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Electrospun nanofibers of polyferrocenylsilanes with different substituents at silicon

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Abstract

The strained silicon-bridged [1]ferrocenophane Fe(η-C_5H_4)$_2$SiBuMe was prepared via a facile chloride substitution reaction at the bridging atom of a readily available SiMeCl-bridged [1]ferrocenophane precursor. Thermal ring-opening polymerization of Fe(η-C_5H_4)$_2$SiBuMe and Fe(η-C_5H_4)$_2$SiMe$_2$ afforded polyferrocenyldimethylsilane (PFDMS) and polyferrocenylbutylmethylsilane (PFBMS), respectively. Polyferrocenylsilane nanofibers were fabricated by electrospinning polymer solutions in 90 wt% tetrahydrofuran and 10 wt% *N*,*N*-dimethylformamide at room temperature. The effect of processing parameters such as concentration of polyferrocenylsilanes solution, applied voltage, and working distance on the diameter and morphology of resulting nanofibers were investigated. Electron diffraction patterns from polymer nanofibers revealed that PFS fibers exhibit different orientation owing to variance of the side groups at silicon.

Keywords: Polyferrocenylsilanes; Electrospinning; Nanofibers; Crystalline

1. Introduction

One-dimensional (1-D) nanomaterials have attracted growing attention due to their unique physical traits including their electronic, magnetic, optical, and mechanical properties [1,2]. Various strategies have been proposed for building these materials. Electrospinning is a versatile top-down method for manufacturing 1-D fibers with diameters ranging from the submicro to nanometer scale [3–7]. Over 100 different polymer solutions or melts have been electrospun into nanoscale fibers [8,9]. Polymeric nanofibers exhibit unusual properties due to their very small diameter, which leads to high surface area, high aspect ratio, and better mechanical properties. These remarkable properties underlie the substantial interests in these materials for industrial, biomedical, and electronic applications. By far the majority of the work to date has focused on polymers with an organic or inorganic backbone [10–12], and only Reneker et al. studied the structure of electrospun PFDMS [12].

Poly(ferrocenylsilanes) (PFS) represent a class of metallopolymers with a main chain that consists of altering organosilane and ferrocene units. As a result of synthetic developments PFS are now available as soluble and readily processable polymers in the past 10–15 years, possessing intriguing redox,

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conductive, precermic, etch-resistant, and catalytic properties [13–15]. The incorporation of Fe atom into 1-D nanofibers would be expected to allow access to a range of distinctive physical and chemical characteristics compared with bulk materials [16].

The electrospinning process provides ample flexibility to control the polymer fiber diameter and morphology by varying several governing parameters. These include solution (solvent, polymer molecular weight, and concentration), process (electric potential, working distance, and hydrostatic press), and environmental (temperature, humidity, and air velocity) parameters [9,17,18]. At the same time the properties of electrospun nanofibers depend significantly on the properties of the backbones and the side groups. In this work we are currently ongoing to explore the feasibility of developing nanofibers from PFS, investigating the effect of process parameters such as concentration of polymer solution, applied voltage, and working distance on the diameter and morphology of resulting nanofibers, and revealing the PFS fibers structure with different side groups.

2. Experiments

2.1. Materials

Hexane, tetrahydrofuran (THF), and diethyl ether dried over Na–K alloy and distilled under argon atmosphere before use. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA), dichlorodimethylsilane, trichloromethylsilane, and chlorotrimethylsilane were purchased from Acros. TMEDA was stored over activated molecular sieves under nitrogen, and trichloromethylsilane was distilled before use. Ferrocene and 1.6 M butyllithium in hexanes were purchased from Acros and used as received. All other chemicals and solvents were obtained from commercial sources and were of analytical grade.

2.2. Syntheses and characterizations

The polymers were synthesized by standard Schlenk technique in an atmosphere of argon or in vacuum. In a typical experiment, PFDMS was synthesized by the thermal ring-opening polymerization (ROP) according to the literature [19]. The ^{1}H NMR spectrum of PFDMS showed the same result as that in the literature [19]. The GPC result of the synthesized PFDMS was: $M_n = 1.81 \times 10^4$, $M_w = 3.29 \times 10^4$, and polydispersity (PDI, M_w/M_n) is 1.8.

PFBMS was synthesized via the nucleophilic substitution of ferrocenophane followed by ROP according to the literature [20]. The ^{1}H NMR spectrum of PFBMS showed the same resonances mentioned as in the literature [20]. GPC experiment showed that the PFBMS has a M_n of 1.94×10^4, M_w of 3.16×10^4, and PDI of 1.6.

