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Metallocene-Catalyzed Copolymerization of Propene with Polystyrene Macromonomers

O. Henschke,* A. Neubauer, and M. Arnold

Institut für Technische Chemie und Makromolekulare Chemie,
Martin-Luther-Universität Halle-Wittenberg, Schlossberg 2, D-06108 Halle, Germany

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ABSTRACT: Graft copolymers poly(propene)-*graft*-poly(styrene) have been synthesized by the copolymerization of propene with polystyrene macromonomers using the catalyst system [$Me_2Si(2\text{-}Me\text{-}Benzind)_2$]-$ZrCl_2$/methylaluminoxane. Due to the high reactivity of allyl-terminated polystyrene in the metallocene-catalyzed copolymerization with propene, application of the macromonomer method for the synthesis of polyolefin graft copolymers was possible. In order to obtain copolymers with well-defined structures, polystyrene macromonomers were made via "living" anionic polymerization and functionalization. In copolymerization reactions, graft copolymers with a polystyrene content of from 7 up to 72 wt % were obtained. The molecular weights as well as the melting points of the copolymers decrease with increasing polystyrene content.

Introduction

Polypropylene is one of the most important commercial plastics. It is a highly versatile material with an outstanding combination of cost performance and excellent physical properties. The property range of polypropylene can be broadened by physically blending it with other polymers, but most of the resulting blends are immiscible. Hence, compatibilization is often necessary for combining the advantageous properties of the blend components.

Compatibilization can be achieved following two strategies. The blends can be compatibilized reactively, by coupling of reactive groups on each of the immiscible polymers.[1] The second way is the addition of premade block or graft copolymers.[2]

Therefore, graft copolymers with polypropylene backbone and chemically different side chains are interesting and desirable products. The chief interest in these graft copolymers originates from their properties as interfacial modifiers. In polypropylene blends they can improve adhesion to and compatibility with other polymers.

The functionalization of polyolefins has long been a field of research, and numerous methods have been employed in forming graft copolymers including free radical initiators in the presence of monomers, hydroperoxidation, halogenation, milling, high energy radiation, and electromagnetic radiation in the visible and UV region.[3,4]

These methods for the chemical modification are usually accompanied by side reactions such as crosslinking and chain cleavage, what results in diminished mechanical properties.[5−7] Graft copolymers PP-*g*-PS are formed during the free radical polymerization of styrene on polypropylene in the solid phase and provide an optimum fine dispersion and phase stability of the resulting polypropylene/polystyrene blends.[8,9] However, in this modification process, the structure and composition of the copolymers are not able to be controlled and characterized. One way to polyolefin graft copolymers with a more defined structure is the use of borane-containing polymers. Borane-group-containing copolymers were obtained by direct copolymerization of an α-olefin and a borane-containing α-olefin with a metallocene catalyst, such as $Et[Ind]_2ZrCl_2$/MAO.[10] A second way is the comonomer/anionic approach. Copolymers of ethylene and *p*-methylstyrene prepared with a metallocene catalyst, such as $Et[Ind]_2ZrCl_2$ or [$C_5Me_4(SiMe_2N\textit{t}Bu)$]$TiCl_2$, were lithiated at the benzyl groups and used as initiators in anionic graft from reactions of styrene, methyl methacrylate, acrylonitrile,

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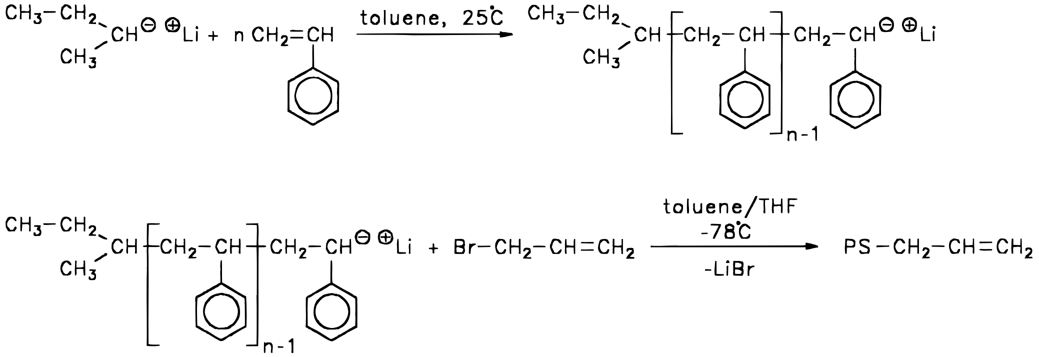
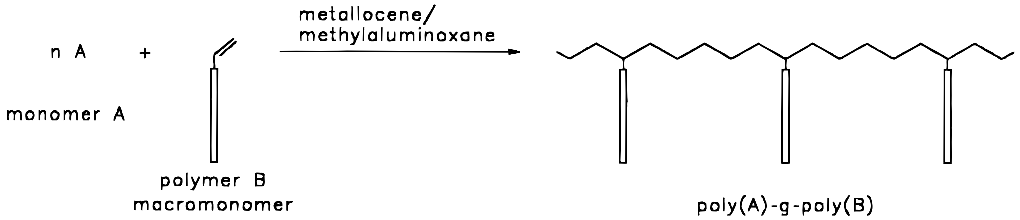
Scheme 1. Synthesis of Polystyrene Macromonomers with Allyl End Groups



