 4-hydroxy styryl 4-carboxy phenyl ketone (0.42 mol) in ethanol (80 ml) were taken in a round bottomed flask and refluxed. 4-Bromobutanol (0.06 ml) and a pinch of KI were added to

this reaction mixture. The reaction was continued for 48 hr, cooled and neutralized with 10% hydrochloric acid. The resultant precipitate was filtered and the residue was washed with distilled water and recrystallized with methanol (m.p. 85°C−90°C). 4-Carboxy (8-hydroxy octyl oxy styryl) phenyl ketone was synthesized by adopting the same procedure. The structure 4-carboxy (4-hydroxy butyl oxy styryl) phenyl ketone was confirmed by the spectroscopy techniques IR, ^{1}H- NMR, and ^{13}C-NMR.

IR (cm^{-1}): 3490 (methylene chain OH), 3000 (acid OH), 1240(ether–o–), 1600 (−CH=CH−), 1710 (acid carbonyl group).

^{1}H-NMR (δ ppm): 3.5 (s 1H,-OH), 3.4(t, 2H-CH_2-OH), 3.6 (t, 2H, ph-o-CH_2-), 1.5 (m, 4H, -CH_2-CH_2-), 5.8 (m, 2H, −CH=CH−), 7.5 (dd, aromatic ring)

^{13}C-NMR (δ ppm): 169 (−COOH), 140–150 (Aromatic protons), 110 (olefinic protons), 10–60 (Aliphatic protons).

Synthesis of 4-carboxy phenyl carbonyl ethylene phenyl oxy m-alkyl meth acrylate. A typical procedure for the synthesis of 4-carboxy phenyl carbonyl ethylene phenyl oxy -4-butyl meth acrylate was as follows. 4-Carboxy (4-hydroxy butyl oxy styryl) phenyl ketone (0.04 mol) in THF (50 ml) was taken in a 250 ml round bottomed flask. Triethylamine (0.03) was added slowly to it. The reaction mixture was cooled at 5°C. Methacryloyl chloride (0.04 mol) was added dropwise and allowed to stirred for 5 hr. The precipitate triethylamine hydrochloride was filtered and the filtrate was evaporated at 40°C under reduced pressure. The residue was washed with petroleum ether to remove unreacted methacryloyl chloride and recrystallized using methanol (m.p. 90°C–95°C). 4-Carboxy phenyl carbonyl ethylene phenyl oxy -8-octyl meth acrylate was synthesized by similar procedure. The structure of 4-carboxy phenyl carbonyl ethylene phenyl oxy -4-butyl meth acrylate was confirmed by the IR, ^{1}H-NMR, and ^{13}C-NMR spectra.

IR (cm^{-1}): 3010 (acid OH), 2852 (aliphatic $-CH_2$), 1705 (carbonyl group), 1625 (−CH=CH−), 1230 (ester–o–ph),

^{1}H-NMR (δ ppm): 1.5 (s, 3H,=C−CH_3−), 3.01 (t, 2H, $-CH_2$−O−methacroyl), 5.5 (s, 2H (−C=CH_2), 3.6 (t, 2H, ph—o−CH_2−), 1.6 (m, 4H, $-CH_2-CH_2$), 6.5 (dd, 2H, −CH=CH−) 9.5 (s, 1H−COOH).

^{13}C-NMR (δ ppm): 172 (−COOH), 120–140 (aromatic protons), 115 (−CH=CH−), 60–20 (aliphatic protons).

Synthesis of 4-[4{biphenyl oxy carbonyl phenyl oxy carbonyl}phenyl carbonyl ethylene phenyl] oxy butyl methacrylate (BOCPOCPCEPOBMA) (Monomer). A mixture of 4-carboxy phenyl carbonyl ethylene phenyl oxy -4-butyl methacrylate (0.005 mol), 4-biphenyl oxy carbonyl phenol (0.005 mol). DMAP (0.0005 mol) and DCC (0.005 mol) in 100 ml of dry methylene chloride were stirred at room temperature over night. The precipitated form of urea was removed by filtration and the filtrate was washed with 5% acetic acid and the saturated sodium chloride solution. The organic layer was then dried over anhydrous sodium sulphate and vacuum distilled. The liquid was purified by column chromatography techniques. Another monomer 4-[4{1-methoxy phenyl oxy carbonyl phenyl oxy carbonyl} phenyl carbonyl ethylene phenyl] oxy octyl methacrylate (MPOCPOCPCEPOOMA) also synthesized by adopting similar procedure.

IR (cm^{-1}):1268 (ether–o–ph), 1610 (−CH=CH− group), 2840 (methylene spacer), 1715 (ester carbonyl), 1540 (−C=CH_2− group) and 830 (aromatic bend).

^{1}H-NMR (δ ppm): 1.5 (δ, 3H, −CH=C−(CH_3)), 3.01(t, 2H, $-CH_2$–o–methacryloyl), 5.2 (s, 2H, (−C=CH_2), 3.5(t, 2H, Ph−o−CH_2−), 1.6 (m, 4H, $-CH_2-CH_2$−), 6.5 (dd, 2H, cinnomoyl−Ph), 7.5 (m, 9 biphenyl ring)

^{13}C-NMR (δ ppm): 175 (−C=O.O), 120–140 (Aromatic carbons), 110 (olefinic carbon), 60–10 (aromatic carbons).

