

Syndiotactic polypropylene nanofibers obtained from solution electrospinning process at ambient temperature

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ABSTRACT: Fabrication of semicrystalline syndiotactic polypropylene (sPP) nanofibers by solution electrospinning was studied. It was found that sPP nanofibers with an average diameter of 230 nm were successfully fabricated via solution electrospinning with methylcyclohexane as solvent at room temperature (25°C). The obtained diameter was significantly thinner than the minimum diameter of 350 nm of PP fibers that were reported previously. It was also found that increasing viscosity of the sPP solution, which was customarily a useful way of fabricating noncrystalline thin fibers, was found ineffectual in producing thinner semicrystalline sPP fibers in our experiments. In fact, a careful selection of solvent by considering the evaporation rate and the specific viscosity could effectively lead to the fabrication of thinner sPP fibers by imposing proper elongation and preventing the sPP solution from gelation. The results could be applied to other semicrystalline polyolefins with similar gelation characteristics analogous to sPP to produce thinner nanofibers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43238.

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INTRODUCTION

Electrospun thin fibers can be practically applied to various functional materials such as separation filters, tissue scaffolds, sensors, and fiber-reinforced composites.^{1–7} In the solution electrospinning in general, the key solution properties for the electrospinning include solution viscosity, conductivity, dielectric constant, volatility, and surface tension.^{8–11} From all these experimental results of the solution properties, it was generally found for noncrystalline polymers that thin nanofibers could be obtained from the solvent with high conductivity,¹² high dielectric constant,¹¹ and low volatility.^{13,14} Selecting a good solvent for polymer could increase the intrinsic viscosity of the polymeric solution and the enhancement of intrinsic viscosity was also considered to be one of the key parameters that could realize the fabrication of thin fibers.¹⁵ All of these reported significant determinants for thin fibers using solution electrospinning processes, however, have been limited to noncrystalline polymers.

Polypropylene (PP) and polyethylene (PE) are semicrystalline polyolefins that have unique properties with outstanding mechanical features and excellent chemical resistance. The chemical resistance, however, causes major difficulty in dissolving polyolefins into commonly used solvents at ambient

temperature due to their chemical stability, which would, therefore, inhibit creating polyolefin nanofibers by electrospinning. To solve the problem, since electrospinning process could only be carried out using liquid-state polymers, the dissolution of the polyolefins into good solvents has generally been attempted. Since a very few solvents were known as the good solvents for polyolefins, the dissolution was normally carried out at substantially elevated temperature.¹⁶ The polyolefin solutions, however, when they were cooled to ambient temperature, could form thermoreversible physical gels due to the nature of their semicrystallinity that could also work as physical crosslinks. Once the solutions transformed into gels, the polymer specimens would not be in the liquid state, which could obviously prevent the synthesis of fine fibers by electrospinning.¹⁷ Because of such difficulties in the solution electrospinning of the polyolefins, the polyolefins were normally spun into fibers through different and sometimes rather complex methods.^{18–21}

Thin polyolefin fibers with the diameter ranging from 0.3 to 1.2 μm have been reported so far using polypropylenes.²² In fact, the fabrication of the thinnest fibers of 286 nm was reported by adding Bu_4NClO_4 as salt during the high-temperature solution-electrospinning.¹⁹ Lee *et al.* reported that syndiotactic PP (sPP) fibers with the average diameter of 650 nm were successfully fabricated at slightly elevated temperature (35°C) using a

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multicomponent solvent system including cyclohexane, acetone, and DMF.^{13,22,23} In this case, the rapid gelation from the heterogeneity of the solution actually led to the formation of the nonuniform fibers. Other than electrospinning, Suzuki *et al.* proposed and developed a new method for the production of isotactic PP (iPP) nano-sheets with a carbon dioxide laser by drawing iPP at a supersonic velocity. They eventually obtained iPP nanofibers with an average diameter of 350 nm, which has become the minimum diameter of PP fibers fabricated at room temperature.²⁰ The solution-electrospinning process for crystalline polymers, including polyolefins, however, has not been systematically studied.

