

Synthesis of Isotactic Polystyrene-block-Polyethylene by the Combination of Sequential Monomer Addition and Hydrogenation of 1,4-*Trans*-polybutadiene Block*

Hua-qing Liang^a, Qi-hua Zhou^a, Yong-jiang Long^a, Wan-chu Wei^a, Guo-dong Liang^{a,b},
Qing Wu^{a,b}, Hai-yang Gao^{a,b} and Fang-ming Zhu^{a,b**}

^a Guangdong Provincial Key Laboratory for High Performance Polymeric Composites, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

^b Key Laboratory for Polymer Composite and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

Abstract Herein, we demonstrate the synthesis of a well-defined diblock copolymer consisting of isotactic polystyrene (*i*PS) and linear polyethylene, isotactic polystyrene-block-polyethylene (*i*PS-*b*-PE), by the combination of sequential monomer addition and hydrogenation. Isospecific living polymerization of styrene and living *trans*-1,4-polymerization of 1,3-butadiene were catalyzed by 1,4-dithiabutanediyl-2,2'-bis(6-cumenyl-4-methylphenoxy) titanium dichloride (complex 1) activated by triisobutyl aluminum modified methylaluminoxane (MMAO) at room temperature to provide highly isotactic polystyrene (*i*PS) and 1,4-*trans*-polybutadiene (1,4-*trans*-PBD) with narrow molecular weight distribution. Furthermore, the *i*PS-*b*-1,4-*trans*-PBD was synthesized *via* sequential monomer addition in the presence of complex 1 and MMAO. The hydrogenation of the 1,4-*trans*-PBD block was promoted by RuCl₂(PPh₃)₃ used as a catalyst to produce *i*PS-*b*-PE.

Keywords Isotactic polystyrene; 1,4-*Trans*-polybutadiene; Linear polyethylene; Diblock copolymer; Sequential monomer addition; Hydrogenation

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INTRODUCTION

The synthesis of block copolymers has attracted much attention due to their unique features to use as compatibilizer for blends and self-assemble into regular nano-structures that can be utilized in diverse fields^[1–8]. The synthesis of block copolymers is always based on controlled/living polymerizations. Active homopolymer chains are obtained with controlled/living polymerizations and can be terminated with functional group. Moreover, it initiates the living copolymerization of another monomer. There are several strategies to design and prepare block copolymers. An effective strategy for the synthesis of block copolymers is sequential monomer addition, which requires the same catalytic or initiating system to promote the living polymerization of both monomers^[9–20]. However, this technology does not work if the catalytic or initiating system can just promote the living polymerization of one monomer.

Some rare earth metal catalysts have been found to catalyze the copolymerization of styrene and butadiene

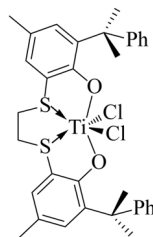
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** Corresponding author: Fang-ming Zhu (祝方明), E-mail: ceszfm@mail.sysu.edu.cn

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(BD)^[21–25]. In recent years, [OSSO]-based titanium complexes were extensively investigated for the isospecific polymerization of styrene^[26–28]. It is worth mentioning that the isospecific living polymerization of styrene was first demonstrated by Beckerle *et al.* in 2006^[28]. Subsequently, the stereospecific living polymerization of styrene and butadiene catalyzed by 1,4-dithiabutandiyl-2,2-bis(6-cumenyl-4-methylphenoxy) titanium dichloride (complex 1, as shown in Scheme 1) activated by methylaluminoxane (MAO) to produce highly isotactic polystyrene (*i*PS) and 1,4-*trans*-polybutadiene (1,4-*trans*-PBD) with narrow molecular weight distribution was reported by Proto *et al.* in 2010^[26]. Moreover, the synthesis of the diblock copolymer of *i*PS-*b*-1,4-*trans*-PBD was also promoted by this catalytic system *via* sequential monomer addition.



Scheme 1 The chemical structure of complex 1

Another strategy, the macroinitiator method, can be employed to solve this problem^[29–38]. The macroinitiators are always prepared from end-functionalized polymers obtained by living polymerizations including living anionic polymerization, living cationic polymerization and living/controlled radical polymerization. Then the prepared macroinitiator was used to initiate the living polymerization of another monomer and provide a block copolymer. Chen *et al.*^[31] has reported the preparation of poly(vinyl acetate) *via* cobalt-mediated radical polymerization as the macroinitiator to synthesize the block copolymers of poly(vinyl acetate)-block-polystyrene and poly(vinyl acetate)-block-polymethacrylate.

