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Noncovalent Side-Wall Functionalization of Single-Walled Carbon Nanotubes

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Received September 3, 2002; Revised Manuscript Received November 21, 2002

ABSTRACT: A family of poly[(*m*-phenylenevinylene)-*co*-(*p*-phenylenevinylene)]s, functionalized in the synthetically accessible C-5 position of the meta-disubstituted phenylene rings have been designed and synthesized: they are essentially poly{(5-alkoxy-*m*-phenylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)-vinylene]} (PAmPV) derivatives. A range of these PAmPV polymers have been prepared both (1) by the polymerization of O-substituted 5-hydroxyisophthalaldehydes and (2) by chemical modifications carried out on polymers bearing reactive groups at the C-5 positions. PAmPV polymers solubilize SWNT bundles in organic solvents by wrapping themselves around the nanotube bundles. PAmPV derivatives which bear tethers or rings form pseudorotaxanes with rings and threads, respectively. The formation of the polypseudorotaxanes has been investigated in solution by NMR and UV/vis spectroscopies, as well as on silicon oxide wafers in the presence of SWNTs by AFM and surface potential microscopy. Wrapping of these functionalized PAmPV polymers around SWNTs results in the grafting of pseudorotaxanes along the walls of the nanotubes in a periodic fashion. The results hold out the prospect of being able to construct arrays of molecular switches and actuators.

Introduction

The small dimensions and remarkable physical properties of single-walled carbon nanotubes (SWNTs) render them unique materials with a wide range of potential applications.¹ However, their lack of solubility in solvents presents a considerable impediment toward harnessing their applications.² Although the covalent functionalization of the sidewalls of SWNTs leads to soluble samples and opens up the possibility of attaching other molecules to nanotubes,^{3,4} all the covalent chemical approaches disrupt the extended π -networks on their surfaces, diminishing both their mechanical and electronic properties. On the other hand, a noncovalent supramolecular approach which involves polymer wrapping^{5–8} of the nanotubes preserves their unique properties.

The creation of polymer-nanotube composites holds out much promise, both for reinforcing the polymers and extending their applications in electronic device settings. Recently, such a scenario has been demonstrated⁵ in the case of the conjugated luminescent polymer poly-[(*m*-phenylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)-vinylene]] (PmPV), filled with either SWNTs or multiwalled carbon nanotubes. Compared with the pristine polymer, these nanotube/PmPV composites have exhibited large increases (by nearly 8 orders of magnitude) in electrical conductivity with little loss in photoluminescence and electroluminescence yields. Moreover, the composite is far more robust than the polymer on its

own when it comes to mechanical strength and photobleaching properties. The coiled morphologies of the polymer chains help them wrap themselves around the nanotubes when they are suspended in dilute solutions of the polymer.

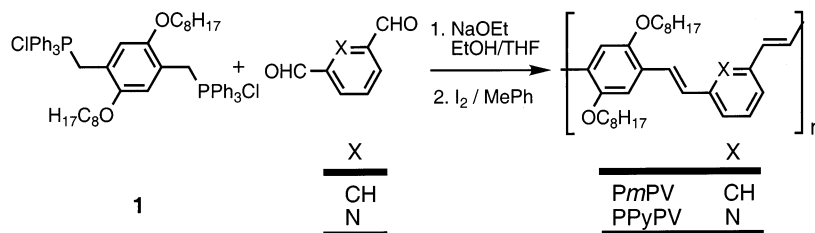
We have also reported⁷ on the use of PmPV for wrapping around SWNTs. Complexes (SWNT/PmPV) are formed on account of stabilizing noncovalent bonding interactions, presumably as a result of π - π stacking and van der Waals interactions between PmPV and the surfaces of the SWNTs. The nature of the interaction of PmPV, as well as that of poly{(2,6-pyridinediyl-enevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)-vinylene]} (PPyPV) (Scheme 1), with SWNTs has been investigated and compared.⁸ Optoelectronic devices have also been fabricated with these complexes. It is clear that noncovalent functionalization of carbon nanotubes can be achieved without disrupting the primary structure of the nanotubes themselves. To this extent, noncovalent functionalization has potentially a virtue that all forms of covalent functionalization lack.

In this paper, we report on the synthesis and characterization of a variety of polymers functionalized in the synthetically accessible C-5 position on the meta-disubstituted phenylene ring, affording poly{(5-alkoxy-*m*-phenylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)-vinylene]} (PAmPV) derivatives. The new polymers were all examined for their interactions with SWNTs. They provide a ready means to change the physical properties of nanotubes, such as their solubilities, as well as the possibility of functionalizing them. PAmPV derivatives, bearing tethers or rings that form pseudorotaxanes with matching rings or threads represent

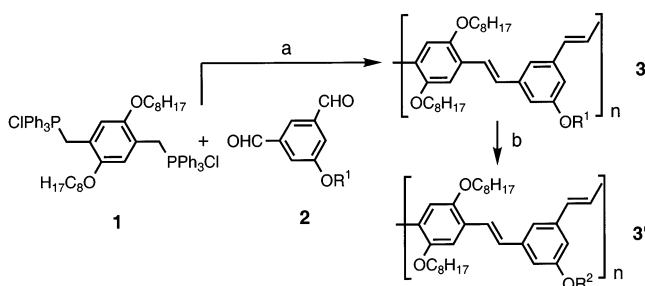
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Scheme 1. Synthesis of Poly{(*m*-phenylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)vinylene]}, or P*m*PV (X = CH), Poly{(2,6-pyridinediylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)vinylene]}, or PPyPV (X = N) by Wittig Polymerization of Diphosphonium Salt **1 from Isophthalaldehyde and 2,6-Pyridinedicarbaldehyde, Respectively**



Scheme 2. Synthesis of Poly{(5-alkoxy-*m*-phenylenevinylene)-*co*[(2,5-dioctyloxy-*p*-phenylene)vinylene]} or P*Am*PV Polymers by (a) Polymerization and (b) Polymer Modification



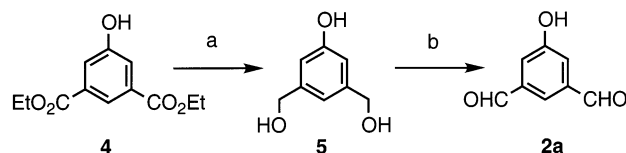
two different types of polypseudorotaxanes.⁹ In this article, we also describe the synthesis of self-assembling pseudorotaxane-containing P*Am*PV polymers based on the two different recognition motifs—(i) one involving hydrogen-bonding interactions between secondary dialkylammonium centers (e.g., dibenzylammonium ions) and suitable crown ethers (e.g., benzo[24]crown-8) and (ii) the other involving π - π stacking, [C-H \cdots O], and [C-H $\cdots\pi$] interactions between π -electron-deficient hosts (e.g., cyclobis(paraquat-*p*-phenylene) and π -electron-rich guests (e.g., 1,5-bis(hydroxyethoxyethoxy)naphthalene). Wrapping these functionalized polymers around SWNTs results, in essence, in the grafting of pseudorotaxanes along the walls of SWNTs in a periodic fashion.

