Synthesis of Well-Defined Polypropylene-*graft*-polystyrene and Relationship between Structure and the Ability To Compatibilize the Polymeric Blends

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ABSTRACT: A new method to prepare polypropylene-*graft*-polystyrene copolymers with tailored structure has been developed. The ability of a series of copolymers with variable structure to compatibilize the polypropylene−polystyrene blends was evaluated through microscopic observation of the morphology of the blends. The synthesis is a two-step process, the first one being the preparation, in the presence of *ansa*-zirconocene-based catalyst, of the backbones formed by i-PP sequences spaced by *p*-methylstyrene−ethylene units. In the second step, the methyl groups in the aromatic rings are reacted with *sec*-butyllithium, and the resulting metalated polymers allowed to add the styrene to initiate the side polystyrene chains growth. This synthesis turns out versatile both in the first step because by changing monomers feed ratio, backbones with different number of the sites of growth of the grafts and with different length of the polypropylene sequences can be obtained, and in the last step because, by tuning styrene concentration and reaction time, the side chains length can be regulated. The PP-*g*-PS copolymers with PP sequences varying in the range of 24−98 units, with number of the side chains from 2 to 14 and with PS side chains length from 0.33×10^2 to 6.9×10^2 units, were obtained and afterward tested as compatibilizers in the PP/PS blends. The morphologies of the blends, analyzed and compared by scanning electron microscopy, suggest that the compatibility of PP/PS blends is improved with increasing either the PP sequences length or the PS side chains length or the number of the side chains in the PP-*g*-PS copolymer.

Introduction

In the past decade the investigations on polymer blends have intensified significantly because they offer a convenient alternative to developing totally new polymers. Polymer blends can be tailored to meet the requirements for specific applications.

However, the ability to produce blends having a desired combination of properties of the individual components depends on the compatibility of the system. For practical applications, the compatibility, and hence the desired properties, must not be time-dependent and must be exhibited at each stage of the blends processing. Unfortunately, most polymers are immiscible, and as a consequence, the majority of polymer blends are weak. The mechanical failure usually arises from low molecular attractive forces between dispersed phase and matrix. However, the properties of immiscible blends would be improved if the interfacial zone could be strenghtened by incorporating on interfacially active block or graft copolymer.[1] Usually such compatibilizers have blocks or graft segments that are chemically identical to those in the respective phases and work by improving the interfacial adhesion. Moreover, they permit a finer dispersion by stabilizing against gross segregation and since the reduction of the interfacial tension tends to make uniform dispersed domains and to reduce phase size. Consequently, it is possible to test the ability of the compatibilizer through the investigation of the morphology and of the size of the dispersed phase using scanning electron microscopy (SEM).[1]

Recent literature addresses the synthesis of polypropylene-*graft*-polystyrene (PP-*g*-PS) copolymers as suitable polypropylene−polystyrene blend compatibilizers. PP-*g*-PS copolymers are commonly obtained by radical polymerization of styrene over functionalized or irradiated PP;[2,3] however, with these methods it is difficult to control the graft density and the graft length, and undesired reticulation reactions may occur.

More recently, the synthesis of PP-*g*-PS from polystyrene macromonomers containing polymerizable end group has been reported by Schulze and co-workers.[4] With this approach it is possible to obtain polypropylene-based copolymers with polystyrene side chains of fixed length in the presence of metallocene catalysts. However, since the content of co-macromonomer in the side chain depends on its length, it is possible to insert only few and short macromonomers per backbone. This drawback is particularly detrimental to the compatibilizing properties of the polymer for which long side chains are instead necessary.

Another method was developed by Chung and coworkers,[5] through the synthesis of copolymers of propylene-*p*-methylstyrene (PP-*co*-*p*-MS) as backbone, by using heterogeneous Ziegler−Natta catalysts. The copolymers were subsequently metalated in the *p*-methyl groups with *sec*-BuLi in order to produce anionic sites for the initiation of living styrene polymerization.[6] This method allows the synthesis of PP-*g*-PS with long grafted chains; however, the backbones obtained in this way are characterized by wide molecular weight distribution and by low (0.5−0.8%) mole content of *p*-MS whatever the polymerization conditions may be. As consequence, the PP-*g*-PS copolymers show a low and narrow range graft density. In addition, the multisite heterogeneous Ziegler−Natta catalysts produce copolymers with broad molecular weight distribution with scarce control of the copolymers composition and consequently of the graft density.

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Chung and co-workers succeeded in preparing P-*co*-*p*-MS copolymer with metallocene catalysts, but such catalysts show low activity and produce copolymers with very low molecular weight.[5]

In the present paper we describe a new method for the synthesis of PP-*g*-PS with tailored structure: the backbone synthesis was carried out according to our previous paper,[7] whereas for the side chain growth, the route described by Chung has been followed.[6] The synthetic strategy proved to be versatile since allowed to obtain PP-*g*-PS with a variable length of polypropylene sequences, a variable length of lateral chains, and a variable number of side chains per backbone; this fact allowed us to study the ability to compatibilize blends of isotactic polypropylene and atactic polystyrene changing the structure PP-*g*-PS.

