

Preparation and Reactions of Epoxy-Modified Polyethylene

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Synopsis

Epoxy-modified polyolefins have been prepared by the radical grafting of glycidyl methacrylate to polymer melts. The reactions of these materials with amines and carboxylic acids were investigated. The modified polymers undergo typical epoxide reactions.

INTRODUCTION

Polyolefin chemical reactivity can be modified without substantial loss of physical properties by grafting various functionalized monomers to the polyolefin. Maleic anhydride^{1,2} and trimethoxysilane-modified polyethylene³ are good examples of these types of materials. Chemically modified polymers have found wide use in a variety of applications, especially polymer blends.⁴

In this context, epoxy-modified polyolefins should be useful materials capable of reacting with both electrophiles and nucleophiles. In this paper, glycidyl methacrylate (GMA) has been grafted to low-density polyethylene (PE) or ethylene propylene rubber (EPR) melts, with radical initiators, to yield glycidyl methacrylate graft polyolefins.

The melt grafting reaction is a facile process for the preparation of epoxy modified polyolefins, avoiding the problems associated with chemical modifications attempted in solution or in copolymerization techniques.^{5,6}

The chemical reactions of glycidyl methacrylate graft polyethylene (PEgGMA) indicate normal epoxy functionality.

EXPERIMENTAL DETAILS AND RESULTS

Grafting of Glycidyl Methacrylate to Polyolefins

The modified polymers were prepared in a Haake® mixing bowl equipped with roller blades and coupled to a Model PL-4000-200 Rheocord® torque rheometer. Temperature and torque were monitored continuously. In all cases blade speed was 40 rpm.

A small electrically heated mixing bowl was preheated to 120°C and filled with 19.0 g low-density PE (Cities Service EH497, density 0.920). After mixing for 5 min, 1.9 g glycidyl methacrylate (stabilized with 50 ppm hydroquinone monomethyl ether, HQME) was added dropwise followed by 0.121 g dicumyl peroxide (DCP). The temperature was increased to 175°C and held there for 5 min. As in all cases of GMA grafting, no torque increase was observed. The modified

polymer was removed from the bowl and analyzed. Analysis of the polymer was done by infrared (IR) spectroscopy using pressed films of the polymer (prepared on a heated press; 120–150°C, 5,000 psi). The modified colorless polymer showed no crosslinking and could easily be pressed into thin films. In all cases, control experiments showed little or no grafting in the absence of peroxide.

The crude polymer was purified by precipitation from hot toluene, chlorobenzene, or phenylcyclohexane solution by addition to methanol, ethanol, alcohol/water mixtures, or chloroform. The procedure was repeated several times until the ratio of carbonyl-containing material to polyethylene (determined by IR spectroscopy) remained unchanged by further precipitation. (This was usually observed after one precipitation). The hot solutions of polymer were filtered through cheesecloth to determine, in a qualitative sense, if any gel was present. In cases of gel formation, quantitative determinations were also made (*vide infra*).

Attempted extraction of PEgGMA with hexafluoroisopropanol (HFIP) resulted in reaction of the polymer bound epoxy groups. No material was extracted from the polymer which had been previously precipitated from toluene with methanol.

The effects of type and concentration of peroxide on grafting are shown in Tables I and II. The percent grafting is an approximate value based on a correlation between oxygen analysis of the polymer and the ratio of the carbonyl stretch in PEgGMA (νCO , 1725 cm^{-1}) to the methyl bend (δCH_3 , 1380 cm^{-1}) in the IR spectrum. This relationship was assumed linear over the range of modification (Table III).

The polyethylene graft glycidyl methacrylate (PEgGMA) prepared in this manner showed good thermal stability below 200°C. No change in the IR spectrum was observed after heating for 1 h at 175°C. Little or no gel was present initially or after heating. (Upon standing for >1 month in sealed jars, a small degree of crosslinking was observed ~5–10% gel.)

The grafting of glycidyl acrylate (GA) to low-density polyethylene was achieved in a manner similar to that described for grafting GMA. The results of grafting are summarized in Table IV.

