

# Synthesis and Physico-Chemical Analysis of Epoxy Methacrylate of (2E, 6E)-2,6-Bis(4-hydroxybenzylidene)cyclohexanone

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## ABSTRACT

*The epoxy methacrylate of (2E,6E)-2, 6-bis(4-hydroxybenzylidene)cyclohexanone (EBHBCMA) was synthesized by condensing 0.02 equi. EBHBC, 0.04 equi. methacrylic acid, 50 mL THF as a solvent and 0.2 mL triethylamine as a catalyst at reflux temperature for 1-5 h to get acid value < 10. EBHBCMA showed good solubility in common solvents. The structure of EBHBCMA was supported by UV-Vis., FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopic techniques. DSC thermogram of EBHBCMA exhibited two endothermic peaks (86.4 and 117.1 °C) and one exothermic peak (142.6°C) due to moisture release, melting and curing of the resin, respectively. EBHBCMA is thermally stable up to about 316 °C and followed single step degradation reaction. EBHBCMA followed apparently second order (1.7) degradation kinetics with 277.69 kJ mol<sup>-1</sup> energy of activation, 5.93 × 10<sup>18</sup> s<sup>-1</sup> frequency factor and entropy change of 107.4 JK<sup>-1</sup>mol<sup>-1</sup>.*

**KEYWORDS:** *Epoxy methacrylate, Acid and hydroxyl values, Thermal stability, Kinetic parameters.*

## INTRODUCTION

Epoxy resins are an important class of thermosetting polymers that are used in diverse fields such as adhesives, advanced composites, coatings, laminates, composite materials in the aerospace and aircraft

industries, nanocomposites and low-stress IC encapsulants<sup>[1-4]</sup>. Epoxy resins are extensively investigated and used frequently in the electronic instruments because of their good electrical and chemical properties, great versatility and superior adherence to many

substrates<sup>[5, 6]</sup>. One of the largest application of epoxy resins is surface coating<sup>[7]</sup>. Because of low resistance to UV radiation, epoxy resins are used mainly as primers and high performance non-decorative protective coating<sup>[8, 9]</sup>. The physicochemical properties of the advanced materials depend upon the chemical structure of the epoxy resins, their functionality, curing agents, curing conditions, curing mechanism, etc.

Unsaturated polyesters are widely used in aerospace, microelectronics, building constructions, automotive industries and furniture industries<sup>[10-13]</sup>. Vinyl ester resins possess excellent corrosion resistance<sup>[14]</sup>. Mostly acrylics are used to modify and improve the performance of the resins. Epoxies and polyesters<sup>[15]</sup> are commonly used in the paint industries. The modification of epoxy resins through acrylate is known to improve flexibility, adhesion, resistance against scratch and resistance to chemicals<sup>[16]</sup>. Epoxy methacrylate resins have terminal reactive double bonds, which can be cross-linked with or without any addition of co-monomer. They possess good toughness, good chemical resistance, improved elongation and better bonding to glass reinforcements. These types of resins are used to fabricate a variety of reinforced composites<sup>[17-20]</sup>.

Recently we have reported some work on epoxy acrylate/methacrylate based on different epoxy resins<sup>[6, 12, 20, 21]</sup>. In this communication we have reported synthesis of methacrylate of (2E, 6E) 2,6-bis(4-hydroxybenzylidene)cyclohexanone and its characterization by acid and hydroxyl values, DSC and TGA.

