Synthesis and characterization of aPP/aPS graft copolymers

M. L. Arnal[1,*], A. J. Müller[1], B. Méndez[2]

[1] Grupo de Polímeros USB, Departamento de Ciencia de los Materiales,
Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela
[2] Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela,
Caracas, Venezuela

Summary

Graft copolymers of atactic polypropylene (aPP) and polystyrene (PS) were synthesized and characterized by ^{13}C NMR analysis. The ^{13}C NMR spectra of the grafts exhibited changes with respect to physical blends of identical compositions. The most important occurred in the meso sequences of the aPP blocks of the copolymer. These changes suggest that some grafting took place during the synthesis. SEM micrographs indicate greater interfacial interaction between phases in the copolymers than in the physical blends. Thermal Analysis showed that the Tg of the copolymers is higher than that of the PS homopolymers prepared under the same conditions. This could be the result of an apparent increased in molecular weight caused by the grafting of the aPS into the aPP chains. TGA results indicated that the thermal stability of the copolymer decreases as the aPP content in the copolymer increases.

Introduction

The compatibilization of immiscible polymer blends is of paramount importance in order to tailor properties for specific applications. The addition of appropriate copolymers that can modify the interfacial activity between the components of the blend (compatibilizing agents) or the chemical modification of one or both components are some of the attractive ways available to optimize properties (1). One of the most successful commercial polymer alloys is high impact polystyrene (HIPS), whose synthesis is based on the mass polymerization of styrene in the presence of an elastomer or an initial mass polymerization followed by a suspension polymerization process. The preparation of HIPS can be summarized in the following sequential stages (2): (a) dissolution of the uncrosslinked elastomer in the monomer styrene, (b) prepolymerization of the monomer under stirring, (c) final polymerization steps with or without stirring, this last stage could be performed by a mass or a suspension process. The polymer final structure is determined by stirring speed; when rubber content is increased, the stirring speed required for phase inversion is lower. The graft reactions before phase inversion tend to reduce the size of polystyrene droplets while after the inversion point these reactions tend to reduce the size of the rubbery phase, both behaviors are a consequence of the emulsifying effect of the graft reactions.

Recently, Trznadel et al. (3) and others (4-5), have studied the modification of polyolefinic matrices (like polyethylene, PE, or polypropylene, PP) by the addition of a second component capable of polymerization, like styrene. These works have concentrated on the morphological changes that swelling, polymerization and subsequent extraction of the PS phase induce in the matrix. They have reported that the diffusion of styrene occurs mainly in the amorphous zones of the matrix and that orientation of the matrix can also have an effect on the diffusion of the monomer. Thermal analysis on such systems indicated that wider fusion endotherms were generated and lower melting points were found for isotactic polypropylene matrices. These results suggested a reduction in polypropylene crystal perfection.

In this work we have employed similar methods to those used to prepare HIPS but we have replaced the usual polybutadiene component by an aPP that due to its lack of structural regularity is soluble in styrene and displays rubbery behavior at room temperature.

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* Corresponding author

Experimental

The polymerization process, purification and separation of the obtained copolymer was performed using the following procedure: (a) dissolution of aPP (Hoescht HN with a viscosity range between 8000 and 30000 mPa x s. and a crystallinity of 3%) in analytical grade styrene at 70 °C, (b) prepolymerization at 70 °C by UV radiation, (c) final polymerization at 100 °C. A purification process was employed whereby the polymer was dissolved in xylene, precipitated in methanol, vacuum filtered and dried for 32 hours at 85 °C under vacuum.

Three variables were studied: The relation of styrene to initiator, the relation of styrene to aPP and the stirring rate. Table 1, shows the eight experiments performed. Finally Two polymerizations of styrene without aPP were also made to have unmodified PS of similar molecular characteristics.

Table 1. Experimental design for PS synthesis in the presence of aPP.

