

# Synthesis, Spectral, and Thermal Characterization of Photoreactive Epoxy Resin Containing Cycloalkanone Moiety in the Main Chain

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**ABSTRACT:** Dual functional epoxy resins were synthesized by solution polycondensation of 2,6-bis(4-hydroxy-3-methoxy benzylidene)cyclohexanone and 2,5-bis(4-hydroxy-3-methoxy benzylidene)cyclopentanone with epichlorohydrin. The synthesized epoxy resins were characterized systematically for their structure by UV, Fourier transform infrared (FTIR),  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopic techniques. Thermal characterization of synthesized epoxy resins was carried out by thermogravimetric analysis, and differential scanning calorimetry (DSC) under nitrogen atmosphere. The self extinguishing property of synthesized oligomers was studied by determining limiting oxygen index (LOI) values using Van Krevelen's equation. X-ray analysis showed that the epoxy resins containing cyclopentanone have higher degree of crystallinity. The photoreactive property of the synthesized epoxy resins in solution and film states was investigated by UV-Vis spectroscopy.

The photocross-linking proceeds through the dimerization of olefinic chromophore present in the main chain of the oligomer via  $2\pi + 2\pi$  cycloaddition reaction. The influence of photoacid generator on the rate of photocross-linking of epoxy resin was studied by FTIR. UV irradiation of the epoxy resin in presence of photoacid generator produces aromatic sulfonium cation radicals and aromatic radicals which initiate the cationic ring-opening polymerization of oxirane ring. The photoreactivity studies of the oligomers by FTIR and DSC indicated the presence of dual functionality in the synthesized epoxy resins. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 58–66, 2012

**Key words:** epoxy resin; photosensitive polymers; photopolymerization; photocross-linking; cationic polymerization; UV-irradiation; photoacid generator; differential scanning calorimetry

## INTRODUCTION

Epoxy resins are widely used as advanced composite matrices in the electronic/electrical industries, owing to their high tensile strength and modulus, low shrinkage in cure, high adhesion property, good chemical and corrosion resistance, and good processability.<sup>1–4</sup> Photoreactive epoxy materials have recently gained a remarkable interest since the photochemical reactions in organic materials can induce many changes in physicochemical properties such as solubility, optical transparency, dielectric constant, and refractive index. These polymers are being used in the fabrication of integrated circuits, printing plates, photocurable coatings, photo recorders, energy exchange materials, and microlithography.<sup>5–8</sup> The photosensitive polymers undergo either photo

polymerization or photocross-linking on UV irradiation. The UV radiation curing process has become a powerful tool to fasten the cross-linking of the epoxy resins. Among many photochemical reactions in organic materials, the cationic photopolymerization by UV light exposure exhibits several advantages in a practical application concern. Crivello et al. have reported two novel classes of photoinitiators, diaryliodonium and triarylsulfonium salts for cationic polymerization, which undergo irreversible photo fragmentation on photolysis producing aryliodonium or arylsulfonium cation radicals.<sup>9,10</sup> Choi et al. synthesized chalcone containing epoxy compounds and studied its photopolymerization ability.<sup>7</sup> Another popular photochemical reaction study is the photocross-linking reactions. Photocross-linkable moieties present in the polymers, on irradiation with UV light can induce significant change in physical properties like solubility, film formation, and optical transparency due to cross-linking nature. The photosensitivity of these materials is mainly attributed to the  $\pi$  electron density of the photoactive chromophore.<sup>11</sup> The common epoxy resin systems cannot satisfy some applications which require high thermal and flame resistance. Traditionally, halogenated

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compounds and/or antimony oxide serving as flame retardants, but disadvantage is the formation of toxic gases during combustion. For this reason, halogen-free flame retardant epoxy polymers have attracted more attention of scientist and engineers in recent years.<sup>12,13</sup>

In this work, we report the synthesis and characterization of dual functional photo reactive epoxy resins containing exocyclic double bonds and oxirane groups in the main chain. Epoxy resins were synthesized from 2,6-bis(4-hydroxy-3-methoxy benzylidene)cyclohexanone (BHMBCH), 2,5-bis(4-hydroxy-3-methoxy benzylidene)cyclopentanone (BHMBCP), and epichlorohydrin. Spectral and thermal characterizations were performed for the synthesized epoxy systems. Photocross-linking property was monitored by UV-Vis spectrophotometer. The effect of photoacid generator on photosensitivity of the resin was investigated by Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

Cyclohexanone (Merck, 99%), cyclopentanone (Aldrich, 99%), BF<sub>3</sub>-diethyl etherate (Fluka, Steinheim, Germany, 99%), triphenylsulphoniumtriflate (Aldrich, Steinheim, Germany, 99%), and sodium hydroxide (Merck, 99%) were used as received. Ethanol (Merck, 99%), methanol (Merck, Mumbai, India, 99%), chloroform (Merck, 99%), and dimethyl sulfoxide (Merck, 99%) were purified by standard procedure. 4-Hydroxy-3-methoxy benzaldehyde (Sd fine, Chemicals, Mumbai, India, 99%) was recrystallized by using standard method.<sup>14,15</sup>

