DOI: 10.1002/masy.200650207

A Novel Route to Graft-Copolymers with Tailored Structures for the Compatibilization of Polymeric Blend

Lucia Caporaso, Nicola Iudici, Leone Oliva*

Summary: A new method to synthesize graft-copolymers based on isotactic polypropylene (iPP) with tailored structure has been developed. The synthesis is a two-step process: synthesis of P-co-(*p*-MS-E) copolymers, by using *ansa*-metallocene catalysts, and metallation of *p*-Me groups followed by living anionic polymerisation for the graft growth. This method turn out to be versatile because, by changing experimental conditions, in the first step backbones with a tuned number of the graft growth sites and polypropylene lengths can be obtained, whereas in the second step, graft chains of different types and lengths can be synthesized. The particular ability of these copolymers to compatibilize polymeric blends was evaluated analyzing the morphology of the products copolymers/blends by using a scanning electron microscopy (SEM).

Keywords: compatibiliser; graft copolymers; polymeric blends

Introduction

Graft copolymers are largely used for the compatibilization of immiscible polymer blends.[1] The compatibilization efficiency of suitable graft copolymers is due to a fine tuning of their main structural parameters as length of the side chain and number of side chains.[1] This is the reason why a synthethic procedure aimed to obtain graft copolymers with a well defined distribution and length of the side chains is mandatory. However, the synthesis of graft copolymers based on isotactic polypropylene (iPP) with well defined structure is complicated because of the inert nature of the polyolefins. Currently, most of the commercial processes are based on post-polymerization processes involving the use of functionalized or irradiated iPP followed by a radical polymerization of the comonomer. Unfortunately, many undesiderable side reactions occur, such as degradation and crosslinking; as consequence it is difficult to control the graft density and the graft length.[2,3]

Recently, a new synthesis of polypropylene-graft-polystyrene through copolymerization of propylene with allyl-terminated polystyrenes macromonomers has been reported in literature.[4] With this approach, in the presence of metallocene catalysts, polypropylene based copolymers with polystyrene side chains of fixed length can be obtained. However, since the incorporation degree of the *co*-macromonomer depends on their length, it is possible to insert only few and short macromonomers for each backbone.

Another method was developed by Chung and coworkers,[5] through the synthesis of copolymers of propylene and *p*-methylstyrene (PP-co-*p*-MS) as backbone, by using heterogeneous Ziegler-Natta catalysts. The copolymers were subsequently methalated in the *p*-methyl groups with *sec*-BuLi and finally the side chain was grown by anionic polymerization of the comonomers.[6] This route allows the tuning of graft length but does not control

---

Dipartimento di Chimica, Università di Salerno. Via S. Allende, I-84081 Baronissi, Salerno (Italy)
E-mail: lcaporaso@unisa.it

the graft density and the compositions due to the wide molecular weight distribution and the low mole content of *p*-MS obtained with heterogeneous Z-N catalysts.

In order to implement a synthetic route able to tune length, distribution and the amount of grafted chains in the resulting graft copolymers, we developed a new synthetic approach.[7] The iPP backbone has been prepared by copolymerization of propylene and *p*-methylstyrene with small amount of ethylene, in presence of homogeneous *ansa*-zirconocene-based catalyst.[8] The ethylene traces in the feed allow to overcome the hindrance to copolymerize propylene and *p*-methylstyrene arising from the opposite insertion regiochemistry of the two monomers. In other words they act as catalyst reactivator. Furthermore, varying polymerization conditions, it is possible to produce isotactic polypropylene containing different amount of isolated *p*-methylstyrene-ethylene units and different polypropylenic sequences length. Since the methyl group in the aromatic ring can be deprotonated, so becoming a centre for the initiation of anionic polymerization, the side chain has been grown following the route described by Chung.[6]

Our synthetic strategy proved to be versatile since allows to obtain graft iPP copolymers varying: a) the chemical nature of the side chains; b) the length of the polypropylene sequence in the backbone; c) the length of the lateral chains; d) the number of side chains per macromolecule.

This allowed us to investigate how changes the compatibilization ability of iPP-based graft copolymers by changing the structural parameters.