Experiment	Variables			Thermal Analysis	
	Styrene/Init. ratio	Stirring rate	Styrene/aPP ratio	Tm (peak)	Tg (peak)
	(weight)	(rpm)	(weight %)	(°C)	(°C)
1	681	300	92.5/7.5	155.0	96.0
2	226	300	92.5/7.5	--	96.0
3	681	500	92.5/7.5	156.8	101.9
4	226	500	92.5/7.5	155.1	84.6
5	681	300	86/14	155.0	95.4
6	226	300	86/14	153.5	98.9
7	681	500	86/14	153.2	95.3
8	226	500	86/14	155.6	92.6
12	681	-----	100/0	--	74.1
13	226	-----	100/0	--	71.7

Benzoyl peroxide was used as initiator, whose decomposition temperature is between 80 and 95°C, at lower temperatures decomposition occurred due to the UV radiation employed.

The samples obtained were characterized by means of Fourier Transform Infrared Spectroscopy (FT-IR) using a Nicolet 550 spectrometer. Nuclear Magnetic Resonance (NMR), spectra were obtained by a Jeol Eclipse 270 spectrometer equipped with a super conducting magnet. The NMR experiments were performed using chloroform solutions, at the following conditions: 6.35 Tesla field, 67.8 MHz for the 13Ctests, 30º pulse and 2 sec. repetition time. Differential Scanning Calorimetry (DSC) was performed with a Perkin-Elmer DSC-7 instrument. Samples were first heated to 200 °C to erase previous thermal history and then cooling scans at 10 °C/min were recorded followed by heating scans also at 10 °C/min. The thermal stability of the samples was examined in air by thermogravimetry between 50 and 500 °C by means of a Polymer Laboratories STA 625 Simultaneous Thermal Analyzer. The morphology of the materials was examined by Scanning Electron Microscopy (SEM) of compression molded cryogenically fractured specimens using a Phillips SEM-50 microscope.

Results and Discussion.

Figure 1 shows the FTIR spectrum of sample P3, a copolymer of composition PS/aPP 92.5/7.5 (Table 1, experiment number 3). This FTIR spectrum was very similar to the FTIR spectrum of sample P12, pure PS, this was to be expected in view of the PS content. A similar result was obtained for the rest of the copolymers from P2 to P8 since the PS content was either 92.5 or 86 %. For these copolymers, the characteristic CH_3 infrared bands of 1300 and 1400 cm^{-1} corresponding to the PP almost totally overlapped with the aromatic bands of the PS component leaving no room for quantitative analysis. Therefore, we turned to ^{13}C NMR in order to examine the
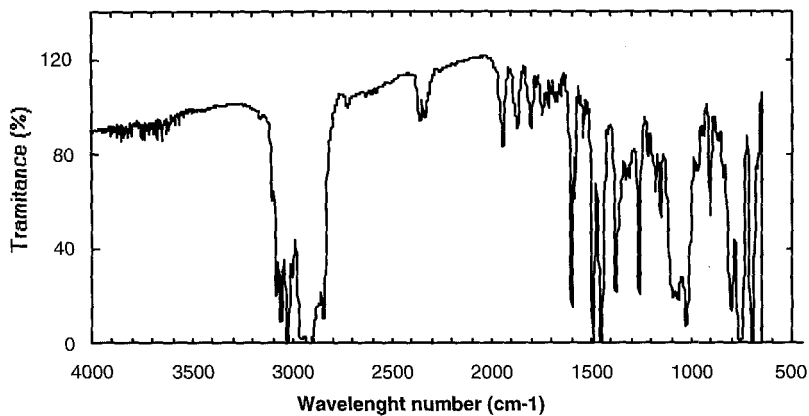
Figure 1. Infrared Spectrum of P3 (PS/aPP 92.5/7.5). Note: The peak at 2300 cm^{-1} is due to background
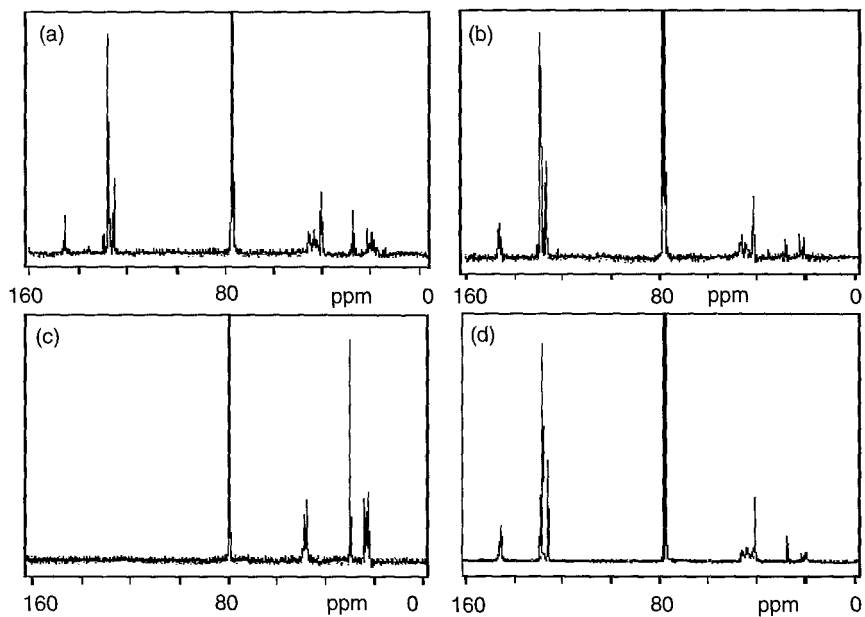

