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The effect of 10,12-pentacosadiynoic acid on the morphology and characteristics of electrospun PDA/PU nanofibers

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Abstract

In this study, the effect of 10,12-pentacosadiynoic acid (PCDA) on the fabrication of PDA/PU nanofibers was examined. The PDA/PU nanofibers were prepared by electrospinning PU and PCDA at different mixing ratios, followed by photopolymerization. The viscosity and conductivity of the spinning solution and the morphology of the fabricated nanofibers were analyzed. We also examined the chemical structure changes, physical structure changes, and color transition characteristics of PDA/PU nanofibers. The concentrations of the spinning solutions and the mixing ratio of PCDA and PU had significant effects on the viscosity of the spinning solution and the diameter and shape of the nanofibers. The optimum conditions for economic efficiency and the practicality of the fabrication of a PDA/PU nano-fibers were 12–14 wt% spinning solution and a ratio of PU to PCDA of 4 to 1 or greater. For these conditions, the viscosity was in the range of 225–290 cP, which resulted in the production of smooth, uniform PDA/PU nanofibers without beads. The diameters of the nanofibers ranged from 270 to 550 nm. The results of FT-IR, XRD and DSC analyses confirmed that the PCDA were well mixed with the PU molecules and were electrospun. The fabricated PDA/PU nanofibers exhibited color transition phenomenon by external temperature stimulation above 70 °C.

Keywords: 10,12-Pentacosadiynoic acid, Polydiacetylene, Polyurethane, Electrospun nanofiber, Color transition

Introduction

The conjugated polymers studied as materials of biosensors are sensitive to external stimuli. The conjugated polymer is superior in thermal properties to low molecular weight materials and is widely used as a material for detecting heavy metals, and noxious gas because it is easily applied to thin films and the like (Son et al. 2015).

Polydiacetylene (PDA) is a conjugated polymer that has an intersection between a double bond and a triple bond. In addition, PDA can be synthesized easily by polymerizing diacetylene monomers through UV light irradiation, free radical polymerization, or plasma treatment (Okada et al. 1998; Lee et al. 2014; Lu et al. 2014). Furthermore, the advantage of diacetylene monomer in the aqueous state is that it has the ability to self-assemble into a three-dimensional structure. The wavelength of the self-assembled, three-dimensional structure is similar to that of a polymer intersecting with a triple

bond around 254 nm, and this transparent substance changes its color to blue at the optimum absorption wavelength at 650 nm (Okada et al. 1998). The color transition of the PDA from blue to red along the electromagnetic spectrum occurs as the result of external environmental factors, for example temperature, pH, chemical substances, and biological substances (antibody, protein, peptide, DNA, bacteria) (Reppy and Pindzola 2007). The mechanism for the color transition of PDA is generally known that the structure of the polymer backbone changes from planar to non-planar by stimulation, resulting in a blue-shift of the spectrum (Qian and Städler 2019; Jelinek and Ritenberg 2013). The degree of the color transition is different according to the kind of external factor, and the fluorescence characteristic, which does not appear in blue, is stronger toward red (Su et al. 2004). The properties of the color transition have been studied in various sensor applications (Okada et al. 1998; Lee et al. 2014).

Electrospinning is a technique that produces polymeric fibers with diameters that range from 2 nm to several micrometers by applying electrical force on natural and synthetic polymer solutions. These nanofibers have smaller voids and surface areas than ordinary fibers. Therefore, these nanofibers can be used in a variety of studies, including nanocatalysts, tissue engineering, protective clothing, filters, pharmaceuticals, bioengineering, and environmental engineering (Bhardwaj and Kundu 2010; He et al. 2018; Kim and Lee 2014; Yoon et al. 2017). There have been recent reports that indicate that the performances of electrospun nanofibers can be improved by adding the new functional materials (Kim and Lee 2018; Lee et al. 2017, 2018). In addition, studies on the feasibility of using electrospun nanofibers as sensors have been made by varying the mixing ratio of PCDA based on polymer (Alam et al. 2016; Yapor et al. 2017). In the previous study Yapor et al. (2017), limited the mixing ratio of PCDA and concentrations of electrospinning solutions to two methods, using PU and PEO as polymers. Alam et al. (2016) extended the concentration of the PEO spinning solution and the mixing ratio of the PCDA into three methods, and examined the effect of the concentration of the spinning solution and the mixing ratio of the PCDA on the size and surface roughness of the nanofibers in detail. PDA-containing nanofibers can be applied to filters or protective clothing that can block harmful substances due to nanostructures as well as a sensing function that can be visually confirmed when exposed to harmful environments. For this reason, it is important to design a detailed experiment on the effect of additive and polymer concentration on the morphology of nanofibers.

Therefore, in this study, we attempted to identify the optimum conditions of PCDA/PU mixtures for the production of PDA/PU nanofibers applicable to colorimetric sensors. The PDA/PU nanofibers were prepared by electrospinning PU and PCDA at different mixing ratios, followed by photopolymerization. Morphological changes, chemical structure change, physical structure change were observed in the PDA/PU nanofibers. We confirmed the color transition of PDA/PU nanofibers by confirming color change by temperature stimulation. The novelty of this study is in a detailed experimental investigation of the effect of additives such as PCDA on the fabrication of PU for colorimetric sensor applications.

