

Polymer Scrambling by Macromolecular Olefin Metathesis

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The authors report the macromolecular olefin metathesis between the main chains of different olefin-containing polymers. The olefin cross metathesis comes down to an apparent interchange of carbon atoms between two double bonds. Polyester containing C=C double bonds in its backbone structure was synthesized by polycondensation reaction of *cis*-2-butene-1,4-diol with adipoyl chloride. A mixture of fractionated polyester ($M_n=12200$, $M_w/M_n=1.14$) and 1,4-polybutadiene ($M_n=128700$, $M_w/M_n=1.18$) showed two apparent peaks in the GPC profile. The metathesis was carried out in dichloromethane using the mixture of polymers in the presence of Grubbs catalyst. As the reaction proceeded, the peaks of the polymer mixture in GPC profiles fused into the single peak ($M_n=17400$, $M_w/M_n=1.46$). The polymer obtained in the reaction was fractionated, and NMR analyses of the fractionated higher molecular weight region ($M_n=77000$, $M_w/M_n=1.17$) were carried out. The peaks assignable to polyester component appeared, although there used to be no polyester component in this region before metathesis. These results indicated that the polymer scrambling reaction proceeded between 1,4-polybutadiene and olefin-containing polyester.

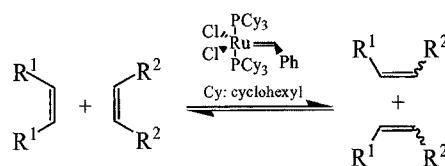
Key words: Polymer reaction, Polymer scrambling, Olefin metathesis, Grubbs catalyst

1. INTRODUCTION

Reorganization of polymer main chains by external stimulation is an attractive method to control the molecular weight and composition of polymer library by combinatorial scrambling. Not only the use of supramolecular chemistry but also the introduction of dynamic covalent chemistry opened the door to the facile reorganization of polymer main chains. Recently, the authors reported that the polyalkoxyamines, in which the initiator units for nitroxide mediated radical polymerization are incorporated, can reorganize upon heating without the formation of any monomeric or oligomeric compounds during the scrambling process.¹ Polyalkoxyamines can be regarded as “dynamic covalent polymer”. However, the concept of dynamic covalent polymer should not be limited in alkoxyamine system.²

The development of well-defined, single-component homogeneous olefin-metathesis catalysts has opened up new horizons in the fields of ring-opening metathesis polymerization (ROMP)³ and ring-closing metathesis (RCM)⁴, affording polymers and cyclic compounds of various ring sizes, respectively. The carbeneruthenium complexes developed by Grubbs and coworkers have found many applications in chemical synthesis as they are commercially available, only moderately air-sensitive, suited for reactions carried out in aqueous media, and tolerant towards many functional groups.⁵ The olefin cross metathesis⁶ has gained importance in organic synthesis as an unique method for the intermolecular exchange of carbon-carbon double bonds (Scheme 1).

In this paper, the authors report the macromolecular olefin metathesis between the main chains of different olefin-containing polymers. The macromolecular olefin metathesis can be expected to consist of three



Scheme 1. Olefin cross metathesis by Grubbs catalyst 1st generation

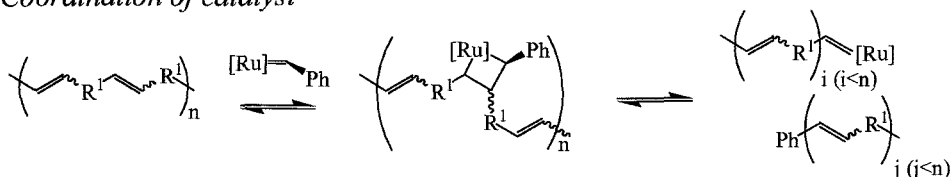
continuous reaction (Scheme 2). First of all, the catalyst coordinates to the double bond in polymer backbone followed by the main chain of the polymer is cut off. Next, active catalyst at the chain end of the polymer attacks a double bond on other polymer backbone. Therefore, two kinds of polymers are conjugated through the metathesis. As a result of the repetition of the reaction, the scrambling of polymers is expected.

