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Photolysis and thermal active polymerization of *bis* (benzylidene) based benzoxazine monomers

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HIGHLIGHTS

- ▶ New class of photoactive benzoxazine monomers has been developed.
- ▶ Upon photolysis on 365 nm, the monomers undergoes photolysis via $[2\pi + 2\pi]$ cycloaddition reaction.
- ▶ The UV irradiated benzoxazine gives a highly thermally stable polybenzoxazine.

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ABSTRACT

A new class of photopolymerizable benzoxazine monomers has been developed, using photoactive bisphenol derivatives such as bis (4-hydroxybenzylidene)-4-phenyl cyclopentanone and bis (4-hydroxybenzylidene)-4-phenyl cyclohexanone, *p*-toludine and formaldehyde (37%). The structure of the benzoxazine monomers has been confirmed by Fourier Transform Infra Red spectroscopy (FTIR) and ^{1}H and ^{13}C Nuclear Magnetic Resonance spectroscopy (NMR). Upon photolysis with radiation of 365 nm, the monomers undergo photolysis via $[2\pi + 2\pi]$ cyclo-addition reaction, which was confirmed by UV spectroscopy. After photolysis, the benzoxazine monomers were subsequently cured at 200 °C for 2 h. The photo irradiated cured products possessed enhanced glass transition temperature and thermal stability, with an increase in the photodimerization time.

1. Introduction

In recent years, the word “polybenzoxazine” is more familiar in the thermosetting world, because it offers a lot of unique properties, such as low moisture absorption, super chemical resistance, good flame retardance, excellent electrical properties, high thermal stability and mechanical properties, which are discussed in several works in literature [1–5]. Polybenzoxazines are prepared from thermal ring opening polymerization of benzoxazine monomers or benzoxazine prepolymers. Due to its numerous advantages, polybenzoxazine based chemistry is one of the growing fields recognized in polymer research. Polybenzoxazine research is going on in several dimensions, among them a new molecular designing is preferable as this one will be very useful to improve the properties of polybenzoxazines.

Currently, photo polymerization attracts more rapid interest in the field of synthetic polymer chemistry. Photo polymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics [6–11]. Thermal polymerization is usually carried out at elevated temperatures, whereas photo polymerization can be performed even at temperatures below the room temperature. The polymerization of benzoxazine, using the combination of mechanism of photo and thermal polymerization has been several additional advantages of high performance applications. Photo chemically active groups are incorporated into the benzoxazine structure; it undergoes sequential photochemical reaction followed by thermal activation and this leads to a highly cross-linked polybenzoxazine network. This would obviously influence the glass transition temperature (T_g) and consequently the mechanical properties of the resultant polymer. Only a few works are available on photo cross linkable benzoxazine [12–17]. A bifunctional benzoxazine monomer containing a coumarin core has been reported, which is capable of undergoing photodimerization, and the thermal ring-opening polymerization processes results highly dense cross-linked networks [12]. Recently, Jin et al. [17] reported a methacrolyl functionalized benzoxazine monomer; it was subjected to photo polymerization followed by thermal polymeriza-

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tion. The photo polymerization was successfully carried out in the presence and absence of a photo initiator, while the thermally activated polymerization is compromised by low temperature degradation [17]. The *bis* (benzylidene) cycloalkanone core in organic monomers is notable mesogenic and having photoactive character. It was used as a photoactive core in wide range of polymer compounds. Several reports are available on photo cross linkable benzylidene based polymers [18–22].

To the best of our knowledge, no reports are available on the photo cross linkable benzylidene based benzoxazine monomer. Hence, in the present work, new *bis* (benzylidene) based benzoxazine monomers were synthesised and their photo polymerization behavior as well as thermal polymerization was studied.

2. Experimental

2.1. Materials

Cyclohexanone, cyclopentanone, 4-hydroxy benzaldehyde, *p*-toluidine, formaldehyde (37%), sodium hydroxide, anhydrous sodium sulfate and all the solvents were used and received from SRL (India) Ltd. 2,6-*bis*(4-hydroxybenzylidene)-cyclohexanone (BBCH), 2,5-*bis*(4-hydroxybenzylidene)-cyclopentanone (BBCP) were used and synthesised as per the literature [18].

