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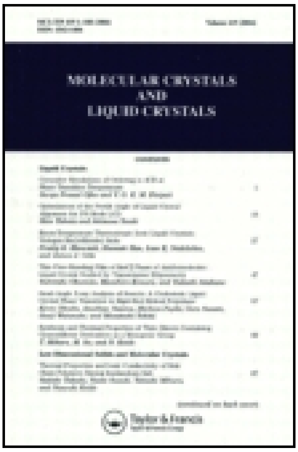

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Synthesis, Characterization, and Properties of Thermotropic Novel Liquid Crystalline Photosensitive Polymer

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Available online: 20 Mar 2012

To cite this article: Sivakumar Jeyasheela & Kathavarayan Subramanian (2012): Synthesis, Characterization, and Properties of Thermotropic Novel Liquid Crystalline Photosensitive Polymer, Molecular Crystals and Liquid Crystals, 557:1, 161-175

To link to this article: http://dx.doi.org/10.1080/15421406.2012.640571

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Mol. Cryst. Liq. Cryst., Vol. 557: pp. 161–175, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.640571

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Synthesis, Characterization, and Properties of Thermotropic Novel Liquid Crystalline Photosensitive Polymer

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Side-chain liquid crystalline photosensitive polymer was synthesized using pendant chalcone moiety. The pendant chalcone moiety was reacted with methylene spacer followed by incorporating methacryloyl chloride which is then reacted with 4-hydroxy phenyl oxycarbonyl acetophenone which is then polymerized using BPO as an initiator. The structures of the synthesized liquid crystalline photosensitive polymer have been confirmed by spectroscopic techniques like IR, ^1H and ^{13}C NMR, and UV visible spectrometer. The thermal stability of the polymer was investigated by thermo gravimetric analysis (TGA). The thermal stability of the polymer decreased with increase in flexible methylene chain. The photochemical properties of this polymer were investigated by UV spectroscopy. Crosslinking proceeds via 2π–2π cycloaddition of the –CH=CH– of the chalcone moieties. Liquid crystalline phase was confirmed by the differential scanning calorimetry (DSC) and hot stage optical polarized microscopy (HOPM).

Keywords Chalcone; crosslinking; liquid crystal; photoresist

1. Introduction

In recent years, polymers containing photosensitive units in the main or side-chain liquid crystal polymer have become attractive due to the photocrosslinking properties offered by the presence of such units. Polymers with pendant cinnamic ester groups have been used as photosensitive polymers [1, 2]. Technological applications of radiation-sensitive polymers have attained considerable interest which has been applied to a wide research area in different fields, such as photolithography [3–6], printing materials [7], and liquid crystalline materials [8–12]. Photolithographic technology has made significant contributions to the microelectronics industry [13–15]. Liquid crystals occupy an important place in modern optical technology. π-Conjugated polymers are promising candidates for thin-film transistors, light-emitting diodes, and organic lasers [16–18]. Attachment of liquid crystalline pendants to conjugated polymer backbones is of interest because the resulting polymers may possess novel electronic and optical properties. Because of the orientability of the mesogens by external forces, the polymers may exhibit both linear and circular polarization [19]. LC

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*Address correspondence to Kathavarayan Subramanian, Department of Chemistry, College of Engineering, Anna University, Chennai 600025, India. E-mail: kathsubramanian@yahoo.com main chain polymers crosslinked networks can be prepared by chemical/thermal/photocrosslinking of reactive double bonds in the chain or by reaction with crosslinking agents or by copolymerization [20–34]. Photolithography is generally based on photocrosslinking reactions of polymeric photoresist. Photoresist materials need to be highly transparent in a visible region in order to be used as display device materials. During the past decade, we worked on several photosensitive polymers [35, 36]. High photosensitivity, thermal stability, and good solubility are the required properties for a photocrosslinkable polymer. In this study, the synthesis, characterization, and properties of thermotropic novel liquid crystalline photosensitive polymers containing pendant chalcone moiety and methylene spacer which shows photosensitive properties as well as liquid crystalline properties are reported. Their structures have been identified/characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR techniques.

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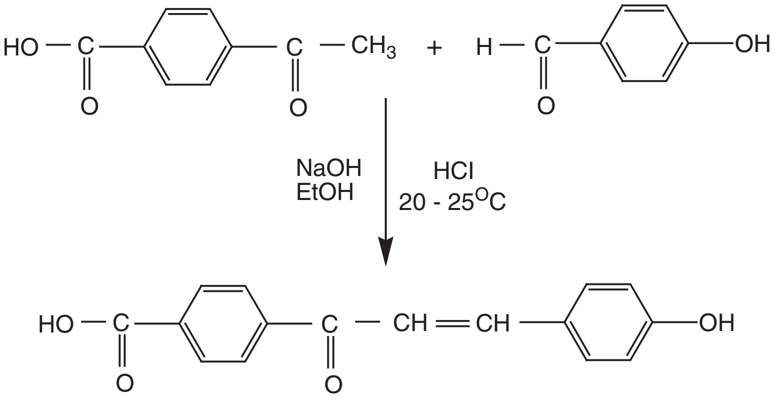
2. Experimental

2.1. Materials

4-Carboxy acetophenone (Aldrich), 2-bromoethanol (Aldrich), and 4-hydroxyl benzaldehyde (Aldrich) were used as received. Triethylamine, 1,3-dicyclohexylcarbodiimide, 4-(*N*, *N′* dimethylaminopyridine, and methacryloyl chloride were purchased from Lancaster. Dichloromethane, ethanol, methanol, tetrahydrofuran (THF), and ethyl methyl ketone (EMK) Super religare laboratories (SRL) were purified by the usual procedure and dried before use [37]. Anhydrous potassium carbonate (Merk) and benzoyl peroxide (BPO) were freshly recrystallized from a chloroform, methanol (1:1) mixture. All other chemicals and solvents were analytical grade samples and were used as received.

2.2. Synthesis of 4-Hydroxy Styryl 4′-Carboxy Phenyl Ketone (HSCPK)

4-Carboxy acetophone (0.05 mol) and 4-hydroxy benzaldehyde (0.05) were dissolved in 50 mL ethanol and cooled at 0ºC–5°C. NaOH (5%) solution was simultaneously added into the reaction mixture. The stirring was continued for 48 h and then the reaction mixture was poured into ice cold water. It was neutralized with dilute HCl to isolate the product. The product was filtered from ethanol (Yield 95%, mp 120ºC–125°C), (Scheme 1) [38].



Scheme 1. Synthesis of 4-hydroxy styryl 4-carboxy phenyl ketone.

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The structure of the compound (HSCPK) was confirmed by IR, ^{1}H NMR, and ^{13}C NMR techniques.

