

Polythiophene-graft-PMMA as a Dispersing Agent for Multi-Walled Carbon Nanotubes in Organic Solvent

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Introduction

Since their discovery,¹ carbon nanotubes (CNTs) with remarkable properties have attracted enormous interest from both academia and industry due to their potential applications in various fields such as field emission devices,²⁻⁴ electrochemical devices,⁵⁻⁷ and polymer composites.⁸⁻¹⁰ However, as-produced CNTs are insoluble in most of organic solvents and aqueous media, since CNTs self-assemble in aggregated bundles where individual CNTs are held together by van der Waals attraction. Thus, the poor solubility of CNTs in solvents has imposed many limitations on their potential applications. Therefore, much effort on improving the solubility of CNTs in solvents has recently been made, which is mainly based on covalent functionalization of the surface of CNTs.¹¹⁻¹⁵ Although this approach is very effective to improve the solubility of CNTs in some organic solvents, it inevitably requires complicated chemical reactions. Furthermore, it usually destroys the π -electron system of CNTs, which very often results in detrimental effect on the intrinsic properties of CNTs. As an alternative, non-covalent functionalization which is more facile approach has recently been used to improve the solubility of CNTs in common organic solvents, where the surface of CNTs is functionalized with various polymeric dispersing agents via π - π interaction or van der Waals interaction.¹⁶⁻²⁹ In particular, the use of conjugated polymers as a dispersing agent for CNTs have recently attracted much attention owing to their ability to strongly adsorb on the surface of CNTs via π - π interaction.²³⁻³¹ However, development of new dispersing agents must be pursued for better and effective dispersion of MWCNTs.

In this study, a graft copolymer (P3HT-g-PMMA) composed of poly(3-hexylthiophene) (P3HT) backbone and poly(methyl methacrylate) (PMMA) graft was synthesized and used as an effective dispersing agent for multi-walled carbon nanotube (MWCNT) in organic solvent. Particularly, we investi-

gate the effect of the graft density of PMMA in P3HT-g-PMMA on the capability to disperse and stabilize the pristine MWCNT in organic solvent. For this purpose, we first synthesize two P3HT-g-PMMA with different graft density of PMMA and then the dispersion capability of these two P3HT-g-PMMA for pristine MWCNT is compared and discussed.

Experimental

MWCNT with a diameter range of 25-70 nm was supplied from Jeio Co. and used as received. The purity of MWCNT used in this study was 92.5%.

Figure 1 shows the chemical structure of P3HT-g-PMMA. The overall synthesis route to P3HT-g-PMMA was described in our previous study in detail.³¹ The molecular characteristics of two P3HT-g-PMMA synthesized in this study are listed in Table I.

The suspension of MWCNT and P3HT-g-PMMA (C1-MWCNT and C2-MWCNT) was prepared as follows: 0.3 mg of C1 (or C2) was added to a solution containing 0.3 mg of MWCNT and 20 mL of toluene, and then the suspension was sonicated in a low-power and high frequency bath sonicator.

The dispersion state of MWCNT in C1-MWCNT and C2-MWCNT was examined using a JEOL-JEM 1010 transmission electron microscopy (TEM), operated at an accelerating voltage of 100 kV.

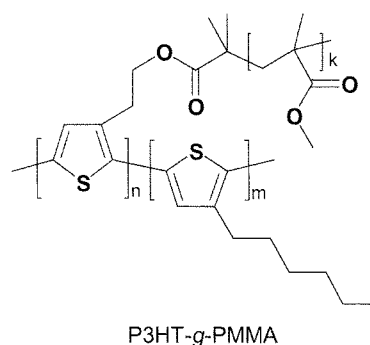


Figure 1. The chemical structure of P3HT-g-PMMA.

Table I. Molecular Characteristics of P3HT-g-PMMA

| Samples | M_n of Polythiophene Backbone (g/mol) ^a | m/n ^b | Number of PMMA Graft per Chain | DP of PMMA ^c |
|---------|--|------------------|--------------------------------|-------------------------|
| C1 | 26,000 | 3 | 33 | 30 |
| C2 | 24,000 | 15 | 8 | 110 |

^aDetermined by gel permeation chromatography.

^bThe molar ratio of two monomeric units in polythiophene backbone.

