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# Investigation on dual functional epoxy resins containing photosensitive group in the main chain for photoresist applications

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## ABSTRACT

Dual functional photosensitive epoxy resins were synthesized by solution polycondensation of 1,3-bis(4-hydroxyphenyl)propanone (BHPP) and 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propanone (HMPHPP) with epichlorohydrin. The characterization of synthesized epoxy resins comprised Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopic techniques. The thermal properties of the epoxy resins were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere and found that the synthesized resins were stable up to 300 °C. The effect of curing agents diamino-diphenylsulfone (DDS) and diaminodiphenylmethane (DDM) on the thermal stability of epoxy resin was compared and found that DDS cured epoxy resin has higher thermal than DDM. The photocrosslinking properties of the epoxy resins were studied with UV-Visible spectroscopy, and we observed that the olefinic double bond undergoes 2π-2π cycloaddition and leads to cyclobutane ring. Also, the effect of solvents on the photocrosslinking of the epoxy resin was also studied. Solvents with higher polarity favored the 2π-2π cycloaddition. The dual functionality of the resins was confirmed by FTIR study. The storage stability of the synthesized epoxy resins remained over more than 60 days. The synthesized epoxy resins successfully applied as negative photoresists.

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## KEYWORDS

Chalcone; photosensitive epoxy resin; negative photoresist; photoinitiator; photocrosslinking

## Introduction

In recent years, the synthesis of polymers containing a reactive functional group has become an active field of research in polymer science since it provides an approach to subsequent modification of the polymer for the required application. The technological applications of such polymers containing photoreactive functional groups are utilized in the fields of microlithography, photocurable coatings, and printing materials, liquid crystalline, and non-linear optical materials.<sup>[1]</sup>

Photosensitive polymers not only enable the production of printed circuits at a microscale<sup>[2]</sup> but also play an important role for additive manufacturing techniques such as stereolithography, inkjet 3D printing, 3D plotting, and bioprinting.<sup>[3]</sup> Polymers containing photosensitive segments

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in the main or side chain have become attractive due to the photocrosslinking properties conferred by the presence of such units.<sup>[4]</sup> Photosensitive polymers are being used as photoresists to make integrated circuits, printing plates, photocurable coatings, photo recorders, and energy exchange materials.<sup>[5]</sup>

The photoresist can be either of the photopolymerizing or of the photocrosslinking type or a combination thereof.<sup>[6]</sup> Among the photochemical reactions, photopolymerization under UV light has been highlighted in practical applications.<sup>[7]</sup> The UV radiation curing process has become a powerful tool to fasten the crosslinking mechanism in the photoresist and to modify selectively the physico-chemical characteristics of the irradiated areas.<sup>[8]</sup> Basically, there are two types of photoresists used for patterning purposes, the positive and the negative types. After light exposure, the positive one becomes more soluble in a proper developing solution, whereas, the negative one undergoes chemical crosslinking and cannot be dissolved in a developing solution.<sup>[9]</sup> Negative photoresists have high chemical resistance and good image reproduction qualities.<sup>[10]</sup> They are widely used in the manufacture of circuit boards and microelectronic devices for these reasons.<sup>[11]</sup> The negative photoresists are generally more difficult to remove than the positive photoresists due to their high chemical resistance. Photosensitive polymers particularly having outstanding physical properties are compatible with existing semiconductor processing techniques.<sup>[12]</sup>

One of the important applications of the UV curing epoxy system is photoinitiated cationic ring-opening polymerization of epoxy compounds.<sup>[13,14]</sup> The cationic photopolymerization of epoxides forms crosslinked 3d polymeric network structures, which provides good chemical resistance and adhesion on different packing materials (metals, glass, and plastics). Free radicals can promote photosensitization of diaryliodonium and triarylsulfonium salts, which enable cationic ring-opening polymerization, as reported by Crivello and Reichmanis.<sup>[15]</sup>

The polymers with pendant chalcone groups undergo crosslinking upon irradiation with UV light and are regarded as negative-type photoresists.<sup>[16]</sup> These polymers are very important for practical use as commercial negative photoresist materials due to their high photosensitivity, ability to form films, good solubility before UV exposure, resistance toward solvents after crosslinking, thermal stability and resistance toward plasmas and etching agents.<sup>[17]</sup>

Previously, we reported the synthesis of polyesters and polyphosphonates from chalcone moieties for various applications.<sup>[18-20]</sup> The purpose of the study reported here is to describe in detail the investigation of dual functional photoreactive epoxy resins containing 1,3-bis(4-hydroxyphenyl)propanone (BHPP) and 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propanone (HMPHPP) and epichlorohydrin. The resins contain both photocrosslinking and cationic photopolymerization functions. Spectral and thermal characterizations were performed for the synthesized epoxy resins. The effect of curing agents on the thermal stability of epoxy resins was examined. The lithographic evaluation using the synthesized epoxy resins was also investigated.

## Experimental

### Materials

4-Hydroxybenzaldehyde (Sd Fine Chemicals, India), vanillin, acetophenone (Sd Fine Chemicals, India), chloroform (Sd Fine Chemicals, India), n-hexane (Merck, India), methanol (Loba Chemie, India) and other solvents were purified by the procedure reported in the literature.<sup>[21]</sup> Boron trifluoride diethyletherate (Fluka, Steinheim, Germany), triphenylsulfonium trifluoroethanesulfonate (Merck, India), diaminodiphenylsulfone (Merck, India), diaminodiphenylmethane (Merck, India) epichlorohydrin (Merck, India) were used as received.

## Characterization

The solubility of the resins was examined with 0.3–0.5 mg of polymer in 5 mL of solvent at room temperature. The number average, weight average molecular weights, and polydispersity index (PDI) of the epoxy resins were estimated using gel permeation chromatography (GPC) using Shimadzu LC-20AD equipment with a RID-10A differential refractive index detector with dual temperature control and flow rate of 0.1 mL/min. THF was used as the eluent at a flow rate of 1.0 mL/min. The GPC calibration curve was done with standard polystyrene samples of different molecular weights (1000 Da–4.5 MDa) dissolved in THF. The infrared spectra were recorded on Shimadzu Fourier transform infrared spectrophotometer using KBr pellet in the range of 4000–400  $\text{cm}^{-1}$  with 32 number of scans and resolution of 4  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on 400 MHz Bruker AV-III 400 NMR spectrometer in DMSO using TMS as an internal standard. The DSC analysis was carried out on a Perkin Elmer Pyris 6 DSC for all samples using the empty aluminum pan as reference with heating rate of 10  $^{\circ}\text{C}/\text{min}$  in nitrogen atmosphere (flow rate 30 mL/min). All the samples were heated from 30 to 100  $^{\circ}\text{C}$  and then cooled to room temperature rapidly to remove the thermal history of the samples. Temperature and heat flow scale of the instrument was calibrated using precrimped In and Zn as standard references. The DSC cell was calibrated with In (*m.p.* 430 K;  $\Delta H_{\text{fus}} = 28.54 \text{ J g}^{-1}$ ) and Zn (*m.p.* 693 K). Thermogravimetric analysis was performed with a Perkin Elmer Diamond TG/DTA equipment, under a dynamic nitrogen atmosphere, using a sample mass of 3–5 mg, at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

The photocrosslinking studies of the synthesized epoxy resins were performed in the solution state using UV-Vis spectrophotometer. The resin 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) by discontinuous mode 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. This procedure was repeated until there was no further considerable decrease in  $\lambda_{\text{max}}$  was observed. The storage stability of the liquid epoxy resin was determined using a Brookfield Viscometer. In Brookfield viscometer, the spindle used for these studies was S61, the speed was maintained constant at 100 rpm. The viscosity of the solvent used was 4.513 cP.

