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# Electrostatic polymer processing of isotactic poly(4-methyl-1-pentene) fibrous membrane

Keun-Hyung Lee [a], Steven Givens [a], D. Bruce Chase [b], John F. Rabolt [a,*]

[a] Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
[b] Central Research and Development, Experimental Station, Dupont, Wilmington, DE 19806, USA

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## Abstract

Isotactic poly(4-methyl-1-pentene) (P4M1P) is a widely used polymer in industrial applications and specifically, in medical products. Producing micro- or nanofibers would expand the usefulness of P4M1P to a broad range of medical applications. The choice and quality of solvent for the solution used for electrospinning can have a dramatic effect on the spinnability of fibers and on their morphological appearance. In this study, four solvent systems: cyclohexane, cyclohexane/acetone mixture, cyclohexane/dimethyl formamide (DMF) mixture and cyclohexane/acetone/DMF mixture have been investigated. As demonstrated by FE-SEM, electrospun fibers with different morphologies including round, twisted with a roughened texture, curled and twisted-ribbon shapes were formed. The fiber shape and morphology depended strongly on the type and amount of non-solvent used.

*Keywords:* Electrospinning; P4M1P; Fibers

## 1. Introduction

Poly(4-methyl-1-pentene), $(-CH_2-CH[CH_2CH(CH_3)_2]-)_n$ (P4M1P), a member of the poly(α-olefin) class, has a wide range of applications, owing to its high optical transparency, due to the similar densities between its crystalline (0.813 g/cm$^3$) and amorphous regions (0.830 g/cm$^3$), excellent dielectric properties, high chemical resistance, and high permeability to gases [1,2]. The high permeability to gases makes it ideal for use as a membrane material in gas separation [3]. In addition, its melting temperature (240 °C) is higher than that of the common polyolefins such as polyethylene (140 °C) and polypropylene (170 °C).

Many methods have been used to produce polymer nanofibers, such as drawing [4], phase separation [5], self assembly [6], and electrospinning [7–11]. Among these methods, electrospinning is very attractive because of its simplicity and flexibility in producing fibers of different diameter and surface texture. Electrospinning is also considered to be one of the most advantageous methods for large-scale production of polymer nanofibers, and recently, many researchers have attempted to improve fiber throughput [12,13].

Since the electrospinning process was first patented in 1934 by Formhals [14], it has been relatively neglected until recently (1970). However, recent interest in the electrospinning process has arisen due, in part, to a surging interest in nanotechnology. A number of synthetic and natural polymers have been successfully spun into micro- and nanodiameter fibers using the electrospinning technique. Moreover, electrospinning studies on polyolefins have been almost non-existent due to their good chemical resistance and poor solubility in the polar solvents, which has limited their utility in appropriate

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* Corresponding author. Department of Materials Science and Engineering, 201 Dupont Hall, University of Delaware, Newark, DE 19716, USA. Tel.: +1 302 831 4476; fax: +1 302 831 4545.
*E-mail address:* rabolt@udel.edu (J.F. Rabolt).

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electrospinning solvents at room temperature. However, some studies reported experiments using melts of polyolefins such as polyethylene and polypropylene that were spun into microfibers at elevated temperature [15–17].

The objective of this study is to determine the relationship between the morphological appearance of polyolefin fibers and the solvent and/or non-solvent used to electrospin them.

## 2. Materials and methods

### 2.1. Materials

Isotactic poly(4-methyl-1-pentene) (P4M1P) with a melt index of 26.00 g/10 min (260 °C, 5.0 kg, ASTM D1238) was purchased from Aldrich Co. along with the reagent grade solvent (cyclohexane) and non-solvents (acetone, dimethylformamide [DMF]) used in this study. All chemicals were used without further purification.

P4M1P was dissolved in cyclohexane and a mixture of cyclohexane and non-solvent (acetone, DMF) at predetermined mixing ratios at about 60 °C in order to prepare clear solutions for electrospinning, and then cooled to near room temperature (below 35 °C).

