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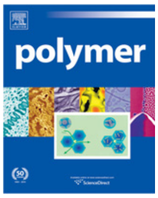

Tailored dispersion of carbon nanotubes in water with pH-responsive polymers

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ABSTRACT

In an effort to control the level of carbon nanotube exfoliation in water, pH-responsive polymers (i.e., weak polyelectrolytes) have been used as stabilizers in water. This noncovalent functionalization of single-walled carbon nanotubes (SWNTs) results in suspensions whose dispersion state can be altered by simply changing pH. In this study poly(acrylic acid), poly(methacrylic acid), poly(allylamine) and polyethyleneimine were used to stabilize aqueous SWNT suspensions. The results indicate that SWNTs stabilized with these polymers show a pH tailorable exfoliation and bundling in water, as evidenced by cryo-TEM images and shifts in suspension viscosity. Composite films prepared by drying these aqueous suspensions suggest that nanotube microstructure in the liquid state is largely preserved in the solid composites, with more bundled/networked structures showing higher electrical conductivity. A stabilization mechanism based upon the results obtained is proposed to explain the exfoliation and aggregation behavior of SWNTs. This method of controlling the microstructure of SWNTs in liquid state with pH could have a significant impact on the ability to tailor the microstructure and properties of composites.

1. Introduction

Single-wall carbon nanotubes (SWNTs) are one-dimensional forms of carbon, which can be visualized as rolled hexagonal carbon networks that are capped by pentagonal carbon rings. Owing to their high aspect ratio (often >1000) and conjugated chemical structure, nanotubes possess unique mechanical [1], thermal [2] and electronic properties [3] that provide a wide range of applications for this material [4]. Nanotube-filled polymer composites, for example, offer tremendous potential for mechanical and transport property improvements, even at very small concentrations of nanotubes [5]. Liquid suspensions of carbon nanotubes are being studied for applications such as biocompatibility [6], drug delivery [7], optical limiting [8] and optical sensors [9]. Despite all of their promise, very limited progress has been made towards realizing the full potential of nanotubes. One key reason for this lack of success is the difficulty associated with the dispersion of otherwise bundled tubes. As produced SWNTs exist in a highly aggregated state because of strong van der Waals attractions that severely limit their dispersion in solvents, especially in water [10,11]. It is important to be able to control the state of nanotube dispersion in order to realize a desired set of properties meant to satisfy a given application.

In recent years, a variety of chemical [12–16] and physical [17–21] stabilization mechanisms have been studied to disperse SWNTs in solvents. For efficient dispersion/solubilization of SWNTs, the above mentioned methods are often used in conjunction with mixing (e.g., ultra-sonication, stirring, etc.). Chemical functionalization or shortened nanotubes is often the result of intense mixing due to the presence of local strain in carbon nanotubes arising from pyramidalization and misalignment of the π-orbitals of the sp^2-hybridized carbon atoms [22]. The presence of local strain in SWNTs makes them more reactive than a flat graphene sheet, which makes it relatively easy for the chemical moieties to attach to the surface [23]. A significant drawback of chemical functionalization is the disruption of the extended π conjugation in nanotubes, which results in inferior electrical properties because each functionalization site scatters electrons [24]. On the other hand, noncovalent stabilization involves physical adsorption of polymers or surfactants on the surface of carbon nanotubes [11]. This method of functionalization does not involve breaking bonds in the nanotube sidewalls and thereby better preserves electrical properties [25,26]. When these stabilizing molecules are stimuli-responsive, there is an opportunity to tailor nanotube dispersion upon exposure to a given stimulus (e.g., pH).

Stimuli-responsive polymers exhibit conformational changes with an applied external stimulus such as pH, temperature or light [27,28]. Weak polyelectrolytes are one class of stimuli-responsive polymers that contain a large number of ionizable groups. These water-soluble polymers typically have pK_a values between 3 and

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10, which make them pH-responsive [29]. These polymers undergo reversible changes in conformation as a function of pH due to changes in charge density of ionizable groups. For example, poly (acrylic acid) (PAA) reversibly transitions between tightly coiled and highly extended conformations(see Fig. 1) [30–32]. Greater chain extension occurs in PAA at high pH due to self-repulsion of the negatively charged carboxylates on its backbone. Weak polyelectrolytes can be positively charged (polycations) or negatively charged (polyanions) or, as in the case of proteins, have groups which can be either positively or negatively charged (amphoteric), depending on pH. The use of weak polyelectrolytes as stabilizers not only results in solubilization of SWNTs in water, but also provides a means for controlling their dispersion state as a function of pH [30,31,33]. In many potential applications, such as SWNT based switching devices, sensors, and drug delivery systems, it may be necessary to control the dispersion or aggregation of SWNTs in solvent with external stimuli [34]. In spite of their immense potential, only a few studies have reported the use of pH-responsive polymers to tailor the dispersion of SWNTs in water [30,31,34,35]. Furthermore, the underlying mechanism of SWNT dispersion and stabilization using pH-responsive polymers seems poorly understood and would benefit from further examination.

In the present study, four different pH-responsive polymers, PAA, poly(methacrylic acid) (PMAA), poly(allylamine) (PAAm), and branched polyethyleneimine (BPEI) were used to stabilize aqueous SWNT suspensions. These polymers exhibit a transition between completely neutral and fully charged states with changing pH. PAA and PMAA are weak polyanions, exhibiting negative and neutral charge at high and low pH [31,36,37], respectively. PAAm and BPEI are weak polycations, exhibiting neutral and positive charge at high and low pH [38], respectively. The focus of this work is to evaluate the effectiveness of these polymers in dispersing SWNTs in water

