Preparation, Alignment, and Optical Properties of Soluble Poly(phenylacetylene)-Wrapped Carbon Nanotubes[†]

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ABSTRACT: Carbon nanotube-containing poly(phenylacetylenes) (NT/PPAs) are prepared by in situ polymerizations of phenylacetylene catalyzed by WCl_6-Ph_4Sn and $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene) in the presence of the nanotubes. The NT/PPAs are characterized by GPC, NMR, UV, FL, TGA, SEM, TEM, and XRD, and it is found that the nanotubes in the NT/PPAs are helically wrapped by the PPA chains. The short nanotubes thickly wrapped in the PPA chains are soluble in common organic solvents including tetrahydrofuran, toluene, chloroform, and 1,4-dioxane. The NT/PPAs are macroscopically processible, and shearing of the NT/PPA solutions readily aligns the nanotubes along the direction of the applied mechanical force. The nanotubes exhibit a strong photostabilization effect, protecting the PPA chains from photodegradation under harsh laser irradiation with incident fluence as high as 10 J/cm^2. The NT/PPA solutions effectively limit intense optical pulses, with the saturation fluence tunable by varying the nanotube contents.

Introduction

The discovery of carbon nanotubes and the prospect of developing carbon-based nanomaterials excited worldwide interest among researchers.[1] Thanks to the enthusiastic research efforts of scientists, the nanotubes have quickly proven to possess exotic properties such as high mechanical strength and flexibility[2] and diameter- and chirality-dependent electrical conductivity.[3] The intractability of the nanotubes, however, poses an obstacle to the further development in nanotube science and significantly limits the scope of their practical applications. No suitable solvents for the nanotubes have been found, and because of the wet nature of chemical research, this has largely blocked chemists' entry to the area of nanotube research. It is envisioned that solubilization of the nanotubes will not only endow the nanotubes with processibility but also open up new avenues in nanotube research.

The nanotubes are sometimes referred to as "quantum wires",[1] and polyacetylenes are the best-known "synthetic metals".[4] Integration of the nanotubes with soluble polyacetylenes is of interest because the resulting nanocomposites may possess novel electrical, optical, magnetic, and mechanical properties. Moreover, the ability to orient the polyacetylene chains by external forces[4,5] may allow alignment of the nanotubes in the polyacetylene matrix by macroscopic means such as mechanical perturbations. In this work, we chose poly(phenylacetylene) (PPA), a soluble photoconductive polyacetylene,[6] as the model polymer. We describe here a simple method for the preparation of soluble nanotube-containing PPAs (NT/PPAs). We demonstrate that the nanotubes in the NT/PPA solutions can be easily aligned by mechanical shear and that the NT/PPA solutions effectively limit intense 532-nm laser pulses.

Experimental Section

The general information on the experimental details including materials, instrumentation, and reaction and analysis procedures can be found in our previous publications.[7−9]

Polymerization of Phenylacetylene in the Presence of Carbon Nanotubes. In a typical run, into a baked 20-mL Schlenk tube under an atmosphere of dry nitrogen were added 100 mg of well-ground multiwalled nanotubes (purchased from MER, Tucson, AZ, and further ground in a smooth agate mortar in our laboratory), 95 mg of WCl_6, 102 mg of Ph_4Sn, 5 mL of toluene, and 0.55 mL of phenylacetylene (all from Aldrich, Milwaukee, WI). The mixture was stirred at room temperature for 24 h. Toluene (5 mL) was then added to the Schlenk tube, and the diluted reaction mixture was filtered by a cotton filter to remove large insoluble nanotube particles. The soluble filtrate was added dropwise into 250 mL of methanol under stirring to precipitate the polymeric product. After standing overnight, the precipitant was isolated using a Gooch-type crucible filter and dried in a vacuum oven. The product was redissolved in tetrahydrofuran (THF), and the resulting solution was centrifuged at 2000 rpm for 16 min. The homogeneous supernatant was added through a cotton filter into hexane under stirring. The precipitant was collected and then dried under vacuum at 40 °C to a constant weight. The NT/PPA was obtained in an isolated yield of 45.3 wt % (Table 1, no. 1).

Purification of the Insoluble Nanotubes Isolated from the Polymerization Reactions. The large insoluble nanotube particles recovered from the polymerization reactions were repeatedly washed by THF. The solvent was tinged yellowish in the beginning of the washing but became colorless at the end. The insoluble nanotubes isolated from reaction 3 of Table 1 were further soaked in THF for a period of 20 days, but the solvent remained uncolored. The black particles separated from the clean supernatant were washed with fresh THF and then dried in vacuo to a constant weight (108 mg).

