Synthesis and Characterization of Liquid Crystalline Polyesters Containing α,β-unsaturated Ketone Moiety in the Main Chain Derived from 2,6-bis(4-hydroxybenzylidene)cyclohexanone

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Abstract—A series of polyesters containing a photosensitive benzylidene chromophore in the main chain were synthesized from 2,6-bis(4-hydroxybenzylidene)cyclohexanone with various aliphatic and aromatic diacid chlorides by interfacial polycondensation technique. The intrinsic viscosity of the synthesized homo and copolymers determined by Ubbelohde viscometer and found to be 0.13−0.18 dL/g. The molecular structure of the monomer and polymers was confirmed by Fourier Transform infrared, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. These polymers were studied for their thermal stability and photochemical properties. Thermal properties were evaluated by thermogravimetric analysis and differential scanning calorimetry. It was found that the polymers were stable up to 238°C and start degrading thereafter. Increase in acid methylene spacer length decreases the thermal stability. The self-extinguishing property of the synthesized polymers was studied by calculating the limiting oxygen index value using Van Krevelen equation. The influence of the length of methylene spacer on phase transition was investigated and it was found that isotropic temperature decreases on increasing the acid methylene spacer length. Hot-stage optical polarizing microscopic study showed that synthesized polymers exhibit grainy texture in the temperature range of 115−127°C. The photolysis of liquid crystalline polyesters revealed that α,β-unsaturated ketone moiety in the main chain dimerizes through 2π+2π cycloaddition reaction to form a cyclobutane derivative that leads to crosslinking.

INTRODUCTION

Thermotropic liquid crystalline (LC) polymers have been one of the important topics to study in polymer chemistry due to a great potential in functional soft materials [1]. In addition to that, photo-crosslinkable LC polymers are also currently attracting significant attention in a wide range of applications such as photoresists to make integrated circuits, printing plates, printing inks, photocurable coatings and energy exchange systems, because of their excellent photoresponsive characteristics, thermal stability and chemical resistance [2]. Photo-crosslinkable liquid crystalline polymers find applications in anisotropic network systems like LC elastomers and LC thermosets, information storage devices and thin films with a controlled orientation of functional groups, which are of interest in microelectronics and optoelectronics [3]. Photosensitivity, solubility and thermal stability are the prime requirements for the use of these polymers in this field.

One condition necessary for organic compounds to exhibit thermotropic liquid-crystalline properties is that the molecule should have either a rod-like or disc-like structure [4, 5]. This is also the case for polymers; nevertheless, polymers tend to decompose even before reaching the melting point. One of the methods by which the high melting point of rod like polymers can be lowered is by introducing flexible aliphatic units into their chains [6, 7]. Another method is by using monomers with pendant groups. However, it should be borne in mind that the behavior of the pendant groups is further complicated by steric and polar effects [8, 9]. While, steric effects generally reduce the thermal stability of the mesophase, on the other hand, substituted units, in which the pendant groups impart increased polarizability and stronger dipolar interactions between the mesogenic groups. The stronger intermolecular attractions, which would result in

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higher thermal stabilities of both the crystalline and liquid-crystalline phases [10].

Main chain liquid crystalline polymers with photo-sensitive groups have attained special attention owing to the presence of dual functionalities. The mesogenic groups contribute to the LC properties and the photo-active groups in the polymer backbone may facilitate photoisomerization, photo-crosslinking, photodimerization, photodissociation and photoassociation of the polymer chains under the influence of UV irradiation [11]. Polymers containing α,β-unsaturated carbonyl groups such as cinnamoyl, benzylidene groups are well studied for their phototransformation phenomena, occurring upon irradiation under UV light and named as negative type photoresists [12]. The photosensitivity of these materials is based on the π-electron density of the chromophores present in the polymer backbone [13]. The literature reveals that the chalcone groups possess higher sensitivity to UV irradiation than that of the cinnamate groups [14].

Several researchers have been actively engaged in the study of main chain thermotropic polyesters containing rodlike mesogens. However, LC polyesters have not been receiving the deserved focus and attention. After performing extensive work on these polymers, Kamal I Aly and coworkers [15—17], observed that the main advantages of benzylidene polyesters are lower melting temperatures, broader mesophase stability range and higher solubility. A pioneering work by Aminabhavi et al. [18, 19] and Percec et al. [20, 21] in the field of liquid crystalline polyethers and polyesters covers many aspects related to this field.

Most of the researchers paid attention to semiflexible polymers in which the hard mesogenic groups are connected by flexible spacer groups. Until now, enormous semiflexible type thermotropic polymers have been reported. The typical examples are polyesters, poly(ether-ester)s, poly(ester-amide)s [22], etc. The various thermotropic polyesters with flexible spacers have been synthesized [23]. The polyesters having the regular sequence of flexible spacer and aromatic group showed the great difference in polarity between the aliphatic spacer and ester linkage to increase the solubility and reduce the transition temperature. Liquid crystalline polyesters have captured the excitement and imagination of contemporary polymer scientists and engineers. These materials exhibit many unique properties and not only challenges for basic research, but also numerous technological opportunities. Liquid crystalline polyesters have provided a number of potential applications in photonics and optoelectronics based technologies such as speed data storage devices and optical fiber communications [24]. The general drawback of this kind of polyesters are poor thermal resistance and fire behavior [25]. This can be minimized by the addition of flame retardants [26].

