

# Synthesis and Characterization of Poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-Graft-Polyoxyethylene

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## SYNOPSIS

This study involved the synthesis and characterization of an amphipathic graft copolymer, poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene. This amphipathic graft copolymer was synthesized utilizing a "grafting-onto" technique in which  $\alpha$ -hydroxy- $\omega$ -methoxypolyoxyethylene was reacted with prepolymerized poly(methyl methacrylate-co-glycidyl methacrylate). Proof of copolymer formation was illustrated using water solubility, GPC, FTIR spectroscopy, and  $^{13}\text{C}$ -NMR spectroscopy. In all cases, proof of copolymer formation is demonstrated unequivocally.

## INTRODUCTION

Methyl methacrylate/oxyethylene graft copolymers have been synthesized using two different techniques: a technique using macromonomers and a "grafting-onto" technique. The first method involves the copolymerization of a monomer with a low molecular weight prepolymer containing a polymerizable double bond. The second method consists of reacting functional end groups of a prepolymer with the functional groups along the chain of another polymer.

Niwa et al.<sup>1</sup> have prepared amphipathic graft copolymers containing polyoxyethylene (PEO) as the hydrophile utilizing macromonomers. In this case, the PEO macromonomer was functionalized with a styrenic group. They found that copolymerizations of styrene-terminated POE with methyl methacrylate (MMA) and styrene afforded copolymers with high molecular weights. Moreover, they found that these macromonomers would homopolymerize, although they described it as difficult to do. Homopolymers were obtained after long reaction time. This observation was attributed to the bulkiness of the macromonomer chain and a lack of accessibility of the active site. Also, Gramain and Frère<sup>2</sup> have

prepared MMA/POE graft copolymers using macromonomers as described above.

Gramain and Frère<sup>3</sup> have prepared graft copolymers with an acrylate backbone by grafting  $\alpha$ -hydroxy- $\omega$ -methoxy-POE onto poly(acryloyl chloride). This graft copolymer was formed by reacting the acid chloride groups with the hydroxyl end group on the POE.

A number of groups have prepared poly(methyl methacrylate) (PMMA)-graft-POE copolymers by a transesterification reaction.<sup>4-6</sup> In these cases, a potassium alkoxide of POE was grafted onto PMMA by the attack of the alkoxide on the carbonyl group of the PMMA with the elimination of the methoxide ion.

Tomoi et al.<sup>7</sup> have polymerized methyl and ethyl methacrylate using alkali-metal alkoxide derivatives of POE. In this case, a copolymer consisting of polymethacrylate and polyether structure was obtained. Moreover, this copolymer contained both block and graft units. The block units were a result of the alkoxide-initiating polymerization of the ethyl methacrylate. The graft units were a result of the alkoxide attacking the carbonyl group of the methacrylate polymer (transesterification reaction).

Gramain and Frère<sup>2,3</sup> found that MMA/POE graft copolymers formed gels, and they concluded that high molecular weight MMA/POE graft copolymers formed "spontaneous gels." The work in this paper demonstrates that high molecular weight

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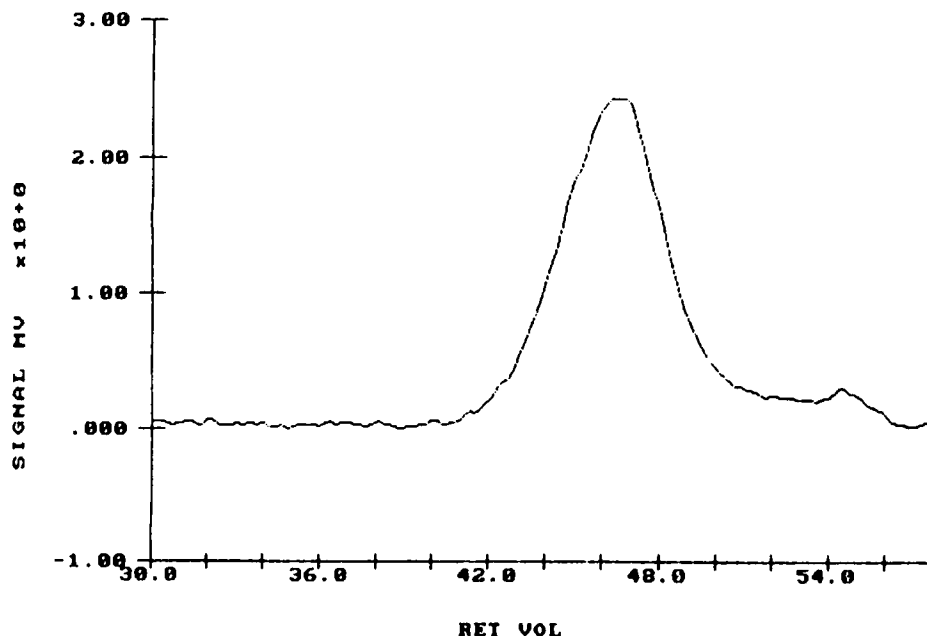