In recent years, the click coupling reaction has been employed for the synthesis of block copolymers^[39–47]. Our group has reported^[48, 49] the synthesis of diblock copolymers polyethylene-block-poly(ethylene oxide) (PE-*b*-PEO) and isotactic polystyrene-block-poly(ethylene oxide) (*i*PS-*b*-PEO) *via* click coupling reactions. The PE-*b*-PEO diblock copolymers were synthesized by the click coupling reaction of azido-terminated polyethylene (PE-N₃) with alkynyl-terminated poly(ethylene oxide) (PEO-≡); the *i*PS-*b*-PEO diblock copolymers were prepared by the click coupling reaction of vinyl-terminated isotactic polystyrene (*i*PS=) with thiol-terminated poly(ethylene oxide) (PEO-SH).

Block copolymers can also be obtained by the chemical modification of other block copolymers. A typical example is the hydrogenation of the polybutadiene-based block copolymers to form polyethylene-based block copolymers. It should be noted that the hydrogenation of polystyrene-block-polybutadiene-block-polystyrene triblock copolymer (SBS) synthesized by living anionic polymerization has been industrialized. The research on the hydrogenation of SBS had begun in 1970s. The nickel and cobalt based catalyst was first used to promote the hydrogenation of SBS by the Shell Oil Company. Then the metallocene catalytic system^[50–52] and the rhodium catalytic system^[53–55] were developed. The diimide catalytic system was also used to promote the hydrogenation of polybutadiene^[56, 57]. However, the hydrogenation of the polybutadiene block of SBS resulted in branched polyethylene with ethyl branch resulting from the anionic 1,2-addition polymerization of butadiene.

Among all these attempts to synthesize block copolymers, nevertheless, the *i*PS-*b*-PE copolymer consisting of a highly isotactic polystyrene block and a linear polyethylene block has hardly been reported^[58]. Fortunately, the synthesis of *i*PS-*b*-1,4-*trans*-PBD reported by Capacchione and his coworkers *via* sequential monomer addition in terms of living coordination polymerization shed a light to the synthesis of *i*PS-*b*-PE. It is reasoned that the selective hydrogenation of the polybutadiene block in *i*PS-*b*-1,4-*trans*-PBD can result in the diblock copolymer of *i*PS-*b*-PE. Herein we report the synthesis of a well-defined block copolymer of *i*PS-*b*-PE with a linear polyethylene block using the ruthenium-based catalyst RuCl₂(PPh₃)₃.

EXPERIMENTAL

Materials

All reagents were purchased from Aladdin and J&K Scientific. Styrene was dried with calcium hydride and distilled on a vacuum line. 1,3-Butadiene was dried with calcium hydride at $-40\text{ }^{\circ}\text{C}$ and distilled at room temperature to form a toluene solution. Toluene was dried by distilling from sodium with benzophenone as an indicator. 1,4-Dimethyl-benzene (*p*-xylene) and chlorobenzene were dried with calcium hydride and distilled on a vacuum line. Ethanol was dried with magnesium ribbon and iodine and distilled on a vacuum line. Ruthenium trichloride hydrate, triphenylphosphine and $1.9\text{ mol}\cdot\text{L}^{-1}$ solution of triisobutyl aluminum modified methylaluminoxane (MMAO) in heptane were used as received.

Synthesis of Isotactic Polystyrene-block-1,4-trans-Polybutadiene (*iPS-b-1,4-trans-PBD*)

iPS-b-1,4-trans-PBD was synthesized as reported in the literature^[26]. A typical example is as follows. A 100 mL flask equipped with a magnetic bar was charged with 6.3 mL of a $1.9\text{ mol}\cdot\text{L}^{-1}$ solution of MMAO in *n*-heptane, 8.7 mL of toluene, and 5.0 mL of solution of $10\text{ }\mu\text{mol}$ 1,4-dithiabutandiyyl-2,2'-bis(6-cumenyl-4-methylphenoxy) titanium dichloride (complex 1) in toluene. The mixture was stirred for 5 min at room temperature. The polymerization was started by injecting 0.7 mL of styrene. After 2 h, 4.6 mL of a $4.3\text{ mol}\cdot\text{L}^{-1}$ solution of 1,3-butadiene in toluene was then rapidly added to this flask. The block copolymerization was continuously proceeded for an additional 2 h. The reaction mixture was terminated by introducing 2 mL of ethanol containing the antioxidant. The polymer was precipitated in ethanol acidified with concentrated hydrochloric acid, recovered by filtration, washed with an excess of ethanol, and dried to constant weight under vacuum at room temperature.

