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Fully-reversible and semi-reversible coordinative chain transfer polymerizations of 1,3-butadiene with neodymium-based catalytic systems

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ABSTRACT

Coordinative chain transfer polymerization (CCTP) of 1,3-butadiene was assessed by employing several traditional Ziegler–Natta type Nd-based catalytic systems. Both the types of alkylaluminum as CTA and chloride donor as third component significantly affected the chain transfer characteristic of the CCTP systems. Among the catalytic systems examined, $Nd(OiPr)_3/Al(iBu)_2H/Me_2SiCl_2$ and $Nd(OiPr)_3/Al(iBu)_2H/Al_2Et_3Cl_3$ systems exhibited the highest catalytic efficiency, yielding 6–10 polymer chains per Nd atom in the presence of 20 *equiv.* CTA. Kinetic examination revealed that $Nd(OiPr)_3/Al(iBu)_2H/Me_2SiCl_2$ and $Nd(OiPr)_3/Al(iBu)_2H/Al_2Et_3Cl_3$ catalytic systems proceeded with fully- and semi-reversible chain transfer reactions, respectively. Quantitative formation of polymers was observed in each step of the 1,3-butadiene seeding polymerization, indicating the living mode of the two catalytic systems. Moreover, the triblock copolymers, PBD-*b*-PIP-*b*-PBD and PBD-*b*-PIP-*b*-PCL, were successfully synthesized with $Nd(OiPr)_3/Al(iBu)_2H/Me_2SiCl_2$ catalytic system.

1. Introduction

Ziegler–Natta type catalytic systems based on neodymium salts represent an important class of catalysts and have been utilized industrially for 1,3-congjugated dienes polymerization in a large capacity due to their high catalytic activity and excellent stereoselectivity [1–3]. However, those catalysts are still suffering from the poor controllability over molecular weight, resulting in the polymers with rather broad molecular weight distribution (MWD) [4,5]. It is reported that high *cis*-1,4 polydienes coupled with narrow MWD are desirable for high abrasion resistance, low heat buildup and high tensile properties [6,7]. Living polymerizations [8–10], including anionic polymerization [11,12], living coordination polymerization [13–16], can feasibly realize controlled polymerization of 1,3-conjugated dienes. However, these living polymerization processes produce only one polymer chain per active metal centre, so searching for adaptive approaches to synthesize polydienes with controlled polymerization behaviors more expediently and economically is still imperative.

As an efficient alternative to living polymerization, the new concept of coordinative chain transfer polymerization (CCTP) has gathered an upsurge in research interest recently [17–20]. Besides sharing some similar features with living polymerization, CCTP preserves various unprecedented advantages such as atom economy, controlling of statistical copolymers composition [21–26], and design of new polymeric materials via chain shuttling polymerization [18,27–30]. CCTP involves the use of a single transition metal-based catalyst and a chain transfer agent (CTA). The heart of CCTP is the highly efficient, rapid and reversible chain transfer reaction between active transition metal-based propagating centers and CTA which is usually in the form of main group metal alkyl such as ZnR_2, MgR_2, and AlR_3 [31,32]. In comparison with classical living polymerization, chain transfer to CTA allows the growth of several polymer chains per active species which has grabbed much attention from industrial point of view. Arriola et al. has derived a mathematical model and put forward three kinds of simulations in olefin polymerizations, that is, fully reversible chain transfer, semi-reversible chain transfer and irreversible chain transfer [32,33]. Experiment examples for irreversible chain transfer [34] and

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reversible chain transfer polymerization [35,36] suitable for the simulations have been accumulated, however, that for semi-reversible chain transfer polymerization has not been disclosed yet.

Tremendous advances of CCTP have been made in the field of olefin polymerization in the past decade, and innovative features such as well-controlling over the microstructure and architecture of polymers have emerged [37,38]. The concept of CCTP was introduced to the field of conjugated dienes polymerization only recently and mainly focused on isoprene polymerization. For instance, $Cp^*La(BH_4)_2(THF)_2/EtMg(nBu)$ [25,39–41], *rac*-$[\{Me_2C(Ind)_2\}Y(1,3\text{-}(SiMe_3)_2\text{–}C_3H_3)]/ZnEt_2$ ($Al(iBu)_3$ or $Mg(nBu)_2$) [26], and bis(allyl)$[(C_5Me_4\text{–}C_6H_4\text{-}o\text{-}NMe_2)Gd\ (\eta^3\text{-}C_3H_5)_2]/AlR_3$ catalytic systems [42] can serve as efficient catalysts for CCTP of isoprene. In addition to these sophisticated lanthanide complexes based catalyst systems, traditional Ziegler–Natta type neodymium (Nd)-based catalytic systems are developed for the CCTP of isoprene by our group [43,44]. However, the CCTP of 1,3-butadiene remained less explored. *Trans*-1,4 stereoselective chain transfer polymerization of butadiene was reported by using $Nd(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me\text{-}Ph)_3(THF)/Mg(n\text{-}Hex)_2$ system [45]. *Cis*-1,4 stereoselective chain transfer polymerization of butadiene was achieved by using $Nd(vers)_3$ based catalyst systems, however the polymerization rate was highly decreased in transfer conditions [46,47]. Recently, chain shutting copolymerization of styrene, isoprene, and 1,3-butadiene was reported by using two different scandium catalysts with $Al(iBu)_3$ as chain shuttling agent [48]. Hence, it is necessary to explore new catalytic systems for CCTP of 1,3-butadiene to get a deep understanding of the polymerization mechanism.