Results and Discussion

Preparation and Characterization of Functional P*Am*PV Polymers. The polymers carrying functional groups and arms have been prepared either (1) by using a functionalized monomer directly or (2) by carrying out subsequent reactions on the polymers. Whereas the first method produces polymers with functional groups present in all the repeating units, the second approach generates randomly substituted polymers where the degree of substitution depends on the efficiencies of the reactions bringing about the modifications. We chose to introduce functionality into the P*m*PV polymer (X = CH in Scheme 1) at the synthetically accessible C-5 position on the meta-substituted phenylene rings along the polymer backbone.

The P*Am*PV polymers **3** were prepared (Scheme 2) from the precursors **2** by a bis-Wittig reaction with the common bisphosphonium salt **1** whose synthesis was described previously.⁸ A range of P*Am*PV polymers **3** have been prepared either (1) by polymerization of the O-substituted 5-hydroxyisophthalaldehydes **2** or (2) by modifications of polymers bearing reactive groups at their C-5 positions. 5-Hydroxyisophthalaldehyde (**2a**) was synthesized (Scheme 3) by employing a variation of a

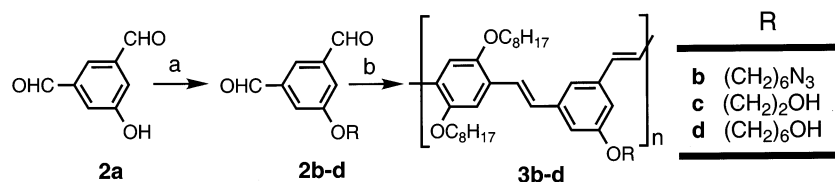
Scheme 3. Synthesis of 5-Hydroxyisophthalaldehyde (2a**)^a**



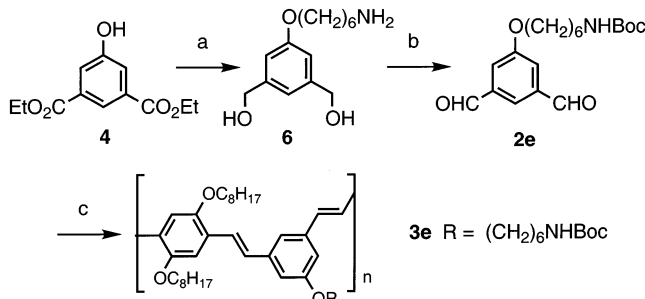
^a Reagents and conditions: (a) LiAlH₄, THF, reflux, 96%; (b) K₂Cr₂O₇, DMSO, 100 °C, 35%.

published procedure.¹⁰ Starting from the commercially available 5-hydroxydiethylisophthalate (**4**), reduction (LiAlH₄/THF) gave (96%) 3,5-bis(hydroxymethyl)phenol (**5**) which was oxidized, on treatment with a Me₂SO solution of potassium dichromate,¹¹ to afford the key monomer **2a**. O-Alkylations of **2a** could be performed (Scheme 4) under relatively mild conditions, i.e., K₂CO₃ in DMF at room temperature using both bromides and iodides as the alkylating agents. Alternatively, O-alkylated 5-hydroxyisophthalaldehydes could be obtained by alkylation of 5-hydroxydiethylisophthalate (**4**); e.g., the Boc-protected derivative **2e** was synthesized (Scheme 5) using this approach: **4** was alkylated with 6-azidotoxylhexanol and then the product was reduced—the azide to an amino function and the ester to alcohols—with LiAlH₄/THF to afford **6** wherein the amino function was protected with a Boc group prior to its being oxidized (PCC/CH₂Cl₂) to the functionalized dialdehyde **2e**. A range of different O-alkylated 5-hydroxyisophthalaldehydes (**2b–e**), including aliphatic alcohols, azides, and protected amines, undergo (Schemes 4 and 5) bis-Wittig-style polymerizations smoothly. However, the parent phenol **2a** did not afford polymers without it first being protected¹² as a methoxymethyl (MOM) ether **2f**, which did undergo (Scheme 6) the polymerization to give the polymer **3f**, from which the MOM-protecting groups could be readily removed to afford **3a**.

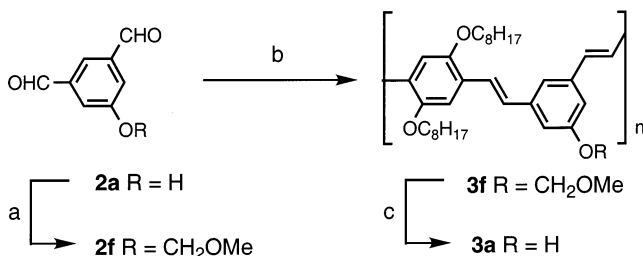
The P*Am*PV polymers were obtained (Table 1A) in yields of 60–80% as a result of reacting the bis-Wittig reagent, generated on treatment of the bisphosphonium salt **1** with NaOEt in ethanolic THF containing the O-substituted 5-hydroxyisophthalaldehydes **2b–f**. In common with Wittig reactions of this type, the new olefinic bonds materialize as a mixture of *cis* and *trans* geometries. However, the *cis* double bonds can be isomerized to *trans* ones, giving the all-*trans* polymers, by heating the crude polymers in PhMe under reflux in the presence of iodine as a catalyst. Although, this step proceeded quantitatively in all cases, one can anticipate a problem when the substituted 5-hydroxyisophthalaldehyde monomers react with iodine.¹³ Theoretically, such P*Am*PV polymers could be prepared using the Wittig–Horner reaction which relies on the use of bisphosphonates to produce olefinic bonds with exclusively the all-*trans* configurations. Indeed, the parent P*m*PV polymer

Scheme 4. Synthesis of the Functional PAmPV Polymers 3b–d^a

^a Reagents and conditions: (a) RI or RBr, K₂CO₃, DMF, room temperature, 60–75%; (b) (i) **1**, EtONa, EtOH/THF, 60%; (ii) I₂ (cat), PhMe, reflux, 100%.

