

Study on a New Kind of Polypropylene-graft-polystyrene: Preparation and Application

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ABSTRACT: A novel synthetic route for preparing polypropylene-graft-polystyrene (PP-g-PSt) was set up. With this synthetic route, a series of PP-g-PSt copolymers containing different percentages of polystyrene chain were synthesized, based on the different reactivities of two kinds of C—C double bonds on 4-(3-butenyl) styrene. Characterization data, including $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, GPC, and DSC, demonstrated that the graft copolymers were all very pure. Furthermore, it was also attempted to use this new kind of

propylene-styrene graft copolymer as a compatibilizer. DMA and SEM results illustrated that the PP-g-PSt obtained is an efficient compatibilizer for the polypropylene-polystyrene blend. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 314–322, 2004

Key words: propylene-styrene copolymer; graft copolymers; blends; compatibility; synthesis

INTRODUCTION

There are some reported methods used for preparing propylene-styrene copolymer. The first is propylene copolymerized directly with styrene by Ziegler-Natta or metallocene catalysts. For example, Roberto et al.¹ prepared 50 : 50 diblock propylene-styrene copolymer with Ti compound supported on Mg halide/(isoBu)₃Al; Talapatra et al.² obtained a propylene-styrene copolymer containing 16 mol % polystyrene chain with TiCl₃ catalyst; Soga and Yanagihara³ synthesized a copolymer with 1 mol % polystyrene content with TiCl₃-Cp₂TiMe₂ catalyst system; Xu and Lin^{4,5} and Chen et al.⁶ prepared polystyrene-block-polypropylene with MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃ and Cp*Ti(Obz)₃/modified MAO catalyst system. The main difficulty of this kind of polymerization is that the difference of the reactive abilities between styrene and propylene is so great that it is difficult for a copolymerization reaction to occur.^{3,4} The purification is complex and difficult, even though a copolymer can be obtained, because the main products are homopolymers.

The second method used for preparing propylene-styrene copolymer is by a living polymerization, as reported in studies by Miwa et al.⁷ and Chung and Dong,⁸ whereas only atactic polystyrene chains can be obtained by this method.

The third method is the copolymerization of propylene with a styrene macromonomer. Henschke et al.⁹ prepared propylene-styrene copolymer based on this method, but unfortunately there were not sufficient characterization data to prove the structure of the copolymer.

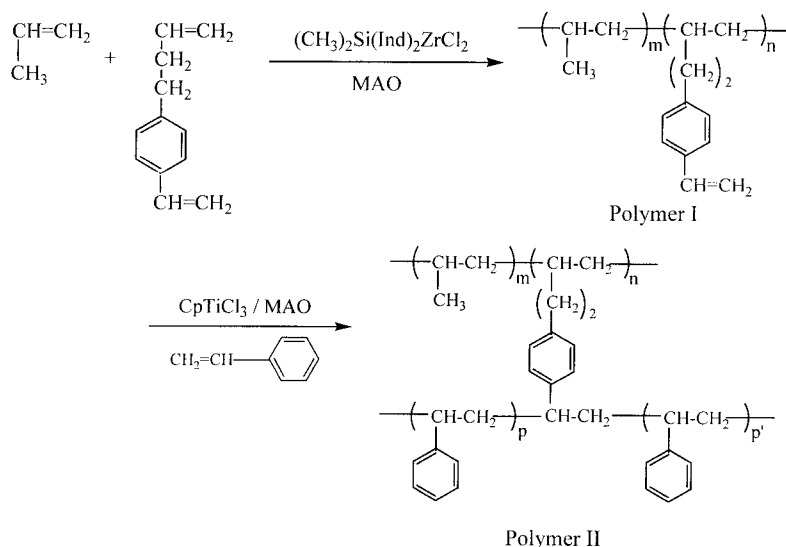
To synthesize propylene-styrene graft copolymer conveniently, we designed a new synthetic route, as shown in Scheme 1. At first, propylene copolymerized with 4-(3-butenyl) styrene, catalyzed by a propylene active catalyst, to form a polymer that has a polypropylene main chain and some styrene side groups. Then, this copolymer reacted with styrene by the styrene active catalyst. Because the motion of polymer chains is much slower than that of small molecules, two polymer chains cannot meet easily. As a result, the side groups of the copolymer react primarily with styrene, and a polypropylene-graft-polystyrene (PP-g-PSt) can be obtained. In this synthetic route, there are two different kinds of carbon-carbon double bonds on the 4-(3-butenyl) styrene molecules. According to the reactivity, one is similar to propylene, and the other is similar to styrene. This difference is the key point in this synthetic route. The polypropylene segment and the polystyrene segment were formed, respectively, and the two sections were linked by a benzene ring. Thus, the stereostructure of the two segments can be controlled with different catalysts. On the other hand,

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Scheme 1 Novel synthetic route for preparing PP-g-PSt.

propylene-4-(3-butenyl) styrene copolymer is a kind of reactive polymer. Polypropylene can easily be functionalized by this reactive copolymer with various monomers possessing polarity or nonpolarity.