2. EXPERIMENTAL SECTION

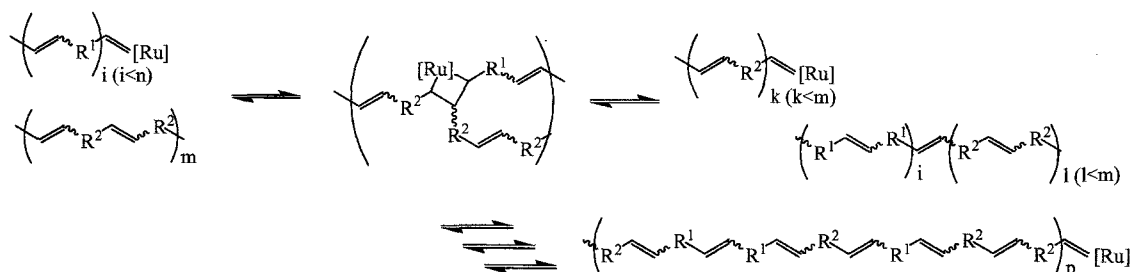
2.1 Synthesis of olefin-containing polyester

Adipoyl chloride (19.25 mL, 100 mmol) was added to the solution of *cis*-2-butene-1,4-diol (8.23 mL, 100 mmol) and pyridine (24.27 mL, 300 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature under nitrogen for 60 h. After the addition of methanol, dichloromethane was added to the reaction mixture and washed with 0.1 mol/L HCl aqueous solution. Then, the organic layer was washed with water five times, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residue was purified by reprecipitation with chloroform/hexane and dried in vacuo to give the olefin-containing polyester as a white powder. Yield

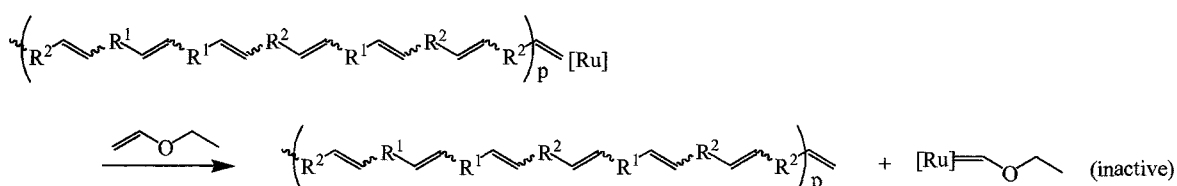
Coordination of catalyst



Polymer scrambling reaction



Elimination of catalyst



Scheme 2. Mechanism of macromolecular olefin cross metathesis

56.0 %, $M_n = 37900$, $M_w/M_n = 1.83$; ^1H NMR: δ / ppm 1.66 (m, 2H), 2.34 (m, 2H), 4.67 (q, $J=3$ Hz 2H), 5.74 (m, 1H); ^{13}C NMR: δ / ppm 24.34, 33.79, 59.96, 127.97, 172.79; FT-IR (film, cm^{-1}): 2944, 2875, 1728, 1470, 1463, 1432, 1407, 1380, 1259, 1177, 1145, 1076, 981, 914, 736, 637, 582.

2.2 Synthesis of 1,4-polybutadiene

1,4-Polybutadiene was synthesized according to the reported method.⁷ Yield 89.2 %, $M_n = 56400$, $M_w/M_n = 1.57$; ^1H NMR: δ / ppm 2.03 (s, 2H), 2.08 (s, 2H), 5.37 (t, $J=4$ Hz, 1H), 5.41 (d, $J=4$ Hz, 1H); ^{13}C NMR: δ / ppm 27.45, 32.72, 32.75, 32.77, 129.33, 129.35, 129.37, 129.53, 129.88, 129.90, 129.93, 129.95, 130.00, 130.03, 130.04, 130.06, 130.08; FT-IR (film, cm^{-1}): 3006, 2917, 2844, 1655, 1448, 1437, 1403, 1352, 1312, 1262, 1236, 1077, 965, 914, 727.

