

Synthesis of Polyethylene-graft-Poly(styrene-co-maleic anhydride) and Its Compatibilizing Effects on Polyethylene/Starch Blends

Eun-Soo Park, Jin-San Yoon

Department of Chemical Science and Engineering, Inha University, 402-751 Incheon, Korea

Received 26 November 2001; accepted 9 September 2002

ABSTRACT: Low density polyethylene (LDPE) was reacted with benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to prepare a latent macroinitiator, PE-TEMPO. Little polymer was synthesized when maleic anhydride (MAH) was bulk polymerized in the presence of the PE-TEMPO. However, addition of styrene accelerated the polymerization rate and PE-grafted-poly(styrene-co-maleic anhydride) [PE-g-P(ST-co-MAH)] was produced to a high yield. Chemical reaction between MAH units and hydroxyl groups of starch was nearly undetectable in the PE/PE-g-

P(ST-co-MAH)/starch blend system, and the tensile properties of the blend were not enhanced significantly. However, addition of tetrabutyl titanate (TNBT) during the blending procedure improved the tensile properties significantly through an increased interfacial adhesion between the components in the blend system. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2434–2438, 2003

Key words: graft copolymers; polyethylene; starch; blends

INTRODUCTION

Introduction of functional groups onto polyolefins has been investigated to improve the compatibility of polyolefins with other synthetic polymers.^{1,2} Graft polymerization is often employed for the functionalization of polyolefins. The conventional graft polymerization on polyolefins using thermal and photoinitiators cannot control graft density and graft length effectively, and sometimes crosslinking or chain scission takes place.

A 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-bound macroinitiator^{3–5} could synthesize various block copolymers such as polystyrene-*b*-polycaprolactone,⁶ polyethylene-*b*-poly(styrene sulfonate),⁷ and polystyrene-*b*-poly(*p*-bromostyrene),⁸ using the living character of the radical polymerization.

In this study, graft copolymerization of styrene (ST) and maleic anhydride (MAH) was carried out using polyethylene (PE)-TEMPO as a macroinitiator.

ST homopolymerization with PE-TEMPO proceeded very slowly and produced a large amount of polystyrene (PS) homopolymer by-product. A negligible amount of MAH was grafted by PE-TEMPO when MAH was homopolymerized. However, the graft copolymerization became fast in the presence of ST/

MAH mixture. The amount of MAH units in the produced PE-g-P(ST-co-MAH) was much larger than that of MAH grafted on PE by using the conventional grafting method with thermal or photoinitiators. The compatibilizing effect of PE-g-P(ST-co-MAH) on a PE/starch blend was investigated for enhancement of mechanical properties.

EXPERIMENTAL

Materials

ST (Junsei, Tokyo, Japan) was purified by two times of vacuum distillation. Benzoyl peroxide (BPO) (Acros Organics, NJ) was purified by precipitation from chloroform into methanol, and recrystallized in methanol at 0°C. TEMPO (Aldrich, Milwaukee, WI) was used as received. Low density polyethylene (LDPE) (MI = 5, MW = 482,000) was donated by Hanhwa (Ulsan, Korea). Corn starch was received by Samyang (Incheon, Korea). Other chemical compounds were of reagent grade and were used as received.

Instrumentation

Molecular weight and its distribution were measured using gel permeation chromatography (GPC) (Waters Instruments, Rochester, MN) model 150C, 1,2,4-trichlorobenzene eluent, 1.0 mL/min, 145°C, column (porosity: 10 μ m, Stragel® HT6E, HT5, HT3) employing PS (Showadenko SL-105, Tokyo, Japan) as a standard.

Correspondence to: J-S. Yoon (jsyoon@inha.ac.kr).

Contract grant sponsor: KOSEF; contract grant number: 1999-2-308-004-3.

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) (Perkin–Elmer DSC 7, Norwalk, CT). Thermal history of the products was removed by scanning to 200°C with the 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 ¹H nuclear magnetic resonance (NMR) spectra recorded at 120°C on a Bruker AC-250 FT-NMR spectrometer (Bruker Instruments, Billerica, MA). Ten milligrams of the copolymer was dissolved in 0.5 mL of 1,2-dichlorobenzene (20 wt/vol %) and was subjected to the ¹H-NMR measurements.

