

REVIEW ARTICLE

Methodology for Homogeneous Dispersion of Single-walled Carbon Nanotubes by Physical Modification

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Science and technology on carbon nanotubes (CNTs) are an expanding field aiming at ascertaining their intrinsic properties and taking advantage of their inviting possibilities. Dealing with CNTs has faced the problem of insolubility in both organic and inorganic solvents due to the strong interaction therein. Here we review the recent progress as well as our approaches to the solubilization of CNTs based on a physical modification method. Especially, the review focuses on the ‘individual’ solubilization of pristine CNTs in solvents. Individual solubilization of CNTs is imperative in many research programs such as chemical modification of CNTs *via* organic reactions, characterization of CNTs chiral indices as well as separation of these mixtures, preparation of composites with polymers, fabrication of CNTs-based nanoelectronics devices and so forth.

KEY WORDS: Carbon Nanotubes / Solubilization / Functionalization / Physical Adsorption / Aromatic Compounds / π - π Interaction / Polymer Nanocomposites /

Carbon nanotubes (CNTs) discovered in 1991 by Iijima are made of rolled-up graphite sheets with one-dimensional large π -conjugated structures.¹ Due to their high aspect ratios and strong van der Waals interaction, as-synthesized CNTs form bundled structures.² One of the key issues in the utilization of CNTs for basic researches and material applications is to develop a methodology to exfoliate the debundled structures and solubilize/disperse them in solvents.^{3–5} Such a solubilization/dispersion technique can be classified mainly into two methods, namely, ‘chemical’ and ‘physical’ modification. Solubilization/dispersion of CNTs based on physical adsorption of dispersant molecules possesses advantages of the ease of preparation process and in maintaining intrinsic CNT properties, which show sharp contrast with the chemical modification.^{4–14}

The mechanism of the debundling of CNTs is believed due to the “unzipping” mechanism proposed by Smalley and co-workers,¹⁵ which is triggered by sonication, followed by the wrapping of CNTs by dispersants. Surfactant micelles, π -aromatic compounds and synthetic and biological polymers can act as dispersants for CNTs *via* physical adsorption.³ Solubility of CNTs in solvents *via* physical modification largely depends on the type of dispersants and purity of CNTs as well. Although numerous papers describing the solubilization/dispersion of CNTs have been published, the degree of solubilization/dispersion varies with the dispersants and the experimental conditions. Here, we focus mainly on individual solubilization of single-walled carbon nanotubes (SWNTs) based on physical modification (Figure 1).

The typical procedures for the preparation of individual solubilization of SWNTs are ultrasonication of the SWNTs in a dispersant solution, followed by centrifugation. Individually

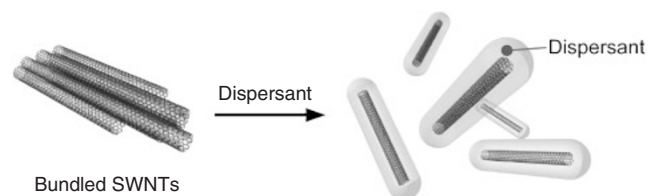


Figure 1. Schematic illustration of individual solubilization of SWNTs through physical modification approach using dispersant molecules.

solubilized/dispersed SWNTs are characterized by near-IR (NIR) absorption and photoluminescence (PL) spectroscopy, atomic force microscope (AFM),^{16,17} small angle neutron scattering (SANS),^{18–20} transmission electron microscope (TEM),^{21,22} and so on. Among them, the PL measurement in the NIR region is a strong tool for determining the dispersion nature of the SWNTs. Wiseman *et al.* found that PL can be detected from individually dissolved SWNTs in the NIR region and then succeeded in the determination of the SWNTs chirality in the solution.^{23,24} It is important to note that only individually dispersed SWNTs respond by PL because the bundled SWNTs end up quenching the PL by the metallic-SWNTs in the bundle. Thus the PL observation provides strong evidence of the individual dispersion in solution as well as in the film.^{25,26} UV-visible NIR absorption spectroscopy is quite helpful in roughly evaluating the existence of individually isolated SWNTs in both the solution and film states.²⁷ In some cases, the electron conductivity measurement allows brief estimation of dispersion of the SWNTs in polymer films by evaluating the concentration of the SWNTs at the electron percolation threshold.^{28,29} A lower threshold concentration is a

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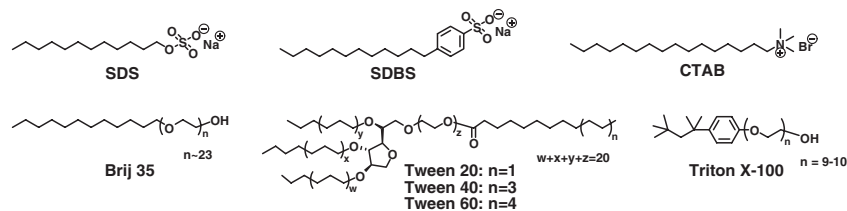