In this work, we attempted to fabricate semicrystalline sPP nanofibers by the solution electrospinning method by simply using single solvent to achieve a homogenous solution system (in contrast to the multi-component solvent system as mentioned above) at ambient temperature (25°C). Cyclohexane, methyl-cyclohexane, ethyl-cyclohexane, propyl-cyclohexane, butyl-cyclohexane, and decahydronaphthalene (decalin) were separately examined as solvent, which possessed similar chemical structures with close solubility parameters. The selection of the solvents was carefully conducted by primarily considering the effects of the solvent properties including conductivity, dielectric constant, evaporation rate, and viscosity on the gelation behavior of the sPP solutions. As a result, sPP nanofibers with an average diameter of 230 nm were successfully fabricated via solution electrospinning by choosing methyl-cyclohexane as solvent at ambient temperature (25°C). It was found that a careful selection of solvent by considering the evaporation rate and the specific viscosity of the solvent could effectively lead to the fabrication of thinner sPP nanofibers through proper elongation and gelation prevention of the sPP solution.

EXPERIMENTAL

Materials

Syndiotactic polypropylene (sPP) was purchased from Sigma-Aldrich. The weight average molecular weight (M_w) and the number average molecular weight (M_n) were 174,000 and 75,000 g/mol, respectively. The melting point was 127°C measured by differential scanning calorimetry (DSC). Cyclohexane, methyl-cyclohexane, and decahydronaphthalene (mixture of *cis*- and *trans*-) (decalin) were purchased from Wako Pure Chemical Industries. Ethyl-cyclohexane, propyl-cyclohexane, and butyl-cyclohexane were purchased from Tokyo Chemical Industry.

Solution Preparations

sPP was dissolved into cyclohexane, methyl-cyclohexane, ethyl-cyclohexane, propyl-cyclohexane, butyl-cyclohexane, and decalin, separately, and stirred at 80°C for overnight. Then the heated solutions were cooled down to room temperature (25°C) in 30 min. The concentration of sPP in the solution was changed from 1 to 5 wt %.

Gelation-Speed Evaluation

The gelation characteristics of sPP largely depended on the concentrations of the solution and the duration of the cooling process from the heated solution. To confirm the sol state of the solution during electrospinning, we performed gelation tests for

sPP solutions by a tube testing method. If the flow of solutions was observed, the solutions were in the sol state, and if not, then the solutions were in the gel state. sPP solutions in glass tubes were kept stationary at the controlled temperature of 25°C for up to 5 days. The tubes were manually reversed every 24 h and checked whether the solutions were in the sol state or in the gel state.

Fabrication of sPP Nanofibers by Electrospinning

sPP nanofibers were fabricated using an electrospinning apparatus (1639, Imoto). Each solution was drawn into a syringe (1005LT, Hamilton) with a capillary tip whose inner diameter was 0.53 mm. The needle tip was connected to a high voltage supply and the positive voltage of 10 kV was applied to the polymer solutions. The grounded metal collector was placed 13 cm off the needle tip. The flow rates of the solution were controlled by syringe pump at 0.20 mL/h.

Morphological Analysis of Electrospun sPP Nanofibers

Electrospun sPP fibers were characterized by the field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi High-Technology). Before SEM observation, all specimens were coated with osmium to prevent electrostatic charge. For each sample, the diameters of the fabricated fibers were measured at 100 different points on each SEM micrograph selected randomly for the calculation of the average diameter of the fibers.

Characterization of Physical Properties of Solvents

To evaluate characteristic features of the used solvents, the conductivity, the dielectric constant, and the evaporation rate of the solvents were individually measured. The conductivity of the solvent was measured using a nonaqueous conductivity meter (DT700, Dispersion Technology) at room temperature (25°C). The dielectric constant of the solvent was also measured using a liquid permittivity meter (Model 871, Nihon Rufuto). Furthermore, the evaporation loss was measured by weighing the mass change of each solvent at 25°C. Each solvent was poured into a ϕ 36 mm glass tube and the tube was left at 25°C under the stable airflow.

Rheological Analysis of sPP Solutions

The zero-shear rate viscosity (η_0) data were obtained by a strain-controlled rheometer (ARES-G2, TA Instruments) under a cone-plate geometry (50.0 mm in diameter and 0.0192 rad in its cone angle). All viscosity data were measured at 25°C. The shear rate was changed from 0.1 to 100 s⁻¹ at 25°C. To evaluate the physical properties of the solution, the specific viscosity (η_{sp}) of the sPP solutions in each solvent was calculated by estimating the zero-shear rate viscosity, analyzed by measured experimental viscosity data. η_{sp} was calculated using the zero-shear rate viscosity (η_0) defined as follows:

$$\eta_{sp} = (\eta_0 - \eta_s) / \eta_s \quad (1)$$

where η_s is the solvent viscosity. η_{sp} represents the rate of increase in solvent viscosity by mixing polymeric solute. The values for the viscosity of solvent were 0.60 mPa s for cyclohexane, 0.77 mPa s for methyl-cyclohexane, 0.85 mPa s for ethyl-cyclohexane, 0.99 mPa s for propyl-cyclohexane, 1.34 mPa s for butyl-cyclohexane, and 2.05 mPa s for decalin.

