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Poly(propylene-*g*-styrene) Graft Copolymers with Well-Defined Microstructure by Metallocene Catalyzed Copolymerization of Propylene with Allyl-Terminated Polystyrene Macromonomers

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ABSTRACT: The synthesis of well-defined poly(propylene-*g*-styrene) (PP-*g*-PS) graft copolymers was investigated by metallocene catalyzed copolymerization of propylene and allyl-terminated polystyrene macromonomer (PS-allyl) obtained via quasiliving atom transfer radical polymerization (ATRP) and subsequent carbocationic allylation. It was found that the structural parameters of PP-*g*-PS can be controlled in a broad range by the variation of reaction conditions. At low conversion the number of polystyrene side chains per 1000 propylene units is proportional to the feed concentration of the PS-allyl macromonomer, while the length of polypropylene backbone decreases with increasing feed concentration. The number-average molecular weight (M_n) of PS-allyl determines the side chain length, but it also affects the side chain density and backbone length. Both decrease with increasing M_n of the macromonomer. At constant pressure, by ensuring the constant concentration ratio of propylene to PS-allyl, the PP backbone length can be varied by alteration of temperature while the side chain density remains nearly uniform. This semicombinatorial library of structural parameters vs reaction conditions affords designed synthesis of PP-*g*-PS graft copolymers with predetermined structure, that is, with desired length of the PS side chains, grafting density, and length of the PP backbone.

Introduction

Polymer blends have attracted significant interest in both academia and industry.[1] However, many beneficial combinations of polymers for blends are not available due to miscibility problems. For compatibilization of immiscible polymers in order to obtain blends with desired properties typically block or graft copolymers are used. In practice, mostly graft copolymers, usually formed by reactive blending processes, are applied. Interestingly, in spite of the pivotal importance of grafts, the effect of AB or ABA block copolymers have been widely studied, while the correlation between structural parameters of graft copolymers, such as the absolute and relative length of side chains and backbone, and their compatibilization efficiency has been hardly investigated. The lack of such systematic studies mainly derives from synthetic difficulties in obtaining structurally well-defined graft copolymers compared to the simple preparation of AB and ABA block copolymers by living polymerization processes. Thus, for studying the relationship between the microstructure and the compatibilization efficiency, new methods for the preparation of well-defined graft copolymers with designed structural parameters, such as length and stereoregularity of side chains and backbone, side chain density, and distribution, must be developed first. Graft copolymers can be obtained by grafting from or grafting onto techniques by utilizing linear polymers with suitable pendent functional groups.[2−4] Another way of graft copolymer synthesis is the macromonomer method,[5−23] i.e., copolymerization of low molecular weight monomers with polymers bearing polymerizable terminal functional groups (macromonomers), which allows the precise regulation of length and size distribution of side chains.

Because of the significant importance of polyolefins, that is polyethylene and polypropylene, their grafts, especially targeting tailor-made graft copolymers, have been the subject of intensive research in recent years (see, e.g., refs 2−21, 24, 25 and references therein). The synthetic approaches mainly apply either the grafting from or the macromonomer methods. For obtaining the polyolefin main chain, both Ziegler−Natta or metallocene catalysts have been used. In the case of ethylene and propylene the homogeneous polymerization catalyzed by metallocenes and other complexes of early and late transition metals is the best known process yielding the most uniform macromolecules with relatively low polydispersities ($M_w/M_n = 2-3$).[26−28] Moreover, this technique is capable to adjust the stereoregularity of polypropylene (PP) and other poly(α-olefin)s. The grafting from and onto approaches[2−4] have certain limitations arising from either the difficulties related to the functionalization of polyolefin chains or solubility problems during the subsequent grafting process. The macromonomer method, that is copolymerization of ethylene or propylene with polymers terminated with alkenes, has already been applied for the preparation of a variety of polyolefin graft copolymers.[5−20]

In a previous study,[20] we reported on the successful synthesis of poly(propylene-*g*-styrene) (PP-*g*-PS) graft copolymers by metallocene catalyzed copolymerization of propylene with allyl-ended polystyrene (PS-allyl) prepared via quasiliving atom transfer radical polymerization (ATRP) and subsequent quantitative chain end functionalization.[29] Our studies on the