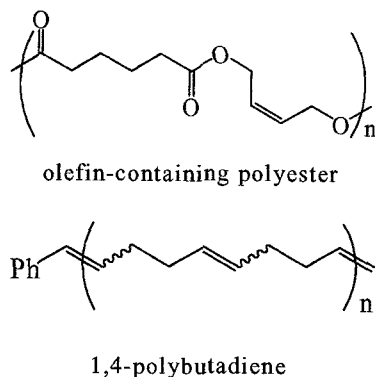


Fig.1 Chemical structures of olefin-containing polyester and 1,4-polybutadiene used in this study.

2.3 Macromolecular olefin metathesis

In a typical experiment, a small vial was charged with Grubbs catalyst (1 mg) under argon. The mixture of equal amounts of polyester (50 mg) and 1,4-polybutadiene (50 mg) was dissolved in dichloromethane (1.85 mL, 3.9 wt%, total concentration of double bond unit: 1 mol/L). The solution was then transferred to the vial containing the catalyst via syringe under vigorous stirring. The reaction was carried out at room temperature. After 24 h, the excess amount of ethyl vinyl ether was added to the reaction mixture and stirred for 2 h, and then characterized by GPC and DSC measurements.

2.4 Measurement

^1H and ^{13}C NMR spectroscopic measurements were carried out with a JEOL JNM-EX400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform- d (CDCl_3). IR spectra were obtained with a Perkin Elmer Spectrum One infrared spectrometer as thin films on NaCl. Number and weight average molecular weights (M_n and M_w , respectively) and the molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a TOSOH system equipped with a refractive index (RI) detector using THF as eluent at a flow rate of 0.8 mL/min, calibrated with polystyrene standards. Fractionation was conducted on a JAI LC-908 HPLC system equipped with two mixed polystyrene gel columns [JAIGEL-2H, JAIGEL-3H (600 x 20 mm)]. Chloroform was used as an eluent at a flow rate of 3.8 mL/min. Differential scanning calorimetry (DSC) was performed by DSC 8230 (Rigaku), using aluminum pan with 3.0 mg of the sample under a nitrogen atmosphere from -140°C to 150°C .

°C at heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1 Polymer scrambling reaction

The synthesized polyester and 1,4-polybutadiene were fractionated by preparative HPLC in order to clarify the progress of polymer scrambling reaction. The two polymers, polyester ($M_n = 13700$, $M_w/M_n = 1.19$) and 1,4-polybutadiene ($M_n = 96100$, $M_w/M_n = 1.23$), were successfully isolated. The mixture of equal amounts of polyester and 1,4-polybutadiene showed two apparent peaks in the GPC profile as shown in Fig.2. The equal amount of polyester and 1,4-polybutadiene was mixed and dissolved in dichloromethane (3.9 wt%, total concentration of double bond unit: 1 mol/L) with Grubbs catalyst. The reaction mixture was stirred at room temperature for 24 h. As the reaction proceeded, the peaks derived from polyester and 1,4-polybutadiene clearly fused into the single peak ($M_n = 17500$, $M_w/M_n = 1.47$).