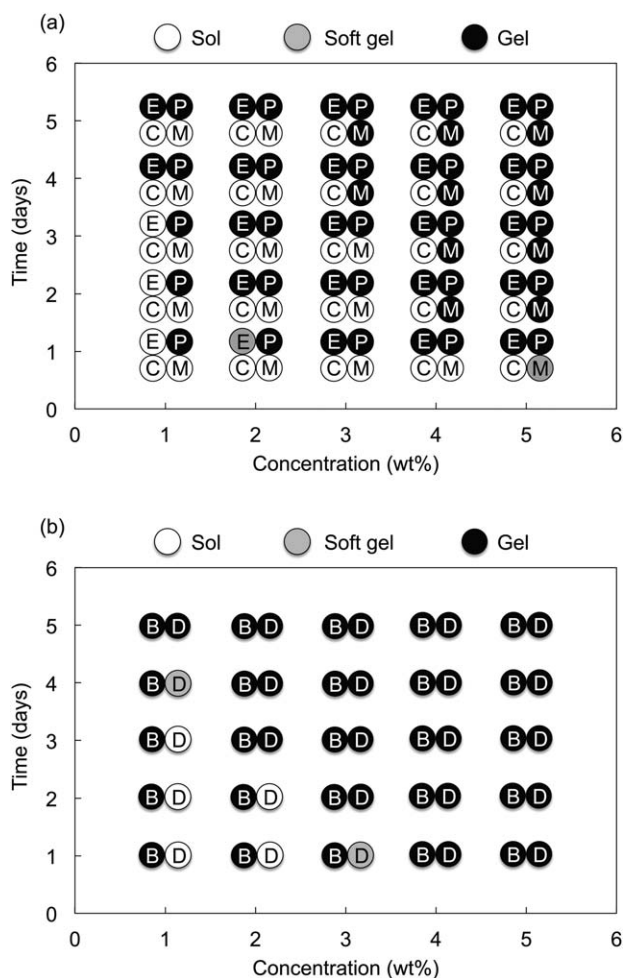


Figure 1. Sol–gel phase changes by concentration and time with different solvents: cyclohexane (C), methyl-cyclohexane (M), ethyl-cyclohexane (E), propyl-cyclohexane (P), butyl-cyclohexane (B), and decalin (D).

RESULTS AND DISCUSSION

Gelation-Speed Evaluation of sPP Solutions

The solution for electrospinning should be in the sol state. The solvent properties and the viscosity of the solution should also be considered. The gelation speed of the crystalline polymer solution is also very important when the solution is used for electrospinning. Figure 1 shows the gelation speed of sPP solutions at the concentration from 1 to 5 wt %. In Figure 1(a), as for the sPP/cyclohexane solution, all 1–5 wt % solutions were in the sol states even 5 days after the preparation, and the sPP solution with cyclohexane showed the widest sol region. The 3–5 wt % methyl-cyclohexane and ethyl-cyclohexane solutions changed from sol to gel states after a few days and the 1–2 wt % solutions were in the sol state even after 5 days. The 3–5 wt % propyl-cyclohexane solution changed from sol to gel states relatively fast in a day and the 1–2 wt % solutions changed to gel states after few days.

As was shown in Figure 1(b), the solution with butyl-cyclohexane was almost in the gel state. It was found that the gelation speed became faster as the length of the alkyl group bonded to cyclohexane increased. The decalin solution

presented sol–gel transitions significantly faster than the other solutions except for the solutions with propyl-cyclohexane and butyl-cyclohexane. The results indicated that the gelation strongly depended on the types of solvents, the concentrations of the solution, and time. It could, therefore, be concluded that the sol solution with cyclohexane, or methyl-cyclohexane and ethyl-cyclohexane that are the cyclohexane with shorter alkyl chains, was a prospective candidate for the solution electrospinning process.