Figure 2. ^{13} C NMR spectra of (a) P3, (b) Physical mixture 1 (PM1), (c) aPP, and (d) Theoretical Mixture (TM 95.5/4.5).

copolymers with the purpose of determining whether small changes in the structure of the aPP resulted as a consequence of PS grafting.^{13}C NMR was performed with samples P3, P7, aPP and PM1, which is a Physical Mixture (PM1) of PS/aPP 92.5/7.5 (see fig 2b). Through analysis of the ^{13}C NMR spectra of aPP the tacticity of this polymer was estimated. It was found that the aPP had 63 % of heterotactic sequences, 18 % syndiotactic and 19 % isotactic sequences. A ^{13}C NMR spectrum of aPP is shown in Figure 2c where the characteristic peaks of CH_3, CH and CH_2 groups can be seen at around 20, 27 and 48 ppm, respectively. These results are consistent with the ^{13}C NMR analysis of PP found in the literature (7). Fig 2 also contains spectra for samples of copolymer P3 (see Fig 2a), PM1 (see Fig 2b) and a Theoretical Mixture 95.5/4.5 (TM, see Fig 2d), where additional peaks that correspond to PS can be observed: between 139 and 144 ppm carbon 1, and between 120 and 130 ppm carbons 2-6 of the aromatic ring; between 40 and 50 ppm main chain CH_2, and finally between 20 and 30 ppm the CH peak.

The Theoretical Mixture consist of a spectrum generated by mathematically averaging the spectra of PS and aPP in different proportions until a composition matching the experimental spectrum is found. The ratio 95.5/4.5 PS/aPP was the best match for the actual spectrum of sample P3. This result is in good agreement with the experimental styrene/aPP ratio of P3, i.e., 92.5/7.5, since after polymerization the sample is washed and purified.

In order to ascertain if grafting of the aPP onto the growing PS took place, the ^{13}C NMR spectra of the copolymers were compared with spectra of Physical Mixtures of PS/aPP with identical nominal composition of the copolymers and with theoretical mixtures generated by mathematical combination of the aPP spectrum and the spectrum of sample P12, i.e., PS under identical conditions. This analysis was performed with samples P3 and P7. The results indicated that appreciable changes could only be found in sample P3, the sample with lower aPP content of the two chosen for this comparison. The explanation of this result can be found in the intrinsic characteristics of the polymerization process utilized. Initially, a one phase solution of aPP in styrene exists until PS start to form. The rapid increase of PS concentration induces the segregation of the aPP component into a second phase. The degree of conversion at which this phenomenon takes place depends on the relative proportions of the solution components; however, at higher aPP concentrations the formation of the second phase will occur sooner. Once the aPP component is part of a second phase, its possibilities of reacting with the growing PS will be reduced. Therefore, in those copolymers with a lower proportion in the reacting mixture of aPP, like P3, the probability of grafting between the growing PS and aPP is higher. It is also important to consider that the number of grafting reactions is expected to be low since the reactivity of styrene is much greater than that of the saturated aPP chains. Additionally, the ^{13}C NMR peaks that correspond to grafted sequences will overlap with those of unmodified aPP chains and the higher the content of the latter ones the more difficult it will be to distinguish them from the grafted chains.

