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A hydrogel with
5·Cl at 10 g L^{-1}

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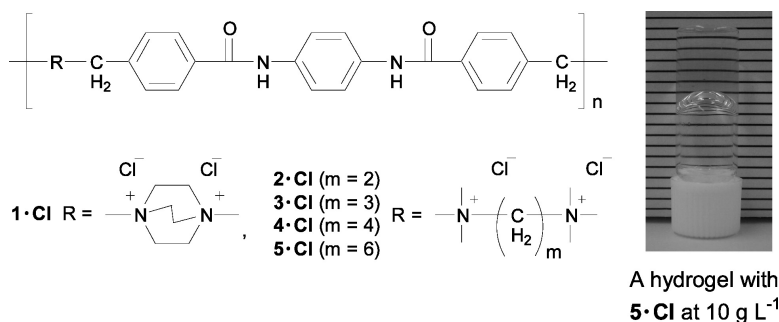- Copyright permission to reproduce figures and/or text from this article

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Hydrogels Based on Surfactant-Free Ionene Polymers with N,N′-(p-Phenylene)dibenzamide Linkages

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ABSTRACT: Ionene polymers with N,N′-(p-phenylene)dibenzamide linkages were synthesized in high yields by the copolymerization of 1,4-bis[4-(chloromethyl)benzamide]benzene and α,ω-ditertiary amines in N,N-dimethylformamide. The ionene polymers provided physical hydrogels under ca. 1–5 wt % of the concentrations after heating and cooling at room temperature without any other additives. The gelation ability was dependent on the diamine spacers and/or the molecular weights, and the ionene polymer with the longest hexylene linker connecting ammonium cations was the most effective gelation capability in water among these ionene polymers. In the rheological measurement, the hydrogel showed a unique thixotropic nature that was a fast self-recovering property after the continuous oscillatory shear stress. Furthermore, the ionene polymer has an additional function as a dispersant for single-walled carbon nanotubes (SWNT) in water.

Introduction

Polymer gels, based on not only biopolymers but also synthetic polymers, have attracted much attention due to the applications in numerous fields, including food, pharmaceuticals, agriculture, chemical processing, and electronics.[1] Especially hydrogels have been of considerable interest due to many biomedical applications. Polymer gels of water strongly depend on the balance between the intrinsic hydrophobicity and hydrophilicity of the polymer. The development of polymers with tunable structure and amphiphilicity thus has been a very important issue for the application of the hydrogels. The cationic polymer containing quaternary ammonium parts not in the substituent but in the main chain, referred to ionene polymer, has attracted much attention due to the various technological applications.[2] Such an amphiphilic polymer can be promising structural motif as the gel-forming agent. Furthermore, it offers the advantage of the ease of synthesis and structural modification by copolymerization of ditertiary amines and dihalides via the intermolecular Menschutkin (quaternization) reaction.[3] So far the interaction of the ionene polymers and n-alkyl surfactants forming micelles and vesicles have been considerably investigated,[4] and the reversible hydrogelation by the ion complex of the aliphatic ionene polymers and sodium dodecyl sulfate (SDS) has been also reported.[5] However, in this case, SDS, i.e., the anionic surfactant with long alkyl chain, was essential to stabilize the hydrogels by the hydrophobic interaction, and to our knowledge, no ionene polymer without the aid of surfactants has formed the hydrogel.

Recently, we first reported the surfactant-free ionene oligomer with pyridinium backbone as a multifunctional gelator which showed unique characteristics such as gelation of water, fast recovery of mechanical strength after continuous large stress in the gel state, and an efficient medium for the dispersion of single-walled carbon nanotubes (SWNT).[6] The oligomer was synthesized by one-pot reaction including amidation and subsequent intermolecular quaternization reaction as a self-condensation of the ampholytic benzamide intermediate. Exploring the synthetic strategy, we designed and prepared the ionene polymers having tetraalkylammonium backbone that can produce the polymer gels without any surfactants. In this report, we describe the ionene polymers with N,N′-(p-phenylene)dibenzamide linkages as key structural moieties prepared by the copolymerization of aliphatic ditertiary amines and the corresponding p-phenylene-based dihalides. We found that most of the ionene polymers gave physical hydrogels under relatively low concentration, and one of them was found to be a dispersant for SWNT in water as observed in our previous study of the oligomer with pyridinium structure.[6]

Experimental Section

Materials. All chemical reagents used for synthesis were purchased from TCI, Kanto Kagaku (Cica), Aldrich, and used without further purification. Deionized water (18.2 MΩ·cm) was prepared by PURELAB Ultra Genetic and PURELAB Option R7B systems (Veolia Water Systems Ltd.). Single-walled carbon nanotubes (HiPco, CNI carbon nanotubes) were purchased from Sumitomo Corp.