Morphology of Electrospun sPP Nanofibers

Figure 2 shows the SEM images of fabricated sPP fibers and the frequency distribution of the fiber diameter prepared via solution electrospinning by different solvents at 25°C. Figure 2(a) showed that the average diameter of sPP fibers by cyclohexane was 720 ± 154 nm. As demonstrated in Figure 2(b), ultrafine sPP fibers with the diameter of 230 ± 57 nm were obtained by electrospinning 3 wt % sPP solution in methyl-cyclohexane with relatively narrow frequency distribution [Figure 2(f)]. It was found that the fibers electrospun from the methyl-cyclohexane solution were connected to each other, while the fibers electrospun from the cyclohexane solution were not connected. Such connection could be due to the wet fibers after reaching the collector probably by the low volatility of methyl-cyclohexane as compared with cyclohexane. Figure 2(c) also showed the average diameter of sPP fibers by ethyl-cyclohexane was 380 ± 130 nm. It was found that the fibers electrospun from the ethyl-cyclohexane solution were not connected to each other. This is probably due to the faster gelation of ethyl-cyclohexane solution before reaching the collector as compared to that of methyl-cyclohexane solution. Figure 2(e) revealed that the solution with decalin forming soft-gel in a day after cooling down to 25°C produced no fibers but microbeads. As mentioned before, since the solution with propyl-cyclohexane and butyl-cyclohexane formed gel relatively fast after cooling to 25°C, the electrospinning process could not be carried out [Figure 2(d)].

All used solvents were classified as alicyclic hydrocarbons with resembling cyclic chemical structures: a slight structural difference between cyclohexane, methyl-cyclohexane, ethyl-cyclohexane, propyl-cyclohexane, and butyl-cyclohexane, for instance, can only be seen in their chemical structures without or with a different length of alkyl group in their side chains. Nevertheless, it was revealed that such slight difference in the chemical structures of the solvents could strongly affect the morphology of the resulting electrospun fibers. The viscous behavior of the solution could be easily controlled by the concentration of the solution and the type of the solvent.^{23,24} Hence, the selection of the solvent was highly significant for the fabrication of thin fibers by electrospinning.

Essential Solvent Properties: Electric Property and Volatility

To evaluate the effects of the essential solvent properties on the obtained fiber morphology, the conductivity, the dielectric constant, and the evaporation rate of the solvents were measured and summarized in Table I. The conductivities of cyclohexane, methyl-cyclohexane, ethyl-cyclohexane, and decalin were found to be fairly close to each other at, 6.62, and 5.20, 10.4, and 5.77 pS/cm, respectively. The dielectric constants of cyclohexane,