In this article, the experimental process of this novel synthetic route to prepare PP-g-PSt and the characterization of the product are described. Furthermore, we attempted to use this new kind of graft copolymer as a compatibilizer for polypropylene and polystyrene blends.

EXPERIMENTAL

Materials and instruments

Toluene was distilled out after being dried over metal sodium. Styrene was obtained by distillation after dried with CaH_2 . 4-(3-Butenyl) styrene was prepared according to the literature.¹⁰ Methylaluminoxane (MAO) solution (1.4 mol/L in toluene) and *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride were purchased from Albemarle Corp. (Tyrone, PA) and Boulder Scientific Co. (Spartanburg, SC), respectively, and used without further purification. CpTiCl_3 was prepared according to the literature.^{11,12} Polypropylene and polystyrene were supplied by Yanshan Petrochemical Corp. (Beijing, China). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker (Billerica, MA) DMX400 spectrometer at 100°C , with *o*-dichlorobenzene- d_4 as a solvent. DSC curves were drawn from a Perkin-Elmer (PE) DSC-7 apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of $20^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) results were carried out on an Alliance GPCV 2000 (Waters Chromatography Division/Millipore, Milford, MA) at 150°C and 1,2,4-trichlorobenzene was used

as solvent. Blends of PP/PSt with and/or without PP-g-PSt were prepared with a Haake (Bersdorff, Germany) RC-90. DMA curves were carried out on a PE DMA-7, and the morphologies of the fracture surfaces of blends were observed on a Hitachi (Osaka, Japan) S-570 scanning electronic microscope. The specimens were fractured by freezing.

Copolymerization of 4-(3-butenyl) styrene and propylene

A 250-mL three-neck flask was purged with nitrogen three times and with propylene two times. Then, 100 mL of toluene, 1.2 mL of 4-(3-butenyl) styrene, 6 mL of MAO, and 6.0 mg of *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (Al/Zr ratio = 3061) were added consecutively to the flask. The polymerization reaction proceeded in propylene atmosphere at 65°C for 10 min. After that, the reaction solution was poured into a 500-mL beaker containing 300 mL 10% (v/v) ethanol solution of hydrochloric acid. Polymer I, a white solid (3.1 g), was

TABLE I
Content and Preparation Condition of PP-PSt Blends^a

Run no.	Content of blends	Weight ratio	Preparation temperature ($^\circ\text{C}$)
1	PP/PS	75/25	180
2	PP/PS	25/75	180
3	PP/PP-g-PSt ^b /PSt	75/5/25	180
4	PP/PP-g-PSt ^b /PSt	25/5/75	180

^aThe mixing time is 5 min.

^bThe copolymer contains 34.8 mol % polystyrene chain and the average molecular weight is 16.8×10^3 g/mol.