### Characterization

Elemental analysis was carried out using Elementar Vario EL III analyzer by taking 0.5 mg of solid sample. UV-visible spectra were recorded on a UV-1700 Pharmaspec Shimadzu spectrophotometer and FTIR on a FTIR-8400S Shimadzu spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 500 MHz Bruker—NMR spectrometer using dimethyl sulphoxide (DMSO)-*d*<sub>6</sub> as solvent and tetramethyl silane (TMS) as an internal standard. DSC traces were obtained on a Perkin-Elmer Pyris 6 instrument at a heating rate of 10°C/min in nitrogen atmosphere to determine the thermal transitions. Thermogravimetric studies were performed on a Perkin-Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min with a sample weight of 3–5 mg. The epoxy content and epoxy equivalent were determined by titration method using pyridinium hydrochloride. The number average, weight average mo-

lecular weights, and polydispersity index (PDI) of the polymers were estimated using gel permeation chromatography (GPC), in THF with a Shimadzu LC-20AD GPC. The X-ray diffraction (XRD) patterns of the oligomers were obtained on Shimadzu XRD-6000. Photolysis of the epoxy resins was carried out in DMSO or in chloroform at 30°C depending on the solubility of the oligomers. The solution was irradiated with medium pressure Hg lamp (Heber Scientific, Chennai, India, photoreactor, 125 W, 280 lux, 280–380 nm) kept at a distance of 10 cm from the sample. Subsequently, the irradiated solution was subjected to UV spectral analysis to study photocross-linking of the oligomers. The photopolymerizing ability of the oligomer through oxirane ring was studied in presence of triphenylsulphoniumtriflate a photoacid generator and analyzed by FTIR and DSC.

### Synthesis of epoxy resins

Two grams (0.00546 mol) of BHMBCH was dissolved in 10.7 mL (0.1365 mol) of epichlorohydrin in a three-necked round bottom flask. 2.04 mol of sodium hydroxide per mole of BHMBCH was added to the reaction mixture with vigorous stirring at 80°C. The stirring was continued for 4 h. The product obtained was kept at room temperature for 12 h and excess epichlorohydrin was separated by vacuum distillation. The final product was washed well with water and methanol to purify the epoxy resin. After the removal of the solvent and water by rotary evaporator, a yellowish solid or liquid product was obtained depending on the ratio of BHMBCH-epichlorohydrin. Yield: 76–80%.

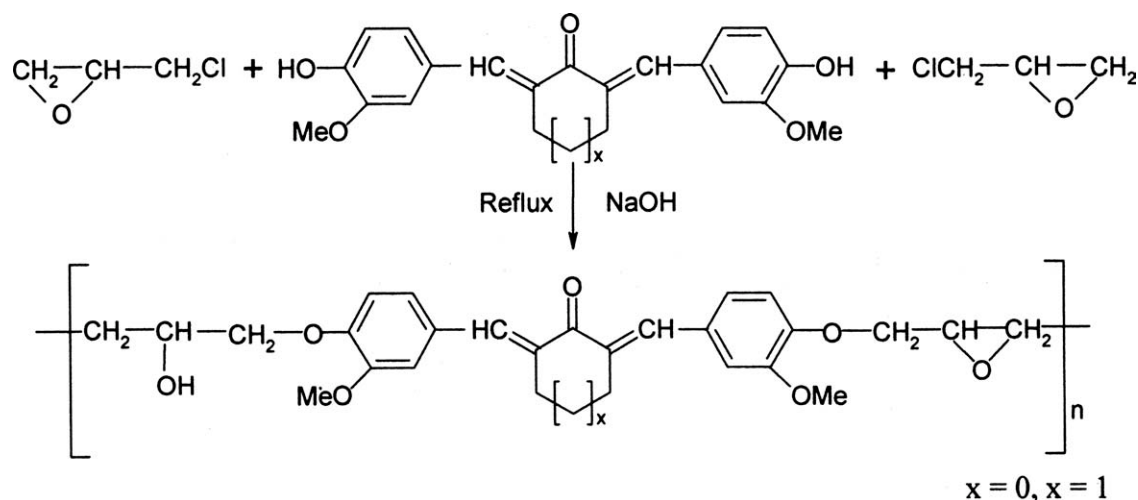
Similar procedure was followed to synthesize BHMBCP based epoxy resins. Yield: 76–85%.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The monomers BHMBCH and BHMBCP were synthesized by condensing 4-hydroxy-3-methoxy benzaldehyde with cyclohexanone and cyclopentanone using borontrifluoride-diethyletherate catalyst as per the previous reports.<sup>6,16,17</sup>

The scheme of preparation of epoxy resins from BHMBCH and BHMBCP is shown in Scheme 1. The solubility of photoreactive oligomers is one of the important criteria for practical use. The solubility of the newly synthesized epoxy resins was tested in various solvents. They were highly soluble in polar aprotic solvents such as DMF, DMSO, dioxane, THF, and chlorinated solvents such as CHCl<sub>3</sub>, dichloromethane, and dichloroethane. They were insoluble in alcohols and hydrocarbons such as benzene, toluene, and *n*-hexane and the results are given in Table I. It



Scheme 1 Scheme of synthesis of BHMBCH- and BHMBCP-based epoxy resins.

was observed that the oligomers containing cyclohexanone moiety are highly soluble than the cyclopentanone containing epoxy resins. This may be attributed to the bulky nature of cyclohexanone which hinders the close packing of oligomers.<sup>18</sup> The epoxy number and epoxy equivalent were determined by titration method using pyridinium hydrochloride.<sup>15</sup> It was found that the epoxy equivalent decreases with increase in epichlorohydrin ratio. This may be due to the formation of diglycidyl structure at higher ratio of epichlorohydrin. The molecular weight results obtained from GPC analysis also support this observation and the results are summarized in the Table II.

### Spectral studies

The infrared spectra of cyclohexanone moiety containing epoxy resins are shown in the Figure 1. The synthesized epoxy resin exhibit absorption band at  $1655\text{ cm}^{-1}$  corresponding to  $\text{C}=\text{O}$  stretching of cyclohexanone.<sup>19</sup> The oligomers showed exocyclic

$\text{C}=\text{C}$ -stretching vibration at around  $1595\text{ cm}^{-1}$ . The sharp distinct absorption bands at  $1253$ ,  $910$ , and  $808\text{ cm}^{-1}$  are due to symmetrical and asymmetrical stretching vibrations of oxirane ring which support the formation of epoxy resins.<sup>4</sup> The presence of  $\text{C}-\text{O}-\text{C}$  stretching was confirmed by the appearance of absorption band at  $1138\text{ cm}^{-1}$ . The aliphatic  $\text{C}-\text{H}$  bending vibrations appeared at  $1420\text{ cm}^{-1}$ . Aromatic  $\text{C}=\text{C}$  stretching appeared at around  $1512\text{ cm}^{-1}$ . All these peaks were also observed for cyclopentanone system. The FTIR spectra of all the epoxy resins showed the disappearance of the phenolic  $\text{OH}$  peak.