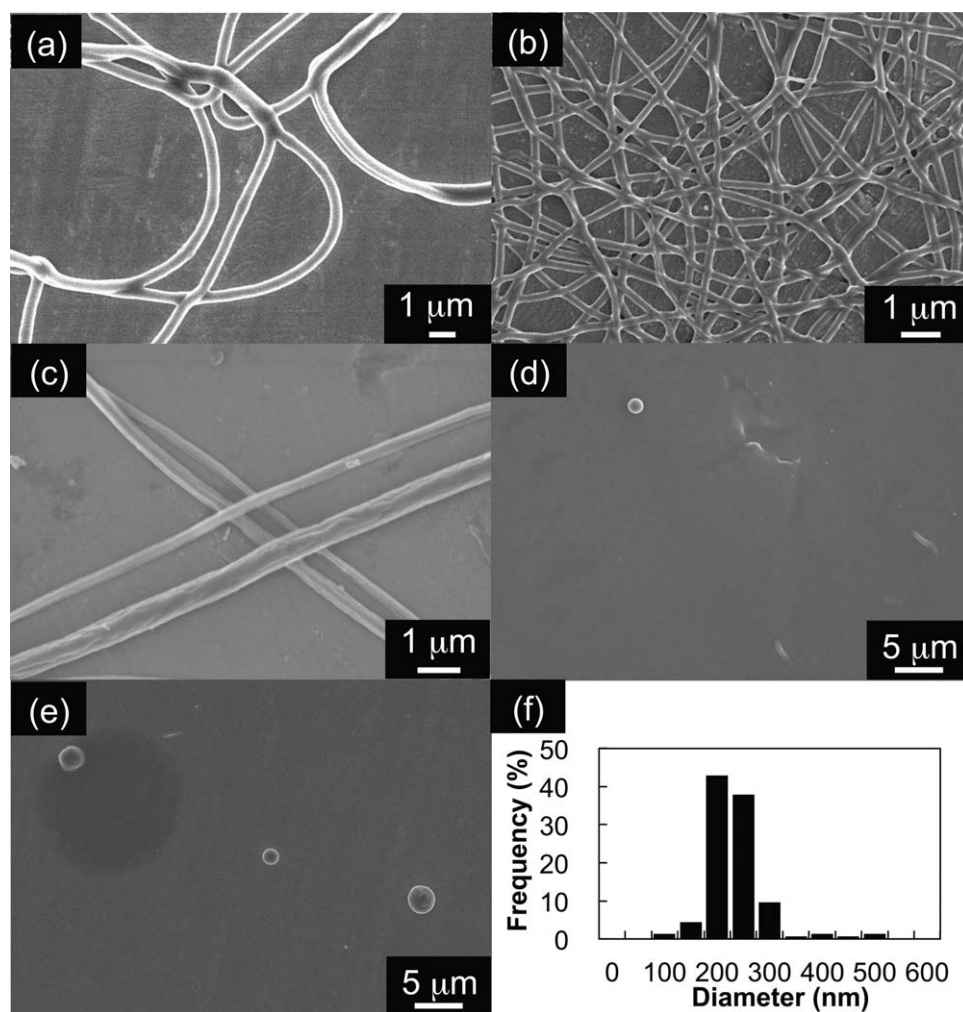


Figure 2. SEM images of electrospun sPP fibers fabricated by different solvents: (a) cyclohexane, (b) methyl-cyclohexane, (c) ethyl-cyclohexane, (d) propyl-cyclohexane, and (e) decalin, with the frequency distribution of the diameter of sPP fibers fabricated by methyl-cyclohexane: (f).

methyl-cyclohexane, ethyl-cyclohexane, and decalin were also very close at 2.04, 2.04, 2.04, and 2.19, respectively. As compared to the previous results using the salt, such as Bu_4NClO_4 or the high-permittivity solvent, such as DMF, in terms of the electric properties, there was not much difference between the solvents.^{21,23} In parallel, the conductivities and the dielectric

constants of 3 wt % sPP solution were measured and summarized in Table II. It was found that the conductivity slightly increased and the dielectric constant remained almost constant. In more detail, the increase in the conductivity was largest for methyl-cyclohexane and smallest for butyl-cyclohexane. Therefore, it was also concluded that the dielectric constants did not

Table I. Physical Properties of Solvents Related to Electrospinning

Name	Molecular weight (g/mol)	Boiling point ^a (°C)	Conductivity (pS/m)	Dielectric constant (-)
Cyclohexane	84.16	81	6.62	2.04
Methyl-cyclohexane	98.19	100	5.20	2.04
Ethyl-cyclohexane	112.22	132	10.4	2.04
Propyl-cyclohexane	126.24	157	12.2	2.05
Butyl-cyclohexane	140.27	180	11.8	2.06
Decahydronaphthalene	138.25	185 (<i>cis</i> -) 193 (<i>trans</i> -)	5.77	2.19

^aFrom SDS data sheet.

Table II. Conductivity and Dielectric Constant of sPP Solutions

Name	Conductivity (pS/m)	Dielectric constant (-)
Cyclohexane	60.4	2.02
Methyl-cyclohexane	70.2	2.03
Ethyl-cyclohexane	65.9	2.05
Propyl-cyclohexane	63.4	2.06
Butyl-cyclohexane	43.2	2.07
Decahydronaphthalene	43.8	2.17

affect the morphology of the fibers in our experiments and that the conductivity enhanced by the interaction between polymer and solvent slightly affected the morphology of the fibers.

Figure 3 shows the evaporation loss of the solvents against time. The evaporation rates of cyclohexane, methyl-cyclohexane, ethyl-cyclohexane, and decalin were calculated as 1.80, 0.94, 0.30, and 0.04 mg/min, respectively. The decrease in the evaporation rates agreed well with the increase in the boiling points as well as the increase in the molecular weights (Table I).

Generally for the *noncrystalline* polymers, it has been reported that using solvent with low volatility would be the key to obtain thin fibers. This is because the elongation process by electrostatic force should be adequately and sufficiently applied to the electrospun fibers before the solidification of the fibers due to the solvent evaporation. Therefore, considering the results of our experiments, thinnest fibers should be obtained from cyclohexane with a longer alkyl group or decalin, which possessed the lowest volatility, whereas thickest fibers should be obtained from the highest volatility cyclohexane. In fact, however, the thinnest fibers were obtained from methyl-cyclohexane, the medium volatility solvent. It was considered that extremely low volatility became rather ineffective in electrospinning semicrystalline polymers because without sufficient solidification, the solution could not form solid fibers before getting to the metal collector.