## EXPERIMENTAL

### Materials and Methods

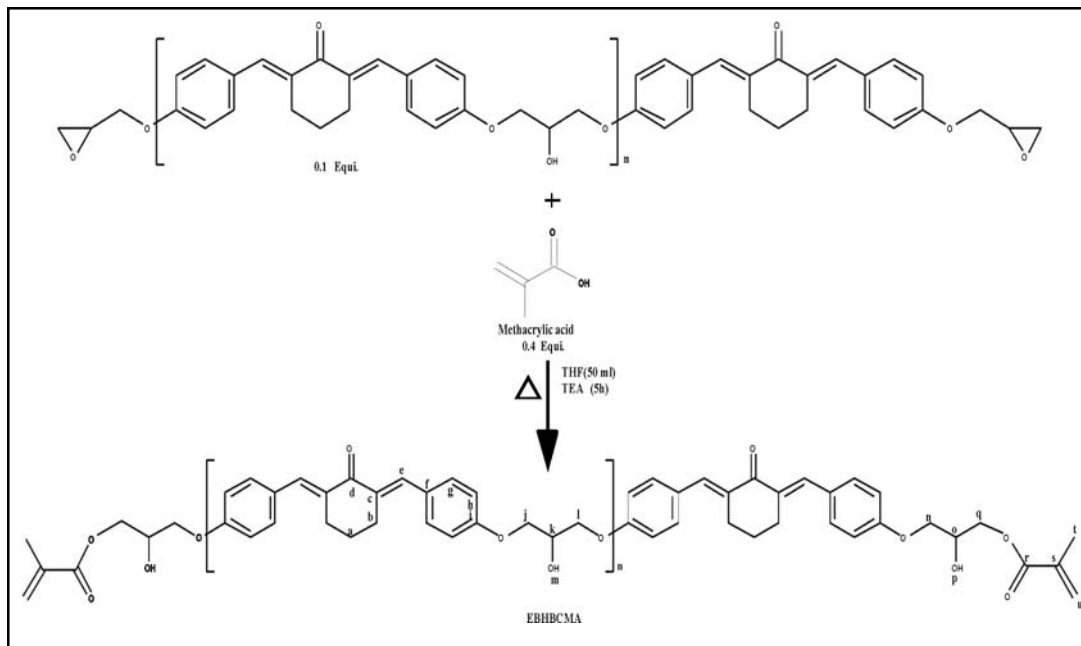
Solvents and chemicals used were of laboratory grade and purified prior to their use<sup>[22]</sup> or used as received. Epoxy resin of (2E, 6E)-2,6-bis(4-hydroxybenzylidene)cyclohexanone (EBHBC) was synthesized and purified according to our recent publication<sup>[23]</sup>. Epoxy equivalent weight of the resin used in the present study was 341.4. Triethylamine (Spectrochem, Mumbai), methylethylketoneperoxide and 6% cobalt naphthenate (free samples from EPP Composites, Rajkot) were used as received.

### Synthesis of Epoxy Methacrylate of (2E, 6E) 2,6-Bis(4-hydroxybenzylidene)cyclohexanone

100 mL round bottomed flasks equipped with condensers are placed in an oil bath. To these flasks 0.02 equi. EBHBC (6.828 g), 0.04 equi. methacrylic acid (3.4 mL), 50 mL THF and 0.2 mL triethylamine (TEA) were charged and the temperature was raised to reflux. The reaction masses were refluxed for 1-5 h, cooled to room temperature and the solid mass was isolated from excess of n-hexane, filtered, washed well with saturated hot bicarbonate solution and finally with distilled water. Crude samples were allowed to dry in an oven at 50°C. The yield of the epoxy methacrylate resin was found to be 6.8-8.7 g. The resin is soluble in common solvents like chloroform, tetrahydrofuran, N, N-dimethylformamide, dimethylsulfoxide, etc. The resin was purified three times from chloroform-n-hexane system. Hereafter resin is designated as EBHBCMA. The reaction scheme is shown in Scheme-1.

### Measurements

The UV-Visible spectrum of EBHBCMA was scanned on a Shimadzu UV1700 over wavelength range from 250-700 nm by using tetrahydrofuran as a solvent. IR spectrum (KBr pellet) of EBHBCMA was scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 600 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>CNMR spectra of EBHBCMA were scanned on a Bruker AVANCE II (400 MHz) spectrometer using DMSO-d<sub>6</sub> as a solvent and TMS as an internal standard. Molecular weights and molecular weight distribution of EBHBCMA were



Scheme 1

determined by gel permeation chromatography (Perkin Elmer GPC) by using THF as a solvent and standard polystyrene mixed bed at 30°C. Differential scanning calorimetric (DSC) measurement was carried out on a Shimadzu DSC 60 (Kyoto, Japan) at heating rate of 10°C min<sup>-1</sup> in nitrogen atmosphere (20mL min<sup>-1</sup> flow rate) by using standard aluminum pan. Thermo gravimetric analysis (TGA) was carried out on a Pyris-1 Perkin Elmer TGA (Massachusetts, USA) at a 10°C min<sup>-1</sup> heating rate in nitrogen atmosphere (20mL min<sup>-1</sup> flow rate).