A series of papers have been published by Abd-Alla and co-workers [27—30] on the synthesis and character-ization of arylidene polyesters containing rigid cycloalkanone moieties. Incorporation of methylene spacer plays a significant role in determining the relationship between thermo-mechanical history, structural and morphological organization of polymers. Such polymers have been reported to possess interesting optical, semiconducting and mechanical properties, attractive morphology and liquid crystalline behavior [31].

In our previous studies, we have synthesized photosensitive poly(benzylidene-ester)s containing methoxy substituent as a pendant group and systematically studied the properties [32]. In the present study, we dealt with the synthesis of photoreactive bisbenzylidene diol containing α,β-unsaturated ketone moiety and polymerized with various aliphatic and aromatic diacid chlorides by interfacial polycondensation technique. Two copolymers containing bisphenol-A were also synthesized for comparing the thermal properties. Spectral, thermal, liquid crystalline and photocrosslinking studies were also carried out in this investigation.

EXPERIMENTAL

Materials

4-Hydroxybenzaldehyde (Sd fine chemicals, India), chloroform (Sd fine chemicals, India), adipic acid (Sd fine chemicals, India), sebacic acid (Sd fine chemicals, India), terephthalic acid (Sd fine chemicals, India), isophthalic acid (Sd fine chemicals, India), cyclohexanone (Merck, India), n-hexane (Merck, India), thionyl chloride (Ranbaxy, India), methanol (Loba Chemie, India) and other solvents were purified by the procedure reported in the literature [33]. Boron trifluoride diethyletherate (Fluka), hexadecyltrimethylammonium bromide (HDTMAB) (Fluka), bisphenol-A (Fluka), subaric acid (Fluka) and azelaic acid (Aldrich, Germany) were used as received.

Characterization

The solubility of the polymers was examined using 0.3—0.5 mg of polymer in 5 mL of solvent at room temperature. The intrinsic viscosity of the synthesized polymers was measured in DMSO at 30°C using Ubbelohde viscometer. The number average, weight average molecular weights and polydispersity index (PDI) of the copolymers were estimated using gel permeation chromatography (GPC) in THF using Shimadzu LC-20AD GPC. Polystyrene standards of known molecular weights were used for calibration. The infrared spectra were recorded on Shimadzu Fourier transform infra red spectrophotometer using KBr pellet in the range of 4000 to 400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Brucker AV-III 400 NMR spectrometer in CDCl$_3$ using TMS as an internal standard. The DSC analysis was carried out on a Perkin Elmer Pyris 6 DSC for all polymers using empty aluminium pan as reference with heating

rate of 10 K/min in nitrogen atmosphere to measure T_g, T_m and T_i values. Temperature and heat flow scale of the instrument was calibrated using pre crimped In and Zn as standard references. Thermogravimetric analysis was performed on Perkin Elmer, Diamond TG/DTA in nitrogen atmosphere with heating rate of 10 K/min. The texture of all the prepared samples was studied using Euromex polarizing microscope equipped with a Linkam heating stage and a TMS 94 temperature programmer. A small quantity of the samples was placed between two thin glass cover slips and heated and subsequently cooled at the rate of 5°C/min and observed the anisotropic behavior. Photographs were taken using a Euromex CCD camera. The photocrosslinking studies of the synthesized polymers were performed in the solution and film state using UV spectrophotometer. The polymer was dissolved in DMSO in a quartz cuvette and irradiated in UV curing reactor with a medium pressure Hg lamp (Heber Scientific Photo reactor, 300−420 nm) exposed at a distance of 10 cm from the sample. Subsequently the irradiated solution was subjected for UV spectral analysis on a Systronics 119 UV spectrophotometer.

Synthesis of Monomer 2,6-Bis(4-hydroxybenzylidene)cyclohexanone (BHBCH)

A mixture of cyclohexanone (50 mmol, 5.2 mL) and 4-hydroxybenzaldehyde (100 mmol, 12.212 g) was dissolved in 50 mL of absolute ethanol with three drops of boron trifluoride diethyl etherate. The solution was stirred for 6 h at 80°C and cooled to room temperature. The solid product formed was filtered off, washed with cold ethanol and dried in vacuum oven. Recrystallization from hot ethanol gave fine yellow color product with more than 85% yield of the title compound. Melting point 285°C. (lit.284°C) [34].

FTIR (KBr): 1637 cm^{-1} ($\gamma_{C=O}$), 1579 cm^{-1} ($\gamma_{C=C}$ exocyclic), 1513 cm^{-1} ($\gamma_{C=C}$ aromatic), 3367 cm^{-1} (γ_{OH}).

^{1}H NMR (CDCl$_3$, TMS), δ_H, ppm: 9.50 (s, 2H, −OH), 6.80−7.20 (m, 6H, aromatic protons), 7.67 (s, 2H, −CH=), 2.92 (s, 4H, βCH$_2$ of cyclohexanone), 1.75 (s, 2H, γCH$_2$ of cyclohexanone).

^{13}C NMR (CDCl$_3$), δ_C, ppm: 188.55 (C=O, ketonic), 133.60 (=CH−), 130.0 (α carbon of cyclohexanone), 115−125 (aromatic carbons), 22.59 (β carbon of cyclohexanone), 27.94 (γ carbon of cyclohexanone).

Preparation of Acid Chlorides

Recrystallized adipic acid (100 mmol, 14.614 g) and distilled thionyl chloride (240 mmol, 14.5 mL) in excess were taken in a 250 mL round bottom flask and refluxed in an oil bath for 4 h. After refluxing, excess thionyl chloride was removed under reduced pressure. Sebacyl chloride, subaryl chloride and azeloyl chloride

were also prepared by adopting similar procedure used in the preparation of adipoyl chloride [35]. Terephthaloyl chloride and isophthaloyl chloride were prepared by refluxing the respective diacids with thionyl chloride with the addition of two drops of pyridine as a catalyst for 12 h. The solid product obtained was recrystallized from n-hexane [36].

