Nano-fiber engineering of microporous polyimides through electrospinning: Influence of electrospinning parameters and salt addition

Fuat Topuz, Mahmoud A. Abdulhamid, Tibor Holtz, Gyorgy Szekely

HIGHLIGHTS
- Five different microporous polyimides having pendant trifluoromethyl groups were synthesized through polycondensation.
- Uniform nanofibers were produced at low polymer concentrations due to improved spinnability in the presence of a salt.
- Higher salt content drastically increased the solution conductivity and led to thinner electrospun fibers.
- A higher flow rate increased fiber diameter due to the higher mass flow.
- Molecular dynamics simulations demonstrated faster solvent evaporation in the presence of salt.

ABSTRACT
The electrospinning of high-performance polyimides (PI) has recently sparked great interest. In this study, we explore the effect of the electrospinning parameters — namely, polymer concentration, voltage, tip-to-collector distance and flow rate — and salt addition on the diameter, morphology, and spinnability of electrospun PI nanofibers. Three different polyimides of intrinsic microporosity (PIM-PIs) with high Brunauer–Emmett–Teller (BET) ranging from 270 to 506 m² g⁻¹, and two microporous polyimides, were synthesized through the polycondensation of 4,4′-(hexafluoroisopropylidene)dipthalic anhydride (6FDA) and aromatic diamines. The addition of tetraethylammonium bromide (TEAB) salt considerably increased the conductivity of all the PI solutions, significantly improved spinnability, and resulted in thinner fibers. We also used molecular dynamic simulations to investigate the macromolecular mechanism of improved spinnability and fiber morphology in the presence of an ammonium salt. The small droplets detached from the parent droplet, followed by the rapid evaporation of the ions through the hydration effect, which facilitated the electrospinning. The resulting uniform nanofibers have great potential in environmental applications due to the presence of microporosity and hydrophobic pendant trifluoromethyl groups, which enhance the sorption performance of the fibers for hydrophobic species.

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1. Introduction

Electrospinning is a method for generating fibers through the formation of a jet from a charged polymer or non-polymeric system under an electrical field [1]. The resultant fiber morphology and diameter vary depending on the intrinsic characteristics of the polymer, the solution properties, and the electrospinning parameters, as well as the used spinneret system [2,3]. Various nanostructures, from beads to bead-free fibers, can be produced by tuning these parameters through a shift from electrohydrodynamic spraying to spinning [4]. While fibers are suitable for applications that require flexibility, such as sorption or wound dressing, beads are mostly used for drug delivery. Beaded fibers are formed by the capillary breakup of the electrospinning jet by surface tension, which reduces the mechanical properties of the resultant fibers. Thus, the engineering of fiber morphology (i.e., controlling the fiber diameter and morphology, as well as spinnability) is a technological bottleneck for the development of electrospun materials.

Polyimides of intrinsic microporosity (PIM-PIs) are porous polyimides with Brunauer–Emmett–Teller (BET) surface area exceeds 200 m$^2$ g$^{-1}$ and contain pores with pore size below 2 nm [5, 6] are high-performance polymers that are synthesized by a conventional cyclodehydration reaction between dianhydrides and diamines (Fig. 1) [7]. In this regard, 4,4′-(hexafluorosopropylidene)diphthalic anhydride (6FDA) has been widely used as a building block for the synthesis of PIM-PIs since it allows producing solution-processable polymers [8]. These PIM-PIs have gained considerable interest in the fields of gas and liquid separations, heterogeneous catalysis, and adsorption-based applications, such as water treatment and hydrogen storage, due to their high surface area, chemical and thermal stability, and tunable molecular structures [9].

PIM-PIs can be electrospun from their concentrated solutions in organic solvents [10], and the resultant nanofibrous mats are employed mainly for oil adsorption [11], lithium-ion batteries [11,12], supercapacitors [13], and protective clothing applications [14]. We recently developed hierarchically porous fluorinated polyimide-based nanofibrous sorbents by electrospinning, which have been deployed in an oil spill remediation scenario to limit ecological damage, as well as being used for the removal of non-polar solvents [15]. Particularly, the presence of microporosity in nanofibers endows them great application potentials in adsorption, separation, catalysis since the microporous network can allow diffusion of molecules of interest. For further reading, a comprehensive review of electrospun polyimide nanofibers has been published [16].