Grafting of GMA to EPR was conducted in a similar manner to the PE grafting reactions. A medium-sized mixing bowl was filled with 42.0 g of talc-covered

TABLE I
% Grafting vs. GMA Concentration

% GMA	DCP:GMA (mol)	$\nu\text{CO}/\delta\text{CH}_3$		Efficiency of Grafting ^a
		Precip	(Crude)	
2	1:30	—	(0.16)	9
5	1:10 ^b	1.04	(1.24)	60
5	1:30	0.64	(0.89)	38
5	1:50	0.51	(0.69)	30
5	1:100	0.39	(0.60)	23
6	1:20	0.92	—	45
10	1:30	2.31	(2.38)	67
10	1:50	2.38	(2.49)	70
10	1:100	2.03	(2.30)	59

^a Estimated from IR data.

^b Some crosslinking.

TABLE II
 % Grafting vs. Peroxide Concentration

BPO:GMA (mol) ^a	$\nu\text{CO}/\delta\text{CH}_3^b$		Efficiency of Grafting ^c
	Precip	(Crude)	
5% GMA—PE			
1:20	1.62	(1.71)	[95]
1:30	1.42	(1.44)	[86]
1:50	1.31	(1.33)	77
1:100	1.21	(1.23)	[67]
1:150	1.14	(1.18)	67
1:200	1.19	(1.25)	70
1:500	1.02	(1.15)	60
10% GMA—PE			
1:30	2.10	(2.21)	[65]

^a At BPO:GMA 1:10 polymer crosslinks with nonuniform dispersion of carbonyl-containing material.

^b Controls show νCO from BPO negligible.

^c Brackets indicate values determined by oxygen analysis; other values extrapolated from IR data.

pelletized EPR. The polymer was melted at 110°C. GMA (4.2 g) was dissolved in the melt followed by 0.475 g DCP. Grafting was accomplished by heating to 175°C. The grafting reaction was accompanied by a small torque increase. Grafting to EPR could be achieved without significant crosslinking (<5% gel); however, the system was more difficult to functionalize than PE. Grafting to ethylene propylene diene rubber (EPDM) was possible; however, EPDM undergoes considerable crosslinking during the grafting reaction.

High density PE gave some functionalization under radical grafting conditions with GMA and DCP, but grafting was less efficient than in low density PE or EPR. Grafting to polypropylene, polystyrene, methyl silicone rubber (SE-30),

 TABLE III
 Oxygen Analysis

Polymer	% Oxygen	$\nu\text{CO}/\delta\text{CH}_3$, precip	Grafting efficiency
5% PEgGMA	1.37	1.36	81
5% PEgGMA	1.61	1.62	95
5% PEgGMA	1.45	1.42	86
5% PEgGMA	1.14	1.21	67
10% PEgGMA	2.94	2.37	87
10% EPRgGMA	2.08	—	62

 TABLE IV
 Grafting of Glycidyl Acrylate

% GA	BPO:GA (mol)	$\nu\text{CO}/\delta\text{CH}_3$, precip 1×
2	1:100	0.3
5	1:20	1.75
5	1:50	1.40
6	1:10	1.52

and hydrogenated butadiene styrene copolymers was not observed under similar conditions.

Grafting of Maleic Anhydride to Polyethylene

Maleic anhydride (0.84 g) was added to a low-density polyethylene melt (42.0 g) which had been heated in a steel mixing bowl at 110°C. DCP was added (0.036 g) and the mixture was heated to 175°C for 5 min. The reaction was accompanied by an initial torque increase then a decrease; at this point, mixing was stopped. Analysis of the product indicated a maleic anhydride graft polyethylene (PEgMA) was formed. The material was uniformly functionalized and showed very little gel (<1%). The IR spectrum was unchanged after precipitation from hot toluene by addition to methanol. Grafting was not observed without peroxide.

Preparation and Separation of Poly(butyl Methacrylate)/Polyethylene Blends

n-Butyl methacrylate (50 ppm HQME) was grafted to a PE melt using 1:20 or 1:30 equivalents benzoyl peroxide (BPO) (decomp 130°C). Nominal grafting would have given 10% polyethylene graft butyl methacrylate (PEgBMA); however, grafting was not efficient. The grafting reaction was accompanied by substantial torque increase. A blend of 10% poly(butyl methacrylate), pBMA (DuPont Elvacite® 2044, Intrinsic viscosity 0.53) was prepared by adding a concentrated tetrahydrofuran solution of the polymer to the melt and heating at 130°C for 30 min. The ratio of carbonyl-containing material to polyethylene was determined from the IR spectra and monitored as the material was precipitated from hot toluene solutions by addition to methanol. The results of repeated precipitations are shown in Table V. Much of the homopolymer was extracted out; the graft showed almost no change.