IR (KBr, cm^{-1}): 3220 (phenolic-OH), 1625 (ethylene –CH=CH–), 1630 (keto>C=O), 1490 (aromatic ring breathing).

^{1}H NMR (CDCl$_3$, δ in ppm): 9.1 (phenolic –OH–), 7.39 (m, 4H, aromatic pendant phenyl), 8.15 (s, aromatic carbon, –OCO– attached), 5.9 (d, 2H; –CH=CH–).

^{13}C NMR (CDCl$_3$, δ in ppm): 169 (keto carbon), 120–140 (aromatic carbon), 115 and 119 (olefinic carbon).

2.3. *Synthesis of 1-Hydroxy Ethyl Oxystyryl-4′-Carboxy Phenyl Ketone (HEOSCPK)*

The compound (HSCPK) (0.01149 mol) was dissolved in dry dimethylformamide (DMF) (20 mL) in a 250 mL two-necked round bottom flask. Anhydrous potassium carbonate (K_2CO_3) (0.0111 mol) and a pinch of KI were added to it. The reaction mixture was continuously heated to 90°C with constant stirring. 2-Bromoethanol (0.011 mol) was added in drops to the reaction mixture and stirred for 48 h. Then, the reaction mixture was poured in to crushed ice and neutralized with 10% HCl to get a product. The precipitated product was filtered, washed, and dried in vacuum (Yield 85%, mp 110ºC–115°C), (Schemes 2 and 3) [39]. The structure of the compound (HEOSCPK) was identified by the spectroscopic techniques (IR, ^{1}H NMR, and ^{13}C NMR).

IR (KBr, cm^{-1}): 3315 (OH), 2245 (C—O stretching), 1610 (olefinic –CH=CH–), 1489 (aromatic ring), 2930 (aliphatic –CH$_2$), 1711 (ester C=O), 1125 and 1030 (O–CH$_2$).

^{1}H NMR (CDCl$_3$, δ in ppm): 9.3 (O–H), 7.7 (m, 4H, aromatic pendent phenyl), 7.1 (m, 4H aromatic carbon, –CO– attached), 6.3 (d, 2H; –CH=CH–), 6.8 (m, 4H phenyl group), 3.5 (m, O–CH$_2$), 1.6 (methylene group).

^{13}C NMR (CDCl$_3$ δ in ppm): 173 (carbonyl carbon), 120–140 (aromatic carbon), 115 and 120 (olefinic carbon), 60–10 (aliphatic carbon).

2.4. *Synthesis of 4-Carboxy Phenyl Carbonyl Ethylene-4-Phenyl Oxyethyl Methacrylate (CPCEPOEMA)*

In a two-necked RB flask (250 mL), the compound HEOSCPK (0.005 mol) and triethylamine (0.005 mol) were dissolved in THF (50 mL) and cooled to 0ºC–5°C. Methacryloyl chloride (0.005) in 50 mL of THF was then added dropwise with stirring. Then, the reaction mixture was stirred for 12 h at room temperature and the precipitated quaternary ammonium salt was filtered off and the filtrate evaporated under reduced pressure by keeping the bath temperature below 40°C. The precipitation, thus obtained, was recrystallized using ethanol (Yield 71%, mp 90ºC–93°C). The structure of the monomer (CPCEPOEMA) was identified by the IR, ^{1}H NMR, and ^{13}C NMR spectra.

IR (KBr, cm^{-1}): 2849 (aliphatic –CH$_2$), 1725 (ester C=OO), 1678 (keto C=O), 1611 (olefinic CH$_2$=CH–), 1560 (aromatic and C=C), 1235 (C–O stretching), 1226 (Ar-O).

^{1}H NMR (CDCl$_3$, δ in ppm): 8.2 (m, 4H, aromatic pendent phenyl), 8.0 (m, 4H aromatic carbon, –CO– attached), 6.7 (m, 2H; –CH=CH–), 7.5 (m, 4H phenyl group), 3.7 (m, O–CH$_2$), 2.1 (methyl group), 1.4 (methylene group).

^{13}C NMR (CDCl$_3$ δ in ppm): 180 (carbonyl) 121–145 (aromatic carbon), 117–119 (olefinic carbon), 60–10 (aliphatic carbon), 68(O–CH$_2$).

