A Dynamic Covalent Polymer Driven by Disulfide Metathesis under Photoirradiation

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Experimental Section.

Materials. 2-Hydroxy ethyldisulfide and diethyl disulfide were purchased from Aldrich and distilled under vacuum over CaH_2. Adipoyl chloride (99%) was purchased from Aldrich and distilled under vacuum over P_2O_5. Dichloromethane (99%) and pyridine (98%) were purchased from Wako Pure Chemical Industries and distilled over CaH_2. All other reagents were purchased from commercial sources and used without further purification.

Measurements. ^{1}H (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 for chloroform-*d* ($CDCl_3$). High-performance liquid chromatography (HPLC) analyses of model disulfides were performed at room temperature on a Shimadzu LC-20AD pump equipped with an SPD-20A variable wavelength detector; the pump operated at a flow rate of 1.0 mL min^{-1} and the detector monitored wavelengths at 254 nm. IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer by the KBr method. Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) were estimated by gel permeation chromatography (GPC) in THF at 40°C on a polystyrene gel column [TOSOH TSKgel SuperH2500, TSKgel SuperH6000 (6-150 mm), maximum molecular weight at which separation is claimed to occur: 40000000]. The column was connected to a TOSOH system equipped with a refractive index (RI) detector at a flow rate of 0.6 mL min^{-1}. The column was calibrated against six standard polystyrene samples (M_n: 1060-3690000; M_w/M_n: 1.02–1.08). Fractionation of **DSPES** was conducted on a JAI LC-9104 HPLC system equipped with two mixed polystyrene gel columns [JAIGEL-3H, JAIGEL-4H (20–600 mm)]. Chloroform was used as an eluent at a flow rate of 14.0 mL min^{-1}. Differential scanning calorimetry (DSC) was performed on an EXSTAR6000 DSC (Seiko Instruments Inc.) under nitrogen atmosphere at a heating rate of 10 K/min. 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 at the glass transition region. Thermogravimetry (TG) was performed on an TG/DTA6200 (Seiko Instruments Inc.) under nitrogen atmosphere at a heating rate of 10 K/min. Photoirradiations of model compounds and polymers were carried out using rotary a photochemical reactor, RH400-10W (Riko-Kagaku Sangyo Co., Ltd.), equipped with a 400-W super-high-pressure mercury lamp (Riko-Kagaku Sangyo Co., Ltd.), in which the maximum peak of the radiation intensity was 365 nm in the range of 312–577 nm, was used. The distance between the sample and the lamp was fixed at 75 mm.

Disulfide exchange reaction of 1 and 2 caused by photoirradiation. Equimolar quantities of disulfide-containing compounds **1** (305.1 mg, 2.5 mmol) and **2** (385.6 mg, 2.5 mmol) were mixed in THF(50 ml) as a 0.10 mol L^{-1} solution. The solution was charged in a glass tube, sealed under vacuum, and then photoirradiated at 30°C. The reaction was followed by HPLC (eluent: water/acetonitrile = 1/3 v/v).

Synthesis of disulfide containing polyester (DSPES). Adipoyl chloride (3.58 mL, 25 mmol) was dissolved in dichloromethane (15 mL), and the solution was added to a mixture of 2-Hydroxyethyldisulfide (3.79 g, 25 mmol), dichloromethane (15 mL), and pyridine (4.05 mL, 50 mmol). The reaction mixture was stirred for 72 h under an argon atmosphere and washed with 0.1 N HCl and water. The solvent was evaporated to dryness. The crude polymer was diluted with chloroform, and the solution was poured into hexane. The precipitate was collected by vacuum filtration and dried in vacuo to yield polyester as a white powder (5.9 g, 89% yield). M_n= 20 700, M_w/M_n= 1.87. ^{1}H NMR: δ/ppm 1.67 (m, 4H, CH3), 2.36 (m, 4H, CH3), 2.92 (t, J = 7 Hz, 4H, CH3), 4.34 (t, J = 7 Hz, 6H, CH3). ^{13}C NMR: δ/ppm 24.31, 33.76, 37.23, 62.16, 172.86. FT-IR (KBr, cm^{-1}): 2947, 2871, 1734, 1453, 1385, 1244, 1166, 1077, 992, 749. Anal. calced for **DSPES**: C,45.43; H,6.10. Found: C,45.21; H,45.43.