Polymerization of 4-[4{biphenyl oxy carbonyl phenyl oxy carbonyl} phenyl carbonyl ethylene phenyl] oxy butyl methacrylate (BOCPOCPCEPOBMA). The polymers were synthesized according to the literature procedure [25]. The polymer was synthesized by free radical polymerization of 4-[4{biphenyl oxy carbonyl phenyl oxy carbonyl} phenyl carbonyl ethylene phenyl] oxy butyl methacrylate (0.01 mol) dissolved in dry oxygen free THF (30 ml) using BPO (1 wt%). At 70°C the reaction was carried out for 24 hr. The mixture was cooled and treated with excess methanol to precipitate the polymer, the polymer was purified by repeated reprecipitation from chloroform using methanol and dried in vacuum at 50°C .The another polymer also synthesized by the same route (Schemes 2, 3).

Measurements

The FT-IR spectra were recorded on a Hitachi 270–50 spectrophotometer using KBr. ^{1}H-NMR was run on a Bruker 270 MHz spectroscopic measurement was recorded with Bruker MSC 300 spectrometer. The molecular weights (M_w and M_n) were determined in the Water 501 gel permeation chromatograph, THF was used as an eluent and poly styrene standards were employed for calibration. Thermal stability of polymers was investigated by TGA on a NETZSCH STA 409 C/CD. Glass transition temperatures of polymer were measured from differential scanning calorimeter (DSC) NETZSCH.DSC.204. UV-visible spectra were recorded on a Hitachi UV-2000 spectrophotometer. The textures of the polymer samples were studied on a Euromax polarizing microscope equipped with a Linken HFS91 heating stage. The samples were prepared by melting the sample between two thin glass cover slips to get uniform film and anisotropic behavior observed by heating and cooling with Kodak film.

Results and Discussion

FT-IR Spectra of Polymer

The FT-IR Spectra of the poly (BOCPOCPCEPOBMA) is shown in Fig. 1(a). The aromatic and CH and olefinic vibrations occurred close to 3010 cm^{-1}. The CH_2– stretching vibration observed at 2927 cm^{-1} and 2849 cm^{-1}. The C=O vibration of the ester occurred at 1718 cm^{-1}. The C=C and aromatic ring vibration yielded their peaks at 1606 cm^{-1}. The peak at 1464 cm^{-1} was due to CH_2 bending and aromatic ring skeletal vibration. The CH_2 bending vibration also gives a shoulder close to 1375 cm^{-1}. The COO vibration gave peak at 1287 cm^{-1}, 1272 cm^{-1} and 1255 cm^{-1}. The phenoxide C=O vibration occurred at 1120 cm^{-1} and 1064 cm^{-1}. The group of peaks occurring below 1000 cm^{-1} was due to aromatic ring CH bending modes.

The olefinic CH− stretching vibration occurs at 3036 cm^{-1}. The corresponding C=C stretching vibration occurs at 1600 cm^{-1}. The C=O stretching occurs at 1734 cm^{-1}. The aromatic ring a vibration occurs at 641 cm^{-1} and 1438 cm^{-1}. The CH_2 bending modes occurs at 1311 cm^{-1}. The ester COO vibration gives a peak at 1291 cm^{-1}. The C−O vibrations gives group of peaks at 1167 cm^{-1}, 1088 cm^{-1}, and 1015 cm^{-1}. The peaks at 949 cm^{-1} and 1311 cm^{-1} illustrates trans position which occurs for the C=C bond substituents. Hence, the IR spectra establish the structure of the poly (MPOCPOCPCEPOOMA) is shown in Fig. 1(b).

