Molecular Ordering of Organic Molten Salts Triggered by Single-Walled Carbon Nanotubes

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When mixed with imidazolium ion-based room-temperature ionic liquids, pristine single-walled carbon nanotubes formed gels after being ground. The heavily entangled nanotube bundles were found to entangle within the gel to form much finer bundles. Phase transition and rheological properties suggest that the gels are formed by physical cross-linking of the nanotube bundles, mediated by local molecular ordering of the ionic liquids rather than by entanglement of the nanotubes. The gels were thermally stable and did not shrivel, even under reduced pressure resulting from the nonvolatility of the ionic liquids, but they would readily undergo a gel-to-solid transition on absorbent materials. The use of a polymerizable ionic liquid as the gelling medium allows for the fabrication of a highly electroconductive polymer/nanotube composite material, which showed a substantial enhancement in dynamic hardness.

Research on single-walled carbon nanotubes (SWNTs) (1) has rapidly grown over the past decade, because of their extraordinary physical properties (2, 3). SWNTs possess a cylindrical nanostructure with a high aspect ratio, and a large π-electronic surface forms by the rolling-up of a two-dimensional (2D) graphene sheet. They typically assemble to give bundles, which are heavily entangled with one another and form 3D networks. These structural aspects provide SWNTs with unique characteristics but also make them difficult to process. Adsorption of organic molecules on SWNTs by means of van der Waals and π-π stacking interactions has been investigated to modify their chemical and physical properties and to improve their processability (4–12). However, the development of much more facile and practical processing methods remains a challenging issue. We focus on organic cations, which potentially interact with π-electronic compounds through so-called “cation-π” interaction (13). From this point of view, ammonium ion-based molten salts (14, 15) are of great interest, because they are fluid at room temperature and can be directly used as media for processing.

We found that room-temperature ionic liquids (RILs) of imidazolium ions (16), upon being ground with SWNTs, form physical gels. When the temperature is lowered, the physically cross-linked gel further orients to form a crystalline material consisting of a long-range unimodal orientation of the RIL molecules. This phenomenon is reminiscent of biological mineralization, during which local clustering of inorganic salts on the surface of an organic scaffold triggers controlled nucleation and growth of inorganic crystals (17). SWNT gels of RILs, which may be called “bucky gels of ionic liquids,” can be prepared readily. Typically, when a suspension of HiPco SWNTs in 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF4) (Fig. 1) was ground with an agate mortar and then centrifuged, a transparent liquid phase, identified as pure BMIBF4, was separated from a black lower gel phase containing both BMIBF4 and SWNTs. The black phase was highly viscous and did not drop when the centrifuge capsule was turned upside down (Fig. S1). The gel phase was estimated to entrapping up to 3 × 10^19 molten salt molecules per 1 mg of SWNTs [1 weight % (wt %)]. As compared with grinding, sonication was ineffective for the gelation, and no phase transition was observed for the suspension of SWNTs in BMIBF4 upon sonication (at 180 W) for 2 hours at 30°C.

We also obtained bucky gels from tetrafluoroborate salts of 1-ethyl-3-methylimidazolium (EMIBF4) and 1-hexyl-3-methylimidazolium (HMIBF4) ions (Fig. 1), for which 1 wt % of SWNTs was required for gelation. Furthermore, when ionic liquids such as bis(trifluoromethylsulfonyl)imide salts of 1-ethyl-3-methylimidazolium (EMITf2N) and 1-butyl-3-methylimidazolium (BMITf2N) ions, and a hexafluorophosphate salt of 1-butyl-3-methylimidazolium ion (BMIPF6) (Fig. 1) were used, the gelation took place more efficiently with 0.5 wt % of SWNTs to give swollen gels. In contrast, common organic solvents such as dichlorobenzene, ethanol, N,N-dimethylformamide, and 1-methylimidazole (a precursor for ionic liquids) did not form gels, even upon prolonged grinding with SWNTs. Likewise, no gelation of ionic liquids took place with other carbon allotropes such as graphite (1 to 2 μm) and C60. We also found that the purity of the nanotubes affects the gelation. Raw-production SWNTs, contaminated with a considerable amount (20 wt %) of granular metal catalyst residue, brought about gelation much less efficiently; BMIBF4 gelled with 2.5 wt % of crude SWNTs. Similarly, BMIBF4 formed a gel upon grinding with 1.5 wt % of laser-ablation SWNTs (18, 19) contaminated with 30 wt % of graphite.

