Grafting of Polystyrene Branches to Polyethylene and Polypropylene

EUN-SOO PARK,[1] HYOUNG-JOON JIN,[1] IK-MO LEE,[2] MAL-NAM KIM,[3] HAN SUP LEE,[1] JIN-SAN YOON[1]

[1] Department of Chemical Science and Engineering, Inha University, 402-751 Inchon, Korea

[2] Department of Chemistry, Inha University, 402-751 Inchon, Korea

[3] Department of Biology, Sangmyung University, 110-743 Seoul, Korea

ABSTRACT: Polyethylene (PE) and polypropylene (PP) were reacted with benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to prepare PE-TEMPO and PP-TEMPO macroinitiators, respectively. Molecular weight of PP decreased, whereas that of PE increased during the reaction with the BPO/TEMPO system. Polystyrene (PS) branches were grafted to PE and PP backbone chains as a result of bulk polymerization of styrene with the PE-TEMPO and PP-TEMPO macroinitiators. A significant amount of PS homopolymer was produced as a byproduct. Weight of the resulting PE-*g*-PS and PP-*g*-PS increased with the polymerization time up to 20 h and then leveled off. Melting point of PE and PP domains in PE-*g*-PS and PP-*g*-PS, respectively, lowered as the content of PS in the copolymers increased. However, glass transition of the copolymers was almost identical with that of PS homopolymer, indicating that the constituents in the copolymers were all phase-separated from each other. In scanning electron microscopy of the incompatible PE/PS, PP/PS, and PE/PP/PS compounded with PE-*g*-PS and PP-*g*-PS, any clear indication of enhanced adhesion between the phases was not observed. However, phase domains in the blends were, nevertheless, reduced significantly to raise mechanical properties such as maximum stress and elongation at break by 20−75%. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1103–1111, 2002

Key words: TEMPO; macroinitiator; polyethylene; polypropylene; polystyrene; graft copolymer

INTRODUCTION

Polyolefins have been used in various applications for daily human life. However, few polymers are compatible with polyolefins because of the absence of any interaction groups in polyolefins. Polyethylene (PE), polypropylene (PP), and polystyrene (PS) are major constituents in commingled waste plastics. Hence, substances compatibilizing the three polymers with each other would be helpful to the recycling of commingled waste plastics without resorting to the tedious and expensive sorting processes. Polyethylene-*g*-polystyrene (PE-*g*-PS) and polypropylene-*g*-polystyrene (PP-*g*-PS) could be effective candidates for the compatibilizer.[1,2]

In general, polyolefin-grafted copolymers are synthesized by the postpolymerization methods. PE-*g*-PS copolymers were synthesized by polymerization of styrene in the presence of PE with photoinitiation or with thermally dissociative initiation.[3–5] However, a systematic study on the effects of molecular structure on the compatibilization with thus synthesized copolymers would be difficult to carry out, because it is very hard to control the graft density and graft length effectively. Moreover, crosslinking reactions often took place concomitantly.

In this study, PE-TEMPO and PP-TEMPO macroinitiators were synthesized, respectively, by reacting PE and PP with benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Styrene bulk polymerization with the macroinitiators produced PE-*g*-PS and PP-*g*-PS, whose molecular structures could be characterized from the concentration of the TEMPO-dormant sites on the macroinitiators.[6–10] The grafting copolymerization was also helpful to investigate the side reactions such as chain-transfer reactions or homopolymerization because PS homopolymer by-product could be easily separated from the copolymers.

EXPERIMENTAL

Materials

Styrene (Junsei) was purified two times by vacuum distillation. BPO (Acros Organics) was purified by precipitation from chloroform into methanol and recrystallized in methanol at 0°C. TEMPO (Aldrich) was used as received. Low-density polyethylene (LDPE; M_w 482,000) and PP (M_w 1,850,000) were donated by Hanhwa (Korea) and Korea Petrochemical (Korea), respectively. PS (M_w 200,000) was received by Hannam Chemical (Korea).

