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**Solubilization of single-walled carbon nanotubes by entanglements between them and hyperbranched phenolic polymer**

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## **Abstract**

Hyperbranched phenolic polymer (HBP) was prepared by Lewis acid-catalyzed polycondensation of bifunctional phenolic monomer with trifunctional phenolic monomer. By choosing an appropriate Lewis acid, HBP was successfully obtained. By using physical adsorption of HBP on a single walled carbon nanotube (SWCNT) surface, solubilization of SWCNTs was examined. SWCNTs were soluble with extended branches of HBP in *N,N*-dimethylformamide (DMF) solution, while they were insoluble in a linear phenolic polymer. In the presence of shrinking branches of HBP in tetrahydrofuran, SWCNTs were hardly soluble. Entanglements between extended branches of HBP and SWCNT in DMF solution resulted in high solubility of SWCNTs.

## 1. Introduction

Since the discovery of single-walled carbon nanotubes (SWCNTs), SWCNTs have raised a great deal of scientific, technological and industrial interests because of their unique one-dimensional structure, superior electrical, and mechanical properties.[1-3] However, they are hardly soluble in organic solvents and aqueous media due to formation of bundles between SWCNTs. Therefore, of particular importance is debundling and solubilization of SWCNTs in solvents. For solubilization of SWCNTs in solvents, chemical modification[4-6] and physical adsorption[7-9] of organic molecules on SWCNT surfaces are useful strategies. Soluble SWCNTs in aqueous media were obtained by using  $\pi$ - $\pi$  interaction between SWCNTs and polynuclear aromatic compounds, such as pyrene and naphthalene derivatives.[7,8] Successful simple solubilization of SWCNTs using several types of surfactant micelles was reported by Smalley and coworkers.[9]

Our current interest is solubilization of SWCNTs by physical adsorption of nanometer scale macromolecules of macrocyclic hosts [10-13]. By using macrocyclic hosts such as water-soluble calixarenes[12] and cucurbiturils[13], water-soluble SWCNTs were successfully obtained. Interestingly, SWCNTs were soluble in aqueous media by using large macrocycles. For solubilization of SWCNTs, nano-architecture and cavity size of macrocycles were extremely important. Thus, in this study, we employed nanoscale macromolecular architecture of hyperbranched phenolic polymer (HBP) for solubilization of SWCNTs. Phenolic polymers, which are typically synthesized by polymerization of phenol derivatives with formaldehyde, exhibit excellent thermal-setting, mechanical and electrical insulating properties.[14-16]

Therefore, in this study, for the construction of insulating conducting wire composed of SWCNT as a conducting wire and phenolic polymers as an insulating coating, we tried to solubilize SWCNTs with phenolic polymers. However, by using typical novolak of linear phenolic polymer (LP), solubilization of SWCNTs *via* physical adsorption of phenolic polymers did not occur due to low physical interaction between SWCNT and phenolic polymer (Figure 1a). On the other hand, in the present research, with hyperbranched phenolic polymer (HBP), homogeneous dispersion of SWCNTs was obtained (Figure 1b). For solubilization of SWCNTs using phenolic polymer, hyperbranched architecture was better than liner chain structure. Moreover, it is interesting to note that nanometric structures of HBP depending on the kinds of solvents resulted in solubilization ability of SWCNTs using HBP. To the best of our knowledge, there are few examples of solubilization of SWCNTs by using physical adsorption of hyperbranched polymer[17], while hyperbranched polymer-functionalized carbon nanotubes *via* covalent bond have been reported.[18-21] Detailed studies about relationships between solubility of SWCNTs and macromolecular architecture have been little known and should lead to be developments for novel solubilization methodology of SWCNTs.

(Insert Figure 1 here)

## **2. Experimental**

### **2.1. Materials**

All solvents and reagents were used as supplied. SWCNTs produced by the method of high-pressure decomposition of carbon monoxide (HiPco Process, the length and diameter of pristine SWCNTs are about 20 - 2000 nm and 0.8 - 1.2 nm, respectively) were obtained by Carbon Nanotechnologies, Inc. The HiPco SWCNTs were purified according to previous paper described.[22]

## **2.2. Measurements**

The  $^1\text{H}$  NMR spectra were recorded at 270 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 67.5 MHz with a JEOL-JNM EX270 spectrometer. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on Shodex GPC LF804 by using THF as an eluent at 25 °C at the flow rate of  $1\text{ mL min}^{-1}$  after calibration with the standard polystyrene samples. The average molecular weight and molecular weight distribution were determined by gel permeation chromatography multiangle laser light scattering (GPC-MALLS) with DAWN HELEOS MALLS detector (Wyatt Technology, Santa Barbara, CA). UV-Vis absorption spectra were recorded with a JASCO V-630 spectrophotometer. Tapping mode atomic force microscopy (TM-AFM) was taken on multimode SPA 400 (SEIKO Instruments). Nanoprobe cantilevers (SI-DF20, SEIKO Instruments) were utilized. For the preparation of samples, one drop of very dilute solution of HBP was deposited on freshly cleaved mica surface and removed the drop by wind pressure immediately. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in nitrogen. The samples were dried at 70 °C for 24 h at reduced pressure before the measurements.