Methods. NMR spectra were recorded on a Bruker Avance 400 spectrometer. The spectra were referenced to tetramethylsilane (TMS) as 0 ppm. Because of the solubility limitation, the mixed solvent of DMSO-d_6 and D_2O (1/1 (v/v)) was often used for the NMR measurements of the polymers. UV–vis–NIR spectra were recorded on a Shimadzu UV-3150 spectrometer. Size exclusion chromatography (SEC) data were obtained using a Shimadzu GPC system equipped with an LC-10ADvp pump unit, a RID-10A refractive index detector, a CTO-10Avp column oven, a SCL-10Avp controller unit, and an Asahipak GF-510 HQ column. The temperature of column oven was maintained 40 °C. 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(methyl methacrylate) standards. Polarized optical microscope images were obtained using an Olympus BH-2 equipped with a FUJIX digital camera HC-300Z/OL. FT-IR spectra were recorded on a Mattson Infinity Gold FTIR spectrometer using CaF$_2$ plates. A field emission scanning electron microscope (FE-SEM) image was obtained using a Topcon DS-720. The Xerogel for the FE-

Scheme 1[a]

[a]Conditions: (i) triethylamine, CH$_2$Cl$_2$, rt, 99%; (ii) diazabicyclo[2.2.2]octane or *N,N,N′,N′*-tetramethylalkylenediamines, DMF, 80 °C, 48 h; yield: 94%, 84%, 83%, 88%, 93% from **1·Cl** to **5·Cl**.

SEM measurement was prepared from the hydrogel with **5·Cl** by freeze-drying in vacuo using an EYELA FDU-1200 lyophilizer. Rheological measurements were performed at 25 °C using an ARES rheometer (TA Instruments). A 50 mm cone plate (0.04 rad) was used for 10 g L^{-1}, while a 25 mm cone plate (0.1 rad) was used for 20 and 30 g L^{-1} concentrations of the gels with **5·Cl**. Gels of ionene polymers were produced as follows: polymers were placed in a vial (diameter 11.7 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: **5·Cl** (50 mg) was dissolved in D$_2$O (2.5 mL) by heating. The hot solution was left at room temperature and then gradually turned into a gel. SWNT (0.5 mg) was added to 2.5 mL of the hydrogel, and the gel containing the SWNT was sonicated for 60 min by an ultrasonicator (Velvo-clear Ultrasonic Cleaner VS-100III, 100 W, 45 kHz) to give a SWNT-dispersed solution.

Synthesis. 1,4-Bis[4-(chloromethyl)benzamido]benzene (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 then washed with dichloromethane to obtain **8** as colorless solid (1.27 g, 99%). ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 10.3 (s, 2H), 7.97 (d, *J* = 8.2 Hz, 4H), 7.75 (s, 4H), 7.59 (d, *J* = 8.2 Hz, 4H), 4.85 (s, 4H). ^{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). Anal. Calcd for C$_{22}$H$_{18}$Cl$_2$N$_2$O$_2$: C, 63.93; H, 4.39; N, 6.78. Found: C, 63.80; H, 4.32; N, 6.48.

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 a precipitate (0.52 g, 94%). ^{1}H NMR (400 MHz, DMSO-d_6/D$_2$O = 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$_2$CH$_2$)$_3$N$^+$−), 3.41 (t, *J* = 7.0 Hz, −N$^+$(CH$_2$CH$_2$)$_3$N), 3.12 (t, *J* = 7.1 Hz, −N$^+$(CH$_2$CH$_2$)$_3$N), IR (10 g L^{-1}, D$_2$O): 1650, 1574, 1516, 1437, 1395 cm^{-1}.

