

Spectral, Thermal, and Photoreactivity Studies on Epoxy Resin Containing Benzylidene Units in the Main Chain

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ABSTRACT: A photosensitive epoxy resin was synthesized from bis(4-hydroxy-3-methoxy benzylidene) acetone and epichlorohydrin using solution polycondensation method. The prepared epoxy resin was characterized by UV, IR, ^1H NMR, and ^{13}C NMR spectroscopy. The thermal stability of the epoxy resin was assessed by thermogravimetric analysis. The glass transition temperature of the polymer was determined by differential scanning calorimetry. The photocrosslinking property and photopolymeriz-

ing ability of the epoxy resin were studied in film and solution state using UV spectroscopy. The effect of photo acid generator and sensitizer on photosensitivity of the resin was also investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2340–2344, 2009

Key words: bis(4-hydroxy-3-methoxy benzylidene) acetone; UV irradiation; epoxy content; photoresist; photo acid generator; photoreactivity

INTRODUCTION

Photosensitive polymers are widely used as polymeric photoresist in the field of microelectronics. They are of broad current interest because they possess a combination of good properties in thermal stability, photosensitivity, and dielectric constant. The photosensitive polymers undergo either photopolymerization or photocrosslinking upon UV irradiation. Among these photochemical reactions, photopolymerization under UV light has been highlighted in practical applications. Because of the rapid cationic polymerization rate and good physical properties of the final products, some of the epoxy compounds have found a considerable use in many applications including photolithography, coating resins, and adhesives.^{1–7} The UV radiation curing process has become a powerful tool to fasten the crosslinking mechanism in the photoresist and to modify selectively the physicochemical characteristics of the irradiated areas. Polymers containing cinnamic ester groups and benzylidene groups have been used for the study of phototransformation phenomena that occurs under the UV irradiation. The photosensitivity of these materials is mainly attributed to the π electron density of the photoactive chromophore. The properties such as high photosensitivity, film forming ability, good solubility before irradiation, resistance toward

solvents, plasmas, and etching agents after UV exposure, and thermal stability are very important for a photopolymer to be used as photoresist.^{8,9}

In the present work, we have synthesized a new photoreactive soluble epoxy resin containing a photoreactive chromophore in the main chain. Spectral and thermal characterizations were performed for the synthesized epoxy resin. The photoreactivity of the synthesized epoxy resin was studied by UV–vis absorption spectroscopy. The effects of photoacid generators and photosensitizers on photoreactivity of the polymer were examined for practical utilization of these polymers as negative photoresists.

EXPERIMENTAL

Materials

Vanillin (S.D. Fine chemicals, India), acetone (S.D. Fine chemicals, India), boric acid (S.D. Fine chemicals, India), epichlorohydrin (S.D. Fine chemicals, India), chloroform (S.D. Fine chemicals, India), and benzene (S.D. Fine chemicals, India) were purified by adopting the standard procedure.^{10,11} Triphenyl sulfonium trifluoromethanesulfonate (Aldrich, Germany) and benzophenone (Fluka, Germany) were used as received.

Monomer preparation

Bis(4-hydroxy-3-methoxy benzylidene) acetone (BH MBA)

15.2 g of 4-Hydroxy-3-methoxy benzaldehyde (0.1 mol) and 6.193 g of boric acid (0.1 mol) were charged into a 250-mL round-bottom flask. To this

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mixture, 50 mL of concentrated HCl was added and the flask was cooled to 0°C. To the reaction mixture 3.7 mL (0.05 mol) of acetone was added dropwise and stirring was continued for 24 h. Then, the reaction mixture was poured into 1 L of cold water. The precipitated product was filtered, washed with distilled water, and dried. Recrystallization from chloroform and xylene mixture gave orange crystals with more than 80% yield of the title compound; mp 159°C. FTIR (KBr): 3391 cm^{-1} (ν_{OH}); 1636 cm^{-1} ($\nu_{\text{C=O}}$); 1585 cm^{-1} ($\nu_{\text{C=C}}$). ^1H NMR (DMSO- d_6): 6.7 ppm (m, 6H, aromatic), 3.7 ppm (s, 6H, $-\text{OCH}_3$), 9.6 ppm (s, 2H, $-\text{OH}$), 7.2–7.7 ppm (d, 4H, $-\text{CH}=\text{CH}-$). UV-vis λ_{max} ($\text{C}_2\text{H}_5\text{OH}$): 353 nm ($-\text{C}=\text{C}-$).¹²

Epoxy resin preparation

The photoreactive epoxy resin was prepared by condensing the aromatic diol, BHMBA, with epichlorohydrin in the presence of base catalyst.¹³ BHMBA (0.815 g, 0.0025 mol) was dissolved in epichlorohydrin (39.1 mL, 0.5 mol) and an aqueous solution of NaOH (10 wt %, 0.005 mol) was added dropwise into the reaction mixture with vigorous stirring. The reaction mixture was stirred at 80°C for 4 h and the 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 solvent using a rotary evaporator, a yellowish viscous liquid resin was obtained, yield: 85%.