Synthesis of Polymers

All the polymers were prepared by the interfacial polycondensation method using HDTMAB as a phase transfer catalyst. A typical procedure for the synthesis of polymer, poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]adipate (P1) is as follows:

0.01 mole (3.06 g) of BHBCH was dissolved in 20 mL of aqueous sodium hydroxide (1 N) solution containing HDTMAB (2 wt % of the diol). The solution turned wine red in color. To this solution 0.01 mol (1.5 mL) of adipoyl chloride in 25 mL of CHCl$_3$ was added with vigorous stirring. After 30 min of stirring the solid polymer was formed in between organic and aqueous layer. It was filtered, washed with ethanol and dried to constant weight in vacuum.

All the other polymers namely, poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]subarate (P2), poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]-azelate (P3), poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]sebacate (P4), poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]terephthalate (P5), and poly[2,6-bis(4-hydroxybenzylidene)cyclohexanone]isophthalate (P6) were also prepared in a similar manner.

Two co-polymers (COP1 and COP2) were synthesized from equimolar quantities of photosensitive diol (BHBCH), acid chlorides (subaryl/sebacyl) and non-photosensitive diol (Bisphenol-A) by adopting the procedure used to synthesize the homopolymers.

RESULTS AND DISCUSSION

Polycondensation is usually carried out by melt, solution or interfacial methods. Since the synthesized monomers and the polymers are sensitive to heat, the room temperature interfacial polycondensation route was selected for the synthesis of polymers in the present study. This technique possesses several advantages over solution polycondensation like using of inexpensive solvents, rapid formation of polymers and good yield. This system by nature is non-equilibrium with reactants and products distributed among various phases. All the polyesters have been prepared by interfacial polycondensation technique using a phase transfer catalyst.

The monomer, BHBCH, was prepared by Claisen−Schmidt condensation of 4-hydroxybenzaldehyde with cyclohexanone using BF$_3$ diethyletherate as a catalyst in ethanol medium (Scheme 1).

It was then polymerized using various aliphatic and aromatic acid chlorides. All the homo and copolymers
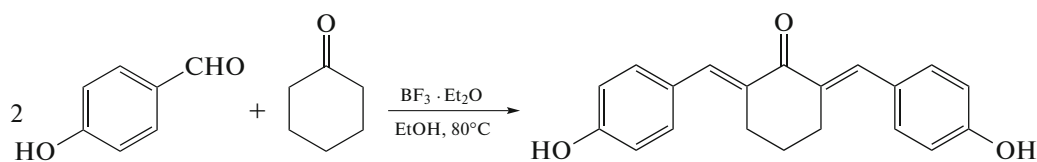
Scheme 1.