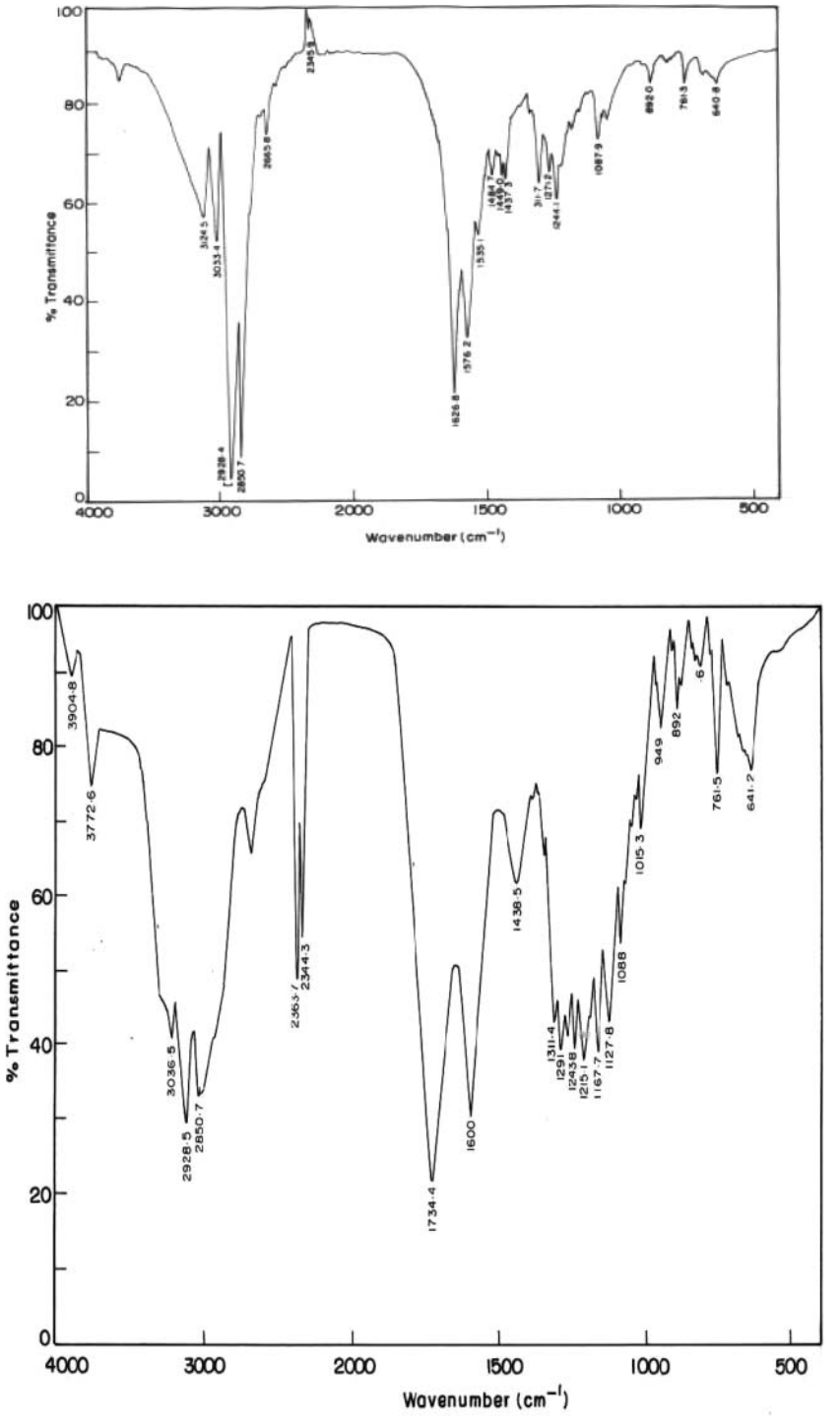


Figure 1. (a) FT-IR spectra of poly (BOCPOCPCEPOBMA). (b) FT-IR spectra of poly (MPOCPOCPCEPOOMA).

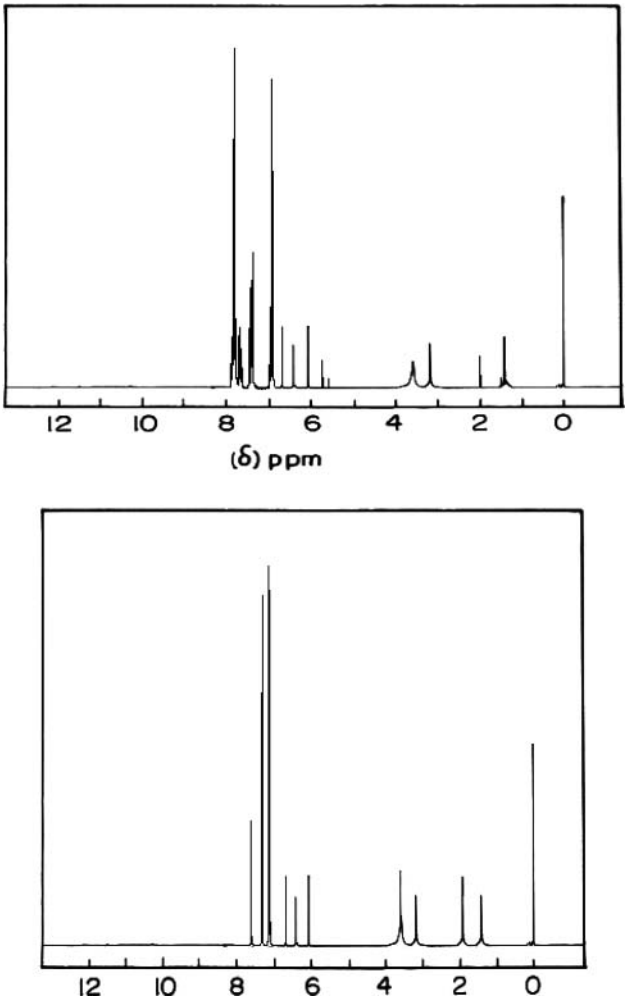


Figure 2. (a) ^{1}H -NMR spectra of poly (BOCPOCPCEPOBMA). (b) ^{1}H -NMR spectra of poly (MPOCPOCPCEPOOMA).

^{1}H-NMR Spectra of Polymer

The ^{1}H-NMR spectrum of poly (BOCPOCPCEPOBMA) is shown in Fig. 2(a). The poly (BOCPOCPCEPOBMA) shows multiplet resonance signals at 6.05–7.99 ppm corresponding to the aromatic protons. The resonance signals of the olefinic protons of the pendant chalcone moiety were observed as doublets at 5.7 ppm and 5.9 ppm. The backbone methylene ($-CH_2$) protons signals appeared at 1.7 ppm. The broad resonance signals at 2.1 ppm were due to the α-CH_3 protons. The resonance signals are at 3.3 ppm and 3.6 ppm were due to methoxy protons.

The ^{1}H-NMR spectrum of poly (MPOCPOCPCEPOOMA) is shown in Fig. 2(b). The olefinic protons produce their signals between 5.8 ppm and 6.1 ppm. All the aromatic ring protons show their peaks between 6.5 ppm and 8 ppm. The alkyl CH_3 and CH_2 protons give peaks at about 2 ppm and 1.8 ppm. The $-CH_2-O-$ and CH_3-O- protons produce

