Efforts to Decrease Crosslinking Extent of Polyethylene in a Reactive Extrusion Grafting Process

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ABSTRACT: Grafting of acrylic acid and glycidyl methacrylate onto low density polyethylene (LDPE) was performed by using a corotating twin-screw extruder. The effects of residence time and concentration of initiator and monomers on degree of grafting and gel content of grafting LDPE were studied systematically. Paraffin, styrene, *p*-benzoquinone, triphenyl phosphite, tetrachloromethane, and oleic acid were added to try to decrease the extent of crosslinking of LDPE. 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (4-hydroxyl-TEMPO) and dipentamethylenethiuram tetrasulfide were also tried to inhibit crosslinking reaction of LDPE during its extruding grafting process. It was found that *p*-benzoquinone, triphenyl phosphite and tetrachloromethane were good inhibitors for crosslinking of LDPE. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 535–543, 2001

Key words: LDPE; reactive extrusion; crosslinking; acrylic acid; glycidyl methacrylate

INTRODUCTION

The modification of polyolefins with polar monomers by reactive extrusion has received much attention in the past several decades. By this method, some properties of polyolefins such as polarity, adhesion with metal, glass or ceramic, and compatibility with polyamides, polyesters, etc. could be greatly improved. Compared with traditional solution graft copolymerization, reactive extruding grafting has obvious advantages, such as reducing the production cost and tailoring polymer properties for special application. The monomers often used for grafting copolymerization are maleic anhydride (MAH), acrylic acid (AA), and its derivatives.[1–3] Among them, glycidyl methacrylate (GMA) has received considerable attention because of its reactivity with many functional groups,[4,5,6] such as carboxyl (—COOH), amino (—NH$_2$), hydroxyl (—OH), etc.

However, side reactions such as crosslinking in polyethylene (PE) or degradation in polypropylene occur, which would detract from their processability and mechanical properties during melt grafting. Many efforts have been made to study the mechanism of melt grafting, with the aim to enhance degree of grafting and reduce the extent of crosslinking in PE.[7,8,9] Melt grafting is a complicated free-radical reaction, including initiator decomposition, radical combination, displacement, addition, etc.. Grafting MAH onto PE molecular chains was initially studied by Gaylord and Mehta[1] They proposed that the presence of nitrogen-, phosphorous-, and sulfur-containing organic electron donors would help to prevent crosslinking of PE and homopolymerization of

MAH. Samay et al.[10] used vinyl monomers incorporated with MAH to modify PE. They found that vinyl comonomers with MAH in an equimolar ratio could form long alternating side groups on PE chains and a considerable amount of MAH could polymerize onto the PE chains without a great probability of recombination.

In this article, the preparation and characterization of new kinds of LDPE-*g*-AA and LDPE-*g*-GMA copolymers are reported. The effects of monomer reactivity, residence time, and concentrations of initiator and monomer on degree of grafting and extent of crosslinking of LDPE copolymers were systematically studied. Several organic compounds such as paraffin, styrene, triphenyl phosphite, *p*-benzoquinone, tetrachloromethane (CCl$_4$), oleic acid, 4-hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (4-hydroxyl-TEMPO), and dipentamethylenethiuram tetrasulfide (DPTT) were adopted in the reactive extruding grafting process to try to inhibit crosslinking of grafted LDPE. The objective is to study and develop a latent commercial functionalized LDPE that owns excellent processability.

EXPERIMENTAL

Materials

LDPE was provided by Yan Shan Petrochemical Co. (Beijing, China), with the trade name PE-FAS-18D075. Its density is 0.923 g/cm^3 and the melt flow rate (MFR) is 7 g/10 min (JIS K6760). Trigonox 101 (92%; Akzo Nobel Chemicals, Deventer, The Netherlands) was used as initiator of the grafting reaction of LDPE. It was not repurified before using.

GMA (95%; Suzhou Anli Chemical Co., Suzhou, China) and AA (A. R.; Tianjin Institute of Chemical Reagents, Tianjin, China) were selected as graft monomers. Other chemical reagents such as paraffin oleic acid, styrene, *p*-benzoquinone, triphenyl phosphite, DPTT, 4-hydroxyl-TEMPO, etc., were commercial products. All reagents were used as received.

Preparation of PE-*g*-AA and PE-*g*-GMA Copolymers

PE-*g*-AA and PE-*g*-GMA were prepared by a reactive extruding process in a homemade corotating twin-screw extruder. The diameter of the screws is 30 mm and the ratio of length to diameter (L/D) is 44. L/D of reactive zone is 24, and 16 for melting zone. The maximum torque of screw is 2 × 147 N · M. The maximum processing temperature is 360°C, and the fluctuation of temperature is within ±5°C. The barrel of the extruder is divided into 11 segments and each segment is heated independently.

