Dispersing as-prepared single-walled carbon nanotube powders with linear conjugated polymers†

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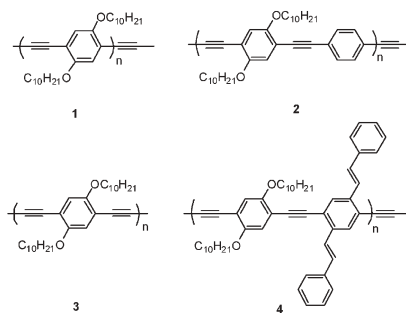
Suitably modified linear conjugated poly(arylene ethynylene)s are able to assist effective debundling and dispersion of crude as-prepared single-walled carbon nanotube powders in organic solvents, the dispersion of which is effected *via* a surface coating mechanism and, to some extent, in a size-selective fashion.

Composite materials of conjugated polymers and carbon nanotubes (CNTs) are of continuous interest in the areas of nanoelectronics and optoelectronics, because they can not only form dramatically reinforced polymer films but also introduce new electronic and photonic properties as a consequence of intimate interactions between the two active components.[1,2] Over the past years, conjugated polymers that can helically wrap themselves around single-walled carbon nanotubes (SWNTs), *e.g.* poly-(*m*-phenylene vinylene) and poly(pyridinylene ethynylene),[3] have been an effective and widely used class of conjugated polymer dispersants for SWNTs. In contrast, conjugated polymers with a rigid and linear-shaped backbone conformation have received much less attention in this regard, although their unique effectiveness in dispersing SWNTs was addressed in several recent reports.[4] The mechanism of solubilizing CNTs with linear conjugated polymers is complicated and not as intuitive as their folding polymer cousins. Surface π-stacking[4a] and steric effects[2b,5] are two rational models developed so far.

To shed more light on the interplay between structurally rigid non-helical conjugated polymers and various CNTs, four representative linear conjugated poly(arylene ethynylene)s (PAEs) **1–4** were investigated in our work. The rigid backbones of these polymers were decorated with long *n*-decyloxy chains for a twofold reason: (i) to impart solubility in organic solvents, and (ii) to stabilize SWNT dispersions by steric repulsion.

The synthesis and characterization of polymers **1–4** are described in the supplementary information.† As-prepared SWNT powders (40–60% purity) were purchased from Carbon Solutions Inc. and used as received in our experiments.

First, the solubilities of as-prepared SWNTs in saturated chloroform solutions of polymers **1–4** were examined. As-prepared SWNT powders of suitable amounts were bath sonicated in each polymer solution for *ca.* 5 min at room temperature. The resultant suspensions were then immediately filtered through a tightly packed cotton plug to remove all insoluble particles. Poly(*p*-phenylene ethynylene)s (PPEs) **1** and **2** were found to

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† Electronic supplementary information (ESI) available: Experimental details and spectroscopic data. See DOI: 10.1039/b612079b

behave poorly in dispersing as-prepared SWNTs, as is evident by UV-Vis analysis (see ESI†). These results are in contrast to what was observed in the dispersion of HiPco SWNTs using structurally similar PPEs.[4] The as-prepared SWNT soot is composed of tubes with different diameters and degree of entanglement than HiPco SWNTs, therefore, the π–π interactions brought about by PPEs **1** and **2** may not be sufficient to cause satisfactory dispersion. Polymers with longer π-extended repeating units, **3** and **4**, were then applied in order to effect stronger π-stacking forces. Indeed, we found that both **3** and **4** could result in very stable dark-colored solutions (which can last for months without precipitation) with the as-prepared SWNT powders after a short period of bath sonication (less than 5 min). Moreover, after slow air drying, these dark solutions turned into high quality black solid films on the walls of glass vials or other smooth substrates. These films were easily redissolved into chloroform to form homogeneous solutions again by sonication. Rheological studies showed that the dynamic viscosities of the SWNT dispersions increased compared with the corresponding polymer solutions. Clearly, polymers **3** and **4** can effectively interact with the as-prepared SWNTs to form stable supramolecular assemblies in chloroform.