Results and Discussion

Preparation and Characterization. During our research program on the development of fullerene-based optical materials,[7,8] we have found that C_{60} can copolymerize with substituted acetylenes such as phenylacetylene and 1-phenyl-1-alkynes.[8] Noting that the nanotubes are conceptually the cylinders of curled graphene sheets capped by the fullerene hemispheres,

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Table 1. Preparation and Solubility of NT/PPAs [Polymerization Reactions Were Carried Out under Nitrogen at Room Temperature in Toluene (5 mL) for 24 h with a Phenylacetylene Concentration of 0.9 M, and the Polymer Products Were Purified by Repeated Precipitation of Their Toluene and THF Solutions into Methanol and Hexane]

no.	nanotube (mg)	catalyst[a]	polymer yield (wt %)	$M_w/10^3$ [b]	PDI[b]	nanotube content[c] (wt %)	solubility[d]			
							THF	toluene	$CHCl_3$	dioxane
1	100	WCl_6-Ph_4Sn	45.3	172	27	6.0	√	√	√	√
2	28	WCl_6-Ph_4Sn	66.8	93	11	1.9	√	√	√	√
3	102	$[Rh(nbd)Cl]_2$	3.4							
4	20	$[Rh(nbd)Cl]_2$	50.2	137	13	2.2	√	√	√	×

[a] $[WCl_6]_0 = [Ph_4Sn]_0 = 43$ mM, $\{[Rh(nbd)Cl]_2\}_0 = 2$ mM (nbd = 2,5-norbornadiene). [b] Estimated by GPC calibrated with 12 monodisperse polystyrene standards (Waters). [c] Estimated by TGA (Perkin-Elmer TGA 7) under nitrogen. [d] Code: √, completely soluble; ×, partially soluble.

we conducted a polymerization of phenylacetylene catalyzed by WCl_6-Ph_4Sn in the presence of the nanotubes. The soluble polymer product isolated from the polymerization reaction was characterized by scanning electron microscopy (SEM), which shows numerous short and somewhat bent tubules with lengths of a few hundred nanometers (Figure 1A). Such tubular images are not observed in the SEM micrograph of the pure PPA obtained from the control experiment, suggesting that the nanotubes are compounded with PPA in situ during the polymerization reaction (Scheme 1). It is not surprising that all of the tubules shown in Figure 1 are short because the long nanotubes have been effectively removed by repeated filtration during the process of polymer purification. The tubules are bent because of the mechanical force exerted by the polymer matrix, indicative of the high flexibility of the nanotubes.[2,10] At high magnification, some tubules are found to be linked up, probably by the PPA chains. The thin string marked by letter "P" in Figure 1B looks like a stretched PPA "rope", with its two ends attaching to two interconnected nanotubes. Closer inspection of the micrograph, especially in those regions marked by the arrows, reveals that the tubules are surrounded by faint veils, intimating that the nanotubes are bundled or wrapped up by the PPA chains. At some spots, tree-like structures are imaged (Figure 1C), in which the "trunks" and "branches" of the isolated and interconnected nanotubes are in all probability sheathed by the "bark" of the PPA chains.

The NT/PPA shows a bimodal gel permeation chromatogram (GPC), with one large peak in the "normal" molecular weight (MW) region and another small peak in the very high MW region (Figure 2). Because the high-MW peak is not observed in the GPC chromatogram of the control PPA, it should be from the nanotubes compounded with PPA. Because of the contribution of the nanotubes, the polystyrene-calibrated weight-average molecular weight (M_w) of the NT/PPA is very high (172 000) and its polydispersity index (PDI) is extremely broad (27; Table 1, no. 1). It is known that the nanotubes are thermally very stable and do not lose any weight below ca. 680 °C even in air.[11] On the other hand, the PPA starts to lose its weight from ca. 200 °C.[12] We thus employed thermogravimetric analysis (TGA) to evaluate the nanotube content of the NT/PPA by heating the nanocomposite to 600 °C under a stream of dry nitrogen. By comparison with the TGA data of the control PPA, it is estimated that the NT/PPA contains 6.0 wt % of the nanotubes.

The parent nanotubes are completely insoluble in THF, even with the aid of prolonged sonication. The NT/PPA, however, readily dissolves in THF, giving macroscopically homogeneous and visually transparent solutions (Figure 3), although its maximum solubility is only about two-thirds of that of the parent PPA in the same solvent. As shown in the lower panel of Figure 3, a PPA solution with a concentration of 4.00 mg/mL is yellow in color, while a NT/PPA solution with a lower concentration (3.18 mg/mL) is orange-colored. The deepening in color is attributable to the dissolved nanotubes, which possess extensively conjugated π electrons. The NT/PPA is also soluble in other common organic solvents including toluene, chloroform, and 1,4-dioxane, as summarized in Table 1.

