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1,3-Butadiene polymerization using binary, ternary and quaternary cobalt catalysts for high 1,4-*trans*polybutadiene



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ABSTRACT

Binary, ternary, and quaternary cobalt catalysts for 1,4-transpolybutadiene were prepared, and their reactivity and microstructure were studied. A novel binary catalytic system composed of cobalt adduct (2-PhC₆H₄O)₃Al·Co(OAc)₂/AlR₃, a ternary system of Co(2-ethylhexanoate)₂/AlEt(OPh)₂/AlEt₃, where OPh is p-dodecyl phenolate, and a quaternary system of cobalt carboxylate (dialkyl phosphite)/AlR₃/(HOPh, p-dodecyl phenol), for high 1,4-transpolybutadiene were compared in polymerization. The binary molecular catalyst, $(2-PhC_6H_4O)_3Al \cdot Co(OAC)_2/AlR_3$, was designed as cobalt and aluminum bimetallic form of an intermediate structure in the active site of 1,3-butadiene polymerization for high trans configuration. The bulky ligand, 2-PhC₆H₄O-, promotes the syn conformation in the active site in favor of trans configuration in polybutadiene. The catalytic activity was reached to 215 kg/(Co mol h) in the quaternary catalytic system. The microstructure consisted of ca. 91% trans, 2% cis and 7% vinyl. Molecular weight was able to be controlled to ca. 700,000 with MWD ca. 2.0. Catalytic reactivity in 1,3-butadiene polymerization was in the order of quaternary > binary > ternary. Diethyl phosphite and triethyl phosphate remarkably reduce molecular weight with high reactivity. The transpolybutadiene prepared by the quaternary catalyst had the glass transition temperature of *ca.* -80 °C, the melting point of *ca.* 30 °C, and possessed a low level of crystallinity at room temperature. In the carbon black composite, transpolybutadiene showed superior abrasion resistance, tear strength and chipping resistance to natural rubber, but exhibited high compound Mooney viscosity and low moduli.

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1. Introduction

1,3-Butadiene polymerization by various catalysts, using Co [1,2], Ln [3,4], Ni [5,6], Fe [7], Li [8,9], generates the three different polymer microstructures, *cis, trans* and vinyl. Among the catalysts, cobalt catalytic system is of particular interest because it shows relatively high reactivity, and provides various microstructures depending on ligand and active site condition. High *cis*polybuta-diene can be obtained from the ternary system of $Co(O_2CC_7H_{15})_2$ -AlEt₂Cl-H₂O ($O_2CC_7H_{15} = 2$ -ethylhexanoate), while 1,2-*syndiotactic* polybutadiene is obtained by Co(ac-ac)₃-AlEt₃-H₂O-CS₂ [10,11]. High *trans*polybutadiene bearing ~80% *trans*-1,4-configuration can be produced by a ternary system: $Co(O_2CC_7H_{15})_2$ -AlEt₃-phenol derivative [12,13].In 1,3-butadiene polymerization with the ternary catalyst for *trans*polybutadiene,

molecular weight control has been very difficult and butadiene oligomer having noxious smell is inevitable. High *trans* microstructure shows interesting properties in terms of its green strength, tear strength, and cut & chip resistance.

In this paper, our aim in the study is to contrive novel cobalt catalyst systems from binary to quaternary, which are able to control molecular weight with high reactivity, and to examine physical properties of high *trans*polybutadiene.

2. Experimental

2.1. Materials

Cyclohexane and toluene (anhydrous grade) used for the polymerization reaction were purchased from Aldrich and purified over Na/K alloy. Co(2-ethyl hexanoate)₂ and Co(acetate)₂ were obtained from Jin Yang Chemicals and Aldrich Chemical, respectively. SMR 20 was employed as the reference natural rubber. All manipulations



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were performed under an inert atmosphere using standard glove box or Schlenk techniques.