The  $^1\text{H}$  NMR spectrum of the representative epoxy resins are shown in the Figures 2 and 3. The aromatic protons resonate as a multiplet at around  $7.2\text{ }\delta$ . The resonance signal as singlet at  $3.8\text{ }\delta$  is due to the presence of methoxy protons. The olefinic protons present in the main chain resonate as a doublet at  $7.6\text{ }\delta$ . The methine and methylene protons of oxirane ring show their resonance peaks at  $4.4$  and  $3.3\text{ }\delta$ , respectively. The methylene protons of glycidyl unit appeared as a

TABLE I  
The Solubility Behavior of the Synthesized Epoxy Resins

Polymer code	Solubility <sup>a</sup>											Dichloro ethane	Dichloro methane
	DMSO	DMF	THF	1,4 dioxane	Acetone	$\text{CHCl}_3$	Ethanol	Benzene	Toluene	n-Hexane	Methanol		
P1	+	+	+	±	-	+	-	-	-	-	-	+	+
P2	+	+	+	+	-	+	-	-	-	-	-	+	+
P3	+	+	+	+	±	+	-	-	-	-	-	+	+
P4	+	+	+	+	+	+	-	-	-	-	-	+	+
P5	+	+	+	±	±	+	-	-	-	-	-	+	+
P6	+	+	+	±	-	+	-	-	-	-	-	+	+
P7	+	+	+	±	-	+	-	-	-	-	-	+	+
P8	+	+	+	±	-	+	-	-	-	-	-	+	+

<sup>a</sup> Qualitative solubility tested with 2–3 mg of sample in 2 ml of the solvent. +, soluble at room temperature; ±, partially soluble; -, insoluble.

TABLE II  
Epoxy Equivalents and Molecular Weight of Oligomers

Polymer code	Monomer	Reactant ratio		Epoxy equivalent	GPC <sup>a</sup>			
		Monomer	Epichlorohydrin		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	PDI <sup>b</sup>
P1	BHMBCH	1	10	732.6	1489	1692	1932	1.14
P2	BHMBCH	1	15	675	1088	1124	1160	1.03
P3	BHMBCH	1	25	500	897	916	936	1.02
P4	BHMBCH	1	200	310	568	550	662	1.02
P5	BHMBCP	1	10	220.2	1280	1357	1441	1.06
P6	BHMBCP	1	15	138.9	1144	1216	1296	1.06
P7	BHMBCP	1	25	145.1	1064	1124	1194	1.06
P8	BHMBCP	1	200	112	856	890	960	1.07

<sup>a</sup> THF as eluent against polystyrene standards.

<sup>b</sup> PDI, polydispersity index.

double doublet at 3.8  $\delta$ .<sup>7</sup> The methylene protons of the cyclohexanone appeared at 1.8 and 2.9  $\delta$ , whereas that of cyclopentanone resonate at 3.1  $\delta$ .<sup>6,20</sup>

The proton decoupled <sup>13</sup>C NMR spectrum of the representative epoxy resins are shown in Figures 4 and 5. The signals at 188.56 and 195  $\delta$  correspond to carbonyl carbon of cyclohexanone and cyclopentanone, respectively.<sup>21</sup> The resonance peaks at 132.42, 124.26, 114.01, 148.90, 149.19, and 113.31  $\delta$  are attributed to aromatic carbons present in the main chain. The exocyclic carbon resonates at around 132  $\delta$ . The signal corresponding to methoxy carbon emerges at 56  $\delta$ . The peaks at 68.5, 40.12, and 39.92  $\delta$  are due to carbons of  $-\text{CH}$  and  $\text{CH}_2$  groups of oxirane ring which are not present in the <sup>13</sup>C NMR spectrum of monomers BHMBCH and BHMBCP. The resonance peaks at 43.79, 27.86, and 22.47  $\delta$  are attributed to  $\alpha$ ,  $\beta$ , and  $\gamma$  carbons of cyclohexanone. For the cyclopentanone moiety containing oligomers  $\alpha$  and  $\beta$  carbons resonate at 38.88 and 25.79  $\delta$ , respectively.<sup>6,22</sup> All the above spectral results confirmed the formation of epoxy resins.

### Thermal studies

The thermal stability of the synthesized oligomers was studied by thermogravimetry in nitrogen atmosphere. The thermogravimetric traces of all the oligomers are shown in Figures 6 and 7. The temperature corresponding to 10, 20, 30, 40, 50% weight loss and char residue at 600°C are summarized in Table III. The temperatures corresponding to 10 and 50% weight loss for the BHMBCH-based epoxy resins were in the range of 370–394°C and 437–487°C, respectively. The initial weight loss observed in epoxy resins P4 and P8 may be due to loss of water molecules occluded in the liquid resins. Further, the thermogravimetric analysis (TGA) data revealed that the BHMBCP-based epoxy resins have higher thermal stability than BHMBCH-based epoxy resins. This may be due to the heat of combustion per methylene unit of cyclopentanone is higher than that of cyclohexanone.<sup>23</sup> It was noticed that the oligomers P4 and P8 synthesized from 1 : 200 of bisphenol and epichlorohydrin have higher thermal stability. Being