Synthesis of macroinitiator

The PE–TEMPO macroinitiator was prepared according to the method described previously.² LDPE (10g) was first dissolved in 50 mL of 1,2,4-trichlorobenzene (TCB) at 170°C and kept under N₂ blanket to prevent oxidation. After stirring for 30 min, the chloroform solution of BPO (1M) was then quickly added to the hot solution and stirred for 2 min. The reaction was terminated with an excess quantity of TCB (2 mL) solution of TEMPO (200 mg). The product was precipitated in methanol and dried *in vacuo* followed by the Soxhlet extraction with boiling methanol for 2 days to remove the unreacted TEMPO.

Polymerization of ST/MAH using PE–TEMPO

Bulk polymerization of ST/MAH was carried out using PE–TEMPO according to the method described previously.¹² The chemistry for the TEMPO-mediated polymerization has been well described by Veregin et al.¹³

MAH (1 g) was first dissolved in ST (20 mL) at room temperature, to which PE–TEMPO (3 g) was added successively. Graft copolymerization was carried out at 120°C for 2 h. The product was precipitated in chloroform and dried *in vacuo* followed by the Soxhlet extraction with boiling chloroform for 2 days to remove ungrafted poly(ST-*co*-MAH) formed during the copolymerization.

Solution polymerization of ST/MAH was carried out in dry xylene using PE–TEMPO. MAH (10 g) and PE–TEMPO (3 g) was first dissolved in xylene (100 mL) at 120°C under N₂ atmosphere. After stirring for 30min, ST (5.2 g) was then added to the hot solution and stirred for 20 h. The product was precipitated in chloroform and dried *in vacuo* followed by the Soxhlet extraction with boiling chloroform for 2 days to remove ungrafted poly(ST-*co*-MAH) formed during the copolymerization. The grafted ST conversion of the copolymers were determined by using

Grafted ST conversion (%) =

$$\frac{\text{Copolymer yield(g)} \times \text{ST content (on weight basis)} - \text{macroinitiator(g)}}{\text{Initial amount of ST(g)}} \times 100 \quad (1)$$

Polymer blending

The PE(6.4 g)/PE-*g*-P(ST-*co*-MAH)(1.0 g) mixture was first dissolved in TCB at 140°C and kept under N₂ atmosphere. After stirring for 30 min, starch (2.6 g) [and tetrabutyl titanate (TNBT) (0.01 g/g of polymer)] was then added to the hot solution and stirred for 20 min. The product was precipitated in methanol and dried *in vacuo* at 60°C.

Blend sheets were made by hot pressing at 200°C for 5 min under 1.55 atm, and quickly immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the film were determined with a tensile test machine (Instron model no. 4200, Canton, MA) at a cross head speed of 50 mm/min according to ASTM D 638 at 20°C, relative humidity 65%.

The film was fractured while immersed in liquid nitrogen. Scanning electron microscopy (SEM) (Hitach S-4200, Tokyo, Japan) was used to observe the fractured surface morphology.

RESULTS AND DISCUSSION

Preparation of PE-*g*-P(ST-*co*-MAH)

Figure 1(a) shows ¹H-NMR spectra of PE–TEMPO. The protons of the tetramethyl groups of the TEMPO units showed their peak at 0.8 ~ 0.9 ppm and 0.37 ppm. Since the PE–homopolymer also exhibited small peaks at 0.8 ~ 0.9, the net contribution of the tetramethyl protons of the TEMPO units in the peak at 0.8 ~ 0.9 ppm was calculated by assuming that the number of methylene protons of PE homopolymer, whose peaks appeared at 1.2 ~ 1.4 ppm, was the same as that of methylene protons of PE–TEMPO.

Styrene bulk polymerization using PE–TEMPO as a macroinitiator proceeded slowly and produced a large amount of polystyrene (PS) homopolymer as by-product, indicating that a thermal initiation of styrene took place significantly. A possible radical chain transfer from PE–TEMPO to styrene should contribute in part to the PS homopolymer production.