Scheme 2. Macromonomer Method for the Synthesis of Graft Copolymers with Well-Defined Graft Length



and *p*-methylstyrene.[10]

Another approach, studied in the present work, is to synthesize polypropylene graft copolymers using the macromonomer method. The copolymerization of propene with macromonomers should allow the synthesis of well-defined graft structures with controlled side chain length and number. These polymers can be used as compatibilizers in polymer blends in order to investigate the influence of molecular parameters of graft copolymers on blend properties and morphology.

In earlier investigations we found a surprisingly high reactivity of higher α-olefins in the metallocene catalyzed copolymerization with propene.[11] Copolymers of ethylene with a polypropylene macromonomer (M_n = 700) could be prepared using different bridged and unbridged metallocene catalysts.[12]

The object of this paper is the synthesis and characterization of well-defined graft copolymers with polypropylene backbone and polystyrene grafts. The copolymerization of propene with polystyrene macromonomers was carried out using the catalyst system [Me_2Si(2-Me-Benzind)$_2$]$ZrCl_2$/methylaluminoxane.

Experimental Section

Materials. [Me_2Si(2-Me-Benzind)$_2$]$ZrCl_2$ was donated by BASF AG and methylaluminoxane (MAO) (10 wt % solution in toluene) by Witco GmbH. Propene was dried by passing through a molecular sieve 3A column. Styrene was purified by distillation over calcium hydride. Toluene was refluxed over sodium/benzophenone.

Macromonomer Synthesis. In a 0.5 dm^3 flask have been introduced, in an argon atmosphere, 200 mL of toluene and 18 mL of styrene. At room temperature 2 mL of a 2 M solution of *sec*-butyllithium in toluene were added. After 1 h the flask was cooled to −78 °C and diluted with 100 mL of tetrahydrofuran. Then, the solution of the "living" anions was added to another flask filled with a solution of 7 mL of allyl bromide in 100 mL of toluene and 100 mL of tetrahydrofuran. The resulting macromonomer (M_n = 4000, M_w/M_n = 1.08), which was completely functionalized was precipitated in methanol, washed with methanol, filtered, and dried in a vacuum.

Copolymerization Procedure. Copolymerization was carried out at 20 °C in a 0.5 dm^3 steel reactor. The reactor was filled with 200 mL of toluene. Then, MAO in toluene, a solution of 2.5 g of polystyrene macromonomer in 50 mL of toluene, and the preactivated metallocene solution were added. The molar ratio methylaluminoxane/metallocene was [Al]:[Zr] = 1000:1. The polymerization was started by adding propene and adjusting the pressure at 0.1 bar. It was terminated by precipitation of the reaction mixture in diluted hydrochloric acid in methanol. The copolymer was filtered, washed with methanol, and dried in a vacuum.

Copolymer Characterization. Copolymer composition, molecular weight, and molecular weight distribution were determined by gel-permeation chromatography (GPC) at 135 °C in 1,2,4-trichlorobenzene. The thermal behavior of the copolymers was investigated using differential scanning calorimetry (DSC).

Results and Discussion

Our studies on tailoring the morphology and mechanical properties of compatibilized polypropylene/polystyrene blends by controlling the molecular structure of the compatibilizing agent require a synthesis method for well-defined polypropylene graft copolymers. The application of the macromonomer method for the synthesis of polyolefins was limited due to the low reactivity of comonomers in the copolymerization with propene using heterogeneous, Ti-containing catalyst systems. Using a highly active metallocene catalyst with strained ligand geometry, such as Me_2Si(2-Me-Benzind)$_2ZrCl_2$, we could overcome this difficulty.

