Hybrid Gels

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Carbon Nanotube Triggered Self-Assembly of Oligo(*p*-phenylene vinylene)s to Stable Hybrid π-Gels**

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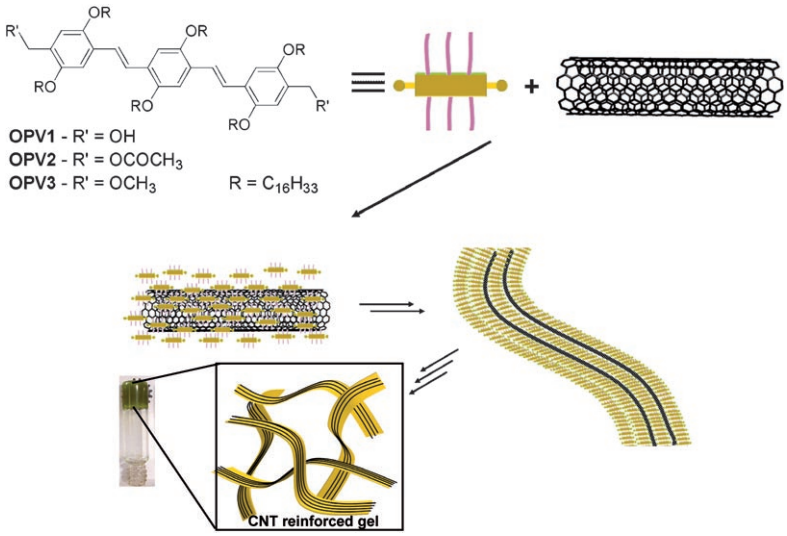
Carbon nanotubes (CNTs) represent a novel class of quasi one-dimensional materials that exhibit unique chemical and physical properties,[1,2] allowing a wide range of applications from optoelectronics to biology.[3,4] The major limitation of CNTs is their poor solubility.[5,6] Although this limitation can be overcome by covalent functionalization, this approach can modulate the chemical and physical properties of CNTs, which in many cases may create defect sites that severely affect their electronic properties.[7–9] An alternative approach is the physical interaction of organic molecules such as polyaromatics, conjugated oligomers, polymers, and DNA with CNTs leading to their dispersion in organic and aqueous solvents.[10–13]

Recently, reports have appeared on the interaction of CNTs with ionic liquids[10a] and organic molecules[10b–f] to form composite gels.[10g–m] These studies prompted us to investigate the influence of CNTs on gel-forming oligo(*p*-phenylene vinylene)s (OPVs), a system in which we have been interested for the past few years.[14a–c] Our studies stem from the hypothesis that planar OPVs with a strong propensity for π-stacking may strongly interact with CNTs. Such an interaction may accelerate their self-assembly, thereby strengthening the gel and leading to reinforced supramolecular architectures as shown in Scheme 1. **OPV1** is known to form organogels above a critical concentration in nonpolar solvents.[14] However, in relatively polar solvents, such as toluene, higher concentrations of **OPV1** lead to the formation of a thixotropic gel that is mechanically unstable. It is therefore necessary to improve the stability and mechanical properties of OPV gels for any potential applications. Herein we report that SWNTs (single-walled carbon nanotubes) and MWNTs (multiwalled carbon nanotubes) accelerate the self-assembly and gelation of OPVs below their normal critical gelation concentration (CGC), resulting in CNT-dispersed stable hybrid π-conjugated gels.



Scheme 1. Chemical structures of OPV derivatives and schematic representation of OPV-CNT gel formation.