As already mentioned Fig 2 shows spectra P3, the Physical Mixture PM1 of composition 92.5/7.5 PS/aPP and the Theoretical Mixture spectrum of composition 92.5/7.5 PS/aPP. For these samples, Figure 3 and 4 present expansions of their ^{13}C NMR spectra for regions associated with the groups CH and CH_3 of their aliphatic fractions. In Fig 3, the expansions correspond to the CH group peaks region and a comparison of the four spectra indicates that the form and size of the bands is very similar for the Physical mixture PM1 (see Fig 3b), the aPP (see Fig 3c), and the Theoretical mixture (see Fig 3d). Nevertheless, in the case of P3 (see Fig 3a), changes in the form and relative size of the bands can be observed. Such changes indicate that in the P3 case grafting could have taken place and that a copolymer has indeed formed.

Having established that there were structural changes in the aPP in copolymer P3, we decided to determine if such changes were also occurring along the aPP chain. A more detailed comparison between the four CH spectra of Fig 3 was then performed. A close inspection of the spectra of P3 and aPP in Fig 3 indicates that there is a reduction in the height of the band associated with the triads mm (between 28 and 27.9 ppm for P3 and 27.9 ppm for PM 1, 27.7 for aPP and between 27.7 and 27.8 ppm for the TM) in relation to the bands attributed to the triads rm (27.7 ppm for P3, and PM 1, 27.5 for aPP and 27.6 for TM) and rr (between 27.3 and 27.5 ppm for all the samples).
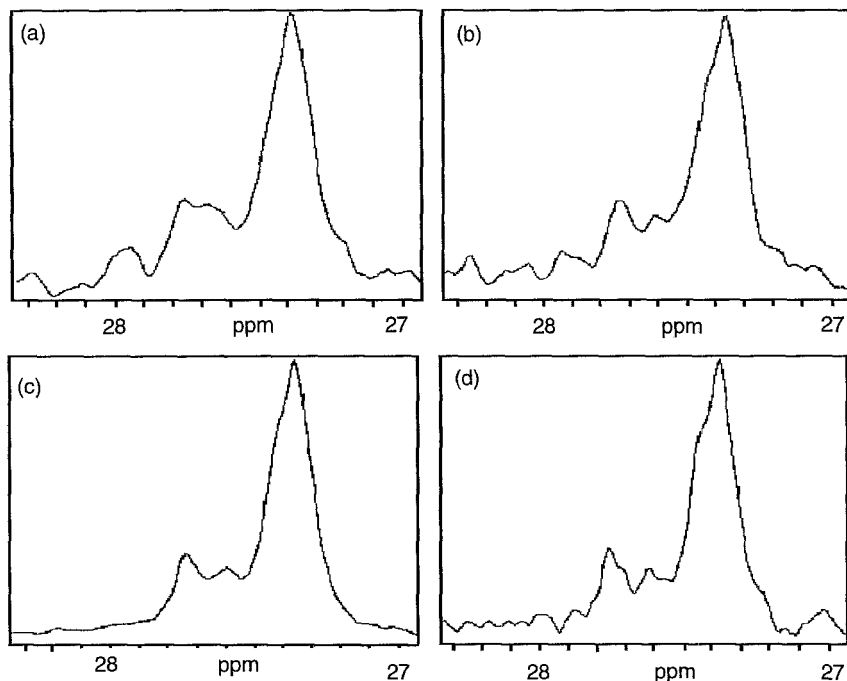
Figure 3. ^{13}C RMN Spectra. Expansions of CH regions: (a) P3, (b) Physical mixture 1 (PM1), (c) aPP, and (d) Theoretical Mixture (TM 95.5/4.5) .

There also seems to be a broadening of the peaks corresponding to the triads mm and rm. Table 2 presents the results of measuring the heights of the three peaks, mr, and rr with respect to a common base line and then normalized by dividing them by the height of the rr peak. As shown in Table 2, the aPP and PM1 samples exhibit the same trend, while in the case of P3, the normalized height of the mm triads is lower than the band corresponding to the mr triads. This result can be interpreted by considering that part of the original mm sequences of the aPP have disappeared when the CH groups that belonged to the meso sequences were replaced by quaternary carbons when the insertion of a growing PS radical took place onto the aPP chain. This preferential insertion of the PS macro radical in the iso sequence of the aPP chain can be rationalized by considering that the polymerization is taken place in solution. In the case of mm sequences, the CH_3 groups of the aPP are spatially oriented on the same side of the chain and therefore the steric hindrance for proton abstraction and the attack of the growing PS macro radical will be lower than for other chain sequences.

