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# Tensile actuators of carbon nanotube coiled yarn based on polydiacetylene–pluronic copolymers as temperature indicators

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## Abstract

Most polydiacetylenes (PDAs) have been studied as chromatic sensors or temperature indicators because of their phase transition that is accompanied by a color change from blue to red. Here, we focus on the structural change based on the polydiacetylene phase transition for a temperature-responsive tensile actuator at low temperature using a copolymer composed of PDA and pluronic in a multi-walled carbon nanotube (MWCNT) coiled yarn. In this paper, we do not focus on the general color change phenomenon of PDA. We demonstrate that the volume change of PDA in the MWCNT coiled yarn provides ~180% tensile strain at low temperature (~53 °C). Insertion of the pluronic copolymer into the coiled yarn composed of PDA and MWCNT caused the tensile actuation temperature to decrease by ~6 °C (with tensile actuation of ~230%) compared to an actuator without pluronic copolymer. Furthermore, we could verify that the large tensile actuation was also predominantly affected by the melting of the nonpolymerized diacetylene (DA) monomer and the pluronic copolymer. MWCNT coiled yarn actuators with PDA-pluronic copolymer can be easily prepared, have a large tensile actuation, and are actuated at low temperature. It could be used as temperature indicators in the food, drugs, and medical fields.

 Online supplementary data available from [stacks.iop.org/SMS/25/075021/mmedia](http://stacks.iop.org/SMS/25/075021/mmedia)

Keywords: polydiacetylene, pluronic copolymer, tensile actuation, temperature indicator, MWCNT

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Various actuators have been continuously studied with new smart materials. In particular, stimuli-responsive polymers that swell, shrink, are tensile, or are torsional in response to environmental changes such as temperature [1], electric fields [2], and light [3] have been applied to actuation devices. In

the past twenty years, numerous researchers have demonstrated an energy conversion system of the transformation of chemical energy into mechanical energy using metal, carbon, polymer, and biopolymer species such as fibers, yarn, and hydrogel [4–7]. Since the introduction of a phase transition related to the volume of the smart polymers, several applications such as artificial muscle [8], robotic hands [3], and a transporting device [9] have been studied in various research fields. The phase transition of a polymer is induced by several

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factors such as hydrogen bonds or coulomb, hydrophobic, and van der Waals interactions. These applications can be realized by changing the external environmental factors.

Polydiacetylenes (PDAs) have attracted a lot of attention in the domain of nonlinear optics because of the important delocalization of the  $\pi$  electrons on conjugated chains [10]. PDAs are crystalline polymers that are obtained by solid-state polymerization of monomer crystals [11, 12]. As the topochemical polymerization proceeds, internal chemical bond strains develop within the crystal lattice because of molecular displacement and changes in bond angles derived from the reaction [13]. As a result, either the crystal lattice dimensions change gradually during the polymerization of diacetylene (DA) units, or thermodynamically metastable polymer crystals are formed by the accumulation of internal strain, even though part of this strain is often released by the cracking of the crystals [13–15]. Topochemically polymerized diene crystals were recently reported to show a very interesting crystalline structure transition according to different temperature [16].

Previous reports revealed that among the various chromatic transitions of PDAs, the mostly studied properties are thermally induced color transitions [17]. Accordingly, to date, PDAs are considered as the representative materials for chromatic sensors. However, because they only display color change, they are difficult to use for some applications that require mechanical work. Here, we introduce an easily fabricated yarn-type tensile actuator using the phase transition of PDA when PDA changes structure (not color) from blue to red. We also used a multi-walled carbon nanotube (MWCNT) sheet with excellent electrical and thermal conductivities and high mechanical strength as the host material. In addition, we improved the tensile actuation performance by making the coiled structure. Currently, PDA actuators with carbon nanotubes or graphene were reported as having bending and torsional actuation [18, 19]. According to a recently published torsional actuating study using PDAs and MWCNTs [19], the actuation was induced by the volume change based on the effect of phase transition of PDAs, and a large volume change of the nonpolymerized DA monomer. The latter monomer could be considered as one of the important actuation factors because the polymerization ratio of the monomer directly influences the tensile actuation.