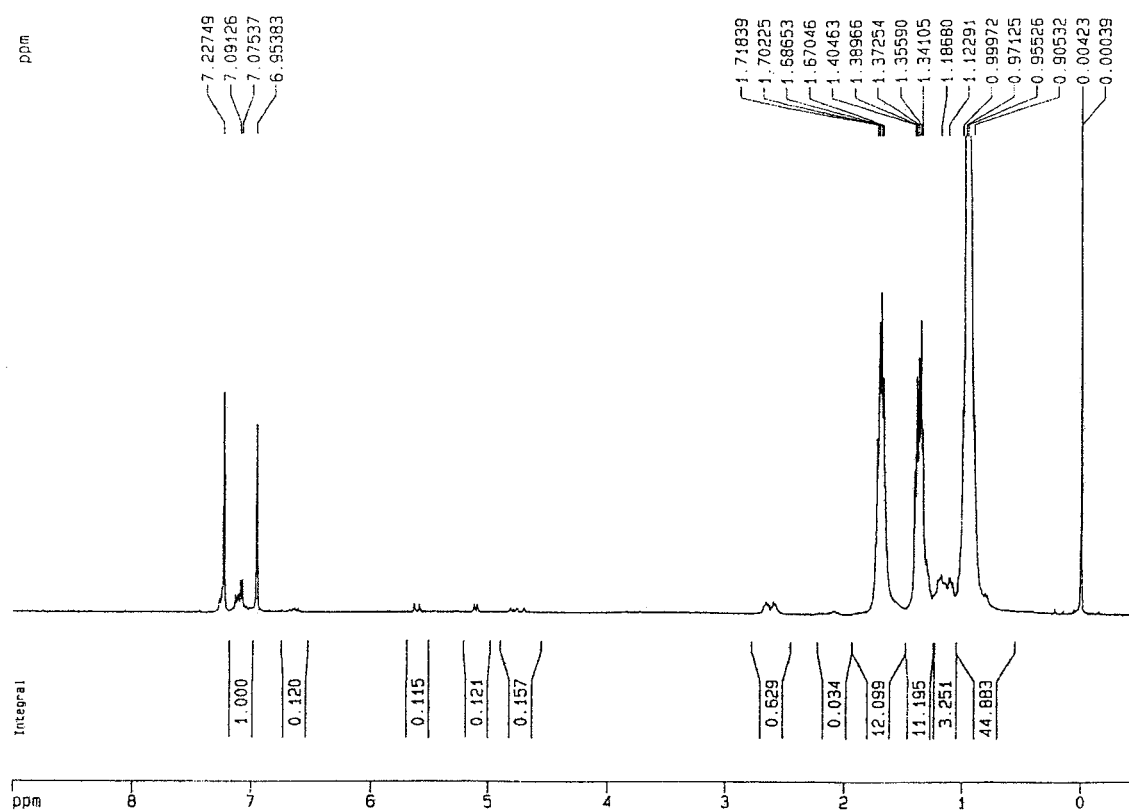


Figure 1 $^1\text{H-NMR}$ spectrum of Polymer I (containing 5 mol % styrene group).

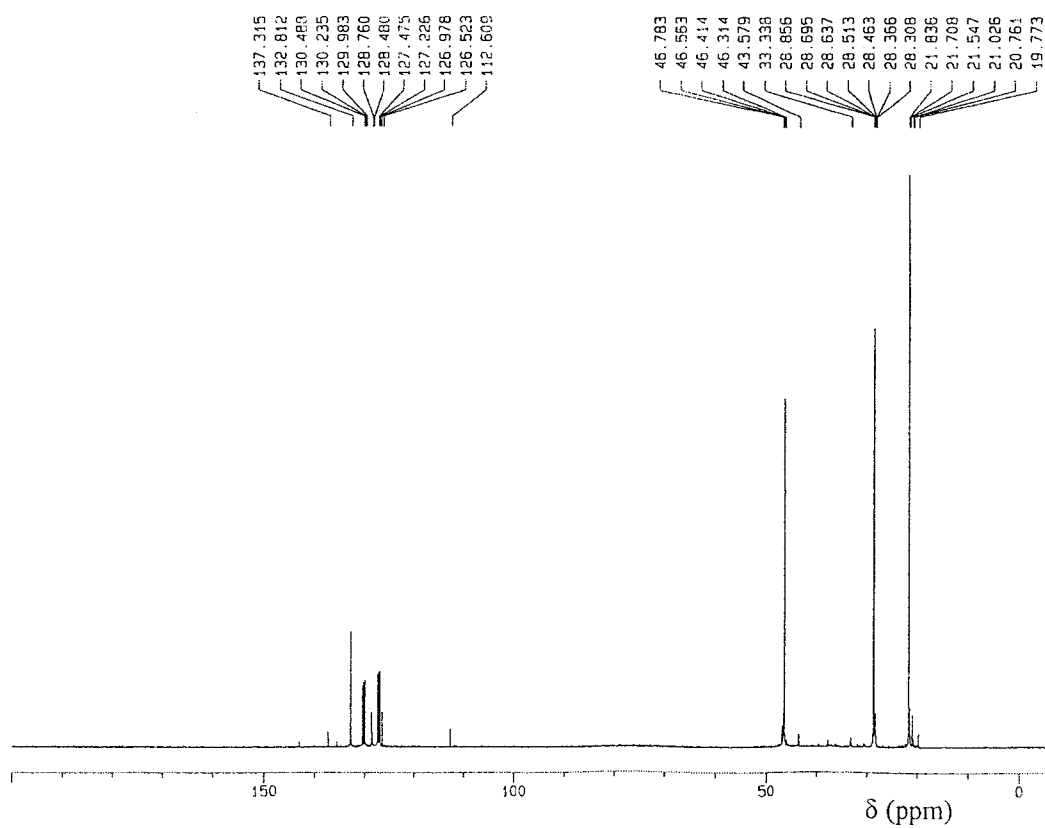


Figure 2 $^{13}\text{C-NMR}$ spectrum of Polymer I (containing 5 mol % styrene group).

