

Peroxide-Initiated Comonomer Grafting of Styrene and Maleic Anhydride onto Polyethylene: Effect of Polyethylene Microstructure

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ABSTRACT: Maleic anhydride has been grafted onto various polyethylenes (PEs) using 2,5-dimethyl-2,5-(di-*t*-butylperoxy)hexane as a free radical initiator in the presence of styrene as a comonomer. Three polyethylenes, differing systematically in their levels of terminal unsaturation and branching, were selected to investigate the effect of these microstructural characteristics on the course of both grafting and crosslinking. It was observed that when polyethylenes containing high levels of terminal unsaturation were reacted in the presence of peroxide or peroxide–maleic anhydride, crosslinking events were enhanced. When styrene was added as comonomer to the reaction medium to eliminate these undesirable side reactions, crosslinking was still observed with those polyethylenes that contained a high concentration of terminal unsaturation. This is attributed to a low reactivity between styrene and the allylic radical generated on the polyethylene backbone, which is believed to be responsible for the increased crosslinking. However, in the presence of high concentrations of styrene, crosslinking was eliminated for PEs containing high degrees of branching. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 96–107, 2001

Key words: grafting; polyethylene; maleic anhydride; free radical

INTRODUCTION

Polyethylene (PE) is one of the most widely used polymers available today. Currently, a number of PE types covering a broad range of flow properties and densities can be prepared using a variety of processes. The three most common types of PE are low-density PE (LDPE), linear low-density PE (LLDPE), and high-density PE (HDPE). Each of these polymers is made using a different process, and as a result, each possesses different micro-

structural characteristics. One method of differentiating among the microstructures of these three particular PEs is the amounts of terminal unsaturation and branching they display.

Although a wide range of PEs can be produced, PE does suffer from shortcomings that limit its involvement in emerging technologies. One obvious example is the nonpolar nature of PE, which results in both poor printability and dyeability. In response, it is common to copolymerize ethylene with polar monomers or to modify the PE by free radically grafting polar moieties onto the backbone of the polymer using organic peroxides. Some examples include the grafting of glycidyl methacrylate (GMA),¹ maleic anhydride (MAN),² diethyl maleate,³ and dimethylamin-

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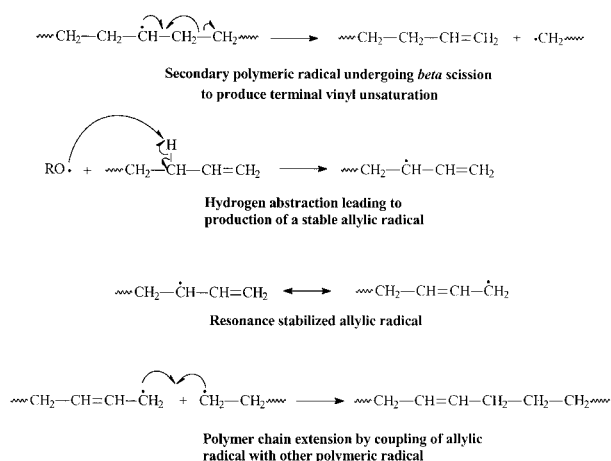


Figure 1 Proposed allylic coupling mechanism of Bremner et al.⁶

ethyl methacrylate.⁴ It has been anticipated that these postpolymerization reactions can be carried out without affecting the molecular architecture of PE; however, this is seldom the case. Generally, it is accepted that PE crosslinks and polypropylene (PP) experience chain scission during the course of these free-radical reactions. Furthermore, in the case of PE, the origin of the observed molecular weight (MW) increases is not well understood from a chemistry viewpoint. However, it is accepted that the microstructure of PE plays an important role, particularly the amount of terminal unsaturation.

In a series of papers by Bremner et al.,^{5,6} the influence of relatively high concentrations of terminal unsaturation on PE crosslinking was investigated. From their results it was observed that high levels of terminal unsaturation in PE increased the amount of crosslinking in the presence of peroxide alone.⁵ For example, when two PEs, LDA and LDB, were heated in the presence of 0.5% peroxide, it was observed that polymer LDB contained more gel than LDA, despite the almost threefold greater MW for LDA. This unexpected result was attributed to the greater level of terminal double bonds in LDB, which were believed to be reacting via an allylic radical coupling mechanism, which is presented in Figure 1. A similar mechanism has been proposed by other researchers.⁷⁻⁹ It should be noted that in the proposed mechanism^{5,6} terminal unsaturation can also be created by scission of a secondary PE radical. However, in this work the results are discussed in terms of the differences in terminal unsaturation in the virgin, unmodified PEs.

