Solid-State Modification of Polypropylene (PP): Grafting of Styrene on Atactic PP

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Summary: Grafting of unsaturated vinyl monomers onto polypropylene (PP) is a convenient route to develop new polymeric materials with synergistic properties. Particular attention must be paid to the formation of graft copolymer relative to the formation of homopolymer, since the final properties are dependent both on the dispersion of the new polymer into the iPP matrix, which is controlled by the degree of grafting, as well as on the chemical nature of the *in-situ* formed polymer chains.
In the present work the grafting reaction of styrene on atactic PP (aPP), considered as good model system for the more studied solid-state modification of isotactic PP (iPP), has been investigated in the presence of two different radical initiators in order to get a first insight into the grafting reactions onto PP. Several grafting reactions were carried out by changing the chemical compositions of the starting polymerization mixture, whose homogeneity was accurately investigated by Raman spectroscopy. Infrared-spectroscopy (FT-IR) was used for qualitative and quantitative characterization of the reaction product. A quantitative separation procedure, based on the concept of selective solvent extraction, has been established which enables the determination of the grafting efficiency (Φ) as well as the exact chemical composition of the final product. Finally, all products were characterized by means of Differential Scanning Calorimetry (DSC) in order to study their thermal behaviour.

Introduction

The modification of polypropylene (PP) in the solid phase is an attractive route to modify the properties of PP at relatively low temperatures through a solvent-free process. In particular, free-radical grafting reactions in solid porous isotactic PP (iPP) were widely studied[1-4] and have been applied on industrial scale[5-9]. In most processes, the porous iPP

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powder is treated with a mixture containing at least one polymerizable vinyl monomer and a free-radical initiator. In particular the grafting reaction of styrene onto iPP has been studied[10-12] extensively for different experimental conditions and compositions of the reactive mixture. In principle, the polymerization reaction can lead to the formation of three different polymer species: unreacted iPP, homopolymerized polystyrene (PS) and graft-copolymer (PP-g-PS). The relative amounts of these three different polymeric species are very crucial for the type and stability of the morphology and, consequently, for the final properties of the blends after processing[13,14].

According to the generally accepted reaction scheme for solid-state grafting[15,16], the styrene monomer can add to the primary radicals generated by the homolytic scission of the initiator leading to the formation of PS homopolymer. On the other hand, the primary radicals can also abstract a hydrogen atom from the PP chain leading to the formation of a macroradical that can also be formed by transfer reactions of the growing chains to the polymer. The macroradical can add styrene molecules to give PP-*g*-PS, but also couple with other growing chains or macroradicals to form crosslinks or eventually terminate by disproportionation. It must be remarked that also thermal polymerization of styrene and PP chain degradation of the macroradical via the β-elimination mechanism are important side-reactions. One of the major problems encountered during processing of PP is the β-scission that is favored by the high temperatures generally required for melt processing (typically 200°C), leading to lower molecular weight products. The modification in the solid phase (at around 100°C) allows a drastic decrease of the degradative behaviour[17].

The use of porous semi-crystalline iPP reactor powders for grafting in solid-state complicates understanding and the optimization of the experimental conditions. For instance the monomer not only may polymerize inside the pores but also on the surface of the iPP particles[12,14]. Moreover[17], the monomer can diffuse and polymerize at the interface between to different iPP particles and/or in the pores of the particles themselves, pores that can have different sizes and provide therefore different constraints to the growing PS chains. The presence of the iPP crystallites provides further constraints to the monomer diffusion, since it is generally accepted[17] that the monomer is prevalently adsorbed in the amorphous iPP regions.

All these physical phenomena complicate the investigation of the chemistry involved in the process. From this point of view, it seems reasonable to use amorphous non-porous atactic

PP (aPP) as a model system for the isotactic isomer, also allowing a comparison with grafting reaction onto aPP in solution[18)]. The choice of the free-radical initiators for the grafting reactions has been made on the basis of the available literature[11)]. BPO decomposes into benzoylic radicals that can eventually undergo CO_2-elimination resulting in the formation of phenyl radicals, the extent of this last reaction depending on the temperature. Both benzoylic and phenyl radicals are good hydrogen abstractors. On the other hand, the primary radicals derived from AIBN have a relatively strong electrophilic character because of the electron-withdrawing effect of the nitrile groups. Taking into account only the chemical structure it seems that primary radicals generated from BPO should be more effective as hydrogen abstractors than those generated from AIBN; i.e. they should be more effective formation of the graft copolymer.