The backbone has been prepared following the synthetic procedure described by the authors for the synthesis of isotactic polypropylene modified with isolated ethylene/styrene units by using *ansa*-zirconocene-based catalyst.[7] A small amount of ethylene in the feed allows to overcome the hindrance to copolymerize propylene and styrene arising from the opposite insertion regiochemistry of the two monomers. Furthermore, varying polymerization conditions, it is possible to produce polypropylene containing a variable content of isolated ethylene−styrene units and characterized by narrow molecular weight distributions. By using *p*-methylstyrene instead of styrene, a backbone composed by isotactic polypropylene containing isolated ethylene/*p*-methylstyrene units is obtained. Since the methyl group in the aromatic ring can be deprotonated, so becoming a center for the initiation of anionic polymerization, copolymers with polystyrene chains grafted on a backbone substantially of isotactic polypropylene have been prepared.

The PP-*g*-PS with variable structure obtained are tested as compatibilizers for blends of isotactic polypropylene and atactic polystyrene by means of the investigation of the morphology and of the size of the dispersed phase and has been performed by using scanning electron microscopy.

Experimental Section

Materials. Ethylene and propylene were purchased from Società Ossigeno Napoli and used without further purification. Toluene and heptane were refluxed over metallic sodium and distilled under nitrogen atmosphere. *p*-Methylstyrene was stirred over CaH_2 and distilled under reduced pressure of nitrogen. Methylalumoxane (MAO), provided by Witco as a 30 wt % solution in toluene, was dried before the use by removing in vacuo the solvent. *rac*-Ethylenebis(1-indenyl)zirconium dichloride was synthesized according to the literature.[8] *sec*-Butylithium (*sec*-BuLi), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and MEK (Aldrich) were purchased and used as received. The PP and PS were produced and provided by Moplefan S.p.A. and Traco S.p.A., respectively.

Propylene-*co*-Ethylene-*p*-Methylstyrene Copolymerization. Copolymerizations were carried out in a 100 mL glass flask thermostated at −25 °C and charged under a nitrogen atmosphere sequentially with *p*-methylstyrene (10 mL), toluene (58 mL), and MAO (8×10^{-3} mol). The mixture was magnetically stirred, and the glass flask was thermostated at −25 °C. A mixture of ethylene and propylene was bubbled through the liquid phase at flow of 0.2 L/min, and then *rac*-ethylenebis(1-indenyl)zirconium dichloride (8×10^{-6} mol) dissolved in 2 mL of toluene was added. The copolymerization products were quenched after 4 h in acidified ethanol, filtered, washed with further ethanol and then with boiling MEK, and dried in vacuo.

The ethylene and propylene concentrations in the liquid phase were calculated through the Lewis and Luke's equation by using the fugacity function chart of ethylene and propylene.[9]

Lithiation Reaction. Under an argon atmosphere, 0.5 g of P-*co*-*p*-MS-E copolymers was suspended in 10 mL of heptane in a 100 mL glass flask with a magnetic stirrer bar; 0.2 mL (1.3 mmol) of TMEDA and 2 mL (2.6 mmol) of 1.3 M *sec*-BuLi solution were added to the flask heated to 60 °C. After 3 h the reaction was cooled to room temperature, and the resulting polymers were filtered and washed with heptane until decoloration of filtrate and then were dried under vacuum.

Graft Reaction. Graft reactions were carried out at room temperature in slurry solutions by reacting 0.25 g of lithiated polymers with 4 mL of styrene in 20 mL of anhydrous heptane. At the appropriate time, the methanol was added to terminate the graft-from reactions. The precipitated polymers were filtered and dried in vacuo and then were subjected to Kumagawa extraction by boiling MEK to remove soluble PS homopolymer.

Polymer Blending. 0.5 g of the PP and 0.5 of PS were dissolved in 20 mL of refluxing 1, 2-dichlorobenzene under N_2 to prevent oxidation. The P-*co*-*p*-MS-E copolymer (0.02 g) was then slowly added to the solution. After the polymer mixture had formed clear homogeneous solution, the blend was precipitated into cold ethanol. The blend, dried under vacuum, was melt-pressed at 200 °C and immediately quenched at 0 °C to form a film. Scanning electron microscopy samples were prepared from films cryofractured in liquid N_2. The surface was coated with a thin golden layer, using a sputter coater (Emscope SC500), to improve the conductivity and prevent charging and then viewed with a scanning electron microscope (SEM), LEICA model S440 operating at 20 kV. The average diameters of the polystyrene dispersed domains were obtained by the SEM micrographs processed by the ImageJ 1.32j program.[10] This program allows to calculate the average surface of the dispersed domains. The average diameters were obtained considering the surfaces as section of the spheres.