In addition, we added the pluronic copolymer to lower the actuating temperature. Pluronic has the conformational orientation of molecular ‘loops,’ ‘tails,’ and ‘trains’ depending on the proportion of poly (ethylene oxide) (PEO) (hydrophilic) and poly(propylene oxide) (PPO) (hydrophobic) blocks [20]. Triblock copolymers of PEO–PPO–PEO are a class of nonionic macromolecular surfactants and amphiphilic molecules widely used in industry, pharmacy, bioprocessing, and separation [21]. The characteristic features of pluronic copolymers are their temperature-dependent self-association in aqueous solutions [22] and the properties of their role in adsorption and adhesion [23, 24] on surfaces. Furthermore, the time- and temperature-dependent properties of PDAs and pluronic copolymers were previously reported by Gou *et al* [25] in detail. They suggested time-dependent temperature

chromatic sensor responding under low temperature between 10 °C–50 °C based on PDA and pluronic copolymer.

Here, we demonstrate that a large tensile actuation ( $\sim 230\%$ ) was provided by a PDA-based MWCNT coiled yarn actuator. This actuator can respond at low temperature ( $\sim 47$  °C) as well. In addition, we suggest that there is an advantage in using this yarn as a mechanical actuator in response to environmental changes with decomposition of materials for applications based on temperature indicators.

## 2. Materials and methods

### 2.1. Materials

The aligned arrays of MWCNT forests were grown on a Si wafer using chemical vapor deposition; 10, 12-pentacosadiynoic acid (PCDA) which is represented by irreversible phase transition as a guest material, tetrahydrofuran (THF), and pluronic copolymer (F127) were purchased from Sigma-Aldrich (USA).

### 2.2. Preparation of PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarn

A DA monomer was dissolved in THF solvent; the final concentration of DA solution was 30 mM, and then the DA solution was filtered by a polytetrafluoroethylene filter (0.2  $\mu\text{m}$  pore size) for purification. The MWCNT sheet of four layers (7 mm  $\times$  7.5 cm) on a slide glass was immersed into 30 mM DA solution and left overnight. After being removed from the DA solution, it was dried at 4 °C for  $\sim 2$  h. After this process, the DA/MWCNT sheet was exposed to 254 nm ultraviolet (UV) light for four time periods (2, 10, 20, and 30 min) at distances of 1 mm and 5 cm, and the MWCNT sheet changed to a dark-blue color by polymerization.

To prepare the PDA/MWCNT coiled yarn, the PDA/MWCNT sheet was first twisted by using a twisting machine based on a two-end tethered structure (twisting insertion: 5300–6000 turns/m using a dual-Archimedean structure). At this time, the PDA/MWCNT yarn length contracted  $\sim 60\%$  of its initial length. To fabricate pluronic copolymer/PDA/MWCNT coiled yarn, the PDA/MWCNT yarn (twisted to  $\sim 1330$  turns/m from the PDA/MWCNT sheet) was immersed in an aqueous solution of pluronic copolymer (10 mM) at 4 °C overnight. After removing the pluronic copolymer-infiltrated yarn from the aqueous solution, the yarn was dried overnight at room temperature. Finally, the pluronic copolymer/PDA/MWCNT yarn was fully twisted until it formed a coiled structure under tethering with 5 mN weight. As with the PDA/MWCNT coiled yarn, the pluronic copolymer/PDA/MWCNT yarn length contracted  $\sim 60\%$ .

### 2.3. Experimental setup

The experimental sample, PDA/MWCNT or pluronic copolymer/PDA/MWCNT coiled yarn, was tethered in a glass cylinder wrapped with Ni/Cr alloy wire for heating, and a thermocouple was attached to the nearest point of the sample

on the noncontact linear displacement sensor which detected the distance between the sensor and the flat metal. A metal flat weight of  $\sim 5$  mN was attached to the end point of the yarn sample (figure S1). The temperature was increased by using a direct current (DC) power supply, and it was controlled by an external variable resistor (in the range of  $3 \Omega$ – $5$  k $\Omega$ ).