At lower concentrations ($< 1 \times 10^{-4}$ M) in toluene, **OPV1** does not favor self-assembly, as shown by its unchanged absorption and emission spectra. Interestingly, addition of small amounts of SWNTs (HiPco) to this solution with sonication and subsequent standing at room temperature resulted in a soft dense solid, thus indicating that gelation had occurred. During the process, the SWNTs become uniformly dispersed in the gel matrix. The absorption spectrum of the composite exhibited a shoulder at 464 nm corresponding to the aggregates of **OPV1** which exhibited thermoreversibility (Figure S1 in the Supporting Information).[15] In addition, the well-resolved electronic absorption bands observed between 500 and 1500 nm indicate the typical van Hove singularities of individually dispersed SWNTs (Figure 1a, inset). A typical absorption spectrum exhibited the characteristic electronic transitions corresponding to the metallic (M_{11}, 400–600 nm) and the semiconducting (S_{22} and S_{11}, 600–900 nm and 1200–1500 nm, respectively) nanotubes, which are in agreement

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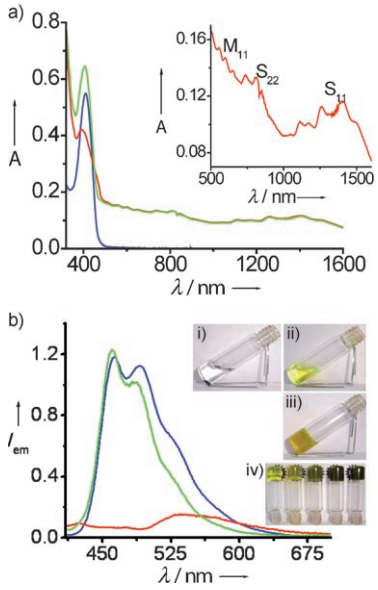

Figure 1. a) Absorption spectra of **OPV1** at 20 °C (blue) and **OPV1-SWNT** in toluene at 55 °C (green) and 20 °C (red). Inset: Zoomed area in the range 500–1600 nm showing van Hove singularities. b) Fluorescence spectra of **OPV1** (blue) and **OPV1-SWNT** in toluene at 55 °C (green) and 20 °C (red). $\lambda_{ex} = 390$ nm ($l = 1$ mm, $c = 1 \times 10^{-4}$ M). Inset: Photographs of i) immiscible SWNTs in toluene, ii) **OPV1** solution in toluene (3×10^{-4} M), iii) gel of **OPV1** in toluene with SWNTs (0.02 mg, total volume = 0.5 mL) and iv) **OPV1** gels in toluene (5×10^{-4} M) with 0, 0.22, 0.45, 0.9, and 1.3 wt% of MWNTs with respect to toluene (left to right).

with the reported spectrum of dispersed HiPco SWNTs.[2b,10a,13d,16]

Addition of SWNTs to a solution of **OPV1** (1×10^{-4} M) in toluene resulted in a decrease of the emission at 464, 500, and 525 nm and a broad emission between 500 and 650 nm was observed which is characteristic of self-assembled OPV aggregates.[14a–c] Upon heating to 55 °C the gel turned into a solution and the emission bands at 464 and 500 nm intensified, indicating a reversal of the self-assembly process. The effect of addition of CNTs on the gelation of **OPV1** in toluene is shown in the inset in Figure 1b. Comparison of the plots of melting temperatures of **OPV1** and **OPV1-CNT** composite gels at different concentrations indicates a higher stability of the composite gels (Figure 2). It is clear that the gel stability increased significantly with the increase in the proportion of CNTs present. Only 8 wt% of the SWNTs is required to form a stable gel of **OPV1** in toluene at a concentration of 3×10^{-4} M. In the cases of **OPV2** and **OPV3**, 14 and 16 wt% of SWNTs respectively, were required to form stable gels,[15] because aggregates of **OPV2** and **OPV3** are much less stable than those of **OPV1**.[14,15] The increased stability of the gel with the increase in CNT concentration indicates the physical reinforcing of the self-assembled 3D gel networks.