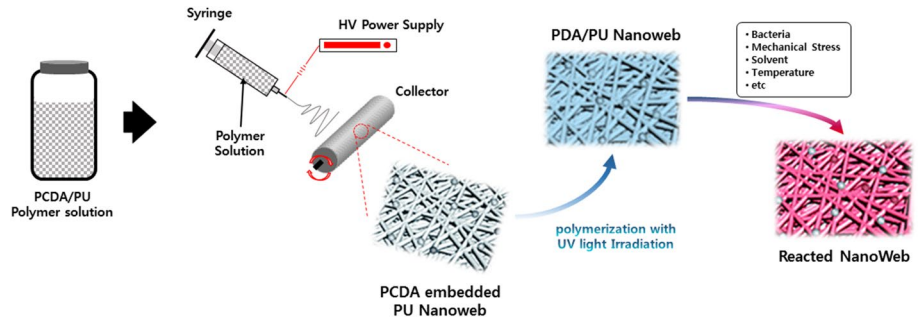

Fig. 1 Method used to fabricate PDA nanofibers

Methods

Materials

We purchased 10,12-pentacosadiynoic acid (PCDA) from Sigma Aldrich (Poland). Polyurethane (PU, pellethane 2103-80AE, MW = 80,000) was obtained from Lubrizol (USA). *N*-Dimethylformamide (DMF, > 98%) was purchased from Daejung Chemicals (Korea).

PCDA and PU were dissolved in DMF by adjusting the PU:PCDA ratio from 1:1 to 6:1 to make concentrations in the range of 8–16 wt%. The solution was stirred for 12 h, sonicated for 1 h, and then stirred for another 12 h to prepare a PU spinning solution that contained PCDA.

Characterization of the spinning solution

The conductivity of the spinning solution was measured using a portable conductivity meter (CD-4303HA, Lutron Electronic, Taiwan). Viscosity changes according to changes in the concentration of the polymer and polymer blend ratio (PU:PCDA) were measured five times using a viscometer (DV-I Prime, Brookfield, USA), and the average value was calculated.

Fabrication of PDA/PU nanofiber

The electrospinning device consisted of a high-voltage DC power supply (High Voltage DC Power Supply Unit, Matsusada Precision Inc., Japan), a collector, a syringe pump (KDS100, NanoNC Co., Ltd., Korea), and a metal syringe needle (21 G). The spinning conditions were a voltage of 12 kV, a tip-to-collector distance of 15 cm, and a fluid velocity of 0.6 ml/h. The weight of the spun nanofibers was adjusted to be 10 g/m^2.

For the photopolymerization of the PCDA that was added to the PCDA/PU nanofibers, UV light of 254 nm was used for 5 s at a distance of 10 cm (Fig. 1). The UV irradiator was manufactured to completely shut off the external light by using an UV C lamp (G40T10, Sankyo Denki, Japan) and a power supply (Arim Industrial Co., Ltd., Korea).

Characterization of the nanofibers

The polymerization of PCDA by photopolymerization was confirmed to change the color of the surfaces of the nanofibers from white to blue, and the change of the

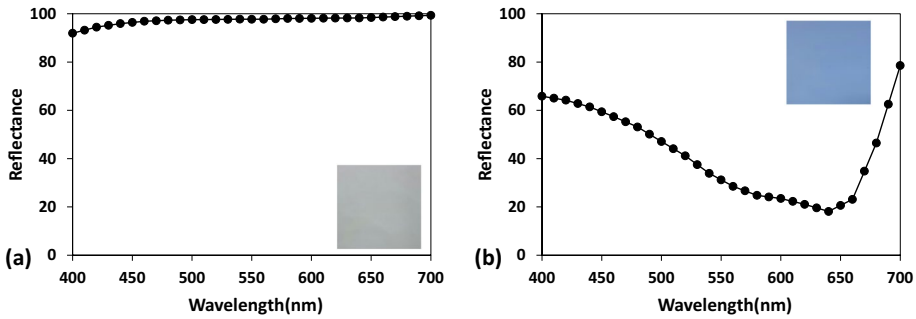

Fig. 2 Reflectance spectra of nanofibers embedded with PCDA: **a** before UV-irradiation; **b** after UV-irradiation (PU:PCDA ratio = 4:1. Spinning solution concentration: 12 wt%)

Table 1 Viscosity and conductivity of 8 wt% spinning solutions

PU:PCDA ratio	Viscosity (cP)	Conductivity (μS/cm)
1:1	158.75 ± 0.96	7.04 ± 0.09
2:1	171.00 ± 0.82	6.84 ± 0.09
3:1	182.25 ± 0.50	6.58 ± 0.13
4:1	190.50 ± 0.58	6.50 ± 0.07
5:1	202.00 ± 0.82	6.36 ± 0.09
6:1	210.00 ± 0.82	6.28 ± 0.04

reflectance of the surface was measured using a colorimeter (JS-555, Color Techno System. co. ltd., Japan). The morphologies of the PDA/PU nanofibers were characterized using a SEM (S-4800, Hitachi, Japan). The diameters of nanofibers that were fabricated were measured, and the formation of the beads and their smoothness were observed. The fabricated nanofibers were examined for chemical structure changes using FT-IR (Nicolet 5700, Thermo Electron Co. USA). We also examined the physical structure changes of nanofibers using an XRD (D/MAX-2500, Rigaku Co., Japan) and a thermal analyzer (TGA/DSC 1, Mettler-Toledo Inc., USA). The interaction between PU and PDA on the fabricated nanofibers was examined. The colorimetric characteristics by temperature stimulation were measured at 50–110 °C by heat treatment at different treatment time and color change was measured.

Results and discussion

The polymerization of polydiacetylene (PDA) by light irradiation

Figure 2 shows that the PCDA/PU nanofibers were white before photopolymerization. However, after photopolymerization, the PCDA contained in the nanofibers was polymerized into PDA, and a clear blue color appeared.