PEgGMA Assay by Titration⁷

A sample of "6.0%" PEgGMA (1.0092 g), which had been precipitated three times from hot toluene by addition to methanol and dried, was dissolved in 25 mL hot chlorobenzene with 25 mL pyridine/HCl, (1.98×10^{-4} M HCl/mL). The solution was heated for 1 h under nitrogen (86–118°C). The polymer was then precipitated from solution by addition to methanol and carefully washed. The

TABLE V
Grafting of Butyl Methacrylate

Precip no.	$\nu_{\text{CO}}/\delta_{\text{CH}_3}$	
	10% <i>p</i> -BMA—PE	10% PEgBMA (1:40, BPO:BMA)
0	3.71	2.33
1	1.55	2.21
2	0.75	2.20
3	0.61	—
4	0.61	—

filtrate was back titrated with 0.1N NaOH/MeOH to a phenolphthalein end point. Analysis indicated 1.67 g oxygen/100 g PE (82% grafting) (3.47×10^{-4} M GMA/gPE). Oxygen analysis indicates 1.87 g oxygen/100 g PE (92% grafting) ($\nu\text{CO}/\delta\text{CH}_3$ ratio in IR spectrum indicates $\sim 87\%$ grafting). The IR spectrum also shows that some reaction of the ester may have taken place in addition to an elimination reaction giving a peak at 1640 cm^{-1} .

Reaction of PEgGMA with Benzoic Acid

A 5.5% PEgGMA melt was allowed to react with 1 eq of benzoic acid at 130°C for 10 min. At this point, a sample was taken and a second equivalent of benzoic acid added. After an additional 10 min, a sample was taken and the temperature increased to 180°C for 10 min. Spectra of the purified samples from this reaction all showed similar features, which were identical to those of a reaction of PEgGMA run with 1 eq of acid at 180°C for 30 min (IR Fig. 3). PEgGMA reacts with benzoic acid to form a β -hydroxy benzoate. A control experiment showed no retention of benzoic acid by a PE melt and no reaction of PEgGMA without the acid. Oxygen analysis of the hydroxy benzoate indicated 96% reaction of the epoxy groups (3.0% oxygen). This value may be a high estimate of epoxy content since other pathways for grafting acid may also occur. A refluxing toluene solution of PEgGMA with benzoic acid showed reaction of the epoxy groups after long heating (>15 h), but little or no grafting of benzoic acid was observed.

A toluene solution of purified hydroxy benzoate graft polymer was reacted with an excess of *n*-butyl isocyanate giving a carbamate-benzoate-modified polymer (IR Fig. 4). Nitrogen analysis (0.344%N) indicates 65% reaction with the hydroxy benzoate (as estimated from oxygen analysis).

Reaction of PEgGMA with Diacids and Diamines

The reactions of PEgGMA melts (5–10% GMA) with adipic acid, 1,3,5-benzenetricarboxylic acid, hexamethylenediamine, *n*-dodecylamine, and methyl benzylamine were run in a manner similar to that for the reaction of PEgGMA with benzoic acid. The reactions involved heating the polymer melts with various amounts of reagent ranging from 0.25 eq to a large excess, for 5–20 min. In some cases, similar reactions were run in toluene solutions of PEgGMA. Reactions were followed by IR spectroscopy, torque value, and percent gel determinations.

Percent Gel Determination

Percent gel values for various modified polymers were determined by placing a sample of the crude material (100–250 mg) between two nickel screens (200 \times 200 mesh) and extracting in a soxhlet for 24 h with toluene. Reaction of the modified polymers during extraction, changing the degree of crosslinking, cannot be excluded.

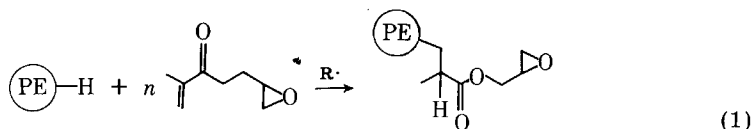
IR Spectra

All samples are pressed films: 120–150°C, 5,000 psi. Absorbances due to PE are omitted. PEgGMA (Fig. 2): 1725, 1265, 1150, 990, 905, 850 cm^{-1} . PEgGA: 1735, 1250, 1170, 910, 850 cm^{-1} . PEgGMA + HFIP: 3480, 1725, 1290, 1220, 1200, 1150, 1105, 690 cm^{-1} . PEgBMA: 1725, 1265, 1240, 1050 cm^{-1} . PEgGMA + PhCOOH (Fig. 3): 3500, 1725, 1605, 1585, 1275, 1115 cm^{-1} . PEgGMA + PhCOOH + $n\text{C}_4\text{H}_9\text{NCO}$ (Fig. 4): 3400, 1720, 1605, 1585, 1520, 1275, 1115 cm^{-1} . PEgMA: 1865, 1785, 1225, 1065, 920 cm^{-1} .