Polypropylene-graft-polystyrene (PP-*g*-PS) with a variety of molecular structures and polypropylene-graft-polymethylmethacrylate (PP-*g*-PMMA) copolymers have been prepared and tested as compatibilisers for polymeric blends. The investigation of the morphology and of the size of the dispersed phase of the compatibilized blends, has been performed by using scanning electron microscopy.

Results and Discussion

a) Synthesis of the Backbone with Well Defined Number of Grafts Growth Sites

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 has been performed under different comonomers feed ratio, in the presence of rac-ethylenebis(1-indenyl)-zirconiumdichloride activated by methylalumoxane, in order to obtain the copolymers with different mole content of p-methylstyrene-ethylene.[7] The p-methylstyrene-ethylene couples interrupt the polypropylene sequences and give rise to the sites of growth of the side chains. The results are summarized in Table 1, where the obtained copolymers contain from 1.0 to 3.9 mol % of p-MS-E units spanning from 98 to 24 units long isotactic PP sequences.

The aliphatic region of the ^{13}CNMR spectrum of the P-co-(*p*-MS-E) copolymer reported in Figure 1 shows the signals at 43.5 ppm (carbon a), 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 iPP sequences at 44.2, 26.5 and 19.5.

Table 1.
Polymerization conditions and P-co-(*p*-MS-E)copolymers composition.

run[a]	[E]/[P]/[*p*-MS][b]	% *p*-MS-E[c]	*Lp*[7]	M_n[d]
1	1/804/63	1.0	98	36150
2	1/804/118	1.6	60	26600
3	1/804/120	1.7	57	18000
4	1/385/62	1.9	51	33050
5	1/390/68	2.0	48	14050
6	1/804/128	2.1	46	9020
7	1/804/136	2.3	42	22400
8	1/804/168	2.6	37	23700
9	1/804/190	2.8	34	26450
10	1/804/236	3.9	24	24750

[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. [d] Molecular weights (g/mol) determined by GPC analysis; the polydispersities (M_w/M_n) were ≤ 2 for all samples.

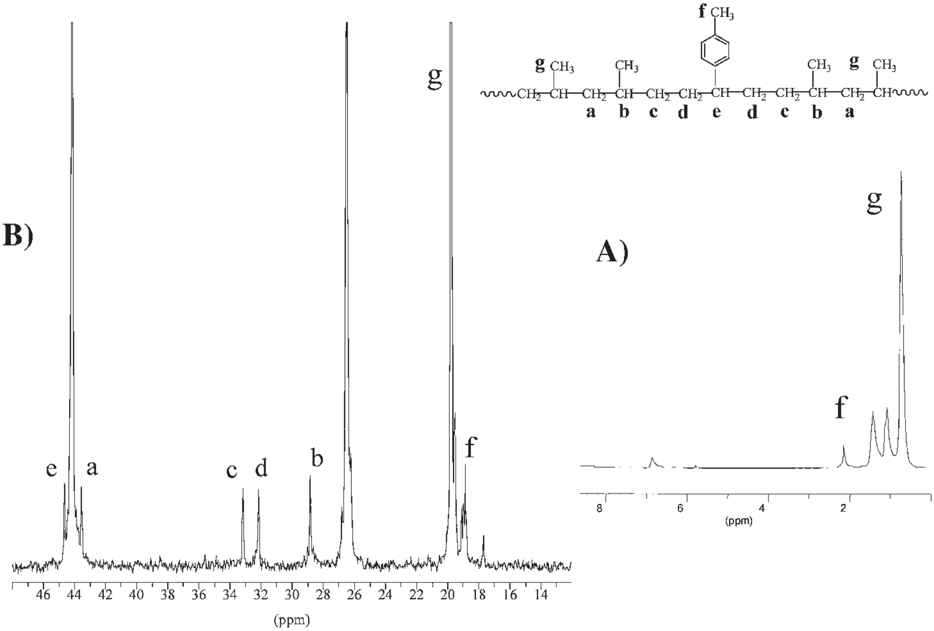


Figure 1.
^{1}H-NMR spectrum A) and aliphatic region of ^{13}C-NMR spectrum B) of a copolymer P-co-(*p*-MS-E) (run 2 of the Tab.1).