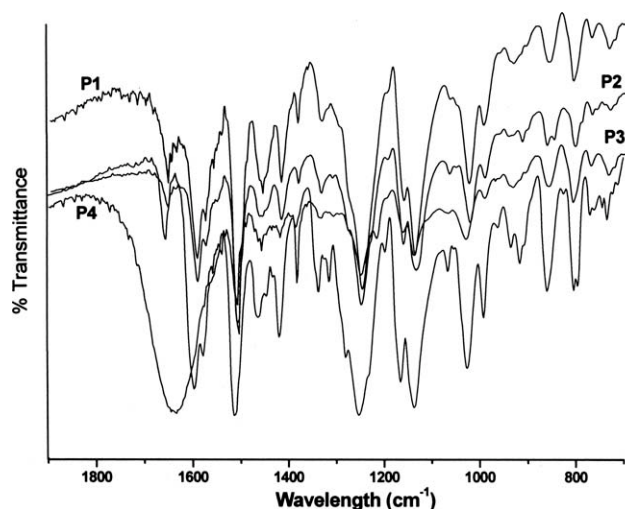


Figure 1 FTIR spectra of BHMBCH-based epoxy resins.

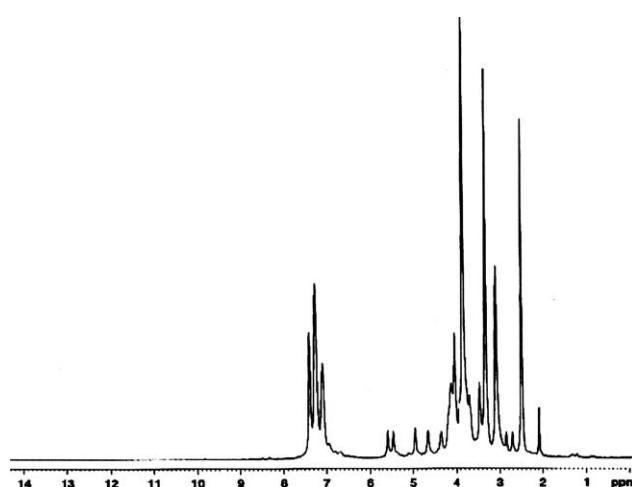


Figure 2 <sup>1</sup>H NMR spectrum of epoxy resin P3.



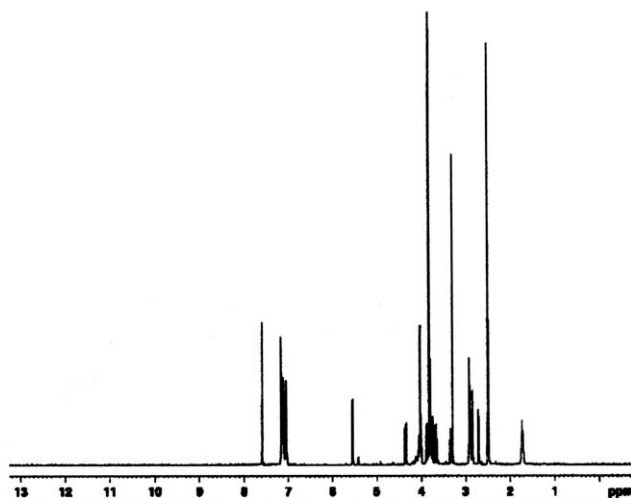


Figure 3  $^1\text{H}$  NMR spectrum of epoxy resin P7.

liquid resins, these oligomers might have undergone thermal cross-linking at higher temperature.

The char yield has been correlated to denote the flame retardancy and has been widely referenced in the studies of the epoxy compounds' flame property. Increasing char formation can limit the production of combustible gases; decrease the exothermicity of the pyrolysis reaction. The flame retardant property of the synthesized epoxy resins was studied by measuring the LOI values by substituting char yield value, obtained from TGA, in Van Krevelen's equation.<sup>24</sup> The LOI values of the non-halogenated polymer systems should be above the threshold value of 26, to render them self-extinguishing. All the synthesized epoxy resins showed high char yield, implying that the epoxy resins would exhibit relatively high

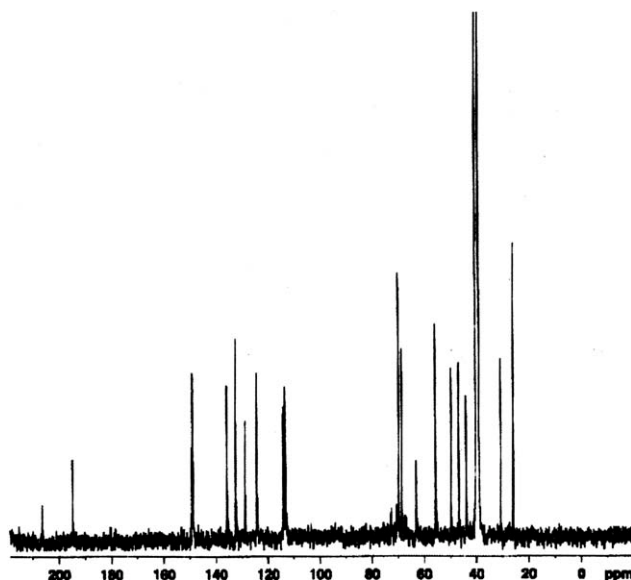


Figure 4  $^{13}\text{C}$  NMR spectrum of BHMBCH-based epoxy resin P3.

