

# Synthesis and Study of the Oligo(ether–ester)s Based on Butylene Oxide

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**ABSTRACT:** Unsaturated oligo(ether–ester) was prepared by ring-opening polymerization of butylene oxide (BO) with glycidyl methacrylate (GMA) in the presence of cationic catalyst  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . The effects of mol ratio of the initial components, amount of catalyst, temperature, and reaction times on the copolymerization reaction were examined. Oligo(ether–ester) were achieved in highest yield of 82% after reaction times of 4 h at 0°C. Synthesized copolymer was characterized using spectroscopic (<sup>1</sup>H

NMR and IR) and chemical analysis methods. The thermal degradation and softening points of oligo(ether–ester)-styrene composites were studied. It is shown that crosslinking of the unsaturated oligo(ether–ester) with styrene takes place through the use of thermostable materials. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2016–2020, 2008

**Key words:** ring-opening polymerization; composites; thermal properties

## INTRODUCTION

Polymeric materials have an extremely important place in modern industry. Unsaturated polyesters are among the most commonly used matrices with a world consumption of approximately 1 million tonnes per year.<sup>1</sup> The synthesis of oligomers having polyfunctional groups is one of the current subjects in polymer chemistry. As known from the literature, the unsaturated oligoesters are synthesized from the copolymerization of alkylene oxides with anhydrides, chloroanhydrides, and esters of unsaturated monocarbonic acids.<sup>2–8</sup> A novel copolymer containing chiral epoxy residues was prepared by free radical initiated copolymerization of glycidyl methacrylate with ethylene glycol dimethacrylate in high yield.<sup>9</sup>

In our previous studies, the copolymerization of propylene oxide with glycidyl methacrylate in the presence of the cationic catalyst was investigated and unsaturated oligomers were synthesized in high yields. The synthesized unsaturated oligomers (oligoesters including unsaturated ester groups) are used in the derivation of polymer materials having high adhesion and physicomechanical properties.<sup>10,11</sup>

Effect of polar compounds on copolymerization of propylene oxide and tetrahydrofuran initiated by  $\text{BF}_3$  was studied by Komratov et al.<sup>12</sup> Copolyethers

were prepared by ring-opening polymerization of two oxiranes, ethylene oxide (EO), and allyl glycidyl ether (AGE), in a high-pressure reactor vessel. The random distribution of AGE units in the copolymers prepared by an anionic route results in a marked decrease of the crystallinity as well as of the melting point.<sup>13</sup>

2-Furyloxirane (FO) was polymerized by various anionic and coordination initiators both in bulk and solution. Propylene oxide did not copolymerize with FO, whereas butylene oxide gave copolymers.<sup>14</sup>

Thermal analysis (TA) has assumed an important role in the study of polymers. TA supplies important information for the evaluation and the development of flame retarded (FR) polymers via the profile of their thermal decomposition.<sup>15–18</sup>

By Yazicigil et al., waste raw materials were transformed into valuable products which are used in polymer chemistry. Soap stock (SS), which is the waste product of oil refinement, was converted to unsaturated ester with epichlorohidrine that has epoxy group and after this unsaturated glycidyl ester copolymers having strength to the thermal destruction and adhesion properties were obtained from its copolymerization with styrene.<sup>19</sup>

## EXPERIMENTAL

### Materials

Glycidyl methacrylate (GMA), butylene oxide (BO), styrene, and cationic catalyst  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  were purchased from Merck (Darmstadt, Germany).

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**TABLE I**  
The Softening Points of Styrene:  
Oligo(ether-ester) Composites

Styrene: oligo(ether-ester) mol ratio	Softening point, °C
9 : 1	61.2
8 : 2	92.7
7 : 3	141.8
6 : 4	34.7
5 : 5	39.8

### Synthesis of unsaturated oligo(ether-ester)s

A 150 mL flask, equipped with a magnetic stirrer and thermometer, was charged with BO : GMA in different ratios from 1 : 1 to 6 : 1. The mixture was heated to C with stirring.  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  (0.5–1.5%) was added to the mixture. After completion of the reaction, methanol (1 mL) was added to mixture to deactivate the catalyst. The starting materials and methanol was removed under reduced pressure (2 mmHg, 53°C). Yield was calculated from final weight.

