Research Article

Two-Dimensional Hexagonal Structure of Boron Nitride Nanotubes and BNNT-Induced Phase Transition of Block Copolymer in BNNT/Block Copolymer Complex for Energy Harvesting

Sang-Woo Jeon,1,2 Heeil Yoo,3 Se Youn Moon,1,3,4 and Tae-Hwan Kim1,2,3,4

1Department of Applied Plasma & Quantum Beam Engineering, Jeonbuk National University, Jeonju, Jeollabukdo 54896, Republic of Korea
2Research Center for Advanced Nuclear Interdisciplinary Technology, Jeonbuk National University, Jeonju, Jeollabukdo 54896, Republic of Korea
3Department of Quantum System Engineering, Jeonbuk National University, Jeonju, Jeollabukdo 54896, Republic of Korea
4High-Enthalpy Plasma Research Center, Jeonbuk National University, Wanju-gun, Jeollabukdo 55317, Republic of Korea

Received 10 February 2023; Revised 6 April 2023; Accepted 19 April 2023; Published 9 May 2023

Abstract

Since boron nitride nanotubes (BNNTs) were first manufactured, they have gained considerable attention for their wide-scale application as reinforcing composites, piezoelectric materials, electrical insulating materials, thermal conductors, and neutron shielding materials because of their excellent mechanical, electrical, thermal, and neutron absorption properties. Despite the remarkable properties and broad application scope of BNNTs, their use has been limited because of their ineffective structural control due to the presence of one-dimensional nanoparticles. To overcome this limitation, we investigated an approach for the collective self-assembly of BNNTs by using block copolymers (Pluronic P65 and Pluronic P85) as a template and studied the BNNT-induced phase behavior of the block copolymer. For homogenous mixtures of BNNTs and block copolymers, the BNNTs were encapsulated by the in situ polymerization of surfactants (p-BNNTs), where their overall structures were confirmed by small-angle neutron scattering (SANS) and atomic force microscopy (AFM) measurements. The p-BNNTs were mixed with the block copolymers (at 50%, Pluronic P65 or Pluronic P85) by centrifugation in alternative directions to form homogeneously mixed complexes. Polarized optical microscopy (POM) and small-angle X-ray scattering (SAXS) measurements confirmed a two-dimensional hexagonal structure of the BNNTs in the block copolymer matrix that self-assembled upon heating, which can give a possibility of being used as effective piezoelectric materials for energy harvesting. Moreover, upon the addition of BNNTs, the phase behavior of the block copolymer can be controlled, allowing the formation of hexagonal, face-centered cubic, and body-centered cubic structures depending on the BNNT concentration and temperature. This study provides a new and simple method to control the collective BNNT structure.

1. Introduction

Boron nitride nanotubes (BNNTs), which are structurally similar to carbon nanotubes (CNTs), were first synthesized in 1994 [1]. BNNTs exhibit excellent mechanical and thermal properties, similar to those of CNTs [2, 3]. However, several physical properties of BNNTs are quite different from those of CNTs. For example, BNNTs are electrically insulative because they have a bandgap energy (5–6 eV) arising from the localization of electrons at the positions of N and B atoms [4–6]. In addition, BNNTs display excellent neutron shielding properties because they are composed of a combination of B (with a thermal neutron absorption cross-sectional area of >3000 barns) and N atoms that can...
be applied to the neutron shielding applications of composites using BNNTs and boron nitride nanosheets (BNNS) [7–12]. Recent studies show that BNNTs displayed piezoelectric and catalytic properties [13–15]. Despite their interesting properties, the practical applications of BNNTs were rather limited. (e.g., it is difficult to disperse BNNTs in aqueous solution or to fabricate highly ordered self-assembly of BNNTs for the enhancement of physical properties of BNNTs) [16–18]. It is rather well known that the BNNTs in aqueous solution can be dispersed by the physical (adsorption using surfactants and block copolymers) and chemical (chemical bonding via acid treatment) methods [19–24]. On the other hand, the methods to improve the physical properties of BNNTs (containing typical one-dimensional nanoparticles) are still in the early stage. Considering that the collective structure of one-dimensional particle can enhance physical properties, the fabrication of the well-defined and highly ordered self-assembly of BNNTs is required. Recently, there were a few reports on the formation of highly ordered self-assembled nanostructures of one-dimensional particles by the application of external forces (flow or electrical and magnetic fields) or through interparticle interactions (template-guided self-assembly, electrostatic interaction, and hydrophobic interaction) [25–31], which have rather complicated procedures to fabricate the highly ordered structure.