### 2.2. Electrospinning

Each P4M1P solution was poured into a 3-ml syringe equipped with a 21-gauge needle (Hamilton). A high-voltage power supply (Gassman High Voltage) capable of generating voltages up to 30 kV was used to generate an 11 kV potential difference between the needle and a grounded metallic plate on which Al-foil was placed. The plate/Al-foil was located 15 cm from the tip of the needle. All fiber spinnings were carried out at slightly elevated temperature (30–35 °C). A schematic diagram of the electrospinning apparatus is shown in Fig. 1.

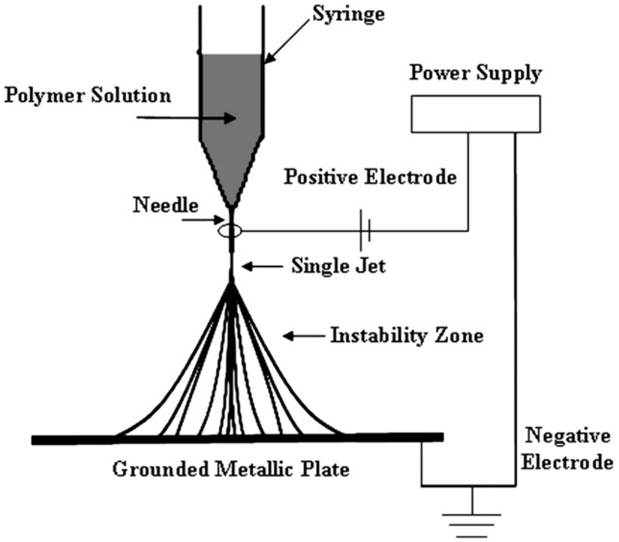

Fig. 1. Schematic diagram of electrospinning process.

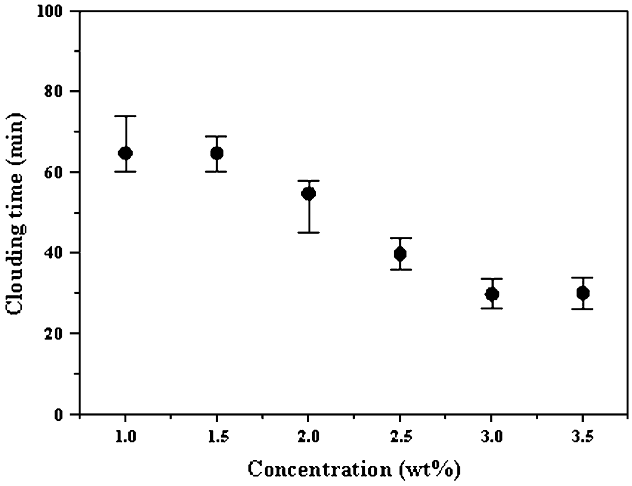

Fig. 2. Clouding time as a function of concentration for P4M1P dissolved in a mixture of cyclohexane, acetone and DMF, 80/10/10 (w/w/w).

### 2.3. Characterization

The P4M1P solutions prepared were placed into a water bath (25 °C) and the clouding time was measured until the onset of turbidity. And the morphologies of electrospun P4M1P fiber membrane were investigated using field emission scanning electron microscopy (FE-SEM, JSM-7400F, JEOL).

## 3. Results and discussion

### 3.1. Characterization of P4M1P solutions

The morphology of polymeric fibers is affected by electrospinning parameters such as solution properties and spinning conditions. The diameter and spinnability of fibers are strongly dependent on solution properties (viscosity, conductivity, dielectric constant, etc) as shown previously [18,19]. These can be altered by changing the solvent type and adding small amounts of non-solvent and/or other additives (e.g. surfactants).

Beck [20] reported various solvents for P4M1P including halogenated hydrocarbons, aromatic hydrocarbons, alkanes and cycloalkanes, etc. He found that no solvent could dissolve any significant amount of P4M1P at room temperature, and that a temperature in excess of about 100 °C was required.