Table 2. Normalized heights of tactic sequences in the CH region.

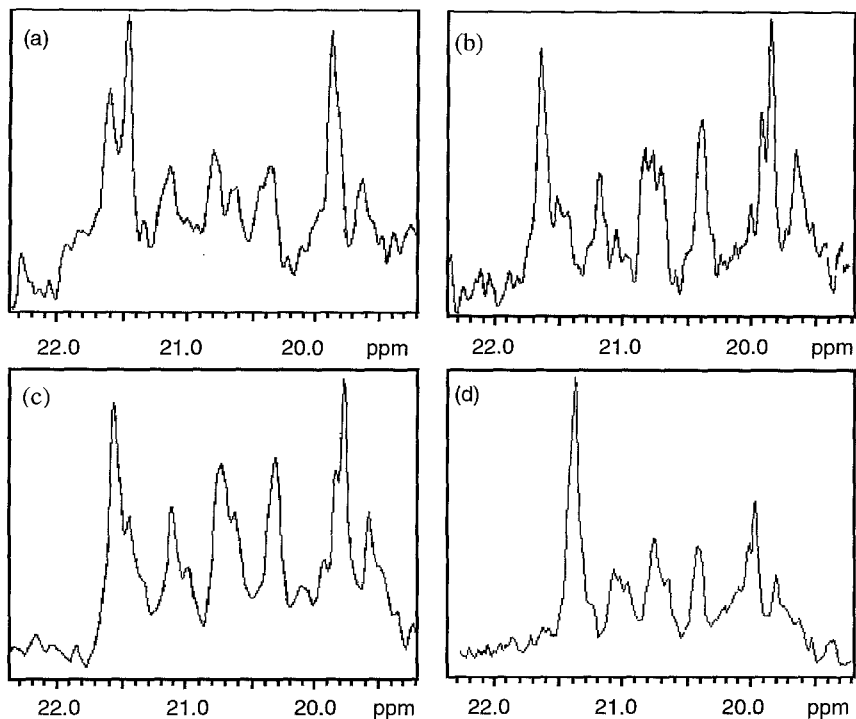| Samples	Triads (normalized height)		
	mm	mr	rr
P3	0.17	0.34	1
aPP	0.26	0.21	1
PM 1	0.31	0.24	1

Figure 4. ^{13}C RMN Spectra. Expansions of CH_3 regions: (a) P3, (b) Physical mixture 1 (PM1), (c) aPP, and (d) Theoretical mixture (TM 95.5/4.5) .

The tendency of greater insertion of PS onto the meso sequences of the aPP can be confirmed by observing the expansion of the ^{13}C NMR spectra around 20 ppm associated with the CH_3 group , see Fig 4. In this Fig it can be seen that the peak shape and relative height are very similar to aPP (see Fig 4c), PM1 (see Fig 4b), and the Theoretical mixture (see Fig 4d), but differs for P3 (see Fig 4a), as was the case of the CH region. The comparison between P3 and aPP indicates that one of the bands that has experienced a bigger change is that corresponding to the meso pentads that occurs between 21.4 - 21.6 ppm and that in the case of P3 exhibits a new peak or shoulder at 21.6 ppm. The peaks associated to mmmr sequences at 21.2 ppm for P3, and between 19.9 and 21.1 for the other samples, mmrr at 20.8 ppm for P3 and between 20.6 and 20.8 for the other samples, and the sum of peaks mmrm and rmrr that occurs at 20.4 ppm appear in sample P3 as broader bands with new peaks or shoulders and between 20.2 and 20.4 ppm for the other samples. The band corresponding to rrrr sequences at 19.8 ppm for P3 and between 20.0 and 19.7 for the other samples also shows some minor changes. The broadening of these bands and/or the appearance of new peaks and shoulders is consistent with the presence of CH_3 groups near the tertiary and quaternary carbons that arose by grafting . Furthermore, in this CH_3 region the bands that have changed are those associated to sequences that contain diads or longer arrangements of units in meso configuration; this is consistent with the tendencies observed above in Fig 3 and Table 2 for the bands corresponding to the CH group.