When the amount of the nanotubes in the mixture of the polymerization reaction decreases from 100 to 28 mg, the yield of the polymer product increases from 45.3% to 66.8% (Table 1, no. 2). In the absence of the nanotubes, the polymer yield is as high as 92.0%. It is thus clear that the presence of the nanotubes in the polymerization mixture decreases the polymer yield. A similar but more pronounced "nanotube effect" is observed when $[Rh(nbd)Cl]_2$ is used as the polymerization catalyst. The polymerization of phenylacetylene in the presence of a large amount (102 mg) of the nanotubes yields little polymer (3.4%; Table 1, no. 3). Decreasing the feed amount of the nanotubes to 20 mg dramatically increases the polymer yield to 50.2%, and the polymerization in the absence of the nanotubes produces PPA in quantitative yield (100%). It is possible that the transition metals and the nanotubes have formed some kinds of complexes of low catalytic activity. The propagation species of the phenylacetylene polymerization, especially when growing in the close vicinity of the tubule shells, may form stable complexes with the nanotubes, thus terminating the polymerization reactions.

From all of the polymerization reactions carried out in the presence of the nanotubes, fair amounts of insoluble nanotube particles were recovered. When the recovered particles were washed by THF, an excellent solvent of PPA, the solvent was tinted, implying that a small amount of PPA had been attached to the nanotubes. Because of the accuracy in weighing and the ease of handling, we chose the particles recovered from the polymerization with the highest nanotube feed ratio (Table 1, no. 3) for detailed investigation. The recovered nanotube particles were washed thoroughly for prolonged time, but the amount of the finally isolated particles (108 mg) was still more than that (102 mg) of the nanotubes initially used in the feed mixture, indicating that the PPA chains had stuck indelibly to the nanotubes.

We thus used transmission electron microscopy (TEM) to "see" how the polymer chains are attached to the nanotubes.[13] As can be clearly seen from Figure 4A, the thinner nanotube is helically wrapped by the PPA coils along the latitudes of tubule shells. Although not so clearly imaged, the tip of the nanotube seems also partially covered by the PPA chains. The thicker

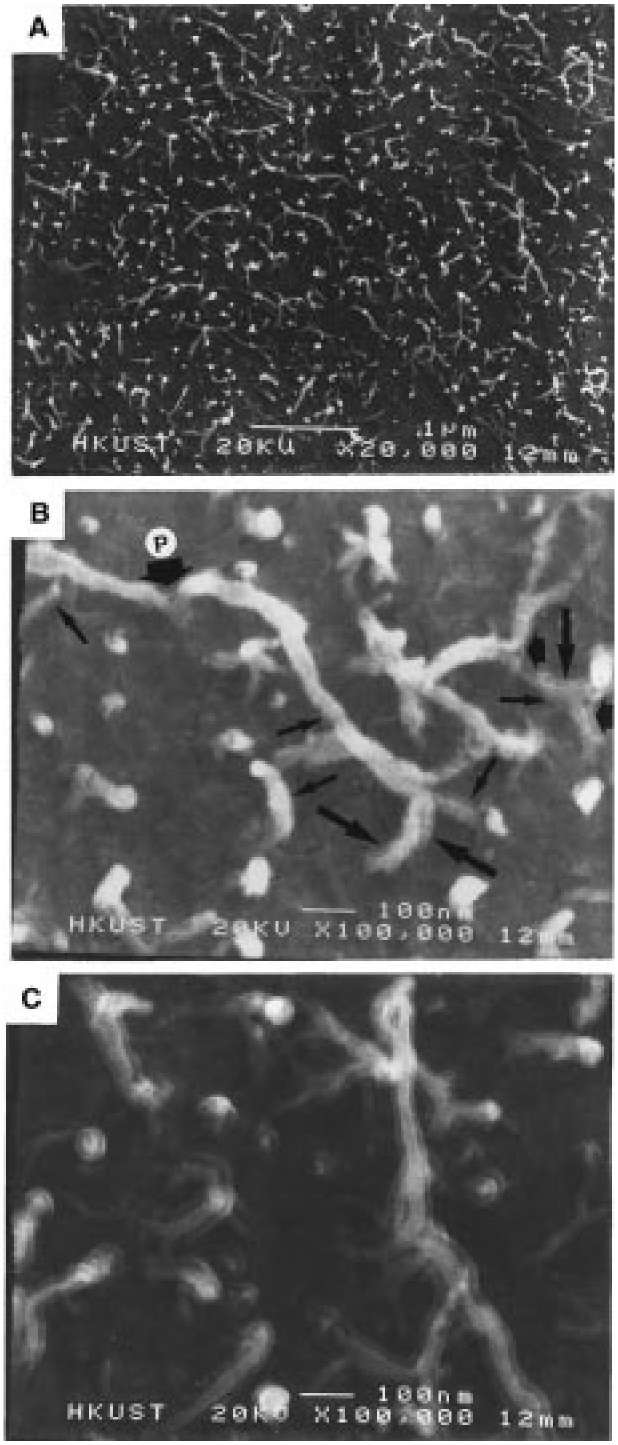
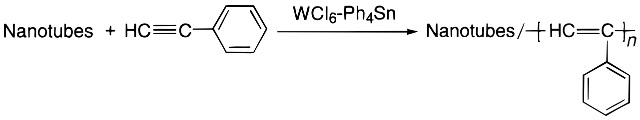


