

# Synthesis, Characterization, and Study of Antibacterial Activity of Homopolymers and Copolymers of 4-Benzyloxyphenylacrylates for Pressure-Sensitive Adhesive Application

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**ABSTRACT:** Poly(4-benzyloxyphenylacrylate) and its copolymers with glycidyl methacrylate were synthesized from the monomer, 4-benzyloxyphenylacrylate (4-BOPA) by free radical solution polymerization. The synthesized homopolymers and copolymers were characterized by UV, FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic techniques. The thermal stability of the polymers was performed by thermogravimetric analysis in inert atmosphere. The glass transition temperatures of the polymers were determined by differential scanning calorimeter. The lap shear strength of the polymers was determined by Universal testing machine. The antibacterial activities of the polymers were also studied by UV spectroscopy. The results of the TGA analysis showed that the polymers possess good stability

even beyond 250°C. Different concentrations of the polymer solutions were prepared and tested for their adhesive strength by applying them between leather strips. Thus, the results of the study reveal that the poly(4-benzyloxyphenylacrylate-co-glycidyl methacrylate) has good adhesive strength compared with poly(4-BOPA), which can be used for its adhesive property suitable for high temperature applications, which can also resist the bacterial growth on the applied surface of the material. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3115–3124, 2012

**Key words:** 4-benzyloxyphenylacrylate; glycidylmethacrylate;  $^1\text{H-NMR}$ ;  $^{13}\text{C-NMR}$ ; TGA

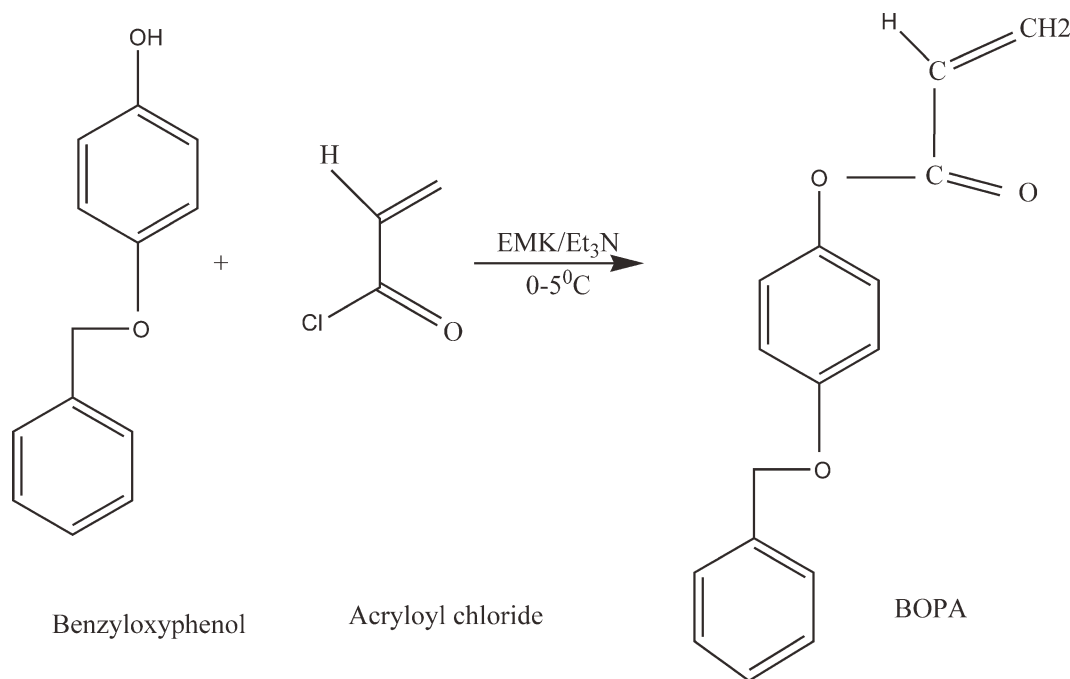
## INTRODUCTION

Phenyl acrylates/methacrylate and vinyl-based copolymers are reported as adhesive polymers for leather to cloth bonding.<sup>1–3</sup> Acrylates containing different functional groups are used in the form of emulsions in coatings, adhesives, and as handling agents for spinning and weaving.<sup>4,5</sup> Copolymerization is one of the important techniques adopted in effecting systematic changes in the properties of commercially important polymers. Phenyl methacrylates are reactive monomers due to the presence of aromatic ring. They have higher thermal stability, which gains much interest due to its potential industrial uses.<sup>6–8</sup> Poly(phenylmethacrylate)s are harder polymers of higher tensile strength and find application in pressure-sensitive, photoimaging materials,<sup>9</sup> and in electro photographic photoreceptors for offset printing plates.<sup>10</sup> They are also used as weather-resistant high-loss topcoats for automobiles.<sup>11</sup>

Copolymers of glycidyl methacrylate (GMA) emulsions without carboxyl groups were prepared by Zurkova et al.<sup>12</sup> and Okubo et al.<sup>13</sup> The reactivity of the oxirane ring toward various nucleophiles was helpful for the chemical modification of the basic polymer for various novel end-use applications. The copolymers based on GMA are, thus, of a great significance for binding enzymes and other biologically active species.<sup>14,15</sup> The oxirane-containing latex can be modified by a number of polymer-analogous reactions, such as hydrolysis, ammonolysis, and aminolysis and by the reaction with hydrogen sulfide in an aqueous solution, thereby yielding active compounds. Antimicrobial polymers play an important role; catheters made from a polymer that slowly recover patients who are dying from infections every year. Antimicrobial polymers could also thwart infections around more permanent implants, such as pacemaker.<sup>16,17</sup> We have reported many polyacrylate and polymethacrylate polymers and copolymers, which were published in reputed journals.<sup>18–22</sup> Among various types of adhesives, pressure-sensitive adhesives form a permanently tacky film after the evaporation of the liquid phase, and bonding is effective by pressing slightly the adhesive surface onto the adherent. They can not only be applied rapidly but also do not need flash off. The significance of these adhesives has, therefore, increased for many

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**Scheme 1** Synthesis of benzyloxyphenylacrylate (4-BOPA) monomer.

applications and these adhesives are also often used in preference to contact or heat sealing adhesives.<sup>23</sup> Acrylate copolymers have gained a considerable significance over other various polymeric raw materials because of their excellent properties, such as, ageing resistance and light stability, good adhesion to various types of substrates, and ease of application. Hence, we have synthesized structurally modified aryl acrylates and their polymers.