Whereas, the low molecular weight peak was also appeared in the GPC profile with the progress of the metathesis. This tailing region was recovered by the preparative HPLC. ^1H -NMR, ^{13}C -NMR, IR measurements were performed to characterize the low molecular weight components. In ^1H -NMR spectrum, the peaks derived from 1,4-polybutadiene was clearly observed at 5.38 and 2.04 ppm as well as the peaks of olefin-containing polyester at 5.74, 4.68, 2.34, and 1.68 ppm. However, the ratio of the peaks of 1,4-polybutadiene to those of polyester is large. Considered from the scheme of macromolecular metathesis reaction and the ^1H -NMR spectra, the peak of the low molecular weight region is expected to be the

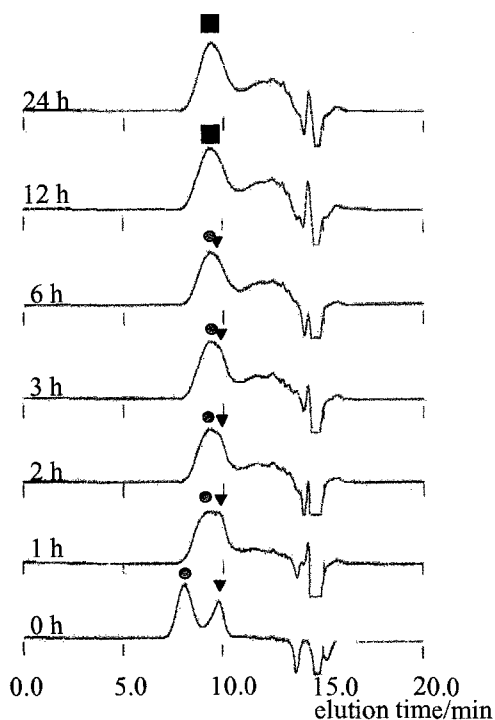


Fig.2 GPC profiles of the mixture of polyester ($M_n=13700$, $M_w/M_n=1.19$) and 1,4-polybutadiene ($M_n=96100$, $M_w/M_n=1.23$) before and after (1, 2, 3, 6, 12, and 24 h) metathesis.

fragment of the polyester and 1,4-polybutadiene with terminated catalyst. The fragmentation was mainly caused by the first scission of main chains and 1,4-polybutadiene is easier to cause the scission of main chain than polyester. The peaks originated to the polyester and 1,4-polybutadiene from ^{13}C -NMR were also observed. In addition, the absorption of the C=O stretching vibration of polyester was observed at 1733 cm^{-1} in IR spectra, and the other peaks were also originated from the polyester and polybutadiene.

3.2 Confirmation of polymer scrambling

Polymer scrambling reaction of the polyester ($M_n = 12200$, $M_w/M_n = 1.14$) and 1,4-polybutadiene ($M_n = 128700$, $M_w/M_n = 1.18$) was conducted in a similar manner. After the reaction, the peaks fused into the single peak of hybrid polymer with $M_n = 17400$, $M_w/M_n = 1.46$ (Fig.3). The resulted polymer was fractionated, and structural confirmation of the fractionated higher molecular weight polymer ($M_n=77000$, $M_w/M_n=1.17$) was conducted by ^1H -NMR measurement. The peaks

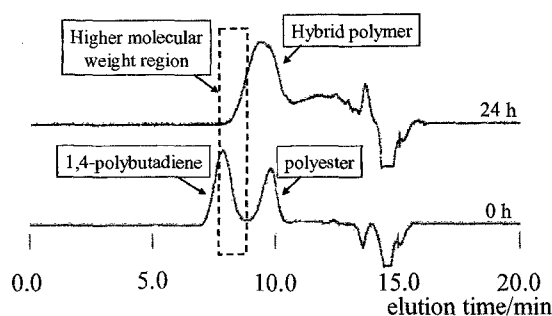


Fig.3 GPC profiles of olefin-containing polyester and 1,4-polybutadiene before and after metathesis in dichloromethane at room temperature.