Figure 2. Chemical structures of surfactants for CNTs solubilization.

consequence of greater dispersion of the SWNTs in the matrices. Scanning probe microscope (SPM) and (high-resolution) TEM are often used to visualize the individually dispersed SWNTs.^{30,31}

Dissolution in Common Organic Solvents

CNTs are colloiddally dispersed in some common organic solvents such as *o*-dichlorobenzene (ODCB), *N*-methylpyrrolidinone (NMP), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) in very limited period of time. Early attempts to disperse CNTs in organic solvents were carried out by Smalley and co-workers.¹⁶ They successfully dispersed SWNTs in DMF and NMP and used them for individual placement on patterned substrates.³² Detailed studies focusing on the ability of dispersion of SWNTs in common organic solvents including chloroform, tetrahydrofuran and pyridine were examined by several groups.^{17,33–38} Dispersion in such solvents is convenient, however we need to recognize that the stability of these suspensions is poor, that is, aggregates of the nanotubes are generated in a few hours or in a couple of days.³⁴

Strong acid treatment of the CNTs causes debundling of CNTs aggregates *via* the introduction of carboxylic acid on the CNTs surfaces. Carboxylic acid groups disturb the charge balance around the CNTs and induce an electronic polarity,³⁹ leading to an enhanced solubility in common organic and inorganic solvents.^{40–46} Initially, a concentrated H₂SO₄:HNO₃ (3:1 by volume) mixture was selected since it has been known to intercalate and exfoliate graphite.⁴⁷ Several kinds of strong acids such as H₂SO₄, trifluoromethanesulfonic acid and chlorosulfonic acid give a similar results.⁴² Acid-treated CNTs thus obtained can disperse in acid to a considerable extent of concentration. Smalley *et al.* carried out rheological studies for the SWNTs dispersion in fuming sulfuric acid and found that the dispersion expresses the lyotropic LC phase above a concentration of 4 vol%.⁴⁸ A similar lyotropic LC nature has been reported for the dispersion of MWNTs.⁴⁹ Although acid treatment of CNTs, especially SWNTs, change their electronic conductivity and optical properties,⁵⁰ carboxyl group-functionalized CNTs are a quite useful material for chemically functionalized CNTs connected by covalent or ionic bonding.¹⁴ Other solvents that can exfoliate and disperse CNTs are ionic liquids. Fukushima *et al.* found that SWNTs are dispersed in some ionic liquids.⁵¹ Wide spreading of this finding are summarized in review article.⁵²

Dissolution Using Surfactants

The most convenient and frequently-used dispersant for CNTs in aqueous media is surfactants including sodium dodecyl sulfate (SDS),^{53–55} sodium dodecylbenzene sulfonate (SDBS),^{21,56–59} cetyltrimethylammonium bromide (CTAB),^{21,60} Brij,^{21,61} Tween,^{21,61} and Triton X^{21,56,61,62} (Figure 2). An early attempt in preparing CNTs dispersions using a surfactant was carried out by Bandow *et al.* in the purification of the SWNTs from carbon soot material.⁶³ The suggested mechanism of the individual dispersion is the encapsulation of SWNTs in the hydrophobic interiors of the micelles, which results in the formation of a stable dispersion. Assembled structures of surfactants on CNTs sidewalls are still under discussion^{15,53,64} and are summarized in a review article.⁶⁵ It should be important to understand that the surfactant molecules are in a dynamic equilibrium between the CNTs surfaces and the bulk solution. Among the conventional surfactants, SDBS is one of most powerful solubilizers for SWNTs, that is, even in the concentration of 20 mg/mL of SWNTs in an SDBS micelle, no aggregation of the SWNTs forms for more than 3 months.⁵⁶

Some biological surfactants such as bile salts are useful molecules for dissolving SWNTs in water (Figure 3).^{61,66,67} Among the biological surfactants, micelles of anionic bio-surfactants including sodium cholate (SC), sodium deoxycholate (SDC), sodium taurocholate (STC), sodium taurodeoxycholate (STDC), sodium glycocholate (SGC), *N,N*-bis(3-D-gluconamidopropyl)cholamide (BIGCHAP) and *N,N*-bis(3-D-gluconamidopropyl)deoxycholamide (deoxy-BIGCHAP) pos-