Characteristics of the manufactured nanofibers

Morphology

Table 1 shows the viscosity and conductivity of the spinning solution based on the ratio of PU to PCDA and the concentration. The PU to PCDA ratio was directly proportional to the viscosity, and the viscosity increased as the PU to PCDA ratio increased in the

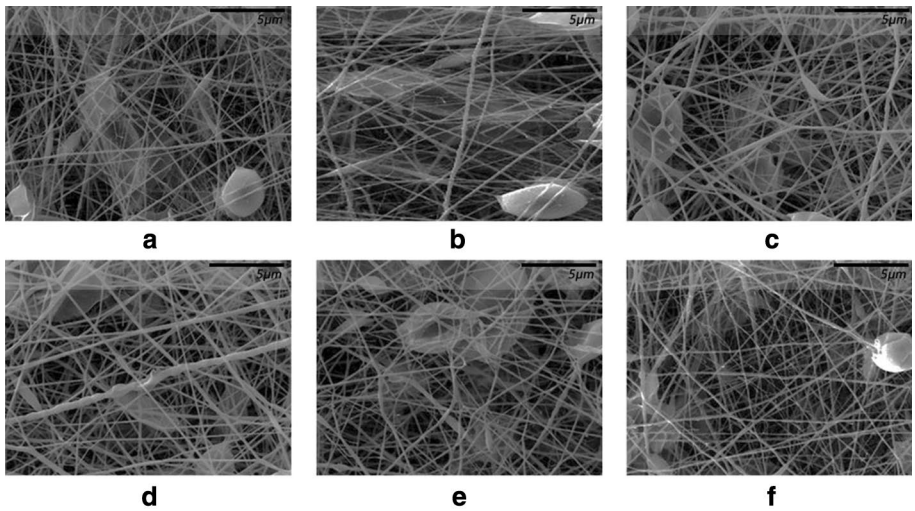

Fig. 3 SEM images of nanofibers fabricated by electrospinning the following PU:PCDA ratios (surface × 10,000): **a** 1:1; **b** 2:1; **c** 3:1; **d** 4:1; **e** 5:1; **f** 6:1 (spinning solution concentration: 8 wt%)

Table 2 Viscosity and conductivity of 10 wt% spinning solutions

PU:PCDA ratio	Viscosity (cP)	Conductivity (μS/cm)
1:1	163.75 ± 1.50	6.92 ± 0.08
2:1	168.00 ± 0.82	6.72 ± 0.08
3:1	179.00 ± 1.15	6.40 ± 0.10
4:1	191.00 ± 0.82	6.32 ± 0.08
5:1	209.00 ± 1.63	6.18 ± 0.11
6:1	220.00 ± 2.71	6.12 ± 0.08

spinning solution. The conductivities of the pure PU solution and the pure PCDA solution were 5.9 and 8 μS/cm, respectively. Therefore, the conductivity of the PCDA/PU solution was greater than that of the pure PU solution. As the amount of PU increased and the amount of PCDA decreased, the conductivity decreased slightly. Figure 3 shows the SEM images of the PCDA/PU nanofibers with various ratios of PU and PCDA in the 8 wt% spinning solution. Beads were generated irrespective of the ratio of PU to PCDA in the 8 wt% spinning solution. This indicated that, when the concentration of the spinning solution was 8%, the viscosity was too low to be suitable for spinning. When the viscosity of the spinning solution was low, there was insufficient spinning, the formation of the fibers was not completely achieved, and the spinning occurred in droplet form.

Table 2 shows the viscosity and electrical conductivity of the solution depending on the ratio of PU to PCDA in the mixture when the spinning solution concentration was 10 wt%. As was shown in Table 1, when the PU/PCDA ratio was increased, the viscosity increased, and decreasing the amount of PCDA resulted in a decrease in conductivity. Figure 4 shows SEM images of the PCDA/PU nanofibers with various contents of PU and PCDA in the mixture of the 10 wt% spinning solution. There also were beads in the 10 wt% spinning solution irrespective of the PU to PCDA ratio in the mixture. However, unlike at 8 wt%, we observed that the shape of the beads changed from circular to a

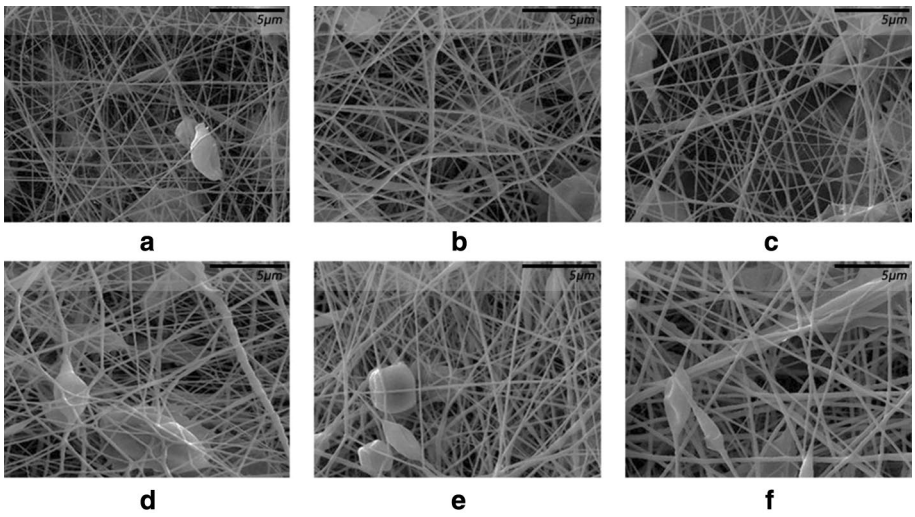

Fig. 4 SEM image of nanofibers fabricated by electrospinning the following PU:PCDA ratios (surface × 10,000): **a** 1:1; **b** 2:1; **c** 3:1; **d** 4:1; **e** 5:1; **f** 6:1 (spinning solution concentration: 10 wt%)

Table 3 Viscosity and conductivity of 12 wt% spinning solutions

PU:PCDA ratio	Viscosity (cP)	Conductivity (μS/cm)
1:1	179.75 ± 1.71	6.84 ± 0.11
2:1	181.75 ± 0.50	6.64 ± 0.11
3:1	198.75 ± 0.96	6.30 ± 0.10
4:1	206.25 ± 0.50	6.24 ± 0.05
5:1	225.25 ± 0.50	6.10 ± 0.07
6:1	237.25 ± 0.50	6.04 ± 0.11

fusiform shape as the content of PU increased. When the spinning solution had a low viscosity, the droplets had a low charge density, and the solution was not significantly dissociated. Also, the lack of polymer entanglements in the solution resulted in insufficient surface tension, and the Taylor Cone became unstable and the jet collapsed (Ryu 2011).