## RESULTS AND DISCUSSION

### Acid and Hydroxyl Values

Acid and hydroxyl values of EBHBCMA were determined at the interval of 1 h and are presented in Table 1. It is observed that acid values decreased and hydroxyl values increased with the extent of the esterification reaction and required acid value is achieved within 1 h and very low value indicated almost completion of the reaction.

TABLE 1. Acid and hydroxyl values of EBHBCMA.

Reaction time, h	1	2	3	4	5
Acid value, mg KOH/ g	10.1	5.6	4.0	2.5	1.5
Hydroxyl value, mg KOH /g	328.1	863.6	1104.8	1616.2	2050.5

### GPC Molecular Weights and Molecular Weight Distribution

The weight average molecular weight  $\bar{M}_w$ , number average molecular weight  $\bar{M}_n$  and molecular weight distribution  $\bar{M}_w/\bar{M}_n$  of EBHBCMA were determined by GPC using THF as a solvent and standard polystyrene mixed bed. Observed values of  $\bar{M}_w$ ,  $\bar{M}_n$  and  $\bar{M}_w/\bar{M}_n$  are 1001, 692 and 1.45, respectively.

### Spectral Analysis

The structure of EBHBCMA is supported by different spectroscopic methods and described in detail as under.

UV-Visible spectrum of  $10^{-3}$  % THF solution of EBHBCMA is presented in Fig. 1. EBHBCMA exhibited two absorption peaks ( $\lambda_{\max}$ ) at 239 and 351 nm. These peaks are assigned as  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transitions due to presence of double bonds and lone pairs of electrons on oxygen atoms.

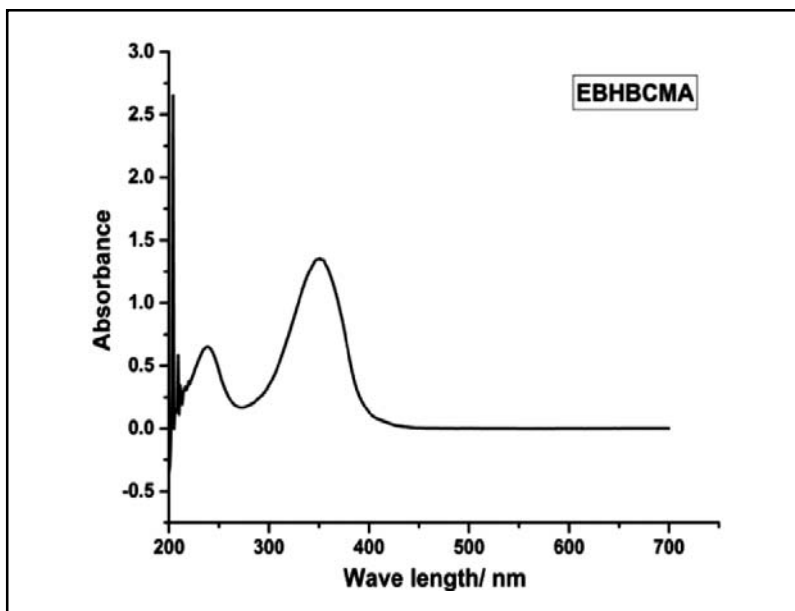


Fig. 1. UV-Visible spectrum of EBHBCMA in THF ( $10^{-3}$  %).

FTIR spectrum of EBHBCMA is shown in Fig. 2. The characteristic absorption peaks ( $\text{cm}^{-1}$ ) are assigned as follow: 3441.12 (O-H str.), 3059.20 (=C-H str.), 2931.80 (C-H asym. str.), 2870.17 (C-H sym. str.), 1712.85 (C=O str. ester), 1654.98 (C=O str.), 1597.11 and 1454.38 (C=C str.), 1423.51 (C-H def.),

1300.07 (C-O str. ester), 1253.77 (C-O-C str.), 1165.04 (C-OH, str.), 941.29 (C-H def. alkene), 833.28 (C-Hoopd.). Disappearance of peaks due to epoxide groups at 970.19 and 914.26  $\text{cm}^{-1}$  and appearance of new peak at 1712.85  $\text{cm}^{-1}$  confirmed formation of EBHBCMA.

