Hydrogels based on surfactant-free ionene polymers with *N,N'*-(*p*-phenylene)dibenzamide linkages

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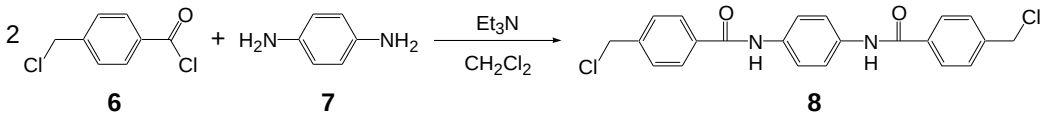
Materials and Methods

All chemical reagents used for synthesis were purchased and used without further purification. Deionized water (18.2 MΩ·cm) was provided by PURELAB Ultra Genetic and PURELAB Option R7B systems (Veolia Water Systems Ltd.). Single walled carbon nanotube (HiPCO, CNI® carbon nanotubes) was purchased from Sumitomo Corporation. ^{1}H NMR, ^{13}C NMR and COSY spectra were recorded on a Bruker Avance 400 spectrometer. The spectra were referenced to tetramethylsilane (TMS) as 0 ppm. UV-Vis-NIR spectra were recorded on a Shimadzu UV-3150 spectrometer. Polarized optical microscope images were obtained using Olympus BH-2 equipped with FUJIX digital camera HC-300Z/OL. FT-IR spectra were recorded on a Mattson Infinity Gold FTIR spectrometer. Field emission scanning electron microscope image was obtained using a Topcon DS-720. The Xerogel for FE-SEM was converted from the hydrogel with **5**·**Cl** by freeze-drying *in vacuo* using an EYELA FDU-1200 instrument. Rheological measurements were performed at 25 ºC using an ARES rheometer (TA instruments). Gels of ionene polymers were produced as follows: polymers were placed in a vial (ϕ11.7 mm × 35 mm) and then dissolved in water (1 mL) by heating, followed by cooling to room temperature. SWNT-dispersed solution was prepared as follows: SWNT (0.5 mg) was added to 2.5 ml of the hydrogel (D_2O, 20 g L^{-1}) with **5**·**Cl** in a vial and the gel sonicated for 60 min (Velvo-clear Ultrasonic Cleaner VS-100III, 100 W, 45 kHz).

Synthesis

1,4-bis[4-(chloromethyl)benzamido]benzene (**8**)

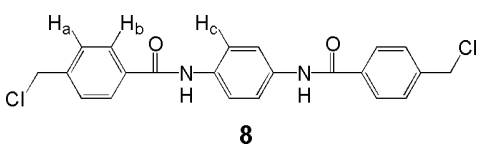


6 **7** **8**

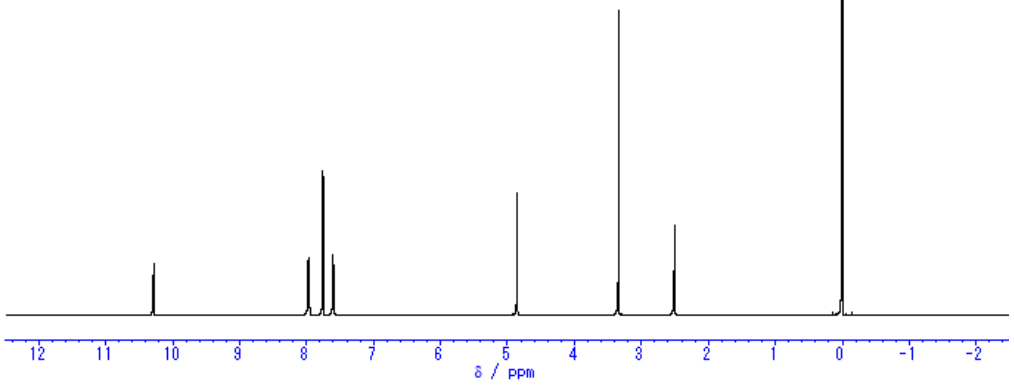
To a suspension of *p*-phenylenediamine (**7**) (331 mg, 3.1 mmol) in anhydrous dichloromethane (30 mL) in the presence of triethylamine (0.63 g, 6.2 mmol) was added a solution of 4-(chloromethyl)benzoyl chloride (**6**) (1.16 g, 6.2 mmol) in anhydrous dichloromethane (20 mL). The mixture was stirred for 18 h at room temperature. The generated precipitate was filtrated off and the washed with dichloromethane to obtain **8** as colorless solid (1.27 g, 99%).

Anal. Calcd for $C_{22}H_{18}Cl_2N_2O_2$: C, 63.93; H, 4.39; N, 6.78. Found: C, 63.80; H, 4.32; N, 6.48.

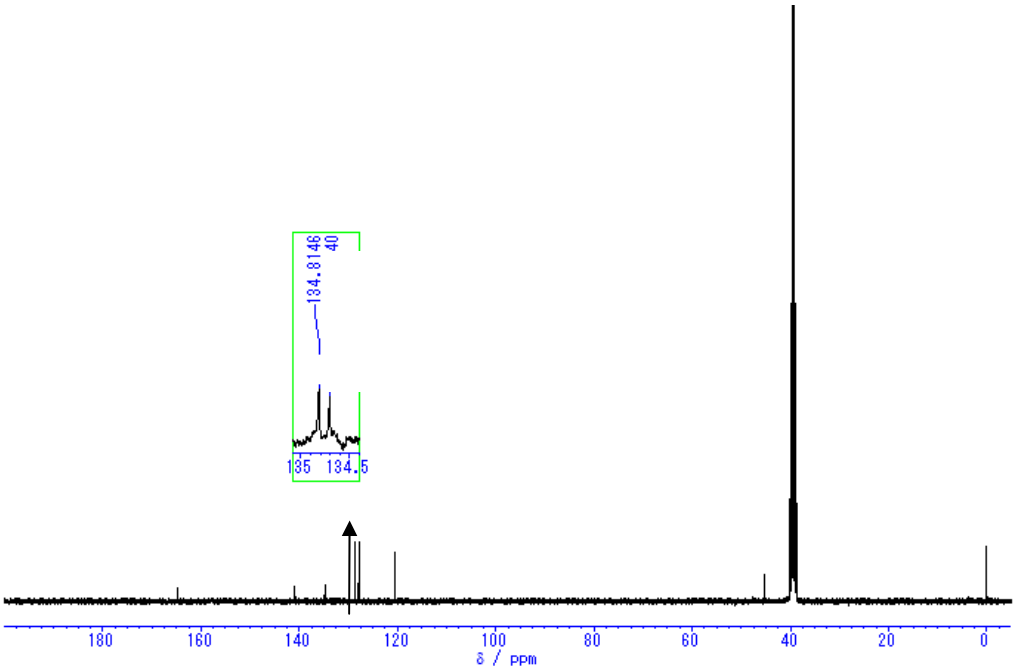
^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.3 (s, 2H, -N*H*), 7.97 (d, J = 8.2 Hz, 4H, Ph-H_b), 7.75 (s, 4H, Ph-H_c), 7.59 (d, J = 8.2 Hz, 4H, Ph-H_a), 4.85 (s, 4H, -CH_2Cl).