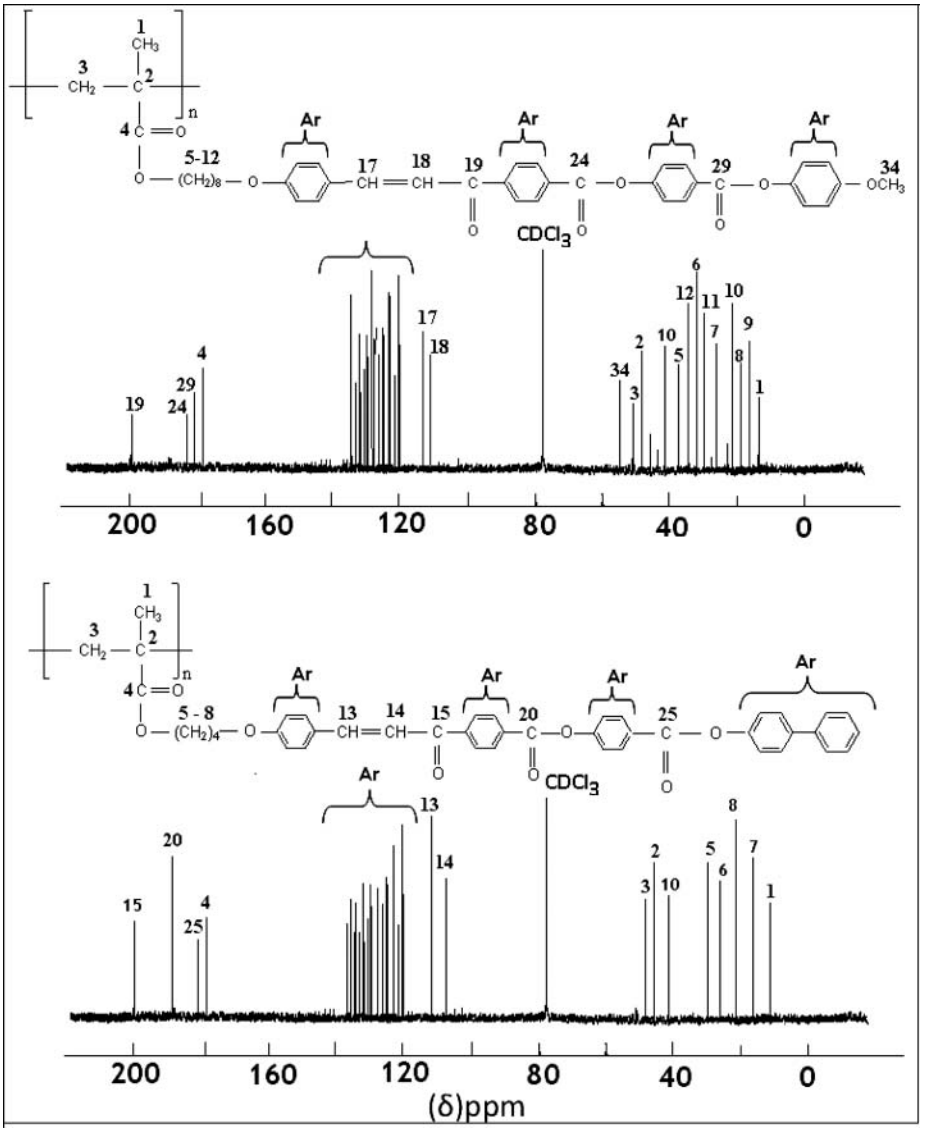


Figure 3. C^{13}NMR spectrum of poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPEPOOMA).

their peaks between 3.5 ppm and 4 ppm. Thus, ^{1}H-NMR spectrum carries signals due to different types of protons of poly (MPOCPOCPCEPOOMA) .

^{13}C NMR Spectra of Polymer

The proton decoupled ^{13}C-NMR spectrum of poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA) is shown in Fig. 3. ^{13}C-NMR chemical shift assignments were made from the off resonance decoupled spectra of the polymers. The keto-carbonyl carbon resonances were observed at 189 ppm and 190 ppm. The ester carbonyl carbon gave their characteristic signals are at 180 ppm and 178 ppm. The signals at 110 ppm are due to

Table 1. TGA and molecular weight data of poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA)

Polymers	$\overline{M_n} \times 10^4$	PDI	IDT	Temperature (°C) at weight loss (%) 20	40	60	80
Poly (BOCPOCPCEPOBMA)	2.69	1.75	200	280	320	370	393
Poly (MPOCPOCPCEPOOMA)	2.44	1.54	190	285	300	355	375

IDT – Initial decomposition temperature (°C).
PDI – Poly dispersity index.
$\overline{M_n}$ and M_w – Number and weight average molecular weight of polymer.

>CH=CH< (olefinic) carbon connected to the benzene ring. The aromatic carbon gave signals at 120–140 ppm and the aliphatic carbon gave signals at 18 ppm, 21 ppm, 29 ppm, 35 ppm, 18 ppm, 43 ppm, and 46 ppm. The signal observed at 40–50 ppm is assignable to the backbone carbon (—C—) of the polymer unit.

Molecular Weight

The values of number average molecular weight ($\overline{M_n}$), weight average molecular weight ($\overline{M_n}$) and polydispersity index (PDI) of polymers were determined by gel permeation chromatography and the data are represented in Table 1. The PDI of polymers are close to the theoretical values of PDI for polymers produced via radical recombination and disproportionation [27 and 28].

$$\overline{M_w} \times 10^{-4} = 4.72;\ \overline{M_n} \times 10^{-4} = 2.69, \qquad \overline{M_w}/\overline{M_n} = 1.75$$
$$\overline{M_w} \times 10^{-4} = 3.78;\ \overline{M_n} \times 10^{-4} = 2.44, \qquad \overline{M_w}/\overline{M_n} = 1.54$$