Amphiphilic molecules, such as block copolymers with hydrophilic and hydrophobic groups, exhibit phase behavior and have been used as templates for constructing highly ordered nanostructures [32–36]. In some studies, block copolymers with amphiphilicity have been used to induce the formation of nanostructures of inorganic nanoparticles (such as gold nanorods, carbon nanotubes, and silica nanoparticles) because these copolymers can induce the selective self-assembly of nanoparticles by controlling the interaction between the block copolymer and nanoparticles [37–43]. However, the formation of highly ordered BNNT nanostructures (which can give a possibility to be used as an effective piezoelectric material) has not yet been explored. To bridge this gap, herein, we form highly ordered nanostructures of BNNTs using a block copolymer system (Pluronic P65 (EO\textsubscript{20}·PO\textsubscript{40}·EO\textsubscript{20}, \(M_w = 3500\ \text{g/mol}\)) and Pluronic P85 (EO\textsubscript{27}·PO\textsubscript{47}·EO\textsubscript{27}, \(M_w = 4600\ \text{g/mol}\)) as template materials by varying the temperature (for the control of hydrophobic interaction). To achieve homogeneous mixtures of BNNTs and block copolymers (Pluronic P65 or Pluronic 85), the BNNTs with a hydrophobic surface were encapsulated by the in situ polymerization of surfactants (p-BNNTs). The p-BNNT/block copolymer complexes self-assemble to form BNNTs with a close-packed hexagonal structure over a specific temperature range, which is attributed to the depletion attraction of the p-BNNTs under the osmotic pressure of the block copolymers. Moreover, upon the addition of BNNTs, the phase behavior of the block copolymer can be controlled, allowing the formation of hexagonal, face-centered cubic (F.C.C), and body-centered cubic (B.C.C) structures, which were caused by the increase of the hydrophobic interaction depending on the BNNT concentration and temperature. To analyze the p-BNNT/block copolymer complex (denoted as P65/Water/p-BNNT and P85/Water/p-BNNT), small-angle X-ray scattering (SAXS) analysis and polarized optical microscopy (POM) were performed. This is the first report on the highly ordered self-assembly of BNNTs and the phase behavior of BNNT/block copolymer complexes and can help in the fabrication and study of self-assembled nanostructures of one-dimensional nanoparticles. Furthermore, the highly ordered BNNT array can give a wide range of potential applications, such as piezoelectric materials for energy harvesting, heat dissipating materials, and neutron shielding materials.

2. Experimental Section

2.1. Materials. BNNTs were purchased from the High-Enthalpy Plasma Research Center of Jeonbuk National University (Iksan, Republic of Korea). 4-Vinylbenzoic acid (VBA) and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma–Aldrich. Cetyltrimethylammonium 4-vinylbenzoate (CTVB) amphiphilic surfactants were fabricated in the laboratory using VBA and CTAB [44]. Triblock copolymers Pluronic P65 (EO\textsubscript{20}·PO\textsubscript{40}·EO\textsubscript{20}) and Pluronic P85 (EO\textsubscript{26}·PO\textsubscript{40}·EO\textsubscript{26}) were obtained from BASF. Pluronic copolymer is an amphiphilic polymer composed of a hydrophilic group, polyethylene oxide (PEO), and a hydrophobic group, polypropylene oxide (PPO), in an A-B-A structure. Purified H\textsubscript{2}O was obtained from ELGA PURELAB Option Q. The VA-044 free radical initiator was purchased by Wako Chemicals.