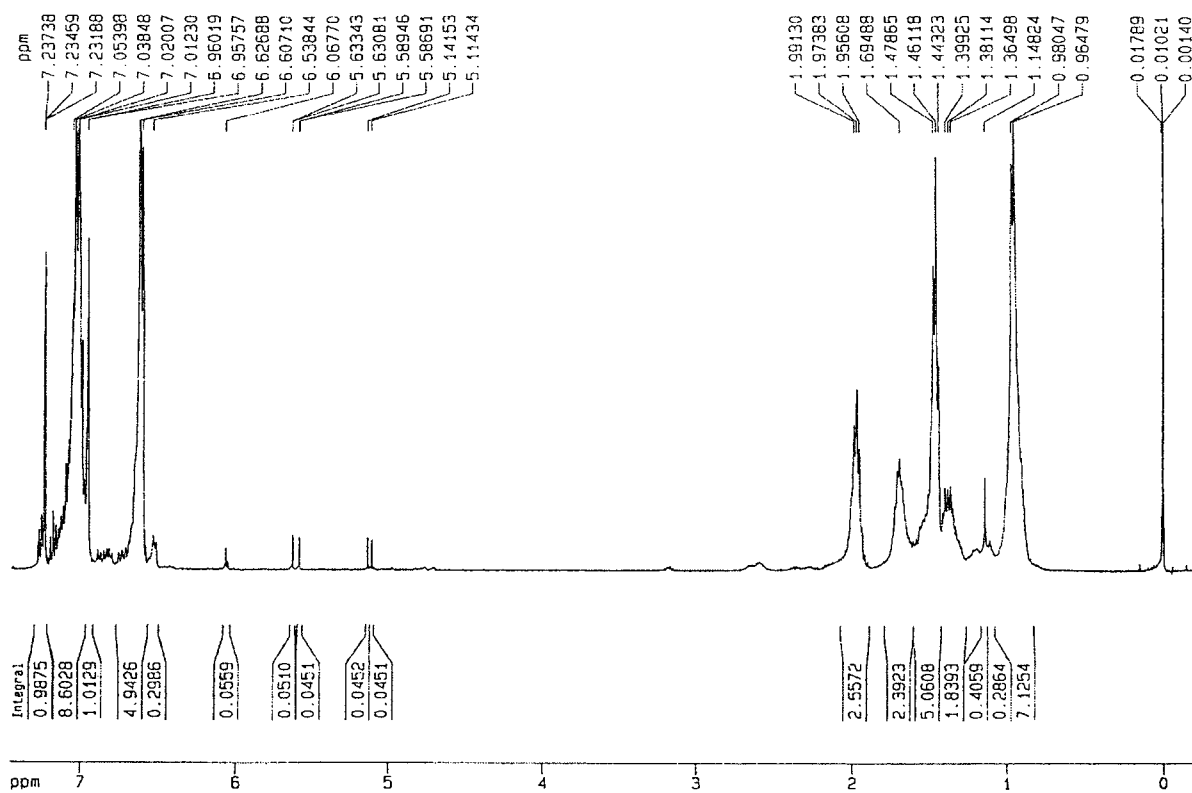


Figure 3 ¹H-NMR spectrum of Polymer II (containing 34.8 mol % polystyrene chain).

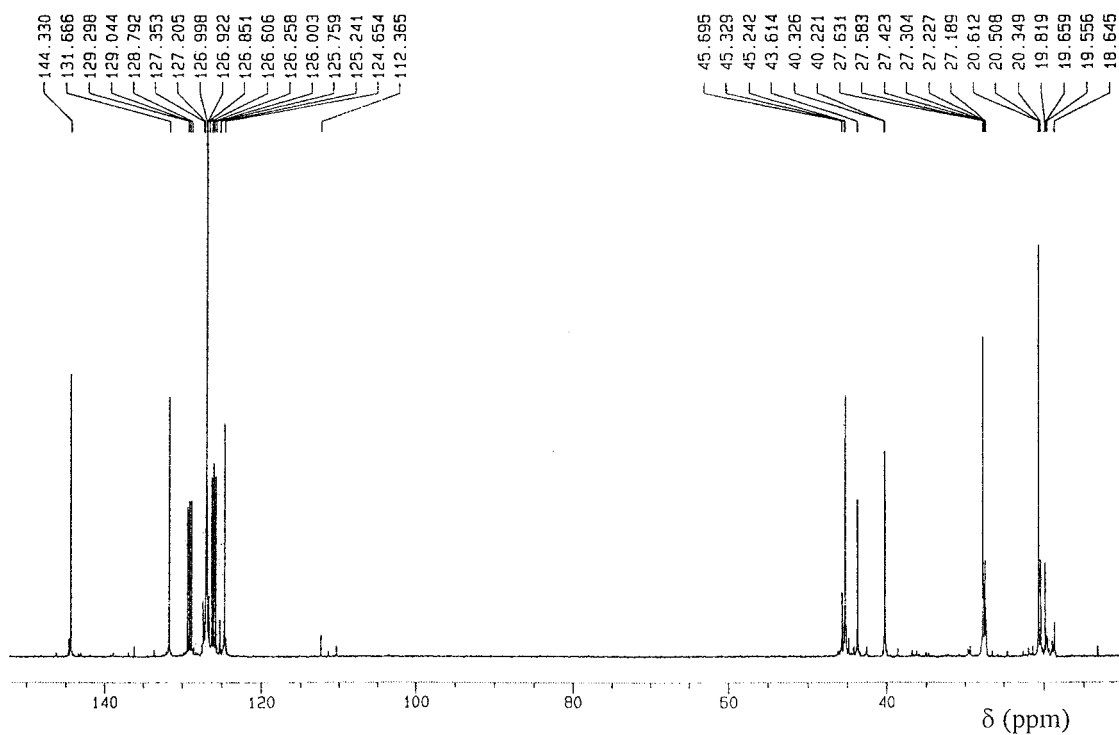


Figure 4 ¹³C-NMR spectrum of Polymer II (containing 34.8 mol % polystyrene chain).