2.2. Synthesis of (2E, 5E)-2, 5-bis ((3, 4-dihydro-3-p-tolyl-2H-benzo[e][1,3]oxazin-6-yl)methylene)cyclopentanone (BZP)

The reaction was conducted in the same manner as the procedure reported in our earlier work [23]. 37% aqueous formaldehyde solution 11 g (0.3666 mol) and *p*-toludine 6.95 g (0.0648 mol) were mixed with 1, 4-dioxane (50 mL) in a 250 ml three necked flask at 0–5 °C for 30 min. Then 10 g (0.0326 mol) of *bis* (benzylidene) cyclopentanone was added. The temperature of the reaction mixture was gradually raised to reflux and maintained for 6 h. After the completion of the reaction, the solvent and water were removed under vacuum and the residue was dissolved in chloroform ($CHCl_3$) (100 mL). The product solution was washed with water and 1 N sodium hydroxide (NaOH) several times, to remove any impurities and unreacted monomers. The product solution was then dried by using anhydrous sodium sulfate and the solvent evaporated at room temperature, to yield a wine red semi solid product (Scheme 1). Yield: 82%.

2.3. Synthesis of (2E, 6E)-2, 6-bis ((3, 4-dihydro-3-p-tolyl-2H-benzo[e][1, 3]oxazin-6-yl) methylene)cyclohexanone (BZH)

BZH was synthesised by using *p*-toludine, *bis* (benzylidene) cyclohexanone and 37% aqueous formaldehyde, the reaction followed as per the procedure reported in Section 2.2 (Scheme 1). Yield: 86% [23].

2.4. Photo polymerization followed by thermal polymerization of benzoxazine

Each 0.001 M $CHCl_3$ solution of benzoxazine monomers (BZP and BZH) was irradiated in a UV photo reactor separately at 5, 30,60 and 120 min intervals each, and the photo chemical activity of benzoxazine monomer was studied, using UV spectroscopy in each time interval. After UV irradiation, the solution was slowly evaporated, and then cured at 200 °C for 2 h.