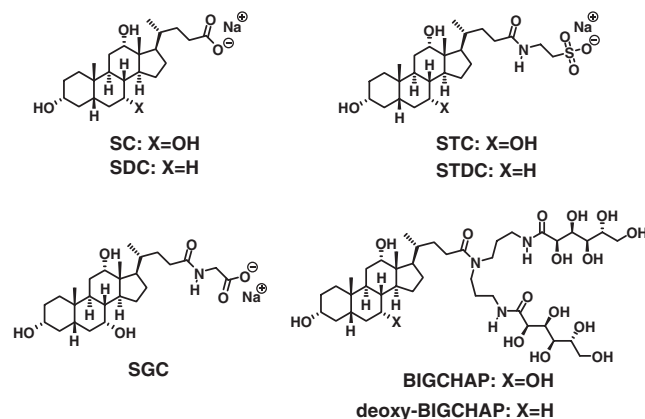


Figure 3. Chemical structures of biological surfactants for CNTs solubilization.

Table I. Pyrene-based dispersants for CNTs

No.	Pyrene Solubilizer	Research Targets	Reference
1		Solubilization of SWNTs into aqueous system Solubilization of C70@SWNTs into aqueous system	71, 73 72
2		ROMP on SWNTs	74
3		Functionalization of MWNTs in supercritical fluids	75
4		Functionalization of MWNTs in supercritical fluids	75
5		Electrochemical response of fullerene/SWNTs hybrid	76
6		Attachment of pyrene-modified chlorophyll derivative	77

sess high solubilization ability, in which the PL in the NIR region guarantees the individual solubilization. The PL spectral analysis has revealed that the chiral indices of the SWNTs solubilized by the biosurfactants depend on their chemical structures.⁶⁷ We used SC as a dispersant for SWNTs for the separation of semiconducting- and metallic-SWNTs based on the preferential coupling reaction of a benzenediazonium salt with the metallic SWNTs.⁶⁸

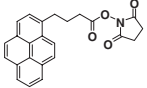
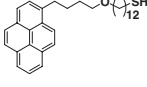
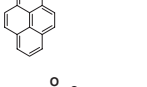
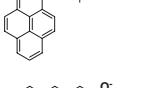
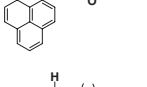
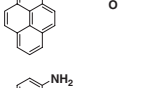
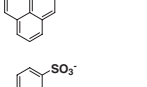
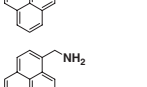
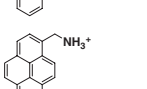
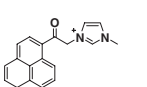
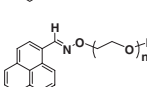
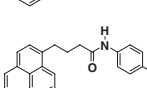
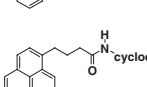
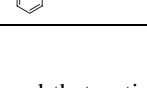
Dissolution Using Polycyclic Aromatic Compounds

The π - π interaction between polycyclic aromatic compounds and CNTs sidewalls has been discussed based on both theoretical⁶⁹ and experimental⁷⁰ approaches. We reported that a pyrene-based ammonium salt (compound **1** in Table I) is able to disperse SWNTs⁷¹ and fullerene-filled CNTs (so-called peapods)⁷² in water. We revealed that the pyrene moiety acts as an efficient functional group compared to naphthyl- and phenyl-based ammonium salts.⁷³ This is due to the strong binding affinity between the pyrene group and the CNTs sidewalls. Since this finding,⁷¹ pyrene derivatives have been widely recognized as excellent solubilizers for CNTs as summarized in Table I.⁷¹⁻⁷⁷ By taking advantage of the efficient adsorbing capability on the CNTs surfaces, pyrene derivatives have been utilized as decent interlinkers to anchor the functional materials that can communicate with CNTs as summarized in Table II.⁷⁸⁻⁹⁵ Pioneering work demonstrating that the pyrene derivative functioned as an interlinker was carried out by Dai *et al.*⁷⁸ They successfully attached a protein on the surface of the SWNTs with the aid of a pyrene-carrying

succinidyl compound (compound **7** in Table II). Pyrene-ammonium **1** was also used by other groups for anchoring anionic functional molecules on the surface of SWNTs as well as that of MWNTs.^{83,84,96} Other polycyclic aromatic moieties such as anthracene,⁹⁷ terphenyl,⁹⁸ perylene,⁹⁹ and phenanthrene¹⁰⁰ also have affinity for the sidewalls of the CNTs. The degree of the interactions between these polycyclic aromatic moieties and the CNTs sidewalls has been evaluated based on Raman spectroscopic analysis.¹⁰¹ Greagan *et al.*¹⁰² revealed the terphenyl group possesses slightly greater affinity than anthracene. The variation of affinity depend on the dispersants is attractive in the view of chirality recognition and separation of CNTs.