^{1}H and ^{13}C Analysis. The spectra of the copolymers were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 393 K. The samples were prepared by dissolving 30 mg of polymer into 0.5 mL of tetrachloro-1,2-dideuterioethane.The pulse interval was 2 s. The reliability of these spectra has been tested by recording the spectrum of the sample 8 also with a pulse interval greater than 2 s without appreciable variation in the relative intensities of the resonances. The chemical shifts are referred to the central peak of $C_2D_2Cl_4$ used as internal reference at $\delta = 74.26$ ppm.

GPC Analyses. GPC measurements were performed by Andries Jekel, Rijksuniversiteit Groningen, Netherlands, at 140 °C using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standard samples as reference. The instrumentation used is a PL-GPC 210 with four PL-gel mixed A columns. The analyses were performed by using a refractive detector at 800 nm (Viscotek) and an H502 viscometer (Viscotek).

Results and Discussion

Synthesis of the Backbone: P-*co*-(*p*-MS-E) Copolymer. The first step in the preparation of the graft copolymer concerns the synthesis of suitable copolymers containing *p*-methylstyrene−ethylene couples spanning long isotactic polypropylene sequences. A series of copolymerizations have been performed under variable monomers feed ratio, in the presence of *rac*-ethylenebis-(1-indenyl)zirconiumdichloride activated by methylalumoxane, to obtain the copolymers with variable composition. In particular, to obtain compatibilizers of isotactic polypropylene−polystyrene blends, polypropylene sequences should not be too short. Therefore, we decided to synthesize copolymers with variable but low content of the comonomer.

Table 1. Polymerization Conditions and P-*co*-(*p*-MS-E) Copolymers Composition

run[a]	[E]/[P]/[*p*-MS][b]	% P[c]	% *p*-MS-E[c]	L_p	M_w/M_n	M_n
1	1/804/63	98.0	1.0	98	1.8	36 150
2	1/804/118	96.8	1.6	60	1.6	26 600
3	1/804/120	96.6	1.7	57	1.7	18 000
4	1/385/62	96.2	1.9	51	1.9	33 050
5	1/390/68	96.0	2.0	48	1.8	14 050
6	1/804/128	95.8	2.1	46	2.0	9 020
7	1/804/136	95.4	2.3	42	1.8	22 400
8	1/804/168	94.8	2.6	37	1.6	23 700
9	1/804/190	94.4	2.8	34	1.5	26 450
10	1/804/236	92.2	3.9	24	1.7	24 750

[a] All the runs have been carried out in the presence of *rac*-ethylenebis(1-indenyl)$ZrCl_2$/MAO at −25 °C and 1 atm. [b] Mole ratio of propylene, ethylene, and *p*-methylstyrene in the feed. [c] Copolymer composition determined by ^{13}C NMR.

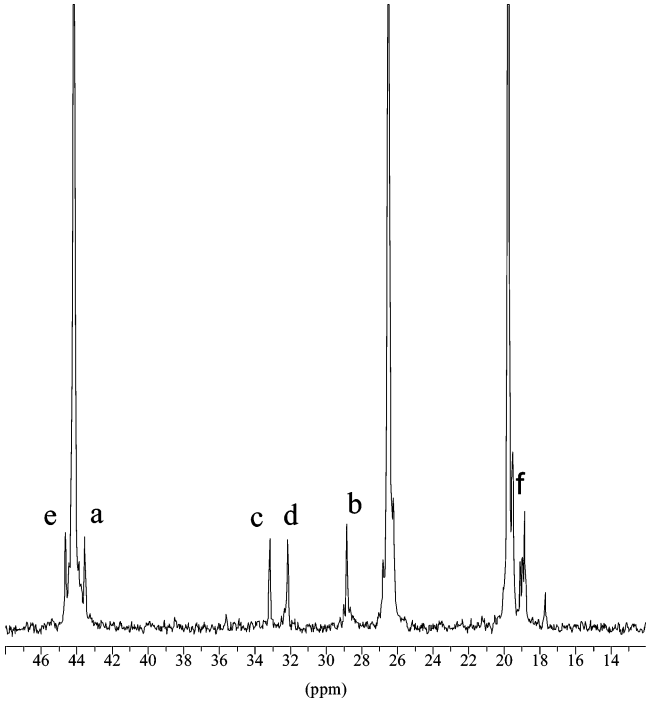
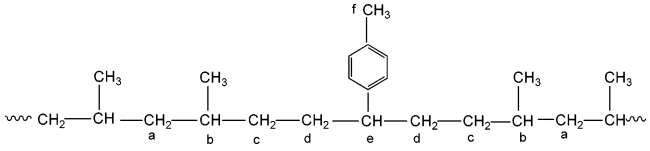


Figure 1. Aliphatic region of ^{13}C NMR spectrum of a copolymer P-*co*-(*p*-MS-E) (run 2 of the Table 1).

