

# Electrospinning of uniform polystyrene fibers: The effect of solvent conductivity

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## ABSTRACT

By means of the electrospinning technique, micron- and nanofibers can be obtained from polymer solutions under a very high electrical field. A special challenge is to produce bead-free uniform fibers since any minor changes in the electrospinning parameters such as slight variations in the polymer solutions and/or electrospinning experimental parameters may result in significant variations in the final nanofiber morphology. Furthermore, it is often not trivial at all to obtain reproducible uniform electrospun nanofibers for the optimized electrospinning conditions. Here we report that the conductivity of the solvent is the key factor for the reproducible electrospinning of uniform polystyrene (PS) fibers from dimethylformamide (DMF) solutions. It is shown that even slight changes in the conductivity of the DMF solutions can greatly affect the morphology of the resulting electrospun PS fibers. Here, we have carried out a thorough and systematic study on the effect of solution conductivity on the electrospinning of bead-free polystyrene (PS) fibers when dimethylformamide (DMF) was used as the solvent. Interestingly, we found out that different grades of solvent as-received (DMF) from various suppliers have slightly different solution conductivities. Consequently, the polymer solutions prepared with the same PS concentration have different conductivities, which are shown to have significant changes on the morphology of the PS fibers resulting in beaded or bead-free uniform fibers when electrospun under the identical electrospinning conditions. Such as, bead-free PS fibers were obtained from PS solutions in the range of 20% (w/v) through 30% (w/v) depending on the DMF grade used. In brief, it was observed that solutions with a higher conductivity yielded bead-free fibers from lower polymer concentrations, which confirms that the solution conductivity plays a very significant role in producing bead-free uniform PS fibers.

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## 1. Introduction

Electrospinning is a handy and cost-effective technique for producing nanowebs where the fiber diameters are in the range of a few hundred nanometers to a few microns. The technique is very promising and versatile since it facilitates the production of multi-functional nanofibers from various polymers, polymer blends, sol-gels, composites and ceramics, etc. [1–4]. With this technique, a continuous filament is electrospun from polymer solutions [1–5] or polymer melts [6] under a very high electrical field, which resulted in the form of nonwovens consisting of nanofibers. Nanowebs produced by the electrospinning technique have several remarkable functional characteristics such as a very large surface area to volume ratio, pore size within the nano range, unique physical and mechanical properties along with the design flexibility for chemical/physical surface functionalization. It has been shown that the outstanding properties and multi-functionality of the

nanowebs make them favorable candidates to be used in many areas including biotechnology (tissue engineering, controlled/sustained release systems) [7–9], membranes/filters [9,10], textiles [11], etc.

Amorphous polystyrene (PS), being a transparent, stiff material with a high electrical resistance and low dielectric loss, is one of the mostly used commodity polymer in the applications for packaging, insulation, filtration, etc. Numerous studies have shown that PS fibers can be produced by means of the electrospinning technique [12–32], and it has been demonstrated that electrospun PS fibers have interesting applications in areas such as tissue engineering [25,26], filtration [27], ion exchanger [28], enzyme immobilization [29], sensors [30], catalysis immobilization [31] and composite materials [32], etc.

It is expected that the morphology of the electrospun PS fibers plays an important role in the physical/mechanical properties of the final products to be used in certain applications; therefore, reproducible electrospinning of uniform PS fibers is essential. With respect to the electrospinning of polystyrene, it has been shown that molecular weight, polymer concentration, solution viscosity [12–15], solution conductivity [16–18] and the type of

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solvent [18–24] all are key parameters which may have a significant influence on the morphology of the electrospun fibers. It has been shown that electrospun PS fibers can be produced by using various solvent systems, and among these, *N,N*-Dimethylformamide (DMF) was found to be the most favorable solvent for producing uniform round fibers with smooth surfaces due to its high boiling point, solution conductivity and high dielectric constant compared to other solvents [19–23].