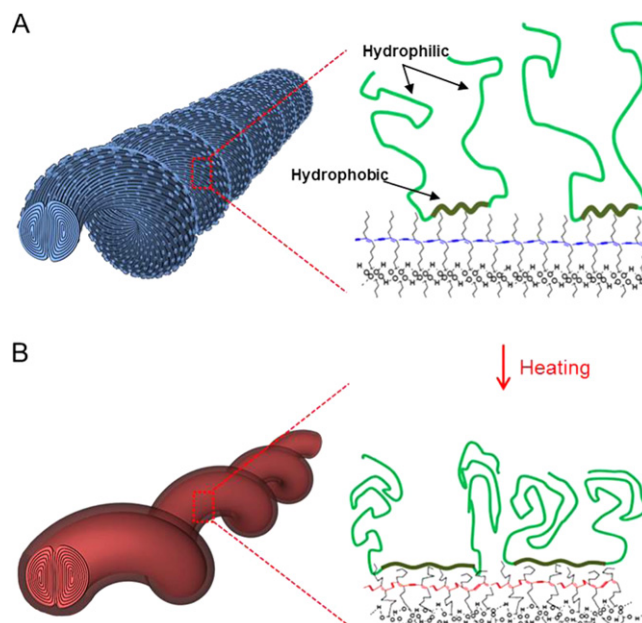
#### 2.4. Characterization

Thermogravimetric analysis (TGA, MAC Science TG-DTA 2000S) was performed to characterize the change in weight of the yarn samples. The temperature was gradually increased from room temperature to  $900$  °C at the rate of  $5$  °C  $\text{min}^{-1}$  in air. Thermal analysis was carried out by differential scanning calorimetry (DSC, TA Instruments, Auto DSC-Q20). The yarn sample was tested in the temperature range between  $20$  °C– $70$  °C under nitrogen conditions with a heating rate of  $1$  °C  $\text{min}^{-1}$ . Raman spectra were obtained with a LabRam Aramis (Horiba Jobin Yvon, France) using a  $633$  nm He-Ne laser. Surface morphology and height profiles were obtained by scanning electron microscopy (SEM, Hitachi S4700, Japan), and atomic force microscopy (AFM, Park Systems XE-100, South Korea). The tensile actuations were measured by a noncontact linear displacement sensor (LD 701) focused on sensing the metal target, which was purchased from Omega Engineering (USA). A Ni/Cr alloy wire was used for heating, and the degree of heating was controlled using an external variable resistor (in the range of  $3 \Omega$ – $5$  k $\Omega$ ). The temperature of each yarn sample was measured by a K-type thermocouple (5SC-TT-K-40-36), also from Omega Engineering.

### 3. Results and discussion

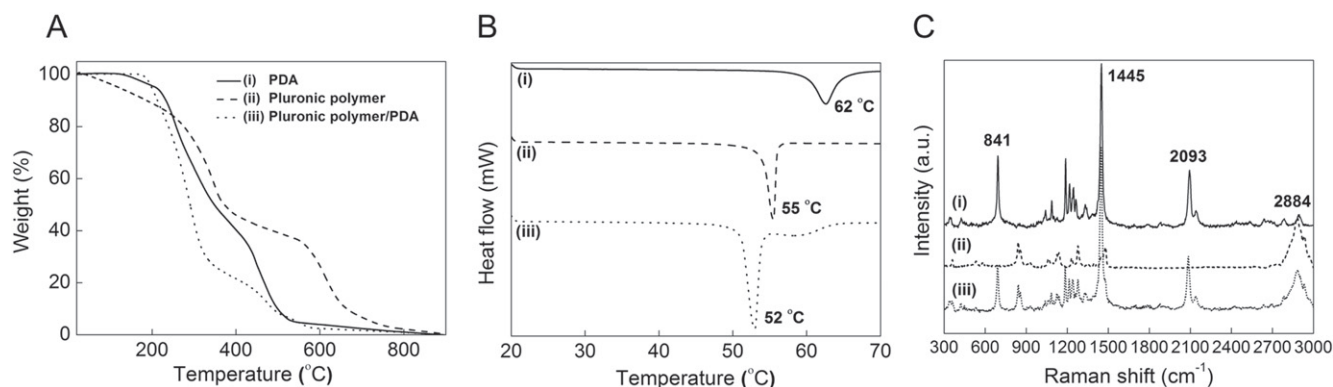
The thermally-responsive PDA/MWCNT coiled yarn was fabricated by PCDA and an MWCNT sheet as the host material. The final PDA/MWCNT coiled yarn contained the pluronic copolymer for inducing the tensile actuation at low temperature. The schematic representation of the PDA/MWCNT coiled yarn containing the pluronic copolymer is shown with two states (based on before/after heating) in figure 1. The structure of the DA was changed to the regular trans-zigzag structure of PDA by UV irradiation, and the PDA backbone keeps its structure with all the trans-alkyl side chains. In addition, the adsorbed pluronic copolymer layer was attached to the trans-alkyl side chains of the PDA with the hydrophobicity of the surface [26] (figure 1(A)). Next, the aggregation properties of the pluronic copolymers affected by concentration and temperature changes are considered, to gain an understanding of the role of the copolymer.