### The preparation of styrene-oligo(ether-ester) composites

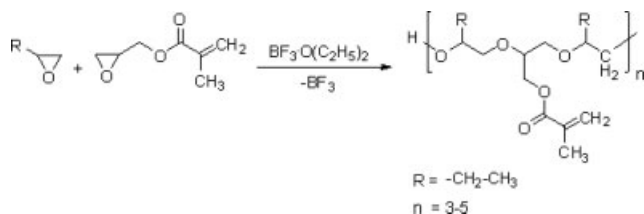
Composite materials of unsaturated oligo(ether-ester)s were prepared with styrene (mol ratios of styrene : oligomer are 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5) in the presence of benzoyl peroxide (1%) and hardened within 1 day increasing temperature from 25 to 95°C.

### Measurements and analysis

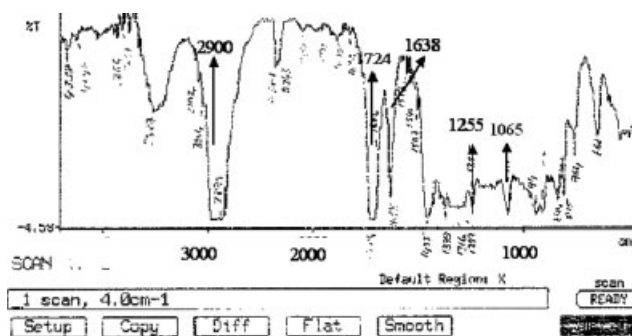
The IR spectra of synthesized copolymers films were recorded with UNICAM SP 1025 spectrometer.  $^1\text{H}$  NMR spectra were performed on Bruker Avance DPX-400 at 400.13 MHz and 25°C. Sample was dissolved in  $\text{CDCl}_3$ .

#### Determination of epoxy group ( $\text{epoxy}$ )

To determine the percentage of the epoxy groups in BO/GMA oligomers, the epoxy group in the sample



**Figure 1** Copolymerization reaction of BO with GMA in the presence of catalyst  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ .



**Figure 2** IR spectrum of oligo(ether-ester).

was cleaved with an excess of HCl and then the remaining HCl was back titrated with KOH (0.1N).<sup>15</sup>

#### Determination of ester groups

To determine number of ester groups in the unsaturated oligo(ether-ester), oligomer (2–3 g) was dissolved in a mixture of ethanol (25 mL) and benzene (50 mL). Twenty five milliliter of an ethanolic solution of KOH (2N) was added. The mixture was refluxed for 1 h. After cooling to room temperature, excess of KOH was titrated with HCl (1N) using phenolphthalein. Number of ester groups was calculated with following equation.

$$\text{Ester group (mg KOH/g oligomer)} = \frac{56.1 \times (V_1 \times N_1 - V_2 \times N_2)}{m}$$

where,  $N_1$  is the normality of the KOH solution,  $N_2$  is the normality of the HCl solution,  $V_1$  is the volume of the added KOH solution (mL),  $V_2$  is the volume of the added HCl solution used for titration (mL),  $m$  is the amount of the sample analyzed (g), 56.1 is the molecular weight of the KOH.

#### Determination of double bonds

Number of double bonds in oligomer was determined by titration method.<sup>20</sup>

#### Determination of molecular weight

To determine average molecular weight of oligomer, cryoscopic method was performed and average molecular weight was calculated with following equation.