In the same procedure for **1·Cl**, poly[(dimethyliminio)ethylene-(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneimino-carbonyl-1,4-phenylenemethylene dichloride] (**2·Cl**), poly[(dimethyliminio)propane-1,3-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl-1,4-phe-

nylenemethylene dichloride] (**3·Cl**), poly[(dimethyliminio)butane-1,4-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenylene-iminocarbonyl-1,4-phenylenemethylene dichloride] (**4·Cl**), and poly[(dimethyliminio)hexane-1,6-diyl(dimethyliminio)methylene-1,4-phenylenecarbonylimino-1,4-phenylene-iminocarbonyl-1,4-phenylenemethylene dichloride] (**5·Cl**) were synthesized. **2·Cl**: 84%. ^{1}H NMR (400 MHz, DMSO-d_6/D$_2$O = 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$_3$)$_2$−). IR (10 g L^{-1}, D$_2$O): 1640, 1572, 1517, 1456, 1434, 1396 cm^{-1}. Anal. Calcd for C: 63.51, H: 6.47, N: 10.58. Found C: 61.00, H: 6.76, N: 10.14. **3·Cl**: 83%. ^{1}H NMR (400 MHz, DMSO-d_6/D$_2$O = 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). IR (10 g L^{-1}, D$_2$O): 1640, 1573, 1517, 1456, 1434, 1396 cm^{-1}. Anal. Calcd for C: 64.08, H: 6.68, N: 10.31. Found C: 60.01, H: 7.03, N: 9.45. **4·Cl**: 88%. ^{1}H NMR (400 MHz, DMSO-d_6/D$_2$O = 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). Anal. Calcd for C: 64.63, H: 6.87, N: 10.05; Found C: 62.17, H: 6.94, N: 9.33. **5·Cl**: 93%. ^{1}H NMR (400 MHz, DMSO-d_6/D$_2$O = 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). UV/vis (H$_2$O) λ_{max} = 228, 292 nm. IR (10 g L^{-1}, D$_2$O): 1645, 1571, 1515, 1485, 1454, 1427, 1390 cm^{-1}. Anal. Calcd for C: 65.63, H: 7.23, N: 9.57. Found C: 62.77, H: 7.54, N: 9.03.

Poly{diazoniabicyclo[2.2.2]octane-1,4-diylmethylene-1,4-phenylenecarbonylimino-1,4-phenyleneiminocarbonyl- 1,4-phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**1·TFSA**). To a solution of **1·Cl** (0.1 g) in water (20 mL) at 90 °C was added a solution of lithium bis(trifluoromethanesulfonyl)amide (1 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$_2$CH$_2$)$_3$N$^+$−), 3.04 (br t, −N$^+$(CH$_2$CH$_2$)$_3$N). SEC data, M_n = 6.19 × 10^3 Da, M_w = 2.11 × 10^4 Da, M_n/M_w = 3.4.

In the same procedure for **1·TFSA**, poly{(dimethyliminio)ethylene (dimethyliminio)methylene - 1,4-phenylenecarbonylimino - 1,4 - phenyleneimino-carbonyl - 1,4 - phenylenemethylene di[bis(tri - fluoromethanesulfonyl)amide]} (**2·TFSA**), poly{(dimethyliminio)-propane - 1,3 - diyl(dimethyliminio)methylene - 1,4-phenylenecarbonylimino - 1,4 - phenyleneiminocarbonyl - 1,4 - phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**3·TFSA**), and poly{(dimethyl-iminio)hexane - 1, 6 - diyl(dimethyliminio)methylene - 1,4 - phenylenecarbonylimino - 1,4 - phenyleneiminocarbonyl - 1,4 - phenylenemethylene di[bis(trifluoromethanesulfonyl)amide]} (**5·TFSA**) were synthesized. **2·TFSA**: 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$_3$)$_2$−). SEC data, M_n = 6.41 × 10^3 Da, M_w = 1.41 × 10^4 Da, M_n/M_w = 2.2. **3·TFSA**: 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$_3$)$_2$−). SEC data, M_n = 6.43 × 10^3 Da, M_w = 4.19 × 10^4 Da, M_n/M_w = 6.5. **5·TFSA**: 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). SEC data, M_n = 1.74 × 10^4 Da, M_w = 7.84 × 10^4 Da, M_n/M_w = 4.5.