As already mentioned, the final product consists of three different polymer species whose relative amounts are important in determining the product morphology and properties after processing. One of the objectives of this work is the development of a fractionation procedure, which can allow the determination of the relative amounts of the three polymer species as well as the graft efficiency (Φ). One of the few attempts described in the literature to achieve such goal was reported by *Huang et al.*[15)], who used a gel permeation chromatography method to determine the graft efficiency without preliminary fractionation of the reaction product. The technique is based on double detection both by means of UV spectroscopy and refractive index. The composition can be then determined via deconvolution of the experimental profiles under the assumptions that the molecular weight of the grafted chains is appreciably different from that of the backbone polymer and that the molecular weight, both the entire distribution and the average values, of the grafted PS chains is the same of the homopolimerized PS ones. Those two assumptions are fulfilled in solution graft polymerization but not hold for melt or solid-state processes. An experimental approach to the problem from a very general point of view is also reliable[20,21)] provided that the two main components of the blend, in this case PP and PS, have a quite different solubility. Such a method is in fact based on the 'selective solvent' concept and can, in principle, be applied when, for example, selective solvents for the two homopolymers (PP and PS) and not for PP-g-PS can be found. The development of such a procedure as well as its evaluation with melt-performed and physically mixed PP/PS blends is described in this work.

Experimental

Materials

aPP (Borealis) was kindly supplied by DSM Research. It possesses a very low crystallinity (at 90°C the crystallinity was measured to be about 10 wt % by DSC) and no porosity. It was milled under N_2(l) into a very fine powder and stored at –4°C before use. Styrene, (Aldrich) containing 10-15 ppm of a radical inhibitor (4-*tert*-butylcatechol), was used without further purification. Toluene (Aldrich), methyl ethyl ketone (MEK) (Aldrich), *n*-heptane (Merck) were used without further purification. Di-benzoyl-peroxide (BPO) (Aldrich) and 2,2'-azobis(2-methylpropionitrile) (AIBN) (Merck) were used as received.

Grafting reactions

aPP, the radical initiator and styrene were introduced in small glass tubes according to the prefixed ratios. The mixtures, approximately 1.5 ml, were then degassed by bubbling through dry N_2(g) for 5 minutes and immediately sealed with a rubber cup. The tubes were then transferred in an ultrasonic bath for 2 hrs at 30°C for homogenization after which they were directly immersed in an oil bath at 90°C. The reactions proceeded without stirring for reaction times equal to six times the half-life time of the radical initiators, i.e. 1 hr for experiments with AIBN and 6 hrs for those with BPO. Then, the temperature was raised to 120°C and the tubes were kept in the oil bath for 10 minutes in order to deactivate any radical species that might still be present. The product was then recovered from the tubes and dried to constant weight. The conversion and total PS content in the final product were evaluated by FTIR and gravimetric analysis according to:

$$\text{conversion }(\%) = \frac{\text{amount of total PS in the reaction product (g)}}{\text{amount of styrene in the starting mixture (g)}} \times 100$$

For the reference samples, which do not contain any aPP, only PS is formed during the reaction: in this case the amount of formed PS is calculated by precipitation of the reaction product from a toluene solution in methanol and successive drying at 40°C to constant weight in a vacuum oven.

Characterization techniques

Raman spectroscopy

Samples for Raman spectroscopy were prepared according to the above described procedure (but without addition of the radical initiator), which was stopped just after the treatment of the polymerization mixtures in the ultrasonic bath. The thus prepared samples were analyzed by Raman spectroscopy using a Dilor Labram dispersive Raman spectrometer. The incident laser excitation line was 532 nm from a Nd:YAG laser source. The instrumental parameters were fixed as follows. The 10x magnification objective was combined with a pinhole diameter of 1000 micrometer. This corresponds to a sample area close to 20 micrometer in diameter within a depth of approx. 20 micrometers. The slit entrance of the detector was set to 300 cm-1, which resulted in a spectral resolution of approx. 3 cm^{-1} using a grating with 1800 lines/mm. The spectra were obtained at two grating positions, one centered around 1200 cm^{-1} and one centered around 3000 cm^{-1} and collected with accumulations of 30 s.

Infrared spectroscopy

Samples for FTIR analysis were prepared by dissolving a small amount of the material in toluene followed by casting on dry KBr pellets. After quick evaporation of the solvent the spectra were recorded by a Mattson FT-IR instrument. The calibration curve, as depicted in Fig. 1, for quantitative analysis was determined by recording spectra of aPP/PS blends prepared by simple dissolution of aPP and PS pellets in prefixed amounts in toluene. The experimental points were then fitted by a non-linear method with an allometric-type function:

$$y = a \times x^{b}$$

where a and b are parameters to be determined by the fitting procedure, y the weight percentage of PS in the sample and x the ratio between the peak area of the absorptions at 700 cm^{-1} (out-of-plane bending mode of the aromatic C-H) and 1370 cm^{-1} (bending aliphatic C-H). The fitting procedure was performed by using Origin 6.0, software by Microcal Origin ®.