Table 3 shows the viscosity and electrical conductivity of the solution as they relate to the ratio of PU to PCDA when the concentration of the spinning solution was 12 wt%. As the ratio of PU to PCDA increased, the viscosity increased from about 180 cP to 237 cP, and the conductivity decreased slightly. Figure 5 shows the shapes of the nanofibers at different ratios of PU to PCDA in the spinning solution. When the mixing ratio of PU to PCDA in the spinning solution was less than 3:1, the shape of the nanofibers that were fabricated was mixed with the shapes of the filaments and the beads. Filaments were formed only when the ratio was 4:1 or more. The viscosity of the filament-formed condition as 200 nm or more. When the mixing ratio of PU was low, the viscosity decreased and, as a result, the fibers were not formed completely due to the lack of radioactivity, and beads were formed. Figure 6 shows that the average diameters of the fibers were 249, 275, and 299 nm at ratios of 4:1, 5:1, and 6:1, respectively.

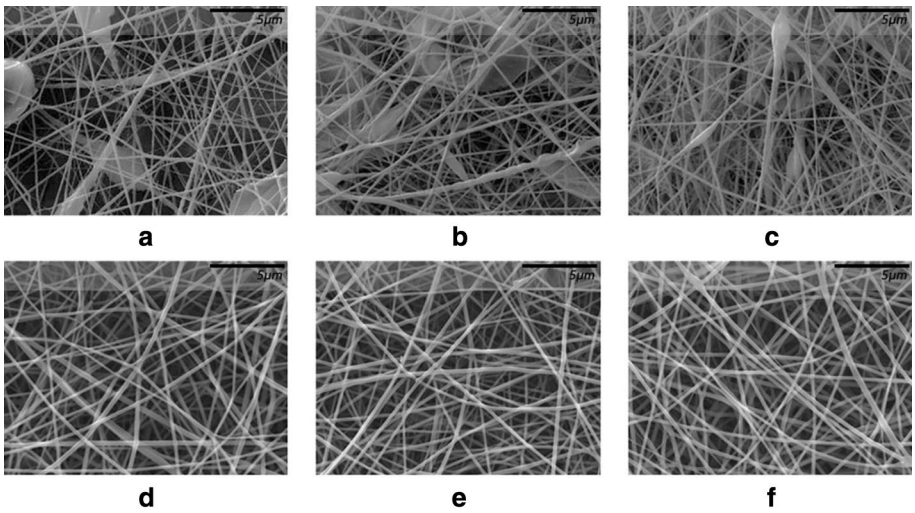

Fig. 5 SEM images of nanofibers fabricated by electrospinning the following PU:PCDA ratios (surface × 10,000): **a** 1:1; **b** 2:1; **c** 3:1; **d** 4:1; **e** 5:1; **f** 6:1 (spinning solution concentration: 12 wt%)

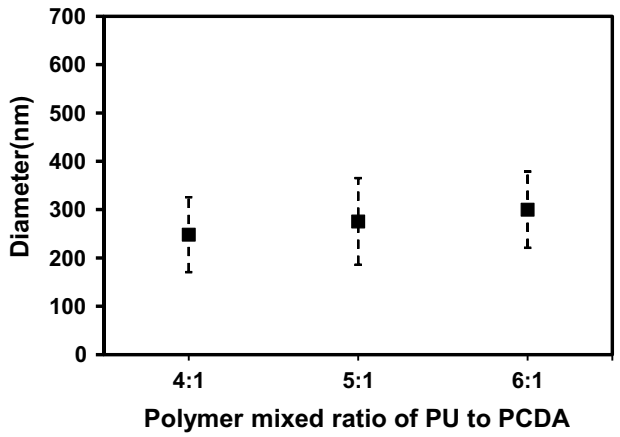

Fig. 6 Diameter (nm) of nanofibers fabricated by electrospinning the polymer mixed ratio (spinning solution concentration: 12 wt%)

Table 4 Viscosity and conductivity of 14 wt% spinning solutions

PU:PCDA ratio	Viscosity (cP)	Conductivity (μS/cm)
1:1	201.50 ± 0.58	6.60 ± 0.10
2:1	223.25 ± 0.50	6.40 ± 0.10
3:1	238.25 ± 0.50	6.18 ± 0.08
4:1	270.50 ± 0.58	6.14 ± 0.05
5:1	284.50 ± 0.58	6.04 ± 0.11
6:1	291.50 ± 0.58	5.98 ± 0.08

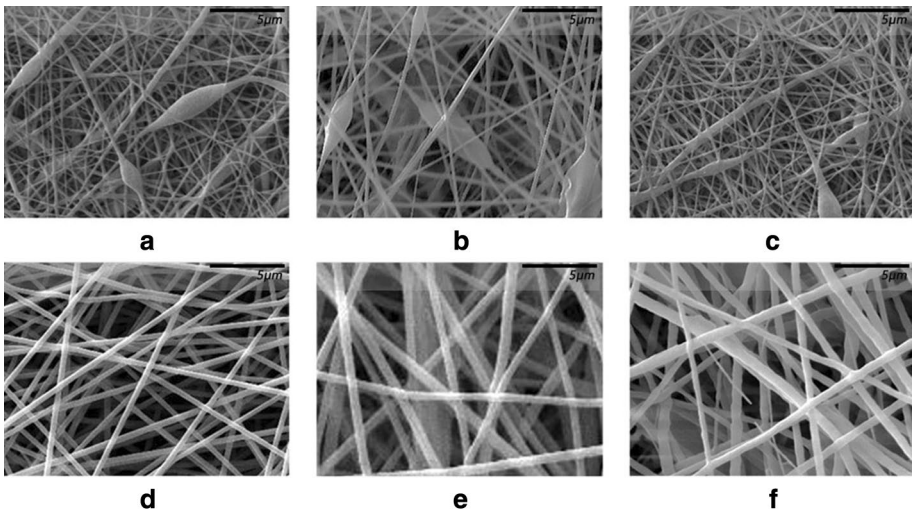

Fig. 7 SEM image of nanofibers fabricated by electrospinning various PU:PCDA ratios (surface × 10,000): **a** 1:1; **b** 2:1; **c** 3:1; **d** 4:1; **e** 5:1; **f** 6:1 (spinning solution concentration: 14 wt%)

