SUPPORTING INFORMATION

A Novel Construction of Reversible Fixation-Release System of Carbon Dioxide by Amidines and Their Polymers

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S1. Introduction of materials and instruments.

S2. Synthetic procedures and characterizations of the monomer and the polymer

Scheme S1. Scheme of synthetic routes for the monomer and the polymer.

S1. Materials and Instruments

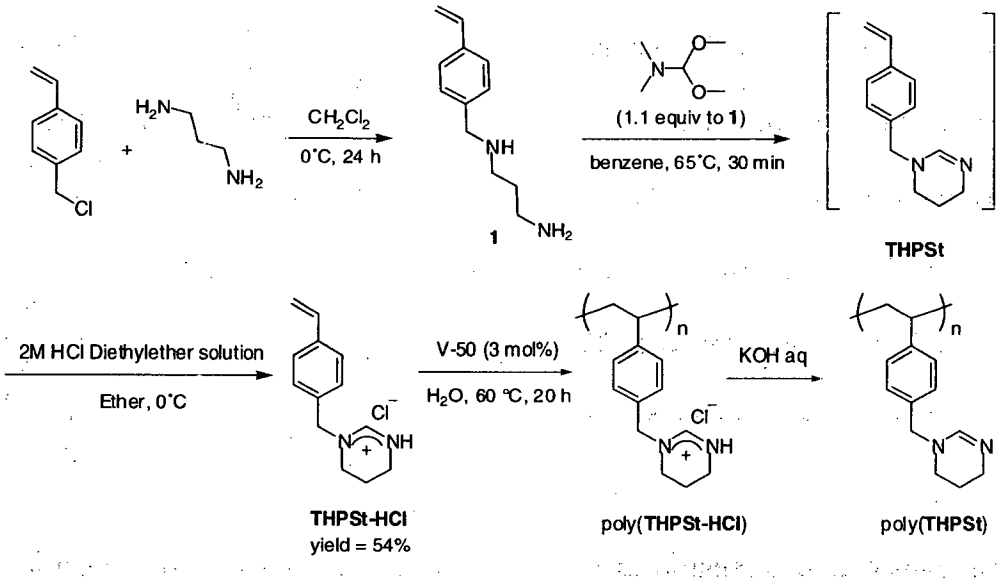
Pyridine (>98.0 %), triethylamine (>99.0 %), 1,4-dimethylaminopyridine (DMAP, 99.0 %), 1,4-diazabicyclo[2,2,2]octane (Dabco, >98.0 %), and 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU, >98.0 %) were purchased from Tokyo Kasei Kogyo Co., Inc., and were used without purification. *N,N*-dimethylformamide (DMF) was dried and distilled from CaH_2 under reduced pressure prior to use. Dimethylacryl amide (DMAAm, Tokyo Kasei Kogyo Co., Inc., >98.0 %) was distilled under reduced pressure prior to use. *N*-vinylacetamide (Showa Denko, Co., >98.0 %) was recrystallized from ethylacetate – hexane.

^{1}H-NMR and ^{13}C-NMR spectra were recorded with JEOL JNM-270EX or JEOL JNM-GX500 spectrometer with tetramethylsilane (TMS) as an internal standard; the δ and J values are given in ppm and Hz, respectively. IR spectra were recorded with a Jasco FT/IR-5300 spectrometer and the values are given in cm^{-1}. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were estimated by size exclusion chromatography (SEC) on a Tosoh HPLC HLC-8120 system equipped with two consecutive hydrophilic vinyl polymer gel columns (TSK gel α-M × 2) and a refractive index detector with phosphate buffer (pH = 7.0) as an eluent at a flow rate of 1.0 mL/min by

poly(ethylene glycol) calibration. Thermogravimetric (TG) analysis was carried out on Tosoh Instruments TG/DTA 220 at a heating rate of 10 °C/min under a nitrogen atmosphere.

S2. Syntheses of the Monomer and the Polymer

Scheme S1



4-(*N*-Aminopropyl)aminomethyl styrene (1)

A solution of 4-chloromethylstyrene (8.53 mL, 0.06 mol) in dichloromethane (60 mL) was added dropwise to a solution of 1,3-diaminopropane (25 mL, 0.3 mol) in dichloromethane (300 mL) at 0 °C.