$$\bar{M}_n = \frac{k \times g \times 1000}{g_1 \times (t_2 - t_1)}$$

where,  $k$  is the cryoscopic constant of solvent,  $g$  is the

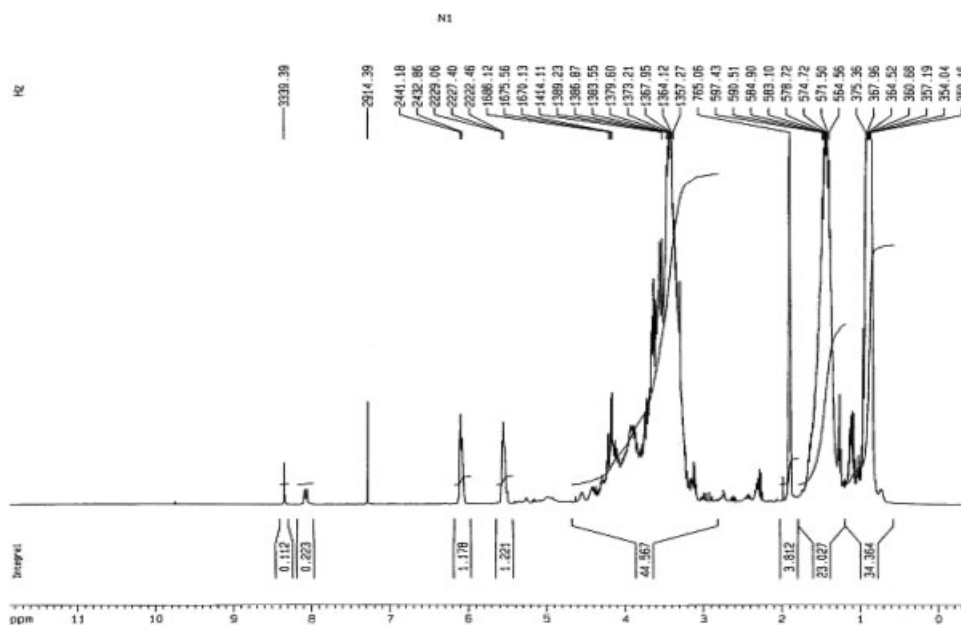


Figure 3  $^1\text{H}$  NMR spectra of oligo(ether-ester).

weight of oligomer,  $g_1$  is the volume of solvent,  $t_1$  is the freezing point of solution, and  $t_2$  is the freezing point of solvent.

#### TGA

Thermogravimetric analysis (TGA) experiments were carried out by use of NETZCH-Geratebau GmbH model thermogravimetric analyzer which was calibrated over all heating rates, using a gas purge, in the same conditions as those of the analysis. Polymer samples, of about 10 mg in a platinum crucible heated in the temperature range 25–500°C using heating rates 10°C min<sup>-1</sup>, with a controlled dry air flow of 120 cm<sup>3</sup> min<sup>-1</sup>.

#### Softening point

Softening points of unsaturated oligo(ether-ester)-styrene composites (Table I) were determined by CEAST HDT-VICAT apparatus at 23–190°C.

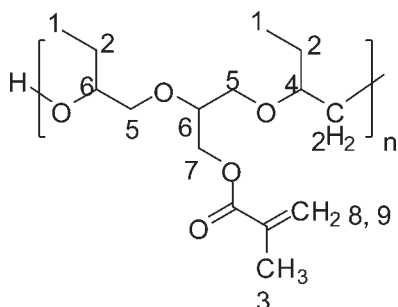


Figure 4 Molecular structure of the unsaturated oligo(ether-ester).

## RESULTS

Copolymerization reaction of BO with GMA was shown in Figure 1. Chemical structure of unsaturated oligomer, determined via IR spectrum. In the IR spectrum, characteristic bands were appeared in the regions of 1065 cm<sup>-1</sup> for —C—O—C—, 1255 cm<sup>-1</sup> for epoxide group, 1638 cm<sup>-1</sup> for C=C and 1724 cm<sup>-1</sup> for C=O of ester (Fig. 2).

$^1\text{H}$  NMR spectrum of the unsaturated oligo(ether-ester) is given in Figure 3. The structure and the numbering of the atoms of unsaturated oligo(ether-ester) is shown in Figure 4. The  $^1\text{H}$  NMR data are collected in Table II.

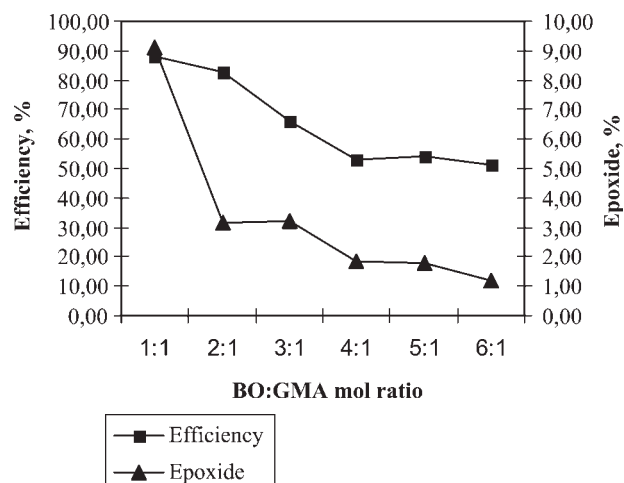


Figure 5 Effect of BO: GMA mol ratio on reaction efficiency and epoxide group.