Recently, Smedberg et al.¹⁰ also studied the effects of terminal unsaturation on PE crosslinking using a series of LLDPEs containing 1,9-decadiene as a comonomer. These PEs contained unsaturation at the ends of the backbone as well as at the end of the short-chain branches. According to the mechanism proposed by Bremner et al., the conversion of a mole of terminal unsaturation should yield a mole of *trans* unsaturation. However, Smedberg et al.¹⁰ found with the aid of FTIR measurements on pressed-out film samples that much larger decreases in terminal unsaturation occurred in contrast to the small observed increases in *trans* unsaturation. From this result they suggested that the decrease in terminal unsaturation (both backbone and short-chain branch) was due to an involvement in polymerization reactions. The formation of internal *trans* unsaturation was thought to be the result of a cage effect on the peroxide-derived radicals.¹⁰ From this brief discussion it can be concluded that although the exact mechanism through which the terminal unsaturation participates is not universally agreed upon, it is clear that PE crosslinking is enhanced when high concentrations are present. However, insight into the mechanism for this has been elucidated using model compounds.¹¹

To complicate matters further, when maleic anhydride (MAN) is added to the reaction, PE crosslinking is observed to increase dramatically.^{12,13} For example, Gaylord et al.¹² observed the gel content of a HDPE polymer increase from ~2% in the presence of 0.125% di-*t*-amyl peroxide alone to 44% when MAN (5% w/w) was added to the system. The increased crosslinking was attributed to two factors: (1) the participation of either free or appended poly(maleic anhydride) chains that could preferentially terminate with PE macroradicals; and (2) the presence of a MAN excimer capable of hydrogen abstraction, thereby increasing the concentration of PE macroradicals. The same observed increases in crosslinking have been observed during the free-radical grafting of MAN onto an ethylene-propylene rubber as well.^{14,15} However, with the addition of polar compounds such as tri(nonylphenyl)phosphite or stearamide, the amount of formed insolubles could be drastically reduced.

A more recent approach to minimize these undesirable side reactions (i.e., PE crosslinking or PP β -scission) is to add a secondary comonomer. In utilizing the comonomer concept, it is postulated that the added comonomer reacts more rap-

Table I Microstructural Characteristics of Polymers Used in This Work

Polymer	Terminal Unsaturation ^a	Density (g/cm ³) ^b	# Tertiary Carbons ^a	MFI (g/10 min.) ^c
Sclair 19C	0.56	0.958	n/a	1.0
Sclair 11E1	0.58	0.920	57	1.2
Nova PF0118F	0.13	0.919	61	1.0

^a Reported as number of terminal olefins (tertiary carbons) per 1000 backbone carbons.

^b Supplied by Nova.

^c ASTM standard D-1238—conditions of 2.16 kg and 190°C.

idly with the polymer macroradical than with the primary monomer of interest. The preferential grafting of the secondary monomer is believed to alter macroradical reactivity, thereby influencing the course of the undesirable side reactions. Styrene has been successfully used to reduce the β -scission of PP^{16–18} and the crosslinking of PE¹⁹ during the free-radical grafting of GMA in both a batch mixer and a twin-screw extruder. Furthermore, styrene was observed to enhance the GMA graft yield. It is of interest to determine whether this comonomer concept involving styrene can be applied to other systems as well.

This article examines the ability of styrene to promote MAn grafting and reduce PE crosslinking. In particular, it is of interest to determine whether this comonomer concept involving styrene is sensitive to the microstructure of the PE. The microstructural characteristics of interest are the amount of terminal unsaturation and branching (tertiary carbons) the PE possesses.

EXPERIMENTAL

Materials

The primary grafting monomer of interest used in this work was MAn. The MAn was obtained from Aldrich (95%+) in briquette form and was recrystallized from chloroform, then stored in a sealed container until needed for the batch mixer studies. Styrene was the comonomer studied in this work. It was obtained from Aldrich (inhibited with 10–15 ppm of *t*-butyl catechol) and used as received.

The free radical initiator 2,5-dimethyl-2,5-(di-*t*-butylperoxy)hexane (Elf Atochem, 92%, L101) was used as received for all batch mixer runs. The half-life time, $t_{1/2}$, of L101 at the temperature used in this work (180°C) was ~ 69 s.²⁰

Three commercially available polymers were kindly supplied by NOVA Chemicals and used in this work. The microstructural characteristics of each polymer are listed in Table I. These polymers were selected so that the terminal unsaturation and branching levels could be systematically varied while keeping the flow characteristics (as measured by the melt flow index) essentially constant.

Typical Batch Mixer Experiment

A Haake Buchler Rheomix 600 internal batch mixer, driven by a Haake Rheocord System 40 microprocessor, was used for all batch mixer melt-grafting reactions. This mixing device is equipped with two roller blades and has an approximate capacity of 56 mL. For all experiments, a fill factor of 75% was used to ensure good distributive mixing of all constituents. A sample size of ~ 40.0 g ensured this requirement was met.

During a typical batch mixer melt-grafting reaction, the PE, monomers, and peroxide were first premixed in a beaker for ~ 5 min to ensure mix uniformity prior to feeding. At time zero of mixing, the ingredients were fed through the top of the mixing chamber with the use of a cold feed chute to facilitate addition of the mixture. Feeding of the mixture took less than 5 sec, so monomer losses were expected to be minimal. Upon completion of feeding, the ram was closed, and the mixture was allowed to react for 8 min. This time frame was sufficient to ensure complete decomposition of the L101 free radical initiator. It typically takes about 2 min for the polymer melt temperature to stabilize (usually 5–10°C greater than the set temperature). During this transient period it is possible that some air-initiated grafting may occur as well as the formation of free styrene–MAn (SMA) copolymer.

During the course of the reaction the rotor speed and mixer wall temperature were kept con-

stant at 70 rpm and 180°C, respectively. During the entire 8-min mixing period, both the melt temperature and mixing torque were continuously recorded. Significant increases in mixing torque are a relatively good indicator (albeit indirect) that an increase in MW of the PE occurred during melt grafting.

