Soluble, Discrete Supramolecular Complexes of Single-Walled Carbon Nanotubes with Fluorene-Based Conjugated Polymers

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The supramolecular functionalization of carbon nanotubes with planar aromatic structures, such as pyrene and porphyrin derivatives, has received significant attention as it allows nanotube modification without the introduction of defects.[1−5] In addition to small molecules with extended conjugation, conjugated polymers have recently been found to strongly interact with the carbon nanotube surface through π-stacking.[6] Indeed, it has been shown that the multivalent nature of the interaction of conjugated polymers with the nanotube surface enhances the binding strength and enables the preparation of discrete polymer−nanotube complexes.[7] If properly modified, these complexes can exhibit high degrees of solubility and excellent conductivity properties,[8] making them potentially interesting for printed electronics, supercapacitors, LEDs, photovoltaic cells, and other optoelectronic devices.

Considering that conjugated polymers prefer a relatively coplanar geometry between monomers in order to maximize π-orbital overlap, only a small number of discrete polymer−nanotube interaction modalities can be expected. Specifically, two general methods by which conjugated polymers can supramolecularly bind to the nanotube surface include helical wrapping and nonhelical adsorption along the nanotube, depending on the flexibility of the polymer backbone.[6] Poly(*m*-phenylenevinylene)[9,10] and poly(phenylacetylene)[11] represent two polymers that are known to adopt helical conformations in solution and have been shown to be ideal for supramolecular nanotube wrapping. Conversely, the rigidity of poly(*p*-phenyleneethynylene) prevents it from adopting helical conformations and therefore limits it to adsorption along the nanotube length as a straight, rodlike chain.[12,13] Along similar lines, we have recently reported a conjugated Zn−porphyrin polymer[7,14] and triply fused porphyrin oligomers[15] that can interact with carbon nanotubes, producing soluble nanotube complexes through a nonwrapping mechanism. Although these structures undergo extremely strong binding to the nanotube surface and have interesting optoelectronic properties, the synthetic challenges associated with their preparation limit their feasibility in practical applications. It is therefore advantageous to explore the interaction of nanotubes with other, more easily accessible conjugated polymers.

Among all the known conjugated polymers, poly(9,9-dialkylfluorene)[16] represents one of the most important families of electroactive polymers due to its conductivity, solubility, and stability properties as well as its intense blue fluorescence. This material has been extensively studied as a component within thin-film transistors (TFTs),[17] light-emitting diodes (LEDs),[18] and photovoltaic (PV) devices.[19] Fluorene−thiophene copolymers, in which the combination of electron-rich thiophene units with relatively electron-deficient fluorene units allows modification of the copolymer bandgap (and thus the maximum fluorescence wavelength), have also been investigated for their charge injection/transport properties.[20] Although these polymers exhibit the extended conjugation required for π-stacking to the nanotube surface, they have thus far attracted limited attention as supramolecular adducts for single-walled carbon nanotubes.[21] In this Communication, we present our recent findings that poly(9,9-dialkylfluorene) (PF) and poly(9,9-dialkylfluorene-*co*-3-alkylthiophene) (PFT) exhibit strong supramolecular binding to the nanotube surface and impart excellent solubility and solution-stability properties even after excess polymer is removed from solution. In addition, thin films cast from these materials were found to exhibit a high degree of electrical conductivity, similar to that of pristine SWNT films.

The PF and PFT polymers were synthesized by the Suzuki polycondensation[22] from diborate **1** and the corresponding dibromides **2** and **3**, as depicted in Figure 1. It was found that the solvent in which the polymerization was carried out dramatically influences the molecular weight of the isolated polymer. For example, the preparation of PF in DMF as the solvent resulted in a poorly soluble product having an M_n of 30 kg/mol and a polydispersity index (PDI) of 2.4. However, the same polymerization in toluene produced PF with an M_n of 9 kg/mol and a PDI of 1.6. Because of the higher solubility of the low molecular weight product, it was preferentially used in the investigation of polymer−nanotube complexes. Preparation of the PFT structure was performed in a mixture of DMF and toluene (4:1 v/v) as the solvent and yielded polymer having an M_n of 15 kg/mol and PDI of 2.7. The high polydispersities in these polymerizations are a result of the uncontrolled step-growth polymerization process and were consistent with literature reports for similar polymers.[23] The ^{1}H NMR spectra of the polymers were also in good agreement with previously reported polymers of this type.[24]

