

Reactive Processing of Polymers: Melt Grafting of Glycidyl Methacrylate on Ethylene Propylene Copolymer in the Presence of a Coagent

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ABSTRACT: Glycidyl methacrylate (GMA) was grafted on ethylene-propylene copolymer during melt processing with peroxide initiation in the presence and absence of a more reactive comonomer (coagent), trimethylolpropane triacrylate (Tris). The characteristics of the grafting systems in terms of the grafting reaction yield and the nature and extent of the competing side reactions were examined. The homopolymers of GMA (Poly-GMA) and Tris (Poly-Tris) and the GMA-Tris copolymer (GMA-co-Tris) were synthesized and characterized. In the absence of the coagent, high levels of poly-GMA, which constituted the major competing reaction, was formed, giving rise to low GMA grafting levels. Further, this grafting system resulted in a high extent of gel formation and polymer crosslinking due to the high levels of peroxide needed to achieve optimum GMA grafting and a consequent large drop in the melt index (increased viscosity) of the polymer. In the presence of the coagent, however, the grafting system required much lower peroxide concentration, by almost an order of magnitude, to achieve the optimum grafting yield. The coagent-containing GMA-grafting system has also resulted in a drastic reduction in the extent of all competing reactions, and in particular, the GMA homopolymerization, leading to improved GMA grafting efficiency with no detectable gel or crosslinking. The mechanisms of the grafting reactions, in the presence and absence of Tris, are proposed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1401–1415, 2001

Key words: reactive processing; grafting of GMA; reactions on EP copolymer; coagent for grafting

INTRODUCTION

The chemical modification of commercial inert hydrocarbon polymers, such as polystyrene (PS), polypropylene (PP), polyethylene (PE), and their copolymers, using reactive functions has been

pursued actively over the last two decades with the aim of producing a new range of specialty materials.¹ Examples of commercial successes include the production of reactively grafted styrenic alloys, silane-modified and moisture-cured polyolefins, maleated polyolefins, supertough nylons, and thermoplastic elastomers.^{2–5} Reactive modification of these polymers was largely achieved either by carrying out the reaction in solution or in the solid state (through *in situ* reactions in polymer melts). The latter route for polymer modification by *in situ* reactive melt grafting has at-

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tracted considerable attention over the last 20 years due to its flexibility and cost benefits. Various reactive modifiers were exploited for the purpose of altering the properties of preformed polymers in a controlled manner and for promoting target reactions to achieve functionalization of polymers, compatibilization of polymer blends, interfacial coupling, crosslinking, and reactive stabilization.^{2,6-8} Examples of some of the most widely used modifiers include maleic acid and its anhydride, fumaric acid and acrylic acid and their corresponding esters, oxazoline, and glycidyl methacrylate.

Glycidyl methacrylate (GMA) is a bifunctional monomer containing an unsaturated group capable of free-radical grafting on hydrocarbon polymers, together with a highly electrophilic epoxide moiety which can react with different nucleophilic functions such as carboxylic, hydroxide, and amine groups. GMA has therefore been largely used to promoting reactive compatibilization in blends and alloys.⁹⁻¹¹ The grafting efficiency of GMA on different hydrocarbon polymers, however, has been shown to be generally low^{7,12,13} due to its low reactivity toward macroradicals and high tendency toward homopolymer formation.

To enhance the free-radical grafting efficiency of GMA on polymers, the grafting process was carried out in the presence of comonomers, such as styrene,^{14,15} and special initiating agents such as acrylamide.¹⁶ In our laboratory, we developed a broad and versatile approach to improving the grafting efficiency of functional modifiers (agents) on polymers by *in situ* cograftering of a small amount of a more reactive (compared to the modifier) bi- or polyfunctional comonomer, a coagent.^{6,17-21} The success of this method, in which the coagent acts as a reactive linker between the modifier and the polymer, relies on achieving a delicate balance between the molar ratios of the reagents (agent, coagent, initiator) and the process variables (e.g., temperature, residence time). It was shown, for example, that the use of the trifunctional coagent, trimethylol propane triacrylate (Tris), with different reactive modifiers, such as maleic anhydride¹⁸ and antioxidants,^{17,19} gave rise to a dramatic increase in the level of grafting of these modifiers on polymers. It was also demonstrated that, for example, in the case of reactive antioxidants, the antioxidant grafts on the polymer are indeed copolymers of the antioxidant and the coagent which are grafted on the polymer via one, or more, of the reactive sites of the coagent.²⁰

We report here our work on peroxide-initiated free-radical melt grafting of GMA on ethylene-propylene copolymer (EP), in the presence and absence of the trifunctional coagent Tris.

EXPERIMENTAL

Materials

Granules of Tafmar P-0480, an EP with a melt-flow rate of 1.7 g/10 min (at 230°C/2.16 kg), was kindly supplied by Mitsui Chemicals, Inc. (UK). GMA (97% purity) and Tris were used as received from Aldrich Chemical Co. (UK). The peroxide, 2,5-dimethyl-2,5-bis(*t*-butylperoxy) hexane (Trigonox 101, T101), kindly donated by Akzo Nobel (Netherlands), was used without further purification. Analytical grade chemicals and reagents were used for titration. All other chemicals and solvents were of general purpose grade.

Free-Radical-Initiated Melt Grafting of GMA on EP

The grafting reaction of GMA on EP was carried out in an internal mixer (RAPRA-Hampden torque rheometer). The preheated mixing chamber was initially flushed with oxygen-free nitrogen before introducing polymer samples containing a mixture of GMA and peroxide (T101) at different molar ratios. Processing was conducted in a closed mixer at 190°C with a rotor speed of 65 rpm. The processed polymer was cooled under a stream of nitrogen and stored in a freezer until required for further analysis. A different method of addition was adopted when the coagent (Tris, used at a ratio to GMA of 1 : 4 unless otherwise specified) was included in the formulation while maintaining the same reaction parameters (i.e., temperature and time).

Separation of Reaction Products

To ensure the accuracy of the reported level of GMA-grafting yield, the reaction products and free (unreacted) reactants were separated and removed prior to the determination of grafting yield of GMA. Initially, grafted polymer samples were either dissolved in hot toluene (in the absence of the coagent) or Soxhlet extracted (24 h) with toluene (in the presence of the coagent). When the coagent (Tris) was used, the homopolymer of Tris (poly-Tris), the copolymer of Tris and GMA (Tris-co-GMA), and crosslinked EP (CL-EP), were separated out as toluene insolubles. The toluene-

soluble fraction was precipitated in excess acetone to give a soluble fraction containing the modifier monomers (GMA, and Tris when used) and GMA homopolymer (poly-GMA) and an insoluble fraction containing the GMA-grafted polymer (EP-g-GMA). The purified acetone-insoluble EP-g-GMA polymer was then dried overnight in a vacuum oven at 80–85°C. This method was used throughout for determining the yield of graft GMA.

To calculate the amount of poly-GMA formed during the grafting reaction, a second separation route was followed. The toluene-soluble fraction was precipitated in this case by using excess methanol. The poly-GMA coprecipitates with the GMA-grafted polymer, and the amount of poly-GMA formed was determined from the difference of the two polymer separation methods.

Determination of the Grafting Yield of GMA

When GMA was grafted onto the polymer in the absence of the coagent, compression-molded films of the separated reaction products (i.e., acetone precipitated polymer) were characterized by FTIR and the grafting degree was determined from FTIR measurements by using a calibration curve which correlates FTIR data to titration results.