Synthesis of Macroinitiator

The LDPE was first dissolved in 1,2,4-trichlorobenzene at 170°C and kept under a N_2 blanket to prevent oxidation. After stirring for 30 min, the chloroform solution of benzoyl peroxide (1*M*) was then quickly added to the hot solution and stirred for 2 min. The reaction was terminated with an excess quantity of 1,2,4-trichlorobenzene solution of TEMPO (2*M*). The product was precipitated in methanol and dried *in vacuo*, followed by Soxhlet extraction with boiling methanol for 2 days to remove the unreacted TEMPO.

Grafting Copolymerization

Styrene was bulk polymerized in the presence of the macroinitiator at 120°C. The product was precipitated in chloroform and dried *in vacuo*, followed by Soxhlet extraction with boiling chloroform for 2 days to remove PS homopolymer formed during the copolymerization.

Instrumentation

Molecular weight and its distribution were measured by using GPC [Waters model 150C, 1,2,4-trichlorobenzene eluent, 1.0 mL/min, 145°C, column (porosity: 10 μm, Stragel® HT6E, HT5, HT3)] employing PS (Showadenko SL-105) as a standard.

The thermal properties of the polymers were determined by DSC (Perkin–Elmer DSC 7). Thermal history of the products was removed by scanning to 200°C with a heating rate of 20°C/min. After cooling down the sample at the rate of 5°C/min to room temperature, it was reheated at 20°C/min to 200°C and the DSC thermograms were obtained.

Graft copolymers were characterized by ^{1}H-NMR spectra recorded at 120°C on a Bruker AC-250 FT-NMR spectrometer. Ten milligrams of the copolymer was dissolved in 0.5 mL 1,2-dichlorobenzene (20 wt/vol %) and was subjected to the ^{1}H-NMR measurements.

Polymer Blending

The LDPE/PP/PS mixture was fed into the cam-type mixing head of a Brabender Plasti-Corder (Western Germany, Type 810602) set at 180°C. The rotor speed was maintained at 60 rpm and the blending was continued for 10 min in the closed mixer. Blend sheets were made by hot pressing at 200°C for 5 min under 1.55 atm and quickly immersed into ice water. PS sheets were prepared on a hot press at 180°C for 5 min under 1.21 atm and then immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the film were determined with a tensile testing machine (Instron 4462) at a crosshead speed of 5 mm/min, according to ASTM D 638 at 20 ± 1°C.

The film was fractured while immersed in liquid nitrogen and then etched with boiling chloroform to dissolve out the PS domains. SEM (Hita-
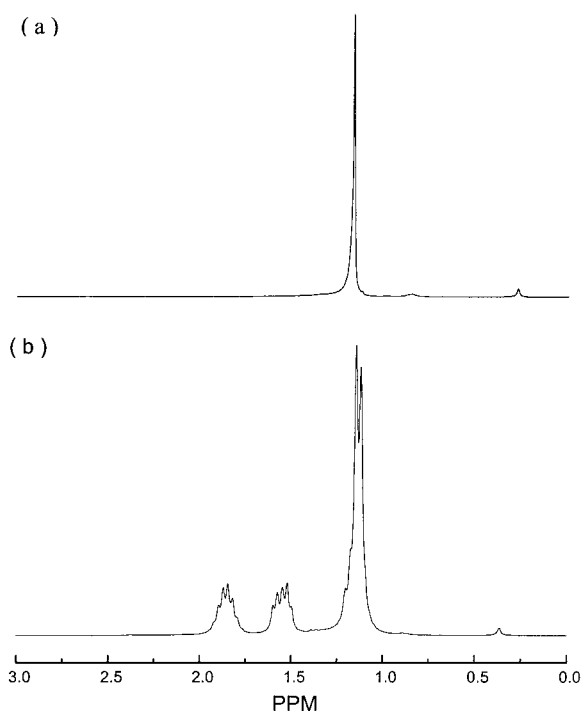
Figure 1 The ^{1}H-NMR spectra of (a) PE-TEMPO, (b) PP-TEMPO.

chi S-4200) was used to observed the fractured surface morphology.