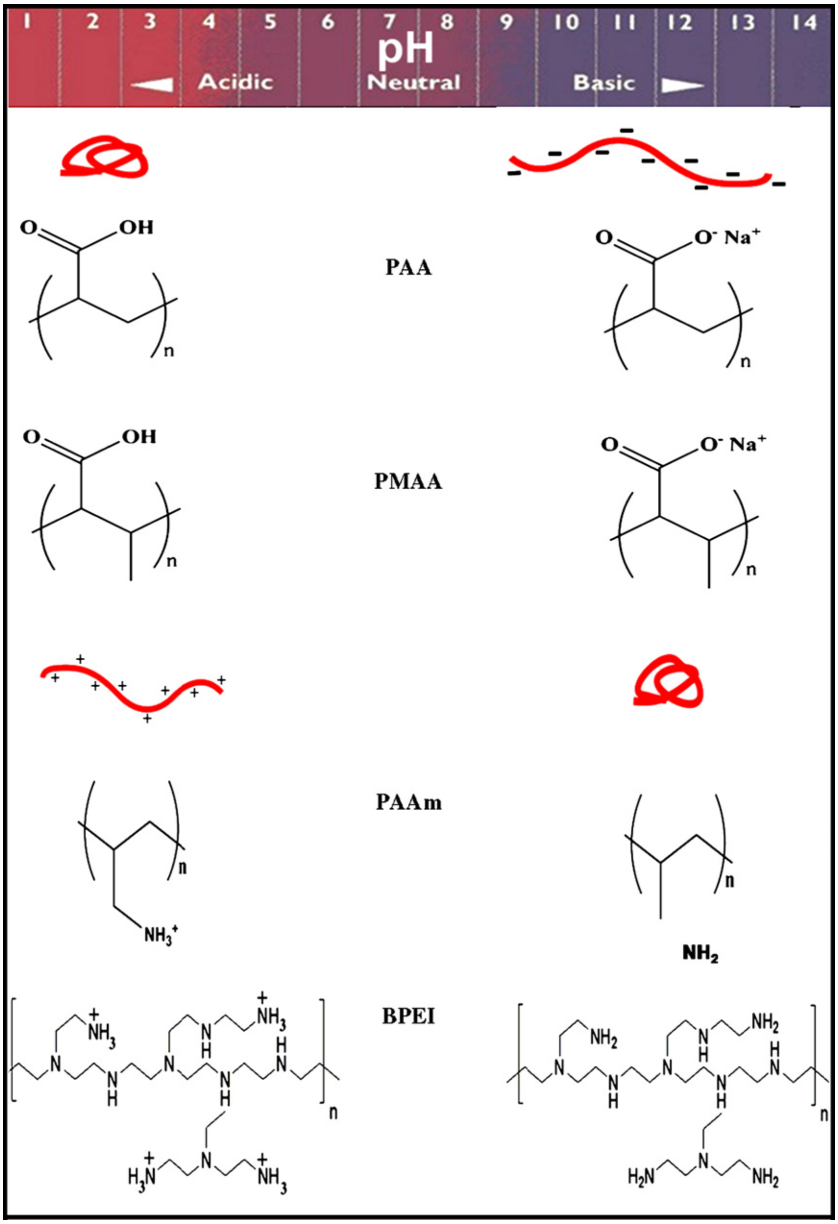


Fig. 1. Effect of pH on the chain conformations of PAA, PMAA, PAAm and BPEI. PAA and PMAA have neutral charge at low pH and become negatively charged at high pH. PAAm and BPEI are neutral at high pH and attain positive charge at low pH.

and to understand the pH-responsive behavior of the stabilized suspensions. Various techniques (rheology, conductivity, microscopy and zeta potential) were used to characterize these stabilized SWNT suspensions stabilized using pH-responsive polymers. The results indicate that pH-responsive polymers are useful for controlling the microstructure of SWNTs in water as a function of pH. Furthermore, polyanions were found to stabilize SWNTs more effectively relative to polycations. Based on the results obtained, a stabilizing mechanism is proposed to explain the pH-responsive dispersion and aggregation of SWNTs in aqueous suspensions that are stabilized using weak polyelectrolytes. This work expands the scope of previous work [30,31] and provides fresh insights on the dispersion and stabilization of SWNTs in water using weak polyelectrolytes. Additionally, this pH tailorability of SWNT dispersion is expected to impact the microstructure and final properties of solution-processed polymer composites.

2. Experimental section

2.1. Materials and methods

Raw single-walled carbon nanotubes (SWNTs) [batch number R0487] were purchased from Carbon Nanotechnologies (Houston, TX) containing 27 wt% impurity (mostly Fe-based catalyst). These nanotubes were used without further purification. PAA ($M_w = 100{,}000$ g/mol) and BPEI ($M_w = 25{,}000$ g/mol) were purchased from Aldrich (Milwaukee, WI), while PAAm ($M_w = 15{,}000$ g/mol) and PMAA ($M_w = 100{,}000$ g/mol) were purchased from PolyScience Inc (Warrington, PA). Aqueous suspensions were prepared by mixing dry SWNTs in 1 wt% aqueous solutions of polymers at their natural (unaltered) pH, followed by sonication for 10 min at 50 W using a VirTis Virsonic 100 ultrasonic cell disrupter (SP industries, Warminster, PA). pH adjustments were made using 1 M NaOH and HCl purchased from Aldrich. Suspensions were sonicated for 5 min at 50 W after pH adjustment. Composites used for electrical conductivity measurements were made by drying 5 ml of suspension on a quartz slide at room temperature (20 °C) for 24 h followed by storing the samples in a dry box for a week before measurements. Dried films were on the order of 0.5 mm thick.

2.2. Characterization

To investigate the relative stability of suspensions, centrifugation was performed at 4500 rpm for 15 min with an accuSpin 400 (Fisher Scientific, Pittsburgh PA). Cryo-TEM images were taken with an FEI Tecnai G2 F20 (Hillsboro, OR) operated at 200 kV and equipped with cryogenic accessories. The samples were frozen in liquid ethane using an FEI Vitrobot apparatus. Images were recorded with a Gatan Tridiem GIF-CCD camera attached to the microscope. UV–vis measurements were made with a USB2000 UV–vis spectrometer (Ocean Optics, Dunedin, FL) using a quartz cuvette. Suspensions that originally contained 1 wt% of polymer and 0.11 wt% SWNT were diluted 10 times for UV–vis measurements. Viscosity of the suspensions as function of shear rate was measured using an AR-G2 rheometer (TA Instruments, Newcastle, DE) equipped with a 40 mm parallel plate geometry. A gap of 1000 μm was maintained for the measurements shown here. Sheet resistance of the composites was measured using a custom-built 4-point probe apparatus. The details of this system and measurement technique have been published elsewhere [39]. The data presented in Fig. 7 are the average values of 16 measurements per sample. Volume conductivity was calculated by taking the inverse of the product of the sheet resistance and composite thickness. To determine suspension stability, zeta potential measurements were made with a Zeta Phase Angle Light Scattering (ZETA PALS) system (Brookhaven Instruments Corporation, Holtsville, NY) using a quartz cuvette. The test chamber was maintained at 25 °C and zeta potentials were determined following the standard operating procedure of the instrument. Scanning electron microscopy was performed with an FEI Quanta 600 FE-SEM on the surface of composites coated with a 5 nm layer of Pt.