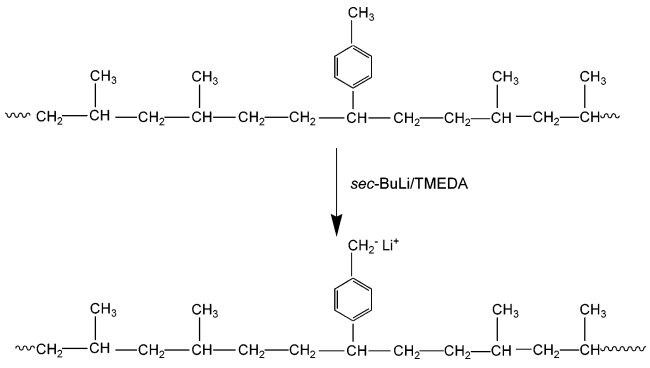
Chart 1



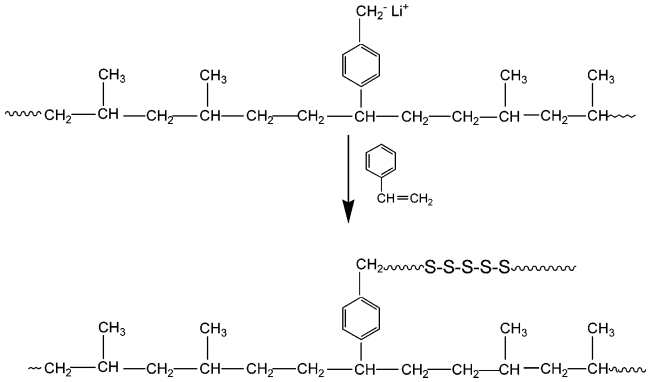
As shown in Table 1, where the results are summarized, the obtained copolymers contain from 1 to 3.9 mol % of *p*-methylstyrene−ethylene couples spanning from 98 to 24 units long isotactic polypropylene sequences.

The aliphatic region of the ^{13}C NMR spectrum of the copolymer P-*co*-(*p*-MS-E) reported in Figure 1 shows the signals at 43.5 ppm (carbon **a** in the Chart 1), 28.8 ppm (carbon **b**), 33.2 and 32.2 (carbon **c** and **d**, respectively) 44.6 ppm (carbon **e**), and 19.1 ppm (carbon **f**), corresponding to the P/*p*-MS-E/P sequences, in addition to the peaks of the isotactic PP sequences at 44.2, 26.5, and 19.5. Accordingly in the ^1H NMR spectrum of the copolymer can be detected signals at $\delta = 0.75$, 1.15, 1.45, and 2.1 ppm, corresponding to C**H**$_3$, C**H**$_2$, C**H**, and ϕ-C**H**$_3$ groups in the backbone, and the peaks between

Scheme 1



Scheme 2



δ = 6.8 and 6.9 ppm corresponding to the aromatic protons.

The copolymer composition as well as the average length of polypropylene sequences has been determined through ^{13}C NMR analysis (see Figure 1) from the relative intensities of the signals by using the following relationships:

$$x_{p-MS} = (0.5A_{32.2})/(A_{32.2} + A_{43.5} + A_{44.2} + 0.5A_{33.2})$$

$$L_P = 2(0.5A_{33.2} + A_{43.5} + A_{44.2})/A_{32.2}$$

PP-*g*-PS Copolymers. The graft copolymers have been obtained through two further steps. In the first step the above-described P-*co*-(*p*-MS-E) copolymers were metalated through reaction with *sec*-butyllithium to obtain stable polymeric anions (see Scheme 1).

The lithiated copolymers were isolated and then allowed to react with styrene (see Scheme 2).

To obtain PP-*g*-PS copolymers with variable length of the side chains (see experimental part), the polymerization of the styrene was carried out at different monomer concentration and with different polymerization time, due to the living character of the anionic styrene polymerization.