RESULTS AND DISCUSSION

Synthesis of PE-TEMPO and PP-TEMPO Macroinitiators

LDPE and PP were reacted with BPO and TEMPO to produce PE-TEMPO and PP-TEMPO, respectively, whose ^{1}H-NMR spectra were shown in Figure 1. Dokolas et al.[12] investigated the chemistry of free-radical graft copolymerization initiated with *t*-butoxy radicals. They provided evidence that grafting on linear low density polyethylene (LLDPE) occurred most frequently from the secondary C—H reaction sites, whereas grafting on PP took place predominantly at the tertiary C—H sites.

Comparing the ^{1}H-NMR signals of LDPE and PP to those of PE-TEMPO and PP-TEMPO, respectively, it can be perceived that a new peak appeared at 0.37 ppm due to the introduction of TEMPO into the polymers. A clear explanation was not provided yet as to why the signal from the tetramethyl protons of TEMPO, whose ^{1}H-NMR peaks usually appeared at 0.8–0.9 ppm, moved upfield as far as to 0.37 ppm.

Yoshida and Fujii[13] performed radical polymerization of methyl styrene by using BPO in the presence of 4-methoxy-2,2′, 6, 6′-tetramethyl-1-piperidinyl-1-oxy (MTEMPO). The tetramethyl protons from MTEMO on the polymer exhibited their ^{1}H-NMR peaks at 0.30, 0.45, 1.00, and 1.15 ppm.

^{1}H-NMR spectra for both LDPE and PP homopolymers also exhibited small peaks at 0.8–0.9 ppm. Therefore, the peaks at 0.8–0.9 ppm appearing in the spectra of PE-TEMPO and PP-TEMPO in Figure 1 were thought to be due not only to the protons of TEMPO but also to those of LDPE and PP themselves.

Contents of the TEMPO units in the macroinitiators were determined from the peaks at 0.37 and 0.8–0.9 ppm, taking into consideration the contribution of LDPE and PP homopolymers to the peaks at 0.8–0.9 ppm, by assuming that the peak intensity of the methylene protons of LDPE and that of the methine protons of PP were the same as that corresponding to PE-TEMPO and to PP-TEMPO, respectively.

The average number of TEMPO units per macroinitiator molecule, θ, was determined from the average number of TEMPO units per repeating unit of the macroinitiator molecule, θ', using eq. (1):

$$\theta = \frac{\theta'}{1 + \theta'} \, \mu_w \tag{1}$$

where μ_w is the weight average degree of polymerization. θ' was calculated, in turn, from the weight average molecular weight, M_w, using eq. (2):

$$\bar{M}_w = M_1 \left\{ \mu_w - \frac{\theta'}{1 + \theta'} \, \mu_w \right\} + M_2 \frac{\theta'}{1 + \theta'} \, \mu_w \tag{2}$$

where M_1 and M_2 are the molar mass of the repeating unit of the backbone polyolefin and that of the repeating unit holding a TEMPO unit, respectively.

On the average, 6.9 TEMPO units and 8.8 TEMPO units were introduced per 1000 repeating units of PE-TEMPO and PP-TEMPO, respectively. More TEMPO units were found on PP-TEMPO than on PE-TEMPO because the tertiary hydrogen of PP was more susceptible to be abstracted by the peroxide radicals compared to the hydrogen of LDPE.

Table I   Characteristics of Macroinitiator

Sample Code	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)	ΔH_f (J/g)	Graft Density (Number of Reacted TEMPO/1000 Repeating Unit)
PE	482	2.09	105.1	69.1	—
PE-TEMPO	597	2.01	106.6	74.8	6.9
PP	1850	5.00	160.9	73.4	—
PP-TEMPO	674	3.66	160.6	83.6	8.8

In contrast, Dokolas et al.[12] predicted that PP was less reactive than LLDPE to free-radical graft copolymerization initiated with *t*-butoxy radicals from their experimental results with 2-methyl pentane and 2,4-dimethyl pentane as models for LLDPE and PP, respectively.