8

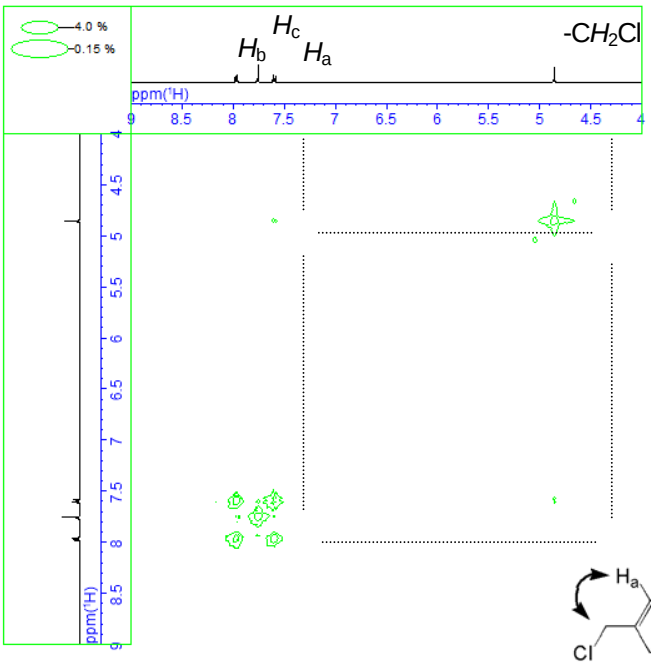


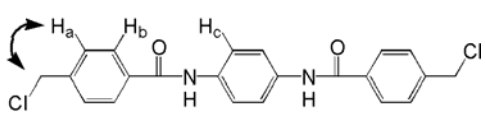
^{13}C NMR (100.6 MHz, DMSO-d_6, TMS) δ 164.7 (*C*=O), 140.9, 134.8, 134.7, 128.7, 127.9, 120.5, 45.3 (Ph-*C*H$_2$Cl).



COSY,

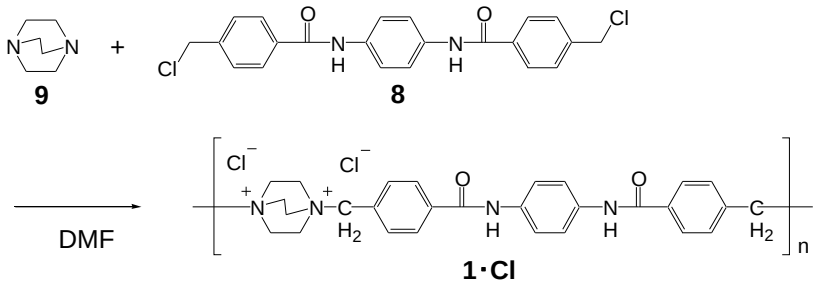
Signals of aromatic protons (H_a and H_b) were assigned by correlation with the signal of methylene proton.





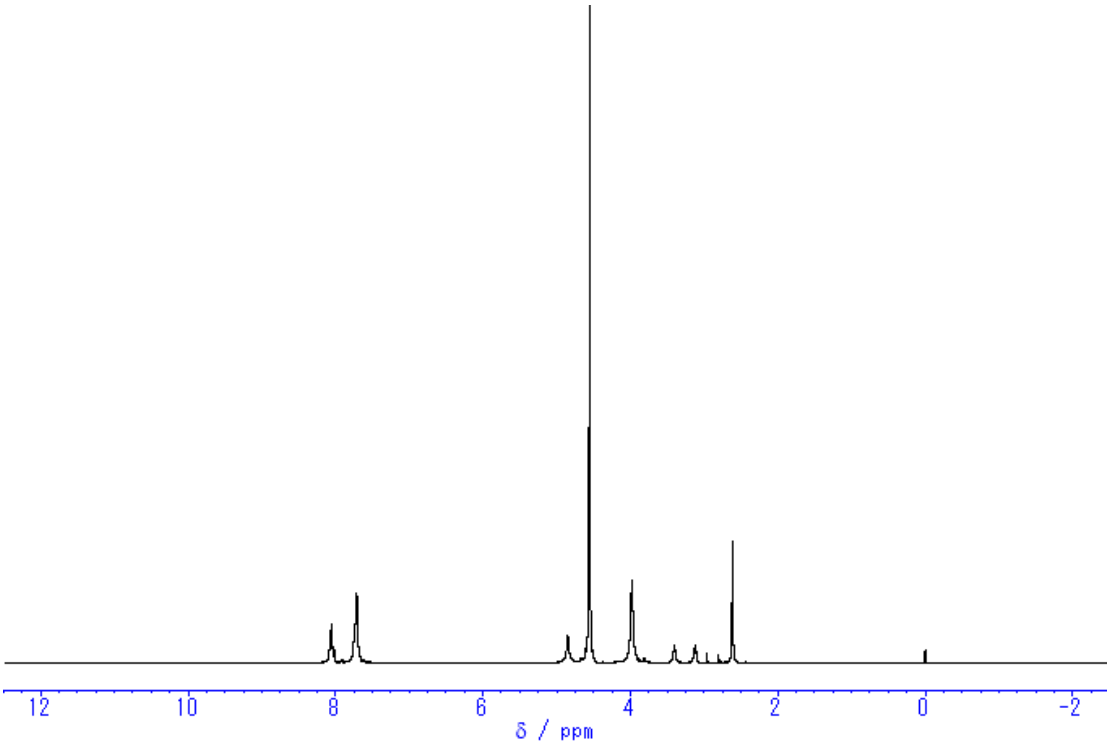
8

Poly[diazoniabicyclo[2.2.2]octane-1,4-diylmethylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4- phenylenemethylene dichloride] (**1·Cl**)

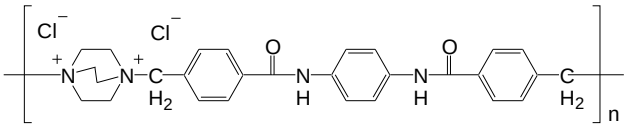


To a stirred solution of **8** (0.41 g, 1.0 mmol) in DMF (40 mL) at 80 °C was added 1,4-diazabicyclo[2.2.2]octane (**9**) (0.11 g, 1.0 mmol). The mixture was stirred at 80 °C for 48 h to give **1·Cl** as precipitate (0.52 g, 94 %).