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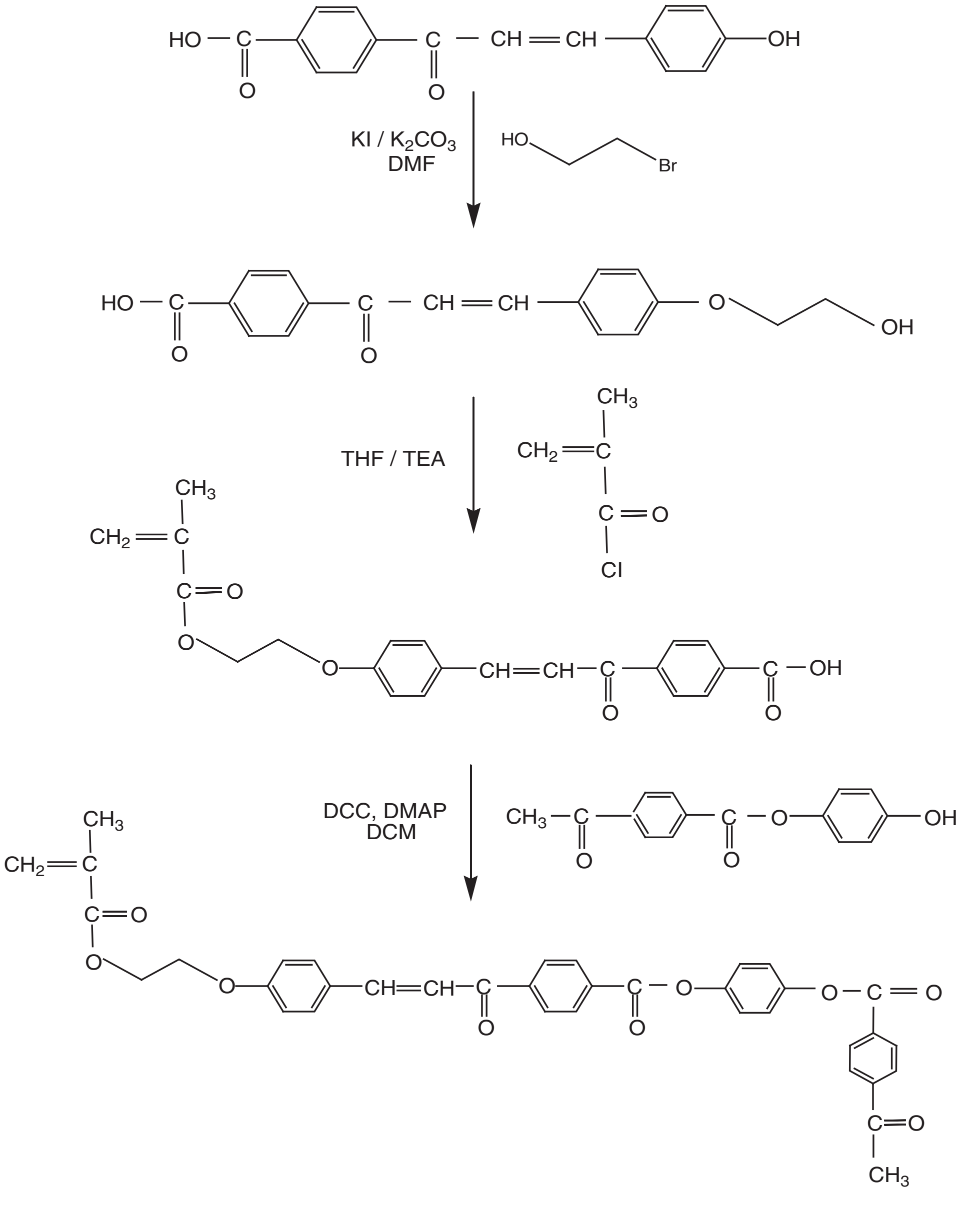
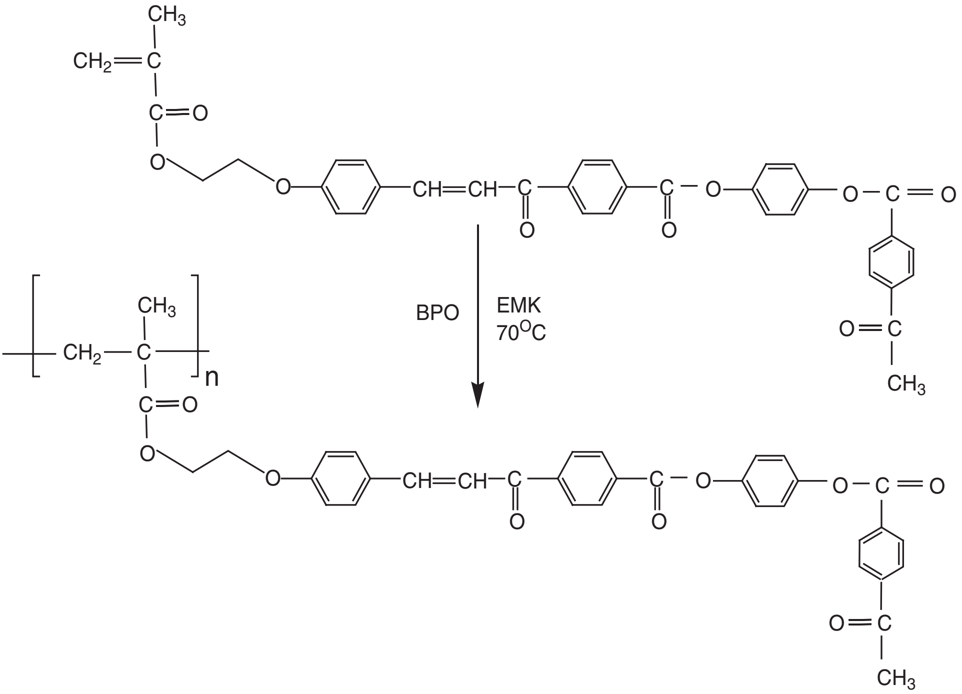


Scheme 2. Synthesis of monomer MPPCEPOEMA.

2.5. Synthesis of 4[4{1-Methyl Carbonyl Phenyl Carbonyl Oxy} 4′ Phenyl Oxycarbonyl] Phenyl Carbonyl Ethylene Phenyl Oxyethyl Methacrylate (MPPCEPOEMA)

The monomer (CPCEPOEMA) (0.0025 mol) and 4-hydroxy phenyl oxycarbonyl acetophenone (0.0025 mol) were dissolved in dichloromethane (20 mL). The solution of *N*,*N*′-dimethylaminopyridine (DMAP) (0.0001 mol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.0001 mol) in absolute dichloromethane (100 mL) was added to the above and kept under



Scheme 3. Synthesis of poly (MPPCEPOEMA).

constant stirring for 24 h. 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 sulphate and removed under vacuum distillation. The residue obtained was purified by column chromatography using 10% methanol in chloroform as eluent. (Yield 69%, mp 75°C –80°C). The structure of the compound (MPPCEPOEMA) was confirmed by the IR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques.

IR (KBr, cm^{-1}): 2842 (aliphatic –CH_2), 1733 (ester C=OO), 1672 (keto C=O), 1596 (olefinic CH_2=CH–), 1585 (aromatic and C=C), 1245 (C–O stretching), 1229 (Ar-O).

^{1}H NMR ($CDCl_3$, δ in ppm): 8.3 (m, 4H, aromatic pendent phenyl), 7.8 (m, 4H aromatic carbon, –CO– attached), 6.9 (m, 2H; –CH=CH–), 7.5 (m, 4H phenyl group), 3.7 (m, O–CH_2), 2 (methyl group), and 1.6 (methylene group).

^{13}C NMR ($CDCl_3$ δ in ppm): 181 (carbonyl), 121–139 (aromatic carbon), 116–120 (olefinic carbon), 68(O-CH_2), and 60–10 (aliphatic carbon).

2.6. Polymerization of 4[4{1-Methyl Carbonyl Phenyl Carbonyl oxy} 4′ Phenyl Oxycarbonyl] Phenyl Carbonyl Ethylene Phenyl Oxyethyl Meth acrylate (MPPCEPOEMA)

The polymer MPPCEPOEMA was polymerized as a 2 M solution in ethyl methyl ketone using BPO as an initiator at 70°C. The predetermined quantities of MPPCEPOEMA, the initiator, and the solvent were placed in polymerization tube and the mixture was flushed with a slow stream of nitrogen for 10 min. Then, the tube was closed and kept in the thermostat at 70°C for 24 h. After that, the contents were cooled and added to excess

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methanol to precipitate the polymer, poly (MPPCEPOEMA). The polymers were purified by dissolving in chloroform and reprecipitating with methanol. The polymers were dried under vacuum at 50°C (Yield 50%, mp 78°C–81°C).