Table 1. Number-Average Molecular Weight (M_n), Number-Average Degree of Polymerization (n), Weight-Average Molecular Weight (M_w), and Polydispersity Index (M_w/M_n) of the Ionene Polymers

compound[a]	M_n	n	M_w	M_w/M_n
1·TFSA	6.19 × 10^3	11	2.11 × 10^4	3.4
2·TFSA	6.41 × 10^3	14	1.41 × 10^4	2.2
3·TFSA	6.43 × 10^3	14	4.19 × 10^4	6.5
5·TFSA	1.74 × 10^4	34	7.84 × 10^4	4.5

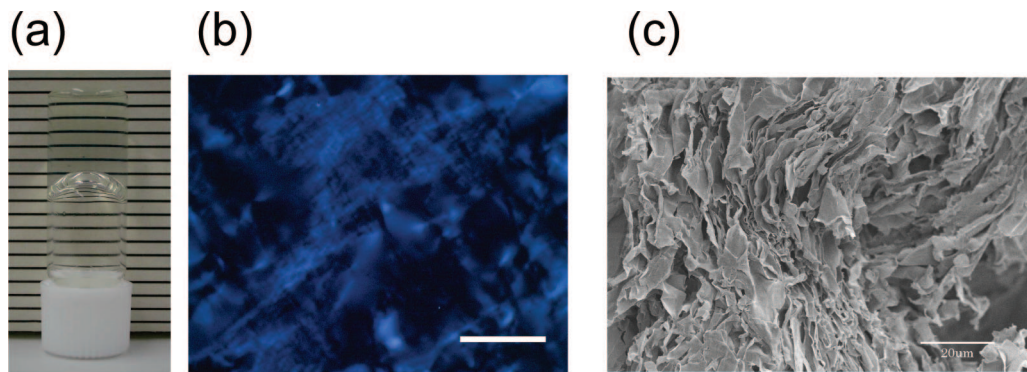[a] Counteranion exchange reaction of **4·Cl** cannot be performed due to the poor solubility even in hot water.

Figure 1. (a) A hydrogel with **5·Cl** at 10 g L^{-1}. (b) Polarized optical micrograph of a hydrogel with **5·Cl** at 10 g L^{-1} (4×, scale bar is 0.5 mm). (c) SEM image of xerogel with **5·Cl** at 10 g L^{-1} (1000×, scale bar is 20 μm).

Results and Discussion

Synthesis and SEC Characterization of Ionene Polymers. The ionene polymers were synthesized according to the two-step reactions as shown in Scheme 1. The amidation reaction of 4-(chloromethyl)benzoyl chloride (**6**) and *p*-phenylenediamine (**7**) in the presence of triethylamine in CH$_2$Cl$_2$ gave 1,4-bis[4-(chloromethyl)benzamido]benzene (**8**) as white precipitate in 99% yield. The product **8** has an electrophilic benzyl part at termini and thus is used as a dielectrophilic monomer for the polymerization reaction. Equimolar mixtures of **8** and diazabicyclo[2.2.2]octane (DABCO) or *N,N,N′,N′*-tetramethylalkylenediamines as dinucleophilic monomers in DMF were stirred at 80 °C for 48 h to give the corresponding ionene polymers (**1·Cl**−**5·Cl**) as precipitate in high yields (83−94%). The structures were identified by ^{1}H NMR using DMSO/D$_2$O (v/v = 1/1) as a solvent. It was very difficult to directly determine the molecular weight of the ionene polymers using an aqueous size exclusion chromatography (SEC) measurement due to the retardation of the polymers in the column. To tune the solubility of the polymers for the SEC measurement, the counteranion exchange reactions from chloride to bis(trifluoromethanesulfonyl)amide (TFSA) were carried out. A solution of LiTFSA in water was added to an aqueous solution of the ionene polymer at 90 °C (except for **4·Cl** due to its poor solubility even in hot water). The molecular weight of the TFSA modified polymers was then determined by the SEC with DMF eluent containing 30 mM LiTFSA (poly(methymethacrylate) standards). The SEC data are shown in Table 1. It was found that the number-average molecular weights increased from 6.19 × 10^3 Da (**1·TFSA**) to 1.74 × 10^4 Da (**5·TFSA**) with increasing the length of the diamine spacer mainly due to the gain of the degree of polymerization.