2.2. Sample Preparation. As described elsewhere [23], permanently isolated BNNTs (p-BNNTs) were synthesized by wrapping the surface with CTVB, followed by in situ polymerization of the head group of CTVB using a VA-044 free radical initiator. To separate the individually present p-BNNTs from the p-BNNT solution, centrifugation was performed at 2504\(g\) (where \(g\) means the gravitational force) for 30 min. After obtaining approximately 80% of the supernatant, the obtained solution was freeze-dried at \(-43^\circ\text{C}\) for 3 days. To the as-prepared p-BNNT powder, Pluronic P65 aqueous solution was added at a fixed concentration of 50%. The block copolymer/water/p-BNNT composition of the complex was 50/50/0, 50/50/5, 50/50/10, 50/50/15, and 50/50/20, wherein the p-BNNT concentration was varied. To homogeneously mix the P65/Water/p-BNNT complexes, which possessed very high viscosity, centrifugation was performed 100 times at 2008\(g\) for 2 min while turning the samples up and down. The Pluronic-P85-based complexes were prepared in the same manner by using the Pluronic P85 aqueous solution.

2.3. SAXS Measurements. SAXS analysis was performed on the 4C beamline of high-resolution X-rays with a wavelength of 0.796 Å (\(\Delta E/E \approx 2 \times 10^{-4}\)) at the Pohang Accelerator Laboratory (PAL) of the Republic of Korea. The sample-to-detector distance (SDD) was fixed at 2 m, and the \(q\) range was 0.014–0.58 Å. Silver behenate (AgBE), a standard sample, was used to calibrate the \(q\) range. The beam size was 100 (vertical) \(\mu\text{m} \times 300\) (horizontal) \(\mu\text{m}\). All SAXS samples...
were measured at 5°C intervals from 25°C to 80°C, and they were slowly heated at 0.3°C/min to make a complete equilibrium state during temperature elevation.

2.4. SANS Measurements. SANS measurements were conducted on the EQ-SANS instrument (BL-6) at the Spallation Neutron Source (SNS) in the USA. Neutrons of a minimum wavelength (2.5 Å, under 60 Hz operation) were used for the SDD of 2.5 m (where the accessible q range is 0.01 Å⁻¹ < q < 0.45 Å⁻¹). The scattering intensity of the sample was corrected for empty cell scattering and background and calibrated for the detector pixel sensitivity. The 1D averaged scattering intensity was calibrated on an absolute scale by using the standard sample through the software provided by SNS [45, 46].

2.5. AFM Measurements. The p-BNNT dispersion in an aqueous solution was spin coated onto a Si wafer cleaned by a piranha solution. The atomic force microscopy (AFM) images were collected in the tapping mode (Bruker, MultiMode 8 model). The coated p-BNNTs on Si wafer were burned for 4 hr at 450°C in air to entirely remove the surfactant covering on the BNNTs, which can characterize the length of the BNNTs.

2.6. POM Measurements. POM was performed using an Olympus BX 53 microscope with cross-polarizers. The sample contained on a glass slide sealed with an epoxy resin was placed on a lab-made heating stage, and the sample temperature was controlled using a Eurotherm 3504 temperature controller.

3. Results and Discussion

Because amphiphilic block copolymers Pluronic P65 and P85, with an equivalent hydrophilic mass fraction (f = 0.5) but different molecular weights, display different phase behavior in an aqueous solution, these block copolymers were used as template material for the self-assembly of BNNTs bearing one-dimensional nanoparticles through hydrophobic interactions, leading to the formation of various nanostructures of BNNTs in the block copolymer matrix. Furthermore, the concentration of BNNTs was controlled to obtain various self-assembled structures of BNNTs depending on its concentration. Pluronic polymers have various self-assembled structures in response to temperature. Therefore, it is possible to form an ordered structure of various one-dimensional nanoparticles by hydrophobic interaction in an aqueous solution. The BNNTs were mixed with the pluronic block copolymers to enhance the hydrophobic interactions, which allow the highly ordered self-assembly of the BNNTs in the block copolymer matrix. However, the BNNTs cannot be easily dispersed in aqueous solutions because of their hydrophobic surfaces and strong van der Waals interactions. To achieve homogeneous BNNTs and block copolymer mixtures, it is essential to form a stable and homogeneous dispersion of BNNTs in aqueous solutions.