DISCUSSION

Radical Grafting to Polyethylene

Experiments were performed in an electrically heated steel mixing bowl using a low-density polyethylene (PE) melt. With benzoyl peroxide (BPO) as an initiator, a mixture of glycidyl methacrylate (GMA) in PE was reacted by heating to 140°C. A mixture of poly(glycidyl methacrylate) (pGMA) in PE was anticipated by a simple radical polymerization of the methacrylate. However, the modified polymer was completely homogeneous and infrared (IR) spectra of the modified PE after repeated precipitation from hot aromatic solvents with a variety of antisolvents showed no appreciable change after the first precipitation. The product appeared to be a graft of the methacrylate to PE.



The grafting of GMA is not accompanied by any torque increase, and high levels of GMA could be grafted to PE ($\leq 10\%$). The monomer was very soluble in the PE melt. At higher levels of GMA (15%), crosslinking was observed, the efficiency of grafting dropped, and a nonuniform distribution of carbonyl containing material was observed. There were problems in mixing the large amount of liquid monomer into the melt. The efficiency of grafting vs. monomer concentration is shown in Table I.

No grafting was observed without peroxide and grafting could be accomplished using monomer with stabilizer (50 ppm hydroxyquinone monomethyl ether, HQME) or without. At equivalent levels, BPO was more efficient than dicumyl peroxide (DCP) in promoting grafting. The effect of peroxide concentration is shown in Table II. Very high levels of peroxide did cause crosslinking. Prolonged heating (>1 h) of the product also caused a small degree of crosslinking.

Both glycidyl acrylate (GA) and glycidyl methacrylate (GMA) grafted to PE equally well (Table IV). After initial experiments, GMA was used in the grafting reactions due to its lower volatility. GMA was successfully grafted to ethylene propylene rubber (EPR) and ethylene propylene diene rubber (EPDM). Little or no grafting was seen using high density polyethylene, polypropylene, polystyrene, methyl silicone rubber (SE-30), or hydrogenated butadiene styrene copolymers. Attempted grafting to a low-viscosity polyethylene wax was un-

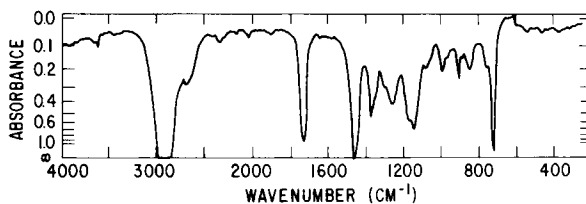


Fig. 1. Glycidyl methacrylate modified PE (PEgGMA).

successful, resulting in the formation of nodules of pGMA. Vinylcyclohexene oxide could not be grafted to low density polyethylene under free radical conditions.

The IR spectra of PEgGMA precipitated from toluene with methanol is shown in Figure 1. Bands at 1000, 900, 850 cm^{-1} clearly indicate the presence of epoxy groups.⁸ Unmodified PE is shown in Figure 2. In most cases grafting was monitored by comparing the carbonyl absorbance of the grafted monomer to the methyl group absorbance of PE. After the first precipitation of PEgGMA, subsequent precipitations had little effect on the ratio. Absolute levels of grafting were determined by oxygen analysis.

In order to prove grafting, attempts were made to prepare polyglycidyl methacrylate (pGMA) and blend it with PE. Separation of the mixture of two polymers under conditions where PEgGMA is not separated would be a good indication of grafting. Attempts to do this were thwarted by our inability to prepare high-molecular-weight noncrosslinked pGMA and blend it into PE. It was shown that unreacted monomer and low molecular weight oligomers could be easily separated from PE.

Addition of a solution of BPO in GMA to a hot melt of PE (175°C) could not be used to prepare a mixture of pGMA in PE. Under similar conditions, *N*-vinyl pyrrolidone and PE did give nodules of homopolymer with no grafting. (Under more favorable conditions, this system also grafts to PE.)