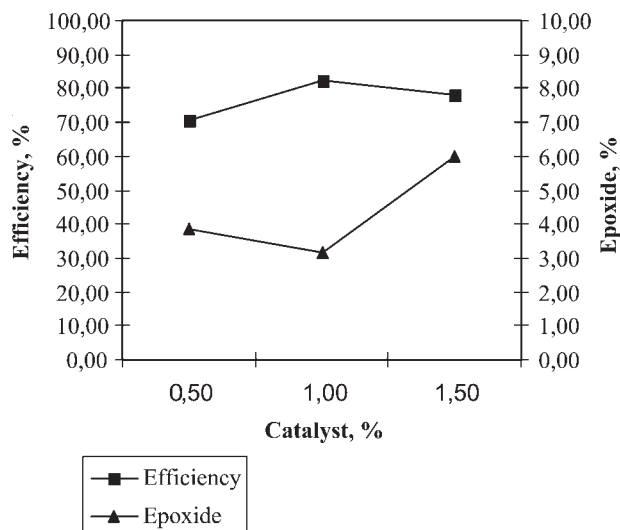


Figure 6 Effect of amount of catalyst on reaction efficiency and epoxide group.

Reactions were carried out according to factors-below: molar ratios of BO:GMA are between 1 : 1 and 6 : 1, amount of catalyst is 0.5–1.5%, temperature is from –5 to 10°C, and reaction periods are 1–8 h.

The optimum reaction conditions for the copolymerization of BO with GMA was obtained according to results presented in Figures 5–8 are following: BO: GMA mol ratio 2:1,  $[BF_3 \cdot O(C_2H_5)_2]$ : 0.030 mol/L; T: 273 K; reaction time: 4 h. In these conditions, yield was 82.5%.

The number of epoxy groups on the oligo(ether-ester) chain was decreased as molar ratio of butylenes oxide to glycidyl methacrylate was increased. Because of this, oligo(ether-ester) chain was mainly formed with cleavage of epoxide ring. The number of epoxy groups was changed by amount of catalyst

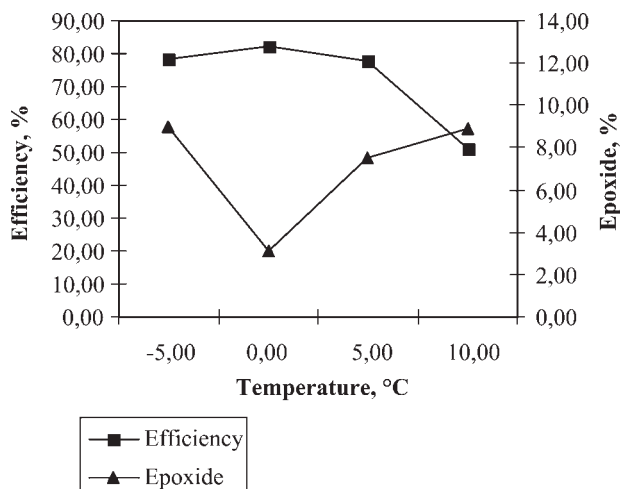


Figure 7 Effect of temperature on reaction efficiency and epoxide group.

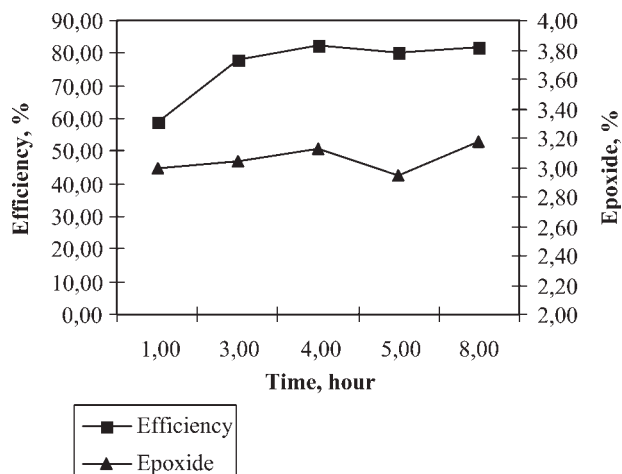


Figure 8 Effect of time on reaction efficiency and epoxide group.

and temperature. However, changes in the reaction time did not affect the epoxy number (Figs. 5–8).

The number of epoxy groups in the structure of unsaturated oligo(ether-ester) obtained in optimum reaction conditions and iodine value were determined as 3.13% and 20.68, respectively. These results showed that the reaction was progressed by cleaving epoxide ring, but it was observed that the reaction was preceded in small amount by extending from the side chain. The ester number in the unsaturated oligo(ether-ester) was calculated as 477.55 mg KOH/g oligo(ether-ester) and average molecular weight of oligomer was determined as 450 g/mol.