The resulting PP-*g*-PS copolymers were extracted with boiling MEK. The ^1H NMR analysis indicated that the soluble fractions are PS homopolymer not chemically linked to the backbone. The insoluble fractions were characterized by several techniques. All PP-*g*-PS copolymers present a narrow molecular weight distribution ($M_w/M_n \approx 2$). Since a PS standard was used for the determination of the molecular weight averages of the copolymers, the calculated values may be not absolutely correct due to the structural differences between the standard and graft copolymers, but the tendencies in the monomodal molecular weight distributions are well

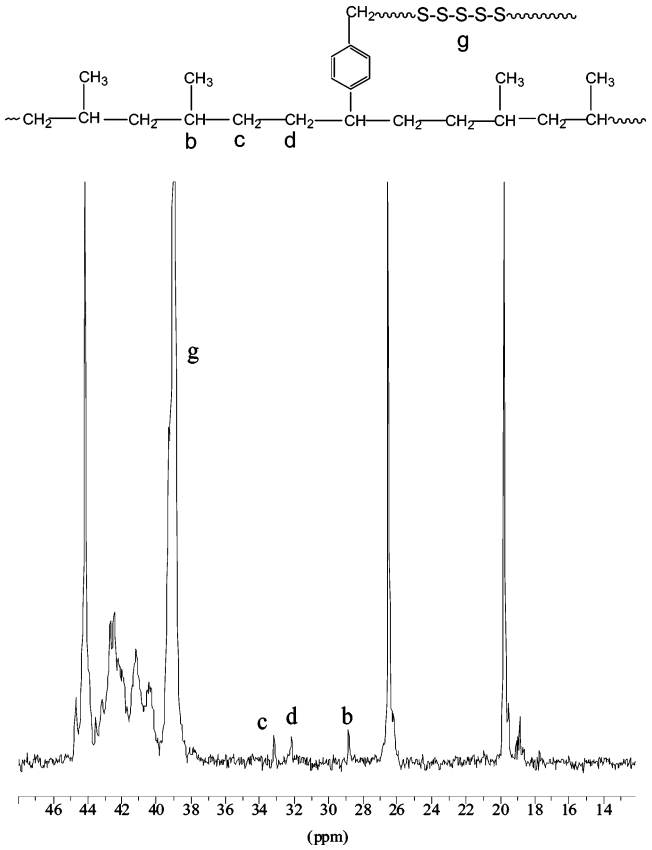


Figure 2. Aliphatic region of ^{13}C NMR spectrum of the sample 8 of Table 2.

Table 2. Polymerization Conditions and Main Results of the ^{13}C NMR Characterization of PP-*g*-PS Copolymers

sample	% *p*-MS-E[a]	[S][b] (mol/L)	L_P[c]	reaction time (min)	Gd[d]	L_S[e] ($\times 10^2$)	N_{SC}[f]
1	1.9	2.6	51	60	1.6	3.5	12
2	1.9	2.6	51	90	1.6	5.2	12
3	1.9	2.6	51	120	1.6	6.9	12
4	2.8	1.8	34	60	2.4	0.33	14
5	2.8	1.8	34	90	2.4	0.57	14
6	1.7	0.8	57	45	1.0	1.1	4
7	2.0	2.6	48	30	1.2	1.1	4
8	1.6	1.8	60	90	0.4	2.6	2
9	2.1	2.4	46	30	1.1	3.1	2
10	2.6	1.8	37	30	0.6	2.2	3
11	3.9	1.8	24	90	3.5	2.1	3
12	2.3	2.5	42	30	2.0	1.0	10
13	1.0	1.8	98	60	0.4	2.8	8

[a] Mole percent of *p*-MS-E in the backbone. [b] In the feed. [c] Average length of polypropylene sequences. [d] Average number of PS grafts respect to hundred propylene units. [e] Average length of the PS sequences. [f] Average number of the side chain for backbone.

indicated. So the contemporary presence of copolymer and homopolymer can be disregarded.

As an example, Figure 2 shows the aliphatic region of the ^{13}C NMR of the PP-*g*-PS copolymer (sample 8 of Table 2) that we have obtained from the P-*co*-(*p*-MS-E) copolymer of run 2 of Table 1. The signals observed in the starting material are still present (see Figure 1) together with additional peaks at 38.9 and 40−42 ppm due to polystyrene sequences. Accordingly, the ^1H NMR spectrum of the PP-*g*-PS copolymer (see Figure 3), when compared with that of the backbone copolymer, shows new resonances at $\delta = 6.8$ and 6.9 ppm assignable to the aromatic protons. Moreover, the reduction of the relative intensity of the peak at 2.1 ppm is also observed.