The pluronic copolymer/PDA/MWCNT coiled yarn provided a large elongation because of the volume change from the MWCNT coiled yarn by heating (figure 1(B)). This large elongation of the pluronic copolymer/PDA/MWCNT coiled yarn was attributed to two factors: the phase transition of PDA interacting with the pluronic copolymer, and the melting phenomena of the nonpolymerized DA monomer.



**Figure 1.** Schematic representation of the pluronic copolymer/PDA/MWCNT yarn. (A) Interfacial absorption of the pluronic copolymer on the PDA; (B) volume contraction of the yarn through the effect of PDA and pluronic copolymer from temperature increases, and the melting effect of the DA monomer and the pluronic copolymer.

First of all, when the temperature increases, the polarity between the ethylene oxide (EO) and propylene oxide (PO) segments change, inducing the pluronic copolymer to aggregate [27]. The phase transition of PDA (from blue to red) was directly affected by the polarity change of the pluronic copolymer. Here, PDA had an important additional role in inducing the phase transition by stress (mechanochromism), as well as by heat (thermochromism). The phase transition of PDA was induced by stress, which was based on the aggregation of the pluronic copolymer with increasing temperature. The regular trans-zigzag structure composed of the trans-alkyl side chains of PDA was accordingly transformed to an irregular structure containing gauche conformations with structural disorder of the side chain group and finally reduced the average conjugation length between the PDA structures [28, 29]. The structural change of the PDA backbone is presented in figure 1(B). During the heating, the nonpolymerized DA monomer and the pluronic copolymer melted simultaneously and trickled out from within the MWCNT yarn due to the volume change induced by the compressed force applied in the coiled yarn. This is closely related to the polymerization ratio of the DA monomer. Although UV irradiation could polymerize the DA monomer, the latter was not deeply and fully polymerized. The polymerization partially occurred on the surface of the coiled yarn, and as a result, unreacted DA monomer could remain with PDA within the yarn. We demonstrated in this study that these two factors in volume change of the phase



**Figure 2.** Analysis of the PDA/MWCNT and pluronic copolymer/PDA/MWCNT composites. (A) TGA of (i) PDA, (ii) pluronic copolymer, and (iii) pluronic copolymer/PDA-infiltrated MWCNT coiled yarn. (B) Micro-DSC curves showing the heat flows during heating for (i) 30 mM PDA/MWCNT, (ii) 10 mM pluronic copolymer/MWCNT, and (iii) 10 mM pluronic copolymer/30 mM PDA MWCNT coiled yarn. (C) Raman spectra of the scattering of (i) PDA, (ii) pluronic copolymer, and (iii) pluronic copolymer/PDA on the MWCNT sheet.

transition and melting of the DA monomer and pluronic copolymer, induced a large elongation.