## **2.3. Synthesis of 1,3,5-Tribromomethyl-2,4,6-trimethoxybenzene ( $\text{B}_3$ )**

To a solution of paraformaldehyde (10.1 g, 60 mmol) in acetic acid (70 mL), sodium bromide (37.0 g, 0.36 mol) was added. To the mixture, sulfuric acid (10 mL) and 1,3,5-trimethoxybenzene were added dropwise at room temperature. The mixture was stirred for 3 h. Then, the resulting solution was poured into water. The precipitate was collected by filtration and washed with water. Column chromatography (silica gel, 60% CH<sub>2</sub>Cl<sub>2</sub> / 40% hexane) afforded a white solid (B<sub>3</sub>, 16.4 g, 36.7 mmol, yield: 61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz, ppm): δ 4.16 (s, 9H, methoxy group), 4.63 (s, 6H, bromomethyl group). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz, ppm): δ 22.7 (C of methoxy group), 62.4 (C of bromomethyl group), 122.8 (aromatic carbons at methoxy group), 159.6 (aromatic carbons at bromomethyl group). FAB mass m/z = 447 (M<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>15</sub>BrO<sub>3</sub>: C, 32.25; H, 3.38; N, 0.00. Found: C, 31.96; H, 3.33; N 0.00.

#### 2.4. Synthesis of Hyperbranched Phenolic Polymer (HBP)

To a mixture of 3,4,5-trimethoxytoluene (A<sub>2</sub>, 0.68 g, 3.8 mol) and zinc chloride (0.34 g, 2.5 mmol) in dichloromethane (2.5 mL), solution of 1,3,5-tribromomethyl-2,4,6-trimethoxybenzene (B<sub>3</sub>, 1.12 g, 2.5 mol) was added dropwise over 6 h at room temperature. The mixture was stirred at room temperature for 3 h. Then, the solution was poured into methanol and the resulting precipitate was collected by filtration (145.2 mg, yield: 12%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz, ppm): δ 1.74 - 2.23 (br, 6H, methyl group from A<sub>2</sub> unit), 2.92 – 3.60 (br, 9H, methoxy group from B<sub>3</sub> unit), 3.60 - 3.73 (br, 8H, methylene bridge), 3.73 - 4.22 (br, 18H, methoxy group from A<sub>2</sub> unit), 4.39 - 4.49 (br, 2H, terminal bromomethyl group from B<sub>3</sub> unit), 5.95 - 6.22 (br, 1H, terminal aromatic proton from A<sub>2</sub> unit). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz, ppm): δ 14.7 – 16.3 (br, C of methyl group from A<sub>2</sub> unit), 19.3 – 24.2 (br, methylene bridge), 52.0 -

64.7 (br, C of methoxy group), 90.9 – 94.6 (br, C of bromomethyl group from B<sub>3</sub> unit), 114.6 - 160.3 (br, C of phenyl).

## **2.5. Synthesis of Linear Phenolic Polymer (LP)**

To a mixture of 3,4,5-trimethoxytoluene (A<sub>2</sub>, 0.91 g, 5 mmol), paraformaldehyde (0.45 g, 15 mmol) in acetonitrile (5 mL), sulfuric acid (0.5 mL) was slowly added at 0 °C. The reaction mixture was heated at 55 °C for 8 h. Then, the solution was poured into water and the resulting precipitate was collected by filtration. The precipitation was dissolved in THF. The mixture was poured into methanol. The solid thus precipitated was filtered off and dried in a vacuum to yield linear phenolic polymer (LP) as a white solid (2.99 g, yield: 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz, ppm): δ 1.90 - 2.11 (br, 3H, methyl group), 3.40 - 3.58 (br, 6H, methoxy group), 3.73 - 3.86 (br, 2H, methylene bridge), 3.89 – 4.01 (br, 3H, methoxy group). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz, ppm): δ 15.0 – 16.3 (C of methylene bridge), 24.5 – 25.7 (C of methyl group), 59.3 – 62.0 (C of methoxy group), 128.7 -152.3 (C of phenyl).

## **2.6. Solubilization of SWCNTs with Phenolic Polymers**

Typical experimental procedure for solubilization of SWCNTs is as follows. To suspension of SWCNTs (1.0 mg) in solution (5.0 mL), phenolic polymer (20 mg) was added and then the resulting solution was sonicated for 2 h at room temperature. After the sonication, insoluble SWCNTs were removed by centrifugation.



### 3. Results and Discussion

#### 3.1. Synthesis of Hyperbranched Phenolic Polymer (HBP)

For the introduction of branching points into linear phenolic polymers, we designed and synthesized hyperbranched phenolic polymers (HBP) by Lewis acid-catalyzed polycondensation of alternatively reactive monomers (Figure 2).

(Insert Figure 2 here)

Polymerization of 3,4,5-trimethoxytoluene ( $A_2$ ) with 1,3,5-tribromomethyl-2,4,6-trimethoxybenzene ( $B_3$ ) was carried out (Table 1). By using Lewis acids such as aluminium(III) chloride, titanium chloride and iron(III) chloride, obtained products were oligomer and soluble in methanol. On the other hand, in the presence of zinc chloride, polymer was found by reprecipitation into methanol (run 1). Reactivity of bromomethyl group as Lewis base should be good compatibility with zinc chloride as Lewis acid. By polymerization of only  $A_2$  (run 2) or  $B_3$  (run 3) in the presence of zinc chloride, no polymer was obtained, indicating that homopolymerization did not proceed and alternative copolymerization between  $A_2$  and  $B_3$  should occur. In addition, by changing feed ratios of  $A_2$  to  $B_3$ , no polymeric products were obtained. The results indicate that stoichiometric balance of the two monomers ( $A_2$  and  $B_3$ ) is important and 3:2 ( $A_2$ : $B_3$ ) feed ratio is suitable condition for polymerization. Content of  $B_3$  unit in HBP (run 1) measured from  $^1\text{H}$  NMR was 39.2% and calculated value from the feed ratio was 40.0%, respectively, indicating that branching points of  $B_3$

unit was ideally contained in HBP. Molecular weight of HBP (run 1) was determined by GPC (polystyrene standard) and GPC-MALLS. Molecular weight of HBP measured by GPC was smaller than that by GPC-MALLS, strongly suggesting that HBP formed compact conformation. The same trends were observed in the other hyperbranched polymers and dendrimers.[23,24]