Figure 1 GPC chromatogram of poly(MMA-*co*-2-hydroxypropyl methacrylate)-graft-POE.

MMA/POE graft copolymers can be synthesized without gel formation.

## EXPERIMENTAL

### Synthesis of Poly(MMA-*co*-2-hydroxy propyl methacrylate)-Graft-POE

#### Preparation of Poly(MMA-*co*-glycidyl methacrylate)

Four samples of poly(MMA-*co*-glycidyl methacrylate) containing different amounts of glycidyl methacrylate were prepared by free radical polymerizations using benzoyl peroxide as initiator. The polymerizations were carried out at 90°C for 16 h under a nitrogen blanket. At the conclusion of this time period, the polymer was precipitated from solution with methanol (1/10 ratio of reaction solution to methanol).

#### Preparation of the Graft Copolymer

POE and poly(MMA-*co*-glycidyl methacrylate) were purified by a freeze-drying technique. The potassium alcoholate of POE was formed by reacting potassium methoxide with  $\alpha$ -hydroxy- $\omega$ -methoxy-POE. A tetrahydrofuran (THF) solution of this

material was placed into a reactor, and a THF solution of poly(MMA-*co*-glycidyl methacrylate) was added dropwise to this reactor. The reaction temperature was raised to 40°C and was held at this temperature for 1 day. After this period, the reaction was quenched by adding dry methanol. The reaction solution was concentrated using a rotary evaporator, and then the graft copolymer was precipitated in

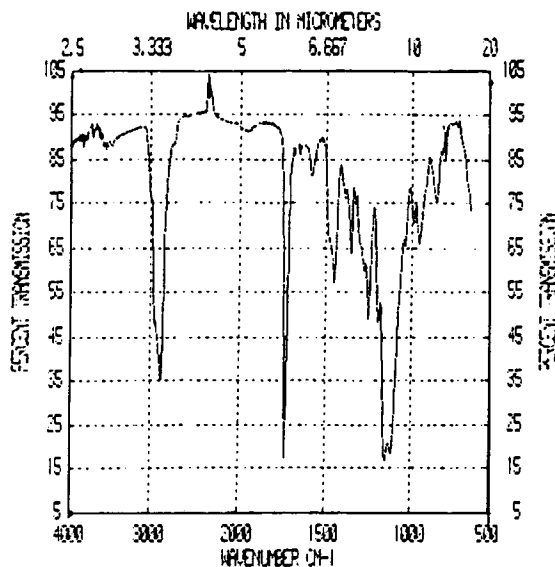


Figure 2 FTIR spectrum of poly(MMA-*co*-2-hydroxypropyl methacrylate)-graft-POE.