Preparation of Tris(triphenylphosphine) Ruthenium Dichloride ($\text{RuCl}_2(\text{PPh}_3)_3$)

2.43 g of triphenylphosphine was added to a branched-neck round bottom flask equipped with a reflux condensing tube and dried under vacuum for several hours. 24 mL of dried ethanol was then added and the flask was heated to $85\text{ }^{\circ}\text{C}$ to completely dissolve the triphenylphosphine. 0.40 g of ruthenium trichloride hydrate was dissolved in 16 mL of dried ethanol and added to the flask to react for 2 h at $85\text{ }^{\circ}\text{C}$. After the ensuing reaction the solution was cooled to room temperature and black crystals were precipitated. The crystalline product were collected by filtration under nitrogen atmosphere and washed with dried ethanol and diethyl ether for several times. Then the crystals were dried under vacuum with a yield of 63.1%.

Preparation of Isotactic Polystyrene-block-Polyethylene (*iPS-b-PE*)

The hydrogenation of 1,4-*trans*-PBD block in *iPS-b-1,4-trans-PBD* was performed in a 250 mL high pressure reactor equipped with a mechanical stirrer. Predetermined amounts of *iPS-b-1,4-trans-PBD* and triphenylphosphine were dissolved in hot dry *p*-xylene and added to the reactor. Then predetermined amount of $\text{RuCl}_2(\text{PPh}_3)_3$ was dissolve in chlorobenzene and added to the reactor. The reactor then was filled with 14–20 MPa pressure of hydrogen and the temperature was raised to the set point to proceed for 5–8 h. Finally, the reaction solvent was poured into 500 mL of ethanol and the white precipitate was collected by filtration and dried under vacuum to constant weight.

Measurements

$^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra were recorded in CDCl_3 at 25 or $50\text{ }^{\circ}\text{C}$ on a Varian Unity Inova 400 spectrometer. Molecular weight and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) against narrow molecular weight distribution polystyrene standards on a Waters 2414 refractive index detector at $40\text{ }^{\circ}\text{C}$ with THF as the eluent or a Waters 150 at $135\text{ }^{\circ}\text{C}$ with 1,2,4-trichlorobenzene as solvent. DSC experiments were carried out on a TA Instruments (New Castle, DE, USA) Q10 calorimeter. Calibration was performed with indium and tin, and all tests were run employing ultrapure nitrogen as the purge gas. DSC heating and cooling scans were performed at 10 K/min over the temperature range $0\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ for standard measurements.

RESULTS AND DISCUSSION

The block copolymer was first synthesized *via* sequential monomer addition (see the supporting information, SI) and the relative length of the blocks in the copolymer can be fine-tuned by changing the monomer composition in the feed. The resulting polymer was characterized by GPC, NMR and DSC. Consider the characterization of one representative block copolymer for example. The GPC (as shown in Fig. 1) shows that the molecular weight of the *i*PS block is 2.9×10^5 and the PBD block is 1.6×10^5 with a molar ratio of 0.8 in narrow molecular weight distribution. The ^{13}C -NMR (as shown in Fig. 2) shows that the PS block is isotactic polystyrene with the characteristic peak of $\delta = 146.5$ and 43.1 (mmm $\geq 95\%$), and the PBD block is 1,4-*trans*-polybutadiene with the characteristic peak of $\delta = 32.9$ and 130.2 (1,4-*trans* addition $\geq 90\%$). Calculated from the ^1H -NMR (as shown in Fig. 3), the molar ratio of styrene/butadiene is 0.8, which is consistent with the results of GPC characterization and indicates the living polymerization of styrene and butadiene. The DSC scan (as shown in Fig. 4) shows the melting temperatures of *i*PS and 1,4-*trans*-PBD blocks, 223°C for *i*PS block and 41°C (76°C) for 1,4-*trans*-PBD block, which confirms the crystallinity of the two blocks.

