

NOTE

Preparation of poly(*N*-isopropylacrylamide)-terminated carbon nanotubes and determining their aggregation properties in response to infrared light and heating

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Polymer Journal (2015) 47, 709–712; doi:10.1038/pj.2015.47; published online 22 July 2015

INTRODUCTION

Carbon nanotubes (CNTs),¹ as well as graphene² and fullerenes,³ are carbon materials with well-established properties of high thermal and electrical conductivity, and they have potential for use as unburnable construction materials, electrical devices and so on. CNTs have high aspect ratios and cylindrical shapes, which can entrap various functional molecules, such as iodine⁴ and fullerenes.⁵ Because of this entrapping property, CNTs are being investigated as a new drug carrier with high stability against harsh conditions⁶ when utilizing the inner space.

Poly(*N*-isopropylacrylamide) (PNIPAM) is an example of a thermally responsive polymer and has a low critical solution temperature (LCST) of 35 °C.⁷ PNIPAM is soluble in water under the LCST. However, PNIPAM aggregates and precipitates in water above the LCST because of dehydration of PNIPAM. Based on this property, various functional thermally responsive materials have been prepared, such as soft actuators and drug carriers.^{8–10}

Infrared light-responsive materials utilizing these two functional polymeric materials, CNTs and PNIPAM, were recently reported.^{11–15} For example, the hybrid material formed from the mixture of PNIPAM and CNTs shrunk in response to irradiation with infrared light.¹⁶ Another example is the infrared light-initiated precipitation of CNTs that have been modified by the attachment of PNIPAM at their surfaces.¹⁷ These materials are interesting from the viewpoint of designing new composite materials. In this study, we newly prepared PNIPAM-terminated CNTs and evaluated their thermal and infrared light responsiveness. The merits of terminal modification of CNTs instead of surface modification are that the π -surfaces of CNTs are less damaged than in the case of surface modification, and additional modifications can still be made to the intact π -surface. Moreover, it is expected that the terminal PNIPAM can be used as a thermally responsive stopper to control the release of drugs from CNTs when CNTs are used as a drug carrier.

In addition, we prepared the hybrid material formed from the PNIPAM-grafted CNTs and poly(vinylalcohol) (PVA) and observed its actuating properties by irradiating it with an infrared laser.

EXPERIMENTAL PROCEDURE

PNIPAM-terminated CNTs were synthesized according to Scheme 1. Purified open-ended multi-walled carbon nanotubes (MCNT) were modified using 1,1-bis(*tert*-butylperoxy)cyclohexane (BBCH) as a radical initiator at the termini according to previous reports,^{18–19} and PNIPAM was grafted by radical polymerization. First, the introduction of polyester (POE) groups onto the termini of CNTs was carried out through trapping of POE radicals formed by the thermal decomposition of BBCH.

CNT (0.2 g) and BBCH (14.5 g, 57 mmol) were loaded into a polymerization tube and heated to 70 °C while stirring for 10 h. After the reaction was complete, the product was repeatedly washed with methanol to remove unreacted initiator until no more initiator was separated by centrifugation. After the separation, peroxide-introduced MCNT (POE-MCNT) was dried *in vacuo*.

Polymerization of NIPAM to MCNT was initiated with radicals formed by the decomposition of the POE groups on the termini of the POE-MCNT. POE-MCNT (0.05 g), *N*-isopropylacrylamide (NIPAM, 0.5 g, 4.4 mmol) and 10 ml of 1,4-dioxane were charged into a polymerization tube. The mixture was heated to 100 °C in an oil bath under stirring for 10 h. After the reaction, the product obtained was repeatedly centrifuged at 1.5×10^4 r.p.m. with methanol and dispersed to remove ungrafted polymer. After the separation, PNIPAM-MCNT was dried *in vacuo* at 100 °C.