3. Results and discussion

Fig. 1 shows a schematic of conformational changes as a function of pH for the polymers studied here. All of these polymers exhibit a transition between completely neutral and fully charged states as pH increases or decreases. In their fully ionized state these polymers exist in an "*extended*" (i.e., looser coil) form and transition to a more coiled (i.e., globule like) conformation as the chain becomes neutralized. It should be noted here that the weak polycations (PAAm and BPEI) and weak polyanions (PAA and PMAA) used in this study achieve neutrality on opposite ends of the pH spectrum. Higher charge density causes the polymer chain to repel itself and leads to a more extended conformation. PAA and PMAA are protonated (neutral) weak polyacids at low pH and exhibit significant intramolecular hydrogen bonding resulting in a globular conformation. At high pH, these polyacids are deprotonated, leading to buildup of negative charge along the polymer backbone that causes extension of the polymer chain through self-repulsion. In contrast, PAAm and BPEI are weak polybases that exhibit globular conformation at high pH and assume an extended conformation with decreasing pH due to ionization. It is this combination of changes in polymer chemistry and conformation that alters their interaction with carbon nanotubes and produces macroscopic changes in suspension properties, as described below.

It was previously shown that suspensions containing exfoliated SWNTs have higher UV absorbance compared to the suspensions containing bundles [40]. The carrier dynamics in SWNT bundles are dominated by tunnel coupling between semi-conducting and metallic SWNTs, which results in reduced interaction with light. As a result, only individual SWNTs can provide a UV–vis signature that suggests an increase in absorbance corresponds to an increase in exfoliation of the SWNT bundles. UV–vis spectroscopy was performed on weak polyelectrolyte suspensions containing SWNTs and the results are shown in Fig. 2. It can be seen that the UV absorption is greater for PAA-stabilized SWNT suspensions at pH 7 as compared to those stabilized at pH 5 and pH 9. This is attributed to the presence of more exfoliated SWNTs at pH 7, than at pH 5 or pH 9 in PAA-stabilized suspensions. A similar observation was made for PAA-stabilized multi-walled carbon nanotubes, where suspensions at pH 5 show better dispersion than those at lower or higher pH [35]. The SWNT suspensions stabilized with PMAA at pH 5 have more absorbance than those at pH 7 and pH 9 suggesting the presence of more exfoliated SWNTs at pH 5. Furthermore, PAAm-stabilized SWNTs suspension has higher absorbance at pH 11 than those at pH 3 or pH 5, suggesting better SWNT exfoliation at high pH. BPEI-stabilized suspensions show only a small increase in absorbance as a function of pH that may be due to the branched structure of BPEI causing weaker interaction with the nanotubes. It was previously shown that dispersion of SWNTs by amines is sensitive to steric hindrance around the nitrogen atom [41]. It should be noted that pH-dependent differences in UV–vis absorption are more prominent for polyanion-stabilized SWNTs as compared to polycations. Furthermore, it was observed that polyanion-based suspensions were stable for a longer period of time relative to polycation-based. Better stabilization of SWNTs with polyanions is presumably because of the Lewis base character