The spinnability of polymers is highly dependent on the properties of their solutions, such as polymer concentration and solution conductivity. The uniformity of the electrospun fibers can be tuned by adjusting the electrospinning process parameters to produce uniform nanofibrous structures in a narrow size range [17–21]. Likewise, the addition of salt significantly improves the spinnability of polymer of intrinsic microporosity–1 [22], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [23] and polystyrene solutions [24]. Improved fiber morphology and spinnability with the addition of salt has been attributed to the accelerated evaporation rate of the solvent [25].

In this study, we investigate the influence of the electrospinning parameters and salt addition on the morphology and diameter of the resulting electrospun nanofibers of PIM-PIs (Fig. 1). All of the studied polymers exhibit porosity, and high BET surface area with exceptions for 6FDA-mPDA and 6FDA-DABA. The polymers are synthesized through the polycondensation of 4,4′-(hexafluorosopropylidene) diphthalic anhydride (6FDA) and a series of aromatic diamines and are characterized by proton nuclear magnetic resonance spectroscopy ($^1$H NMR), gel permeation chromatography (GPC), Brunauer–Emmett–Teller (BET), fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analyzer (TGA). Viscosity and conductivity measurements for the salt-containing polyimide solutions were carried out. The polymers are dissolved in N,N-dimethylformamide (DMF) and electrospun into nanofibers either in the presence or the absence of a quaternary ammonium salt. The electrospinning parameters were systematically altered to explore their effects on the morphology and diameters of the fiber. Finally, molecular dynamics (MD) simulations were performed to elucidate the impact of salt addition on the spinnability of the polymer solutions.

2. Experimental

2.1. Materials

2,4,6-Trimethyl-m-phenylenediamine (TrMPD, 96%), 4,4′-(hexafluorosopropylidene) diphthalic anhydride (6FDA, 99%), m-phenylenediamine (mPDA, 99%), 2,4,6-trimethylbenzoic acid (TMBA, 99%), 3,3′-dimethyl-naphthidine (DMN), 3,5-diaminobenzoic acid (DABA), isoquinoline (97%) and m-cresol (99%) were purchased from Merck. N,
N-Dimethylformamide (DMF, 99.9%) was received from Fisher Scientific. Tetraethylammonium bromide (TEAB, 99%) was received from Sigma Aldrich.

2.2. Characterizations

The electrospun fibers were analyzed by scanning electron microscopy (SEM, Magellan FEI). Before analysis, the fibers were coated with Pt (5 nm) using a K575X sputter. The mean fiber diameter was calculated from the respective SEM images over approx. 100 fibers using ImageJ (NIH, US). The infrared spectra of the polyimides were recorded for powder samples using a Varian 670-IR ATR-FTIR spectrometer. The spectra were recorded as the average of 128 scans at 4 cm⁻¹ resolution.

1H Nuclear magnetic resonance (NMR) spectra of the polyimides were recorded on a 500 MHz Bruker AVANCE-III spectrometer in deuterated dimethylsulfoxide (DMSO-d₆) solvent, and each spectrum was the sum of 128 scans. Number average molecular weight (Mn), molecular weight (Mw), and polydispersity index (PDI) of the polyimides were obtained by gel permeation chromatography (GPC) in an Agilent 1200 system using polystyrene standard calibration and DMF as the eluent. The thermal stability of these polymers was evaluated using a thermal gravimetric analyzer (TGA) and a Model Q5000 system (TA Instruments) at a rate of 5 °C min⁻¹ up to 800 °C. Brunauer-Emmett-Teller (BET) surface area experiments were conducted on Micrometrics ASAP 2020 porosimetry analyzer. The BET surface areas were determined from N₂ adsorption isotherms measured at −196 °C. Before the experiments, all samples were degassed for 12 h at 150 °C under a high vacuum. Conductivity measurements were performed in triplicates by Accumet – Excel XL20 (Fisher Scientific) using DMF solutions, and the mean data are reported with standard deviations. The viscosity of the polyimide solutions was recorded by an electromagnetically spinning viscometer (EMS viscometer) (EMS-1000, Kyoto Electronics) at 25 °C. It measured the viscosity of liquids through observation of the rotation of a sphere, which is driven by electromagnetic interaction. During the measurement, aluminum spheres (diameter = 2 mm) were used, and the measurements were carried out five times continuously without changing the equipment conditions (i.e., sample, spherical probe, and container combination). The viscosity of the solutions was measured at constant rotation as a function of time. The thermal stability of these polymers was evaluated using thermal gravimetric analysis (TGA) Model Q5000 system (TA Instruments) at a rate of 5 °C min⁻¹ and up to 800 °C.