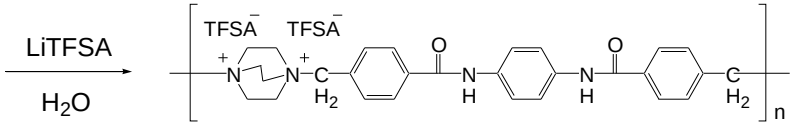
^{1}H NMR (400 MHz, DMSO-d_6/D_2O = 1/1 (v/v), TMS) δ 8.07-8.02 (m), 7.74-7.65 (m), 4.85 (br s), 3.98 (s, -$N^+(CH_2CH_2)_3N^+$-), 3.41 (t, J = 7.0 Hz, -$N^+(CH_2CH_2)_3N$), 3.12 (t, J = 7.1 Hz, -$N^+(CH_2CH_2)_3N$).



Poly{diazoniabicyclo[2.2.2]octane-1,4-diylmethylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4-phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**1·TFSA**)



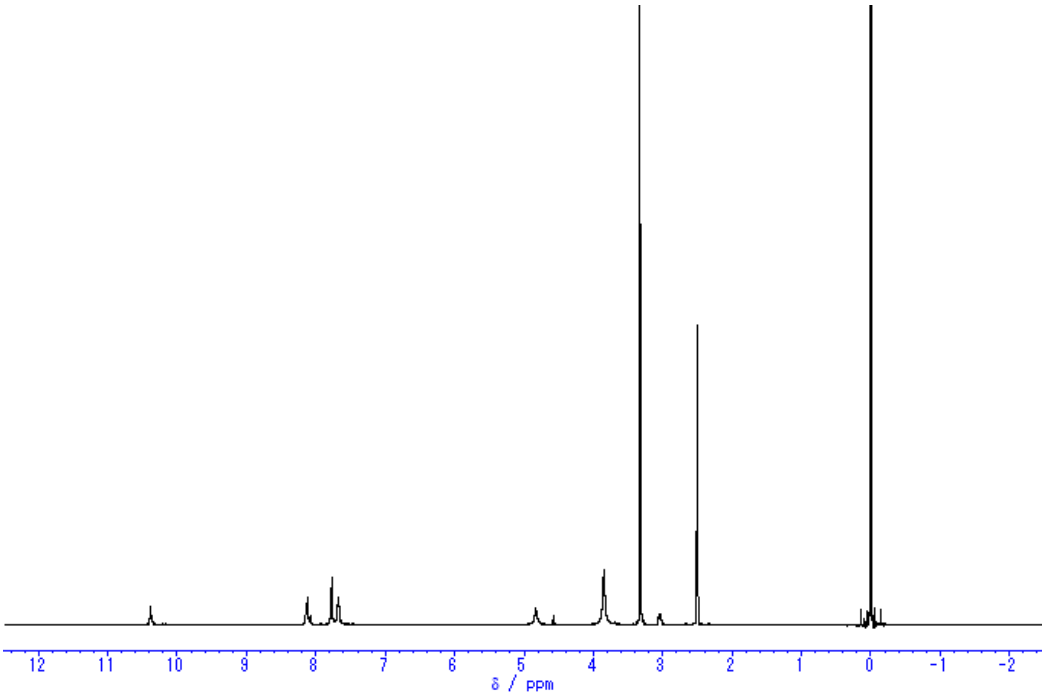
1·Cl



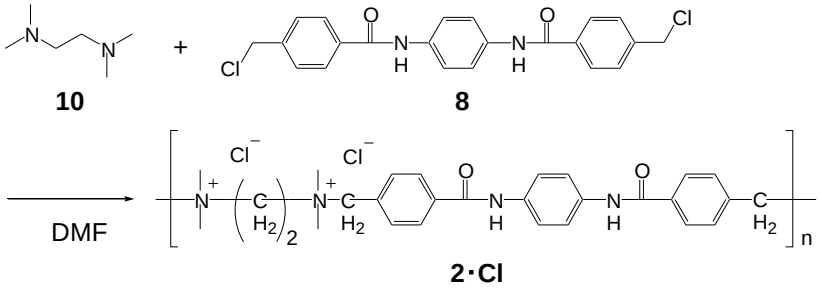
1·TFSA

To a solution of **1·Cl** (0.10 g) in water (20 mL) at 90 ℃ was added a solution of lithium bis(trifluoromethanesulfonyl)amide (1.0 g) in water (2 mL). The mixture was stirred for 32 min to give **1·TFSA** as precipitate (0.154 g, 80 %).

^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.4 (s, -NH), 8.14-8.08 (m), 7.77 (s), 7.68-7.66 (br d), 4.82 (br s), 4.58 (br s), 3.85 (s, -$N^+(CH_2CH_2)_3N^+$-), 3.04 (br t, -$N^+(CH_2CH_2)_3N$).

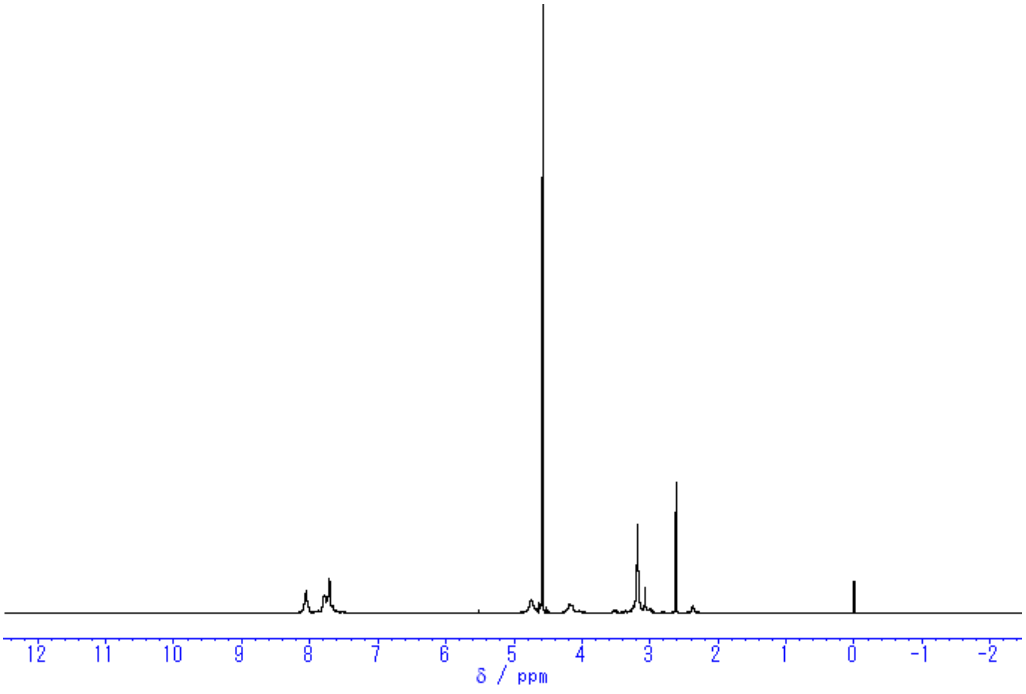


Poly[(dimethyliminio)ethylene(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneimino-carbonyl-1,4-phenylenemethylene dichloride] (**2·Cl**)

