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Communication

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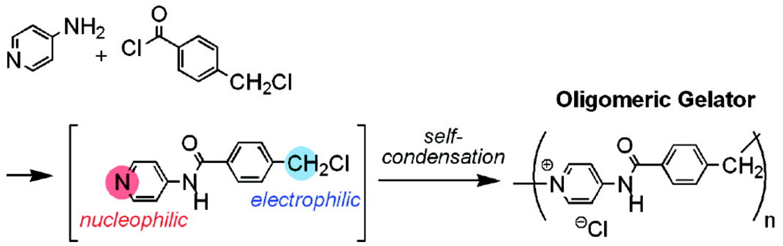

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COMMUNICATIONS

Oligomeric Electrolyte as a Multifunctional Gelator

Masaru Yoshida,*,† Nagatoshi Koumura,‡ Yoshihiro Misawa,† Nobuyuki Tamaoki,†
Hajime Matsumoto,§ Hajime Kawanami,|| Said Kazaoui,⊥ and Nobutsugu Minami†

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, Photonics Research Institute, AIST, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, Research Institute for Ubiquitous Energy Devices, AIST, 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan, Research Center For Compact Chemical Process, AIST, 4-2-1, Nigatake, Miyaginoku, Sendai, Miyagi 983-8551, Japan, and Research Center for Advanced Carbon Materials, AIST, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

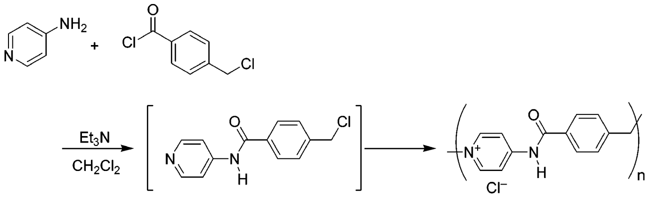
Received May 29, 2007; E-mail: masaru.yoshida@aist.go.jp

Hydrogels derived from natural (e.g., gelatin) and synthetic compounds are very important in biological, medical, and pharmaceutical products. In particular, synthetic gelators are extremely promising because their properties are readily tunable by chemical functionalization.[1] However, these syntheses often require multisteps and therefore tend to hinder large-scale production. In addition, except for a few amphiphilic gelators,[2] direct utilization of the hydrogelators in other fluids, e.g., organic solvents, ionic liquids, is generally limited due to their low solubility.

In this communication we describe a novel oligomeric electrolyte as a new structural motif in gelators that has the following notable characteristics: (1) facile preparation in one pot involving condensation and subsequent intermolecular quaternization reaction; (2) tunable solubility to apply to various solvents (e.g., organic, aqueous) and ionic liquids by a simple anion-exchange reaction; (3) resistance to acids; (4) fast recovery of the mechanical strength after stress; (5) synergistic use as a dispersant for single-walled carbon nanotubes (SWNT).

The amidation reaction of commercially available 4-aminopyridine and 4-(chloromethyl)benzoyl chloride in dichloromethane with a slight excess of triethylamine directly gave a white precipitate described as the ionic oligomer **1·Cl** (poly[pyridinium-1,4-diyl-iminocarbonyl-1,4-phenylene-methylene chloride]) in 80% yield (Scheme 1). The expected ampholytic amide intermediate having both the nucleophilic and the electrophilic parts at the termini was not isolated because the polymerization (intermolecular quaternization reaction) is very fast and occurs immediately after the condensation reaction. The compound **1·Cl** is soluble only in water, and its structure was assigned by NMR spectroscopy in D_2O. Functionalizations using anion-exchange reactions of **1·Cl** were easily carried out by adding an appropriate salt with perfluoro anion to a hot solution of **1·Cl** in water. New ionic oligomers such as **1·PF₆** and **1·TFSI** were prepared with a PF_6 and TFSI ($N(SO_2CF_3)_2$) anions, respectively. Since those products were insoluble and precipitated in water, they were isolated and redispersed in organic solvents such as DMSO and DMF. The oligomeric nature of the electrolytes was confirmed by SEC of **1·TFSI**. The weight-averaged molecular weight (M_w) of **1·TFSI** was approximately 2.80×10^3 Da (PDI = 1.66, polystyrene standards, DMF eluent containing 30 mM of LiTFSI).[3] The degree of polymerization was apparently calculated to be 13 using the formal M_w and the molecular weight of the cationic part of the monomer unit (211 Da). This oligomeric electrolyte carries a positive charge on the main chain as already reported for viologen polymers.[4] To the best of our knowledge, however, **1·Cl** is one of rare examples of the main-chain polyelectrolyte synthesized by "self-condensation" through the intermolecular quaternization as is known for the thermal polymerization of 4-bromo- and 4-chloropyridine.[5]