Therefore, the surface of the BNNTs was covered with a polymerizable surfactant and then radically polymerized in situ to enhance the stability of the dispersion. The detailed structural information of polymerized BNNTs (p-BNNT) was characterized by small-angle neutron scattering (SANS) and atomic force microscopy (AFM) measurements (Figures 1(a) and 1(b)). The length evaluation of BNNTs in the AFM images revealed that the peak of the length distribution of BNNT was 450 ± 50 nm. Herein, the length distribution of BNNT was obtained from the analysis of the 63 AFM images by using NanoScope Analysis Software supplied from Bruker. The mean length of BNNTs, which is estimated from a simple fitting with a log-normal distribution, was 536.8 ± 76.5 nm. The cross-sectional distribution of p-BNNTs was determined by the SANS form factor analysis (radius of BNNT = 1.46 ± 0.29 nm and thickness of surfactant adsorbed on BNNT surface = 0.93 ± 0.10 nm) by using the sum of the core-shell cylinder model (for p-BNNTs) and cylinder model (for micelles that are not involved in the encapsulation of BNNT) [47], which was reported in the previous study [23]. This result is nearly identical to the previous study [19] and is schematically summarized in Figure 1(c). The p-BNNTs had a hydrophilic surface; hence, their dispersion was highly stable. Additionally, the p-BNNTs were redispersible in aqueous solutions even after freeze-drying, providing an easy method to prepare a homogeneous and highly concentrated BNNT dispersion in an aqueous solution. The prepared p-BNNTs (5, 10, 15, and 20 wt%) were mixed with Pluronic P65 and P85 block copolymers by alternative centrifugation (Figure S1). The structural changes in the BNNT/block copolymer complexes upon varying the concentration of p-BNNTs were confirmed by POM and SAXS analysis.

First of all, the structural information of the Pluronic P65/Water/p-BNNT complexes, which have relatively low block copolymer molecular weights of the block copolymer, was acquired by POM and SAXS analysis. To identify the overall phase behaviors of the highly concentrated P65 in an aqueous solution and the P65/Water/p-BNNT complexes with temperature increment, the POM images of each sample under the cross polarizer (0° rotated polarizer-sample-90° rotated polarizer) were acquired from 25°C to 80°C (Figure 2). For the P65/Water/p-BNNT (50/50/0 and 50/50/5) complexes, which contain no or relatively low amount of p-BNNT particles, a sequential image change representing dark (25–45°C) to partially bright (50–70°C) to dark (75°C) textures and partially bright (25–75°C) to dark (80°C) textures, respectively, was observed. This result indicates the formation of an anisotropic ordered phase in the temperature range at which the samples show a bright texture upon birefringence [48]. In contrast, the P65/Water/p-BNNT (50/50/10, 50/50/15, and 50/50/20) complexes, which have a relatively high number of p-BNNT particles, showed partially bright (that is, birefringent) textures over the entire temperature range (25–80°C). This result implies that the p-BNNT particles led to a change in the overall phase behavior of the Pluronic P65 block copolymer or the formation of the anisotropic ordered phase of the P65/p-BNNT complexes.