Upon completion of the reaction, the roller blades were stopped, and the mixing chamber was pulled off so the contents could be removed. PE samples were removed from the mixing chamber and placed in liquid nitrogen to quench the reaction. The resulting sample was then purified to remove any unreacted monomer and free copolymer for subsequent graft content analysis.

Sample Purification

Approximately 2.5 g of the crude reaction product was dissolved in 150 mL of boiling xylene to permit separation of any unreacted monomer and free SMA copolymer. The dissolution process took about 1–1.5 h because of the high MWs of the reaction products. The solution was then added to ~800 mL of acetone and allowed to stir for ~4 h. PE and grafted-PE precipitated while the unreacted monomers and free SMA copolymer remained in solution. Only one purification step was deemed necessary because a graft-modified sample was carried through two dissolution/precipitation steps and no change in the degree of grafting of MAn was observed. Finally, the precipitate was suction-filtered and placed in a vacuum oven overnight to remove any remaining solvent.

Sample Analysis

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectra were recorded using a Bomem MB-1200 FTIR spectrophotometer at a resolution of 1 cm⁻¹. The spectra of grafted polymer samples were obtained using thin films pressed out using a hydraulic press at a temperature of 180°C and a pressure of 300 psi. Films obtained by this technique were 100–200 μm thick. MAn and styrene graft levels were determined using a FTIR calibration technique developed by Sun et al.²¹ The peaks at 700 cm⁻¹ and 1865 cm⁻¹ were used to determine the degrees of grafting of styrene and MAn, respectively. The CH₂ rocking peak at 720 cm⁻¹ was used as an internal standard to account for variations in PE film thickness. FTIR spectra were obtained for

both purified and unpurified samples so that a measure of the styrene and MAn graft efficiency (GE) could be determined. The GE was determined by dividing the degree of grafting (DG) of the purified sample by the apparent DG of the unpurified sample for either MAn or styrene. FTIR was also used to assess the nature of the styrene and MAn grafts on the backbone of the PE.

Quantification of the terminal vinyl groups in each of the virgin PEs was also completed according to an FTIR technique of Haslam et al.²² Absorbance of the terminal vinyl occurs at 909 cm⁻¹, while internal *trans* unsaturation occurs at 965 cm⁻¹. Extinction coefficients used in the determination of the terminal unsaturation concentrations were also obtained from Haslam et al.²²

¹³C-Nuclear Magnetic Resonance

Short-chain branch contents for each of the virgin PEs were determined by ¹³C-nuclear magnetic resonance (NMR) on a Bruker AM-400 MHz spectrometer at a temperature of 130°C in *o*-dichlorobenzene solvent.²³

Gel Permeation Chromatography

For the polymer-melt grafting studies, high-temperature gel permeation chromatography (GPC) was utilized in the evaluation of the MW of the final graft-modified PE. A Waters 150 CV+ high-temperature gel permeation chromatograph (HT-GPC) equipped with three Waters Styragel HT6E linear columns and a differential refractive index detector was used. The mobile phase was 1,2,4-trichlorobenzene at a temperature of 140°C containing 0.02% by weight Irganox 1010 antioxidant. HTGPC samples were prepared at a concentration of ~0.5 mg/mL. MWs were determined using a universal calibration curve with narrow MW polystyrene standards.

Melt Flow Index

The melt flow indexes (MFIs) of the crude melt-grafted samples were determined to obtain an indirect measure of the change in the MW and the MW distribution (MWD) of the PE samples. All MFI data were obtained using a Tinius-Olsen extrusion plastometer. MFI values of the virgin PE samples were obtained according to ASTM D-1238 (190°C and 2.16 kg). Because of much higher melt viscosities, the MFI values of the peroxide-modified PE samples had to be obtained

using conditions of 190°C and 10.0 kg. In most cases, 1- or 2-min extrudates were collected.

Gel Content Analysis

The gel content of the peroxide-modified PE samples was obtained according to an ASTM D-238. In a typical gel test, ~0.6 g of crude sample was cut into small cubes (typically 1 mm × 1 mm × 1 mm) and placed within a 120-mesh steel basket. The exact weights of both the PE sample (w_1) and the PE sample and steel basket (w_2) were taken so the gel content could be determined later. The steel basket containing the crude PE sample was then immersed in boiling xylene, and the PE was allowed to dissolve for 8 h. The ASTM standard calls for 12 h, but it was found that there was no weight change after 8 h, so 12 h was deemed unnecessary. After 8 h, the sample was placed in a vacuum oven and allowed to dry for 24 h at 90°C to remove any residual solvent. Once the sample was completely dry, the sample was allowed to cool down to room temperature and then reweighed (w_3). The gel content was then determined using eq. (1):

$$\% \text{ Gel} = 100 - [(w_2 - w_3)/w_1 \times 100] \quad (1)$$

Selected samples were reproduced so a statistical analysis of the data could be carried out.