Figure 1. Nanotubes dispersed in a PPA matrix (sample from Table 1, no. 1). Micrographs were taken on a JEOL 6300L ultrahigh-resolution scanning electron microscope operating at an accelerating voltage of 20 kV. Scale bar: (A) 1 μm, (B) 100 nm, (C) 100 nm.

Scheme 1



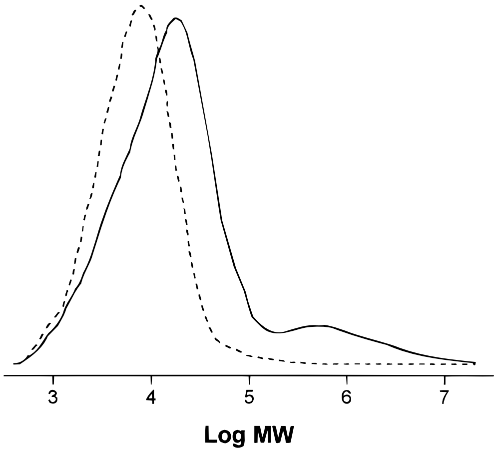


Figure 2. Gel permeation chromatograms of NT/PPA (solid line; sample from Table 1, no. 1) and PPA (dotted line) recorded on a Waters 510 GPC system with a set of Styragel columns (HT3, HT4, and HT6) covering a MW range of 10^2-10^7.

Figure 3. Homogeneous and transparent solutions of NT/PPA (sample from Table 1, no. 1) in THF with concentrations (*c*) of (upper panel from left) 19.07, 10.59, 7.15, 5.45, and 3.18 mg/mL. For comparison, THF solutions of NT/PPA and PPA with similar concentrations are given in the lower panel with *c* (mg/mL; from left) of 5.45 (NT/PPA), 4.00 (PPA), and 3.18 (NT/PPA).

neighboring nanotube looks naked, indicating that not all of the recovered insoluble nanotubes are wrapped by the PPA chains. Similarly, the thinner nanotube in Figure 4B is coiled by the PPA helices. In this case, however, the attachment of the PPA chains to the tip of the nanotube is clearly imaged. Because the prolonged washing by THF should have cleaned away the polymer chains physically stuck to the tube *tip*, it is thus likely that the PPA chains are chemically bound to the fullerene hemisphere, probably by the polymerization of phenylacetylene with the C_{60} moiety.[8] At other spots, some tubules are completely wrapped by the PPA chains, with the helices running perpendicular to the long axes of the nanotubes (Figure 4C).

To further confirm the identity of the TEM images, we carried out powder X-ray diffraction (XRD) analysis