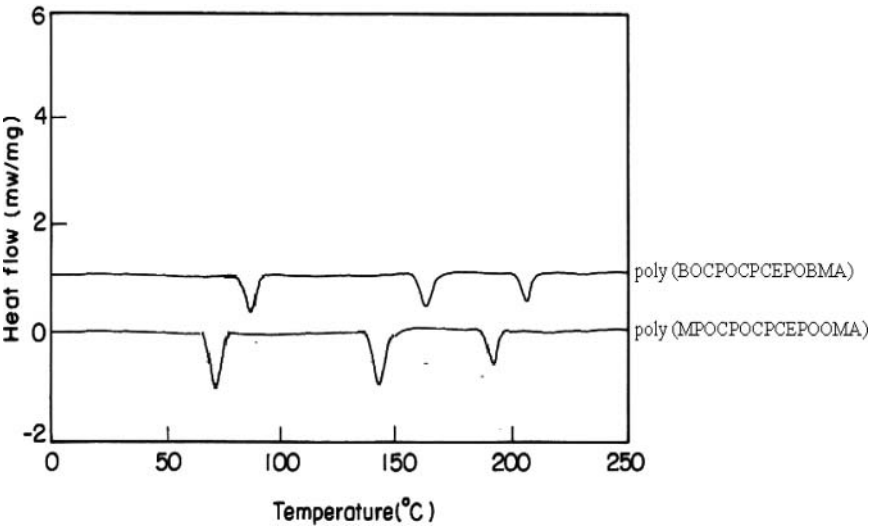


Figure 4. DSC trace of poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA).

Table 2. DSC and HOPM data of poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA)

Polymers	DSC				HOPM
	T_m °C	T_i	δT	T_g	Mesophase
Poly (BOCPOCPCEPOBMA)	169	210	41	87	Nematic
Poly (MPOCPOCPCEPOOMA)	145	190	45	75	Nematic

T_m – Crystal–liquid melting temperature.
T_i – Mesophase-isotropic phase transition temperature.
T_g – Glass transition temperature.

Hence, the PDI value of termination by disproportionation was more than that for dimerisation.

Thermal Studies

DSC Analysis

DSC analysis investigates the mesogenic transition of the polymers. The DSC thermogram of the polymers was measured at a heating rate of 10°C min^{-1} and representative thermogram of polymers has been shown in Fig. 4. The phase transition temperature of the polymers was summarized in Table 1. The DSC thermograms show three endothermic

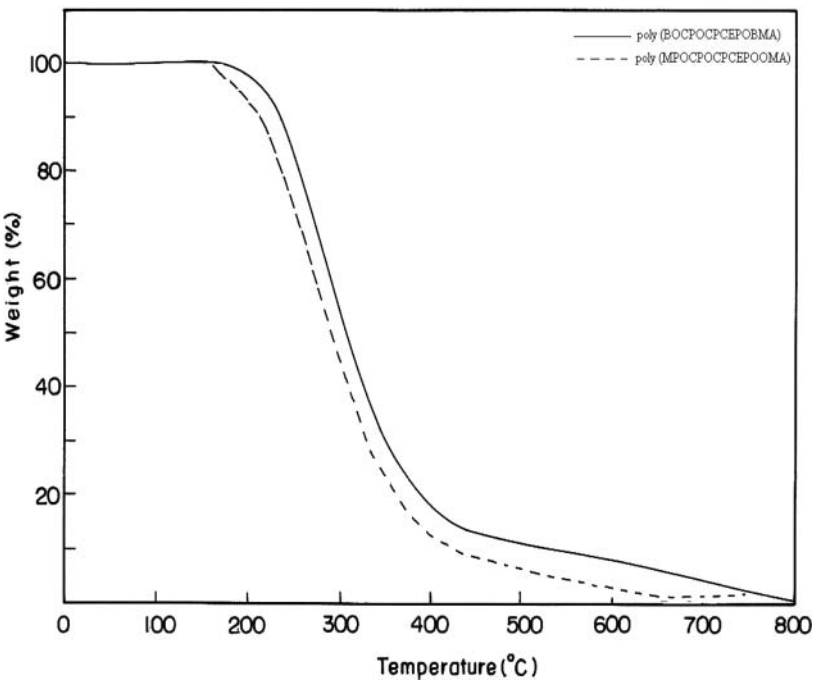


Figure 5. TGA thermogram of the poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA).