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Table 1. Conditions for the Synthesis of Allyl-Terminated Polystyrene Macromonomers (PS-allyl) by Quasiliving Atom Transfer Radical Polymerization (in Toluene, 110 °C) and Subsequent Carbocationic Allylation, the Number Average Molecular Weight (M_n) and Polydispersity (M_w/M_n) of the Resulting PS-allyl Macromonomers, and Concentrations of Styrene (c_{St}), Initiator (c_{PhEtBr}), Catalyst ($c_{CuBr} = c_{PMDETA}$), Allyltrimethylsilane (c_{ATMS}), and Titanium Tetrachloride (c_{TiCl_4})

	polymerization				allylation			
macromonomer	c_{St} [mol/L]	c_{PhEtBr} [mmol/L]	$c_{CuBr} = c_{PMDETA}$ [mmol/L]	t [min]	c_{ATMS} [equiv]	c_{TiCl_4} [equiv]	M_n [g/mol]	M_w/M_n
PS(1500)	6.27	422	139	135	1.5	1.5	1500	1.07
PS(3000)	5.87	253	164	120	3	1.5	3000	1.06
PS(11900)	8.56	58.3	63.1	260	10	6	11 900	1.08
PS(29900)	8.64	35.5	31.4	960	12	9	29 900	1.15

Table 2. Conditions of Programmed Precipitations for PP-*g*-PS Graft Copolymers with PS-allyl Macromonomers of Different Molecular Weights

macromonomer M_n (PS-allyl)	solvent for graft copolymer	initial composition of selective solvent/precipitant mixture	modification of the solution composition by addition of solvent
1500	100 mL of xylene	400 mL of acetone + 100 mL of ethanol	100 mL of ethanol
3000	100 mL of xylene	400 mL of acetone + 100 mL of ethanol	100 mL of ethanol
11 900	100 mL of xylene	500 mL of acetone	100 mL of ethanol
29 900	194 mL of xylene	50 mL of acetone + 6 mL of xylene	350 mL of acetone + 140 mL of ethanol

compatibilization of PP and PS by the resulting PP-*g*-PS graft copolymers showed an unexpected relation between the average PS side chain length and blending efficiency. In contrast to expectations, the efficiency of compatibilization increased with decreasing molecular weight of the PS chains. It has been also found that the incorporation ratio of the PS-allyl macromonomers in the PP-*g*-PS grafts might strongly depend on the reaction conditions. Therefore, in order to obtain a reliable database for designing and preparing PP-*g*-PS graft copolymers with desired structural parameters, we have decided to carry out systematic research to reveal the relationships between reaction conditions and the structural parameters of the resulting PP-*g*-PS graft copolymers synthesized by metallocene catalyzed copolymerization of propylene with PS-allyl macromonomers. Here we report on the effect of polymerization temperature, the number-average molecular weight (M_n) and concentration of PS-allyl on the structure of PP-*g*-PS formed in this process, and based on these new results on the synthesis possibilities for obtaining well-defined PP-*g*-PS graft copolymers by this method.

Experimental Section

Materials. Styrene (Aldrich) was distilled under reduced pressure at room temperature. Dichloromethane (Chemolab, Hungary) was dried by refluxing over calcium hydride and was distilled under nitrogen atmosphere. Toluene (Fluka, p.a.) was dried by refluxing over Na/K alloy and finally distilled under argon atmosphere. Propylene (2.8 grade) was purchased from Riessner-Gase and was purified by passing through 3 Å molecular sieves followed by R3−11 copper oxide catalysts (BASF). Toluene for macromonomer preparation, methanol, tetrahydrofuran, hexane (all from Chemolab, Hungary), (1-bromoethyl)benzene, pentamethyldiethylenetriamine (PMDETA), copper(I) bromide, titanium tetrachloride, neutral aluminum oxide (all from Aldrich), allyltrimethylsilane (ATMS) (Fluka), methylaluminoxane (MAO) solution (10 wt % in toluene) (Crompton), and *rac*-$Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzInd]_2ZrCl_2$ (MBI) (Boulder) were used as received.

Synthesis of Macromonomers. Polystyrenes with 2-bromo-2-phenylethyl chain end were synthesized by quasiliving atom transfer radical polymerization (ATRP) of styrene. The initiator was (1-bromoethyl)benzene and the catalyst was copper(I) bromide complexed with PMDETA, the polymerization was conducted at 110 °C in toluene. The halogen terminated polymers were dissolved in dichloromethane (∼200 g/L) and were transformed to allyl-ended polystyrene macromonomers (PS-allyl) by reaction with ATMS in the presence of $TiCl_4$. Other details of the macromonomer preparation and purification were described recently.[20] The concentrations of reagents and other reaction conditions applied in the synthesis of PS-allyl macromonomers are summarized in Table 1.