The present article describes the synthesis, characterization, monomers reactivity ratios, and thermal properties of novel copolymers of 4-benzyloxyphenylacrylate (4-BOPA) with GMA. As there are no reports have been found about these polymeric systems in chemical abstracts, we have synthesized these newer homo and copolymers. We have studied the antibacterial activity and also found their adhesive strength of the above said polymeric systems in the present investigation.

## EXPERIMENT

### Materials

4-Benzyloxy phenol (Aldrich) was used as received. GMA from SRL was purified by distillation under reduced pressure. AIBN initiator (Aldrich) was recrystallized from ethanol. All solvents were purified by distillation prior to their use.

### Synthesis of 4-BOPA

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel et al.<sup>24</sup> For the synthesis of 4-BOPA, a three-necked round-bot-

tomed flask (500 mL) fitted with thermometer, stirrer, dropping funnel containing of 4-benzyloxyphenol (8.012 g), triethylamine (6.69 mL), hydroquinone (0.5 g), and 2-butanone (200 mL) was cooled at  $-5$  to  $0^{\circ}\text{C}$ . Acryloyl chloride (3.74 mL) dissolved in 2-butanone (20 mL) was added slowly with stirring, and the temperature was maintained at  $-5$  to  $0^{\circ}\text{C}$  (Scheme 1). The stirring was continued for 1 h. The reaction mixture was stirred for another 2 h at room temperature and precipitated quaternary ammonium salt was filtered off. The unreacted contents and hydroquinone were removed by successive extraction with 5% sodium hydroxide and distilled water. After drying over anhydrous sodium sulfate, 2-butanone was evaporated on rotary evaporator. The crude product was then recrystallized from ethanol to give 4.1 g (yield 50%) of pale yellow crystals. Melting point was  $89$ – $93^{\circ}\text{C}$ .

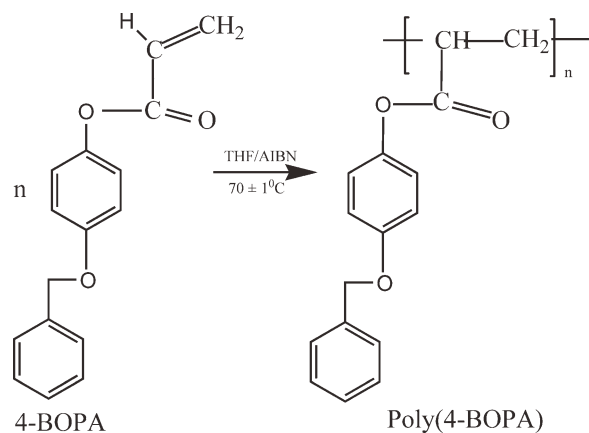
The monomer was examined by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectra.

IR (KBr,  $\text{cm}^{-1}$ ):  $3,436$   $\text{cm}^{-1}$ ; Ar-C-H;  $1,505$   $\text{cm}^{-1}$ ; Ar-C=C;  $1,732$   $\text{cm}^{-1}$ : ester carbonyl C=O stretching;  $1,027$   $\text{cm}^{-1}$ : C-O alcoholic part of ester;  $1,188$   $\text{cm}^{-1}$  and  $1,297$   $\text{cm}^{-1}$ : acid part of ester;  $1,243.5$   $\text{cm}^{-1}$  and  $1,103$   $\text{cm}^{-1}$ : C-O-C stretching;  $3,070$  and  $3,030$   $\text{cm}^{-1}$ : =C-H and =CH<sub>2</sub>.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): Ar-H: 6.7–7.5; =CH<sub>2</sub>: 6.1 (d, 2H); =CH-: (t, 1H); O-CH<sub>2</sub>: 5.0 (s, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 165.08 (C=O, ester); 124–150 (aromatic carbons); 117 (=C-); 124 (=CH<sub>2</sub>); 70.1 (CH<sub>2</sub>).

### Homopolymerization

Five grams of monomer 4-BOPA and free radical initiator AIBN (0.5% wt of monomer) dissolved in

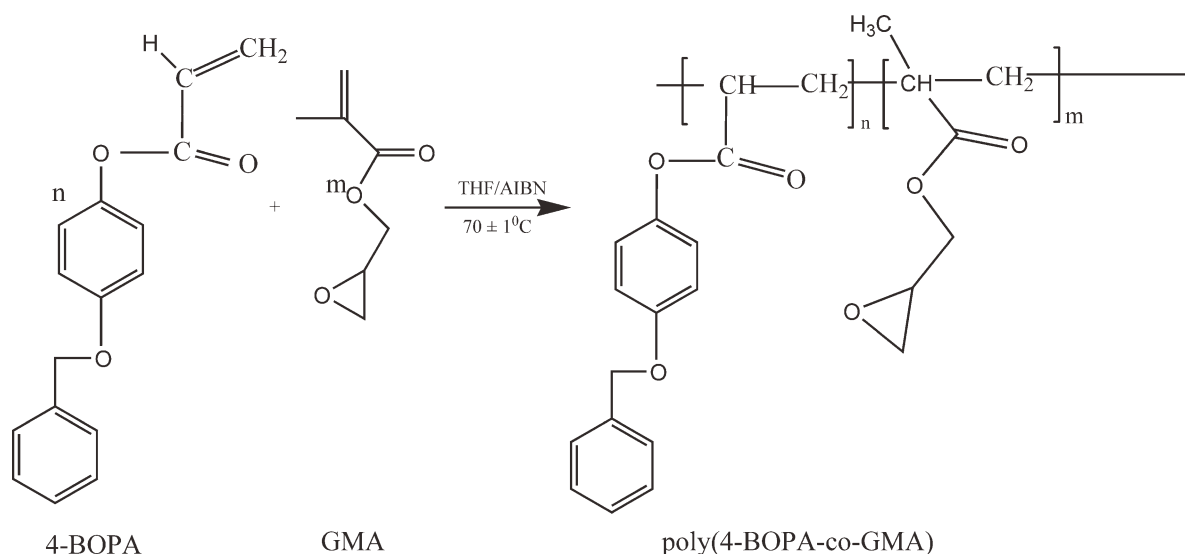


**Scheme 2** Homopolymerization of 4-BOPA.

40 mL THF were taken in a polymerization tube, and  $O_2$ -free  $N_2$  was purged through the solution for 20 min. Then, the solution was thermostated at  $70^\circ C$ . After 8 h, the polymer was precipitated by adding methanol to the reaction mixture (Scheme 2). The polymer was purified by repeated reprecipitation using methanol, and the product was dried at ambient temperature (yield = 70%).

