

Supporting Information

Double stimuli-responsive behavior of aliphatic poly(urethane-amine)s derived from supercritical carbon dioxide

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General Information. ^1H NMR spectra were recorded on a JEOL Lambda 300 spectrometer using CDCl_3 with Me_4Si as an internal standard. Infrared spectra of KBr pellet samples were recorded by a spectrophotometer JASCO FTIR-610. Urethane contents of the products listed in Table 1 were calculated from the elemental analyses under the assumption of the copolymeric structures containing urethane and amine moieties prepared from corresponding aziridine monomers. The light transmittances of the product solution were measured by a JASCO V-530 UV-Vis spectrometer with an ETC-505T temperature controller. The phase transition temperatures are defined as onset points in their transmittance curves measured for their warm-up period.

Materials. 2-Methylaziridine was purchased from Tokyo Kasei Co. and purified by distillation under reduced pressure. Liquefied carbon dioxide (99.999%) was purchased from Showa Tansan.

Experimental procedure. *CAUTION: Since operations under high gas pressure are involved, safety precautions must be taken at all stages of studies.* Reactions were carried out in a 50 mL stainless autoclave. The autoclave was filled with argon gas and 2-methylaziridine (8.8 mmol) was introduced in the autoclave with a syringe. Then CO_2 was charged through cooling apparatus with an HPLC pump until reaching 3-22 MPa in a steady state. After stirring at 100 °C for 24 h, the reaction was stopped by cooling the autoclave with a dry ice-methanol bath followed by release of gaseous CO_2 slowly. The polymeric product was purified by reprecipitation from methanol solution into diethyl ether to remove low-molecular-weight products and dried in vacuo. The molecular weights of these products were assembled in the range of 10^4 - 10^5 . For **5**, mean M_w was calculated as 2.7×10^4 .

Analyses of the products. In the ^1H NMR spectrum of **5** shown in Figure S1, formation of urethane units by incorporation of CO_2 molecules into the polymer can be confirmed by the signals at 3.6-4.3 ppm attributable to protons at the carbon adjacent to the urethane's oxygen. Furthermore, the signals at $\delta = 3.8-4.2$ and 2.3-2.6 ppm which are corresponding to the methylene protons adjacent to the urethane oxygen and amine nitrogen respectively are also exhibited. In Figure S2, the product **5** should contain urethane group according to the sharp peaks at 1710 cm^{-1} and 1540 cm^{-1} for carbonyl groups as well as the peaks at 1250 cm^{-1} and 1080 cm^{-1} assignable to urethane C–O–C symmetric and asymmetric bending vibrations. Similar results are shown for products **1-4**. These analytical results by ^1H NMR and IR spectroscopies were consistent with the proposed poly(urethane-amine) structure derived from 2-methylaziridine and CO_2 . In Figure S3 and S4, the temperature variable light transmittances of the aqueous solutions of product **5** at various concentration were measured. The LCSTs were tabulated in Table 2 in the main text.

Measurement of Molecular Weight. The molar mass distributions of the products were determined at $35.0\text{ }^\circ\text{C}$ by a SEC using Shodex OHpak SB-806MHQ and SB-804HQ columns at the polymer concentration of 10 mg/mL and dual-detector system consisting of a MALLS device model DAWN-EOS (Wyatt Technology) and a refractive index detector set in the direction of flow. An eluent was an aqueous solution of 0.2 M NaNO_3 /0.5 M CH_3COOH at a flow rate of 0.5 mL/min. All samples were filtered through Millipore Millex-LG (0.20 μm) before analyses.