## Syntheses of monomers

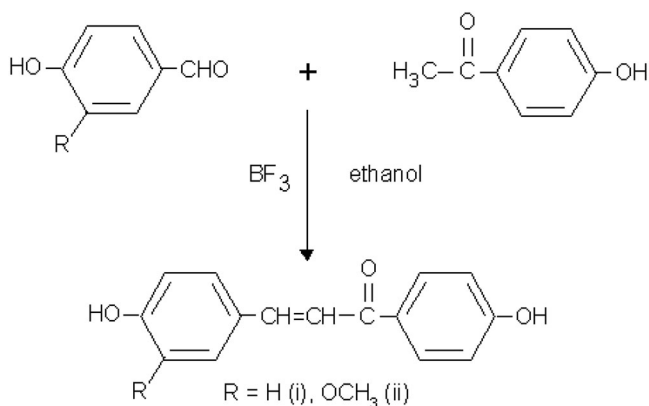
Synthetic procedures for the preparation of two monomers, 1,3-bis(4-hydroxyphenyl)propanone (BHPP), and 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propanone (HMPHPP) were well described in our previous reports<sup>[18–20,22,23]</sup>.

The scheme of synthesis of monomers, BHPP and HMPHPP is shown in [Scheme 1](#).

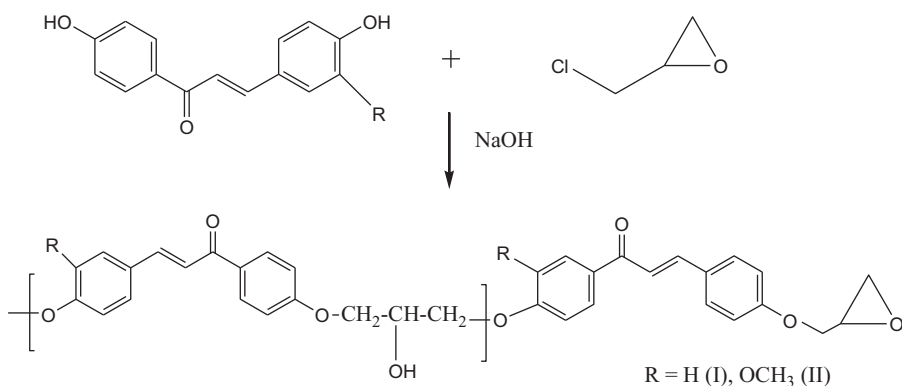
## Synthesis of epoxy resins

The photosensitive epoxy resin was synthesized by condensing the aromatic diol, BHPP, with epichlorohydrin in the presence of base catalyst. BHPP (2.5 mmol) was dissolved in epichlorohydrin (500 mmol) and an aqueous solution of NaOH (10 wt%, 5 mmol) was added dropwise into the reaction mixture with vigorous stirring. The reaction mixture was stirred at 80  $^{\circ}\text{C}$  for 4 h and then unreacted epichlorohydrin was separated by distillation. The crude product was extracted with THF, washed with distilled water, and dried over molecular sieves. After the removal of the solvent using a rotary evaporator, a yellowish viscous liquid resin was obtained, yield: 80%.

Another epoxy resin (II) was also prepared similarly manner from HMPHPP and epichlorohydrin.



**Scheme 1.** Synthesis of diol monomers (i) BHPP and (ii) HMPHPP.



**Scheme 2.** Synthesis of epoxy resins I and II.

To investigate the effect of the epoxy content on the photosensitivity of the synthesized epoxy resin, the above said procedure was repeated with the feeding composition of 1:200 HMPHPP (0.675 g, 0.0025 mol) and epichlorohydrin (39.10 ml, 0.5 mol.).

The synthetic pathway adopted for the synthesis of photosensitive epoxy resins (I and II) is shown in [Scheme 2](#).

### **Estimation of epoxy content**

The epoxy content was determined by refluxing 1 g of resin for 20 min with 50 mL of a pyridinium hydrochloride solution. (Pyridinium hydrochloride solution was prepared from 16 ml concentrated hydrochloric acid diluted with pyridine to one liter.) After cooling, excess hydrochloric acid is back-titrated with 0.1 N sodium hydroxide in methanol to a phenolphthalein endpoint.<sup>[24]</sup>

### **Preparation of lithographic plates**

A stoichiometric amount of photoinitiator (triphenylsulfonium trifluoroethanesulfonate) was added to 20 wt% photosensitive epoxy resin in THF. The viscous solution was filtered through a 2.5  $\mu\text{m}$  filter paper. The resin solution was spin-coated on the aluminum substrate at 50 °C using a spin coating machine. The speed of spinning was gradually increased to 400 rpm in 5 min and was kept at this speed for more than 5 min to dry completely. A thin film was obtained which

**Table 1.** Effect of monomer-epichlorohydrin ratio on the epoxy content of the resin II.

| S. no. | Monomers ratio |                 | Epoxy content | Epoxy equivalent |
|--------|----------------|-----------------|---------------|------------------|
|        | HMPHPP         | Epichlorohydrin |               |                  |
| 1      | 1              | 1.22            | 0.116         | 862.07           |
| 2      | 1              | 15.00           | 0.119         | 840.34           |
| 3      | 1              | 50.00           | 0.135         | 740.74           |
| 4      | 1              | 75.00           | 0.157         | 636.94           |
| 5      | 1              | 100.00          | 0.253         | 395.26           |
| 6      | 1              | 200.00          | 0.274         | 364.96           |

was then soft-baked at 85 °C for 15 min. The substrate with the film was exposed to a UV source for spot curing at ambient temperature. The exposed film was developed with a THF solvent. In this step, the unpolymerized resin was washed out.<sup>[25]</sup>

## Results and discussion

### Synthesis of epoxy resins

The photosensitive epoxy resins were synthesized by condensing the aromatic diol monomers and epichlorohydrin in the presence of a base catalyst. Before introducing the results of specific experiments, it is worth making a few general comments on these resins. Both the synthesized resins were viscous, yellow in color and obtained in good yield. The solubility of the epoxy resin is one of the important requirements for practical uses of resin. The solubility of the epoxy resins in various solvents was tested at room temperature. The photosensitive resins were soluble in polar solvents like DMSO, DMF, chloroform, acetone, 1,4-dioxane and THF, partially soluble in ethanol, and *p*-cresol and insoluble in benzene, toluene, *n*-hexane, and other hydrocarbon solvents. The solubility test shows that there are high chances of using many solvents required for practical uses.