^cDetermined by ¹H NMR.

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Results and Discussion

The molecular weights of two polythiophene backbones of P3HT-*g*-PMMA as measured by gel permeation chromatography were 2.6×10^4 and 2.4×10^4 g/mol, respectively. Analysis of ^1H NMR spectra of two polythiophene backbones revealed that the molar ratios (*m/n* in Figure 1) of two monomeric units were 3 and 15, respectively. Consequently, two polythiophenes with similar molecular weight but different molar ratio of two monomeric units were synthesized. MMA was graft copolymerized onto two polythiophene backbones via atom transfer radical polymerization (ATRP). The degree of polymerization (DP) of PMMA graft was controlled for two P3HT-*g*-PMMA to have nearly equal total mass of PMMA (see Table I).

To evaluate the capability of C1 and C2 to disperse MWCNT in toluene, the C1-MWCNT (or C2-MWCNT) suspension is sonicated for 1 h. For comparison, MWCNT suspension without the addition of dispersing agent is also prepared under the same experimental condition. When MWCNT, C1-MWCNT, and C2-MWCNT suspensions stand for 3 days after sonication for 1 h, as shown in Figure 2, MWCNTs in C1-MWCNT and C2-MWCNT suspensions have not been precipitated into the bottom of suspensions during still-standing of 3 days, indicating formation of the stable suspension, whereas MWCNTs in the MWCNT suspension precipitate immediately after sonication stops and the precipitation is completed within 30 min. This demonstrates that C1 and C2 act as an effective dispersing agent for MWCNT. The effectiveness of C1 and C2 as a dispersing agent for pristine MWCNT arises from the π - π interaction between polythiophene backbone of dispersing agent and the surface of MWCNT, as shown in Figure 3. Our recent report has also shown that there exists a strong π - π interaction between polythiophene backbone and MWCNT.³¹ It should be noted here that although toluene is used as a solvent to disperse and stabilize MWCNT in this study, it is

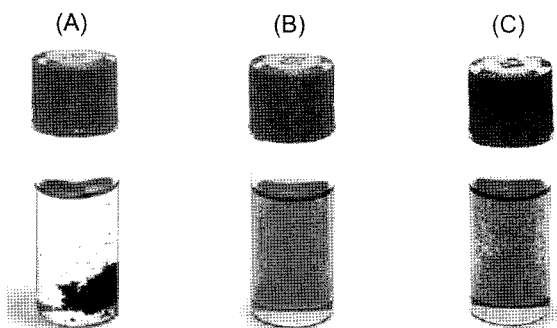


Figure 2. The photographs of (A) MWCNT, (B) C1-MWCNT, and (C) C2-MWCNT suspensions in toluene. All suspensions contain the same amount of MWCNT (0.3 mg) and dispersing agent (0.3 mg) in toluene of 20 mL. The photograph is taken from the suspensions still-standing for 3 days after sonication.

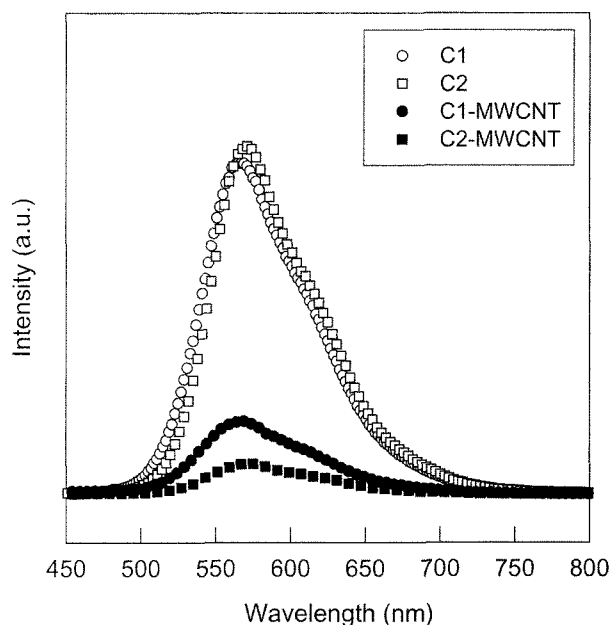


Figure 3. Fluorescence emission spectra of dispersing agent (C1 and C2), C1-MWCNT, and C2-MWCNT suspensions. For measurement of fluorescence emission spectra, 0.3 mg of dispersing agent and a mixture of 0.3 mg of dispersing agent and 0.3 mg of MWCNT are dissolved in 20 mL of toluene, and then they are sonicated for 1 h.

easily expected that the use of any other organic solvent such as ethyl acetate, chloroform and acetone, which can dissolve PMMA graft of P3HT-*g*-PMMA, leads to the similar result.