One of the challenges in the formation of nanofibers by means of the electrospinning technique is the reproducible production of bead-free uniform fibers since any small changes in numerous electrospinning parameters such as viscosity, surface tension, solution conductivity, type of solvent, etc. may result in significant changes in the final fiber morphology. For example beaded fibers often result for otherwise optimized electrospinning conditions due to small changes in the polymer solutions and/or the electrospinning setup. From detailed studies of the electrospinning of PS fibers from a DMF solution, we have experienced such reproducibility problems and revealed that the electrospinning conditions must be optimized in order to produce bead-free electrospun PS fibers. However, even when the electrospinning experiments were

subsequently repeated using the same solvent (DMF) but from different grades and/or suppliers, we may again obtain beaded fibers instead of uniform bead-free fibers. This unanticipated and surprising result inspired us to carry out an extensive and systematic study in order to try to understand this unexpected behavior. We here report on the morphological differences of PS fibers when electrospun under the same conditions but using different grades of DMFs with slightly different solution conductivities. It is shown that any slight changes in solution conductivity indeed greatly affect the final morphology of the electrospun PS fibers yielding beaded or bead-free fibers.

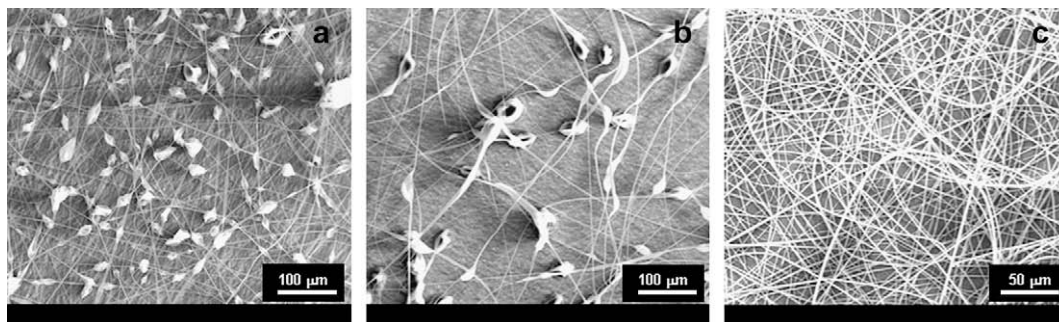
## 2. Experimental

### 2.1. Materials

The amorphous polystyrene (PS) ( $M_w \sim 280,000$ , Sigma) was used for electrospinning. Different grades of *N,N*-Dimethylformamide (DMF) were used, namely; DMF ( $\geq 99.8\%$ , ACS reagent, Sigma-Aldrich, Germany), DMF (99%, Aldrich, Germany), DMF ( $\geq 98.0\%$  (GC), Fluka, Germany), DMF ( $\geq 99.8\%$  (GC), Fluka, Germany). In the