We revealed that porphyrin compounds are able to individually solubilize SWNTs.¹⁰³ We first used zinc protoporphyrin IX (compound **20** in Table III) for the study and found that a **20**/SWNTs solution is stable even after 6 months. Fluorescence quenching of the porphyrin in the **20**/SWNTs evidenced the adsorption of the porphyrin onto the SWNTs. We tested a series of porphyrin derivatives and revealed that a wide range of porphyrin derivatives including **21** and **22** (Table III) can also act as effective dispersants for SWNTs.¹⁰⁴ The finding lead the theoretical as well as experimental attempts to understand the interaction between porphyrin and CNTs.¹⁰⁵⁻¹⁰⁷ The combination of porphyrin and CNTs has attracted extensive interest due to their unique photophysical,^{81,108,109} electrochemical,¹¹⁰⁻¹¹² electronic,^{108,113-115} and optical^{116,117} properties. One of the striking results realized in these studies is the separation of optical active SWNTs reported by Osuka *et al.*¹¹⁸

Table II. Pyrene-based interlinkers for immobilizing functional molecules on the CNTs surface

No.	Pyrene interlinker	Immobilized materials	Research Target	Reference
7		Proteins	Immobilization of protein onto SWNTs surface	78
8		Au nanoparticles	Au nanoparticle immobilization on MWNTs	79
9		Poly(sodium <i>p</i> -styrenesulfonate)	Layer-by-layer assembly of SWNTs with polyanion	80
1		Anionic Porphyrin CdTe Anionic Polythiophene	Photoinduced electron transfer from porphyrin to SWNTs Photoinduced electron transfer between CdTe and MWNTs Photoinduced electron transfer between polythiophene and SWNTs	81, 82, 83, 84 85 86
10		Cationic porphyrin	Photoinduced electron transfer from porphyrin to SWNTs	87
11		Fe ₃ O ₄	Immobilization of magnetic particle	88
12		Metal nanoparticles	Immobilization of metal nanoparticles onto SWNTs	89
13		Polyaniline	Enhancing of bioelectrocatalyzed oxidation	90
14		Au nanoparticles	Immobilization of Au nanoparticle onto MWNTs surface	91
15		Poly(sodium <i>p</i> -styrenesulfonate)	Layer-by-layer assembly of polyelectrolytes	92
16		Poly(sodium <i>p</i> -styrenesulfonate)	Layer-by-layer assembly of polyelectrolytes	92
17		Tabacco mosaic virus	Immobilization of tobacco mosaic virus onto SWNTs	93
18		Naphthalocyanine	Photoinduced electron transfer from naphthalocyanine to SWNTs	94
19		Adamantane derivative	Modification of cyclodextrin on SWNTs surface	95

They found that optically active porphyrin dimers (compound **35** in Table III) could separately pick up SWNTs with right- and left-handed helicities structures from racemic mixtures depending on the chirality of the dimers. Porphyrin derivatives^{114,119–126} as well as their analog molecules such as phthalocyanines^{127–129} and sapphyrin¹³⁰ have been reported to serve as dispersants for the CNTs.

Dissolution Using Natural Polymers

The combinations of CNTs and biological molecules are of interest in many chemical and biochemical areas from the viewpoints of both fundamentals and applications.¹³¹ Biological molecules including peptides^{132–137} and proteins^{138–140} have been reported to have interactions with CNTs sidewalls. In these systems, the hydrophobic interaction between the

Table III. Porphyrin-based solubilizers for CNTs

No.	Porphyrin	M	R	Research Target	Reference
20		Zn		First porphyrin-based solubilizer for SWNTs	103
21		2H		Solubilization of SWNTs	104
22		FeCl		Electrochemical response for SWNTs/Porphyrin hybrid	105
23		2H		Photoinduced charge Injection from excited porphyrin into SWNTs	108
24		2H		Porphyrin driven supramolecular assembly of SWNTs	124
25		Zn		Direct observation of adsorbed porphyrin on SWNTs and evaluation of the composite as nanoelectronics device	113
26		2H		Photoinduced charge injection from excited porphyrin into SWNTs	108
27		2H, Zn		Nonlinear optical properties of SWNTs/Porphyrin composite	117
28		2H, Zn		Investigation of interaction between porphyrin and SWNTs	107
29		2H		Photoinduced charge injection from excited porphyrin into SWNTs	108
30		4H ²⁺		Solubilization of SWNTs in water	119
31		2H, Zn		Separation of semiconducting SWNTs	120
32		Zn		Solubilization by conjugated porphyrin polymer	122
33		Zn		Supramolecular solubilization	121
34			 R ₁ =	Solubilization by fully-fused porphyrin	125
35				Separation of optically active SWNTs	118
36		2H		Long-lived charge separation between porphyrin and SWNTs	126

hydrophobic domains and the CNTs sidewall plays a significant role in the dispersion.¹⁴⁰ Dieckmann *et al.* used a cyclic peptide for the diameter recognition of the SWNTs and found that the diameters of the solubilized SWNTs vary with the diameter of the peptide macrocycle.¹³⁵ It can be said that 'individual dispersion' is the essential step for the solution-based separation and purification of the SWNTs.