Accordingly in the ^{1}H NMR spectrum of the copolymer can be detected signals at $\delta = 0.75, 1.15, 1.45$ and 2.1 ppm, corresponding to CH_3, CH_2, CH and ϕ-CH_3 groups in the backbone, and the peaks between $\delta = 6.8$ and 6.9 ppm corresponding to the aromatic protons.

The copolymer composition as well as the average length of the polypropylene sequences has been determined through ^{1}H NMR and ^{13}C NMR analysis from the relative intensities of the signals assigned to polypropylene sequences and to *p*-methylstyrene-ethylene isolated units, as reported in reference 7.

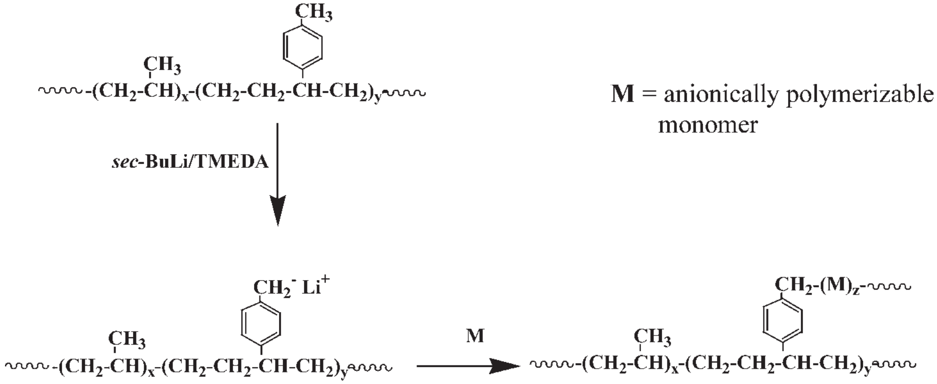
b) Synthesis of iPP-graft Copolymers with Different Structure and Chemical Nature of the Side Chains

The second step concerns the preparation of graft copolymers involving the metallation of P-co-(*p*-MS-E) copolymers with large excess of *sec*-BuLi and subsequent living anionic graft-from reaction, as illustrated in Scheme 1.[7]

In order to evaluate the versatility of our synthetic approach, the lithiated polymers was reacted with: a) styrene by varying the concentration and the reaction time, so to produce copolymers with well-defined number of the side chains for backbones and well-defined length; b) a polar monomer, such as MMA, producing copolymers with different chemical nature of the side chains.

The PP-*g*-PS and PP-*g*-MMA copolymers were washed with boiling MEK to remove any ungrafted homopolymer. The insoluble fractions were characterized by GPC technique. The copolymers present a narrow and unimodal molecular weight distributions ($M_w/M_n \approx 2$), so the contemporary presence of copolymers and homopolymers can be disregarded. The experimental results of the synthesis of PP-*g*-PS and PP-*g*-PMMA copolymers are summarized in Table 2 and 3 respectively.

As an example, in Figure 2 is reported the aliphatic region of the ^{13}C NMR of a PP-*g*-PS copolymer. This copolymer, characterized by two side chains per backbone,



Scheme 1.

as long as 260 styrene units on average, was synthesized at 25 °C for 90 minutes with $[S] = 1.8$ mol/L starting from the P-co-(*p*-MS-E) copolymer of run 2 of the Table 1. The ^{13}C NMR spectra, in addition to the signals due to the P-co-(*p*-MS-E) backbone, show new resonances at 38.9 ppm and 40–42 ppm corresponding to the polystyrene side chains. In accordance with ^{13}C NMR, the ^{1}H NMR spectrum of the PP-*g*-PS copolymer also shows new resonances between $\delta = 6.8$ and 6.9 ppm assignable to the polystyrene units, in addition to the signals of the backbone.

As consequence of the reaction of methyl groups of *p*-MS units to connect graft polystyrene chains, can be observed the reduction of the relative intensity of the peak at 2.1 ppm of the PP-g-PS copolymer (b), reported in Figure 2A, with respect to that of the starting copolymer (a) show in Figure 1A.