In this contribution, we examined the ability of several typical Ziegler–Natta Nd-based catalytic systems for the CCTP of 1,3-butadiene. The effects of various chain transfer agents based on alkylaluminum and chloride donors on the chain transfer ability of catalytic systems were firstly assessed. The kinetic experiments were designed and carried out to examine the polymerization process with different catalytic systems. We report notably herein fully-reversible and semi-reversible coordinative chain transfer polymerizations of 1,3-butadiene, which have never been reported as far as we are aware. Moreover, the living metal-polybutadienyl species could further initiate block copolymerization, affording PBD-*b*-PIP-*b*-PBD and PBD-*b*-PIP-*b*-PCL triblock copolymers.

2. Experimental

2.1. Materials

$Nd(OiPr)_3$ was purchased from J&K Chemical Co. and used as a toluene solution (0.10 mol/L). This compound is actually an oxo-isopropoxide cluster of the type $[Nd_5(\mu_5\text{-}O)(\mu_2\text{-}OiPr)_4(\mu_3\text{-}OiPr)_4(OiPr)_5]$ [49] and generally denoted as $Nd(OiPr)_3$ [50,51]. We added this sentence into the experiment part. Neodymium versatate $[Nd(vers)_3]$ was synthesized according to the literature [52] and diluted to 0.1 mol/L by toluene. Alkylaluminum [$AlEt_3$, $AlEt_2H$, $Al(iBu)_3$, $Al(iBu)_2H$, and $Al(Oct)_3$] were commercial products of Akzo Nobel and diluted with toluene into 2.0 mol/L solution. Me_2SiCl_2, CCl_4, $tBuCl$, $Al(iBu)_2Cl$, $AlEt_2Cl$, $AlEtCl_2$, and $Al_2Et_3Cl_3$ were purchased from Sigma–Aldrich and diluted with toluene into 0.20 mol/L solution. 1,3-Butadiene was supplied by Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å and KOH prior to use. Isoprene was purchased from Fluka and refluxed over CaH_2 for 2 h, and distilled prior to use. ε-Caprolactone (ε-CL) was purchased from Alfa, dried over CaH_2 and then distilled under reduced pressure before use. Toluene was refluxed over sodium/diphenylketyl under nitrogen and then distilled before use.

2.2. Polymerization procedures

All the manipulations were performed under a dry nitrogen atmosphere. A detailed polymerization procedure is described as a typical example. $Nd(OiPr)_3$, 1,3-butadiene, $Al(iBu)_2H$, and $Al_2Et_3Cl_3$ in toluene solution at designed ratios were injected into a glass tube with septum via syringes and then aged at 50 °C for 40 min before use. The additional alkylaluminum supplied by alkylaluminum chloride was not taken into account when calculating the aluminum level in the catalyst.

A toluene solution of 1,3-butadiene (1.85 mol/L, 20 mL) was placed in an oxygen- and moisture-free ampule capped with a rubber septum. After the monomer solution was brought to a desired temperature, the preformed catalyst solution was added. Polymerization was carried out at 50 °C for 5 h and quenched by adding 2.0 mL acidified ethanol containing 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. The polymer was washed with ethanol repeatedly, and then dried in vacuum at 40 °C to constant weight. The polymer yield was determined by gravimetric analysis. For the synthesis of triblock copolymer PBD-*b*-PIP-*b*-PBD, firstly, the living polybutadiene was prepared as described above, and then a toluene solution of isoprene (24 mL, 1.5 mol/L) was added into the ampule, after the system kept for 5 h, a toluene solution of 1,3-butadiene (1.85 mol/L, 20 mL) was added. The precipitation and dry procedures of block copolymer is the same as that of polybutadiene preparation. The experimental procedure for the synthesis of triblock copolymer PBD-*b*-PIP-*b*-PCL is similar to that described for PBD-*b*-PIP-*b*-PBD triblock copolymer.

2.3. Characterization

The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured at 30 °C by using gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF), and a Waters 2414 refractive index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min. Sample solutions were filtered through a 0.45 μm microfilter before injection. The values of M_n and M_w/M_n were calculated by using polystyrene calibration. The column was calibrated with monodisperse polystyrene (PS) standards having the Mark-Houwink constants $K = 1.05 \times 10^{-4}$, $\alpha = 0.731$ for PS, and $K = 2.46 \times 10^{-4}$, $\alpha = 0.732$ for polybutadiene. The microstructure of polymers was determined by ^1H NMR and ^{13}C NMR recorded on a Varian Unity 400 MHz spectrometer in $CDCl_3$ at room temperature [51]. IR spectra measured with BRUKE Vertex-70 FTIR spectrophotometer and films were cast from CS_2 solution onto KBr plates. The isomer units' proportions of polymers were determined as reported in literatures [53,54]. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Diamond DSC apparatus at a heating rate of 10 °C/min under a continuous flow of helium, using aluminum capsules. Glass transition temperatures were determined from the second cycle.

3. Results and discussion

3.1. Screening out catalytic systems for 1,3-butadiene polymerization

It is known alkylaluminum and halide donor are essential for 1,3-conjugated dienes polymerizations by using Nd-based Ziegler–Natta catalyst to achieve high activity and *cis*-1,4 selectivity [55]. It has been proved that the nature of alkylaluminum remarkably influences the chain transfer rate and polymerization rate in the polymerization process [46], consequently, affording polymers