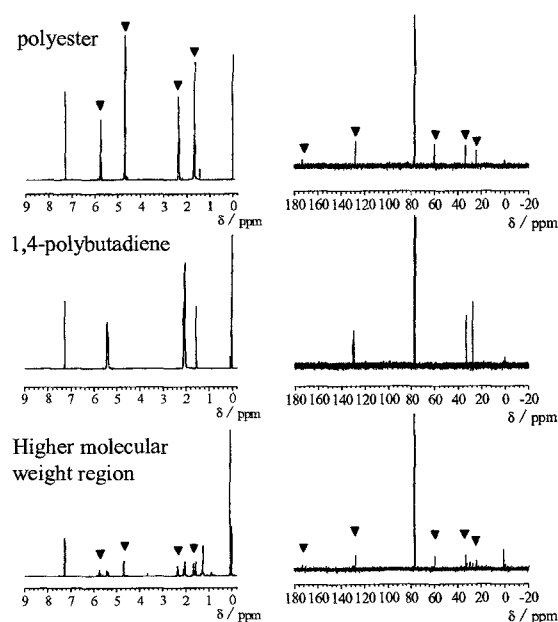


Fig.4 ^1H - and ^{13}C -NMR spectra of olefin-containing polyester, 1,4-polybutadiene, and higher molecular weight region of the hybrid polymer. ▼ denotes the peaks derived from the polyester.

assignable to the polyester were clearly observed, although there used to be no polyester component in this higher molecular weight region before metathesis (Fig.4).

Thermal properties of 1,4-polybutadiene, polyester, polyester/polybutadiene blend polymer, and hybrid polymer were characterized by differential scanning calorimetry (DSC). The hybrid polymer was fractionated to remove the tailing peak. Fig.5 shows the DSC curves of the samples. In the case of olefin-containing polyester, an endothermic peak was observed with a peak at 56.5 °C. This is due to the melting of the crystalline part in the polyester. In the case of 1,4-polybutadiene, a step decrease in the heat flow was observed at -98.6 °C and -51.7 °C. The former is due to a glass transition of the *cis* content of polybutadiene from the glass to rubber state and the latter is due to the *trans* content of that.⁸

For polyester/polybutadiene blend polymer, melting endothermic peak and glass transition temperatures derived from polyester and polybutadiene were observed at same temperature, indicating that these polymers form the macroscopic phase-separation. On the other hand, the melting endothermic peak of the hybrid polymer shifted from 56.5 °C to 45.7 °C. The lowering of melting point was confirmed in hybrid polymer after macromolecular metathesis.

This result indicates that the length of the main chain of polyester is shorter than that of polyester before metathesis, and the lamellar thickness of the polyester crystal decreased in the hybrid polymer. Consequently, the polymer scrambling reaction seems to form random multiblock copolymer with 1,4-polybutadiene and olefin-containing polyester.

4.CONCLUSIONS

The present paper has demonstrated that polymer scrambling reaction proceeds between 1,4-polybutadiene and olefin-containing polyester. By adding the catalyst as an external stimulation, macromolecular olefin cross metathesis proceeded between the different polymers with double bonds in the main chain, and the reorganization after the polymer synthesis of the structure was achieved. This method is quite useful for hybridization of different polymers because one can

readily control the composition and the degree of scrambling.

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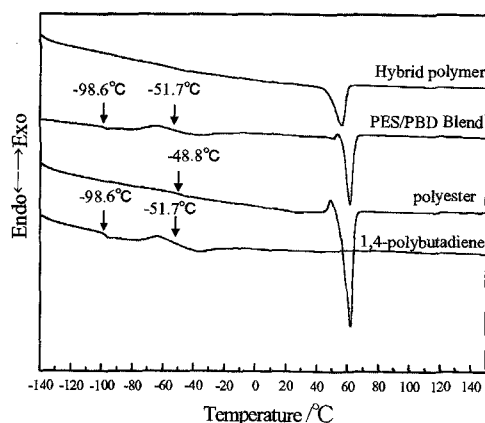


Fig.5 DSC curves of polyester, 1,4-polybutadiene, mixture of polyester and 1,4-polybutadiene, and hybrid polymer after metathesis.