RESULTS AND DISCUSSION

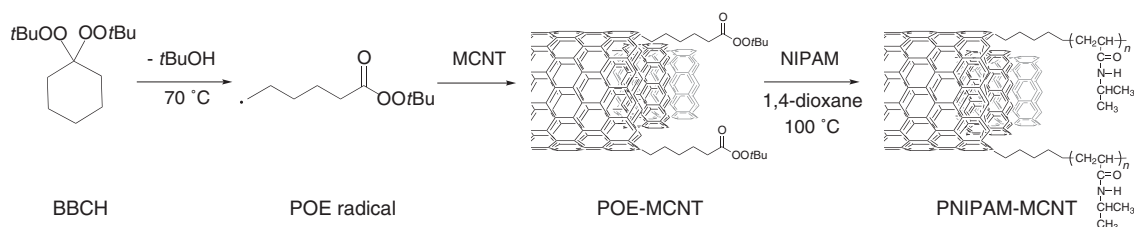
Identification of the terminated CNTs was carried out with Fourier Transform-Infrared (FT-IR), thermogravimetric analysis (TGA), gas chromatography–mass spectrometry (GC-MS) and Raman spectroscopy. FT-IR spectra of the PNIPAM-MCNT and unmodified MCNT samples are shown in Figure 1a. The FT-IR spectrum of the MCNT sample exhibited no significant absorption band. In contrast, the characteristic absorption bands associated with the amide bond were

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Received 22 April 2015; revised 14 May 2015; accepted 17 May 2015; published online 22 July 2015



Scheme 1 Synthesis of PNIPAM-MCNT.

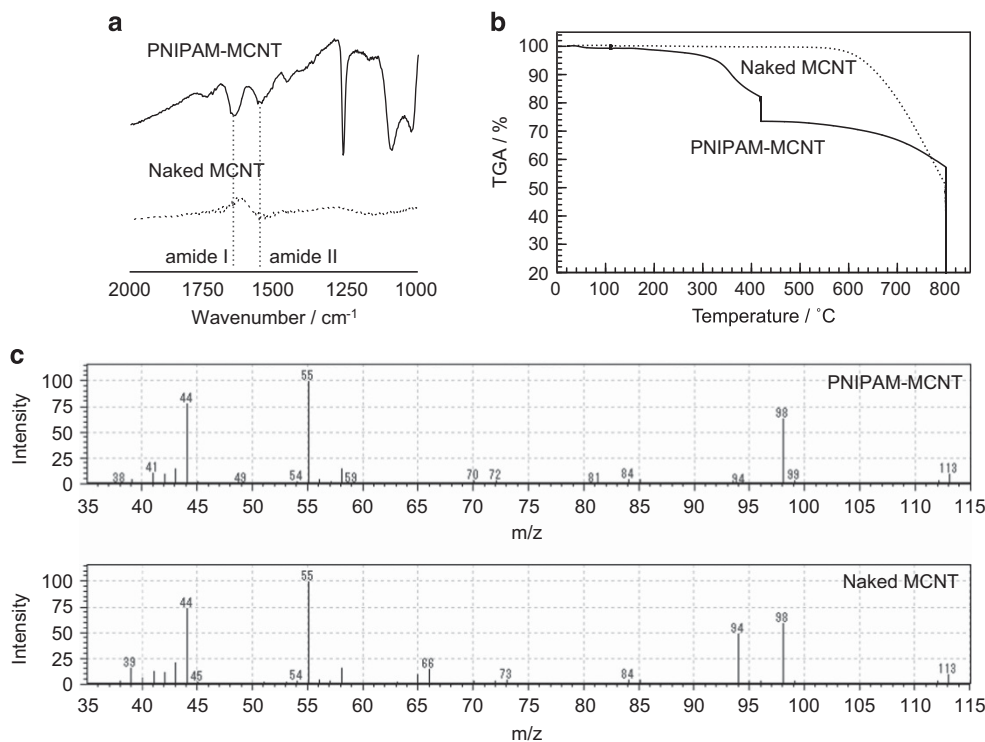


Figure 1 (a) FT-IR (KBr pellet) spectra, (b) TGA data and (c) GC-MS spectra of the synthesized PNIPAM-MCNT and unmodified MCNT. A full color version of this figure is available at the *Polymer Journal* online.