Rheological Aspects of sPP Solutions

The viscosity of each solution, which could normally be one of the key parameters that determined the morphology of fibers,

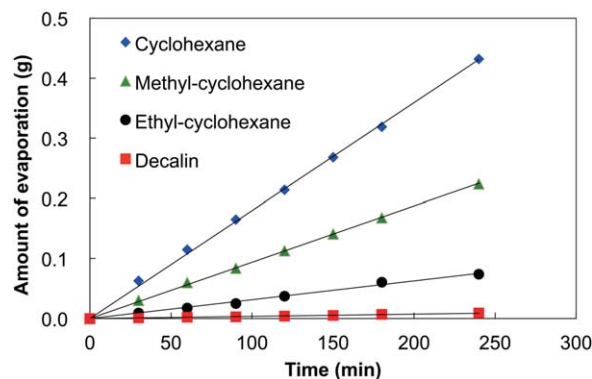


Figure 3. Evaporation loss against time using different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

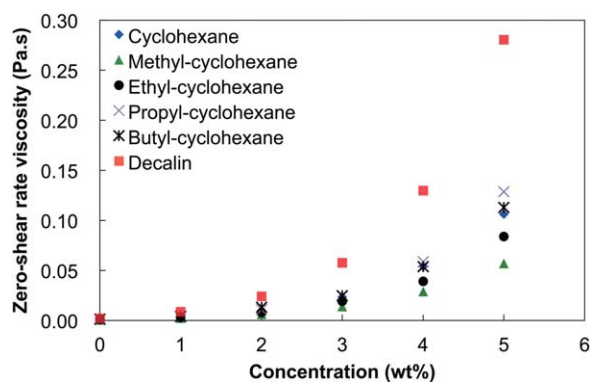


Figure 4. Zero shear-rate viscosity as a function of concentration by different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was measured by changing the shear rates from 0.1 to 100 s^{-1} at 25°C. The concentration of the solutions was changed from 1 to 5 wt %. Figure 4 shows the zero-shear rate viscosity (η_0) as a function of shear rate at different concentrations. η_0 increased as the concentration increased from 1 to 5 wt %. Figure 5 shows the specific viscosity (η_{sp}) as a function of concentration. η_{sp} of cyclohexane was the highest, η_{sp} of methyl-cyclohexane was the lowest, and η_{sp} of ethyl-cyclohexane, propyl-cyclohexane, butyl-cyclohexane, and decalin were in between those of cyclohexane and methyl-cyclohexane at every concentration. Considering the previous studies on the intrinsic viscosity of noncrystalline polymers,¹⁵ our viscometric results could suggest that cyclohexane with the highest viscosity should be the best solvent for the thinnest fiber fabrication, which, however, could not be applied to our experiments [Figure 2(a)].

To discuss the deviation of the fiber morphology observed in our fiber fabrications from the other preceding results suggesting a fairly strong relation between thinner fibers and higher viscosity of noncrystalline polymers, we considered the molecular entanglements. In fact, the entanglements generally took an important role in constructing uniform fibers. Colby *et al.* defined the entanglement concentration C_e at the slope change of η_{sp} , which was also at the exact boundary between the semidilute-unentangled and semidilute-entangled regimes.²⁴ At

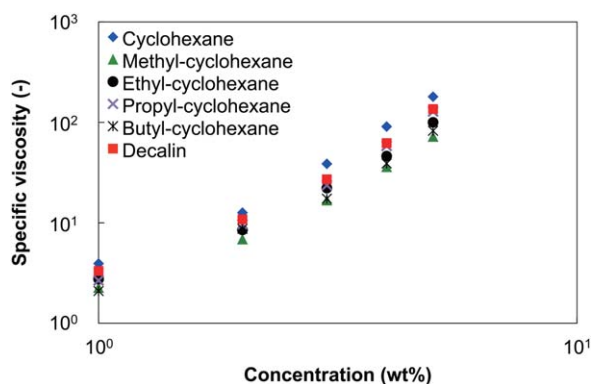


Figure 5. Specific viscosity as a function of concentration by different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