RESULTS AND DISCUSSION

Styrene and MAn Grafting Analysis

Styrene was selected as comonomer for this work because it has been demonstrated in the literature that it can minimize crosslinking during grafting of MAn onto PE^{24,25} and β -scission during grafting of GMA onto PP.^{16,18} However, this is the first reported work to study the relationship between PE microstructure and the effect of styrene's ability to reduce crosslinking and enhance MAn grafting. It was postulated that the degree of grafting (DG) of MAn would also increase because of a strong propensity of both MAn and styrene to copolymerize.²⁶

Evidence for Grafting

FTIR is a simple technique for detecting the presence of grafted monomers on polymer backbones. For example, it has been used to observe the grafting of MAn,^{25,27} GMA,^{17,21} styrene,²⁸ dim-

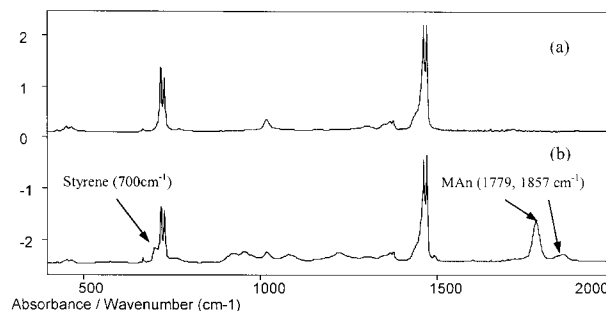


Figure 2 FTIR spectra of (a) virgin PF0118F and (b) PF0118F graft modified with styrene and MAn.

ethylaminoethyl methacrylate,⁴ and diethyl maleate.³ Therefore, it was used in this work to detect the presence of grafted styrene and MAn. Figure 2(a,b) shows FTIR spectra of virgin PF0118F and of PF0118F that has been graft-modified with L101 (0.25% w/w), MAn (5% w/w), and styrene (9% w/w). It can be seen in Figure 2(b) that new FTIR stretching vibrations appear at ~700 cm⁻¹ and 1865 cm⁻¹, which are indicative of grafted styrene and MAn, respectively. Since any copolymer, homopolymer, and unreacted monomer were removed (as shown by no change in graft level after a second extraction), this was sufficient evidence to confirm that both styrene and MAn had been grafted to PE.

To elucidate the nature of the SMA grafts on the backbone of the PF0118F (equally applicable to the other PEs), a comparison of the SMA graft-modified PF0118F FTIR spectra was made with a typical commercial SMA copolymer. The position of the symmetric anhydride stretching vibration was observed to be at ~1779 cm⁻¹ for both these samples. The FTIR spectrum of a sample of PF0118F grafted with MAn displayed a stretching vibration only at 1786 cm⁻¹. These results suggest that styrene and MAn graft onto the backbone of PE as an SMA copolymer.

Degree of Grafting

FTIR was also used to quantify the degree of grafting of both styrene and MAn onto each of the PEs. A calibration technique developed by Sun et al.²¹ was utilized in determining the DGs for each of the grafted monomers. The DGs for styrene and MAn are presented in Table II. The DG of styrene is the bracketed value, while the unbracketed values are for MAn. The DGs of styrene and MAn were also determined for unpurified films so that a measure of the graft efficiency (GE) could be

Table II Summary of Degrees of Grafting for MAn^a (and Styrene)—Purified and Unpurified for Each PE (Styrene Levels in Brackets)

Added Styrene (wt %)	SC19C (wt %) ^b		SC11E1 (wt %)		PF0118F (wt %)	
	P ^c	U/P	P	U/P	P	U/P
0	n/a	n/a	n/a	n/a	n/a	n/a
3	n/a	n/a	n/a	n/a	n/a	n/a
6	1.8 (1.3)	2.3 (1.9)	2.1 (1.8)	2.7 (2.3)	1.8 (1.8)	2.5 (2.3)
9	2.1 (3.5)	2.9 (4.4)	1.9 (3.0)	2.6 (4.0)	2.0 (3.5)	2.7 (4.6)

^a 5% w/w MAn in all experiments.

^b 95% confidence intervals found by adding ± 0.2 for styrene and MAn respectively.

^c P represents purified and U/P is unpurified.

determined. The GE was determined by dividing the DG of the purified sample by the apparent value of the unpurified sample for each monomer. It can be observed from the data in Table II that the DG of styrene and MAn could not be determined at added styrene levels of 0 (represents addition of L101 and MAn only) and 3%. As will be demonstrated shortly, these runs contained appreciable amounts of gel; therefore, good films could not be pressed out for subsequent FTIR analysis.

It can also be seen from the data in Table II that both styrene and MAn appear to graft with rather high efficiencies regardless of the type of PE. The graft efficiencies were determined to be $\sim 75\%$ and $\sim 72\%$ for styrene and MAn, respectively, when an average was taken over all the PEs. The DG values in Table II may appear rather high, but similar MAn grafting levels were observed by Gaylord when MAn was grafted onto PE using a Haake-type batch mixer with no comonomer.¹² In the work of Gaylord,¹² in the presence of 0.125% w/w di-*t*-amyl peroxide and 5% MAn w/w, the DG of MAn was observed to be 2.8% in the xylene-soluble fraction, so the numbers appear reasonable. It can also be observed that styrene has not enhanced the degree of grafting of MAn if the data in the 6% and 9% columns are compared. It is possible that a plateau exists in the relationship between added styrene and MAn graft level enhancement, and this is what is observed in Table II for styrene levels of 6% or greater. Qualitatively, a similar trend was observed by Cartier and Hu¹⁹ for the grafting of GMA onto PE using styrene as comonomer.

Finally, it should be noted that at the 9% styrene level, it appeared that the degree of grafting of both styrene and MAn was equivalent for each PE (within experimental error) regardless of mi-

crostructure. Therefore, the presence of differing microstructures does not have an influence on the grafting of MAn or styrene. This will prove to be an interesting result when the crosslinking analysis is discussed in the next section.