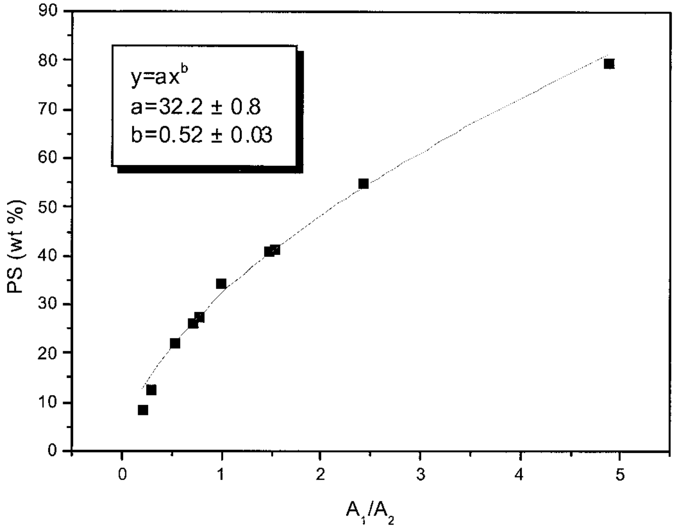


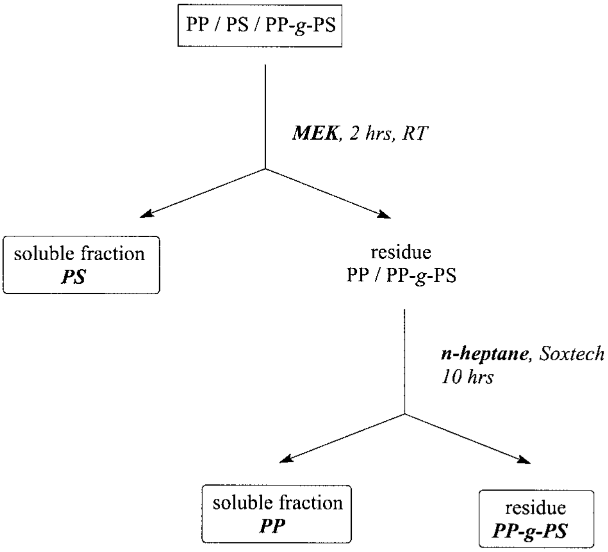
Fig. 1: FT-IR calibration curve for aPP/PS mixtures. A_1=area of the peak at 700 cm^{-1}; A_2=area of the peak at 1370 cm^{-1}.

Selective solvents extraction

The separation procedure consisted of two steps (Scheme 1):

-extraction in MEK: about 0.8 g of the graft product, cut into small pieces, was dispersed in about 50 ml of MEK in a small flask. The dispersion was stirred at R.T. for 2 hrs and then filtered. The solid on the filter was repeatedly washed with MEK. Both the residue and the extracted fractions were then dried in a vacuum oven at 40°C to constant weight.

-extraction in *n*-heptane: the dried residues from the MEK extractions were directly extracted by *n*-heptane vapors for 10 hrs using a Soxtech apparatus. Both the residue and extracted fractions were dried in a vacuum oven at 40°C to constant weight.



Scheme 1: Fractionation procedure.

Once dried, all extracted and residual fractions were weighted and the composition was determined by FTIR spectroscopy. The last technique is used to verify whether the extraction in MEK is selective towards the formed PS homopolymer and the one in *n*-heptane is selective towards unreacted aPP. Furthermore, the selectivity of the separation procedure was tested both quantitatively (mass balance) and qualitatively (FTIR) on solution cast and melt (in a mini-extruder at 140°C) aPP/PS blends.The mass balance is used to evaluate the grafting efficiency (Φ) defined as follows:

$$\Phi = \frac{\text{amount of grafted PS (g)}}{\text{amount of total formed PS (g)}} \times 100$$

where the amount of grafted PS was calculated from the total PS content determined by FT-IR and the amount of PS homopolymer extracted in MEK. In order to get an estimate of the quality of the separation procedure, the mass balance could be used to calculate the extraction efficiency (Γ) defined as:

$$\Gamma = \Gamma_{MEK} \times \Gamma_{hept}$$

where Γ_x, i.e. the extraction efficiency for solvent x, is defined as:

$$\Gamma_x = \frac{\text{amount of extracted fraction (g)} + \text{amount of residue (g)}}{\text{total amount of material before extraction in x (g)}}$$

DSC analysis

Differential Scanning Calorimetry was performed on a Perkin Elmer Pyris 1 DSC. Temperature calibration was performed with indium, hexatriacontane and dodecane. Calibration of the heat of fusion was performed using the heat of fusion of Indium. The baseline was obtained by performing a run with two empty pans using the same heating/cooling rate (10°C/min) as employed for the sample run.

