



Synthesis of isotactic polypropylene-*block*-polystyrene block copolymers as compatibilizers for isotactic polypropylene/polyphenylene oxide blends

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ABSTRACT

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and isotactic polypropylene (iPP) are highly incompatible and consequently their uncompatibilized blends are quite brittle regardless of the molecular weights and ductility of the individual components. Isotactic polypropylene-polystyrene block copolymers, to be applied as compatibilizers for a broad range of PPO/iPP blend compositions, were prepared by mechanism transformation from coordination polymerization (iPP) to Activators Regenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization of styrene. The effect of the block copolymer composition and loading on the mechanical, thermal and morphological properties of the blends was studied. The addition of compatibilizer resulted in significant decreased domain size of the dispersed phase and improved mechanical properties. An unexpected phenomenon was observed for some compatibilized iPP-rich blends with only 20% PPO, which were characterized by an even higher impact resistance than that of pure PPO.

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1. Introduction

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a high-performance thermoplastic material useful for applications requiring high temperature resistance. Despite the fact that PPO shows high strength, excellent heat resistance, inherent flame resistance, good water resistance and good dimensional stability, the application of neat PPO is limited due to its natural brittleness, poor processability (high melt viscosity and poor melt stability) and limited solvent resistance [1]. Isotactic polypropylene on the other hand is a low cost commodity polymer with good solvent/hydrolytic resistance owing to its semicrystallinity combined with easy processability [2,3]. Increasing the iPP impact strength at temperatures close to room temperature would considerably upgrade this polymer. Rubber modification has been shown to be effective in toughening iPP even at low temperatures (i.e. -20°C), but it

unfortunately involves a noticeable reduction in modulus [4].

In this work, PPO and iPP were blended in order to combine the best properties of both polymers in a cost-effective way [3,4]. It is well known that PPO and iPP are highly incompatible due to the difference in polarity and solubility parameters, resulting in quite brittle blends with low impact resistance [5]. In order to overcome the incompatibility and thus improve the mechanical properties of such a blend, it is highly desirable to reduce the size and morphology of the phase-separated domains, and in particular to strengthen the interfacial adhesion between the dispersed phase and the matrix such that the blend can withstand stresses applied in the normal use of the product [3]. It is generally known that block or graft copolymers with segments identical to or at least miscible with the polymer components forming the blend can improve the compatibility of the blend's morphological and mechanical properties since they are capable to improve the dispersion, reduce the phase sizes and increase the interfacial interaction between domains [4,6]. Typical compatibilizers reported for PPO/iPP blends are polystyrene-*block*-polyolefin block copolymers like styrene-ethylene-propylene (SEP) diblock copolymers, styrene-

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ethylene/butylene-styrene (SEBS) or styrene-ethylene/propylene-styrene (SEPS) triblock copolymers [5,7–12]. Those polymers are typically produced by a two-step process that involves anionic polymerization of styrene and butadiene or isoprene followed by a costly partial hydrogenation step. However, recently Kim et al. developed a one-pot system for the synthesis of polystyrene-*block*-polyolefin-*block*-polystyrene block copolymers via coordinative chain transfer polymerization (CCTP) of ethylene/propylene and subsequent anionic polymerization of styrene [13]. The polystyrene block in polystyrene-*block*-polyolefin block copolymers is thermodynamically miscible with the PPO phase and the rubbery block is at least partially compatible with the amorphous fraction of the iPP matrix, although not truly miscible with iPP [11]. A disadvantage is that rather large quantities of these styrene-diene rubbers have to be added to be efficient, which significantly affects the stiffness of the final product. Therefore, in this work, a series of isotactic polypropylene-*block*-polystyrene (iPP-*b*-PS) block copolymers (Scheme 1) was synthesized with iPP as olefinic block such that full compatibility and miscibility with the iPP phase in the blends is ensured and loss of stiffness is overcome. Olefinic block copolymers are generally prepared by a mechanism transformation [14], which requires a macroinitiator with a reactive functional group that can be transformed into or used as an initiator for the second block [15]. Initially, polyolefins with borane end groups were used as macroinitiator for free radical polymerization of styrene or polyolefins with *p*-methylstyrene end groups for anionic polymerization of styrene [16]. More recently, controlled radical polymerization methods like atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) and reversible addition-fragmentation chain transfer (RAFT) are on the march for the synthesis of well-defined polyolefin block copolymers with styrene [17]. Among those CRP methods, ATRP is generally known as one of the most attractive and convenient tools for synthesizing a variety of styrenic and (meth)acrylate block copolymers. Up to now, however, no reports could be found on the use of Activators Regenerated by Electron Transfer (ARGET) ATRP [18,19] for the synthesis of the polystyrene part in olefinic block copolymers. ARGET ATRP is a very interesting method since it requires much less metal catalyst (e.g. CuBr) than normal ATRP and by consequence nearly does not contaminate the final product with metal traces. This is especially an advantage in the case of polyolefin copolymers due to their poor solubility, which makes it tough to remove catalyst traces from the polymer.