Considering half time of initiator is about 75 s at 180°C, we set a sequence of segment temperatures at 130, 140, 185, 185, 190, 190, 195, 195, 190, and 180°C from feeder to die and die temperature at 170°C. The premixed PE, monomer, and initiator were added through the feeder, then pelletized after extrusion. By adjusting residence time (from 50 to 160 s), monomer concentration (1–5 wt %, based on PE as 100 wt %), and initiator concentration (0.05–1 wt %, based on PE as 100 wt %), PE graft copolymers were obtained with different degrees of grafting and gel content.

Purification of PE Graft Copolymer

Approximately 3–5 g PE graft sample was dissolved in 150 mL of xylene, then the solution was poured into 500 mL of acetone with stirring. The precipitate was filtered by vacuum and washed with acetone, then dried in a vacuum oven at 60°C for 24 h.

Determination of Degree of Grafting

Chemical Titration

PE-g-GMA. The degree of grafting of GMA was determined by a nonaqueous back-titration.[6] Approximately 1 g of the purified sample was dissolved in 50 mL of hot xylene, followed by the addition of 5 mL ($1.95 \times 10^{-2}M$) of trichloroacetic acid solution in xylene. The solution was kept refluxing for 90 min, then titrated with 0.1N KOH in methanol using phenolphthalein as an indicator. The blank titration with plain PE was performed under the same conditions.

The equation to calculate degree of grafting of GMA can be expressed as:

$$\text{DG (wt \%)} = \frac{(V_s - V_b) \times N \times M}{W} \times 100 \quad (1)$$

where V_s and V_b represent the volume of KOH/MeOH solution used for titration of grafted PE and plain PE, N is molar concentration of KOH/MeOH solution, M is the molecular weight of GMA, and W is the weight of grafted PE.

PE-g-AA. Approximately 0.5 g of the purified PE-*g*-AA sample was dissolved in 50 mL of hot

xylene, then titrated with 0.05N KOH in methanol using phenolphthalein as an indicator.

The equation to calculate degree of grafting of AA can be expressed as:

$$DG \ (wt \ \%) = \frac{V \times N \times M}{W} \times 100 \qquad (2)$$

where V represents the volume of KOH/MeOH solution used for titration of grafted PE, N is molar concentration of KOH/MeOH solution, M is the molecular weight of AA, and W is the weight of grafted PE.

Fourier Transform Infrared (FTIR) Spectrum

FTIR spectra were also used to determine the degree of grafting of PE grafted copolymers. Calibration equations were obtained by using the following procedure: A series of samples in which degrees of grafting had been determined by chemical titration were pressed into film at 180°C. A BIO-RAD FTS-135 IR spectrometer was adopted for the measurements. Its resolution is 4 cm^{-1} and the number of scans is 16. Ratios of A$_{1736}$ to A$_{1378}$ and A$_{1716}$ to A$_{1378}$ for PE-g-GMA and PE-g-AA, respectively, were plotted versus degrees of grafting samples. By linear fit, the relationship between IR spectrum and degree of grafting was obtained.

Determination of Gel Content and MFR

A unpurified sample (100–150 mg) was packed in a preweighed nickel net and put in a Soxhlet extractor, extracted with xylene for 24 h, then dried in a vacuum oven at 60°C until its weight was constant. The gel content was calculated by the following equation:

$$gel \ content \ (\%) = \frac{W_s - W_n}{W_p} \times 100 \qquad (3)$$

where W_s, W_n, and W_p represent the total weight of polymer and nickel net after being extracted, the weight of nickel net, and the weight of polymer, respectively.

MFR was measured at 190°C under the weight of a piston weighing, in combination with its plunger, 2160 g. The diameter of orifice was 2.095 mm and length was 8 mm.