were prepared by interfacial polycondensation technique and the synthetic route for the preparation is depicted in Scheme 2.
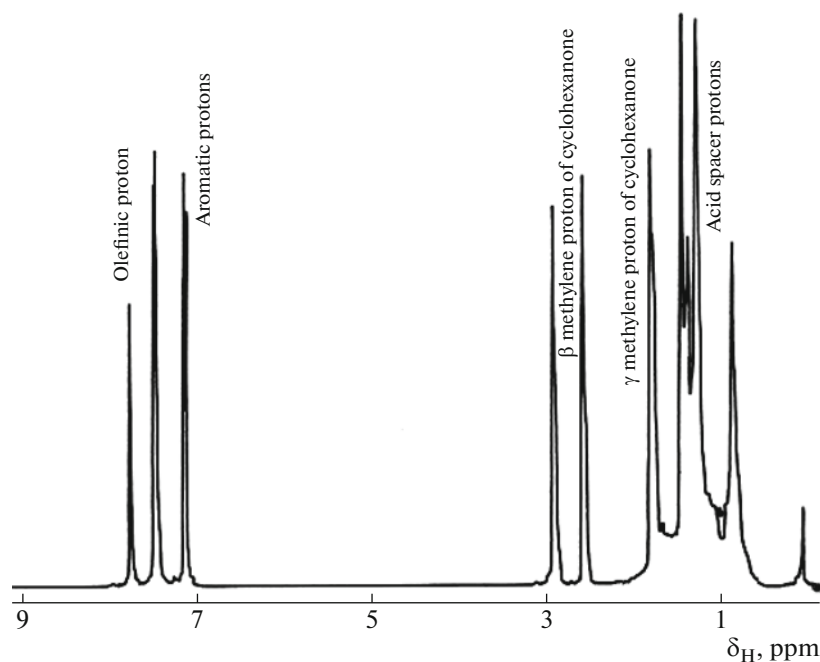
All the polymers were obtained fairly in good yield and yellow in color. All the aliphatic polyesters were soluble in polar solvents like DMSO, DMF, CHCl$_3$ in room temperature and insoluble in ethanol, methanol toluene and n-hexane. The solubility increases in polar aprotic solvents with the increase of polarity index. This may be due to the intermolecular interactions of polar solvents with ester linkage of the polymer molecules [35]. Molecular weights of the resulting polymers were determined by using GPC. Number and weight average molecular weights of polymers were in the range of 8000−8200 g/mol and 9800 g/mol respectively with polydispersity of 1.19−1.22. The intrinsic viscosities of the polymers were found to be in the range of 0.13−0.18 dL/g.
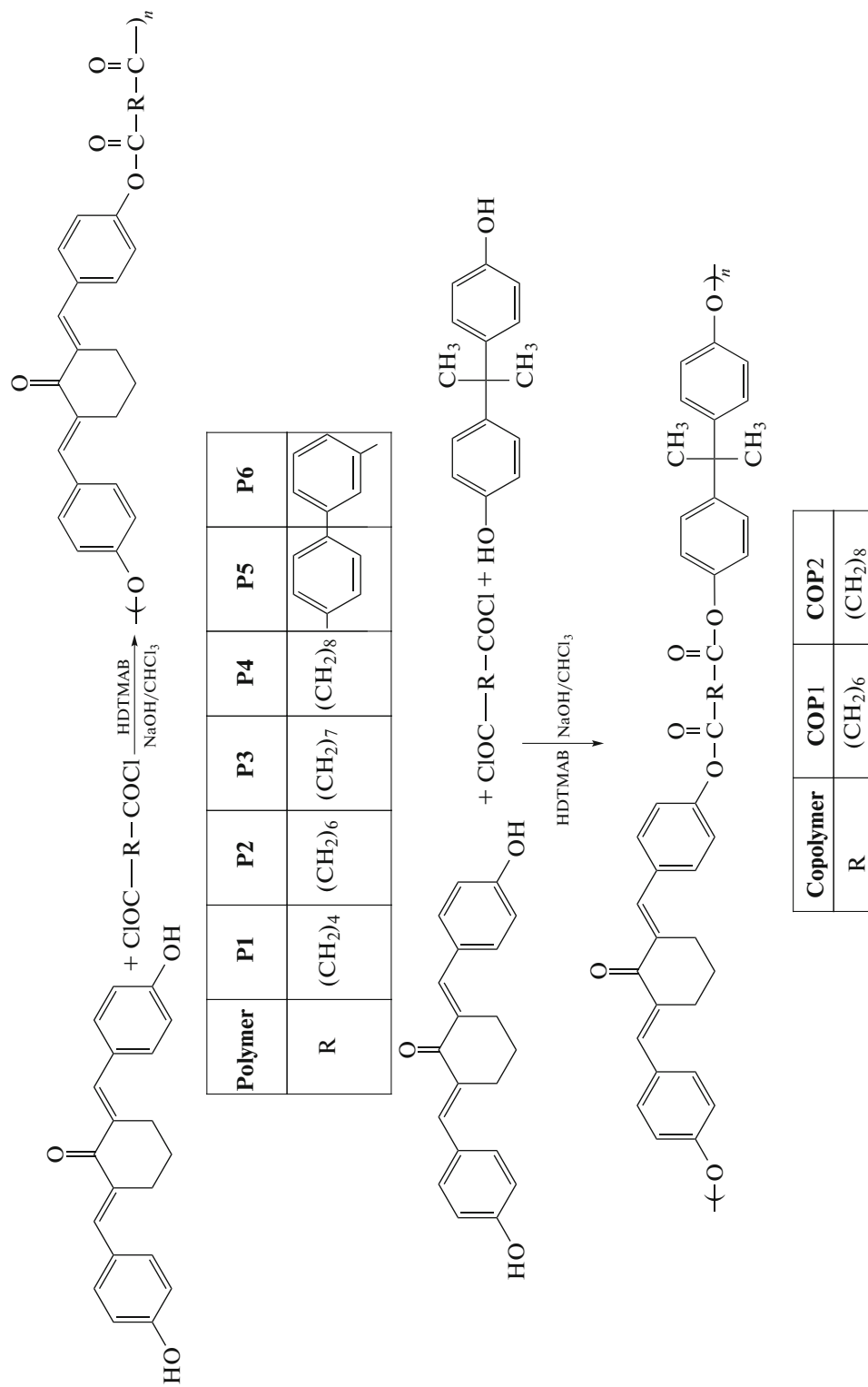
Structural Characterization

The structure of the polyesters was studied by FTIR and NMR spectroscopic techniques. All the polyesters exhibited characteristic medium absorption bands in the region of 1650−1689 cm^{-1} corresponding to carbonyl (C=O) stretching of the cyclohexanone group. The lowering of carbonyl stretching vibration can be attributed to the mesomeric effect and the π-orbital conjugation induced by the unsaturation in the α-carbon atoms and co-planarity of the (−CH=C−(C=O)−C=CH−) group [37]. A stretching peak at around 1595 cm^{-1} is attributed to the olefinic double bonds of benzylidene unit [38]. All the polymers showed a strong absorption at around 1716−1751 cm^{-1} characteristic of >C=O stretching vibrations of ester carbonyl group which is absent in FTIR spectrum of monomer, BHBCH. This confirmed the formation of the polyester. The C−O stretching due to the ester groups appeared at around 1240 cm^{-1}. The prominent bands occurred in the low frequency region of 900−650 cm^{-1} are due to the C−H out of plane bending of the benzene ring.

The representative ^{1}H NMR spectrum of the polymer (P2) is shown in Fig. 1. The olefinic protons appeared as a singlet around 7.7 ppm in all the poly-

Fig. 1. ^{1}H NMR spectrum of polyester (P2).