Characterization

The synthesized epoxy resin was characterized systematically. The epoxy content was determined by pyridiniumhydrochloride titration method. The solubility of the synthesized epoxy resin was tested in various organic solvents.

The chemical structure of the resin was confirmed by UV, FTIR, and NMR spectroscopy. IR spectrum was recorded on a Bruker IFS 66V FTIR spectrophotometer. ^1H NMR spectrum was taken in CDCl_3 on a AMX400 NMR spectrometer. ^{13}C NMR spectrum was recorded in CDCl_3 on a AMX400 NMR spectrometer. The UV spectra were recorded on a Systronics 119 UV spectrophotometer. The thermal properties of the synthesized resin were determined by thermogravimetric analysis and differential scanning calorimeter. DSC traces were obtained on Perkin-Elmer Pyris 6 differential scanning calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. TGA measurements were performed on STA 409C at a heating rate of 10°C/min under nitrogen atmosphere.

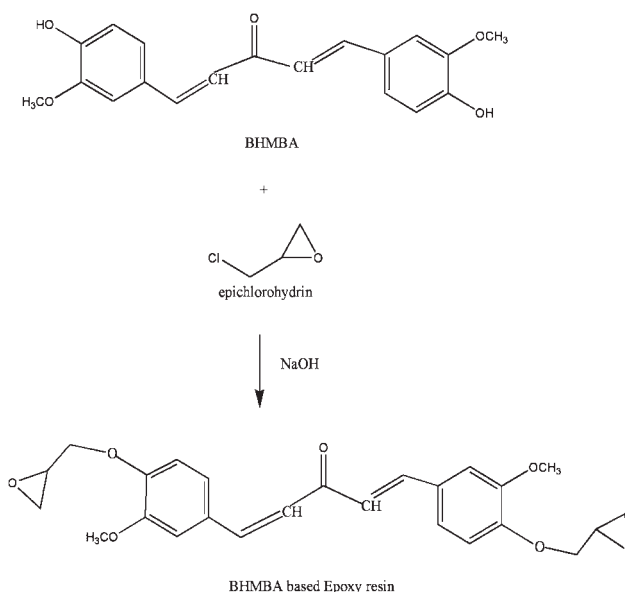


Figure 1 Scheme of synthesis of BHMBA-based epoxy resin.

The photoreactivity of prepared epoxy resin in solution and film states was studied by UV spectrophotometer. The epoxy resin was dissolved in chloroform (0.005%) in a quartz cuvette and irradiated in UV curing reactor with a medium pressure Hg lamp (Heber Scientific Photo reactor, 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. The same study was conducted for film state also. A thin film was cast on the outer surface of the quartz cuvette from chloroform solution and irradiated with the UV lamp.¹⁴ Further, the effects of sensitizers, free radical initiator, and photo acid generator on the photo reactivity of the polymer were also investigated.

RESULTS AND DISCUSSION

The monomer, BHMBA, was synthesized from 4-hydroxy-3-methoxy benzaldehyde and acetone using boric acid and hydrochloric acid. IR, UV, and NMR spectral analyses confirmed the formation of the monomer. The epoxy resin containing benzyldiene moieties was synthesized by solution polycondensation of BHMBA with epichlorohydrin using NaOH as catalyst (Fig. 1). The epoxy content was determined by titration method using pyridiniumhydrochloride and observed as 0.1668 and epoxy equivalent was 600. The solubility of the prepared epoxy resin in various organic solvents was tested. It was found that the epoxy resin is highly soluble in polar aprotic solvents such as DMF, DMSO, 1,4-dioxane, THF, and CHCl_3 and insoluble in methanol, ethanol, and hydrocarbons.

