Manuscript for Supporting Information

Reversible Chain Association/Dissociation in an Aqueous Medium via a CO_2 Responsive Crosslinking/Decrosslinking System

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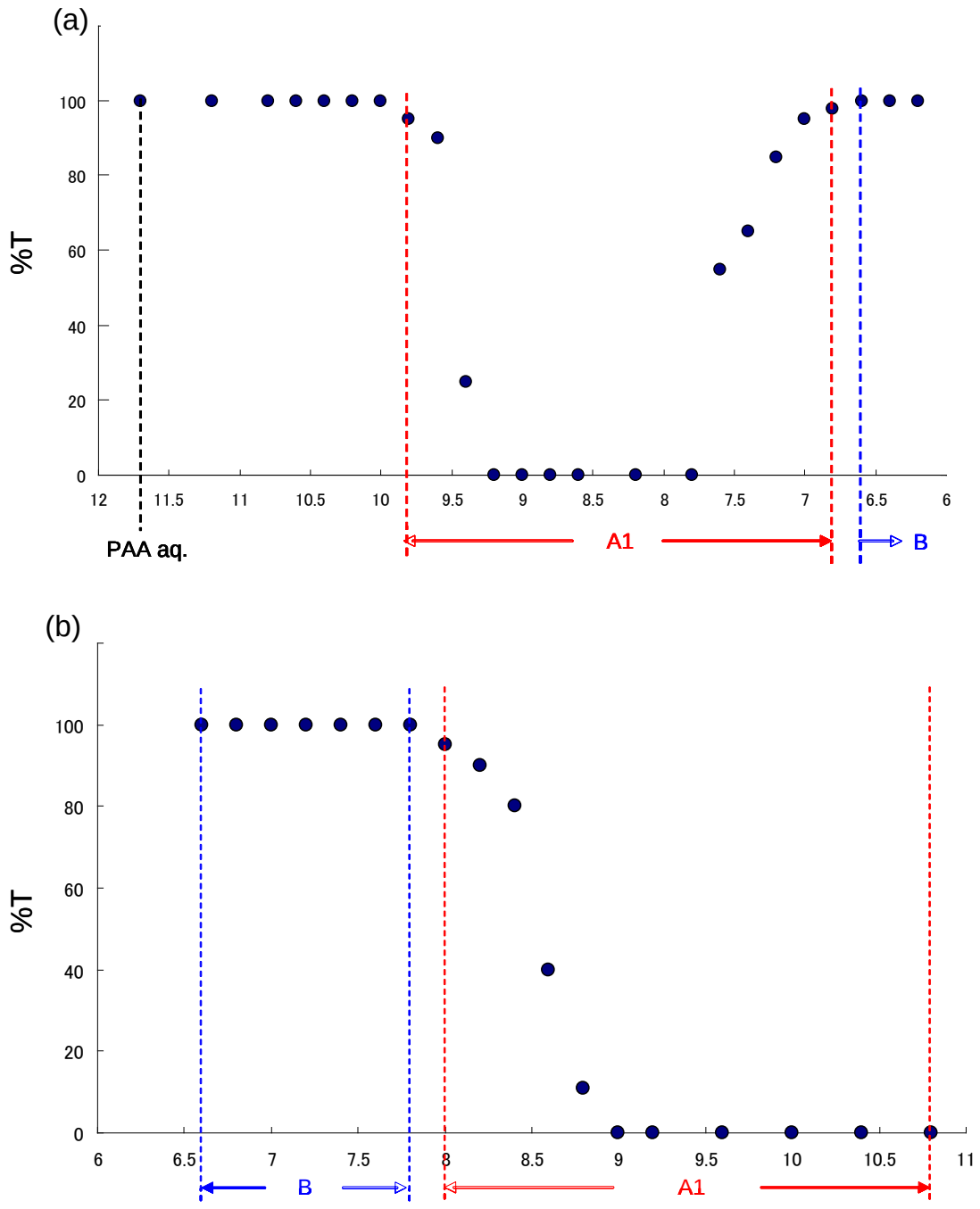

Fig. S1. Change of percent transmittance in PAA aqueous solution as a function of pH at ambient temperature. (a) Change of %T in PAA aqueous solution with addition of CO_2; (b) Change of %T in B with addition of 0.2 M NaOH aq.

Materials. Polyallylamine (PAA, 10.4 wt % aqueous solution, M_w = 25000) was supplied by Nittobo (sample code PAA-25). Styrene (Tokyo Kasei Kogyo, >99.0 %) and divinylbenzene (Aldrich, >80.0 %) were purified by distillation. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (Wako Pure Chemical, >95.0 %) were commercially available and used as received.

Instruments. ^{13}C NMR spectra were recorded with a JEOL JNM-λ500 using D_2O as a solvent; the δ values are given in parts per million (ppm). Optical microscope was performed using an OLYMPUS BXP instrument. Scanning electron microscopy (SEM) was performed using a Hitachi S3000N instrument at an acceleration voltage of 1.5 kV.

Dynmamic light scattering (DLS) measurements. In order to study the association and dissociation of PAA chains under various CO_2 concentration, dynamic light scattering (DLS) measurements were performed with the Zetasizer Nano ZS system (Malvern). In the system, a He-Ne laser is used as a light source and the scattering angle is 173°. The distribution of hydrodynamic diameter was calculated by Laplace inversion of intensity-intensity autocorrelation function $g^{(2)}(\tau)$ with the COTIN program.