We have found that clear solutions can be obtained by dissolving P4M1P in a solvent, cyclohexane, and in a mixture of cyclohexane and non-solvents (acetone and/or DMF) at 60 °C. When the temperature of the clear solutions was lowered to room temperature (about 25 °C), these solutions remained clear for a short time and then turned turbid. Clouding time, defined as the onset of turbidity, is strongly dependent on the solvent type (data not shown) and the polymer concentration (Fig. 2). All P4M1P solutions were immediately brought to ambient conditions and the time taken for clouding was measured. The properties of solvent and non-solvents used in this study are shown in Table 1.

Table 1
Properties of solvents used in this study

| | Solubility | Boiling point (°C) | $\varepsilon^{a}$ | $\mu^{b}$ |
|---|---|---|---|---|
| Cyclohexane | Solvent | 80.7 | 2.0 | 0.6 |
| Acetone | Non-solvent | 56.5 | 20.7 | 3.0 |
| DMF | Non-solvent | 153.0 | 36.7 | 3.9 |

[a] Dielectric constant at 20 °C.
[b] Dipole moment in Debyes.

### *3.2. Effect of solvent/non-solvent used*

#### *3.2.1. Cyclohexane*

Cyclohexane is a solvent for P4M1P, but it is not an ideal solvent for electrospinning of P4M1P due to its low-polarity and low-volatility. P4M1P solutions in cyclohexane exhibit very poor spinnability of fibers at all concentrations primarily due to non-ideal solvent properties such as low dielectric constant, low dipole moment (Table 1), low-polarity and low-volatility. Only a very small quantity of smooth fiber with diameters of 300–600 nm was observed among the electrosprayed droplets at weight concentration of 2%. An example of one such fiber is shown in Fig. 3A.

#### *3.2.2. Mixture of cyclohexane and acetone*

To introduce polarity and volatility, a mixture of cyclohexane and acetone, 80/20 (w/w) has also been used to electrospin P4M1P. Acetone is a non-solvent for P4M1P, but it has excellent volatility, a high dielectric constant and a large dipole moment (Table 1) as well as being readily miscible in cyclohexane by stirring. Interestingly, twisted fibers are formed and a roughened texture is introduced on the surface of the electrospun fibers spun from this mixture (Fig. 3B). The formation of the roughened surface texture is very similar to that observed for polymer fibers with pore structure generated by the use of a volatile solvent [21]. Although acetone is miscible in cyclohexane, acetone rich regions exist. These regions can produce a roughened surface texture and twisted-ribbon shaped fibers, which will be discussed in a later section.

While electrospinning the P4M1P solutions using a mixture of cyclohexane and acetone, the fibers appeared to deposit on the grounded collector in a very small confined area independent of the concentration prepared. This is illustrated in the schematic diagram in Fig. 3B. A greater quantity of spun fibers versus electrosprayed droplets was observed in the P4M1P/cyclohexane/acetone as compared to the P4M1P/cyclohexane system.

#### *3.2.3. Mixture of cyclohexane and DMF*

In general, DMF is known to help the formation of electrospun fibers in selected polymer systems [10]. Although DMF is a non-solvent for P4M1P and is immiscible in cyclohexane, it is readily dispersed in cyclohexane by stirring and is included as a part of a multi-component mixture (cyclohexane, DMF) to improve the spinnability of P4M1P. In particular, we observed that the collection area increased substantially (see schematic Fig. 3C) and was no longer confined. However, it was not easy to evaporate the DMF due to its high boiling point. Interestingly, the formation of curled and twisted-ribbon shaped fibers (see arrow in Fig. 3C) was observed. The curled structure is most likely the result of relaxation caused by small amount of the residual DMF in the interior of the fiber. Ribbon shapes, generated by the lateral force produced by an electric charge uniformly distributed on the jet flowing to both margins of the fiber when the fiber center collapses were previously reported by Koombhongse et al. [22].