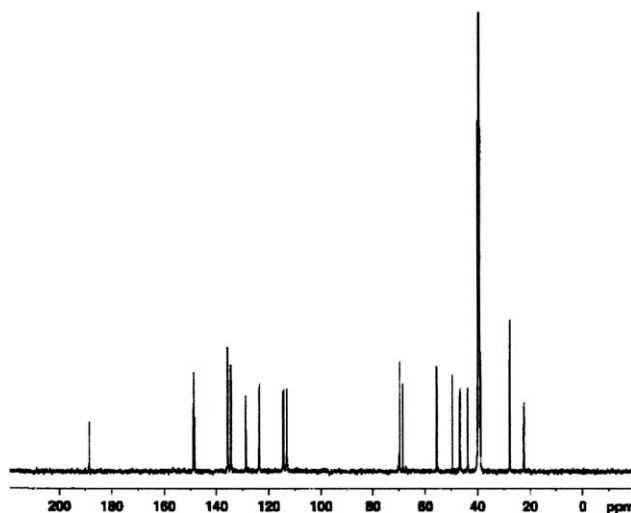


Figure 5  $^{13}\text{C}$  NMR spectrum of BHMBCP-based epoxy resin P7.

flame retardancy. The LOI values of BHMBCH- and BHMBCP-based epoxy resins were found to be in the range of 26.1–32.89 and 30.3–40.7°C, respectively. These results are shown in Table III. The LOI values of the cyclopentanone based resins are found to be comparatively higher than that of the cyclohexanone-based resins. This may be due to high thermal stability of the cyclopentanone-based resins which is reflected in TGA results. The flame retardancy and thermal stability indicate that these epoxy resins can be used in green electrical/electronic materials.

The DSC traces of the synthesized oligomers are shown in Figures 8 and 9 and their glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and exothermic temperature are presented in the Table III. The DSC traces indicated that the  $T_g$  and  $T_m$  of the BHMBCH- and BHMBCP-based epoxy resins are in the range of 106–107°C and 126–156°C, respectively.

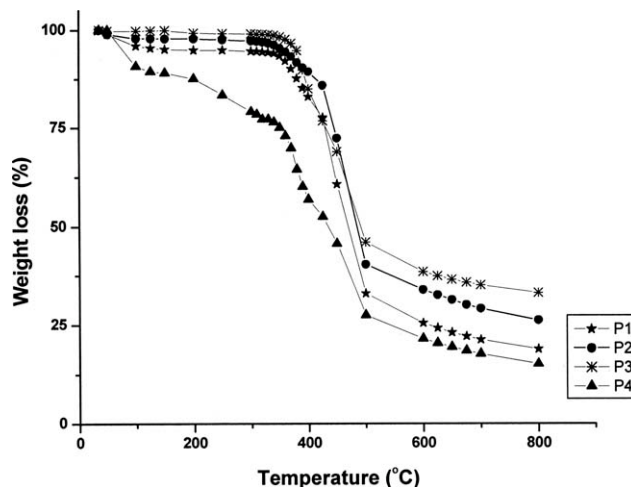
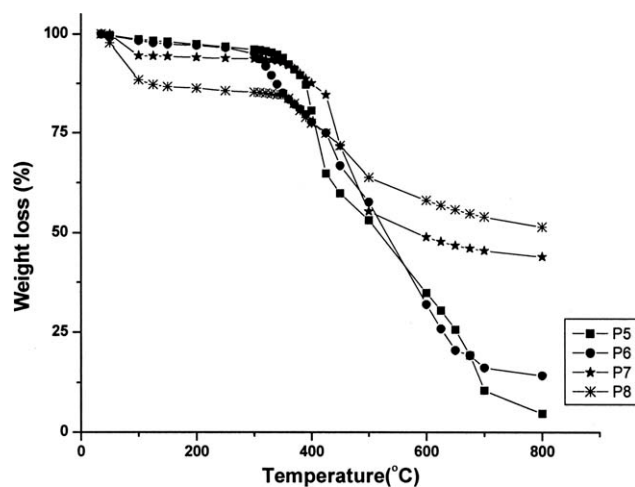


Figure 6 Thermogravimetric traces of BHMBCH-based epoxy resins.



**Figure 7** Thermogravimetric traces of BHMBCHP-based epoxy resins.

Further, it was noticed that the cyclopentanone-containing epoxy oligomers possess higher  $T_g$  and  $T_m$  values. This may be due to higher crystallinity of the cyclopentanone containing oligomers. The existence of multiple endotherms in the DSC traces (Fig. 9) may be due to the melting of micro crystalline units inside the hard macrodomains.<sup>25–27</sup> From the results obtained, it was seen that the transition temperatures are inversely proportional with the size of the cycloalkanone ring. A plausible explanation could be that, the smaller the ring size, the more linear and rigid is the hard segment, which leads to closer packing of the chains and hence higher transition temperatures. As the ring size increases, the hard segments start losing their linear rigid structure, which can reduce the transition temperature.<sup>17</sup> The DSC traces of the oligomers P1–P4 and P5–P8 also exhibited a broad exothermic peak in the range of 325–335°C, and 399–408°C, respectively. This may be

attributed to the thermal cross-linking of the polymer backbone.

### X-ray diffraction studies

XRD patterns of P1 and P5 are shown in Figure 10. According to Bragg diffractions formula ( $2d\sin\theta = n\lambda$ ), the XRD pattern of P1 shows smaller diffraction peaks at about  $2\theta = 12.92^\circ$  ( $d = 7.95$  a.u),  $14.38^\circ$  ( $d = 7.14$  a.u), and  $2\theta = 15.4^\circ$  ( $d = 6.67$  a.u), which show the semicrystalline nature of the epoxy resins. Oligomer P5 showed sharp diffraction peaks at  $2\theta = 31.88^\circ$  ( $d = 3.25$  a.u),  $2\theta = 53.35^\circ$  ( $d = 1.99$  a.u), and  $2\theta = 36.99^\circ$  ( $d = 2.81$  a.u), indicating the higher crystallinity nature of oligomers. These results indicate that the degree of crystallinity is higher in cyclopentanone containing epoxy resins than cyclohexanone which is in good agreement with DSC results.<sup>28</sup>

### Photocross-linking behavior of epoxy resins

The UV-induced photocross-linking of the epoxy resins was carried out in solution and film states using 125W medium pressure mercury vapor lamp. The absorption changes in the epoxy resin caused by photoreaction were monitored by UV–Vis spectrophotometer. The UV spectra of BHMBCHP-based epoxy resins showed an absorption maximum at around 379 nm in solution and film states due to  $\pi \rightarrow \pi^*$  transition of the olefinic double bond present in the main chain of the oligomers. On successive irradiation, the peak maximum decreased. This behavior clearly indicates the  $2\pi + 2\pi$  cycloaddition of olefinic double bond leading to the formation of cyclobutane ring.<sup>29</sup> The UV–Vis spectra representing the photocross-linking behavior of the oligomers P3 and P7 are shown in Figures 11 and 12.