2.3. Processing

The diagram of the electrospinning apparatus used in present work is shown in Fig. 1. Electrospinning was performed in a horizontal configuration where the fibers were electrostatically conveyed to the grounded target at ambient temperature and air pressure. The apparatus consists of a 2 mL capillary tube equipped with a Taylor cone and a grounded target of steel wire mesh. The inner diameter of Taylor cone is 0.6 mm. The grounded electrode covered with aluminum foil and carbon films was placed at a predetermined distance (working distance) from the cone tip. A Cu electrode dipped in the PFS solution was connected to a high voltage power supply with positive polarity. The capillary tube was fixed perpendicular to the collection screen and the polymer solution was allowed to flow under gravity and electrical pressure. A Dong-Wen High Voltage Power Supply DW-P503-4AC (0–50 kV, Dong-Wen High Voltage Power Supply Factory) with a low current output was used as the power source.

In this work, electrospinning was conducted by varying processing parameters such as concentration of the PFS solution, working distance, and applied electric field. The applied electric field was varied from 5 to 35 kV, the concentration of the PFS solution was varied from 15% to 25% (wt/v) in co-solvent system consisting of THF and *N*,*N*-dimethylformamide (DMF) in a 9:1 weight ratio,

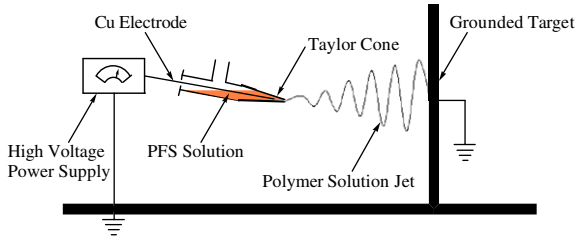

Fig. 1. Schematic of the electrospinning apparatus.

and the working distance was varied from 5 to 30 cm.

2.4. Instrumentation

^{1}H NMR spectra of PFS were recorded with a 400 MHz UNITY INOVA NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Molecular weights were measured by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 515 HPLC pump, Ultrastryragel columns, and a Waters 2410 differential refractometer. THF was used as the eluent at the flow rate of 1.0 mL/min. Monodisperse polystyrenes were used as standards for calibration purposes.

The diameter, morphology ((bead/non-bead), shape (circular/irregular cross-section), and surface topography (rough/smooth) of the fibers were examined using scanning electron microscopy (SEM) after the fibers were coated with gold. Average fiber diameters were determined by measuring 50 fibers selected randomly from each electrospun mats. The solidified fibers were collected with the carbon-coated copper grids for transmission electron microscopy (TEM) measurement. Electron diffraction patterns were recorded on photographic film and scanned using a digital image scanner.

3. Results and discussion

3.1. Synthesis of PFDMS and PFBMS

Since the discovery of thermal ROP by Manners et al. [21], various other ROP techniques have been developed. The high molecular weight PFDMS and PFBMS were synthesized via a convenient thermal ROP route as shown in Fig. 2 [19,20]. The nucleophilic substitution of Fe(η-C_5H_4)$_2$SiMeCl with BuLi smoothly provided to Fe(η-C_5H_4)$_2$SiBuMe at low temperature. By varying the thermal polymerization time, PFDMS and PFBMS with analogue molecular weight and polydispersity were achieved [19,20].

The ferrocenophane reaction and subsequent ROP allow us to introduce different side groups onto PFS. The physical characteristics of PFS have been found to be significantly affected by the side groups attached to silicon. Two methyls are attached to the Si atom of PFDMS, and a methyl and a butyl are attached to the Si atom of PFBMS.

3.2. Effect of electrospinning parameters on the morphology of PFS nanofibers

Various electrospinning parameters can affect the formation of nanofibers from a special polymer [17,18]. The object of this work was to evaluate the feasibility of developing ultrafine fibers from PFS by electrospinning and to find out the optimal parameters including concentration of the PFS solution, applied potential, and working distance. SEM results for the nanofibers produced from PFDMS solution are shown in Fig. 3.

We found that the threshold voltage of PFDMS was about 6 kV when polymer concentration was 20% (wt/v) at room temperature. The potential difference must be high enough that electrical forces overcame the forces associated with surface tension and viscoelastic forces [22]. The threshold voltage to start the jet formation was shown to be a linear function of polymer concentration [23]. Fig. 3a–c depicts the electrospun nanofibers formed at different applied potentials from a constant polymer concentration of 20% (wt/v) at a working distance of 15 cm. Previous studies showed that the electrospinning voltage has a significant influence on the diameter and shape of the resulting nanofibers [3,9,11]. Electrospun fibers at an applied potential

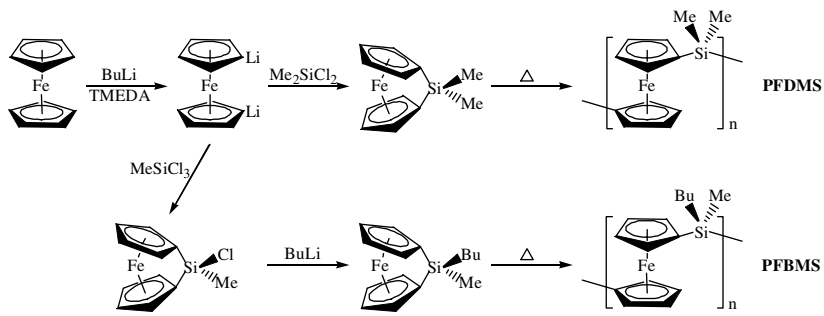

Fig. 2. Synthesis of PFDMS and PFBMS.