In order to obtain graft copolymers with uniform polystyrene side chain length we prepared macromonomers via "living" anionic polymerization of styrene with *sec*-butyllithium as initiator. The polymerizable end group was introduced in a second, functionalization step by reacting the "living" chain ends with allyl bromide according to Scheme 1.

For the copolymerization reactions with propene we used a completely allyl terminated polystyrene macromonomer with a molecular weight of M_n = 4000 and a molecular weight distribution of M_w/M_n = 1.08. The functionality was determined by comparing the signals of the initiating group and of the allyl end group in the 500 MHz ^{1}H NMR spectrum.

Scheme 2 shows the macromonomer method that was used for the copolymerization of propene with polystyrene. The highly isospecific catalyst Me_2Si(2-Me-

Table 1. Synthesis of Graft Copolymers with Polypropylene Backbone and Polystyrene Grafts

copolymer	catalyst concentration (μmol/L)	polymerization time (h)	product + macromonomer (g)	macromonomer conversion (%)	polystyrene content (wt %)
PPgPS 1	40	7,5	8.9	24.3	7
PPgPS 2	20	15	5.6	49.4	20
PPgPS 3	20	48	3.1	26.2	72

Table 2. Properties of Graft Copolymers with Polypropylene Backbone and Polystyrene Grafts

copolymer	polystyrene content (wt %)	M_w (kg/mol)	D	no. of grafts per molecule	PP sequence length M_{nPP} (kg/mol)	mp (°C)
PPgPS 1	7	310	2.5	2.2	41	153.4
PPgPS 2	20	158	2.2	3.6	16	151.9
PPgPS 3	72	23	1.4	2.9	4	122.2

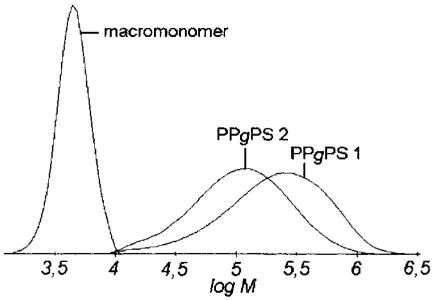


Figure 1. GPC curves of the macromonomer and graft copolymers PPgPS (macromonomer curve mirrored for comparison).

Benzind)$_2$]ZrCl$_2$ was chosen because of its open ligand structure with good accessibility of the active zirconium center in the polymerization even for long olefins.

The results of the copolymerization runs are summarized in Table 1. At a constant propene pressure of 0.1 bar we found the polystyrene macromonomer to be quite reactive. A conversion from 24% up to 49% was observed.

At a high catalyst concentration the polymerization rate is rather high and 7 wt % polystyrene is incorporated into the copolymer. Much higher polystyrene contents up to 72 wt % can be achieved using a lower catalyst concentration and lower polymerization rates.

The graft copolymer composition was determined from the results of the high temperature GPC (RI/viscosity detection, PS beads with pore sizes of 500, 10^4, 10^5, and 10^6 Å). With 1,2,4−trichlorobenzene as eluent, a polypropylene standard gave a positive peak and a polystyrene standard a negative peak. The polystyrene content of the copolymers was calculated from the comparison of the peak areas. The copolymer peak in the GPC curve was compared with polypropylene and polystyrene standards, and the polystyrene content was calculated. From this macromonomer content and the peak area of the unreacted polystyrene (Figure 1), we calculated the macromonomer conversion.

As can be seen from Figure 1 (where the negative peak of the polystyrene macromonomer is mirrored) the GPC curves of the copolymers polypropylene-*graft*-polystyrene exhibit a shape that is typical for metallocene polyolefins. There is no polystyrene rich fraction detectable as a negative peak either in the low molecular weight nor in the high molecular weight part of the curves. Therefore it can be concluded that the polystyrene grafts are randomly distributed. The molecular weight distribution was found to be narrow (1.4−2.5) as expected for metallocene products.

The molecular weights of the copolymers are given in Table 2. It is obvious that with increasing polystyrene content in the graft copolymer the molecular weight decreases from about 300 000 g for the copolymer with 7 wt % polystyrene to only 23 000 for a polystyrene content of 72 wt %.