The molecular weight was decreased and the polydispersity became narrower during the reaction of PP with the BPO/TEMPO system. In contrast, the same reaction increased the molecular weight of LDPE (Table I).

Roover et al.[14] grafted maleic anhydride (MAH) on PP by using 1,3-di-*t*-butyl peroxyisopropyl benzene. They found the molecular weight of PP decreased exponentially with the peroxide concentration irrespective of the MAH concentration.
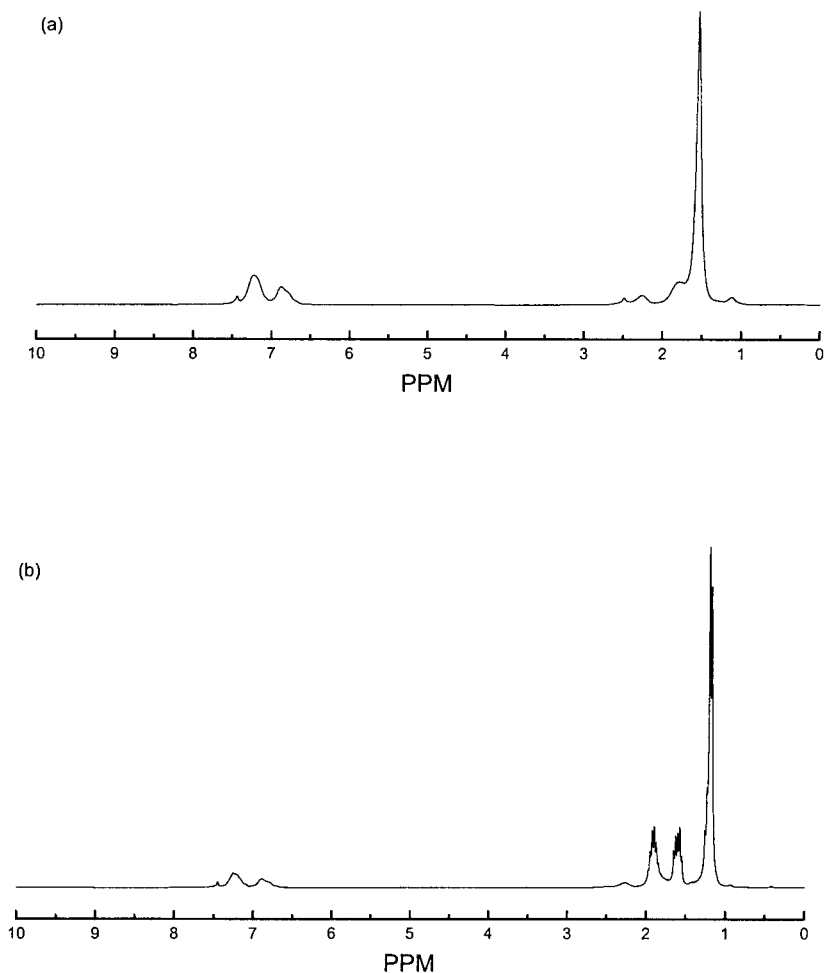

Figure 2 ^{1}H-NMR spectra of (a) PE-*g*-PS (PE-*g*-PS03) and (b) PP-*g*-PS (PP-*g*-PS03).

Table II   Bulk Polymerization of Styrene in the Presence of PE-TEMPO

Sample Code	Polymer Time (h)	Copolymer Yield (g)	Content of Styrene Unit (mol %)[a]	T_m (PE) (°C)	ΔH_f (J/g PE)	M_w ($\times 10^{-3}$)	PS Homopolymer Weight (g)	M_n	M_w
PE-TEMPO	—	—	—	106.6	74.8	597	—	—	—
PE-g-PS01	2	8.9	3.2	105.7	49.0	768	9.8	193	395
PE-g-PS02	5	9.6	4.7	105.4	48.3	813	13.5	250	478
PE-g-PS03	20	12.6	12.3	104.3	46.2	1097	19.3	252	598
PE-g-PS04	40	12.8	—	104.8	—	—	22.0	322	744

[PE-TEMPO] = 8 g; polymerization temperature, 120°C.
[a] Measured from ^{1}H-NMR spectra.