To further understand the supramolecular interactions between SWNTs and polymers **3** and **4**, UV-Vis spectra for the polymers as well as the polymer and SWNT assemblies (henceforth referred to as [polymer + SWNTs]) were measured in various solvents at room temperature. As shown in Fig. 1a and c, characteristic absorption features of SWNTs, particularly those in the NIR region, were observed in the chloroform solutions of [3 + SWNTs] and [4 + SWNTs], indicating significant dissolution of SWNTs. Moreover, a new weak absorption band appeared at *ca.* 502 nm for [3 + SWNTs] and *ca.* 494 nm for [4 + SWNTs], respectively. Such bands are consistent with the aggregation bands induced by progressively adding acetonitrile into the chloroform solutions of polymers **3** and **4** (see ESI†), and are indicative of π–π interactions between the polymers and SWNTs.

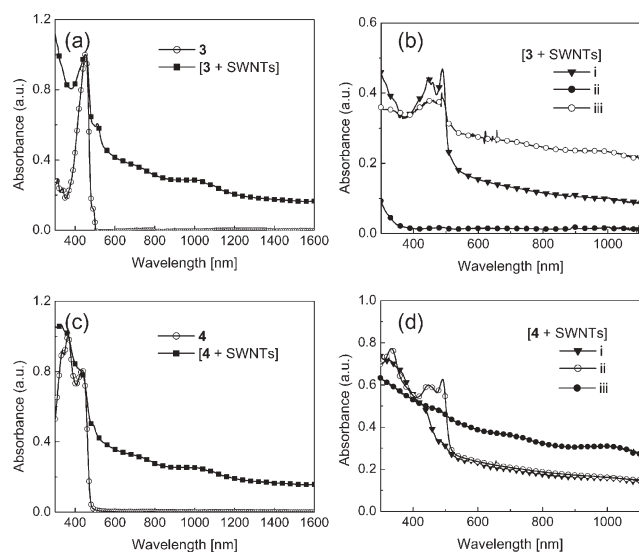When an equivolume amount of acetonitrile was added to a chloroform solution of [polymer + SWNTs], significant amounts

of SWNTs precipitated immediately in both the cases of **3** and **4**, resulting in light-colored solutions after filtration. Interestingly, the UV-Vis absorption of the resultant solutions gave outcomes in stark contrast. For polymer **3**, the aggregation band at 502 nm became more intense (Fig. 1b, (i)), signifying pronounced interpolymer aggregation, whereas for polymer **4** the absorption (Fig. 1d, (i)) showed no significant changes compared to [**4** + SWNTs] in chloroform (Fig. 1c). A similar trend of aggregation band variance was also detected in the absorption spectra of the solid films of both [polymer + SWNTs] assemblies (Fig. 1b, (iii) and Fig. 1d, (iii)). A rational explanation for this is that the association between polymer **3** and SWNTs is relatively weak and hence more susceptible to solvent polarity. Polar solvent environment could partially break down the [polymer + SWNTs] assemblies and subsequently induced interpolymer aggregation of **3**. Polymer **4**, on the other hand, has much stronger interactions/affinity with SWNTs, owing to its highly delocalized polymer backbone, such that change of solvent polarity has little effect to cause dissociation of the [**4** + SWNTs] assembly.

The interactions between already aggregated polymers and as-prepared SWNTs in a more polar solvent environment were also examined by UV-Vis absorption analyses. Polymer solutions in these experiments were first prepared in chloroform–acetonitrile (1 : 1, v/v); as such, significant polymer aggregation had already occurred before adding SWNTs. When as-prepared SWNTs were added into the solution of polymer **3** in 1 : 1 chloroform–acetonitrile, pronounced polymer precipitation was induced. The resultant filtrate barely contained any detectable amounts of polymers and/or SWNTs as monitored by UV-Vis analysis (Fig. 1b, (ii)), which is evidence that aggregated polymer **3** has no or very limited dispersing ability for SWNTs. In contrast,
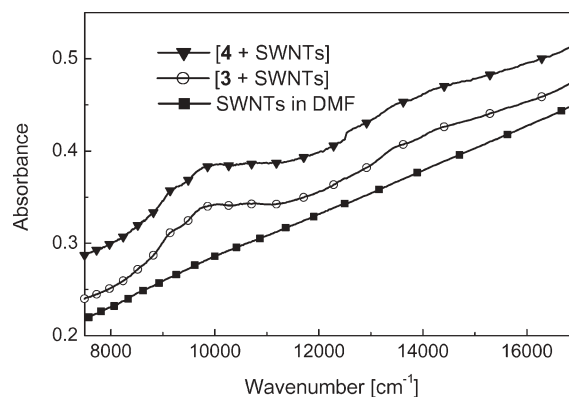
aggregated polymer **4** in 1 : 1 chloroform–acetonitrile was still able to disperse SWNTs into solution (Fig. 1d, (ii)), albeit to a degree substantially lower than its non-aggregated form in chloroform.