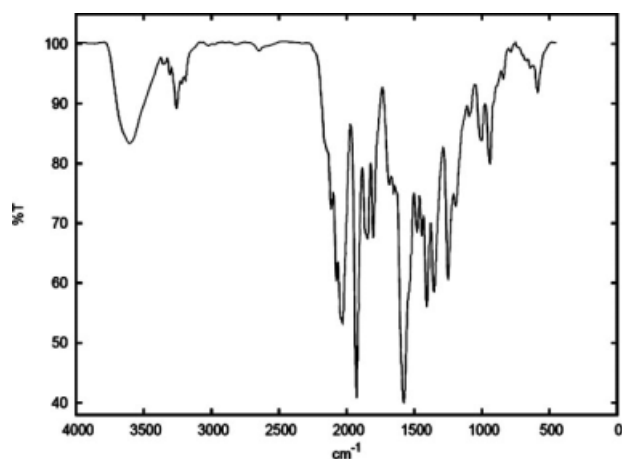


Figure 2 IR spectrum of epoxy resin.

The IR spectrum of synthesized epoxy resin is shown in Figure 2. The absorption band at 1681 cm^{-1} corresponds to the C=O stretching, and those at 1644 and 1616 cm^{-1} correspond to C=C stretching. The symmetric stretching vibration of C—O (epoxy ring) is observed at 913 cm^{-1} . The broad band at 3428 cm^{-1} is attributed to stretching vibrations of the hydroxyl group and a strong band due to the C—H stretching vibration was observed at 2930 cm^{-1} . The aliphatic C—H bending vibrations appear at 1421 cm^{-1} . The epoxy resin exhibits an absorption peak at 1188 cm^{-1} due to the O—C stretching of methoxy group.

The ^1H NMR spectrum of resin is shown in Figure 3. The aromatic protons of phenyl ring appear as broad multiplet in the region of 7.0–7.8 ppm. The chemical shifts at 2.5 and 2.7 ppm correspond to methine and methylene protons of epoxy resin, respectively. The protons of —CH₂—O— moiety resonate at 2.9 ppm. The olefinic protons and methoxy protons resonate at 5.8 and 3.3 ppm, respectively.

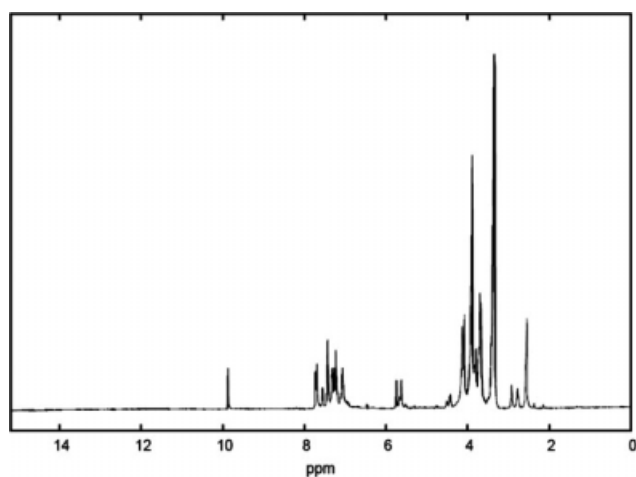


Figure 3 ^1H NMR spectrum of epoxy resin.

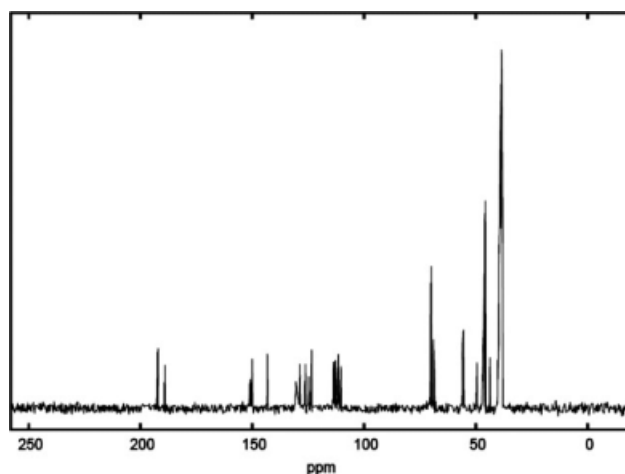


Figure 4 ^{13}C NMR spectrum of epoxy resin.

A typical proton decoupled ^{13}C NMR spectrum of epoxy resin in CDCl_3 is shown in Figure 4. The aromatic carbons of the phenyl group are centered around $115\text{--}124\text{ ppm}$. The signal at 189 ppm corresponds to the carbonyl carbon present in the main chain of the polymer and 127 ppm peak belong to carbon double bond. The signals at 54 ppm is due to methoxy carbon and the resonance peaks at 40 ppm is assigned to epoxy methylene carbon. These spectral results confirmed the formation of epoxy resin.