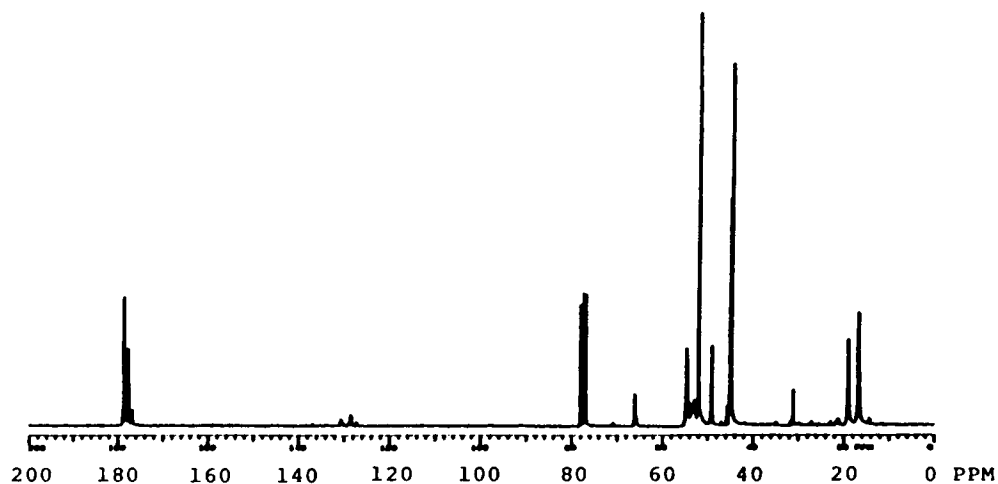


Figure 3 Decoupled  $^{13}\text{C}$ -NMR spectrum of poly(MMA-co-glycidyl methacrylate).

hexane. The precipitate was a light brown viscous mass with a pasty consistency. It was washed with ether so that the precipitate would completely solidify. The graft copolymer was purified by a fractionation technique. A total of six graft copolymers were synthesized, and their recipes are outlined in Ref. 8.

#### Characterization

The molecular weight of the graft copolymer was determined using gel permeation chromatography (GPC) with a Waters Associates 15C ALC/GPC instrument. Proof of copolymer formation was accomplished using Fourier transform infrared spec-

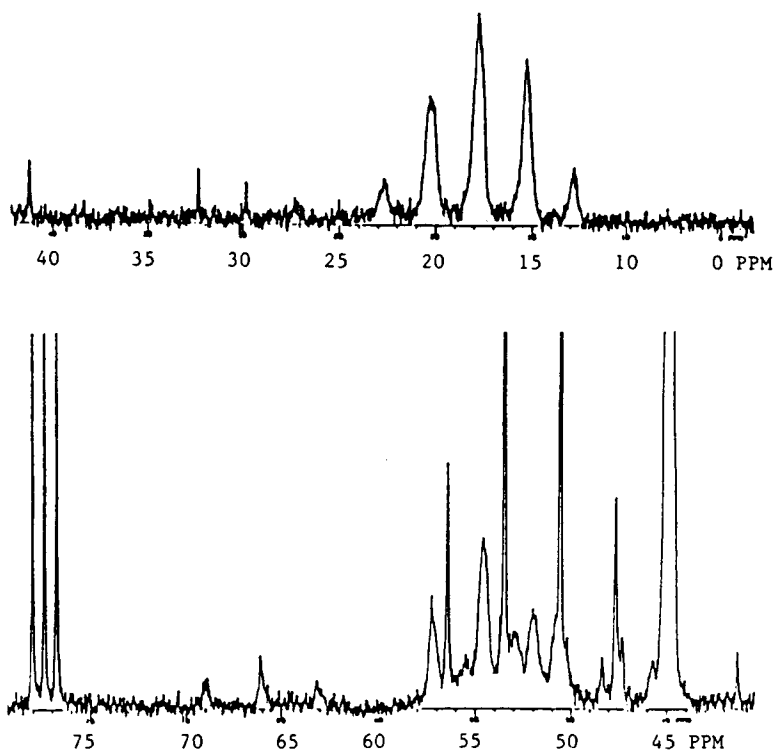


Figure 4 Coupled  $^{13}\text{C}$ -NMR spectrum of poly(MMA-co-glycidyl methacrylate).

**Table I**  $^{13}\text{C}$ -NMR Data for Poly(MMA-*co*-glycidyl methacrylate)

Carbon	Decoupling conditions chemical shift (ppm)	Coupling conditions chemical shift (ppm)
$\begin{array}{c} \text{CH}_3 \\   \end{array}$	18–20	Quartet 13–23
$\begin{array}{c}   \\ -\text{C}- \\   \end{array}$	44–44.5	Singlet 44–45
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -^*\text{CH}-\text{CH}_2 \end{array}$	49	Doublet <sup>a</sup> 46–53
$\begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ -\text{CH}-\text{CH}_2^* \end{array}$	45 <sup>a</sup>	Triplet <sup>a</sup>
$\begin{array}{c} \text{CH}_3 \\   \\ \text{O} \end{array}$	52–53	Quartet 47.5, 50.5, 53.5, 56.5
$-\text{CH}_2-$	54.5–55	Triplet 52, 54.5, 57.0
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -^*\text{CH}_2-\text{CH}-\text{CH}_2 \\ \text{C}=\text{O} \end{array}$	66	Triplet 63, 66, 69
	177–179.5	

\* = assignment for this carbon atom.