Table 4 shows the viscosity and electrical conductivity of solutions depending on the ratio of PU to PCDA when the concentration of the spinning solution was 14 wt%. As with the previous concentrations, the viscosity increased as the percentage of PU increases, and the conductivity decreased slightly. At a concentration of 14%, the viscosity is above 200 nm in all proportions of PU and PCDA.

Figure 7 shows the morphology of the nanofibers based on the mixing ratio of PU to PCDA in the 14 wt% spinning solution. As in the case of the 12 wt% spinning solution, the nanofibers were well formed without beads at PU/PCDA ratios greater than 4:1. The viscosity of the fiber-forming conditions ranged from 270 to 290 cp. However, when compared with the viscosity of the 12 wt% spinning solution, the nanofibers of the filaments were well formed at viscosities of 200 cP or more in the case of the 12 wt% spinning solution, but, in the 14 wt% spinning solution, beads were formed when the ratio of PU to PCDA was 3:1 or less even if the viscosity was 200 cp or greater. As the concentration of the spinning solution increased, the amount of PCDA increased even if the ratio of PU to PCDA was the same. This indicated that, in addition to the viscosity, the amount of PCDA influenced the fabrication of the nanofibers. Since the formation of the beads is due to polymer entanglement insufficient at low concentrations, there is a critical concentration that allows sufficient entanglement of the polymer chains to form continuous fibers. As the amount of PCDA added increases, there appears to be a larger attractive force between PCDA monomers with self-assembled structure than PCDA and PU matrix, leading to a higher critical concentration allowing polymer chain entanglement (Alam et al. 2016; Yapor et al. 2017). That is, as the amount of PCDA increases, the hydrogen-bonding of the carboxylic headgroups of the polymerized PCDA increases. Increased hydrogen-bonding requires additional functional groups to be boned, so the amount of PU must be added as well to maintain proper molecular organization (Ahn et al. 2003).

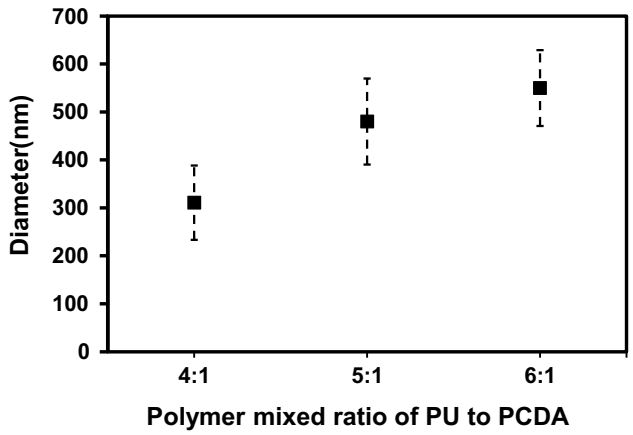

Fig. 8 Diameter (nm) of nanofibers fabricated by electrospinning the mixed polymer ratio (spinning solution concentration: 14 wt%)

Table 5 Viscosity and conductivity of 16 wt% spinning solutions

PU:PCDA ratio	Viscosity (cP)	Conductivity (μS/cm)
1:1	224.00 ± 1.41	6.36 ± 0.11
2:1	248.50 ± 0.58	6.16 ± 0.11
3:1	281.25 ± 0.50	6.14 ± 0.05
4:1	308.00 ± 1.15	6.12 ± 0.04
5:1	332.25 ± 0.50	5.98 ± 0.04
6:1	340.00 ± 0.82	5.92 ± 0.04

Figure 8 shows the diameters of the nanofibers at the mixing ratio of 4:1 or greater, and they were prepared smoothly without the beads. The increase in the concentration of PU in the spinning solution increased the diameters of the nanofibers to the range of 300–550 nm. As the viscosity increased, the diameters of the nanofibers also increased. This tendency was due to the fact that the increasing the viscosity of the solution increases the degree of entanglement of the polymer chains in the solvent and hinders the collapse of the jet (Andrady 2008).

Table 5 shows the viscosity and conductivity of the solution depending on the ratio of PU to PCDA in the mixture when the concentration of the spinning solution was 16 wt%. The viscosity increased significantly and ranged from 224 to 340 cP. In particular, when the ratio of PU to PCDA was 4:1 or more, the viscosity was 300 nm or more. The variation of the conductivity was smaller at other concentrations.