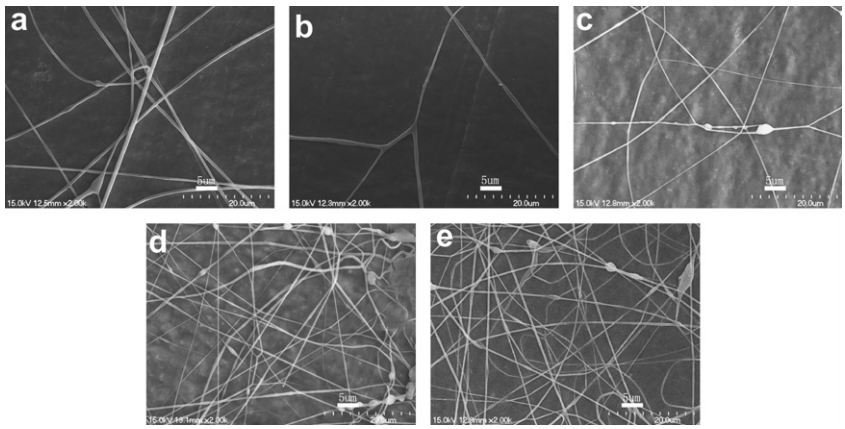

Fig. 3. SEM images of electrospun PFDMS nanofibers from 20% (wt/v) THF/DMF at different voltages and distances. (a) 7 kV and 15 cm, (b) 10 kV and 15 cm, (c) 16 kV and 15 cm, (d) 10 kV and 5 cm, (e) 10 kV and 25 cm.

of 7 kV resulted in the formation of 450–950 nm fibers as shown in Fig. 3a, while 16 kV of voltage produced fibers with diameters of 200–400 nm in Fig. 3c. It was obvious that the average diameters of fibers decreased when the applied potentials was increased from 7 to 16 kV. A higher applied voltage increased the net charge experienced by the jet, resulting in enhanced fiber drawing to narrow diameters.

Lower fields result in electrospun fibers with an irregular shape or cross-section, Fig. 3a and b; however, an increase (Fig. 3a and b) in the electric field from 10 to 16 kV improved the shape of the fibers, which assumed a more cylindrical structure. Though the increased electrostatic force exerted on the jet at higher applied potential seemed to improve the shape of the electrospun fibers, the distinct beads formed along the fibers can be attributed to unsteady jet and deposition of the jet into droplets.

Working distance is known to play a significant role in determining fiber diameter and morphology during electrospinning [9,11,17]. Fig. 3d, b, and e shows the effect of working distance on the shape and diameters of electrospun nanofibers from a constant polymer concentration of 20% (wt/v) at the applied potentials of 10 kV. In the case of 5 cm working distance, the beaded fibers showed a highly irregular morphology with large variations in diameter (Fig. 3d), and spun fibers tended to stick to each other due to incomplete solvent evaporation. Increasing the working distance to 25 cm did not show any statistically significant differences in the fiber diameters compared to fibers obtained at 5 cm, however beads formation along the fibers and cross-section decreased. Previous studies have shown that bending instability occurred at high charge densities and field, and they can typically be enhanced by increasing the electric conductivity of the polymer solution [18,24]. In the present work when the distance between the spinnerette and the collecting screen was long at comparatively low applied potential of 10 kV, the jet was moved, formed a series of coils, and resulted in loops in the collecting screen (Fig. 3e).

Another interesting feature observed in Fig. 3b is branching and/or splitting from the primary jet. The phenomena were found in electrospinning a number of polymer solutions such as HEMA [poly (2-hydroxethyl methacrylate)], PS (polystyrene), PVDF [poly(vinylidene fluoride)], and PEI [poly(ether imide)], with weight concentrations of more than 10% [9,24,25]. Polyferrocenylsilanes containing Fe atoms in the main chain behaves as redox activity, so the high electric conductivity of PFS solution could result in more unstable jet fluid toward the collecting screen by the electric force, then branching from the elongating primary jet occurred in Fig. 3b. As the concentration of PFS solution was decreased, the secondary jet was still found, which showed that concentration did not relate to the splitting phenomenon directly.