(Insert Table 1 here)

### **3.2. Solubilization of SWCNTs with Linear (LP) and Hyperbranched Phenolic Polymer (HBP)**

Solubilization of SWCNTs with HBP *via* physical adsorption was investigated. As a control experiment, linear phenolic polymer with almost similar molecular weight and constituents to HBP (LP,  $M_n = 5,100$ ,  $M_w/M_n = 1.3$ , Figure 1) was employed. Typical solubilization procedure for solubilization of SWCNTs is as follows. To suspension of SWCNTs in solution (5 mL), phenolic polymer (20 mg) was added and then the resulting solution was sonicated for 2 h at room temperature. By using HBP as solubilizer of SWCNTs, SWCNTs were homogeneously dispersed in *N,N*-dimethylformamide (DMF) solution. After the sonication, insoluble SWCNTs were removed by centrifugation. The supernatant using HBP was extremely stable for more than a month (Figure 3a). In contrast, in the presence of LP, SWCNTs were insoluble in DMF even after sonication (Figure 3b). Figure 4 shows UV-Vis spectra of the supernatants after centrifugation. In the region of 500 – 900 nm, typical SWCNT van

Hove singularities were observed in the presence of HBP (Figure 4a), while no absorption bands were found in the presence of LP (Figure 4b). From these data, SWCNTs were soluble in DMF solution with HBP and insoluble with LP. Entanglements between SWCNTs and branches of HBP resulted in high solubility of SWCNTs, whereas SWCNT was hardly entangled with LP (Figure 1). We examined effect of the concentration of HBP on solubility of SWCNTs in DMF. As the concentration of HBP increased, solubility of SWCNTs also increased (Supplementary Data).

(Insert Figures 3 and 4 here)

### **3.3. Solvent Effects on solubility of SWCNTs with HBP**

Solubility of SWCNTs with HBP depending on the kinds of solvents was investigated. As described in above, SWCNTs were soluble in DMF solution with HBP (Figure 3a). In contrast, SWCNTs were hardly soluble in tetrahydrofuran (THF) solution even with HBP (Figure 3c). Typical SWCNT van Hove singularities were found with HBP in DMF (Figure 4a), while the absorption from SWCNTs was not observed with HBP in THF (Figure 4c). From these observations, with HBP as solubilizer, SWCNTs were soluble in DMF but insoluble in THF solutions.

To reveal the solvent effects on solubility of SWCNTs, changes in conformation of HBP depending on the kinds of the solvents were investigated by tapping mode atomic force microscopy (TM-AFM) measurements. To inhibit aggregation of HBP during

solvent evaporation, one drop of very dilute solution of HBP was deposited on freshly cleaved mica surface and removed the drop by wind pressure immediately. In THF solution, particles of HBP were observed (Figure 5a). In contrast, in DMF solution, morphology of HBP was fluffy structures (Figure 5b). Average sizes of HBP particles in THF and fluffy structures of HBP in DMF were found to be 20 nm and 250 nm, respectively. These sizes observed were almost similar to sizes determined from DLS (Supplementary Data), indicating that the structures on mica substrate reflected HBP structures in these solutions. Moreover, HBP in THF showed significant higher height than that in DMF (Figure 5c and 5d, 2.6 vs. 1.4 nm). Flexible HBP in DMF can flatten on the mica surface (Figure 5f), whereas the shrinking HBP particles in THF stand rigidly (Figure 5e). From these data, HBP forms expanded branches in DMF but shrinking structure in THF. Therefore, entanglements between SWCNTs and expanded polymer branches of HBP in DMF easily occurred, while SWCNTs were insoluble with shrinking branches of HBP in THF (Figure 1b).

(Insert Figure 5 here)

### **3.4. AFM Study of SWCNT-HBP Hybrids**

To investigate nanostructure of SWCNTs solubilized by HBP in DMF (SWCNT-HBP hybrids), TM-AFM measurements were carried out. As seen in Figure 6a, nanotubes were observed and free expanded branches of HBP were also found around the tubes. The average size of the tubes was about 2.3 – 2.5 nm (Figure 6b).

Since the average diameter of Hipco SWCNT and height of extended polymer branches of HBP is 0.8 – 1.2 nm[25] and 1.3 – 1.4 nm (Figure 6b), respectively, the nanotube observed is individual SWCNTs (Proposed structure of SWCNT-HBP hybrids was shown in Figure 6c). From the expanded height (Figure 6d) and phase (Figure 6e) images, covering SWCNT surface by HBPs was observed, indicating solubilization of SWCNTs with physical adsorption of HBPs.

(Insert Figure 6 here)

### **3.5. Thermal Property of SWCNT-HBP Hybrids**

Thermal property of SWCNT-HBP hybrids was checked by TGA measurements (Figure 7). To remove free HBP, SWCNT-HBP hybrids were collected by filtration (pore diameter: 0.45  $\mu\text{m}$ ) and washed with DMF repeatedly. The curve of weight loss of SWCNT-HBP hybrids was shifted to high temperature compared to the pristine HBP. Ten weight percentage loss temperature ( $T_{10}$ ) of SWCNT-HBP hybrids and HBP was 363  $^{\circ}\text{C}$  and 335  $^{\circ}\text{C}$ , respectively, indicating that the thermal stability of HBP was improved by hybridization with SWCNT at nanometer level. From char yields of HBP and SWCNT-HBP hybrids, weight percentage of HBP in SWCNT-HBP hybrids was calculated to be ca. 64 wt%.