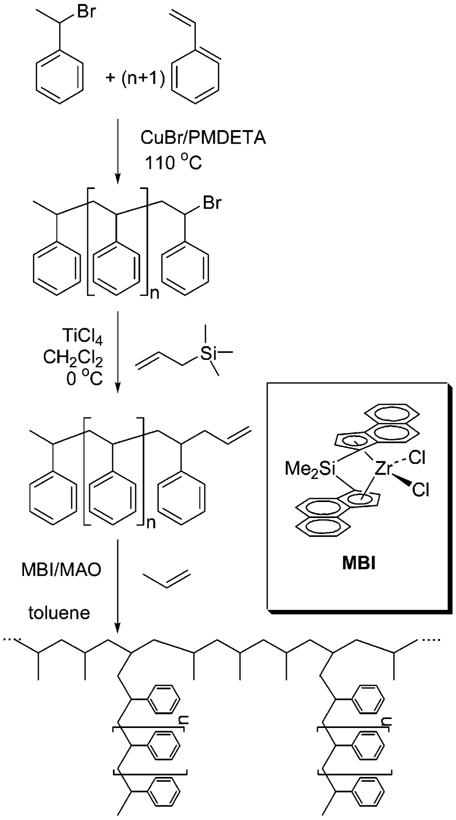
Copolymerization. Copolymerizations of propylene and PS-allyl were carried out in 200 mL of toluene in a 1 L glass autoclave (Büchi) equipped with a stirrer, manometer, thermocouple, and heating and cooling units. The reactor was first charged with the corresponding macromonomer, toluene, and the cocatalyst solution (MAO). The reactor was kept at the desired temperature (40−70 °C), and the solution was saturated with propylene at 1.2 bar total pressure. The polymerization was initiated by injecting the metallocene (MBI) solution into the reactor. The catalyst concentration was 1.6×10^{-5} mol/L (sample 4: 3.2×10^{-5} mol/L). After consumption of 0.2 mol of propylene the polymerization was terminated by injecting a small amount of ethanol. Further conditions of the copolymerization are described in more details in our previous publication.[20]

The purification of copolymers was carried out by the following programmed precipitations: The mixture of graft copolymer and unreacted PS macromonomer containing 2 g polypropylene calculated from feed ratio was dissolved in hot xylene. After filtration the solution was dropped into a selective precipitant/solvent mixture and simultaneously the composition of this mixture was modified with continuous addition of a corrective precipitant (ethanol) to offset the increasing polypropylene solubilizing ability of the solvent mixture caused by the increasing concentration of xylene. The initial composition of the selective precipitant and the composition of the corrective solvent were dependent on the M_n of macromonomer applied in the corresponding copolymerization as listed in Table 2.

Polymer Characterization. ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. The samples were measured at 120 °C in $C_2D_2Cl_4$ which also was used as reference ($\delta(^1H) = 5.98$ ppm) and lock.

Molecular weights of PP-*g*-PSs were determined using high-temperature gel permeation chromatography performed with a PL-GPC 220 (Polymer Laboratories) chromatograph connected to a DAWN EOS multiangle laser light scattering (MALLS) detector (Wyatt Technologies) at 150 °C using 1,2,4-trichlorobenzene (stabilized by diphenyl amine) as mobile phase with a flow rate of 1.0 mL/min. The column set contained two PL MIXED-B-LS columns (Polymer Laboratories). For detection MALLS were used. The concentration of the unfiltered polymer solutions was 0.025 g/mL. The calibration was carried out using PP with known molecular weight and distribution or with calculation of a product-specific refraction increment from the RI chromatograms used for the MALLS analysis provided that complete elution of the polymer exists.

Scheme 1. Synthesis of Allyl-Terminated Polystyrene Macromonomers and Their Copolymerization with Propylene



Molecular weights of PS-allyl macromonomers were determined by gel permeation chromatography with a Waters/Millipore liquid chromatograph equipped with a Waters 515 pump, UltraStyragel columns of pore sizes 1 × 10^5, 1 × 10^4, 1 × 10^3, and 500 Å, and a Viscotek parallel differential refractometer/viscometer detector. Measurements were carried out at room temperature. Tetrahydrofuran was used as the mobile phase with a flow rate of 1.5 mL/min. Calibration was made with narrow MWD polystyrene standards.

Results and Discussion

Scheme 1 shows the reaction route for the synthesis of poly(propylene-*g*-styrene) (PP-*g*-PS) graft copolymers. First, polystyrenes with 2-bromo-2-phenylethyl termini (PS−Br) by quasiliving atom transfer radical polymerization (ATRP) were prepared using the (1-bromoethyl)benzene/CuBr/PMDETA initiating system. The variation of the monomer/initiator ratio and reaction time led to PS−Br with different molecular weights as listed in Table 1. Polystyrenes with allyl chain end (PS-allyl) were synthesized by quantitative carbocationic allylation of halogen ended polystyrenes with allyltrimethylsilane in the presence of $TiCl_4$ Lewis acid.[29] These processes yielded PS-allyls with different molecular weights (M_n = 1500, 3000, 11900, and 29900) and narrow molecular weight distributions (M_w/M_n = 1.06−1.15). Then these PS-allyl macromonomers were copolymerized with propylene in the presence of *rac*-$Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzInd]_2ZrCl_2$ (MBI) catalyst in conjunction with methylaluminoxane (MAO) under various conditions (Table 3).