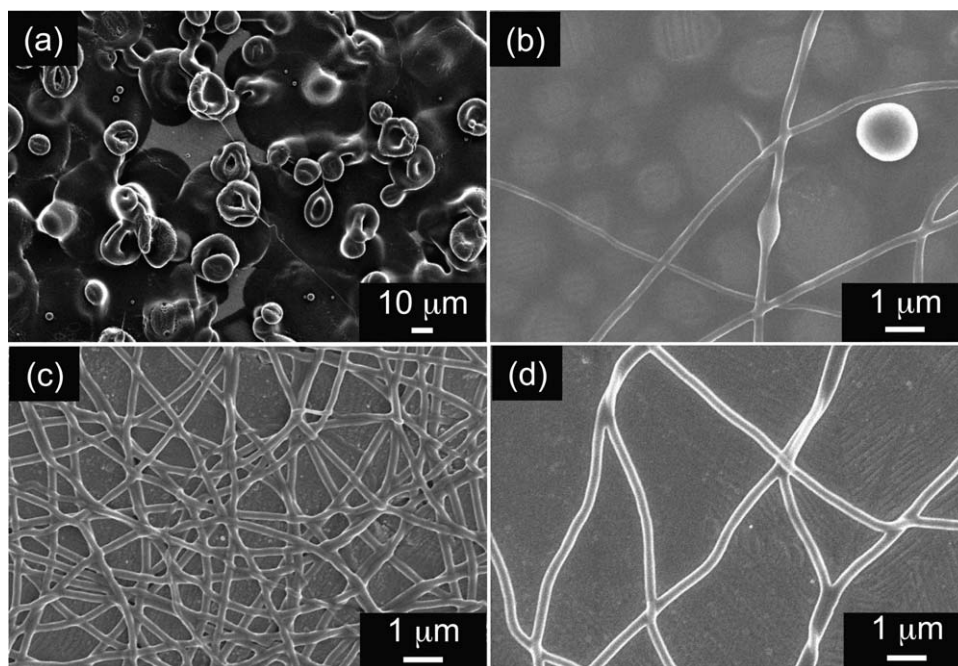


Figure 6. SEM micrograph of sPP nanofibers fabricated by sPP/methyl-cyclohexane solution at different concentrations: (a) 1 wt %, (b) 2 wt %, (c) 3 wt %, and (d) 4 wt %.

C_e , a significant overlap of the polymer chains began to constrain the molecular chain motions. Considering the electrospinning process from the viewpoint of C_e , no morphology should be observed when the experimental concentration was below C_e , i.e., without entanglements, where the unentangled-polymer jet could not still withstand the excessive force of the electrostatic field and the jet would break up into droplets to finally construct beads instead of fibers. As the concentration increased to $\sim C_e$, fiber-like structures could be obtained. As the concentration further increased to become kC_e , where the constant k was 2.0–2.5 according to the paper by McKee *et al.* and 1.2–2.7 according to the paper by Kong *et al.*, uniform and bead-free fibers could generally be obtained.^{25,26} However, above kC_e , due to the abundant entanglements, the fiber diameter simply became large according to the concentration. Thus, the favorable concentration for the fabrication of the thinnest fibers may highly be obtained around kC_e for the electrospinning process.

Figure 6 shows the SEM images of the fabricated nanofibers from the sPP solution in methylcyclohexane with different concentrations: from 1 wt %, beads appeared which was shown in Figure 6(a); from 2 wt %, beaded nanofibers were found [Figure 6(b)]; from 3 wt %, uniform nanofibers were fabricated [Figure 6(c)]; and above 4 wt %, uniform nanofibers with larger diameter by sPP concentrations were found [Figure 6(d)]. From these results, it was estimated that the C_e was 1–2 wt % and kC_e was ~ 3 wt %. The C_e for sPP/methyl-cyclohexane solution was also confirmed to be 1.9 wt % from Figure 7. In the semidilute unentangled regimes, η_{sp} was proportional to $C^{-1.41}$, whereas in the semidilute entangled regimes, η_{sp} was proportional to $C^{2.55}$. The concentration dependence was similar to the experimental values reported by McKee *et al.* and by Kong

et al.^{25,26} The C_e for sPP/cyclohexane solution and sPP/ethyl-cyclohexane solution were confirmed and determined to be 1.6 wt % (please refer to Supporting Information Figs. S1 and S2). It was also found that our kC_e/C_e was 1.6–1.9, close to the values reported by McKee *et al.* and by Kong *et al.*^{25,26}