Hydrogels. The gelation ability of the ionene polymers for water was tested by a vial inversion method. The ionene polymers except for **4·Cl** could be dissolved in the deionized water by heating, followed by cooling to room temperature to obtain gels. It was found that the spacer and/or the molecular weight significantly influenced the gelation process. The **1·Cl** having DABCO spacer produced turbid hydrogels at 50 g L^{-1} after standing for 3 days, while it took over a week for 40 g L^{-1} concentration. On the other hand, **2·Cl** having flexible ethylene linker produced a hydrogel at 30 g L^{-1} within 5 h. The **3·Cl** gave a translucent hydrogel at 30 g L^{-1} after standing for 3−4 days. Interestingly, the **5·Cl** having the longest diamine spacer and the highest molecular weight produced a transparent gel at relatively lower concentration of 10 g L^{-1} within 3 h, showing the highest gelation ability among these ionene polymers (Figure 1a).

Since none of the conventional ionene polymers has shown the gelation property, it is apparent that the *N,N′*-(*p*-phenylene)dibenzamide linkages in the main chain are crucial for the hydrogelation. Although the gelation mechanism has not been clear so far, the intermolecular hydrogen bond interaction, π−π interaction, cation−π interaction, and electrostatic interaction relating to the "polyelectrolyte effect"[7] on the viscosity of polymer solution would be important. The FT-IR spectrum of **5·Cl** (10 g L^{-1}) in D$_2$O showed a broad peak of the carbonyl stretching around 1645 cm^{-1}, similar to the low-molecular-weight hydrogelator based on the benzamide structure.[8] The result would likely indicate the intermolecular hydrogen bonding between amide groups to give gel networks. However, the strong interaction between the protic hydrogen of the amide group and halide anion, which might overcome the conventional hydrogen bond interaction between amide groups, has been suggested not only theoretically[9] but also experimentally[10] in the literature. So far we should not ignore the possibility of the *indirect* hydrogen-bonding interaction between amide groups through the anions and/or water molecules even in the gel state. The polarized optical micrograph of the transparent gel showed birefringence under the crossed nicols condition, clearly showing the formation of anisotropic aggregation (Figure 1b). It is noteworthy that the physical hydrogel of poly(*p*-sulfophenylene terephthalamide) based on the similar benzamide structure in the backbone to the present polymers also showed birefringence in the gel state.[11,12] The SEM image of the xerogel prepared by freeze-drying of the transparent gel of **5·Cl** revealed the formation of layered filmlike structures instead of the fibrous structure, as in case of our previous report[6] (Figure 1c). As for the acid resistance, which is not observed for most of the natural compounds forming hydrogels, the **5·Cl** can gelatinize 0.1 M HCl solution (pH = 1) at 10 g L^{-1}, forming a turbid gel. This result evidently reflects that there is not any acid labile moiety in the structure of **5·Cl**.