After stirring at the same temperature for 24 h, the reaction mixture was filtered with sintered glass to remove 1,3-diaminopropane hydrochloride. The filtrate was concentrated by a rotary evaporator under reduced pressure, and the residue was dried under vacuum to obtain 4-(*N*-aminopropyl)aminomethyl styrene (**1**) (9.89 g, 0.052 mol, 87 %) as an orange syrup.

^{1}H NMR (270 MHz, $CDCl_3$): δ 1.27 (3H, s), 1.65 (1H, m), 2.69 (2H, t, J = 6.75), 2.77 (2H, t, J = 7.02), 3.78 (2H, s), 5.21 (1H, dd, J = 10.9, 0.41), 5.73 (1H, dd, J = 17.4, 0.95), 6.70 (1H, dd, J = 17.4, 10.9), 7.26–7.39 (4H, m).

4-(1,4,5,6-tetrahydropyrimide-1-yl)methylstyrene hydrochloride (THPSt-HCl)

N,N-Dimethylformamide dimethylacetal (5.98 mL , 45 mmol) was added to a solution of **1** (8.56 g, 45 mmol) in benzene (190 mL) at room temperature, and the mixture was stirred at 65 °C for 30 min. The mixture was concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (3 mL) and poured into diethylether (500 mL), and insoluble parts were filtered off. To the filtrate, 2 M HCl diethylether solution (18 mL) was added dropwise at 0 °C, and the resulting precipitate was corrected by

filtration with suction, recrystallized from ethanol–hexane (v/v = 1/9) to give 4-(1,4,5,6-tetrahydropyrimide-1-yl)methylstyrene hydrochloride (**THPSt-HCl**) (5.66 g, 23.9 mmol, 53 %) as a white powder.

mp: 192.0–193.5 °C. IR (KBr) 1681 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 2.00 (2H, m), 3.26 (2H, t, J = 5.94), 3.46 (2H, t, J = 5.67), 4.71 (2H, s), 5.32 (1H, dd, J = 10.8, 0.54), 5.79 (1H, dd, J = 17.6, 0.81), 6.71 (1H, dd, J = 17.6, 10.8) 7.26–7.44 (4H, m), 8.76 (1H, s), 11.51 (1H, s). ^{13}C NMR (67.5 MHz, CD_3OD,): δ 19.46, 38.31, 44.29, 58.99, 115.30, 128.10, 129.99, 134.56, 137.54, 139.80, 153.80. Anal. Calcd for $C_{13}H_{17}N_2Cl$: C, 65.95; H, 7.24; N, 11.83. Found: C, 65.61; H, 7.34; N, 11.64.

Radical Polymerizarion (Typical Procedure)

THPSt-HCl (237 mg, 1.0 mmol), 2,2'-azobis(2-amidinopropane)dihydrochloride (8 mg, 0.03 mmol), and H_2O (2 mL) were fed into a glass ampule. The ampule was cooled, degassed, sealed off, and heated at 60 °C for 20 h. The mixture was poured into THF (100 mL), and the resulting precipitate was collected by filtration with suction and dried under vacuum to obtain poly(**THPSt-HCl**) (230 mg, 97% yield) as a white powder. SEC-analysis (eluent: H_2O, poly(ethylene glycol)

standards) of the formed polymer was carried out to estimate the number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) (M_n = 45600, M_w/M_n = 1.64).

IR (KBr): 1681 cm^{-1}. ^1H NMR (270 MHz, D_2O): δ 0.85–2.44 (5H, br, m), 3.13-(4H, br, m). 4.51 (2H, br, s,), 6.57–7.10 (2H, br, m), 8.16 (1H, br, s).

Dehydrochlorination of poly(THPSt-HCl)

Poly(**THPSt-HCl**) (100 mg) was dissolved in H_2O (5 mL) and precipitated with 1.5 wt % aqueous KOH (2 mL) to obtain poly(**THPSt**), which was collected by filtration with suction and dried under vacuum.

IR (KBr): 1627 cm^{-1}. ^1H NMR (270 MHz, CD_3OD): δ 0.85–2.20 (5H, br, m), 3.30 (2H, br, s), 3.64 (2H, br, m), 4.43 (2H, br, s), 6.55–8.30 (4H, br, m), 8.30 (1H, br, s).