The supramolecular interaction of PF (9 kg/mol) and PFT (15 kg/mol) with SWNTs was studied using our previously reported methods.[7,14] In a typical experiment, a SWNT sample (10 mg) was added to a solution of polymer in THF (30 mg/20 mL), and the mixture was sonicated for 1 h. The resulting suspension was centrifuged for 20 min at 5000 rpm[25] and allowed to stand overnight. The clear, dark supernatant was carefully decanted, and nanotube solubility within the sample was measured without removal of the excess free polymer present in solution. Then, the isolated supernatant was filtered through a 200 nm pore diameter Teflon membrane and repeatedly washed with THF (4 × 250 mL) to remove all excess polymer. Polymer removal was monitored by measuring the fluorescence of the filtrate, which decreased dramatically with continued washing. Once no fluorescence from the filtrate was observable, it was deemed that all free polymer had been washed out of the nanotube sample. The nanotube residue was then peeled away from the Teflon membrane and added to 5 mL of THF, followed by sonication for 5 min to disperse the nanotubes. After sonication, the resulting dark suspension of nanotubes was

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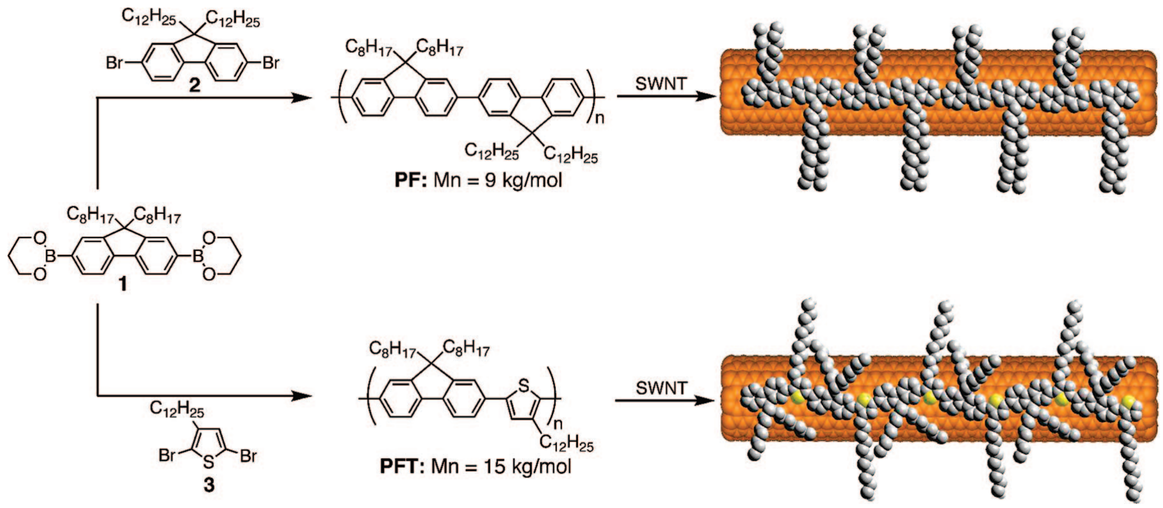

Figure 1. Preparation of conjugated PF and PFT polymers and a cartoon representation of their interaction with SWNTs.