RESULTS AND DISCUSSION

Formation of LDPE-g-GMA and LDPE-g-AA

FTIR spectra of PE, PE-g-AA, and PE-g-GMA are shown in Figure 1. Compared with the spectrum
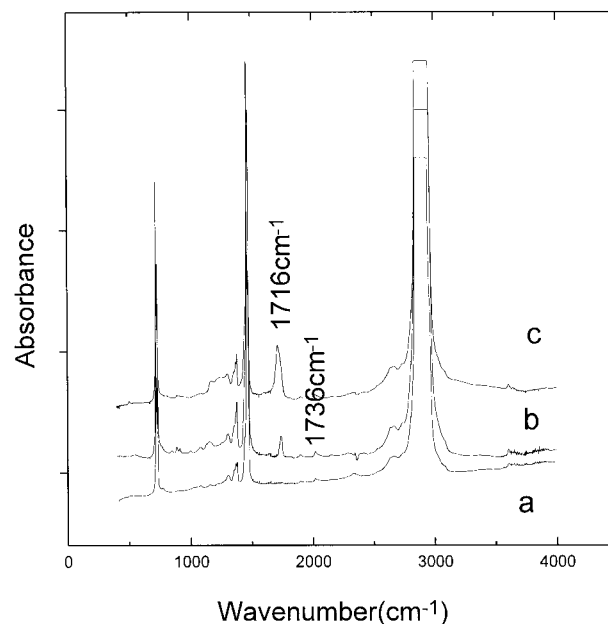

Figure 1 FTIR spectra of (a) LDPE, (b) LDPE-g-GMA, and (c) LDPE-g-AA.

of the plain PE, new peaks at 1716 and 1736 cm^{-1}, corresponding to the carbonyl groups of AA and GMA, respectively, appeared in PE-g-AA and PE-g-GMA samples, which indicated that AA and GMA had been grafted onto the molecular chains of PE.

By determining the spectra of a series of samples in which degrees of grafting had been determined by chemical titration, FTIR calibration equations for determining degree of grafting were obtained, as shown in eqs. (4) and (5):

$$degree \ of \ grafted \ AA \ (\%) = 1.024 \ A_{1716}/A_{1378} \quad (4)$$

$$degree \ of \ grafted \ GMA \ (\%) = 2.050 \ A_{1736}/A_{1378} \qquad (5)$$

where A_{1716}/A_{1378} and A_{1736}/A_{1378} were the ratio of the height of carbonyl stretch peaks (1716 cm^{-1} for AA and 1736 cm^{-1} for GMA, respectively) to methyl peak (1378 cm^{-1}).

Mechanism of Melt Graft Copolymerization

The mechanism of melt grafting of AA and GMA monomers onto PE backbone with a peroxide initiator is very complicated, and can be tentatively expressed in the following Scheme:
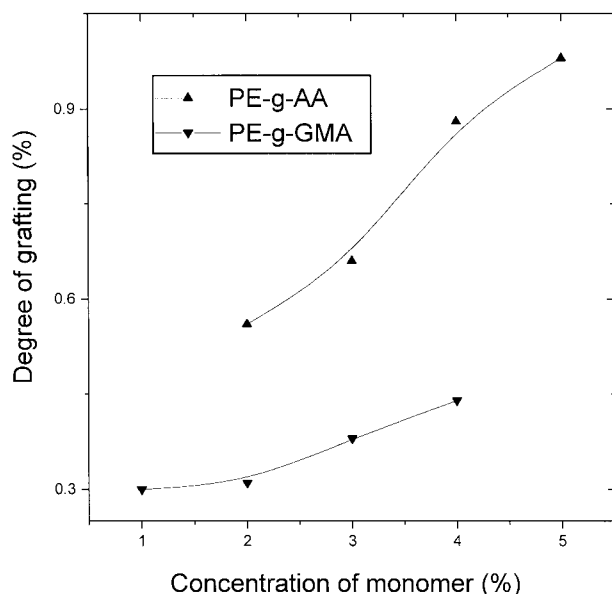
Figure 2   Effect of concentration of monomer on degrees of grafting of LDPE-*g*-GMA and LDPE-*g*-AA. Concentration of initiator, 0.3%; residence time, 160 s.

Peroxide decomposition: ROOR $\rightarrow$ 2RO · [1]
Initiation: RO · + M $\rightarrow$ M · [2a];
                                          RO · + P $\rightarrow$ P · [2b]
Propagation: M · + M$_{n-1}$ $\rightarrow$ M ·$_n$ [3a];
                                          P · + M $\rightarrow$ P − M · [3b];
                                          P − M · +M$_{n-1}$ $\rightarrow$
                                                      P − M ·$_n$ [3c]
Termination: M·$_n$ + M·$_m$ $\rightarrow$ M$_{n+m}$ [4a];
                                          P · + P · $\rightarrow$ P − P [4b];
                                          P − M·$_n$ + P − M·$_m$ $\rightarrow$
                                                      P − M$_{n+m}$ − P [4c]

M · , M ·$_n$, and P · represent monomer radical, homopolymer radical, and PE macroradical, respectively. The schematic reaction path is just a main part of the total reactions happening in the extrusion process during melt grafting copolymerization. There should be some other reactions such as chain transfer, disproportionation, etc. This scheme is used to explain qualitatively some factors that affect the grafting degree and the gel content in this system.