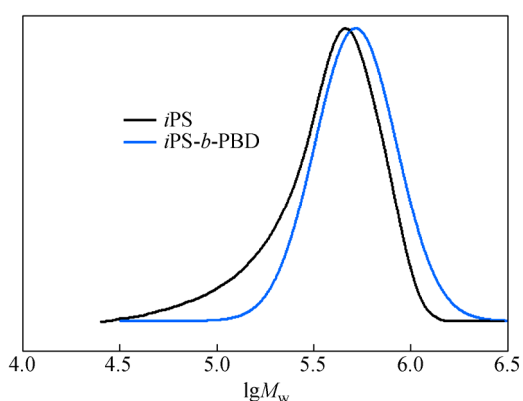


Fig. 1 GPC profiles of the *i*PS block before feeding butadiene and the final *i*PS-*b*-1,4-*trans*-PBD

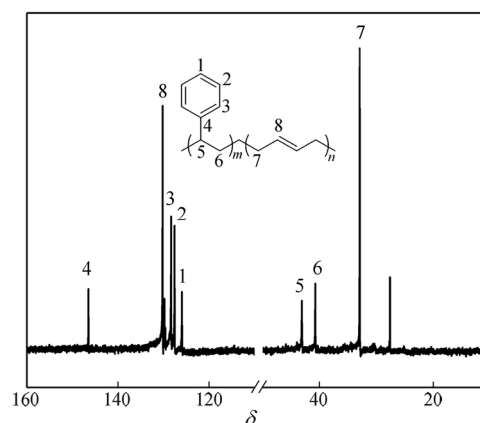


Fig. 2 ^{13}C -NMR spectrum of *i*PS-*b*-1,4-*trans*-PBD

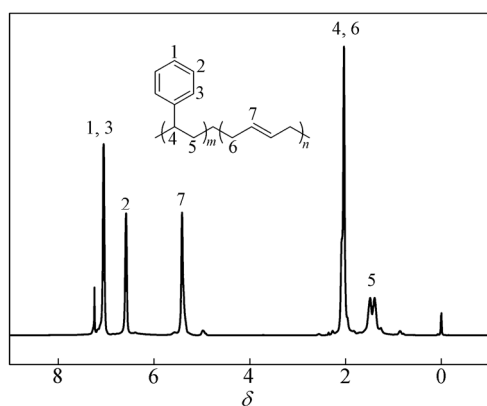


Fig. 3 ^1H -NMR spectrum of *i*PS-*b*-1,4-*trans*-PBD

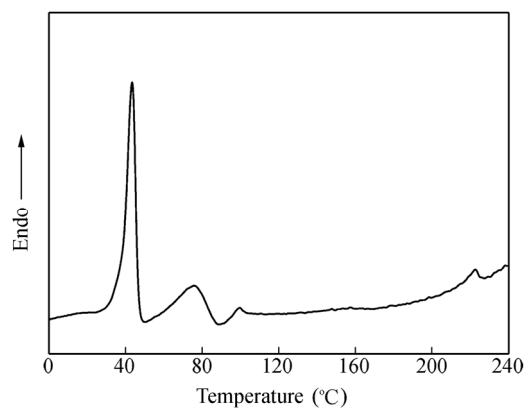
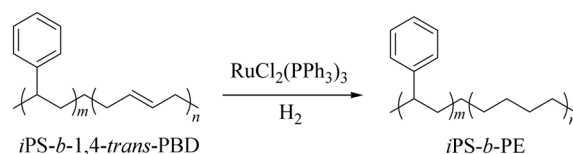