Scheme 1. Synthesis of the Oligomeric Gelator **1·Cl**



1·Cl

The **1·Cl** produces a translucent gel at concentrations above 7.5 g/L in water (Figure 1a). The apparent gel−sol transition temperature (T_{g-s}) was estimated to be 77−80 °C in case of 20 g/L of **1·Cl**. The **1·Cl** was not able to be applied for the gelation of any organic solvents due to its low solubility. However, a transparent gel was obtained based on the anion-exchanged ionic oligomer **1·TFSI** at a concentration of 50 g/L in methanol. In addition, **1·PF₆** acted as a specific gelator for several ionic liquids,[6] e.g., 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm-BF_4) and 1-butylpyridinium tetrafluoroborate (1-BuPy-BF_4). When we tried to use **1·Cl** directly for the ionic liquids, the **1·Cl** never dissolved into the media even after an intensive heating. However, **1·PF₆** can dissolve in those ionic liquids by heating and gelatinizes them. It should be pointed out the ion exchange between PF_6 of **1·PF₆** and an excess amount of BF_4 may occur during the formation of the gels of ionic liquids. It is thus noteworthy that the miscibility of the ionic gelator **1·Cl** is well tunable by the counteranion-exchange reaction. It is also important that the ionic liquid was gelatinized without impairing its ionic conductivity (σ). The σ of the ionic gel (σ_{gel}) (EMIm-BF_4 + **1·PF₆**, $c = 20$ g/L, at 25 °C) was measured to be 14.1 mS/cm, almost identical with that for the neat ionic liquid ($\sigma_{gel}/\sigma_{neat} = 0.98$) despite the formation of stiff gel. The σ_{gel} slightly decreases with increasing the concentration of **1·PF₆** (13.2 mS/cm, $c = 40$ g/L, at 25 °C) and increases with increasing temperature (25.1 mS/cm, $c = 20$ g/L, at 45 °C).

Although the gelation mechanism has not been clear so far, the intermolecular hydrogen-bond interaction, $\pi-\pi$ interaction, cation−π interaction, and electrostatic interaction relating to the "polyelectrolyte effect"[7] on the viscosity of the polymer solution would be effective. As for the hydrogen-bond interaction, two $\nu_{(C=O)}$ bands were observed at 1691 and 1634 cm^{-1}, respectively,

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† Nanotechnology Research Institute.
‡ Photonics Research Institute.
§ Research Institute for Ubiquitous Energy Devices.
|| Research Center for Compact Chemical Process.
⊥ Research Center for Advanced Carbon Materials.

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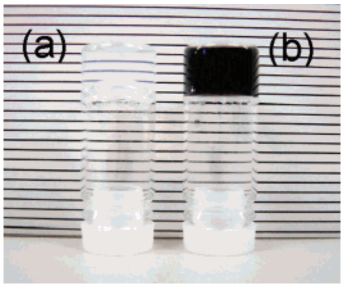

Figure 1. (a) Hydrogel with **1·Cl** (10 g/L). (b) Hybrid hydrogel with **1·Cl** (20 g/L) and single-walled carbon nanotubes (0.1 g/L).

in the FT-IR spectrum of the D_2O gel of **1·Cl**. The wavenumber of the latter band is well consistent with the literature value (1641 cm^{-1}) of the hydrogen-bonded carbonyl band of a structurally similar hydrogelator based on a benzamide derivative.[8] This result indicates the amide groups partially interact with each other by hydrogen bonding for the gel formation. The **1·Cl** also showed unique concentration-dependent absorption spectra in water (see Supporting Information). In a dilute condition ($c \approx 10^{-4}$ M (based on the monomer unit including the chloride anion)), two distinct absorption peaks were observed at 347 and 297 nm, respectively. However, the former peak observed at longer wavelength completely disappeared at a high concentration ($c > 3 \times 10^{-3}$ M (0.74 g/L)). This unusual absorption change may be attributed to the delocalized conjugation by the enolization of amide moiety in the main chain, if low concentration conditions lead to the enolization stabilized by the tautomerism between the pyridinium and the pyridinylidene structures of the cationic part. However, at higher concentrations, the keto form with a localized conjugation would be likely to become dominant due to the intermolecular hydrogen-bond interaction largely contributing the hydrogel formation.[9]