(Insert Figure 7 here)

#### **4. Conclusions**

We successfully synthesized HBP by choosing an appropriate Lewis acid. By using HBP as solubilizer of SWCNTs, SWCNTs were soluble in DMF. In contrast, in the presence of LP, SWCNTs were insoluble in DMF. It was found that hyperbranched structure of HBP was effective for solubilization of SWCNTs by using phenolic polymers. Moreover, solubility of SWCNTs with HBP was depended on the kinds of solvents. In DMF, expanded branches of HBP were easily stacked to SWCNT surface. In contrast, entanglement of HBP with SWCNT should not occur due to shrinking polymer branches of HBP in THF solution. To the best of our knowledge, revelation of solubilization ability of SWCNTs depending on macromolecular structures and solubilization of SWCNTs with phenolic polymer are the first example. Because HBP exhibits excellent thermal, mechanical and insulating properties, SWCNT-HBP hybrids made from core of SWCNT and shell of HBP should be applied for nano-insulating conducting wire to create nanodevices and nanomachines.

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We thank Prof. Kohshin Takahashi (Kanazawa University) for TM-AFM measurements and Dr. Masa-aki Ozawa (Nissan Chemical Industries, LTD.) for GPC-MALLS measurements. This work was supported by a Grant-in-Aid for Young Scientist

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## **Appendix A. Supplementary Data**

Effect of the concentration of HBP on solubility of SWCNTs (Figure 1S) and size distributions of HBP in THF and DMF by DLS measurements (Figure 2S).

## **References**

- [1] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. *Chem Rev* 2006;106:1105-1136.
- [2] Baughman NR, Zakhidov AA, de Heer WA. Carbon nanotubes-the route toward applications. *Science* 2002;297:787-792.
- [3] Chen J, Hamon MA, Hu H, Chen YS, Rao AM, Eklund PC, et al. Solution properties of single-walled carbon nanotubes. *Science* 1998;282:95-98.
- [4] Hu H, Zhao B, Hamon MA, Kamaras K, Itkis ME, Haddon RC. Sidewall functionalization of single-walled carbon nanotubes by addition of dichlorocarbene. *J Am Chem Soc* 2003;125:14893-14900.
- [5] Holozinger M, Abraham J, Whelan P, Graupner P, Ley L, Hennrich F, et al. functionalization of single-walled carbon nanotubes with (R-)oxycarbonyl nitrenes. *J Am Chem Soc* 2003;125:8566-8580.

- [6] Hamon MA, Chen J, Hu H, Chen YS, Itkis ME, Rao AM, et al. Dissolution of single-walled carbon nanotubes. *Adv Mater* 1999;11:834-840.
- [7] Nakashima N, Tomonari Y, Murakami H, Yoshinaga K. Water-soluble single-walled carbon nanotubes via noncovalent sidewall-functionalization with a pyrene-carrying ammonium ion. *Chem Lett* 2002;638-639.
- [8] Nakashima N, Tanaka Y, Tomonari Y, Murakami H, Kataura H, Sakaue T, et al. Helical superstructures of fullerene peapods and empty single-walled carbon nanotubes formed in water. *J Phys Chem B* 2005;109:13076-13082.
- [9] Moore VC, Strano MS, Haroz RH, Hauge RH, Smalley RE, Schmidt J, et al. Individually suspended single-walled carbon nanotubes in various surfactants. *Nano Lett* 2003;3:1379-1382.
- [10] Ogoshi T, Takashima Y, Yamaguchi H, Harada A. Chemically-responsive sol-gel transition of supramolecular single-walled carbon nanotubes (SWNTs) hydrogel made by hybrids of SWNTs and cyclodextrins. *J Am Chem Soc* 2007;129:4878-4879.
- [11] Ogoshi T, Yamagishi T, Nakamoto Y, Harada A. Water soluble single-walled carbon nanotubes using inclusion complex of cyclodextrin with an adamantane derivative. *Chem Lett* 2007;36:1026-1027.
- [12] Ogoshi T, Yamagishi T, Nakamoto Y. Supramolecular single-walled carbon nanotubes (SWCNTs) network polymer made by hybrids of SWCNTs and water-soluble calix[8]arenes. *Chem Commun* 2007;4776-4778.



- [13] Ogoshi T, Inagaki A, Yamagishi T, Nakamoto Y. Defection-selective solubilization and chemically-responsive solubility switching of single-walled carbon nanotubes with cucurbit[7]uril. *Chem Commun* 2008;2245-2247.
- [14] Yamagishi T, Nomoto M, Yamashita S, Yamazaki T, Nakamoto Y, Ishida S. Characterization of high molecular weight novolak. *Macromol Chem Phys* 1998;199:423-428.
- [15] Fahrenholtz SR, Kwei TK. Compatibility of polymer mixtures containing novolac resins. *Macromolecules* 1981;14:1076-1079.
- [16] Yang TP, Pearce EM, Kwei TK, Yang NL. Complexation of poly(N,N-dimethylacrylamide) and phenol-formaldehyde resins. *Macromolecules* 1989;22:1813-1818.
- [17] Star A, Stoddart JF. Dispersion and solubilization of single-walled carbon nanotubes with a hyperbranched polymer. *Macromolecules* 2002;35:7516-7520.
- [18] Choi JY, Oh SJ, Lee HJ, Wang DH, Tan LS, Baek JB. In-situ grafting of hyperbranched poly(ether ketone)s onto multiwalled carbon nanotubes via the A3 + B2 approach. *Macromolecules* 2007;40:4474-4480.
- [19] Gao C, Muthukrishnan S, Li W, Yuan J, Xu Y, Muller AHE. Linear and hyperbranched glycopolymer-functionalized carbon nanotubes: synthesis, kinetics, and characterization. *Macromolecules* 2007;40:1803-1815.