Polymerization of Styrene Using PE-TEMPO and PP-TEMPO

Styrene was bulk-polymerized in the presence of PE-TEMPO and PP-TEMPO in an attempt to synthesize PE-g-PS and PP-g-PS, respectively, whose ^{1}H-NMR spectra were demonstrated in Figure 2.

These experiments were designed to measure the amount of styrene polymerized as a result of the contribution of the reversible cleavage of the TEMPO–polymeric radical adduct, because styrene could be consumed also by the thermal self-initiation and by the radicals produced by the chain transfer reactions.[15] PS homopolymers produced could be easily removed from PE-g-PS and PP-g-PS by using chloroform.

The results of the styrene bulk polymerization with the PE-TEMPO and PP-TEMPO were collected in Tables II and III, respectively.

When the weight increase was plotted as a function of polymerization time for the above two styrene polymerizations, it increased up to 20 h and then leveled off (Fig. 3).

The plateauing behavior is also seen in the plot of grafting conversion as a function of total conversion (Fig. 4). This substantiates the fact that the chain transfer and the thermal self-initiation took place in addition to the reversible cleavage of the TEMPO–polymeric radical adduct, because in the absence of the chain transfer or the thermal self-initiation, the weight increase would rise linearly with conversion.

Tables II and III demonstrate that a huge amount of PS homopolymer was formed as byproducts. Greszta and Matyjaszewski[15] incorporated the transfer to the Mayo dimer into their model, which was 20 times faster than the transfer to styrene, and their model fit accurately both

Table III   Bulk Polymerization of Styrene in the Presence of PP-TEMPO

Sample Code	Polymer Time (h)	Copolymer Yield (g)	Content of Styrene Unit (mol %)[a]	T_g (PS) (°C)	T_m (PP) (°C)	ΔH_f (J/g PP)	M_w ($\times 10^{-3}$)	PS Homopolymer Weight (g)	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)
PP-TEMPO	—	—	—	—	160.6	83.6	674	—	—	—
PP-g-PS01	2	9.0	6.1	105.9	161.5	72.5	800	7.4	136	239
PP-g-PS02	5	9.4	8.8	106.1	158.8	66.1	1106	12.0	215	406
PP-g-PS03	20	10.1	11.3	106.0	156.6	55.0	1550	16.3	243	562
PP-g-PS04	40	10.1	—	104.7	157.3	49.2	—	20.1	294	630
PP-g-PS05[b]	20	9.4	6.0	106.5	156.9	64.6	—	22.0	233	516

[PP-TEMPO] = 8 g; polymerization temperature, 120°C.
[a] Measured from ^{1}H-NMR spectra.
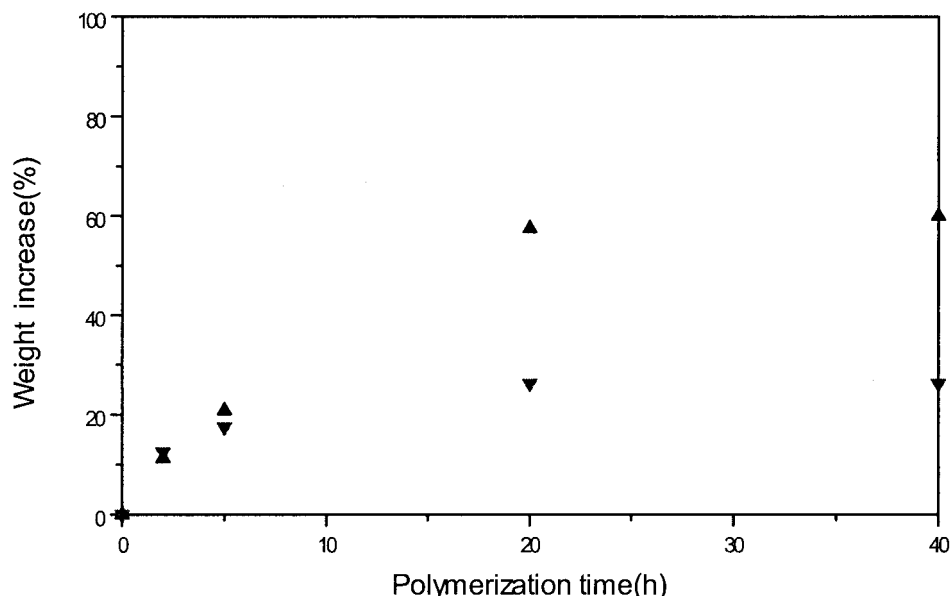[b] Polymerization temperature, 130°C.