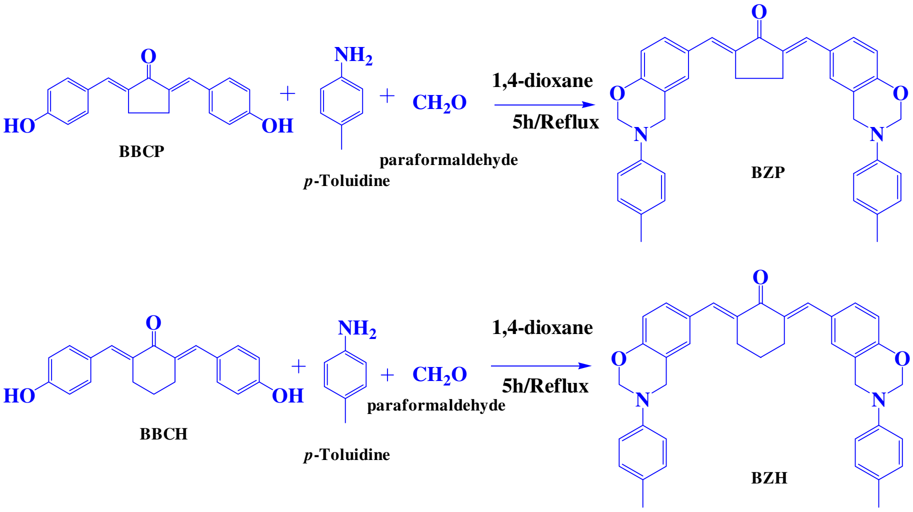
2.5. Characterization

2.5.1. Spectroscopy

The FT-IR spectrum was recorded on a Perkin Elmer 6X FT-IR spectrometer. About 100 mg of optical-grade KBr was ground with a sufficient quantity of the solid sample to make the wt.% mixture for making KBr pellets. After the sample was loaded, a minimum of 16 scans were collected for each sample at a resolution of ±4 cm^{-1}. The ^{1}HNMR and ^{13}CNMR spectra of benzoxazine monomers (BZP and BZH) were recorded with a BRUCKER 300 MHz NMR spectrometer. Samples were diluted using deuterated chloroform ($CDCl_3$), and tetramethylsilane (TMS) was used as an internal standard. The photo cross linking behavior was monitored by the absorptions between 320 nm and 420 nm on a Shimadzu UV-160A UV visible recording spectrophotometer in a chloroform solution (0.001 M).

2.5.2. Thermal properties

The Glass transition temperature (T_g) of the samples was determined, using DSC 200 PC differential scanning calorimeter (Netzsch Gerateban GmbH) in the temperature range between 25 °C and 300 °C at a heating rate of 10 °C per min in a nitrogen atmosphere. The thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 thermogravimetric analyzer. The instrument was calibrated with calcium oxalate and aluminum supplied by



Scheme 1. Synthesis of photo active benzoxazine monomers (BZP and BZH).

Netzsch. The samples (about 50 mg) were heated from ambient temperature to 800 °C under a continuous flow of nitrogen (60 mL/min), at 10 °C/min.

3. Results and discussion

3.1. Spectral analysis of bis (benzylidene)based benzoxazine monomers

Photoactive benzoxazine monomers (BZP and BZH) were synthesised from appropriate photoactive bisphenols, *p*-toluidine and paraformaldehyde; it has been presented in Scheme 1. The FT-IR spectrum of (BZP and BZH) is presented in Fig. S1. A strong intensive band appeared at 2942 and 2852 cm^{-1} and it represent the symmetric and asymmetric stretching frequency of the cyclopentanone moiety. The formation of a strong intensive band at 1500 cm^{-1} indicates the presence of a tri substituted benzene ring of benzoxazine monomer. The band appeared at 1247 cm^{-1} indicating the carbonyl stretching frequency of the benzylidene unit. The appearance of a strong intensive band at 992 cm^{-1} confirms the presence of *bis* benzylidene group in the benzoxazine monomers. The appearance of a band at 930 cm^{-1} indicates N–C–O stretching, which in turn, confirms the formation of benzoxazine monomer. The ^1H NMR spectra of BZP and BZH are presented in Figs S2 and S4. The benzylidene protons of the benzoxazine monomer appear as a singlet at 7.72 ppm. The methylene protons of $–N–CH_2–O–$ and $–N–CH_2–Ar$ appear as a singlet at 5.3–5.4 ppm and 4.3–4.6 ppm respectively which confirmed the formation of benzoxazine monomer. The cyclic protons are appearing as multiplet in the range between 1.2 and 1.7 ppm. The ^{13}C Spectrum of BZP is presented in Fig. S3. The two types of methylene bridge carbon ($–N–CH_2–O–$ and $–N–CH_2–Ar$) appears in range between 50 and 80 ppm respectively and the carbonyl carbon appear at 181 ppm.

3.2. Photo cross linking studies of benzoxazine monomers

Two independent reactions, such as photo induced dimerization and ring-opening polymerization of photo active monomers, were investigated. The benzoxazine monomer in a chloroform solution was irradiated in a UV photo reactor and its structural changes were monitored by UV spectrophotometer. The representative spectral changes in the photolysis of benzoxazine monomers are shown in Figs. 1 and 2 respectively. The UV spectra of benzoxazine monomer in a chloroform solution showed that there is a decrease in the intensity of absorption at 360 nm. This may be ascribed to the formation of the dimerization of olefinic double bond of bis (benzylidene) cycloalkanone chromophores, which involves the $2\pi + 2\pi$ cycloaddition reactions (Figs. 1 and 2). The absorption at 360 nm disappeared completely after 120 min of irradiation. The relative rate of photo cross linking of benzoxazine monomers are shown in Fig. 3, where the relative reactivity $A_o–A_t/A_o$ is plotted against the irradiation time, in which, "A_o" is the absorption before irradiation and "A_t" is the absorption after irradiation at time "t". It is observed that, among the two types of benzoxazine monomers, the cyclopentanone containing monomer undergoes photolysis faster than the cyclohexanone containing monomer. This may be attributed to an increase in the unfavorable geometry for $2\pi + 2\pi$ cycloaddition reactions in cyclohexanone containing monomer [18].