To confirm the structural changes of the P65/Water/p-BNNT (50/50/0, 50/50/5, 50/50/10, 50/50/15, and 50/50/20) complexes as a function of temperature, the SAXS intensities of the complexes were acquired at 25–80°C. In these, the representative SAXS intensities of the P65/Water/p-BNNT (50/50/0, 50/50/5, 50/50/10, and 50/50/20) complexes are
presented (the other complex (50/50/15) is presented in the Supporting Information (Figure S2)). The SAXS intensities of the P65/Water/p-BNNT (50/50/0) complex indicate the sequential phase behavior in the isotropic micelle (25–30°C) \(\rightarrow\) hexagonal (peak position ratio of 1: \(\sqrt{3}: 2: \sqrt{7}: 3\), 35–70°C) \(\rightarrow\) isotropic micelle (75°C) \(\rightarrow\) lamellar (peak position ratio of 1: 2: 3: 4, 80°C) structures upon heating (Figure 3(a)). The center-to-center distance of the particles of the Pluronic P65 micelle with the hexagonal structure \(d_{\text{hex}} = \frac{4\pi}{\sqrt{3}q_1}\), where \(q_1\) is the 1st peak position of the hexagonal structure) increases from 9.3 to 10.4 nm upon heating from 35 to 70°C. At 75°C, the Pluronic P65 micelle possessed an isotropic phase again, indicating no Bragg reflection, followed by a lamellar structure, which had a repeat distance \(d_{\text{lam}} = \frac{2\pi}{q_1}\) of 9.5 nm at 80°C (Figure 3(e)). These results are similar to the previous study [38].

When the p-BNNT particles were added to the Pluronic P65 block polymer, the SAXS intensity differed from that of the Pluronic P65 block polymer to which no particles were added. The SAXS intensities of the P65/Water/p-BNNT (50/50/5) complex showed the sequential phase behavior of the hexagonal (25°C) \(\rightarrow\) two different sets of hexagonal (30–70°C) \(\rightarrow\) hexagonal (75°C) \(\rightarrow\) isotropic micelle (80°C) structures with increasing temperature (Figure 3(b)). Considering the molecular weight of the Pluronic P65 block copolymer and the diameter of the p-BNNT particles (4.6 nm), it is expected that the formation of the close-packed hexagonal structure with the center-to-center distance of the particle \(d_{\text{p-BNNT}} = \frac{4\pi}{\sqrt{3}q_1} = 4.85 – 5.43\) nm, which is observed at 30–75°C, is attributed to the presence of the p-BNNT particles (Figure 3(f)). Considering that p-BNNTs are colloidal particles and the Pluronic P65 block copolymer has a sufficient volume fraction in solution, it is understood that the formation of the close-packed hexagonal structure of p-BNNTs is attributed to the depletion attraction of the p-BNNTs under the osmotic pressure of the block copolymers, which has been reported in previous studies [38–43]. Since the osmotic pressure of the PEO block polymer (50 wt%) in aqueous solution is more than 100 atm at room temperature and slightly decreases with temperature [49], it is expected that the depletion attraction is enough, leading to the formation of hexagonal array of BNNT. At 30–70°C, a different set of hexagonal structures with particles having \(d_{\text{hex}}\) of 8.76–9.87 nm was observed, together with the close-packed hexagonal structure of p-BNNTs, which arose from the Pluronic P65 block copolymer (similar to the \(d_{\text{hex}}\) of Pluronic P65 only; Figure 3(e)). The center-to-center distances of the particles \(d_{\text{p-BNNT}}\) in the hexagonal structure of the block copolymer and p-BNNT (low concentration) gradually increase, which can be explained by the decrease in osmotic pressure of the block copolymer when heated.

