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Metathesis-driven scrambling reactions between polybutadiene or naturally occurring polyisoprene and olefin-containing polyurethane

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ABSTRACT

Controlled scrambling reactions of polybutadiene and olefin-containing polyurethane prepared by step-growth or chain-growth polymerization were accomplished via macromolecular olefin cross-metathesis in the presence of Grubbs' second-generation catalyst to yield scrambled copolymers with different thermal and mechanical properties. In addition, naturally occurring polyisoprene and olefin-containing polyurethane were successfully scrambled, demonstrating that these polymers can be used to synthesize natural/synthetic hybrid materials by the cross-metathesis reaction. Effects of reaction time, solvent, and homopolymer structure on these scrambling reactions were investigated. This metathesis-based approach facilitates the precise control of the scrambling reactions under the applied reaction conditions, thus affording the desired polymer structures with compositions ranging from multiblock to random compositions and enhanced mechanical properties.

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1. Introduction

Synthetic polymers made from oil resources have many applications as foams, plastics, elastic fibers, adhesive materials, or biomedical materials [1,2]. Since a single polymer (homopolymer) provides a limited number of material properties [3], copolymerization and formation of polymer blends are practical approaches to produce various structural materials with new properties from a limited number of existing monomers and polymers [4]. These methods, however, cannot change the primary polymer structure after polymerization. In addition, since oil resources will run out in the near future, a new method to exploit biological and natural resources is required [5].

Recently, polymer reactions based on dynamic covalent chemistry enabled the facile reorganization of polymer structures [6–8]. Polymers containing reversible dynamic covalent bonds offer the possibility to rebuild their structures and to realize facile scrambling between different polymers at the nanometer scale. This can be achieved by exchange reactions between the dynamic covalent bonds, which can be triggered by appropriate external stimuli. This scrambling method promises to be useful in producing new polymers that cannot be prepared by conventional synthetic routes. For instance, alkoxyamine-containing polyesters and polyurethanes have been scrambled by a heat-induced radical exchange process [7c].

Olefin cross-metathesis reactions can also be used in polymer chemistry. Carbon–carbon double bonds exchange in the presence of Grubbs' catalysts (ruthenium carbene complexes) [9]. Originally, the metathesis reaction had been developed for organic synthesis, novel ring-opening polymerizations, and ring-closing reactions, which benefit from the selectivity of the metathesis reaction for carbon–carbon double bonds while leaving any additional functional groups unaffected [10,11]. Diverse olefin cross-metathesis reactions of monomers and polymer containing carbon–carbon double bonds to prepare various polymers have been reported [12–18].

We have previously reported the controlled scrambling of 1,4-polybutadiene and an olefin-containing polyester based on the macromolecular olefin cross-metathesis reaction [19]. This previous study demonstrated that the degree of scrambling can be

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controlled by the reaction time, and therefore, we could tune the copolymer structures from multiblock to random compositions and adjust the thermal properties, the glass-transition and melting temperatures of the scrambled polymers. However, the polymers used in this reaction were synthetic polymers, and unknown effects of the solvent and the homopolymer structure on the scrambling system cannot be excluded. In this paper, we report the polymer scrambling reactions between polybutadiene or naturally occurring polyisoprene (PI), and olefin-containing polyurethane (Scheme 1). The effects of the reaction solvent and the homopolymer structure on the degree of exchange estimated from the change in the polymer structures and the thermal and mechanical properties of the resulting scrambled polymers are discussed.

2. Experimental

2.1. Materials

Grubbs' second-generation catalyst, trimethyl-1,6-diisocyanatohexane, and tris(hydroxymethyl)phosphine (THP) were purchased from Sigma–Aldrich Co. LLC. *N*,*N*-Dimethylformamide (DMF, 99.5%), methylene chloride (CH_2Cl_2, ≥99.9%), and tetrahydrofuran (THF, ≥ 99.9%) were purchased from Kishida Chemical Co., Ltd., and purified with a Glass Counter Solvent Purification System. 1,4-Butadiene and ethyl vinyl ether were purchased from Wako Pure Chemical Industries Ltd. Di-*n*-butyltin dilaurate (DBTDL) was purchased from Tokyo Chemical Industry Co., Ltd. Naturally occurring polyisoprene (PI) was commercial high-ammonia natural rubber latex. The natural rubber was deproteinized by incubating the latex with 0.1% w/v urea (Nacalai Tesque, Inc., 99.5%) and 1.0% w/v sodium dodecyl sulfate (Kishida Reagents Chemicals Co., Ltd., 99%) for 1 h at 30 °C followed by centrifugation at 10^4 G [20,21].