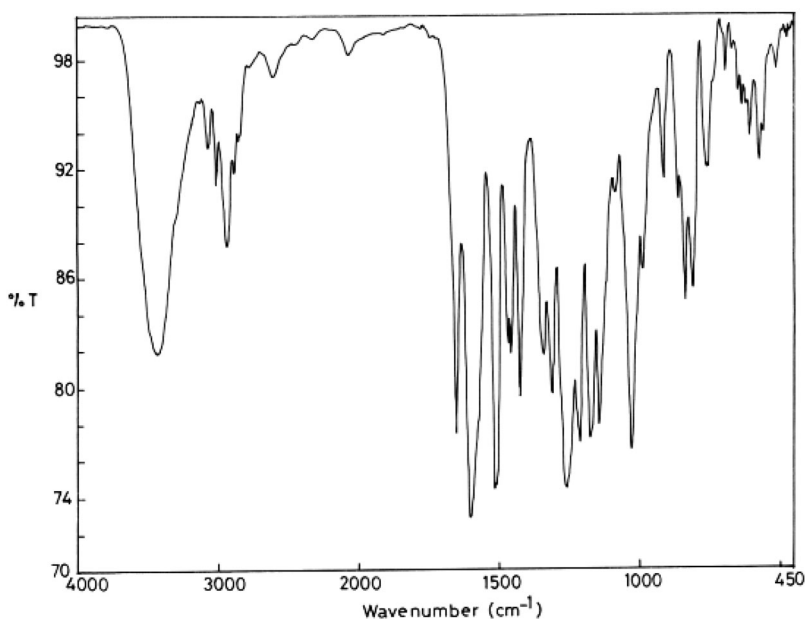
The average molecular weights of the resins were obtained from GPC and the number average molecular weight ( $M_n$ ) of BHPP based epoxy resin is 345 g/mole and the weight average molecular weight ( $M_w$ ) is 435 g/mole. The ( $M_n$ ) of HMPHPP based epoxy resin is 356 g/mole and the ( $M_w$ ) is 448 g/mole.

To order to investigate the effect of the diol-epichlorohydrin ratio on epoxy content, the resin II was synthesized at different ratios of epichlorohydrin by adopting the procedure, mentioned in the experimental part. The results are summarized in Table 1.

It was found that the diol-epichlorohydrin feed ratio changes the epoxy content. From the epoxy content results, the 1:200 ratio of diol and epichlorohydrin was fixed for preparing BHPP based epoxy resin I. The inherent viscosity of the resin is 0.10 dL/g in DMSO solvent. The epoxy content and an epoxy equivalent of the resin I are 0.2290 and 436.6 respectively.

### Spectral studies

The chemical structure of the synthesized resins was confirmed by the FTIR and NMR spectroscopic techniques. A representative FTIR spectrum of HMPHPP based epoxy resins II is shown in Figure 1. The absorptions around 1651 and 1600  $\text{cm}^{-1}$  correspond to carbonyl ( $\nu_{\text{C=O}}$ ) and olefinic ( $\nu_{\text{C=C}}$ ) stretchings, respectively.<sup>[26]</sup> The symmetric stretching vibration of the epoxy ring is observed at 914  $\text{cm}^{-1}$ . The epoxy resin showed a strong absorption band at around 2931  $\text{cm}^{-1}$  corresponding to the stretching vibration of  $\nu_{\text{Ar-O-CH}_2}$ . The resin exhibits an absorption peak at 1141  $\text{cm}^{-1}$  due to the O-C stretching of the methoxy group. The broad band at 3435  $\text{cm}^{-1}$  is attributed to the stretching band of the free hydroxyl group.



**Figure 1.** The representative FTIR spectrum of HMPHPP based epoxy resin II.

The  $^1\text{H-NMR}$  spectra of epoxy resins I and II are shown in [Figures 2 and 3](#). The aromatic protons of phenyl ring appear as a broad multiplet in the region of 6.8–7.4 ppm and 8.0 ppm. The olefinic protons and methoxy protons resonate at around 7.66 and 3.85 ppm respectively. The chemical shift at 2.72 and 2.85 ppm correspond to the methylene protons of the epoxide groups. The  $-\text{CH}$  proton of the oxirane ring appeared as a multiplet at 3.35 ppm.<sup>[27]</sup>

A typical proton decoupled  $^{13}\text{C-NMR}$  spectra of epoxy resins are shown in [Figures 4 and 5](#). In epoxy resins, the aromatic carbons of the phenyl group are centered around 117–137 ppm. The signal at 189 ppm corresponds to the carbonyl carbon present in the main chain of the epoxy resin. The resonance peaks at 44 and 47 ppm may be assigned to  $-\text{CH}$  and  $-\text{CH}_2$  carbons of oxirane ring respectively. In epoxy resin II a signal corresponding to methoxy carbon emerges at 56 ppm. The spectral results indicated that the targeted photosensitive epoxy resins were synthesized successfully.

### **Thermal studies**

The DSC trace of the epoxy resin I is shown in [Figure 6](#). The glass transition temperature ( $T_g$ ) of the resin is observed at 94 °C. The resin I shows an exothermic peak at 335 °C corresponding to thermal curing. In [Figure 7](#), epoxy resin II,  $T_g$  is observed at around 78 °C and an exothermic peak was observed at 324 °C. The exothermic peak may be due to the thermal curing of the epoxy resin.

[Figure 8](#) represents the DSC trace of resin II with an amine curing agent, DDS. In the presence of DDS, a resin undergoes ring polymerization through the epoxy group and gives an exothermic peak at 314 °C. The  $T_g$  observed at 78 °C was disappeared when DDS was used. This may be due to the curing of epoxy resin by DDS. Three exothermic peaks were observed in DSC trace of epoxy resin II with DDS. The first peak starts around 120 °C and ends at around 230 °C. The second and third exothermic peaks were observed at 314 °C and 389 °C. The first and second exothermic peaks are attributed to chemical curing of the epoxy ring. The third peak may be due to thermal decomposition. This observation is reflected in the TGA thermogram also.