<sup>a</sup> Difficult to ascertain because of multiple chemical shifts in the region.

troscopy (FTIR) and carbon-13 nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$ -NMR) as described previously.<sup>8</sup>

## RESULTS AND DISCUSSION

### Synthesis of Poly(MMA-*co*-2-hydroxypropyl methacrylate)-Graft-POE

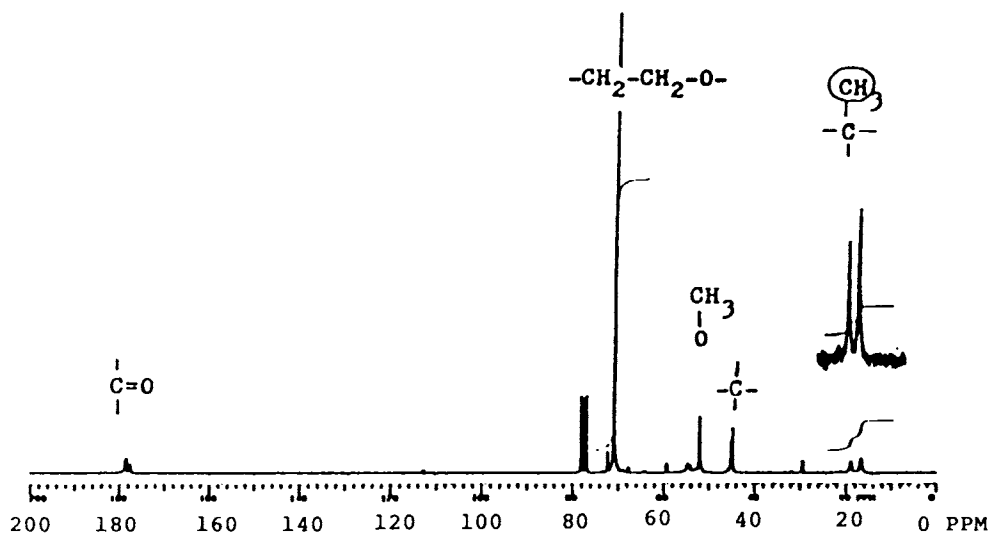
Poly(MMA-*co*-2-hydroxypropyl methacrylate)-graft-POE was synthesized by a "grafting-onto" technique. In this case, monofunctional POE was reacted with the epoxy groups in a copolymer of MMA and glycidyl methacrylate to form the graft copolymer with a methacrylate backbone and oxyethylene graft units.

### Preparation of Poly(MMA-*co*-glycidyl methacrylate)

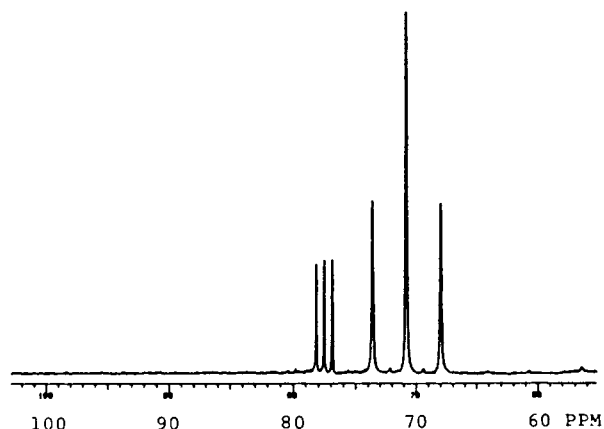
This random copolymer was prepared by the free radical polymerization of MMA and glycidyl methacrylate using benzoyl peroxide as the initiator. Since free radical polymerization was used, the molecular weight of the copolymer was fairly broad: MWD = 2.4. This distribution was made more narrow by using a fractionation technique.