2.3. Polyimide synthesis

The synthesis of microporous polyimides was performed through the polycondensation of monomers. The following synthesis approach was applied for the preparation of the polyimides. In a one-step high-temperature polymerization, an equimolar amount of 4,4’-(hexafluoroisopropylidene) phthalic anhydride (6FDA) and the diamine (i.e., mPDA, DABA, TrMCA, TrMPD, or DMN) were added to a Schlenk tube equipped with a nitrogen inlet, a magnetic stirrer, and an oil bubbler, followed by the addition of m-cresol solvent. The solution was heated to 80 °C, and isoquinoline (0.1 mL) was added to the solution, and the temperature was increased gradually to 200 °C to ensure complete imidization and total conversion of poly(amic acid) to polyimide. The highly viscous solution was then poured into methanol, followed by stirring for 4 h and then collection by filtration. Further purification of the polymer powder was achieved by re-precipitation of the polymer solution in methanol. The polymers were characterized by 1H NMR, FTIR, BET, and TGA (Figs. S1–4). The physical characteristics and solubility of the polyimides are given in Table 2 and Table S1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>6FDA-TrMCA, 6FDA-mPDA, 6FDA-DABA, 6FDA-DMN</td>
</tr>
<tr>
<td>Electrical field (kV)</td>
<td>7.5, 10, 12.5, 17.5, 20</td>
</tr>
<tr>
<td>Flow rate (mL h⁻¹)</td>
<td>0.25, 0.5, 1, 2</td>
</tr>
<tr>
<td>Tip-to-collector distance (TCD, cm)</td>
<td>5, 10, 15, 20</td>
</tr>
<tr>
<td>Polymer concentration (% w/w)</td>
<td>5, 7.5, 10, 15</td>
</tr>
<tr>
<td>TEAB content (wt%)</td>
<td>0, 1, 2.5, 5, 10</td>
</tr>
</tbody>
</table>

* With respect to the polymer content.
atomic coordinates for the initial configuration were set up using the Packmol [37] and the Moltemplate [38] software suites, while the Ovito [39] program was used to visualize the results. Constant temperature simulations were performed using the Berendsen thermostat [31]. The initial droplet configuration consisted of a polymer of 30 monomer units, which were folded by simulated annealing and 1448 DMF solvents, while 4 TEAB molecules were also added to investigate the salt effect. The droplet was pre-equilibrated at 300 K and was immersed in 3000 N2 molecules in a 30·30·100 nm periodic simulation box (Fig. S5). The whole system was equilibrated for 300 ps at 300 K and 1 atm.

A unidirectional electric field of 0.8 V/nm was applied in the electrospinning simulations, and the nitrogen bath gas was thermostated at 600 K to provide heat for the evaporation [25]. The applied electrical field and the temperature are certainly higher than those in the experimental conditions, but they were necessary due to the available time scales in the molecular dynamics simulations. Nevertheless, a previous study has shown that these settings give realistic results [25].