Scheme 5. Synthesis of PAmPV Polymer 3e^a

^a Reagents and conditions: (a) (i) 6-azido-1-(*p*-toluenesulfonyloxy)hexane, K₂CO₃, DMF, 90%; (ii) LiAlH₄, THF, reflux, 61%; (b) (i) Boc₂O, NaHCO₃, Na₂CO₃, 67%; (ii) PCC, CH₂Cl₂, 60%; (c) (i) **1**, EtONa, EtOH/THF, 60%; (ii) I₂ (cat), PhMe, reflux, 100%.

Scheme 6. Synthesis of the Phenol-Containing PAmPV Polymer 3a^a

^a Reagents and conditions: (a) ClCH₂OMe, Me₂CO, K₂CO₃, 78%; (b) (i) **1**, EtONa, EtOH/THF, 84%; (ii) I₂ (cat), PhMe, reflux, 100%; (c) HCl, *i*PrOH/THF, 92%.

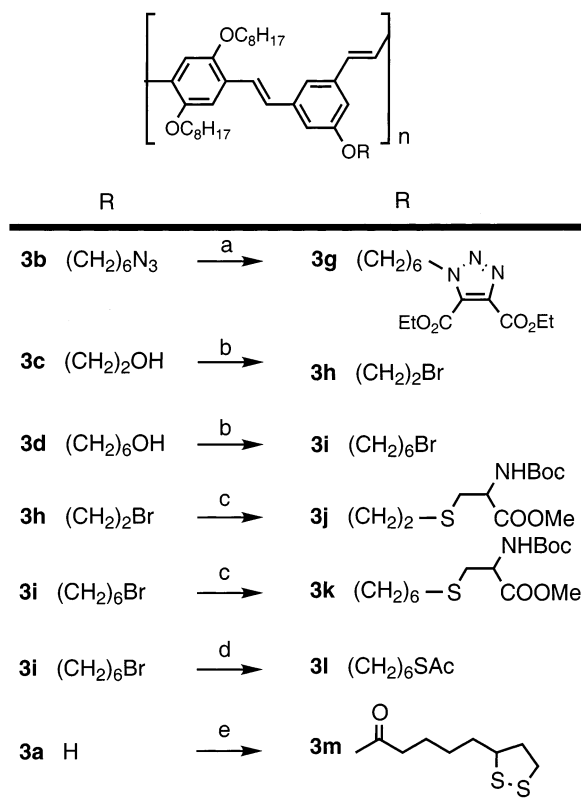
Table 1. Selected PAmPV Polymers

| polymer | fw ^b | yield (%) | M _n / PDI | n |
|---|-----------------|-----------|----------------------|----|
| (A) Polymers (3a–f) Prepared by Polymerization of O-Substituted 5-Hydroxyisophthalaldehydes (2a–f) ^a | | | | |
| PmPV ⁸ | 460.69 | 60 | 11 900/1.6 | 26 |
| 3a ^c | 476.69 | 0 | - | - |
| 3b | 601.86 | 77 | 23 900/1.7 | 40 |
| 3d | 576.85 | 73 | 26 000/1.8 | 45 |
| 3e | 675.98 | 77 | 16 960/1.6 | 25 |
| 3f | 520.74 | 84 | 10 400/1.7 | 20 |
| (B) Selected PAmPV Polymers Prepared by Polymer Modifications ^d | | | | |
| 3a | 476.69 | 92 | 8700/2.2 | 18 |
| 3g | 772.02 | 90 | 21 700/1.6 | 28 |
| 3i | 639.75 | 94 | 4900/2.24 | 8 |
| 3l | 634.95 | 95 | 5500/1.7 | 9 |
| 3m | 665.00 | 93 | 14 000/1.8 | 21 |

^a Reagents and conditions: (i) **1**, EtONa, EtOH/THF, 60%; (ii) I₂ (catalytic), PhMe, reflux, 100%. See Schemes 4–6. ^b Formula weight of the polymer repeating unit. ^c No polymerization was observed for the unprotected monomer. ^d See Schemes 6 and 7.

has been prepared^{13,14} with a high degree of polymerization using the Wittig–Horner approach.

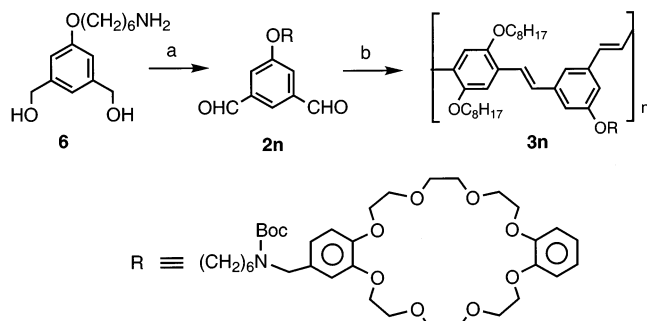
We have carried out (Scheme 7) a number of different reactions on PmPV derivatives to obtain further chemi-

Scheme 7. Polymer Modifications^a

^a Reagents and conditions: (a) diethyl acetylenedicarboxylate, PhMe, reflux, 90%; (b) CBr₄, PPh₃, THF, 0 °C to room temperature, 92–94%; (c) *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester, Et₃N, CHCl₃, room temperature, 88–91%; (d) thioacetic acid, Et₃N, CHCl₃, room temperature, 95%; (e) thioctic acid, DCC, DMAP, CH₂Cl₂, room temperature, 93%.

