Spectroscopic Evaluation of the Length of Poly(ethylene glycol) Covalently Attached to Multiwalled Carbon Nanotubes

Satoshi Kubota,[1] Takafumi Maruyama,[1] Hiromasa Nishikiori,[1]
Nobuaki Tanaka,[1] Morinobu Endo,[2] and Tsuneo Fujii*[1]
[1]*Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University,*
4-17-1 Wakasato, Nagano 380-8553
[2]*Department of Electrical and Electronic Engineering, Faculty of Engineering, Shinshu University,*
4-17-1 Wakasato, Nagano 380-8553

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Multiwalled carbon nanotubes (MWNTs) were covalently functionalized by poly(ethylene glycol) (PEG) of different molecular weights. The lengths of the PEG on each sample were evaluated using 1-naphthol as a fluorescence probe. The intensity of ion-pair fluorescence of the 1-naphthol increased with the length of the attached PEG due to interaction between the 1-naphthol and ether groups of the PEG. This increase indicated that fluorescence measurement using 1-naphthol is an excellent tool to evaluate the length of PEG on the MWNTs.

Carbon nanotubes (CNTs) have attracted much attention due to their unique properties.[1,2] These properties of the CNTs provide potential applications in a significant number of fields.[3,4] Recently, research on CNT-based drug delivery vehicles for the transport of therapeutics has been noteworthy.[5,6] However, due to the hydrophobic surface and highly nonspecific uptake by biological species of pristine CNTs, modifications of the CNT surfaces by poly(ethylene glycol) (PEG) are preferred.[5,6] Furthermore, the functionalization by longer PEG chains enables the CNTs to enhance their ability to block any nonspecific uptake by a cell.

It is important to evaluate the length of the PEG attached to the CNTs, because the PEG is hydrolyzed in a strong acid or basic environment and fragmented by OH radicals.[7] In this letter, we report the evaluation of the length of PEG attached to multiwalled carbon nanotubes (MWNTs) by the following two spectroscopic measurements: One is UV–vis absorption measurement of various PEG-modified MWNTs. The other is fluorescence measurement using 1-naphthol which emits the original fluorescence from excited-state charge-transfer species in the hydrogen-bonded complex.[8] The reason for using the MWNTs as a substrate is that they have high commercial viability due to the suitability of mass production.

MWNTs (ILJIN Nanotech CM-95, diameter 10–30 nm) were treated in a mixture of concentrated sulfuric acid and nitric acid with ultrasonication for 48 h in order to introduce the carboxyl groups (MWNT-COOH). The PEG-modified MWNTs were prepared in accordance with the following procedure, and a detailed procedure is described elsewhere.[9] In order to convert the MWNT-COOH into MWNT-COCl, MWNT-COOH was treated in $SOCl_2$ at 343 K for 24 h. The MWNT-COCl in liquid PEG ($M_w = 400$) or solid PEG ($M_w = 4000, 20000$) was dissolved in a benzene/THF solvent mixture (v/v = 3/1), then ultrasonicated at 343 K for 72 h. The samples obtained by the reaction of MWNT-COCl with the PEGs of $M_w = 400$, 4000, and 20000 were labeled MWNT-P400, MWNT-P4000, and MWNT-P20000, respectively.

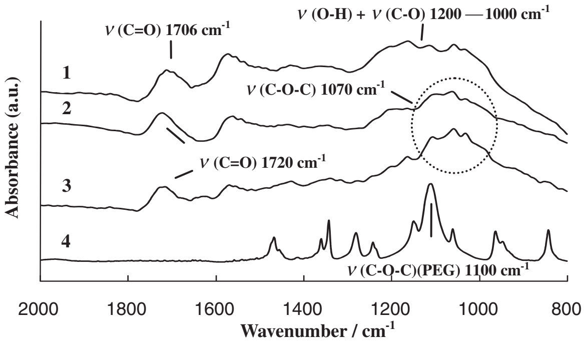

Figure 1. FT-IR speactra of (1) MWNT-COOH, (2) MWNT-P400, (3) MWNT-P20000, and (4) PEG4000.

The prepared MWNT samples (0.2 mg) were individually dispersed in an aqueous solution of 1-naphthol (10 mL, 3.0×10^{-4} mol dm^{-3}) by mild ultrasonication. The resulting suspensions were centrifuged to remove any precipitates. The absorption and fluorescence spectra of the resulting supernatants were then measured. The pH of the all supernatants was ca. 6.

We first characterized the surface chemical species of the MWNT-COOH and the PEG-modified MWNTs. Figure 1 shows FT-IR spectra of MWNT-COOH, MWNT-P400, MWNT-P20000, and PEG4000. All samples were pressed in KBr for the FT-IR analysis. In the higher wavenumber region, a peak at 1706 cm^{-1} assigned to the C=O stretching mode of the carboxyl group appeared in the MWNT-COOH spectrum. On the other hand, in the PEG-modified MWNTs, a peak at 1720 cm^{-1} assigned to the C=O stretching mode of an ester appeared. In the lower wavenumber region, the bands at 1200–1000 cm^{-1}, which are due to the O–H bending modes and C–O stretching modes of the carboxyl group, appeared in the MWNT-COOH spectrum. On the other hand, in the PEG-modified MWNTs, a peak around 1070 cm^{-1} assigned to the C–O–C stretching mode due to the ether group of the PEG appeared. This peak shift of the C–O–C stretching vibration in the PEG-modified MWNT from that in the parent PEG at around 1100 cm^{-1} may be attributed to the hydrophobic interaction between the graphite surface of MWNT and the hydrophobic part of PEG because the peak of C–H stretching vibration at around 2900 cm^{-1} was also shifted. Furthermore, the absorbance around 1070 cm^{-1} in the MWNT-P20000 was higher than that in the MWNT-P400. Thus, it is found that each PEG was chemically attached to the MWNTs.