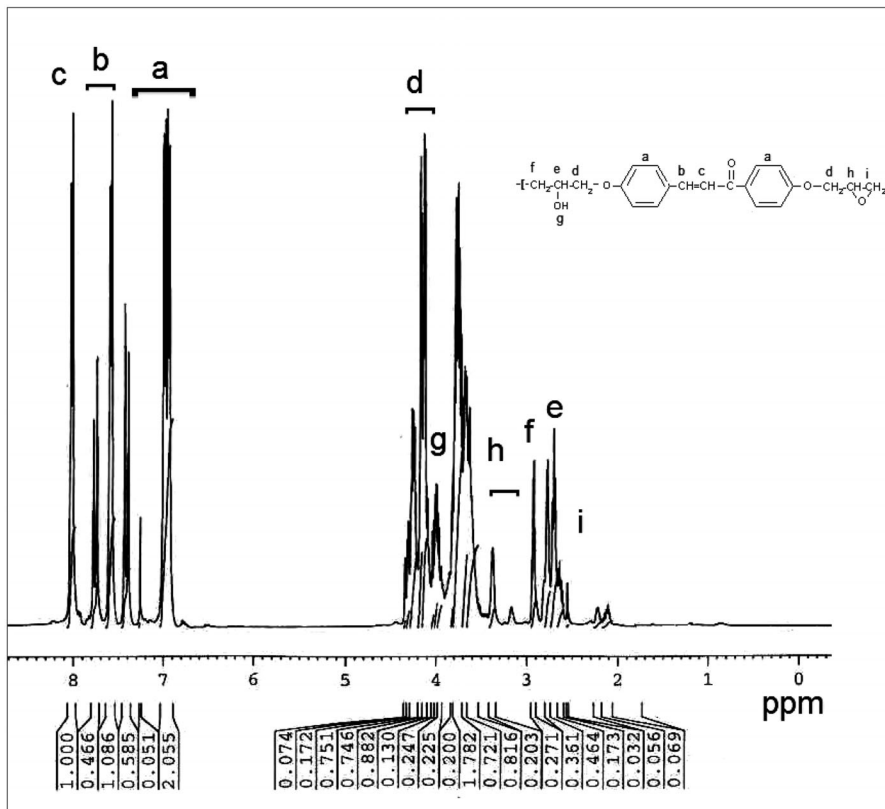


Figure 2. <sup>1</sup>H-NMR spectrum of epoxy resin I.

The epoxy resin II, having methoxy substituent shows lower glass transition temperature than the corresponding unsubstituted resin I. This may be due to the presence of  $-\text{OCH}_3$  group in the aromatic ring which hinders the close packing of molecules and enhance the amorphous nature of the resin. It is also known that methoxy substituent may reduce the coplanarity of the adjacent chain (mesogenic group) and increase the diameter or decrease the axial ratio of the chalcone group (mesogenic unit).<sup>[28]</sup>

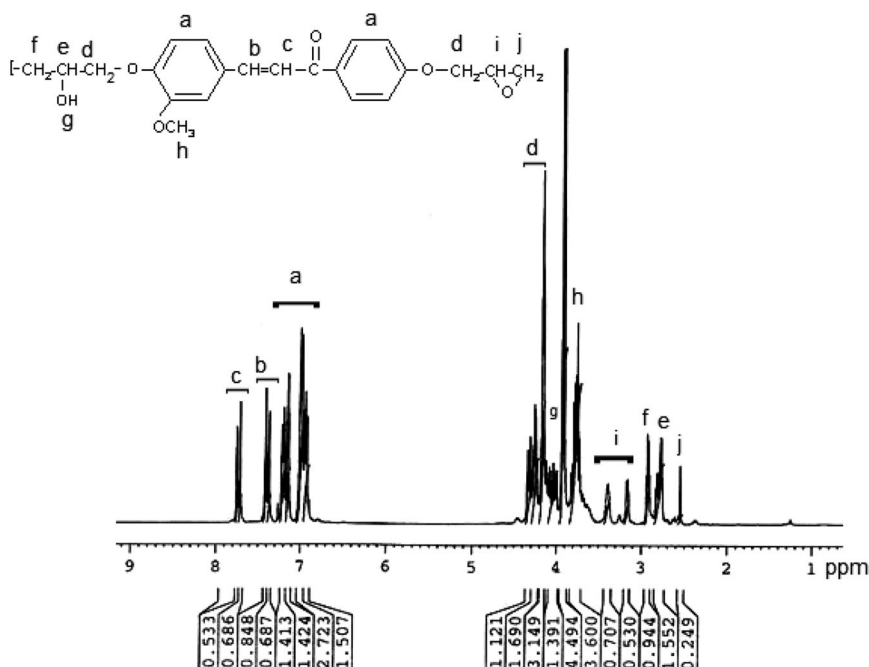
The thermal stability of the synthesized epoxy resins was studied by thermogravimetry in the nitrogen atmosphere. The TGA trace of the synthesized epoxy resins I and II are shown in Figures 9 and 10. The temperature corresponding to 25% and 50% weight loss and char residue at 550 °C are summarized in Table 2.

It was observed that the methoxy substituted HMPHPP based epoxy resin II is more stable than the corresponding unsubstituted BHPP based resin I. It has char residue of 48% at 550 °C.

Figure 11 reflects the thermal stability of epoxy resin II cured by DDS and DDM. The results revealed that resin II cured with DDS has comparatively higher thermal stability than DDM cured. The presence of a sulfone group in DDS may attract the chains and increases the network structure. So, this may be the reason for the higher thermal stability of DDS cured epoxy resin II.<sup>[29]</sup>

Flame retardancy of the synthesized epoxy resins was evaluated by Van Krevelen's method using char residue data from TGA study. Van Krevelen established a linear relationship for the limiting oxygen index (LOI) of halogen-free polymers.<sup>[30]</sup>  $\text{LOI} = 17.5 + 0.4(\sigma)$ , where  $\sigma$  is the percentage of char yield. According to Van Krevelen's theory, an increase in the char formation will depress the flammability of the materials. The LOI values of the product should be above the

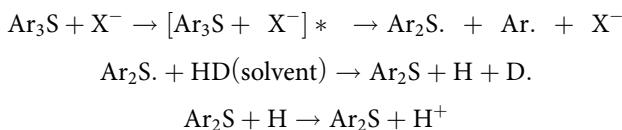




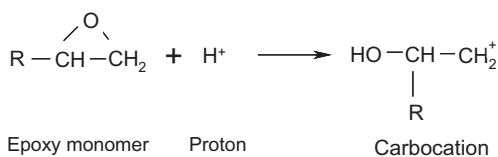
**Figure 3.** <sup>1</sup>H-NMR spectrum of epoxy resin II.

threshold value of 26, to render them self-extinguishing. The char yield and the calculated LOI values are given in Table 2. The LOI values indicate that both epoxy resins I & II have self-extinguishing property it will be suitably exploited for self-extinguishing resins and the detailed analysis is in-progress will be reported in future publications.

The dual functionality, photocrosslinking and photo polymerization, of the resin were confirmed by FTIR analysis. Figure 12 shows the FTIR spectrum of UV exposed epoxy resin II with triphenylsulfonium trifluoroethanesulfonate photoinitiator and the reaction is described by the following mechanism.



The  $\text{H}^+$  ion initiates cationic ring-opening polymerization of the epoxy group.



In the FTIR spectrum, the characteristic absorption band corresponding to epoxide group observed at  $914\text{ cm}^{-1}$  had disappeared. This may be attributed to the photopolymerization of epoxy groups.<sup>[31]</sup> Further, the intensity of the absorption band due to the double bond at  $1649\text{ cm}^{-1}$  was also reduced. This may be due to the photocrosslinking of the olefinic double bond present in the main chain of the oligomer.<sup>[32]</sup> These results reveal that both photopolymerization and photocrosslinking reactions take place during UV irradiation.