2.7. Experimental Techniques

FT-IR spectra were recorded in a Nicolet 510P FT-IR Spectrometer. Polymer and monomer sample films used for measurements have been obtained by casting on a KBr pellet. High resolution ^{1}H, ^{13}C NMR Spectra were recorded on a Brucker spectrometer of 300. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) were determined from gel permeation chromatography (GPC) measurements, which were carried out in THF on a water 2410 instrument equipped with three waters μ-Styragel columns at 35°C, with water and 2410 RI detector. Phase transitions and thermodynamic parameters were determined by using a Perkin Elmer DSC-7 equipped with a liquid nitrogen cooling system with heating and cooling rates being kept at 20°C min. The thermal stabilities of polymer were measured with a Perkin Elmer TGA-7 thermogravimetric analyzer using nitrogen atmosphere and a 20°C min heating rate. The thermal transition and optical textures of the polymer were observed with a Ziss-Jena POM equipped with a Mettler FP 82 hot stage. The LC properties of all the polymer samples were examined by using Euromex polarizing microscope equipped with a Linkem HGS91 heating stage and a TP-93 temperature programmer. The photographs were taken with a Nikon FM 10 camera and printed on a Konica film. The photolysis studies were performed in thin films of the polymer by irradiating under UV light at 365 nm wavelength on a Hitachi U2000UV spectrophotometer.

3. Results and Discussion

3.1. Characterization

The solubility of the polymer was tested in various organic solvents. The polymer was dissolved in aprotic polar solvents, such as N-methyl-2-pyrrolidene, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, and tetrahydrofuron and in chlorinated solvents such as chloroform and methylene dichloride. They were insoluble in hydrocarbons such as benzene, toluene, and xylene and in protic solvents such as methanol, ethanol, and 2-propanol.

3.2. FT-IR Studies

Figure 1 shows the IR spectrum of the poly (MPPCEPOEMA). The olefinic C–H stretching vibrations gave their peaks at 3024 cm^{-1}. The –CH$_2$ peak occurs at 2888, 2750, and 2658 cm^{-1}. The C=O stretching vibration of the ester group occurs at 1628 and 1602 cm^{-1}. The group of peaks between 1587, 1484, and 1457 cm^{-1} induces aromatic ring R–O vibration and –COO– vibrations. The peak at 1317 cm^{-1} is due to –CH$_2$ bending vibration. The peak at 1272 and 1244 cm^{-1} is due to alkoxy C–O stretching vibration. The group of peaks occurring at 1067 cm^{-1} is due to aromatic ring C–H bending modes. The ring with two adjacent hydrogen atoms gives its C–H bending vibration at 892 cm^{-1}. The other ring with five adjacent hydrogen atoms gives its C–H bending vibrations at 761 and 540 cm^{-1}.

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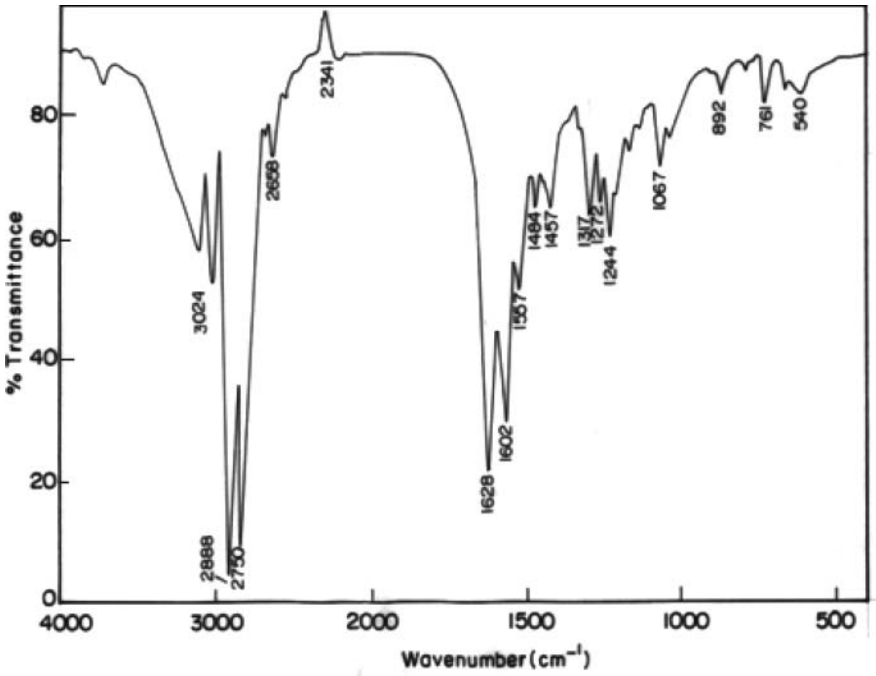

Figure 1. FT-IR spectrum of poly (MPPCEPOEMA).

3.3. ^{1}H NMR Spectra of Poly (MPPCEPOEMA)

The ^{1}H NMR spectrum of poly (MPPCEPOEMA) is shown in Fig. 2. The multiplet resonance signals at 8.15–7.25 ppm corresponding to the aromatic protons. The resonance signals of the olefinic protons of the pendant chalcone moiety were observed at 6.8 ppm.

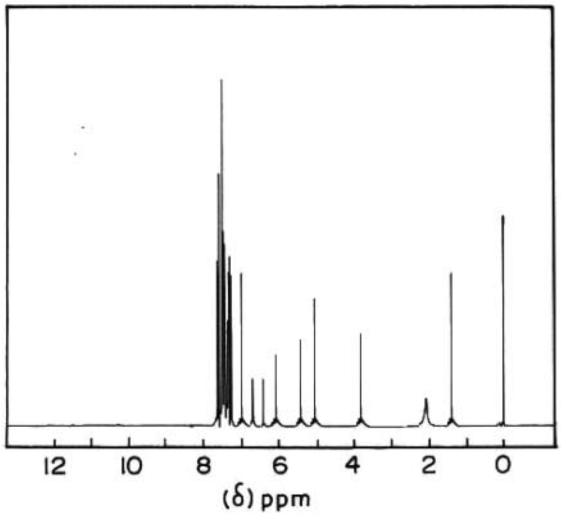

Figure 2. Proton NMR spectrum of poly (MPPCEPOEMA).

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The resonance signals at 4.2 ppm and at 2 ppm are due to the alkoxy and methyl protons. The backbone methylene (–CH_2) occurs at 1.7 ppm.

3.4. ^{13}C NMR Spectra of Poly (MPPCEPOEMA)

The proton decoupled ^{13}C NMR spectrum of poly (MPPCEPOEMA) is presented in Fig. 3. ^{13}C NMR chemical shift assignment was made from the off resonance decoupled spectra of the polymer. The resonance signals appear at 178 ppm corresponding to esteric carbonyl carbon. The ketone carbon signal is observed at 190 ppm. The signals at 110 ppm are due to $>CH{=}CH<$ (olefinic) carbon connected to the benzene ring. The aromatic carbon gave signals at 120–140 ppm and the aliphatic carbon gave signals between 60 ppm and 10 ppm. The signal observed at 40–50 ppm is assignable to the backbone carbon (–C–) of the poly (MPPCEPOEMA) unit.