observed from the PNIPAM-MCNT sample at 1540 and 1630 cm^{-1} , respectively. This result indicated that the process of grafting PNIPAM to CNTs was carried out successfully. TGA showed a decrease in weight at 375 and 600 °C for the PNIPAM-MCNT sample, as shown in Figure 1b. The unmodified MCNT sample exhibited only one decreasing band at 600 °C . On the other hand, the decreasing band of pure PNIPAM was observed at approximately $350\text{--}400\text{ °C}$ in previous reports.²⁰ Consequently, it was confirmed that CNTs were terminated by PNIPAM because the decomposition bands at 375 °C associated with PNIPAM were observed in the PNIPAM-MCNT sample. The grafting ratio was estimated at 20.7 wt\% based on the calculation with the TGA data shown in Supplementary Figure S1.

In addition, peaks associated with PNIPAM were observed in the mass spectrum of PNIPAM-MCNT obtained with GC-MS. PNIPAM showed the fraction peaks at $m/z=44$, 55 and 98 , as shown in Figure 1c. The PNIPAM-MCNT sample also showed these peaks at $m/z=44$, 55 and 98 . This result clearly supports the conclusion that PNIPAM was grafted to the CNTs.

Raman spectra of the unmodified MCNT sample and the PNIPAM-MCNT sample are shown in Supplementary Figure S1. The D band at approximately 1330 cm^{-1} and the G band at approximately 1570 cm^{-1} correspond to the defects in the π -surface

of the MCNT and the surface vibrations of a six-membered carbon ring, respectively. Because the intensity ratio of the D band to the G band hardly changed before and after the modification of the MCNT with PNIPAM, it is considered that π -surface of the MCNT was not damaged by the PNIPAM modification and that PNIPAM was mainly attached at the termini of the MCNT. Details of the chemicals and apparatus utilized in this research and the conditions of the experiments are described in Supplementary Information.

The synthesized PNIPAM-MCNT dispersed well into water, as shown in Figure 2a, while the unmodified CNTs precipitated rapidly in water. In this way, the hydrophilicity was enhanced due to grafting PNIPAM to the termini of the CNTs. An aqueous dispersion of the PNIPAM-MCNT did not precipitate at room temperature even after standing for 60 min , as shown in Figure 2b, and remained in suspension for no less than 2 weeks . In contrast, PNIPAM-MCNT started to precipitate rapidly at 50 °C , and almost all of the PNIPAM-MCNT had precipitated after 60 min . Accordingly, it was confirmed that PNIPAM-MCNT had a thermally responsive aggregation property. The decrease in the aqueous dispersiveness of the PNIPAM-MCNT may be because the PNIPAM polymer chains terminating the CNTs aggregated at 50 °C , which is higher than the LCST of PNIPAM (35 °C). The PNIPAM-MCNT that precipitated

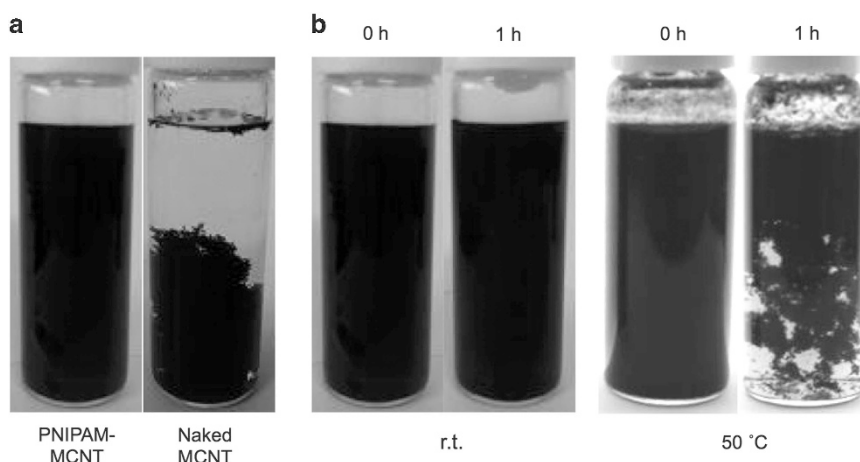


Figure 2 (a) Photographs of PNIPAM-MCNT and MCNT in water and (b) PNIPAM-MCNT before and after standing for 1 h at room temperature and at 50 °C. The concentration is 0.2 g l^{-1} for both the PNIPAM-MCNT and MCNT samples. A full color version of this figure is available at the *Polymer Journal* online.