For the P65/Water/p-BNNT complexes with higher p-BNNT concentrations (50/50/10 and 50/50/20), the SAXS intensities were not significantly different, indicating the sequential phase behavior of two different sets of the hexagonal (25–70°C) \(\rightarrow\) hexagonal (75–80°C) structures (Figures 3(c) and 3(d)). At 25–70°C, two different sets of the
Figure 2: POM images of the P65/Water/p-BNNT complexes having the composition of (a) 50/50/0, (b) 50/50/5, (c) 50/50/10, (d) 50/50/15, and (e) 50/50/20.
Figure 3: Continued.
hexagonal structures (the hexagonal structure of p-BNNTs and Pluronic P65 micelles) were observed, which is similar to the result for P65/Water/p-BNNT (50/50/5). The $d_{\text{p-BNNT}}$ and $d_{\text{hex}}$ of the P65/Water/p-BNNT ((50/50/10) and (50/50/20)) complexes were summarized in Figures 3(e) and 3(f), indicating 4.87–5.17 nm and 8.65–9.43 nm for the P65/Water/p-BNNT (50/50/10) complex and 4.96–4.98 nm and 8.6–9.13 nm for the P65/Water/p-BNNT (50/50/20) complex, respectively, depending on temperature (25–70°C). At 75–80°C, only one hexagonal structure of p-BNNTs was observed. The $d_{\text{p-BNNT}}$ of the P65/Water/p-BNNT ((50/50/10) and (50/50/20)) complexes was 4.96–5.07 nm and 4.98 nm, respectively. It should be noted that the $d_{\text{p-BNNT}}$ slightly increases with temperature (25–80°C, Figure 3), which was not much larger than that of low concentrations of p-BNNTs. This is explained by the interplay between the increase in the particle volume fraction (which leads to an increase in depletion attraction) and the decrease in the osmotic pressure of the block copolymer upon heating (due to micellization by increasing the hydrophobic interaction) [50, 51]. Because the hydrophobic interaction of the block copolymer increases with temperature, the osmotic pressure of Pluronic P65 decreases with the concentration of the free block copolymers, which do not contribute to the formation of a micellar or ordered structure. For the P65/Water/p-BNNT (50/50/15) complex, both $d_{\text{p-BNNT}}$ and $d_{\text{hex}}$ were similar to those of the P65/Water/p-BNNT (50/50/10) complex.

The structural information of the Pluronic P85 aqueous solution and the P85/Water/p-BNNT complexes was confirmed by POM and SAXS analysis. To identify the overall phase behavior of the highly concentrated P85 aqueous solution (50/50/5) and the P85/Water/p-BNNT (50/50/5, 50/50/10, 50/50/15, and 50/50/20) complexes upon temperature increment, POM measurements under the cross polarizer (0° rotated polarizer-sample-90° rotated polarizer) were performed for each complex at 25–80°C (Figure 4). The results confirmed that both the Pluronic P85 aqueous solution (50/50/5) and the P85/Water/p-BNNT (50/50/5, 50/50/10, 50/50/15, and 50/50/20) complexes displayed partially bright (birefringent) textures throughout the entire temperature range (25–80°C). This result indicates that all samples form an anisotropic ordered phase across the entire temperature range [48]. To obtain the detailed structural information of the high-concentration Pluronic P85 aqueous solution and the P85/Water/p-BNNT complexes, a series of SAXS measurements was performed upon heating (25–80°C). In Figure 5, the representative SAXS intensities of the P85/Water/p-BNNT (50/50/0, 50/50/5, 50/50/10, and 50/50/20) complexes are presented (the other complex (50/50/15) is presented in the Supporting Information (Figure S2)). The SAXS intensities of the P85/Water/p-BNNT (50/50/0) complex indicate the sequential phase behavior of the hexagonal (peak position ratio of $\sqrt{3}:2\sqrt{7}$; 25–70°C) → F.C.C (peak position ratio of $\sqrt{3}:\sqrt{4}:\sqrt{8}$; 80°C) structures upon heating (Figure 5(a)). The center-to-center distance of the particles in the hexagonal structure of Pluronic P85 ($d_{\text{hex}} = 4\pi/\sqrt{3}q_1$, $q_1$ is 1st peak position) increases from 11.3 to 12.4 nm upon heating from 25 to 70°C.
Figure 4: POM images of the P85/Water/p-BNNT complex having the composition of (a) 50/50/0, (b) 50/50/5, (c) 50/50/10, (d) 50/50/15, and (e) 50/50/20.
Figure 5: Continued.
At 80°C, the center-to-center distance of the particles in the F.C.C structure of Pluronic P85 \(d_{\text{F.C.C}} = 2\pi \sqrt{3}/q_1\) was 19.5 nm (Figure 5(e)).