Crosslinking Analysis

The main objective of this work was to assess whether the influence of styrene on crosslinking was sensitive to the microstructure (terminal unsaturation and branching) of the PE being grafted. In this section styrene's ability to reduce crosslinking has been assessed based on measurements of Haake mixing torque, melt flow index, gel content, and MW. The first three measurements are indirect measures of the changes in MW, while the last examines the true changes that occurred as a result of the peroxide modification.

Haake Mixing Torque

During the course of a typical batch-mixer reaction, the Haake mixing torque is constantly recorded. Since torque is directly related to the viscosity of the material being processed and hence its MW, any significant increase in torque should reflect an increase in the MW of the material. A similar analysis was adopted by Xie et al.²⁹ for studying the effects of various initiators on the crosslinking of PE and the degradation of PP. Therefore, the efficacy of styrene to reduce crosslinking was assessed through its ability to reduce the Haake mixing torque.

Figure 3 depicts typical torque versus time traces for the reaction of each PE with L101 (0.25% w/w). The horizontal line at ~ 1200 m-gf represents the average baseline torque for each

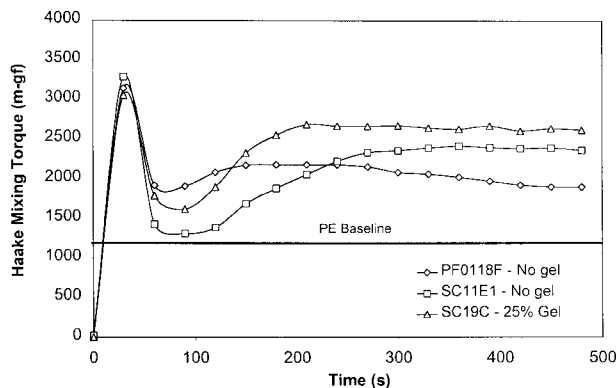


Figure 3 Effect of L101 (0.25% w/w) on the Haake torque profile for each PE (baseline calculated from average steady-state torques for all three grades).

PE after steady state has been achieved in the mixer. It can be observed that the presence of L101 has caused each PE to undergo an increase in mixing torque (in comparison to the PE baseline), which is attributed to a crosslinking reaction between PE macroradicals. It can also be observed that in the high terminally unsaturated PEs, SC19C and SC11E1 have experienced the greatest torque increases, suggesting the importance of terminal unsaturation during crosslinking. In fact, the reaction between SC19C and L101 has resulted in the formation of $\sim 25\%$ gel. This result would suggest that allylic radical coupling occurred with this highly terminally unsaturated polymer.⁶

Figure 4 represents torque versus time traces for each of the PEs after the addition of L101 (0.25% w/w) and MAn (5% w/w). It can be seen that significantly different torque profiles are obtained when MAn is added to the system. For both SC19C and SC11E1, after the melting peak is completed (~ 70 – 80 s), a significant increase in torque occurs that reaches a maximum at ~ 200 s and then gradually decreases. It is also observed from Figure 4 that the decrease in torque is much more rapid for the SC19C compared to the SC11E1. The presence of a second maximum in these torque profiles is from the formation of a severely crosslinked material. The torque drops off with time after the maximum is reached because the material has become so severely crosslinked it is crumbly in nature and is detached from the walls leading to lower torque. In contrast, PF0118F did not experience a torque maximum, suggesting that crosslinking was not as severe with this PE. These results suggest that

allylic radical coupling (i.e., crosslinking) also occurred during the grafting of MAn. A similar result was observed by Marquez et al.³⁰ during the grafting of DEM onto LLDPE.

A similar increase in the amount of crosslinked material in the presence of MAn has also been observed by with both PE¹² and EPDM rubber³¹ according to other researchers. The exact mechanism of the observed increase in crosslinking is not well understood. However, researchers have attributed the increase to (1) the formation of an excimer during peroxide decomposition that has the ability to abstract hydrogen atoms, resulting in an increased macroradical concentration³²; (2) preferential coupling between MAn-centered PE and PE macroradicals³³; and (3) inter- and intramolecular hydrogen abstraction by MAn-centered macroradicals to regenerate PE macroradicals capable of coupling.³⁴

Figure 5 represents the torque profiles for each of three PEs after addition of styrene (9% w/w) to the reaction. The reactions involving L101 and MAn alone (shown as the gray lines) are also provided for comparative purposes. Results are presented only for the addition of 9% w/w styrene because it was observed that relatively small changes in torque were occurring at lower styrene concentrations (3% and 6% w/w) in comparison to the MAn/L101 torque-versus-time traces. It can be seen from Figure 5 that greater reductions in torque were observed for the SC11E1 and the PF0118F. The SC19C, which contains a high concentration of terminal unsaturation and low levels of branching, possessed the highest steady-state torque. Therefore, despite similar graft levels of both MAn and styrene, the Haake torque

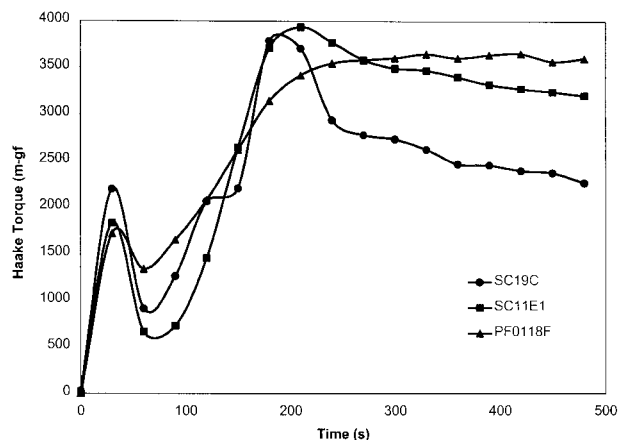


Figure 4 Effect of MAn (5% w/w) on the torque-versus-time profile for each PE (0.25% L101).