To overcome the problem of low average number of side chains per molecule found during our recent investigations,[20] the increase in the backbone length and PS side chain density were targeted first. The standard temperature of copolymerizations was chosen to be 40 °C. This provided relatively long PP backbones but still did not lead to graft copolymers with too high molecular weights making the purification process difficult. Furthermore, the effect of feed concentration of PS-allyl macromonomers on composition, backbone length and grafting density was studied. As shown in Table 3, the overall polystyrene content of the resulting PP-*g*-PS graft copolymers increased with increasing feed concentration of PS-allyl, and in some cases (samples 4, 10, and 11) it was in the range of 30 wt %.

In the cases of PP-*g*-PS with high PS contents the purification process, i.e., precipitation from hot xylene into cold acetone, developed for graft copolymers with lower than 10 wt % polystyrene, was not effective. In addition to the risk of the presence of PS macromonomer residue in the insoluble part the increased solubility of the graft copolymer with higher PS contents in acetone/xylene mixtures had to be taken into account as well. Thus, the further optimization of the precipitation method, that is, the decrease of PP-*g*-PS solubility in such solvent mixtures was necessary for all the macromonomers used for the graft copolymer syntheses. From the feed ratio of PS-allyl and propylene, the expected weight of the products (mixture of unreacted PS macromonomer and PP-*g*-PS copolymer) containing 2 grams of PP was calculated. Samples of this quantity were dissolved in 100 mL xylene (or 194 mL, for PS-allyl with M_n = 29 900) and precipitated into nearly 600 mL of a mixture of acetone (cosolvent for the macromonomer) and ethanol. The composition of this precipitant/solvent mixture was continuously modified by balanced addition of the polymer solution in xylene, on the one hand, and by adding the corrective solvent (ethanol) to suppress the solubility of PP-*g*-PS graft copolymers, on the other hand. The final composition of the solvent mixtures was determined for the different macromonomers to be barely able to solve PS-allyl with appropriate M_n in a given concentration calculated as an upper estimation from the feed ratio assuming no incorporation into the graft copolymers. The details of the corresponding precipitation programs are listed in Table 2. The efficiency of the developed purification methods was confirmed by ^{1}H NMR spectroscopy. The analysis of precipitates revealed that unreacted PS macromonomer residues in PP-*g*-PS samples were not detectable, since no signals were found in the region of allyl protons between 4.7 and 5.6 ppm in the ^{1}H NMR spectra (Figure 1). The characterization of the soluble part (Figure 2) indicated that it contains only low amounts of polypropylene; usually less than 5% of formed polypropylene was dissolved in the solvent mixture.

As already mentioned, the main goal of our study was finding correlation between the reaction conditions and the resulting microstructure of PP-*g*-PS graft copolymers. Thus, our experiments were planned to establish relationships between the M_n of PS-allyl ($M_{n,PS}$), the feed ratio of PS macromonomer and propylene, and the copolymerization temperature on the microstructure of the resulting graft copolymers by keeping other parameters constant. The structural parameters of graft copolymers were partly determined directly by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC), partly calculated from the results of these measurements. The styrene content (x_{St}) and polystyrene weight content of the graft copolymers (w_{PS}) were determined from the ^{1}H NMR spectra by eqs 1 and 2, respectively

$$x_{St} = \frac{A_{6.23-7.44}/5}{A_{6.23-7.44}/5 + \left(A_{0.43-2.61} - \frac{3}{5}A_{6.23-7.44}\right)/6} \qquad (1)$$

$$w_{PS} = \frac{x_{St}M_{St}}{x_{St}M_{St} + (1 - x_{St})M_P} \qquad (2)$$

Table 3. Reaction Conditions of Copolymerization of Propylene and PS-allyl (Polymerization Temperature (T_{pol}), Concentration of Propylene (c_p) and PS-allyl ($c_{0,PS}$) in the Feed, Number Average Molecular Weight of PS-allyl ($M_{n,PS}$), Conversion of PS-allyls (convn) and PP Loss upon Precipitation) and Parameters of the Resulting PP-*g*-PS Graft Copolymers (Polystyrene Content (w_{PS}), Average Number of Polystyrene Side Chains Per 1000 Propylene Units (n_{1000}), Average Molecular Weight of PP-*g*-PS (M_n) and PP Backbone ($M_{n,PP}$), Polydispersity (M_w/M_n), and Average Number of Grafts per Molecule ($n_{PP-g-PS}$)) for Catalyst (MBI) Concentration $c_{cat} = 1.6 \times 10^{-5}$ mol/L and Al/Zr = 4000 or 8000 (Samples 3, 7−11)