Figure 3 Weight increase as a function of polymerization time for bulk polymerization of styrene using PE-TEMPO (▲) and PP-TEMPO (▼) at 120°C.

the kinetic data and the molecular weight of the thermal self-initiated styrene homopolymerization. The alkoxyamines could also be irreversibly decomposed to the hydroxylamine and the macromolecular species.[15]

Admitting that the rate of transfer to polymer is much slower than the other transfer reactions, the PE-*g*-PS and PP-*g*-PS should cease to grow once the chain breaking reactions took place. At the polymerization temperature (120°C), the
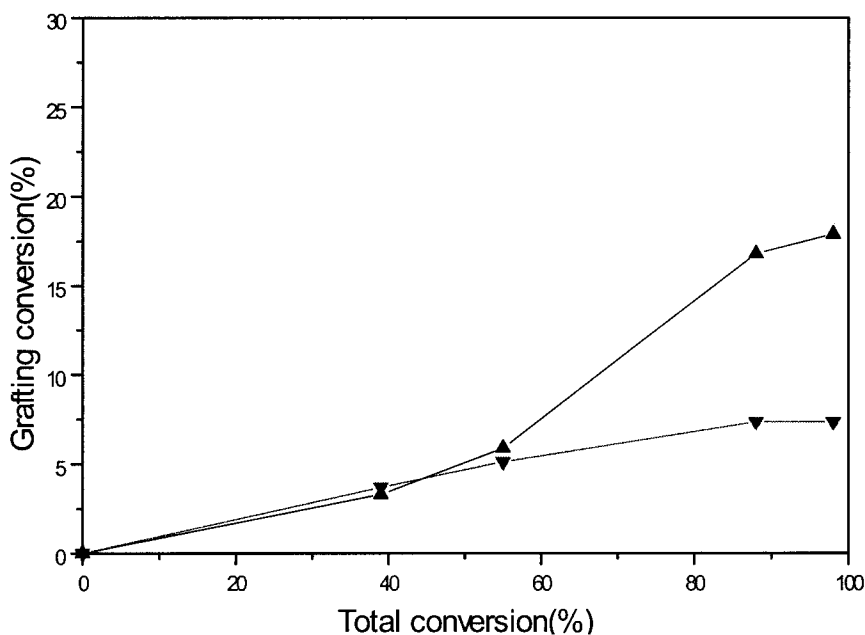

Figure 4 Grafting of polystyrene to PE-TEMPO (▲) and PP-TEMPO (▼). Graft conversion: (weight increase of the copolymer)/(initial weight of styrene).

Table IV   Thermal Properties of PP/PE/PS Blend System

Blend System	Blend Composition (wt %)	PS (T_g) (°C)	PE (T_m) (°C)	PP (T_m) (°C)	PE (T_c) (°C)	PP (T_c) (°C)
PP/PE/PS	33/34/33	—	105.5	157.7	85.8	105.0
PP/PE/PS/PP-g-PS/PE-g-PS	30/30/30/5/5	—	106.5	159.7	86.4	109.1
PP/PS	50/50	103.1	—	155.6	—	106.2
PP/PS/PP-g-PS	45/45/10	103.4	—	157.3	—	108.4
PE/PS	50/50	—	105.6	—	85.1	—
PE/PS/PE-g-PS	45/45/10	—	105.5	—	86.2	—

polymer radicals and the free TEMPO molecules are in equilibrium with the TEMPO-dormant site with equilibrium constant of 10^{11} L/mol.[15]

While the free TEMPO molecules, which are approximately 0.1% based on the initial concentration of the alkoxyamine, are cleaved off from the alkoxyamine dormant site, propagation takes place by the radicals on the copolymer molecules.