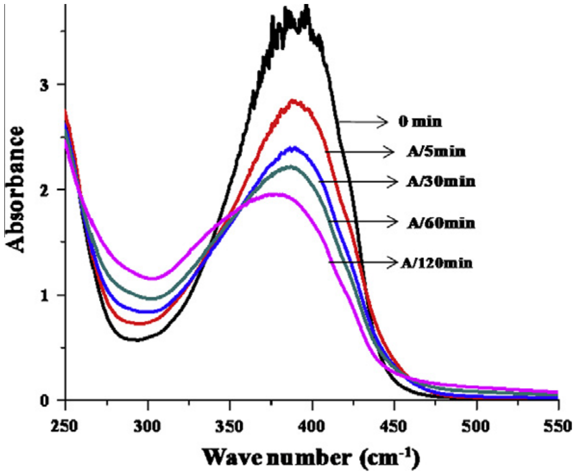


Fig. 2. Changes in UV spectral characteristics during photolysis of BZH in $CHCl_3$ at various time intervals.

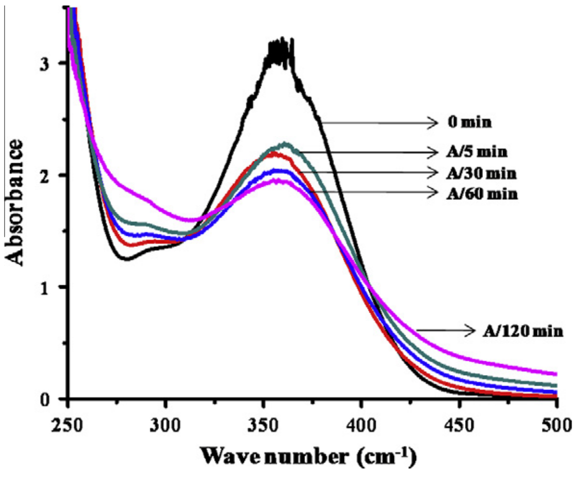


Fig. 1. Changes in UV spectral characteristics during photolysis of BZP in $CHCl_3$ at various time intervals.

3.3. Effect of photo irradiation on the curing behavior of benzoxazine monomers

The DSC thermograms taken before and after the UV irradiation of benzoxazine monomers (BZP and BZH) and the data are presented in Table 1. All the monomers show a single exothermic peak. Before UV irradiation, the DSC thermogram of benzoxazine (BZP) exhibits an onset, and the maximum curing temperature at

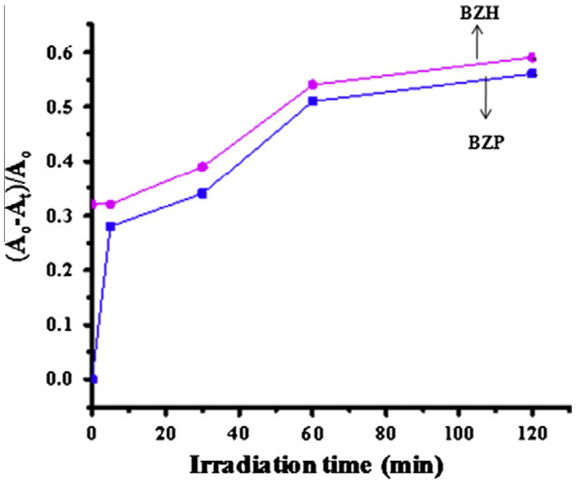


Fig. 3. Rate of photo cross linking of BZP and BZH under UV irradiation in different time intervals (A_0 and A_t are the absorbance at time 0 min and absorbance at time *t*).