cally modified PAmPV derivatives. As a general rule, treatment of these derivatives with either strong acid or strong base resulted in insoluble products. For example, attempts (1) to reduce the azido group in polymer **3b** and (2) to remove the Boc protecting group from polymer **3e** were unsuccessful. Those reactions which could be carried out successfully are summarized in Scheme 7. These reactions were followed by ¹H NMR spectroscopy (see Table 2 in Supporting Information). Changes in the molecular weights of the polymers were assessed by GPC (Table 1B). Polymer **3b** was found to undergo a 1,3-dipolar cycloaddition with diethylacetylenedicarboxylate almost quantitatively to afford polymer **3g**. The hydroxymethyl groups in polymers **3c** and **3d** could be converted easily and efficiently into the corresponding polymers **3h** and **3i**, respectively, with bromomethyl functions. These bromides react well with good nucleophiles, such as the thiol group in L-cysteine to give, respectively, the polymers **3j** and **3k** and thioacetic acid to give the polymer **3l**. However, it should be noted that the brominations (CBr₄/Ph₃P) of polymers

Scheme 8. Synthesis of Dibenzo[24]crown-8-Containing PAmPV Polymer **3n^a**



^a Reagents and conditions: (a) (i) 2-Formyldibenzo-[24]-crown-8, PhMe, reflux; (ii) NaBH₄, MeOH; (iii) Boc₂O, NaHCO₃, Na₂CO₃, the total yield for the 3 steps is 67%; (iv) PCC, CH₂Cl₂, 60%; (b) (i) **1**, EtONa, EtOH/THF, 53%; (ii) I₂ (cat), PhMe, reflux, 100%.

3c and **3d** are accompanied by losses in molecular weight: see Table 1, parts A and B, which show, for example, that conversion of **3d** into **3i** is accompanied by a decrease from 45 to 8 in the polymer repeating unit. A more promising approach to polymer modification is the esterification of the phenol-containing polymer **3a**, using mild activated-coupling conditions with carboxylic acids, such as thioctic acid where polymer **3m** was obtained without any degradation of the polymer chain having occurred (Table 1B). It is worth noting that this polymer could be used to assist in the anchoring of SWNT/PAmPV bundles onto gold surfaces.

Design and Synthesis of Polypseudorotaxanes.

The approach we have used for the grafting of pseudorotaxanes onto PAmPV polymers has been to attach neutral recognition units to the C-5 position of 5-hydroxyisophthalaldehyde (**2a**) and then carry out polymerizations with the bis-Wittig reagent derived from the bisphosphonium salt **1**. Two pseudorotaxanes were targeted—one involving the tethering of dibenzo[24]-crown-8 (DB24C8) macrocycles to the polymer backbone for threading by dibenzylammonium (DBA⁺) ions¹⁵ and the other involving a polyether chain incorporating a 1,5-dioxynaphthalene ring system for encircling by cyclobis(paraquat-*p*-phenylene).¹⁶

Since all our initial attempts to introduce crown ether rings onto the side chains of PAmPV polymers were unsuccessful, we decided to incorporate the DB24C8 appendages into a dialdehyde monomer **2n** prior to polymerization (Scheme 8). The synthesis of the monomer relied upon starting with a formylated DB24C8 derivative¹⁷ which was treated with the amine **6** to produce an imine which was reduced in situ to an amine that was Boc-protected, before being subjected to the polymerization conditions. The molecular weight of the resulting polymer **3n** was determined by GPC and found to be 12 300 (*M_n*) with a polydispersity index (PDI) of 1.8. Although the peaks in the ¹H NMR spectrum (Figure 1a) of the polymer were broadened sufficiently to obscure all the coupling constant information, they could still be assigned unequivocally to protons in the polymer. Significant movement of signals in the region δ 3.0–4.6 was evident when DBA·PF₆ was added to the solution of the PAmPV polymer **3n** in CDCl₃, indicating (Figure 1b) the formation of polypseudorotaxanes in the solution.

The 1,5-dioxynaphthalene-containing PAmPV polymer **3p** was obtained (Scheme 9) by polymerizing the

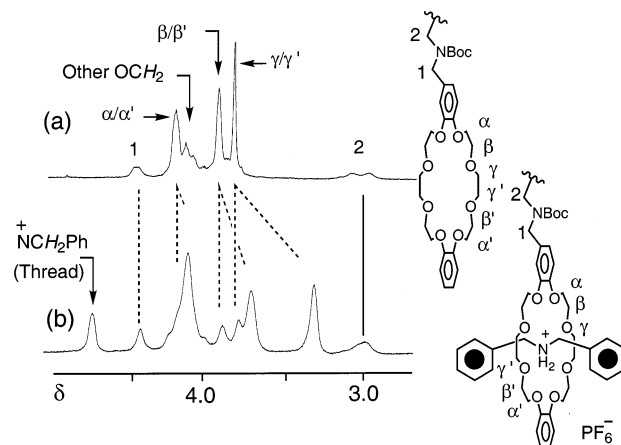
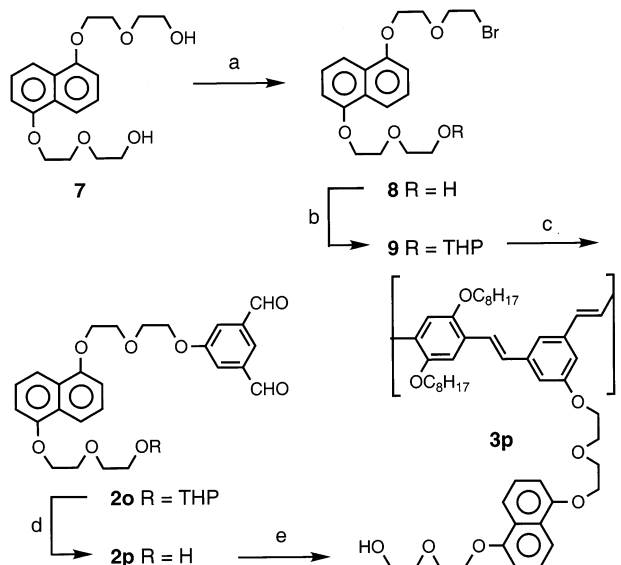


Figure 1. ¹H NMR spectra (500 MHz, CD₃CN/CDCl₃) of dibenzo[24]crown-8-containing polymer (**3n**) before (a) and after (b) addition of dibenzoammonium hexafluorophosphate.