Results and Discussion

The results of the grafting reactions on aPP will be described according to the following: first the homogeneity of the starting reaction mixtures will be discussed according to Raman analysis and next the results of the polymerization reactions will be discussed from the point of view of the styrene conversion and the total PS content in the reaction product as determined by FTIR and gravimetric analysis. Next the development of the fractionation procedure will be described including its testing on solution cast and melt aPP/PS blends, and then the results obtained by such procedure for the grafted products. Finally, some preliminary data on the thermal behaviour of the reaction products, as determined by DSC, will be presented.

The polymerization of styrene in the presence of aPP was carried out in small glass tubes under a dry $N_2(g)$ atmosphere. This method is quite different from the common experimental methodologies for the solid-state grafting onto iPP, in which the monomer and the radical initiator are slowly added to the stirred iPP powder. The reason for choosing a different experimental procedure is found in the fact that the aPP powder becomes very sticky at 90°C, which reduces the mixing efficiency drastically. Since the homogeneity of the starting solution is a very important parameter in order to obtain reproducible results, it was tested by means of Raman microscopy. Samples analogous to those successively polymerized except for the presence of the radical initiator were prepared and analyzed by recording different Raman spectra along vertical and horizontal lines (typical length of about 1 cm) as depicted in Fig. 2 within the sample tube. All the recorded spectra (one spectrum representative of a 50/50 wt/wt styrene/aPP mixture is depicted in Fig.2) are very similar. In order to get more insight in the composition, a quantitative analysis has been performed: the ratio between the peak heights at 3063 cm^{-1} and 2960 cm^{-1} as well as that between the peak heights at 1630 cm^{-1} and 1325 cm^{-1} is representative for the styrene/aPP ratio. It is then possible to calculate these ratios for every spectrum, at least 15 for every composition, referred to every single sample and then calculate the average concentration fluctuations as standard deviations from the mean value. The results, as given in Table 1, clearly show that the solution can be regarded as homogeneous as long as concentration variations up to 2% are tolerated. As expected, the largest change is observed for the styrene/aPP 30/70 wt/wt sample. On increasing the styrene percentage the concentration fluctuations level down between 1 and 2%, suggesting that the experimental error threshold has been reached.

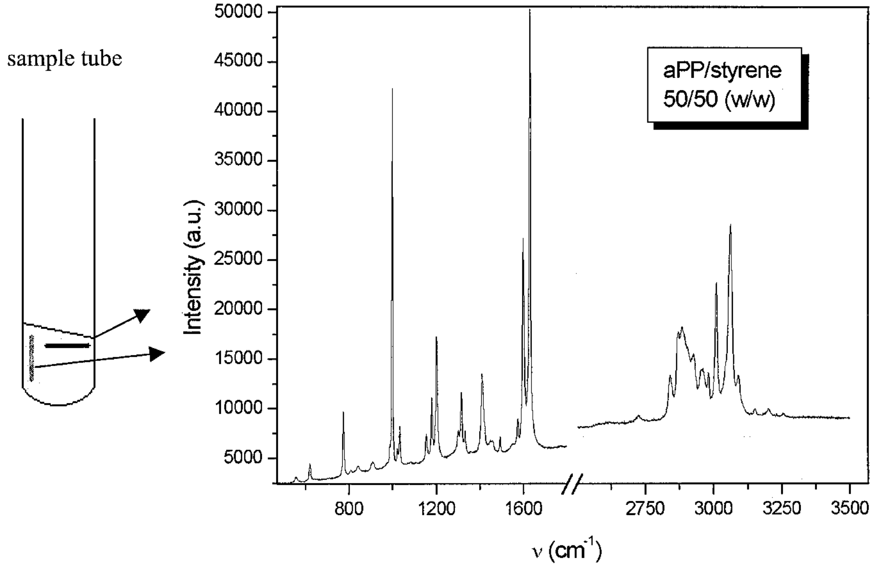


Fig. 2: Raman analysis of the initial aPP/styrene solutions.

