

Supplementary Information for:

**Scrambling Reaction between Polymers Prepared by Step-growth and
Chain-growth Polymerizations: Macromolecular Cross-metathesis
between 1,4-Polybutadiene and Olefin-containing Polyester**

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1. Instruments

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C 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) in THF at 40 °C on a polystyrene gel column [Shodex GPC KF-804L column (300 x 8.0 mm), molecular weight range which is claimed to separate is 100–400000] that was connected to a TOSOH system equipped with a refractive index (RI) detector at a flow rate of 0.8 mL/min. The column was calibrated against six standard polystyrene samples (M_n 800–152000; M_w/M_n 1.03–1.10). 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), with 3.0 mg of the sample under a nitrogen atmosphere from –140 °C to 150 °C at heating rate of 10 °C/min.

2. Materials

Adipoyl chloride, pyridine, *cis*-2-butene-1,4-diol, dichloromethane, and 1,5-cyclooctadiene were purified by distillation. Grubbs catalyst (1st generation, Aldrich) was used as received. Other reagents were used as received without purification.

3. Synthetic Procedures

3-1. Synthesis of 1,4-polybutadiene (PBD)

1,4-Polybutadiene (**PBD**) was synthesized from 1,5-cyclooctadiene according to the reported method.¹ Yield 89 %, $M_n = 56400$, $M_w/M_n = 1.57$; $^1\text{H-NMR}$: δ / ppm 2.03 (s, 2H, CH_2), 2.08 (s, 2H, CH_2), 5.37 (t, $J=4$ Hz, 1H, CH), 5.41 (d, $J=4$ Hz, 1H, CH); $^{13}\text{C-NMR}$: 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 (cm⁻¹): 3006, 2917, 2844, 1655, 1448, 1437, 1403, 1352, 1312, 1262, 1236, 1077, 965, 914, 727.

3-2. Synthesis of unsaturated polyester (PES)

Adipoyl chloride (9.15 mL, 50 mmol) was added to the solution of *cis*-2-butene-1,4-diol (4.41 mL, 50 mmol) and pyridine (8.1 mL, 100 mmol) in dichloromethane (50 mL). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 72 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 the filtrate was evaporated to dryness. The residue was purified by reprecipitation from chloroform/hexane and dried in vacuo to give olefin-containing polyester (**PES**) as a white powder in 91 % yield. $M_n = 22000$, $M_w/M_n = 1.90$; ¹H-NMR: δ / ppm 1.66 (m, 2H, CH₂), 2.34 (m, 2H, CH₂), 4.67 (q, $J=3$ Hz, 2H, CH₂), 5.74 (m, 1H, CH); ¹³C-NMR: δ / ppm 24.34, 33.79, 59.96, 127.97, 172.79; FT-IR (cm⁻¹): 2944, 2875, 1728 (C=O), 1470, 1463, 1432, 1407, 1380, 1259, 1177, 1145, 1076, 981, 914, 736, 637, 582.

3-3. Macromolecular metathesis of PBD and PES

In a typical experiment, a small vial was charged with Grubbs catalyst 1st generation (9.8 mg; 1 mol% against the total double bond units in the main chain of polymers) under argon. The mixture of equal amounts of **PBD** (50 mg) and **PES** (50 mg) was dissolved in dichloromethane (1.85 mL, concentration of polymers were 3.9 wt%). The solution was then transferred to the vial containing the catalyst via syringe and vigorously stirred at room temperature. After 24 h, the excess amount of ethyl vinyl ether was added to the reaction mixture and stirred for 2 h. Then, the mixture was evaporated to dryness and dried in vacuo. Molecular weight was measured by GPC without purification. The obtained hybrid polymers were purified by preparative HPLC with SEC column. The product was fractionated to remove the low molecular weight components and evaporated to dryness and dried in vacuo to give **PBD/PES** hybrid polymer in 68% yield.

The yields of the hybrid polymers were approximately 70% at all reaction time.

The macromolecular metathesis of **PBD** and **PES** was also carried out in the presence of 0.1 mol% Grubbs catalyst 1st generation. The DSC profile of the resulting hybrid polymer shows a melting point of a crystalline part even after the reaction time of 24 h. Systematic wide-angle X-ray diffraction and small angle X-ray scattering data were successfully collected throughout the scrambling process. We will report the detailed data on the change of the crystallinity in the near future.