When the p-BNNT particles were added to the highly concentrated Pluronic P85 aqueous solution, the SAXS intensities of the P85/Water/p-BNNT (50/50/5) complex showed the sequential phase behavior of the multiphase (B.C.C (peak position ratio of 1: √2 : √3) and hexagonal; 25–30°C) → hexagonal (35–45°C) → two different sets of hexagonal (50–55°C) → hexagonal (60–80°C) structures upon heating (Figure 5(b)). At 25–30°C, the center-to-center distance of the particles in the B.C.C structure of Pluronic P85 \(d_{\text{B.C.C}} = 2\pi \sqrt{3}/q_1\) increased from 13.3 to 13.5 nm. At 35–45°C, an isotropic micellar phase was observed. The \(d_{\text{hex}}\) increased from 11.7 to 12.5 nm upon heating (50–80°C). Likewise, for the P65/Water/p-BNNT complex, considering the SAXS intensity of the Pluronic P85 aqueous solution and the diameter of p-BNNT particles (4.6 nm), the close-packed hexagonal structure with \(d_{\text{p-BNNT}} = 5.19 – 5.51\) nm, which is observed at 25–55°C, is attributed to the p-BNNT particles (Figure 5(f)). It was confirmed that the hexagonal structure of p-BNNTs disappeared as the temperature increased from 60 to 80°C. Because the molecular weight of Pluronic P85 is higher than that of Pluronic P65, the number of Pluronic P85 micelles in the complex was lower than that of Pluronic P65 micelles in the P65/Water/p-BNNT complex. Considering that the osmotic pressure of the Pluronic P85 block copolymer decreases upon heating [49], therefore, the hexagonal structure of p-BNNT is not maintained at high temperatures.

The SAXS intensities of P85/Water/p-BNNT with higher p-BNNT concentrations (50/50/10 and 50/50/20) showed the sequential phase behavior of two different sets of hexagonal (25–70°C) → multiphase (F.C.C and hexagonal, 80°C) structures (Figures 5(c) and 5(d)). At 25–70°C, two different sets of the hexagonal structures (p-BNNT and Pluronic P85) were observed. The \(d_{\text{p-BNNT}}\) and \(d_{\text{hex}}\) of the P85/Water/p-BNNT ((50/50/10) and (50/50/20)) complexes are summarized in Figures 5(e) and 5(f). The \(d_{\text{p-BNNT}}\) and the \(d_{\text{hex}}\) are 4.98–5.36 nm and 10.9–11.8 nm for the P85/Water/p-BNNT (50/50/10) complex and 4.89–4.91 nm and 10.6–10.9 nm for the P85/Water/p-BNNT (50/50/20), respectively. These values depend on the temperature range (25–70°C). At 80°C, a multiphase (F.C.C structure of Pluronic P85 and hexagonal structure of p-BNNT) structure was observed, indicating that the \(d_{\text{F.C.C}}\) and the \(d_{\text{p-BNNT}}\) are 18.2 nm and 5.36 nm for the P85/Water/p-BNNT (50/50/10) and 16.7 nm and 4.91 nm for the P85/Water/p-BNNT (50/50/20), respectively (Figures 5(e) and 5(f)).

Similar to those of the P65/Water/p-BNNT complexes, the \(d_{\text{hex}}, d_{\text{F.C.C}},\) and \(d_{\text{p-BNNT}}\) of the P85/Water/p-BNNT complex slightly increased with temperature (25–80°C) (Figure 5). This phenomenon can be explained by the interplay between the increase in the overlapped exclusive volume fraction between the p-BNNT particles (the depletion attraction is enhanced) and the decrease in the osmotic pressure of the
block copolymer upon heating, which is similar to the result for the P65/Water/p-BNNT complex.