**Table 1**  
The characteristics of PS solutions and the resulting electrospun PS fibers

Name	DMF grade	% PS (w/v)	Fiber morphology	Fiber diameter (nm)	Bead size (l/w) (micron)	Bead aspect ratio (micron)	Viscosity (cP)	Conductivity ( $\mu\text{S}/\text{cm}$ )
DMF1-Aldrich99	Aldrich, 99%	0	–	–	–	–	–	15.9
DMF1-A99-PS10	Aldrich, 99%	10	Nano-fibers with few beads	481 ± 93	8.43 ± 1.48/3.60 ± 0.79	2.41 ± 0.51	21.2 ± 0.1	10.1
DMF1-A99-PS15	Aldrich, 99%	15	Nano-fibers, very few beads	958 ± 200	17.27 ± 5.83/5.18 ± 1.37	3.39 ± 1.16	60.0 ± 0.7	8.6
DMF1-A99-PS20	Aldrich, 99%	20	Micro-fibers only	1470 ± 256	–	–	139.7 ± 0.7	7.3
DMF2-Aldrich99	Aldrich, 99%	0	–	–	–	–	–	5.6
DMF2-A99-PS10	Aldrich, 99%	10	Nano-fibers with many beads	373 ± 112	9.39 ± 1.62/4.60 ± 1.42	2.18 ± 0.63	22.9 ± 0.1	2.5
DMF2-A99-PS15	Aldrich, 99%	15	Micro-fibers with beads	1229 ± 319	15.42 ± 2.62/6.36 ± 1.11	2.48 ± 0.49	59.9 ± 0.5	1.35
DMF2-A99-PS20	Aldrich, 99%	20	Micro-fibers with few beads	2370 ± 445	21.70 ± 2.34/6.86 ± 1.24	3.23 ± 0.60	129.8 ± 0.4	1.1
DMF2-A99-PS25	Aldrich, 99%	25	Micro-fibers only	1882 ± 277	–	–	342.6 ± 1.8	1.1
DMF-Sigma998	Sigma, 99.8%	0	–	–	–	–	–	1.3
DMF-S998-PS10	Sigma, 99.8%	10	Nano-fibers with many beads	367 ± 120	10.76 ± 2.80/6.01 ± 1.59	1.87 ± 0.52	21.6 ± 0.2	0.9
DMF-S998-PS15	Sigma, 99.8%	15	Nano-fibers with beads	922 ± 274	15.92 ± 4.36/9.85 ± 1.28	1.62 ± 0.39	62.5 ± 0.5	0.8
DMF-S998-PS20	Sigma, 99.8%	20	Micro-fibers with few beads	2788 ± 374	26.01 ± 3.56/10.77 ± 0.30	2.46 ± 0.30	136.4 ± 0.5	0.8
DMF-S998-PS25	Sigma, 99.8%	25	Micro-fibers only	1872 ± 223	–	–	338.9 ± 1.1	0.8
DMF-Fluka98	Fluka, 98%	0	–	–	–	–	–	0.5
DMF-F98-PS10	Fluka, 98%	10	Nano-fibers with many beads	351 ± 97	7.87 ± 1.86/3.38 ± 1.22	2.50 ± 0.72	21.2 ± 0.1	0.5
DMF-F98-PS15	Fluka, 98%	15	Nano-fibers with beads	942 ± 171	21.66 ± 3.91/10.47 ± 2.52	2.12 ± 0.38	55.3 ± 0.2	0.4
DMF-F98-PS20	Fluka, 98%	20	Micro-fibers with beads	1376 ± 272	21.69 ± 5.74/11.88 ± 2.72	1.87 ± 0.52	122.8 ± 0.6	0.4
DMF-F98-PS25	Fluka, 98%	25	Micro-fibers with few beads	2661 ± 529	32.57 ± 6.05/14.74 ± 3.10	2.28 ± 0.53	336.3 ± 3.5	0.4
DMF-F98-PS30	Fluka, 98%	30	Micro-fibers only	4284 ± 413	–	–	604	0.4
DMF-Fluka998	Fluka, 99.8%	0	–	–	–	–	–	1.0
DMF-F998-PS10	Fluka, 99.8%	10	Nano-fibers with many beads	292 ± 48	12.85 ± 2.56/6.60 ± 1.20	2.01 ± 0.51	22.2 ± 0.1	0.7
DMF-F998-PS15	Fluka, 99.8%	15	Nano-fibers with beads	942 ± 248	16.97 ± 3.27/8.48 ± 1.72	2.01 ± 0.58	62.5 ± 0.7	0.7
DMF-F998-PS20	Fluka, 99.8%	20	Micro-fibers with beads	1534 ± 366	27.34 ± 5.21/13.49 ± 2.09	2.04 ± 0.37	129.6 ± 0.7	0.7
DMF-F998-PS25	Fluka, 99.8%	25	Micro-fibers with few beads	1656 ± 218	14.93 ± 1.51/5.42 ± 0.64	2.78 ± 0.37	354.8 ± 2.8	0.7
DMF-F998-PS30	Fluka, 99.8%	30	Micro-fibers only	3803 ± 596	–	–	666	0.7



**Fig. 1.** SEM images of electrospun PS fibers obtained from 20% (w/v) PS solution in (a) THF, (b)  $\text{CHCl}_3$ , (c) DMF (DMF1-Aldrich99). Electrospinning parameters: applied voltage = 15 kV, tip-to-collector distance = 10 cm, feeding rate = 1 mL/h.

case of DMF (99%, Aldrich, Germany), two different bottles were used, and it was observed that these two DMFs have different solution conductivities. Tetrahydrofuran (Fluka,  $\geq 99.0\%$ , Germany), chloroform (Fluka,  $\geq 99.5\%$ , Germany) and tetrabutylammonium bromide ( $\geq 98.0\%$ , Fluka, Germany) were also used in this study. All the materials were used as-received without any purification.