### Copolymerization

Predetermined quantities of 4-BOPA, GMA, MEK, and AIBN were placed in a standard reaction tube (100 mL), and the mixture was flushed with  $O_2$  free  $N_2$  for 20 min. The copolymer reported here has 50 : 50 molar volumes of the monomers. The tube was tightly sealed and immersed in a water bath at  $70 \pm 1^\circ C$ . After the required time (7–10 h), the polymer was precipitated in methanol (Scheme 3). The precipitated polymer was filtered off and purified by



**Scheme 3** Copolymerization of 4-BOPA with GMA.

repeated reprecipitation by using methanol and finally dried in vacuum at  $50^\circ C$  for 24 h. The polymers are prepared to get high conversions for adhesive applications. The epoxy group of the poly(4-BOPA-co-GMA) was cured using 40% of diethanolamine (based on GMA content of the polymers) in chloroform as solvent.

### Solubility test

The solubility of the poly(4-BOPA) and the poly(4-BOPA-co-GMA) was tested by mixing 20 mg of the polymer with 2 mL of various solvents in test tubes. After setting aside the closed tubes for 1 day, the solubility was noticed.

### Characterization techniques

UV spectra were recorded in Hitachi RS1 spectrophotometer. IR spectra were recorded with a Nicolet 360 FTIR ESP spectrophotometer as KBr pellets.  $^1H$ -NMR spectra of all the monomer and polymer samples in  $CDCl_3$  were recorded on a Bruker 300 MHz FT NMR spectrometer at room temperature using tetramethylsilane as internal standard. The proton-decoupled  $^{13}C$ -NMR spectrum was run on the same instrument operating at 22.63 MHz at room temperature and the chemical shifts were recorded under similar conditions. Thermogravimetric analysis was performed with a Mettler TA 3000 thermal analyzer in air at a heating rate of  $10^\circ C/min$ . The glass transition temperature was determined with a NETZSCH-Geratebau GmbH DSC 204 thermal analyzer at a heating rate of  $10^\circ C/min$  in nitrogen. SEM analysis was carried out for the polymers FEI Quanta FEG 200 high-resolution scanning electron microscope.

### Evaluation of lap shear strength

Polymers obtained by the copolymerization of 4-BOPA and GMA to high conversion and having the molar composition 0.5 : 0.5 were used for making the adhesive formulations. Appropriate amount of the polymers are crosslinked with ethanolamine (40% of the weight of GMA) in 10 mL of chloroform solvent to obtain an adhesive paste. Three concentrations of poly/(4-BOPA) and poly(4-BOPA-co-GMA) solutions were prepared. Sheep side leather strips of 15 cm length and 2.5 cm width were used for the determination of shear strength of the prepared adhesive. After the removal of the grain from the leather using emery paper, the adhesive paste was applied over an area of 7.5–2.5 cm at one end of the buffed surface of each strip to form a uniform layer of adhesive. The adhesive coated surfaces of the leather strips were aligned, one over the other and pressed in such a way that the free ends of the leather strips were in opposite direction. The shear strength of the adhesives on leather strips was evaluated by following British standard SATRA TM123 in Universal testing machine (UTM).

### Evaluation of antibacterial properties of poly(4-BOPA) and poly(4-BOPA-co-GMA)

The synthesized polymers of different concentrations of polymers were tested against *Pseudomonas aeruginosa* (a Gram-negative bacterium) and *Staphylococcus aureus* (a Gram-positive bacterium). The antibacterial spectrum of the prepared polymers was determined against the aforementioned test bacteria on powdery samples by the cut-plug method<sup>25</sup> on nutrient agar that contained per liter, 10 g of peptone, 5.0 g of NaCl, 5 g of beef extract, and 20.0 g of agar at pH = 7. After solidification, the assay plates were seeded with the test bacteria by using a cotton swab, and the wells were made and filled with different concentrations of polymer solution. The plates were incubated at 30°C for 24 h, after which the diameter of the inhibition zones were measured at first and further assayed at different concentrations in aqueous suspensions for quantification of their inhibitory effects by UV studies.

Bacterial strains were grown in nutrient broth. Five percent (v/v) inoculums of bacterial culture was used to inoculate solution of nutrient broth (control) and test media (100-mL solution of nutrient broth + *x* mg polymer sample) and incubated on rotary shaker (200 rpm) at 37°C. Half millilitre of liquid was withdrawn at specified time intervals (24–48 h) from the test media. After suitable dilution with DNS reagent and distilled water, optical density was measured at 600 nm and calculated as opti-

cal density per millilitre (i.e., growth). The inhibition percentage (*I*) was obtained as follows:

$$\% \text{Viable cells}(I) = \frac{\text{Test O.D} \times 100}{\text{Control O.D}};$$

O.D = Optical density

This method is based on the principle that as the growth proceeds, cell number increases, which leads to increase in the optical density of the medium.

### Analysis of water absorption

Water absorption was determined gravimetrically. Previously weighed polymers were immersed in distilled water at room temperature for 24 h. Percentage absorption was calculated using the formula

$$\text{Percentage of water absorption} = \frac{\text{Wet } M - \text{Dry } M}{\text{Dry } M} \times 100,$$

where Wet *M* is the weight of wet polymer and Dry *M* is the weight of dry polymer.

## RESULTS AND DISCUSSION

### Characterization of polymers

#### Solubility

The poly(4-BOPA) and poly(4-BOPA-co-GMA) were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethylsulfoxide, tetrahydrofuran, benzene, toluene, and xylene but insoluble in *n*-hexane, water, and hydroxy-group-containing solvents such as methanol and ethanol.

