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Synthesis of spherical *trans*-1,4-polyisoprene/*trans*-1,4-poly(butadiene-*co*-isoprene) rubber alloys within reactor

Qingtao Niu, Xiubo Jiang, Aihua He*

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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Trans-polydiene rubber family as high-performance tire stock possessed excellent dynamic properties, including excellent anti fatigue, low rolling resistance, low heat buildup, good green strength, and low abrasion loss. Here, Reactor Granule Technology (RGT) was introduced into the field of synthetic rubber for the first time to produce *trans*-1.4-polyisoprene/*trans*-1,4-poly(butadiene-co-isoprene) rubber alloy, which showed significant improvement in rubber synthetic technologies and great development in abundance of *trans*-rubber family. A series of *trans*-polyisoprene alloys with excellent spherical morphology were successfully synthesized by using sequential multistage polymerization. The alloy was fractionated into four fractions by temperature-gradient fractionation, and the fractionation was analyzed by ^{1}H NMR, ^{13}C NMR, DSC and WAXD.

1. Introduction

Polymer alloy materials with excellent comprehensive performance have the potential to fulfill new challenges in material field nowadays and in the future, such as low cost, environmentally friendly, high-performance, etc. [1–4]. As the most widely applied materials, polyolefin alloys have gained great attention and play a crucial role for the development of plastic materials.

At present, mechanical blending was one of the most adopted methods to achieve polymer alloys, which has a great significance for the improvement of the processing performance of materials, preparation of new materials to meet a particular need and reduction of production costs [5–10]. But due to great difference of the polymer structure, polarity and so on, it is not easy to achieve microscopic homogeneous system only by mechanical blending, even under strong mechanical shear. In particular, a family of in-reactor prepared improved/innovative propylene-based products normally called polypropylene (PP) alloys have been synthesized based on Reactor Granule Technology (RGT) [11–16] considered to be a fundamental polyolefin synthetic technically milestone. The technology can be directly used to synthetic multicomponent alloy materials in the polymerization reactor with the dispersed phase in the scale of less than micron dimension, which is much smaller than that prepared by the traditional mechanical blending technology. So the comprehensive performance of alloy materials improves significantly. Anyway, up to now, the researches based on RGT mainly concentrated on the synthesis of polypropylene [17–21] and polybutene-1 [22] alloy materials, while rubber alloy or polydiene alloy materials prepared with RGT technology have not been reported yet.

Trans-1,4-polyisoprene (TPI) synthesized by bulk precipitation technology instead of traditionally solution polymerization [23,24] showed great potential as high-performance tire materials due to its low production cost and excellent dynamic properties, including excellent anti-fatigue, low rolling resistance, good green strength, and low abrasion loss. Also as another member of *trans*-polydiene families, *trans*-1,4-poly(butadiene-co-isoprene) rubber (TBIR) [25–27] as a new kind of elastomers showed more outstanding anti-fatigue properties, good comprehensive mechanical properties. Anyway, due to the fact that TBIR is easy to dissolve in the monomer and solvent, solution polymerization involves extra postprocessing procedures like flocculation, steam stripping, etc. has to be used.

Here in order to merge so many advantages of *trans*-polydiene family and simplify the synthesis procedure, we introduced in-reactor alloy technology into the synthesis of high-performance TPI alloys with sequential multistage polymerization process (Scheme 1) for the first time. As Scheme 1 shown, in the first stage, active TPI particles with spherical morphology are synthesized by the bulk precipitation polymerization of isoprene with supported Ti-based Ziegler–Natta (Z–N) catalyst, and then the formed TPI

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* Corresponding author. Tel./fax: +86 (0) 532 84022951.
E-mail addresses: ahhe@qust.edu.cn, aihuahe@iccas.ac.cn (A. He).

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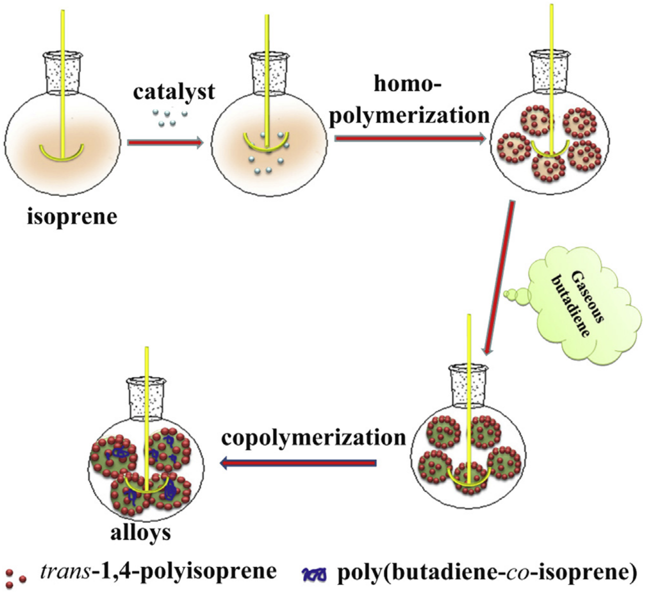

Scheme 1. Schematic illustration of synthesis of *trans*-polyisoprenes alloys.

granules containing active species are used as microreactors to initiate the copolymerization of butadiene and isoprene in the second stage. A series of TPI alloys with different content of elastomers are synthesized successfully by changing copolymerization time and feed ratio of isoprene to butadiene.