From the application standpoint, the hydrogel from **1·Cl** has several unique characteristics. First, the **1·Cl** is remarkably resistant to acid in contrast to the some natural gelators, for example, agarose and gelatin. The natural ones, in the acidic solution due to the acid-catalyzed hydrolysis at the ester or ketal moieties, tend to lose their gelation property. The ionic gelator **1·Cl** can form a gel in acidic water even at pH = 1 (0.1 N of aq HCl or 45 wt% of H_3PO_4). On the other hand, **1·Cl** was found to lose its solubility when an equivalent molar amount of basic or neutral inorganic salts, such as NaOH and NaCl, was added into water. Since **1·Cl** (c = 10 g/L) was able to gelatinize a diluted tetrabutylammonium hydroxide solution (pH = 10) containing no metal ion, we conclude that the existence of metal cations significantly decreases the solubility and thus the gelation ability of **1·Cl**. Although the origin of the specific effect of the metal cations is still unclear, this effect may be related to a kind of a salt-out (deswelling) phenomenon reported for several polymer hydrogels.[10]

Second, the rheological property of the hydrogel consisting of **1·Cl** was also investigated. In Figure 2a the storage moduli (G') and loss moduli (G'') are shown as a function of angular frequency (ω) for three different concentrations of **1·Cl** (γ = 0.2%). All of the samples showed the plateau regions of the dynamic moduli. The G' numbers showed a substantial elastic response, which are larger than the G'' over the entire range of frequencies. Strain amplitude sweeps shown in Figure 2b also revealed the elastic response of the hydrogel (c = 30 g/L). The G' rapidly decreased above the critical strain regions ($\gamma > 10\%$), showing a collapse of the gel state. Interestingly, the gel exhibits a very rapid recovery of the mechanical strength after large amplitude oscillatory breakdown (Figure 2c). When nonlinear, large-amplitude oscillations ($\gamma = 100\%$, $\omega = 6$ rad/s (1 Hz)) were applied, the G' decreases to ca. 10 Pa, resulting in a quasi-liquid state (tan δ (G''/G') $\approx$ 10). However, the G' immediately recovered close to 1×10^4 Pa within 10 s, showing a quasi-solid state (tan $\delta \approx 0.1$), when the amplitude oscillations changed to a small value (γ = 0.1%) at the same frequency. The recovery was fully reproducible for at least three cycles. The rheological measurement indicates that these gels are thixotropic and the **1·Cl** is a promising candidate as a novel fast-recovering hydrogel scaffold. Nowak et al. have already reported a similar behavior for hydrogel made from self-assembled diblock copolypeptide having an ammonium side chain.[11] It is noteworthy that the G' of the quasi-solid state of the present hydrogel was almost one magnitude higher than that reported in their study.

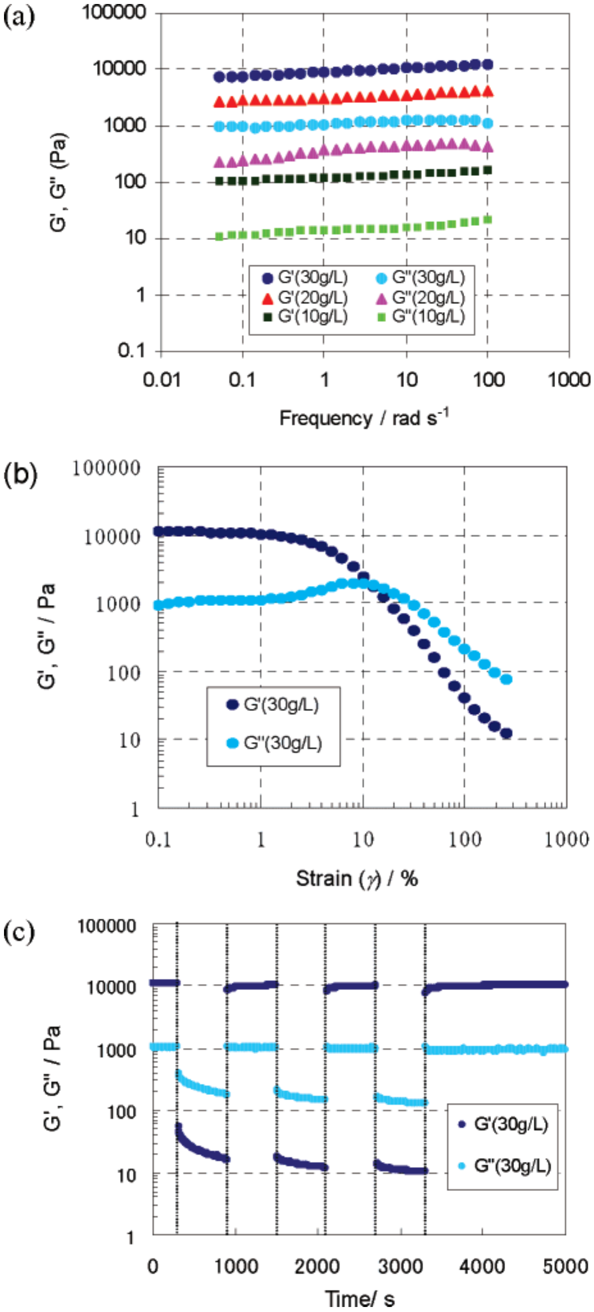

Figure 2. Rheological data of the hydrogels prepared by **1·Cl**. (a) Frequency sweeps (ω = 0.05−100 rad/s) of three samples of the hydrogels with different concentrations. (c = 10, 20, and 30 g/L) (b) Strain amplitude sweeps and (c) step strain measurement of the hydrogel (c = 30 g/L). Step strain was a continuous measurement (three cycles)).