$+ \ ClOC\!-\!\!-R\!-\!COCl \xrightarrow[\text{NaOH/CHCl}_3]{\text{HDTMAB}}$

Polymer	P1	P2	P3	P4	P5	P6
R	$(CH_2)_4$	$(CH_2)_6$	$(CH_2)_7$	$(CH_2)_8$		

$+ \ ClOC\!-\!\!-R\!-\!COCl + HO \qquad \xrightarrow[\text{NaOH/CHCl}_3]{\text{HDTMAB}}$

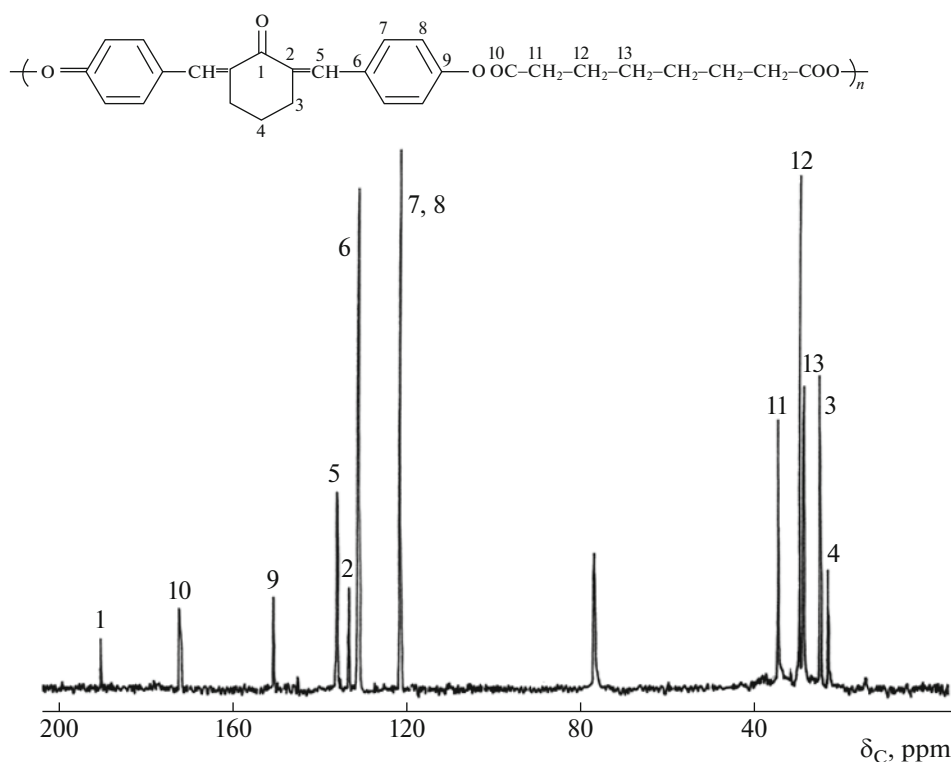| Copolymer	COP1	COP2
R	$(CH_2)_6$	$(CH_2)_8$

Scheme 2.

Fig. 2. ^{13}C NMR spectrum of polyester (P2).

mers as in the monomer. This indicates the existence of E configuration [39] in the backbone of the polymers. The singlet peaks appearing at 2.85–2.95 ppm and 1.72–1.90 ppm correspond to β and γ methylene protons of cyclohexanone respectively [40]. The multiplet at 6.89–7.14 ppm was attributed to aromatic protons. Whereas, the strongly shielded aliphatic acid spacer protons appeared as multiplet at around 0.80–2.90 ppm and confirmed the presence of the acid spacer protons in polymers P1–P4. These data strongly confirmed the formation of the polyesters.

The proton decoupled ^{13}C NMR spectra of polyester P4 is shown in Fig. 2. The ^{13}C NMR spectrum exhibited the expected peaks for every carbon atoms of the polymers. The chemical shift assignments were carried out using normal additive parameter of the substituent in the benzene ring and the considerations of the off resonance spectra in conjugation with the difference in the intensities among the quaternary, methane, methylene and methyl carbons [38]. The α,β-unsaturation in the carbonyl compound makes the carbonyl carbon to resonate in the upfield. The ketonic carbonyl carbon of the polymer appeared around 191 ppm. The β and γ methylenic carbons of cyclohexanone resonate in the region of 24.1–28.4 ppm and 21.8–24.9 ppm respectively. The exocyclic olefinic α and β carbons are appearing in the range of 127.4–134.8 ppm and 135.1–139.6 ppm respectively. The resonance peaks appearing at around 112–124 ppm were attributed to the aromatic carbons present in the polymer. A peak appeared at around 173.5 ppm in all the polymers signified the presence of ester carbon. The aliphatic polyesters showed a resonance signal at around 22.2–34.0 ppm corresponding to methylenic acid spacer.

Thermogravimetric Analysis

The TGA data revealed that all the homo polymers are stable up to 275°C and that 10% weight loss occurred around 280°C. The 50% weight loss was observed around 434–600°C for all the polymers which may be attributed to the decomposition of rigid cyclohexanone segment [41]. The char yield of the aliphatic polymers was around 15–27%. The date is summarized in Table 1. The thermal stability of the polymers decreases as the acid methylene spacer length increases [42]. The presence of methylene spacer units is expected to introduce flexibility to the polymer chain and bring down thermal stability [43]. The char yield among the aliphatic polyesters at 650°C is given as P1 > P2 > P3 > P4. A polymer forming high char yield in thermogravimetric analysis under nitrogen atmosphere indicates that the polymer may be a fire retardant. Thick char becomes a better thermal insulating layer and undergoes slow oxidative degradation, protecting the remaining polymer from heat radiation [44].