2. Experimental

2.1. Materials

The spherical $TiCl_4/MgCl_2$ Z–N catalyst containing 2.34 wt% Ti content was supplied by Oriental Hongye Chemical Company. Triisobutyl aluminum ($Al(i\text{-}Bu)_3$, >98%) was purchased from Yanshan Petrochemical Co., China. Natural rubber (NR, $ML^{100°C}_{(1+4)} = 54$) was the standard stock SCR5 from Hainai, China. Isoprene (Ip) (polymerization grade, Jinshan Petrochemical Company, PetroChina) was distilled over molecularsieve before using. Butadiene (Bd) (polymerization grade) was supplied by the Qilu Petrochemical Company, PetroChina.

2.2. Polymerization procedure

The Ziegler–Natta catalyst was used in the polymerization with $Al(i\text{-}Bu)_3$ as a cocatalyst. The TPI/TBIR in-reactor alloys were synthesized by sequential multistage polymerization process. In the first stage, isoprene, $Al(i\text{-}Bu)_3$ were successively introduced into the reactor, and then the solid catalyst powder was added to start prepolymerization for 1 h at 0 °C, then the temperature of polymerization raised to 20 °C, isoprene bulk precipitation homopolymerization was carried out for 28 h (the conversion was 50.25%), and no residual isoprene monomer outside the TPI particles (the residual monomers were completely absorbed inside the TPI particles) could be observed at this state. Then a certain amount of gas phase butadiene was added into the reactor to copolymerize with the unreacted isoprene inside the active TPI particles at 20 °C for a predetermined reaction time. The copolymerization was finally terminated by adding an excess amount of hydrochloric acid solution diluted with ethanol. The granular products were washed with plenty of ethanol, filtered, and dried in a vacuum oven at 45 °C for 24 h.

2.3. Fractionation procedure of TPI alloys

About 1.1 g of the alloy samples were dissolved in the mixed solvent containing 130 mL of toluene and 130 mL of *n*-heptane at 80 °C for 6 h. After filtration for removing of gel, the flask containing the homogeneous solution of TPI alloy was immersed in a water bath at 60 °C for 30 min, and then cooled down to 20 °C at a rate of 0.75 °C/min and maintained statically at 20 °C for 24 h for isothermal crystallization. The insoluble fraction was collected. The remaining solution was cooled down to 10 °C at the same rate of 0.75 °C/min and maintained statically at 10 °C for 24 h for isothermal crystallization. Later, with repetition of the above process all insoluble fractions under different temperatures (0 °C, −10 °C, −20 °C) were obtained, respectively. Finally, the soluble fraction in the mixed solvent at −20 °C was collected by precipitation with plenty of alcohol. All the fractions were dried at 40 °C in a vacuum for 48 h before weighting and testing.

2.4. Characterization

Weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) (HLC-8320GPC) fitted with a refractive index detector with samples in tetrahydrofuran at 40 °C calibrated by polystyrene standards. Differential scanning calorimetry (DSC) analysis of the alloys was made by a NETZSCH DSC-204 Differential Scanning Calorimeter under N_2 atmosphere. About 5 mg of sample was sealed in aluminum sample pan. The sample was heated from −100 to 180 °C at a heating rate of 10 °C/min to eliminate the thermal history, and then cooled to −100 °C at 10 °C/min. Then the samples were heated from −100 to 180 °C at 10 °C min^{-1}, the heat flow versus time were recorded and T_m was determined in the second scan. Fourier transform infrared (FTIR) spectra of the alloy samples were recorded on TENSOR27 FTIR spectrometer (Bruker, Germany). The samples were dissolved in $CHCl_3$ at 45 °C, then the dissolved polymers were coated on the potassium bromide salt tablet to prepare thin films. X-ray diffraction (XRD) studies of the samples were carried out with a Rigaku D/MAX-2500 X-ray diffractometer (Japan) (45 kV, 300 mA). The scanning range was 5°–40° at a rate of 8°/min. ^1H NMR (500 MHz) spectra were recorded at 25 °C with a Bruker 500 MHz spectrometer with samples in $CDCl_3$ containing tetramethylsilane as standard. The morphology of Bd/Ip in-reactor alloy particle was observed using SMZ1500 stereology microscopy and Jeol 7500F scanning electronmicroscope at an acceleration voltage of 1.0 kV. The Mooney viscosity (ML^{100}_{3+4}) was measured with an EK-2000M Mooney viscometer (Ektron tek, Taiwan) at 100 °C according to GB/T1232-1992. The tensile testing of the copolymers was carried out on a Zwick/Roell: Z005 testing machine (Germany) with dumbbell-shaped specimens at a crosshead speed of 500 mm min^{-1} according to GB/T528-1992.

3. Results and discussion

3.1. Synthesis of in-reactor TPI alloy

A series of TPI alloys were synthesized under different polymerization conditions. Firstly, isoprene homopolymerization was carried out and active TPI particles were obtained with supported Z–N catalyst. Secondly, the active TPI granules were used as microreactors to initiate the copolymerization of butadiene and isoprene. A series of TPI alloys with different content of elastomers are synthesized successfully by changing copolymerization time and feed ratio of isoprene to butadiene. The polymerization results of the synthetic alloy granules were summarized in Table 1. The

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