Attempted soxhlet extraction of PEgGMA with hexafluoroisopropanol (HFIP) led to incorporation of the solvent into the polymer. The IR spectra still retained a strong carbonyl absorbance.

Failure to retain any carbonyl-containing material in the attempted grafting to polystyrene and polypropylene along with the physical properties of PEgGMA point strongly to a graft. Even in the unlikely event that PEgGMA is not a graft, the two materials are very compatible and not easily separated.

The radical grafting of *n*-butyl methacrylate to PE melts was investigated as a model for the GMA grafting reaction.

The grafting of *n*-butyl methacrylate to PE melts was accomplished under

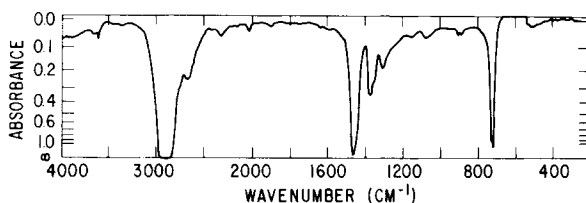
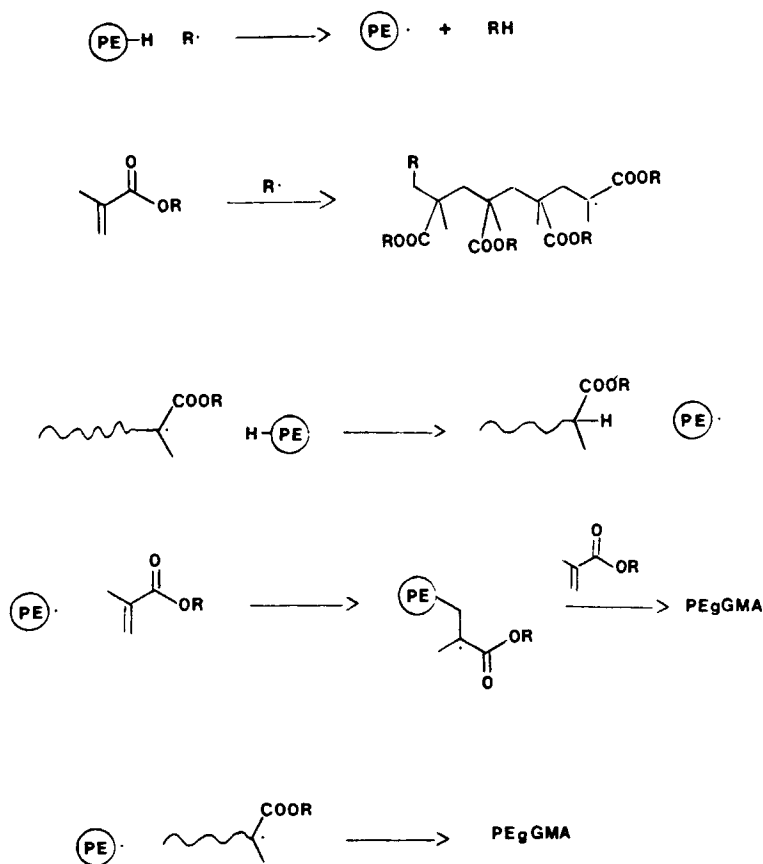


Fig. 2. Unmodified PE.

radical conditions, but the efficiency of the reaction was somewhat lower than the GMA case. The *n*-butyl methacrylate modified polymer, PEgBMA, contained some extractable material. Purification of the monomer or higher levels of peroxide had little effect on these results. (Very high levels of peroxide resulted in crosslinking.) Comparison of a blend of polybutyl methacrylate (pBMA) with PE, and PEgBMA were performed. The graft showed little change upon precipitation while the carbonyl absorbance in the pBMA—PE blend continued to diminish. After four precipitations, the homopolymer blend showed a small carbonyl absorbance which remained unchanged upon subsequent precipitation (Table V). A small amount of homopolymer is retained (grafted?) in the PE. The alkyl methacrylate showed no grafting in the absence of peroxide.

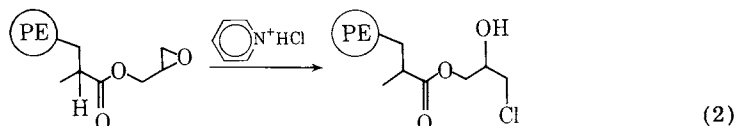
The grafting of GMA to PE is consistent with the reactions shown in Scheme I. All the reactions listed can occur; however, the rapid polymerization of methacrylates under radical conditions points to chain transfer as the key reaction.⁹ The formation of reactive sites on the polyolefin backbone is probably the result of chain transfer rather than abstraction by the direct products of peroxide decomposition. These reactive sites either add to vinyl monomer allowing the growth of a methacrylate chain or capture a growing methacrylate chain, resulting in grafting.