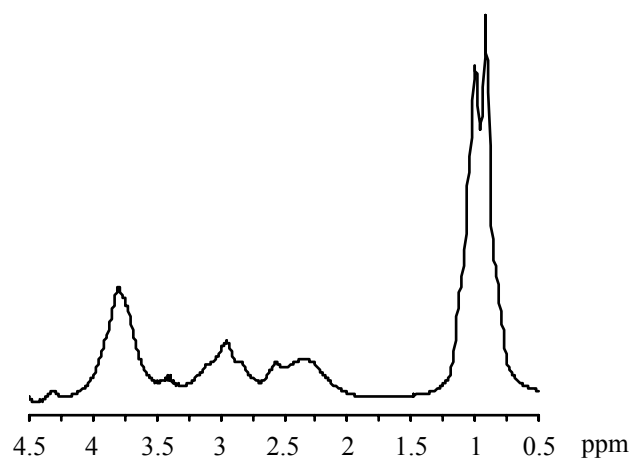


Fig. S1. ¹H NMR spectrum of the product **5**

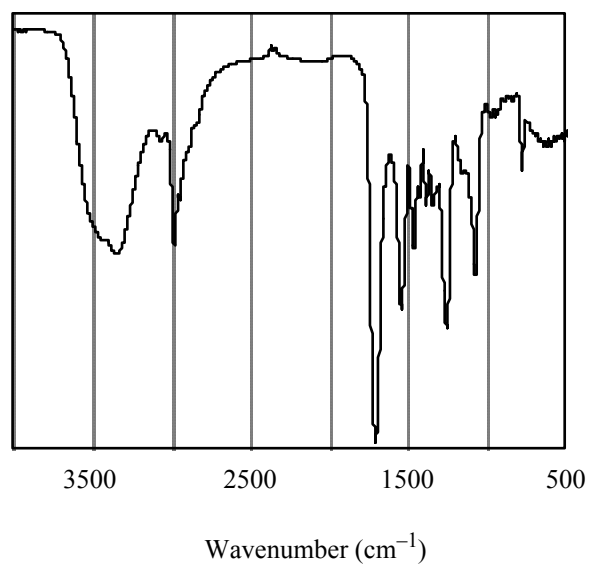


Fig. S2. IR spectrum of the product **5**

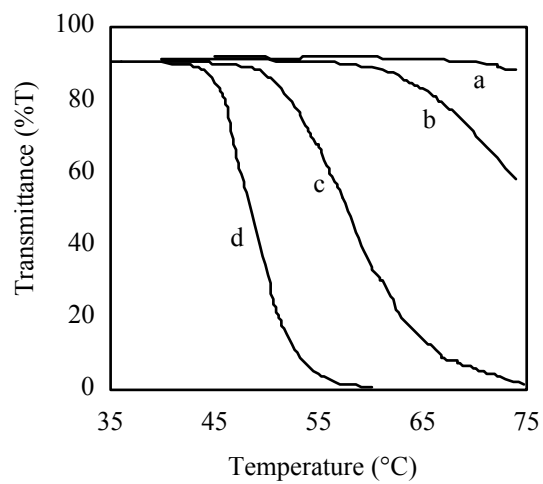


Fig. S3. Light transmittances of the aqueous solutions of product **5**. Each concentration of the solution is (a) 0.10 wt%, (b) 0.20 wt%, (c) 0.40 wt%, and (d) 0.80 wt%.

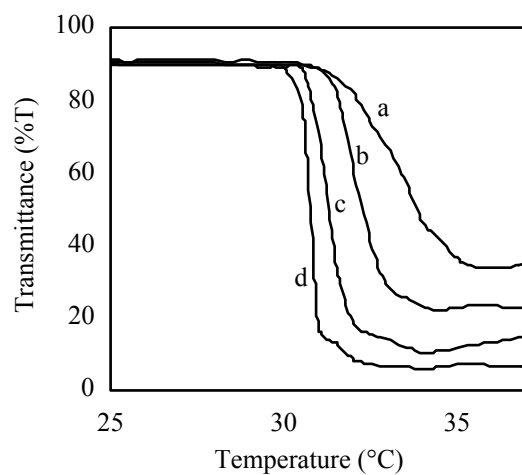


Fig. S4. Light transmittances of the aqueous solutions of **5** adjusted to pH 10.0 by $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ standard solution. Each concentration of the solution is (a) 0.10 wt%, (b) 0.20 wt%, (c) 0.40 wt%, and (d) 0.80 wt%.