Effect of Monomer Concentration on Degree of Grafting and Gel Content

As shown in Figures 2 and 3, when the concentration of the initiator was fixed at 0.3% (by weight), the degree of grafting of PE-*g*-AA increased and gel content decreased with increasing monomer concentration. This feature can be ten-

tatively explained as follows: During reactive extrusion, primary radicals, coming from the initiator decomposition, could react either with monomer AA (reaction [2a] in scheme) to form monomer radicals, or with PE molecular chains to form PE macroradicals (reaction [2b] in scheme). The monomer radical would participate in grafting reaction on PE molecular chains or form AA homopolymer. With increasing concentration of the AA monomer, the possibility and rate of grafting reaction and homopolymerization of AA would increase, and the coupling reactions between PE macroradicals would decrease.

In the PE-*g*-GMA system, a similar trend was observed for grafting of GMA, but its value was much lower than AA. The gel content of PE-*g*-GMA was very low, and not much difference could be found when the monomer content was increased. This could be attributed to the fact that the activity and rate of homopolymerization of GMA were higher than AA.[11]

Effect of the Initiator Concentration on Degree of Grafting and Gel Content

When the concentrations of AA and GMA were fixed at 4% (by weight), degrees of grafting of both PE-*g*-AA and PE-*g*-GMA increased with enhancement of the initiator, as shown in Figure 4. There seems to be a critical concentration of the initiator
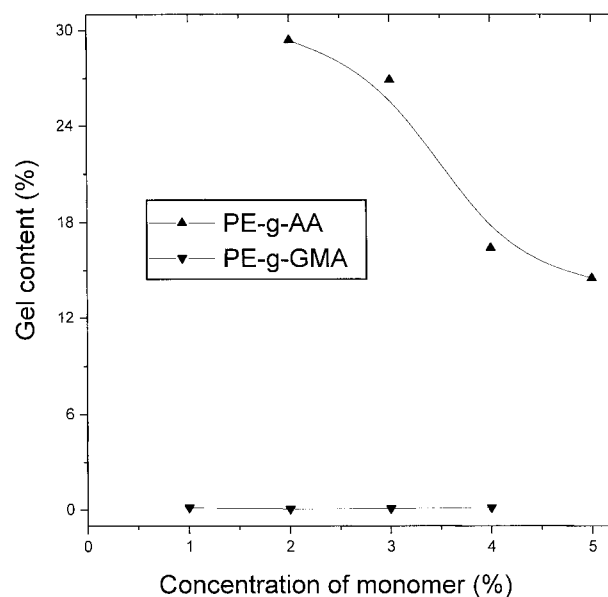

Figure 3   Effect of concentration of monomer on gel content of LDPE-*g*-GMA and LDPE-*g*-AA. Concentration of initiator, 0.3%; residence time, 160 s.
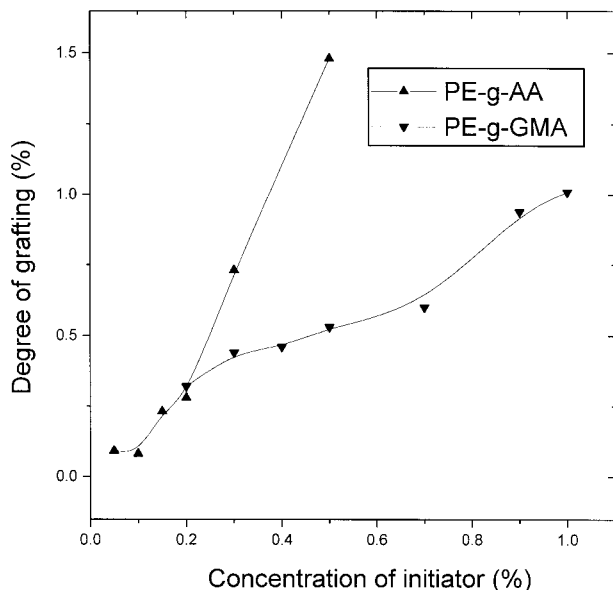
Figure 4 Effect of concentration of initiator on degree of grafting of LDPE-*g*-GMA and LDPE-*g*-AA. Residence time, 160 s; concentration of monomer, 4%.
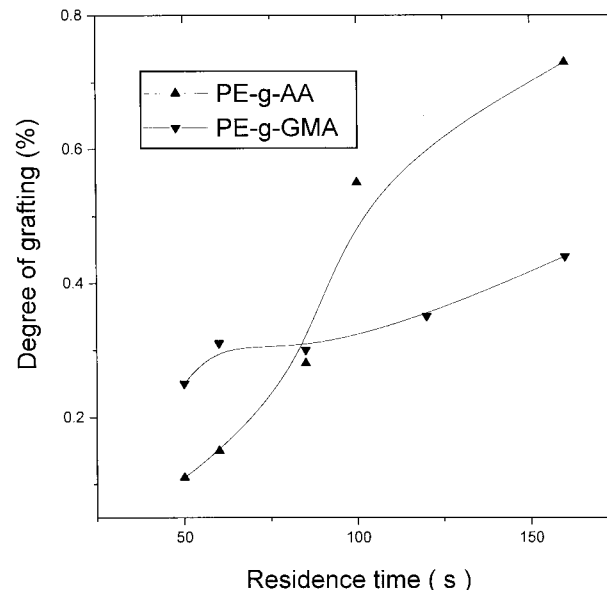