Scheme I

Reactions of Polyethylene Graft Glycidyl Methacrylate

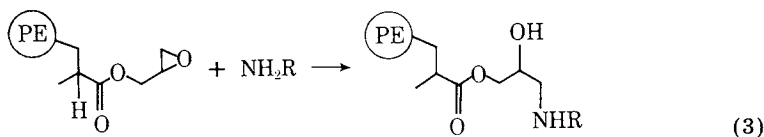
Several different methods were used to determine the extent of epoxy functionalization of PEgGMA. The IR spectrum showed the presence of epoxy groups, and oxygen analysis gave an upper limit to the extent of grafting. In an attempt to directly assay the epoxy groups on PEgGMA, a nonaqueous titration system was used. A hot chlorobenzene solution of PEgGMA was reacted with a standardized solution of pyridine hydrochloride in pyridine. After precipitation of the polymer, the solution was back titrated to determine the level of HCl addition to the polymer⁷ [eq. (2)]. IR analysis of this



material showed reaction of the epoxide, but formation of a 1640 cm^{-1} band in the IR spectra suggests elimination to form an olefin also. In addition, only a small amount of reagent was consumed, making very accurate determinations of epoxy number difficult.

Oxygen analysis of the PEgGMA used for the above reaction shows 5.3% GMA. Results of titration indicate 4.9% GMA, indicating that 92% of the GMA groups grafted to PE have epoxy functionality. This value is subject to error as discussed; oxygen analysis is not specific for epoxy content and is always a high estimate. Titration may not be 100% efficient and is accompanied by side reactions. The good agreement between these numbers (5.3, 4.9%) is heartening but may be fortuitous.

Other attempts to assay the epoxy content of PEgGMA were made by reacting the polymer with amines and determining the level of functionalization by nitrogen analysis¹⁰:



Reaction of an excess of *n*-dodecylamine with molten PEgGMA was slower than anticipated. After 5 min mixing at 110°C , the IR spectra still showed epoxy bands. Heating for 10 min ($110\text{--}150^{\circ}\text{C}$) resulted in complete disappearance of the epoxy bands. No amide formation was observed. The stability of the addition product under the reaction conditions was of some concern; further reaction of the initially formed adduct with a second epoxy group is possible.

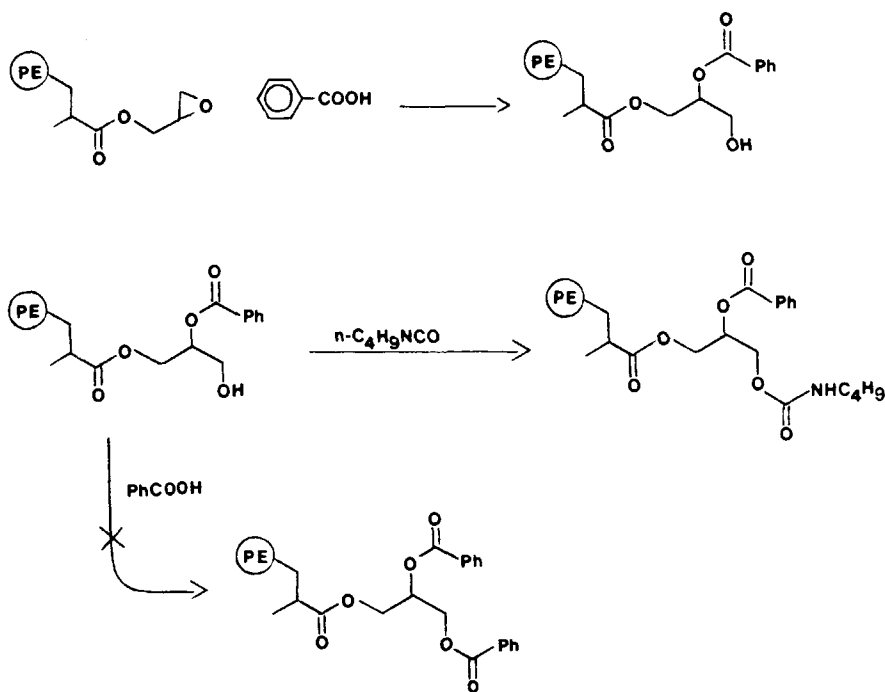
The results of nitrogen analyses of the product of the reaction of a PEgGMA melt with *n*-dodecylamine show a low level of epoxy functionalization. Assuming reaction of one epoxy group per equivalent of amine, 33% of the GMA grafted (determined by oxygen analysis) bear epoxy groups. The same reaction run overnight in a hot toluene solution of PEgGMA showed 44% epoxy functionalization. After 2 h the above reaction showed only 16% epoxy functionalization. (A second overnight run showed 47% functionalization.)