The thermal properties of the resulting polymer were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry. TGA analysis revealed that the degradation of **DSPES** started around 275 ºC (**Figure S1**). High char content of DSPES was found at 500 °C. DSC thermograms of **DSPES** showed a sharp endothermic peak at 41 ºC, together with exothermic peaks and a baseline shift that originated from the glass transition point of **DSPES** at –50ºC during the heating process (**Figure S2**). Although we have changed molecular weights and molecular weight distribution of the samples, the two exothermic peaks were always observed. The results of TGA and DSC measurements indicated that **DSPES** was stable enough for the heating conditions. It remained unmelted at 30 ºC, which was the temperature for the main chain exchange reactions initiated by photoirradiation.

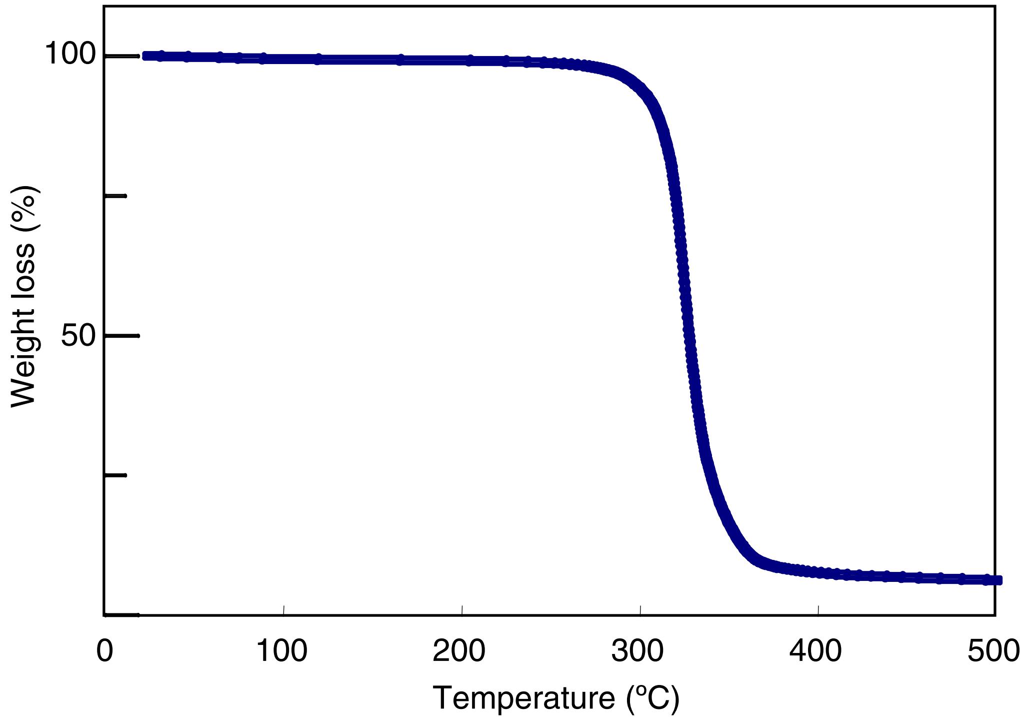

Figure S1. TGA analysis of **DSPES**

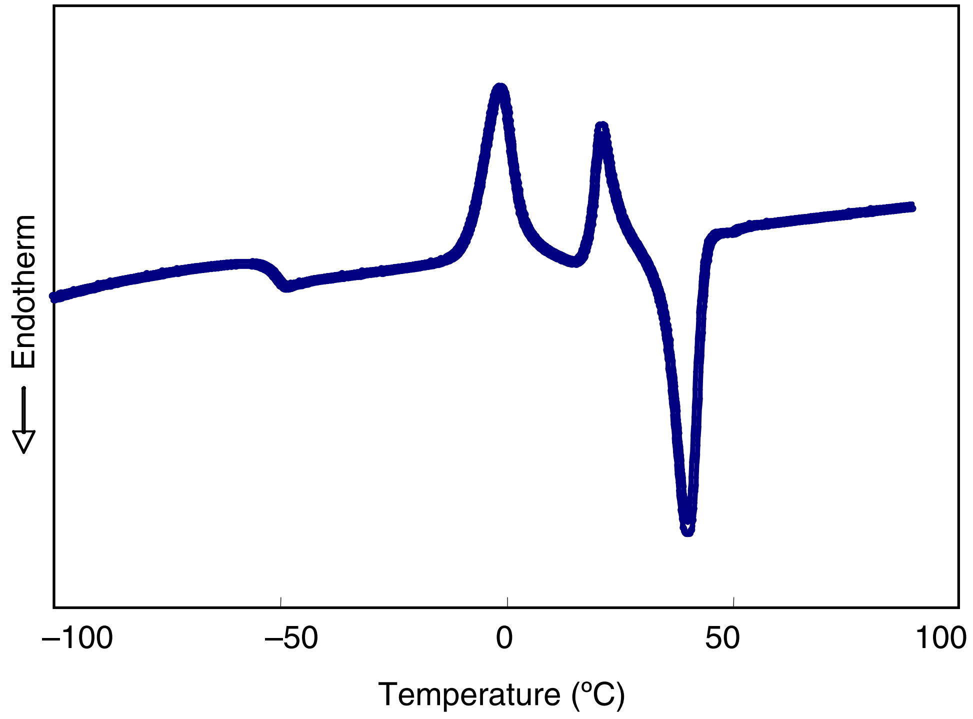

Figure S2. DSC thermogram of **DSPES** at heating rate of 10 °C/min.

Main chain exchange reaction of a film of fractionated DSPES. Fractionated polyester film [Mn = 20000, M_w/M_n= 1.21] was photoirradiated in hexane at 30 °C under an argon atmosphere. GPC and NMR measurements of the resulting polymers were carried out. **Figure S3** shows NMR and spectra of **DSPES** before and after photoirradiation. As can be seen from the spectra, we can conclude that no photochemistry happens at the ester position. This is also confirmed by IR spectra of **DSPES** before and after photoirradiation as shown in **Figure S4**.

