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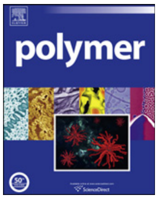

Synthesis and characterization of stereotriblock polybutadiene containing crystallizable high *trans*-1,4-polybutadiene block by barium salt of di(ethylene glycol) ethylether/triisobutylaluminium/dilithium

Xuetao Zhang, Yang Li*, Chunqing Zhang, Yanming Hu, Shunxi Song, Huanhuan Guo, Yurong Wang

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, Dalian University of Technology, Dalian, 116012, China

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ABSTRACT

A series of high *trans*-1,4-low-*cis*-1,4-high *trans*-1,4-stereotriblock polybutadienes (HTPB-*b*-LCPB-*b*-HTPBs) were synthesized through a sequential anionic polymerization of butadiene (Bd) initiated by barium salt of di(ethylene glycol) ethylether/triisobutylaluminium/dilithium (BaDEGEE/TIBA/DLi). The polymers consisted of elastic low-*cis*-1,4-polybutadiene (LCPB) chemically bonded with crystallizable high *trans*-1,4-polybutadiene (HTPB). The block ratios (HTPB:LCPB:HTPB) were designed at 25:50:25 (molar ratio) and finally determined by SEC. The microstructures and sequences of the specimens were investigated by FTIR and NMR. The resultant HTPB-*b*-LCPB-*b*-HTPBs consisted of LCPB block with 52.5% *trans*-1,4 content and HTPB block with 55.9–85.8% *trans*-1,4 content. According to differential scanning calorimetry (DSC), HTPB-*b*-LCPB-*b*-HTPB showed a significant cold crystallization which was discussed in terms of entanglement concept. The cold crystallization temperature (T_{cc}) decreased whereas the melting temperature (T_m) increased with the increasing *trans*-1,4 content of HTPB block.

1. Introduction

Stereo block polybutadiene often exhibits micro-phase separation transition and allows the new complex morphologies due to the balance of relative incompatibility and molecular architectures with unique qualities, which the classical polymer blend cannot show [1–4]. However, up to now, only a few kinds of stereotriblock polybutadiene have been reported. By means of anionic polymerization, 1,2-1,4-1,2-stereotriblock polybutadiene was prepared by Wang [3] and Xie [4], respectively. The polymer had two T_gs and two loss moduli and exhibited micro-phase separation. Further more, 1,2-1,4-1,2-stereotriblock polybutadiene was hydrogenated to be (butene-1-ethylene-butene-1) tri-block copolymer which consisted of more than 30% crystallinity and exhibited the behavior of a thermoplastic elastomer [4].

Consequently, it is significant to synthesize stereotriblock polybutadiene containing crystallizable high *trans*-1,4-polybutadiene (HTPB) block due to the excellent mechanical properties of HTPB, including excellent antifatigue, low rolling resistance, low heat buildup, good green strength and low abrasion loss, which are necessary for the manufacture of products such as high performance tires [5–7].

It has been demonstrated that HTPB can be obtained by titanium [8,9], vanadium [10], and neodymium [11] catalyst systems. The *trans*-1,4 content of HTPB obtained by these catalyst systems is more than 90%, and great crystalline tendency is observed. However, these methods are inferior to anionic polymerization for synthesizing block copolymers, since they produce significant amount of homopolymers.

Potassium-based anionic initiation system can prepare HTPB with 80–95% of *trans*-1,4 content and has acceptable activity. However, they do not hold a “living” character, and the polymer is a heterogeneous mixture due to a number of insoluble HTPB [12,13]. Furthermore, a new anionic initiation system had been reported to obtain HTPB [14–19]. This initiation system showed good solubility in non-polar hydrocarbon solvents (such as cyclohexane), as well as reproducibility, commercial availability, and “living” character. However, to our knowledge, there is no report on the preparation of stereotriblock polybutadiene containing HTPB block.

The aim of the present article is to synthesize stereotriblock polybutadiene containing HTPB block. In this study, the preparation and characterization of high *trans*-1,4-low-*cis*-1,4-high *trans*-1,4-stereotriblock polybutadiene (HTPB-*b*- LCPB-*b*-HTPB) using barium salt of di(ethyleneglycol) ethylether (BaDEGEE)/triisobutylaluminum

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* Corresponding author. Tel.: +86 0411 39893856; fax: +86 0411 83633080.
E-mail address: liyang@dlut.edu.cn (Y. Li).

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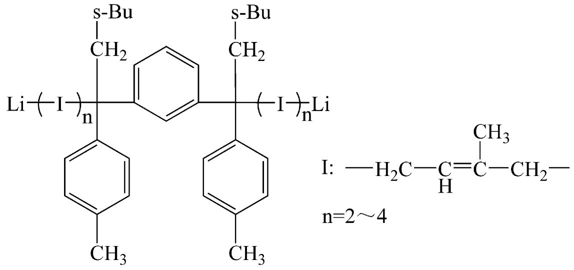


Chart 1. Structure of DLi.

(TIBA)/dilithium (DLi) as initiation system were described. The polymers had well controlled microstructures and macromolecular architecture determined by FTIR, NMR, and SEC. The thermal behaviors were recorded by differential scanning calorimetry (DSC), and the cold crystallization and melting were discussed in detail.