#### UV spectroscopy studies

The UV absorbance values for the monomer, poly(4-BOPA) and copolymer have been observed between 200–400 nm. The 4-BOPA, poly(4-BOPA), and poly(4-BOPA-co-GMA) show UV<sub>max</sub> at 371 nm, 275–286 nm, and 278 nm, respectively.

#### Infrared spectroscopy of poly(4-BOPA)

IR spectrum of poly(4-BOPA) showing absorption peaks at 3,404 cm<sup>-1</sup> corresponds to aromatic C–H stretching. C=C aromatic stretching absorption is observed at 1,511 cm<sup>-1</sup> and out of plane bending absorption in the region 697–900 cm<sup>-1</sup>. The strong absorption peak at 1,752 cm<sup>-1</sup> is due to ester carbonyl C=O stretching vibrations. C–O stretching frequency of alcoholic part of ester is observed at 1,016 cm<sup>-1</sup>. The ring stretching vibrations of the

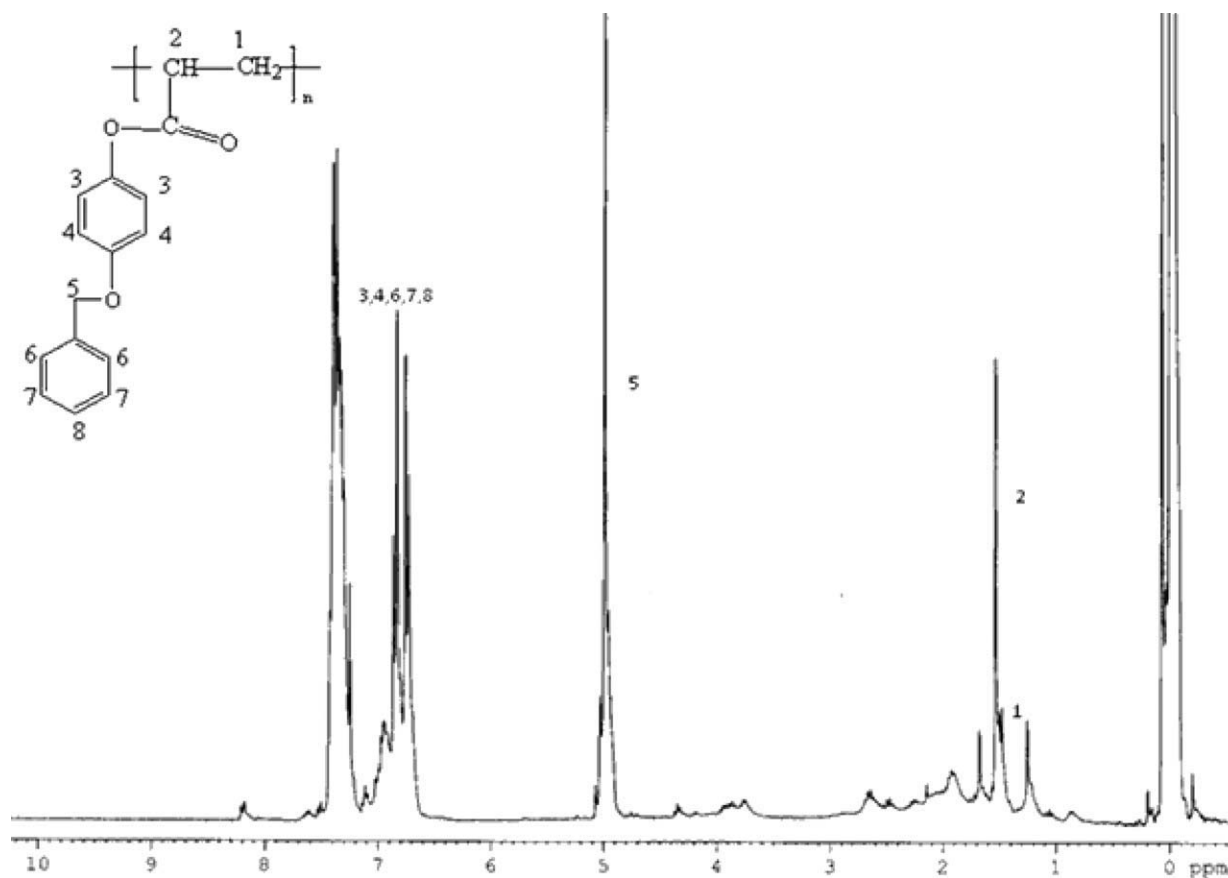


Figure 1  $^1\text{H-NMR}$  spectra of homopolymer 4-BOPA.

aromatic nuclei are observed at  $1604$ ,  $1511\text{ cm}^{-1}$ . C—O—C stretching frequency of ether is observed in the region between  $1,243.8$  and  $1,103\text{ cm}^{-1}$ . The

bending vibrations of methylene group are observed at  $1,452.9\text{ cm}^{-1}$ . The peaks at  $2963\text{ cm}^{-1}$  correspond to symmetrical and asymmetrical stretchings due to