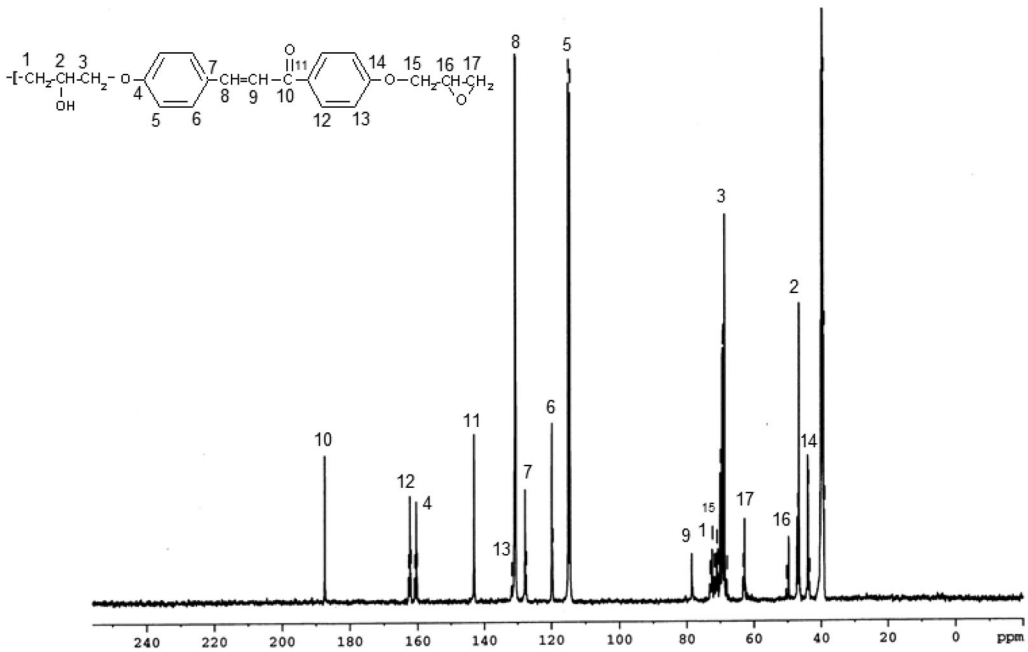


Figure 4. <sup>13</sup>C-NMR spectrum of epoxy resin I.

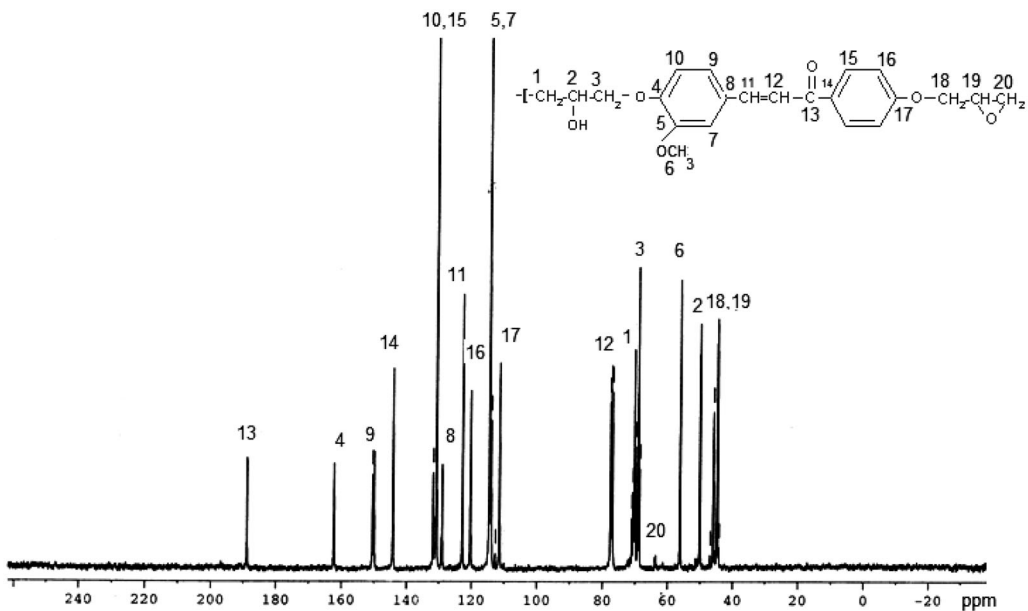


Figure 5. <sup>13</sup>C-NMR spectrum of epoxy resin II.

### Photoreactive studies

The photocrosslinking of the synthesized epoxy resins in solution state was investigated by irradiating with UV light using a medium pressure Hg lamp. The change in absorption maximum ( $\lambda_{\max}$ ) was measured using UV-Vis spectrophotometer and shown in Figures 13 and 14. The UV-Vis spectra of resins showed an absorption maximum at around 325–335 nm due to  $\pi \rightarrow \pi^*$  transition of the olefinic double bonds present in the chain. On successive irradiation of epoxy

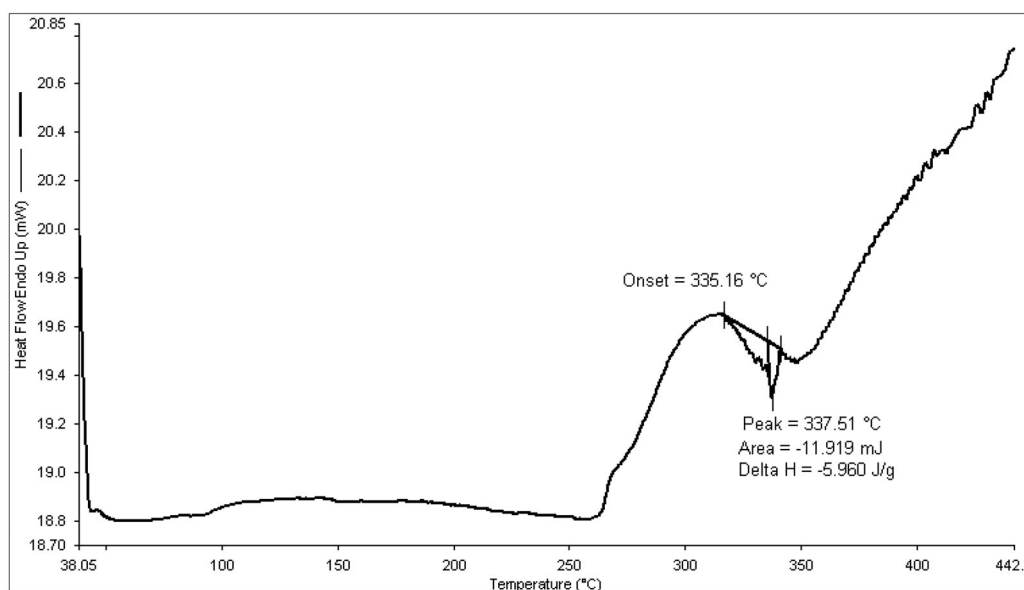


Figure 6. DSC trace of epoxy resin I.