Fig. 4 DSC profile of *i*PS-*b*-1,4-*trans*-PBD at 10 K/min heating rate

The hydrogenation of 1,4-*trans*-PBD block in *i*PS-*b*-1,4-*trans*-PBD was carried out as per the procedures^[53] (as shown in Scheme 2). $\text{RhCl}(\text{PPh}_3)_3$ is an effective catalyst for the hydrogenation of polybutadiene but rhodium is a precious metal^[54, 55]. As an element of the same subgroup, ruthenium has a similar property as rhodium but is less expensive. Therefore, we chose $\text{RuCl}_2(\text{PPh}_3)_3$ as the catalyst for the selective hydrogenation of *i*PS-*b*-1,4-

trans-PBD. The stereoregular diblock polymer of *iPS-b-1,4-trans*-PBD was hard to dissolve in *p*-xylene at room temperature. After heating to 125 °C for several hours, the polymer gradually got dissolved and was transferred to the reactor. Since the catalyst $\text{RuCl}_2(\text{PPh}_3)_3$ was more soluble in chlorobenzene than in *p*-xylene, chlorobenzene was chosen to be the solvent of $\text{RuCl}_2(\text{PPh}_3)_3$.



Scheme 2 The hydrogenation of 1,4-*trans*-PBD block in *iPS-b-1,4-trans*-PBD

It is noted that the amount of the catalyst, the reaction temperature, the reaction time and the hydrogen pressure affect the hydrogenation efficiency. Generally, the hydrogenation of SBS was performed at 150 °C with a hydrogen pressure of 1.4 MPa for 5 h to reach a degree of hydrogenation of 98%. When the polymer was *iPS-b-1,4-trans*-PBD with a styrene/butadiene molar ratio of 0.21:0.79 (denoted by *iPS*_{0.21}-*b*-PBD_{0.79}), the degree of hydrogenation was 92.1% under the same reaction conditions (as shown in Fig. 5). Nevertheless, as the polystyrene block became longer (*iPS*_{0.30}-*b*-PBD_{0.70}), the degree of hydrogenation was reduced to 70.5% (as shown in Fig. 6). It is supposed that the reduction of the hydrogenation efficiency was caused by the increase of the steric effects of the aromatic ring in the polystyrene block. To accelerate the reaction rate of hydrogenation, the reaction condition was raised to 170 °C with a hydrogen pressure of 1.8 MPa for 8 h, under which the polymer *iPS*_{0.61}-*b*-PBD_{0.39} with a higher styrene content could be hydrogenated with a degree of 95.4% (as shown in Fig. 7). It indicates that the raising of temperature, hydrogen pressure and reaction time could increase the efficiency of hydrogenation.

To determine the microstructure of the hydrogenated polymer, ¹H-NMR and ¹³C-NMR characterization were performed. Figure 5 is the ¹H-NMR spectra of *iPS*_{0.21}-PBD_{0.79} before and after hydrogenation. The characteristic peak of 1,4-*trans*-PBD at $\delta = 5.40$ almost disappears and the characteristic peak of polyethylene appears after hydrogenation. Figure 8 is the ¹³C-NMR spectra of *iPS*_{0.21}-PBD_{0.79} before and after hydrogenation. The chemical shifts of $\delta = 32.9$ and 130.3 are the characteristic peaks of 1,4-*trans*-PBD, which almost disappear after hydrogenation. Moreover, a new peak at $\delta = 30.0$, the characteristic peak of polyethylene, appears after

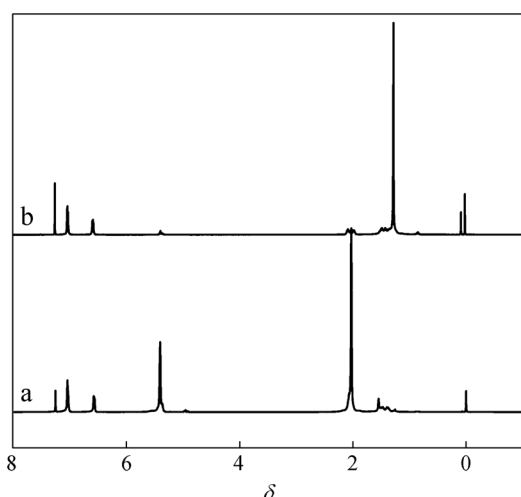


Fig. 5 ¹H-NMR spectra of *iPS*_{0.21}-*b*-PBD_{0.79} before (a) and after (b) hydrogenation at 150 °C with a hydrogen pressure of 1.4 MPa for 5 h