One of the most noteworthy molecules that can individually dissolve SWNTs in water is DNA. Individual dissolution of

SWNTs using double-strand DNA (dsDNA) and single-strand DNA (ssDNA) were reported from our group¹⁴¹ and Zheng *et al.*,¹⁴² respectively. The typical procedure of ultrasonication and successive ultracentrifugation give black-transparent supernatant solutions. As for the mechanism of the individual dissolution with ssDNA, the interaction between the SWNTs sidewall and the DNA nucleobase has been proposed both experimentally^{143–145} and theoretically.¹⁴⁶ Indeed, SWNTs that are helically wrapped by the ssDNA have been observed by

means of the AFM technique.¹⁴⁷ On the other hand, the interaction between the SWNTs and the DNA groove¹⁴⁸ as well as the nucleobase¹⁴⁹ has been suggested for the solubilization with dsDNA. High dispersability of the SWNTs by DNA allows to give the formation of the lyotropic liquid crystalline phase at high concentration.¹⁵⁰ Vast numbers of research studies have been carried out concerning DNA/CNTs composites in view of the biological applications, such as the conformation transition monitoring occurring at DNA,¹⁵¹ hybridization detection between ssDNA and their complementary DNA¹⁵² and uptake estimation of DNA/SWNTs into the cell hybrid as a novel gene delivery.¹⁵³ Zheng *et al.*¹⁵⁴ achieved chromatography-based enrichment of chiral indices for ssDNA/SWNTs complex. In this work, inherent properties of DNA were not utilized but the individual isolation of the SWNTs realized by DNA solubilizer play a crucial role.

Other helical natural polymers such as amylose^{155,156} and β -1,3-glucans^{157,158} also wrap SWNTs and individually dissolve them in water. Impressive evidence for the helical wrapping of the polymer onto the SWNTs is the TEM images of the schizophyllan/SWNTs hybrid presented by Shinkai *et al.*¹⁵⁸ SWNTs solutions individually dispersed in an aqueous system obtained with the aid of biopolymers such as chitosan¹⁵⁹ and gelatin¹⁶⁰ have been reported and used for a wide range of applications. Recently, our combinatorial investigations elucidate that green tea also function as a good dispersant for SWNTs.¹⁶¹ Our hypothesis is that catechin, a polycyclic aromatic compound, mainly contributes to the dispersion because epigallocatechin gallate also disperses the SWNTs into water.

Dissolution Using Synthetic Polymers

Efficient dispersion of CNTs in polymers enhances and/or reinforces the intrinsic properties of the polymer such as the mechanical properties.^{14,162–166} Although numerous papers describing polymer/CNTs composites have been reported, unfortunately, not all of the research considered the degree of the dispersion of the nanotubes in the matrices. Individual dispersion of CNTs in the polymer composites in solutions is considered to be essential for efficient dispersion in the composite films. Many different kinds of synthetic polymers have been reported to disperse SWNTs in solvents. The π - π interaction between the polymers and the CNTs surfaces contributes to the solubilization of the CNTs. Pioneering studies dispersing SWNTs in solvents were carried out using *p*-phenylenevinylene derivatives (PPVs).^{167–169} The SWNTs formed stable suspensions in the presence of PPVs in organic solvents such as chloroform, suggesting that the polymer wrapped around the tubes. SWNTs complexes with π -conjugated PPVs have been the intriguing materials because of their unique optoelectronic properties.^{170–186} Up to date, wide variety of aromatic polymers have been reported to serve as an excellent dispersant for CNTs. And extensive researches to achieve further reinforcement of the aromatic polymers were carried out since CNTs are expected to act as ideal filler materials for polymer films due to their high tensile modulus

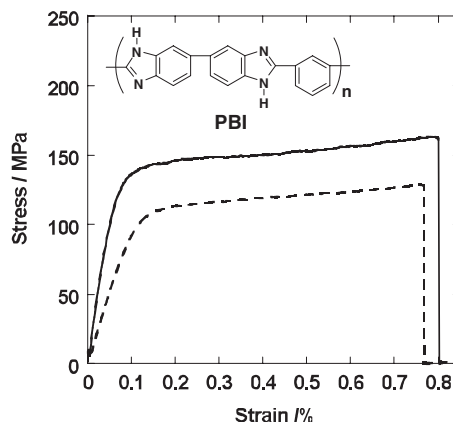


Figure 4. Typical strain-stress curves for PBI (dotted line) and 0.06 wt % of PBI/SWNTs (solid line) films.