The graft efficiency - the amount of the methyl groups of *p*-MS in the starting P-co-(*p*-MS-E) copolymers that reacted producing graft chains - depends principally on the efficiency of the lithiation reaction and can be valuated from the intensities of the ^{1}H NMR signals by using the following relationship:

$$\mathrm{Eg} = [(\mathrm{A}_{2.1}/\mathrm{A}_{0.75})_a - (\mathrm{A}_{2.1}/\mathrm{A}_{0.75})_b]/(\mathrm{A}_{2.1}/\mathrm{A}_{0.75})_a$$

The occurrence that, in some cases, a very high graft efficiency has be obtained (up to 89%) suggests that, in spite of the heterogeneous system, the internal methyl groups are involved as well as the external ones in the grafting reaction. On the other hand the polydispersity evaluated through

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)	Eg[d)]	L_S[e)] ($\times 10^2$)	N_{SC}[f]
1	1.9	2.6	51	60	0.8	3.5	12
2	1.9	2.6	51	90	0.8	5.2	12
3	1.9	2.6	51	120	0.8	6.9	12
4	2.8	1.8	34	60	0.9	0.33	14
5	2.8	1.8	34	90	0.9	0.57	14
6	1.7	0.8	57	45	0.6	1.1	4
7	2.0	2.6	48	30	0.6	1.1	4
8	1.6	1.8	60	90	0.3	2.6	2
9	2.1	2.4	46	30	0.5	3.1	2
10	2.6	1.8	37	30	0.9	2.2	3
11	3.9	1.8	24	90	0.5	2.1	3
12	2.3	2.5	42	30	0.9	1.0	10
13	1.0	1.8	98	60	0.4	2.8	8

[a)] Mole per cent of *p*-MS-E in the backbone; [b)]In the feed; [c)]Average length of polypropylene sequences;[7] [d)] The graft efficiency [e)]Average length of the PS sequences [7] [f)]Average number of the side chain for backbone.[7]

Table 3.
Polymerization conditions and main results of the ^{13}C NMR characterization of PP-*g*-PMMA copolymers.

Sample	% *p*-MS-E[a]	[MMA] (mol/L)[b]	L_P[c]	Reaction time (min)	Eg[d]	L_{MMA}[e] ($\times 10^2$)	N_{SC}[f]
1	1.7	1.8	57	30	0.6	0.43	4
2	1.7	1.8	57	60	0.6	0.87	4
3	1.7	1.8	57	90	0.6	1.3	4
4	2.3	1.8	42	90	0.9	0.51	10

[a] Mole per cent of *p*-MS-E in the backbone; [b]9In the feed; [c]9Average length of polypropylene sequences;[7] [d] The graft efficiency [e]Average length of the PMMA sequences;[7] [f]Average number of the side chain for backbone.[7]

GPC analysis (Mw/Mn ≤ 2) shows the homogeneity of the samples.

For all the samples the average length of the side chains (L_S) and the average number of the side chains (N_{SC}) were calculated by NMR and GPC analysis, in agreement with reference 7.

On the other hand the experimental results of the synthesis of PP-*g*-PMMA copolymers are show in Table 3.

The ^{13}C NMR of a PP-*g*-PMMA copolymer is shown in Figure 3. This sample (run 4 of the Table 3), characterized by 10 side chains per backbones of methyl methacrylate (51 units long on average), was obtained by anionic polymerization of MMA over the P-co-(*p*-MS-E) copolymer (run 7 of Table 1) obtained after lithiation reaction, in the same reaction condition as the PP-*g*-PS copolymer reported in Figure 2. In this spectrum the signals observed in the starting material (see Figure 1) and the peaks due to polymethylmethacrylate sequences are both present. The corresponding ^{1}H NMR spectrum (not reported here) of the same PP-*g*-PMMA copolymer shows new resonances at $\delta = 3.5$ ppm due to methyl groups (CH_3–O) of MMA sequences in the side chains. Moreover a considerable reduction of the relative intensity of the peak at 2.1 ppm is also observed. In fact, the intensity ratio of $-CH_{3\,(p\mathrm{MS})}$ and $-CH_{3\,(\mathrm{PP})}$ peaks changes from $2.3 \cdot 10^{-2}$ in the P-co-(*p*-MS-E) copolymer (a) to $2.1 \cdot 10^{-3}$ in the PP-*g*-PMMA copolymer (b) as consequence of that 90% of methyl