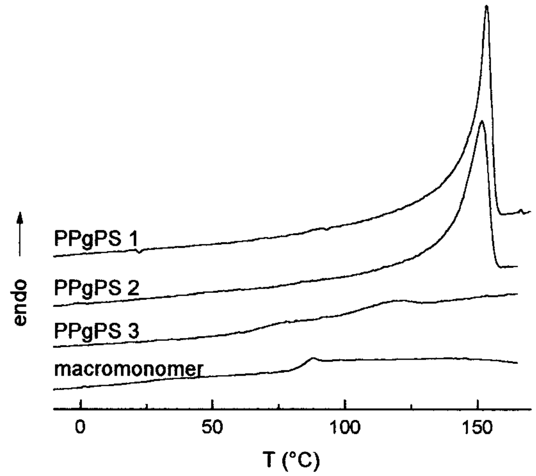


Figure 2. DSC curves of the macromonomer and graft copolymers PP*g*PS.

The average number of grafts per molecule was calculated using the polystyrene content, the macromonomer molecular weight, and the total molecular weight of the graft copolymer. Because of the decreasing total molecular weight with increasing polystyrene content the values are similar between 2.2 and 3.6 grafts per main chain.

The average length of the polypropylene sequences between two grafts in the copolymer backbone could be calculated, too. Of course this length is reduced with increasing polystyrene content and decreasing total molecular weight from 41 000 to 4000. This great reduction causes a change in the thermal properties of the graft copolymers. Figure 2 illustrates this fact.

The DSC curves show that melting point and crystallinity of the copolymers are influenced by macromonomer incorporation. If the polystyrene content is increased from 7 to 20 wt %, the melting point is changed not much. That may be due to phase separation in these copolymers where polypropylene crystallization is only slightly affected by the polystyrene phase. On the other hand the glass transition of a separate polystyrene phase could not be detected. In contrast to that the DSC curve of the graft copolymer with a polypropylene content of only 28 wt % (PP*g*PS 3) indicates a strong influence of the polystyrene grafts on the backbone melting. There is only a small melting peak at about 120 °C visible. The low crystallinity corresponds to the value for the average propene sequence length of 4000. Furthermore, a single glass transition was found at 70 °C that can be assigned to a mixed polystyrene rich phase. The glass transition temperature of the pure macromonomer at 86 °C is significantly shifted due to the phase interaction in this copolymer.

Summary

Graft copolymers with polypropylene backbone and polystyrene grafts could be made by the metallocene-catalyzed copolymerization of propene with an allyl-terminated polystyrene macromonomer prepared via anionic polymerization. The use of this macromonomer method leads to defined copolymer structures with uniform graft length and randomly distributed grafts. The molecular weight as well as the melting behavior is influenced by the macromonomer incorporation into the polypropylene chain. The results of our investigations on the use of the synthesized graft copolymers as compatibilizers in polypropylene/polystyrene blends will be published elsewhere.

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References and Notes

(1) Bidaux, J.; Smith, G. D.; Bernet, N.; Manson, J. E.; Hilborn, J. *Polymer* **1996**, *37*, 1129.
(2) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(3) Mukherjee, A. K.; Gupta, B. D. *J. Macromol. Sci., Chem.* **1983**, *A19*, 1069.
(4) Ranby, B. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 55.
(5) Fritz, H.; Cai, Q.; Bölz, U. *Kunststoffe* **1993**, *83*, 439.
(6) Heinen, W.; Rosenmöller, C. H.; Wenzel, C. B.; de Groot, H. J. M.; Lugtenburg, J.; van Duin, M. *Macromolecules* **1996**, *29*, 1151.
(7) Ho, R. M.; Su, A. C.; Wu, C. H.; Chen, S. I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 941.
(8) Galli, P.; Haylock, J. C.; DeNicola, A. *Macromol. Symp.* **1995**, *100*, 95.
(9) Beenen, W.; v.d. Wal, D. J.; Janssen, L. P. B. M.; Buijtenhuijs, A.; Hogt, A. H. *Macromol. Symp.* **1996**, *102*, 255.
(10) Chung, T. C. *Worldwide Metallocene Conference MetCon '96*; June 12–13, 1996; Houston, TX.
(11) Arnold, M.; Henschke, O.; Knorr, J. *Macromol. Chem. Phys.* **1996**, *197*, 563.
(12) Shiono, T.; Moriki, Y.; Soga, K. *Macromol. Symp.* **1995**, *97*, 161.

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