The information about the experimentally identified structure of the block copolymer/BNNT complex and the phase behavior of the block copolymers themselves obtained by SAXS and POM measurements is summarized in Figure 6. Depending on the molecular weight of the block copolymer used as a template material, BNNTs, which contain a one-dimensional nanoparticle, self-assemble to form a two-dimensional hexagonal structure depending on the temperature, and the collective phase behavior of the block copolymer/BNNT is controlled. Notably, the phase transition (isotropic to hexagonal and hexagonal to isotropic) of the BNNTs is dependent on the molecular weight of the template materials.

4. Conclusion

In summary, we investigated highly ordered nanostructures of Pluronic P65/water/p-BNNT and P85/water/p-BNNT complexes through POM and SAXS analysis. The structures of the complexes prepared using Pluronic P65 and Pluronic P85 with different molecular weights as templates were analyzed upon heating. The results confirmed the sequential phase behavior, wherein the structure of the P65/Water/p-BNNT complex changed from the isotropic micelle-hexagonal to two different sets of hexagonal structures with increasing p-BNNT concentration. In addition, it was confirmed that the phase behavior of the P85/Water/p-BNNT complex changed from hexagonal–F.C.C to two different sets of hexagonal–multiphase (F.C.C with hexagonal) with increasing p-BNNT concentration. Moreover, the close-packed hexagonal structure of p-BNNTs in highly concentrated Pluronic P65 and P85 aqueous solutions was maintained over a wide temperature range. As the concentration of the BNNTs in the complex increased, the \( d_{p-BNNT} \) slightly increased, which is due to the depletion attraction because of an increase in the overlapped exclusive volume fraction between the p-BNNT particles and a decrease in the osmotic pressure of the block copolymer. Considering the various phase behaviors of the block copolymers, to the best of our knowledge, this novel approach for the highly ordered self-assembly of the BNNTs may provide new opportunities for the fabrication of highly ordered BNNT superstructures with various phases, which can be widely applied to the fabrication of complex materials. Moreover, the temperature-dependent self-assembly of the BNNTs in the polymer matrix promotes the development of thermosensitive, multifunctional hybrid materials. Based on the morphology control of BNNTs, we think that it needs to additionally perform on the neutron shielding and the energy harvesting studies according to the structure of BNNTs in the composite.
Abbreviations

BNNTs: Boron nitride nanotubes
CNTs: Carbon nanotubes
F.C.C: Face-centered cubic
B.C.C: Body-centered cubic
SAXS: Small-angle X-ray scattering
POM: Polarized optical microscopy
AFM: Atomic force microscopy
SANS: Small-angle neutron scattering.

Data Availability

The (SANS, AFM, SAXS, and POM) data used to support the findings of this study are included within the article. The (SAXS and photography) data used to support the findings of this study are included within the supplementary information file.

Conflicts of Interest

The authors declare no competing financial interest.

Authors’ Contributions

The manuscript writing was done by SWJ and THK. The experimental discussion was conducted by SWJ, HY, SYM, and THK. The experimental design and measurements were performed by SWJ and THK.

Acknowledgments

This research was supported by the Korea Basic Science Institute (National Research Facilities and Equipment Center) grant funded by the Ministry of Education and by the National Research Foundation of Korea (NRF) grants funded by the Korea government (NRF-2021M2D2A1A02041482, NRF-2020M2D6A1044636, NRF-2020R1I1A3A04036603, NRF-2021R1A6C101B383, and RS-2022-0014435).

Supplementary Materials

Additional supporting information can be found online in the Supporting Information section at the end of this article. Photographs of P65/Water/p-BNNT (50/50/0 and 50/50/20) and P85/Water/p-BNNT (50/50/0 and 50/50/20) complexes (PDF). Additional SAXS results for P65/Water/p-BNNT (50/50/15) and P85/Water/p-BNNT (50/50/15) complexes (PDF). (Supplementary Materials)

References