It was thought that the apparent low levels of epoxy functionalization might

reflect a second addition of the initial amine adduct to epoxide. If this occurs, each equivalent of amine will consume two epoxy groups, and the percentages determined above should be doubled (giving good agreement with the epoxy functionalization levels determined by other methods). This possibility was explored by treating a hot toluene solution of PEGGMA with methyl benzylamine. In this case, the amine should add to only one epoxy group. Nitrogen analysis of the precipitated product indicates 41% epoxy functionalization. This value is consistent with the assumption that the reaction with the primary amine consumes one epoxy group; however, it may also reflect lower reactivity of the secondary vs. primary amine.

The reaction of amines with PEGGMA leaves much to be desired as a method of determining the degree of epoxy functionalization. However, even if the lowest levels of epoxy functionalization determined are accurate, there is still 1.5–2.0% active GMA (by weight) bound to the polymer. Attempts to use nuclear magnetic resonance spectroscopy (NMR) to elucidate polymer structure did not yield useful results.

The reaction of PEGGMA and benzoic acid was investigated as a model for the reaction of polyester resins with PEGGMA. Under a variety of conditions in the melt, benzoic acid was added to PEGGMA to form a polymer bound hydroxy benzoate (Scheme II).¹¹ IR spectra (Fig. 3) indicate addition of only 1 eq of acid to the epoxide. Further reaction of the hydroxy group with benzoic acid was not observed even at long reaction times with a large excess of acid. The adduct showed good thermal stability, and the IR spectrum showed no change on heating at 185°C for 30 min.



Scheme II

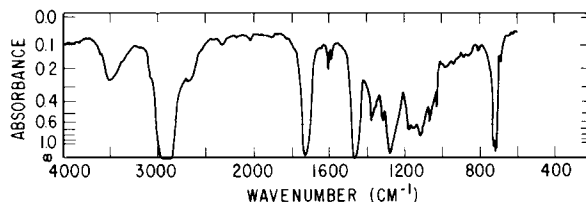


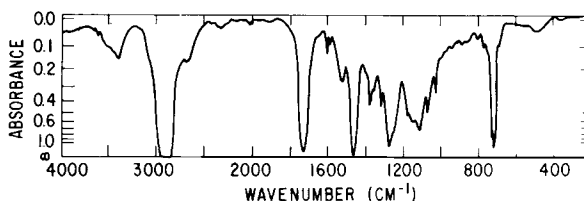
Fig. 3. PEGGMA + benzoic acid.