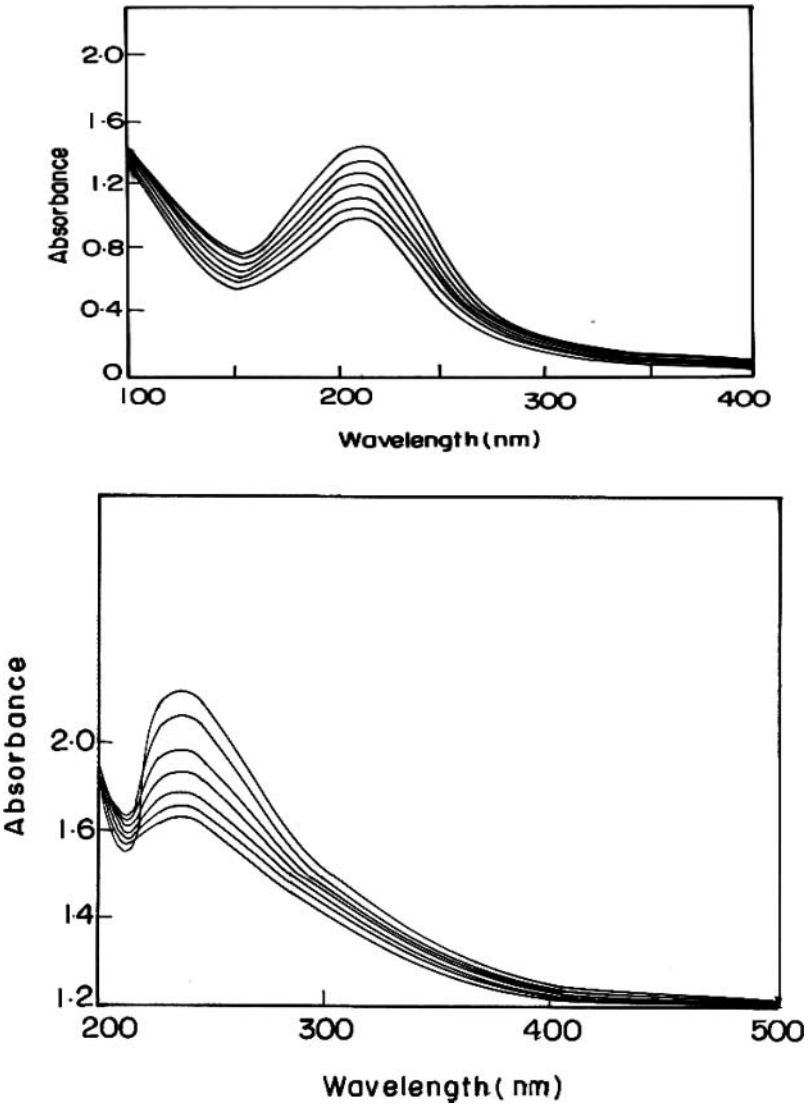


Figure 6. (a) Change in UV spectral characteristics, during the photolysis of the polymer poly (BOCPOCPCEPOBMA). (b) Change in UV spectral characteristics, during the photolysis of the polymer poly (MPOCPOCPCEPOOMA).

peaks which reveals that the mesogenic transition values decreases with increase in methylene group. The synthesized polymers show higher mesogenic transition temperature due to the effect of substituent of biphenyl ring on the thermal properties of the polymer. The poly (BOCPOCPCEPOBMA) exhibits higher glass transition temperature due to the presence of shorter methylene chain and rigidity of the biphenyl ring. The poly (MPOCPOCPCE-POOMA) shows lower glass transition temperature due to the presence of longer methylene chain of the polymer backbone.

Thermogravimetric Analysis

The thermal stability of the polymer was studied by thermogravimetric analysis in nitrogen atmosphere. Temperatures corresponding weight loss between 10% and 80% were given in Table 2. The representative thermograms are shown in Fig. 5. The poly (BOCPOCP-CEPOBMA) was showing good thermal stability up to 190°C due to the presence of rigid biphenyl ring, increase in the aromaticity and shorter methylene chain. The poly (MPOCPOCPCEPOOMA) shows lower thermal stability due to the presence of longer methylene chain of the polymer backbone.