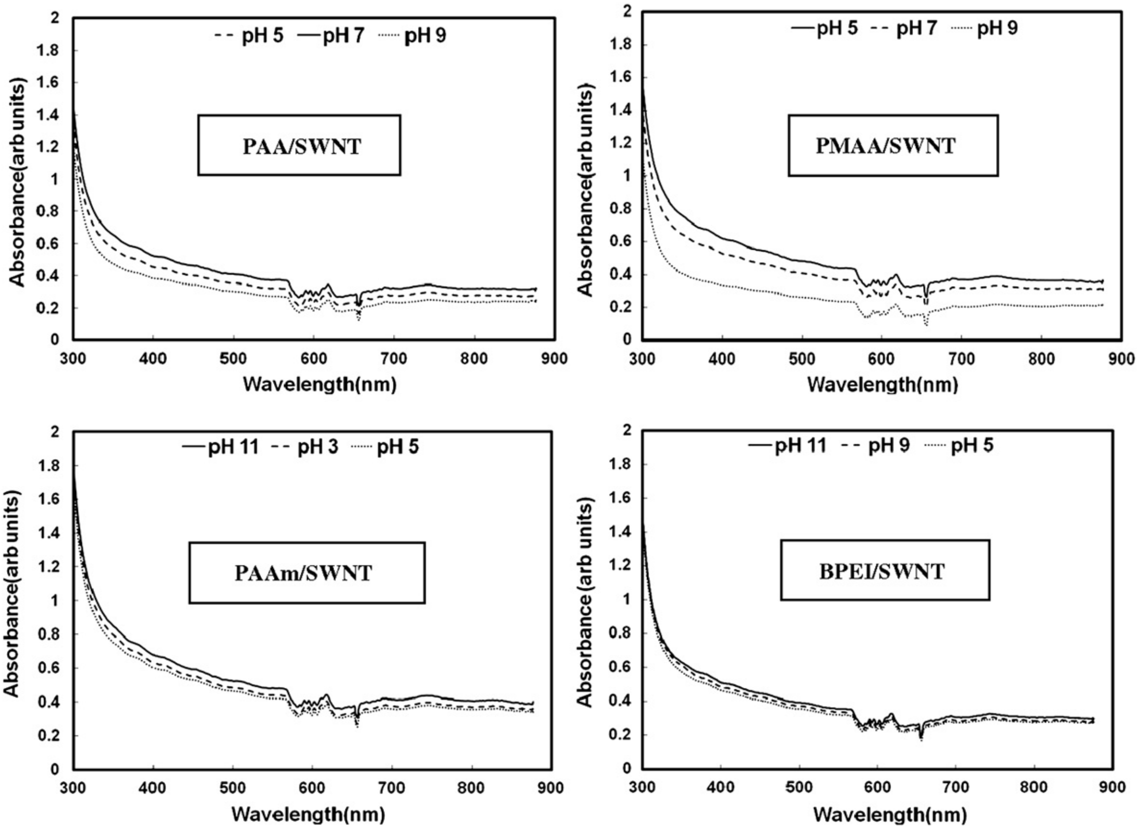


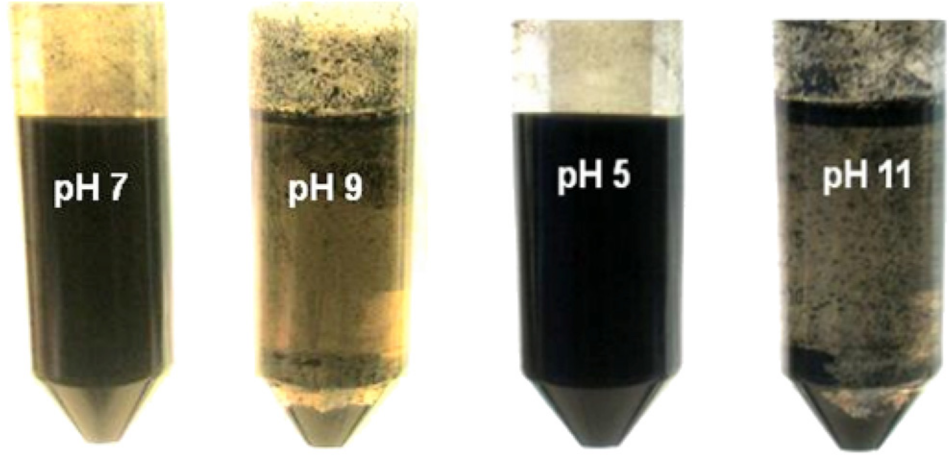
Fig. 2. UV–vis spectra of aqueous suspensions containing 0.01 wt% pH-responsive polymer and 0.0011 wt% single-walled carbon nanotubes at various pH levels.

of the graphene sidewalls of SWNTs, which results in stronger adsorption of polyacids [42].

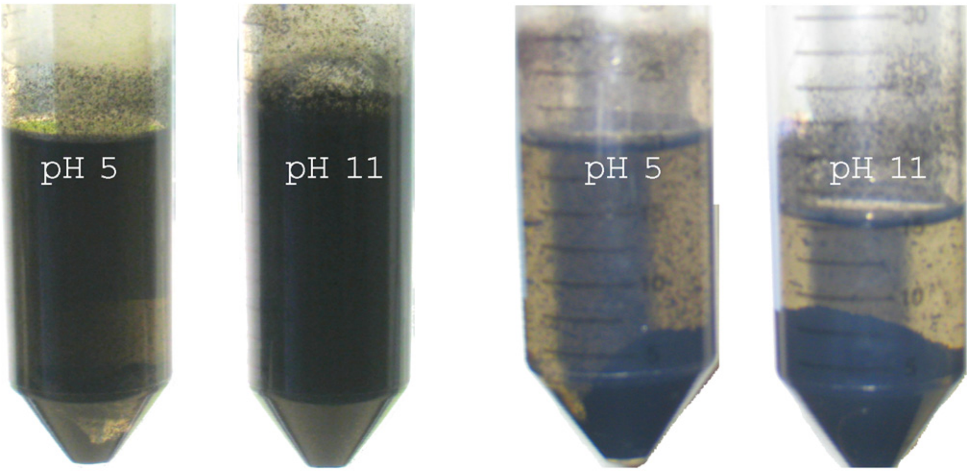
Suspensions at pH levels corresponding to maximum and minimum UV–vis absorption were chosen for further characterization. Fig. 3 shows the relative stability of SWNT-stabilized suspensions at different pH. The suspensions were sonicated for 10 min at 50 W prior to centrifugation at 4500 rpm for 15 min. As shown in Fig. 3, PAA-stabilized suspensions at pH 7 are relatively homogeneous after centrifugation, but those at pH 9 show significant sedimentation. It should be noted here that PAA/SWNT suspensions at pH < 7 were slightly less stable than those at pH 7, although they are relatively similar compared to the pH 9 suspensions. The PMAA-stabilized suspensions show similar pH-dependent stability, with suspensions at pH 5 being stable after centrifugation, while those at pH 9 show significant sedimentation. As expected, PAAm-stabilized suspensions show the opposite trend. PAAm-based suspensions are stable at pH 11, while those at pH 5 show significant sedimentation. BPEI-stabilized suspensions show poor stabilization at both high and low pH. As already mentioned, this may be due to the branched structure of BPEI that sterically diminishes interaction.

In an effort to visualize the SWNT nanostructure in water, cryo-TEM was done with SWNT/PAA and SWNT/PAAm suspensions. Fig. 4 shows these images, where it is obvious that PAA-stabilized SWNTs exist in a relatively exfoliated state at pH 7 and are more bundled at pH 9. The images of PAAm-stabilized SWNT suspensions show more exfoliation at pH 11(Fig. 4(c)) than at pH 5 (Fig. 4(d)). Significant exfoliation of nanotubes is possible when sufficient inter-tube repulsion is introduced by the dispersant. The repulsion can be electrostatic, steric or a combination of both (i.e., electrosteric) based on the charged state and conformation of the adsorbed dispersant [43]. Since the polyelectrolytes used in this study are weak polyacids and polybases, the electrostatic stabilization mechanism alone may be not sufficient for stable dispersion of SWNTs. The observation of aggregated SWNTs at the pH corresponding to the charged state of PAA and PAAm strengthens this claim. Exfoliated nanotubes observed at conditions corresponding to more globular polymer conformation suggests the presence of a thicker steric layer on the SWNT surface. Both PAA and PAAm have globule like conformation at low and high pH, respectively, that can lead to thicker steric layer coverage on the nanotubes. Additionally, these polymers undergo pH-dependent ionization that leads to a charge buildup along the polymer backbone. The presence of a steric layer of partially ionized polymers on SWNTs counteracts the inter-tube van der Waals force of attraction through what is believed to be an electrosteric stabilization mechanism. The cryo-TEM micrographs of PMAA-stabilized suspensions (not shown here) also show exfoliated and aggregated SWNTs as a function of pH. The observation of exfoliated and aggregated SWNTs, depending on the type of stabilizing polymer used, as a function of pH (in the cryo-TEM micrographs) provides direct evidence of pH-responsive SWNT stabilization in water.

Suspensions with well-dispersed SWNTs are known to have lower viscosities as compared to those that have agglomerated or bundled tubes, due to lack of entanglements [30]. Furthermore, it was shown that concentrated solutions of nanotubes show *shear-thinning* behavior because of the high degree of physical entanglements that are akin to polymeric solutions [44]. The observation of shear-thinning behavior in SWNT suspensions stabilized with pH-responsive polymers should therefore suggest the presence of highly networked SWNT structure. At high shear rates these networks are broken, which results in lower suspension viscosity.