TABLE II
 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ Data of Polymer I and Polymer II

Polymer	$^1\text{H-NMR}$ (δ in ppm)	$^{13}\text{C-NMR}$ (δ in ppm)
I	Polypropylene segment: 1.0, 1.4, 1.7 Styrene groups: 4.7, 5.1, 5.6, 6.6, 7.08	Polypropylene segment: 21.8, 28.6, 46.3 Styrene groups: 112.6, 135.6, 126.2, 128.5, 133.2, 137.3
	Methylene groups linking the two parts of the copolymer: 1.2, 2.6	Methylene groups: 33.5, 37.7
II	Polypropylene segment: 1.0, 1.4, 1.7 Polystyrene segment: 6.6, 7.0	Polypropylene segment: 20.3, 27.3, 45.3 Polystyrene segment: 40.2, 43.6, 124.7, 126.9, 144.3
	Methylene groups: 1.1, 2.6	Methylene groups: 38

obtained after filtration, washed thoroughly with water and ethanol, and dried under vacuum at 70°C overnight. The styrene group content, which can be obtained from the $^1\text{H-NMR}$ spectrum, is 5.0 mol %, and this content can be controlled with addition of differing amounts of raw materials. The illustration here is just a typical example.

Preparation of [PP-g-PSt]

A 250-mL two-neck flask, containing 2 g of Polymer I, was purged with dry nitrogen three times. Then, 100 mL of toluene was added to the flask, and the reaction system was warmed up to 50°C . After the solid was dissolved, 0.5 mL of styrene was added to the reaction solution. After that, 2.0 mL of MAO and 1.8 mg of CpTiCl_3 (Al/Ti ratio = 1573) were added consecutively to the flask. The reaction solution was stirred at 50°C for 30 min. Then, the reaction was terminated by the addition of 300 mL 10% (v/v)

ethanol solution of hydrochloric acid. Polymer II, a white solid (1.9 g) containing 4.6 mol % polystyrene chain, was obtained after filtration, washed thoroughly with water and ethanol, and dried under vacuum at 70°C . A series of samples with different contents of polystyrene segment were obtained according to the addition of differing amounts of raw materials.

Preparation of [PP-g-PSt] by a "one-pot" process

A 2-L stainless reactor was purged with nitrogen three times and propylene two times. Then 500 mL of toluene, 3.2 mL of 4-(3-butenyl) styrene, 42 mL of MAO, and 41 mg of *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (Al/Zr ratio = 3136) were added consecutively to the reactor. Keeping the pressure of propylene at 1 atm, the polymerization proceeded at 60°C for 50 min. After that, the propylene flow was replaced with nitrogen. Styrene (150 mL), MAO (35

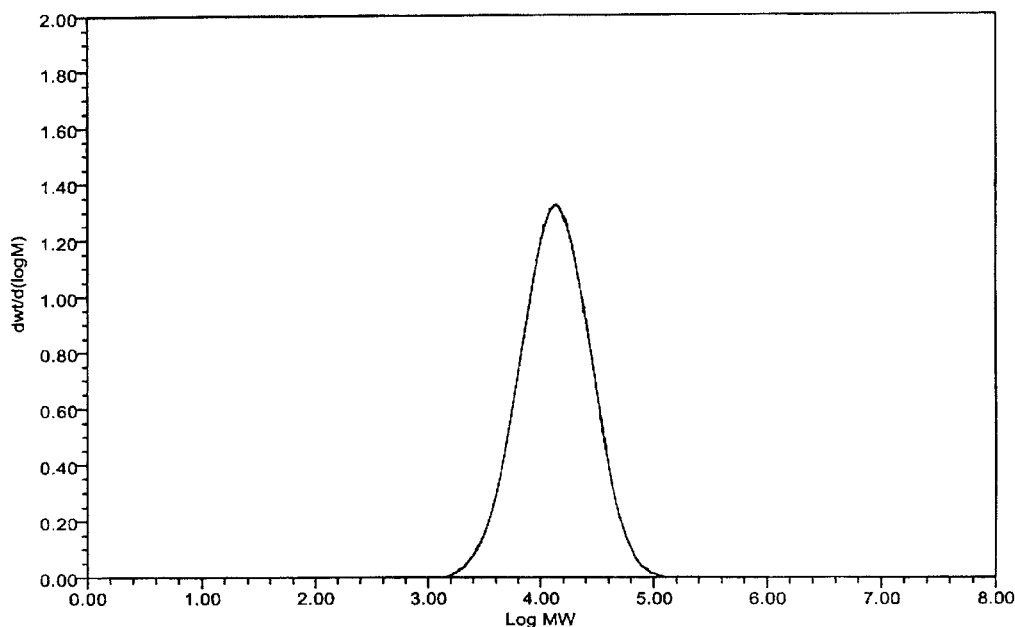


Figure 5 GPC curve of Polymer II (containing 34.8 mol % polystyrene chain).