#### *3.2.4. Mixture of cyclohexane, acetone, and DMF*

To introduce volatility and to improve the spinnability of P4M1P solutions, solvents comprised of a mixture of

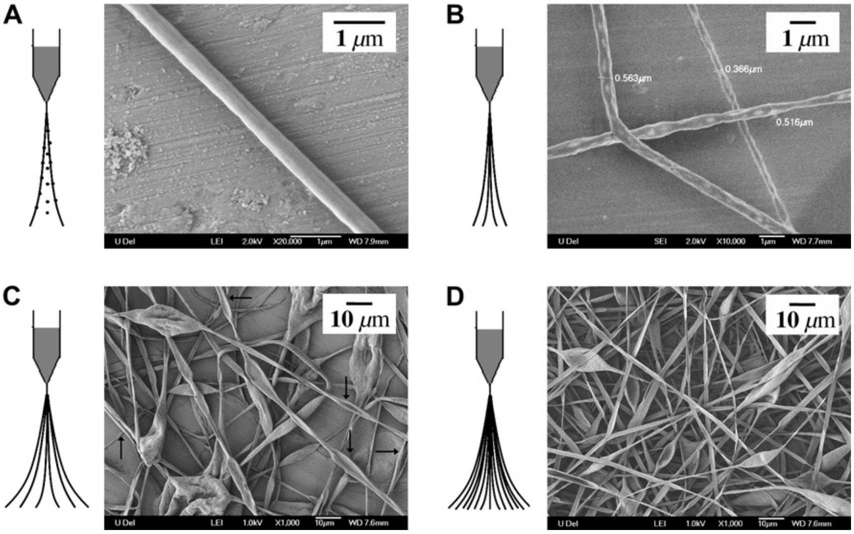

Fig. 3. Schematic diagram of electrospinning results and FE-SEM images of electrospun fibers from solutions of P4M1P in: (A) cyclohexane, (B) a mixture of cyclohexane and acetone (80/20, w/w), (C) a mixture of cyclohexane and DMF (80/20, w/w) and (D) a mixture of cyclohexane, acetone and DMF (80/10/10, w/w/w). The arrows in (C) illustrate curled and/or twisted fibers.

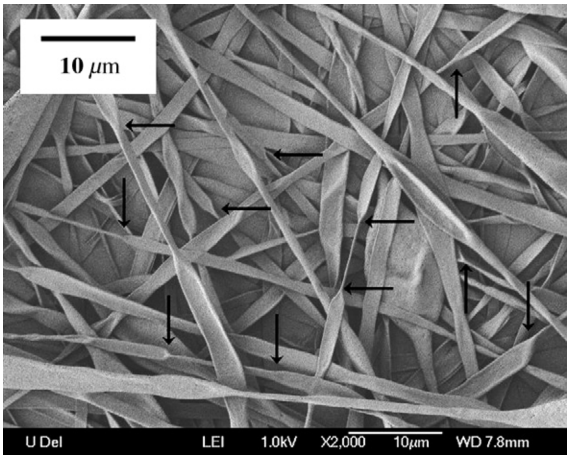

Fig. 4. FE-SEM image of twisted-ribbon shaped fibers; arrows indicate the twisting point.

cyclohexane, acetone and DMF, 80/10/10 (w/w/w) were used. It was observed that the spinnability was greatly improved and that the solvent evaporation occurred at a faster rate. A large deposition area on the grounded collector was also observed (Fig. 3D).

As shown in Figs. 3D and 4, the appearance of fibers electrospun from P4M1P multi-component solutions (cyclohexane, acetone and DMF) has a twisted-ribbon shape with irregular twisting points (see the arrows in Fig. 4). This effect is the result of the non-solvent added. In the early stage of electrospinning, small amounts of solvent can exist inside a thin skin formed on the surface of a jet due to rapid phase separation and evaporation of solvent. Solvents used in this study have widely different characteristic properties such as boiling point, volatility, dielectric constant, dipole moment and polyelectrolyte behavior. Among them, acetone has a low boiling point (56.5 °C), is more volatile and is much easier to evaporate than other solvents such as DMF and cyclohexane. DMF, on the other hand, does not easily evaporate due to its high boiling point (153 °C). During fiber formation in the electrospinning process, each solvent rich region will be present. An acetone rich region is rapidly evaporated due to high volatility and low boiling point resulting in a roughened texture. A DMF rich region is slowly evaporated due to the high boiling point of DMF when compared to acetone. The phenomenon of twisting could occur due to the different evaporation times of the different solvents used. For example, the jet path could be rotated toward the evaporating acetone region, and this results in the twisted-ribbon shaped fibers. For this mixed solvent system, the frequency distribution of fiber diameters is very broad and is observed in the range from 0.6 to 3 μm. The range of fiber diameters for each solvent system is summarized in Table 2.