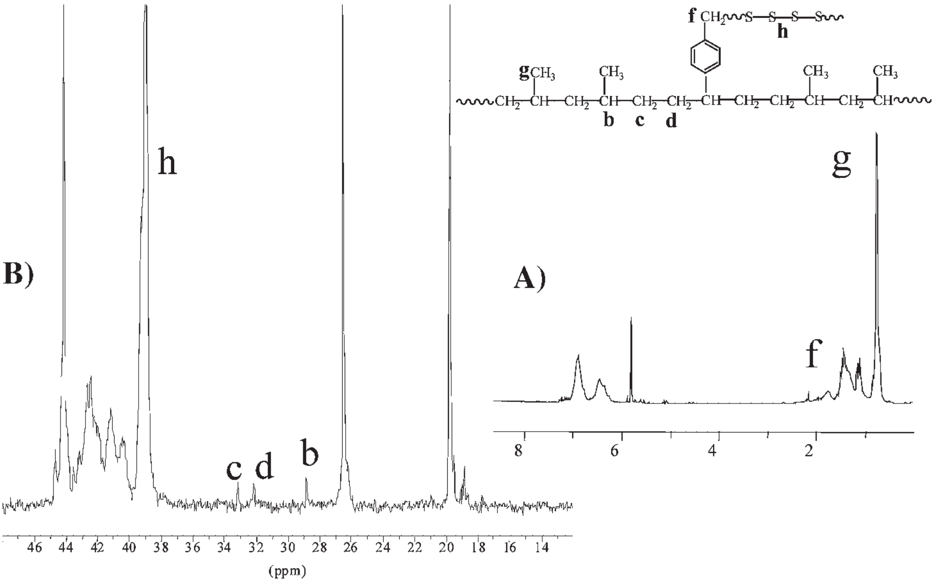


Figure 2.
A) ^{1}H NMR spectrum and B) Aliphatic region of ^{13}C-NMR spectrum of sample 8 of Table 2.

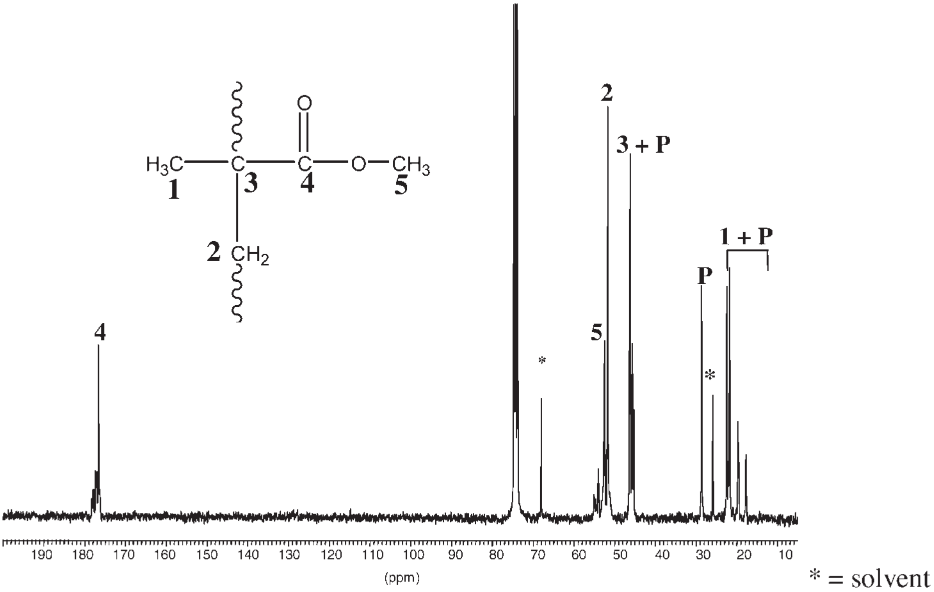


Figure 3.
The ^{13}C NMR of a PP-*g*-PMMA copolymer (sample 4 of the Table 3).

groups of the *p*-MS units reacted to connected to graft side polymethylmethacrylate chains.