- [20] Xu Y, Gao C, Kong H, Yan D, Jin YZ, Watts PCP. Growing multihydroxyl hyperbranched polymers on the surfaces of carbon nanotubes by in situ ring-opening polymerization. *Macromolecules* 2004;37:8846-8853.
- [21] Campidelli S, Sooambar C, Lozano DE, Ehli C, Guldi DM, Prato M. Dendrimer-functionalized single-wall carbon nanotubes: synthesis, characterization, and photoinduced electron transfer. *J Am Chem Soc* 2006;128:12544-12552.
- [22] Zhou W, Ooi YH, Russo R, Papanek P, Luzzi DE, Fischer JE, et al. Structural characterization and diameter-dependent oxidative stability of single wall carbon nanotubes synthesized by the catalytic decomposition of CO. *Chem Phys Lett* 2001;350:6-14.
- [23] Chen G, Huynh D, Felgner PL, Guan Z. Tandem chain walking polymerization and atom transfer radical polymerization for efficient synthesis of dendritic nanoparticles for bioconjugation. *J Am Chem Soc* 2006;128:4298-4302.
- [24] Xue L, Agarwal US, Zhang M, Staal BBP, Muller AHE, Bailly CME, et al. Synthesis and direct topology visualization of high-molecular-weight star PMMA. *Macromolecules* 2005;38:2093-2100.
- [25] Nikolaev P, Bronikowski M, Bradley R, Rohmund F, Colbert D, Smith K, et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem Phys Lett* 1999;313:91-97.

## **Lists of Captions for Figures and Tables**

**Figure 1.** Solubilization of SWCNTs using (a) linear phenolic polymer (LP) and (b) hyperbranched phenolic polymer (HBP).

**Figure 2.** Synthesis of HBP.

**Figure 3.** Photos of SWCNTs supernatants with (a) HBP in DMF, (b) LP in DMF and (c) HBP in THF after sonication.

**Figure 4.** UV-Vis spectra of SWCNTs supernatants with (a) HBP in DMF, (b) LP in DMF and (c) HBP in THF after sonication.

**Figure 5.** TM-AFM height images of (a) the HBP particles from THF and (b) the fluffy structures of HBP from DMF. (c) Height profile along dash line in (a). (d) Height profile along dash line in (b). (e) Model showing standing of HBP on mica surface. (f) Model showing flattening of HBP on mica surface.

**Figure 6.** (a) TM-AFM height image of SWCNTs solubilized by extended HBP. (b) Height profile along dash line in (a). (c) Proposed structure of hybrids composed of HBP and SWCNTs on mica surface. The extended TM-AFM (d) height and (e) phase images in box area in (a).

**Figure 7.** TGA thermograms of (a) HBP and (b) SWCNT-HBP hybrids under nitrogen.

**Table 1.** Synthesis of hyperbranched phenolic polymer (HBP)

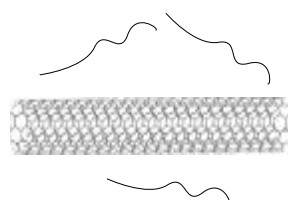
**Table 1.** Synthesis of hyperbranched phenolic polymer (HBP)

run	<b>A<sub>2</sub></b> (mmol)	<b>B<sub>3</sub></b> (mmol)	feed ratio <b>A<sub>2</sub> : B<sub>3</sub></b>	catalyst	yield (%)	$M_n^a$	$M_w/M_n^a$	$M_n^b$	$M_w/M_n^b$
1	3.8	2.5	3 : 2	ZnCl <sub>2</sub>	12	2,400	1.6	3,400	1.2
2	3.8	-	3 : 0	ZnCl <sub>2</sub>	no polymer	-	-	-	-
3	-	2.5	0 : 2	ZnCl <sub>2</sub>	no polymer	-	-	-	-

<sup>a</sup> Measured by GPC (Polystyrene standard).

<sup>b</sup> Measured by GPC-MALLS.

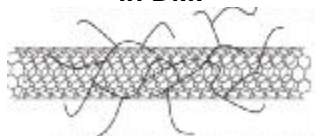
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***Weak  
Entanglement***