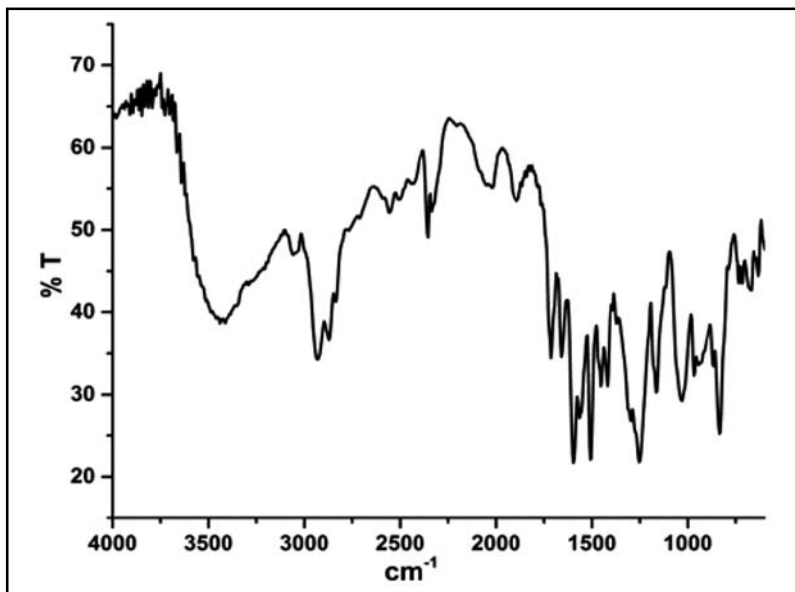


Fig. 2. FT-IR spectrum of EBHBCMA.

<sup>1</sup>HNMR spectrum of EBHBCMA is shown in spectrum is complex. An effort has been made Fig. 3 from which it is confirmed that the to assign chemical shifts and types of protons

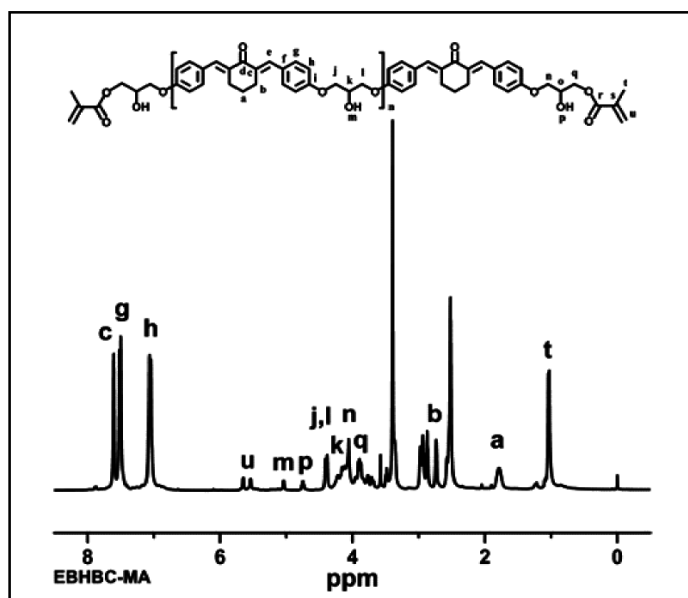


Fig. 3. <sup>1</sup>HNMR (400 MHz) spectrum of EBHBCMA in DMSO-d<sub>6</sub>.

as follow: 1.028 [s, 3H(t)], 1.783 [br s, H(a)], 2.972-2.738 [m, H(b)], 3.910-3.866 [m, OCH<sub>2</sub> (q)], 4.155-4.058 [m, OCH<sub>2</sub> (n), CH-OH (k, o)], 4.410-4.382 [d, OCH<sub>2</sub> (j, l)], 4.747 [br s, CH-OH(p)], 5.045 [br s, CH-OH(m)], 5.542-5.432 [d, =CH<sub>2</sub>(u)] and 5.652-5.645 [d, =CH<sub>2</sub> (u)], 7.063-7.044 [d, ArH (h), J= 7.6], 7.516-7.496 [d, ArH (g), J=8] and 7.604 [s, 2H (e)].