3.5. Molecular Weight

The weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) are the polydispersity index. Poly (BCPMA) determined by the GPC are as follows:

$$\bar{M}_w \times 10^{-4} = 4.15; \bar{M}_n \times 10^{-4} = 2.65; \bar{M}_w/\bar{M}_n = 1.56.$$

The theoretical values of $\bar{M}_w/\bar{M}_n$ for polymer produced via radical recombination and disproportionation are 1.5 and 2.0, respectively [40,41]. Usually, the polydispersity index $\bar{M}_w/\bar{M}_n$ of poly (meth) acrylates [42] prepared by free radical polymerization of the

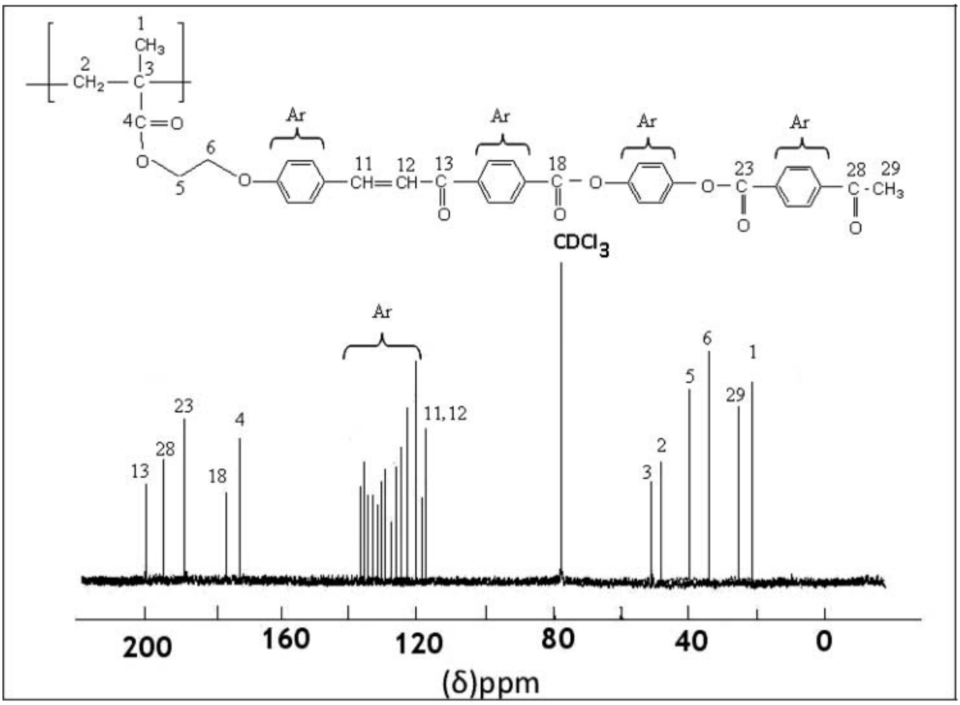

Figure 3. ^{13}C NMR spectrum of poly (MPPCEPOEMA).

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

					Temperature (°C) at weight loss (%)			
Polymers	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	PDI	IDT	10	30	50	90
Poly (MPPCEPOEMA)	4.15	2.65	1.56	192	208	224	247	270

Note: IDT – Initial Decomposition Temperature (°C), PDI – Polydispersity index, $\bar{M}_n$ & $\bar{M}_w$ – Number and Weight average molecular weight of polymer.

monomer depends on the chain termination mechanism. The polydispersity index value of poly (MPPCEPOEMA) suggests that the tendency for chain termination by disproportionation is more than that for dimerization.

3.6. Thermal Analysis

The rapid evaluation of the thermal stability of the polymer was done by TGA technique in air atmosphere and the data are presented in Table 1, and TGA traces are shown in Fig. 4. Poly (MPPCEPOEMA) undergoes decomposition in a single stage between 208°C and 410°C. The initial decomposition and 10% weight loss of polymer occur at about 210°C and the polymer was stable up to 260°C. The phase transition and corresponding enthalpy changes of the obtained polymers are shown in Table 2. DSC curve of the polymer obtained during heating is shown in Fig. 5. The phase transition temperature and mesophase of the poly (MPPCEPOEMA) are evaluated by the DSC thermogram. The DSC trace of the polymer shows three endothermic peaks, corresponding to glass transition (T_g), melting (T_m), and isotropic (T_i) transition temperature. Generally, the melting transition temperature decreases with increase in aliphatic spacers as expected. The T_g is an important parameter in

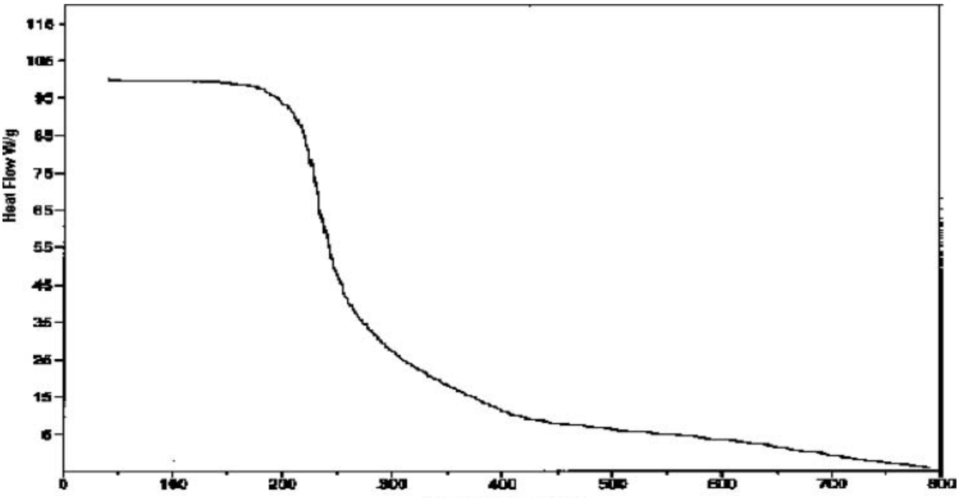

Figure 4. TGA trace of poly (MPPCEPOEMA).

Table 2. DSC and HOPM data of poly (MPPCEPOEMA)

	DSC				HOPM
Polymers	T_m°C	T_i	ΔT	T_g	Mesophase
Poly (MPPCEPOEMA)	136	167	31	67	Nematic

T_m – Crystal–liquid melting temperature, T_i – Mesophase–isotropic phase transition temperature, T_g – glass transition temperature.