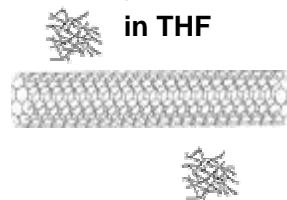
**(b) Using HBP**

***Expanded Branches  
in DMF***

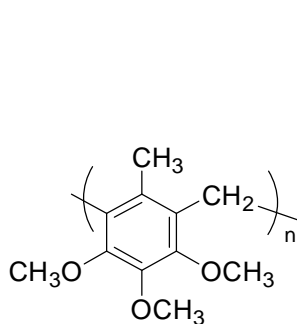


***Weak Binding***

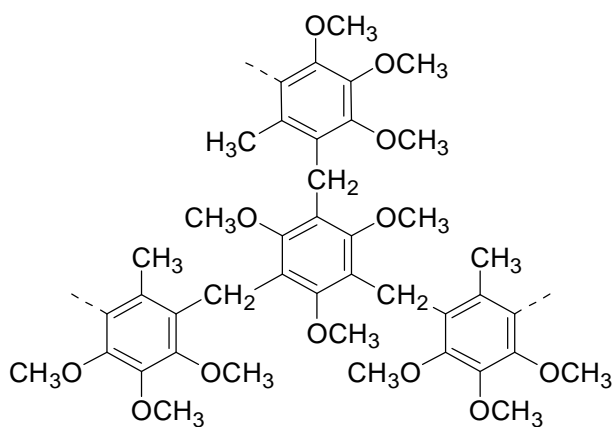
***Shrinking Branches  
in THF***



***Entanglement***

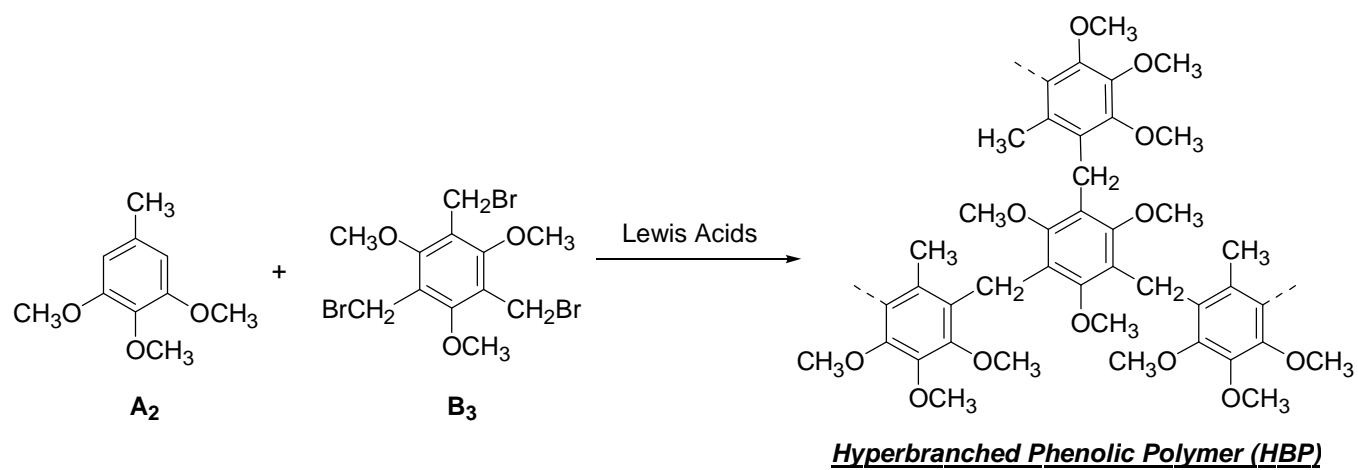


Linear Phenolic Polymer (LP)



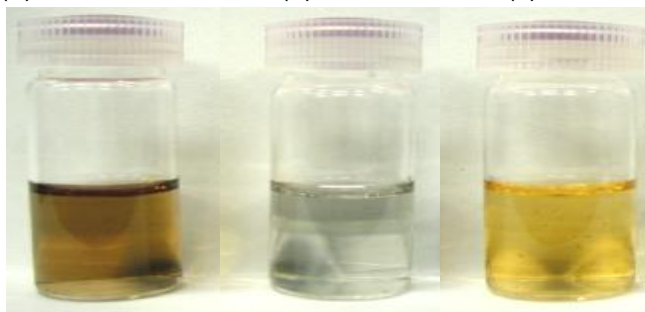
Hyperbranched Phenolic Polymer (HBP)

**Figure 1.** Solubilization of SWCNTs using (a) linear phenolic polymer (LP) and (b) hyperbranched phenolic polymer (HBP)