### Preparation of the Graft Copolymers

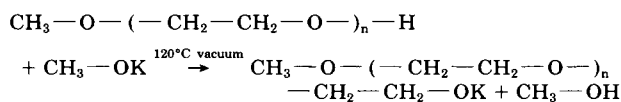
During this step, the functional end group of the POE was reacted with the epoxy groups of the poly(MMA-*co*-glycidyl methacrylate) to form the graft copolymers. Since the hydroxyl group exhibited a low reactivity toward the epoxy group, the hydroxyl group was modified so that it would become more reactive. This was accomplished by forming the potassium salt:



**Figure 5** Decoupled  $^{13}\text{C}$ -NMR spectrum of graft copolymer.

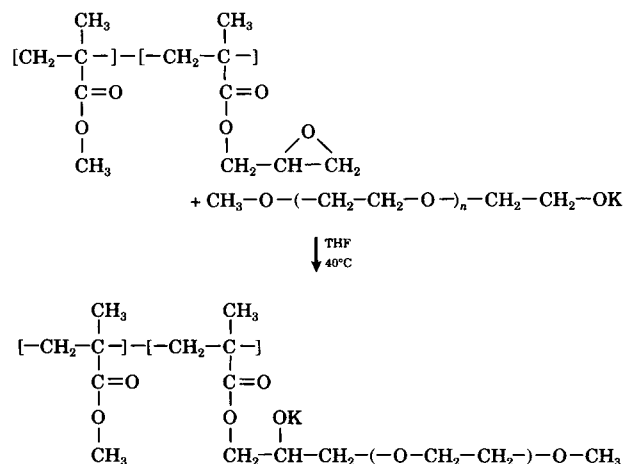


**Figure 6** Coupled  $^{13}\text{C}$ -NMR spectrum of graft copolymer.



As expected, the potassium alcoholate exhibited a much higher reactivity toward the epoxy group than did the hydroxyl group.

The poly(MMA-*co*-glycidyl methacrylate) was reacted with the potassium salt of POE in THF under argon at  $40^\circ\text{C}$ . The formation of the graft copolymer occurs according to the following reaction:



Then, the alkoxide was converted to the hydroxyl group by the addition of dry methanol.

During this grafting reaction, there are three side reactions that could occur: (1) Since commercially available POE was used, a small fraction of this polymer was difunctional. If both functional groups react, then this could result in the formation of cross-

links. To circumvent this problem, a 2.5 molar excess of the POE was used. By using an excess, there was predominantly unreacted POE available for the grafting reaction, and this reduced the probability of cross-link formation. (2) After the ring opening reaction occurred, a pendant alkoxide was formed on the backbone of the graft copolymer. This alkoxide could attack another epoxy group. If this reaction occurred intermolecularly, then the formation of cross-links would also result. This side reaction was prevented by adding the backbone copolymer to a reactor containing a solution of the POE. (3) Finally, the pendant alkoxide formed in the ring opening reaction could also attack the ester group in the methacrylate portion of the molecule. A low reaction temperature ( $40^\circ\text{C}$ ) was used to minimize this side reaction.

### Characterization of Methacrylate Copolymers

After precipitation of the crude reaction product, it was found to be 100% water soluble. This finding certainly indicates that all of the methacrylate copolymer was incorporated into the graft copolymer.

### Gel Permeation Chromatography of the Methacrylate Copolymers

After purification of the crude graft copolymers, they were studied using gel permeation chromatography (GPC). A typical chromatogram is shown in Figure 1. Proof of graft copolymer formation is illustrated by the peak in the high molecular weight region of 31,000 g/mol. In this case, the reaction between POE with a molecular weight of 2000 g/mol and

**Table II**  $^{13}\text{C}$ -NMR Data for Poly(MMA-*co*-2-hydroxypropyl methacrylate)-Graft-POE

Carbon	Decoupling Conditions Chemical Shift (ppm)	Coupling Conditions Chemical Shift (ppm)
CH <sub>3</sub>	18–20	
—C—	44–45	
CH <sub>3</sub>	52–53	
O		
—CH <sub>2</sub> —	54–55	
—CH <sub>2</sub> —CH <sub>2</sub> —O—	70–71	Triplet 68, 71, 74
—C=O	177–180	

poly(MMA-*co*-glycidyl methacrylate) with a molecular weight of less than 20,000 g/mol yielded a product with a much higher molecular weight. Moreover, this chromatogram showed that only a very small amount (less than a few percent) of the unreacted POE remained in the purified graft copolymer.