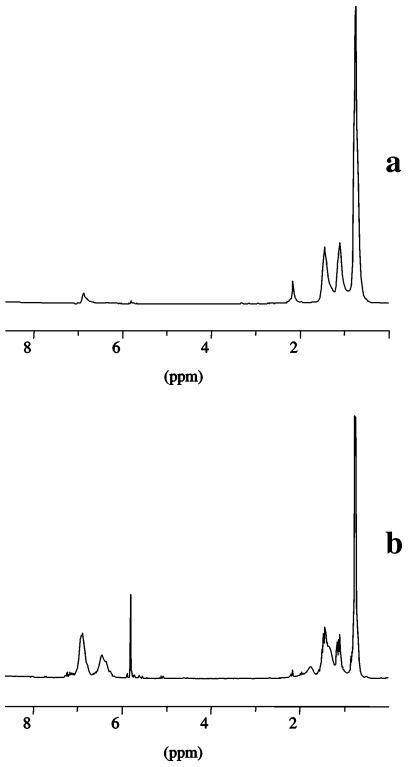


Figure 3. Comparison of ^1H NMR spectra of (a) P-*co*-(*p*-MS-E) copolymer with 1.6 mol % of *p*-MS (run 2 of Table 1) and (b) the corresponding PP-*g*-PS (sample 8 of Table 2).

In fact, the intensity ratio of $-C\mathbf{H_3}_{(p\mathrm{MS})}$ and $-C\mathbf{H_3}_{(\mathrm{PP})}$ peaks changes from 1/66 in the P-*co*-(*p*-MS-E) copolymer (a) to 1/93 in the PP-*g*-PS copolymer (b). The smaller ratio is the consequence of the partial reaction of methyl groups of the *p*-MS units to connect graft side polystyrene chains. The graft density, Gd (defined as average number of PS grafts per hundred propylene units), has been evaluated from the intensities of the ^1H NMR signals by using the following relationship:

$$\mathrm{Gd} = [(A_{2.1}/A_{0.75})_a - (A_{2.1}/A_{0.75})_b)] \times 100$$

On the contrary the average length of the PS sequences can be properly calculated from the intensities of signals of the ^{13}C NMR spectrum through the equation

$$L_S = (A_{38.9}/A_{26.5})_b/0.01\mathrm{Gd}$$

The L_S values (see Table 2) increase with increasing either the reaction time or the concentration of styrene in the feed, as one can expect for a living anionic polymerization. The graft density depends on the efficiency of the lithiation reaction.

The average number of the side chains for backbone can be calculated from

$$N_{SC} = 0.01 M_n F_P \mathrm{Gd}/(42F_P + 146)$$

where F_P is molar ratio of P to *p*-MS-E units in the copolymer determined by ^{13}C NMR; 42 and 146 are the molecular weight of the P unit and of the *p*-MS-E unit, respectively.

Upon inspection of Table 2, one can note that the composition of the PP-*g*-PS copolymers differs in average length of the PS sequences, in average length of polypropylene sequences, and in average number of the

Table 3. Structural Characteristics of PP-*g*-PS Copolymers and the Results of the SEM Characterization of the Blends

blend	L_P[a]	L_S[b] ($\times 10^2$)	N_{SC}[c]	d_d[d] (μm)
1	51	3.5	12	$6._0$
2	51	5.2	12	$4._2$
3	51	6.9	12	$2._6$
4	34	0.33	14	$8._4$
5	34	0.57	14	$6._8$
6	57	1.1	4	$5._4$
7	48	1.1	4	$6._8$
8	60	2.6	2	$3._6$
9	46	3.1	2	$5._8$
10	37	2.2	3	$5._2$
11	24	2.1	3	$6._6$
12	42	1.0	10	$5._8$
13	98	2.8	8	$2._8$

[a] Average length of polypropylene sequences of the PP-*g*-PS copolymer in the blends. [b] Average length of the PS sequences of the PP-*g*-PS copolymer in the blends. [c] Average number of the side chain for backbone of the PP-*g*-PS copolymer in the blends. [d] Average diameter of the PS phase in the blends.

side chains for backbone. In particular, by comparing the samples 1, 2, and 3, it is possible to observe that the L_P and the N_{SC} values are the same, but their L_S values are different and increase with increasing the polymerization time. The same can be noted for the samples 4 and 5. On the other hand, samples 6 and 7 are identical in the average number of the side chains for backbone and comparable in the average length of the PS sequences, but the average length of the PP sequences of the sample 6 is about 10 units greater than sample 7. The couple of samples 8 and 9, as well as that of samples 10 and 11, presents the same N_{SC} values, but their L_S and L_P values are very different. Samples 12 and 7 are different in the average number of the side chains for backbone, but their average length of the PS sequences as well as of the PP sequences is quite similar. Finally, the couple 11 and 13 presents the more relevant variation of N_{SC} value.

PS−PP Polymer Blends. The graft copolymers have been tested as compatibilizers of isotactic polypropylene−polystyrene blends. Blends composed by the 49/49/2 weight ratio of PP, PS, and PP-*g*-PS and, for comparison purpose, a 50/50 blend of PP and PS were prepared. 2 mm thin films were obtained from the blends that where cryofractured in liquid N_2, and the surface of the edges was observed through scanning electron micrographs (SEM) to examine the bulk morphologies. Two phases can be recognized. The size of the domain of the dispersed phase (d_d, average diameter of domain) was calculated (see experimental part) for each sample in order to establish how the ability to compatibilize depends on the structure of the PP-*g*-PS. The results are displayed in Table 3.