SWNTs usually exist as bundles, which are heavily entangled with one another to form 3D networks. Upon gelation, the entangled SWNT bundles exfoliated to form much finer bundles. In transmission electron microscopy (TEM), the bucky gel of BMIBF4 (Fig. 2A), in contrast with as-
received SWNTs (Fig. 2B), showed highly untangled small bundles of SWNTs. The gel also displayed well-resolved electronic absorption bands (Fig. 2C), comparable to those reported for a homogeneous thin film of SWNTs, prepared by a spray-deposition method (20). The absorption bands of SWNTs remained unchanged without any shifts upon grinding with ionic liquids. Raman spectroscopy showed that the radial breathing and tangential modes, typical of HiPco SWNTs, remain unchanged upon gelation (Fig. 2D). From these spectral profiles, we conclude that the gelation is triggered only physically, without chemical denaturation of SWNTs.

We found that bucky gels of RILs show differential scanning calorimetry (DSC) and x-ray diffraction (XRD) profiles that are essentially different from those of RILs alone (figs. S2 to S6). For example, a gel of BMITf$_2$N, on cooling, was simply supercooled to reach a glass transition point at $-85^\circ$C, whereas on heating, it showed sharp exothermic and endothermic peaks at $-52^\circ$ and $-4^\circ$C, respectively (Fig. 3A). However, BMITf$_2$N alone displayed a very broad exothermic peak from $-45^\circ$C until the beginning of an endothermic peak at $-6^\circ$C (Fig. 3C). Also, XRD analysis of BMITf$_2$N at $-25^\circ$C exhibited many weak diffraction peaks as a result of its polycrystalline structure (Fig. 3D). In contrast, the mesophase between $-52^\circ$ and $-4^\circ$C, observed for the bucky gel of BMITf$_2$N, displayed a very simple XRD pattern that had an intense diffraction peak, with a $d$ spacing of 4.60 Å (Fig. 3B). This observation is interesting, considering that such distinct changes in physical properties are induced by only 0.5 wt % of SWNTs. Because HiPco SWNTs showed no XRD peaks, the simplicity of the XRD profile in Fig. 3B indicates that the system consists of a unimodal long-range molecular ordering of the molten salt without polycrystalline character. The $d$ spacing of 4.60 Å, thus observed, is comparable to plane-to-plane separations of interionically paired imidazolium ions (21), reported for single crystals of imidazolium hexafluorophosphate (22) and nitrate salts (23).

With all the above features in mind, we investigated rheological properties of the bucky gels of ionic liquids. At an applied strain ($\gamma$) of 0.01, the dynamic storage modulus $G'$ curve of a bucky gel of BMIBF$_4$ showed a plateau region in the frequency dispersion curves (Fig. 4), indicating the existence of an elastic network structure in the system. Over a wide range of angular frequencies ($\omega$) from 100 to 0.04 rad s$^{-1}$, the loss modulus $G''$ curve showed only a shallow minimum without any signature of relaxation, indicating that the sys-

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**Fig. 2.** Morphological and spectral change profiles of SWNT bundles upon gelation. (A) TEM image of SWNTs obtained by dispersing a bucky gel of BMIBF$_4$ in deionized water. Scale bar, 100 nm. (B) TEM image of as-received SWNTs as reference, after sonication in ethanol. Scale bar, 100 nm. (C) Electronic absorption spectrum of a bucky gel of BMIBF$_4$ sandwiched by quartz plates. (D) Raman spectrum of a bucky gel of BMIBF$_4$ upon excitation at 488 nm. Raman bands at 1588 and 201 cm$^{-1}$ are a result of tangential and radial breathing modes, respectively, which are essentially identical to those of as-received SWNTs (1589 and 200 cm$^{-1}$).