Considering the η_{sp} of different solvents at the same kC_e in Figure 5, the η_{sp} of methyl-cyclohexane was the lowest throughout the whole range of concentrations. The solution with the lowest viscosity would be the prospective candidate for the thinnest fibers, since higher mobility of molecules with the same number of entanglements could produce higher extension of polymers for the synthesis of thinner fibers.²⁷

As was presented above, increasing viscosity of the sPP solution did not produce thinner sPP fibers. In fact, electrospinning of the sPP fibers was unsuccessful for the sPP/decalin solution,

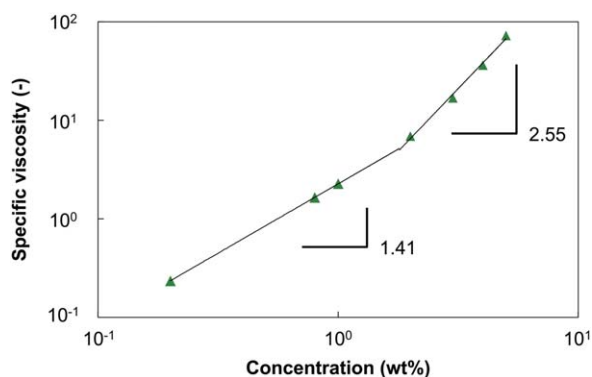


Figure 7. Specific viscosity as a function of concentration for sPP/methyl-cyclohexane solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

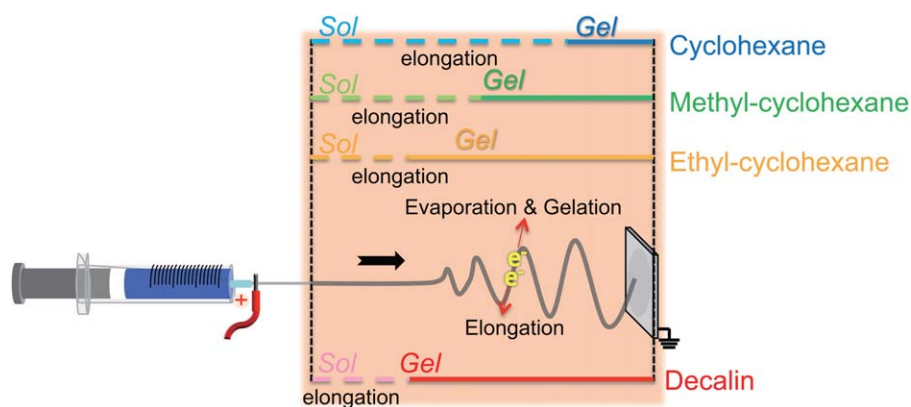


Figure 8. Schematic image of evaporation, gelation, and elongation of semicrystalline solutions during electrospinning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which possessed the highest viscosity as well as the lowest evaporation rate, which should normally be a good condition to fabricate fine fibers. Here, the evaporation of the solvent directly led to a higher concentration of the solution, which raised the viscosity and hence caused the gelation of the solution.

The sPP gel eventually inhibited the fabrication of the sPP nanofibers due to the solidification of the electrospun sPP solution, which hindered the extension of polymers caused by the loss of mobility of the molecules during electrospinning (Figure 8). It was also found that the gelation speed of the sPP dissolved in ethyl-cyclohexane and decalin was substantially higher than those dissolved in cyclohexane and methyl-cyclohexane. It is therefore surmised for our sPP solution that lowering the specific viscosity by selecting solvent at the concentration above C_e could effectively produce bead-free and thinner sPP nanofibers. Additionally, it was found that avoiding the gelation of the semicrystalline polymer solution without using the solvent with extremely low volatility such as decalin was essential in the electrospinning of the semicrystalline sPP.

CONCLUSIONS

Fabrication of sPP nanofibers by solution electrospinning using single solvent at room temperature (25°C) was examined. sPP nanofibers with the average diameter of 230 nm were successfully fabricated using methylcyclohexane for the solvent. The obtained diameter was significantly thinner than the minimum diameter of 350 nm of polypropylene fibers reported previously. Just by selecting lower volatility and higher viscosity, as was suggested by noncrystalline polymer experiments, thinner semicrystalline sPP fibers could not be fabricated, which was highly due to the gelation caused by the crystallinity of sPP. For the fabrication of nanofibers of semicrystalline polymers, it is crucial to consider the entanglement of the molecules and hence to choose the moderate gelation speed and the lower specific viscosity of the semicrystalline solution at the favorable entanglement concentration $\sim kC_e$.

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