sample	T_{pol} [°C]	$c_p{}^b/c_{0,PS}$	$c_{0,PS}$ [mmol/L]	$M_{n,PS}$ [g/mol]	convn [%]	PP loss [%]	w_{PS} [wt %]	n_{1000}	M_n [g/mol]	M_w/M_n	$M_{n,PP}$ [g/mol]	$n_{PP-g-PS}$
1	40	100.2	7.3	1500	17.4	3.4	4.7	1.38	123 000	1.4	117 000	3.8
2	40	31.2	23.4	1500	19.6	2.3	15.1	5.0	82 000	1.6	71 000	8.4
3	40	16.3	44.8	1500	17.5	1.8	24.1	8.8	63 000	1.6	47 000	9.8
4[a]	40	10.6	67.8	1500	16.7	3.7	33.5	13.9	59 000	1.5	37 000	12.4
5	40	102.1	7.15	3000	14.7	3.9	7.4	1.11	98 000	1.7	90 000	2.4
6a	40	31.5	23.2	3000	14.7	1.3	20.9	3.7	68 000	1.9	54 000	4.8
6b	40	31.5	23.2	3000	13.5	2.5	19.5	3.4	84 000	1.7	66 000	5.3
7	40	102.1	7.15	11 900	10.5	3.6	19.4	0.85	83 000	1.6	67 000	1.4
8	40	102.1	7.06	29 900	6.1	13.2	25.6	0.48	220 000	1.3	163 000	1.9
9	50	16.3	35.6	1500	24.7	3.2	25.9	9.7	40 000	1.5	30 000	6.8
10	60	16.2	29.1	1500	32.8	3.4	27.7	10.6	36 000	1.6	26 000	6.5
11	70	16.3	24.1	1500	38.7	11.8	27.2	10.3	36 000	2.2	26 000	6.4

[a] $c_{cat} = 3.2 \times 10^{-5}$ mol/L [b] Samples 1−8: c_p = 730 mmol/L. Sample 9: 580 mmol/L. Sample 10: 472 mmol/L. Sample 11: 393 mmol/L.

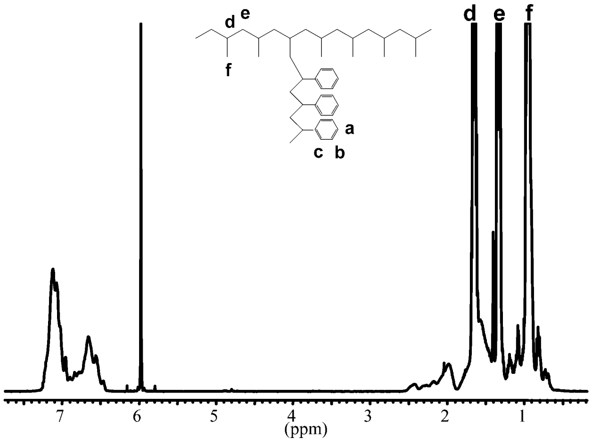


Figure 1. ^{1}H NMR spectrum of the PP-*g*-PS graft copolymer **4** containing 33.5 wt % PS: PS(1500); $c_{0,PS}$ = 67.8 mmol/L; T_{pol} = 40 °C.

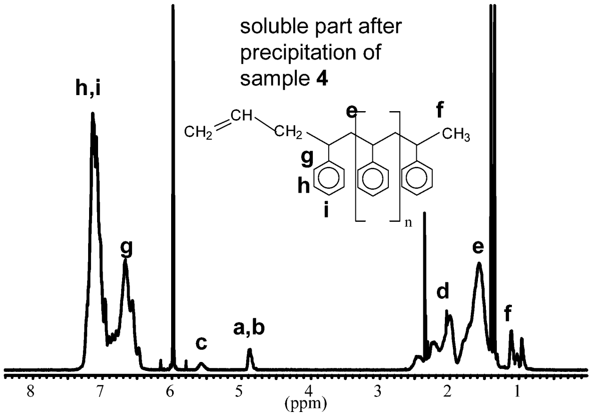


Figure 2. ^{1}H NMR spectrum of the soluble fraction after precipitation of PP-*g*-PS graft copolymer **4**.