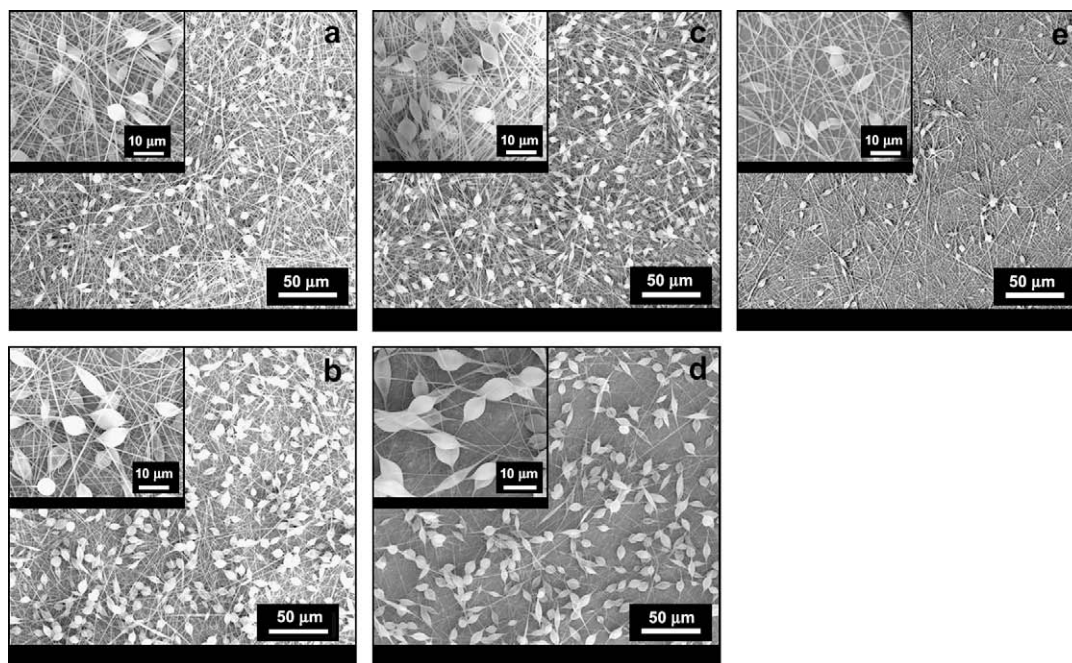
## 2.2. Solvent conductivity

It was observed that the solution conductivities of as-received DMFs were different from each other. The two DMFs from Aldrich (99%) had different solution conductivities of  $15.9 \mu\text{S}/\text{cm}$  and  $5.6 \mu\text{S}/\text{cm}$  and named as DMF1-Aldrich99 and DMF2-Aldrich99, respectively. The other DMFs from Sigma-Aldrich (99.8%), Fluka (99.8%) and Fluka (98%) had solution conductivities of  $1.3 \mu\text{S}/\text{cm}$ ,  $1.0 \mu\text{S}/\text{cm}$  and  $0.5 \mu\text{S}/\text{cm}$ , respectively, and named as DMF-Sigma998, DMF-Fluka998 and DMF-Fluka98, respectively. The conductivities of as-received DMFs and the resulting polystyrene solution are summarized in Table 1. It is worth mentioning that the conductivities of as-received DMFs were checked regularly prior to preparation of polymer solutions to