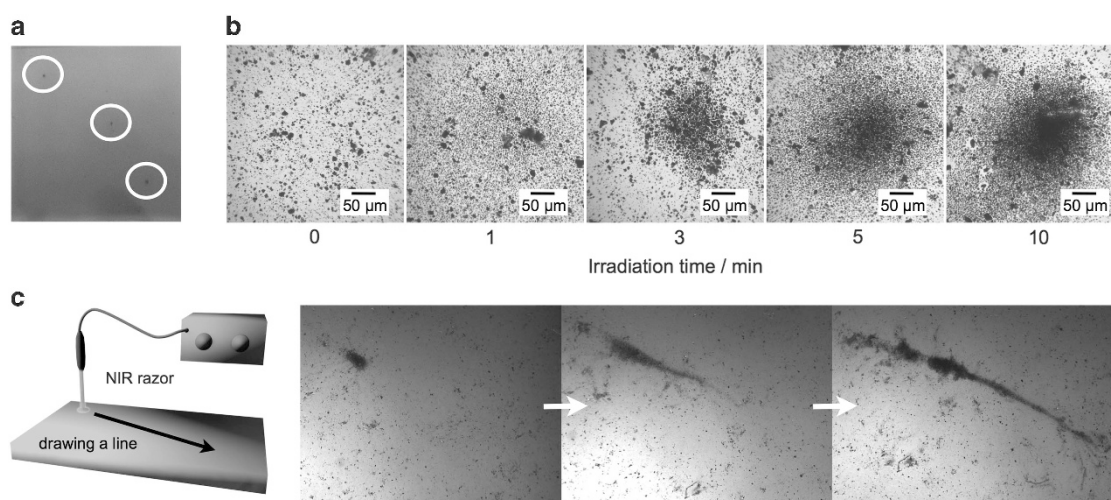


Figure 3 (a) Photograph of the aqueous dispersion of PNIPAM-MCNT (0.2 g l^{-1}) after infrared laser irradiation inside the white circles for 10 min, (b) microscopic images of the assembly of PNIPAM-MCNT (0.2 g l^{-1}) after infrared laser irradiation for 0, 1, 3, 5 and 10 min and (c) schematic illustration of the apparatus and photographs of the line drawing of the PNIPAM-MCNT using the infrared laser. A full color version of this figure is available at the *Polymer Journal* online.

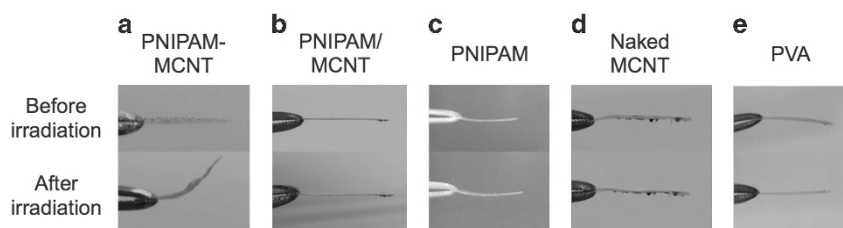


Figure 4 Photograph of the respective films before and after irradiation with the infrared laser: (a) PNIPAM-MCNT/PVA hybrid film, (b) PVA film mixed with PNIPAM and unmodified MCNT, (c) PVA film containing PNIPAM, (d) PVA film containing unmodified MCNTs, and (e) pure PVA film. The pure PVA film was stained with a food-safe red dye because it was difficult to take a photo due to its high transparency. Only the PNIPAM-MCNT/PVA hybrid film exhibited bending actuation behavior as a result of irradiation with the infrared laser. A full color version of this figure is available at the *Polymer Journal* online.

above the LCST can be re-dispersed by sonication at room temperature.