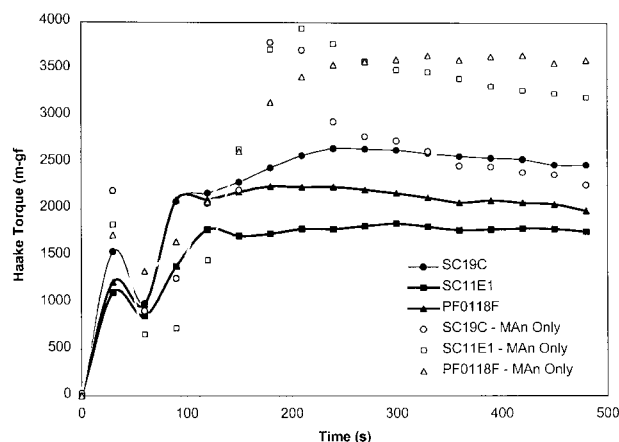


Figure 5 Comparison of the torque reduction for each PE in the presence of styrene (9% w/w based on PE). (Runs involving MAn–L101 without styrene are shown with open symbols for comparison.)

results suggest that utilizing styrene to reduce crosslinking is more beneficial with branched PEs. Overall, the addition of styrene has led to a decrease in crosslinking for all three PEs.

To confirm these results, MFI measurements on the crude product of each batch-mixer reaction were also obtained. Qualitatively, the same trends observed with the Haake mixing torque were also observed in the MFI studies. Therefore, an in-depth explanation of the data is not required. A summary of the MFI results is presented in Table III.

Gel Content

The gel content of each graft-modified PE sample was also analyzed to assess the influence of styrene on PE crosslinking. It is often noted that gel-content values are a function of many parameters, such as dissolution time and the solvent within which the test is conducted. These variables can influence the reproducibility of the test. Therefore, the reproducibility of select runs was determined to ensure the validity of the technique. The results can be found in Table IV. The numbers are presented such that they display replicate measurements from three different runs carried out on three different days. Therefore, the reproducibility from both run-to-run experiments and the gel-measurement technique was evaluated. It is evident from the data in Table IV that the reproducibility of the gel-content test is acceptable. When a pooled estimate of the standard deviation for each replicate run is taken, the 95%

confidence-interval limits for the test were determined to be $\pm 2.7\%$.

The effect of added styrene on the gel content of each of the SMA-modified samples is presented in Figure 6. It can be seen that at the 0% added level of styrene (L101 and MAn only), the highly terminally unsaturated PEs—SC19C and SC11E1—possess the highest gel content. These results are in good qualitative agreement with both the torque and MFI measurements. It can also be seen that at low levels of styrene (i.e., 3% w/w) a small but statistically significant drop in gel content occurs for each PE, with the greatest decrease observed for SC19C and SC11E1. It is only when higher levels (6% and 9% w/w) are used that statistically significant reductions in gel content occur. In fact, at the 9% w/w level of added styrene, gel was eliminated from the SC11E1 and PF0118F resins. Once again, it is the highly branched PEs that have experienced the greatest reduction because of added styrene. The highly terminally unsaturated PE, SC19C, still contains $\sim 25\%$ gel even after the addition of 9% w/w styrene.

MW and MWD

To probe the true changes in MW that occurred as a result of the presence of styrene, high-temperature GPC was conducted. Since this technique requires the sample to be gel-free, only those samples that contained 0% gel could be analyzed (Fig. 6). All runs involving L101–MAn resulted in the formation of gel, so the product from this reaction could not be used as a baseline for assessing the influence of styrene on the MWD. Therefore, the reactions involving only L101 were used for comparison. Figure 7 shows the effect of added styrene (9% w/w) on the MW and MWD of PF0118F. As can be seen from Figure 7, with the addition of

Table III Effect of Styrene on the MFI of the Crude Reaction Product

Sample Description	SC19C	SC11E1	PF0118F
PE	8.35	10.69	7.54
L101	n/a ^a	0.07	0.94
L101/MAn	n/a	n/a	n/a
L101/MAn/3% Styrene	n/a	n/a	n/a
L101/MAn/6% Styrene	n/a	0.17	0.10
L101/MAn/9% Styrene	0.21	0.97	1.07

^a Could not measure even under a 10.0 kg load at 190°C.

Table IV Summary of Gel Test Reproducibility

Run Description	Gel Content (Run 1/Run 2/Run 3)
PF0118F, 0.25% L101, 5% MAn, 9% Styrene	0.0, 0.0/0.0, 0.0/0.0, 0.0
SC11E1, 0.25% L101, 5% MAn, 6% Styrene	35.3, 32.8/33.1, 34.6/35.9, 32.7
SC19C, 0.25% L101, 5% MAn	57.4, 59.8/49.8, 51.9/53.1, 56.1

L101 (0.25% w/w) to PF0118F, the chromatogram depicts a shift to much lower MWs. This result was not expected because with the addition of L101 to PF0118F, both a higher Haake torque and a lower MFI were observed in comparison to those of the virgin material, suggesting that an increase in MW had occurred. It is possible that some fractionation may have occurred in the GPC, through removal of gel or higher MW material, but this sample was observed to be soluble (0% gel content) in boiling xylene and trichlorobenzene. Furthermore, the expected increase in MW as a result of peroxide modification is observed for SC19C (Fig. 8), so another explanation is required.