### 3.1. Characterization of PDA, pluronic copolymer, and MWCNT yarn

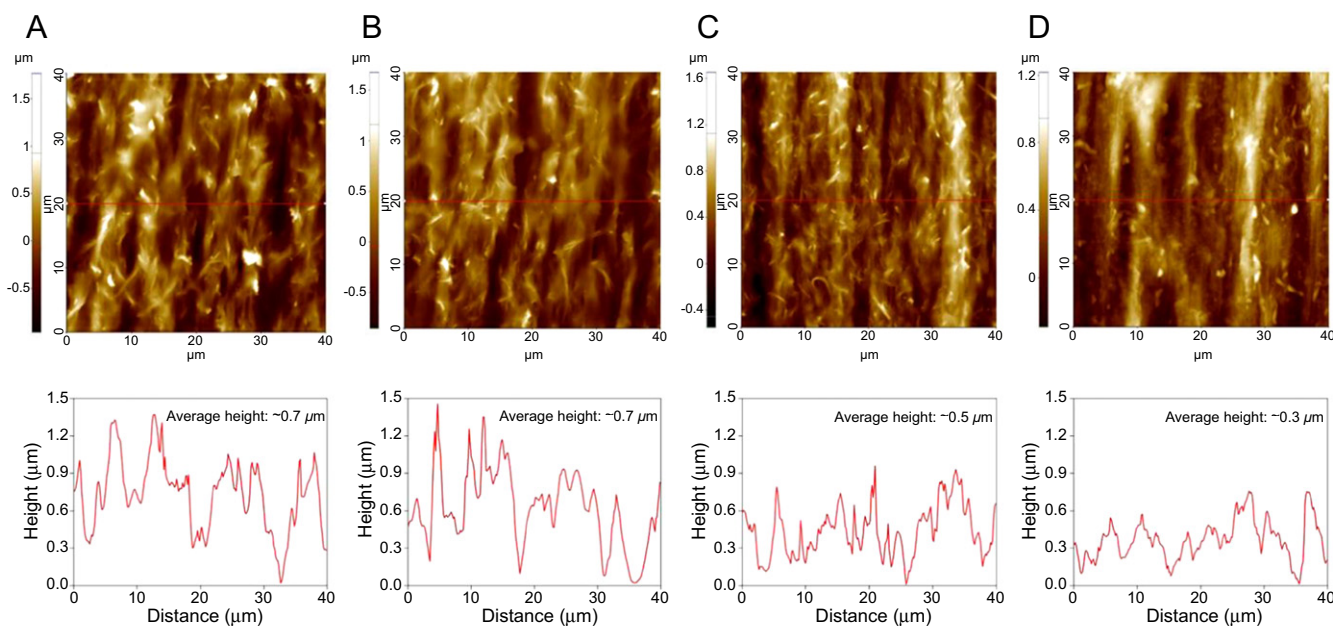
To measure the thermal stability and content of polymer of the coiled yarn, which contained three constituents (PDA, pluronic copolymer, and pluronic copolymer/PDA) in the MWCNT coiled yarn, the temperature was increased from room temperature to 900 °C. TGA results of the three conditions are shown in figure 2(A). The starting temperature point showing weight loss was ~140 °C, and significant weight loss (~60%) of the PDA/MWCNT coiled yarn occurred between ~220 °C–~400 °C while increasing the temperature. The weight of the pluronic copolymer coiled yarn decreased to ~60% between room temperature and ~480 °C. Comparing the PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarns, the latter yarn showed thermal stability up to ~180 °C, and a ~80 wt% weight loss was observed at ~400 °C. Also, high loading of guest material up to ~80% achieved by the biscrolling (PDA) and dipping method (pluronic copolymer) is one of the advantages for actuation, because tensile actuation results from the volume change of guest materials in the MWCNT coiled yarn. The second shoulder peaks for the three conditions were only attributed to the weight loss of the MWCNTs over a temperature of ~400 °C [30].

The endothermic peaks of the DSC curves for PDA (i), pluronic copolymer (ii), and pluronic copolymer/PDA (iii) in the MWCNT coiled yarn are shown in figure 2(B). The PDA and pluronic copolymer in the MWCNT coiled yarn had a main endothermic peak at 62 and 55 °C during heating, respectively. These endothermic peak points (62 °C for PDA and 55 °C for the pluronic copolymer) were closely related to the melting points of DA (~63 °C) and the pluronic copolymer (~55 °C). In the case of the endothermic peak of the composite with pluronic copolymer and PDA in the MWCNT yarn, we confirmed the shift of the endothermic peak to 52 °C.