Photochemical Properties

The photocrosslinking reactions of the synthesized liquid crystalline photosensitive polymers were studied in polymer solutions. The polymers showed the absorbance band at 230 due to the π–π^* transition of the exocyclic double bond, during this absorption intensity was decreased. The change in UV spectral pattern during the photolysis of polymer at various intervals of time is shown in Fig. 6(a) and 6(b). The corresponding photo-crosslinking rate on irradiation time of the polymer is shown in Fig. 7. The photocrosslinking of the polymer chain, which involves the $2\pi + 2\pi$ cycloaddition leading to the formation of the cyclobutane ring [29 and 30]. The UV spectrum of the polymer solution was recorded at a definite intervals and the rate of disappearance of >C=C< of the pendant α,β-unsaturated ketone unit of the polymer was followed by measuring the UV absorption intensity of the solution (Schemas 4 and 5) after each exposure interval using the following

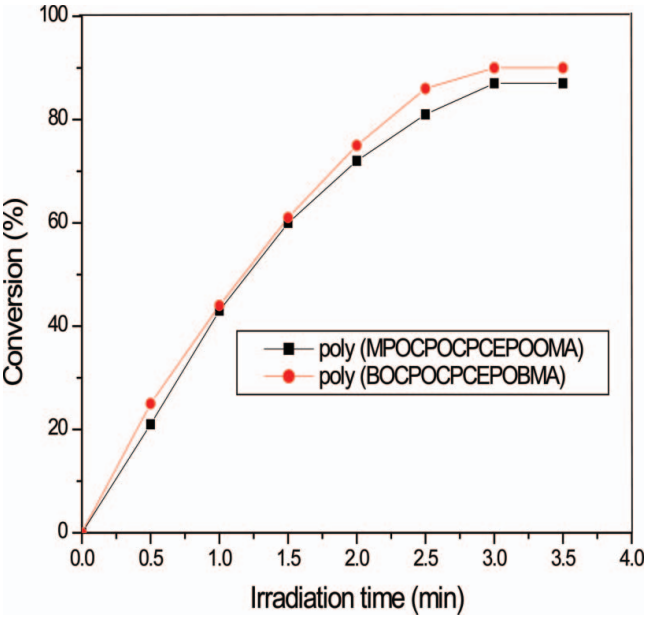
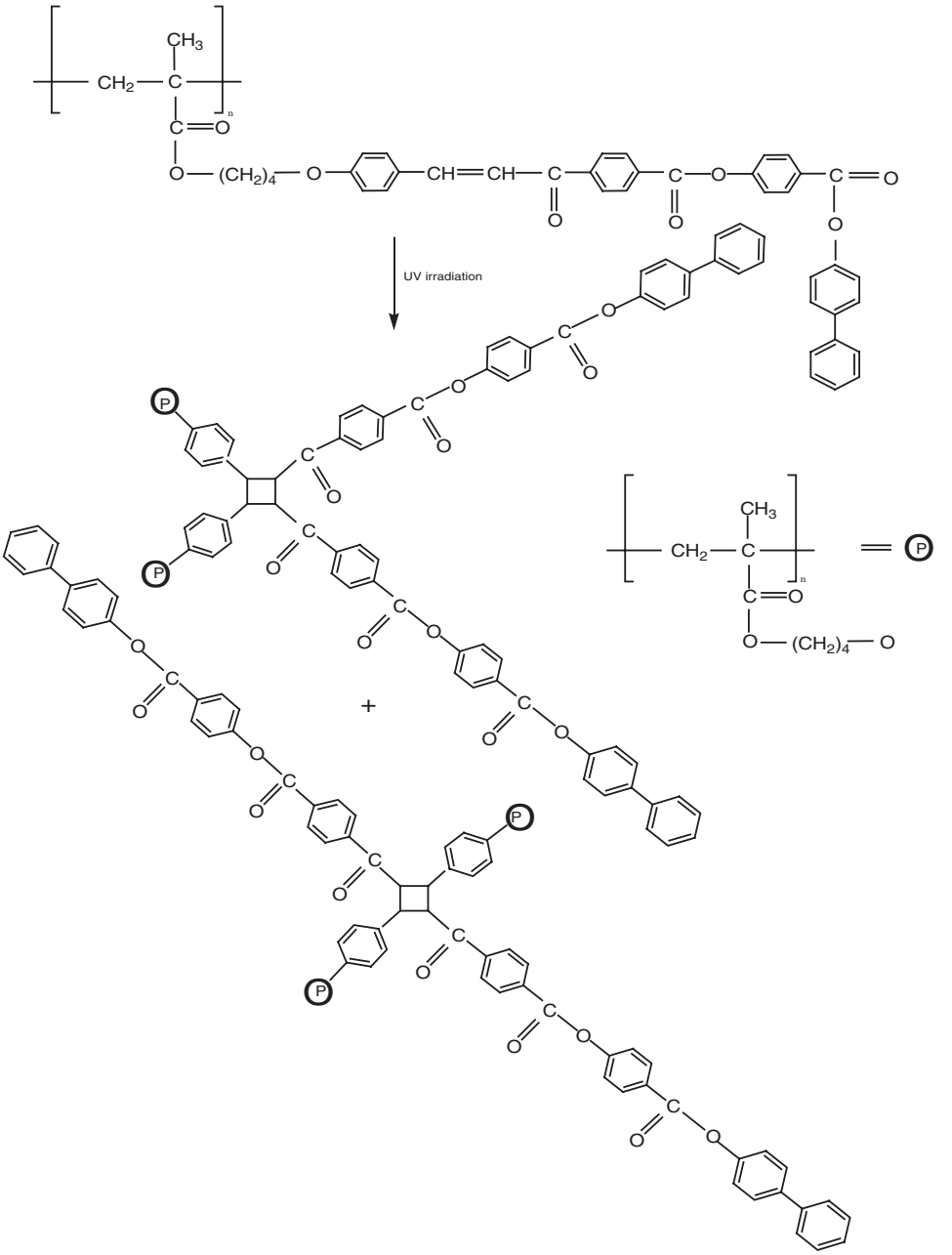