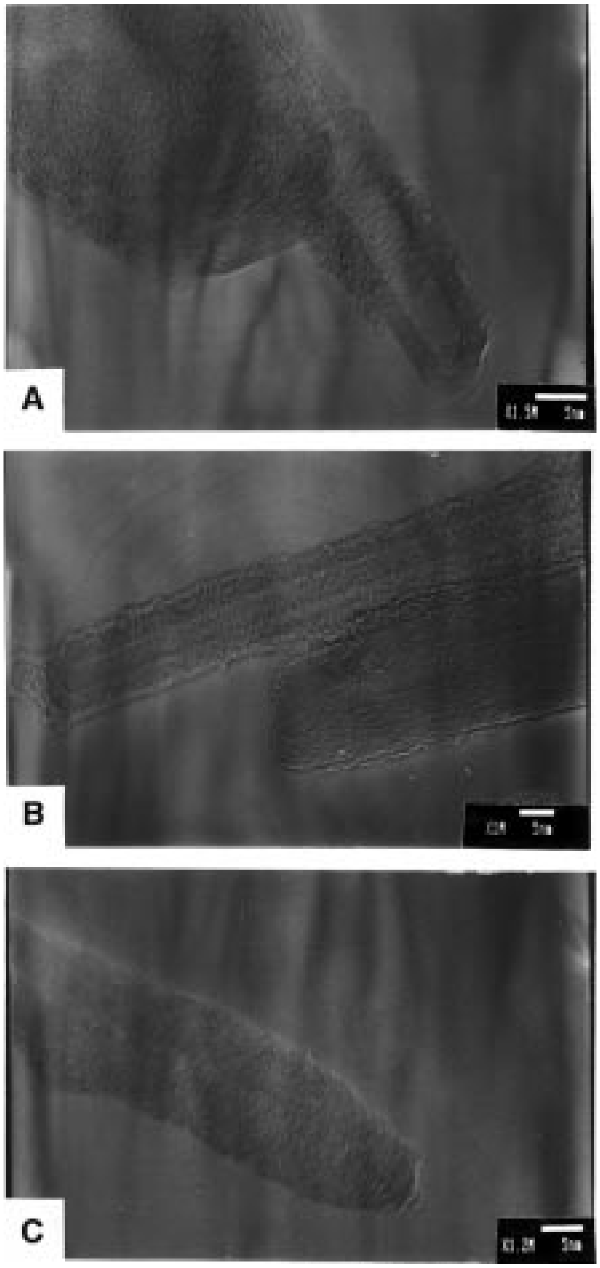


Figure 4. Wrapping of PPA chains around nanotube shells. Micrographs were taken on a JEOL 2010 transmission electron microscope operating at an accelerating voltage of 200 kV (scale bar 5 nm).

of the recovered insoluble nanotube particles. The XRD pattern of the parent nanotubes exhibits an intense (002) Bragg reflection at $2\theta = 26.1°$ (Figure 5A), corresponding to the intershell spacing ($d = 3.4$ Å) of the concentric cylinders of graphitic carbon.[14] The recovered nanotube particles show, in addition to the nanotube reflection, two new weak and broad peaks at low angles, which, by comparison with the diffractogram of the pure PPA shown in Figure 5C, are clearly the reflection peaks of the PPA chains. The XRD data thus support the correlation of the TEM images; that is, the coils wrapping around the tubule shells and attaching to the tubule tips are the amorphous PPA chains.

To check whether the PPA chains can be attached to the nanotubes by simple physical blending, a control experiment was conducted, in which the nanotubes and the preformed (pure) PPA were admixed and stirred in toluene for 24 h. Following the filtration and precipitation procedures detailed in the Experimental Section for the purification of NT/PPAs, all of the nanotubes were recovered and the color of the PPA solution remained unchanged. The microscopic analyses show neither the PPA chains in the recovered nanotubes nor the tubular entity in the recovered PPA. The nanotubes thus may be wrapped by the propagating species of the PPA chains in situ during the polymerization reactions.

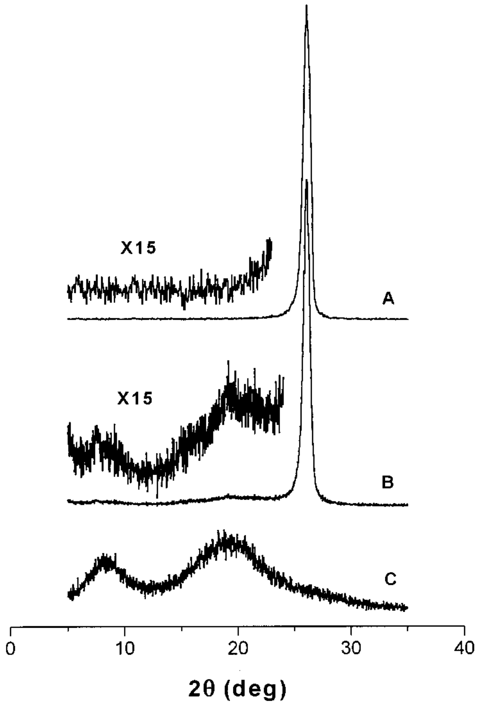


Figure 5. X-ray diffraction patterns of (A) nanotubes, (B) PPA-wrapped nanotubes, and (C) PPA. Diffratograms were recorded on a powder diffractometer (Philips PW1830) with Cu $K\alpha$ radiation.

It is well-known that terminal alkynes ($RC{\equiv}C{-}H$) often form $\equiv C{-}H{\cdots}\pi$ hydrogen bonds with molecules and/or groups that are rich in π electrons.[5,15] Because the nanotubes are full of π electrons, the phenylacetylene monomers are likely to “wet” the surfaces of the tubule shells through the $\equiv C{-}H{\cdots}\pi$ hydrogen bonds, and polymerization of such absorbed monomers would produce PPA chains wrapping up the nanotubes. Polymerizations of internal alkynes without the acidic acetylene hydrogen such as $CH_3C{\equiv}CPh$ fail to incorporate any nanotubes into the resulting polyacetylenes, further suggesting the important role of the $\equiv C{-}H{\cdots}\pi$ hydrogen bonds in the wrapping processes of the nanotubes by the PPA chains. Trans-cisoidal and trans-transoidal PPAs can form helices with 3−12 monomer units per coil,[16] polyacetylenes with chiral substituents possess helical conformation,[17] and complexation of PPA derivatives with chiral molecules can induce helix formation.[18] The nanotubes are cylinders of rolled-up graphene sheets with various chiralities,[3] and the propagating species of the polymer chains may experience steric and electronic interaction with the chiral tubules, thus generating the PPA helices spiraling around the nanotubes. When the short nanotubes are thickly wrapped by the PPA chains, the solvation of the polymer molecules may drag the tubules into the solvent, thus making the nanotubes “soluble”. On the other hand, the long tubules not wrapped or thinly wrapped by the PPA chains would remain insoluble in the organic solvents.