(640 GP)¹⁸⁷ and tensile strength (≈ 100 GPa)¹⁸⁸ together with a high aspect ratio (typically *ca.* 300–1000) of CNTs. Kumar *et al.*¹⁸⁹ described that the tensile strength of polybenzoxazole (PBO) fiber was reinforced by 1.5 times with the addition of a 10 wt %-addition of SWNTs. We recently found that the only a 0.06 wt % addition of SWNTs into polybenzimidazole (PBI) (Figure 4. inset) reinforces the mechanical properties of the original polymer by 1.5 times (Figure 4).¹⁹⁰ It is reasoned that the SWNTs are dispersed efficiently in the polymer film by the interaction between the sidewalls of the SWNTs and PBI. In fact, PBI individually dissolves the SWNTs in an organic solvent, which was proved by photoluminescence measurement.

Polyimide/CNTs composites are fascinating materials for use under severe conditions such as aerospace applications. Composite preparations *via in situ* polymerization of polyimide in the presence of CNTs have been employed for various combinations of monomers.^{30,31,191,192} We have reported that polyimide having a sulfonic acid salt (PI-1 in Figure 5) possess high capability for stabilizing the individually exfoliated SWNTs in organic solvents for long periods of time.¹⁹³ It is interesting to note that the concentration of SWNTs in dimethyl sulfoxide (DMSO) solution of the PI-1 can reach as high as 2–3 mg/mL, and the mixtures form physical gels above 1.8 mg/mL (Figure 5). To our surprise, PL spectra revealed that the SWNTs/PI-1 solution at the highest concentration retains the individual isolation of the SWNTs.

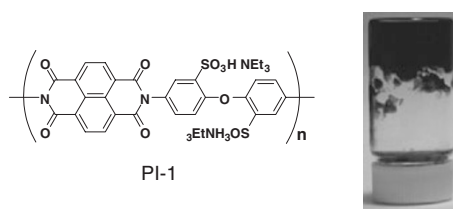


Figure 5. Chemical structure of PI-1 (left) and photograph of SWNTs (2.1 mg/mL) individually dispersed in DMSO solution of PI-1 (1.0 mg/mL).

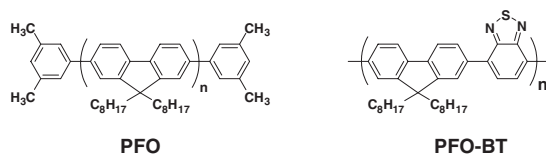


Figure 6. Chemical structures of PFO and PFO-BT.

Aromatic polymers with a rigid-backbone have an opportunity to disperse the SWNTs with specific chiral indices by aligning their backbones along the SWNTs surfaces in order to maximize the interaction between π -bonds.¹⁹⁴ Coleman *et al.* used the conjugated polymer poly(*m*-phenylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV) to preferentially disperse SWNTs with specific chiral indices leaving the others in the precipitate.^{195–198} Quite recently, two different groups reported impressive papers, in which they described that the poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(1,4-benzo-2,1,3-thiadiazole)] (PFO-BT) (Figure 6) have strong selectivity to enrich the SWNTs with a single chirality index.^{199,200} Of interest, PFO selectively wraps only SWNTs with high chiral angles (close to an armchair configuration) and PFO-BT preferentially wraps the SWNTs with a certain diameter of around 1.05 nm. Further understanding of the mechanism of the SWNTs-polymer selective interaction could lead to a properly-designed polymer able to recognize SWNTs down to a single chirality index at one's request.

As for the vinyl polymers, commercially available poly(styrene sulfonate),²⁰¹ poly(vinyl alcohol),²⁰² poly(vinylpyrrolidone)²⁰¹ enable CNTs to be dispersible in solution. Baskaran *et al.* successfully prepared a stable dispersion of MWNTs in organic solvent with the aid of polymers such as polybutadiene, polyisoprene, polystyrene, poly(methyl methacrylate), and poly(ethylene oxide) through two mixing steps (solution blending followed by melt mixing).²⁰³ They claimed the importance of the CH- π interaction for the dispersion mechanism with non-aromatic polymers. On the other hand, introduction of π - π interaction are the promising strategy for vinyl polymers. For example, pyrene moieties employed in the polymer structure as the pendant group offered the better dispersion of CNTs (Figure 7).^{204–209} We synthesized a pyrene-carrying copolymer of (Figure 7. compound **38**) and found that the copolymer helped to form a stable aqueous dispersion of SWNTs.²⁰⁶ No precipitate was observed on heating up to 95 °C, while dispersion in the corresponding monomer pro-