Figure 6 Effect of residence time on degree of grafting of LDPE-*g*-GMA and LDPE-*g*-AA. Concentration of initiator, 0.3%; concentration of monomer, 4%.

for the relationship between the gel content and the initiator concentration. As shown in Figure 5, it is 0.2% for PE-*g*-AA and 0.9% for PE-*g*-GMA. When the initiator concentration was beyond the critical value, their gel contents were sharply increased.

Effect of Residence Time on Degree of Grafting and Gel Content

As shown in Figures 6 and 7, at fixed concentrations of grafting monomers (4% by weight) and initiator (0.3% by weight), both the degrees of grafting and the gel content of PE-*g*-AA and PE-
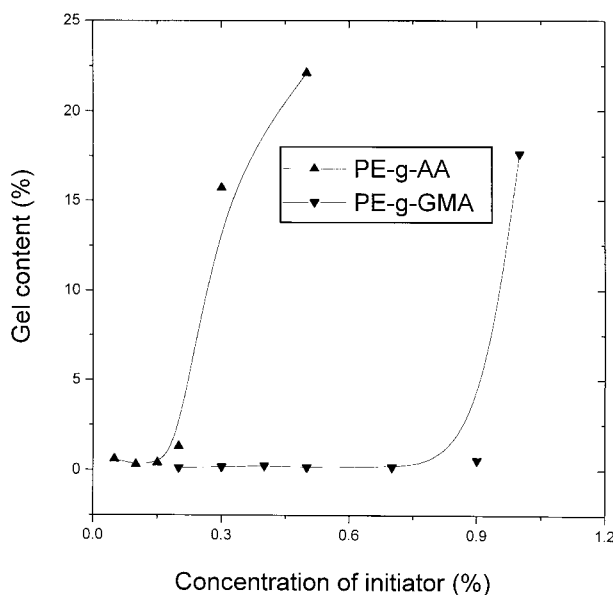

Figure 5 Effect of concentration of initiator on gel content of LDPE-*g*-GMA and LDPE-*g*-AA. Residence time, 160 s; concentration of monomer, 4%.
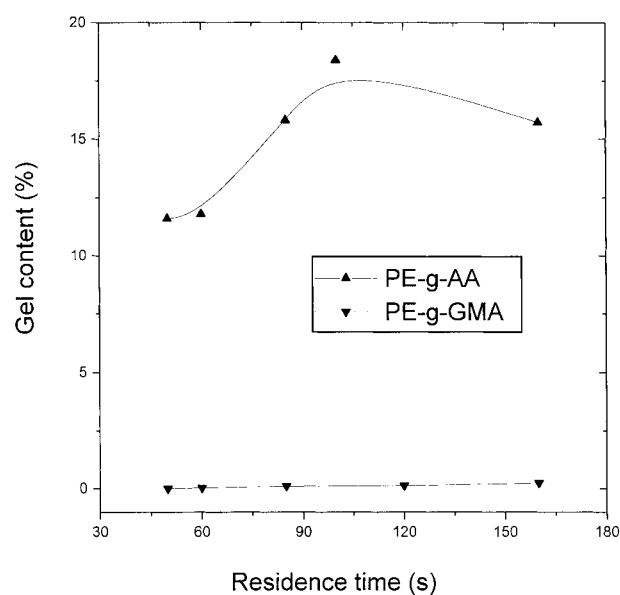

Figure 7 Effect of residence time on gel content of LDPE-*g*-GMA and LDPE-AA. Concentration of initiator, 0.3%; concentration of monomer, 4%.