It is worth noting that the solutions of [**3** + SWNTs] and [**4** + SWNTs] in chloroform gave much better resolved absorption bands in the visible-NIR region, attributable to the interband transitions among van Hove singularities, than the dispersion of as-prepared SWNTs in DMF (Fig. 2). Such prominent features are suggestive that the SWNTs dispersed by polymers **3** and **4** are of higher purity[6] and, very likely, exist in the form of individual or very fine bundles in the solutions.[7]

The strong interactions between SWNTs with polymers **3** and **4** were also supported by fluorescence analysis (see ESI†). The emission intensities of polymers **3** and **4** were found to be considerably quenched after complexing with as-prepared SWNTs. The quenching effect is presumably due to photoinduced charge transfer, as the polymers are good electron donors and SWNTs are good electron acceptors.[8] The fluorescence results in turn suggest potential applications in photovoltaic and photoconducting devices.[1]

More information about the polymer–SWNT interactions at the microscopic level was obtained by imaging dried films of dilute suspensions on mica using an atomic force microscope (AFM). As shown in Fig. 3a and c, distinctive nanoscopic tubular features together with randomly scattered polymer aggregates can be clearly observed in both of the samples of [**3** + SWNTs] and [**4** + SWNTs]. The co-location of large aggregates and tubular objects in Fig. 3 is simply a result of the drying process, but a close look at the tubular features (Fig. 4) shows clear evidence for a coating (thicker diameter region) on a tube (thinner diameter region). The height distribution analyses in Fig. 3b and d and the height profile in Fig. 4b show diameters consistent with coated nanotubes, where heights are used rather than widths to avoid AFM tip-induced broadening. It is reasonable to ascribe the nanotubes of 2–5 nm in the AFM images to individual tubes (1–2 nm in diameter) partially or completely coated with a single (2–3 nm thick) layer of polymers (see Fig. 4). The states of larger-sized (6–10 nm) tubes, however, could not be clearly identified. Either tiny bundles or individual tubes coated with multiple polymer layers were possible.

Finally, Raman spectroscopic analysis was performed on as-prepared SWNT powders and the composite thin films of [**3** + SWNTs] and [**4** + SWNTs] with an excitation wavelength at

Fig. 1 (a) Comparison of UV-Vis-NIR spectra of polymer **3** and [**3** + SWNTs] in chloroform. (b) UV-Vis spectra of (i) an equivolume amount of acetonitrile added into a solution of [**3** + SWNTs] in chloroform, (ii) SWNTs added into a solution of [**3** + SWNTs] in 1 : 1 chloroform–acetonitrile, and (iii) a solid film of [**3** + SWNTs]. (c) UV-Vis-NIR spectra of polymer **4** and [**4** + SWNTs] in chloroform. (d) UV-Vis spectra of (i) an equivolume amount of acetonitrile added into a solution of [**4** + SWNTs] in chloroform, (ii) SWNTs added into a solution of [**4** + SWNTs] in 1 : 1 chloroform–acetonitrile, and (iii) a solid film of [**4** + SWNTs].