Table 1. Transition behavior of polymers

Polymer code	Temperature[a], °C corresponding to		Char residue[a], % at 650°C	DSC[b], °C				HOPM[c], °C			Stirred opalescence
	10% wt loss	50% wt loss		T_g	T_m	T_i	ΔT	T_m	T_i	ΔT	
P1	339	460	27.3	108	131	189	58	127	185	58	Strong
P2	398	475	19.1	101	126	173	47	122	170	48	Strong
P3	282	434	17.1	92	113	140	27	115	142	27	Strong
P4	275	475	15.4	104	–	138	–	–	141	–	Strong
P5	400	575	43.6	–	–	250	–	–	253	–	Strong
P6	425	600	47.6	–	–	–	-	–	*	*	Nil
COP1	239	408	17.7	59	–	113	–	–	120	–	Strong
COP2	215	400	12.6	–	–	110	–	–	113	–	Strong

[a]The values were determined using TGA (at heating rate of 10 K/min under N_2 atmosphere).

[b]Transition temperature identified using DSC (at heating rate of 10 K/min under N_2 atmosphere).

[c]Transition temperature identified with HOPM at a heating rate of 5 K/min.

*Unable to determine since HOPM can be operable only below 300°C.

A copolymer, COP1 derived from suberyl chloride showed considerably less thermal stability than its homo polymer, P2. This may be due to the flexibility of the non-photosensitive diol (Bisphenol-A) which decreased the thermal stability. Another plausible explanation might be that in copolymers there are more ester groups in the mass unit than in homo polymers. The ester group may decompose in the early stage. The 10% weight loss occurred around 239°C and char yield at 650°C was found to be 17.75%. For aromatic polymers (P5, P6), the data revealed that the char yields were quite higher than aliphatic polymers. Among the aromatic polymers, the polymer P6, containing isophthaloyl units showed a higher stability and char yield compared to the polyester containing terephthaloyl units. This may be ascribed to the higher crystallinity inside the hard domain of the polyester derived from terephthalic acid compared to that of the polyester derived from isophthalic acid which is reflected in the DSC results also.

Limiting oxygen index for all the polymers was determined using Van Krevelen equation [45] and is in the range of 23.6–36.5. According to Van Krevelen, polymers having LOI above threshold value of 26 possess self-extinguishing property. LOI data indicates that among the aliphatic polyesters adipoyl unit containing polyester (P1) exhibited the LOI value of 28.41 has only self extinguishing property and the rest of the aliphatic polyesters (P2, P3, P4) and copolyesters (COP1 and COP2) showed LOI below the threshold value. This may be due to the more number of methylene units in homo polymers and the presence of flexible bisphenol-A moiety in the main chain of copolymer increases the flexibility and reduced the thermal stability as we observed in the TGA studies. Aromatic polyesters derived from terephthaloyl and isophthaloyl

groups exhibited LOI above the threshold value of 34.9 and 36.5 respectively. This showed that both the aromatic polyesters exhibited self-extinguishing property due to more stability and rigidity.

The DSC data of the synthesized polymers is given in Table 1. Except P4, all the aliphatic polymers showed double endotherms and the phase transitions, which are reversible during cooling cycle; they are enantiotropic in nature.

The melting transition temperature T_m of the polymers was obtained in the range of 113–131°C and the isotropic transition temperature T_i was observed in the region of 138–250°C. The polymers exhibiting double endotherms showed well-defined mesophase separation [46]. A representative DSC trace of polymer P3 is shown in Fig. 3a. On increase in the spacer length from P1 to P4, isotropic temperature T_i decreases. All the aliphatic polymers showed a glass transition temperature T_g in the region of 92–108°C. It was observed that aromatic polyesters containing terephthaloyl showed a melting transition whereas, isophthaloyl containing polyester did not show any melting transition. This may be due to the higher thermal stability of the polyester which resulted in the TGA results.

The copolymer COP1 and COP2 showed melting T_i at 113 and 110°C and COP1 exhibited T_g at 59°C. On comparing, corresponding homo and co-polymers we observed that the presence of bisphenol-A in the copolymers may increases the flexibility in the main chain and reduced the melting transition. The another explanation might be that in copolymers there are more ester groups in the mass unit than in homo polymers, due to lower molecular mass of bisphenol-A reduces T_i. The Fig. 3b showed the correlation
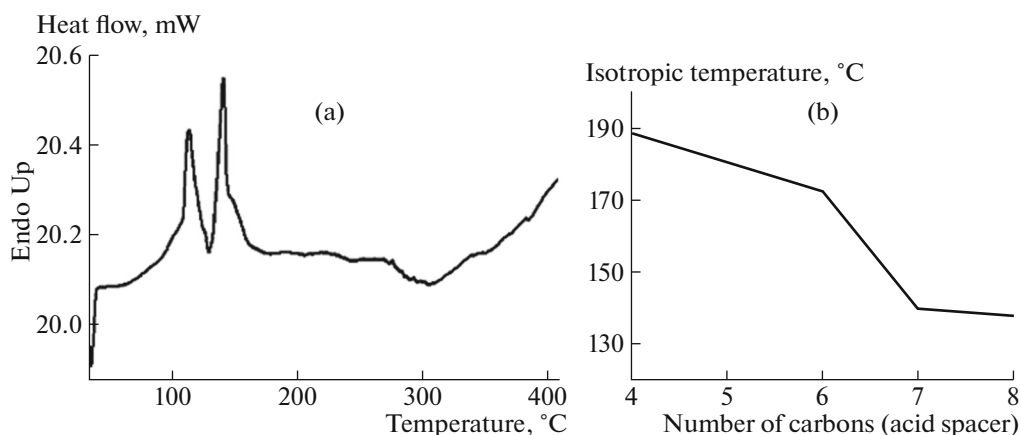
Fig. 3 (a) DSC trace of polymer (P3). (b) Correlation between isotropic temperature of aliphatic polyesters and number of acid spacer carbon atoms.
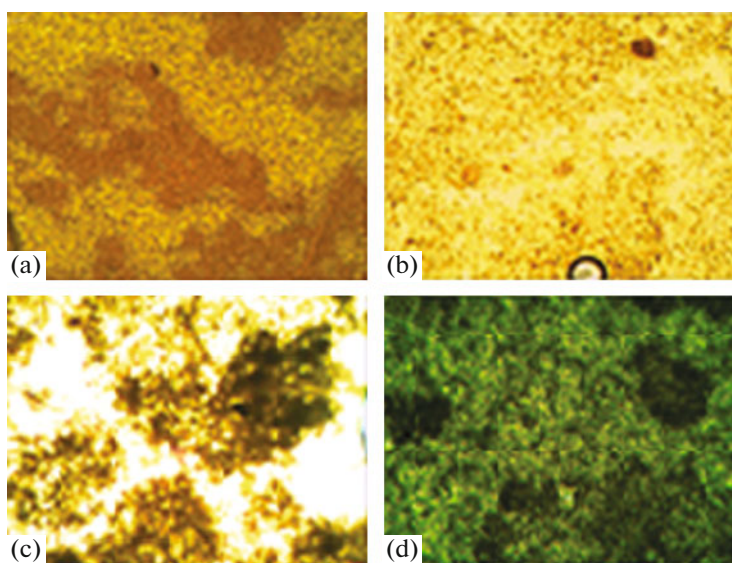