Infrared measurements were performed on a Perkin-Elmer FTIR Paragon 1000 (4000–400 cm^{-1}) spectrophotometer at a 1- cm^{-1} resolution and spectral collection over 10 scans. The epoxy ring absorption at 909 cm^{-1} was used to determine the extent of grafting by using the 720- cm^{-1} band (due to $-\text{CH}_2-$ absorption of the EP polymer) as a reference. The relative amount of grafted GMA was calculated from the ratio of absorption areas of peaks at 909 and 720 cm^{-1} ($A_{909\text{cm}^{-1}}/A_{720\text{cm}^{-1}}$). The level of grafting was determined from the calibration curve of the relative amount obtained by FTIR with the amount of grafted GMA determined by titration. The degree of grafting (yield) is the mass percentage of grafted monomer in the polymer, whereas the grafting efficiency is defined as the percentage

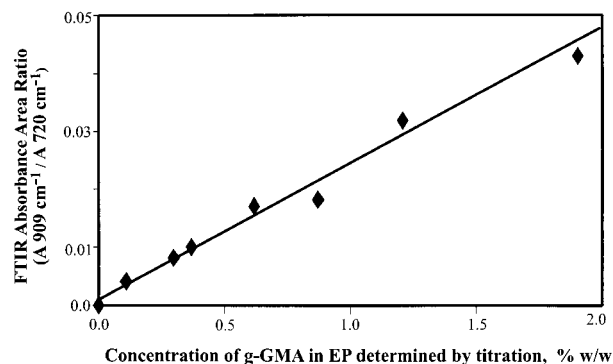
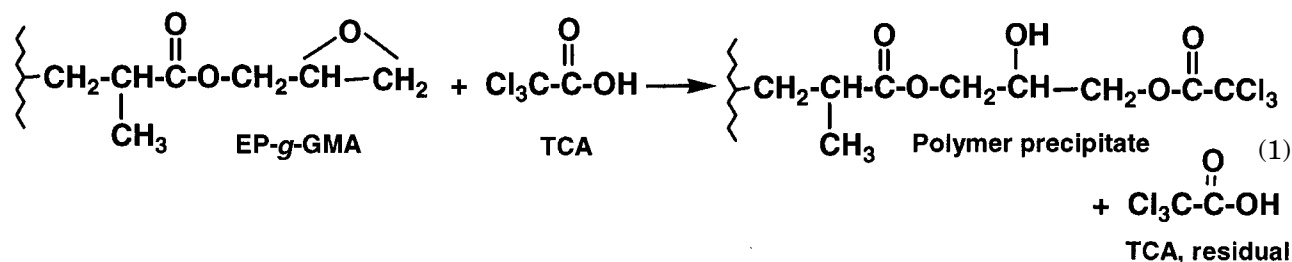


Figure 1 Calibration curve correlating the relative amount of *graft*-GMA determined from FTIR to that obtained by titration.

conversion of the total functional monomer initially added to the actual amount of grafted monomer achieved.

Calibration of FTIR Versus Titration Data for Grafted GMA Determination

A nonaqueous back-titration method was used to determine the degree of grafting of GMA.^{7,16} A calibration curve was developed to correlate the relative amount of *graft*-GMA as determined from FTIR measurements to that obtained by the titration method (Fig. 1). A sample of the purified GMA-g-EP polymer (1 g) was dissolved in hot toluene, followed by the addition of an excess amount of 0.3M trichloroacetic acid (TCA) solution in toluene. The mixture was stirred and maintained at 100–110°C for over 90 min to drive the ring opening reaction of the epoxy group (with the acid) to completion (reaction 1). The solution was then precipitated into excess ethyl acetate, filtered, and washed. The filtrate (residual TCA) was titrated with 0.1M KOH solution in methanol by using phenolphthalein as an indicator. Corrections were made on the basis of results from analogous experimental procedures using the unmodified polymer.



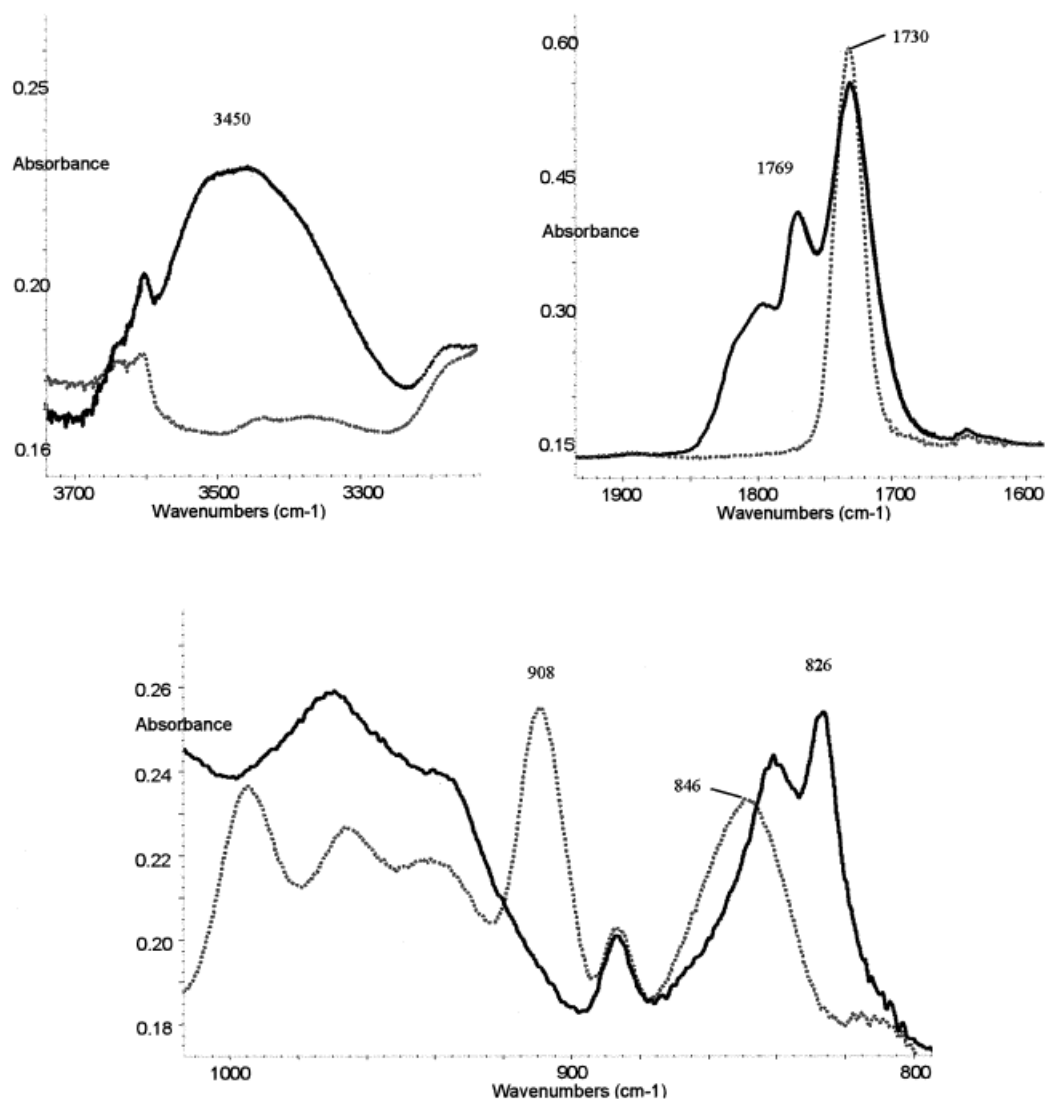


Figure 2 FTIR spectra of purified EP-g-GMA (---) film and that of the epoxide-ring open product precipitated during the nonaqueous back titration (—).