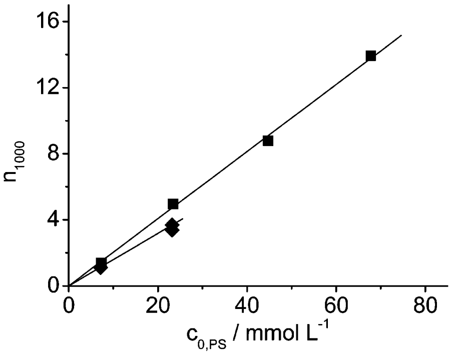


Figure 3. Effect of the initial concentration ($c_{0,PS}$) of PS(1500) (■) and PS(3000) (◆) on the number of polystyrene side chains per 1000 propylene units in PP-*g*-PS graft copolymers obtained at T_{pol} = 40 °C.

where A with the subscript is the integration of the corresponding signals in the denoted range of the ^{1}H NMR spectra, M_{St}, M_P, x_{St}, and $1 - x_{St}$ are the molecular weights of styrene and propylene and the styrene and propylene contents, respectively. The composition of the soluble polymer upon precipitation was calculated in a similar way by comparing the integrals of the NMR signals at 0.88−0.99 and 6.23−7.44 ppm deriving from protons of propylene and styrene monomer units. The M_n of the PP backbone ($M_{n,PP}$) was calculated by multiplying the M_n of the PP-*g*-PS graft copolymers determined by GPC with the polypropylene content. The average number of side chains per 1000 propylene unit (n_{1000}) and per molecule ($n_{PP-g-PS}$) were calculated by eqs 3 and 4, respectively, wherein $M_{n,PS}$ is the number-average molecular weight of the macromonomer, i.e., the PS side chains of the graft copolymer. The above molecular parameters together with reaction conditions are listed in Table 3.

$$n_{1000} = \frac{x_{St}M_{St}}{(1 - x_{St})M_{n,PS}} \times 1000 \tag{3}$$

$$n_{PP-g-PS} = \frac{n_{1000}}{1000}\frac{M_{n,PP}}{M_p} \tag{4}$$

First, the effect of feed ratio of the PS-allyl macromonomer to propylene was investigated (samples 1−6 in Table 3). Propylene was copolymerized with various concentrations of PS(1500) and PS(3000) at a total pressure of 1.2 bar at 40 °C. The propylene concentration in toluene was calculated on the basis of eq 5 giving the dependence of propylene concentration (c_p) on total pressure (p/bar) and temperature (T/K).[30]

$$c_p = \frac{p^{1.058}}{\exp\left(7.4048 - \dfrac{932.68}{T - 109.65}\right)} \tag{5}$$

According to this equation the propylene concentration was 730 mmol/L at 40 °C. Figure 3 shows that linear relationship exists between the number of polystyrene side chains per 1000 propylene units and the initial concentration of PS-allyls. This

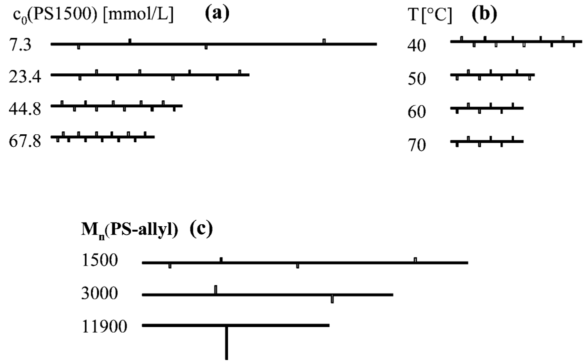


Figure 4. Schematic structure of PP-*g*-PS graft copolymers obtained (a) with different initial concentrations of PS(1500) at 40 °C, (b) at different polymerization temperatures with constant initial ratio of propylene and PS(1500) and (c) with different PS-allyl molecular weights but constant initial concentrations of the PS macromonomers at $T_{pol} = 40$ °C.

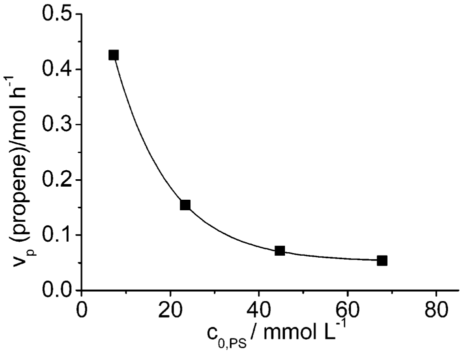


Figure 5. Polymerization rate of propylene vs PS(1500) macromonomer concentration in the feed, $T_{pol} = 40$ °C.

