



Synthesis of polyethylene/polyester copolymers through main chain exchange reactions via olefin metathesis



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ABSTRACT

The synthesis and characterization of linear polyethylene/polyester copolymers produced by olefin cross metathesis and subsequent catalytic hydrogenation are described. The success of the scrambling reaction between 1,4-polybutadiene and unsaturated polyester via olefin cross metathesis was confirmed by ¹H NMR. Differential scanning calorimetric (DSC) measurements indicated that the size of the copolymer blocks varied gradually with the exchange ratio. Catalytic hydrogenation of the unsaturated copolymers with different exchange ratios was carried out using Pd–Al₂O₃. The crystallinity of the resulting hydrogenated polymers depended on the exchange ratios achieved during olefin cross metathesis. This suggests that the unique sequential structure imparted to the unsaturated polymers during metathesis was retained during the hydrogenation process.

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1. Introduction

Physicochemical characteristics of polymeric materials, including their mechanical, thermal, and optical properties, can be controlled by combining different types of polymers. Polymer blending and copolymerization are frequently used to combine different polymer types. Polymer blending, which involves adjusting the feed ratio of homopolymers, offers the possibility for controlling the properties of polymeric materials. Advancements in polymer synthesis have facilitated the development of a variety of copolymerization methods, which involve the chain-growth polymerization of an appropriate set of comonomers or the step-growth polymerization of monomers that include heteroatoms, aromatics, and even organometallic complexes. Recently, however, polymer reactions based on dynamic covalent chemistry have received much attention as an alternative method for accessing copolymers [1–4].

Polymer backbones with reversible and exchangeable covalent bonds can be reconstructed by external stimuli, even after polymerization. It is possible to scramble different polymer chains through the exchange of these reversible covalent bonds. For example, scrambling of alkoxyamine-containing polyester and polyurethane via thermal radical exchange reactions successfully afforded the corresponding copolymers, which are stable at ambient temperature [5]. Similarly, polymers containing acylhydrazone groups can be scrambled upon heating or in the presence of a pentadecafluorooctanoic acid catalyst to yield scrambled copolymers that exhibit unique mechanical and optical properties [6]. Unlike polymer blending methods, scrambling of polymer chains via dynamic covalent chemistry affords novel, reorganizable copolymers. This method can be used to synthesize copolymers that are difficult to obtain by conventional polymerization methods, such as copolymers that consist of polymers prepared by step-growth polymerization and chain-growth polymerization. Some transition metal-based catalysts have been used to directly synthesize polyethylene-based copolymers via coordination polymerization of ethylene and comonomers that include α -olefins, olefin monomers with polar pendent groups, and cycloolefins [7–10]. However, the synthesis of polyolefins with polar groups in the main chain is still a challenging issue.

Olefin metathesis, which is catalyzed by organometallic complexes, is a powerful method for the reversible formation of

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carbon–carbon double bonds [11]. The development of highly active transition metal carbene complexes as catalysts for metathesis has enabled the synthesis of a variety of olefin-containing polymers with a wide range of functional groups. The reactions proceed by means of acyclic diene metathesis (ADMET) polymerization of α,ω -diene monomers containing functional groups or ring-opening metathesis polymerization (ROMP) of common cyclic olefin monomers bearing functional groups [12–15]. The resulting copolymers have attracted increased attention due to the possibility of further modification or hydrogenation of the olefins in the polymer backbones [16,17]. Moreover, growing interest in the use of plant oils as feedstock for the production of bio-based polymers has made synthetic approaches to aliphatic long-chain polyesters via olefin metathesis increasingly important [18–23].

When viewed from the perspective of catalyzed, reversible bonding, carbon–carbon double bonds can be treated as a type of dynamic covalent bond that facilitates polymer backbone exchangeability [24]. We reported preliminary results on the scrambling reactions of different olefin-containing polymers that were prepared by step-growth polymerization and chain-growth polymerization. These reactions were performed by a main chain exchange using olefin metathesis catalyzed by Grubbs' first-generation catalyst [25]. More recently, olefin metathesis of polymer chains was applied to topological polymers [26] and cross-linked polymers with malleable and self-healing properties [27].

In this paper, we report the success of systematic scrambling reactions between 1,4-polybutadiene (PBD) and unsaturated polyesters (PEs) via olefin metathesis, as well as the hydrogenation of the scrambled copolymers into the corresponding saturated copolymers. Unlike copolymers synthesized by ADMET polymerization and ROMP, this two-step approach of olefin metathesis followed by catalytic hydrogenation allowed for control over the degree of polyethylene and polyester scrambling. Moreover, a statistical distribution of the functional group sequence on the copolymers could be obtained. Consequently, the sequence imparted during the olefin metathesis affects the crystallinity of the scrambled polymer. In addition, this work describes how the degree of scrambling affects the thermal characteristics and crystallinity of the scrambled polymers of polyethylene and polyester.