PAA / SWNT **PMAA / SWNT**



PAAm / SWNT **BPEI / SWNT**

Fig. 3. Images of aqueous nanotube suspensions after centrifugation at different pH. All suspensions contained 0.11 wt% of SWNT in 1 wt% of the aqueous polymer solution.

On the other hand, the absence of a networked SWNT structure, found in suspensions containing highly exfoliated SWNTs, should lead to a more shear rate independent behavior (i.e., Newtonian). In an effort to investigate this pH-dependent behavior, viscosity measurements were made on aqueous suspensions containing 0.11 wt% SWNTs and 1 wt% of the stabilizing polymer as shown in Fig. 5. Both PAA and PMAA-stabilized SWNT suspensions show *shear-thinning* behavior at pH 9, further confirming the presence of a networked structure. Newtonian behavior arising due to the presence of exfoliated nanotubes is observed at low pH (i.e., pH 7 for PAA and pH 5 for PMAA). PAAm and BPEI-stabilized SWNT suspensions show strong *shear-thinning* behavior at pH 5 and pH 3, respectively, also suggesting the presence of networked SWNTs. At high pH, the PAAm-based suspension still shows *shear-thinning* behavior, although it is closer to Newtonian than low pH. BPEI-based suspensions actually get slightly more shear-thinning at high pH. This lack of transition to fully Newtonian behavior suggests weaker polymer–nanotube interaction for weak polycations, which may be expected due to both entities having basic chemistry. It should be noted here that aggregated and exfoliated microstructure of SWNTs was observed in cryo-TEM images (see Fig. 4) for suspensions showing shear-thinning and Newtonian behavior, respectively. Therefore, it is reasonable to suggest that SWNTs stabilized with pH-responsive polymers exhibit pH-dependent dispersion in aqueous suspensions.

Zeta potential is another property used to characterize the stability of colloidal suspensions. Suspensions with large zeta potential values ($>+25$ mV or <-25 mV) signify good stability [45]. Furthermore, the sign of the potential may indicate the nature of the stabilizing species. Table 1 shows the zeta potential results for the SWNT suspensions studied here. As expected, suspensions stabilized using PAA and PMAA have high negative zeta potential, whereas those stabilized using PAAm and BPEI show positive zeta potential values. It should be noted that zeta potential measurements were made only on the suspensions that contained highly exfoliated SWNTs, as the suspensions containing more bundled and aggregated SWNTs were too irreproducible. One of the most interesting observations is the stabilizing polymer dependent polarity of the zeta potential values. The use of negatively charged polymers (PAA and PMAA) and positively charged polymers (PAAm and BPEI) results in negative and positive zeta potentials, respectively. It is known that the polarity of the zeta potential is

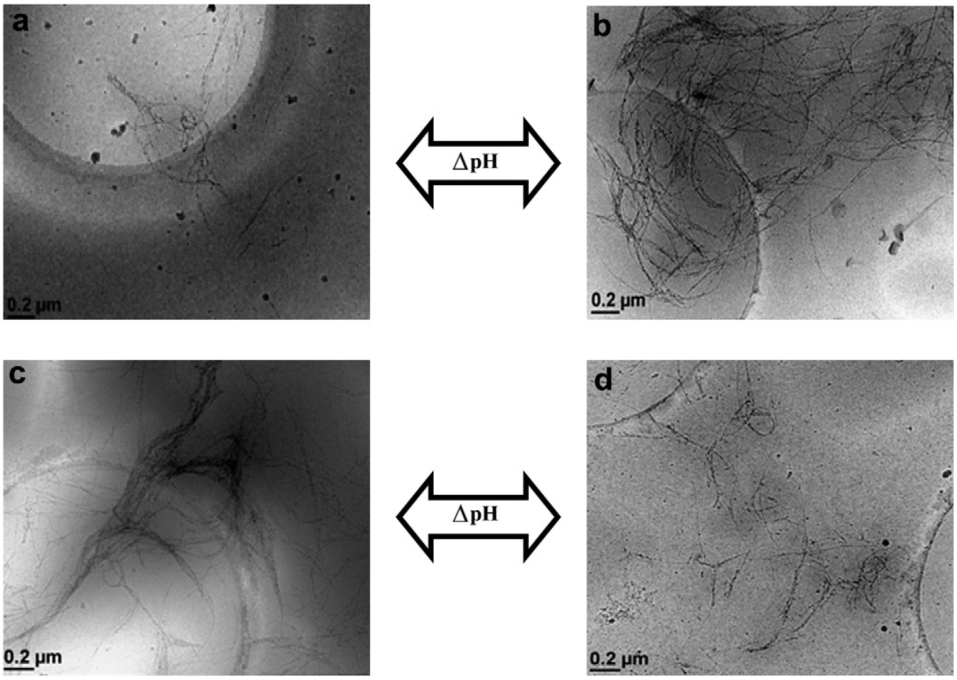


Fig. 4. Cryo-TEM images of SWNT/PAA suspensions at pH 7 (a) and pH 9 (b) and SWNT/PAAm suspensions at pH 5 (c) and pH 11 (d).

dependent on the charge of the adsorbed polymer on particles [46,47]. This suggests that the weak polyelectrolytes used in this study are adsorbed onto the SWNT surface, which imparts surface charge depending on the nature of the polymer. Although the BPEI-stabilized SWNTs show positive zeta potential values, significant scatter was observed in the measurements. This is attributed to weaker stability of BPEI-based suspensions that results in variable SWNT aggregation during measurements.