It is well known that highly branched polymers tend to conform more tightly in solution than linear polymers of an equivalent MW. This "molecular contraction" usually manifests itself as lower observed values for both the radius of gyration and intrinsic viscosity.³⁵ As a result of the tighter conformation, branched molecules will tend to elute at longer times in HTGPC than expected and therefore appear to have smaller MWs. This seems to be the case with PF0118F

and leads to a conclusion that the crosslinking reaction with L101 resulted in a highly branched structure for PF0118F. In light of this result, it is obvious from Figure 7 that with the addition of styrene (9% w/w), the original MWD was being approached and less structural change had occurred.

Unfortunately, most of the runs involving SC19C contained gel and therefore could not be analyzed using HTGPC. However, results were obtained with the soluble product from the experiment involving styrene (9% w/w). The results are presented in Figure 8, from which it is evident that the soluble portion of this particular run has a MW (115,000 g/mol) very similar to that of the original SC19C (126,000 g/mol). Evidently styrene had some impact on controlling the MW increase in a portion of SC19C as well. These results demonstrate that the reductions in torque and increases in MFI can be at least partially attributed to a reduction in MW and not solely to the presence of a free SMA copolymer.

Similar results to that obtained for SC19C were also observed for SC11E1. The original MW of the unmodified polymer was determined to be 81,000 g/mol, and with the addition of 0.25%

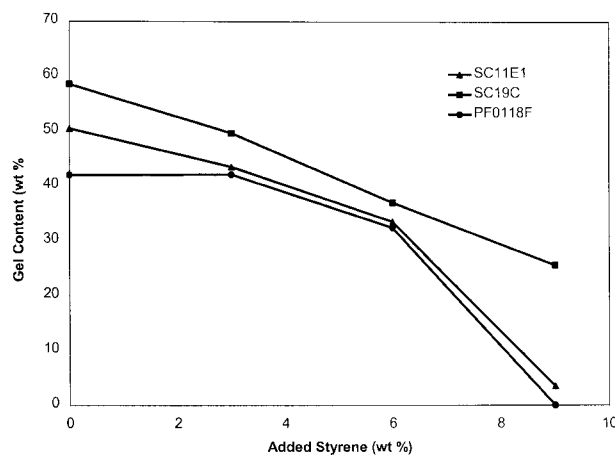


Figure 6 Effect of added styrene on the gel content of SC11E1, SC19C and PF0118F (with 0.25% w/w L101 and 5% w/w MAn).

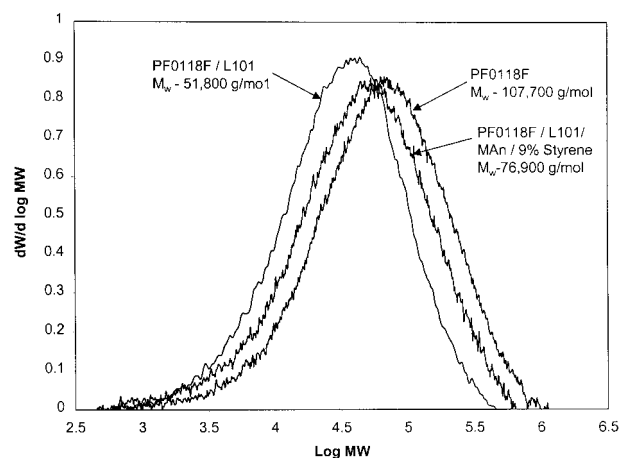


Figure 7 Effect of styrene on the MW and MWD of PF0118F.

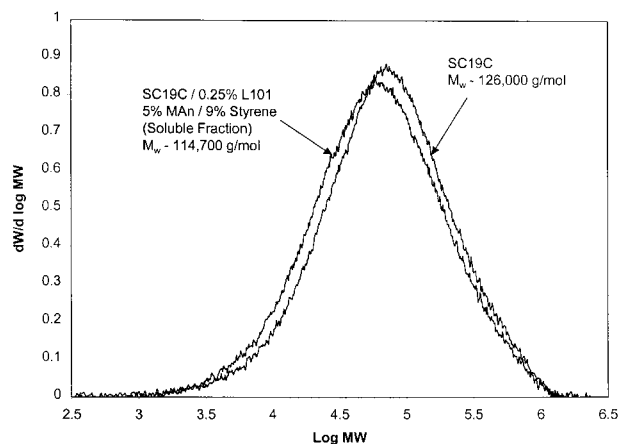


Figure 8 Effect of styrene on the MW and MWD of SC19C (soluble fraction only).

L101, the MW increased to 143,000 g/mol. However, when 9% w/w styrene was added to the mixture to reduce the observed crosslinking, the MW was reduced to 101,000 g/mol.

Proposed Mechanism for PE Crosslink Reduction in the Presence of Styrene

Styrene has been shown to be an efficient comonomer for reducing crosslinking for the PEs examined in this work. However, all results clearly show that styrene had a greater impact on those PEs that possessed a significant level of branching, despite similar grafting levels of both styrene and MAn. It is believed the differences can be partially attributed to the varying microstructures of the PEs. To fully understand why this is true, an understanding of the free-radical chemistry involved in these reactions is essential.