Table 1: Concentration variation for different styrene/aPP weight ratios.

Sample[a]	Approximate variation in the styrene concentration[b] (%)
Styrene/aPP 30/70	2-3
Styrene/aPP 40/60	1-2
Styrene/aPP 50/50	1-2
Styrene/aPP 60/40	1-2

[a] compositions are expressed by weight ratios

[b] calculated as standard deviation from the mean value for the peak height ratios in the Raman spectra

Table 2: Solid-state grafting reactions on aPP by using AIBN or BPO as radical initiators.

Run	Feed (wt %)[a]		Conversion (%)	
	aPP[b]	styrene[b]	FT-IR	Gravimetric
Aa1	100	-	-	-
Aa2	40	60	44	41
Aa3	-	100	-	95
Aa10	-	100	-	6
Aa5	68	32	53	57
Aa7	59	41	43	50
Aa6	46	54	70	65
Aa8	38	62	54	55
Aa4	30	70	76	83
Aa9	23	77	61	67
Ba1	100	-	-	-
Ba2	49	51	43	47
Ba3	-	100	-	99
Ba4	-	100	-	7
Ba5	67	33	95	94
Ba6	57	43	85	91
Ba7	48	52	79	79
Ba8	39	61	81	80
Ba9	29	71	60	72
Ba10	23	77	100	83

[a] the amount of free-radical initiator is 1 wt % of the amount of styrene in the feed

[b] compositions are expressed as weight percentages referred only to the total amount of aPP/styrene mixture

The grafting reactions were carried out using both AIBN and BPO (Table 2) but also varying the styrene/aPP ratio. Concerning the experiments with AIBN (coded as Aax with x=1-10) it must be outlined that the conversion, as calculated by both methods, is never complete (from 50 to about 80 %) depending on the feed composition. On the other hand, the experiment carried out in absence of aPP (Aa3) shows a quite high conversion, suggesting that the presence of aPP strongly inhibits the styrene polymerization. This behaviour can be explained either by retardation of the chain propagation reactions or by a decrease in the overall reaction rate due to the competition of the polymer chain to the primary radicals. Of course, both factors can influence the reaction at the same time resulting in an ill-defined dependence of the conversion on the feed composition. It must also be stressed that some influence of the thermal polymerization of styrene can be expected as suggested by runs Aa10 and Aa2.

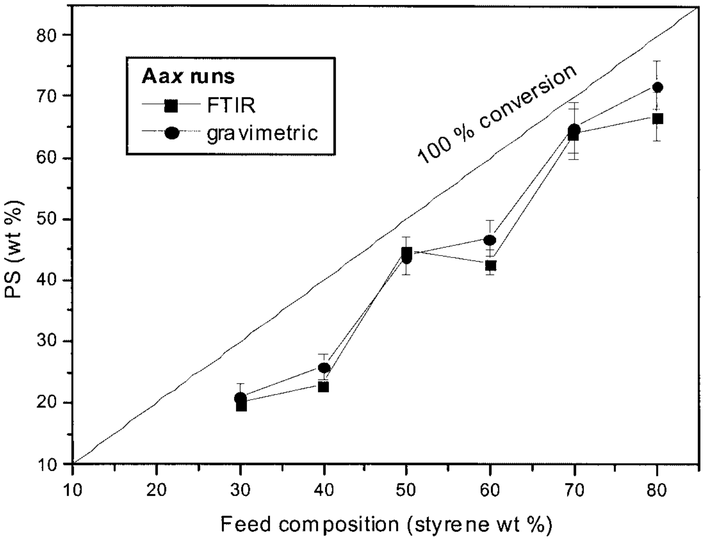


Fig. 3: Total PS content of solid-state grafted aPP, initiated by AIBN, as determined by FT-IR and gravimetric analysis.

All the above considerations hold in the case of BPO-based experiments (coded as Bax with x=1-10) except that the conversion values are in general higher than those achieved with AIBN. Such difference can be ascribed prevalently to the different efficiency of the two initiators: it is in fact not possible to infer a different extent by which thermal polymerization of styrene can occur depending on the longer reaction time (6 hrs vs. 1 hr). A simple comparison between conversion values for Aa10, Aa2, Ba2 and Ba4 clearly shows a similar behavior with respect to the styrene conversion. It must be also stressed that the conversion as measured by gravimetry and FT-IR is in good agreement. This also holds for the determination of the total PS content in the product (Fig. 3 and 4). In this case it is possible to clearly address that the differences in the determined values by the two different techniques are within the correspondent experimental errors.