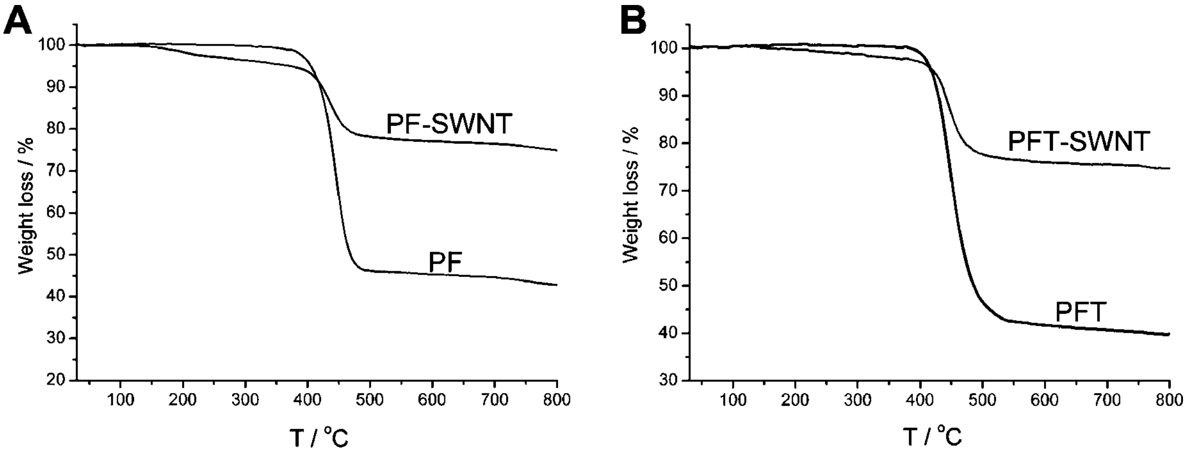

Figure 2. Thermogravimetric analysis data for polymer PF (A) and PFT (B), showing thermal decomposition profiles for the free polymer and polymer–nanotube complexes.

centrifuged at 5000 rpm for 20 min and allowed to stand undisturbed overnight. Again, the supernatant was carefully transferred by pipet to a clean vial, and nanotube solubility in this solution was also measured.

It was found that, using both PF and PFT, it was possible to produce a homogeneous, dark and stable solution even after removal of the excess free polymer, as described above.[26] This indicates that the majority of adsorbed polymer does not desorb from the nanotube surface once it is bound, and the π-stacking interaction between the polymer and the nanotube surface is strong enough to prevent reaggregation of nanotubes into large bundles. All solutions remained stable for periods of at least 4 weeks, with no observable precipitation. Nanotube solubility was initially quantified using a spectrophotometric method in which a specific extinction coefficient for SWNTs at 700 nm, $\epsilon_{700} = 2.35 \times 10^4$ cm^2 g^{-1}, was utilized. [27] It was necessary to use this extinction coefficient rather than the more commonly used value at 500 nm[28–32] because of interference from the absorption of PFT, which tails off at just above 500 nm. From these measurements, it was found that all of the polymer–SWNT complexes exhibited high solubility in THF, where the solubility in the presence of free polymer (PF–SWNT, 603 mg L^{-1}; PFT–SWNT, 718 mg L^{-1}) was much higher than that in the absence of free polymer (PF–SWNT, 209 mg L^{-1}; PFT–SWNT, 384 mg L^{-1}). This result indicates that a dynamic equilibrium between bound and unbound polymer exists, and the presence of excess polymer favors the formation of the soluble polymer–nanotube complexes. The spectrophotometrically determined solubilities were found to be in good agreement with a more traditional gravimetric method, in which dissolved material was isolated by filtration and weighed. For the gravimetric measurements, it was necessary to subtract the mass of polymer within the dissolved material. The polymer content was calculated by thermogravimetric analysis (TGA), which provided the weight fraction of the polymer. TGA data for the free polymers PF and PFT, as well as the corresponding polymer–nanotube complexes, are provided in Figure 2. These data indicate that it is not possible to completely decompose the conjugated polymers by heating to 800 °C under Ar. Instead, the major mass loss for the polymer occurs at ca. 450 °C, corresponding to the loss of alkyl side chains within these polymers.[33] Indeed, the observed mass-loss values of 57% (PF) and 60% (PFT) are in agreement with calculated weight percentages for the alkyl side chains of 63% for PF and 61% for PFT. On the basis of the observed thermograms of the free polymers, the polymer content in the two polymer–nanotube complexes could be calculated and was found to be 38% and 42% for PF–SWNT and PFT–SWNT, respectively. Gravimetric measurements of solubility were done by filtering an exact volume of the saturated solution obtained after removal of excess free polymer (see above), drying the nanotube residue to constant mass, and measuring the mass of the isolated