The average length of the PMMA sequences can be properly calculated from the intensities of signals of the ^{1}H and ^{13}C NMR spectra through the equation:

$$L_{\mathrm{MMA}} = (A_{50.4}/A_{26.5})_b/[(A_{2.1}/A_{0.75})_a - (A_{2.1}/A_{0.75})_b]$$

The L_{MMA} values (see Table 3) increase with increasing the reaction time of MMA, as one can expect for a living anionic polymerization. The average number of the side chains for backbone that depends on the efficiency of the lithiation reaction can be calculated from:

$$N_{\mathrm{SC}} = Mn\,F_{\mathrm{P}}[(A_{2.1}/A_{0.75})_a - (A_{2.1}/A_{0.75})_b]/(42F_{\mathrm{P}} + 146)$$

were 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.[7]

It is worth to note that the L_{P} and N_{SC} parameters depends principally on the starting backbones while, by tuning the reaction time in the anionic graft polymerization, the average side length can be regulated (see e.g., samples 1–5 and 8, 9 in Table 2 and sample 1–3 in Table 3). Therefore, by changing the starting backbones, the comonomer and graft reaction conditions, iPP-graft copolymers that differs in average length of polypropylene sequences, in the chemical nature, in average length and in average number of the side chains per backbone have been synthesized.

c) Polymers Blend

The PP-*g*-PS and PP-*g*-PMMA copolymers have been tested as compatibilisers of isotactic polypropylene-polystyrene and polypropylene-polymethylmethacrylate blends, respectively.

Therefore, PP/PS and PP/PMMA blends without and with addition of PP-*g*-PS and PP-*g*-MMA graft copolymers respectively, were prepared by dissolving the components in 20 mL refluxing 1, 2-dichlorobenzene under N_2. After the polymer mixture had formed a clear solution, the blend was precipitated by pouring the solution into cold ethanol. The blends, dried under vacuum, were melt pressed at 200 °C and quickly quenched at 0 °C to form a 2 mm thin film.

The films obtained were cryo-fracturated in liquid N_2 and the surface of the edges was observed through scanning electron micrographs (SEM) to examine the bulk morphologies.

The SEM imagines of two blends composed by a) 50/50 of PP and PS and b) by 49/49/2 weight ratio of iPP, PS and PP-*g*-PS are reported in Figures 4. The gross phase separation between disperse PS and continuous PP phase can be observed in Figure 4a. The size and the shape of the PS phases are variable owing to the lack of interaction with the PP matrix. On the other hand, the imagine of the compatibilized blend (Figure 4b) is far more uniform. This result indicates that the PP-*g*-PS is able to increase the interfacial interaction between the iPP matrix and the PS dispersed phase, and consequently to reduce the domain size.

The SEM imagines of a) the blend composed by 70/50 weight ratio of PP and PMMA and b) the corresponding blend with 5 weight % of PP-*g*-PMMA (sample 4 of Table 3), are reported in Figure 5. Also in this case the imagine of the blend with PP-*g*-PMMA (see Figure 5b) shows more uniformity; the compatibilizing effects due to the copolymer addition is clearly visible.

In order to study the influence of graft copolymers parameters L_P, L_S, N_{SC} on their compatibilizing efficiency, the PP-g-PS copolymers with different microstructure were used to prepare PP/PP-*g*-PS/ PS blends 49/2/49 and their cross-sections were analyzed and compared by SEM.

For this purpose, the size of the domain of the dispersed phase (d_d, average diameter of domain) was calculated[9] and compared in all the SEM imagines showing two distinct phases, the iPP matrix and the PS dispersed phase (see Table 4).

One can observe that the PP-*g*-PS's employed in the entry 1, 2, and 3, differ only for the L_S values that is growing from 1 to 3. In particular L_S of blend $1 < L_S$ of blend $2 < L_S$ of blend 3.