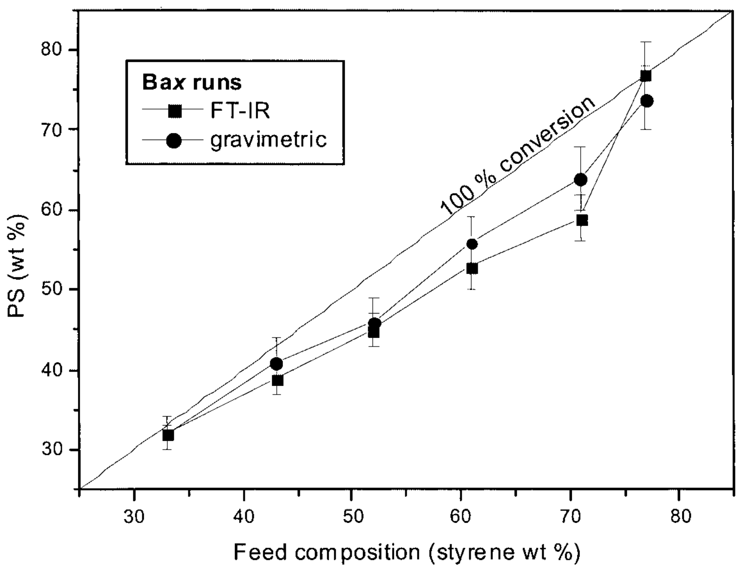


Fig. 4: Total PS content of solid-state grafted aPP, initiated by BPO, as determined by FT-IR and gravimetric analysis.

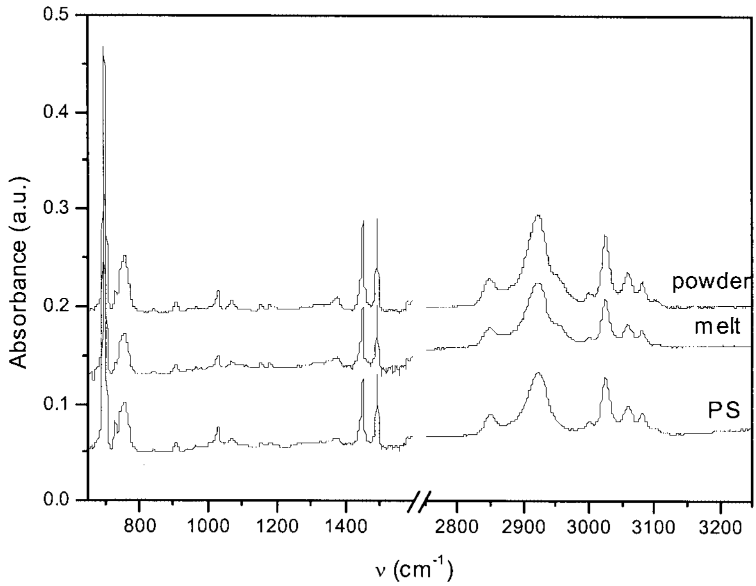


Fig. 5: FT-IR spectra for MEK extracted fractions for solution cast and melt aPP/PS blends.

All the reaction products were fractionated by selective solvent extractions according to the procedure given in Scheme 1. The extraction procedure was qualitatively (FT-IR) and quantitatively (mass balance) tested on solution cast (powder mixing) and melt aPP/PS blends. In both cases no detectable residue was observed upon extracting with *n*-heptane. Both MEK and n-heptane extracted fractions were analyzed by FT-IR and compared respectively to the neat PS and aPP (Fig. 5 and 6).

No traces of aPP could be observed in the MEK extracted fraction and no traces of PS in the *n*-heptane fraction. Of course, the fractionation procedure was also qualitatively tested in the case of Aax and Bax runs by means of FT-IR spectroscopy on all residues and extracted fractions.