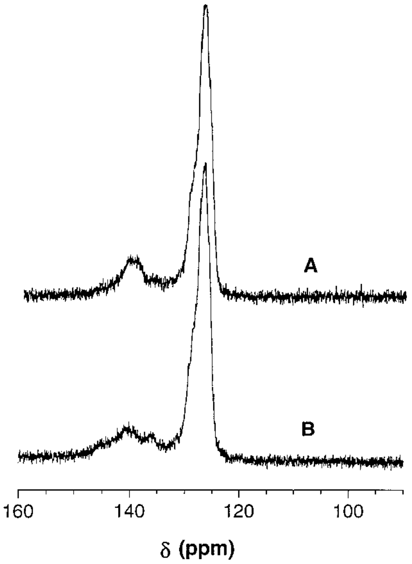


Figure 6. ^{13}C NMR spectra of (A) NT/PPA (sample from Table 1, no. 1) and (B) PPA recorded on a Bruker ARX300 NMR spectrometer using chloroform-*d* as the solvent and tetramethylsilane as the internal reference.

The solubility of the short nanotubes wrapped by the PPA chains enables structural characterization by wet spectroscopy and investigation of their solution properties. The ^{13}C nuclear magnetic resonance (NMR) spectrum of the chloroform solution of the NT/PPA is almost identical to that of the parent PPA, except for that the peak of the NT/PPA at ca. δ 140 becomes more intense (Figure 6). The solid-state NMR spectrum of the parent nanotubes shows a broad peak centered at δ 130, and the acid-functionalized nanotubes absorb at ca. δ 145.[19] The increase in the peak intensity at ca. δ 140 thus may be attributed to the absorption of the nanotubes wrapped by the PPA chains.

Shear-Induced Alignment. We have recently found that liquid-crystalline polyacetylenes can be oriented by external forces,[5] and it is of interest to know whether the nanotubes in the NT/PPA solutions can be aligned by macroscopic processing means[20] such as mechanical shear. We thus applied a shear force to a thin layer of a concentrated THF solution of NT/PPA sandwiched between two pieces of glass slides. After a while, the initially uniform background of the homogeneous solution was found to be embellished with numerous parallel spots aligning along the shear direction (Figure 7A). Such texture is not observable in the control experiment using a THF solution of pure PPA, implying that the tiny spots are the aggregates of the nanotubes in the NT/PPA. As the solvent of the sheared NT/PPA solution in the glass cell slowly evaporates, the nanotubes oriented by the shear force would gradually aggregate. The surrounding PPA chains, however, would prevent the aggregates from growing bigger, thus resulting in the formation of tiny micelle-like spots. During the emerging stage of the aggregates from the homogeneous solution, necklace-like texture forms, in which the tiny black "pearls" of the nanotube clusters are strung together, probably by the oriented PPA chains (Figure 7B). This suggests that the alignment of the nanotube aggregates along the shear direction is assisted, at least in part, by the shear-induced orientation of the stiff polyacetylene chains.[5]

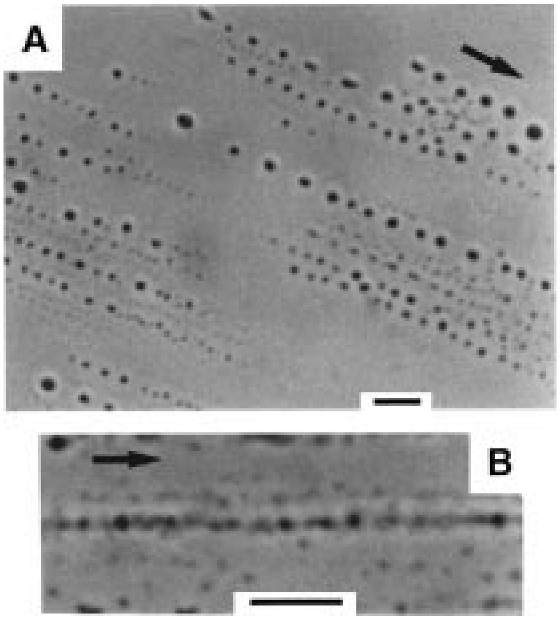


Figure 7. Alignment of nanotubes induced by mechanical shear (directions of the shear force being indicated by the arrows). Photomicrographs were taken on an Olympus BX60 optical microscope (scale bar 10 μm).