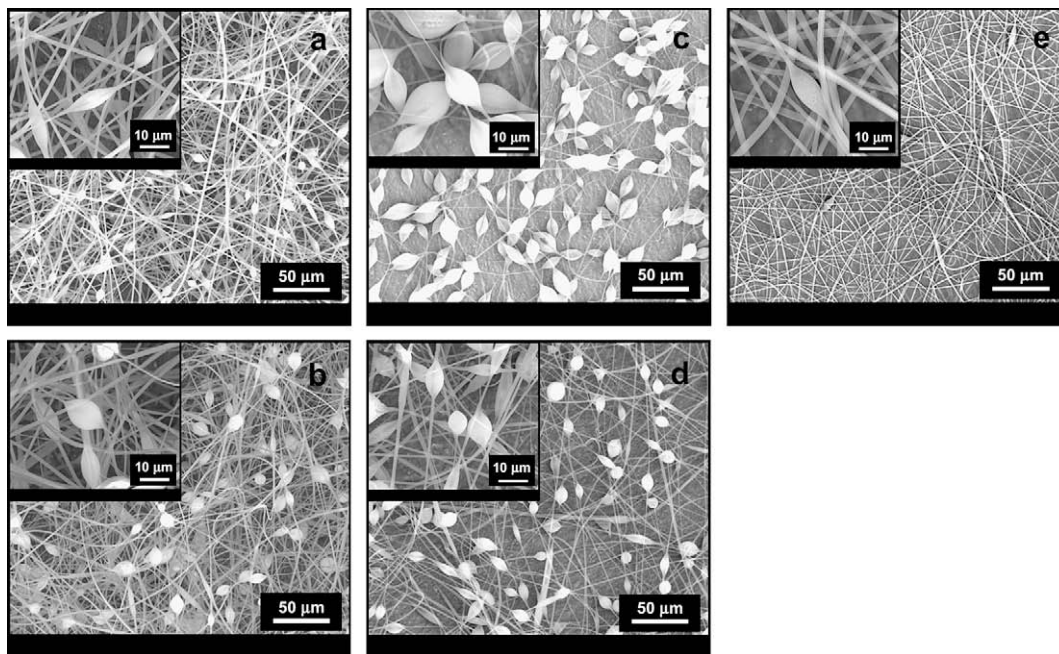
make sure that no change in conductivity of the solvents occurred during time.

## 2.3. Electrospinning

Homogeneous and clear polymer solutions were prepared by dissolving PS in DMF at room temperature after stirring for 5 h. The polymer concentration was varied from 10% (w/v) up to 30% (w/v). The PS solutions were placed in a 1 mL syringe fitted with a metallic needle of 0.4 mm of inner diameter. The syringe was fixed horizontally on the syringe pump (Model: KDS 101, KD Scientific) and the electrode of the high voltage power supply (Spellman High Voltage Electronics Corporation, MP Series) was clamped to the metal needle tip. The flow rate of polymer solution was varied from 0.5 to 2 mL/h, and the applied voltage was varied from 10 to 20 kV. The tip-to-collector distance was varied from 5 to 20 cm, and a grounded stationary rectangular metal collector ( $15 \text{ cm} \times 20 \text{ cm}$ ) covered by a piece of aluminum foil was used for the fiber deposition. The complete electrospinning apparatus was enclosed in glass box and the electrospinning was carried out in a horizontal position at room temperature. The best results were obtained when the flow



**Fig. 2.** SEM images of electrospun PS fibers obtained from 10% (w/v) PS solution prepared by using different grades of DMF (a) DMF2-Aldrich 99%, (b) Sigma 99.8%, (c) Fluka 98%, (d) Fluka 99.8%, (e) DMF1-Aldrich 99%. The inset image shows the same sample with a higher magnification.