Table 1
Curing studies of benzoxazine monomers before and after UV irradiation.

Sample code	T_i (°C)	T_{max} (°C)
BZP	163	229
BZP[a]	166	232
BZP[b]	177	251
BZH	169	235
BZH[a]	169	238
BZH[b]	181	255

T_i – initial polymerization temperature; T_{max} – maximum curing temperature.

[a] BZP (BZP subjected to UV irradiation for 5 min).

[b] BZP (BZP subjected to UV irradiation for 120 min).

163 °C and 229 °C respectively (Table 1), whereas the monomer BZH exhibits then at 169 °C and 235 °C respectively (Table 1). The photolysis was performed in a UV reactor using irradiation of $CHCl_3$ solution (0.001 M) of benzoxazine monomers (BZP and BZH) at 365 nm for 5 min and 120 min. After solvent evaporation, the curing behaviors of both the irradiated solid samples were analyzed using the DSC instrument. The onset and peak at the maximum curing exotherm of BZP[a] (BZP subjected to UV irradiation for 5 min) are 166 °C and 242 °C respectively. The values are almost similar to the onset and peak at the maximum curing exotherm of BZH[a] (BZH subjected to UV irradiation for 5 min) viz, 168 °C and 237 °C respectively. The curing behavior of the 5 min UV irradiated benzoxazine monomers (BZP[a] and BZH[a]) is not much varied, while the monomers irradiated for 120 min (BZP[b] and BZH[b]), exhibited a significant variation in the onset and maximum curing temperatures (Table 1). Fig. 4 shows the variation of the maximum curing temperature with respect to UV irradiation time of benzoxazine monomers. The changes occurring in the curing exotherm are due to the dimerization and higher cross-linking formation of the UV irradiated samples. The cross-linking of benzoxazine could be due to the hydrogen abstraction from the carbon atom adjacent to the nitrogen atom or from the vinylene proton of bisbenzylidene. Due to this hydrogen abstraction, a new free radical species has been generated that result in two reacting sites in one molecule [17].

3.4. Effect of photo cross linking on thermal properties of polybenzoxazines

The photo-polybenzoxazines (P-PBZs) obtained from benzoxazine involved to UV irradiation exposed by thermal curing, possess higher values of T_g than those of polybenzoxazine (PBZ) obtained from non irradiated benzoxazine monomer. The T_g values of P-PBZs increased linearly with an increase in the UV irradiation time of benzoxazine monomers (Fig. 5). The increase in the T_g value may be ascribed to the higher cross linking density of P-PBZs. The thermal behavior of polybenzoxazines was evaluated by the TGA in a nitrogen atmosphere at the heating rate of 10 °C/min and the data are presented in Table 2. Twenty percent weight loss temperatures of the photo-polybenzoxazine (P-PBZP$_1$ and P-PBZH$_1$) were observed at 442 °C and 428 °C, which are in the higher region than that of neat polybenzoxazine (Table 2). The results indicate that, the photo-polybenzoxazines were stable up to 247 °C and start degrading thereafter in a nitrogen atmosphere. When the photo irradiation time of benzoxazine monomer increases, its cross linking density may also increase. Therefore the highly cross linkable benzoxazine undergoes thermal polymerization resulting in thermally stable polybenzoxazine. The thermal stability of polybenzoxazines increased linearly with an increase in the irradiation time of the benzoxazine monomers. From the data, it was observed that the 20% wt loss temperature of the PBZP (435–473 °C) is more stable than that of PBZH (414–451 °C) (Table 2). This may be explained on the basis of the Baeyer's strain theory, that the heat of combustion per methylene unit of cyclopentanone was higher than that of cyclohexanone [18].