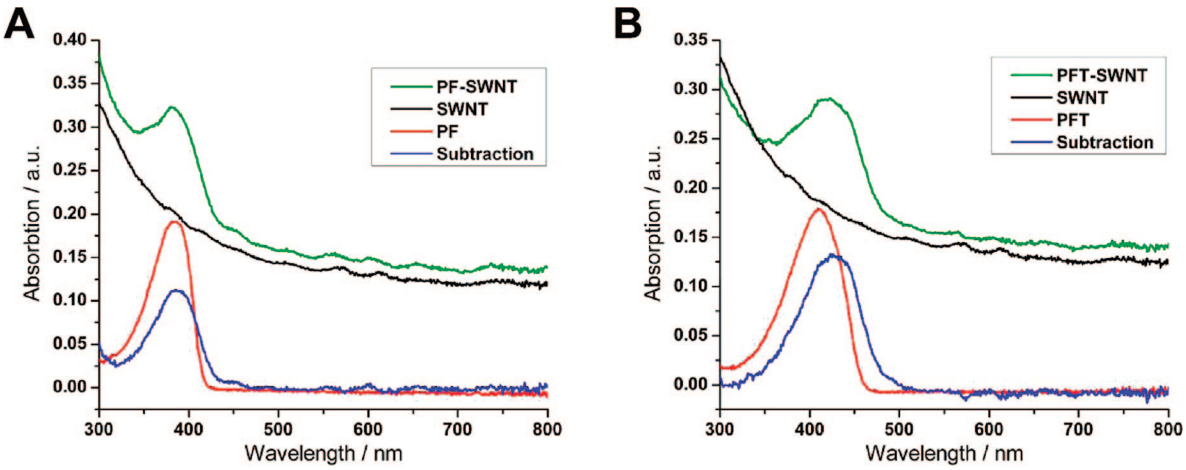

Figure 3. UV–vis absorption data from polymer−nanotube complexes, SWNTs, free polymer, and the polymer contribution to the polymer−nanotube complex spectrum (labeled "subtraction") for PF (A) and PFT (B).

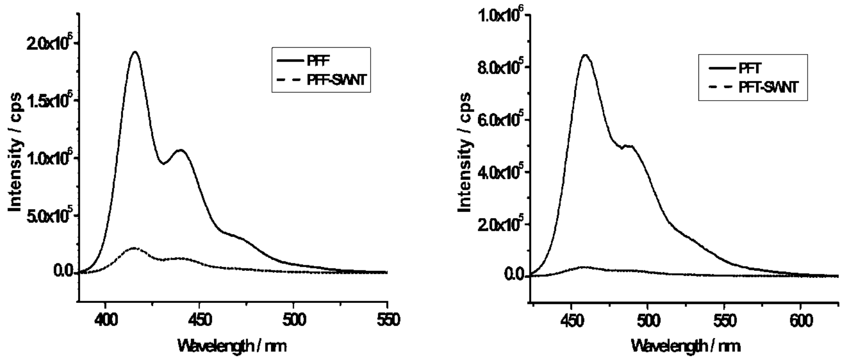

Figure 4. Emission spectra of free polymer and polymer−nanotube complexes using PF (A) and PFT (B) polymers, with the excitation wavelength set to the λ_{max} of each sample (382 nm for PF and PF−SWNT, 409 nm for PFT, and 425 nm for PFT−SWNT).

polymer−nanotube complex. The weight percentage of polymer within these complexes was then subtracted from the measured mass to determine the mass of nanotubes within the isolated sample. This method gave nanotube solubility values of 322 and 360 mgL^{-1} for PF−SWNT and PFT−SWNT, respectively, which were in reasonable agreement with the spectrophotometrically determined values. It should be noted that other carbonaceous material (amorphous carbon, turbostratic graphite, etc.) may be present in these solutions, augmenting our solubility values. However, the purified grade of the SWNT sample used, our TEM and AFM data (see below), and previous reports with other conjugated polymers[34] suggest the amount of such non-nanotube material is negligible.

