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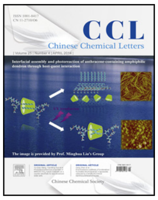

Original article

A convenient, highly-efficient method for preparation of hydroxyl-terminated isotactic poly(propylene) and functional di-block copolymer

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ABSTRACT

Both terminated functional isotactic polypropylene (*i*PP) and block copolymers containing *i*PP segment are desirable for commercial applications. This paper provides a convenient, highly-efficient method to prepare hydroxyl-terminated isotactic polypropylene (*i*PP-*t*-OH) and functional di-block copolymer containing the *i*PP segment through a combination of coordination polymerization and coupling reaction. The coordination polymerization was catalyzed by $TiCl_4/MgCl_2/AlEt_3$ catalyst system using $ZnEt_2$ as chain transfer agent. Further, the Zn-terminated *i*PP was oxidized and subsequently hydrolyzed to provide *i*PP-*t*-OH. Soxhlet extraction and ^{13}C NMR were used to calculate the isotacticity of *i*PP-*t*-OH. The degree of polymerization and the number of hydroxyl groups at the chain end of *i*PP-*t*-OH were measured by GPC and ^{1}H NMR. Despite the high molecular weight and heterogeneous reaction, *i*PP-*t*-OH is effectively linked with PEG-*t*-NCO to produce di-block copolymers. DSC analysis of the di-block copolymer shows an obvious decrease in T_m and T_c, which indicated that PEG was successfully linked to the terminal end of *i*PP.

1. Introduction

Isotactic polypropylene (*i*PP) is one of the most in-demand polymeric materials due to its excellent physical properties and high performances in commercial applications. However, some inherent shortages of *i*PP, such as poor adhesion, incompatibility, low surface energy and difficulty for chemical modification due to semicrystalline morphology and the lack of chemical functionality, obstruct its commercial success in other fields [1–3]. Therefore one hot topic in present research is to prepare polar functional polypropylene or polypropylene copolymers without disturbing the isotactic chain structure [4]. To improve the compatibility, one possible way is to synthesize the block or graft copolymers, but it is a challenging task for synthetic chemistry due to *i*PP's special property [5].

It is a very beneficial task to prepare *i*PP containing terminal functional groups [6,7] because it can guarantee isotactic chain structure unperturbed, and consequently maintains the functionalized *i*PP with high crystallinity. Moreover, the terminal functional group, having good mobility and reactivity, can endow *i*PP with desirable interactive properties, forming graft and block copolymers, which can be widely used in many fields [8–11]. Therefore, various functional groups have been introduced to the end of polypropylene chain [12–17], such as amino, vinyl, halogen and metal (Al, Zn). However, there are few methods to prepare block copolymers originating from terminal-functionalized *i*PP due to the large steric hindrance and heterogeneous reaction conditions.

Free-radical reaction is a common technique [8,9,18,19] used to synthesize graft or block copolymers, however, it is not easy to prepare well-defined copolymers, because the existence of β-hydrogen on the polypropylene chain can result in side reactions, such as chain scission and crosslinking. Furthermore, the high molecular weight and crystallization of terminated functional *i*PP also result in a reduced reactivity. Although ionic polymerization [11,20] and controlled/living free radical techniques [21,22] are mostly employed in the functionalization of *i*PP in order to get well-defined copolymer structure. Both reactions mentioned above need strict conditions, such as complete absence of moisture

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and other acidic impurities, which impede their industrialization applications. Furthermore, there are few transition metal coordination catalysts that exhibit living polymerization behavior, and most of them are limited to the preparation of polyethylene and poly(1-hexene) [5,23–26].

In recent years, the coupling reaction, one of the most significant but non-mainstream methods, was introduced in PP functionalization to produce novel PP copolymer structures. Soga *et al.* [12] successfully introduced the coupling reaction into the functionalization of PP. They synthesized the Zn-terminated PP by the $TiCl_3/Al(C_2H_5)_2Cl$ catalyst system using $ZnEt_2$ as chain transfer reagent. Then the Zn-terminated PP was transformed into vinyl-terminated PP by a coupling reaction. Lu [10] prepared long chain branched PP with a relatively well-defined molecular structure using a coupling reaction, whose backbone molecular weight, graft length, and graft density can be well controlled by modulating the ratio between PP-*g*-maleic anhydride and PP-*t*-NH_2. The metal catalyzed azide/alkyne 'click' reaction represents an important contribution to the functionalization of *i*PP due to its high reactivity. Huang *et al.* [27] synthesized a star *i*PP by coupling the azide-terminated-*i*PP with the trialkyne-containing multifunctional compound. Dong *et al.* [28] fabricated azide and alkyne functional *i*PP, with azide at the chain end of *i*PP while alkyne at the side chain, and then coupled them effectively by click chemistry. From previous works one conclusion can be drawn that the key to coupling reaction applied to polypropylene is to maximize the reactive activity because the reaction agent used is of low reaction activity due to the large spacial steric hindrance and heterogeneous reaction.

In this paper, we report an efficient method to synthesize *i*PP-*t*-OH and the subsequent *i*PP-*b*-PEG copolymers by a combination of coordination polymerization and coupling reaction. The iPP-*b*-PEG is an excellent compatilizer for polypropylene matrix composites with polar filler or other polar polymers. Furthermore, it was proposed for use in coating applications that the iPP-*b*-PEG can be employed as an interlayer, or prime coat, between the polar substrate and a polypropylene topcoat. The coordination polymerization was catalyzed by $TiCl_4/MgCl_2/AlEt_3$ catalyst system and $ZnEt_2$ as chain transfer agent, since $MgCl_2$-supported Ziegler–Natta catalysts are playing major roles in the production of polyolefins, including more than 50 million tons of PP each year. The resultant Zn-terminated PP was oxidized and hydrolyzed to provide a monohydroxyl-terminated PP (*i*PP-*t*-OH). Then *i*PP-*t*-OH was successfully reacted with isocyanate-terminated poly(ethylene glycol) (PEG-*t*-NCO) to prepare di-block copolymer containing the *i*PP segment via coupling reaction due to high reactivity between –OH and –NCO. Thus, a simple but highly-efficient method for preparation of di-block copolymer containing *i*PP segment was achieved.