Fig. 2 Comparison of visible-NIR absorption spectra of [**3** + SWNTs] in chloroform, [**4** + SWNTs] in chloroform, and SWNTs in DMF.
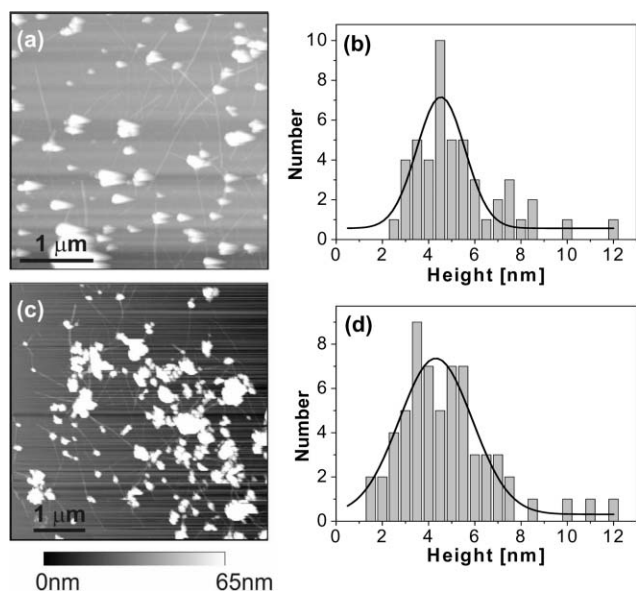
Fig. 3 AFM images (tapping mode) of polymer and SWNT assemblies on mica, and nanotube height distribution analysis. (a) and (b): [3 + SWNTs], and (c) and (d): [4 + SWNTs]. The solid-lined curves are Gaussian fits.
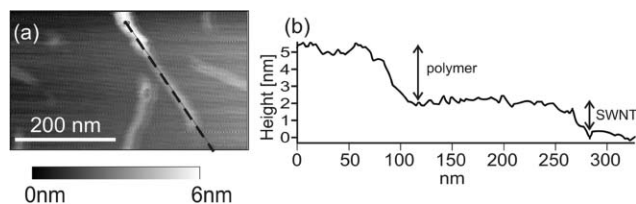
Fig. 4 (a) AFM image of [3 + SWNTs] and (b) height profile along the heavy dashed line in (a) showing the features of an individual nanotube (*ca.* 1.2 nm in diameter) partially coated with a polymer (*ca.* 3 nm in thickness) at one end.

532 nm. As shown in Fig. 5a, in the radial breathing mode (RBM), as-prepared SWNT powders gave an intense and relatively symmetrical peak at 162 cm^{-1}. The peak shifted slightly by 4 cm^{-1} for [4 + SWNTs] in conjunction with a notable shoulder at *ca.* 138 cm^{-1}. [3 + SWNTs] assemblies gave a peak at 161 cm^{-1} which is similar to that of as-prepared SWNTs, and a noticeable shoulder emerged at 178 cm^{-1}. Considering the inversely proportional correlation between diameter and RBM frequency,[9] these results suggested that, to some extent, polymers **3** and **4** may have different diameter selectivity for SWNTs during the formation of supramolecular assemblies. In the G-band region (Fig. 5b), however, no significant differences were observed among the three samples, implying that the polymers have no particular discrimination between semiconducting or metallic types of nanotubes.

Collectively, our studies have shown that linear conjugated polymers, upon rational backbone modifications, can form stable and soluble supramolecular assemblies with as-prepared SWNT powders in organic solutions *via* a surface coating mechanism. The satisfactory dispersing and debundling results of polymers **3** and **4** manifest that such type of polymers can constitute a novel generic platform for SWNT dispersants. The strength of π–π interactions between the SWNT surface and the polymer is determinative to the outcomes of dispersion as well as stabilization. The long alkyl
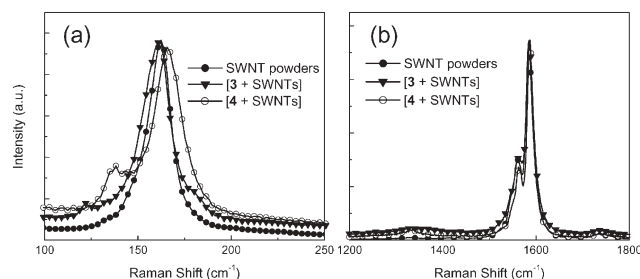
Fig. 5 Raman spectra for as-prepared SWNT powders, [3 + SWNTs], and [4 + SWNTs] showing (a) the RBM region, and (b) the G-band region.

chains are also believed to be indispensable as they can provide repulsive forces to prevent re-aggregation of individual tubes.[2a,5] These two factors may operate synergetically to achieve good dispersing outcomes. In this vein, further efforts to systematically evaluate analogous linear conjugated polymers in terms of their dispersing abilities for assorted CNTs could open a new avenue to practically useful techniques for processing and purifying CNT materials.

Notes and references

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