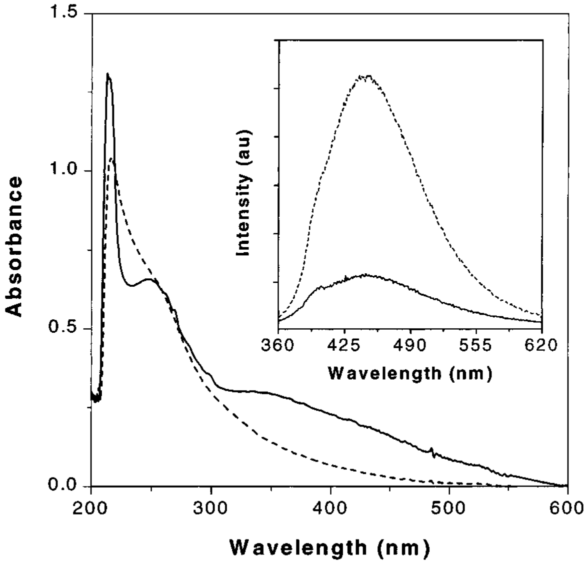


Figure 8. Electronic absorption and fluorescence emission (inset) spectra of THF solutions of NT/PPA (solid line; sample from Table 1, no. 1) and PPA (dotted line) recorded on a Milton Roy 3000 array spectrophotometer and a SLM Aminco JD-490 spectrofluorometer (excited at 350 nm). Concentration (mg/mL): 0.01 (absorption) and 0.10 (emission).

Electronic and Optical Properties. While the parent PPA weakly absorbs in the visible spectral region, the absorption of the NT/PPA well extends to ca. 600 nm (Figure 8), in agreement with its deeper color. When the PPA is excited at 350 nm, it emits fluorescence with a peak maximum at ca. 450 nm.[21] The fluorescence spectral profile of the NT/PPA is similar to that of the PPA, but with much lower quantum yield. Quite recently, Curran et al. have observed similar phenomenon in their nanotube/poly(*m*-phenylenevinylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) (NT/PPV) nanocomposite system.[22] The fluorescence of the NT/PPV was much weaker than that of the parent polymer, "caused", as the authors proposed, "by absorption, quenching, and scattering from the nanotubes present".[22] Similar mechanisms may be applicable to the decrease in the fluorescence intensity in our NT/PPA system.

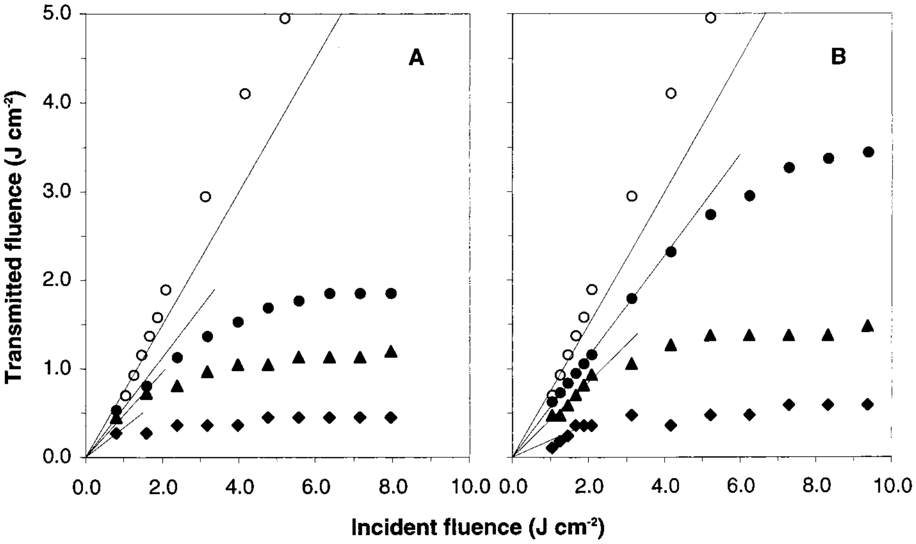


Figure 9. Optical-limiting responses of THF solutions of the NT/PPAs prepared by (A) WCl_6−Ph_4Sn (sample from Table 1, no. 1) and (B) $[Rh(nbd)Cl]_2$ (Table 1, no. 4). Concentration (*c*; mg/mL)/linear transmittance (*T*; %): (A) 0.4/57 (●), 0.5/48 (▲), 0.6/34 (◆); (B) 1.0/57 (●), 2.0/42 (▲), 3.0/19 (◆). Optical responses of a THF solution of PPA are shown for comparison [*c* (mg/mL)/*T* (%): 4.0/75 (○)]. The 8-ns pulses of 532-nm light were generated from a Quanta Ray GCR 3 frequency-doubled Q-switched Nd:YAG laser (ref 25).