The resistance results of crosslinked styrene-oligo(ether-ester)s to heat between 150°C and 450°C were presented in Figures 9 and 10. The resistance of oligomers to heat is increased as the ratio of oligo(ether-ester) in composite material is increased. These polymers are thermally stable to more than 300°C in the air. The composite prepared with styrene-

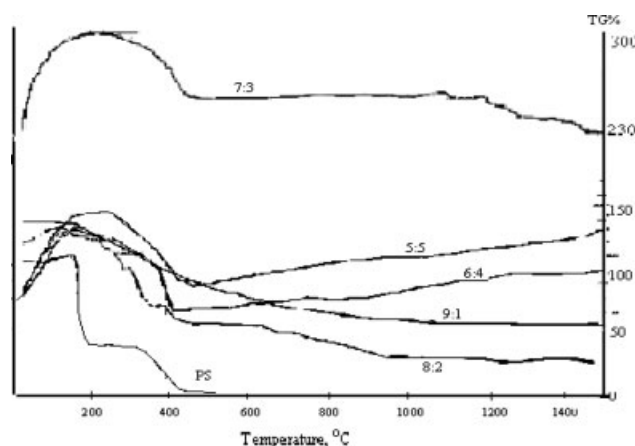


Figure 9 TGA curves of styrene: unsaturated oligo(ether-ester) composites and PS.

**TABLE II**  
 $^1\text{H}$  NMR Chemical Shifts (ppm) of Unsaturated  
 Oligo(ether-ester)

No. of atom	$^1\text{H}$
1	0.87–0.94 (6H, t, $\text{CH}_3$ )
2	1.40–1.61 (6H, m, $\text{CH}_2$ )
3	1.91 (3H, s, $\text{CH}_3$ )
4	3.10–3.18 (1H, m, CH)
5	3.21–3.26 (4H, m, $\text{CH}_2$ )
6	3.65–3.74 (2H, m, CH)
7	4.07–4.13 (2H, m, $\text{CH}_2$ )
8	5.55 (1H, d, $=\text{C}-\text{H}$ )
9	6.10 (1H, d, $=\text{C}-\text{H}$ )

ne:oligo(ether-ester) (mol ratio 7 : 3) gave a best thermal analysis result. Weight loss of that material was least (45%) at 450°C. The resistance of them to thermal degradation depending on the number of functional groups in all unsaturated oligo(ether-ester) composites was higher than that of polystyrene. Thermal analysis results were showed that weight loss was began at 150°C, reached to 50% at 300°C and 95% at 450°C. Weight loss of oligo(ether-ester) composites is about 50% at 450°C.

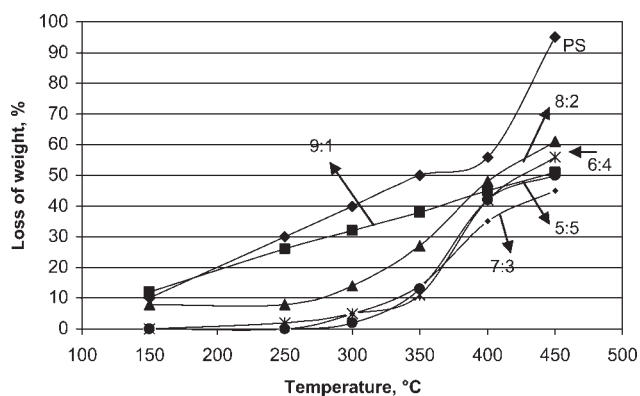
Softening point of styrene : oligo(ether-ester) composite (mol ratio 7 : 3) is 141.8°C and it was determined that this material is more resistant to temperature (Table I).

## CONCLUSIONS

The optimum reaction conditions for the copolymerization of BO with GMA are following: BO: GMA mol ratio 2 : 1,  $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_0$ : 0.030 mol/L;  $T$ : 273 K; reaction time: 4 h. In these conditions, yield was 82.5%.

The results obtained for epoxy group and iodine value showed that the reaction was progressed by cleaving epoxide ring, but it was observed that the reaction was preceded in small amount by extending from the side chain.

The resistance of crosslinked styrene-oligo(ether-ester)s to thermal degradation depending on the number of functional groups in all composites was higher than that of polystyrene. These polymers are thermally stable to more than 300°C in the air. Weight loss of oligo(ether-ester) composites is about 50% at 450°C.



**Figure 10** Weight loss variation of styrene: unsaturated oligo(ether-ester) composites.

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