Figure 9 shows the shape of the nanofibers that were produced when the concentration of the spinning solution was 16 wt%. The nanofibers were prepared smoothly without beads when the ratios of PU to PCDA in the spinning solution were 2:1 and 3:1. In these cases, the amount of PCDA to be added was increased than other concentration conditions at which fibers are formed well. Viscosity is higher than other concentration solutions with similar amounts of PCDA. As discussed above, when the amount of PCDA was increased, nanofibers are formed well at a certain high

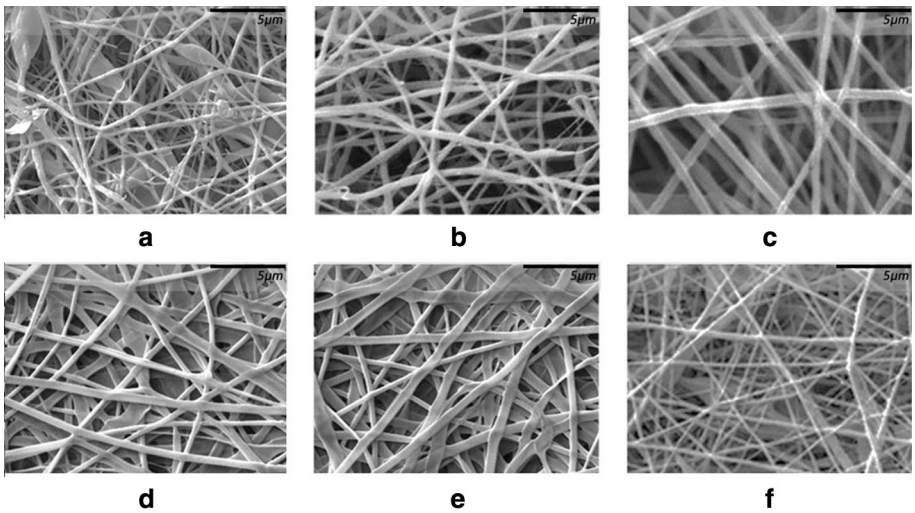

Fig. 9 SEM images of nanofibers fabricated by electrospinning the following various PU:PCDA ratios (surface × 10,000): **a** 1:1; **b** 2:1; **c** 3:1; **d** 4:1; **e** 5:1; **f** 6:1 (spinning solution concentration: 16 wt%)

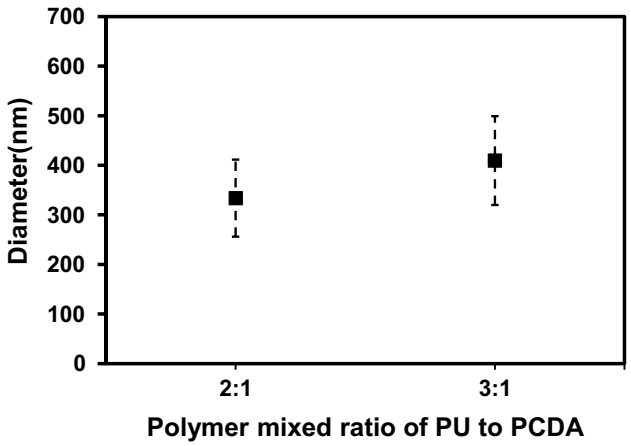

Fig. 10 Diameter (nm) of nanofibers fabricated by electrospinning two different ratios of PU:PCDA (spinning solution concentration: 16 wt%)

viscosity. However, the increase in the amount of PCDA is disadvantageous in economic terms.

Figure 10 shows that, when the ratios of PCDA to PDA were 2:1 and 3:1, the average diameters of the nanofibers were about 330 and 400 nm, respectively. When the ratio of PCDA to PDA in the spinning solution was 4:1 to 5:1, the shapes of the spun nanofibers were distorted, and the nanofibers were fused to each other. When the viscosity of the spinning solution was high, the size of the droplets became large, and the solvent is not volatilized completely even when it reached the collector. When the ratio of PU to PCDA was 6:1, the spinning was interrupted at times. If the viscosity of the spinning solution is too high, it is difficult to form the Taylor Cone, and the

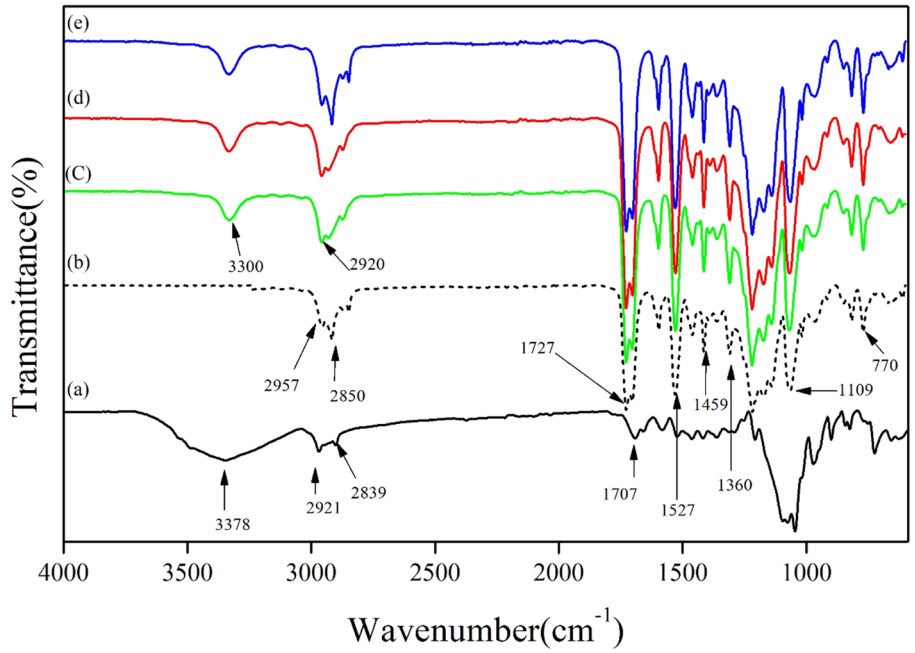

Fig. 11 FT-IR spectra of PU nanofibers and nanofibers according to different ratio of PU to PCDA. **a** Pure PDA **b** pure PU, **c** 6:1, **d** 5:1 and **e** 4:1 (spinning solution concentration: 12 wt%)

surface of the droplet solidifies at the tip of the nozzle (Andrady 2008; Satapathy et al. 2011).

Conductivity was about 6–7 μS/cm at all concentrations and PU to PCDA mixing ratios. It has been reported that this degree of variation of the conductivity has no significant effect on electric spinning (Cengiz and Jirsak 2009).