Scheme 9. Synthesis of the Naphthalene-Containing PAmPV Polymer **3p^a**



^a Reagents and conditions: (a) PPh₃, CBr₄, THF, 26%; (b) THP, TsOH, CH₂Cl₂, 85%; (c) **2a**, K₂CO₃, DMF, 58%; (d) HCl, THF, 83%; (e) (i) **1**, EtONa, EtOH/THF, 53%; (ii) I₂ (cat), PhMe, reflux, 100%.

monomer **2p** which was synthesized in four steps from 1,5-dihydroxyethoxyethoxynaphthalene¹⁸ (**7**). Compound **7** was monobrominated to give **8** which was converted to its THP-protected derivative **9** before being used to alkylate (K₂CO₃/DMF) 5-hydroxyisophthalaldehyde (**2a**) at room temperature. Deprotection of the product **2o** yielded the monomer **2p** which was subjected to the usual polymerization conditions to give the polymer **3p** with *M_n* = 14,050, corresponding to a repeating unit of 18. The ¹H NMR spectrum recorded in CDCl₃/CD₃CN is shown in Figure 2c. Upon addition of CBPQT·4PF₆, with the ¹H NMR spectra shown in Figure 2a, the polypseudorotaxane is formed: the signals (Figure 2b) for protons in CBPQT⁴⁺ are broadened and shifted together with those for the 1,5-dioxynaphthalene ring system. The signal broadening is probably related in part to slow complexation–decomplexation of CBPQT⁴⁺ with the side chains tangling from the polymer backbone. UV/vis spectroscopy provides (Figure 3) further evidence for polypseudorotaxane formation. In common with other PAmPV polymers **3a–3m** (see Table 3 in

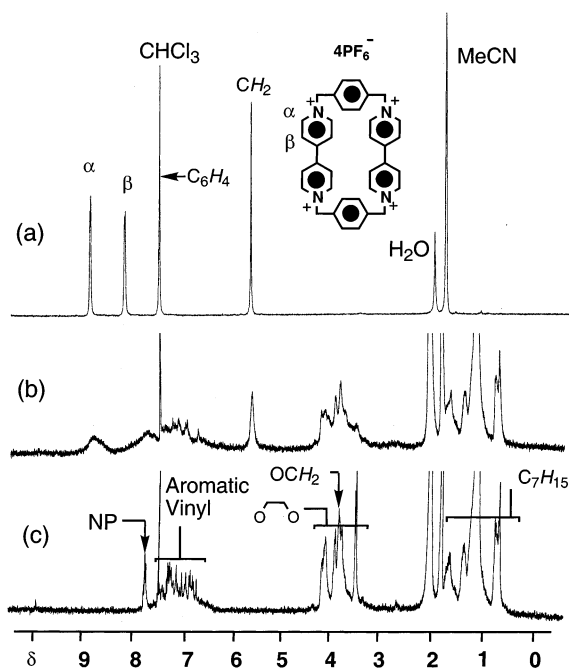


Figure 2. ^1H NMR spectra (500 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$) of 1,5-dihydroxyethoxyethoxynaphthalene-containing polymer (**3p**) before (c) and after (b) addition of cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}), the spectrum of which is presented above (a).

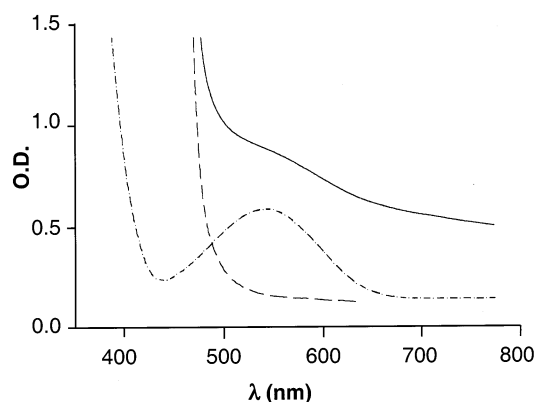


Figure 3. UV-vis spectra of the 1,5-dihydroxyethoxyethoxynaphthalene-containing polymer (**3p**) before (dashed line, a) and after (solid line, b) addition of cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}). UV-vis spectra of a charge-transfer band of the pseudorotaxane formed by 1,5-dihydroxyethoxyethoxynaphthalene and CBPQT^{4+} presented as (c) a dashed and dotted line.

Supporting Information), polymer **3p** absorbs strongly at just above 400 nm. It does not absorb in the 520–540 nm region where the 1,5-dioxynaphthalene/ CBPQT^{4+} charge-transfer band is expected.¹⁹ However, addition of $\text{CBPQT}\cdot 4\text{PF}_6$ to the polymer solution produces a shoulder centered on 520 nm, indicating the threading of CBPQT^{4+} cyclophanes onto the 1,5-dihydroxynaphthalene-containing polyether sidearms on the polymer **3p**. This polypseudorotaxane formation can also be detected by the naked eye since the color of the polymer solution changes from greenish-yellow to orange on addition of $\text{CBPQT}\cdot 4\text{PF}_6$.

Interaction of PAmPV Polymers with Single-Walled Carbon Nanotubes (SWNTs). The polymers were tested for their abilities to solubilize bundles of SWNTs. We have shown that the PAmPV derivatives **3a–p** form stable solutions with the bundles in CHCl_3