<sup>13</sup>CNMR spectrum of EBHBCMA is presented in Fig.4 from which it is confirmed that the resin contains a large number of different types of carbon atoms. An effort has been made to assign each types of carbon atoms. The

chemical shifts of different carbon atoms are as follow: 21.35 (t), 28.7 (a), 35.78 (b), 62.61 (q), 66.32 (o), 67.28 (k), 68.52(n), 69.85 (j, l), 114.97 (h), 128.01 (u), 128.20 (f), 132.20 (g), 133.32 (s), 133.44 (e), 135.60 (c), 158.64 (i), 158.98 (r), 188.29 (d).

### Thermal Analysis

Thermal analysis of polymers is very important in understanding molecular architecture, environmental condition for manufacture and application of these polymer materials. DSC thermogram of EBHBCMA is presented in Fig. 5. EBHBCMA showed two endothermic

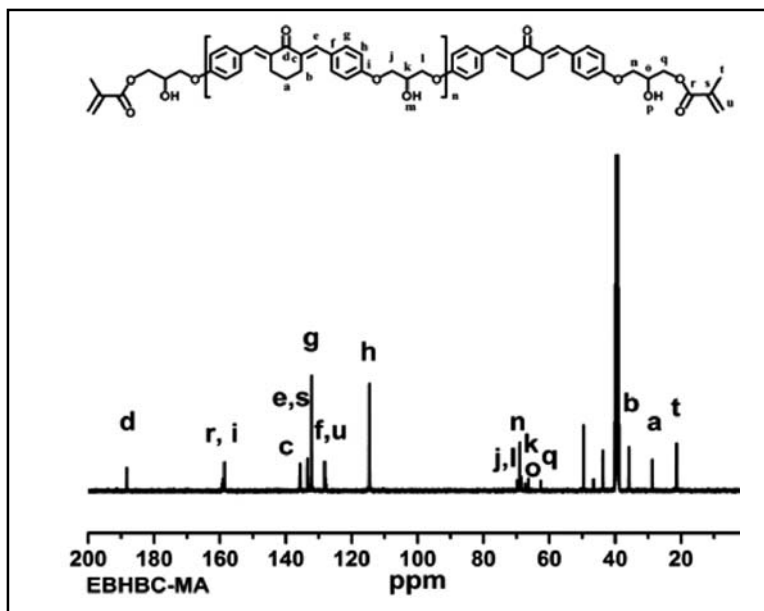


Fig. 4. <sup>13</sup>C NMR (400 MHz) spectrum of EBHBCMA in DMSO-d<sub>6</sub>.

transitions centered at 86.4 and 117.1 °C due to moisture release and melting, respectively. EBHBCMA exhibited one exothermic transition centered at 142.6 °C due to curing reaction.

TG thermogram of EBHBCMA is presented in Fig. 6 from which it is observed that it is thermally stable up to about 316 °C and followed single step degradation reaction. It involved 62 % weight loss over 316-500°C with temperature

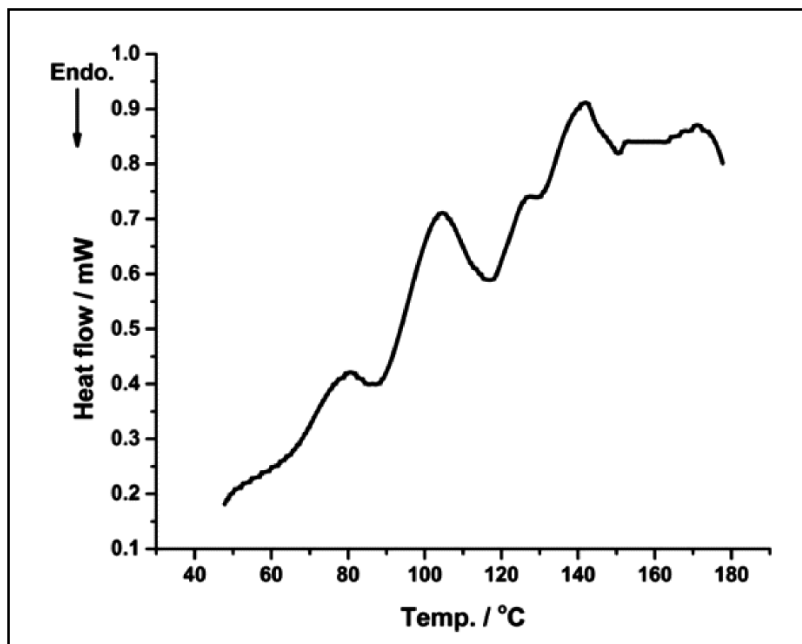


Fig. 5. DSC thermogram of EBHBCMA at 10°C min<sup>-1</sup> heating rate in nitrogen atmosphere.

of maximum weight loss at 427°C. A 27.9 % residue remained at 700°C.