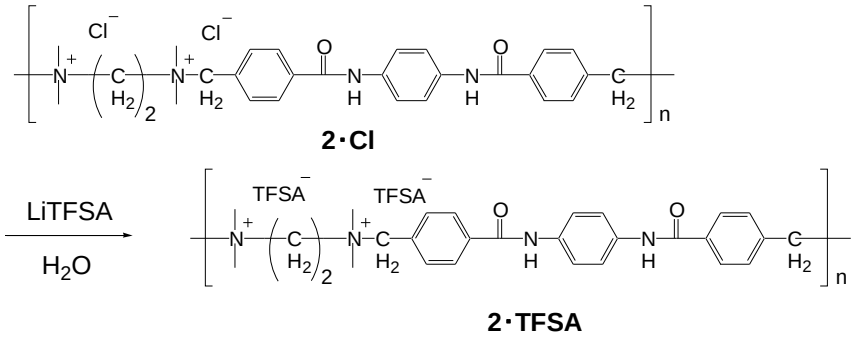


To a solution of **8** (1.65 g, 4.0 mmol) in DMF (150 mL) at 80 °C was added a solution of *N*,*N*,*N*',*N*'-tetramethyl-1,2-diaminoethane (**10**) (0.46 g, 4.0 mmol) in DMF (5 ml). The mixture was stirred for 48 h at 80 °C to give **2·Cl** as precipitate (1.76 g, 84 %).

^{1}H NMR (400 MHz, DMSO-d_6/D_2O = 1/1 (v/v), TMS) δ 8.05-8.01 (m), 7.78-7.66 (m), 4.75 (br s), 4.18-4.14 (br d), 3.18 (s, -$N^+(CH_3)_2$-).

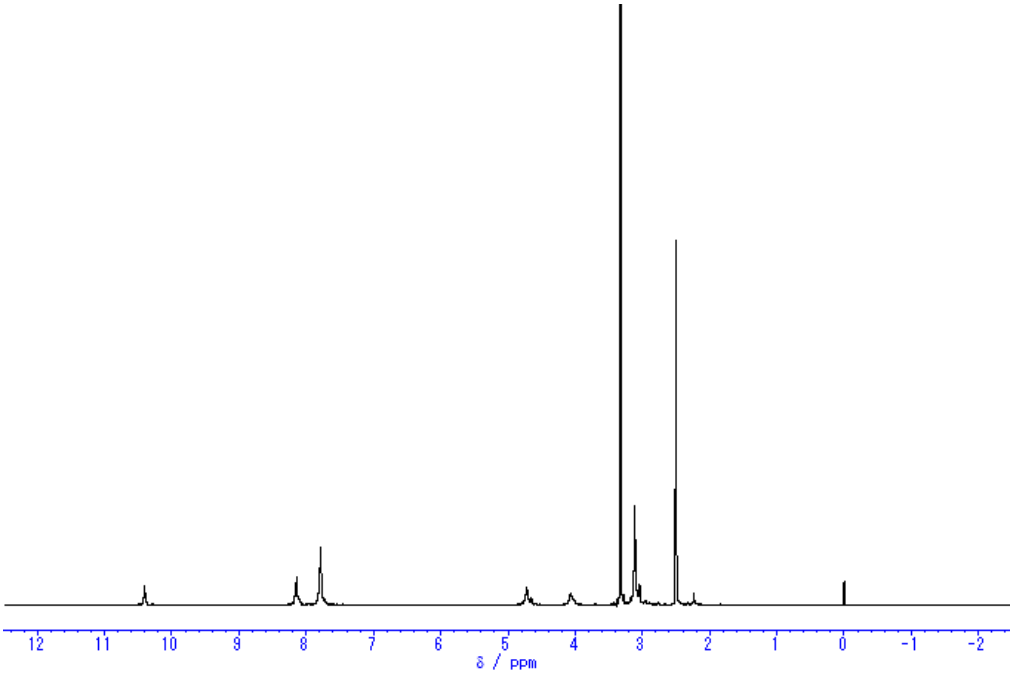


Poly{(dimethyliminio)ethylene(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneimino-carbonyl-1,4-phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**2·TFSA**)

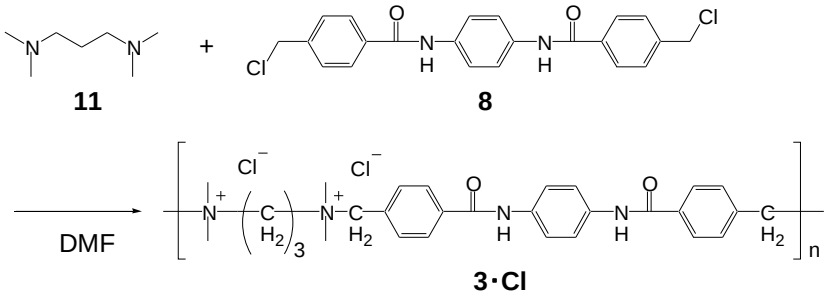


To a solution of **2·Cl** (0.10 g) in water (100 mL) at 80 °C was added a solution of lithium bis(trifluoromethanesulfonyl)amide (1.0 g) in water (10 mL) .The mixture was stirred for 1 min to give **2·TFSA** as precipitate (0.156 g, 81 %).

^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.4 (s, -N*H*), 8.16-8.09 (m), 7.79 (s), 4.72 (br s), 4.07 (br s), 3.11 (s, -$N^+(CH_3)_2$-).