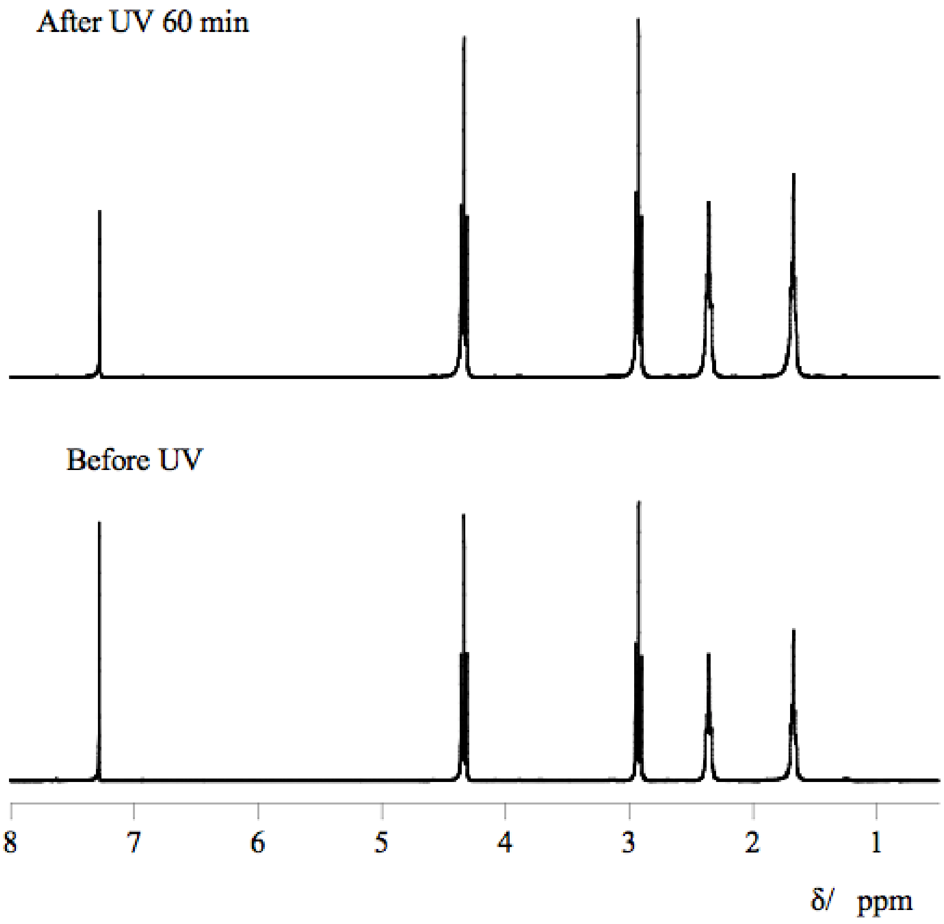

Figure S3. NMR spectra of **DSPES** before and after photoirradiation.