Associated kinetic parameters such as energy of activation ( $E_a$ ), frequency factor (A), order of reaction (n), and entropy change ( $\Delta S^*$ ) are determined according to the Anderson-Freeman method [27]:

$$\Delta \ln dw/dt = n \Delta \ln W - (E_a/R) \Delta (1/T) \quad (3)$$

$$A = E_a \beta / RT^2 e^{E_a / RT} \quad (4)$$

$$\Delta S^* = R \ln(Ah / kT) \quad (5)$$

Where,  $dw/dt$  is the weight loss with time,  $W$  is the active weight of the substance,  $\beta$  is the heating rate,  $R$  is the gas constant,  $h$  is the Planck's constant,  $T$  is the temperature, and  $k$  is the Boltzmann constant. The derived least squared values

of  $n$ ,  $E_a$ ,  $A$  and  $R^2$  are 1.7, 277.69 kJ mol<sup>-1</sup>,  $5.93 \times 10^{18}$  s<sup>-1</sup> and 0.976  $R^2$ . The value of  $\Delta S^*$  was derived at  $T_{max}$  and observed value is 107.4 JK<sup>-1</sup> mol<sup>-1</sup>. The large and positive value of  $\Delta S^*$  indicated that the transition state is more in disorderly state than that of individual molecules of EBHBCMA [27].

Ether and ester linkages are weak points in the resin molecule and therefore selective degradation starts from such weak points on heating and results into the formation of free radicals with release of low molecular weight hydrocarbons. Formed radicals may further undergo secondary reactions namely recombination, crosslinking, branching, rearrangements, etc. A considerable (27.9 %) residue left at 700 °C confirmed the formation of highly thermally stable crosslinked product.

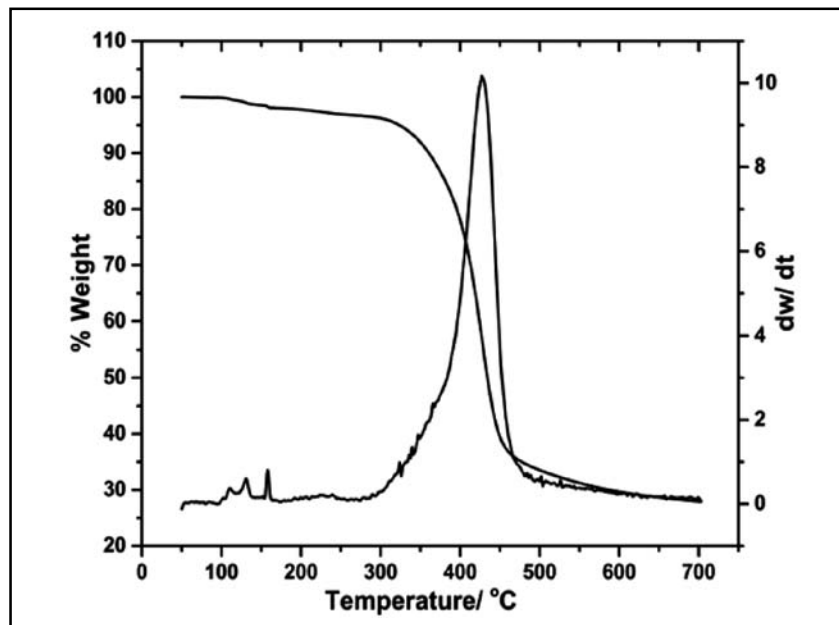


Fig. 6. TG and DTG thermograms of EBHBCMA at  $10^{\circ}\text{C min}^{-1}$  heating rate in nitrogen atmosphere.

### CONCLUSIONS

EBHBCMA possesses good solubility in common solvents and excellent thermal stability. It followed single step degradation kinetics and followed apparently second order degradation kinetics. A considerable amount of residue (27.9 %) left at  $700^{\circ}\text{C}$  confirmed the formation of highly thermally stable crosslinked product.

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