Evidence for the interaction of SWNTs with **OPV1** is obtained from FTIR, and ^{1}H NMR analyses of the composites.[11c,15] The aromatic C-H bending mode between 700–900 cm^{-1} in the FTIR spectrum of **OPV1** almost vanishes in the presence of SWNTs. The ^{1}H NMR signals of **OPV1** became significantly broader in the presence of SWNTs. For

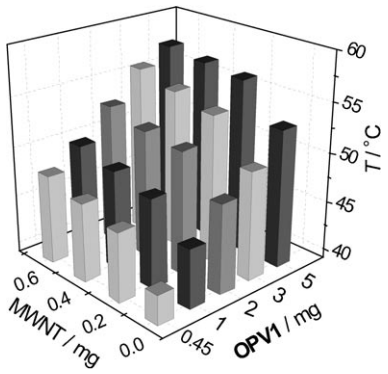

Figure 2. 3D plot of T_{gel} of toluene gel (0.5 mL) with increasing concentrations of MWNTs and **OPV1**.

example, the signals of the aromatic protons at $\delta = 6.86$ ppm are broadened, and the peaks at $\delta = 7.12$ and 7.14 ppm merged into a broad single peak. Similarly, the vinylic proton peaks at $\delta = 7.45$ ppm are also broadened. These observations indicate a strong interaction between the π-conjugated backbone of the OPVs with the SWNTs. Thermogravimetric analysis (TGA) reveals that the pyrolysis temperature of the **OPV1-SWNT** composite gel is different from those of the **OPV1** gel and the SWNTs, which is clear from differential thermal analysis (DTA).[15,17] Differential scanning calorimetry (DSC) analysis of **OPV1** showed a melting transition at 118 °C in the heating cycle, whereas a sharp phase transition at 108 °C was observed in the cooling cycle. The composite showed a relatively broad melting transition at 117 °C in the heating cycle, whereas a broad exotherm around 96 °C is observed in the cooling cycle.[10a,15,18] These differences in the TGA and DSC phase transitions indicate the physical interaction of **OPV1** with the CNTs leading to self-assembled composites.

The storage modulus (G') and loss modulus (G'') of **OPV1** and nanocomposite gel **OPV1-SWNT** (containing 1.5 wt% of SWNT with respect to **OPV1**) are shown as a function of angular frequency (ω) at 0.01% strain (γ) amplitude in Figure 3. **OPV1** and the nanocomposite gels showed a plateau region when the angular frequency was varied from 100 to 0.1 rad s^{-1}. The G' value showed a substantial elastic response to the gels, which are larger than G'' over the entire frequency range. Rheological parameters of the composite gel **OPV1-SWNT** indicate enhanced solid-like character relative to the

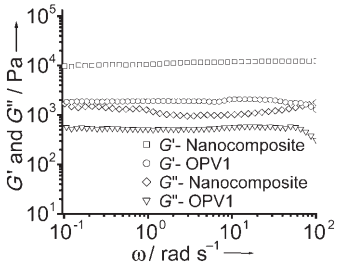

Figure 3. Angular frequency (ω) dependencies of dynamic storage (G') and loss modules (G'') of **OPV1** (1×10^{-3} M) and the nanocomposite gel (1.5 wt% of SWNT) at 25 °C with strain amplitude (γ) at 0.01.

OPV1 gel. The ratio of G' to G'' for **OPV1-SWNT** is 11.48, while that of the **OPV1** gel is 3.14, indicating enhanced stability and elastic response of the former. When the strain amplitude values were varied from 0.01 to 1, the angular frequency dependence plots showed significant changes in the G' values whereas the G'' values remained almost unchanged. The ratio of G' to G'' decreased in the order 11.48, 6.39 and 2.6 when the strain value was increased from 0.01, 0.1, and 1, respectively.[10a,15] The fact that the G'/G'' values are greater than 1 indicates that the **OPV1-SWNT** composite retained gel-like nature for a wide range of strain amplitudes, which excludes the possibility that the entanglement of SWNT bundles governs the rheological properties. Rather, the physical reinforcement of the self-assembled OPV tapes is considered to be responsible for the improved rheological properties.[10a,k]

When viewed through a cross polarizer, **OPV1** showed birefringent tape-like texture upon cooling from the isotropic melt (Figure 4a) which indicates the linear anisotropic growth