In addition, Raman spectra were measured for PDA (i), pluronic copolymer (ii), and pluronic copolymer/PDA (iii) in solid state on the MWCNT sheet (figure 2(C)). The most prominent peaks within the PDA spectrum were the carbon triple-bond stretch at 2093  $\text{cm}^{-1}$  and the carbon double-bond stretch at 1445  $\text{cm}^{-1}$ . Spectral peaks within these regions are correlated to the state before the reaction, which is the planar structure of the PDA backbone [31]. The pluronic copolymer spectrum generated C-H stretching vibrations of pluronic polyalkyleneoxide moieties of 2884  $\text{cm}^{-1}$  with absorption peaks from 2800–3000  $\text{cm}^{-1}$  [32]. Upon adsorption of the pluronic copolymers on the PDA (see figures 2(C) (iii)), the bands were associated with  $\text{CH}_2$  rocking, wagging, or twisting, and antisymmetric stretching vibrational modes could be found at 841, 1021–1348, and ~2884  $\text{cm}^{-1}$ . The prominent vibrational bands at 1445 and 2093  $\text{cm}^{-1}$  could be assigned to the  $\nu$  (C=C) and  $\nu$  (C≡C) bands, respectively [29]. After heating the pluronic copolymer/PDA/MWCNT sheet, the typical red phase appeared in the carbon triple-bond at 2121  $\text{cm}^{-1}$  and carbon double-bond at 1515  $\text{cm}^{-1}$  which relate to the alkyne–alkene band (figure S2) [33]. For this result, the structural change of PDA is confirmed by raman spectra when heating.

### 3.2. Height changes for the pluronic copolymer/PDA/MWCNT sheet

The height change of the PDA films by temperature has been previously reported by using AFM [34]. To verify the height changes of the pluronic copolymer/PDA on the MWCNT sheet based on surface morphologies, we used AFM for four temperature conditions, i.e. 25, 45, 55, and 65 °C (figure 3). At the temperatures of 25 and 45 °C (blue phase, unreacted condition, which is indicated by color change), the height averages were  $0.7 \pm 0.31$  and  $0.7 \pm 0.34$   $\mu\text{m}$ , respectively. At 55 °C (red phase, active condition indicated by color change), the pluronic copolymer/PDA/MWCNT surface height change was shown to decrease, and the average height change was  $0.5 \pm 0.23$   $\mu\text{m}$ . When the temperature increased to 65 °C, the height profile of the pluronic copolymer/PDA/MWCNT



**Figure 3.** AFM images for height changes of pluronic copolymer/PDA on the MWCNT sheet at (A) 25 °C, (B) 45 °C, (C) 55 °C, and (D) 65 °C.