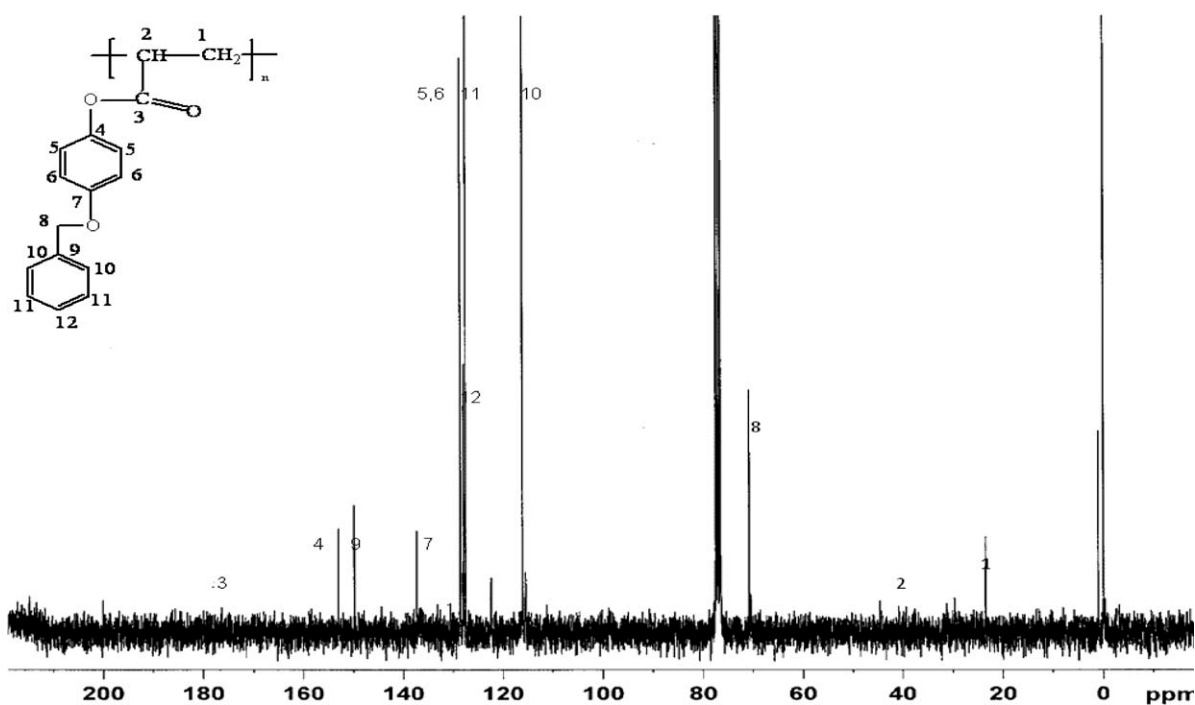


Figure 2  $^{13}\text{C-NMR}$  spectra of poly(4-BOPA).

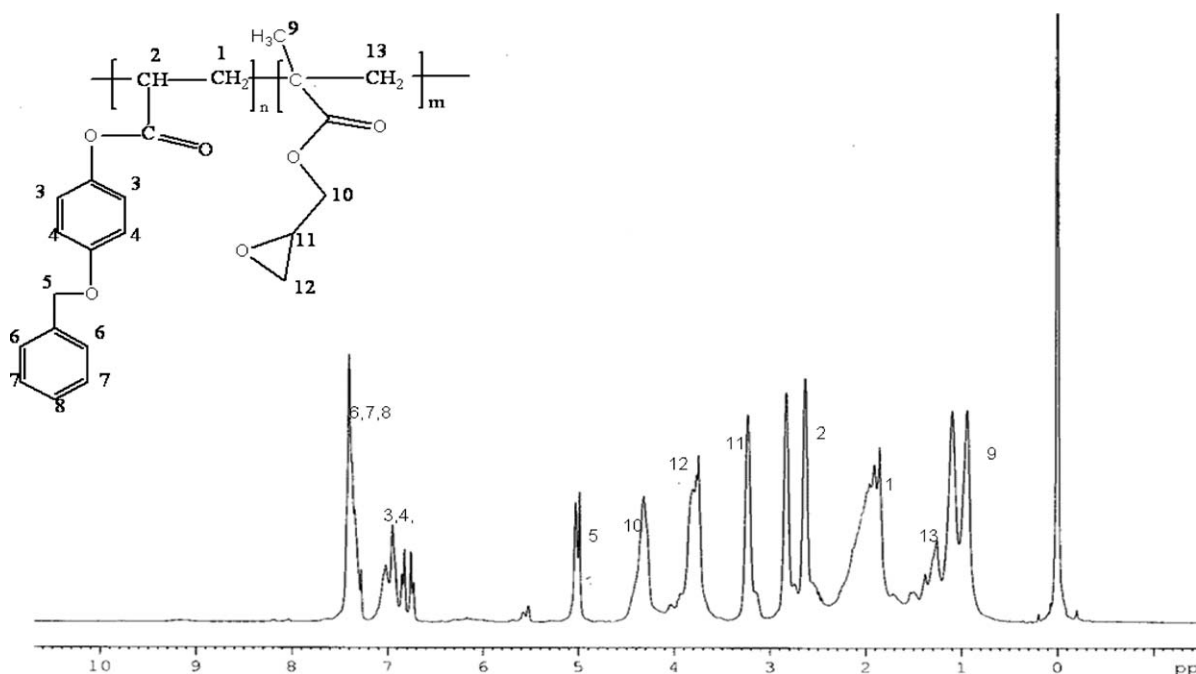


Figure 3  $^1\text{H-NMR}$  spectrum of poly(4-BOPA-co-GMA).

methylene group. Peak at  $521\text{ cm}^{-1}$  corresponds to  $\text{C}=\text{C}$  out of plane bending vibrations.

#### $^1\text{H-NMR}$ spectrum of poly(4-BOPA)

$^1\text{H-NMR}$  spectrum of the poly(4-BOPA) shown in Figure 1. The chemical shift of multiplet in the region 6.7–7.5 ppm corresponds to aromatic protons. The resonance signal at 5 ppm corresponds to ben-

zyloxy protons ( $\text{O-CH}_2\text{-Ar}$ ). The methylene groups ( $-\text{CH}_2-$  and  $-\text{CH}-$ ) show signals between 1.2 and 1.5 ppm, respectively.