Photoinduced charge transfer process may be involved in the fluorescence quenching, in which the electrons in the excited PPA chains are effectively transferred to the nearby shells of the nanotubes.

Fullerenes[23] and polyacene-based oligomers with graphite-like structures[24] are known to limit intense optical pulses by reverse saturable absorption mechanisms. The fullerene tips and the graphene sheets of the short carbon nanotubes may undergo nonlinear optical (NLO) absorption processes. Moreover, the cylindrical bodies of the nanotubes, albeit with a high length/diameter ratio, may function as light scattering centers. Both the NLO absorption and scattering would make the nanotubes promising candidates for optical limiters. We thus investigated optical responses of the NT/PPA solutions to laser pulses, employing a similar experimental setup used in our previous studies on the optical limiting properties of fullerene materials.[25]

When a THF solution of the parent PPA is shot by the 8-ns pulses of 532-nm laser light, the transmitted fluence linearly increases in the region of low incident fluence (linear transmittance 75%; Figure 9). The output starts and continues to deviate from the linear-transmission line from the input of ca. 1.7 J/cm^2, implying that the intense illumination gradually bleaches the PPA to transparency, probably by the laser-induced photolysis of the polyacetylene chains. The NT/PPA solutions, however, respond to the optical pulses in a strikingly different way. The linear transmittance of a dilute NT/PPA solution (0.4 mg/mL) is only 57% (Figure 9A), although its concentration is only one-tenth of that (4 mg/mL) of the parent PPA, probably because of the optical losses caused by the nanotube absorption and scattering. As the incident fluence increases, the NT/PPA solution becomes opaque, instead of transparent, with its transmitted fluence eventually leveling off or saturating at 1.85 J/cm^2 (saturation fluence). Clearly, the nanotubes have endowed the NT/PPA with optical limiting power. While the PPA is liable to photolysis, the NT/PPA is stable at very high incident fluence. The energy-sinking and radical-trapping functions of aromatic rings often protect polymer molecules from photodegradation,[26] and the extensively conjugated graphitic aromatic system of the nanotubes may have enhanced the resistance of the PPA chains against the harsh laser irradiation.[22] As the concentration of the NT/PPA solution increases, its saturation fluence decreases. Increasing the concentration to 0.6 mg/mL readily decreases the saturation fluence to as low as 0.45 J/cm^2.

Similarly, the NT/PPA prepared by the $[Rh(nbd)Cl]_2$ catalyst also limits the intense optical pulses (Figure 9B). A THF solution of the NT/PPA with a concentration of 1.0 mg/mL exhibits a saturation fluence of 3.44 mg/cm^2, which is much higher than those of the THF solutions of the NT/PPA prepared by WCl_6−Ph_4Sn with lower concentrations (cf. Figure 9A). The major difference between the two NT/PPAs is their nanotube contents. The NT/PPA with lower nanotube content shows higher saturation fluence, further confirming that the nanotubes are responsible for the optical limiting in the NT/PPA solutions. In this case again, increasing the concentration decreases the saturation fluence. A low saturation fluence of 0.58 J/cm^2 is achieved when the concentration is increased to 3.0 mg/mL.

Concluding Remarks

In summary, in this study, short carbon nanotubes have been solubilized by wrapping them with soluble PPA chains. Solubility is the primary requirement for studying wet chemistry, and this work paves the way for new developments in nanotube research. The PPA is stable at room temperature but gradually degrades at high temperature. Heating a NT/PPA solution under controlled conditions will partially unwrap the nanotubes and allow the naked part of the nanotubes to react with chemical reagents in solution, thus making it possible to study the chemistry of the nanotubes in homogeneous media.

The helical wrapping of the PPA chains along the latitudes of the nanotubes is of technological interest. One intriguing possibility is the creation of molecular-level electromagnetic devices such as “nanomotors” by magnetizing the nanotubes by the electrical field generated by the photoconductive PPA coils. Ready alignment of the nanotubes has been demonstrated, and this provides a versatile means for macroscopically manipulating the nanotubes. Moreover, the NT/PPA solutions have been found to effectively limit the intense 532-nm optical pulses. Because the control of light intensity is of fundamental importance in optics engineering, the NT/PPAs examined in this work may find an array of potential applications in optics-related, especially laser-based, technologies.

The nanotubes dramatically stabilize the PPA chains against the harsh laser irradiation. Such a stabilization effect is of academic interest and practical importance, which may not only trigger basic research on the understanding of electronic properties of the nanotubes in solutions by wet spectroscopy but also help find technological applications for the nanotubes in electronic and optical systems. For example, short lifetime has been a thorny problem in the optical-limiting and light-emitting devices consisting of organic (polymer) materials, and incorporation of the nanotubes into such devices may help develop organic photonic systems with long life spans and thus commercial value.

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