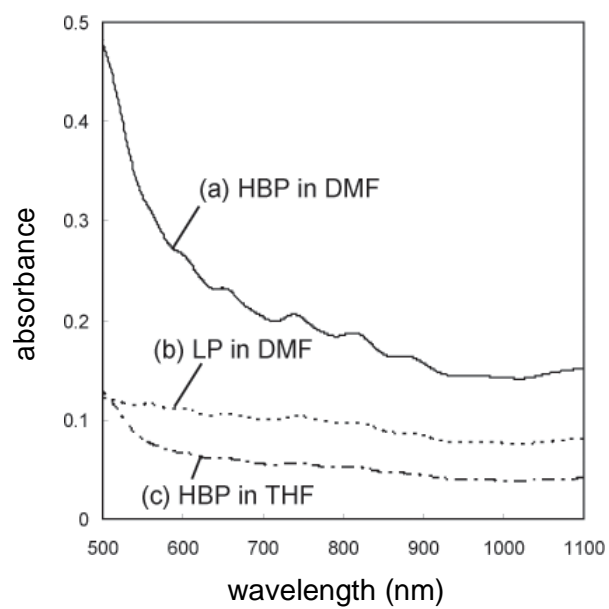


**Figure 2.** Synthesis of HBP

(a) HBP in DMF      (b) LP in DMF      (c) HBP in THF

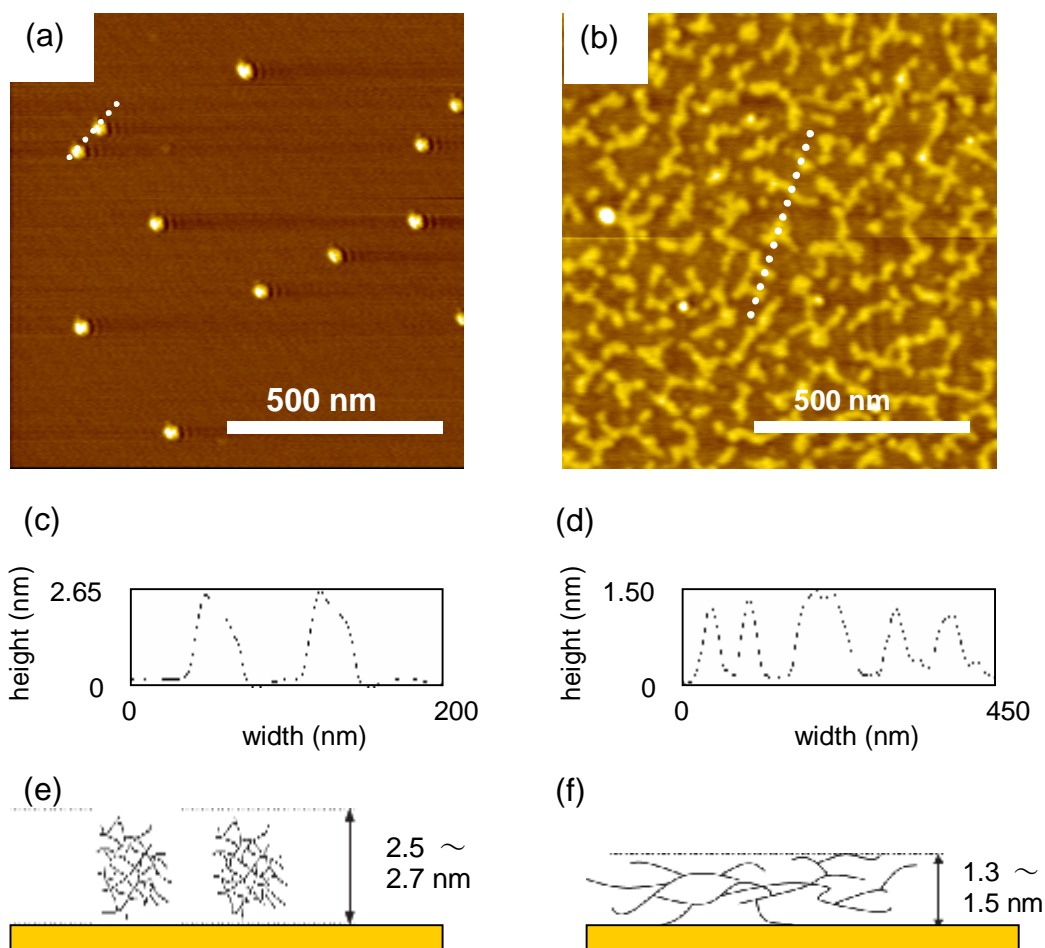


**Figure 3.** Photos of SWCNTs supernatants with (a) HBP in DMF, (b) LP in DMF and (c) HBP in THF after sonication.

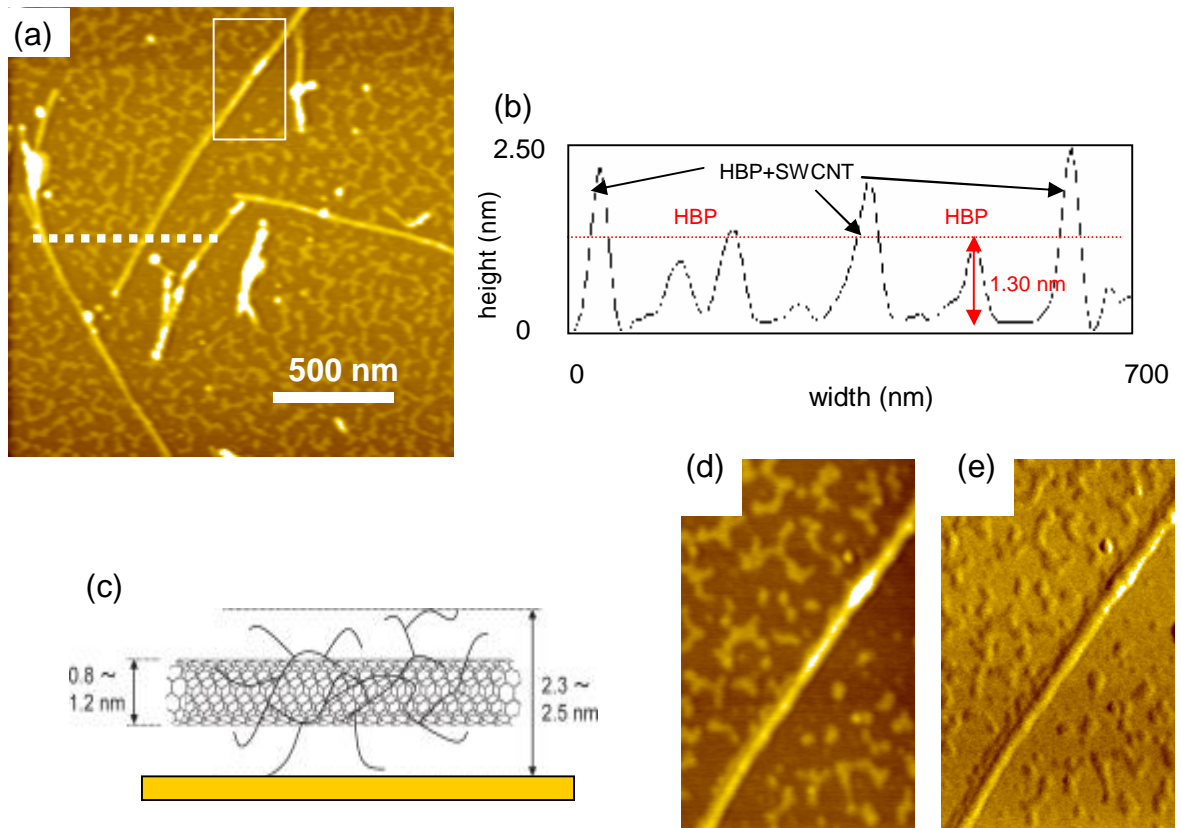


**Figure 4.** UV-Vis spectra of SWCNTs supernatants with (a) HBP in DMF, (b) LP in DMF and (c) HBP in THF after sonication.

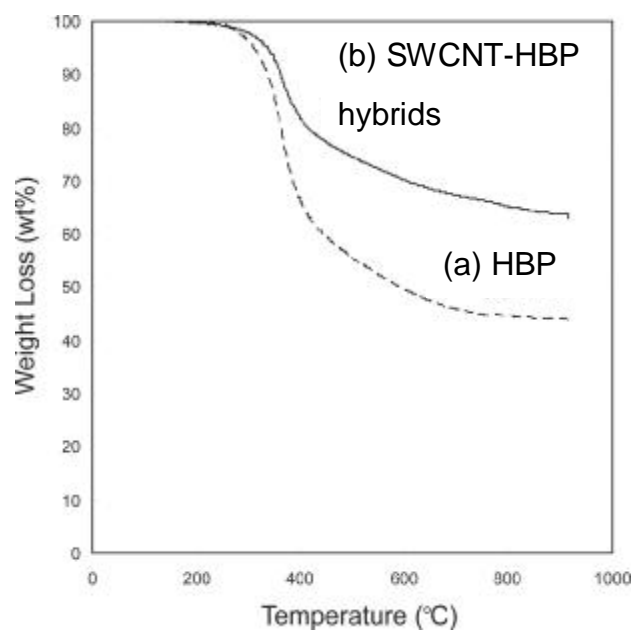




**Figure 5.** TM-AFM height images of (a) the HBP particles from THF and (b) the fluffy structures of HBP from DMF. (c) Height profile along dash line in (a). (d) Height profile along dash line in (b). (e) Model showing standing of HBP on mica surface. (f) Model showing flattening of HBP on mica surface.



**Figure 6.