Table I   Effect of Additives on Degree of Grafting and Gel Content[a]

Additives	Gel Content (%)	Degree of Grafting (%)
None	17.6	1.01
p-Benzoquinone (0.1 wt %)	3.6	0.76
Triphenyl phosphite (1 wt %)	0.9	0.82
CCl$_4$ (4 wt %)	0.3	0.80
Styrene (4 wt %)	36.7	2.65
Paraffin (4 wt %)	14.1	1.45
Oleic acid (4 wt %)	16.7	1.30

[a] Residence time, 160 s; concentration of initiator, 1%; concentration of monomer (GMA), 4%.

g-GMA samples increased with extension of residence time of PE in the twin-screw extruder. The residence time of PE material in the extruder defines the time of the grafting or crosslinking reactions. For the PE-g-GMA system, to get a high grafting degree, longer residence time could be adopted. This was because there was a negligible enhancement of the gel content.

Addition of Additives and Their Effect on Degree of Grafting and Gel Content

As mentioned in the previous paragraphs, for the PE-g-GMA system, it is difficult to get PE grafted copolymers with high grafting degree and acceptable crosslinking extent by changing processing parameters. To reduce the crosslinking reaction, we selected several other chemical agents such as paraffin, oleic acid, styrene, p-benzoquinone, tetrachloromethane (CCl$_4$) and triphenyl phosphite as additives during the melt grafting process. As is well known, CCl$_4$ and p-benzoquinone are often used as chain transfer agent and inhibitor in free radical polymerization, respectively. Triphenyl phosphite is a common antioxidant in the plastics industry: it can react rapidly with different types of radicals. During melt grafting copolymerization, it reacts with primary radicals, PE macroradicals, and monomer radicals. It could be predicted that both the crosslinking reaction and graft copolymerization might be prohibited. The effect of several additives on degree of grafting and gel content of PE-g-GMA copolymers is shown in Table I.

It seems that p-benzoquinone, triphenyl phosphite, and tetrachloromethane are good additives to reduce crosslinking of PE macroradicals, and the obtained PE-g-GMA copolymers have higher degrees of grafting. As shown in Table I, when styrene was added, both degree of grafting and gel content of PE-g-GMA increased.

The addition of paraffin and oleic acid increases the grafting degree of PE graft copolymers and decreases its gel content somewhat. However, if the concentration of the initiator was decreased to 0.1–0.2%, by addition of 1–2% oleic acid, the grafting degree of PE graft copolymers increased dramatically. Their gel content could be controlled to a very low level, as shown in Table II. This finding should be important in applications.

Addition of Iniferters and Their Effect on Degree of Grafting and Gel Content

Living free radical polymerization has been widely investigated to obtain polymers with designed structures. One of the methods involves the repeated reinitiation of polymer propagation by thermolysis or photolysis of weak linkages in polymer, such as S—S bonds or C—S bonds. Among the thio-initiators used are disulphides, xanthates, and carbamates, which are often called iniferters,[12] 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) had been found to act in a similar manner to the iniferters in living free radical polymerization.[13–15] TEMPO reacts only with carbon-centered radicals, not oxygen-centered radicals. We attempted to use 4-hydroxyl-TEMPO to control the crosslinking reaction. The result is shown in Table III. The gel content was little changed, whereas degree of grafting reduced remarkably. It can be tentatively explained that: 4-hydroxyl-TEMPO is dissolved in monomers, reacts preferentially with monomer radical, and slows down monomer homopolymerization.

DPTT can also be used as an iniferter in living free radical polymerization. It has been reported that sulphur can make saturated polyolefins crosslink above 200°C.[16] This means that sulphur radicals can abstract hydrogen from saturated polyolefins to form macroradicals. DPTT could

Table II   Effect of Oleic Acid on Degree of Grafting and Gel Content of PE-*g*-AA Copolymer[a]

Sample	Initiator (%)	Degree of Grafting (%)	Gel Content (%)	MFR (g/10 min)
AA (4%)[b]	0.1	0.08	0.3	2.12
AA (1%) Oleic acid (2%)	0.1	0.33	0.1	2.61
AA (2%) Oleic acid (2%)	0.1	0.73	0.3	1.88
AA (4%)[b]	0.15	0.23	0.4	1.38
AA (1%) Oleic acid (2%)	0.15	0.48	0.3	1.29
AA (2%) Oleic acid (2%)	0.15	0.89	3.8	1.07
AA (4%)[b]	0.2	0.28	1.3	1.39
AA (1%) Oleic acid (2%)	0.2	0.51	0.5	1.17
AA (2%) Oleic acid (2%)	0.2	0.94	9.3	0.65