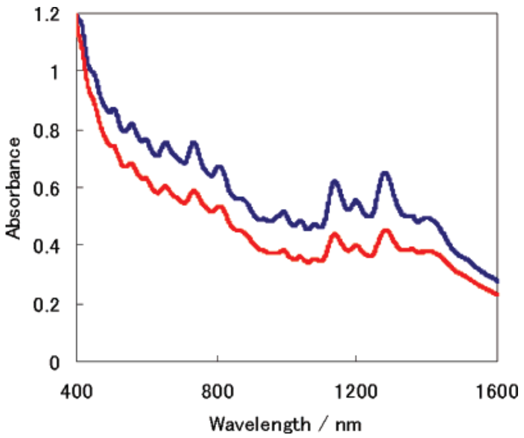

Figure 3. UV−vis−NIR spectra of the D_2O solution based on **1·Cl** (7.5 g/L) with SWNT (0.1 g/L) (blue) and D_2O gel based on **1·Cl** (20 g/L) with SWNT (0.1 g/L) (red).

Last, SWNT composite gels are of potential interest for various applications.[12] In this context, it is intriguing to study the basic properties of the SWNT gel system prepared from **1·Cl**. A mixture of 37.5 mg of **1·Cl** and 0.5 mg of SWNT (HiPco, CNI) in 5 mL of water was sonicated for 1 h using a low-power bath sonication (130 W, 35 kHz). A stable dispersion was obtained under these mild conditions without high-power sonication (using an immersed horn) that is known to damage the nanotubes.[13] A well-resolved optical absorption spectrum (400−1600 nm) clearly demonstrates that a substantial amount of SWNT can be unbundled and dispersed in an aqueous solution of **1·Cl** (Figure 3, blue line). The degree of dispersion was further improved by the centrifugation (at 160,000*g*, 1 h) to discard slightly remaining large aggregates of **1·Cl** and bundled SWNT. The obtained supernatant solution shows the typical optical absorption features of further molecularly dispersed SWNT. Dispersion of SWNT using a slightly concentrated solution of **1·Cl** was enough to form a SWNT-containing gel without any other additives (Figure 1b). The shape of the UV−vis−NIR spectrum of the gel was found to be essentially the same as that of the solution (Figure 3, red line). We observed that T_{g-s} of the hydrogel decreases to some extent in the presence of SWNT. For instance, in case of the hydrogel with 20 g/L of **1·Cl**, the apparent T_{g-s} changed from 77−80 °C to 44−56 °C after the addition of 0.1 g/L of SWNT. The main reason for the softening of the SWNT hybrid hydrogel would be the long-time sonication that is necessary to obtain the dispersion of SWNT, because the control experiment using the native hydrogel without SWNT shows a similar decrease of the gel strength after sonication. However, further careful investigation should be required to know the pristine effect of SWNT on the strength of the current hydrogels. Nevertheless, the bifunctional behavior of **1·Cl** as a "dispersant" and as a "gelator" may contribute to the development of a novel, hybrid hydrogel filled with SWNT.

In summary, (1) we successfully prepared a new ionic gelator by a very simple one-pot condensation and intermolecular quaternization reaction; (2) this gelator is applicable to a broad range of solvents (e.g., organic, aqueous) and ionic liquids by anion-exchange reaction; (3) and thus a composite material including well-dispersed SWNT is produced. The gelator is characterized by relatively high ionic conductivity of the ionic liquid gel and by a fast recovery of its rheological properties. Future work will focus on the applications of these gels from the oligomeric electrolytes, for example the use of the ionic gels in quasi-solid-electrolyte dye-sensitized solar cells, electrochemical actuators, and electric double-layer capacitors (EDLC) and the use of SWNT gel for electrochemical separation and modification of SWNT. These investigations are in progress.

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Supporting Information Available: Synthesis, ^{1}H NMR and UV spectra, SEC profiles and characterization of the ionic oligomers, SEM image of xerogel with **1·Cl**, ionic conductivity measurements of ionic gels with **1·PF$_6$**, and complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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