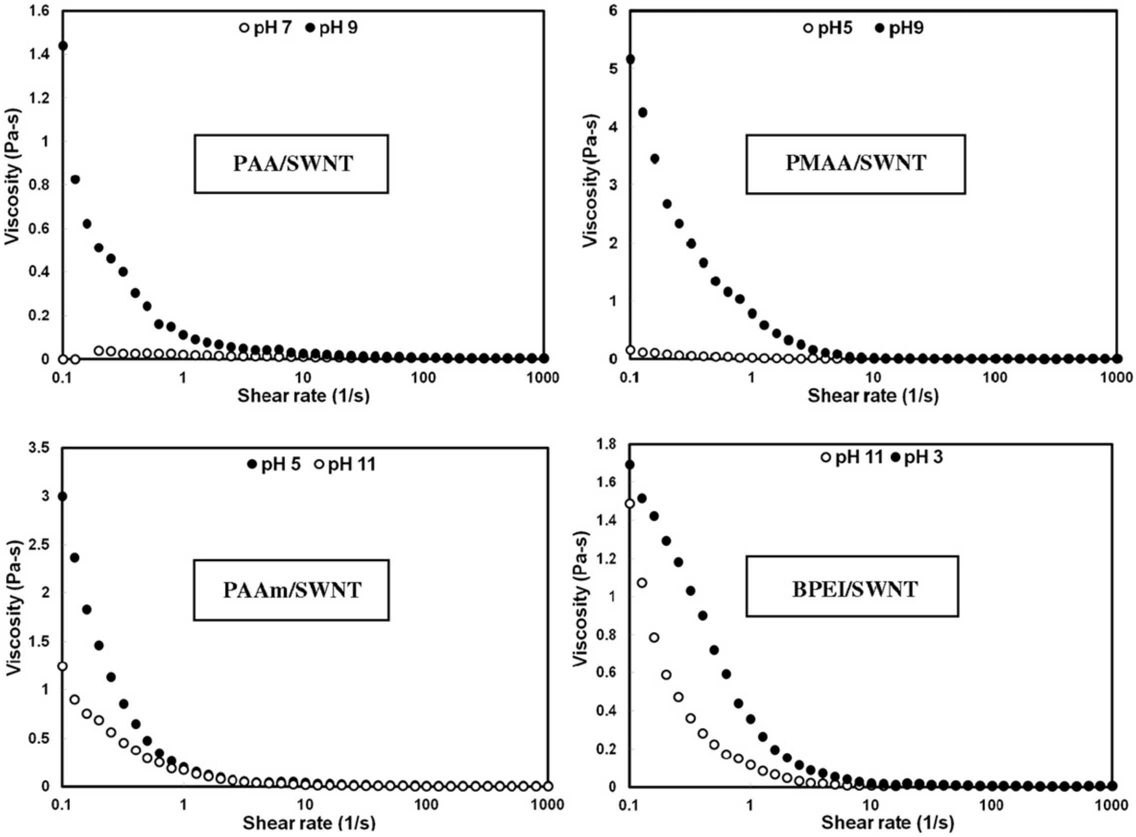


Fig. 5. Viscosity as a function of shear rate at varying pH levels for PAA, PMAA, PAAm and BPEI-stabilized aqueous suspensions of single-walled carbon nanotubes.

Table 1
Zeta potentials of aqueous SWNT suspensions stabilized with pH-responsive polymers.

Suspension	pH	Zeta potential (mV)
PAA/SWNT	7	−82
PMAA/SWNT	5	−62
PAAm/SWNT	11	43
BPEI	11	14–74

It was previously shown that this dispersion state of SWNTs in solution influences their microstructure in solid polymer composites upon drying the suspension [30,35]. To investigate the solid state microstructure of SWNTs in polymer composites, suspensions containing 1 wt% of a pH-responsive polymer and 0.11 wt% SWNT, at different pH, were dried at room temperature. Scanning electron microscopy was performed on the surface of PAA and PAAm matrix composites and the images obtained are shown in Fig. 6. As expected, nanotube microstructure in these composites is dependent on the pH of the suspensions used. It is clear that the PAA-based composite made with a pH 7 suspension has fairly homogenous and uniform SWNT dispersion (Fig. 6(a)), whereas that made with pH 9 shows extensively aggregated SWNTs (Fig. 6(b)). PAAm-based composites also show similar behavior, where composites made with pH 11 and pH 5 suspensions have homogeneous and aggregated SWNT dispersion, respectively. It should be noted here that PAA-based composites have better overall SWNT distribution as compared to PAAm-based composites at both pH levels. This again suggests that polyacids are better stabilizers for SWNTs than polybases. BPEI-based composites (not shown here) have non-uniform SWNT distribution where large areas with no nanotubes can be seen. This is because of poor interaction between SWNTs and BPEI.

Electrical conductivity measurements were made on these dried composite films and the results are shown in Fig. 7. It can be seen that the pH of the SWNT/polymer suspensions ultimately influences the electrical conductivity of the composite. The SWNT/PAA composite prepared at pH 7 has an order of magnitude lower conductivity as compared to that made from a pH 9 suspension. Similar observations were made for SWNT/PMAA and SWNT/PAAm composites. It should be pointed out that all composite films contained 10 wt% of SWNT, which is well above the percolation threshold reported for nanotube–polymer composites [48,49]. This point suggests the difference in the electrical conductivity in these composites is the result of altered nanotube–nanotube interaction and network formation in the presence of the stabilizing polymer. The increased conductivity for the composites made from suspensions that contained bundled SWNTs is attributed to more intimate nanotube–nanotube contacts resulting from the extended structure of the polymer, as shown in Fig. 8. When the polymer assumes an extended conformation, the steric hindrance necessary for generating exfoliated SWNTs is reduced, which leads to SWNT aggregation and a greater number of contacts for electrical transport [50]. The observed lower conductivities for the composites made from the suspensions containing exfoliated SWNTs are due to the presence of a thicker layer of adsorbed polymer, which results in effective shielding of the nanotubes–nanotube contacts and also reduces the total number of contacts due to better dispersion. Much like with viscosity (see Fig.