Table 2
Observed fiber diameters for different solvent systems

| Solvent(s) | Fiber diameter (μm) |
|---|---|
| Cyclohexane | 0.3–0.6 |
| Cyclohexane/acetone (80/20, w/w) | 0.3–0.6 |
| Cyclohexane/DMF (80/20, w/w) | 0.8–6.0 |
| Cyclohexane/acetone/DMF (80/10/10, w/w/w) | 0.6–3.0 |

Fig. 5 shows a cross-sectional view of the twisted-ribbon shaped P4M1P fibers. Various cross-sectional shapes such as circular, elliptic and flat ribbon have been observed [22–24]. One of these, the flat ribbon morphology is induced by the collapse of a polymer skin and tube formed on the liquid jet, which is induced by rapid solvent evaporation during electrospinning [22]. As can be seen in Fig. 5, the fibers have a flat ribbon with two small hollow or filled tubes at each edge. The thickness of the ribbon is about 200 nm. Small amounts of an elliptical shape have also been observed while the circular shape was not observed in our studies.

The number of twisted-ribbon shaped fibers decreased with increasing polymer concentration. In general, the relationship between viscosity and polymer concentration determined the diameter of the electrospun fibers. In this study, the ribbon thickness and width increased with increasing polymer concentration, as shown in Fig. 6. As observed by FE-SEM, the surface of the ribbon spun from P4M1P concentrations in cyclohexane/acetone/DMF (80/10/10, w/w/w) below 2.0 wt% is very smooth, while that of a ribbon spun from P4M1P

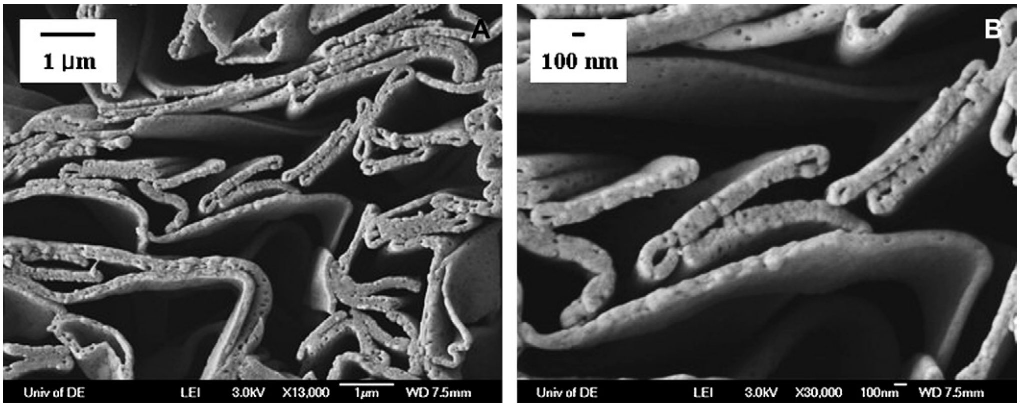

Fig. 5. FE-SEM images of a cross-section of P4M1P fibers electrospun from the mixture of cyclohexane, acetone, and DMF (80/10/10, w/w/w): (A) ×13,000 and (B) ×30,000.