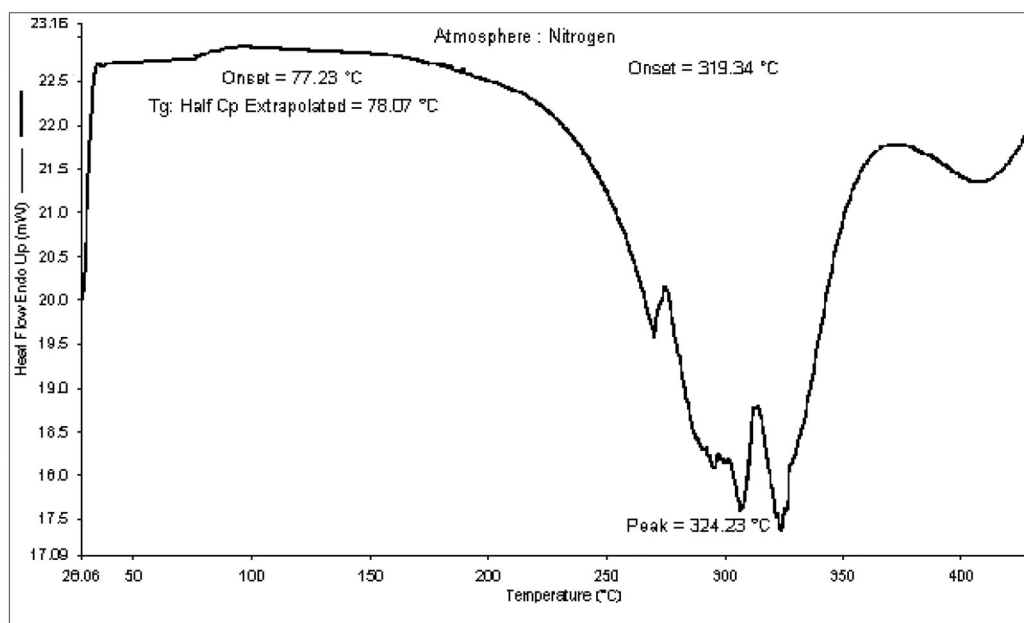


Figure 7. DSC trace of epoxy resin II.

resins, a decrease in the intensity of absorbance was observed. This may be due to  $2\pi + 2\pi$  cycloaddition of olefinic double bond leading to the formation of cyclobutane ring.<sup>[33]</sup> Scheme 3 represents the expected photocrosslinked structure.

The photocrosslinking efficiency of the prepared resins was determined by calculating the conversion of the photoreactive olefinic chromophore ( $-\text{CH}=\text{CH}-$ ) to the cyclobutane ring using the following 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

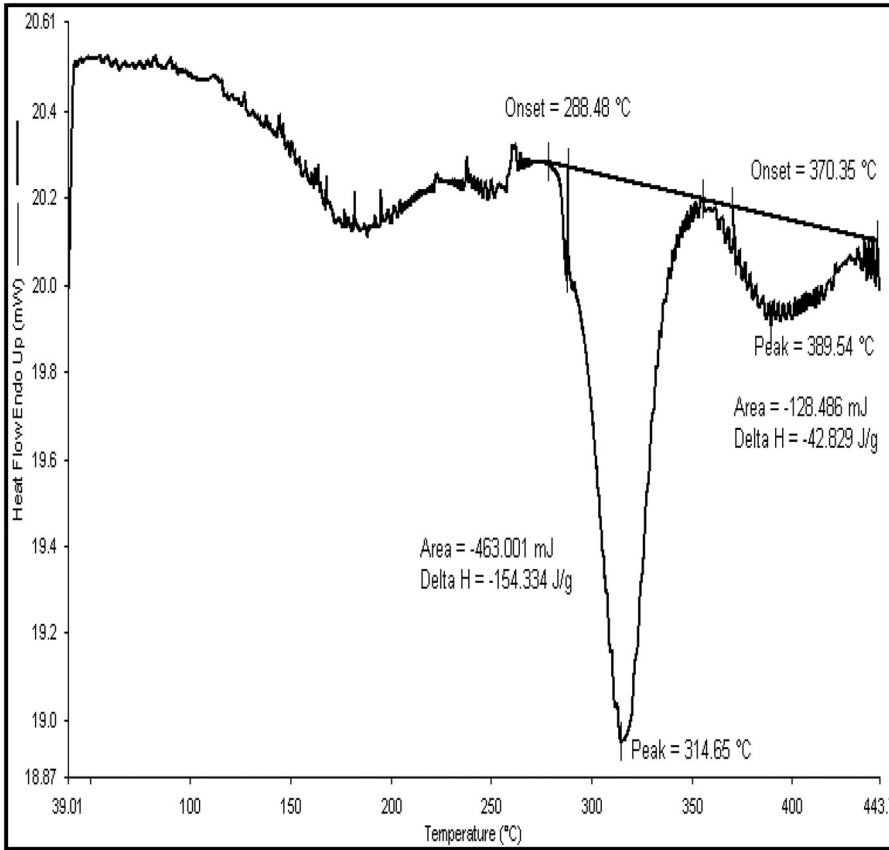


Figure 8. DSC trace of DDS cured epoxy resin II.

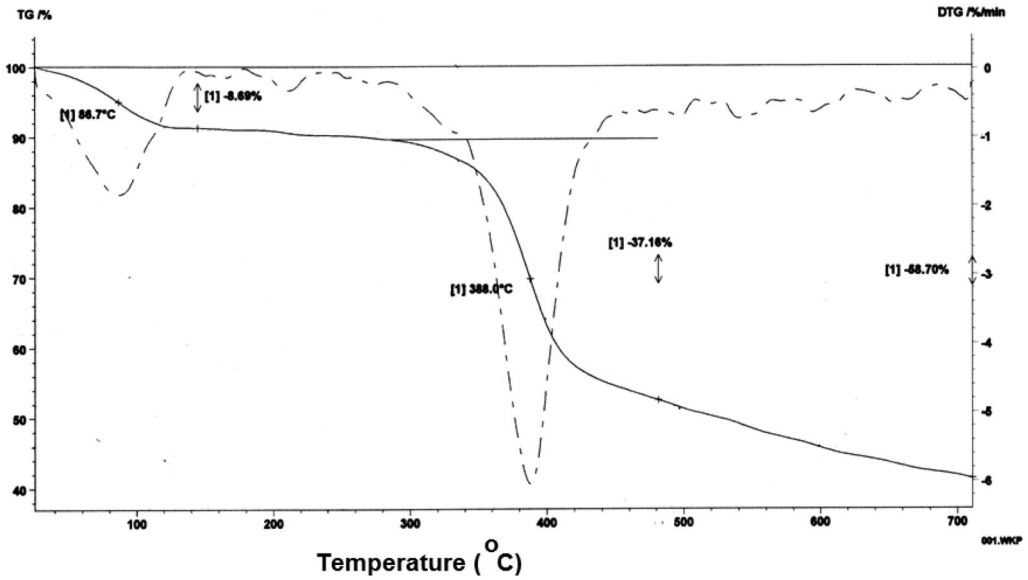


Figure 9. TGA trace of epoxy resin I.