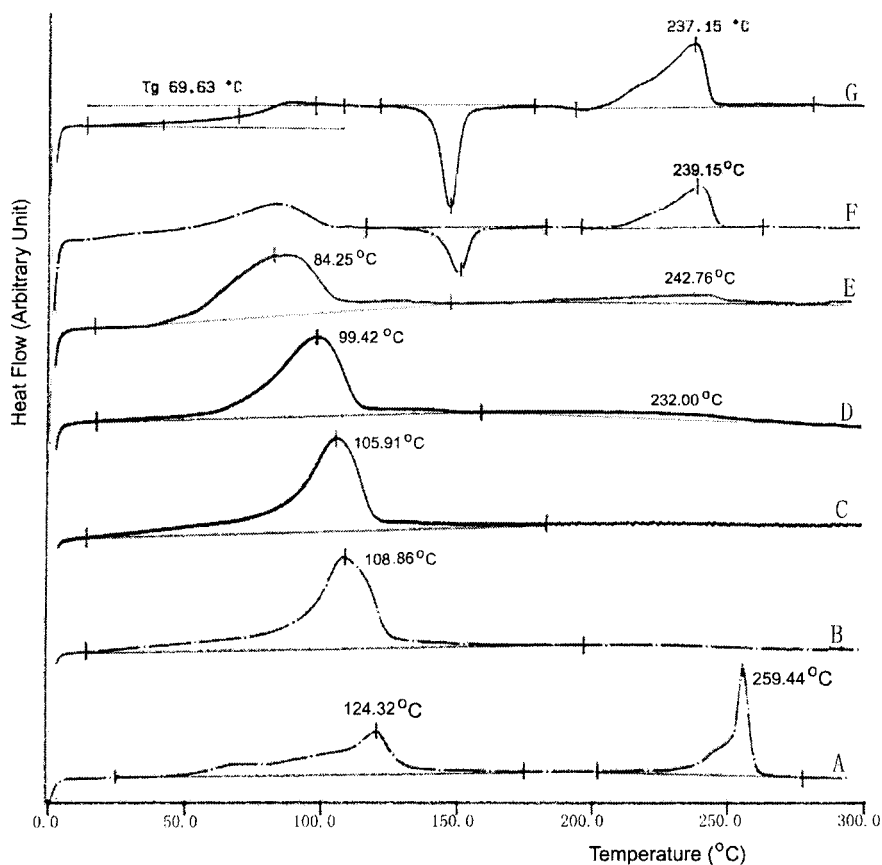


Figure 6 DSC curves of Polymer II: (A) blend of iPP and sPSt; (B)–(G): copolymers, with varying contents of PSt chain (in mol %): (B) 1.7; (C) 2.3; (D) 4.6; (E) 10.1; (F) 12.1; (G) 34.8.

mL), and CpTiCl₃ (106.8 mg) (Al/Ti ratio = 1021) were added to the reaction solution. After the reaction solution was stirred at 60°C for 2 h, the reaction was stopped by pouring the reaction solution into a 10% (v/v) ethanol solution of hydrochloric acid. Graft co-

polymer (44.4 g), with 34.8 mol % of polystyrene chain, was obtained after being thoroughly washed with ethanol and water, and dried under the vacuum. The product was characterized with ¹H-NMR, ¹³C-NMR, GPC, and DSC and the results are similar to the

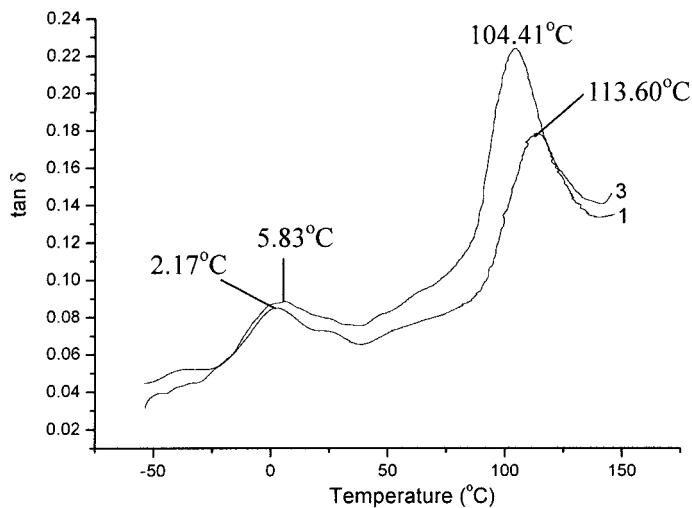


Figure 7 DMA curves of PP/PSt(75/25) blends (3: containing 5 wt % PP-g-PSt).