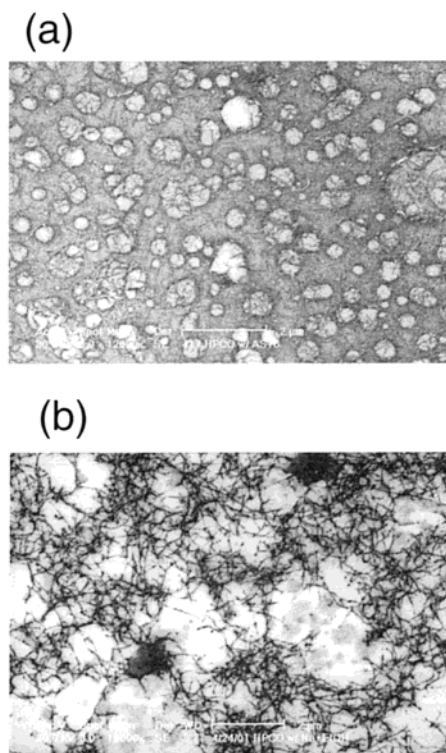


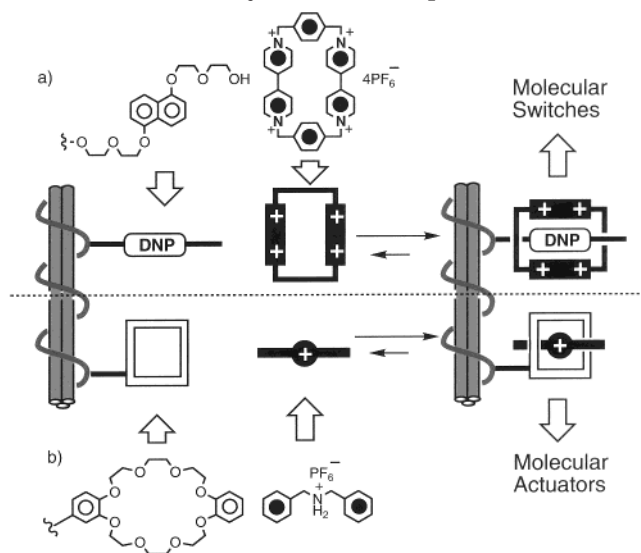
Figure 4. Scanning electron microscopy (SEM) images of (a) the CHCl_3 -soluble complex of SWNTs, wrapped with PAmPV (**3a**), and (b) the EtOH-soluble complex of SWNTs, wrapped with the sodium salt of **3a**.

and other organic solvents. In the case of the derivative **3a** containing phenolic residues, the sodium phenoxide derived polymer was found to solubilize the bundles in protic solvents, e.g., EtOH. Figure 4 provides an example of a scanning electron microscopy (SEM) image of bundles of SWNTs coated with the PAmPV derivative **3a**. Other derivatives, namely **3d**, **3e**, **3g**, **3i**, and **3l**, afforded (see Figures 6 and 7 in Supporting Information) similar images, all suggestive of the solubilization of the nanotube bundles in CHCl_3 . However, in the case of the sodium salt of **3a**, EtOH affords an image (Figure 4b) commensurate with it having solubilized the bundles. SWNTs wrapped with the PAmPV polymer **3a** containing reactive phenolic hydroxyl groups were also examined for their ability to react with dicarboxylic acids as cross-linking agents. When the CHCl_3 soluble composite was treated with dodecanedioic acid, an insoluble cross-linked resin was formed. The SEM images (Figure 8 in Supporting Information) of this composite resin show that the SWNT bundles are included in the polymer network.

Although the polypseudorotaxane formed between the PAmPV derivative **3n** and $\text{DBA}\cdot\text{PF}_6$ in CHCl_3 (Scheme 10) can also solubilize SWNTs on sonication only 1 min after sonication is halted, the SWNTs start to precipitate out of solution. Presumably, the introduction of positive charges on the sidearms of the polymer decrease the solubility of the polypseudorotaxane composite in CHCl_3 .

In the case of the PAmPV derivative **3p** and $\text{CBPQT}\cdot 4\text{PF}_6$ (Scheme 10), a solvent mismatch (SWNT bundles wrapped with **3p** are soluble in CHCl_3 but not in MeCN, whereas $\text{CBPQT}\cdot 4\text{PF}_6$ is soluble in MeCN but not in CHCl_3) has prevented us from studying the solubilization of SWNTs with this polypseudorotaxane. Indeed, the polymer-wrapped SWNTs which are soluble in

Scheme 10. Polypseudorotaxane Formation from Polymers **3n** and **3p**



CHCl_3 precipitate their SWNTs on addition of an MeCN solution of $\text{CBPQT} \cdot 4\text{PF}_6$. The precipitation may be another example where addition of positive charge to the sidearms of the polymer is the cause or it may simply be a solvent effect.

On account of solvent constraints, the traditional observation of a CT band resulting from the threading of the CBPQT^{4+} by the 1,5-dioxynaphthalene-containing polyether side chains on the PAmPV derivative **3p** could not be performed in the presence of SWNTs, the reason being that, on the addition of MeCN or Me_2CO the SWNTs precipitate from solution. Scanning probe microscopy provides an alternative means to investigate this triply supramolecular bundle. In particular, tapping mode atomic force microscopy (AFM) and surface potential (SP) microscopy were informative. Dilute solutions of the polymer **3p** and SWNTs in CHCl_3 were spin-coated onto silicon oxide wafers that were pre-patterned with alignment markers. After the supramolecular bundles had been characterized by AFM and SP, the wafers were placed in a 0.1 mM solution of $\text{CBPQT} \cdot 4\text{PF}_6$ in MeCN for 12 h.²⁰ Individual bundles were identifiable as a result of their fixed proximity to the alignment markers. A series of AFM images is shown in Figure 5, starting with the topography (Figure 5a) of the supramolecular bundle and its corresponding SP (Figure 5b). After exposure of the wafer to the MeCN solution of $\text{CBPQT} \cdot 4\text{PF}_6$, while there was no change in the topography, there was a significant change in the SP. It is evident from a comparison of the images portrayed in Figure 5, parts b and c, that the addition of the $\text{CBPQT} \cdot 4\text{PF}_6$ solution affects the dipole density of the bundle. Although this observation does not prove that CBPQT^{4+} has threaded onto the **3p** polymer-coated bundles, we believe that the tetracationic cyclophane has become associated in some way with the bundles.

Conclusions

The noncovalent functionalization of bundles of carbon nanotubes with conducting polymers that have the capacity to form pseudorotaxanes represents the operation of supramolecular forces at three different levels of superstructure, viz., (1) the aggregation of the nanotubes into bundles, (2) the wrapping of the bundles by the polymer, and (3) the formation through the sidearms