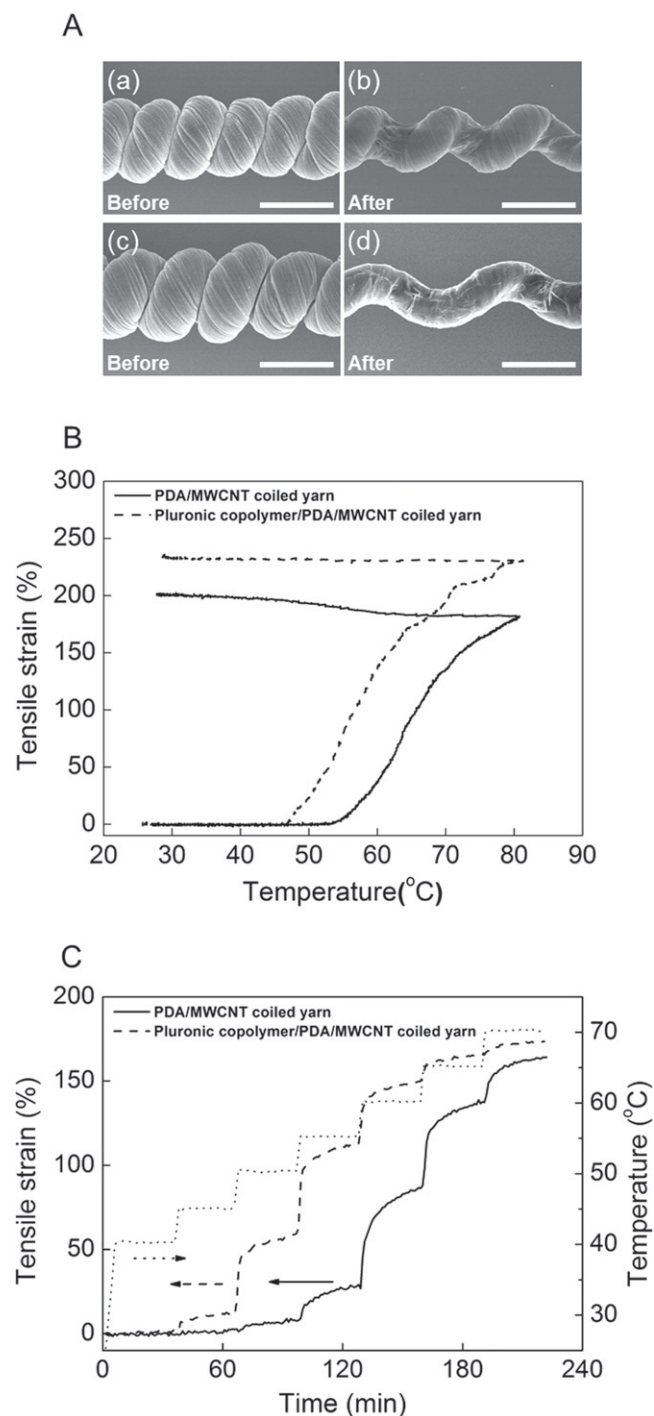
surface decreased to  $0.3 \pm 0.17 \mu\text{m}$ . These decrements in height changes of the pluronic copolymer/PDA/MWCNT surface meant that the pluronic copolymer and PDA melted on the MWCNT sheet with the phase change, and the average height change decreased (see figures 3(A)–(D)). In addition, as the height profile of the pluronic copolymer/PDA/MWCNT decreased, the average height change of PDA on the MWCNT sheet also decreased when the temperature was over 55 °C (figure S3). When the temperature was increased to 65 °C, the average morphological height for the PDA on the MWCNT sheet decreased from  $0.6 \pm 0.50 \mu\text{m}$  (25 °C) to  $0.4 \pm 0.22 \mu\text{m}$  (65 °C). Although the height changes of the pluronic copolymer/PDA (figure 3) and PDA (figure S3) on the MWCNT sheet were dramatic, these large height changes were mainly attributed to the melting of the DA monomer and the pluronic copolymer. Based on the analysis of data (in particular TGA, DSC, and the Raman spectrum) for both composites (pluronic copolymer/PDA/MWCNT and PDA/MWCNT) shown in figures 2 and 3, much of the DA monomer and pluronic copolymer remained in the MWCNT coiled yarn. Hence, we confirmed that the strong actuation of the pluronic copolymer/PDA/MWCNT and PDA/MWCNT coiled yarns was predominantly caused by the melting of the DA monomer and the pluronic copolymer rather than by phase transition.

### 3.3. Thermal actuation for PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarn

The thermally-responsive tensile actuations were shown in the temperature range between room temperature and 80 °C (figure 4). SEM images of the PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarns (before and after heating) that were irradiated for 2 min with 5 cm distance

from the UV source are shown in figure 4(A). About 180% tensile actuation of PDA/MWCNT was achieved, and the pluronic copolymer/PDA/MWCNT coiled yarn was actuated  $\sim 230\%$  at 80 °C. We recognized that the DA monomer stagnated between the coil structure shown in figures 4(A) (a) and (b), which was related to the melting phenomenon from inside to outside in the SEM image of the PDA/MWCNT coiled yarn after heating. In the pluronic copolymer/PDA/MWCNT coiled yarn, the DA monomer and the pluronic copolymer fully coated the MWCNT coiled yarn, as shown in figures 4(A) (c) and (d). We also checked the effect of tensile strain by changing the UV polymerization (figure S4) for verification of the DA melting effect. Tensile actuation was obtained according to the distance from the UV source (1 mm and 5 cm). As a result, the tensile actuation decreased depending on the UV exposure time and distance. When the distance between the UV source and the PDA/MWCNT coiled yarn was 5 cm, the tensile actuations obtained were about 180% (for 2 min) as a maximum, 125% (for 10 min), 120% (for 20 min), and 45% (30 min). Similarly, 105%, 85%, 35%, and 26% tensile actuation results were observed for the same time periods, respectively, at a distance of 1 mm. After  $\sim 20$  min, the polymerization was almost saturated because a long irradiation time and a short irradiation distance strongly induce polymerization. Therefore, the degree of melting of the DA monomer could be decreased by applying a long UV irradiation time.

