Hydrogels Based on Surfactant-Free Ionene Polymers with $N,N\#-(p\text{-}Phenylene)dibenzamide$ Linkages

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A hydrogel with 5·Cl at 10 g L$^{-1}$

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ABSTRACT: Ionene polymers with \(N,N'(p\text{-phenylene})\)dibenzamide linkages were synthesized in high yields by the copolymerization of 1,4-bis[4-(chloromethyl)benzamide]benzene and \(\alpha,\omega\)-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 amiation 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 \(N,N'(p\text{-phenylene})\)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\(_2\)O (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-
SEM measurement was prepared from the hydrogel with 5·Cl by freeze-drying in vacuo using an EYELA FDU-1200 lyophylizer. 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 ionone polymers were produced as follows: polymers were placed in a vial (diameter 17.7 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 D₂O (2.5 mL) by heating. The hot solution was left at room temperature and then gradually turned into a gel. SWNT containing the SWNT was sonicated for 60 min by an ultrasonicator for 60 min. 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. SWNT or N₃,N₃,N₃,N₄,N₄,N₄-tetramethyldialkylenediamines, DMF, 80 °C, 48 h; yield: 94%, 84%, 83%, 88%, 93% from 1·Cl to 5·Cl.

Synthesis. 1,4-Bis[4-(chloromethyl)benzamido]benzene (8). To a suspension of p-phenylelenediamine (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)benzyloxyl 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%). ¹H NMR (400 MHz, DMSO-d₆, 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). ¹³C NMR (100.6 MHz, DMSO-d₆, TMS): δ 164.7 (C=O), 140.9, 134.8, 134.7, 128.7, 127.9, 120.5, 45.3 (Ph—CH₂Cl). Anal. Calcd for C₂₂H₁₈Cl₄N₆O: C, 63.93; H, 4.39; N, 6.78. Found: C, 63.80; H, 4.32; N, 6.48.

Poly[diazeniacyclo[2.2.2][octane-1,4-diylmethylene-1,4-phe

nylenemethylene dichloride] (3·Cl), poly[(dimethyliminio)butane-1,4-diyl(dimethyliminio)methylene-1,4-phenylene-carbonyl-1,4-phenylene-iminocarboxyl-1,4-phenyleneimethylene dichloride] (4·Cl), and poly[(dimethyliminio)hexane-1,6-diyl(dimethyliminio)methylene-1,4-phenylene-carbonyl-1,4-phenyleneimethylene dichloride] (5·Cl) were synthesized. 2·Cl. 84%. ¹H NMR (400 MHz, DMSO-d₆, 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(CH₂Cl)₂). IR (10 g L⁻¹, D₂O): 1640, 1572, 1517, 1456, 1434, 1396 cm⁻¹. Anal. Calcd for C₆₃H₄₅N₃O₇: 61.67, 6.47, 10.58. Found: C, 61.00; H, 6.76; N, 10.14. 3·Cl: 83%. ¹H NMR (400 MHz, DMSO-d₆, TMS): δ 8.06—7.96 (m), 7.77—7.62 (m), 4.66 (br s), 3.48 (br s), 3.11 (s, —N(CH₂Cl)₂). IR (10 g L⁻¹, D₂O): 1640, 1573, 1517, 1456, 1434, 1396 cm⁻¹. Anal. Calcd for C₆₃H₄₅N₃O₇: 61.67, 6.47, 10.58. Found: C, 61.00; H, 6.76; N, 10.14. 4·Cl: 88%. ¹H NMR (400 MHz, DMSO-d₆, TMS): δ 8.05 (s), 7.74—7.68 (m), 3.46 (br s), 3.05 (s, —N(CH₂Cl)₂), 1.97 (br s). Anal. Calcd for C₆₄H₄₆N₄O₈: 62.67, 6.84, 9.33. 5·Cl: 93%. ¹H NMR (400 MHz, DMSO-d₆, TMS): δ 8.04 (s), 7.73—7.67 (m), 3.35 (br s), 3.01 (s, —N(CH₂Cl)₂), 1.90 (br s). IR (10 g L⁻¹, D₂O): 1654, 1571, 1515, 1485, 1454, 1427, 1390 cm⁻¹. Anal. Calcd for C₆₅H₄₇N₄O₈: 62.67, 7.23, 9.57. Found: C, 62.77; H, 7.54; N, 9.03.

Poly[diazeniacyclo[2.2.2][octane-1,4-diylmethylene-1,4-phenylene-carbonylino-1,4-phenyleneimino-carboxyl-1,4-phenylene-imethylene dibi(s 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 dibi(s 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%). ¹H NMR (400 MHz, DMSO-d₆, 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(CH₂H₂)₂N⁺Cl⁻, 3.04 (br t, —N(CH₂H₂)₂N⁺Cl⁻), 1.90 (br s). IR (10 g L⁻¹, D₂O): 1645, 1571, 1515, 1485, 1454, 1427, 1390 cm⁻¹. Anal. Calcd for C₆₅H₄₇N₄O₈: 62.67, 7.23, 9.57. Found: C, 62.77; H, 7.54; N, 9.03.

In the same procedure for 1·TfSA, poly[(dimethyliminio)ethylen

Table 1. Number-Average Molecular Weight (Mₙ), Weight-Average Molecular Weight (Mₙ), and Polydispersity Index (Mₙ/Mₙ) of the Ionene Polymers

<table>
<thead>
<tr>
<th>compound</th>
<th>Mₙ (Da)</th>
<th>n</th>
<th>Mₙ (Da)</th>
<th>Mₙ/Mₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·TfSA</td>
<td>6.19 × 10⁴</td>
<td>11</td>
<td>2.11 × 10⁴</td>
<td>3.4</td>
</tr>
<tr>
<td>2·TfSA</td>
<td>6.41 × 10⁴</td>
<td>14</td>
<td>1.41 × 10⁴</td>
<td>2.2</td>
</tr>
<tr>
<td>3·TfSA</td>
<td>6.43 × 10⁴</td>
<td>14</td>
<td>4.19 × 10⁴</td>
<td>6.5</td>
</tr>
<tr>
<td>5·TfSA</td>
<td>1.74 × 10⁵</td>
<td>34</td>
<td>7.84 × 10⁴</td>
<td>4.5</td>
</tr>
</tbody>
</table>

⁶ Counterion exchange reaction of 4·Cl cannot be performed due to the poor solubility even in hot water.
that the number-average molecular weights increased from 6.19
standards). The SEC data are shown in Table 1. It was found
modified polymers was then determined by the SEC with DMF
solubility even in hot water). The molecular weight of the TFSA
 spacer and the highest molecular weight produced a transparent
result evident from LiTFSA in water was added to an aqueous solution of
the ionene polymer at 90
°C (except for
 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
diluent 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” on the viscosity of
polymer solution would be important. The FT-IR spectrum of
5·Cl (10 g L
−1
) in D2O showed a broad peak of the carbonyl
stretching around 1645 cm
−1
, similar to the low-molecular-
weight hydrogelator based on the benzamide structure. 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
 but also experimentally
 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.

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. 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.
The dynamic strain amplitude sweep profiles of 5·Cl also 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, 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 than that of $G''$, indicating the quasi-solid nature of the gel in the whole range of the measured frequency. Nowak et al. and we 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, 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
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\(^{\prime}\)-(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\(^{\prime}\),N\(^{\prime}\)-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.

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**Supporting Information Available:** Detailed syntheses, NMR spectra, SEC profiles, rheological data of ionene polymers, and IR spectra of 5·Cl in D\(_2\)O. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