The precipitated polymer was dried and pressed into a thin film for characterization by FTIR. It was shown that the epoxide ring opening reaction goes to completion as can be seen from a comparison of the infrared spectra of the ring-open product (precipitated polymer film) with that of the original purified EP-g-GMA polymer film (Fig. 2). The infrared spectrum of the ring-open product shows a complete absence of the epoxide ring absorption (908 cm^{-1}) and retention of the GMA ester carbonyl absorption (1731 cm^{-1}), which is concomitant with the appearance of new bands at about 3450 and 1769 cm^{-1} , due to formation of an —OH group as a result of an epoxide ring opening and that of a chlorinated acetate ester carbonyl absorption, respectively (see reaction 1 and Fig. 2).

Polymerization of Agent and Coagent and Their Copolymerization

The homopolymerization of GMA was initiated by azoisobutyronitrile (AIBN, $0.1M$ ratio) under reflux with chloroform (argon atmosphere) for 4 h. The product, a white powder, was characterized as poly-GMA by using FTIR (formation of saturated carbonyl absorption at 1731 cm^{-1} , disappearance of unsaturation at 1637 cm^{-1} , presence of epoxide ring, 909 and 845 cm^{-1}) and $^{13}\text{C-NMR}$ to follow the disappearance of the double bond peaks at 125 and 136 ppm and appearance of saturated quaternary carbon and methylene carbon at 45 and 18 ppm, respectively. Poly-GMA was found to be soluble in acetone and chloroform

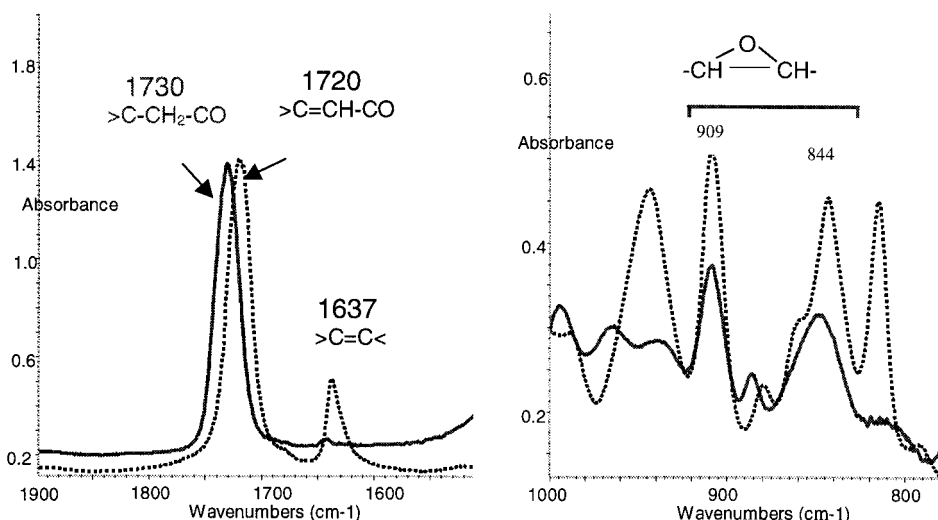


Figure 3 FTIR spectra of purified EP-*g*-GMA (—) thin film and that of GMA (---) measured in KBr disc.

at room temperature and in hot toluene but insoluble in methanol.

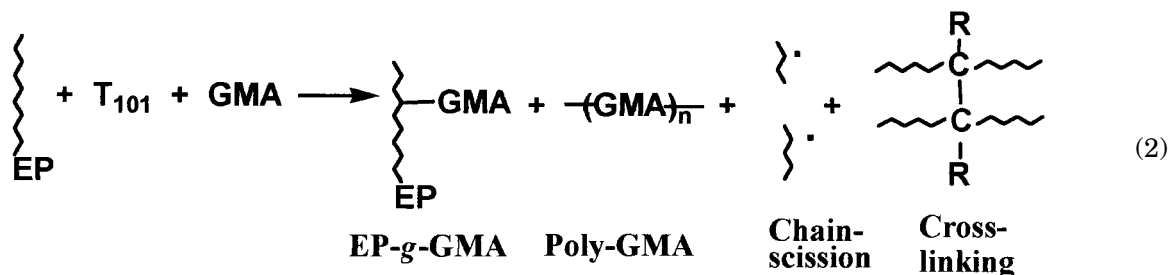
The homopolymerization of Tris was similarly carried out by using AIBN (0.3*M* ratio) under reflux with benzene (under argon) for 5 h. After evaporation of the solvent and drying, a white powder was obtained; this was characterized by FTIR and NMR as poly-Tris.²⁰ Poly-Tris was found to be insoluble in most organic solvents.

A mixture of GMA and Tris (weight ratio of 7/3) was heated in the presence of AIBN (0.1*M* ratio) in toluene at 70°C under argon for 5 h. After evaporation of the solvent, washing with acetone (to remove any free GMA, free Tris, and poly-GMA), and drying, a white powder was obtained; this was characterized by FTIR and NMR as GMA-*co*-Tris.

RESULTS AND DISCUSSION

Peroxide-Initiated Grafting System Containing Monomer, GMA, Only: Effect of Concentration on the Nature and Yield of the Grafting Reaction

Alongside the target melt free-radical-initiated grafting reaction of GMA on EP (EP-*g*-GMA), there are at least three other undesirable competing side reactions: homopolymerization of GMA (poly-GMA) and crosslinking and chain scission of EP (reaction 2). The relative contribution of these reactions depends both on the chemical composition of the grafting system and on the melt processing conditions. The main aim of this work is to optimize these conditions in favor of the target grafting reaction.



GMA was melt processed in EP in the presence of a peroxide (T101) and the GMA-grafted polymer was characterized by FTIR after purification. The purification method resulted in the separa-

tion and complete removal of the homopolymer, poly-GMA, which was characterized (by FTIR) and found to have identical spectral characteristics to that of the synthesized poly-GMA sample.