Rheology of Hydrogels. We have previously reported the unique rheological property of the oligomeric electrolyte hydrogel showing a rapid recovery of storage module after continuous shear stress.[6] In this study, we also examined the rheology of the hydrogels based on the ionene polymers. In dynamic strain amplitude sweep measurements at 1 Hz frequency, the hydrogel with **1·Cl** (50 g L^{-1}), **2·Cl** (30 g L^{-1}), and **3·Cl** (40 g L^{-1}) showed relatively weak gel strength with storage modulus (*G*′) to be less than 100 Pa in plateau regions (see Supporting Information). On the other hand, the hydrogel with **5·Cl** showed higher *G*′ values than 100 Pa above 20 g L^{-1} of concentration (Figure 2a), which indicated **5·Cl** effectively solidified water compared to the other ionene polymers.
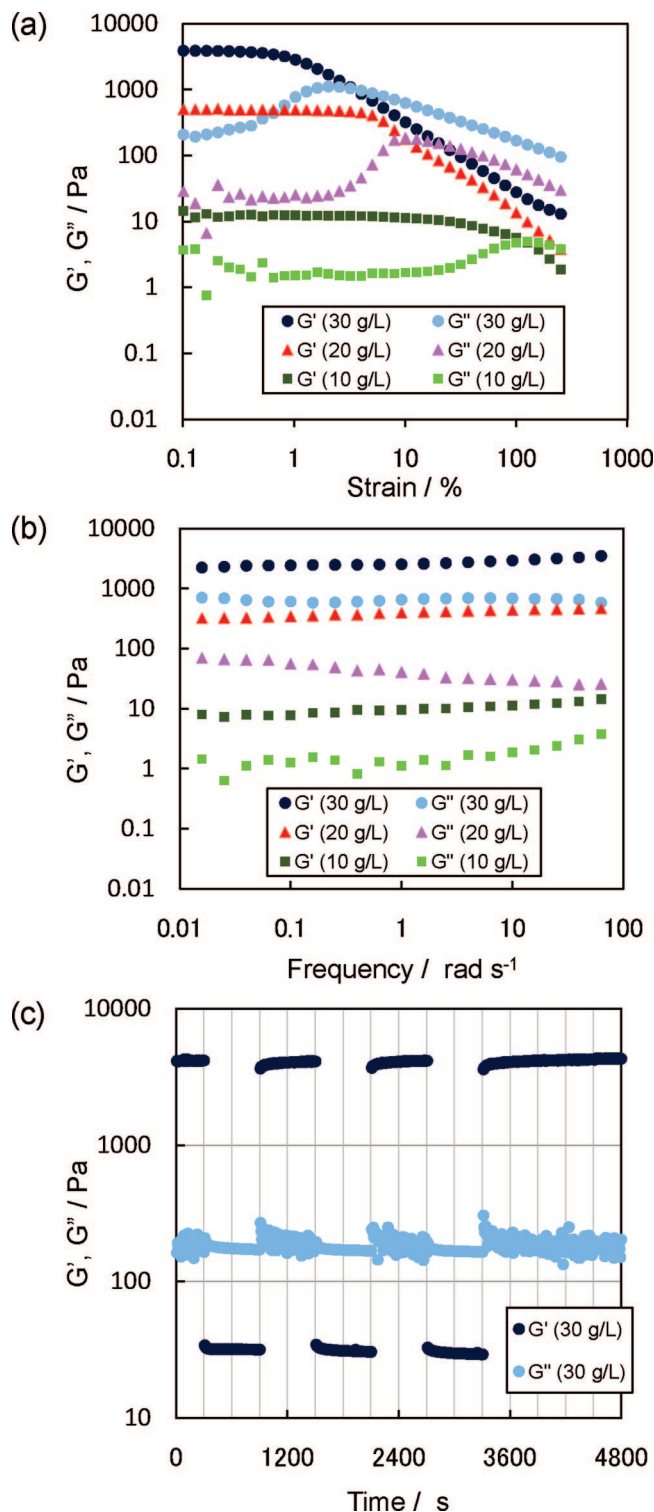
(a)

(b)

(c)

Figure 2. Rheological experiments for the hydrogel with **5·Cl**: (a) dynamic strain amplitude sweep tests at 1 Hz (= 6.28 rad s^{-1}); (b) dynamic frequency sweep tests at 1% strain; (c) dynamic step strain amplitude test ($\gamma = 0.1\%$ or 100%).

The dynamic strain amplitude sweep profiles of **5·Cl** also well indicated the thixotropic property of the gel. The crossover point of storage modulus (G') and loss modulus (G'') moved to the lower strain region when the concentration of **5·Cl** was increased. This trend is very similar to the cationic polypeptide hydrogels,[13] and thus the polymer gel becomes more brittle, in the sense of the gel structure collapsing at smaller strains, as the **5·Cl** concentration increases. In dynamic frequency sweep at 1% strain (Figure 2b), the value of G' was consistently larger

(a)