Chemical structure change of nanofibers

The FT-IR spectra of pure PU nanofibers, nanofibers with PDA and pure polydiacetylenes as colorimetric polymers are shown in Fig. 11. The absorption band of pure PDA was found at 3378 cm^{-1} due to O–H stretching vibration, and the peak due to stretching vibration of C–H group was 2921 cm^{-1} and 2839 cm^{-1}. The absorption band of pure PU nanofibers was found to be 2957 cm^{-1} (asymmetric stretching vibration) and 2850 cm^{-1} (symmetric stretching vibration) due to the C–H group. Urethane, urea, and –(C=O)– carbonyl in the ester group showed a stretching vibration of 1727 cm^{-1}. Also, the vibration peak due to –(CONH) group appeared at 1527 cm^{-1}, bending vibration by CH_3 group was observed at 1459 cm^{-1}. And we founded bending vibration due to –(CNH)– group at 1360 cm^{-1}, and a stretching vibration due to ester linkages at 1109 cm^{-1}. And the absorption band by C–H was 770 cm^{-1}.

The absorption spectra of PDA-containing PU nanofibers show that the spectra at 3300 cm^{-1} and 2920 cm^{-1} due to the PDA were overlapped on PU absorption spectrum (Kim and Lee 2017; Barikani et al. 2015; Da Silva et al. 2011; Paul et al. 2013; Wu et al. 2013). The peak of the spectrum, which did not exist in pure PU nanofibers, appears in

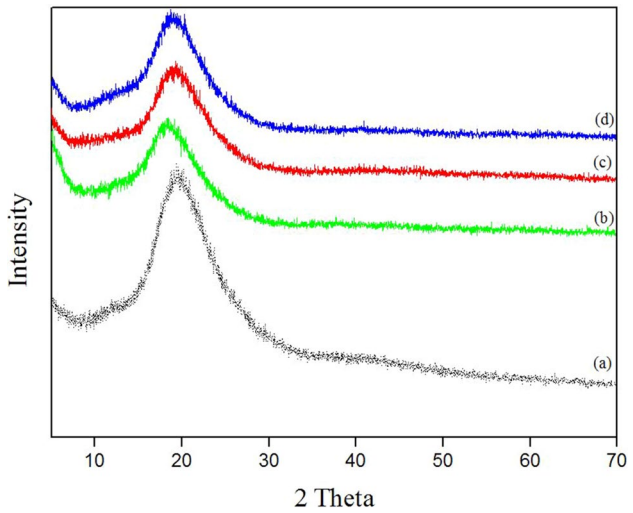

Fig. 12 XRD spectra of PU nanofibers and nanofibers according to different ratio of PU to PCDA. **a** Pure PU, **b** 6:1, **c** 5:1 and **d** 4:1 (spinning solution concentration: 12 wt%)

Table 6 Thermal analysis of nanofiber prepared from different ratio of PU to PCDA (spinning solution concentration: 12 wt%)

PU: PCDA ratio	T_m (°C)	ΔH_m (J/g^{-1})
Pure PU	407.03	520.14
6:1	406.32	512.66
5:1	405.81	497.37
4:1	404.10	486.01

the PDA/PU nanofiber, which means that the PDA was uniformly dispersed in the PU (Gregorio and Cestari 1994; Kim et al. 2014).

Physical structure change of nanofibers

Comparing the XRD spectra of Fig. 12, $2\theta = 20°$ peaks due to the PU diffraction pattern appears in all samples. The broad diffraction peak of the PU nanofiber was due to the low crystallinity of the PU. Also, the addition of PCDA decreased the specific peak of PU. It was the result of intermolecular force reduction due to the interval between the polymer chains as the PCDA and PU are bonded (Hong et al. 2016; Shin and Kim 2016; Kew and Hall 2006).

Table 6 shows the results of thermal analysis of nanofibers with pure PU nanofibers and PDA-added nanofibers. The melting point of pure PU nanofibers was 407.03 °C and the nanofibers containing PDA were slightly lowered to 404–406 °C depending on the content of PDA. Also, the amount of heat required for pyrolysis decreased somewhat. It was the result of a decrease in intermolecular force and a decrease in degree of crystallization due to the combination of PDA and PU, as shown in the results of the XRD analysis (Hong et al. 2016; Shin and Kim 2016; Kew and Hall 2006).

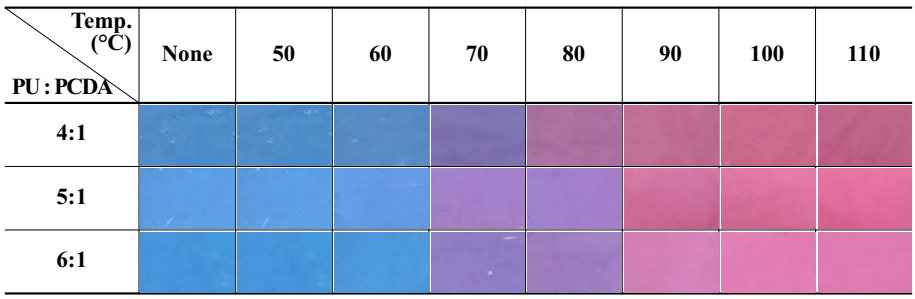

Fig. 13 Photographic images of PDA/PU nanofibers responded to heat treated according to different ratio of PU and PCDA (spinning solution concentration: 12 wt%, heat treated time: 10 s.)

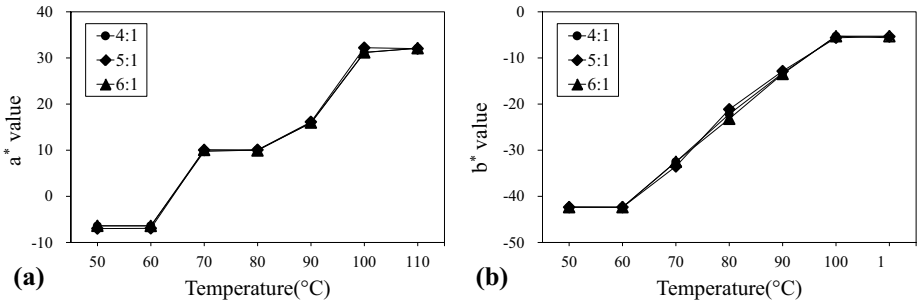

Fig. 14 Change of a* and b* Value of PDA/PU nanofibers by treated temperature; **a** a* value **b** b* value (spinning solution concentration: 12 wt%, heat treated time: 10 s.)