clearly indicates that the density of side chains in PP-*g*-PS graft copolymers can be easily regulated by varying the feed concentration of PS-allyl, i.e., the concentration ratio of propylene to PS-allyl. However, the feed concentration of PS-allyl influences not only the number of PS side chains, but also the M_n of the polypropylene backbone ($M_{n,PP}$ in Table 3). Figure 4a shows schematically that the length of the backbone decreases with increasing feed concentration of PS(1500) which is linked to the increased PS incorporation. In other words, increasing the feed ratio of PS-allyl macromonomers in the propylene/PS-allyl copolymerization systems leads to higher grafting density but shorter polypropylene backbones. Presumably the decrease in $M_{n,PP}$ is caused by the sterical hindrance of the PS side chains, which hampers the addition of propylene. Consequently, the higher the density of side chains, the lower the overall propagation rate. This is confirmed by the observed reduced rate of propylene consumption with increasing macromonomer concentration (Figure 5). However, the exact dependence of the chain propagation rate on the macromonomer concentration could not been determined since partial deactivation of the metallocene catalyst by contaminants of macromonomer occurs, which cannot be quantified.

The effect of M_n of PS-allyls on their reactivity in the copolymerization reaction and the microstructure of the resulting PP-*g*-PS graft copolymers was also investigated. These copolymerizations (samples 1, 5, 7, and 8 in Table 3) were conducted with nearly the same initial concentrations of PS-allyls at 1.2 bar total pressure at 40 °C. The length of PS side chains of PP-*g*-PS graft copolymers is determined by the M_n of PS-allyls. The average number of PS side chains per 1000 propylene units (n_{1000}) in PP-*g*-PS graft copolymers as a function of M_n of the PS-allyl macromonomers is plotted in Figure 6. This figure reveals that the reactivity of PS-allyl macromonomers depends on molecular weight. Although the initial concentration of macromonomers were the same in the corresponding experiments, the increase in M_n(PS-allyl) resulted in significant decrease in side chain density. This indicates the decrease in the relative reactivity of PS-allyls with increasing molecular weight which can be explained by the increasing sterical hindrance of polystyrene chains attached to the polymerizable allyl group. This is in good accordance with previous studies by Radke and Müller on the effect of molecular weight on the reactivity of macromonomers.[31]

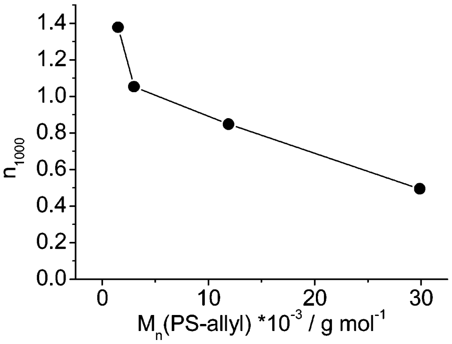


Figure 6. Dependence of the number of polystyrene side chains per 1000 propylene units in PP-*g*-PS graft copolymers on the molecular weight of PS macromonomers. $c_{0,PS} \approx 7.2$ mmol/L; $T_{pol} = 40$ °C.

Figure 4c and data in Table 3 show that not only the side chain density but also the length of PP backbone of PP-*g*-PS graft copolymers depends on the M_n of the PS-allyl macromonomers. In the range of 1500−11900 g/mol of M_n(PS-allyl) the backbone length decreases with increasing M_n. Surprisingly, the copolymerization of propylene with PS(29900) yielded PP-*g*-PS with much higher PP backbone length than that determined in the experiment with PS(11900). It is thought that the backbone length should indeed decrease with increasing M_n of PS side chains, as it is indicated by experiments with M_n(PS-allyl) of 1500−11900 g/mol, since the longer pendent chains decreases the overall propagation more effectively. It is likely that the M_n and backbone length of PP-*g*-PS obtained by copolymerization of PS(29900) were overestimated (and the PS content was underestimated). This statement is based on the fact that the PP loss was rather high (see sample 8 in Table 3) during purification of this sample. Presumably the PP-*g*-PS copolymers with shorter PP backbones and higher PS contents dissolved preferably in the toluene/acetone/ethanol mixture, thus, these molecules were principally lost upon precipitation. The loss of 13 wt % PP, which should be incorporated in molecules with high n_{1000} and low $M_{n,PP}$ values resulted in a considerable overestimation of M_n of this PP-*g*-PS. Fractionation of such graft copolymer during the work up is also suggested by the low polydispersity ($M_w/M_n = 1.3$) of the product PP-*g*-PS. Overall, it can be concluded from the results of these copolymerizations that the backbone length in PP-*g*-PS graft copolymers decreases with increasing M_n of the PS-allyl macromonomers.