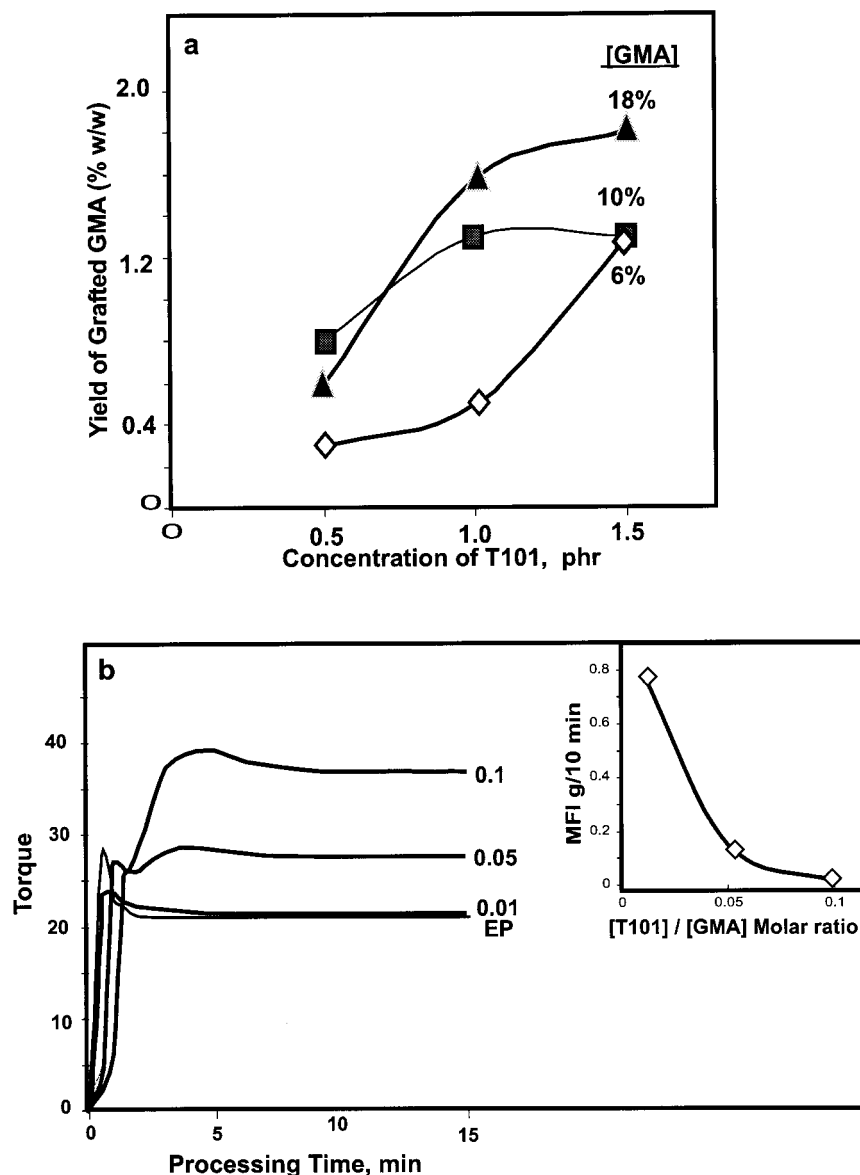
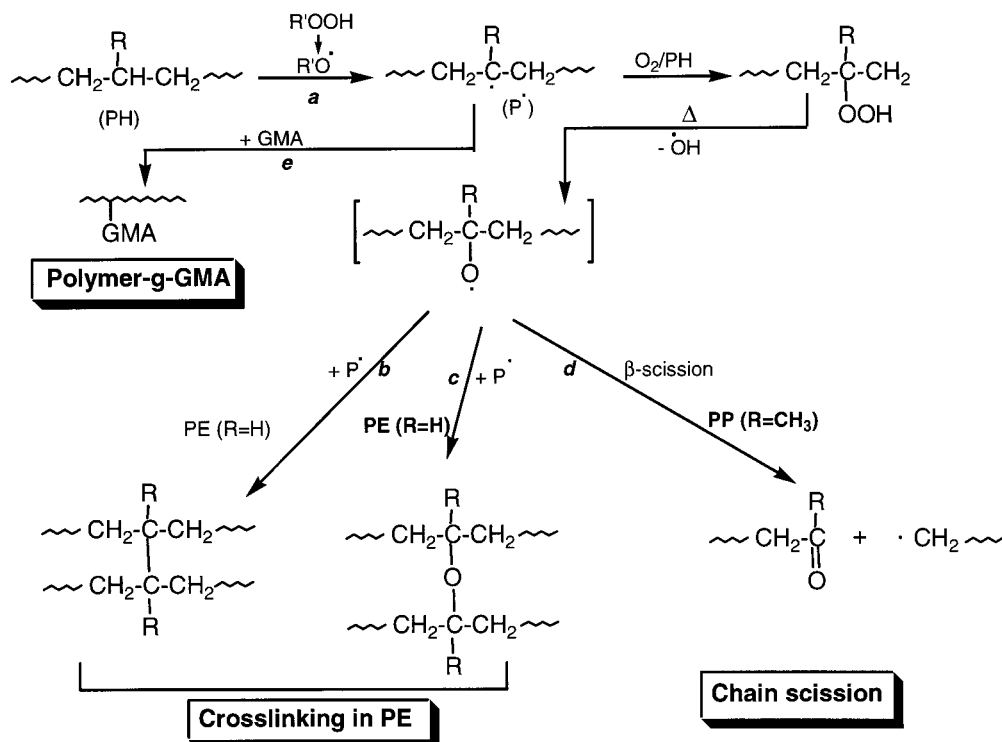


Figure 4 (a) Effect of peroxide concentration on the grafting yield of GMA in EP; numbers on curves are the initial concentration of GMA. (b) Effect of peroxide-to-GMA molar ratios (numbers on curves) on changes of torque during melt processing of EP; inset shows the corresponding changes in the melt flow index measured at the end of processing.

Figure 3 shows the FTIR spectra of a purified EP-g-GMA sample and that of GMA. A comparison of the FTIR spectra shows clearly the absence of absorption at 1637 cm^{-1} ($>\text{C}=\text{C}<$ of GMA) in the grafted polymer, together with a red-shift in the ester carbonyl absorption (shift from 1720 to 1730 cm^{-1}), which is ascribed to the formation of a saturated ester. Further, the presence of the epoxide ring (with absorptions at 908 and 844 cm^{-1}) in the EP-g-GMA polymer shows the avail-

ability of the epoxide functionality for further reactions.

The effect of peroxide concentration on the grafting yield of GMA on EP can be seen clearly from Figure 4(a), where the grafting yield of GMA shows an overall increase at higher peroxide concentration. However, closer examination of the torque behavior during melt reactive processing reveals that higher peroxide concentrations give rise to higher torque values, indicating an in-



Scheme 1 Oxidative degradation reactions of EP and grafting of GMA.

crease in polymer viscosity, whereas much lower peroxide concentrations show only a slight effect [Fig. 4(b)]. The type of polymer used in a grafting system is expected to affect the nature of polymer side reactions. In this study, the EP polymer used has a high-ethylene content (ethylene/propylene = 4). It is well known that polyethylene undergoes predominantly crosslinking reactions (through the secondary macroalkyl radicals) during melt processing (see Scheme 1, rns b and c), resulting in an increase in molar mass and viscosity of the polymer, whereas polypropylene undergoes primarily β -chain scission (via the tertiary macroalkyl radicals; see Scheme 1, rn d), leading to reduction in the molar mass.²² The higher peroxide concentrations, which are needed in this system to achieve higher grafting levels, appear to give rise to oxidative degradation of the polymer which is dominated by crosslinking reactions as indicated by the observed higher torque levels [e.g., Fig. 4(b), curve 0.1] associated with higher polymer viscosity. Further evidence of polymer crosslinking at higher peroxide concentrations was obtained from measurement of the extent of insoluble gel determined by extraction in hot toluene (note that the unmodified polymer is completely soluble under these conditions). For

example, a peroxide-to-GMA molar ratio of 0.1 gave higher grafting with 10% gel, whereas very little grafting and no measurable amount of gel was formed at a molar ratio of 0.01.

Overall, therefore, an increase in peroxide concentration in the grafting system leads to the generation of more macroradical sites (Scheme 1, reaction a) resulting in higher GMA-grafting yield (reaction e). However, high initiator concentrations would induce a higher degree of polymer degradation and, in the case of the EP copolymer used here, the above experimental results support the view that crosslinking reactions of the ethylene units predominate the overall degradation process (see Scheme 1, reactions b and c). Similar observations were reported for polypropylene,^{13,23} where high GMA grafting levels were achieved in the polymer at high initiator concentrations, giving rise to severe polymer degradation concomitant with a reduction in molar mass.