Figure 4 compares the suspensions of C1-MWCNT and C2-MWCNT in toluene sonicated for 10 min, where the samples for TEM observation are prepared by depositing droplets of the C1-MWCNT and C2-MWCNT suspensions onto carbon-coated copper grids. Figure 4(A) clearly shows that some MWCNTs in C1-MWCNT suspension are still entangled and/or aggregated into the bundle, while the entanglement and/or aggregation of MWCNTs are not

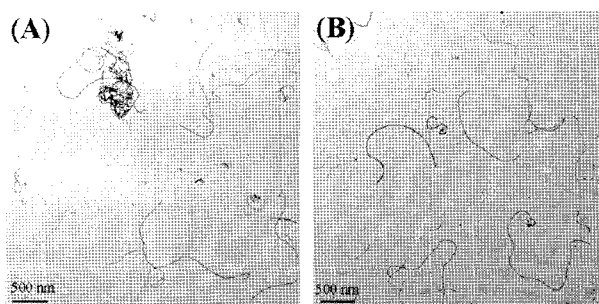


Figure 4. TEM images for (A) C1-MWCNT and (B) C2-MWCNT suspensions sonicated for 10 min. Both suspensions contain the same amount of MWCNT (0.3 mg) and dispersing agent (0.3 mg) in toluene of 20 mL.

observed in C2-MWCNT suspension, as shown in Figure 4(B). This result indicates that the C2 dispersing agent with lower graft density and higher DP of PMMA is more effective and thus requires less sonication time to separate and/or disperse the individual MWCNTs from their bundles than the C1 dispersing agent with higher graft density and lower DP of PMMA.

The long-term stability of C1-MWCNT and C2-MWCNT suspensions is also investigated by observing the TEM images for the suspensions still-standing for several days. For the TEM observation, the C1-MWCNT and C2-MWCNT suspensions are first sonicated for 1 h, and then TEM images are taken from the suspensions still-standing for 1 and 2 week, as shown in Figures 5(A) and 5(B), respectively. The TEM images (Figure 5(A)) of C1-MWCNT suspension clearly show that MWCNTs are well-separated and dispersed in C1-MWCNT suspension still-standing for 1 week without forming aggregated bundles, while some aggregated bundles are observed in the C2-MWCNT suspension still-standing for 1 week, as can be seen in Figure 5(B). The formation of aggregated bundles observed in the C2-MWCNT suspension becomes more severe as the still-standing time increases, as shown in Figure 5(B). Although some aggregated bundles are also observed in the C1-MWCNT suspension still-standing for 2 week, the extent of aggregation observed in the C1-MWCNT suspension is very low as compared to that observed in the C2-MWCNT suspension, indicating that the long-term stability of C1-MWCNT suspension is better than that of C2-MWCNT suspension.

Consequently, the integration of TEM results in Figures 4 and 5 lead us to conclude that the C1 dispersing agent is less effective to separate individual MWCNTs from their aggregated bundles than the C2 dispersing agent, but the C1 dispersing agent stabilizes more effectively individual MWCNTs for long term after aggregated bundles are separated into individual MWCNTs. One possible explanation for this result is that the C1 dispersing agent with higher graft density of PMMA is expected to require more conformational energy to wrap the surface of MWCNT than the C2 dispersing agent with lower graft density, because a large number of graft site may prohibit polythiophene backbone from chain torsion required for wrapping. As a result, the C1 dispersing agent becomes less effective for wrapping the surface of MWCNT. In the same reason, the C1 dispersing agent is also expected to require more energy to unwrap the surface of MWCNT than the C2 dispersing agent, since the wrapping/unwrapping is an equilibrium process. Therefore, unwrapping the C1 dispersing agent from the surface of MWCNT is not expected to occur readily after the C1 wraps MWCNT, which may give better long term stability for MWCNTs suspension. In short, the C2 is kinetically favorable for dispersion of MWCNTs whereas the C2 is thermodynamically favorable for dispersion of MWCNTs.