However, styrene/maleic anhydride(ST/MAH) copolymerization with the PE–TEMPO progressed much more rapidly than ST homopolymerization did.⁹ And the amount of PS homopolymer by-product decreased as the mole fraction of MAH increased in the reaction medium.

Figure 1(b) exhibits ¹H-NMR spectra of ST/MAH copolymers produced over the PE–TEMPO. The ST/

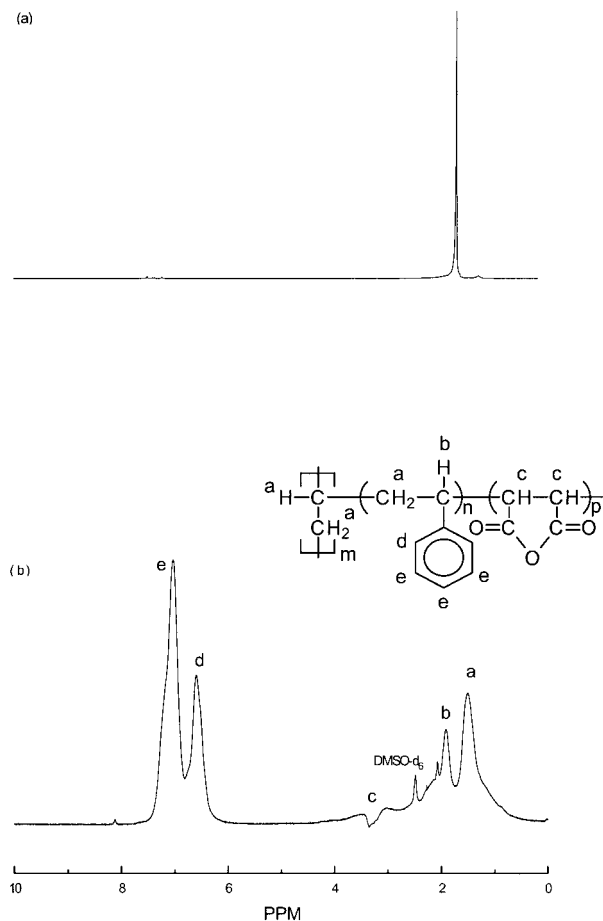


Figure 1 $^1\text{H-NMR}$ of (a) PE-TEMPO and (b) PE-g-P(ST-co-MAH)₃.

MAH copolymers should be graft copolymers because the PE-TEMPO contained 6.9 TEMPO units per 1000 repeating units. Methylene protons of ethylene and those of ST units exhibit their peaks at 1.2 ~ 1.4 and 1.7 ~ 2.0 ppm, respectively. Phenyl ring protons of ST units appeared at 6.6 ~ 7.4 ppm. The peaks at 2.4 ~ 3.4 ppm correspond to the methine protons of MAH units.

Table I demonstrates the results of ST/MAH copolymerization with the PE-TEMPO. The copolymerization was carried out in bulk state, but xylene solution polymerization was employed for the copolymerization when MAH concentration was higher than 2.5M, where MAH began to be insoluble in ST.

Since the formation of ST/MAH charge transfer complex became a rare event above 80°C, ST/MAH copolymerization at 120°C or higher should proceed randomly rather than in an alternating manner.¹⁰

MAH content in the copolymer was determined from the Fourier transform infrared (FTIR) spectra using the peak intensity at 1780 cm^{-1} (stretching of carbonyl group of MAH) and that at 719 cm^{-1} (C—H stretching of ethylene units).¹¹ As the MAH anhydride ring could be opened during the copolymerization,