Fig. 4. HOPM photographs of polymers (a) P1 at 127°C, (b) P2 at 122°C, (c) P3 at 115°C, (d) COP1 at 120°C.

between isotropic temperature of aliphatic polyesters and number of acid spacer carbon atoms.

Hot-stage optical polarizing microscopic (HOPM) observations were performed to study the liquid crystal texture of the polymers. Table 1 shows the transition temperatures and their differences. The phase transition temperature determined by DSC are consistent with those observed by HOPM. Observation of polyesters under a polarizing microscope revealed that polymers, P1, P2 and P3 exhibited grainy texture [47] at 127, 122, and 115°C respectively (Fig. 4) and on further heating it will changed to isotropic state. Except polymer P6, the rest of the polymers and copolymers exhibited melt birefringence and stirred opalescence properties.

Photo-Crosslinking Studies

Polymers having olefinic groups are sensitive to ultraviolet irradiation. The peculiar property of these types of polymers is the tendency to proceed rapid photocrosslinking without the addition of any photoinitiators [48]. The scope of the present investigation is to study the photoreactivity of the polymers in solution and film states by UV spectrophotometry. Figures 5 and 6 shows the changes in the UV spectral pattern during the photolyses of polymer P2 in DMSO solution and P4 in film state at various intervals of time. The absorption bands observed at around 340–350 nm for the polymers correspond to $\pi \rightarrow \pi^*$ transition of the olefinic double bond present in the main chain of the polymer. During the successive UV irradiation of polymer a decrease in intensity of the absorption was noted. This may be attributed to the
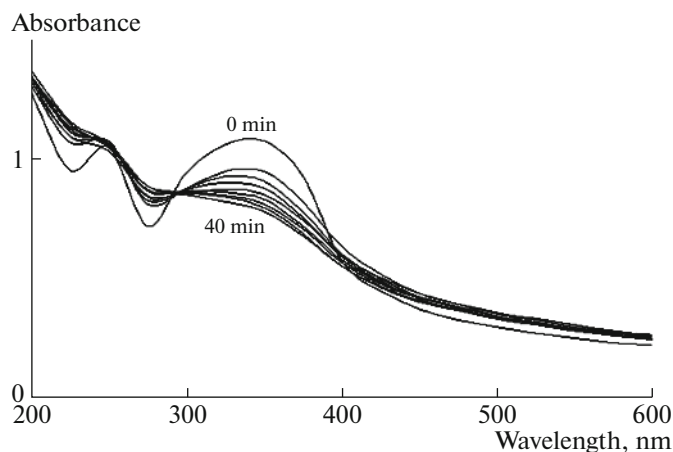
Fig. 5. Photo-crosslinking of polymer P2 in DMSO. Reaction time: 0, 5, 10, 15, 20, 25, 30, 35, and 40 min.
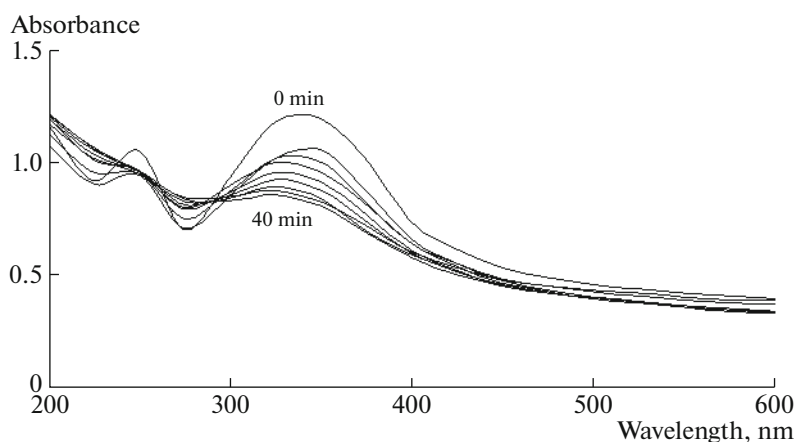

Fig. 6. Photocrosslinking of polymer P4 in film state (0, 5, 10, 15, 20, 25, 30, 35, 40 min).