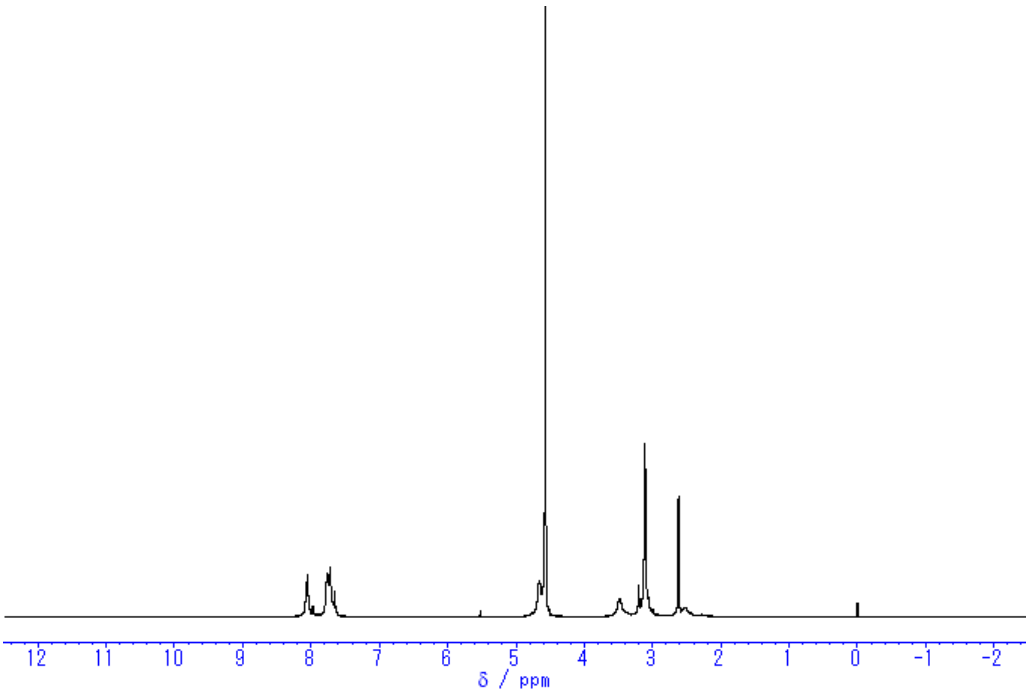


Poly[(dimethyliminio)propane-1,3-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4-phenylenemethylene dichloride] (**3·Cl**)

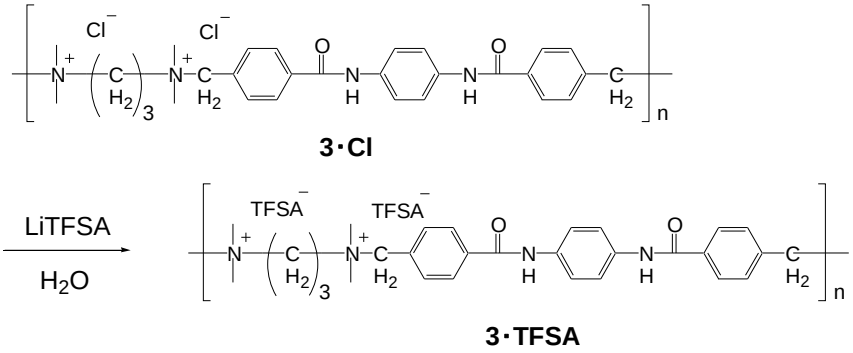


To a solution of **8** (0.41 g, 1.0 mmol) in DMF (40 mL) at 80 °C was added a solution of *N*,*N*,*N*',*N*'-tetramethyl-1,3-diaminopropane (**11**) (0.13 g, 1.0 mmol) in DMF (1 ml). The mixture was stirred for 48 h at 80 °C to give **3·Cl** as precipitate (0.45 g, 83 %).

^{1}H NMR (400 MHz, DMSO-d_6/D_2O = 1/1 (v/v), TMS) δ 8.06-7.96 (m), 7.77-7.62 (m), 4.66 (br s), 3.48 (br s), 3.11 (s, -$N^+(CH_3)_2$-), 2.53 (br s).

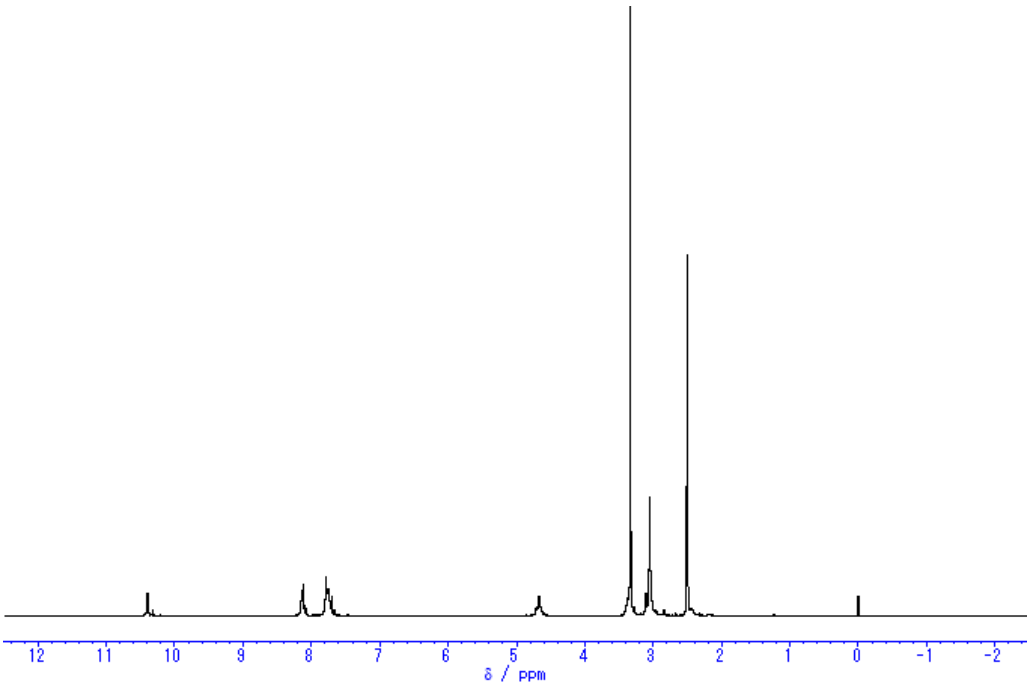


Poly{(dimethyliminio)propane-1,3-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4-phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**3·TFSA**)

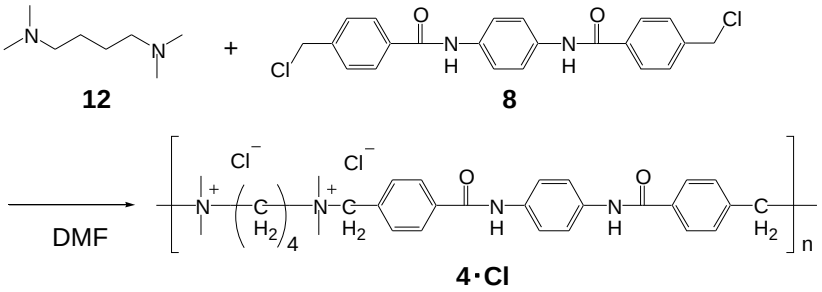


To a solution of **3·Cl** (0.10 g) in water (100 mL) at 90 °C was added a solution of lithium bis(trifluoromethanesulfonyl)amide (1.0 g) in water (10 mL). The mixture was stirred for 10 min to give **3·TFSA** as preipitate (0.135 g, 71 %).