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connection with the structure and properties of polymer. This high T_g value of the polymer is attributed to the inflexible and bulky pendant chalcone units and the presence of short side chain which facilitates the chain entanglement. In general, T_g-value of the side-chain LCP is strongly influenced by the polymeric chain flexibility, molecular weight, the mesogenic group, and the length of the spacer group [43].

3.7. Photocrosslinking Studies

The photochemical studies have been carried out in a discontinuous mode. The sample was exposed to UV radiation by using a 125 W medium-pressure mercury lamp for varying intervals of time. The irradiated solution was subsequently subjected to UV spectral analysis and the photocrosslinking property of polymer was observed. Figure 6 shows the changes in the UV spectral pattern during the photolysis of poly (MPPCEPOEMA) at various intervals of time. The absorbance bond at 275 nm corresponds to the $\pi \rightarrow \pi^*$ transition of pendent chalcone moiety. The relative reactivity $(A_0–A_t)/A_0$ is plotted against the different time of irradiation, where A_0 is the absorbance before irradiation, and A_t after irradiation for time t. The substitution on the pendant phenyl ring does not have a significant effect on the rate of photolysis. An isobestic point occurs at 240 nm due to *cis–trans* isomerization during initial irradiation. The absorption intensity at 275 nm decreases immediately with irradiation time

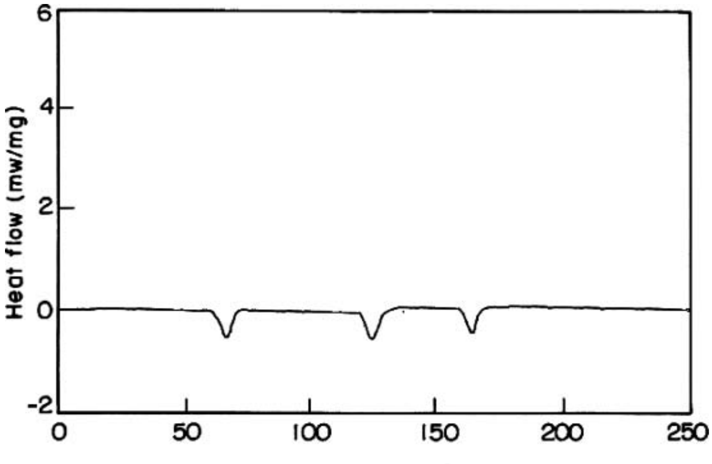

Figure 5. DSC thermogram of poly (MPPCEPOEMA).

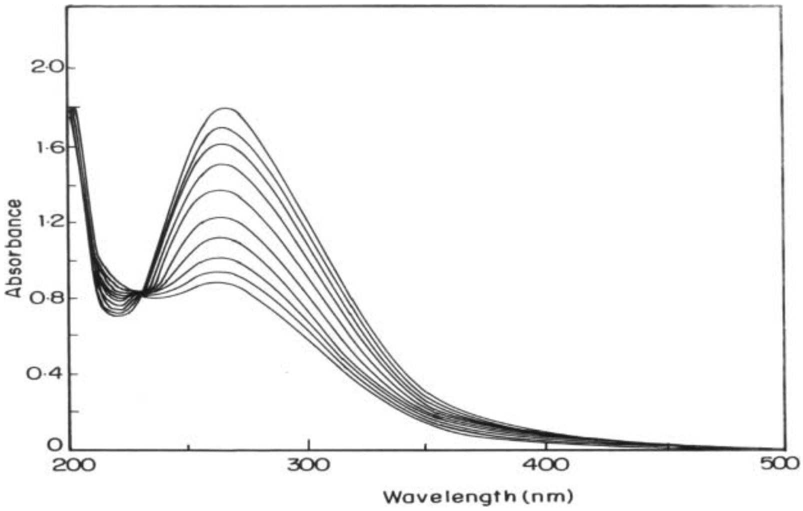

Figure 6. Change in UV spectral characteristics, during the photolysis of poly (MPPCEPOEMA).

and disappears almost completely within 10 min of irradiation time. The rate of crosslinking increases with increase in methylene chain length in the polymer backbone. Photoreactive polymer containing chalcone moiety behaves as a negative photoresist as result of $2\pi + 2\pi$ photocycloaddition between an excited chalcone of one chain with ground state chalcone of another chain [44, 45]. As the $2\pi + 2\pi$ cycloaddition destroys the conjugation in the

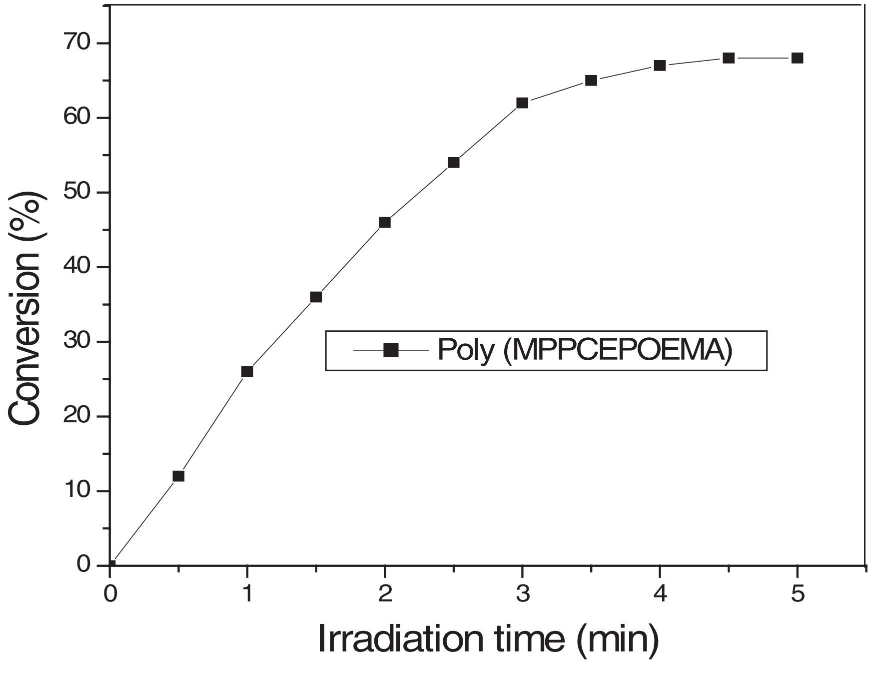

Figure 7. Dependence of the photocrosslinking rate on irradiation time poly (MPPCEPOEMA).