duced a precipitate around 50 °C. This result clearly indicates the advantage of polymer-based solubilizers when it compared to the monomeric type. Porphyrin was also employed as a pendant group as well.¹²⁶ We also reported that an anthracene-carrying polymer led to the individual solubilization of SWNTs in DMF. In the course of the studies, we noticed that SWNTs acted as an effective “molecular heater” triggered by the NIR irradiation.²¹⁰ Photothermal conversion occurred due to the effective nonradiative process of excited-SWNTs generating intense heat in a very short period. As a result, the wrapped polymer is dissociated from the composites and the SWNTs start to re-aggregate through strong van der Waals interactions. In fact, we observed the temperature increase of the composite solution upon photo-irradiation. A similar NIR induced release of the wrapping polymer was reported in the system of SWNTs/DNA composites by Dai *et al.*²¹¹ The wide range of absorption on CNTs provides an opportunity for the “molecular heater” to work at the various wavelengths of the light source.

It is also believed that the amphiphilicity of the polymers may contribute to the dispersion of CNTs through a micelle-encapsulation mechanism. Taton and co-worker found that the micelle formation in a DMF solution of polystyrene-*b*-poly(acrylic acid)²¹² induced by water addition enabled the dispersion of SWNTs. Up to date, wide range of block copolymers have been reported to disperse CNTs through the micelle encapsulation mechanism, especially polystyrene (PS) containing copolymers, such as polystyrene-*b*-poly(methacrylic acid) (PS-PMAA),²¹³ polystyrene-*b*-polybutadiene-*b*-polystyrene (PS-PBD-PS),^{212,214,215} polystyrene-*b*-poly(ethylene oxide) (PS-PEO),²¹⁶ polystyrene-*b*-poly(*tert*-butyl acrylate) (PS-PBA),²¹⁷ polystyrene-*b*-polyisoprene (PS-PI),²¹⁸ polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP),²¹⁹ polystyrene-*b*-poly[sodium(2-sulfamate-3-carboxylate)isoprene] (PS-PSCI).^{220,221} Polyethylene oxide blocks are also considered as an effective segment for the CNTs wrapping, and numbers of block copolymers such as poly(ethylene oxide)-*b*-poly(propylene oxide) (PEO-PPO),²¹⁷ poly(methylmethacrylate)-*b*-poly(ethylene oxide) (PMMA-PEO),²¹⁶ poly(ethyleneoxide)-*b*-poly(dimethylsiloxane)-*b*-poly(ethylene oxide) (PEO-PDMS-PEO),^{213,217} poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO),²¹⁷ poly(ethylene oxide)-*b*-poly[2-(*N,N*-dimethylamino)ethyl methacrylate] (PEO-PDEM)²²² have been reported as dispersants (Figure 8). An interesting example of the dispersion with the aid of block copolymers is the PS-P4VP dispersion reported by Shin *et al.*,

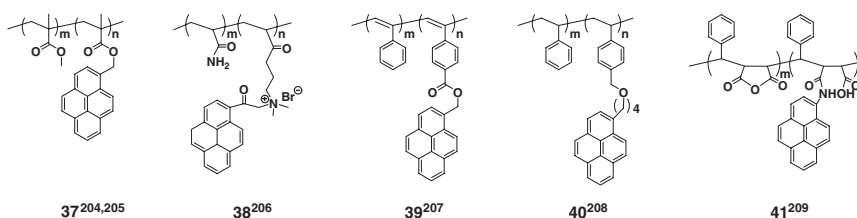


Figure 7. Chemical structures of pyrene-based copolymers for CNTs solubilization.