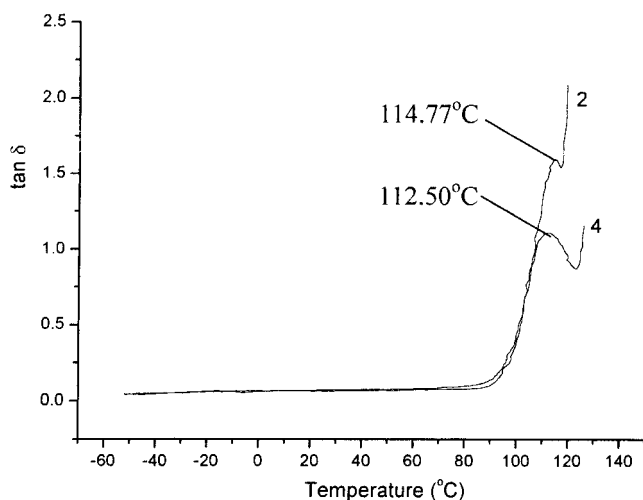


Figure 8 DMA curves of PP/PSt(25/75) blends (4: containing 5 wt % PP-g-PSt).

product obtained by the two-step process illustrated above.

Preparation of blends

Blends of PP/PSt were prepared on a Haake RC-90 apparatus. The content of blends and preparation conditions are shown in Table I.

RESULTS AND DISCUSSION

Characterization of polymers

The chemical structures of Polymers I and II were characterized with $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, GPC, and DSC. The spectra and curves are shown in Figures 1–6.

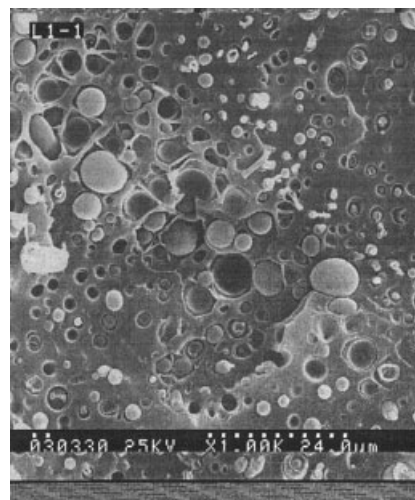


Figure 9 SEM image of PP/PSt(75/25) blend without PP-g-PSt.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data of Polymer I and Polymer II are listed in Table II. These results demonstrate that Polymer I has a polypropylene main chain and some styrene side groups, and Polymer II contains a polypropylene segment and a polystyrene segment. Furthermore, because the GPC of the polymer II exhibits a narrow distribution (polydispersity = 1.59), as shown in Figure 5, then the main product thus obtained is a copolymer, in which there are either no homopolymers, such as PSt and PP, or if there are any, only a negligible amount.

Figure 6 shows the DSC traces of the resulting copolymers containing various compositions. For convenience of comparison, the DSC of sPSt/iPP blend with molar ratio of 30% is also illustrated in Figure 6. On this curve, the melting points (T_m) of neat sPSt and neat iPP are at 259.44 and 124.32°C, respectively.

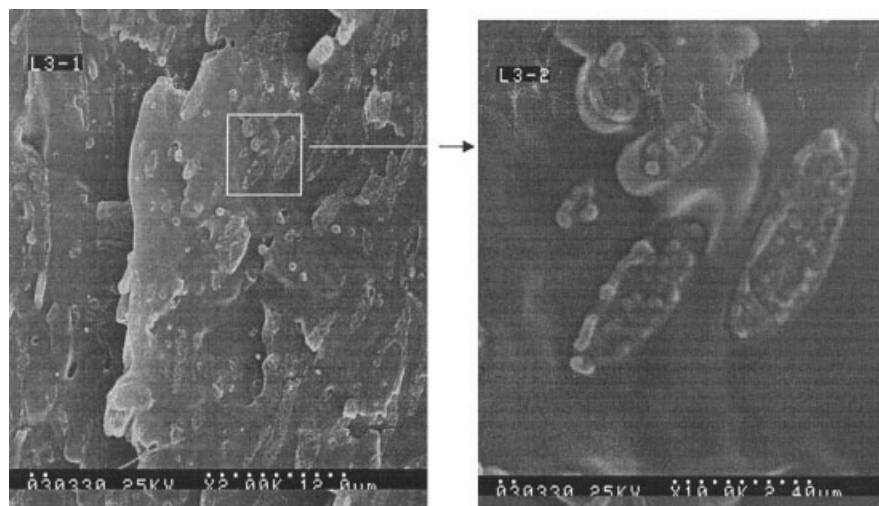


Figure 10 SEM images of PP/PSt(75/25) blends containing 5 wt % PP-g-PSt.