2. Experimental section

2.1. Materials

1,3-Butadiene (Bd, polymerization grade, Beijing Yanshan Petrochemical Co., China) was purified with a small amount of *sec*-butyllithium (*s*-BuLi) and then vaporized to keep water content below 10 ppm. *s*-BuLi (1.3 M solution in cyclohexane/hexane (92/8), Acros Organics Co., Geel, Belgium) and triisobutylaluminium (TIBA, 1.1 M solution in toluene, Acros Organics Co., Geel, Belgium) were diluted in dry cyclohexane under dry nitrogen, respectively. The concentration of *s*-BuLi was calibrated by Gilman double titration method [20]. The concentration of TIBA was calibrated by EDTA complexation titration method [21]. Cyclohexane (analytical reagent, Liaoyang Petrochemical Co., China) was dried and kept over molecular sieves (5Å) to keep water content below 5 ppm, and then it was purged with highly purified nitrogen for more than 15 min prior use to keep oxygen content below 10 ppm.

Barium di(ethylene glycol) ethyl ether (BaDEGEE) was synthesized according to the literature procedure [19].

2.2. The synthesis of dilithium

The synthesis of dilithium was described in the literatures [22,23]. Further more, several isoprene (Ip) units were added to

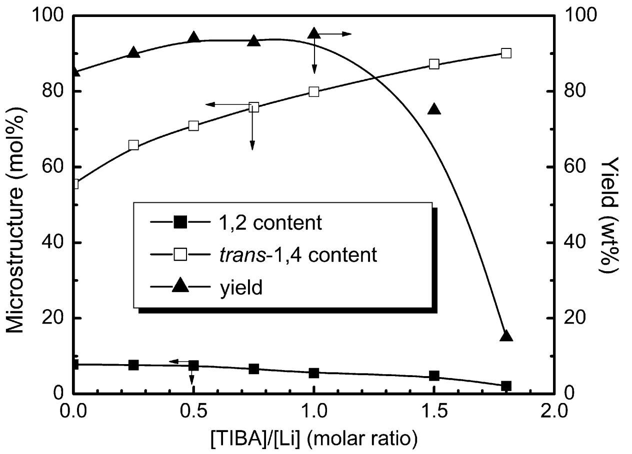
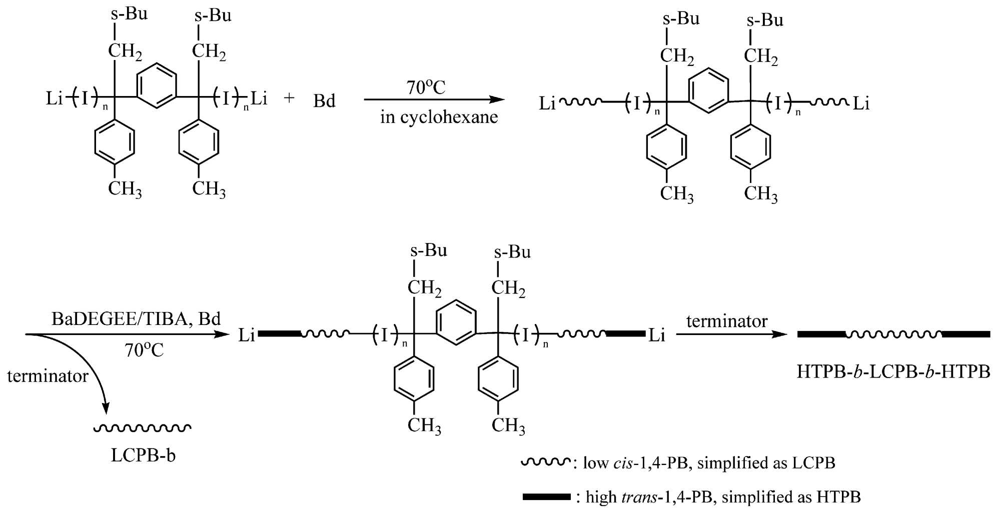


Fig. 1. Effects of [TIBA]/[Li] on microstructures and yield ([BaDEGEE]/[Li] = 0.25, [DLi]/Bd = 1.0 mmol/100 g, 70 °C).

C$^-$Li$^+$ bond to enhance the solubility of the dilithium in cyclohexane. The dilithium we adopted in the polymerization was simplified as DLi (Chart 1). The concentration of DLi was approximately 0.06 mol/L determined by the double titration method of Gilman [20].

2.3. Synthesis of HTPB-b-LCPB-b-HTPB

The synthesis of HTPB-*b*-LCPB-*b*-HTPB (simplified as HLH) was presented in Scheme 1. The LCPB block was prepared with Bd (30.0 g, 10 wt% in cyclohexane) initiated by DLi (0.3 mmol, 0.06 mol/L in cyclohexane) at 70 °C, which results in approximately 52.5% *trans*-1,4 units, 39.7% *cis*-1,4 units, and 7.8% 1,2 units. After completion of the polymerization, the temperature was lowered to 20 ± 1 °C and 6.0 g of the living polymer was terminated by degassed isopropanol for further analysis. The remaining living polymer was divided into six approximately equal parts, and each part was added into a stoichiometric amount of BaDEGEE ([BaDEGEE]/[Li] = 0.25) and TIBA ([TIBA]/[Li] = 0–1.5), which have been shown to produce high *trans*-1,4 addition under the conditions employed. Then quantitive Bd (equals to the remaining living polymer in the reactor) in cyclohexane, which had been purified by *s*-BuLi, was introduced into the reactor. The polymerization proceeded for another 3 h at 70 °C. After finishing the polymerization,



Scheme 1. Schematic presentation for the synthesis of HTPB-*b*-LCPB-*b*-HTPB.