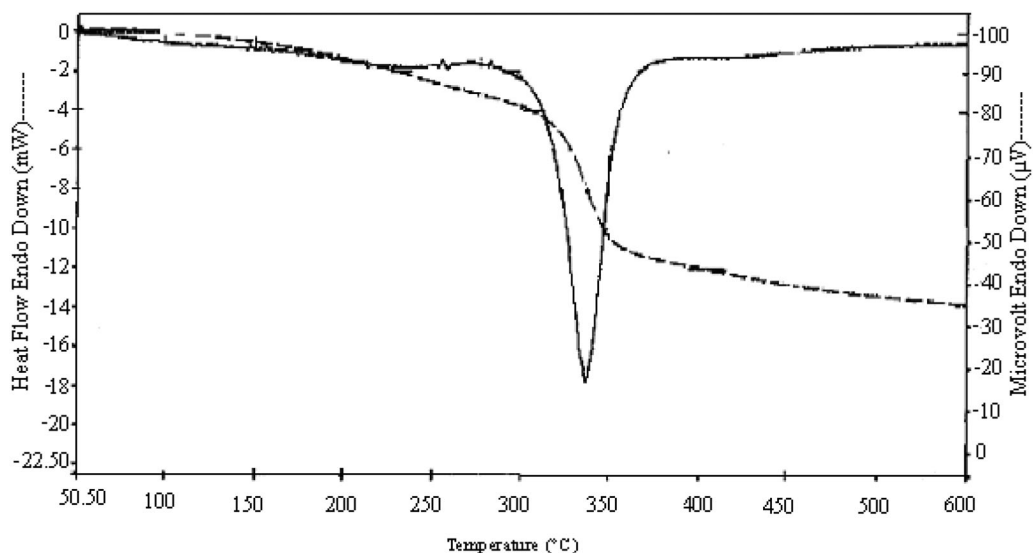


Figure 10. TGA trace of epoxy resin II.

Table 2. Thermal stability of epoxy resins.

| Resins | Temperature (°C) corresponding to |              | Char residue (%) at 550 °C ( $\sigma$ ) | LOI ( $17.5 + 0.4\sigma$ ) |
|--------|-----------------------------------|--------------|---|----------------------------|
|        | 25% Wt. loss                      | 50% Wt. loss |   |                            |
| I      | 325                               | 336          | 30                                      | 29.5                       |
| II     | 375                               | 480          | 48                                      | 36.7                       |

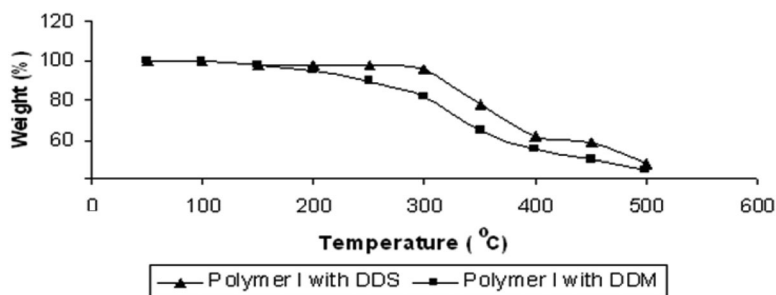


Figure 11. TGA traces of DDS and DDM cured epoxy resin II.

change in the absorption, respectively. The rate of photocrosslinking of HMPHPP based epoxy resin II is higher than BHPP based epoxy resin I. The plausible explanation could be that this may be due to the electron releasing nature of methoxy group facilitates the cycloaddition and it will be further investigated and reported in our future publications.

Figure 15 represents the effect of solvents on the rate of photocrosslinking of epoxy resin II. This analysis revealed that the polarity of the solvents influences the photocrosslinking property of the synthesized resins. Photoreactivity is in the order of DMSO > chloroform > dioxane. The more polar the solvent polarity may make the molecules come closer and facilitate  $2\pi + 2\pi$  cycloaddition.

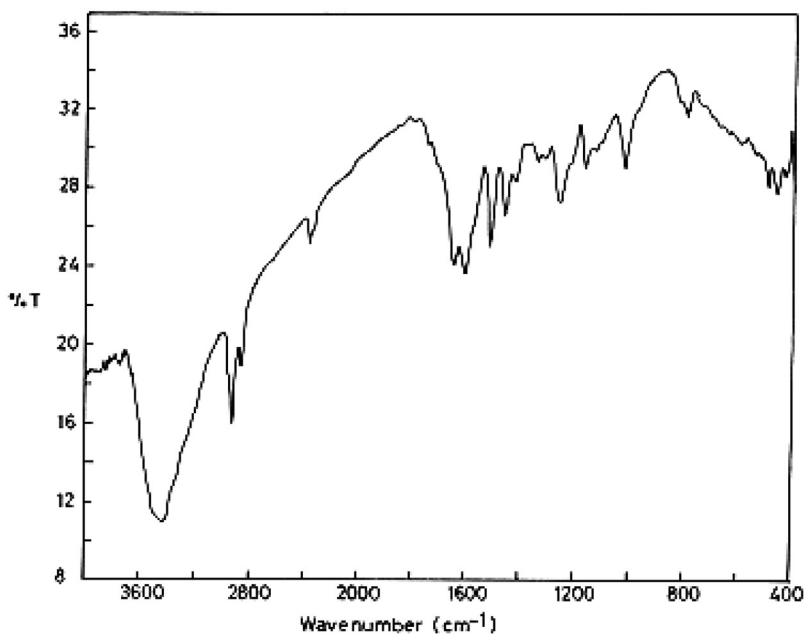


Figure 12. FTIR spectrum of UV exposed epoxy resin II.

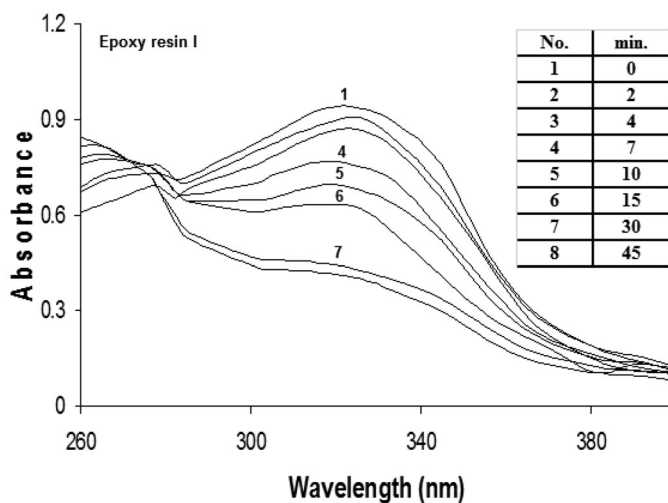


Figure 13. Changes in UV-Vis spectral characteristics during photolysis of epoxy resin I in DMSO solution at various intervals of time.

### Storage stability of the epoxy resin

Storage stability is one of the important properties of the epoxy resins for their practical applications. To determine this property, 1% of epoxy resin I in DMSO was prepared with and without a photoinitiator. The viscosity of the solution was monitored using a Brookfield viscometer at various time intervals. The viscosity data are shown in Table 3.