To compare the thermal actuation of the PDA/MWCNT coiled yarn with the noncomposite and composite pluronic copolymers, figure 4(B) presents the tensile strain change depending on the temperature for 2 min with UV irradiation for the PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarns. Here, the applied load was 5 mN for both systems. The coiled PDA/MWCNT yarn started to



**Figure 4.** Thermal actuation of PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarn. (A) SEM images of PDA/MWCNT before and after heating (a), (b), and pluronic copolymer/PDA/MWCNT yarn (c), (d) (scale bar: 100  $\mu\text{m}$ ). (B) Thermal actuation of PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarn for 2 min with UV irradiation under 5 mN until 80  $^{\circ}\text{C}$ . (C) The tensile strain depending on the temperature by applying the exposure time. Each temperature was maintained for  $\sim 30$  min with a gap of 5  $^{\circ}\text{C}$  under 5 mN.

actuate at  $\sim 53$   $^{\circ}\text{C}$  and elongated  $\sim 180\%$  up to 80  $^{\circ}\text{C}$ . Likewise, the pluronic copolymer/PDA/MWCNT coiled yarn started to actuate at  $\sim 47$   $^{\circ}\text{C}$  and elongated  $\sim 230\%$  from room temperature to 80  $^{\circ}\text{C}$ . The starting temperature for the

actuation of the pluronic copolymer/PDA/MWCNT coiled yarn decreased  $\sim 6$   $^{\circ}\text{C}$  compared with the PDA/MWCNT coiled yarn. In addition, the diameter of the pluronic copolymer/PDA/MWCNT coiled yarn decreased from  $\sim 80$  to  $\sim 60$   $\mu\text{m}$  and elongated  $\sim 50\%$  more than the PDA/MWCNT coiled yarn because of the melting of the pluronic copolymer.

We also measured the thermal actuation of the PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarns under 5  $^{\circ}\text{C}$  temperature changes, starting at 40  $^{\circ}\text{C}$  and rising to 70  $^{\circ}\text{C}$ , every 30 min (figure 4(C)). The PDA/MWCNT and pluronic copolymer/PDA/MWCNT coiled yarn actuation started at  $\sim 55$   $^{\circ}\text{C}$  ( $\sim 25\%$ ) and 45  $^{\circ}\text{C}$  ( $\sim 10\%$ ), respectively. The significant strain change occurred between 55  $^{\circ}\text{C}$ –65  $^{\circ}\text{C}$  for the PDA/MWCNT coiled yarn and between 45  $^{\circ}\text{C}$ –60  $^{\circ}\text{C}$  for the pluronic copolymer/PDA/MWCNT coiled yarn. The tensile actuation gradually decreased above 65  $^{\circ}\text{C}$  because of the melting of both the DA monomer and the pluronic copolymer from the coiled yarn.

In summary, thermal actuation of melting effects was observed by the endothermic peak of DSC curves, height change of AFM data, SEM image of before and after heating, and the actuation performance by UV polymerization time. The melting effects result from the remaining DA monomer after UV polymerization. Simultaneously, pluronic copolymer which is not attached on PDA induces additional melting effects. As a result, melted DA monomer and pluronic copolymer flow out from the inside of the pluronic copolymer/PDA/MWCNT coiled yarn when heating.

#### 4. Conclusion

We fabricated an irreversible thermally-responsive tensile actuator based on a PDA and MWCNT sheet, and induced actuation at low temperature ( $\sim 47$   $^{\circ}\text{C}$ ) by adding a pluronic copolymer. We confirmed that the tensile actuation with changing polymerization ratio was predominantly influenced by the melting of the nonpolymerized PDA and pluronic copolymer compared with the phase transition of the PDA. Accordingly, it is capable of being used as temperature indicators for preventing the opening of bottle lids which contain denaturalized medicine, food, and proteins or as a shut-off from a dangerous situation such as fire when exposed to high temperature.

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