dimerization of the olefinic double bond of the polymer chain, which involves the $2\pi+2\pi$ cycloaddition reaction of the same leading to the formation of cyclobutane ring [49] (Scheme 3).
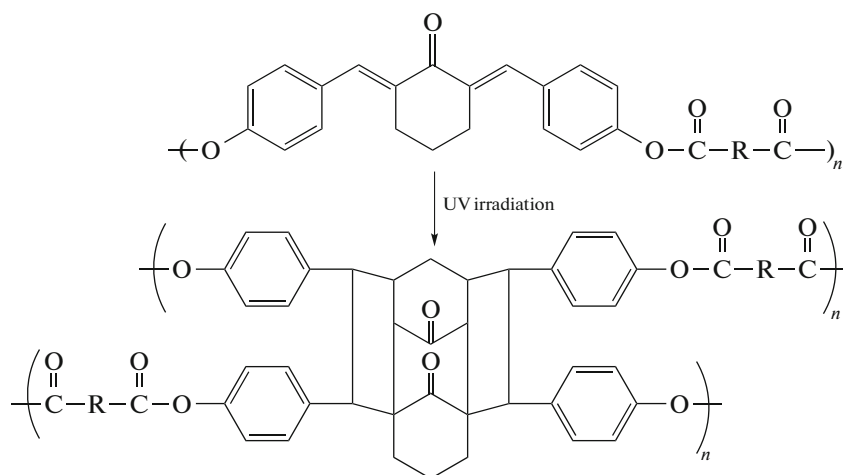
The rate of photo-crosslinking in solution state is faster than the film state. This may be due to the restricted chain mobility of polymer in film state; it takes more time than the solution state for crosslinking.

The relative reactivity rate $[(A_0 - A_t)/A_0$ where A_0 is the absorbance before irradiation and A_t is the absorbance after irradiation time t] was plotted against the time of irradiation. From Table 2 and Fig. 7, in film state, it is clear that the relative reactivity rate of photo-crosslinking of polymer P4 in film state increases significantly on increasing methylene carbon chain length of acid spacer. However, the cause of this effect is not well understood and it needs further investigation.

The photo-crosslinking ability of a polymer was also studied by monitoring with FTIR spectroscopy. There are significant changes in the FTIR spectra of α,β-unsaturated carbonyl group containing polymers occurred upon the UV exposure. The >C=C< stretching vibration at around 350 nm was observed to decrease after UV exposure and a new absorption band corresponding to a saturated carbonyl stretching vibration was appeared like our previously reported work [32].

In order to understand this type of polymers to be used as a negative photoresist compounds, the polymer samples were irradiated with UV light for 3 h and the crosslinked polymer was obtained by evaporating the solvents. The residue obtained was tested for solubility in various solvents. It was found that the UV irradiated polymer becomes insoluble in the solvents in which they were soluble before irradiation. The irradiated samples were further subjected for HOPM and DSC analysis and found that they lost their LC properties with increase in transition temperatures. This study confirmed the formation of crosslinked network
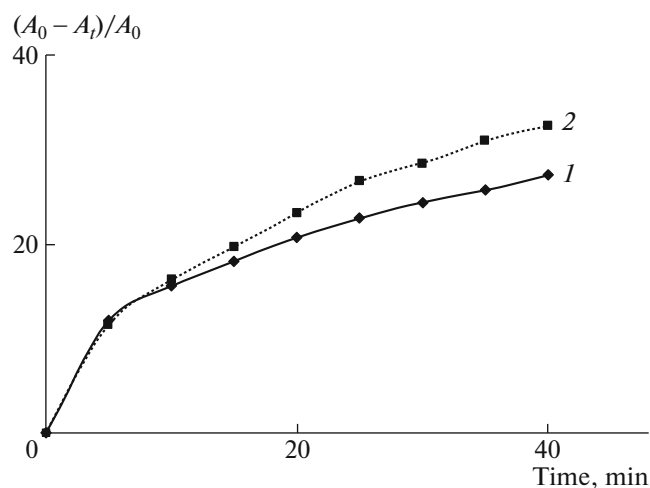
Scheme 3.

CONCLUSIONS

Photosensitive polymers were synthesized from 2,6-bis(4-hydroxybenzylidene)cyclohexanone and aliphatic/aromatic acid chlorides by interfacial polycondensation. It was observed that the aliphatic polyesters are soluble in most of the polar solvents and insoluble in non-polar solvents. The formation of polyesters was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR spectral techniques. The TGA results clearly indicated that these homo polymers are stable up to 275°C and copolymer start degrading at 239°C due to the introduction of bisphenol-A. The thermal stability of the homo polymers decreases as the acid methylene spacer length increases. In DSC analysis, on increase in acid spacer length decreases T_i. In HOPM analysis the synthesized polymers showed grainy texture, birefringence and stirred opalescence properties. The UV spectral studies revealed that the polymer undergoes photocrosslinking under the influence of UV radiation and showed that rate of photocrosslinking increases significantly on increasing methylene carbon chain length of acid spacer. This type of compounds can be suitably exploited for the negative photoresist applications.

Fig. 7. Rate of photolysis on irradiation of polymers (*1*) P2 and (*2*) P4 in film state.

structure upon UV irradiation. Also, it was observed from the work [50] that −C=C− at the terminal only helped to stabilise the LC phase.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

Table 2. Relative reactivity rate of photo-crosslinking

Time, min	Relative reactivity rate	
	P2	P4
5	12	11
10	14	15
15	18	20
20	21	24
25	23	27
30	23	28
35	26	31
40	27	33

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