[a] Residence time, 85 s.
[b] Residence time, 160 s.

produce sulphur radicals by thermolysis and it is not dissolved in monomers. We adopted the mixture of DPTT and Trigonox 101 to initiate the grafting reaction. The relative concentration of DPTT in the mixture was from zero to 100% (by weight) and total concentration of the mixture was 1% (by weight). The temperature was set at 220°C. Figure 8 shows that DPTT was capable of initiating graft copolymerization. When DPTT was used alone, both the degree of grafting and crosslinking extent of PE-*g*-GMA copolymer was very low. With increasing relative concentration of DPTT in the mixture, the degree of grafting decreased and MFR increased (Fig. 9), which indicated that DPTT could retard radical reactions.

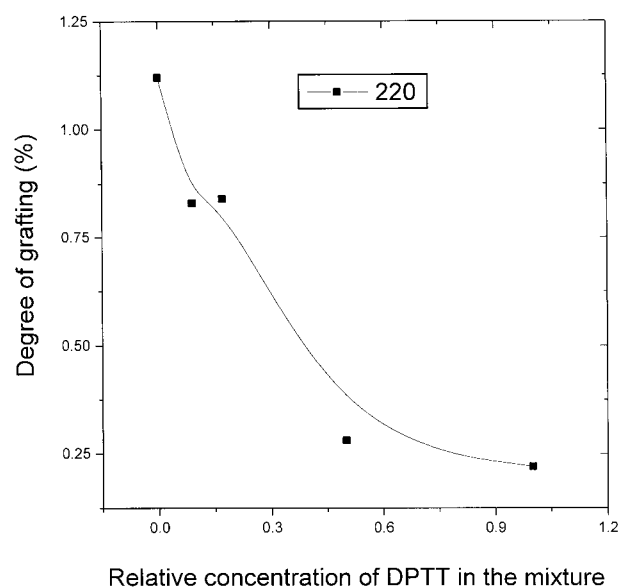### Effect of Concentration of Styrene on Degree of Grafting and Gel Content

As mentioned in the previous paragraph, the addition of styrene alone could increase both the

Table III   Effect of TEMPO on Degree of Grafting and Gel Content[a]

Sample	Gel Content (%)	Degree of Grafting (%)
Initiator (0.3%)	16.5	1.37
Initiator (0.3%) TEMPO (0.3%)	16.6	0.67
Initiator (0.3%) TEMPO (0.6%)	11.6	0.20

[a] Residence time, 160 s; concentration of monomer (AA), 4%.

grafting degree and the gel content of the PE-*g*-GMA copolymer. But, if it was used with DPTT, the gel content of the copolymer could be sharply decreased. As shown in Figures 10 and 11, when adding 1% (wt %) mixture of DPTT and Trigonox 101 (weight ratio of DPTT to Trigonox 101 was 1:10), the grafting degree of the PE-*g*-GMA copolymers increased with increasing content of styrene. Little change occurred for the parameter, MFR.