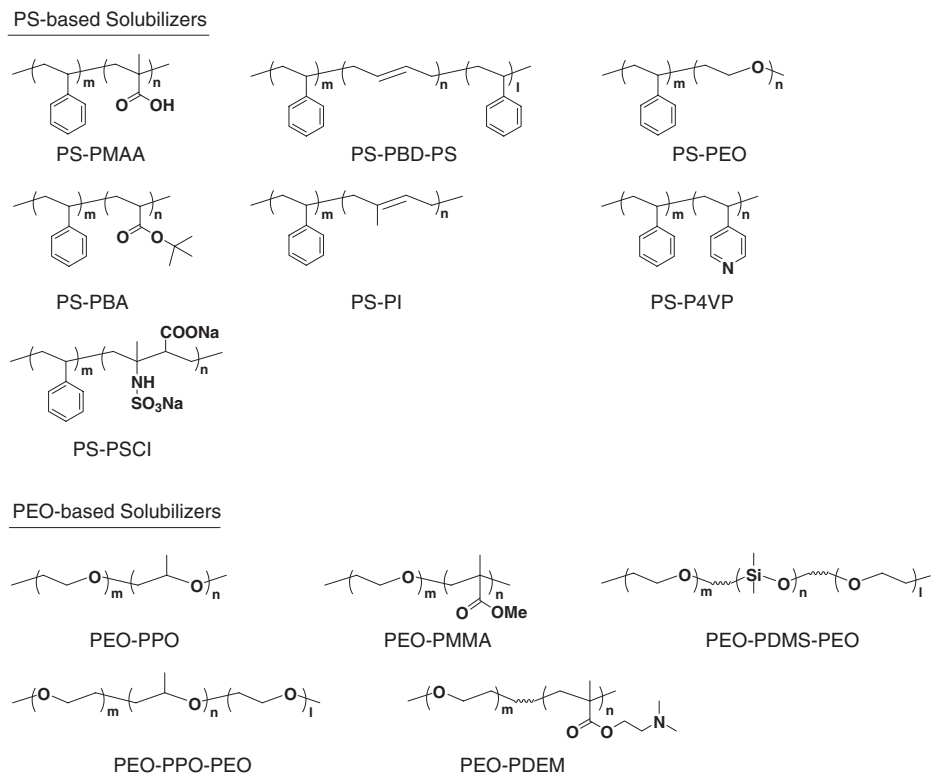


Figure 8. Chemical structures of copolymer-based solubilizers.

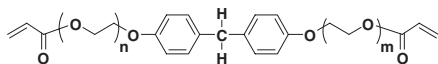


Figure 9. Chemical structure of UV-1 used for the preparation of composites with SWNTs.

where the SWNTs are exfoliated both in polar and non-polar solvents.²¹⁹ TEM observation revealed that the PS block contributes to the dissolution in toluene by exposing the segment outside, while the P4VP formed a shell in an ethanol solution resulting in the stable dissolution of the SWNTs.

A major issue in the preparation of the composite film involves re-aggregation of the CNTs during evaporation of the solvent or cooling of the melt mixture of the composites. Quite recently, we proposed a new strategy for preventing the re-aggregation during film formation.²²³ We dispersed SWNTs into an UV-curable monomer (UV-1 in Figure 9) and successive irradiation in the presence of a photo-initiator yielded a homogeneous black film without any sign of re-aggregation during the film formation. By comparison of the visible-NIR absorption spectra of the composite before and after the photopolymerization (Figure 10), it is clear that the dispersed state retained during the polymerization. Such an immediate immobilization by quick solidification is considered a new methodology for hampering the aggregation of CNTs. By virtue of their fluidic nature and high processability, we successfully fabricate 500-nm-sized patterns of SWNTs composite *via* nanoimprint lithography using PDMS as a stamp (Figure 11).

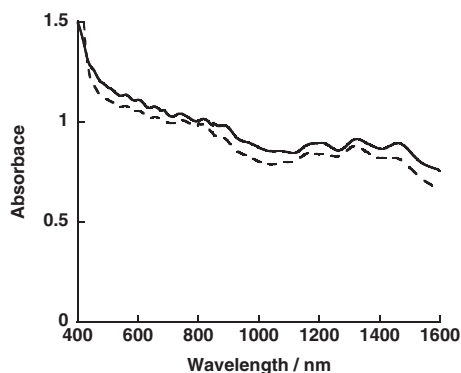


Figure 10. Visible-NIR spectra of UV-1/SWNTs composite before (dotted line) and after (solid line) photopolymerization.

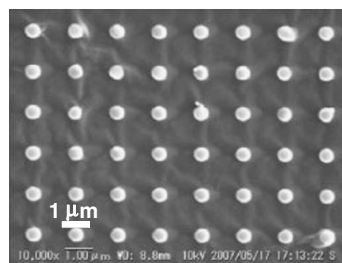


Figure 11. SEM picture of nanoimprinted patterns formed by UV-1/SWNTs composite.

SUMMARY

We summarized the solubilization/dispersion of pristine CNTs based on physical adsorption using dispersant molecules. Wrapping of CNTs by dispersants based on π - π , CH- π and micelle encapsulation of CNTs are considered the typical strategies for CNTs solubilization/dispersion. Individual solubilization of CNTs is necessary for a wide range of science and technology because the preparation of individually dissolved SWNTs is the first step to put CNTs to practical use as well as fundamental studies. The individual solubilization based on physical modification can maintain CNTs intact and is an attractive route for taking advantage of their intrinsic properties.

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