**TABLE III**  
Thermal Behavior of Epoxy Resins P1–P8

Polymer code	TGA					Char residue <sup>a</sup> (%) at 600°C	LOI <sup>b</sup>	DSC		
	Temperature (°C) corresponding to weight loss <sup>a</sup>							$T_g$ (°C) <sup>c</sup>	$T_m$ (°C) <sup>c</sup>	Exothermic peak (°C) <sup>c</sup>
	10%	20%	30%	40%	50%					
P1	370	415	439	450	459	25.5	27.7	107.7	155.90	332.33
P2	394	439	452	459	470	33.9	31.06	107.66	152.43	325.23
P3	389	413	447	467	487	38.48	32.89	–	126.78	335.26
P4	108	288	369	390	437	21.56	26.1	106.12	–	328.56
P5	378	400	413	449	520	34.74	31.4	103.47	244	399.58
P6	328	388	431	490	532	31.9	30.3	129.03	240	408.35
P7	380	438	452	472	576	48.83	37.0	–	112.16	405.06
P8	85	384	458	563	854	58.03	40.7	126.23	240	402.17

<sup>a</sup> The values were determined by TGA at a heating rate of 10°C/min in nitrogen atmosphere.

<sup>b</sup> Determined using Van Krevelen's equation.

<sup>c</sup> Measured by DSC at a heating rate of 10°C/min in nitrogen atmosphere.

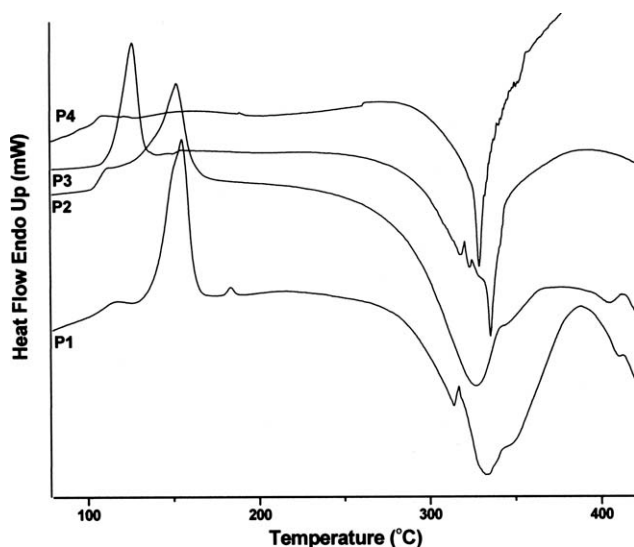


Figure 8 DSC traces of BHMBCH-based epoxy resins.

The photocross-linking efficiency of the epoxy resins were determined by calculating the conversion of the photoreactive olefinic chromophore ( $-\text{CH}=\text{CH}-$ ) to the cyclobutane ring using the expression  $[(A_0 - A_t) \times 100]/[A_0 - A]$ , where,  $A_0$ ,  $A_t$ , and  $A$  are the absorption intensities of  $>\text{C}=\text{C}<$  at irradiation times 0,  $t$  and a time after which there is no further significant change in the absorption, respectively. Figures 13 and 14 represent the rate of photocross-linking of the oligomers. It was observed that the maximum cross-linking occur within 10 min of irradiation. From Figure 15, it was noticed that the rate of photocross-linking of epoxy resins in solution state was higher than in film state. This may be due to the ease of orientation of chromophoric olefinic groups in solution phase for photocross-linking.<sup>30</sup> And also it was noticed that the cyclopentanone moiety containing epoxy resins have higher photocross-linking ability than the cyclohexanone containing epoxy resins.

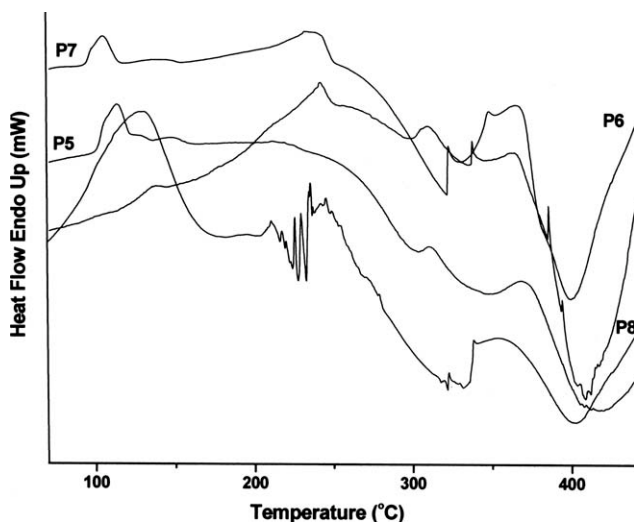


Figure 9 DSC traces of BHMBCP-based epoxy resins.

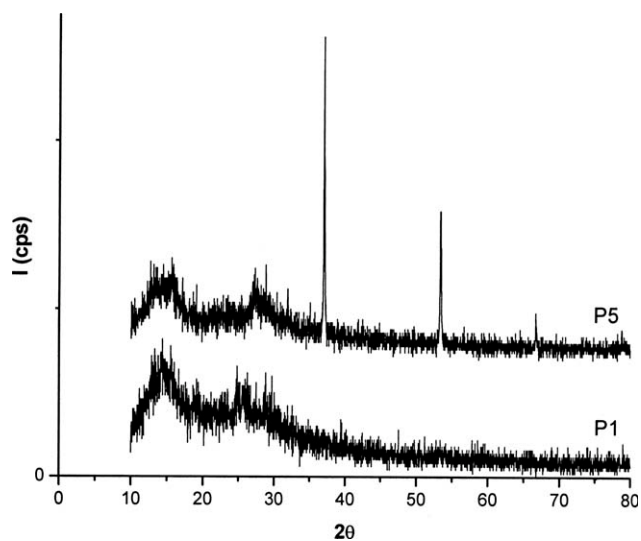


Figure 10 XRD patterns of P1 and P5.