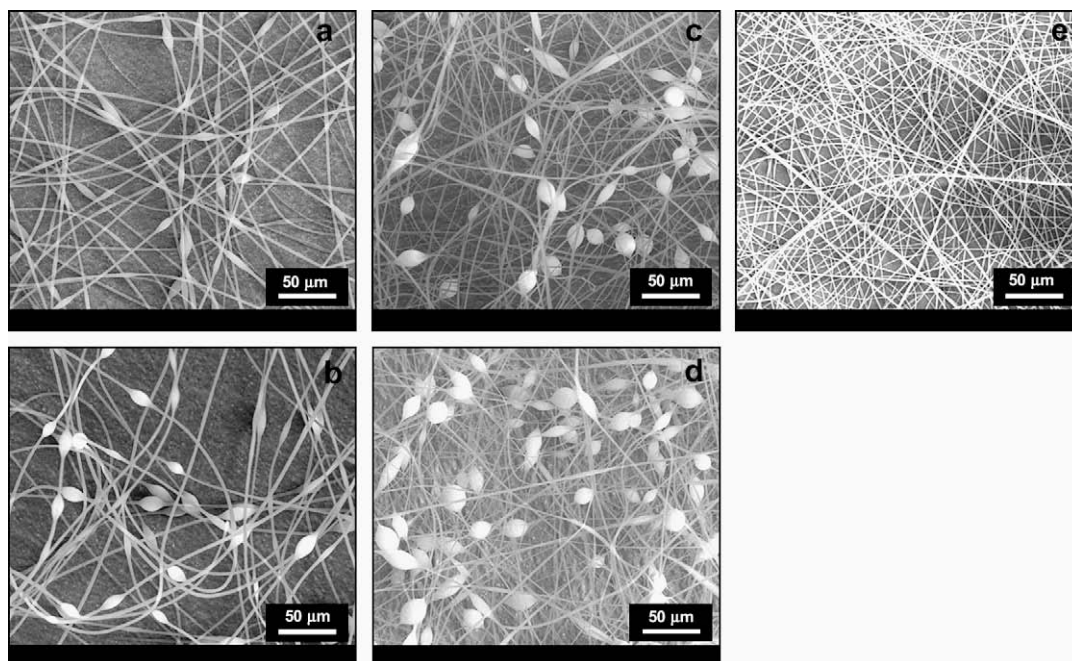


**Fig. 3.** SEM images of electrospun PS fibers obtained from 15% (w/v) PS solution prepared by using different grades of DMF (a) DMF2-Aldrich 99%, (b) Sigma 99.8%, (c) Fluka 98%, (d) Fluka 99.8%, (e) DMF1-Aldrich 99%. The inset image shows the same sample with a higher magnification.

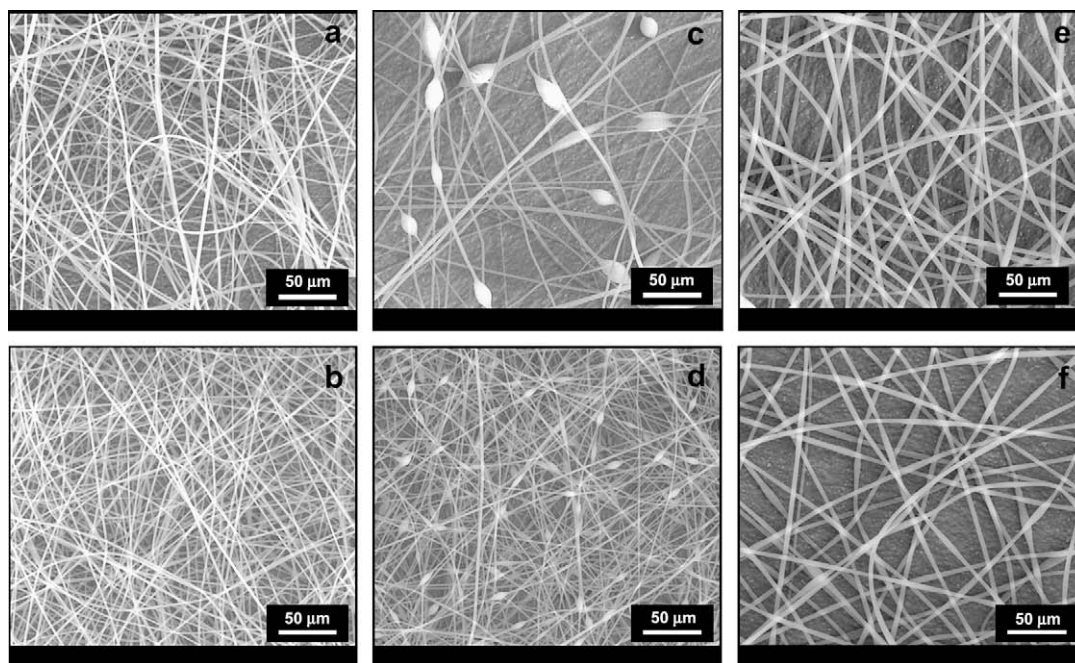
rate of polymer solution was kept at 1 mL/h, the applied voltage was 15 kV and the tip-to-collector distance was 10 cm. Therefore, all the experiments were done at these electrospinning parameters and kept constant for all PS solutions mentioned in this study. The electrospinning of each PS solution in different DMFs was carried out at least three times to make sure that the results for the fibers are reproducible and that no significant variation was observed with respect to the fiber morphology and the fiber diameter.