### ***Infrared Spectroscopy of the Graft Copolymers***

Infrared spectra were obtained for the graft copolymers as shown in Figure 2. As can be seen, this spectrum exhibits absorption bands that are characteristic of the oxyethylene polymer and the methacrylate polymer. The strong absorption band at 2900  $\text{cm}^{-1}$  is attributed to the C—H stretch in the oxyethylene group. Moreover, the strong absorption band at 1720  $\text{cm}^{-1}$  is attributed to the carbonyl stretch for the ester group in the methacrylate portion of the molecule. These absorption bands clearly show the presence of both the oxyethylene units and the methacrylate units in the purified reaction product and, thus, provide evidence for the formation of the graft copolymer.

### ***Carbon-13 Nuclear Magnetic Resonance Spectroscopy of the Methacrylate Copolymers***

Carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) spectra were obtained for the poly(MMA-*co*-glycidyl methacrylate) under decoupling and coupling conditions using a Varian Gemini-200. Typical spectra are shown in Figures 3 and 4 for the decoupling and coupling experiment, respectively. Spectra acquired under coupling conditions appear very different from spectra acquired under decoupling conditions. The difference is that the chemical shifts are sensitive to the coupling of the carbon atoms to specific nuclei bonded to the carbon atoms. In this case, the chemical shifts appear as lines that are equally spaced from the chemical shifts in the decoupled spectrum. This spectrum provides information as to the number of protons attached to a particular carbon atom. Thus, in most cases, methyl, methylene, methine, and quaternary carbons can readily be distinguished.<sup>9</sup> As can be seen from Figure 4, the methyl carbon resonance is now represented by a quartet, the methylene carbon resonance is represented by a triplet, the methine carbon resonance is represented by a doublet, and the quaternary carbon resonance is a singlet.

The chemical shift assignments and verification of each assignment are listed in Table I. Verification of these assignments can be obtained from the literature<sup>10-15</sup> and by comparing the spectra acquired

under decoupling and coupling conditions. Chemical shifts characteristic to poly(MMA-*co*-glycidyl methacrylate) are present as shown in Figure 3 and listed in Table I.

The  $^{13}\text{C}$ -NMR spectra were obtained for the graft copolymer under decoupled and coupling conditions as shown in Figures 5 and 6, respectively. The assignments of the chemical shifts are shown in Table II. These assignments were ascertained from the literature references.<sup>10-17</sup> Moreover, the spectra acquired under coupling conditions (Fig. 6) provide evidence that the chemical shift at 70–71 ppm in Figure 5 is a methylene carbon resonance for the methylene groups in the POE.

Proof of copolymer formation can be illustrated unequivocally by the identification of chemical shifts in Figure 5 that are characteristic to the methacrylate and the oxyethylene portions of the molecule. As listed in Table II, the chemical shifts at 18–20 ppm, 44–45 ppm, and 54–55 ppm represent the carbon atoms in the methyl, quaternary carbon, and methylene carbons of the methacrylate portion of the molecule, respectively. Also, the chemical shift for the carbon atom in the methoxy group of the MMA portion of the molecule appears at 52–53 ppm. The carbon atoms of the oxyethylene group are seen at 70–71 ppm. Appearance and disappearance of appropriate chemical shifts can illustrate that certain groups have reacted and, thus, provide evidence of copolymer formation. Disappearance of the chemical shift for the methine of the epoxy at 49 ppm shows that the epoxy group has reacted. Moreover, disappearance of the chemical shift for the terminal carbon atom containing the hydroxyl group in POE at 62 ppm illustrates that this hydroxyl group in the POE has reacted.

## **CONCLUSIONS**

This work shows that high molecular weight poly(MMA-*co*-2-hydroxypropyl methacrylate)-graft-POE copolymers can be prepared without the formation of gelled material. These graft copolymers were synthesized by a unique "grafting-onto" reaction. The number of grafts was easily controlled by controlling the number of glycidyl methacrylate units in the prepolymer used to prepare the graft copolymer. Since there was no byproduct formed during the grafting reactions, the grafting efficiency was quite high, as illustrated by the absence of the chemical shifts for the glycidyl group in the  $^{13}\text{C}$ -NMR spectra.

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