3. Results and discussion

3.1. Synthesis of microporous polyimides

Five 6FDA-based polyimides were synthesized by a one-pot polycondensation reaction between 6FDA dianhydride and four planar diamines (mPDA, DABA, TrMCA, and TrMPD) and one contorted diamine (DMN) in m-cresol and the presence of isoquinoline at 200 °C (Scheme 1). The chemical structures of the polyimides were confirmed by 1H nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR). The total conversion of poly(amic) acid to polyimide was confirmed by 1H NMR through the absence of peaks above 10 ppm (Fig. S1). The FTIR was used to detect the characteristic absorption bands of the functional groups of 6FDA-based polyimides. The carbonyl (C=O) band appeared at 1786–1790 cm\(^{-1}\) and 1713–1726 cm\(^{-1}\) for asymmetric and symmetric stretching, respectively, while the characteristic stretching band of the imide bond (C–N) was observed at 1350–1357 cm\(^{-1}\). The obtained polyimides demonstrated high thermal stability, as confirmed by the thermogravimetric (TGA) analysis (Table 2, Fig. S3). The carboxyl functionalized polyimides (i.e., 6FDA-DABA and 6FDA-TrMCA) demonstrated lower decomposition temperature relative to the non-functionalized polyimides, resulted from the early degradation of –COOH group. 6FDA-mPDA exhibited the highest thermal stability in this series with \(T_{d,5\%}\) of 516 °C, while 6FDA-DABA was the least stable with \(T_{d,5\%}\) of 390 °C, as shown in Table 2.

We carefully selected the diamines to show the difference between polyimides bearing functionalities and non-functionalized polyimides and to explore the effect of using planar versus contorted diamines. The obtained polyimides had different BET surface areas, ranging from 36 to 506 m\(^2\) g\(^{-1}\), with the highest surface area for 6FDA-DMN, which was constructed from the contorted DMN (Table 2).

The presence of methyl groups at the ortho position to the imide linkage can lock the imide bond rotation and produce a more rigid polymer backbone, which leads to an increase in the BET surface area and fractional free volume (FFV) [40]. For instance, the presence of trimethyl side chains boosted the BET surface area from 36 (6FDA-mPDA) to 455 m\(^2\) g\(^{-1}\) (6FDA-TrMPD), and from 40 (6FDA-DABA) to 270 m\(^2\) g\(^{-1}\) (6FDA-TrMCA). The presence of –COOH groups in the polymer backbone can enhance the polymer chains packing due to the formation of hydrogen bonds, which result in the reduction of the BET surface area and FFV. The presence of the –COOH group led to a notable reduction
in the BET surface area from 455 (6FDA-TrMPD) to 270 m² g⁻¹ (6FDA-TrMCA).

3.2. Electrospinning: influence of process parameters and salt addition

First, we found that the optimum polymer concentration produced fibers by screening the concentration range of 5–20% (w/v). Bead-free fibers were produced at concentrations of 15% (6FDA-DABA), 10% (6FDA-DMN), 20% (6FDA-mPDA), 20% (6FDA-TrMCA) and 10% (6FDA-TrMPD) (w/v). Afterward, the influence of the process parameters on the electrospinning of the polyimides was studied by changing a single parameter while keeping other parameters constant (Table 2). The optimization experiments began with the effect of the applied voltage on the diameter and morphology of the resultant fibers. Fig. S6 shows the SEM images of the five polymers spun by the stepwise increase of the applied voltage from 7.5 to 20 kV. The diameter distribution plots of the respective fibers are shown in Fig. S7. At the voltage of 7.5 kV, the electrospinning yield was low, with fewer fibers formed on the collector during a given time for all polymers. However, an increase in the applied voltage significantly enhanced the electrospinning yield. The impact of the voltage was most pronounced on the fiber diameter, which revealed a decreasing trend as a result of higher jet stretch. For instance, for the 6FDA-DABA, the mean fiber diameter decreased from 570 ± 120 to 410 ± 80 nm as a result of increasing the voltage from 7.5 to 12.5 kV. However, a further increase in the voltage increased the fiber diameter, which can be attributed to the occurrence of higher mass flow at high voltages. The most uniform nanofibers with a low diameter distribution were produced at 12.5 kV. We also studied the effects of applied voltage on the morphology and diameter of other polyimides. The mean diameter of the polyimide fibers decreased from 380 ± 170, 370 ± 110, 420 ± 145, and 290 ± 80 nm to 250 ± 65, 370 ± 80, 280 ± 75 nm, and 280 ± 75 nm as the applied voltage increased from 7.5 to 17.5 kV for 6FDA-DMN, 6FDA-mPDA, 6FDA-TrMCA, and 6FDA-TrMPD, respectively (Fig. S7). The lower applied voltage resulted in the formation of uniform fibers, while the increase in the voltage adversely affected the fiber morphology. At 20 kV, we observed the formation of beaded-fibers, which can be credited to the decline in the size of the Taylor cone and a rise in the jet velocity for the identical flow rate [4]. Similar findings have been reported for the electrospinning of poly(vinyl alcohol) [41] and poly(caprolactone) [42].