PNIPAM-MCNT was dispersed into water and put between a glass slide and a glass coverslip. After exposing the aqueous dispersion inside the circle area shown in Figure 3a to infrared laser irradiation,

PNIPAM-MCNT was assembled. Figure 3b shows photographs that illustrate the time dependency of assembling PNIPAM-MCNT by irradiation with an infrared laser. As time passed, the size of the assembly increased. Finally, the diameter of the aggregation reached $260 \mu\text{m}$ after 10 min. In a similar way, a line of the PNIPAM-MCNT

floating at the surface of water could be drawn with the infrared laser, as shown in Figure 3c. In contrast, unmodified CNTs did not show such floating behavior. In this way, it was confirmed that the assembly of PNIPAM-MCNT can be regulated. Additionally, this result indicates the possibility that circuits of CNTs can be made by drawing the circuit pathways with an infrared laser.

PNIPAM-MCNT can form composite materials by blending with various monomeric or polymeric materials. Thus PNIPAM-MCNT was blended into a PVA film. An aqueous dispersion of PNIPAM-MCNT (0.2 g l^{-1} , 5.0 ml) was blended with an aqueous solution of PVA (2.0 wt%, 0.48 ml) using a kneading machine for 1 min. The water in the dispersion was evaporated at ambient temperature, and finally a PNIPAM-MCNT/PVA hybrid film was obtained. Similarly, PVA films containing unmodified MCNTs, PNIPAM, an unreacted mixture of MCNTs and PNIPAM and a pure PVA film were also prepared. The PNIPAM-MCNT/PVA hybrid film was irradiated with an infrared laser at a power level of 100 mW. Consequently, the PVA film containing PNIPAM-MCNT exhibited a bending motion, as shown in Figure 4a. In contrast, the PVA film containing unmodified MCNTs or PNIPAM and the PVA film containing no other material did not exhibit any significant response following infrared laser irradiation, as shown in Figures 4c–e. Moreover, interestingly, the PVA film containing CNTs and PNIPAM separately did not exhibit the bending motion at this concentration ratio, as shown in Figure 4b. In addition, the PVA film containing unmodified MCNTs and PNIPAM separately was brittle because MCNTs do not disperse well in the PVA film. It was suggested that, when the PNIPAM-MCNT blended into the PVA film was irradiated with the infrared laser, heat generated from the CNTs made the PNIPAM grafted at their termini shrink due to the dehydration of the small amount of water remaining inside the hybrid PVA film; thus the hybrid PVA film was bent. Water remaining in the film was estimated at 1.59 wt% by utilizing TGA, as shown in Supplementary Figure S4. Furthermore, it is considered that the direct modification to the termini of the CNTs made the transmission of heat from the CNT to the PNIPAM more effective than in the case of just mixing the unmodified MCNTs and PNIPAM. From these results, compared with the materials formed from the mixture of unmodified CNTs and PNIPAM polymer, PNIPAM-MCNT has the ability to create stable hybrid materials by mixing various monomers and polymers.

In this research, we prepared CNTs with PNIPAM grafted to their termini utilizing a radical reaction. PNIPAM-MCNT reported in this research was responsive to heat and infrared light. Moreover, PNIPAM-MCNT could form a stable hybrid film with PVA, and the hybrid PVA film exhibited bending actuation in response to infrared light. Interestingly, the PVA film mixed with unmodified MCNTs and PNIPAM did not show such bending actuation behavior because the distance between the MCNT and PNIPAM was large and the transmission of heat from the CNTs to PNIPAM was less effective.

It is expected that the PNIPAM-MCNT prepared in this research can be used in a drug delivery application. PNIPAM grafted onto the termini of CNTs can act as a thermally responsive valve, and the CNTs can function as a high-stability capsule. PNIPAM-MCNT can also be used for photodynamic cancer therapy, wherein infrared light and our photoresponsive material can be used to clog and destroy the blood

vessels of tumors. Moreover, PNIPAM-MCNT can be further functionalized by modification to the intact surface of the CNT with any of the various surface modification reactions previously reported in the field.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

We appreciate the kind help from Dr T Kawahara, Niigata University. This work was supported by JSPS Kakenhi (Grant Number: 2412001) from the MEXT in Japan.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)