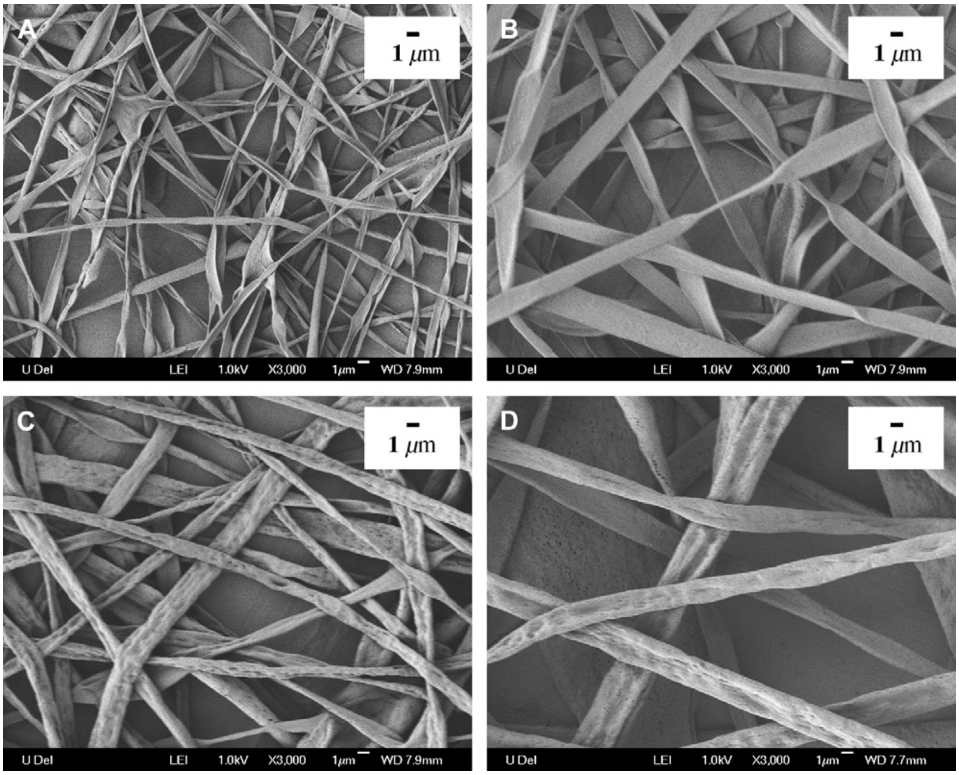

Fig. 6. FE-SEM images of electrospun P4M1P fibers as a function of the concentration: (A) 1.5 wt%, (B) 2.0 wt%, (C) 2.5 wt%, and (D) 3.0 wt%. The solvent composition is a mixture of the cyclohexane, acetone and DMF (80/10/10, w/w/w).

concentrations above 2.5 wt% is more textured. This could be the result of P4M1P coming out of solution during the electrospinning process since it appears to correlate with clouding time, which decreased with increasing polymer concentration (Fig. 2). Lowering the temperature and then adding a non-solvent resulted in a decrease in P4M1P solubility in the solvent/non-solvent mixture and phase separation occurred. Using a higher concentration of polymer, especially in those solutions with non-solvent, produced a roughened surface morphology due to rapid evaporation at the fiber surface. This rapid evaporation of the non-solvent produced a supercooling effect, which resulted in phase separation at the fiber surface. Solutions of lower polymer concentration produced a smoother surface morphology due to a more uniform evaporation of solvent and non-solvent at the fiber surface.

## 4. Conclusions

In this study, electrospun fibers of P4M1P have been successfully prepared from solutions of varying solvent systems via electrospinning. We have shown that solvent and non-solvent mixtures for electrospinning P4M1P can have a dramatic effect on the spinnability and morphological appearance of electrospun fibers. Four different solvent systems (cyclohexane, cyclohexane/acetone mixture, cyclohexane/DMF mixture and cyclohexane/acetone/DMF mixture) were studied. P4M1P fibers were generated at ambient temperature using these mixed solvent systems. Fiber morphology, as demonstrated by FE-SEM was primarily influenced by the type of solvent/non-solvent used. Specifically, the morphological appearance of electrospun fibers varied from round to twisted-ribbon shape by adding a small amount of non-solvent. Acetone and DMF have been found to help solvent evaporation and spinnability due to high volatility and high electrolyte properties during electrospinning. This was observed to be strongly dependent on the type and amount of non-solvent used.

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