We also studied the influence of the flow rate on the fiber morphology and diameter. Usually, a higher flow rate results in thicker fibers due to the higher mass flow, and, above a critical value, the formation of bead-free fibers may occur due to unstable jet formation. Fig. S8 shows the SEM photos of polyimide fibers electrospun at flow rates in the range of 0.25–2 mL h⁻¹. The diameter distributions of the respective fibers are shown in Fig. S9. The mean diameters of the nanofibers increased from 320 ± 125, 420 ± 105, and 390 ± 110 nm to 440 ± 85, 590 ± 295, and 460 ± 300 nm as a result of the increase in the flow rate from 0.25 to 2 mL h⁻¹ for 6FDA-DMN, 6FDA-mPDA, and 6FDA-TrMCA, respectively. At high flow rates, non-uniform nanofibers were formed due to the incomplete stretching of the jet in the flight between the metallic collector and the needle. At a flow rate of 2 mL h⁻¹, the formation of beads was obvious, while most uniform fibers obtained at a flow rate of 0.25 mL h⁻¹. Next, the effect of the tip-to-collector distance on the fiber morphology and diameter was studied. In the electrospinning process, an ideal tip-to-collector distance (TCD) should be long enough to allow the solvent from the electrospun jet to vaporize before the solidified fiber strand is collected on the metal plate. If the TCD distance is too short, insufficient vaporization of the solvent molecules from the jet may lead to fused fibers. During the experiments, the applied voltage (12.5 kV) and the flow rate (0.25 mL h⁻¹) were kept constant, while the TCD was increased from 5 to 20 cm. Fig. S10 shows the SEM images of the electrospun polyimide fibers produced at various TCDs. The mean diameter of the fibers showed a decreasing trend with an increase in the TCD (Fig. S11). For instance, the mean diameter of the 6FDA-DABA, 6FDA-DMN, 6FDA-mPDA, 6FDA-TrMCA, and 6FDA-TrMPD fibers decreased from 350 ± 40, 350 ± 40, 420 ± 105, 540 ± 165, 530 ± 90 nm to 310 ± 35, 280 ± 100, 420 ± 160, 480 ± 160, and 460 ± 160 nm by increasing the TCD two-fold from 5 to 10 cm, respectively. This observation is in line with previous reports that observed thinner fibers with increasing TCDs [43]. However, at high TCD (i.e., 20 cm), we observed a rise in the fiber diameter, which could be attributed to the lower stretching because of the lower electrical field and viscoelastic forces opposing stretching.

After exploring the effect of changing the electrospinning process parameters on the diameter and morphology of the electrospun fibers, we used a salt additive (TEAB) to study the impact of solution conductivity on the solution properties and spinability of the microporous polyimides. Fig. 2a shows the conductivity of the polyimide solutions as a function of TEAB content. Higher TEAB content prominently increased the conductivity of polyimide solutions. The conductivity of the 6FDA-TrMPD, 6FDA-DABA, 6FDA-TrMCA, 6FDA-DMN and 6FDA-mPDA solution increased from 66.84 ± 0.25, 58.94 ± 0.31, 37.52 ± 0.18, 31.80 ± 0.06 and 46.34 ± 0.16 μS cm⁻¹ to 998.06 ± 2.22, 1336 ± 8.49, 925.2 ± 1.44, 964.6 ± 1.80 and 1027 ± 0.81 μS cm⁻¹ with a gradual rise in the TEAB content from 0 to 10 wt%, respectively.