#### 2.4. Characterization and measurements

The viscosity of the polymer solutions was measured at 24 °C by using Brookfield DV-III Ultra Rheometer equipped with cone/plate accessory using the spindle type CPE-41. The viscosity measurements were repeated three times or more to make sure that the viscosity reading was consistent. The conductivity of the solutions was measured with Multiparameter meter Ino Lab® Multi 720



**Fig. 4.** SEM images of electrospun PS fibers obtained from 20% (w/v) PS solution prepared by using different grades of DMF (a) DMF2-Aldrich 99%, (b) Sigma 99.8%, (c) Fluka 98%, (d) Fluka 99.8%, (e) DMF1-Aldrich 99%.



**Fig. 5.** SEM images of electrospun PS fibers obtained from 25% (w/v) PS solution prepared by using different grades of DMF (a) Sigma 99%, (b) Sigma 99.8%, (c) Fluka 98%, (d) Fluka 99.8%. SEM images of electrospun PS fibers obtained from 30% (w/v) PS solution in DMF of (e) Fluka 98%, (f) Fluka 99.8%.

(WTW) at room temperature. The morphology of the polystyrene (PS) fibers was examined by high-resolution scanning electron microscopy (SEM) (FEI, Nova 600 NanoSEM). The fibers collected onto aluminum foil were directly put into SEM chamber without any metal sputtering/coating on them. The average fiber diameter and the aspect ratio of the beads were calculated from the SEM images. Up to 50 fibers and 25 beads were analyzed for measuring the fiber diameter and the aspect ratio of beads.

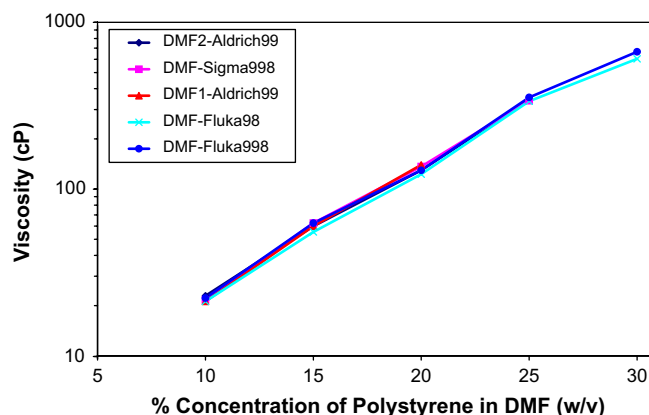
### 3. Results and discussion

Among the solvents used; tetrahydrofuran (THF), chloroform and *N,N*-Dimethylformamide (DMF), for electrospinning of polystyrene (PS), DMF was found to be the optimal solvent producing bead-free uniform electrospun PS fibers. SEM images showed that the DMF solvent yielded bead-free PS fibers but fibers with irregular structures were obtained when THF and chloroform were used as solvents (Fig. 1). These results are in very good accordance with the literature findings where DMF was reported to be the most favorable solvent yielding uniform PS fibers due to its solution conductivity, high dielectric constant and high boiling point [15,19–23]. The measured viscosity and conductivity of 20% (w/v) PS solution in DMF (DMF1-Aldrich99) was  $139.7 \pm 0.7$  cP and  $7.3 \mu\text{S}/\text{cm}$ , respectively, whereas the viscosity of PS solutions in THF and chloroform was  $210 \pm 1.1$  cP and  $246.3 \pm 1.5$  cP, respectively, and these PS solutions have zero conductivity. Despite the low viscosity of the PS solution in DMF, this result indicated that the conductivity of the polymer solution is one of the key factors in the production of uniform electrospun PS fibers.