#### $^{13}\text{C-NMR}$ spectrum of poly(4-BOPA)

The proton decoupled  $^{13}\text{C-NMR}$  spectrum of poly(4-BOPA) is shown in Figure 2. The resonance signals at 176 ppm correspond to ester carbonyl carbon. The

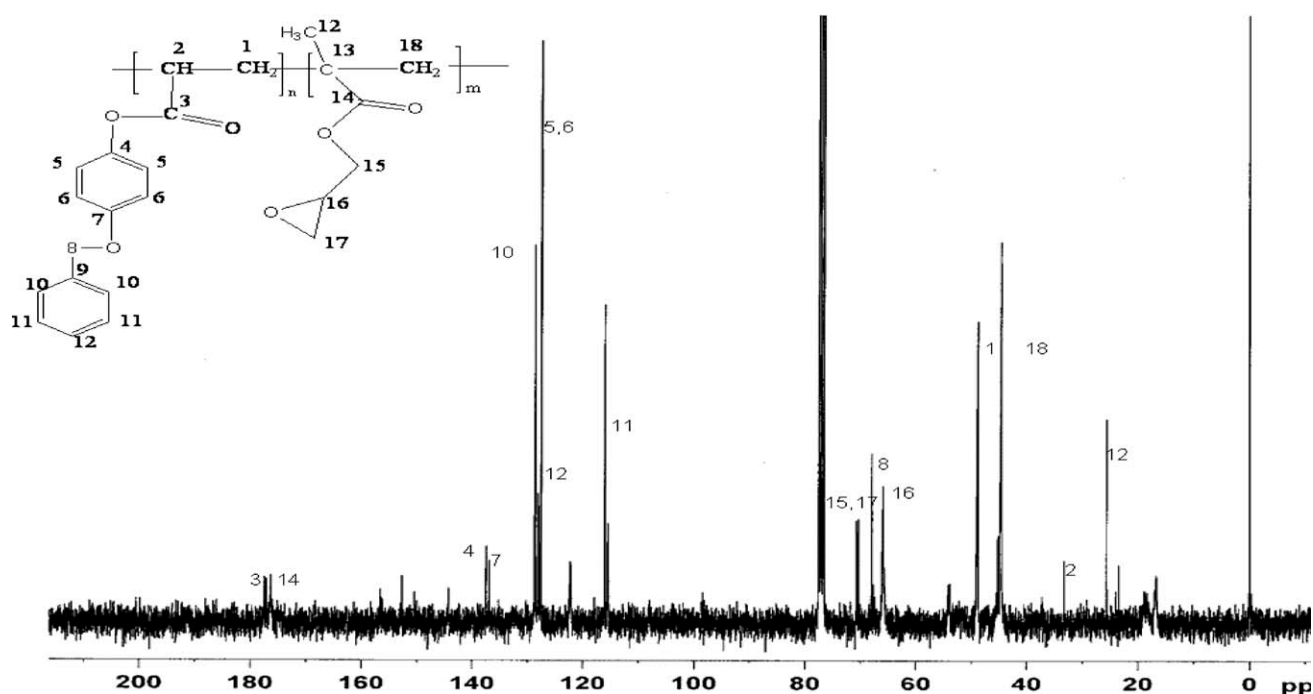
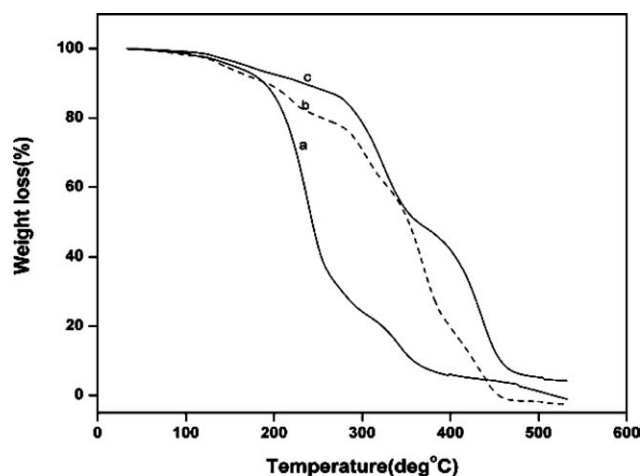


Figure 4  $^{13}\text{C-NMR}$  spectrum of poly(4-BOPA-co-GMA).



**Figure 5** TGA curves of poly(GMA) (a), poly(4-BOPA) (b), and poly(4-BOPA-co-GMA) (c).

aromatic resonance signals are observed at 115–155 ppm. The upfield shift of some aromatic carbons is due to the presence of ester group. Signals at 30.1 and 24 ppm can be assigned to backbone carbon  $-\text{CH}_2$  and  $-\text{CH}-$ , respectively. In addition, the benzyloxy-carbon ( $-\text{O}-\text{CH}_2$ ) shows resonance signal at 70 ppm.

#### Infrared spectroscopy of poly(4-BOPA-co-GMA)

IR spectrum of poly(4-BOPA-co-GMA) is shows absorption at  $3,004\text{ cm}^{-1}$  corresponds to aromatic C-H stretching.  $\text{C}=\text{C}$  aromatic stretching absorption is observed at  $1,470\text{ cm}^{-1}$  and out of plane bending absorption in the region  $697\text{--}900\text{ cm}^{-1}$ . The strong absorption peak at  $1,766.6\text{ cm}^{-1}$  is due to ester carbonyl  $\text{C}=\text{O}$  stretching vibrations. The peaks at around  $2800\text{ cm}^{-1}$  correspond to symmetrical and asymmetrical stretchings due to methylene group.

#### $^1\text{H}$ -NMR spectrum of poly(4-BOPA-co-GMA)

$^1\text{H}$ -NMR spectrum of the poly(4-BOPA-co-GMA) (0.5 : 0.5) is shown in Figure 3. The chemical shift of multiplet in the region 6.7–7.5 ppm corresponds to aromatic protons. The resonance signal at 5 ppm corresponds to benzyloxy protons ( $\text{O}-\text{CH}_2$ ). The methylene groups ( $-\text{CH}_2$  and  $-\text{CH}-$ ) show signals between 1.0, 2.0, and 1.8 ppm, respectively. The  $\alpha$ -methyl group of GMA is observed at 1.2 ppm, the

esteric  $-\text{CH}_2$  show signal at 4.3 ppm and the peaks at 2.7 and 3.8 ppm corresponds to epoxy protons.

#### $^{13}\text{C}$ -NMR spectrum of poly(4-BOPA-co-GMA)

The proton-decoupled  $^{13}\text{C}$ -NMR spectrum of poly(4-BOPA-co-GMA) (0.5 : 0.5) is shown in Figure 4. The resonance signals at 175 and 176 ppm are due to the ester carbonyl carbon of 4-BOPA and GMA units, respectively. The aromatic carbons show signals between 115 and 140. The methylenoxy group flanked between the carbonyl group and epoxy group gives a signal at 70 ppm. The epoxy ring methyne and methylene carbons of GMA unit give signals at above 55 ppm, respectively. The signals due to the backbone methylene and tertiary carbon atoms are observed between 20 and 50 ppm, respectively. The  $\alpha$ -methyl groups of GMA units show a resonance signal at 28 ppm.