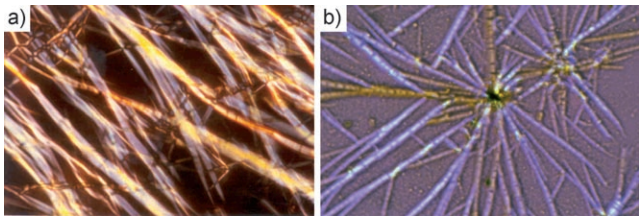

Figure 4. Polarizing optical micrographs of the xerogels of a) **OPV1** (400×), b) **OPV1-SWNT** (400×), when cooled from the corresponding isotropic melts.

of H-bonded assemblies of the OPV molecules.[14a,18c] Interestingly, the xerogel of **OPV1-SWNT** exhibited a branched fibrous birefringent texture (Figure 4b), indicating the anisotropic self-assembly of **OPV1** over the SWNT surface. The optical micrograph of **OPV1** gel and the nanocomposite gel in toluene at a cooling rate of 5 °C min^{-1} from the corresponding isotropic solution showed significant differences in their textures.[15]

A transmission electron microscopic (TEM) image of SWNTs shows the presence of bundled nanotubes (Figure 5a). A TEM image of the self-assembled OPV exhibited the characteristic nanotape morphology (Figure 5b) with a width of 10–200 nm and length of several micrometers. Unbundled nanotubes are seen for the **OPV1-SWNT** composite and these are aligned in a side-wise fashion within the self-assembled OPV (Figure 5c). The magnified TEM images indicate that the nanotube-encapsulated OPV self-assembled structures appear like fiber-reinforced supramolecular tapes (Figure 5d). The inset in Figure 5d shows an isolated HiPco SWNT with 1–2 nm diameter within the self-assembled tape of **OPV1**.[19]

In conclusion, we have shown that the self-assembly of OPV molecules is accelerated through physical interaction with CNTs in hydrocarbon solvents. As a result the CNTs are dispersed in the solvent, which facilitates the self-assembly processes and leads to the formation of hybrid π-conjugated gels. The individually dispersed CNTs are significantly

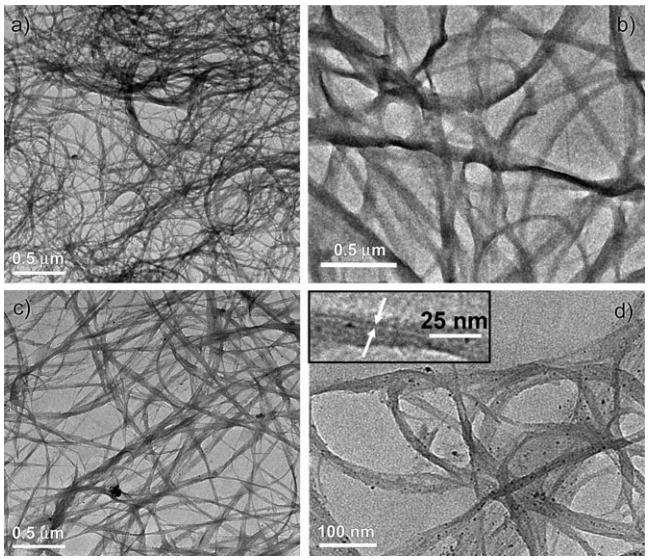

Figure 5. TEM images (unstained) of a) SWNT b) **OPV1** c) and d) **OPV1-SWNT** nanocomposite. All samples are drop casted from toluene on carbon-coated TEM grids.

aligned within the OPV gel, thereby reinforcing the OPV supramolecular tapes. CNTs may also act as physical cross-links between the tapes, thus enhancing gel stability. This new strategy to make CNT-OPV hybrid π-conjugated gels allows the CNTs to retain their long aspect ratio as well as their electronic properties in the gel state. This design of a hybrid gel consisting of a total π-system, CNTs, OPVs, and an aromatic solvent (toluene) is expected to lead to further studies on the potential use of CNT-OPV nanocomposite gels as optoelectronic materials.

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