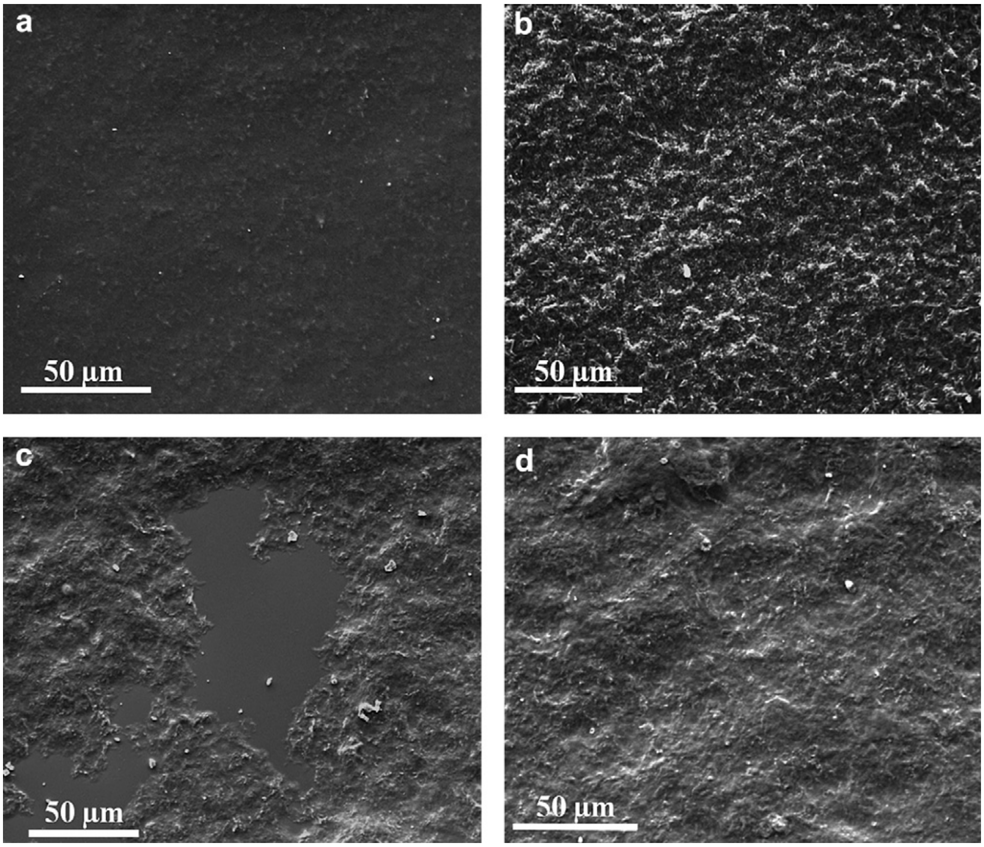


Fig. 6. SEM images of composites containing 10 wt% SWNT that were made by drying aqueous PAA-based suspension at pH 7 (a) or pH 9 (b) and PAAm-based suspensions at pH5 (c) or pH 11(d).

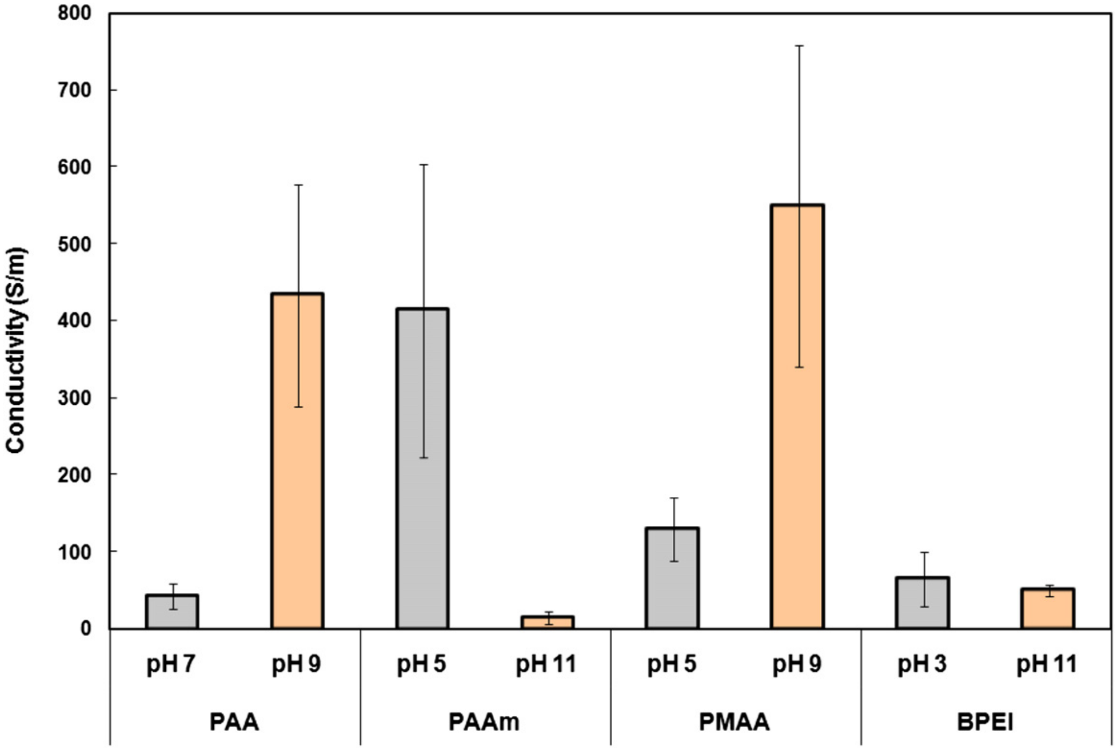


Fig. 7. Electrical conductivity of solution-processed 10 wt% SWNT/pH-responsive polymer composites as a function of pH.

5), BPEI/SWNT composites show only a small difference in electrical conductivity as a function of pH. This may be due to poor interaction between BPEI and SWNT. The results obtained from these measurements suggest that interactions and microstructure in the liquid suspensions are at least partially preserved in the solid composites. This method of tailoring microstructure in the liquid state to control the microstructure in the solid state holds significant potential for the preparation of polymer nanocomposites.

Based on the above results, the scheme shown in Fig. 8 is postulated to explain the stabilizing mechanism by pH-responsive polymers. SWNT stabilization with polymers is believed to be due to polymer wrapping on the nanotube surfaces, which results in extended coverage of the polymer along the tube axis [26,51]. Despite this generally accepted mechanism, at low ionizations, weak polyelectrolytes assume a coiled conformation at the adsorbed surface in order to maximize configurational entropy and assume a random walk configuration [32]. Therefore, at these conditions it would be difficult for the polymer to wrap around the SWNTs. Superior stability of SWNT suspensions, stabilized with partially ionized polymers, suggests that polymers are adsorbed on to the SWNT surface in globular form, as shown schematically in Fig. 8. The globular conformation of the polymer results in a smaller radius of gyration (R_g) that creates a thicker steric layer on the SWNT sidewall. Upon complete ionization, the polymer assumes an extended conformation and results in a flatter coverage on the SWNT sidewall. This conformation of the polymer reduces the steric layer thickness and results in SWNT aggregation. It is true that fully ionized polymers adsorbing on the SWNT sidewall should impart inter-tube electrostatic repulsion, thereby preventing aggregation, but at these conditions the nanotubes exist in aggregated state (as evidenced in cryo-TEM images shown in Fig. 4). This suggests that electrostatic repulsion alone is not sufficient for exfoliation of SWNTs. The SWNT microstructure in these suspensions is believed to be influenced by a combination of electrostatic and steric forces and is more sensitive to the steric layer thickness variations. A similar steric layer thickness dependent stabilization was observed for polystyrene latex stabilized with acidic polysaccharides [52].