^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.4 (s, -N*H*), 8.14-8.08 (m), 7.78-7.71 (m), 4.67 (br s), 3.05 (s, -$N^+(CH_3)_2$-).

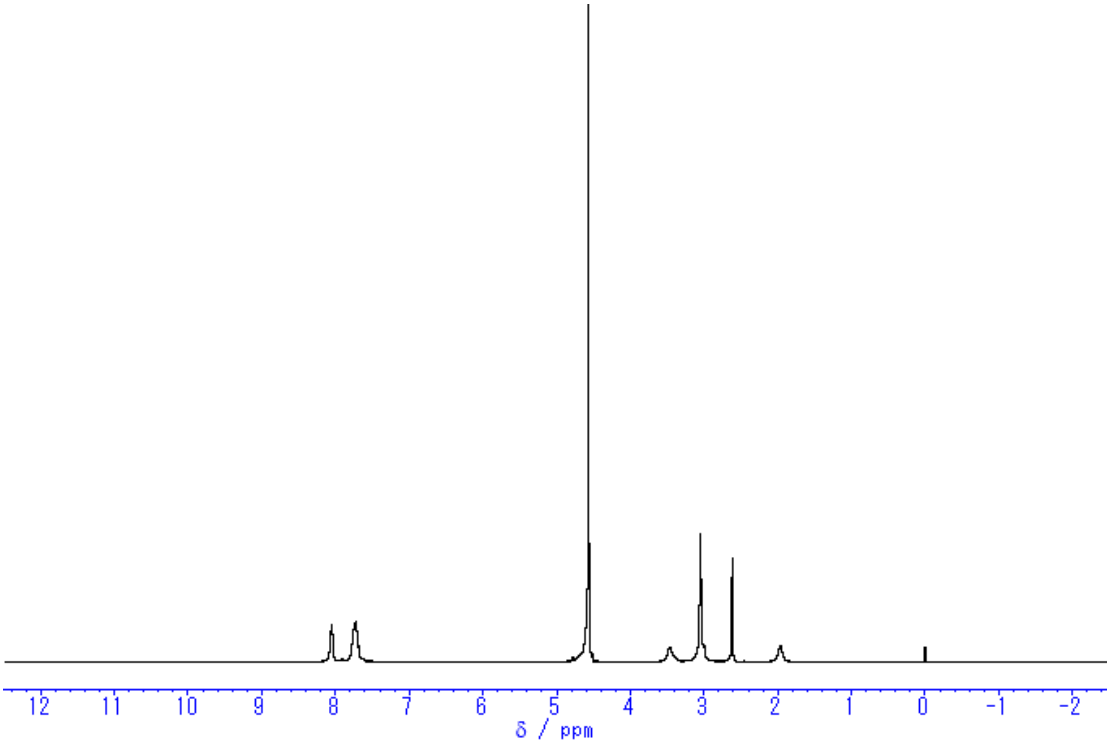


Poly[(dimethyliminio)butane-1,4-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenylene-iminocarbonyl-1,4-phenylenemethylene dichloride] (**4·Cl**)

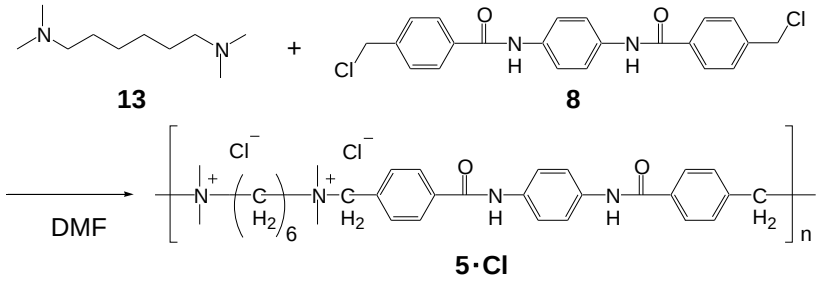


To a solution of **8** (0.42 g, 1.0 mmol) in DMF (40 mL) at 80 °C was added a solution of *N*,*N*,*N*',*N*'-tetramethyl-1,4-diaminobutane (**12**) (0.15 g, 1.0 mmol) in DMF (1 ml). The mixture was stirred for 48 h at 80 °C to give **4·Cl** as precipitate (0.50 g, 88 %).

^{1}H NMR (400 MHz, DMSO-d_6/D_2O = 1/1 (v/v), TMS) δ 8.05 (s), 7.74-7.68 (m), 3.46 (br s), 3.05 (s, -$N^+(CH_3)_2$-), 1.97 (br s).



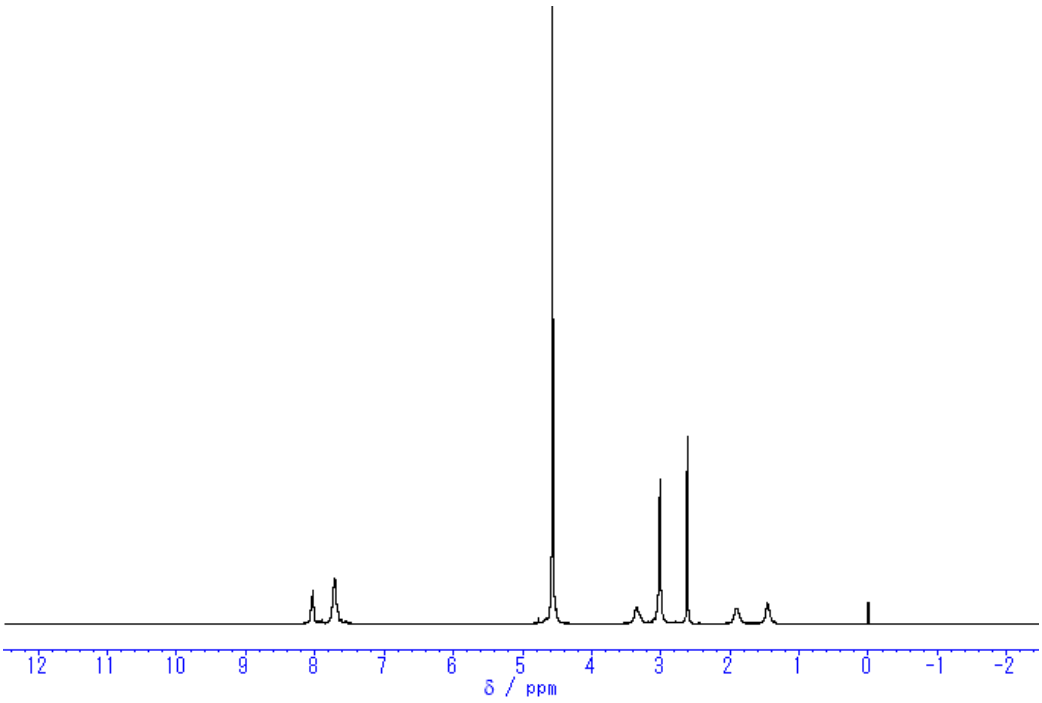
Poly[(dimethyliminio)hexane-1,6-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenylene-iminocarbonyl-1,4-phenylenemethylene dichloride] (**5·Cl**)