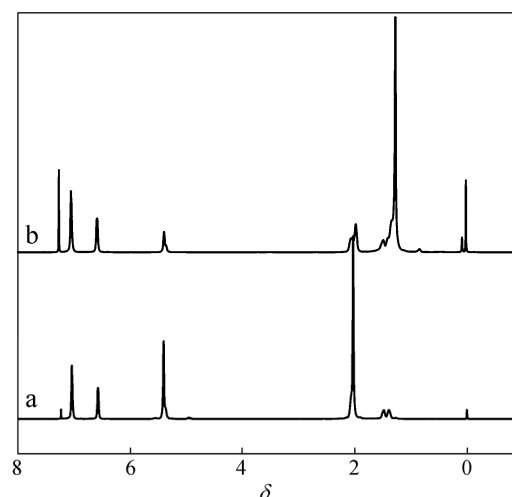


Fig. 6 ¹H-NMR spectra of *iPS*_{0.30}-*b*-PBD_{0.70} before (a) and after (b) hydrogenation at 150 °C with a hydrogen pressure of 1.4 MPa for 5 h

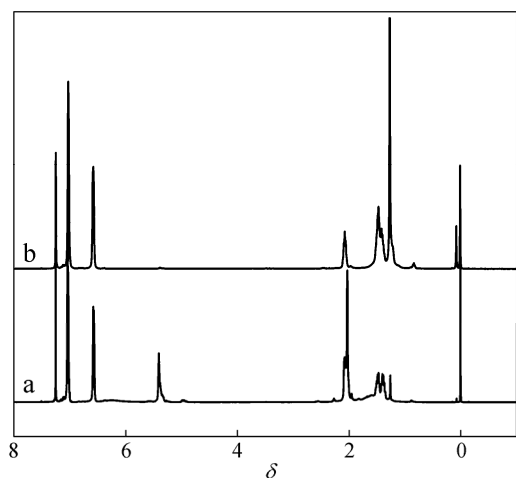


Fig. 7 ^1H -NMR spectra of $i\text{PS}_{0.61}\text{-}b\text{-PBD}_{0.39}$ before (a) and after (b) hydrogenation at $170\text{ }^\circ\text{C}$ with a hydrogen pressure of 1.8 MPa for 8 h

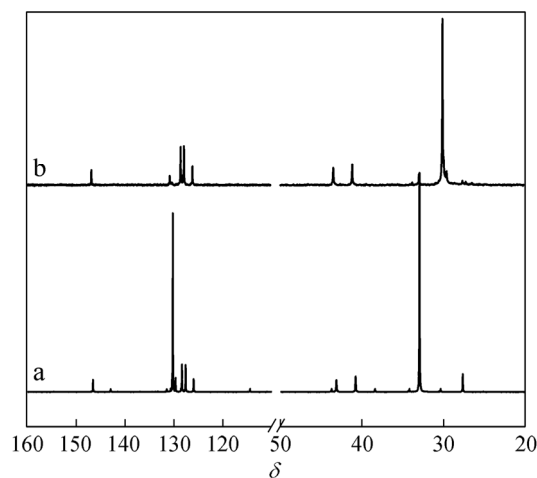


Fig. 8 ^{13}C -NMR spectra of $i\text{PS}_{0.21}\text{-}b\text{-PBD}_{0.79}$ before (a) and after (b) hydrogenation at $150\text{ }^\circ\text{C}$ with a hydrogen pressure of 1.4 MPa for 5 h

hydrogenation. Next to the peak at $\delta = 30$ there are no other peaks and the characteristic peak of isotactic polystyrene remains unchanged, which demonstrates that the polyethylene block formed was linear polyethylene and no other side reaction took place except the selective hydrogenation of polybutadiene. GPC (as shown in Fig. 9) showed that the molecular weight of the hydrogenated copolymer $i\text{PS-PE}$ ($M_n = 5.3 \times 10^5$) was slightly higher than that of the initial copolymer $i\text{PS-PBD}$ ($M_n = 5.1 \times 10^5$) as the hydrogen was added to the polymer chain. In addition, the polydispersity indexes of these two polymers were almost the same (1.21 and 1.28, respectively) and suggested that no crosslinking or chain scission took place during the hydrogenation.