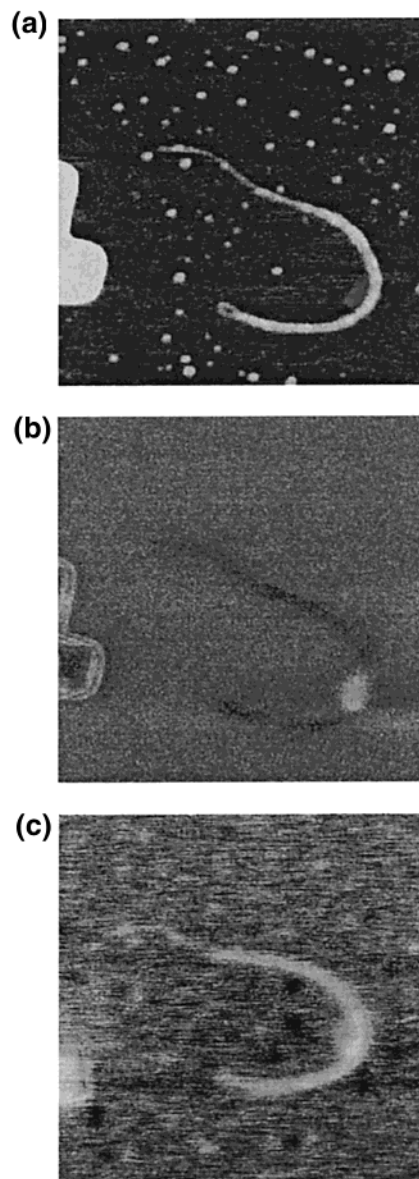
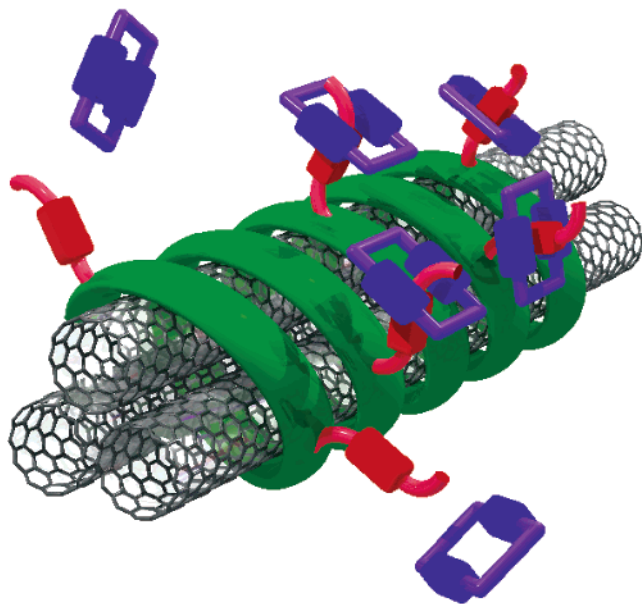


Figure 5. Atomic Force Microscopy (AFM) tapping mode images of an SWNT bundle wrapped with the polymer **3p**, which is soluble in CHCl_3 , and treated subsequently with cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}). (a) Topography of a bundle of SWNTs wrapped with the polymer **3p** on a silicon oxide substrate after spin-coating. (b) Surface potential of this same sample. (c) Surface potential of the same SWNT polymer-wrapped bundle after a 12 h exposure to a MeCN solution of $\text{CBPQT} \cdot 4\text{PF}_6$. The feature on the left represents the alignment marker in the $4 \times 4 \mu\text{m}$ images.

attached to the polymer of threaded complexes. The results conjure up the prospect of developing arrays of molecular actuators and switches in the future.

Experimental Section

Materials and Instrumentation. Chemicals were purchased from Aldrich and used as received. Syntheses of 2,5-bis(methyltriphenylphosphonium chloride)-1,4-bis(octyloxy)-benzene (**1**) have previously been reported by us.⁸ Cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}) was synthesized according to the literature procedures.¹⁶ Sodium ethoxide was freshly prepared prior to use from Na metal and anhydrous EtOH. Solvents were dried, distilled, and stored under argon. UV/visible spectra were obtained using a Varian Cary 100 Bio spectrophotometer. Absorption measurements of polymeric sample



solutions were carried out in CHCl_3 with concentrations of 1.0×10^{-4} and 1×10^{-5} M relative to repeating units in a polymer. Molecular weights of polymers were determined by using a Dynamax solvent delivery module system, a Styragel HR3 column, and a Dynamax PDA-2 diode array detector, at a flow rate of 1.0 mL/min. All molecular weights were measured against polystyrene standards in THF. Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) spectra were recorded on a Bruker ARX400 or ARX500 at 25 $^\circ\text{C}$, using the deuterated solvent as lock and the residual solvent as internal standard. Elemental analyses were performed by Quantitative Technologies Inc.

General Polymerization Procedure. A solution of NaOEt in EtOH (1 M, 2.5 mL) was added dropwise to a solution of 2,5-dioctyloxy-1,4-bis(triphenylphosphonium) dichloride (**1**) (1 mmol) and substituted 5-hydroxyisophthalaldehyde (**2**) (1 mmol) in a mixture of anhydrous EtOH (10 mL) and THF (10 mL) at ambient temperature. The reaction mixture was stirred for an additional 24 h and then evaporated to dryness. The residue was dissolved in a minimum amount of CHCl_3 (1 mL), and the crude polymer was precipitated out by addition of MeOH (20 mL) as a yellow resin, which was filtered and dried. A sample of the crude polymer (50 mmol) and I_2 (0.5 mg) was refluxed in PhMe (15 mL) for 4 h. The solvent was evaporated off under vacuum, and the polymer was precipitated from CHCl_3 by the addition of an excess of MeOH. The polymer was filtered and dried to afford PAmPV (**3**) as a yellow resin. Typical yields are 60–80%. See Table 1.

3n. Following the general polymerization procedure, this polymer was obtained from **1** (0.96 g, 1.0 mmol) and **2n** (0.81 g, 1 mmol) as a yellow sticky solid (0.74 g, 65%). Data for **3n** follow. ^1H NMR (500 MHz, CDCl_3): δ = 7.52 (s, 1H), 7.42 (s, 1H), 7.19–7.06 (m, 5H), 6.96 (s, 2H), 6.79 (brs, 4H, Ar–H, crown), 6.68 (brd, 3H, Ar–H, crown), 4.33 (brs, 2H, $>\text{NCH}_2\text{Ar}$), 4.12 (brs, 8H, $\alpha\text{-H}$ crown), 4.07–4.03 (m, 6H, $-\text{OCH}_2\text{-(CH}_2)_5\text{-}$), 3.90 (brs, 8H, $\beta\text{-H}$ crown), 3.82 (brs, 8H, $\gamma\text{-H}$ crown), 3.19 (brd, 2H, $-\text{O(CH}_2)_5\text{CH}_2\text{N}<$), 1.88–1.85 (m, 6H, $-\text{OCH}_2\text{CH}_2\text{-}$), 1.54–1.28 (m, 26H, $-\text{CH}_2\text{-}$), 1.45 (s, 9H, *t*-Bu), 0.85 (brt, 6H, $-\text{O(CH}_2)_7\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ = 160.0, 159.0, 151.17, 148.95, 148.88, 148.0, 139.6, 131.5, 128.9, 127.0, 124.1, 121.4, 113.99, 113.67, 110.8, 79.5, 71.25, 69.93, 69.62, 69.46, 69.34, 67.90, 53.0, 31.85, 29.71, 29.51, 29.44, 29.34, 28.51, 26.76, 26.30, 25.96, 22.67, 14.12. Anal. Calcd for $\text{C}_{68}\text{H}_{97}\text{NO}_3$ (1136.5): C, 71.86; H, 8.60; N, 1.23. Found: C, 71.21; H, 8.61; N, 1.25.