Secondly, we investigated whether or not the dispersion degree of the PEG-modified MWNTs correlates with the length of the attached PEG. Figure 2 shows the absorbance at 500 nm ob-

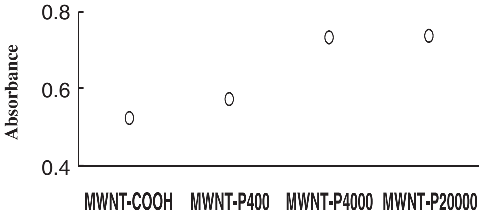

Figure 2. Absorbance at 500 nm observed for aqueous suspensions containing 1-naphthol and MWNT samples.

served in the aqueous 1-naphthol suspensions containing MWNT-COOH or PEG-modified MWNTs. The value of the absorbance at 500 nm of the suspensions containing the MWNTs is directly proportional to the dispersion degree of the MWNTs in the water phase.[10] The dispersion degree of all of the PEG-modified MWNT samples is higher compared to that of the MWNT-COOH. This increase is attributed to the interaction between the hydrophilic PEG and water. The dispersion degree of the MWNT-P4000 system is significantly enhanced compared to that of the MWNT-P400 system. On the other hand, the dispersion degree of the MWNT-P20000 system is almost the same as that of the MWNT-P4000 system. This means that there is a limitation to the dispersion of the PEG-modified MWNTs into water. Therefore, the change in the length of the PEG chain attached to the MWNTs can be evaluated to a certain extent from the dispersion degree of the PEG-modified MWNTs, though there is a limitation to the evaluation due to saturation of the dispersibility.

In order to identify the length of the PEG attached to the MWNTs, the fluorescence spectra of 1-naphthol in water were observed. Figure 3a shows the fluorescence spectra of 1-naphthol in aqueous suspensions containing MWNT-COOH or the PEG-modified MWNTs.

There are three main fluorescent species and they show peaks at around 460, 390–450, and 330–350 nm, respectively. The fluorescence spectrum of 1-naphthol in water shows a peak at around 460 nm originating from its anion species. On the other hand, dual fluorescence of 1-naphthol was observed in a suspension containing MWNTs.[8] The fluorescence observed at 330–350 nm is assigned to the ^1L_b fluorescence of 1-naphthol. This fluorescence of 1-naphthol appears in a nonpolar environment, indicating that the 1-naphthol molecules were adsorbed on the MWNTs surface through a π–π interaction.[8] The other is a broad band having peaks at 390–450 nm. Since the ion-pair fluorescence of 1-naphthol derived from excited-state charge-transfer species in the hydrogen-bonded complex exhibits a peak at around 390 nm, these broad bands are attributed to the superposition of the ion-pair and the anionic fluorescences.[8] The spectral shift in the peak from 450 to 390 nm was observed with an increase in the molecular weight of the PEG attached to the MWNTs.

The intensity ratio of ion-pair fluorescence to anion fluorescence was evaluated and the results are shown in Figure 3b. The relative intensity of the ion-pair fluorescence increased with an increase in the molecular weight of the PEG attached to the MWNTs due to increase in the hydrogen-bonded complex of 1-naphthol. This result can reasonably be explained as follows: the ion-pair fluorescence observed in a suspension containing MWNT-COOH originated from excited-state charge-transfer species in the hydrogen-bonded complex of 1-naphthol and the carboxyl group on the MWNTs. On the other hand, the ion-pair fluorescence observed in a suspension containing PEG-modified MWNTs originated from excited-state charge-transfer species in the hydrogen-bonded complex of 1-naphthol and the ether group in PEG on the MWNTs. These results indicated that the relative intensity of the ion-pair fluorescence of the 1-naphthol reflects the length of the attached PEG chain on the MWNTs. Therefore, whether or not the PEG chain on the MWNTs is shortened under harsh conditions can be evaluated by this method.

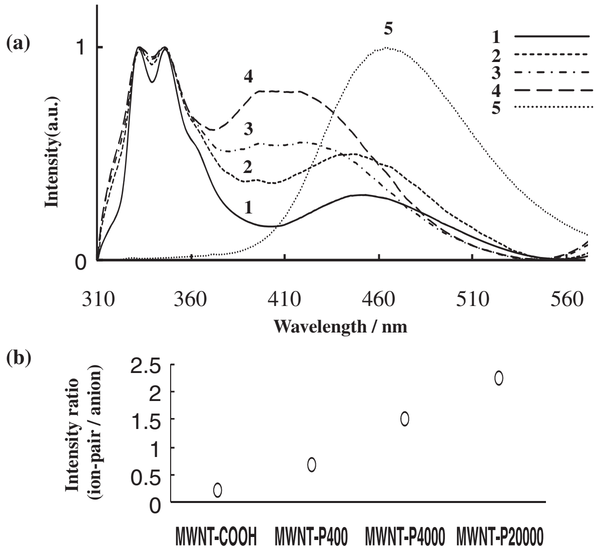

Figure 3. (a) The fluorescence spectra of aqueous 1-naphthol suspension containing (1) MWNT-COOH, (2) MWNT-P400, (3) MWNT-P4000, (4) MWNT-P20000, and (5) 1-naphthol in water. (b) The relative intensity of the ion-pair band to that of the anion band for each system.

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