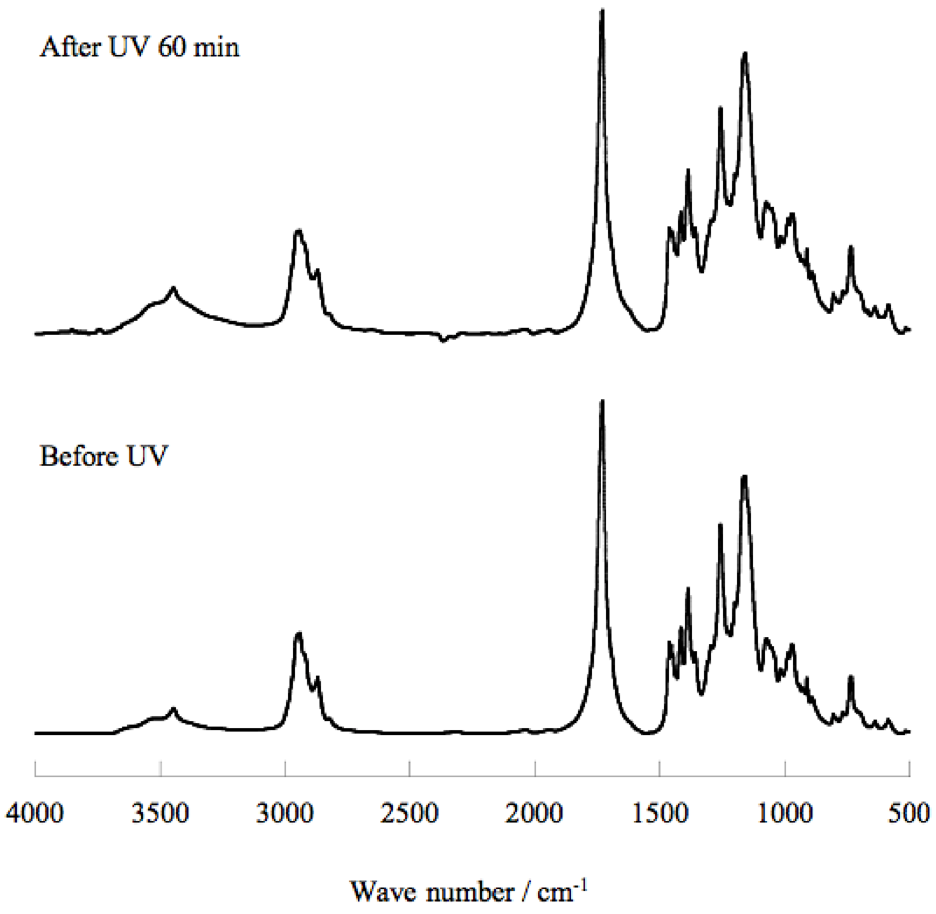

Figure S4. IR spectra of **DSPES** before and after photoirradiation.

Main chain exchange reaction of a film of the mixture of DSPES with different molecular weights. Polyester films (M_n = 64000, M_w/M_n = 1.06 was used as a high molecular weight sample; M_n = 8700, M_w/M_n = 1.54 was used as a low molecular weight sample) were photoirradiated in hexane at 30 °C under an argon atmosphere for 1 h. GPC and NMR measurements of the resulting polymers were performed.

Exchange reaction of DSPES in the presence of benzoyl peroxide.

In order to indicate the radical reactivity of DSPES, we carried out the exchange reaction in the presence of a radical