It is important to point out that over the entire range of peroxide concentrations examined, the GMA-grafting efficiency is shown to be low; for example, at the low-molar ratio (peroxide-to-GMA) of 0.01, where polymer degradation is minimal, the GMA grafting efficiency was found to be

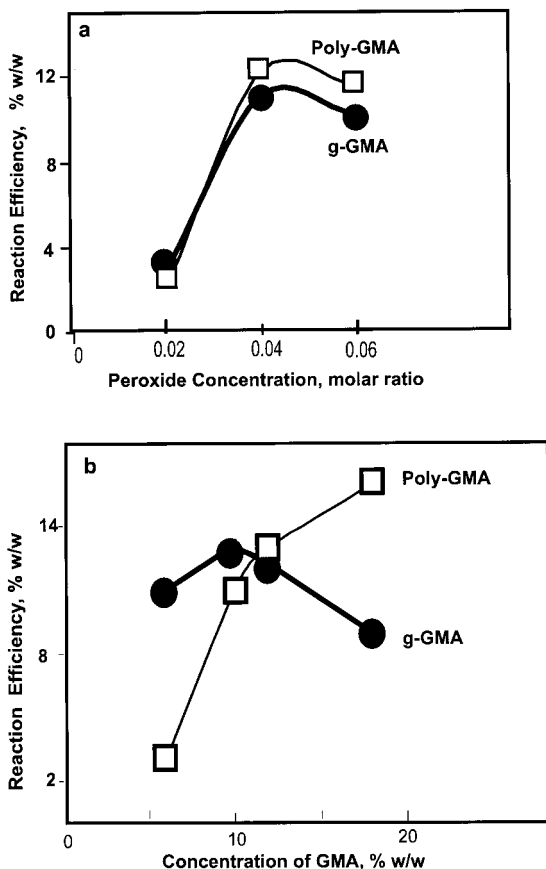


Figure 5 Effect of (a) peroxide concentration and (b) GMA concentration ($[T_{101}] = 1$ phr), on the extent of grafting and homopolymerization of GMA.

only 3%. Low-grafting efficiency of GMA in polyolefins has also been reported by others.^{12,13} The observed low grafting yield of GMA is almost certainly due to the predominance of the main competing side reaction, the GMA-homopolymerization (poly-GMA). Homopolymerization of different modifiers containing unsaturated reactivity has been shown previously in many other systems to be the one most important contributory factor to low levels of grafting.^{24,19} Figure 5 illustrates this clearly in the case of GMA and shows that the amount of poly-GMA formed exceeds the level of grafting, particularly at higher GMA concentrations. It is also clear [Fig. 5(b)] that the grafting efficiency of GMA is not directly proportional to GMA concentration; it shows a maximum at an initial GMA concentration of about 10% followed by a drop at higher GMA levels. This drop in grafting yield is paralleled by a large increase in the amount of homopolymer formation. The presence of a maximum in the grafting efficiency

curve must, therefore, be due to the greater propensity of the GMA-radical coupling reaction at the higher GMA levels, which facilitates further the GMA-homopolymer formation at the expense of the target GMA-EP grafting reaction.

Examination of the kinetics of GMA homopolymer and graft formation (e.g., in a grafting system containing a molar ratio of peroxide-to-GMA of 0.05) shows clearly that from the onset of the reaction the homopolymerization is in direct competition with grafting (see Fig. 6). In this system, the initial rate of formation of poly-GMA at the beginning of the reaction is slower than the rate of its grafting but, as the melt processing operation continues, the concentration of the homopolymer continues to rise, whereas the grafting reaction reaches its maximum level within the first 5 min of the reaction.

Peroxide-Initiated Grafting System Containing Monomer and Coagent, GMA, and Tris

Effect of the Coagent on the Nature of the Grafting Reaction

The above discussion shows that the overall grafting efficiency (conversion) of GMA on EP is low and that much higher peroxide concentrations are needed to achieve higher conversion rates, albeit at the expense of degradation of the polymer. We have shown previously^{6,17,18,20} that the free-radical grafting yield in polymer melts of modifiers with free-radical reactivity (e.g., an ethylenically

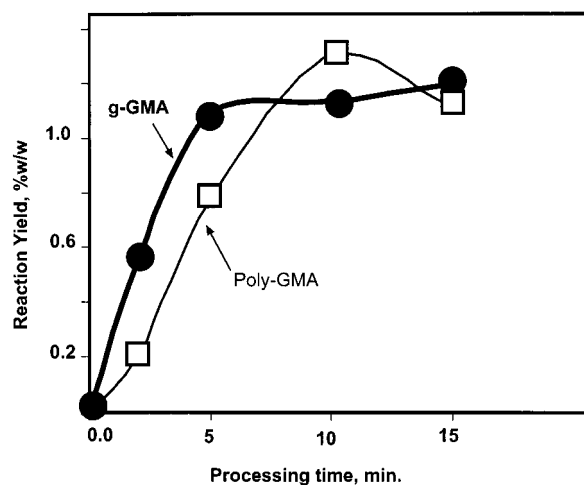


Figure 6 Rate of GMA graft and homopolymer formation during the melt processing of EP containing an initial GMA concentration of 10% and peroxide-to-GMA molar ratio of 0.05.

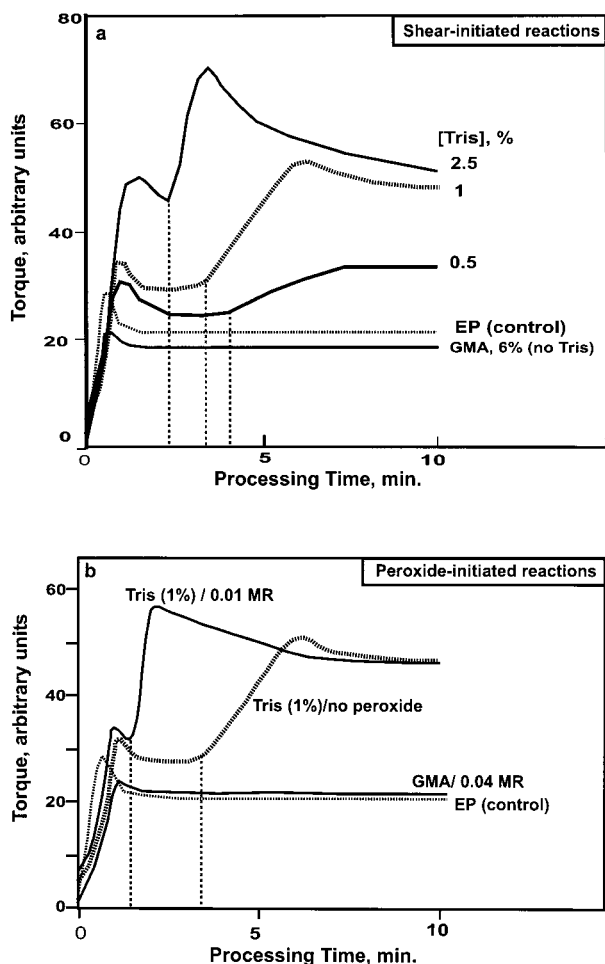


Figure 7 Torque–time curves for (a) shear-initiated reactions and (b) peroxide-initiated reactions in EP containing Tris and GMA separately (MR is molar ratio of peroxide to monomer).

unsaturated group) and functional reactivity (e.g., antioxidant, acid, or anhydride function) is substantially improved by the addition of a small concentration of a highly reactive comonomer (co-agent) containing no functional reactivity but having two or three unsaturated polymerizable functions with strong free-radical reactivity (e.g., Tris). It was shown that the grafting efficiency of, for example, monofunctional antioxidants can be improved from as low as 10–40% to in excess of 80–90%.^{17,20} The key to this approach is the *in situ* cografting of a small amount of the reactive coagent (linker) that can be achieved through a delicate balance between the composition of the chemical system and process conditions.