TABLE I
Characteristics of the PE-g-P(ST-co-MAH) Copolymers

Sample code	Polymerization time (h)	Copolymer yield (g)	MAH ([M])	ST ([M])	Conversion ^c	MAHcontent (wt %)		DSC data			
						NMR ^d	FTIR ^b	T_m (°C)	ΔH (J/g of PE)	T_c (°C)	
PE	—	—	—	—	—	—	—	—	—	—	—
PE-TEMPO	—	—	—	—	—	—	—	—	79.0	90.0	—
PE-g-PS ^a	—	—	—	—	—	—	—	—	101.5	91.2	—
PE-g-P(ST-co-MAH) ¹	0.5	3.0	—	—	—	—	—	—	—	—	—
PE-g-P(ST-co-MAH) ²	2	6.4	1.02	—	17.5	—	3.72	106.1	45.7	87.1	—
PE-g-P(ST-co-MAH) ³	0.5	12.0	2.55	—	47.7	4.30	3.30	106.2	85.6	87.4	—
PE-g-P(ST-co-MAH) ^{3a}	0.5	21.4	5.10	—	92.3	12.3	8.23	104.8	152.7	87.2	—
PE-g-P(ST-co-MAH) ⁴	20	3.0	1.0	0	0	0	0	106.1	100.4	90.8	—
PE-g-P(ST-co-MAH) ⁵	20	6.5	1.0	0.5	65.0	—	3.48	105.6	46.4	87.7	—
PE-g-P(ST-co-MAH) ⁶	2	6.2	1.0	1.0	63.0	5.80	3.20	104.9	44.2	87.8	—
PE-g-P(ST-co-MAH) ⁷	20	13.0	1.0	1.0	93.8	6.95	4.75	105.1	92.7	86.2	—

^a Polymerization in pure styrene at 120°C. (Initial amount of styrene: 18.2 g).

^b Polymerization in xylene solution at 120°C. (Initial amount of styrene and that of MAH was 10.4 and 10.0 g respectively, in 100 mL of xylene.)

^c See eq. (1).

^d Measured from $^1\text{H-NMR}$ spectra.

^e Measured from FTIR spectra.

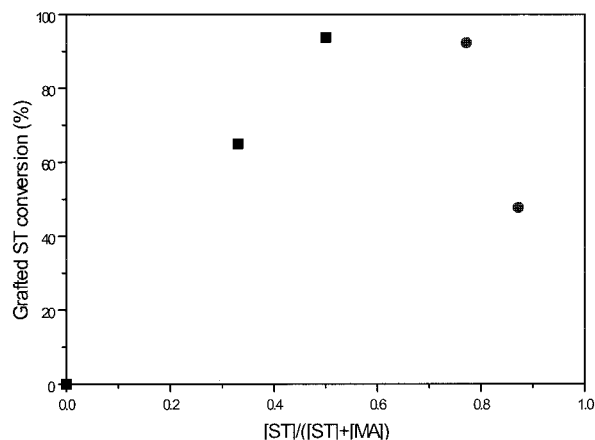


Figure 2 Grafted ST conversion [see eq. (1)] of the copolymerization in the presence of PE-TEMPO as a function of $[ST]/([ST] + [MAH])$. (■) Polymerization in xylene solution for 20 h; (●) polymerization in pure styrene for 0.5 h.

the copolymer was heated at 180°C for 4 h under vacuum before the FTIR measurements. MAH content thus obtained was lower than that determined from $^1\text{H-NMR}$ spectra. We place more confidence in the FTIR results than in the $^1\text{H-NMR}$ ones, because $^1\text{H-NMR}$ peaks of MAH units were poorly resolved.

Figure 2 shows conversion of ST/MAH copolymerization as a function of ST mole fraction in the reaction medium. It is immediately evident that the copolymerization became faster as the concentration of ST and that of MAH became equimolar.

Melting point of PE moiety in PE-*g*-P(ST-*co*-MAH) decreased, and crystallization peak, observed during cooling at $-5^\circ\text{C}/\text{min}$ on DSC, appeared at a lower temperature, as the amount of the grafted ST/MAH copolymer increased, indicating that the grafted copolymer reduced the crystallization rate of the PE phase (Table I).

Mechanical properties of PE/starch/PE-*g*-P(ST-*co*-MAH) blends

Table II demonstrates the tensile properties of PE/starch/PE-*g*-P(ST-*co*-MAH) blends. The average of at least five measurements was taken. Addition of PE-*g*-P(ST-*co*-MAH) increased the elongation at break of the blends to a slight extent.