The thermal analysis of the hydrogenated polymer was characterized by DSC (as shown in Fig. 10). After hydrogenation, the two exothermal peaks of $1,4\text{-}trans\text{-PBD}$ almost disappear and a new exothermal peak at $98.8\text{ }^\circ\text{C}$ appears, which indicated the formation of the linear polyethylene block. The thermal stability of the hydrogenated polymer was studied by TGA. The initial decomposition temperature of hydrogenated polymer $i\text{PS-}b\text{-PE}$ is $450\text{ }^\circ\text{C}$, which is improved by $40\text{ }^\circ\text{C}$ compared with the initial polymer $i\text{PS-}b\text{-PBD}$ (the initial decomposition temperature is $410\text{ }^\circ\text{C}$). SEM was used to examine the phase structure of the hydrogenated polymer $i\text{PS-}b\text{-PE}$ (as shown in Fig. 11). The bulk $i\text{PS-}b\text{-PE}$ showed a remarkable phase-separated morphology as $i\text{PS}$ was incompatible with PE in microstructure.

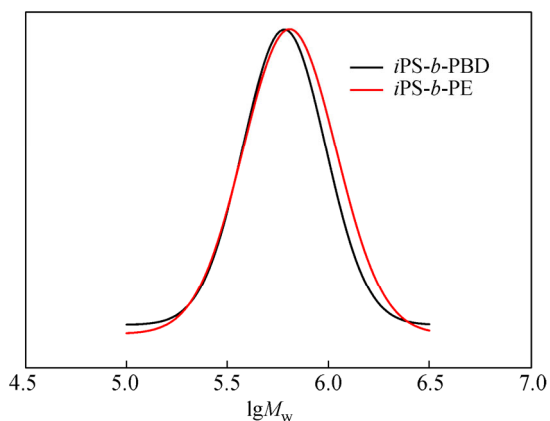


Fig. 9 GPC profiles of $i\text{PS-}b\text{-}1,4\text{-}trans\text{-PBD}$ and its hydrogenated product $i\text{PS-}b\text{-PE}$

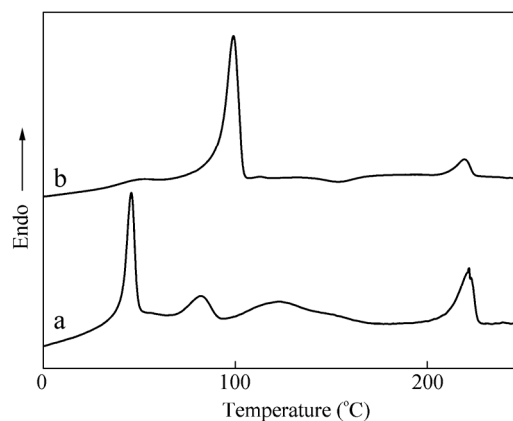


Fig. 10 DSC profiles of $i\text{PS}_{0.21}\text{-}b\text{-PBD}_{0.79}$ before (a) and after (b) hydrogenation at a heating rate of 10 K/min

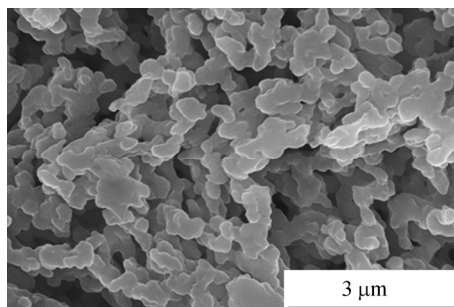


Fig. 11 SEM image of the bulk *iPS-b-PE*

CONCLUSIONS

1,4-Dithiabutandiyyl-2,2'-bis(6-cumenyl-4-methylphenoxy) titanium dichloride (complex 1) activated by triisobutyl aluminum modified methylaluminoxane (MMAO) can serve as excellent catalysts not only for the isospecific living polymerization of styrene and living *trans*-1,4-polymerization of butadiene but also for the block copolymerization of these two monomers *via* sequential monomer addition, affording the diblock copolymer of isotactic polystyrene-block-1,4-*trans*-polybutadiene (*iPS-b-1,4-trans-PBD*) with well-controlled molecular weight and narrow molecular weight distribution and a wide range of *iPS*/1,4-*trans*-PBD contents. Moreover, the 1,4-*trans*-PBD block was highly efficiently hydrogenated by $\text{RuCl}_2(\text{PPh}_3)_3$ which was used as a catalyst to form isotactic polystyrene-block-polyethylene (*iPS-b-PE*).

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