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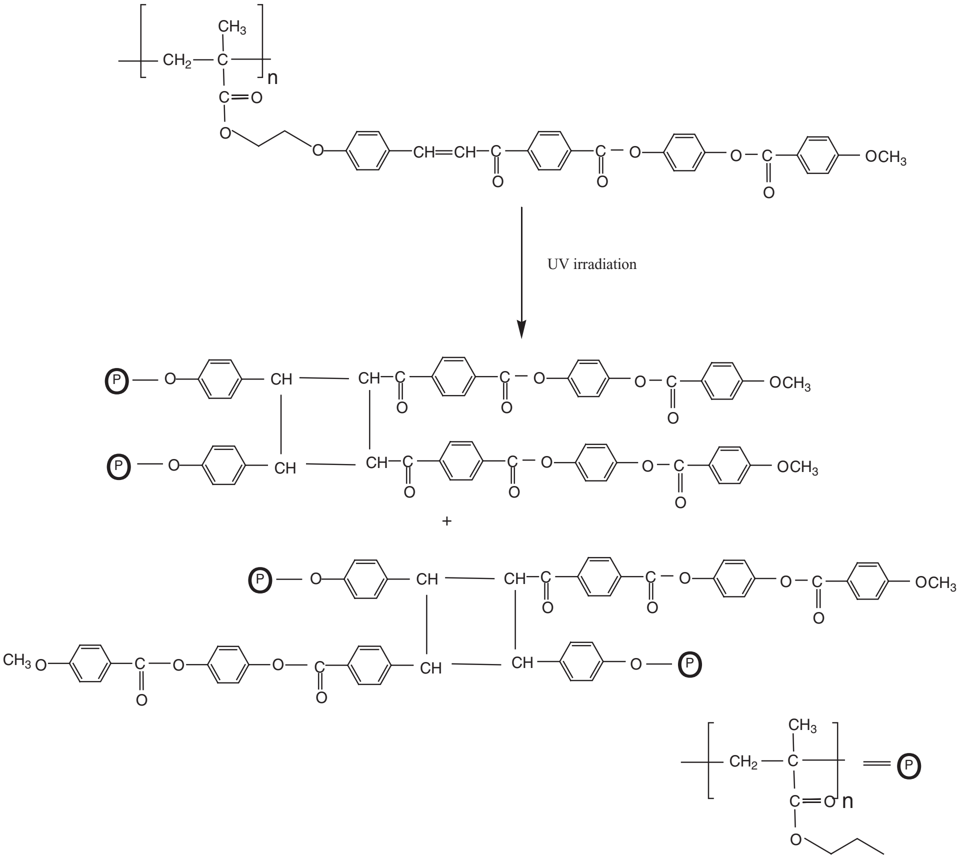
entire π electron system, the UV absorbtion intensity decreases with irradiation time [46] which leads to cyclobutadiene ring formation. The photosensitivity of the poly (MPPCE-POEMA) containing an α, β-unsaturated carbonyl carbon was measured in terms of the rate of disappearance of (>C=C<) with irradiation time and the results are illustrated in Fig. 7. The polymer after irradiation was insoluble in solvents in which it had been soluble before irradiation and this may be due to crosslinking of polymer chain through 2π–2π cycloaddition of olefinic double bond of the pendant chalcone unit. Thus, the polymer might be useful in negative photoresist in photolithography application (Scheme 4) [38].



Scheme 4. Chemical structure of $(2\pi + 2\pi)$ cycloaddition of poly (MPPCEPOEMA).

3.8. *Liquid Crystalline Properties of Polymer*

The development of photosensitive liquid crystalline compounds for data recording optical storage and reproduction is one of the most rapidly developing areas in the physical chemistry of low molecular mass and polymer liquid crystals [47]. The optical textures of the poly (MPPCEPOEMA) are observed by HOPM with hot stage process. The poly (MPPCEPOEMA) is heated to 147°C whereupon it exhibits Nematic texture as shown in Fig. 8. The optical texture is always stable through the whole mesogenic range. The phase transition temperature values noted in DSC thermogram are almost equivalent to that of the transition temperature. The rigidity of the mesogenic core with the flexible spacer length

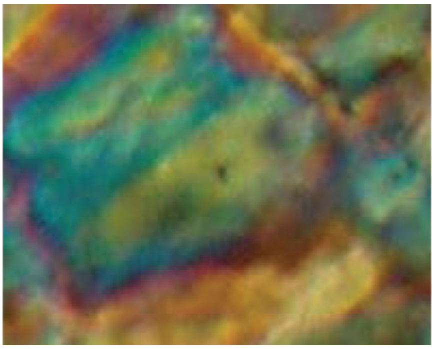


Figure 8. HOPM photograph of polymer poly (MPPCEPOEMA).

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and terminal units highly influence the melting temperature, mesophase temperature, and even molecular arrangement. Highly polar hindered pendant group revealed to have high interaction leading to formation of liquid crystalline phase [48]. Some polymers take the effect of mesogen and when they are spaced together, a polymer having rigid mesogen and short spacer shows the higher transition temperature [49].

4. Conclusion

The side-chain liquid crystalline photosensitive polymer was synthesized by free radical polymerization in solution using BPO as an initiator. The synthesized polymer was characterized by IR, ^{1}H NMR and ^{13}C NMR, and UV spectral techniques. The solubility of the polymer was tested in different organic solvents. The polydispersity index value obtained from GPC indicates that polymerization was terminated by disproportionation rather than dimerization. The TGA analysis clearly shows that the polymer possesses good thermal stability. The polymer exhibits a high thermal stability due to the presence of shorter methylene chain of the polymer backbone. The $>C=C<$ group of the polymer pendant can be readily crosslinked by UV irradiation to form cyclobutane via $(2\pi + 2\pi)$ cycloaddition. The photocrosslinking of the polymers occurs even in the absence of photosensitizers, and it would be useful in negative photoresists. HOPM studies indicate that the prepared polymer exhibits good LC properties with nematic textures.

References

[1] Minsk, L. M., Smith, J. G., Van Deusen, W. P., & Wright, J. F. (1959). *J. Appl. Polym. Sci.*, *2*, 302.

[2] Kato, M., Ichijo, T., Ishii, K., & Hasegawa, M. (1971). *J. Polym. Sci., A-I*, *9*, 2109.

[3] Thompson, L. F., Wilson, C. G., & Tarawa, S. (Eds.). (1994). *Polymers for Microelectronics—Resists and Dielectrics*, ACS Symp. Ser. 537, Am. Chem. Soc.: Washington, DC.

[4] Thompson, L. F., Wilson, C. G., & Bowden, M. J. (Eds.). (1994). *Introduction to Microlithography*, Am. Chem. Soc.: Washington, DC.

[5] Reiser, A. (1989). *Photo Reactive Polymers—The Science and Technology of Resists*, J. Polym. Sci., Part C, New York.