Scheme 1 summarizes the approach used in this work to synthesize iPP-*b*-PS block copolymeric compatibilizers prepared in three steps starting from hydroxyl chain-end functionalized iPP polymer (iPP-OH), which was synthesized by CCTP using aluminum and zinc alkyls as chain transfer agents, followed by oxidation with oxygen [20]. The hydroxyl end-group of iPP chains was transformed into an alkylhalogenide (iPP-Br), which was subsequently used as a macroinitiator for the ARGET ATRP of styrene.

To the best of our knowledge, this is the first report about the use of iPP-*b*-PS block copolymers as compatibilizers for PPO/iPP blends.

Here we discuss the effects of the composition and segmental chain lengths of those new iPP-*b*-PS compatibilizers as well as the amount of block copolymer on the PPO/iPP compatibilization by comparing the morphology, mechanical properties, melting characteristics and crystallization behavior of the PPO/iPP blends. The morphology and properties of binary PPO/iPP blends without compatibilizers will be compared as benchmark.

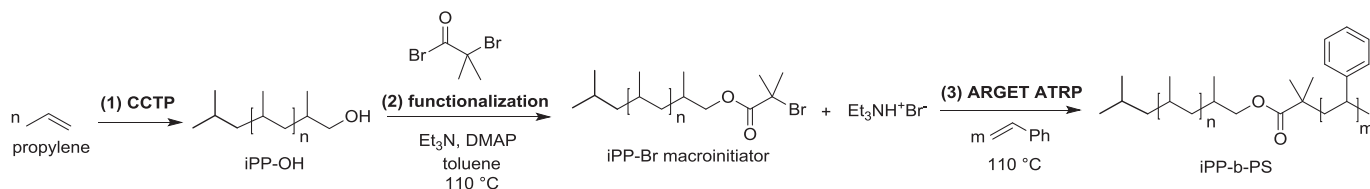
2 Experimental part

2.1 Materials

Ethyl α -bromoisobutyrate (Sigma Aldrich, 98%), basic alumina oxide (Sigma Aldrich), 4-dimethylaminopyridine (Acros Organics, 99%), α -bromoisobutyryl bromide (Acros Organics, 98%), copper(II) bromide (Sigma Aldrich, 99%), tin(II)ethylhexanoate (Sn(EH)₂; Sigma Aldrich, 95%), pentamethyldiethylenetriamine (PMDETA; Acros, 99%), tris(2-pyridylmethyl)amine [TPMA; Sigma Aldrich, 98%), tetrahydrofuran (Biosolve, 99.8+%), methanol (Acros Organics, 99+%), toluene (VWR, 100%), anisole (Acros Organics, 99%), dimethyl acetamide (Acros Organics, 99%), triethylamine, chloroform-*d* (VWR, 99.8%), 1,1,2,2-tetrachloroethane-*d*₂ (Cambridge Isotope Laboratories, 99.6%), 1,2-dichlorobenzene (VWR, \geq 99%), MAO (Chemtura, 30 wt% solution in toluene), diethyl zinc (DEZ; 1.0 M solution in hexanes, Sigma-Aldrich), triisobutylaluminum (TiBA; 1.0 M solution in hexanes, Sigma-Aldrich), benzophenone (Acros Organics, 99%), calcium hydride (Acros Organics, 93%), styrene (Sigma Aldrich, 98%) and Irganox 1010 (BASF) were used as received unless stated otherwise. Toluene was dried over sodium/benzophenone and triethylamine was dried over calcium hydride. Cu(I)Br (Aldrich, 98%) was purified by stirring with acetic acid. After filtration, it was washed with methanol and ether and then dried under vacuum at 70 °C. Catalyst precursor *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ was purchased from MCAT GmbH, Konstanz, Germany. Isotactic polypropylene PP520P (SABIC) and poly(2,6-dimethyl-1,4-phenylene ether) Noryl 640 (SABIC) were used to make blends. The homopolymers have the following characteristics (datasheets). Noryl 640: $M_n = 19,900$ g/mol, $\bar{D} = 2.8$, intrinsic viscosity = 0.4 dL/g at 25 °C in chloroform, $T_g = 216$ °C PP520P: $M_n = 56,200$ g/mol, $\bar{D} = 7.4$, MFI = 3 g/10 min at 230 °C, 2.16 kg, $T_g \approx -5$ °C and $T_m = 163$ °C.

2.2. Methods

Typical procedure for the synthesis of OH functionalized iPP macroinitiator (iPP-OH). The polymerization reaction was carried out in a stainless steel Büchi reactor (300 mL). Prior to the polymerization, the reactor was dried in vacuo at 40 °C and flushed with nitrogen. Toluene (100 mL) and MAO (30 wt% solution in toluene, 0.25 mL) were added and stirred at 50 rpm for 20–30 min. TiBA (1.0 M solution in hexane, 2 mL) and DEZ (1.0 M solution in hexane, 0.5 mL) were added and the solution was saturated with propylene and stirred for 10 min. In a glove box, *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂



Scheme 1. Mechanism transformation for the synthesis of iPP-*b*-PS block copolymers via (1) coordinative chain transfer polymerization (CCTP) of propylene towards OH-end functionalized iPP polymer (iPP-OH), (2) functionalization of the OH end group in iPP-OH to an alkylhalogenide initiator function (iPP-Br) for ATRP and (3) use of iPP-Br macroinitiator for the initiation of ARGET ATRP of styrene.

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