** (a) TM-AFM height image of SWCNTs solubilized by extended HBP. (b) Height profile along dash line in (a). (c) Proposed structure of hybrids composed of HBP and SWCNTs on mica surface. The extended TM-AFM (d) height and (e) phase images in box area in (a).



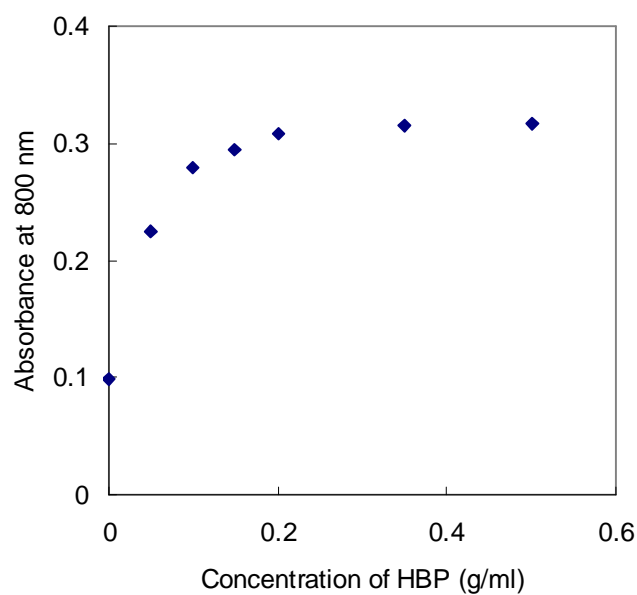
**Figure 7.** TGA thermograms of (a) HBP and (b) SWCNT-HBP hybrids under nitrogen.

## Supplementary Data

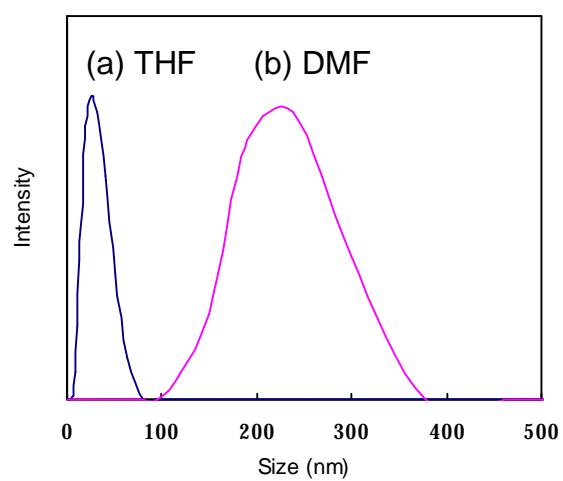
### **Solubilization of single-walled carbon nanotubes by entanglements between them and hyperbranched phenolic polymer**

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**Figure 1S.** Absorbance at 800 nm from dispersed SWCNTs in DMF solution vs. concentration of HBP used.



**Figure 2S.** Size distributions obtained by dynamic light scattering: HBP in (a) THF and (b) DMF.