2. Experimental

2.1. Measurements and equipment

NMR spectra were obtained using a JEOL JNM-EX400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C . Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) as the internal standard in CDCl_3 . The IR spectra were recorded using a Perkin–Elmer Spectrum One infrared spectrometer. The size-exclusion chromatography (SEC) measurements were carried out at 40 °C on a TOSOH HLC-8220 gel permeation chromatography (GPC) system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSKgel SuperH-2500, –4000, and –6000 (6.0 \times 150 mm); the claimed molecular weight range of separation is up to 40,000,000), and a refractive index (RI) detector. Tetrahydrofuran (THF) was used as the eluant at a flow rate of 0.6 mL min^{-1} . The molecular weight calibration curves were obtained using polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed on an EXSTAR6000 DSC (Seiko Instruments Inc.) under a nitrogen atmosphere at a heating rate of 10 °C/min. The samples were sealed in aluminum pans. Thermograms of the third heating process were stored and analyzed. The glass transition temperature was evaluated as an extrapolated

onset temperature of the transition from the intersection of the inflection line with the linear extrapolated specific heat curve encompassing the glass transition region. Thermogravimetry (TG) was performed on a TG/DTA6200 (Seiko Instruments Inc.) under a nitrogen atmosphere at a heating rate of 10 °C/min. The wide-angle X-ray diffraction (WAXD) measurements were carried out using a Rigaku RINT 2500V (Rigaku Co., Ltd.) with a Cu K_α X-ray source (40 kV, 200 mA) on polymer powders. The wavelength, λ , of the incident X-ray was 0.1542 nm. The data collection rate was 3 s per step using 0.05° intervals.

2.2. Preparation of homopolymers

PBD and unsaturated PEs were employed as olefin-containing polymers for polymer scrambling. Polybutadienes can be synthesized by chain-growth polymerization methods, including anionic, radical, and ROMP. In contrast, polyesters, which are representative step-growth polymers, are primarily prepared by polycondensation. The controlled synthesis of copolymers composed of these two polymers is rarely performed. To avoid cross-linking reactions during olefin metathesis, PBD containing no other isomeric butadiene units was prepared via ROMP of 1,5-cyclooctadiene using Grubbs' first-generation catalyst [28]. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PBD were 54,000 and 2.2, respectively. PEs were prepared by the polycondensation of *trans*-3-hexenediyl dichloride and 1,4-butanediol [29]. The chemical structures of the PEs were confirmed by NMR and IR measurements. The M_n and M_w/M_n were 9100 and 2.03, respectively. PBDs with different molecular weights ($M_n = 27,000$, $M_w/M_n = 1.8$ and $M_n = 47,000$, $M_w/M_n = 1.8$) were obtained using the same reaction procedure with varying reaction times.

2.3. Typical procedure for olefin metathesis of PBD

Olefin metathesis of PBD was carried out under modified conditions for ROMP of 1,5-cyclooctadiene [28,30]. PBD (0.44 g, $M_n = 27,000$, $M_w/M_n = 1.8$) was dissolved in dichloromethane (final concentrations: 7, 14, and 20 wt%) within a Schlenk flask, and the solution degassed by three freeze–pump–thaw cycles and stored under argon. A first-generation Grubbs' catalyst (0.1, 0.4, and 0.8 mol% with respect to the total number double bond units in the main chains of polymers, respectively) was then added to the solution. At specific time points, excess amounts of ethyl vinyl ether (2 mL), 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT, 4 mg), and dichloromethane (2 mL) were added to the reaction mixture and stirred for 2 h. The mixture was purified by column chromatography (SiO_2 ; eluant: hexane/chloroform), and the resulting polymer was characterized by GPC.

2.4. Scrambling of PBD and PEs via olefin metathesis

Scrambling of PBD and PEs via olefin metathesis was carried out under modified conditions for ROMP of 1,5-cyclooctadiene [28,30]. In a 10 mL Schlenk flask, equal amounts of PBD (0.80 g, $M_n = 54,000$, $M_w/M_n = 2.2$) and PEs (0.80 g, $M_n = 9100$, $M_w/M_n = 2.0$) were dissolved in dichloromethane (5.4 mL, final concentration of polymers was 18 wt%). The solution was degassed by three freeze–pump–thaw cycles and stored under argon. A second-generation Grubbs' catalyst (80 mg; 0.5 mol% with respect to the total number of double bond units in the main chains of polymers) was then added to the solution. After 12 h, excess amounts of ethyl vinyl ether and 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) were added to the reaction mixture and stirred for 2 h. Tris(2-hydroxymethyl)phosphine (50 eq. with respect to

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