generator in the dark. The reaction was carried out in the presence and absence of benzoylperoxide (BPO) in anisole at 80 °C in the dark. In the absence of BPO, no exchange reaction occurred. In contrast, as shown in **Figure S5**, in the presence of BPO, the exchange reaction of the disulfide-containing polyester did occur.

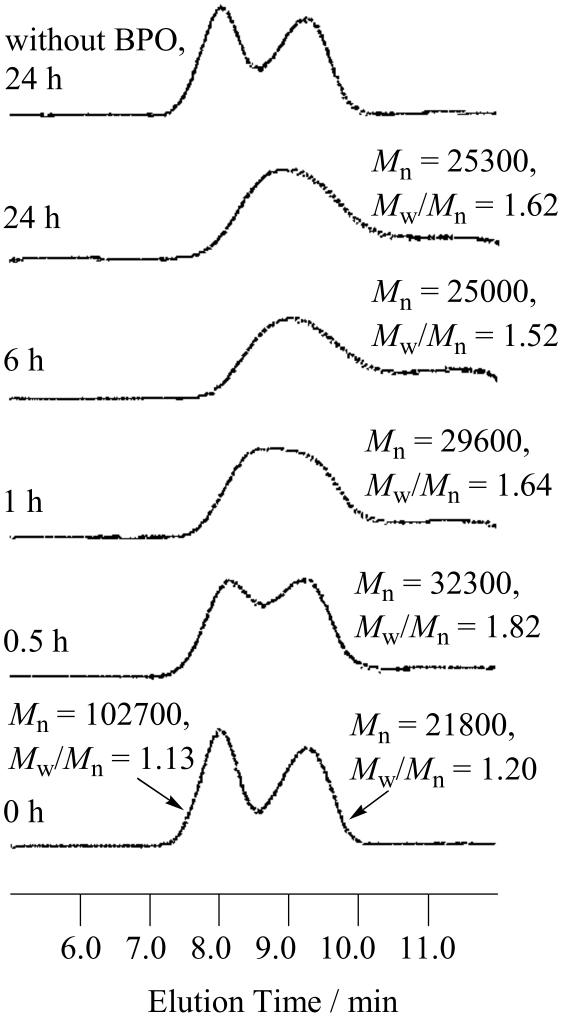

Figure S5. GPC profiles of the mixture of the fractionated disulfide-containing polyester with different molecular weight (M_n = 102700, M_w/M_n = 1.13 and M_n = 21800, M_w/M_n = 1.20) after the reaction in the presence and absence of benzoyl peroxide (1mol% per disulfide) heated at 80 °C in anisole solution (0.20 mol disulfide/L).