Figure 4 shows scanning electron micrograph of the reference blend composed by 50/50 weight ratio of PP and PS. Two distinct phases can be detected: a disperse PS phase and a continuous PP phase. The big size of the dispersed domain (d_d is 10.4 μm) with irregular shape and the holes formed during fracture indicate low adhesion between the phases and poor stress transfer across the interface, as a consequence of the two homopolymers incompatibility.

In Figure 5 the imagines obtained by scanning electron micrographs of the blends of 49/49/2 weight ratio of PP, PS and PP-*g*-PS (sample 1, 2, and 3 of Table 2) are compared.

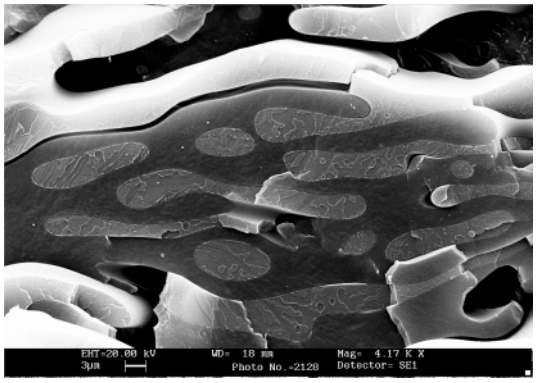


Figure 4. SEM micrograph of the cross section of two homopolymers with PP/PS = 50/50.

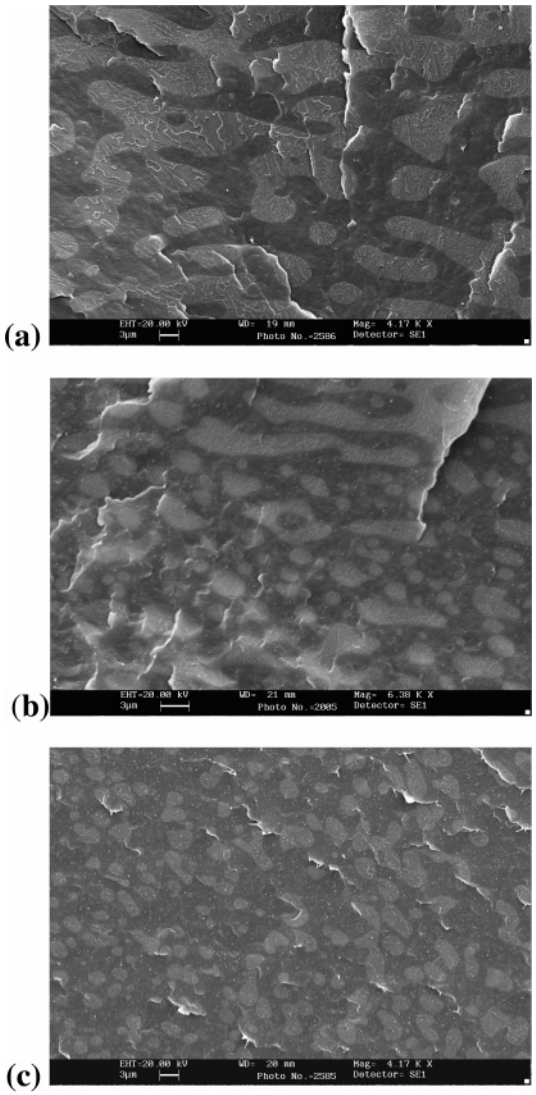


Figure 5. SEM micrographs of the cross section of the (a) blend 1, (b) blend 2, and (c) blend 3 of Table 3, with PP/PP-*g*-PS/PS = 49/2/49.

The images of the compatibilized blends (Figure 5) are highly uniform and do not present holes. Moreover, the sizes of the dispersed domain are smaller (see Table 3) and more regular compared to the PS phase of the homopolymer blend previously discussed (Figure 4).

This result indicates that these PP-*g*-PS copolymers are able to reduce the domain size and consequently are able to improve the compatibility between the two homopolymers.