The solubility of the UV-exposed resins was tested with common solvents. The photo-irradiated samples were found to be insoluble in organic solvents due to the formation of cross-linked structure. The photocross-linking of the olefinic  $-\text{C}=\text{C}-$  double bonds of the epoxy resins was also monitored by FTIR spectroscopy. The representative FTIR spectra of oligomer P3 before and after UV exposure are shown in Figure 16. The intensity of  $-\text{C}=\text{C}-$  stretching vibration at  $1595\text{ cm}^{-1}$  decreases significantly on UV exposure, whereas the intensity of the peaks corresponding to epoxy group were unaltered.

#### Photopolymerizing behavior of epoxy resins

The most important constituent in a UV-initiated cationic polymerization is the photoinitiator, because the most reactive epoxy compounds can hardly be

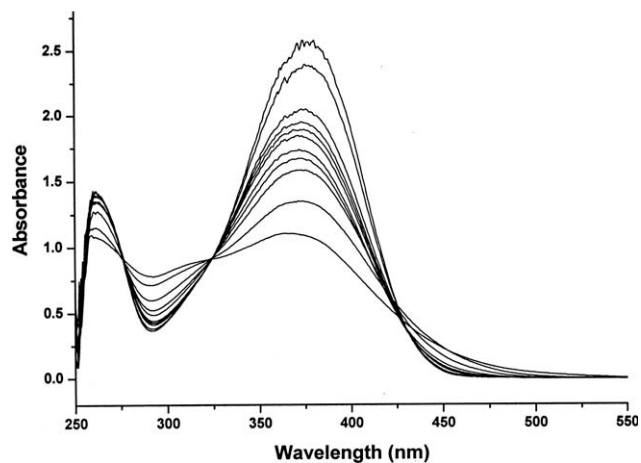


Figure 11 Change of UV-vis absorption spectral characteristics of BHMBCH-based epoxy resin P3 during photolysis, top to bottom, irradiation time  $t = 0, 5, 10, 15, 20, 25, 30, 45,$  and  $60$  min.

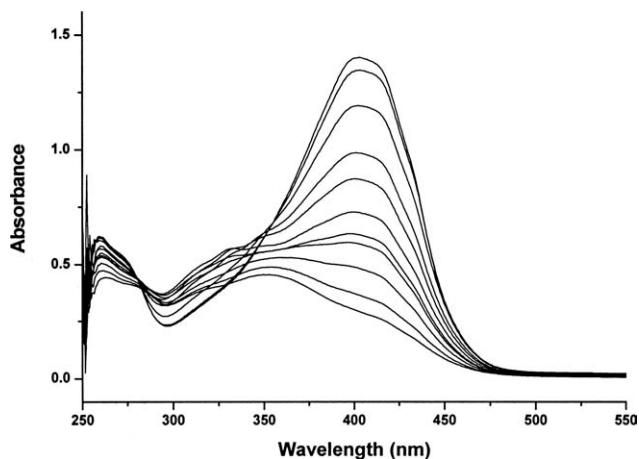


Figure 12 Change of UV-vis absorption spectral characteristics of BHMBCP-based epoxy resin P7 during photolysis, top to bottom, irradiation time  $t = 0, 5, 10, 15, 20, 25, 30, 45,$  and  $60$  min.

polymerized without any photoinitiator on UV irradiation. Therefore, to examine the photoreactive nature of the epoxy group present in the main chain, a photoinitiator, triphenylsulphoniumtriflate, was used. A thin film, prepared from epoxy resin P3 containing photoacid generator (PAG) on the quartz plate, was subjected to UV irradiation. The concentration of photoacid initiator was  $0.01 \text{ mol } \%$  and the UV exposure time was set to be  $1 \text{ h}$ . On exposure to UV irradiation of the mixture of epoxy resin and PAG, aromatic sulonium cation radical and aromatic radical are generated and then proceed to the cationic ring-opening polymerization.<sup>9,10</sup> In the FTIR spectrum, Figure 16, the characteristic peaks for epoxy group at  $910$  and  $808 \text{ cm}^{-1}$  diminished significantly on exposure to UV light. From these results,

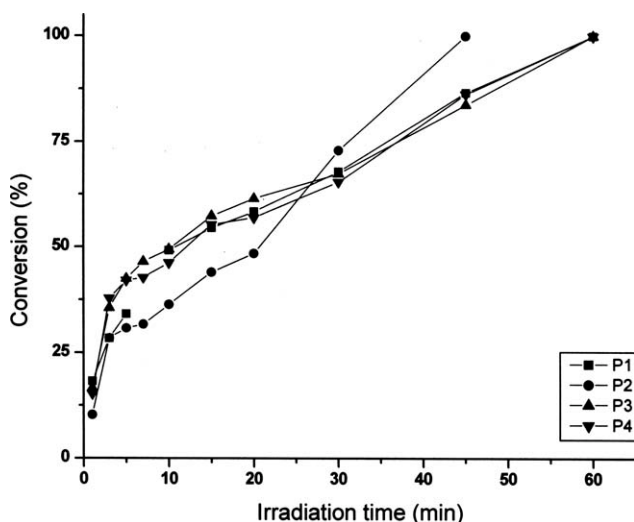


Figure 13 Rate of disappearance of  $>C=C<$  of photo-reactive group of BHMBCP-based epoxy resins in DMSO solution.