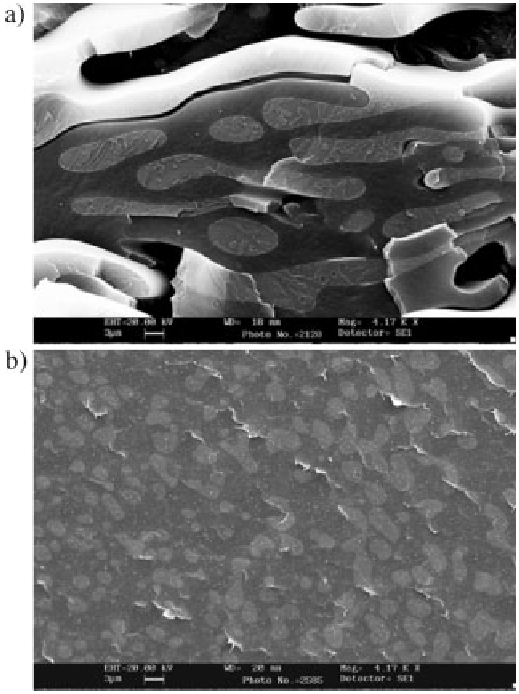


Figure 4.
SEM micrographs of the cross-section of two polymer blends: a) two homopolymers with PP/PS = 50/50 and b) two homopolymers and 2 wt % of PP-*g*-PS copolymer(sample 3 of the Table 2).

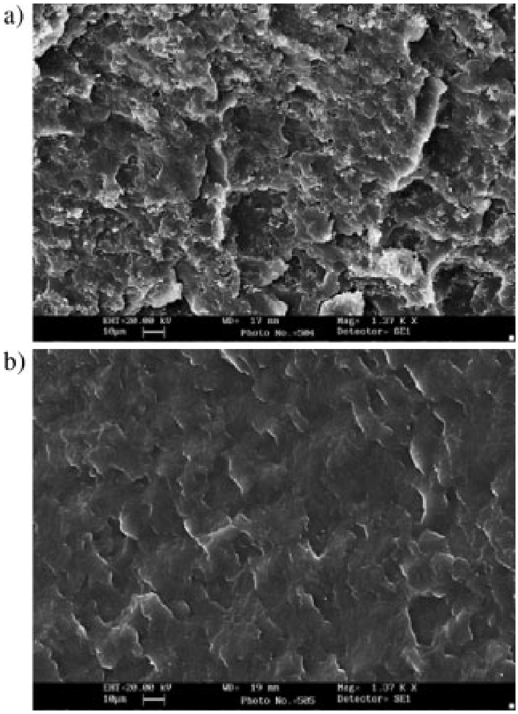


Figure 5.
SEM micrographs of the cross-section of two polymer blends: a) two homopolymers with PP/PMMA = 70/30 and b) two homopolymers and 5 wt % of PP-*g*-PMMA copolymer (sample 4 of the Table 3).

In the corresponding blends, the particle size of the dispersed PS phase is gradually reduced in the opposite order: d_d of blend $1 > d_d$ of blend $2 > d_d$ of blend 3.

Table 4.
The structural characteristics of PP-*g*-PS copolymers and the results of the SEM characterization of the blends.

Entry	L_P[a)]	L_S[b)] ($\times10^2$)	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 compatibiliser;[7] [b)] Average length of the PS sequences of the PP-*g*-PS compatibiliser;[7] [c)] Average number of the side chain for backbone of the PP-*g*-PS compatibiliser in the blends;[7] [d)] Average diameter of the PS phase in the blends.[7]

The blends of the entries 4 and 5 behave in accordance with this trend (Table 4).

On the basis of these experimental data, we can conclude that the PP-g-PS compatibilization efficiency increases with increasing the average length of the side chain.

The particle size of the PS phase of blend 6 is smaller than that of blend 7, as pointed out by the values d_d reported in the Table 4. Such a reduction in phase size can be related to the average length of the *i*PP sequence that is longer in the PP-*g*-PS copolymer employed for the blend 6 respect to PP-*g*-PS copolymer employed for the blend 7.

With the same account, can be justified the occurrence that 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 4).

Besides, Table 4 shows that the size of the dispersed domain of the blends 3 and 13 is similar in spite of a marked difference in the structures of the corresponding PP-*g*-PS copolymer employed. In particular the compatibiliser used for the blend 3 presents the L_S value of 6.9×10^2 and L_P value of 51, on the contrary the copolymer employed for the blend 13 presents L_S value of 2.8×10^2 and L_P value of 98. It is evident that in order to improve the compatibility of two homopolymers are relevant not only the length of the side chains of the PP-*g*-PS compatibiliser, as above reported but also the length of iPP sequences.