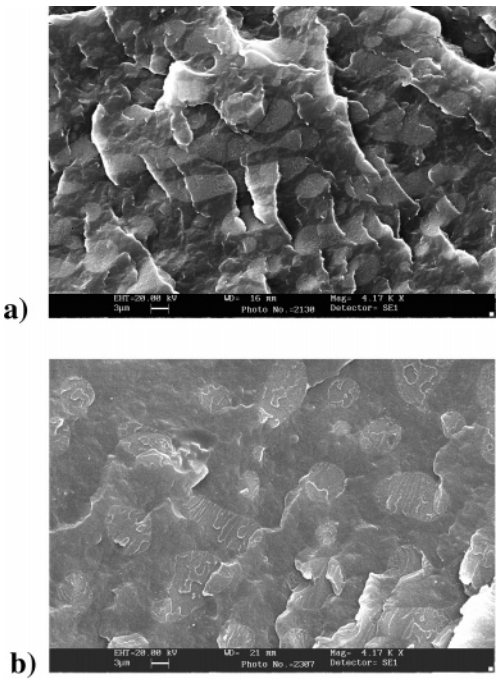


Figure 6. SEM micrographs of the cross section of the (a) blend 6 of Table 3 and (b) blend 7 of Table 3, with PP/PP-*g*-PS/PS = 49/2/49.

Moreover, as reported in Table 3, the PP-*g*-PS is employed in the blends 1, 2, and 3 differ only for the L_S values and in particular L_S of blend 1 < L_S of blend 2 < L_S of blend 3.

In the corresponded blends, as evident from the SEM micrographs in Figure 5 and from the values of d_d of Table 3, the particle size of the dispersed PS phase is gradually reduced in the opposite order: d_d of blend 1 (Figure 5a) > d_d of blend 2 (Figure 5b) > d_d of blend 3 (Figure 5c).

Blends 4 and 5 behave in accordance with this trend (Table 3).

These observations suggested that, at least in the composition range investigated, the compatibility between the two homopolymers increases with increasing the average length of the side chain of the PP-*g*-PS.

The morphology of the blends 6 and 7 are compared in Figure 6. The particle size of the PS phase of blends 6 is clearly smaller than that of the blend 7, as also pointed out by the values d_d reported in Table 3. Such a reduction in phase size can be related to the average length of the PP sequence that is longer in the PP-*g*-PS copolymer of the blend 6 respect to PP-*g*-PS copolymer of the blend 7.

With the same account, the reason for which the particle sizes of the PS phase of the blends 8 and 10 are smaller than those of the blends 9 and 11, respectively (see Table 3), can be explained.

Besides, Table 3 shows that the size of the dispersed domain of the blends 3 and 13 is similar despite a marked difference in the structures of the corresponded PP-*g*-PS copolymer employed. In particular, the copolymer of the blend 3 presents the L_S value of 6.9×10^2 and L_P value of 51; on the contrary, the copolymer of the blend 13 presents L_S value of 2.8×10^2 and L_P value of 98. It is evident that for improving of the compatibility of two homopolymers are relevant not only the length of the side chains of the PP-*g*-PS compatibilizer, as above-reported but also the length of PP sequences.

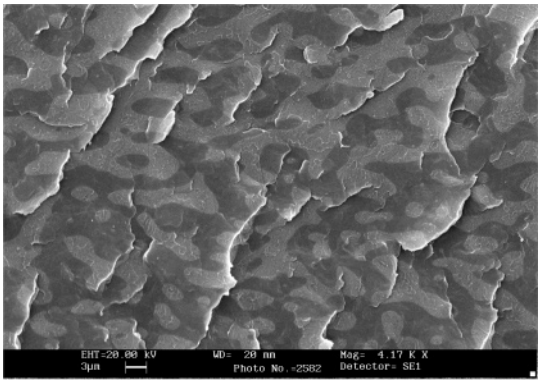


Figure 7. SEM micrograph of the cross section of the blend 12 with PP/PP-*g*-PS/PS = 49/2/49.

These results indicate that the ability to compatibilize the two homopolymers depends markedly on the length of the PP sequence and increases with increasing the average length of the PP sequence at least in the range of 24−98 units.

The blend 12 and 7 are selected as examples to illustrate the effect of the number of the side chains for the backbone on the improvement of the compatibility of the PP/PS blends. The PP-*g*-PS used in both blends present L_S and L_P values quit similar, but the N_{sc} values are different and being the double in the former. The consequence is that the size of PS phase of the blend 12 (Figure 7) is smaller to the size of the blend 7 (Figure 6b).

Finally, the compatibility between polypropylene and polystyrene also improves with increasing the average number of the side chains for backbone of the PP-*g*-PS.

Conclusions

The way we used for the synthesis of polypropylene-*graft*-polystyrene copolymers seems to work properly. As a matter of fact, it is possible to tune the density of the point of growth of the grafts and the length of the polypropylene sequences through a suitable monomer feed in the step of the backbone synthesis. On the other hand, the living styrene polymerization step allows the regulation of the grafts length through the control of the reaction time.

The compatibilization test carried out on polypropylene−polystyrene blends shows a remarkable reduction of the phase separation. The results of the morphologic characterization of the blends clearly indicate that the compatibilization ability of the PP-*g*-PS improves with increasing either the length of the polypropylene sequences or the length of the polystyrene sequences or the number of the side chains for backbone, at least in the composition range investigated.

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