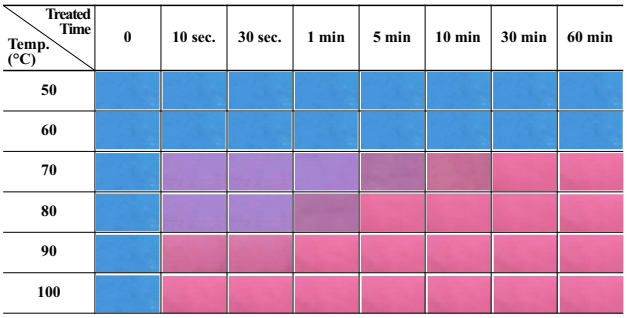

Fig. 15 Photographic images of PDA/PU nanofibers responded to heat treated according to heat treated time (spinning solution concentration: 12 wt%, ratio of PU to PCDA: 6:1)

Color transition by temperature stimulation of nanofibers

Figures 13 and 14 show the results of the blending ratio of PU to PCDA and the colorimetric characteristics of nanofibers according to the heat treatment temperature. Regardless of the content of PCDA, no color change was observed at temperatures below 60 °C. However, as the temperature increased above 70 °C, the redness of the nanofibers increased. Comparing the values of a* and b* in Fig. 14, the content of PDA was not significantly affected. Therefore, it was expected that sufficient color transition effect can be obtained with a small amount of PDA.

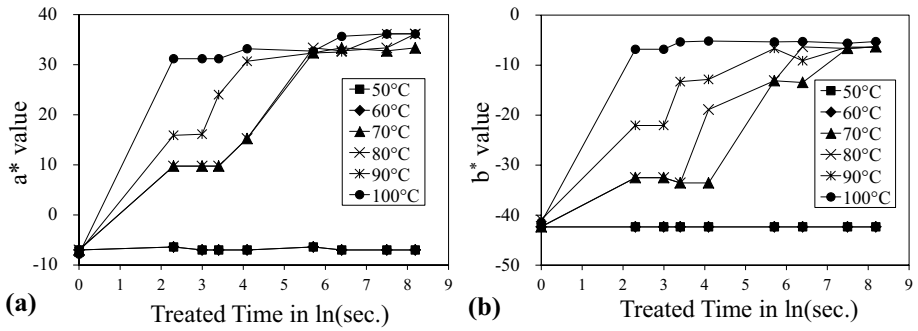

Fig. 16 Change of a* and b* value of PDA/PU nanofibers by treated time; **a** a* value, **b** b* value (spinning solution concentration: 12 wt%, ratio of PU to PCDA: 6:1)

Figures 15 and 16 show the results of examining the colorimetric characteristics of nanofibers according to heat treated temperature and treated time. Comparing the values of a* and b* in Fig. 16, the color change was not observed at temperatures below 60 °C even when the heat treated time was increased. At the treated temperature from 70 to 90 °C were different reaction rates depending on the treated time. The higher the temperature, the less time it takes to change to red. When the temperature was over 100 °C, it immediately turned red. From the above results, it was confirmed that the PDA/PU nanofibers produced exhibited color transition upon exposure to a temperature of 70 °C or higher, and that the reaction rate varied depending on the temperature. The color change at 70 °C is in a good agreement with the previous paper (Alam et al. 2016).

Conclusions

The effect of the concentration of spinning solution and the mixing ratio of PU and PCDA on the morphology of the PDA/PU nanofibers were studied. As the mixing ratio of PCDA decreased, the viscosity increased and the conductivity decreased. If the viscosity of the spinning solution was inadequate, beads were formed, and nanofibers with the desired shapes were not produced. The range of change in the conductivity of the solution did not affect the fabrication of the nanofibers. It was found that the PDA/PU nanofibers were influenced both by the proper concentration of the spinning solution and by the content of PCDA. Increasing the amount of PCDA also increased the viscosity required for spinning. The optimum conditions for economic efficiency and practicality of the production of the PDA/PU nanofibers a spinning-solution concentration in the range of 12–14 wt%, a PU/PCDA ratio greater than 4:1, and a viscosity in the range of 225 to 290 cP. With these conditions, it is possible to make a bead-less, smooth PDA/PU nanofibers that is well formed and has PDA/PU nanofibers with diameters in the range of 270–550 nm. The FT-IR spectra of the PU nanofibers containing the colorimetric polymers show that the spectrum due to the PDA overlaps the band of the PU nanofibers. It was confirmed that the PDA was uniformly dispersed in the PU nanofiber. From the results of XRD spectrum and DSC analysis, intermolecular force reduction due to the bonded of PDA and PU was confirmed. When the PU nanofibers containing PDA were exposed to heat, a color change from blue to red was observed at 70 °C or higher, and the higher the temperature, the faster the color transition reaction rate. Also, it was confirmed that PU/

PCDA nanofiber of 6:1 ratio including a small amount of PCDA had sufficiently color transition effect by temperature stimulation.

Abbreviations
PCDA: 10,12-pentacosadiynoic acid; PDA: polydiacetylene; PU: polyureathane; DMF: *N*-dimethylformamide.

Authors' contributions
KMO and LJS were contributed to the conception of the study, designed the experiment, conducted the work and drafted the manuscript. Both authors read and approved the final manuscript.

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Competing interests
The authors declare that they have no competing interests.

Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Consent for publication
Not applicable.

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Not applicable.

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