Protection of the radicals on the copolymer molecules by the free TEMPO molecules becomes less probable and they are more susceptible to the chain breaking reactions, because radicals are continuously generated in styrene monomer moiety and share the TEMPO molecules with the radicals on the copolymer molecules.

The macroinitiators were used on an equal weight basis; molar concentration of TEMPO dormant sites of PE-TEMPO was 1.2 times higher than that of PP-TEMPO. However, this does not provide a full explanation for the curious fact that the weight increase in the polymerizations with PE-TEMPO was much greater than that with PP-TEMPO.

Aside from the TEMPO-dormant sites, the copolymer molecules could also become active for styrene polymerization once the radicals were transferred from the styrene moiety to the copol-ymer molecules. We do not have at present any logical reasoning why the radicals are more easily transferred to PE-g-PS than to PP-g-PS, or why the TEMPO–polymer radical intermediates in the PP-g-PS are more susceptible to the chain breaking reactions than those in PE-g-PS.

The molecular weight of the PS homopolymer in Tables II and III was much higher than that of PS produced during the styrene polymerization with TEMPO/BPO system.[16]

Hui and Hamielec[17] reported that molecular weight of PS produced by thermal self-initiation decreased slightly or remained almost constant depending on polymerization temperature as the conversion rose. In direct contrast, molecular weight of PS homopolymer in Tables II and III increased with the conversion.

This implies that some radicals on PS homopolymer molecules were protected by the free TEMPO molecules from the chain-breaking reactions.

The glass transition temperature of PP-g-PS appeared at 105°C irrespective of the copolymer composition, indicating that PS and PP moieties in the copolymer were separated from each other, because the glass transition temperature was the same as that of PS homopolymer (Table IV). The

Table V   UTM Data of PP/PE/PS Blend System

Blend System	E. Modulus (MPa)	Max Stress (MPa)	Elongation at Break (%)
PP/PE/PS	798	9.8	2.04
PP/PE/PS/PP-g-PS/PE-g-PS	742	12.9	2.44
PP/PS	1238	12.2	1.51
PP/PS/PP-g-PS	1238	21.4	2.12
PE/PS	475	6.6	2.11
PE/PS/PE-g-PS	568	10.1	2.56
PS	1805	31.8	2.10

(a) PP/PE/PS(33/33/34)

(b) PP/PE/PS/PP-*g*-PS/PE-*g*-PS (30/30/30/5/5)

(c) PP/PS(50/50)

(d) PP/PS/PP-*g*-PS(45/45/10)

(e) PE:PS(50/50)