Reactive monomers containing more than one polymerizable group have been used previously as crosslinking agents for polymers (due to their

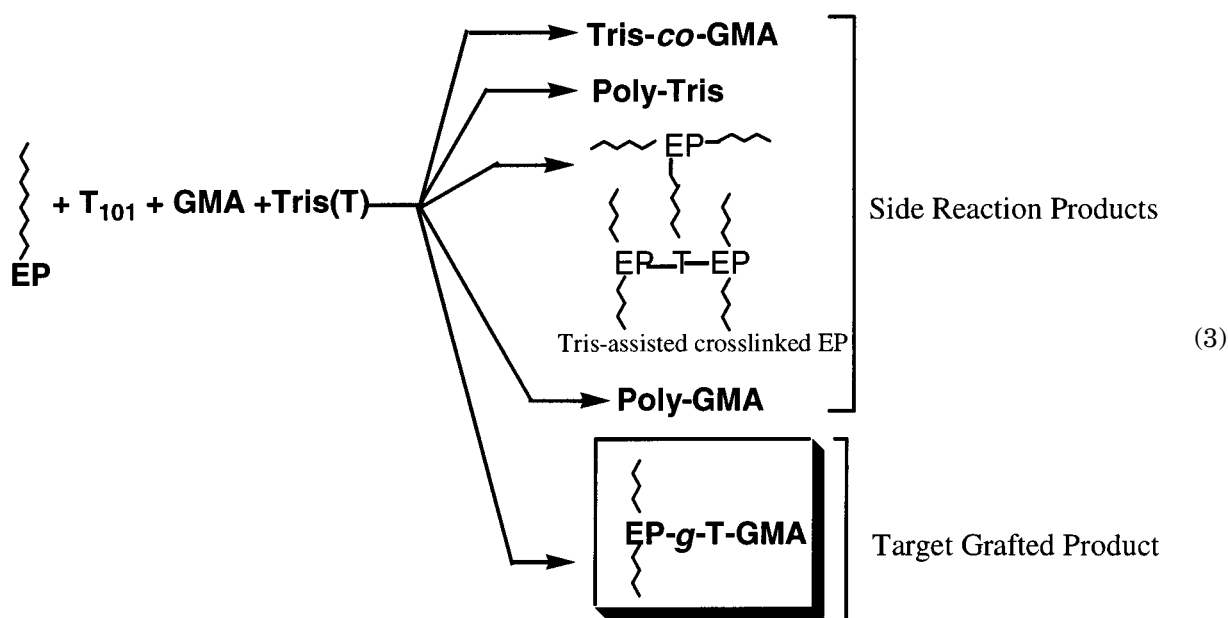
high free-radical reactivity).²⁵ The novelty of the approach that exploits such reactive molecules to assist in the melt grafting of less reactive functional monomers arises from the finding that not only higher levels of grafting can be achieved but also with minimum, or no crosslinking or degradation to the modified polymers.^{17,20} To understand the role of one such reactive comonomer (Tris) on the grafting reaction of GMA in EP, the torque behavior of the polymer melt was initially investigated in the presence of Tris and GMA separately, both in peroxide-initiated and shear-initiated (i.e., in the absence of peroxides) grafting systems. In the shear-initiated system [Fig. 7(a)] for EP-containing GMA, the torque shows a leveling off after a slight initial decrease which is comparable overall to the torque behavior observed for the unmodified virgin EP (control) sample. In the presence of Tris, however, the torque values reach a maximum after an initial slight drop. The effect of Tris concentration appears to result in the displacement of the onset of the torque maximum to shorter times (e.g., 4 min at 0.5% w/w and 2.5 min at 2.5% w/w Tris) while, at the same time, showing higher maximum torque values. This observation suggests that, in the presence of shear-induced polymer macroradicals, higher concentrations of Tris give rise to an increase in both the rate and yield of its reaction with the polymer.

In the case of a free-radical-initiated reaction [see Fig. 7(b)], the use of a very small concentration of a free-radical initiator (T101) with Tris causes an even more noticeable shift to the onset of the torque peak to shorter times, as well as a further increase in the maximum torque (peak) value; this will then drop to lower values at longer reaction times. This behavior illustrates clearly the much faster rate of peroxide-initiated Tris reaction (than shear-initiation) with polymer macroradicals. For example, for the same Tris concentration of 1%, in the absence of peroxide, the onset of the torque peak occurred at 3.5 min (peak maximum at 6 min), compared to an onset at 1.5 min (and peak maximum at 2 min) in the presence of 0.01M ratio of peroxide [see Fig. 7(b)]. The torque changes were very different when the polymer was processed with GMA by using the same peroxide-initiation conditions: here there is no observed torque peak and the overall changes in the torque are quite similar to that of the unmodified polymer. It is evident from this drastic difference in the torque behavior of Tris compared to GMA, that the free-radical reactivity of

Tris toward the polymer macroradicals is much higher than that of GMA macroradicals under both shear-initiated and free-radical-initiated melt-grafting processes.

The torque behavior of Tris, therefore, indicates an initial occurrence of both grafting/branching and crosslinking reactions (torque peak) followed by some chain scission (subsequent torque reduction). The use of such a reactive multifunctional comonomer in the GMA grafting system may be expected, therefore, to result in a more complicated grafting system. Thus, in addition to the formation of poly-GMA, a number of other side reactions involving the Tris

coagent are expected to compete with the target GMA-grafting reaction, including the formation of ungrafted copolymer of Tris and GMA (Tris-co-GMA) as well as a Tris homopolymer (poly-Tris), together with possible polymer crosslinking that may occur via reaction of the reactive functions of the coagent with the polymer macroradicals (see rn 3). Provided that the contribution from these undesirable side reactions can be controlled and kept to a minimum, the higher reactivity of the coagent Tris could, therefore, be exploited suitably to enhancing the grafting of a less reactive monomer such as GMA on polymers.



The extent of competition from the Tris-GMA copolymerization side reaction was found to depend on the method of mixing. Introducing a pre-mix of all the reactants (GMA, Tris, and peroxide) into the mixing chamber in single shot resulted in an increase in the copolymerization yield and was paralleled by a decrease in the extent of GMA homopolymerization. To confirm the identity of the free copolymer formed, the polymer products obtained by using this mixing methodology were purified and the toluene-insoluble material was separated out from the EP polymer and was characterized by FTIR; for example, 11% insoluble material was formed when using a molar ratio of 0.05 of Tris/GMA. The infrared spectrum of the isolated (toluene-insoluble white powder) mate-

rial revealed that it does not contain any EP polymer (i.e., no crosslinked EP); its spectral characteristics were identical to that of a synthesized Tris-co-GMA copolymer, which confirms the high extent of free copolymer formation by this method of mixing. The formation of ungrafted Tris-co-GMA copolymer was, however, greatly minimized and in most cases eliminated, by altering the addition sequence of the reactive components. When GMA and peroxide were incorporated in the polymer melt subsequent (after 1 min) to the addition of Tris, practically no free copolymer formation was formed and this was also associated with an appreciable improvement in the GMA-grafting efficiency. This addition sequence was, therefore, subsequently adopted for all the Tris-containing

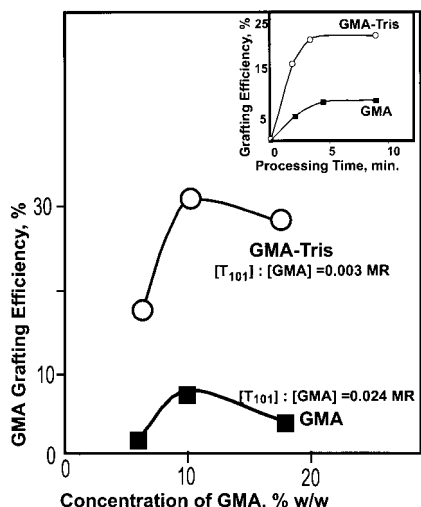


Figure 8 (a) Effect of GMA concentration EP in the presence and absence of Tris on its grafting efficiency; inset shows the rate of the grafting reactions. (b) Grafting efficiency and the concentration of peroxide required for GMA grafting in the presence and absence of Tris.

sample preparations, which were found to be free from the ungrafted Tris-GMA copolymer.

The finding that the former mixing methodology (as pointed out above) results in the formation of an appreciable amount of free Tris *co*-GMA copolymer but with no poly-GMA is both interesting and important. It suggests that the reactivity of Tris radicals toward GMA (i.e., copolymerization) is higher than the reactivity of GMA radicals toward GMA (homopropagation resulting in poly-GMA). Although the presence of an ungrafted (free) Tris-*co*-GMA copolymer is undesirable (and this has been eliminated successfully in optimized systems), the differences in reactivities is in itself an important finding because the aim in using the co-reactive monomer (Tris) is to enhance the reactivity of GMA and its grafting on the polymer while decreasing the extent of GMA homopolymerization and contributions from other side reactions. As to whether this overall aim can be achieved will be tested experimentally (see below).