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**Fig. 3.** DSC thermograms and XRD profiles at $-25^\circ$C on heating from $-110^\circ$C (second heating and cooling). (A and B) A bucky gel of BMITf$_2$N containing 0.5 wt % of SWNTs. (C and D) BMITf$_2$N alone as a reference. Heating and cooling rates in both DSC and XRD measurements were $10^\circ$C min$^{-1}$. Before measurements, the samples were heated once at $100^\circ$C to remove water, if any. The XRD measurements were performed on a Cu substrate at a scan rate of 2$^\circ$ min$^{-1}$ using a Rigaku model RINT–Ultima II system equipped with a temperature controller. $\Delta H$ values for exothermic/endothermic DSC peaks were 16.0/–21.9 and 10.9/–14.8 kJ mol$^{-1}$ for the gel and BMITf$_2$N alone, respectively. $T_g$, glass transition temperature; exo., exothermic; cps, count per second.
tem has permanent networks and therefore behaves as a gel. At $\gamma = 0.1$, the $G'$ curve still showed a plateau region. However, when $\gamma$ was further increased to 1.0, the system began to behave like a critical gel, where the $G'$ and $G''$ values both dropped to low modulus levels and changed with angular frequency ($\omega$) in a power law manner without any plateau. One of the important observations in the above rheological study is the large dependence of storage modulus $G'$ on $\gamma$ at such low strain amplitudes ($\gamma < 1.0$). This feature excludes a possibility that the entanglement of SWNT bundles governs the rheological properties of the gel (24). The system is more likely ruled by a large number of weak physical cross-links among the SWNT bundles, for which molecular ordering of ionic liquids is considered responsible. SWNTs can orient imidazolium ions on their $\pi$-electronic surfaces by way of a possible “cation-$$\pi$$ interaction (13). Such a molecular ordering may trigger clustering of the surrounding imidazolium ions cumbically (21) and consequently interconnect neighboring SWNT bundles. The unimodal crystal growth in the gel at a low temperature (Fig. 3B) most likely results from a controlled nucleation initiated by this local molecular orientation around the SWNT surfaces. After grinding, the large SWNT bundles are disentangled into many finer bundles, which efficiently promote the ordering of ionic liquids.

As an extension of this finding, we synthesized a bucky gel of a polymerizable ionic liquid and attempted in situ polymerization of the ionic liquid component with an expectation that the SWNTs included can enhance mechanical properties of the polymer. Thus, 102 mg (3.8 wt %) of SWNTs was added to a polymerizable molten salt such as 1-(4-acryloyloxybutyl)-3-methylimidazolium hexafluorophosphate (ABMIPF$_6$; 2.56 g) (Fig. 1), and the resulting suspension, containing 2,2'-azobisisobutyronitrile (AIBN; 15 mg), was ground for 1 hour to prepare a black gel. Then, the gel was heated for 10 hours at 75°C, at which point the polymerization of ABMIPF$_6$ took place to give a homogeneous black polymer composite of SWNTs. Although the content of SWNTs was only 3.8 wt %, a sheet fabricated from this composite material displayed a nearly 400% increase in dynamic hardness (DHT115) compared with a reference polymer sheet prepared solely from ABMIPF$_6$ (26). Although SWNTs have been expected to be used as reinforcing materials for polymers, successful examples are very limited (27, 28), resulting from a rather poor adhesion at the polymer/SWNT interface. However, the bucky gel-based composite polymer is efficiently reinforced by taking advantage of a strong affinity of the imidazolium ion toward the $\pi$-electronic SWNT surface. We also found that the polymer/SWNT composite, thus fabricated, is highly electroconductive. For example, a composite polymer sheet, containing 3.8 wt % of SWNTs, showed a conductivity of 0.56 S cm$^{-1}$ at room temperature (29). In contrast, a polymer of ABMIPF$_6$ was substantially an insulator.

The electroconductivity of the SWNT-reinforced polymer composite indicates its potential utility as a component in, for example, novel electronic devices, coating materials, and antistatic materials.

References and Notes
21. For example, crystallographic studies on single crystals of EMIPF$_6$ [melting point (mp) 58$^\circ$ to 60°C] and EMINO$_3$ (mp 38°C) have shown stacking of the EMI$^+$ ions with plane-to-plane separations of 4.53 (22) and 4.54 Å (23), respectively.
25. Materials and methods are available as supporting material on Science Online.
26. Sheet samples (0.6 mm thick and 1 cm$^2$ wide) of an ABMIPF$_6$ polymer/SWNT (3.8 weight %) composite and an ABMIPF$_6$ polymer were fabricated by compression molding upon heating at 200°C for 2 min with a Teflon mold, and then cut into small pieces, which were subjected to a Simadzu Dynamic Ultra Micro Hardness Tester model DUH-201S with a 115° triangular pyramid indenter at 23 ± 2°C. Dynamic hardness (DHT115) values were calculated from test forces (P, measured in millinewtons) and indentation depths (h, measured in micrometers) by using an equation $DHT_{115} = 3.8584 P/h^0.15$. The DHT115 values were measured at three different areas on each sample and averaged to give 0.074 and 0.019 for the composite and the polymer, respectively.
27. In order to circumvent a problem of poor matrix-SWNT connectivity, a special processing technique called "layer-by-layer assembly" has recently been reported for the fabrication of high-strength polymer composites of SWNTs (28).
29. The electrical resistance was measured by a standard four-probe method on a sheet sample. Gold wires (20 μm in diameter) were attached to the sheet with a gold paste. A direct current was generated by an Advantest model R6412 power source, and the potential difference was measured on an Advantest model R6452A digital multimeter.
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