2.2. Measurement

¹H-and ¹³C NMR spectra were recorded on a Bruker 400 MHz Advance III NMR spectrometer (100 MHz for ¹³C{¹H}, CDCl₃). Differential Scanning Calorimetry (DSC) thermograms were obtained from a second heating at a heating rate of 10 °C/min with Thermal Analysis Q10 instrument. Mooney viscosity was measured at 100 °C with a Mooney MV 2000 of Alpha Technologies. Physical properties of the compounds were measured with a universal testing machine (Instron 6021). Dynamic mechanical analysis was employed to characterize the compounds using a Rheo metric Scientific[™] Model DMTA V at a fixed frequency of 10 Hz with 3 $^\circ$ C/min heating rate (sample dimension $8.0 \times 5.0 \times 2.0$ mm). The thermal stability of the samples was conducted with a PerkinElmer TGA with a heating rate of 10 °C/min under a nitrogen atmosphere. Gel permeation chromatography data were obtained using a Waters 2690 system employing connected Waters ultra styregel columns, HMW7 and HMW6E, with a refractive index detector. Tetrahydrofuran was used as solvent at the flow rate of 1.0 mL/min. To monitor crystal growth of *trans*polybutadiene, a sample was filmed on a cover glass by solvent casting (toluene), and the glass was mounted on a polarized optical microscopy (LEICA, DM4000M) equipped with a temperature controller. The sample was heated to 120 °C, and cooled to room temperature, and slowly heated to 80 °C at a heating rate of 10 °C/min to monitor melting of *trans*polybutadiene.

2.3. Calculation

Geometry optimization for our molecular model of the activated catalyst was performed within the DFT formalism, with the hybrid functional mixing the Lee, Yang and Parr function for the correlation part and Becke's three-parameter function for exchange (B3LYP) [14]. The molecular orbitals were constructed with a Gaussian 6-311G** basis set, including polarization p-type functions on hydrogen atoms and d-type functions on C, O, and Al atoms [15]. For cobalt atom, the Wachters-Hay all electron basis set was used [16]. The geometry optimization with no symmetry constraints was carried out by calculating analytical gradients and Hessians. We confirmed that the ground-state geometries had all positive vibrational frequencies. The DFT calculations were performed using the GAUSSIAN 09 program [17]. We built a PBC cell composed of 10 cis/transpolybutadiene polymer units using Amorphous cell. We have the system equilibrated at 298 K by running NPT dynamics on the system for some suitable number of steps. From the equilibrated system, cis and transpolybutadiene polymer molecules in the system are obtained after additional geometry optimization using Forcite plus.

2.4. Catalyst

Binary catalyst activation [18]. To a stirred solution of $(2-PhC_6H_4O)_3Al \cdot Co(OAc)_2$ (560 mg, 0.80 mmol) in toluene (8.0 mL) was added a solution of $(2-PhC_6H_4O)AlEt_2$ (200 mg, 0.80 mmol) in toluene (2.0 mL), and then the mixture was stirred in order for activation for 2 h at room temperature.

Ternary catalyst activation. Added were Al(iBu)₂H, *p*-dodecyl phenol and cobalt (2-ethyl hexanoate)₂ in the order (Co = 0.80 mmol, Co:phenol:Al, 1:10:20 mol ratio). The mixture was stirred in order for activation for 2 h at room temperature.

Quaternary catalyst activation. Added were $Al(iBu)_2H$, *p*-dodecyl phenol, cobalt (2-ethyl hexanoate)₂ and dialkyl phosphite in the order (Co = 0.80 mmol, Co:phosphine:phenol:Al, 1:1:10:20 mol

Table 1

Compounds of natural rubber and transpolybutadiene in carbon black.

| Component (phr) | Natural rubber | TransPBD |
|----------------------------|----------------|----------|
| Natural rubber (SMR-20) | 100 | 0 |
| <i>trans</i> polybutadiene | 0 | 100 |
| Carbon black (N220) | 50 | 50 |
| Zinc oxide | 5 | 5 |
| Stearic acid | 2 | 2 |
| Sulfur | 2.2 | 2.2 |
| TBBS | 0.9 | 0.9 |

phr: per hundred gram rubber.

ratio). The mixture was stirred in order for activation for 2 h at room temperature.

2.5. Polymerization

In cyclohexane (500 g), the activated cobalt catalyst and 1,3butadiene (100 g) were sequentially added to a 5-L pressure glass reactor under a nitrogen atmosphere, and reacted at 60 °C for 2 h. The resulting polybutadiene was terminated by adding methanol, and dried.

2.6. Compounding

The compound recipes of the blends are tabulated in Table 1. Rubber, carbon black (N220), zinc oxide, and stearic acid were placed in a 0.5 L-kneader. In the first mixing step, the rubber



Fig. 1. DFT calculated structure of cobalt alkoxoaluminum complex, $(2-PhC_6H_4O)_3Al\cdot Co(OAc) (C_2H_5)$.

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