Because viscosity is one of the critical parameters that affects electrospinning, we studied the influence of salt addition on the viscosity of the polyimide solutions. Fig. 2b shows the viscosity of each polymer solution as a function of salt content. Increasing the TEAB content first increased the solution viscosity, followed by a significant drop in the viscosity, except for the solutions of the 6FDA-mPDA, which revealed an increasing trend with increasing TEAB. This increase in viscosity can be attributed to interactions between the polymer and the TEAB. In contrast, the decrease might be attributed to the negative interference of salt ions between the polymer chains, thus disrupting intermolecular interactions. A similar observation was recently reported for the solutions of PIM-1 and TEAB, where higher TEAB content decreased the viscosity of PIM-1 solutions [22]. Likewise, Su et al. reported that lower viscosity with increasing salt content as a result of disruption of hydrogen bonds between chitosan chains by metal ions may be the key reasons for the improved spinability [44].

Fig. 3 shows the SEM photos of the structures obtained by the electrospraying/electrospinning at various concentrations of mPDA but with the TEAB content held constant. The results demonstrate the improved spinability of the fibers as a result of the salt addition. The electrospinning at 10 and 15% (w/v) resulted in bead-free fibers, while the incorporation of 10 wt% TEAB directly influenced the fiber morphology, and bead-free fibers were produced. Even at lower concentrations, a transition from beads to bead-free fibers was observed, demonstrating the improved spinability in the presence of salt.

Fig. 4 shows the effect of TEAB addition on the electrospinning of the 6FDA-DABA solutions of various concentrations. The incorporation of the TEAB significantly improved the spinability, which manifested in very thin fibers at lower polymer concentrations. In contrast, at the polymer concentration of 7.5% (w/v), electrospayed beads were formed without salt addition. However, the addition of 10 wt% TEAB
resulted in electrospun fibers, which demonstrates the enhanced spinnability in the presence of TEAB. At high TEAB contents, thinner fibers were formed as a result of the lower viscosity of the respective solution. On the other hand, thicker fibers were spun at higher polymer concentrations as a result of the higher viscosity. The fiber diameter of the 6FDA-DABA fibers at 15% (w/v) decreased from 200 ± 45 to 180 ± 50 nm with the incorporation of 10 wt% TEAB. We observed a similar trend for the enhanced spinnability of 6FDA-DMN, which formed beads at a concentration of 5% (w/v) (Fig. S12). In contrast, we observed beaded-fibers after the addition of 10 wt% TEAB. Increasing the polymer content further to 10% (w/v) led to thick fibers, whereas the addition of 10 wt% TEAB resulted in thinner fibers. The addition of TEAB clearly improved the spinnability and drastically reduced the fiber diameter. For instance, the mean diameter of the fibers spun at 10% (w/v) decreased from 365 ± 165 to 190 ± 80 nm with the addition of 10 wt% TEAB. Likewise, a three-fold decrease in the diameter was observed for the fibers spun at 15% (i.e., from 940 ± 205 to 340 ± 140 nm) with the salt incorporation.

The impact of salt addition on the electrospinning of the 6FDA-TrMPD was more pronounced. We performed the electrospinning of the 6FDA-TrMPD of various concentrations in the presence of 10 wt% TEAB (with respect to the polymer) (Fig. 5). At 5 and 7.5% (w/v) of the 6FDA-TrMPD, beaded-fibers were obtained in the absence of TEAB, whereas increasing the polymer content to 10% (w/v) led to beaded-fibers. A further increase in the polymer concentration to 15% (w/v) led to thick fibers of 360 ± 75 nm. On the other hand, the addition of TEAB significantly improved the spinnability and led to the production of fibers, even at 5% (w/v), which is the lowest polymer concentration that yielded fibers among all the polymers screened. Furthermore, because of the low polymer concentrations, ultrathin fibers were formed with a mean diameter of 40 ± 11 nm in the presence of 10 wt% TEAB. In contrast, a two-fold increase in the polymer concentration increased the fiber diameter to 90 ± 60 nm, while the mean diameter of the salt-free fibers was 190 ± 65 nm. At very high polymer concentrations (i.e., 15% (w/v), the influence of TEAB addition was relatively reduced, and the mean diameter of the fibers decreased slightly from 360 ± 75 to 320 ± 65 nm with 10 wt% TEAB.
The effect of TEAB on the spinnability of the TrMCA fibers was also studied at various concentrations of the polymer and at constant TEAB content. SEM images of the respective fibers are shown in Fig. 13. We found that the effect of TEAB on the morphology of the structures obtained by electrosprining/electrospraying was negligible compared to other polymers. Furthermore, no clear transition with the TEAB addition was observed. Even at a polymer concentration of 15%, bead-free fibers could not be obtained with the addition of salt.