#### Thermogravimetric analysis

Thermogravimetric analysis was used in estimating the percentage weight loss of the poly(4-BOPA), poly(GMA), and poly(4-BOPA-co-GMA) against temperature were given in Figure 5. The initial decomposition temperature (IDT) of poly(4-BOPA) is  $175^\circ\text{C}$ . Poly(4-BOPA) undergoes two stages of decomposition, showing first stage decomposition occurs between  $208\text{--}254^\circ\text{C}$  with a weight loss of 50% and second stage decomposition undergoes between  $280\text{--}350^\circ\text{C}$  with a weight loss of 85%. The IDT of poly(4-BOPA-co-GMA) is  $225^\circ\text{C}$ . It also undergoes two stages of decomposition, showing first stage decomposition occurs between 254 and  $373^\circ\text{C}$  with a weight loss of 50% and second stage decomposition undergoes between 375 and  $480^\circ\text{C}$  with a weight loss of 90%. The poly(4-BOPA-co-GMA) is found to be more stable toward temperature than poly(4-BOPA) and poly(GMA), the higher thermal stability of the copolymer is due to benzyloxy carbon backbone and the lesser steric hinderance among the monomer units than the poly(4-BOPA).

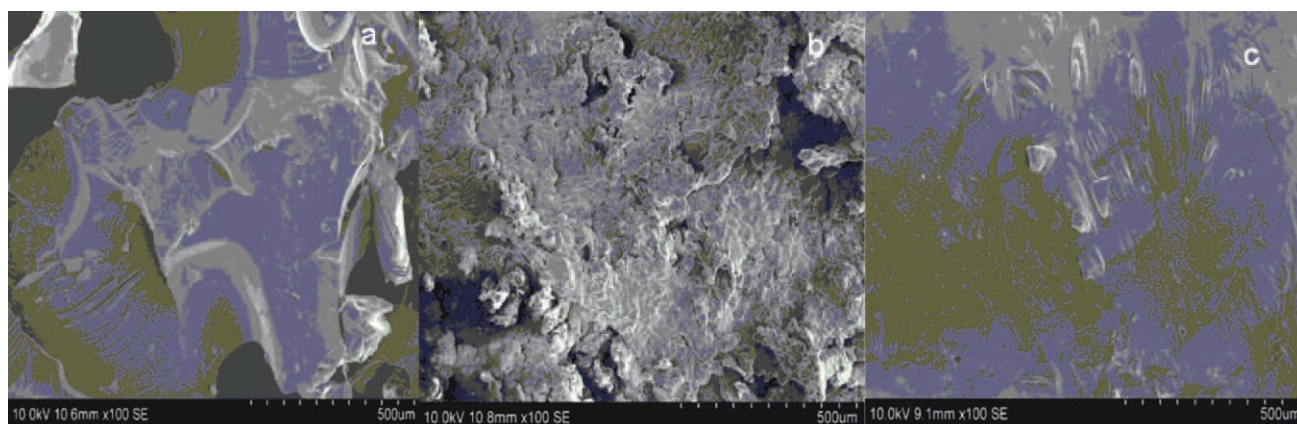
#### Glass transition temperature

The glass transition temperature of polymer is determined by differential scanning calorimeter. The

**TABLE I**  
Degradation of Polymers with Increase in Temperature

Polymer	$m_1$	$T_g$ ( $^\circ\text{C}$ )	IDT ( $^\circ\text{C}$ )	Temperature ( $^\circ\text{C}$ ) at different weight loss (%)				
				10	25	50	75	90
Poly(4-BOPA)	1	93.6	175	200	235	255	330	390
Poly(GMA)	1	76.0	133.4	186.76	250.1	360.2	400	440
Poly(4-BOPA-co-GMA)	0.5	86.6	225	248	308.15	373.5	433.5	480.24

$m_1$  is the mole fraction of monomers.



**Figure 6** SEM images of poly(GMA) (a), poly(4-BOPA) (b), and poly(4-BOPA-co-GMA) (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

polymers show single glass transition temperature, thus indicating the absence of formation of block copolymers or a mixture of homopolymers. The  $T_g$  value of poly(4-BOPA) is 93.6°C. The relatively high value of  $T_g$  for the poly(4-BOPA) is due to  $\alpha$ -methyl group introduced into the backbone, which leads to chain entanglement and shows amorphous nature of the poly(4-BOPA). The poly(GMA) showed its  $T_g$  at 76°C. The poly(4-BOPA-co-GMA) showed  $T_g$  is 86.6°C lies in between the  $T_g$ s of poly(4-BOPA) and poly(GMA). The results obtained from DSC are given in Table I.

#### SEM analysis

The SEM analysis (Figure 6) shows that the surface morphology of the poly(4-BOPA-co-GMA) is uniform than both the poly(4-BOPA) and poly(GMA). These polymers also exhibit the amorphous nature.

#### Lap shear strength

The synthesized polymers were tested for their adhesive strength by preparing various concentrations (1–5%) with the diethanolamine solutions (40% in  $\text{CHCl}_3$ ) by following the method of British standard SATRA TM 123 in UTM. The maximum tensile stress value obtained are given in Table II shows that the maximum tensile stress increases with the

**TABLE II**  
Evaluation of Lap Shear Strength

Conc. (%)	Maximum tensile stress (kPa)		
	Poly(4-BOPA)	Poly(GMA)	Poly(4-BOPA-co-GMA)
1	407.87	526.56	647.32
2	485.07	623.48	666.46
3	532.21	637.45	785.55
4	582.34	682.52	842.34
5	631.12	747.23	896.22

concentration for both the polymers and also the poly(4-BOPA-co-GMA) shows maximum tensile stress than poly(4-BOPA). These compositions showed good adhesive characteristics even at room temperature. The enhanced tensile stress for the copolymer was due to the higher number of epoxy group content in the poly(4-BOPA-co-GMA). When the poly(4-BOPA-co-GMA) solution in chloroform was treated with ethanolamine, the amino group of the later readily reacts with the epoxy group of the poly(4-BOPA-co-GMA) to give a pasty product having more free volume and lower  $T_g$  compared with the poly(4-BOPMA), which can form a temporary hydrogen bonding with the diethanolamine. The paste still contains some unreacted epoxy groups, which when applied over leather would react with the functional groups in its surface to form a chemical bonding through crosslinking with the diethanol amine, which readily enhances the tensile stress of the copolymer.