2. Experimental

2.1. Materials and equipments

$TiCl_4/MgCl_2$/diester catalyst was kindly donated by SINOPEC Catalyst Co., Ltd., Beijing, China. The catalyst had a Ti content of 2.7 wt%. Triethylaluminium (TEA) was purchased from Albemarle. Cyclohexyl(dimethoxy)methylsilane (C-donor) was purchased from Huabang Chemistry Ltd., Hubei, China. Diethylzinc (15 wt% in toluene) was purchased from Aldrich. Propylene (purity >99.9%) and O_2 (purity >99.5%) were purchased from Hangzhou Minxing Gas Co., Ltd., China. Toluene, acetone, monohydroxyl-terminated poly(ethylene glycol) (PEG-*t*-OH, $M_n = 2000$ g/mol, $M_w/M_n = 1.1$), dichloromethane, dibutyltin dilaurate (DBTDL), 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, purity >99.5%), hydrochloric acid were purchased from Aldrich. Toluene was purified over sodium/benzophenone ketyl and distilled under a dry N_2 atmosphere prior to use. PEG was distilled in toluene for 6 h to remove water before reaction. Extra-pure-grade (99.99%) nitrogen was further purified by passing through two columns of de-oxygen catalysts and pre-activated 4 Å molecular sieves to remove the residual moisture and oxygen. All moisture-sensitive manipulations were carried out through Schlenk technique.

Fourier transform infrared spectroscopy was performed on a Bruker Vector 22 FT-IR spectrometer (Germany). DSC measurement was carried out on a Q100 MDSC (TA Instruments Corporation, USA) under a nitrogen flow of 50 mL/min. It was operated from −20 °C to 200 °C at a heating/cooling rate of 10 °C/min. Molecular weight and polydispersity index were measured with gel permeation chromatography on a PL-GPC220 at 120 °C using 1,2,4-trichlorobenzene as eluent and polystyrene as standard. The ^1H NMR measurement of PEG-*t*-NCO was conducted on a Varian-Inova-500 HZ spectrometer using deuterated chloroform ($CDCl_3$) as solvent. The other ^1H NMR and ^{13}C NMR spectra were performed on a Varian Mercury 300 Plus instrument in the pulse Fourier mode and recorded with deuterated 1,2-dichlorobenzene at 120 °C. In the case of ^{13}C NMR, the parameter of pulse repetition and scanning times is set to 20 s and 8000 s, respectively, for the purpose of getting high resolution spectra.

2.2. Synthesis of hydroxyl-terminated iPP

In a typical propylene coordination polymerization, 50 mL toluene, a specific amount of triethylaluminium (Al/Ti = 100), C-donor (Si/Ti = 5) and $ZnEt_2$ (Zn/Ti = 3–40) were injected into a 100 mL Schlenk flask under propylene atmosphere at 1 atm. About 40 mg of $TiCl_4/MgCl_2$ catalyst was added into the mixed solution to initiate the polymerization at 60 °C. 30 min later, the reaction mixture was heated to 100 °C and contacted with dry oxygen gas for another 30 min. Finally, the reaction was quenching by hydrochloride acidified methanol. The solvent was removed by rotary evaporator and the polymer was washed with acetone–water mixture and dried in vacuum at 60 °C for 24 h. With the purpose of determining the influence of chain transfer on the isotactic index (*II*) of *i*PP-*t*-OH, a series of Soxhlet extraction experiments were performed at 100 °C (near the boiling point of *n*-heptane) for 24 h. The isotactic index (*II*) was defined as the weight percentage of *n*-heptane insoluble fraction in the sample. Both the *n*-heptane soluble fraction and *n*-heptane insoluble fraction were evaporated and then dried in vacuum at 60 °C for 24 h.

2.3. Synthesis of isocyanate-terminated PEG

DBTDL (20 mg [1 wt% (PEG-*t*-OH)]), IPDI (0.222 g, 1 mmol) and 5 mL CH_2Cl_2 were added into a 100 mL Schlenk flask at 55 °C. Then 2 g (1 mmol) PEG-*t*-OH dissolved in 50 mL dichloromethane was injected into the 100 mL Schlenk flask slowly by a micro injection pump at a rate of 0.2 mL/min. Then, the mixture was refluxed at 55 °C for 4 h. Finally, the mixture solution was precipitated by *n*-heptane and dissolved in dichloromethane repeatedly to remove impurities and then dried in vacuum at 30 °C for 24 h. PEG-*t*-NCO (2.09 g, $M_n = 2200$ g/mol, $M_w/M_n = 1.03$) was obtained.

2.4. Synthesis of iPP-b-PEG via coupling reaction

PEG-*t*-NCO (1.32 g, 0.6 mmol), 0.5 mmol *i*PP-*t*-OH (entry 2, 3, 5 and 7 in Table 1) and 50 mL toluene were added into a 100 mL Schlenk flask and stirred for 1 h at 110 °C. Subsequently, 1 wt% (*i*PP-*t*-OH) of DBTDL was added into the Schlenk flask and the mixture was stirred for 8 h. Finally the mixture solution was precipitated by *n*-heptane and dissolved in dichloromethane repeatedly to remove impurities and dried in vacuum at 60 °C for 24 h.