To explore the effect of salt content on the morphology and spinnability of the polyimides, we carried out electrosprining at various concentrations of TEAB, but with a constant polyimide concentration. Fig. 6 shows the structures of the electrosprayed fibers and electrosprayed particles produced at concentrations of TEAB in the range 0–5 wt% with respect to the polymer content. In the absence of TEAB, uniform fibers could not be obtained. Moreover, some of the fibers even exhibited bead formation; for instance, we observed the formation of electrosprayed beads of 6FDA-DABA due to the low concentration of the polymer (i.e., 10% (w/v)). The addition of salt did not provide a clear transition from beads to fibers; however, smaller beads were formed with increasing concentrations of TEAB. At 5 wt% TEAB, beaded-fibers were observed owing to the occurrence of partial electrospinning. On the other hand, the electrospinning of the 6FDA-DMN at 10% (w/v) led to thick and non-uniform fibers. The increase in salt content induced thinner fibers as a result of the enhanced conductivity in the respective solutions.

Fig. 4. SEM images of the electrosprayed/electrospun structures of the 6FDA-DABA of various concentrations but at constant salt content. c_{TEAB} = 10 wt% (with respect to the polymer content). The insets show the statistical distributions of fiber diameters. The TCD and flow rates were 15 cm and 0.25 mL h^{-1}, respectively.

Fig. 5. SEM images of the electrosprayed/electrospun structures of the 6FDA-TrMPD of various concentrations at constant salt content. c_{TEAB} = 10 wt% (with respect to the polymer content). The insets show the statistical distributions of fiber diameters. The TCD and flow rates were 15 cm and 0.25 mL h^{-1}, respectively.
The benefit of salt addition was evident for both 6FDA-mPDA and 6FDA-TrMCA. The electrospinning of both polymers at the concentration of 15% (w/v) in the absence of TEAB led to beaded fibers. However, with the addition of TEAB, bead-free fibers were formed because of the improved spinnability of the respective polymer solutions. Higher salt content (i.e., 5 wt%) led to thinner fibers of diameters 220 ± 75 and 190 ± 55 nm for 6FDA-mPDA and 6FDA-TrMCA, respectively. Unlike other polyimides, the spinnability of the 6FDA-TrMPD was significantly influenced by the salt addition. Even a small addition of TEAB (1 wt%) led to the formation of thin fibers (120 ± 45 nm) at polymer concentrations of 10% (w/v). Further increasing the TEAB content decreased the fiber diameter considerably (i.e., 80 ± 30 nm for 2.5 wt% TEAB), culminating in the formation of beaded-fibers at 5 wt% TEAB. Overall, we found the impact of salt addition on the spinnability of polyimides to be significant, and we observed that salt addition improved the spinnability and formed thinner fibers.

Fig. 6. The effect of salt concentration on the electrospun polyimide fibers. The polymer concentrations are as follows; (a) 6FDA-DABA (7.5% (w/v)), (b) 6FDA-DMN (10% (w/v)), (c) 6FDA-mPDA (15% (w/v)), (d) 6FDA-TrMCA (15% (w/v)), and (e) 6FDA-TrMPD (10% (w/v)), respectively. The insets show the statistical distributions of fiber diameters.
3.3. Molecular modeling studies

The effect of salt addition on the electrospinning of polyimides was explored through molecular dynamics (MD) simulations. The size and shape evolution of the droplet with and without TEAB salt is depicted in Fig. 9. We investigated the droplet size by clustering and counting the corresponding atoms with a 5 Å cutoff radius, while we used the radius of gyration (\(R_G\), Eq. 1) to analyze the spatial extent of the droplet.

\[
R_G = \left( \frac{\sum m_i \cdot r_i^2}{\sum m_i} \right)^{1/2}
\]