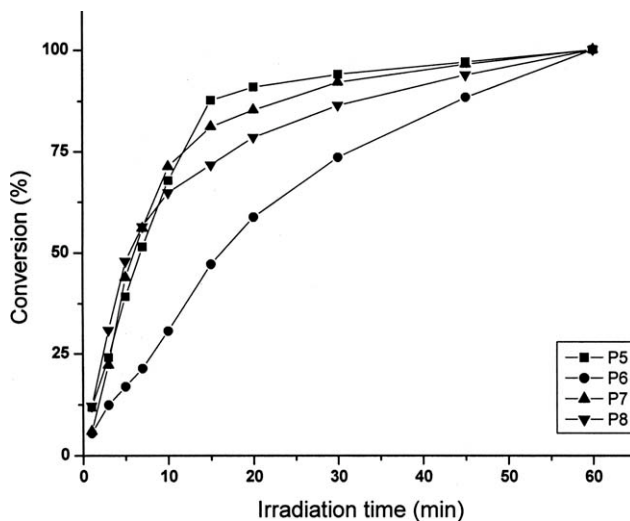


Figure 14 Rate of disappearance of  $>C=C<$  of photo-reactive group of BHMBCP-based epoxy resins in DMSO solution.

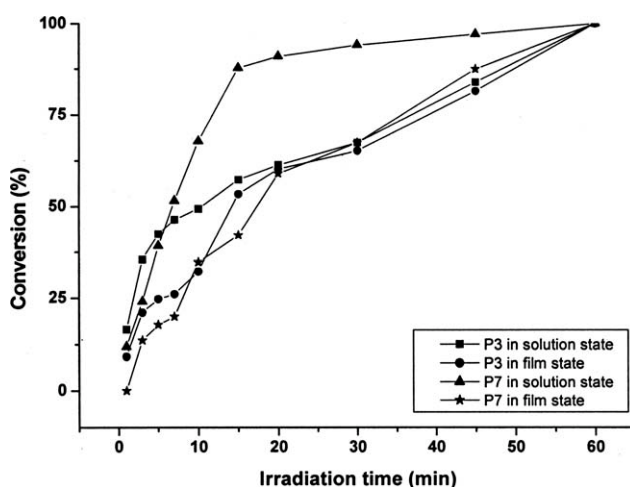


Figure 15 Rate of disappearance of  $>C=C<$  of photo-reactive group of P3 and P7 in solution and film state.

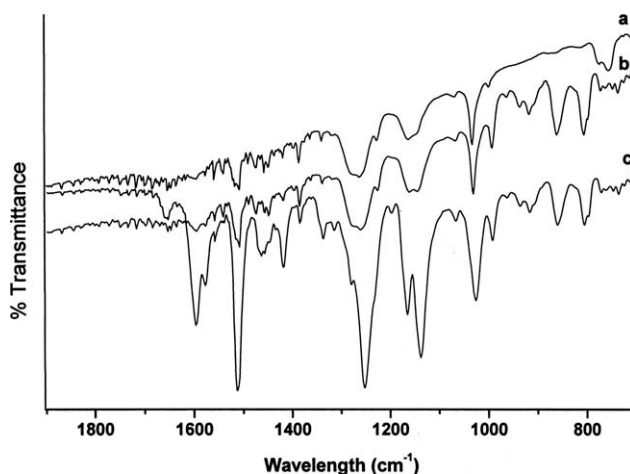
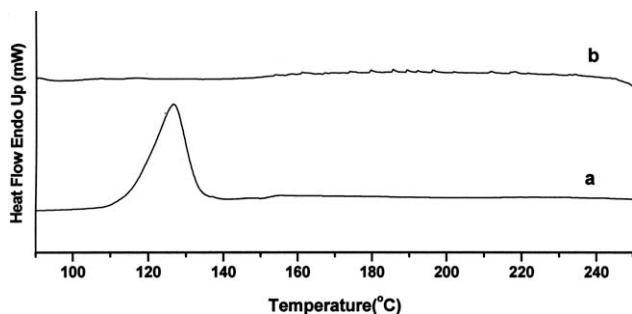


Figure 16 FTIR spectra of epoxy resin (a) P3 +PAG UV exposed; (b) P3 UV exposed; (c) P3 UV unexposed.





**Figure 17** DSC traces of epoxy resin (a) P3 UV unexposed; (b) P3 +PAG UV exposed.

it is observed that the epoxy resin with PAG can undergo photopolymerization upon UV exposure. The UV exposed oligomer P3 was also analyzed for its thermal property using DSC. The absence of  $T_m$  in the DSC traces was observed (Figure 17). This may be due to the formation of network structure by photopolymerization which reduced the crystallinity of the oligomer.

These observations substantiated that the synthesized epoxy resin can undergo both photocross-linking reaction between the  $-C=C-$  olefinic bonds and photopolymerization of the epoxy rings. These results revealed the dual functionality of synthesized epoxy resins.

## CONCLUSIONS

Dual functional photoreactive epoxy resins were synthesized from BHMBCH and BHMBCP by solution polycondensation with epichlorohydrin. The structures of monomers and oligomers were confirmed by spectroscopic techniques. The epoxy equivalent, molecular weight, and the physical state of the epoxy resins varied with the diol and epichlorohydrin ratio. It was observed that the oligomeric epoxy resin is highly soluble in aprotic polar solvents and insoluble in nonpolar solvents. TGA results clearly indicated that the BHMBCP-based polymers are highly stable than the BHMBCH-based polymers. The UV, FTIR, and DSC studies revealed that the oligomers undergo photocross-linking and photopolymerization under the influence of UV radiation, confirmed the presence of dual functionality. The char yield and LOI values indicated that the synthesized epoxy resins have good thermal stability and flame retardant properties which can be used in electrical and electronic industries.

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