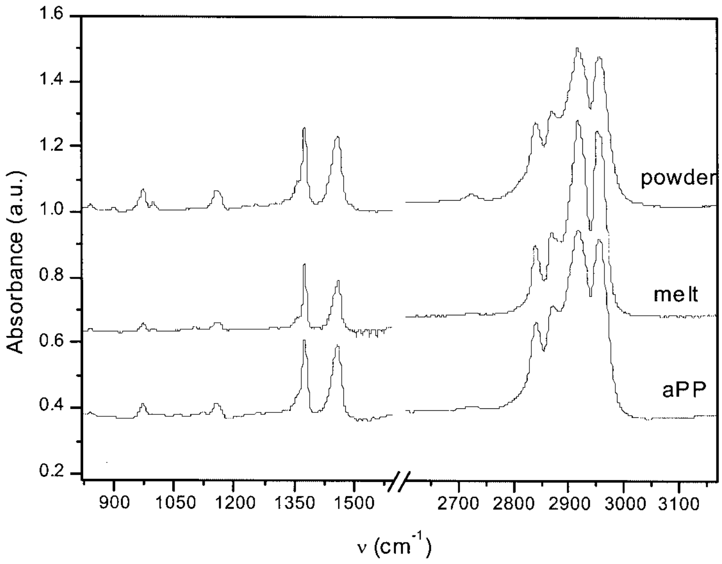


Fig. 6: FT-IR spectra for *n*-heptane extracted fractions for solution cast and melt aPP/PS blends.

The spectra clearly demonstrate that the extraction with *n*-heptane is selective for the aPP, but the one in MEK is not fully selective for PS. If one compares the FT-IR spectra (Fig. 7) of the neat PS and of the MEK extracted fractions, for example the one for run Aa9 but the same considerations hold for all the other, is then possible to infer the presence of a small amount of aPP material: both the peak area and height of the absorption located at about 1370 cm^{-1} (bending vibration mode of the aliphatic C-H bond) are relatively higher in the spectrum of the extracted fraction than in that of the neat PS. On the other hand, such enhanced absorption can only be detected at very high magnification of the spectrum and it seems then indicative of a very small contamination (<1%) of the MEK extracted fractions by aPP.

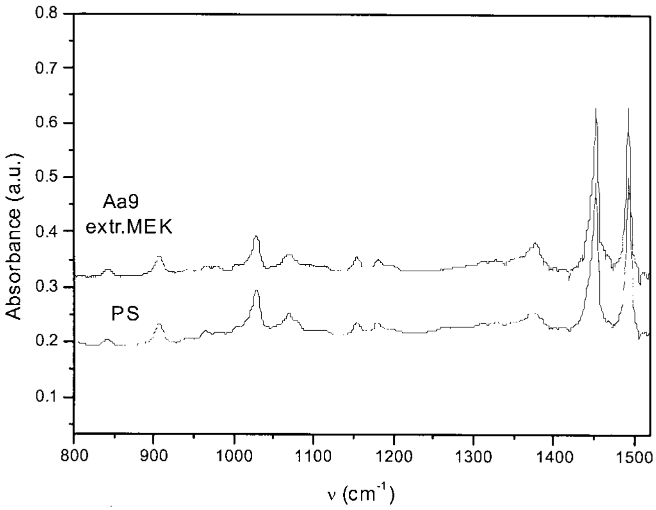


Fig. 7: FT-IR spectra of PS and MEK extracted fraction for run Aa9.

The results of the fractionation procedure (Table 3) clearly demonstrate that the extraction procedure has a good overall efficiency, since the minimum value for Γ is 0.93. The values of grafting efficiency are particularly interesting. First of all a positive value of Φ is detected even in the absence of the initiators (runs Aa2 and Ba2). This clearly suggests that transfer reaction of the growing PS chains to the polymer take place and that they became more important with the reaction time. It is also observed that Φ has in general a maximum for a certain feed composition. The occurrence of this maximum can be explained by assuming that, for high styrene/aPP ratios, the primary radicals derived from the initiator will preferentially undergo addition reaction to the styrene leading to the preferential formation of the free PS homopolymer over the PP-g-PS. On the other hand, for low styrene/aPP ratios, the formed macroradicals can easily undergo secondary reactions (coupling, transfer, disproportionation ...) instead of addition to the styrene monomer. The same consideration holds for the amount of PP-*g*-PS as a function of composition: in both cases BPO is more efficient than AIBN in promoting the graft-polymerization of styrene with respect to the homo-polymerization.

Table 3: Fractionation by selective solvents extraction.