3p. Following the general polymerization procedure, this polymer was obtained from **1** (65 mg, 0.07 mmol) and **2n** (32 mg, 0.07 mmol) as a yellow resin; yield 52 mg (0.06 mmol, 53%). Data for **3p** follow. ^1H NMR (400 MHz, CDCl_3): δ =

9.97 (s, 0.08H, CHO end groups), 7.91 (d, 1H, J = 8.6 Hz, Ar–H, NP), 7.87 (d, 1H, J = 8.4 Hz, Ar–H, NP), 7.51–7.44 (m, 1H), 7.37 (t, 1H, J_{ave} = 8.0 Hz, Ar–H, NP), 7.33 (t, 1H, J_{ave} = 8.2 Hz, Ar–H, NP), 7.28 (s, 1H), 7.17–7.04 (m, 5H), 6.88 (d, 1H, J = 7.6 Hz, Ar–H, NP), 6.83 (d, 1H, J = 7.6 Hz, Ar–H, NP), 6.85–6.70 (m, 2H), 4.37 (t, 2H, J = 4.6 Hz, $-\text{OCH}_2\text{CH}_2\text{O-}$), 4.29 (t, 4H, J = 4.6 Hz, $-\text{OCH}_2\text{CH}_2\text{O-}$), 4.12 (t, 2H, J = 4.6 Hz, $-\text{OCH}_2\text{CH}_2\text{O-}$), 4.07 (t, 4H, J = 6.0 Hz, $-\text{OCH}_2\text{(CH}_2)_6\text{CH}_3$), 3.99 (t, 4H, J = 4.6 Hz, $-\text{OCH}_2\text{CH}_2\text{O-}$), 3.78–3.72 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{O-}$), 2.02 (brs, 1H, $-\text{OH}$), 1.89 (p, 4H, J = 6.8 Hz, $-\text{OCH}_2\text{CH}_2\text{(CH}_2)_5\text{CH}_3$), 1.54 (p, 4H, J = 6.8 Hz, $-\text{O(CH}_2)_2\text{CH}_2\text{(CH}_2)_4\text{CH}_3$), 1.38–1.27 (m, 16H, $-\text{O(CH}_2)_3\text{(CH}_2)_4\text{CH}_3$), 0.85 (t, 6H, J = 6.8 Hz, $-\text{O(CH}_2)_7\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ = 154.38 (Ar–C, NP), 154.27 (Ar–C, NP), 151.17, 139.6, 128.9, 126.85 (Ar–C, NP), 126.79 (Ar–C, NP), 125.22 (Ar–CH, NP), 125.15 (Ar–CH, NP), 124.1, 114.8, 114.56 (Ar–CH, NP), 114.55 (Ar–CH, NP), 108.7, 105.80 (Ar–CH, NP, 2 overlapping), 72.60 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 70.18 ($\text{OCH}_2\text{CH}_2\text{O}$), 70.10 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 69.78 ($-\text{OCH}_2\text{(CH}_2)_6\text{CH}_3$), 69.61 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 68.02 ($\text{OCH}_2\text{CH}_2\text{O}$, 2 overlapping), 67.90 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 61.86 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 31.85, 29.51, 29.49, 29.44, 26.27, 22.68, 14.12. Anal. Calcd for $\text{C}_{50}\text{H}_{66}\text{O}_8$ (795.05): C, 75.53; H, 8.37. Found: C, 74.92; H, 8.40.

Molecular Weight Determinations. The molecular weights and polydispersity (PDI) of **3n** (M_w = 22 100; DPI = 1.8) and **3p** (M_w = 24 720; DPI = 1.76) were determined in THF by using a size-exclusion chromatograph (SEC) equipped with a UV detector. The SEC system was calibrated by using polystyrene standards prior to use. The GPC measurements of **3n** show that its number-average molecular weight (M_n) is 12 300, corresponding to 11 repeating units. The GPC measurements of **3p** show that the number-average molecular weight (M_n) is 14 045, corresponding to 18 repeating units. The presence of the aldehyde end groups is evident from ^1H NMR spectroscopy. The degree of polymerization of **3p** was estimated as $n \approx 25$ by NMR end group analysis.

Preparation of the SWNT/Polymer Complex. The SWNTs were produced by the HiPco method and used as received from Rice University. SWNTs (0.3 mg) were added to a solution of the polymer in CHCl_3 solution (1 mg in 5 mL). Sonication (30 min) in a water bath (Branson model 1510, 40 kHz) gave a stable transparent solution.

Preparation of the SWNT/Polymer Samples Prior to Atomic Force Microscopy (AFM). After sonication, 1 drop of the SWNT/PAmPV solution was placed on a freshly cleaved 1 cm^2 mica wafer, which was subsequently washed with 5 drops of CHCl_3 while spinning at 750 rpm to wash off excess of the polymer. AFM images were collected in tapping mode.

Acknowledgment. This work was supported by the Office of Naval Research and by the National Science Foundation.

Supporting Information Available: Text giving experimental procedures for 5-hydroxyisophthalaldehyde (**2a**), O-alkylated 5-hydroxyisophthalaldehyde (**2b–p**), and PAmPV polymers (**3a–m**), tables giving ^1H NMR and UV–vis spectral data of PAmPV polymers (**3a–m**) and figures giving SEM images of SWNTs/PAmPV complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA021417N