Comparing the thermal behavior of the copolymers with the homopolymers by DSC (Table 1) it can be seen that the copolymers exhibit higher glass transition temperatures than any of the

two homopolymers (P9 and P10). Higher Tg's could be due to grafting that causes an apparent increase in the molecular weight thereby raising the Tg as compared with the homopolymer obtained under identical conditions (e.g., see Table 1, copolymer P1, Tg=96 °C and homopolymer P9, Tg=74 °C).

The thermal stability of the copolymers was found to decrease with increasing aPP content. TGA indicated differences of at least 50 °C in the temperature at which degradation initiates between the homopolymers (for P9, polystyrene, 319 °C was the limit of thermal stability while for aPP it wasonly 271 °C). In the case of copolymer P3 of composition 92.5/7.5 PS/aPP, the thermal stability limit was 305 °C, while for P7 it was 270 °C. The temperatures reported correspond to the 10 % initial weight loss.

SEM analysis of cryogenically fractured specimens was performed of the copolymers and of mixed melt blends of approximately the same composition but with an added compatibilizer (an styrene-isoprene-styrene block copolymer). Figure 5 shows representative micrographs of two samples. In the case of the copolymers, the dispersed phase particles seem to be embedded in the matrix and no detachment of particles was observed after cryogenic fracture. The melt mixed blend, on the other hand, exhibits clean holes that indicate particle detachment. The homogeneous morphology of the copolymer and the apparent interface adhesion indicated by the lack of interfacial failure can also be considered as evidence for grafting during the polymerization.
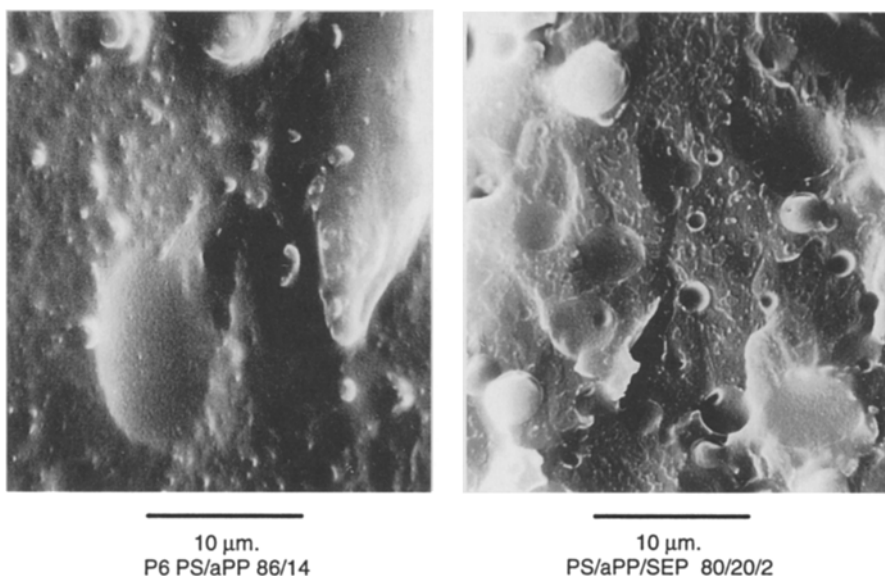

| 10 µm. | 10 µm. |
| P6 PS/aPP 86/14 | PS/aPP/SEP 80/20/2 |

Figure 5. Morphology of P6 copolymer and polyblend PS/aPP/SEP 80/20/2 obtained by SEM.

Conclusions

The polymerization of styrene in the presence of aPP by means of UV light radiation and temperature causes grafting between the aPP and the growing PS chain. The grafting was detected by the changes exhibited in the ^{13}C NMR spectra of the copolymers as compared to Physical Mixtures and to theoretical expectations based on the composition ratios. The changes observed in the ^{13}C NMR spectrum of a 92.5/7.5 PS/aPP copolymer indicated that some aPP was inserted in the growing PS chains and that the sequences most affected in the aPP are those isotactic sequences associated with n-ads of the meso type. The morphology of these graft

copolymers indicates better phase interactions than compatibilized melt mixed blends of similar compositions. These grafts could be of interest for the preparation of toughened PS and as compatibilizers for PP/PS blends.

Acknowledgments

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