4. GPC results

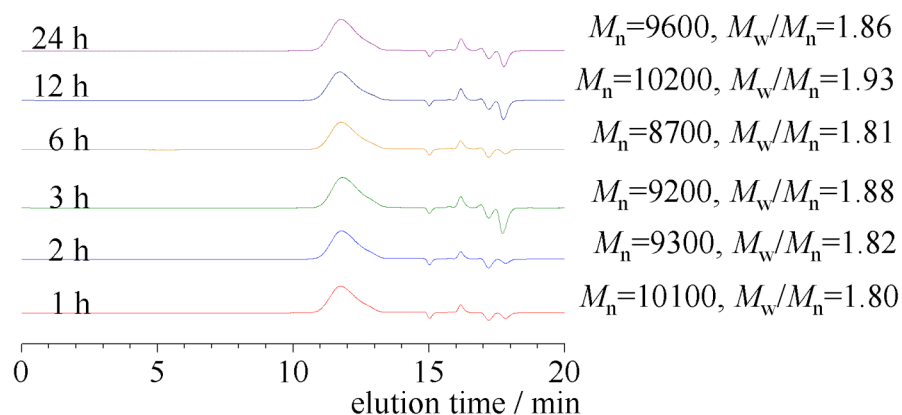


Figure S1. GPC profiles of hybrid polymers prepared by macromolecular olefin cross metathesis with Grubbs catalyst 1st generation (1 mol%); reaction time for 1 h – 24 h.

5. $^1\text{H-NMR}$ spectral change in macromolecular metathesis of PBD and PES

5-1. H-H COSY of a scrambled polymer of PBD and PES

H-H COSY measurement was carried out in order to identify the new peaks. The newly appeared peaks were assigned to the signals that derived from the position generated by the metathesis reaction.

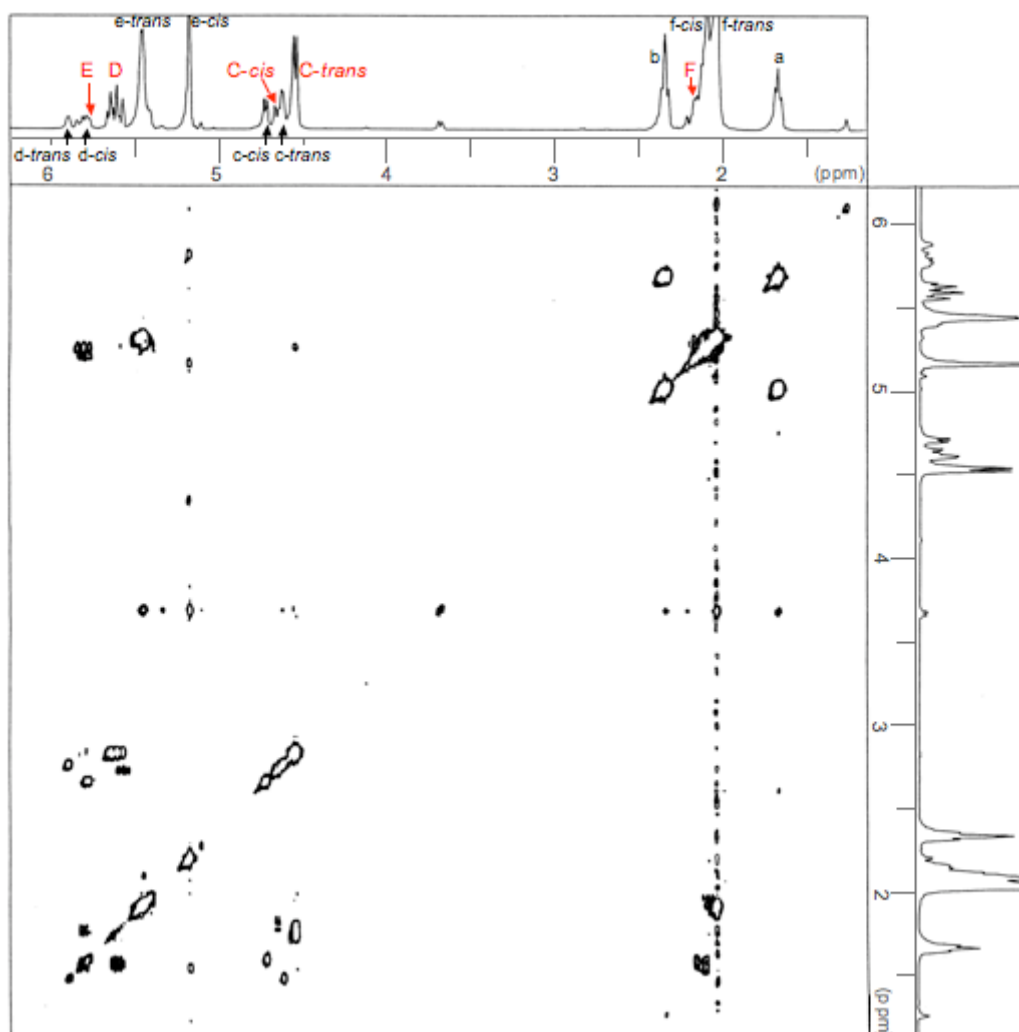


Figure S2. H-H COSY spectrum of hybrid polymer prepared by macromolecular olefin cross-metathesis for 24 h with Grubbs catalyst 1st generation (1 mol%).