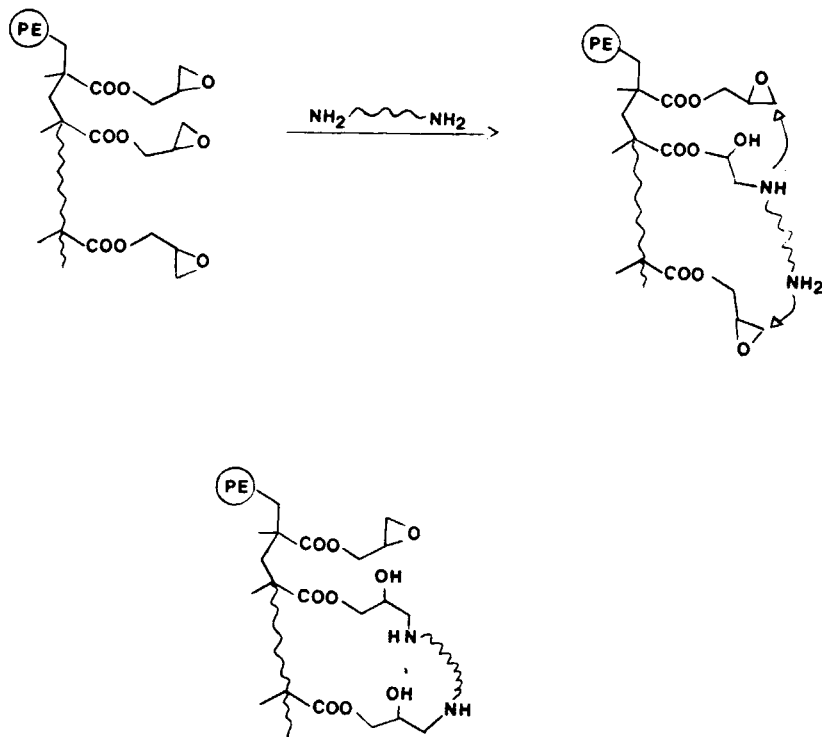
Oxygen analysis of the hydroxy benzoate indicated 96.0% reaction, assuming that one third of all oxygen initially present is epoxide, and that only 1 eq of acid adds to an epoxide group. The nature of the hydroxy benzoate was further elucidated by its reaction with *n*-butyl isocyanate (Scheme II). Both IR spectra (Fig. 4) and nitrogen analysis support the formation of the benzoate carbamate adduct. Assuming quantitative addition of isocyanate to alcohol and estimating alcohol concentration by oxygen analysis of the hydroxy benzoate, 65% of the hydroxy groups react to form carbamate. Another way to look at the results is that if the reaction of both the benzoic acid with epoxide and the isocyanate with hydroxy benzoate are quantitative, then about 62% of the GMA grafted had reactive epoxy groups.

Crosslinking of 10% PEGGMA using hexamethylenediamine (HMDA) was attempted. Half an equivalent of diamine, based on epoxy group content, was added to a polymer melt. A blend of the two materials heated to 180°C showed no substantial torque increase. IR spectra showed slow reaction of the epoxy groups with no amide formation. Percent gel was determined to be 54.2%. Higher or lower levels of diamine did not have substantial effects on the results. Similar results were seen in blends of 10% PEGGMA with adipic acid or 1,3,5-benzenetricarboxylic acid.

It was expected that in some instances crosslinking of PEGGMA would be very rapid and give percent gel values of 90% or higher, an indication of a very high degree of crosslinking. One explanation of the low degree of crosslinking is that the chemical reactions occurring are inefficient in forming bonds between the polyolefin chains. This inefficiency may be inherent in the chemical reactions used to achieve crosslinking; however, it may also be caused by the structure of the graft copolymer.

While there is no definite proof, it is reasonable to expect PEGGMA to contain long chains of grafted methacrylate. The rapid homopolymerization of PE primarily by chain transfer and capture of a growing GMA polymer chain.¹⁰ If this is the case, and the grafted GMA chains are isolated from each other, a large portion

Fig. 4. PEGGMA + benzoic acid + *n*-butyl isocyanate.



Scheme III

of the crosslinking reactions will result in addition to the same grafted polymer chain. This mechanism will result in the formation of loops in the grafted GMA chain without crosslinking (Scheme III).¹²

In order to test this hypothesis, the crosslinking of another modified polyethylene was examined. In maleic anhydride graft polyethylene,^{1,2} where the level of functionalization is low (1–2%) and the graft chain length is short, addition of a diamine gives highly crosslinked material. While the reaction giving rise to crosslinking is different from that in the epoxy-modified polymer, this result does give some support to the explanation of why extensive crosslinking is not observed in PEGMA reactions with diacids and diamines.

CONCLUSION

In summary, epoxy modified polyolefins can be prepared in the melt by radical grafting of glycidyl methacrylate. The material appears to be a graft rather than a mixture of homopolymers and has high levels of functionalization. *n*-Alkyl-methacrylate- and maleic-anhydride-modified polyolefins were prepared in a similar manner. The glycidyl methacrylate modified polyolefins undergo reactions typical of epoxides. The melt reaction with benzoic acid results in ring opening and attachment of the acid, via the reacted glycidyl methacrylate, to the polyolefin backbone. Addition of amines to the polymer-bound epoxy groups results in formation of a polymer bound amino alcohol. The addition of difunctional carboxylic acids or amines to PEGMA did not result in effective crosslinking. A related system, maleic anhydride graft polyethylene, is very

efficiently crosslinked by diamines. The inefficient crosslinking of PEGGMA is attributed to the longer length of the grafted polymer chain compared to the maleic anhydride case.

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