When L101 decomposes to form *t*-butoxy (or methyl radicals), there are four types of hydrogen available for abstraction: tertiary, secondary, primary, and allylic. Whether abstraction occurs at any of these positions is governed by both thermodynamic and kinetic factors. The easiest way to examine the reactivities of these various hydrogens is to look at their selectivity ratios. A selec-

tivity ratio is a measure of the kinetic reactivity of each hydrogen toward transfer by an attacking radical, as determined by either spin-trapping experiments or product yields. Table V presents the selectivity ratios of the *t*-butoxy radical toward primary, secondary, tertiary, and allylic hydrogens at 40°C. These ratios were determined from product yields from the reaction of *t*-butyl hypochlorite (TBH) with the various radicals. Despite these values being measured at 40°C (reactions in this work are at 180°C), it is clear that the *t*-butoxy radical shows a preference for attack at the tertiary and allylic protons. It is interesting to note that this selectivity trend closely correlates with the order of bond dissociation energies for each of these hydrogens. Tertiary and allylic hydrogens have lower BDE values (93.3 and 82.5 kcal/mol at 298 K)³⁷ in comparison to secondary and primary protons (96.4 and 110.3 kcal/mol),³⁷ so this order is somewhat expected. Abstraction of the allylic hydrogen is also facilitated by its location at a highly mobile chain end.

The probability of hydrogen abstraction is also influenced by statistical factors. Since the number of secondary hydrogens is much greater than the number of tertiary hydrogens, it is postulated that abstraction will be preferred at the secondary position. This result has been observed by other research groups.^{30,38,39} Therefore, from this discussion it is postulated that hydrogen abstraction occurs predominantly at allylic and secondary carbons along the PE backbone.

With an understanding that hydrogen abstraction is expected to occur at allylic and secondary carbons, why is styrene ineffective in reducing SC19C's gel content at high concentrations? To answer this question, it is necessary to look at the reactivity of styrene toward each of these radicals. However, a difficulty arises in finding a suitable model for each of these radicals. From a review of the literature, it appears as though the best models for studying the reaction of styrene with an allylic and a secondary radical are butadiene and ethylene, respectively. Although ethyl-

Table V Selectivity Ratios of *t*-Butoxy Radical Towards Primary, Secondary, Tertiary and Allylic Hydrogens³⁶

Attacking Radical	1° R—CH ₂ —H	2° R ₂ CH—H	3° R ₃ C—H	Allylic CH ₂ =CH—CH ₂ —R
(CH ₃) ₃ CO• (40°C)	1	12	44	60

Table VI Estimated Rate Constants for the Addition of Styrene to an Ethyl and Butenyl Radical

Radical	$r_2(k_{22}/k_{21})$	k_{22}^a ($M^{-1} s^{-1}$)	k_{21} ($M^{-1} \cdot s^{-1}$)
Ethyl	0.016	0.242 (10^3)	~ 1.6 (10^4)
Butenyl	1.98	0.1 (10^3)	~ 5 (10^1)

^a Values are at 60°C.⁴⁰

ene is the source of a primary radical, it should serve as an appropriate model for these calculations. The rate constants for the addition of styrene to each of the radicals were determined using eq. (2), below:

$$k_{21} = k_{22}/r_2 \quad (2)$$

Therefore, if the reactivity ratio (r_2) is known along with an estimate for the butadiene and ethylene propagation rate constants (k_{22}), the desired rate constant (k_{21}) is easily determined. The results of the calculations are presented in Table VI.

It can be observed from the data in Table VI that styrene has an almost three order of magnitude greater reactivity toward the ethyl radical compared to the butenyl radical. If this result is coupled with the expected low concentration of allylic radicals, it is clear that styrene will have a low propensity to react at this site. Therefore, it can be concluded that styrene will graft almost exclusively at secondary carbons. The allylic radicals are left to couple via the allylic coupling mechanism proposed by Bremner et al.,⁶ resulting in the formation of crosslinked material. This is why styrene is ineffective at reducing the gel content of SC19C. A question may arise as to why styrene was effective in reducing the gel content of SC11E1, which had a level of terminal unsaturation similar to that of SC19C. As Figure 8 shows, the MW of SC11E1 (81,000 g/mol) is lower in comparison to either PF0118F (108,000 g/mol) or SC19C (124,000 g/mol). Since crosslinking is also expected to be MW dependent, it appears that the reduction in gel for SC11E1 is due to its lower MW.

CONCLUSIONS

Styrene has been employed as comonomer in an attempt to reduce the amount of crosslinking usu-

ally observed during free-radical grafting of MAn onto PE. Several conclusions can be drawn based on the work carried out:

1. Terminal unsaturation increases the amount of crosslinking during the peroxide modification of PE. Enhanced levels of crosslinking are expected during the reaction in the presence of peroxide and peroxide-MAn. Crosslinking is believed to occur as a result of coupling between allylic and secondary PE radicals.
2. Styrene is ineffective in reducing the gel content of PEs that contain high concentrations of terminal unsaturation. This is attributed to low reactivity between styrene and the allylic radical.
3. With the concentrations examined in this work, styrene did not enhance the grafting of MAn onto PE. This is attributed to a plateau in the relationship between added styrene and the DG of MAn.

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