Sample	Extr. MEK (wt %)[a]	Extr. Heptane (wt %)[a]	Residue (wt %)[a]	Γ^b	Φ (%)[b]
Aa2	39.7	58.9	1.4	0.93	0.1
Aa5	19.5	76.5	4.0	0.97	2.5
Aa7	21.5	72.6	5.9	0.95	6.5
Aa6	39.4	51.7	8.9	0.94	12.4
Aa8	39.5	54.1	6.4	0.93	8.1
Aa4	59.3	38.2	2.5	0.96	7.3
Aa9	64.0	30.9	5.1	0.95	4.5
Ba2	28.3	69.1	2.6	0.95	8.7
Ba5	29.0	65.5	5.5	0.98	9.4
Ba6	33.2	60.1	6.8	0.93	14.9
Ba7	35.1	52.5	12.4	0.96	22.0
Ba8	47.7	43.1	9.2	0.99	10.0
Ba9	55.4	35.9	8.7	0.98	6.1
Ba10	73.3	19.5	7.2	0.94	4.8

[a] all percentages were renormalized to 100% after the fractionation procedure

[b] calculated as reported in the Experimental Section

All samples were analyzed by means of DSC analysis (Table 4) to investigate their thermal behaviour. In particular it was interesting to evaluate the influence, if any, of the presence of the *in-situ* formed PS phase on the aPP crystallinity and melting behaviour. Unfortunately the aPP sample displays a very broad endothermic melting transition: this makes the calculations on the melting endotherms not fully reproducible and at least characterized by a high relative error. For this reason we performed the analysis on the 1st-cool curves where the crystallization exotherm is sharp enough to allow easy and reproducible calculation of the peak area. If one compares the normalized crystallization enthalpies (ΔH_c expressed in J/g_{aPP}) of the aPP (runs Aa1 and Ba1, processed under the same experimental conditions as the others) with those of the processed samples, it is possible first of all to stress that the reaction time has very little influence on the sample crystallinity since ΔH_c for runs Aa1 and Ba1 are quite similar.

Table 4: DSC analysis: crystallization behaviour.

Sample	Composition (wt %)		Experimental[a]	
	aPP	PS	T_c (°C)	ΔH_c (J/g_{aPP})
Aa1	100	0	76.1	12.9
Aa5	80	20	69.0	13.6
Aa7	77	23	67.4	12.9
Aa8	57	43	65.0	7.4
Aa6	55	45	71.0	10.0
Aa4	36	64	62.7	11.7
Aa9	33	67	62.7	7.3
Ba1	100	0	74.1	12.4
Ba5	68	32	69.3	10.1
Ba6	61	39	68.2	10.7
Ba7	55	45	67.6	11.7
Ba8	47	53	63.6	11.1
Ba9	41	59	64.5	5.6
Ba10	23	77	60.4	4.3

[a] determined from 1st-cool DSC curves

Moreover, ΔH_c decreases upon grafting for all the samples even if there is no clear trend as a function of the feed composition or of the chemical kind of the used initiator. The only exception to this behaviour can be detected for the run Aa5 which displays a slightly higher value than the neat aPP. Although the exact reason for such deviation needs further investigation, it can be outlined that similar results were previously observed[19)] for the grafting reaction of styrene on LLDPE for low styrene content like in our case. In that case a Swelling Induced Crystallization (SIC) mechanism was proposed based on the fact that the monomer can diffuse in the amorphous LLDPE but also, due to the very low crystallinity of the polymer, into the crystalline phase, in particular into the less perfect crystals.

Conclusions

The grafting reaction of styrene onto aPP was performed under quiescent conditions at 90°C using AIBN or BPO as free-radical initiator. The conversion of styrene is remarkably lowered by the presence of aPP: this behaviour can be explained by the fact that the viscosity of the system increases on the addition of aPP, which changes the apparent kinetic rate constant for the chain propagation. On the other hand, the presence of aPP leads to new reactions (transfer to the polymer, hydrogen abstraction) which are in competition with the chain propagation step. The spectroscopic techniques, i.e. Raman and FT-IR, were used to determine the homogeneity of the initial reaction mixtures as well as the styrene conversion and total PS content in the final product. Accurate results are obtained, which are in good agreement with the gravimetric analysis.

The fractionation by selective solvents extractions allowed to determine the grafting efficiency and the relative amount of graft-copolymer formed during the polymerization. In both cases the use of BPO results in higher grafting efficiencies and higher amounts of PP-g-PS, which is due to the formation of primary radicals that strongly abstract hydrogen atoms form the aPP chains. However, in this stage of the investigation, it is not possible to fully exclude an influence of the different reaction time on the extent of grafting. The definition of an exact theoretical kinetic model is probably needed in order to get a deeper insight into the contributions of each parameter on the grafting efficiency and the amount of formed PP-g-PS.

The DSC analysis demonstrated an overall decrease of both T_C and ΔH_C suggesting an hindered crystallization of the PP phase in the presence of PS. Exceptions to this behaviour were detected for low contents of styrene in the initial mixture and could be related to similar systems described in the literature. The use of an aPP sample with a more defined melting behaviour is probably needed to better characterize the thermal properties of the final product.

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