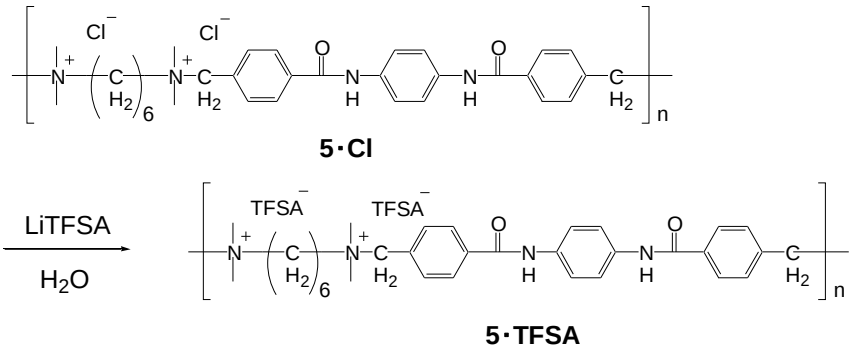
To a solution of **8** (0.43 g, 1.0 mmol) in DMF (40 mL) at 80 °C was added a solution of *N*,*N*,*N*',*N*'-tetramethyl-1,6-diaminohexane (**13**) (0.18 g, 1.0 mmol) in DMF (5 ml). The mixture was stirred for 48 h at 80 °C to give **5·Cl** as precipitate (0.57 g, 93 %).

UV/Vis (H_2O) λ_{max} = 228, 292 nm; IR (10 g L^{-1}, D_2O) 1645 cm^{-1} (C=O).

^{1}H NMR (400 MHz, DMSO-d_6/D_2O = 1/1 (v/v), TMS) δ 8.03 (br), 7.72-7.67 (m), 3.35 (br s), 3.01 (s, -$N^+(CH_3)_2$-), 1.90 (br s), 1.46 (br s).

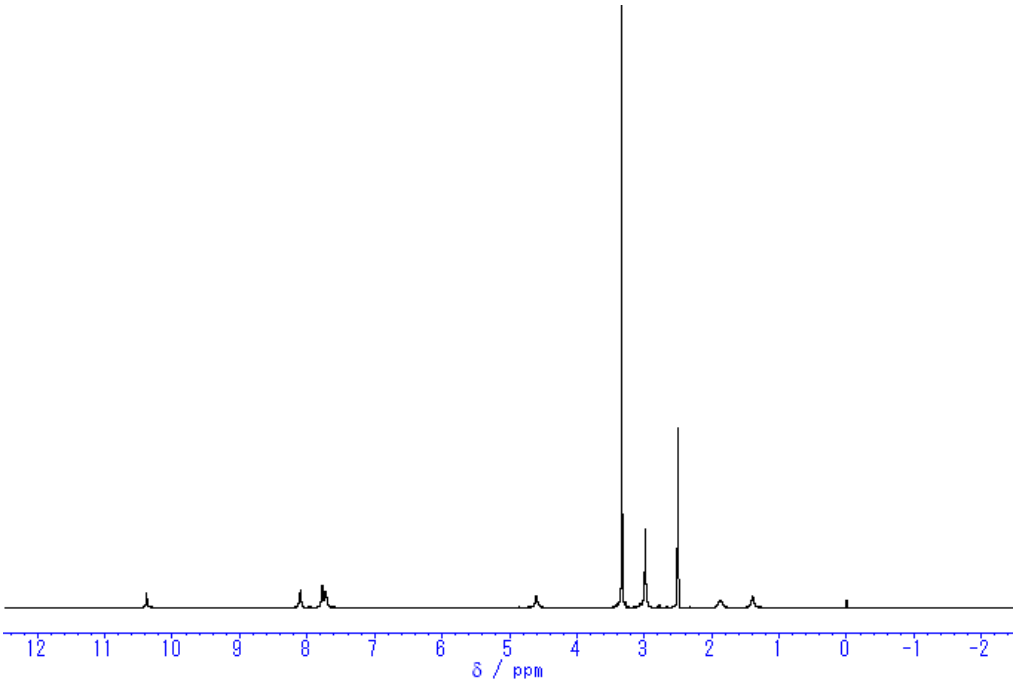


Poly{(dimethyliminio)hexane-1,6-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4-phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**5·TFSA**)

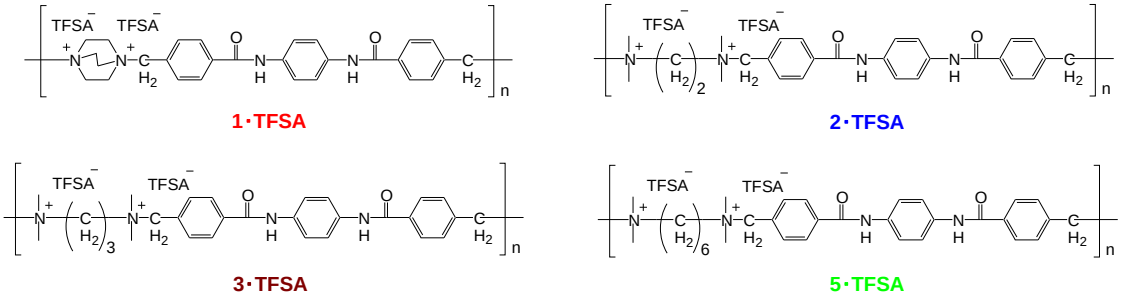


To a stirred solution of **5·Cl** (0.1 g) in water (100 mL) at 80 °C was added a solution of lithium bis(trifluoromethanesulfonyl)amide (1.0 g) in water (10 mL). The mixture was stirred for 18 min to give **5·TFSA** as precipitate (0.153 g, 83 %).

^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.4 (s, -NH), 8.11 (d, J = 7.6 Hz), 7.78 (s), 7.75 (d, J = 7.8 Hz), 4.60 (br s), 2.99 (s, -N$^+$(CH_3)$_2$-), 1.87 (br s), 1.39 (br s).