(b)
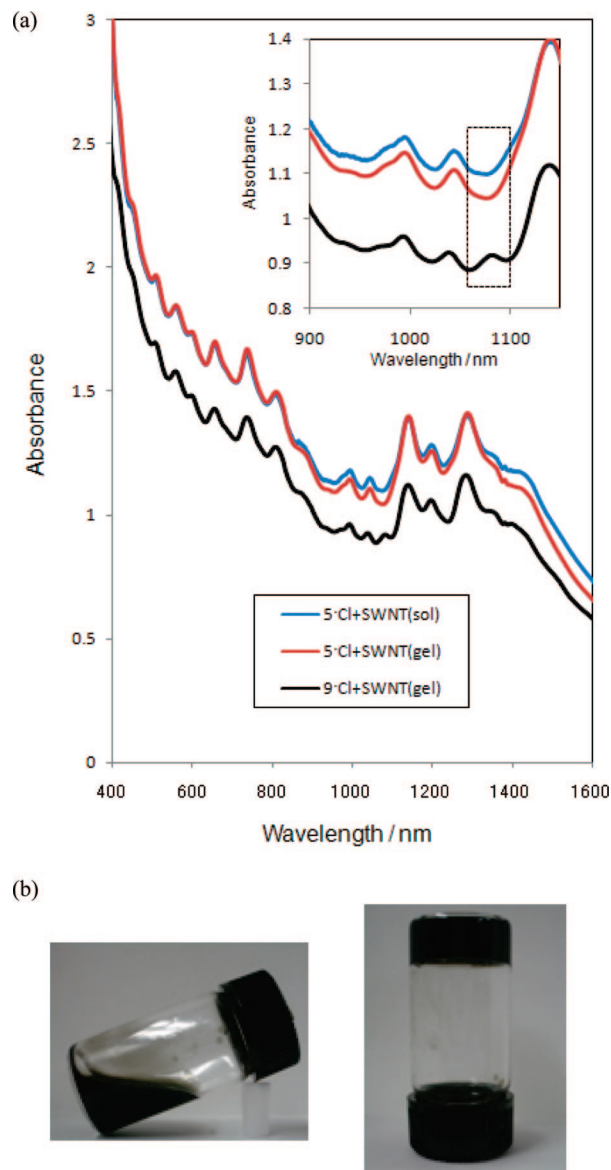
Figure 3. (a) Vis−NIR spectra of fluid (blue line) and gels (red and black lines) with dispersed SWNT (0.2 g L^{-1}) with **5·Cl** or **9·Cl** (20 g L^{-1}) in D$_2$O. (b) Pictures of a fluid (left) and a gel state (right, the upturned flask) containing SWNT with **5·Cl** (20 g L^{-1}) in D$_2$O.

than that of G'', indicating the quasi-solid nature of the gel in the whole range of the measured frequency. Nowak et al.[13−15] and we[6] have reported hydrogels composed of poly- or oligo-electrolytes showing a rapidly recovering property after the mechanical decomposition. It is quite interesting because this recovering behavior should be "self-healing" of the artificial gel materials. We found that the hydrogel of **5·Cl** also showed a fast recovering property against the mechanical stress by continuous oscillation. In the recovery measurements for the gel of **5·Cl** at 30 g L^{-1} (Figure 2c), the initial G' was observed to be 4.16×10^3 Pa at the small strain ($\gamma = 0.1\%$). When large strain ($\gamma = 100\%$) was given to the gel, G' was immediately decreased by more than 10^2 times to be ca. 30 Pa. When the strain was returned to the small value ($\gamma = 0.1\%$) again after 600 s of the continuous stress, the G' was rapidly recovered within 10 s to be 3.64×10^3 Pa which is estimated to be 87% of the initial G'. The fast recovery of the gel strength was repeatedly confirmed for three cycles. Considering both the present and previous results,[6] it is thus suggested that the rapid recovery behavior of the hydrogel would be a common property for the hydrogels based on the ionene polymers. Because the

9·Cl
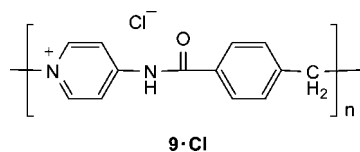
recovery behavior of gels is certainly liked to the gel topology and nature of the cross-links between the structure elements, we assume the amide−anion interaction[9,10] should be crucial not only for the gel network formation as already pointed out in the former section but also for the rapid recovery of the hydrogel.