These results indicate that the ability to compatibilize the two homopolymers depends markedly on the length of the iPP sequence and it increases with increasing the average length of the iPP sequence.

The blends of the entries 12 and 7 can illustrate the effect of the number of the side chains per backbone of graft copolymer on the compatibility of the PP/PS blends. The PP-*g*-PS used in both blends present similar L_S and L_P values but different N_{SC} values. The consequence is that the size of PS phase of the blend of entry 12 is smaller than that of the blend of the entry 7 (see Table 4).

Finally the PP-g-PS compatibilization efficiency also improves with increasing the average number of the side chains for backbone.

Conclusions

The combination of the synthesis of P-co-(*p*-MS-E) copolymers by coordination catalysis with anionic polymerization of different comonomers, is a suitable route to synthesis of polypropylene graft copolymers with defined structure and with variable chemical nature of the side chains.

As a matter of fact, the route we have described make possible to tune the density of the grafts growth and the length of the polypropylene sequences simply changing the monomer feed in the step of the backbone synthesis. On the other hand, also the chemical nature and the graft lengths of the side chains can be tuned varying the comonomer used and the reaction conditions in the second step of anionic polymerization.

The compatibilization tests carried out on polypropylene-polystyrene blends, as well as on polypropylene-polymethylmethacrylate, show a remarkable reduction of the phase separation. Finally, the results of the morphologic characterization of the PP/PS blends clearly indicate that, in the composition range investigated, 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.

[1] R. D. Paul, S. Newman, "*Polymer Blends*", Academic Press Inc:, New York 1978. (b) E. L. Thomas, In: "*Materials Science and Technology: A Comprehensive Treatment*" R. W. Cahn, P. Haasen, E. J. Kramer, Eds.; VCH Publishers: Weinheim, **1991**; Vol. *12*, p 251. (c) O. Olabisi, L. M. Robeson, M. T. Shaw, *Polymer-Polymer Miscibility*; Academic Press Inc: New York, **1979**. (d) G. Riess, Y. Jolivet, In: "*Polyblends and Composites*" N. A. J. Platzer, Ed., ACS Advances in Chemistry Series, American Chemical Society: Washington, DC, **1975**, Vol. *142*. (e) R. Fayt, P. Hadjiandreou, P. Teyssie, *J. Polym. Sci. Pol. Chem.* **1985**, *23*, 337. (f) B. D. Edgecombe, J. A. Stein, J. M. J. Fréchet, Z. Xu, E. J. Kramer, *Macromolecules* **1998**, *31*, 1292. (g) E. A. Eastwood, M. D. Dadmun, *Macromolecules* **2002**, *35*, 5069.

[2] P. Galli, J. C. Haylock, A. De Nicola, *Macromolecular Symposia* **1995**, *100*, 95.

[3] E. S. Park, H. J. Jin, I. M. Lee, M. N. Kim, H. S. Lee, J. S Yoon, *J. Appl. Polym. Sci.* **2002**, *83*, 1103.

[4] U. Schulze, T. Fónagy, H. Komber, G. Pompe, J. Pionteck, B. Iván, *Macromolecules* **2003**, *36*, 4719.

[5] H. L. Lu, S. Hong, T. C. Chung, *J. Polym. Sci. Pol. Chem.* **1999**, *37*, 2795.

[6] H. L. Lu, T. C. Chung, *J. Polym. Sci. Pol. Chem.* **1999**, *37*, 4176.

[7] L. Caporaso, N. Iudici, L. Oliva, *Macromolecules* **2005**, *38*, 4894.

[8] (a) L. Caporaso, L. Izzo, L. Oliva, *Macromolecules* **1999**, *32*, 7329. (b) L. Oliva, G. Guerra, L. Caporaso, L. Izzo, L. Resconi, (Montell Technology Company Bv, Neth.). PCT Int. Appl. WO 0047643 A1, 2000.

[9] The average diameters of the polystyrene dispersed domains were obtained by the SEM micrographs processed by ImageJ 1.32j program (W. Rasband, *ImageJ 1.32j* National Institute of Health, Bethesda, Maryland, USA). This program allows to calculate the average surface of the dispersed domains. The average diameters were obtained considering the surfaces as section of spheres.