Phase behavior of PAA aqueous solution in the presence of CO_2. An aqueous solution of PAA (1.0 wt%, 2.0 mL) was placed in a vial with a rubber septum. A balloon with a needle attached was filled with CO_2 (1 atm), and the needle was inserted into the rubber septum of the vial to allow the CO_2 to enter. The mixture was stirred, and the phase behavior of ~A1, A1, ~B, and B was observed; then, the rubber septum was opened, the mixture was stirred, and the phase behavior of A2 was observed.

^{13}C NMR (500 MHz, D_2O, rt, δ in ppm): PAA: 35.20–35.75 (br, $-CH_2CH(CH_2NH_2)-$), 44.73 (s, $-CH_2NH_2-$).

~A1 (prepared by centrifugation, followed by lyophilization): 32.59–40.00 (br m, $-CH_2CH(CH_2NH_2)-$, $-CH_2CH(CH_2NHCOO^-)-$, $-CH_2CH(CH_2NH_3^+)-$), 44.73 (br, $-CH_2NH_2-$, $-CH_2NHCOO^-$, $-CH_2NH_3^+$), 165.26 (s, $-NHCOO^-\cdot H_3N^+-$)

A1 (prepared by centrifugation, followed by lyophilization): 31.21–38.51 (br m, –*C*H$_2$*C*H(CH$_2$NH$_2$)–, –*C*H$_2$*C*H(CH$_2$NHCOO$^-$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$)–), 42.88–47.20 (br m, –*C*H$_2$NH$_2$, –*C*H$_2$NHCOO$^-$, –*C*H$_2$NH$_3^+$), 165.22 (s, –NH*C*OO$^-$·H$_3$N$^+$–).

~B (prepared by lyophilization): 29.10–37.51 (br m, –*C*H$_2$*C*H(CH$_2$NH$_2$)–, –*C*H$_2$*C*H(CH$_2$NHCOO$^-$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$·HCO$_3^-$)–), 41.67–46.89 (br m, –*C*H$_2$NH$_2$, –*C*H$_2$NHCOO$^-$, –*C*H$_2$NH$_3^+$, –*C*H$_2$NH$_3^+$·HCO$_3^-$), 161.20 (s, –CH$_2$NH$_3^+$·H*C*O$_3^-$), 165.15 (s. –NH*C*OO$^-$·H$_3$N$^+$–).

B (prepared by lyophilization): 30.88–39.00 (br m, –*C*H$_2$*C*H(CH$_2$NH$_2$)–, –*C*H$_2$*C*H(CH$_2$NHCOO$^-$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$·HCO$_3^-$)–), 42.00–48.02 (br m, –*C*H$_2$NH$_2$, –*C*H$_2$NHCOO$^-$, –*C*H$_2$NH$_3^+$, –*C*H$_2$NH$_3^+$·HCO$_3^-$), 161.00 ((s, –CH$_2$NH$_3^+$·H*C*O$_3^-$), 165.00 (s. –NH*C*OO$^-$·H$_3$N$^+$–).

~A2 (prepared by centrifugation, followed by lyophilization): 29.10–37.51 (br m, –*C*H$_2$*C*H(CH$_2$NH$_2$)–, –*C*H$_2$*C*H(CH$_2$NHCOO$^-$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$·HCO$_3^-$)–), 41.67–46.89 (br m, –*C*H$_2$NH$_2$, –*C*H$_2$NHCOO$^-$, –*C*H$_2$NH$_3^+$, –*C*H$_2$NH$_3^+$·HCO$_3^-$), 161.20 (s, –*C*H$_2$NH$_3^+$·H*C*O$_3^-$), 165.15 (s. –NH*C*OO$^-$).

A2 (prepared by centrifugation, followed by lyophilization): 31.00–37.50 (br m, –*C*H$_2$*C*H(CH$_2$NH$_2$)–, –*C*H$_2$*C*H(CH$_2$NHCOO$^-$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$)–, –*C*H$_2$*C*H(CH$_2$NH$_3^+$·HCO$_3^-$)–), 42.00–47.00 (br m, –*C*H$_2$NH$_2$, –*C*H$_2$NHCOO$^-$, –*C*H$_2$NH$_3^+$, –*C*H$_2$NH$_3^+$·HCO$_3^-$), 161.80 ((s, –CH$_2$NH$_3^+$·H*C*O$_3^-$), 165.20 (s. –NH*C*OO$^-$·H$_3$N$^+$–).

Synthesis of porous crosslinked polystyrene. Styrene (0.12 mL, 1.05 mmol), divinylbenzene (10.0 mg, 0.06 mmol), and A1 particles (100 mg), which was prepared by centrifugation, followed by freeze dry, were fed into a test tube, and mixed by vigorous stirring. The test tube was cooled, degassed, and the atmosphere was replaced with nitrogen. To the mixture, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (3.00 mg, 0.01 mmol) was added, and the mixture was stirred at 25°C for 20 h.

The mixture was added into distilled water (100 mL), and the resulting precipitate was collected by filtration with suction. The solid was washed with distilled water (50.0 mL) in the presence of CO_2 for 24 h, and collected by filtration with suction and dried by lyophilization to obtain the products as a white powder (80.0 g).