Figure 3 exhibits FTIR spectra of PE-*g*-P(ST-*co*-MAH)(a), PE/starch/PE-*g*-P(ST-*co*-MAH)(b) and PE/starch blends(c). The stretching vibration peak of carbonyl group of MAH appears at 1790 and 1865 cm^{-1} . The peak at 1730 cm^{-1} corresponds to stretching of carbonyl groups in the ester groups. Carboxylic groups of MAH exhibits its peak at 1710 cm^{-1} . The intensity of the peak at 1650 cm^{-1} due to the absorbed water decreased after the blending process.

PE-*g*-P(ST-*co*-MAH) showed peaks not only at 1730, 1790, and 1865 cm^{-1} but also at 1710 cm^{-1} as a shoulder. It can be perceived from Figure 3 that decrease of

TABLE II
Tensile Properties of PE/Starch/PE-*g*-P(ST-*co*-MAH)7

Blend composition (wt %)	Tensile properties		
	Elongation modulus (MPa)	Stress at maximum load (MPa)	Elongation at break (%)
100/0/0	53.2	10.4	476
70/30/0	95.4	2.51	7.08
68/27/5	87.5	3.11	11.7
64/26/10	82.7	2.64	10.7
64/26/10-Ti(OBu) ₄	126.3	1.27	17.7

the peak intensity corresponding to the anhydride carbonyl of MAH or increase of the peak height of the ester carbonyl groups was not discernible after the blending, saying that the esterification reaction between MAH and starch did not take place appreciably. Morphology of the fractured surface of the blends demonstrated in Figure 4 does not provide any clear evidence of enhanced interfacial adhesion owing to PE-*g*-P(ST-*co*-MAH).

Tetrabutyl titanate(TNBT, $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$)(0.01g/g of polymer) was added to 1,2,4-trichlorobenzene solution of PE/starch/PE-*g*-P(ST-*co*-MAH)(64/26/10), and the solution was kept at 170°C for 20 min and then was precipitated quickly in methanol. The specimens prepared by hot pressing the precipitated solid after drying were subjected to the measurements of the tensile properties, and the results are shown in Table II.

Morphology of fractured surface of PE/starch/PE-*g*-P(ST-*co*-MAH) specimens (64/26/10) prepared by compounding in the absence of TNBT [(Fig. 4(c)) shows that many starch particles protruded on the fractured surface, which evidenced that weak points were concentrated at the interface, and that cracks were propagated mainly through the interface. In sharp contrast, Figure 4(e) shows that the number of starch particles protruded on the fractured surface of the same blend but

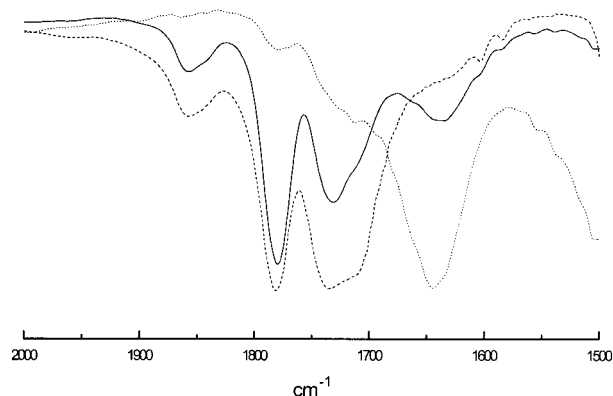


Figure 3 FTIR spectrum of blend system. Dotted line: PE/starch; solid line: PE/starch/PE-*g*-P(ST-*co*-MAH)7; dashed line: PE-*g*-P(ST-*co*-MAH)7.