When the content of the sPSt is very low in the copolymer system, the sample exhibits the melting point of the PP crystallite only and vice versa. It can be shown that the T_m of iPP (or sPSt) substantially decreases with increasing content of sPSt (or iPP). This is because the melting point can easily be influenced by the other component¹³; in the system of copolymers, in particular, the one component chain will inhibit the other molecular chains folding into growing crystal lamellae, thus making it difficult to form larger crystals and, in turn, more significantly decreasing the T_m of components of the copolymers than that of components of the blends. This phenomenon also illustrates that the resulting product is a copolymer rather than a blend.

Preparation of [PP-g-PSt] by a "one-pot" process

PP-g-PSt was successfully obtained by a "one-pot" process with a 2-L reactor, which demonstrates that the synthetic route we designed is rather reasonable, and suitable for use in industrial-scale processes.

Characterization of PP/PSt blends

The DMA curves and SEM images of PP/PSt blends are shown in Figures 7–12. From the DMA curves, one can observe that the polypropylene glass transition of the synthesized blends containing PP-g-PSt is higher than that of blends without PP-g-PSt. Meanwhile, the glass transition of polystyrene decreases. This phenomenon demonstrates that the compatibility of polypropylene and polystyrene was improved when

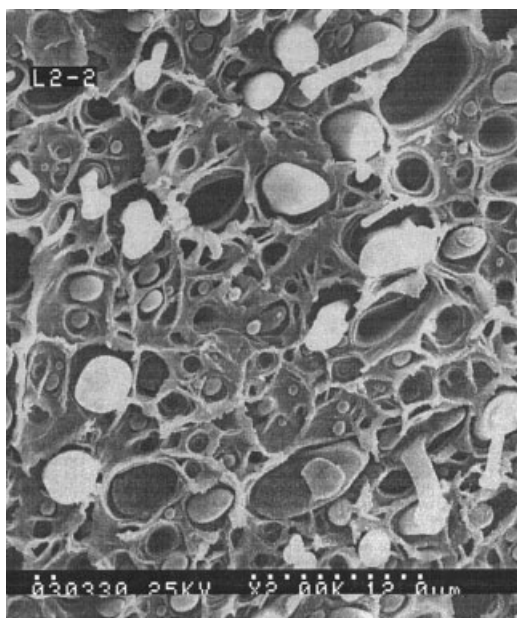


Figure 11 SEM image of PP/PSt(25/75) blend without PP-g-PSt.

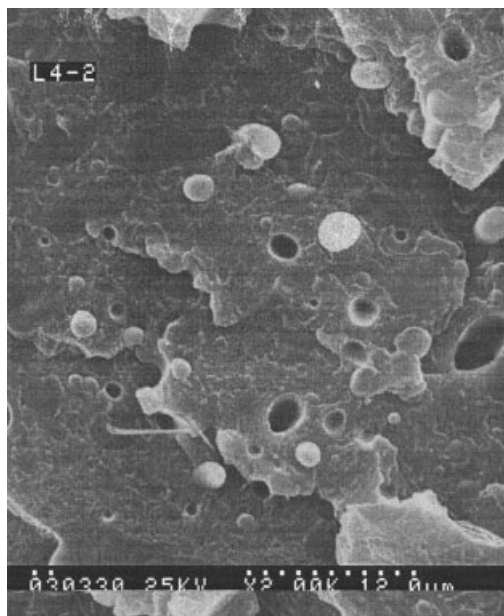


Figure 12 SEM image of PP/PSt(25/75) blend containing 5 wt % PP-g-PSt.

PP-g-PSt was added. This can also be confirmed by SEM images. From the images, it may be observed that the phase separation decreased when PP-g-PSt was added. This phenomenon is much clearer when the PP/PSt ratio is 75/25. From Figure 10, some "cell" structure can be observed. Consequently, the obtained PP-g-PSt is an efficient compatibilizer of the PP/PSt blend.

CONCLUSIONS

The characterization data demonstrate that the PP-g-PSt is easily prepared by the novel synthetic route. Furthermore, this synthetic route is also suitable for synthesizing other kinds of graft copolymers; for example, the main chains constitute the other polyolefins and the side chains constitute polystyrene or the other groups, that is, the functionalization of polyolefins can be achieved conveniently by this synthetic route.

DMA and SEM results illustrate that the PP-g-PSt obtained by the novel synthetic route is an efficient compatibilizer of the PP/PSt blend.

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