Figure 7. Dependence of the photocrosslinking rate on irradiation time of the polymer poly (BOCPOCPCEPOBMA) and poly (MPOCPOCPCEPOOMA).

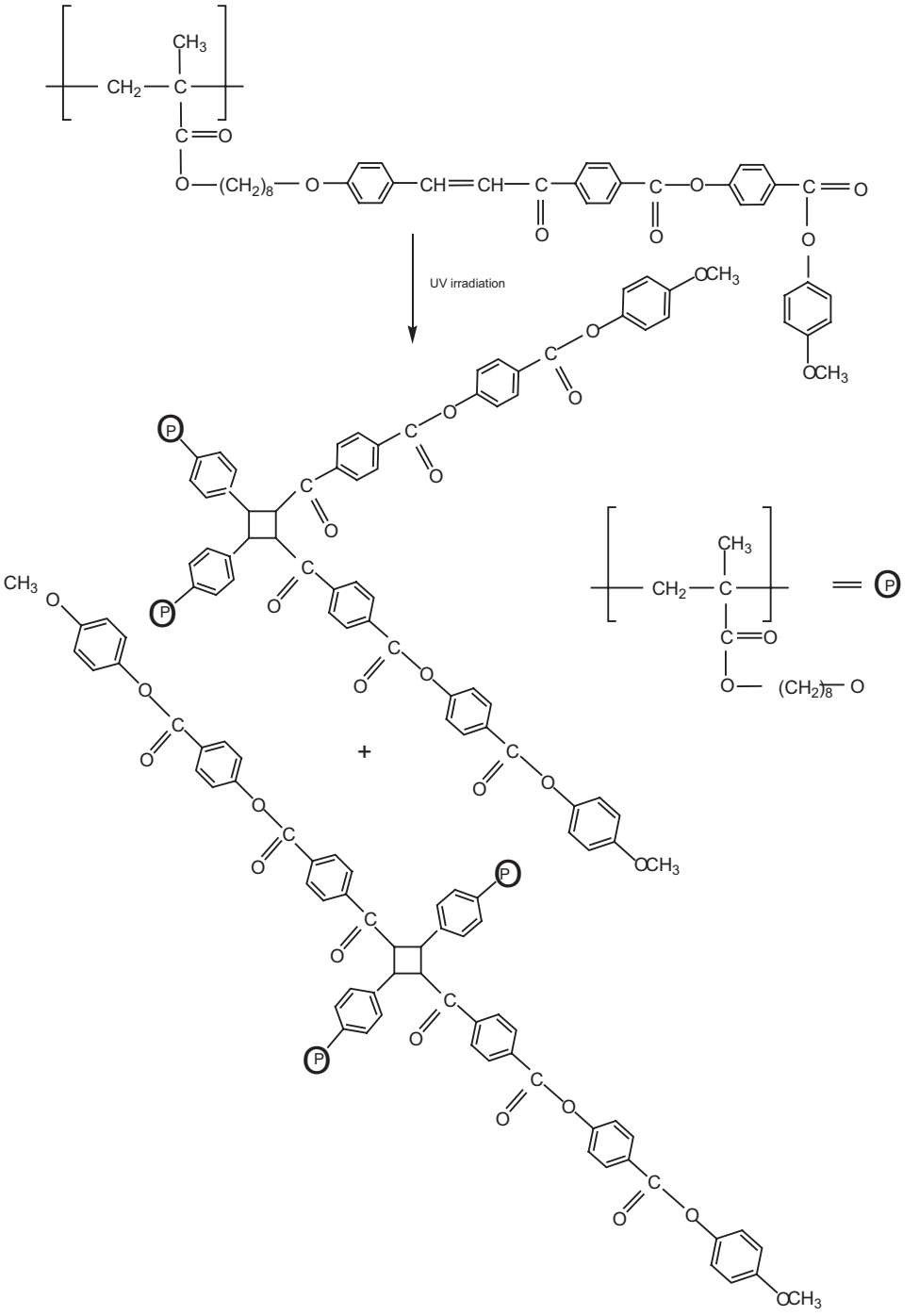


Scheme 4. Photocrosslinking reaction ($2\pi + 2\pi$ cycloaddition) of poly (BOCPOCPCEPOBMA).

expression:

$$\text{Rate of conversion}\,(\%) = (A_0 - A_T)/(A_0 - A_\alpha) \times 100$$

Where A_0, A_T, and A_α are absorption intensities due to the C=C group after the irradiation times $t = 0$, $t = T$, and $t = \alpha$ (maximum irradiation time), respectively.



Scheme 5. Photocrosslinking reaction ($2\pi + 2\pi$ cycloaddition) of poly (MPOCPOCPCEPOOMA).

Polarized Optical Microscopy Analysis

The DSC trace of the polymer shows three endothermic peaks, corresponding to glass transition temperature, melting (T_m) and isotropic (T_i) transition temperature. Generally, the melting transition temperature decreases with increase in aliphatic spacers as expected. The polymers exhibited liquid crystalline nature with nematic textures on heating. The polymer was heated to 191°C which exhibits Nematic texture as shown in Figs. 8(a) and (b). On the cooling of the polymer from isotropic melt (T_i), the reproducibility of the phase was satisfactory. The rigidity of the mesogenic core with the flexible spacer length and

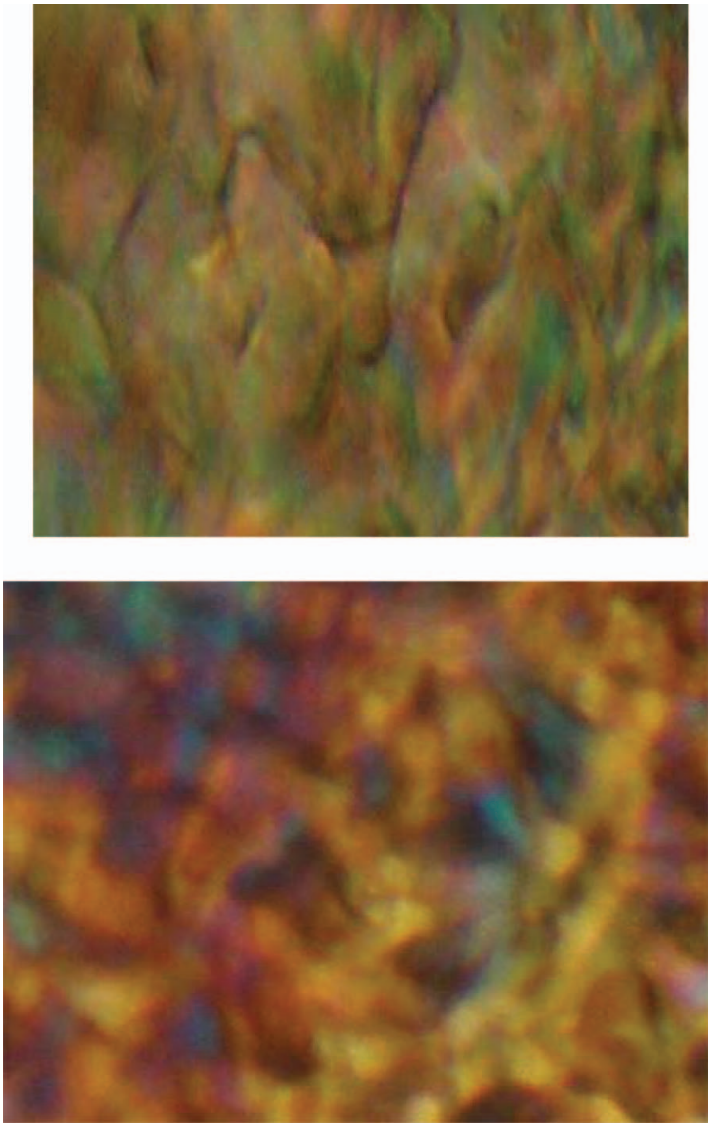


Figure 8. (a) HOPM photograph of poly (BOCPOCPCEPOBMA). (b) HOPM photograph of poly (MPOCPOCPCEPOOMA).

terminal units highly influence the melting temperature, mesophase temperature, and even molecular arrangement.

Conclusions

The novel liquid crystalline photoactive was synthesized by free radical polymerization method. The polymers were synthesized and characterized by spectroscopically. The spectral data supported the structural assignment of the polymers. Glass transition temperatures were determined by DSC analysis. The synthesized polymers have higher thermal stability due to the presence of increase in the aromaticity of the polymer backbone. The polymers showed photocrosslinking behavior via. $2\pi + 2\pi$ cycloaddition under UV irradiation. The poly (MPOCPOCPCEPOOMA) containing the longer methylene chain unit showed faster photolysis than that of lower methylene chain of the poly (BOCPOCPCEPOBMA). The HOPM analysis showed that the synthesized polymers were exhibited LC properties with nematic texture.

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