Conclusions

We investigate the effect of the graft density of PMMA in P3HT-g-PMMA on the capability to disperse pristine MWCNT

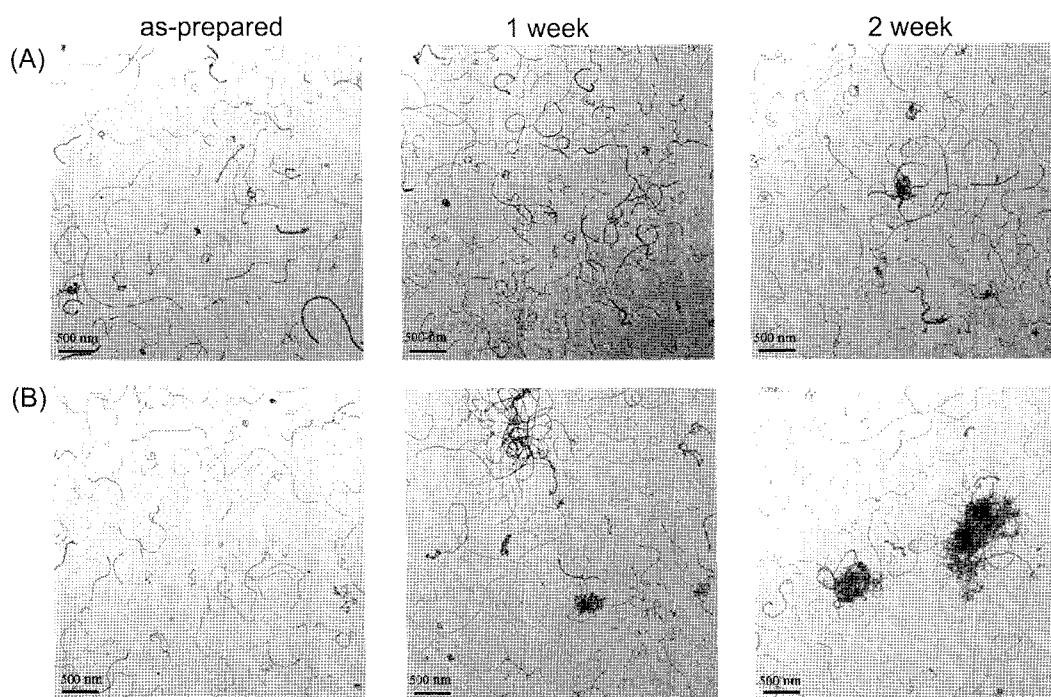


Figure 5. TEM images for (A) C1-MWCNT and (B) C2-MWCNT suspensions still-standing for 1 and 2 week, respectively. Both suspensions contain the same amount of MWCNT (0.3 mg) and dispersing agent (0.3 mg) in toluene of 20 mL.

in organic solvent. TEM images taken from the suspension sonicated for 10 min clearly show that the C2 dispersing agent with lower graft density and higher DP of PMMA graft separates and disperses more effectively MWCNTs from their bundles than C1. On the other hand, the long-term stability of C1-MWCNT suspension is better than that of C2-MWCNT suspension after MWCNTs are separated from their aggregated bundles. This indicates that the C2 is kinetically favorable for dispersion of MWCNTs whereas the C2 is thermodynamically favorable for dispersion of MWCNTs.