Size exclusion chromatography (SEC) data were obtained using a Shimadzu GPC system equipped with LC-10ADvp pump unit, RID-10A reflux index detector, CTO-10Avp column oven and SCL-10Avp controller unit. The temperature of column oven was maintained 40 ºC. Asahipak GF-510 HQ column was used. DMF including 30 mM lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) was used as eluent and the flow rate was maintained at 0.5 mL min^{-1}. Molecular weights of ionene polymers were calibrated using poly(methylmethacrylate) standards.



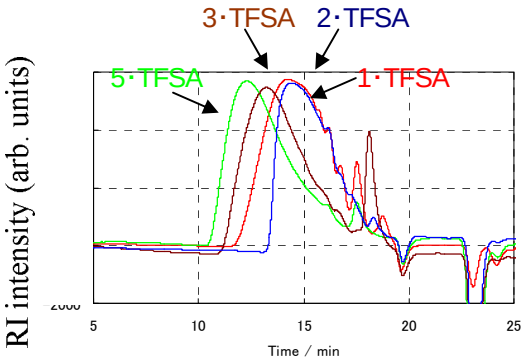


Figure S1. SEC profiles of ionene polymers.

Rheorogical measurements were performed at 25 °C using an ARES rheometer (TA instruments) with a 50 mm cone plate. In the case of a dynamic strain sweep test, frequency was maintained at 1 Hz.

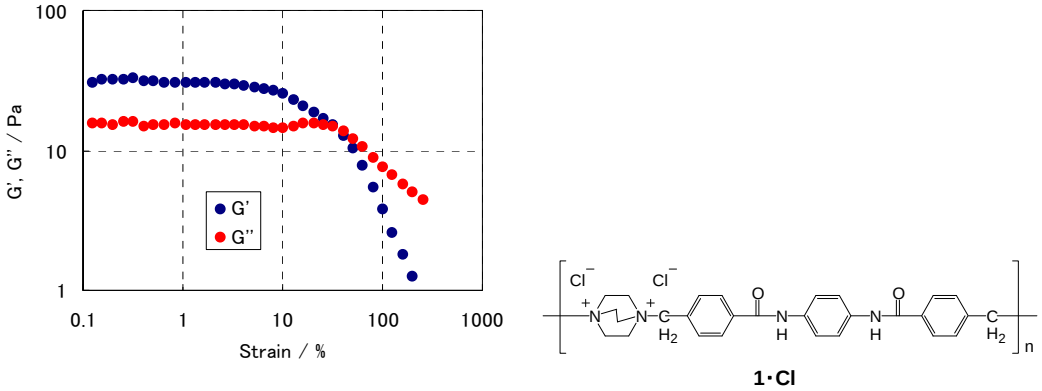


Figure S2. A dynamic strain amplitude sweep test for a hydrogel with **1·Cl** at 50 g L^{-1}.

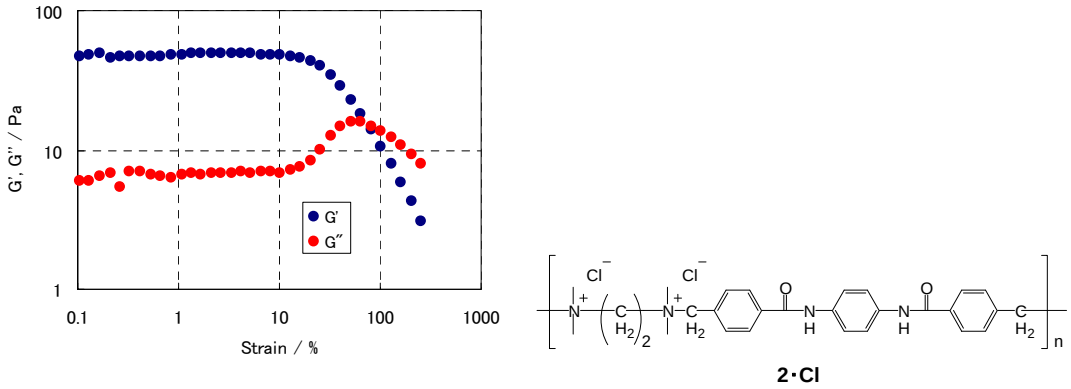


Figure S3. A dynamic strain amplitude sweep test for a hydrogel with **2·Cl** at 30 g L^{-1}.

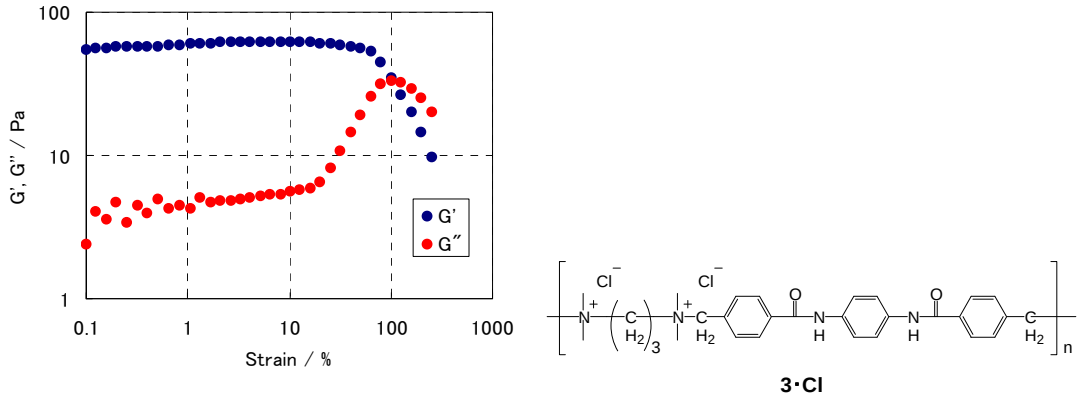


Figure S4. A dynamic strain amplitude sweep test for a hydrogel with **3**·**Cl** at 40 g L^{-1}.

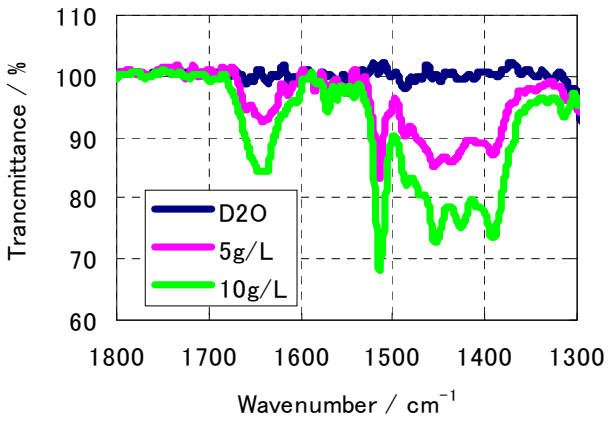


Figure S5. IR spectra of **5**·**Cl** in D_2O (1800-1300 cm^{-1} region).