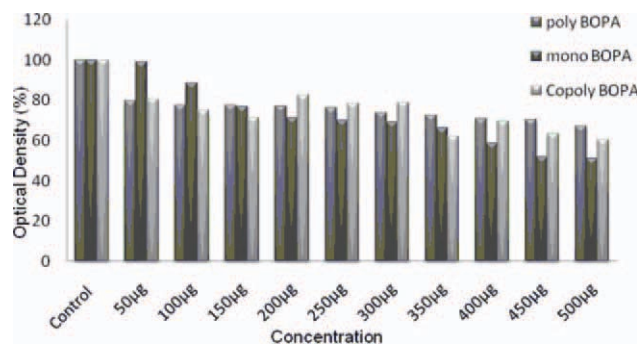
#### Water absorption analysis

Water absorption of the polymers was tested by gravimetric method. The results show that the water resistance follows poly(4-BOPA) > Poly(4-BOPA-co-GMA) > poly(GMA). This trend is because of reduction in the number of epoxy unit in the polymer. The percentage of water absorption is listed in the Table III.

**TABLE III**  
Evaluation of Percentage of Water Absorption of Polymers

Sample	Water absorption (%)
Poly(4-BOPA)	6%
Poly(GMA)	12%
Poly(4-BOPA-co-GMA)	24%





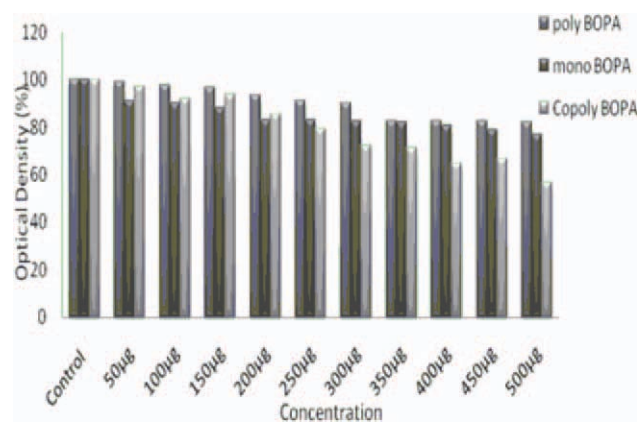
**Figure 7** Effect of polymers against the gram positive bacteria, *Staph.aureus* at different concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Antibacterial assessment of polymers

The antibacterial activities of poly(4-BOPA) and poly(4-BOPA-co-GMA) against *P. aeruginosa* and *S. aureus* were explored by the cut plug method and broth dilution methods as described previously (Figure 7 and Figure 8).

A control experiment was carried out with only DMSO solution in cut plug method. The poly(4-BOPA) shows inhibition zones, which vary with respect to their concentration. The poly(4-BOPA-co-GMA) does not show any measurable inhibition zones with exact diameter in cut plug method but shows antibacterial effect in broth dilution method.

The ability of the prepared polymers to inhibit the growth of the tested microorganisms on solid media is shown in Table IV. The diameter of the inhibition zone varied according to the active group in the polymer and their concentration. The Poly(4-BOPA) was found to be more effective than poly(4-BOPA-co-GMA), against Gram-positive bacteria as its concentration has been increased, but it is vice versa against Gram-negative bacteria.



**Figure 8** Effect of polymers against the gram negative bacteria, *Ps.aeruginosa* at different concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE IV**  
Antibacterial Evaluation of Polymers—By Cut Plug Method

Samples	Zone of inhibition (mm)							
	Against <i>S. aureus</i> ( $\mu\text{g}$ )				Against <i>P. aeruginosa</i> ( $\mu\text{g}$ )			
	100	200	300	400	100	200	300	400
4-BOPA	12	15	18	19	14	16	21	21
Poly(4-BOPA)	12	14	14	17	14	19	23	23

Poly(4-BOPA-co-GMA) does not show any proper zone of inhibition though it has some antibacterial activity.

It may be because of the presence of both hydrophilic and hydrophobic groups in poly(4-BOPA-co-GMA) in which the hydrophilic groups were interacted by water and hydrophobic groups were interacted by the Gram-negative bacterial cell wall, which has more lipid in them and thus gets penetrated into and thus destroys them.

#### CONCLUSIONS

The poly(4-BOPA) and poly(4-BOPA-co-GMA) having equal composition were synthesized in solution by free radical polymerization. The structures of the poly(4-BOPA) and poly(4-BOPA-co-GMA) were confirmed by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic techniques. The poly(4-BOPA) and poly(4-BOPA-co-GMA)s soluble in polar aprotic and non-polar solvents such as tetrahydrofuran, dimethylformamide, dimethylsulphoxide, chloroform, and methylene dichloride. They are insoluble in hydroxyl group containing solvents such as methanol, ethanol, and 2-isopropanol. Thermal studies indicate that poly(4-BOPA) and poly(4-BOPA-co-GMA) show two stage decomposition and thus showing higher thermal stability. The weight loss of the poly(4-BOPA-co-GMA) at various temperatures indicates higher thermal stability. The SEM analysis results reveal that the poly(4-BOPA-co-GMA) has uniform surface morphology and the antibacterial study shows these polymers also resist the growth of bacteria and thus they can be used for coating applications also. These poly(4-BOPA-co-GMA) may be used for pressure sensitive applications due to its bulky benzyloxy group. Poly(4-BOPA-co-GMA) dissolved in  $\text{CHCl}_3$  and partially crosslinked with diethanolamine was found to be a good adhesive for leather. The peel strength of the adhesive was found to increase with increase in concentration with respect to GMA in the poly(4-BOPA-co-GMA). These copolymers exhibit good adhesive characteristics even at room temperature, which also shows better antibacterial activity against the bacterial growth.

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