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References

- (1) S. Iijima, *Nature*, **354**, 56 (1991).
- (2) R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, *Science*, **297**, 787 (2002).
- (3) C. V. Nguyen, C. So, R. M. Stevens, Y. Li, L. Delziet, and P. Sarrazin, *J. Phys. Chem. B*, **108**, 2816 (2004).
- (4) Y. C. Kim, K. H. Sohn, Y. M. Cho, and E. H. Yoo, *Appl. Phys. Lett.*, **84**, 5350 (2004).
- (5) J. Wang, R. P. Deo, P. Poulin, and M. Mangey, *J. Am. Chem. Soc.*, **125**, 14706 (2003).
- (6) J. Wang and M. Musameh, *Anal. Chem.*, **75**, 2075 (2003).
- (7) M. Zhang and W. Gorski, *Anal. Chem.*, **77**, 3960 (2005).
- (8) H. Zengin, W. Zhou, J. Jin, R. Czerw, D. W. Smith, and L. Echegoyen, *Adv. Mater.*, **14**, 1480 (2002).
- (9) N. Saran, K. Parikh, D. S. Suh, E. Munoz, H. Kolla, and S. K. Manohar, *J. Am. Chem. Soc.*, **126**, 4462 (2004).
- (10) O. Regev, P. N. B. Elkati, J. Loos, and C. E. Koning, *Adv. Mater.*, **16**, 248 (2004).
- (11) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, and P. C. Eklund, *Science*, **282**, 95 (1998).
- (12) C. A. Dyke and J. M. Tour, *Chem. Eur. J.*, **10**, 813 (2004).
- (13) C. A. Dyke and J. M. Tour, *J. Am. Chem. Soc.*, **125**, 1156 (2003).
- (14) J. L. Bahr, J. P. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, and J. M. Tour, *J. Am. Chem. Soc.*, **123**, 6536 (2001).
- (15) G. Xu, W. T. Wu, Y. Wang, W. Pang, Q. Zhu, P. Wang, and Y. You, *Polymer*, **47**, 5909 (2006).
- (16) N. Sluzarenko, B. Heurtefeu, M. Maugey, C. Zakri, P. Poulin, and S. Lecommandoux, *Carbon*, **44**, 3207 (2006).
- (17) G. J. Bahun, C. Wang, and A. Adronov, *J. Polym. Sci. Polym. Chem.*, **44**, 1941 (2006).
- (18) R. J. Chen, Y. Zhang, D. Wang, and H. Dai, *J. Am. Chem. Soc.*, **123**, 3838 (2001).
- (19) R. Shvartzman-Cohen, Y. Levi-Kalishman, E. Nativ-Roth, and R. Yerushalmi-Rozen, *Langmuir*, **20**, 6085 (2004).
- (20) X. Lou, R. Daussin, S. Cuenot, A. S. Duwez, C. Pagnouille, and C. Detrembleur, *Chem. Mater.*, **16**, 4005 (2004).
- (21) P. Petrov, F. Stassin, C. Pagnouille, and R. Jérôme, *Chem. Comm.*, 2904 (2003).
- (22) J. Sung, J. M. Park, U. H. Choi, J. Huh, B. Jung, B. G. Min, C. H. Ahn, and C. Park, *Macromol. Rapid Commun.*, **28**, 176 (2007).
- (23) A. Star and J. F. Stoddart, *Macromolecules*, **35**, 7516 (2002).
- (24) A. B. Dalton, C. Stephan, J. N. Coleman, B. McCarthy, P. M. Ajayan, and S. Lefrant, *J. Phys. Chem. B*, **104**, 10012 (2000).
- (25) A. Star, Y. Liu, K. Grant, L. Ridvan, F. J. Stoddart, D. Steuerman, M. R. Diehl, A. Boukai, and J. R. Heath, *Macromolecules*, **36**, 553 (2003).
- (26) A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S. W. Chung, H. Choi, and J. R. Heath, *Angew. Chem. Int. Ed.*, **40**, 1721 (2001).
- (27) D. W. Steuerman, A. Star, R. Narizzano, H. Choi, R. S. Ries, C. Nicolini, J. F. Stoddart, and J. R. Heath, *J. Phys. Chem. B*, **106**, 3124 (2002).
- (28) J. Chen, H. Y. Liu, W. A. Weimer, M. D. Halls, D. H. Waldeck, and G. C. Walker, *J. Am. Chem. Soc.*, **124**, 9034 (2002).
- (29) Z. Tang and H. Xu, *Macromolecules*, **32**, 2569 (1999).
- (30) J. U. Lee, J. Huh, K. H. Kim, C. Park, and W. H. Jo, *Carbon*, **45**, 1051 (2007).
- (31) K. H. Kim and W. H. Jo, *Macromolecules*, **40**, 3708 (2007).