3.3. Structure of PFDMS and PFBMS fibers

The physical characteristics of PFS have been found to significantly depend on the side groups attached to silicon [26,27]. PFDMS and PFBMS were electrospun by the processes of the evaporation of the solvent and the extreme elongation of the semi-solidifying fibers in less than 0.01 s. PFS

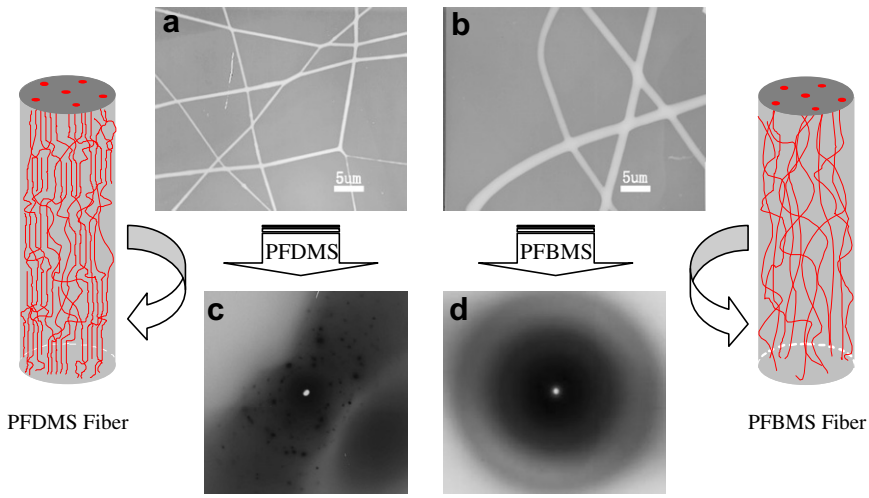

Fig. 4. Typical TEM images, electron diffraction patterns, and corresponding structure models of electrospun PFS nanofibers from 20% (wt/v) THF/DMF at 20 kV and 20 cm. (a) and (c): PFDMS, (b) and (d): PFBMS.

nanofibers were formed from 20% (wt/v) THF/DMF at 20 kV and 20 cm. Typical TEM images are shown in Fig. 4a and b. After the resulting fibers were annealed for a week at room temperature, electron diffraction patterns of nanofibers were measured and shown in Fig. 4c and d.

Keeping all the other parameters unchanged, the substitution of one methyl group in PFDMS with a butyl group obviously showed bigger diameters of the electrospun fibers from PFBMS than those from PFDMS, which indicated that the side groups considerably affected the electrospun fibers diameter. PFDMS is a crystallizable thermoplastic with a melt transition (122–145 °C) [27], but PFBMS is a amorphous gum at room temperature [20]. Butyl substitution of Si perhaps decreased the electrical conductivity of the polymer solution, at the same time viscosity and elastic forces counteracted the electrical forces, as a result the fiber diameters increased. Substitution of the silicon atom offers an alternative opportunity to control the properties of PFS fibers.

The degree of orientation could be substantially increased by annealing the fibers. From Fig. 4c, the sharp diffraction pattern was found. The high degree of crystallite orientation reveals itself in the inhomogeneous azimuthal distribution. Previous studies concluded that the PFDMS molecules adopt a monoclinic unit cell in the nanofibers [12]. Polyferrocenyldibutylsilane is capable of showing significant order, particularly when samples were annealed, however there are not diffraction spots and rings Fig. 4d, which shows typically amorphous fibers. The structure model of PFDMS fibers was different from that of PFBMS fibers. For PFBMS the only chain orientations lies in fibers (Fig. 4 right). Symmetrically substituted PFDMS and high magnitude of elongation favor the chain orientation and the crystallite orientation in the electrospun fibers (Fig. 4 left) [28,29]. Manners and Wang et al. have reported that a dramatic increase in the electrical conductivity for PFS films doped with I_2 [30], so 1-D periodic PFS fibers is attractive for fabricating low-cost logic and switching circuit. Further studies of PFS fibers and related materials are in progress.

4. Conclusion

Polyferrocenyldimethylsilane and polyferrocenylbutylmethylsilane were synthesized respectively by the nucleophilic substitution for sila[1]ferrocenophane and the thermal ring-opening polymerization. This work demonstrated the feasibility of developing PFS fibers in the nano-micrometer range through electrospinning polymer solutions in tetrahydrofuran and *N*,*N*-dimethylformamide in a 9:1 weight ratio at room temperature. The effect of process parameters such as concentration of polyferrocenylsilanes solution, applied voltage, and working distance on the diameter and morphology of resulting nanofibers were investigated. Electron diffraction patterns of the cylindrical fibers formed under optimized condition revealed that PFDMS

fibers were crystalline, but PFBMS fibers were amorphous. Substitution of the silicon atom offers an alternative opportunity to control the properties of PFS fibers.

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