Effect of the Coagent on the Grafting Efficiency and the Yield of the GMA Homopolymer

In view of the high reactivity of the coagent Tris toward both the polymer macroradicals and GMA, its effect on the GMA-grafting efficiency and the fate of the most important undesirable

side reaction (i.e., GMA homopolymerization) are examined. Figure 8 shows clearly that the use of the coagent leads to a significant improvement in the grafting efficiency of GMA on EP as well as to increasing the rate of the grafting reaction (see inset). Another advantage in using the Tris coagent is that the higher levels of grafting observed are achieved at much lower peroxide concentrations, resulting in a negligible amount of peroxide-initiated polymer degradation; for example, in the presence of Tris over 30% grafting efficiency is achieved by using 0.003 peroxide molar ratio, whereas less than 9% efficiency is achieved by using more than an order of magnitude higher peroxide concentration (0.02M ratio of peroxide-to-GMA) in the absence of Tris (see Fig. 8).

Although the grafting efficiency is clearly improved in the presence of Tris, the question still remains as to whether this apparently complex system could lead to simple grafting without the persistence of side reactions that would adversely affect the polymer properties. Both the torque behavior and the amount of toluene-insoluble gel (determined chemically) formed in the presence and absence of Tris were examined. The Tris-containing GMA system produced no measurable amounts of gel (completely toluene soluble) under all conditions tested, in contrast to grafting systems containing no Tris, where significant amounts of gel were formed. For example, in a system containing 6% GMA and 1.5 phr peroxide, 10% insoluble gel was formed and this system

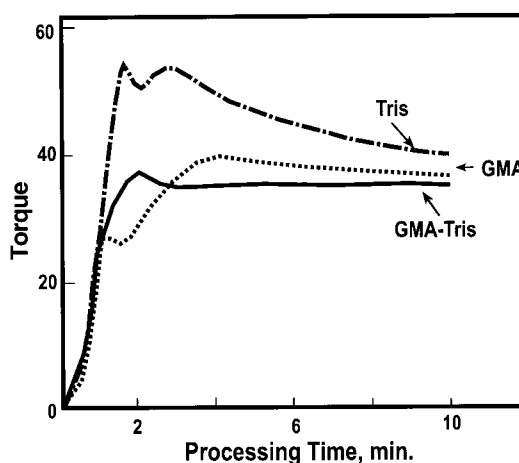


Figure 9 Torque-time curves for EP processed with GMA ($[peroxide] = 1.5$ phr) and Tris ($[peroxide] = 0.05$ phr) separately and with Tris and GMA together ($[peroxide] = 0.13$ phr). Concentration of GMA = 6 phr in all cases.

showed high torque values [see Fig. 4(b), curve 0.1, and Fig. 9 curve GMA]. The torque behavior in the presence of Tris in a system containing the same amount of GMA (6%) but having an order of magnitude lower peroxide concentration (0.13 phr) is not too dissimilar except that the overall torque is slightly lower and the torque peak occurs much earlier, confirming the faster rate of the reaction in the presence of Tris. In addition, the grafting efficiency in the above Tris-GMA system was in excess of 40% compared to 19% in the GMA system (with no Tris). Overall, therefore, in this case for example, the coagent Tris has contributed to more than doubling the grafting efficiency achieved under conditions of much lower peroxide concentration (e.g., an order of magnitude) and yielded a GMA-grafted polymer which has not suffered from degradation or crosslinking (no measurable insoluble gel). The overall high values of the torque observed in the presence of Tris must, therefore, be due to some branching reactions which occur through the multifunctionality of the Tris coagent (see mechanism later) and is certainly not due to polymer crosslinking.

Under the optimized mixing route used in this work, the homopolymer of the coagent (poly-Tris) was not formed (not detected) in all the samples. Having now eliminated the possibility of formation of three of the side reaction products [i.e., the insoluble Tris-assisted-crosslinked polymer, the poly-Tris, and the ungrafted Tris-co-GMA copolymer (see reaction 3)], an examination of the extent of contribution of the most important side reaction product, the GMA homopolymer, is needed now. To examine the extent of poly-GMA formation in the Tris-containing system, the kinetics of its formation was investigated by sampling at different time intervals during reactive processing followed by purification and analysis for poly-GMA. It was shown that the Tris-GMA system gives rise to very low yield of poly-GMA, which is produced at a slow rate (Fig. 10). This behavior clearly contrasts that of GMA grafting in the absence of Tris where the concentration of poly-GMA formed is much higher and occurs at a faster rate (Fig. 10). It is also interesting to note that the poly-GMA formed in the presence of Tris (at different Tris-GMA ratios examined, see inset as an example) goes through a maximum at early stages of the melt reaction before decreasing to its final very low concentration. This suggests that in the Tris-containing system, the poly-GMA formed has a lower molar mass than in the absence of Tris and hence may undergo depropagation, lead-

ing to a reduction in its final concentration in the polymer. On further processing, the GMA radicals produced from this depropagation reaction would then undergo further graft reaction through the intermediacy of the more reactive Tris-graft-macroradical, resulting in the higher grafting efficiency observed in the presence of Tris (see Fig. 8).

The Mechanisms of GMA-Grafting Process in the Absence and Presence of a Coagent

Although both secondary and tertiary macroradicals are formed during the radical-initiated melt grafting reactions of GMA in EP, the evidence suggests that for the EP used in this study which contain a higher ethylene content, crosslinking is the predominant degradation reaction at higher peroxide concentrations (Scheme 2, rn b). This is reflected from both the torque-time curves (final torque values increase) and the melt flow index (decrease melt index; see Fig. 4). Further, in the absence of a coagent, the peroxide would initiate both the target grafting reaction of GMA on EP macroradicals (via inter- and/or intramolecular hydrogen abstraction, Scheme 2, rns d, e, respectively), and the undesirable homopolymerization reaction of GMA (reaction f). Further grafting via reaction of the propagating GMA radical with EP