The supramolecular interaction of the polymers with SWNTs was further investigated by UV/vis absorption spectroscopy. Figure 3 depicts the spectra of the polymers, SWNTs (measured in an aqueous solution using sodium dodecyl sulfate as a surfactant),[35] and the polymer−SWNT complexes in THF. In addition, by subtracting the normalized spectrum of the SWNTs alone from that of the polymer−SWNT complexes, it was possible to generate a spectrum that corresponds to just the polymer contribution to the absorption of the polymer−SWNT complexes (labeled "subtraction" in Figure 3). By comparing this subtraction spectrum to that of the free polymer, it was found that a bathochromic shift in the polymer absorption occurs upon nanotube complexation. This shift may arise from an increased effective conjugation length within the polymers, caused by a more planar structure of its backbone after it has interacted with the SWNT surface.[7] Alternatively, the bathochromic shift may also be due to the π-stacking interaction, resulting in delocalization of π electrons onto the SWNT surface. Interestingly, a larger red shift (18 nm) was observed for the PFT−SWNT complex, as compared to the PF−SWNT complex (4 nm). This indicates that the electronic structure of the polymers has an effect on the interaction strength with carbon nanotubes, where the relatively electron-rich PFT may exhibit stronger supramolecular complexation with SWNTs, consistent with the observed higher solubility of the PFT−SWNT complex.

The fluorescence spectra of the free polymers and polymer−SWNT complexes were also measured and quantitatively compared (Figure 4). By normalizing the absorption spectrum of the free polymer and the polymer contribution to the absorption of the polymer−SWNT complex (subtraction file in Figure 3), it was possible to determine normalization factors that could be applied to the fluorescence spectra of the two samples. From the normalized emission spectra, it is clear that highly efficient quenching of fluorescence occurs when the polymers assemble on the carbon nanotube surface. The calculated quenching efficiency was measured to be 96% and 89% for PFT−SWNT and PF−SWNT complexes, respectively, which again indicated that the PFT exhibits a stronger interaction with carbon nanotubes than PF. The fluorescence quenching is likely a result of photoinduced energy or electron transfer between the excited conjugated polymer and the SWNTs, as previously reported for other systems.[12,36–40] Interestingly, no shifts in the λ_{max} values of emission from the polymer−nanotube complexes, relative to the free polymer, were observed, indicating that the observed emission of the polymer−nanotube complexes is actually emanating from a small amount of free polymer that has desorbed from the nanotube surface and likely

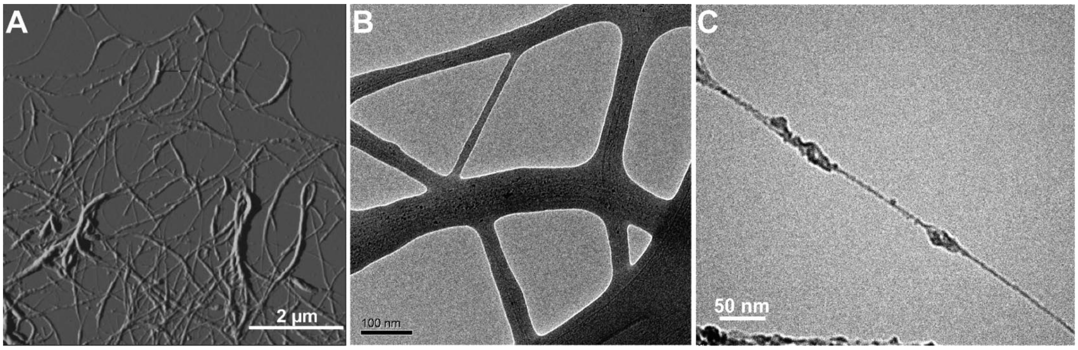

Figure 5. AFM image of a PF−SWNT sample on freshly cleaved mica (A); high-resolution TEM image of PFT−SWNT prior to plasma cleaning (B) and post plasma cleaning (C).

formed a dynamic equilibrium with bound polymer. This implies that the actual fluorescence quenching efficiencies for nanotube-bound polymers are likely to be higher than what were calculated from this data, most probably reaching unit efficiencies.