For studying the effect of temperature, the ratio of propylene concentration (c_p) and the feed concentration of PS(1500) ($c_{0,PS}$) was kept constant (samples 3 and 9−11 in Table 3). The solubility of propylene in toluene and thus c_p was calculated according to eq 5 at 1.2 bar total pressure and at the applied polymerization temperature. Then $c_{0,PS}$ was calculated so that the final ratio of $c_p/c_{0,PS}$ was about 16.3. In Figure 7, the n_{1000} values of the resulting PP-*g*-PS copolymers vs temperature are plotted. As shown in this Figure, the side chain density of the PP-*g*-PS graft copolymers slightly increases with increasing

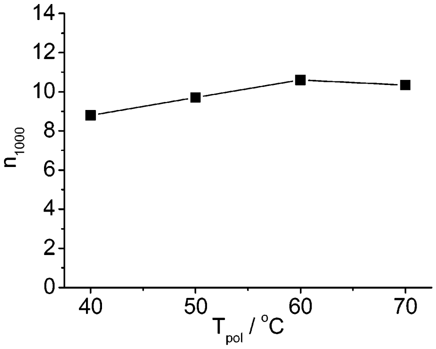


Figure 7. Influence of polymerization temperature on the number of polystyrene side chains per 1000 propylene units in PP-*g*-PS graft copolymers obtained in copolymerizations of propylene and PS(1500) with constant initial propylene/PS macromonomer ratio of 16.3 at 1.2 bar total pressure.

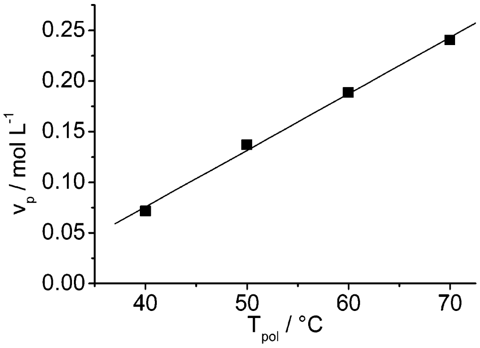


Figure 8. Polymerization rate of propylene as a function of polymerization temperature in the copolymerization with PS-allyl. M_n(PS-allyl) = 1500 g/mol; $c_p/c_{0,PS}$ = 16.3.

temperature indicating that there is some increase in the relative reactivity of PS-allyl to propylene. The effect of temperature on the length of the PP backbone is more considerable. Figure 4b shows schematically that beside the nearly constant side chain density the length of the PP backbone significantly decreases with increasing temperature. This molecular weight decrease with increasing polymerization temperature is typical for the metallocene catalyzed polymerization of propylene.[32] With increasing temperature, the probability of transfer reactions is higher, the propagating chains are terminated earlier, and consequently the molecular weight of the PP backbone decreases. As shown in Figure 8, the rate of propylene consumption (v_p) increases linearly with increasing temperature in the copolymerization of propylene with PS-allyl in the investigated temperature range (40−70 °C). This dependence is caused by several factors including the change in the total concentration of propylene and the rate constants of the elementary copolymerization reactions, such as propagation, cross propagation, chain transfer, and termination, by variation of the polymerization temperature. Nevertheless, this approach, i.e., the variation of temperature (and alternatively the alteration of pressure) at constant propylene to PS-allyl concentration ratio is a tool for regulating the length of the PP backbone while the side chain density is kept nearly constant.

Conclusions

The microstructure of poly(propylene-*g*-styrene) (PP-*g*-PS) graft copolymers obtained by metallocene catalyzed copolymerization of propylene and allyl-terminated polystyrene (PS-allyl) macromonomers can be controlled by the variation of reaction conditions. At low PS-allyl conversions the number of polystyrene side chains per 1000 propylene units in the PP-*g*-PS grafts is proportional to the feed concentration of the PS macromonomer, while the length of polypropylene backbone decreases with increasing feed concentration. The side chain length is predetermined by the M_n of PS-allyl, but it also affects the side chain density and backbone length. Both decrease with increasing M_n of the PS macromonomer. At constant concentration ratio of propylene to PS-allyl, the backbone length can be controlled by the reaction temperature while the side chain density is nearly constant. This semicombinatorial approach provides a library of data on the relation between the structure of PP-*g*-PS graft copolymers vs reaction conditions and average length of PS-allyl macromonomers as shown in Figure 4. These new findings thus offer the opportunity to prepare well-defined PP-*g*-PS graft copolymers with designed structural parameters, such as side chain length, grafting density and average length of the PP backbone by selecting the appropriate conditions. Such series of samples, especially with relatively high PS contents, may provide us the opportunity to carry out further studies on the correlation between the microstructure and macroscopic properties of graft copolymers.

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