The thermal properties of the polymer were studied by thermo gravimetric analysis and differential scanning calorimetry in nitrogen atmosphere. Figure 5 shows the thermogram of synthesized resin. It is observed that the synthesized epoxy resin is stable upto 350°C . DSC trace of HMPHPP epoxy resin is shown in Figure 6. The glass transition temperature is observed at around 140°C and the thermal decomposition starts at 350°C .

The photoreactive property of the new epoxy resin in solution and film state was studied by a UV spectrophotometer. The change in the UV spectral

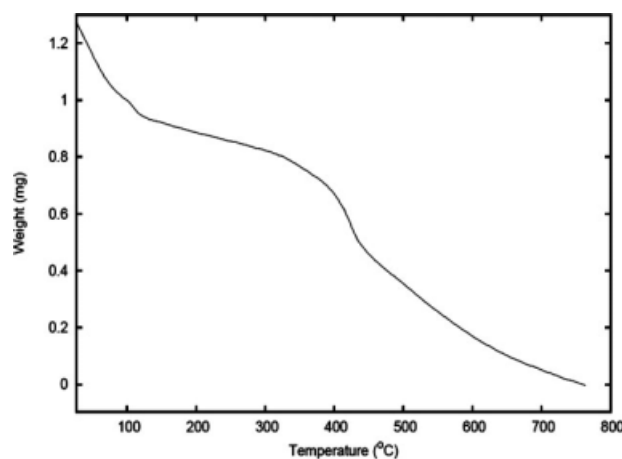


Figure 5 Thermo gravimetric trace of epoxy resin.

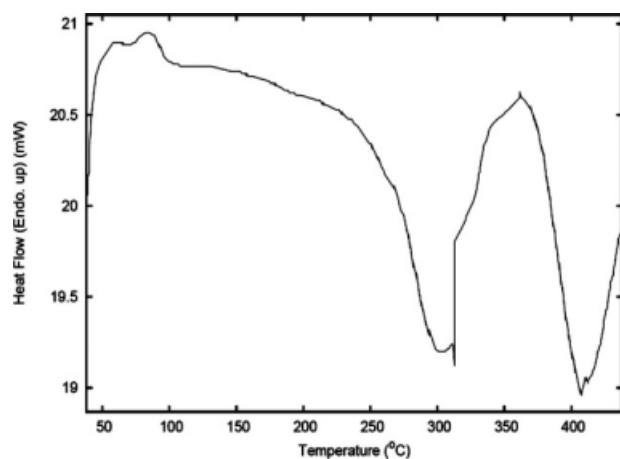


Figure 6 DSC trace of epoxy resin.

pattern during the photolysis of epoxy resin in solution state at various intervals of time is shown in Figure 7. The absorption maximum at around 360 nm corresponds to $\pi \rightarrow \pi^*$ transition of the olefinic double bond present in the oligomer chain. A decrease in the intensity of absorbance was observed during successive irradiation with regular intervals of time. This may be attributed to the formation of cyclobutane ring by the $2\pi + 2\pi$ cycloaddition reaction of the olefinic double bonds upon UV irradiation.¹⁵ An isobestic point was observed at around 280 nm which may be due to the cis-trans isomerization of olefinic double bond present in the main chain. The rate of conversion of $>C=C<$ to $-C-C-$ was calculated using the expression, $[(A_0 - A_t)/(A_0 - A)] \times 100$, where A_0 , A_t , and A are the absorption intensities of $>C=C<$ at irradiation times 0, t and a time after which there is no further significant change in the absorption. The conversion percentage is plotted against the time of irradiation. The results are shown in Figure 8. Further, it is noted that the rate of photocrosslinking of epoxy resin in film state

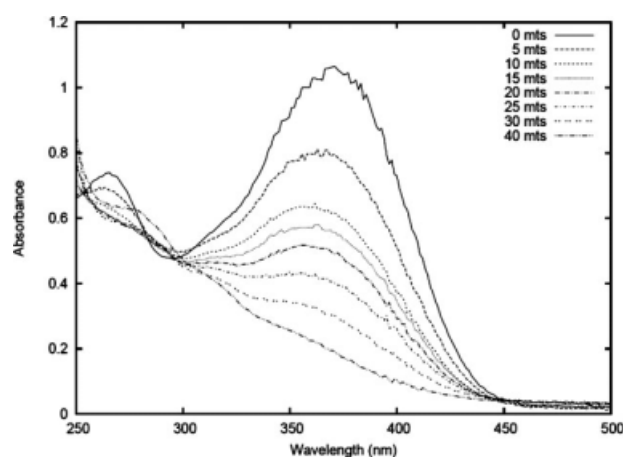


Figure 7 Change of UV-vis absorption spectral characteristics of epoxy resin during UV irradiation.