Microstructural characterization of polymer−nanotube complexes was performed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The AFM image of a PF−SWNT sample (Figure 5A), prepared by spin-casting a dilute solution of the sample in THF onto a freshly cleaved mica disk, shows a large number of entangled "nanofibers". Height analysis of these features indicated that most of the fibers ranged in height from ca. 2 to ca. 17 nm, presumably corresponding to a mixture of individual and aggregated polymer-functionalized nanotubes. Considering that, as solvent evaporates on the substrate, individual nanotubes can be pushed together into larger aggregates, the observed mixture of differently aggregated features is not surprising. Using TEM, it is also possible to observe features corresponding to nanotube fibers that are coated with polymer (Figure 5B). Although, from this image, it is possible to observe SWNTs as well as Fe catalyst particles underneath the polymer coating, the large amount of polymer present hinders our ability to discern individual nanotubes from nanotube bundles. The samples were therefore treated with a plasma cleaning procedure, after deposition on the TEM grid, in order to degrade the polymer coating prior to microscopy. Following plasma cleaning for 30 s, it was found that the majority of the polymer was removed from the sample, leaving only the underlying nanotubes exposed (Figure 5C). The resulting image shows an individual, bare SWNT with only small patches of polymer left on its surface. This image provides evidence that the polymer was able to exfoliate nanotube bundles, and the fibers observed by AFM and TEM (prior to plasma cleaning) were composed of single SWNTs coated with polymer.

The conductivity properties of the polymer−SWNT complexes were evaluated by measuring the sheet resistance of thin films made from these materials. The thin films were prepared by previously reported methods involving vacuum filtration of the nanotube solutions through a 200 nm pore diameter Teflon membrane.[41] Briefly, the purified polymer−SWNT complexes in THF solution were carefully poured into the filtration apparatus, avoiding bubble formation on the solution surface. Each solution was filtered and washed with THF (4 × 250 mL), after which the residue was allowed to air-dry while pulling vacuum on the sample for 30 min. The films were then subjected to further drying in a vacuum oven at 50 °C for 24 h. Although the films could be peeled from the membrane as intact, flexible sheets, it was found that electrical contact with electrodes was easier to achieve if the films remained on the Teflon membrane, which provided extra support. Standard four-point-probe measurements were performed under ambient conditions to determine sheet resistance values, which could be converted to conductivities after determination of film thickness according to eq 1

Table 1. Conductivity data for Nanotube Thin Films

sample	sheet resistance (Ω)	film thickness (cm)	conductivity (S cm^{-1})
SWNT	0.52	0.009 ± 0.002	210 ± 40
PF−SWNT	1.23	0.024 ± 0.003	34 ± 4
PFT−SWNT	1.07	0.018 ± 0.001	52 ± 3

$$\sigma = \frac{1}{R_s t} \tag{1}$$

where σ is the conductivity in S cm^{-1}, R_s is the sheet resistance in ohms/square (Ω/square), and t is the film thickness in cm. On the basis of these measurements, it was found that the supramolecular polymer−nanotube complexes can be used to produce homogeneous films having conductivities similar to those of pristine nanotubes (Table 1). The measured conductivity of a 240 μm thick film of the PF−SWNT complex was 34 ± 4 S cm^{-1}, while a 180 μm thick film of the PFT−SWNT complex was 52 ± 3 S cm^{-1}. A control film of pristine SWNTs, with a thickness of 90 μm, was also measured and exhibited a conductivity of 210 ± 40 S cm^{-1}. The 4−6-fold lower conductivity for the polymer−SWNT complexes is not surprising, considering that these samples are composed of ca. 40% polymer.

In conclusion, fluorene-based conjugated polymers were synthesized and used to prepare discrete polymer−SWNT complexes. The conjugated polymers were found to form strong supramolecular complexes with SWNTs, imparting excellent solubility in organic solvents in the absence of excess free polymer. Thermogravimetric analysis indicated that the polymer−nanotube complexes were composed of ~40 wt % polymer. UV–vis absorption measurements revealed a bathochromic shift in the absorption spectrum of the polymers as a result of nanotube complexation, while fluorescence measurements showed that polymer fluorescence is highly quenched in the complexes. Microstructural analysis (AFM and TEM) was used to demonstrate that the polymer chains can exfoliate SWNT bundles, resulting in individual nanotubes that are uniformly coated with polymer. Using four-point-probe measurements, it was found that the conductivity of thin films of polymer−nanotube complexes was only slightly lower than what was observed for films of pristine nanotubes. The high conductivity and solubility of the supramolecular polymer−nanotube complexes opens the door to their application in a variety of applications, such as in printed electronics.

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Supporting Information Available: All experimental procedures for polymer preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Note that when high molecular weight PF (M_n, 30K) was used to produce a polymer—nanotube complex, no soluble carbon nanotube material could be isolated after removing excess free polymer, which is likely due to the relatively poor solubility of the high molecular weight PF.

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