Figure 8   Effect of DPTT relative content on degree of grating of LDPE-*g*-GMA. Total concentration of DPTT and peroxide mixture, 1%; Residence time, 85 s; concentration of monomer (GMA), 4%.
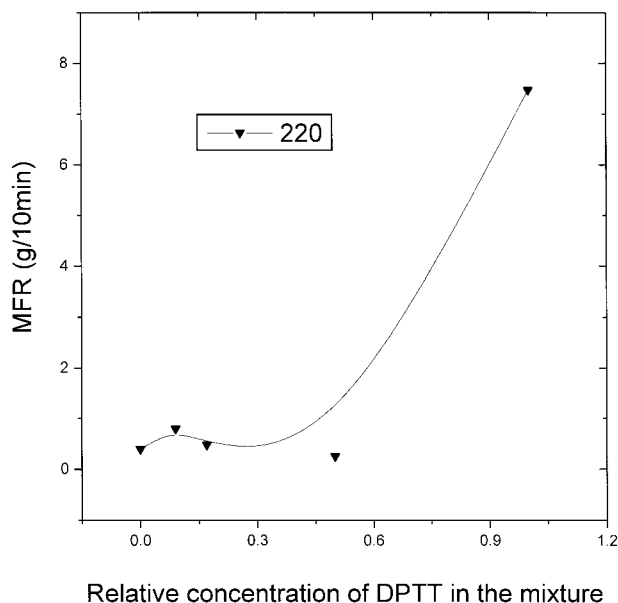
Figure 9   Effect of relative content of DPTT on gel content of LDPE-*g*-GMA. Total concentration of DPTT and peroxide mixture, 1%; Residence time, 85 s; concentration of monomer (GMA), 4%.
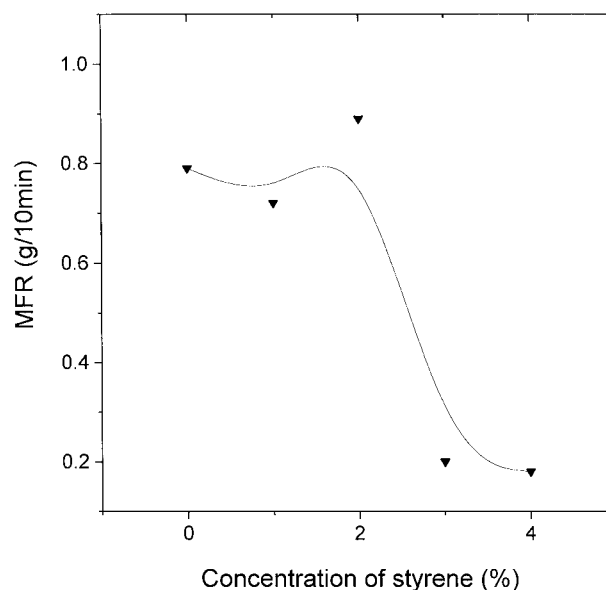
Figure 11   Effect of concentration of styrene on gel content of LDPE-*g*-GMA. DPTT/peroxide = 1:10 (total concentration of mixture is 1% by weight); concentration of monomer, 4%.

CONCLUSIONS

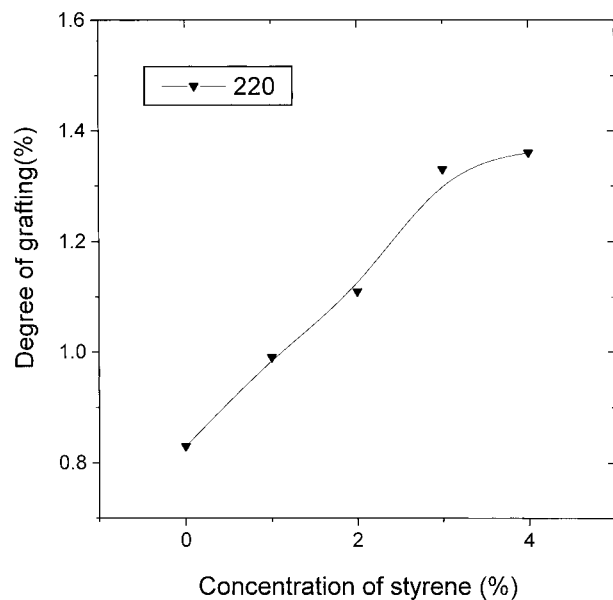1. LDPE-*g*-GMA and LDPE-*g*-AA copolymers were prepared by using a reactive extrusion

Figure 10   Effect of concentration of styrene on degree of grafting of LDPE-*g*-GMA. DPTT/peroxide = 1:10 (total concentration of mixture is 1% by weight); concentration of monomer, 4%.

method. FTIR spectra verified that GMA and AA were grafted onto PE molecular chains. Their grafting degrees could be determined by using both chemical titration methods and IR calibration equations.

2. The degree of grafting and gel contents of two copolymers increased with increasing concentration of the initiator and residence time of melting materials in the twin-screw extruder. But, with increasing concentration of monomers, their degrees of grafting increased whereas their gel contents decreased. A critical concentration of the initiator was found in this work. When its concentration was lower than this critical value, grafted LDPE copolymers with low gel contents and relatively high degrees of grafting could be obtained.

3. Additives such as *p*-benzoquinone, triphenyl phosphite, and tetrachloromethane could be used as good inhibitors to decrease the crosslinking extent of LDPE-*g*-GMA and LDPE-*g*-AA copolymers. The addition of 1–2% oleic acid, and a decrease of the concentration of the initiator to 1 or 2 tenths of normal dose, gave LDPE grafted copolymers with acceptable grafting degree and less gel content.

4. It was found that TEMPO had a notable

effect on the degrees of grafting and the gel contents of the grafted copolymers. DPTT could initiate the grafting copolymerization, but its reactive activity was very low in the melt grafting process. Incorporation of DPTT with Trigonox 101 and styrene yielded LDPE-*g*-GMA copolymer with a higher grafting degree and less gel content.

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