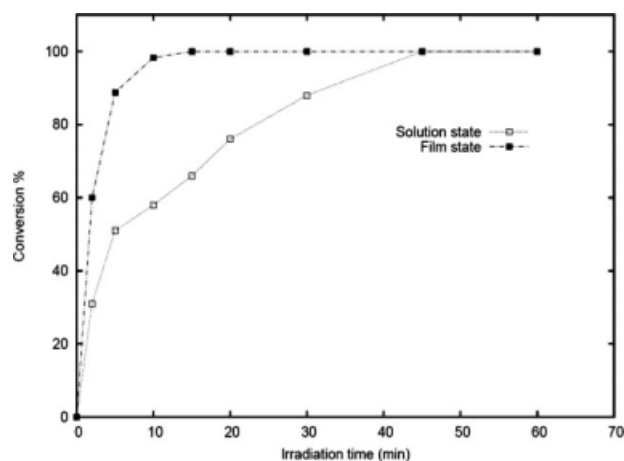


Figure 8 Rate of disappearance of $>C=C<$ of epoxy resin in solution (\square) and film state (\blacksquare).

is higher than in solution state. In solution state, trans-cis isomerization cannot be ruled out, which takes precedence over photocrosslinking through intermolecular cycloaddition. Further, there is no orderly arrangement or aggregation of the chromophore in dilute solution than in film state. Figure 9 indicates the effect of photo acid generator on photosensitivity of the synthesized epoxy resin. The most important constituent in a UV initiated cationic polymerization is the photoinitiator, because the most reactive epoxy compounds can be hardly polymerized without any photoinitiator upon UV irradiation. Therefore, it can be said that the depth of penetration of UV radiation and curing are dependent on the photoinitiator. During the UV irradiation of the epoxy resin and photo acid generator, aromatic sulfonium cation radicals and aromatic radicals are generated which then initiate the cationic ring opening polymerization. The UV results indicate that the

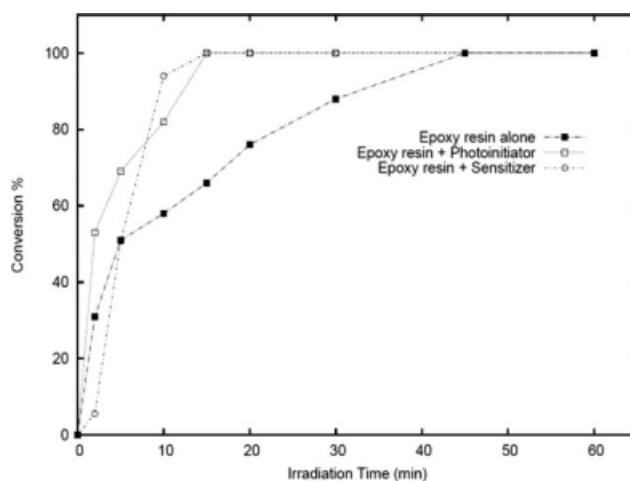


Figure 9 Rate of disappearance of $>C=C<$ of epoxy resin, epoxy resin alone (\blacksquare), with photoinitiator (\square), and with sensitizer (\circ).

addition of photoinitiator influence the rate of photocrosslinking.

It was also found that the photocrosslinking of the polymers is influenced by sensitizers. From Figure 9, it is observed that with the presence of sensitizer the rate of photocrosslinking was increased significantly. After UV irradiation for 10 min, the epoxy resin in the presence of sensitizer turned completely insoluble.

CONCLUSIONS

Photosensitive epoxy resin was synthesized from bis(4-hydroxy-3-methoxy benzylidene) acetone and epichlorohydrin by solution polycondensation. The epoxy equivalent of the synthesized epoxy resin was determined by pyridiniumhydrochloride titration method. The formation of resin was confirmed by UV, FTIR, ^1H NMR, and ^{13}C NMR spectral techniques. It was observed that the resin is highly soluble in polar solvents and insoluble in nonpolar solvents. TGA results clearly indicate that this polymer is stable up to 350°C. The T_g of the epoxy resin was determined by DSC and is observed at 130°C. The UV spectral studies revealed that the polymer undergoes photocrosslinking under the influence of UV radiation. The photocrosslinking rate of the polymer is influenced by sensitizer and photo acid generator. The photoinduced cycloaddition proceeds at a slightly faster rate in film than in solution state. The photo reactivity studies of the polymer in solution

and film state strongly suggest that the polymer has high photosensitivity. The observed solubility, thermal stability, and photoreactivity of the synthesized epoxy resin suggest that this epoxy resin may be used as a negative photoresist.

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