Fig. 8. (a) The evolution of the droplet shape with TEAB and (b) the final polymer configuration with TEAB. (c) The droplet shape evolution without TEAB and (d) final polymer configuration without TEAB. Color coding: grey – carbon, red – oxygen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
where \( m_i \) and \( r_i \) are the mass and distance from the center of mass of each atomic nuclei, respectively. We investigated the particle shape using the covariance of the atomic coordinates measured from the center of the atomic coordinates, as it is implemented in the Molmod library. We computed the shape factor \( S \) as defined in Eq. 2.

\[
S = \frac{2 \cdot \lambda_1}{\lambda_2 + \lambda_3}
\]  

(2)

where \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are the eigenvalues of the covariance matrix in descending order. Averaging of the smaller eigenvalues was specifically defined due to the ellipsoid shape of the particles. \( S = 1 \) indicates a spherical particle, which increases with its distortion into an ellipsoid shape.

Fig. 7a shows a remarkable increase in the droplet evaporation rate with the addition of TEAB salt. The electrospinning process begins similarly, irrespective of the salt addition. The radius of gyration (Fig. 7b) indicates the spatial increase of the droplet, while the shape factor (Fig. 7c) clearly shows that this was caused by the distortion of the elongated ellipsoid shape due to the external electric field. The extent of the distortion was smaller when TEAB was added to the system, which we postulate was the result of the higher evaporation rate.

However, the evaporation mechanism depends considerably on the presence of the TEAB salt. With TEAB salt addition, the electrical field accelerates the ions, and DMF was removed rapidly in the form of secondary droplets from the tip of the ellipsoid shape particle (Fig. 8a). On the contrary, without TEAB salt, DMF was evaporated at the molecular level (Fig. 8b), which explains the remarkable difference in their evaporation rates. Similar effects have been observed in the case of polyethylene-glycol/H2O/NaCl system. [25] Interestingly, the addition of TEAB salt resulted in a less compact polymer structure after the electrospinning process (Fig. 8c) compared to that without TEAB salt (Fig. 8d). The interactions between the polymer and the salt lead to a less compact polymer structure because the electrical field accelerates the ions, and thereby extends the polymer chain. In this regard, a similar finding was reported for the electrospinning of polyethylene oxide in the presence of sodium chloride [25]. The authors performed molecular dynamic simulations and found that some sodium ions coordinate with the ether oxygen group in the PEO chain. Under the electrical field, these ions are accelerated, resulting in the stretching of PEO chains while improving the fiber morphology. Furthermore, this supports the fast evaporation of solvent molecules from the fiber matrix as a result of the formation of wide pores.

4. Conclusion

The influence of process parameters and salt addition on the electrospinning of five different porous polyimides was studied. The fiber morphology and diameter were affected by the electrospinning parameters, and their adjustment enabled the formation of thinner and uniform nanofibers. The impact of salt addition on the spinnability and fiber morphology was substantial, boosting the solution conductivity and enhancing the spinnability. With the addition of TEAB salt, the formation of fibers even at low polymer concentrations could be succeeded. In contrast, at the same concentrations in the absence of salt, electrospayed beads were formed. The higher salt content decreased the fiber diameter and led to nanofibers as thin as 40 ± 11 nm. We observed the most considerable changes for the electrospinning of 6FDA-TrMPD. Molecular dynamics simulations revealed the detachment of secondary droplets from the primary droplet due to the evaporation of ions and the hydration effect. This phenomenon rapidly accelerated water evaporation and therefore improved the spinnability of the solution. Our results reveal that when salt ions are accelerated by an electric field, the polymer chain follows the motion of the ions, and ultimately improving the fiber morphology. These uniform, porous nanofibers featuring pendant trifluoromethyl groups have a high potential to be employed in various applications, including water treatment. Furthermore, the presented approach can be employed for the electrospinning of other polymers to produce uniform thin fibers at lower polymer concentrations.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CRediT authorship contribution statement

Fuat Topuz: Conceptualization, Investigation, Formal analysis, Writing - original draft. Mahmoud A. Abdulhamid: Investigation, Writing - review & editing. Tibor Holtzl: Investigation, Writing - review & editing. Gyorgy Szekely: Conceptualization, Funding acquisition, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2020.109280.

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