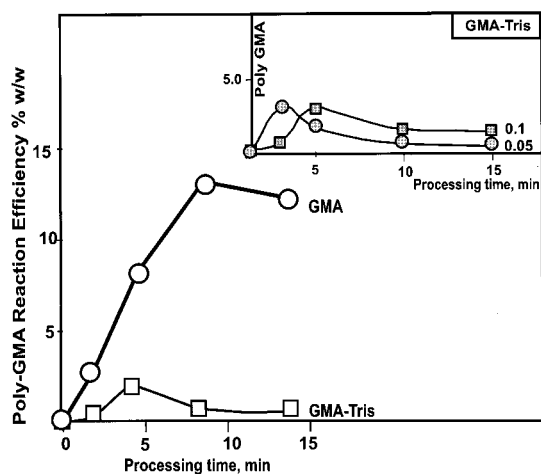
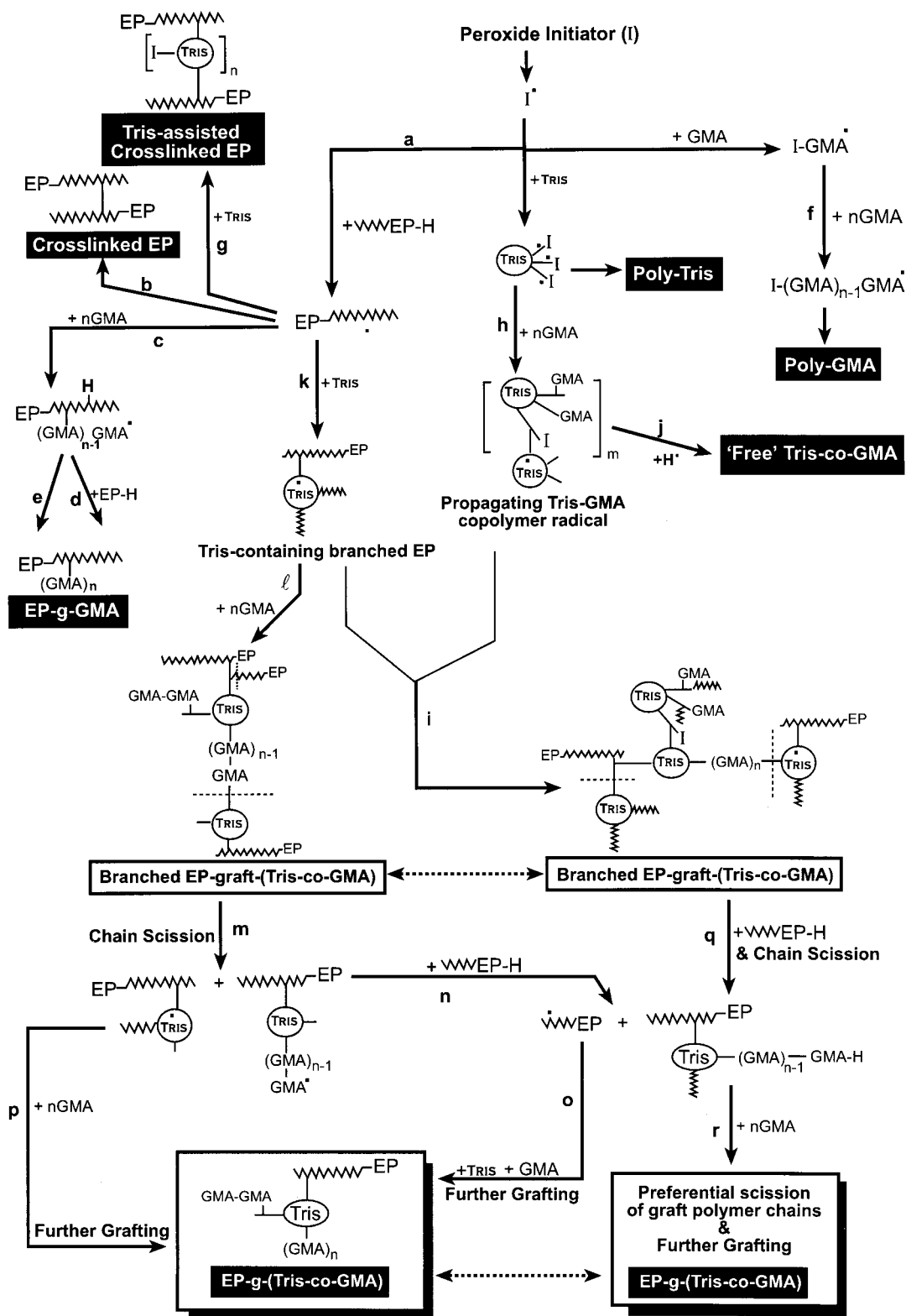


Figure 10 The difference in the rate and efficiency of GMA homopolymerization (poly-GMA formation) during grafting of GMA when used separately ([peroxide]-to-[GMA] = 0.05 MR) and with Tris ([peroxide]-to-[GMA] = 0.02 MR). Inset compares the rate of poly-GMA formation in GMA-Tris system containing two different GMA-to-Tris molar ratios (numbers on curves).



Scheme 2 Reaction mechanism for the melt grafting of GMA in the absence and presence of the coagent Tris.

macroradical is unlikely due to its low H-abstracting ability, hence the GMA graft length is expected to be short. It is clear that the overall low grafting yield of GMA on EP [Fig. 4(a)] is not only due to the known low free-radical grafting reactivity of GMA,²⁶ but also due to the high competitiveness of GMA-homopolymerization (reaction f), especially at high initial GMA concentrations, resulting in the observed high concentration of poly-GMA in the grafting system (Fig. 5).

The incorporation of a small concentration of the highly reactive coagent Tris in the GMA-grafting system brings about important changes characterized by a clear improvement in the grafting efficiency which is achieved at a faster rate and which requires a much lower peroxide initiator concentration (Fig. 8). Another important difference is the absence of undesirable insoluble crosslinked gel (reactions b and g), in the polymer as well as a substantial reduction (almost the absence) of the main competing side reaction, the GMA-homopolymerization (Fig. 10). The very low concentration of Poly-GMA formed in the Tris-containing system is almost certainly due to the higher reactivity of Tris toward GMA radicals compared to the reactivity of GMA toward GMA radicals. This results in the predominance of copolymerization reaction between Tris and GMA (Tris-co-GMA), which occurs at the expense of the GMA-homopolymerization reaction. In spite of this, the experimental evidence presented showed clearly that no free Tris-GMA copolymer was detected at the end of the grafting reactions. The high reactivity of Tris would suggest that the propagation reaction between Tris radicals and GMA (reaction h) would indeed take place during the early stages of the melt reaction. On the basis of the evidence presented (no free copolymer and high grafting yield), it appears that, on further processing, the propagating Tris-GMA copolymer radical reacts with Tris-containing branched macroradicals, giving rise to a branched EP-graft-(Tris-co-GMA) (reaction i), rather than terminating to give the free Tris-co-GMA copolymer (reaction j).

In addition, the high reactivity of Tris toward EP macroradicals (see Fig. 7) results in a fast rate of formation of Tris-containing branched EP (reaction k) in the early stages of the melt processing, which would also be expected to react rapidly with GMA, resulting in the formation of more branched EP-graft-(Tris-co-GMA) (see reaction l). The fact that the Tris-GMA grafting system does not result in any insoluble gel suggests that the

branched EP-graft-(Tris-co-GMA) chains formed in the initial stages of the melt reaction would undergo, on further processing, preferential chain scission and restructuring. This process would be followed by further GMA grafting (reactions m to r), which is responsible for the final increase in the grafting efficiency observed (see Fig. 8).

CONCLUSION

The melt free-radical grafting of GMA on EP was found to be generally low, even though higher peroxide concentrations were found to yield higher conversions at the expense of polymer degradation (in the form of crosslinking). Furthermore, high yield of GMA homopolymerization, the major competing reaction, was shown to accompany the grafting reaction and to predominate at higher GMA concentrations.

Incorporation of the highly reactive coagent Tris to the GMA-grafting system gives rise to an increase in the rate and yield of the grafting reaction associated with a significant reduction or elimination of the GMA homopolymer. In addition, because a much lower concentration of the peroxide is needed in the presence of Tris, the grafted polymer does not undergo peroxide-initiated degradation and crosslinking reactions. The higher reactivity of Tris toward GMA, compared to the reactivity of GMA toward its own radicals, is responsible for the observed drastic reduction in the yield of Poly-GMA as well as formation of copolymer of Tris and GMA (Tris-co-GMA). In view of the absence of free Tris-co-GMA in the grafting system and the high reactivity of Tris toward the EP macroradicals and GMA, it is proposed that the grafted macromolecular structure is based on a copolymer of Tris and GMA [EP-g-(Tris-co-GMA)]. Overall, the polyfunctional coagent Tris appears to act as a promoter for the grafting reaction of GMA via an *in situ* cograftering process resulting in a noncrosslinked polymer containing highly grafted GMA. The use of this Tris-assisted GMA grafted polymer as a compatibilizer in EP/PET (polyethylene terephthalate) blends has resulted in improved adhesion and enhanced mechanical properties and will be reported separately.²⁷

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