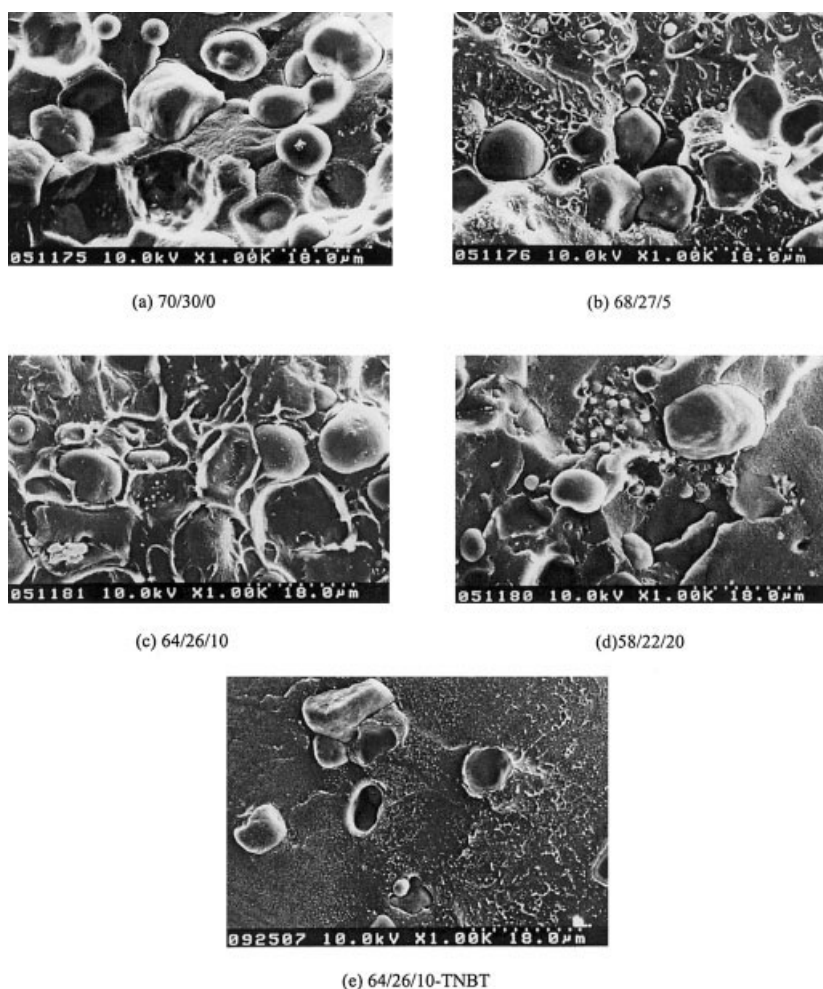


Figure 4 SEM of the fractured surface [PE/starch/PE-g-P(ST-co-MAH)7].

prepared in the presence of TNBT decreased significantly compared to that in Figure 4(c). This clearly substantiates that concentration of weak points at the interface was mitigated by enhancing the interfacial adhesion through the esterification reaction between MAH and starch catalyzed by TNBT. Improvement of elongation at break of PE/starch/ PE-g-P(ST-co-MAH)-TNBT compared to that of the same blend but without TNBT, as shown in Table II, should also be ascribed to the enhanced interfacial adhesion.

References

1. Riess, G.; Periard, J.; Banderet, A. *A Colloidal and Morphological Behavior of Block and Graft Copolymer*; Plenum Press: New York, 1971.
2. Lohse, D. J.; Datta, S.; Kresge, E. N. *Macromolecules* 1991, 24, 561.
3. Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Polym Mater Sci Eng* 1993, 68, 8.
4. Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 5316.
5. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* 1994, 27, 7228.
6. Hawker, C. J.; Hedrick, J. L.; Malmström, E.; Trolls, M. *Polym Prepr* 1997, 38(2), 412.
7. Keoshkerian, B.; Georges, M. K.; Boissier, D. B. *Macromolecules* 1995, 28, 6381.
8. Yoshida, E. *J Polym Sci, Part A: Polym Chem* 1996, 34, 2937.
9. Park, E. S.; Kim, M. N.; Lee, I.-M.; Lee, H. S.; Yoon, J. S. *J Polym Sci, Part A: Polym Chem Ed* 2000, 38, 2239.
10. Kroschwitz, J. I. *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1985; Vol 9, p 262.
11. Wang, Y.; Ji, D.; Yang, C.; Zhang, H.; Qin, C. *J Appl Polym Sci* 1994, 52, 1411.
12. Park, E. S.; Jin, H. J.; Lee, I.-M.; Kim, M. N.; Lee, H. S.; Yoon, J. S. *J. Applied Polym. Sci* 2002, 83, 1103.
13. Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 5316.