SWNT suspensions stabilized using polyanions show superior stability as compared to those stabilized with polycations (see Fig. 2). This may be due to better interaction between polyanions and SWNTs owing to the Lewis base character of the nanotube graphene sidewalls [42]. Additionally, the stabilizing polymer charge, observed in zeta potential measurements (see Table 1) on the suspensions, suggests the adsorption of the stabilizing polymer onto the SWNT sidewalls. Therefore, it is reasonable to assume that polyanions are adsorbed more strongly to the SWNT surface than polycations. Furthermore, the weak polyelectrolytes used in this study (PAA, PMAA, PAAm and BPEI) exist in a partially ionized state at the pH corresponding to high SWNT exfoliation (i.e., low pH for polyanions and high pH for polycations), so it is reasonable to assume a conformation of the polymer that is intermediate between tight globule and extended coil (i.e., a combination of *coiled and uncoiled* domains shown in Fig. 8). These polymer conformations result in thicker steric layer coverage on the SWNT surface, thereby providing superior stability of suspensions. On the contrary, the weaker adsorption of polycations to the SWNT surface may result in desorption upon standing. Sedimentation of SWNT upon standing is observed in both PAAm and BPEI-stabilized suspensions at high pH, which is attributed to desorption of polymer from the SWNT surface. When these polyelectrolytes are fully charged, they assume an extended conformation, thereby reducing the steric layer thickness on the SWNT surface that leads to the aggregated microstructure shown in Fig. 8.

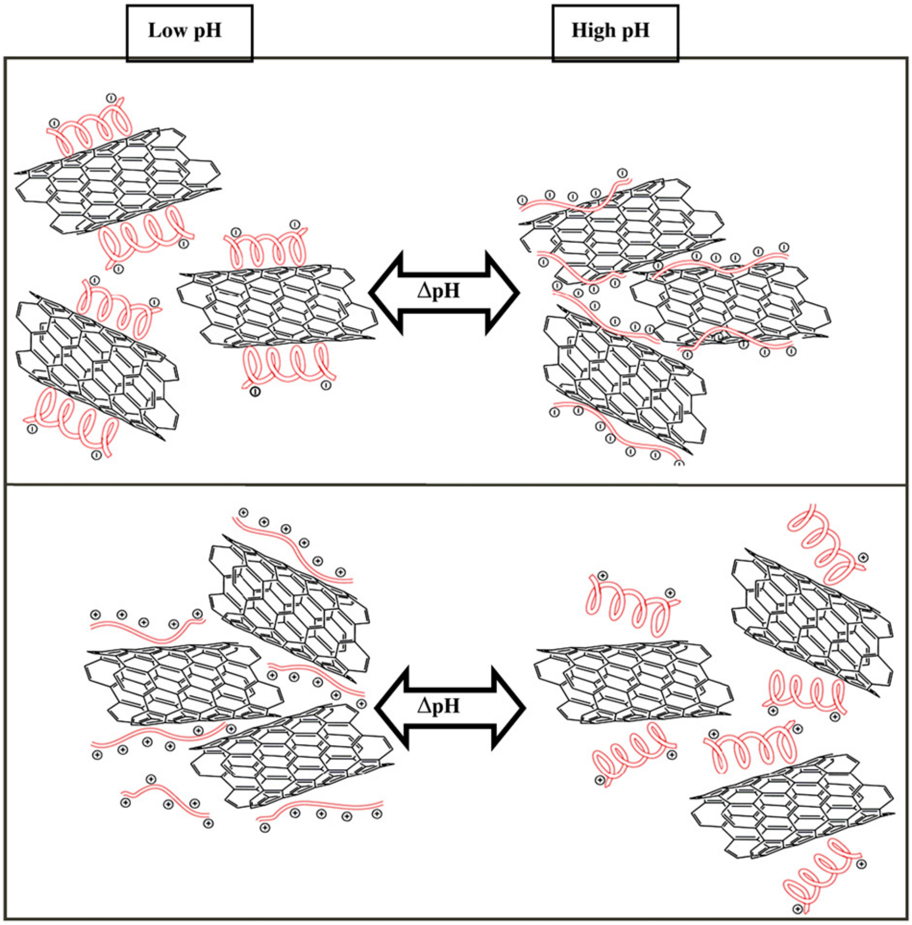


Fig. 8. Schematic of SWNT dispersion and aggregation as a function of pH in aqueous suspensions using weak polyanions (a) and weak polycations (b). Both polycations and polyanions transition between weakly and fully ionized states along the pH spectrum. In the weakly ionized state, these polyelectrolytes exfoliate and stabilize SWNTs in water, whereas aggregated and bundled nanotubes are observed when polymer electrolytes are fully ionized.

4. Conclusions

The ability to control the dispersion state of carbon nanotubes in water was demonstrated with four different pH-responsive polymers (PAA, PMAA, PAAm and BPEI). These weak polyelectrolytes exhibit pH-dependent conformational transitions in water (i.e., extended coil-to-globule) with changing pH. The stability of SWNT suspensions was characterized using UV–vis spectroscopy, cryo-TEM and centrifugation. Suspensions containing exfoliated SWNTs show more UV–vis absorption than those having bundles. Viscosity measurements of aqueous suspensions indicate that nanotubes exists in exfoliated and aggregated state depending upon pH. Zeta potential measurements of these same suspensions suggest adsorption of polymer on the SWNT surface. Electrical conductivity measurements on the composites made by drying the suspensions demonstrate that nanotube microstructure in the liquid state is preserved to a large extent in the solid state. These results indicate that SWNTs can be stabilized in water using pH-responsive polymers and the dispersion state can be tailored between bundled and exfoliated states. Based on these results, a stabilization mechanism is hypothesized where pH induced conformational changes of a polymer adsorbed on the SWNT sidewalls influences their dispersion state. This ability to control nanotube microstructure in the liquid state holds significant promise for the processing of solution-based composites. Tailoring SWNT structure ultimately suggests composite properties (conductivity, strength, etc.) can be precisely tailored, which could lead to improved (and better controlled) behaviors in these nanotube-filled materials.

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