[6] Reichmanis, E., & Thompson, L. F. (1989). *Polymers in Microlithography, Materials and Processes*, ACS Symp. Ser. 412, Am. Chem. Soc. 1: Washington, DC.

[7] Tazuke, S. (1982). *Developments in Polymer Photochemistry*, Applied Science: London.

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[8] Kawatsuki, N., Sakashita, S., Takatani, K., Yamamoto, T., & Sangen, O. (1996). *Macromol. Chem. Phys.*, *197*, 1919.

[9] Chien, L. C., & Cada, L. G. (1994). *Macromolecules*, *27*, 3721.

[10] Yamashita, K., Kyo, S., Miyagawa, Y., Nango, M., & Tsuda, K. (1994). *J. Appl. Polym. Sci.*, *52*, 577.

[11] Whitcombe, M. J., Gilbert, A., & Mitchell, G. R. (1992). *J. Polym. Sci: Part A: Polym. Chem.*, *30*, 1681.

[12] Stumpe, J., Zaplo, O., & Kreysing, D. (1992). *Macromol. Chem.*, *193*, 1567.

[13] Reichmanis, E., & Thompson, L. F. (1989). *Chem. Rev.*, *89*, 1273.

[14] Reichmanis, E., Nalamasu, O., & Houlihan, F. M. (1999). *Acc. Chem. Res.*, *32*, 659.

[15] Cry, P. W., Rider, D. A., Kulbaba, K., & Manners, I. (2004). *Macromolecules*, *37*, 3959.

[16] Katz, H. E. (1997). *J. Mater. Chem.*, *7*, 369.

[17] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, K. H., Burn, P. L., Kraft, A., & Holmes, A. B. (1990). *Nature*, *347*, 539.

[18] Gustatsson, G., Cao, Y., Treacy, G. M., Klavetter, F., Colaneri, N., & Heeger, A. J. (1992). *Nature*, *357*, 477.

[19] Chen, S. H., Conger, B. M., Mastrangelo, J. C., Kenda, A. S., & Kim, D. U. (1998). *Macromolecules*, *31*, 8051.

[20] Morman, W., & Zimmermann, J. G. (1996). *Macromolecules*, *29*, 1949.

[21] Koner, H., & Ober, C. K. (1995). *Polym. Mater. Sci. Eng. Prepr.*, *73*, 456.

[22] Wang, Y. H., Hong, H. L., Yang, F. S., & Hong, I. L. (1994). *Polym. Mater. Sci. Eng. Prepr.*, *71*, 678.

[23] Melissaris, A. P., Sutter, J. K., Litt, M. H., Scheiman, D. A., & Srheiman, M. (1995). *Macromolecules*, *28*, 860.

[24] Hoyt, A. E., & Huang, S. J. (1995). *J. Macromol. Sci.: Pure Appl. Chem.*, *32*, 1931.

[25] Hikmet, R. A. M., Lub, J., & Tol, A. J. W. (1995). *Macromolecules*, *28*, 3313.

[26] Lai, W. W., & Chang, T. C. (1995). *J. Polym. Sci. Polym. Chem. Ed.*, *33*, 1075.

[27] Douglas, E. P., Langlois, D. A., & Benicewice, B. C. (1994). *Chem. Mater.*, *6*, 1295.

[28] Mallon, J. J., & Adams, P. M. (1993). *J. Polym. Sci., Polym. Chem. Ed.*, *31*, 2249.

[29] Navarro, F. (1991). *Macromolecules*, *246*, 622.

[30] Peter, K., & Ratzsch, M. (1990). *Macromol. Chem.*, *191*, 1021.

[31] Taroze, R. V., Gubiuna, T. I., Shibaev, V. P., Plate, N. A., Pakin, V. I., Shamakova, N. A., & Shukov, F. (1990). *Macromol. Chem. Rapid. Commun.*, *11*, 67.

[32] Mitchel, G. R., & Davis, F. J. (1987). *Ashman. Polymer.*, *28*, 639.

[33] Zentel, R., & Reckert, G. (1986). *Macromol. Chem.*, *187*, 1915.

[34] Finkelmann, H., Kock, H. J., & Rehage, G. (1981). *Macromol. Chem. Rapid. Commun.*, *2*, 317.

[35] Rami Reddy, A. V., Subramanian, K., Krishanasamy, V., & Ravichandrandran, J. (1996). *Eur. Polym. J.*, *32*, 919.

[36] Subramanian, K., Rami Reddy, A. V., Krishanasamy, V., & Ravichandrandran, J. (1991). *Macromol. Chem. Rapid. Commun.*, *12*, 211.

[37] Perrin, D. D., & Armarigo, W. L. F. (1988). *Purification of laboratory chemicals*. 3rd Ed., Pergamon Press: New York.

[38] Subramanian, K., Krishnaswamy, V., Nanjundan, S., & Rami Reddy, A. V. (2000). *Eur. Polym. J.*, *36*, 2343–2350.

[39] Mohan Kumar, R., Saravanan, C., Senthil, S., & Kannan, P. (2007). *Eur. Polym. J.*, *43*, 2648–2659.

[40] Teramachi, S., Hasegava, A., Akatsuka, M., Yamashita, A., & Takemoto, N. (1978). *Macromolecules*, *11*, 1206.

[41] Lenz, R. W. (1967). *Organic Chemistry of Synthetic High Polymers*, Wiley/Interscience: New York.

[42] Melville, H. W., Nobe, B., & Watson, W. F. (1946). *J. Polym. Sci.*, *4*, 629.

[43] Hirschrmann, H., Roberts, P., & Davis, F. J. (2001). Liquid crystalline elastomers: The relationship between macroscopic behavior and the level of backbone anisotropy. *J. Polym.*, *42*, 7063–7071.
[44] Kim, S. H., Ahn, C. H., Keum, S. R., & Koh, K. (2005). *Dye Pigm.*, *65*, 179–182.
[45] Zhang, Y. D., Hreha, R. D., Jabbour, G. E., Kippelen, B., Peyghambarian, N., & Marder, S. R. (2002). *J. Mater. Chem.*, *12*, 1703–1708.
[46] Yang, P.-C., & Wu, M.-Z., & Liu, J.-H. (2008). *Polymer*, *49*, 2851.
[47] Watanabe, S., & Kato, M. (1984). *J. Polym. Sci., Polym. Chem. Ed.*, *22*, 2801.
[48] Curme, H. G., Natale, C. C., & Kelley, D. T. (1976). *J. Phys. Chem.*, *71*, 767.
[49] Nishikubo, T., Jchijyo, T., & Takaodo, T. (2009). *J. Appl. Polym. Sci.*, 18.

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