2.2. Measurement

^{1}H NMR (400 MHz) spectroscopic measurements were carried out at 25 °C with Bruker AVANCE-III 400 MHz using tetramethylsilane (TMS) in chloroform-*d* ($CDCl_3$) as an internal standard. Gel permeation chromatography (GPC) was carried out at 40 °C on a Tosoh HLC-8220 GPC system equipped with a guard column (Tosoh TSK guard column Super H-L), three GPC columns (Tosoh TSK gel SuperH 6000, 4000, and 2500), and a UV–Vis detector. THF was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4920–3,000,000; M_w/M_n = 1.02–1.03) were used to calibrate the GPC system. Differential scanning calorimetry (DSC) was performed on an EXSTAR6000 DSC (Seiko Instruments Inc.) under nitrogen atmosphere at a heating rate of 10 °C/min. Thermograms of the third heating process were stored and analyzed. The glass transition temperature was evaluated as the extrapolated onset temperature of the transition of the intersection of the

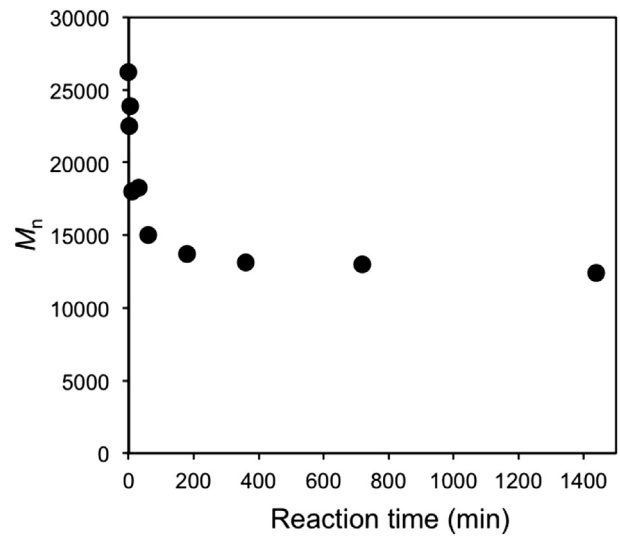


Fig. 1. Time dependence of the number average molecular weight of PBD–*cis*-PU scrambled copolymers prepared by macromolecular metathesis in the presence of Grubbs' second-generation catalyst (1 mol% per total number of double bonds).

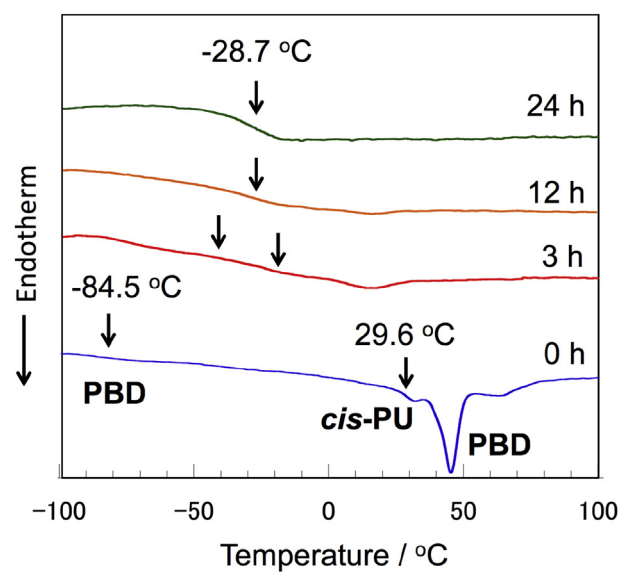
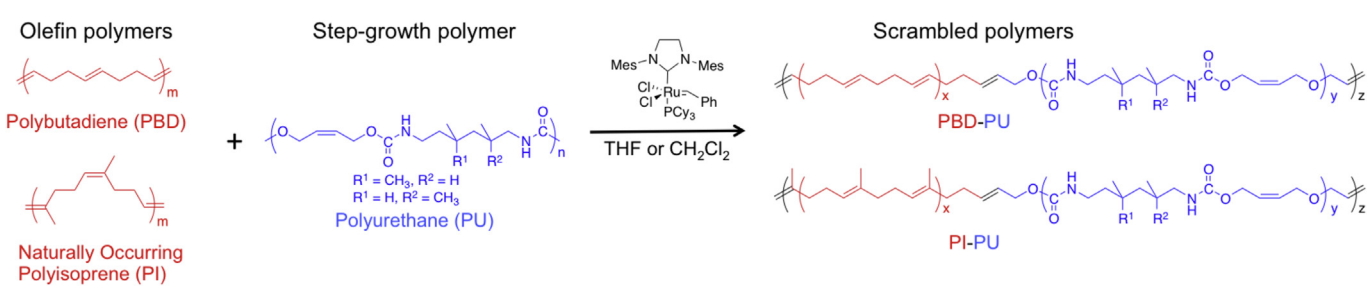


Fig. 2. DSC thermograms of PBD–*cis*-PU scrambled copolymers prepared by macromolecular metathesis in the presence of Grubbs' second-generation catalyst (1 mol% per total number of double bonds). Arrows indicate glass transition temperatures.



Scheme 1. Polymer scrambling between olefin-containing polymers by cross-metathesis reactions.

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