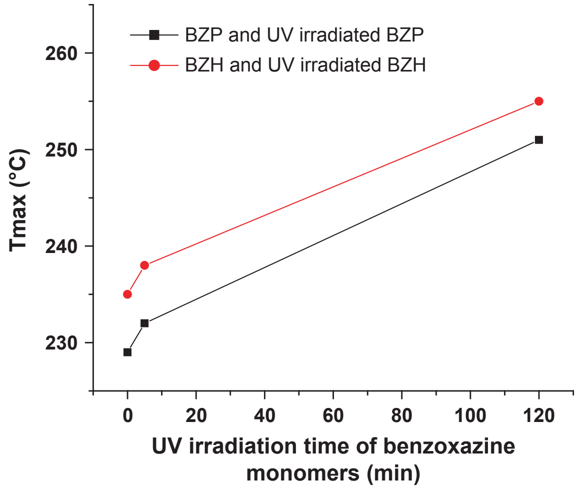


Fig. 4. A plot of T_{max} vs. UV irradiation time of benzoxazine monomers.

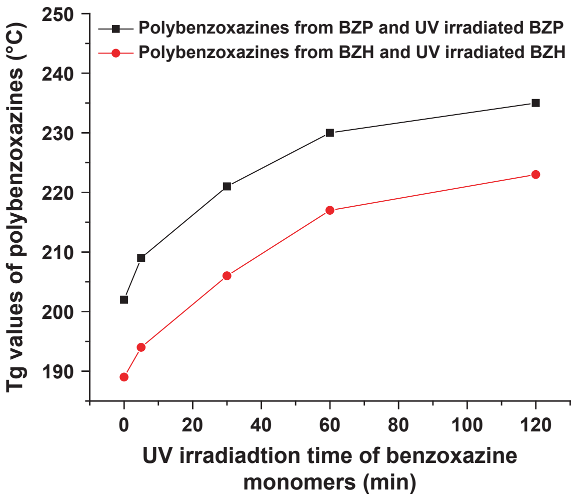


Fig. 5. A plot of T_g values of polybenzoxazines vs. irradiation time of benzoxazine monomers.

Table 2
Thermal properties of polybenzoxazines (PBZP and PBZH).

Sample code	T_g (°C)	T_5	T_{20}	Char yield (wt.%) at 800 °C
PBZP	202	259	435	29
P-PBZP$_1$	209	273	442	33
P-PBZP$_2$	221	280	459	38
P-PBZP$_3$	230	284	466	42
P-PBZP$_4$	235	291	473	45
PBZH	189	247	414	24
P-PBZH$_1$	194	258	428	27
P-PBZH$_2$	206	267	434	32
P-PBZH$_3$	217	275	446	36
P-PBZH$_4$	223	280	451	39

PBZP: Thermal curing of BZP monomer without UV irradiation; P-PBZP$_1$: BZP monomer UV irradiated for 5 min followed by thermal curing; P-PBZP$_2$: BZP monomer UV irradiated for 30 min followed by thermal curing; P-PBZP$_3$: BZP monomer UV irradiated for 60 min followed by thermal curing; P-PBZP$_4$: BZP monomer UV irradiated for 120 min followed by thermal curing; PBZH: Thermal curing of BZH monomer without UV irradiation.; P-PBZH$_1$: BZH monomer UV irradiated for 5 min followed by thermal curing; P-PBZH$_2$: BZH monomer UV irradiated for 30 min followed by thermal curing; P-PBZH$_3$: BZH monomer UV irradiated for 60 min followed by thermal curing; P-PBZH$_4$: BZH monomer UV irradiated for 120 min followed by thermal curing.

4. Conclusion

In the present work, two types of *bis* (benzylidene) based benzoxazine monomers have been synthesised, and the molecular structure of benzoxazine was confirmed using the FT-IR and NMR spectroscopy analyses. Between the two types of benzoxazine monomers, the BZP undergoes photolysis faster than the BZH. The onset and curing temperature of the benzoxazine monomers were increased with an increase in the irradiation time. The UV irradiated benzoxazine gives a highly thermally stable polybenzoxazine, when compared to non-irradiated benzoxazine. The UV irradiated BZP monomer gives highly thermally stable polybenzoxazine compared to the UV irradiated BZH monomer.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.06.002.

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