From the above studies, it is found that the viscosity of synthesized epoxy resin doesn't change appreciably for more than 60 days in the absence of a photoinitiator. It indicates that the epoxy resin has good storage stability in the absence of a photoinitiator. In the presence of a

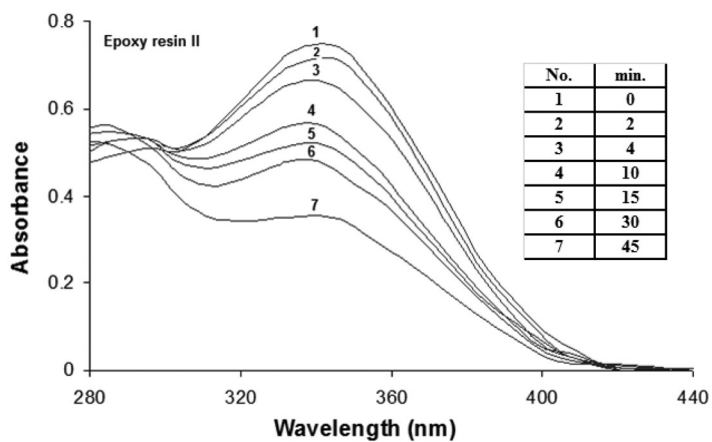
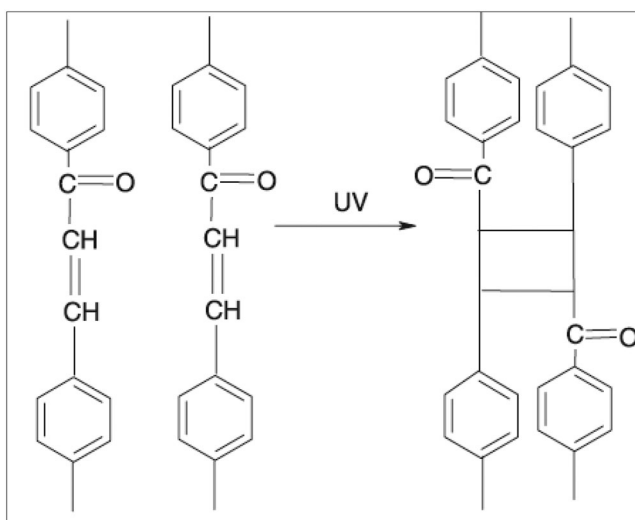


Figure 14. Changes in UV-Vis spectral characteristics during photolysis of epoxy resin II in DMSO solution at various intervals of time.



Scheme 3. Expected photocrosslinking structure of epoxy resin.

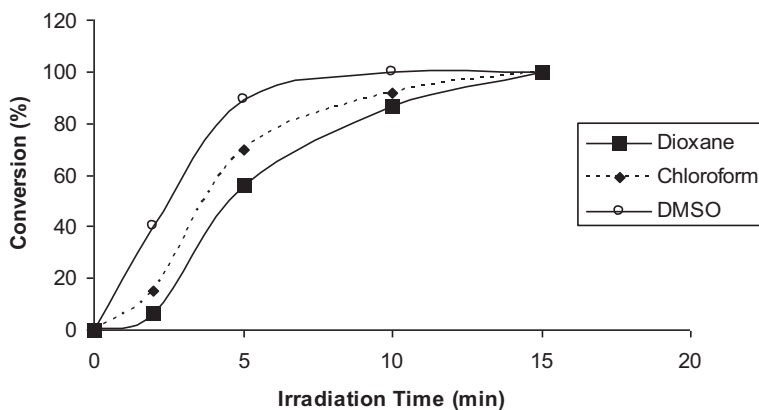
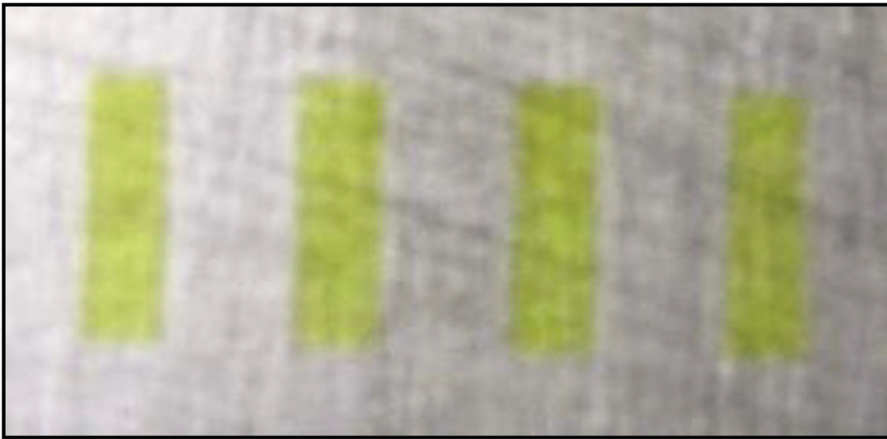


Figure 15. The effect of solvent on the rate of photocrosslinking of epoxy resin II.

**Table 3.** Viscosity of epoxy resin I at various days.

| Duration (days) | Viscosity of resin without photoinitiator (cP) | Viscosity of polymer with 0.1% photoinitiator (cP) |
|-----------------|--|--|
| 1               | 4.666  | 4.700  |
| 3               | 4.666  | 4.709  |
| 5               | 4.669  | 4.739  |
| 7               | 4.672  | 4.782  |
| 14              | 4.675  | 4.895  |
| 20              | 4.675  | 4.921  |
| 60              | 4.677  | –  |

**Figure 16.** The photograph of negative image obtained from epoxy resin I coated on aluminum plates.**Figure 17.** The photograph of negative image obtained from epoxy resin II coated on aluminum plates.



photoinitiator, the resin undergoes curing and the viscosity increases. This indicates that the mixture of synthesized epoxy resin and photoinitiator should be kept in a dark container to avoid photopolymerization.

### **Lithographic evaluation**

Resist film was prepared by spin coating the photosensitive epoxy resin I and II in THF solvent containing photoinitiator on aluminum plate to get a thin film. The film was prebaked and exposed to UV mercury lamp. Development was done in DMSO solvent. Figures 16 and 17 show the photograph of a negative pattern on aluminum plate.

The results of this study indicate that the resin works in negative mode. The poor resolution of these photoresists in despite the high sensitivity appears to be due to the poor adhesion properties of the resin to the substrate.

### **Conclusion**

In this work, we successfully synthesized dual functional photo reactive epoxy resins containing  $\alpha,\beta$ -unsaturated carbonyl group in the main chain from 1,3-bis(4-hydroxyphenyl)propanone (BHPP), 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)propanone (HMPHPP) with epichlorohydrin. The structure of the resins was confirmed by spectral techniques. TGA results clearly indicate that these resins are stable up to 300 °C. The photochemical studies revealed that the resins underwent photocrosslinking under the influence of UV irradiation. Thus photocrosslinking and photopolymerization occurring in the resins have been confirmed by FTIR analysis. Hence, the resins possess dual functionality. The studies confirmed that the photocrosslinking behavior was influenced by solvent polarity also. The storage stability of the resins was found to be more than 60 days. A lithographic study reveals that synthesized epoxy resins exhibit negative resist property. In conclusion, we are successful in developing photosensitive epoxy resins belong to a class of photocrosslinkable materials. From the present investigation, it may be concluded that these resins can be suitably exploited for negative photoresists, where solubility, thermal stability, flame retardancy, and photoreactivity are collectively required, and thereby proving to be potential futuristic photoreactive material.

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