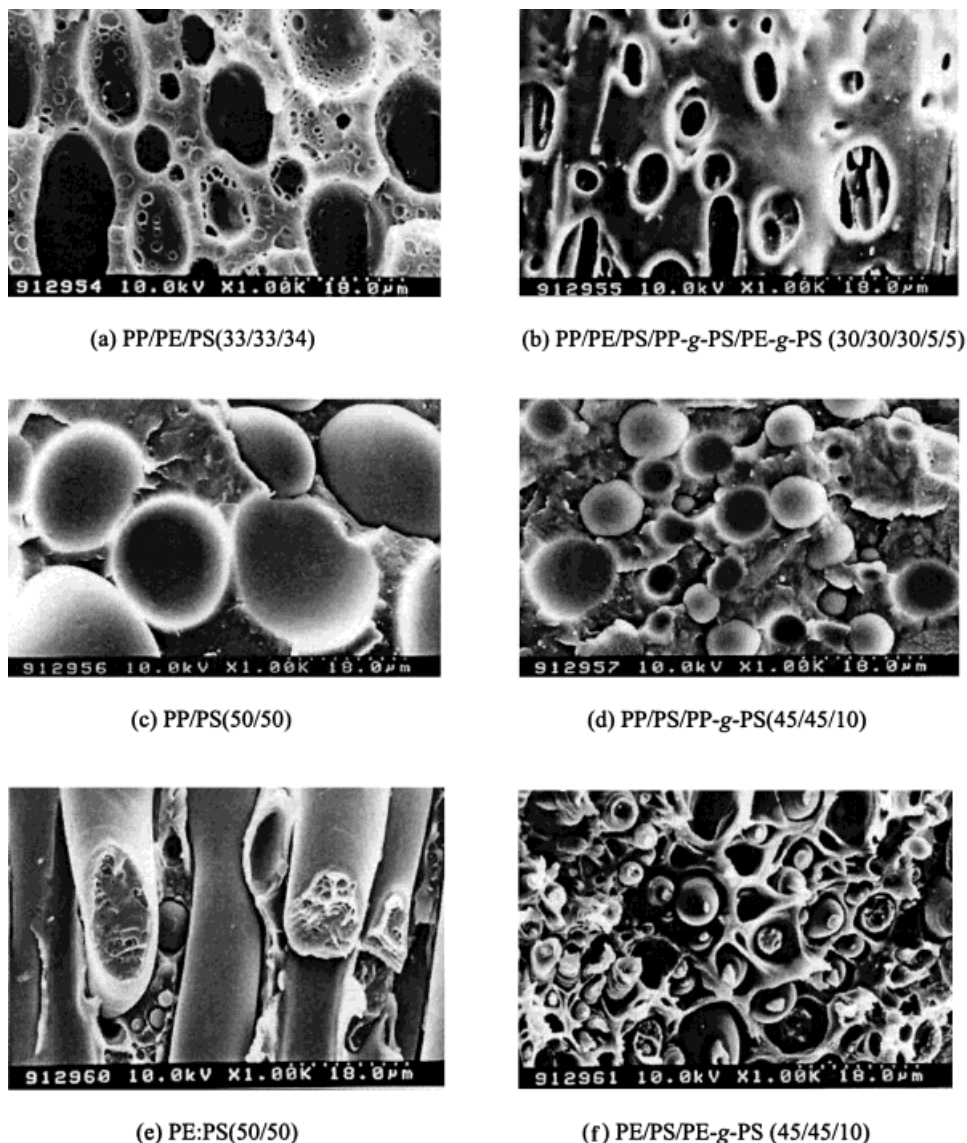(f) PE/PS/PE-*g*-PS (45/45/10)

Figure 5 Scanning electron photomicrographs of the fractured surface.

glass transition temperature of the PS phase in PE-*g*-PS was covered up by the melting peak of the PE phase.

It is to be noted that the melting temperature of both PE-*g*-PS and PP-*g*-PS decreased as the PS content increased, which was ascribed to the fact that the PS moieties seized hold of the crystallizable PE and PP parts to reduce the crystallization rate of the latter.

Chung et al.[11] also observed that the melting temperature of PE-*g*-PS synthesized by an anionic polymerization decreased with an increase of the PS content.

Compatibilizing Effect of PE-*g*-PS and PP-*g*-PS

PE-*g*-PS03 and PP-*g*-PS03 were compounded with the incompatible PP/PE/PS, PP/PS, and PE/PS blend systems, and the results were collected in Tables IV and V. The glass transition peak of the PS phase, the melting peaks of the PE and PP phase, and the crystallization peaks appeared well separated from each other, except that the T_g of the PS phase was masked by the melting peak of the blends containing PE moiety.

Incorporation of the graft copolymers enhanced significantly the mechanical properties of the blends such as the maximum stress and the elon-

gation at break (Table V), in spite of the fact that the SEM micrograph in Figure 5 did not show any clear indication of improved adhesion between the separated phases. However, the domain size of the dispersed phase was reduced in the presence of the graft copolymers.

The crystallization temperature in Table III was obtained during cooling at $-5°C$/min from the melt state. Hence, the higher the crystallization temperature, the more easily the crystallization takes place. It is interesting to observe that the addition of the graft copolymer rendered the blends more crystallizable, which should be at least partly ascribed to the increased interfacial area for the crystal nucleation sites.

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