SWNT Dispersion and Gel. The dispersion of SWNT has attracted much attention because of the limitation of processing methods caused by the intractable property due to the heavy aggregation.[16−19] SWNT composite gels are also of potential interest for various applications.[20−24] We have already reported the pyridinium oligomer, **9·Cl**, can be used for the dispersant for SWNT and easily give both SWNT dispersed solution and gel.[6]

In this study, we found the polymeric electrolyte **5·Cl** also showed an additional property as a dispersant for SWNT in water. SWNT (0.5 mg, HiPCO, CNI carbon nanotubes) was added to 2.5 mL of the hydrogel of **5·Cl** (D_2O, 20 g L^{-1}), and the gel was sonicated for 60 min (100 W, 45 kHz). The vis−NIR spectrum of a resulting black solution even without the ultracentrifugation shows sharp peaks from 400 to 1600 nm assigned to the absorption of the molecularly dispersed SWNT (Figure 3a, blue line).[6] Although the polymeric dispersant having tetraalkylammonium part for SWNT has been reported, it was a vinyl polymer and the ammonium moiety located at a substituent.[19] In addition, the pyrene pendant group is obviously crucial for the interaction between the polymer and SWNT in that case. Therefore, to the best of our knowledge, the simple ionene polymer based on tetraalkylammonium backbone without any polycyclic aromatic groups has not been used for the purpose of the SWNT dispersion. It is also worth noting that the present result clearly showed that a planar pyridinium cation moiety, which was thought to be essential for the cation−π interaction with SWNT π-surface in our previous study,[6] is proved to be not always necessary to form stable SWNT dispersion. We assume the planar π−surface of the N,N'-(p-phenylene)dibenzamide moiety would be crucial for the π−π interaction with SWNT, similar to the polymeric SWNT dispersant based on polyimides that works well in DMSO.[17] Actually, when we compared the vis−NIR spectra between the SWNT with **5·Cl** and **9·Cl** (Figure 3a, blue and black lines), the spectra were almost identical each other, but there was found to be a small difference. The absorption at 1082 nm observed for SWNT with **9·Cl** has disappeared in case of the SWNT with **5·Cl** (Figure 3a, inset). The disappearance might be caused by the difference between the cation−π and π−π interactions as main driving forces for the dispersion formation when we compare the two dispersants. The absorption at The SWNT solution prepared by sonication did not spontaneously recover to a gel. However, after heating and the subsequent cooling, the solution turned into a black gel retaining the dispersed SWNT in it. The repetitive sol−gel transition induced by a sonication and the following heating/cooling process was reproducible even after several weeks. It was confirmed that the sol−gel transition did not change the degree of dispersion of SWNT by the comparison of the vis−NIR spectrum of the solution and the gel (Figure 3). It is worth noting here that the similar reversible sol−gel change by sonication was observed in hydrogel with only **5·Cl** at 20 g L^{-1} without SWNT. It is known that sonication can cleave noncovalent bonds and the

reversible sol−gel/gel−sol change by ultrasound is of considerable interest for the external stimuli responsive gel.[25]

Conclusions

In conclusion, we synthesized the ionene polymers based on tetraalkylammonium backbone with N,N'-(p-phenylene)dibenzamide linkages in high yields by an intermolecular quaternization reaction using 1,4-bis[4-(chloromethyl)benzamido]benzene and commercially available N,N,N',N'-tetramethylalkylenediamines as monomers. Most of the ionene polymers showed the efficient ability to gelate water under the mild condition without any additives, i.e., anionic surfactants. We found the spacer and/or the molecular weight significantly influenced the gelation behavior. The ionene polymer **5·Cl** having the longest diamine spacer and the highest molecular weight produced a transparent gel at relatively lower concentration of 10 g L^{-1}, showing the highest gelation ability among these ionene polymers. One of these ionene polymers also impart many unique properties such as gelation of acidic solution, fast recovery property after mechanical stress, dispersion of SWNT both in fluid and gel state, and external stimuli responsibility of the hydrogel by ultrasound. We believe that the present results present not only structural motif but also a facile synthetic procedure for the polymer hydrogels. Further modification of the hydrogels with the cationic polymers by the coupling of the other dielectrophilic and dinucleophilic monomers are now in progress.

Supporting Information Available: Detailed syntheses, NMR spectra, SEC profiles, rheological data of ionene polymers, and IR spectra of **5·Cl** in D_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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