5-2. $^1\text{H-NMR}$ spectra of scrambled polymers

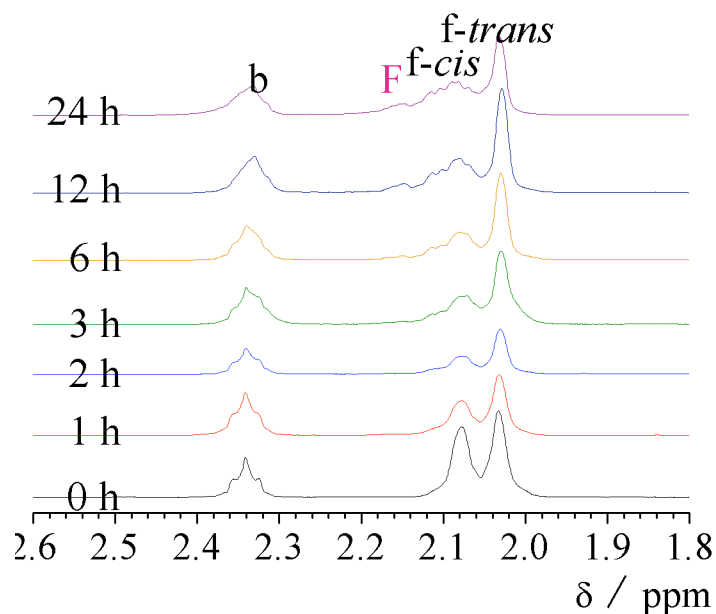


Figure S3. $^1\text{H-NMR}$ spectra at 1.8-2.6 ppm of polyester/1,4-polybutadiene hybrid polymers prepared by macromolecular olefin cross metathesis with Grubbs catalyst (1 mol%).

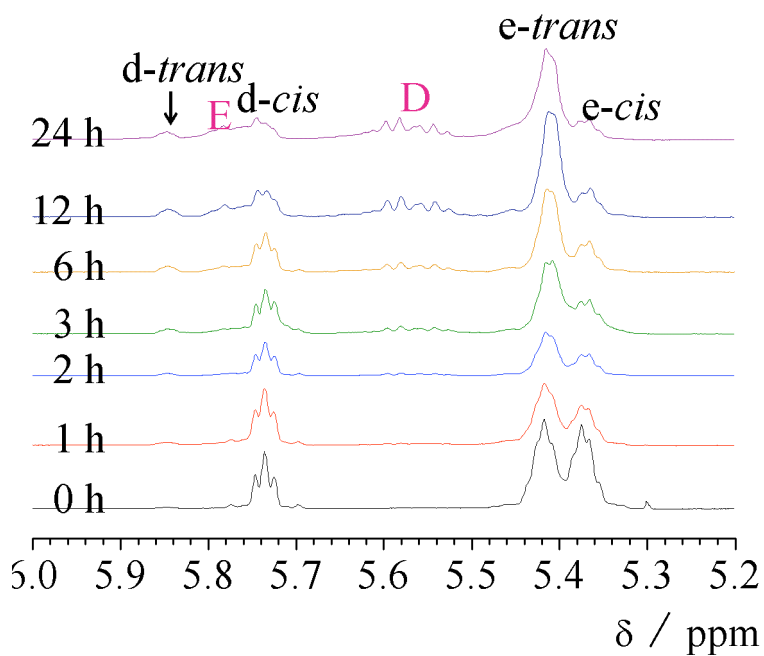


Figure S4. $^1\text{H-NMR}$ spectra at 5.2-6.0 ppm of polyester/1,4-polybutadiene hybrid polymers prepared by macromolecular olefin cross metathesis with Grubbs catalyst (1 mol%).

5-3. Changes in conversion and average segmental length with metathesis reaction time

The newly appeared peaks were assigned to the signals that derived from the position generated by the metathesis reaction. The exchange degree of polyester is calculated from the integral ratio between original peak and exchange peak. An average segment length of polyester was also calculated from the degree of exchange. The exchange degree of polyester can be calculated by the following equation.

$$\text{Exchange degree (\%)} = \frac{I(C)}{I(C) + I(c)} \times 100 (\%) \quad (\text{eq. 1})$$

Here, $I(C)$ represents the integral ratio of exchange peak for polyester (C), and $I(c)$ represents that of original peak for polyester (c). Additionally, an average segment length of polyester is calculated by the following equation.

$$\text{Average segment length; } X(\text{unit}) = \frac{DP_0}{DP_0 \times \frac{I(C)}{I(C) + I(c)} + 1} \quad (\text{eq. 2})$$

6. Supplementary Reference

- 1) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.*, **1996**, 118, 100-110.