The electrospinning of PS solutions prepared by using different grades of DMFs; (Aldrich (99%), Sigma-Aldrich ( $\geq 99.8\%$ ), Fluka ( $\geq 99.8\%$ ) and Fluka ( $\geq 98\%$ )) were used as solvent for polymer solutions. The concentration of the PS solutions was varied from 10% (w/v) up to 30% (w/v). The characteristics of PS solutions and the resulting PS fibers are summarized in Table 1. The scanning electron microscopy (SEM) images of electrospun PS fibers from 10% (w/v) through 30% (w/v) polymer solution in different grades of DMFs are shown in Figs. 2–5. It was found that the viscosity

increased as the concentration of polymer solution increased from 10% to 30% (w/v) due to the higher number of polymer chain entanglements. SEM images depicted in Figs. 2 and 3 showed that beaded fiber structures were obtained at lower polymer concentrations but an increase in the polymer concentration to 20–30% (w/v) yielded bead-free fibers (Figs. 4 and 5), which indicates that a high viscosity is required to obtain uniform PS fibers. These findings are consistent with previous findings in the literature where bead-free PS fibers were obtained only at the high viscosity range [12–15,22]. Interestingly, significant morphological variations were observed for electrospun PS fibers at the same polymer concentrations but using different DMFs under the same electrospinning conditions.

In Fig. 6 is depicted how the viscosity varies as a function of the PS concentration prepared by using different grades of DMF solvents. It is observed that the measured viscosities for same concentration of PS solutions are basically very close when different grades of DMFs are used. This finding shows that the viscosity



**Fig. 6.** Viscosity of various concentrations of PS solution prepared by using different grades of DMF.

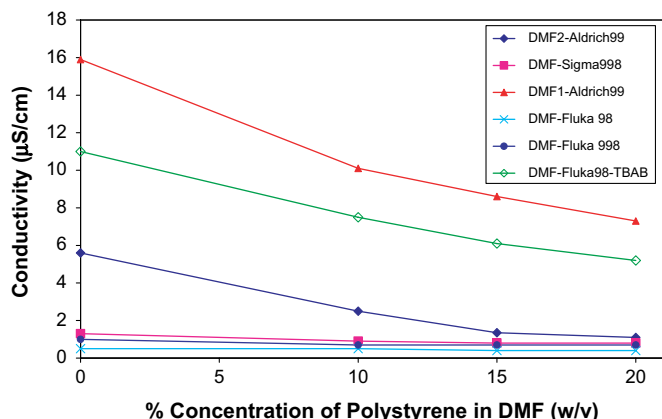


Fig. 7. The change in the conductivity of the PS solutions at various concentrations prepared by using different grades of DMF.

cannot be the main reason for the yield of different fiber morphologies when different grades of DMF are used.

However, when the solution conductivities of the pure DMF solvents were measured, we observed that they were indeed slightly different. *DMF1-Aldrich99* having the highest conductivity of 15.9  $\mu\text{S}/\text{cm}$  and the other DMFs: *DMF2-Aldrich99*, *DMF-Sigma998*, *DMF-Fluka998* and *DMF-Fluka98* having solution conductivities of 5.6  $\mu\text{S}/\text{cm}$ , 1.3  $\mu\text{S}/\text{cm}$ , 1.0  $\mu\text{S}/\text{cm}$  and 0.5  $\mu\text{S}/\text{cm}$ , respectively. The addition of PS, a non-conducting polymer, lowers the conductivity of the solution but still the conductivity of each solution at the same concentration is slightly different from each other (Table 1). Fig. 7 shows the variations in conductivity of the polymer solution as a function of the PS concentration. *DMF1-Aldrich99* polymer solutions have the highest conductivity (10.1–7.3  $\mu\text{S}/\text{cm}$ ) at all concentrations of PS followed by the *DMF2-Aldrich99* solutions (2.5–1.1  $\mu\text{S}/\text{cm}$ ), *DMF-Sigma998* solutions (0.9–0.8  $\mu\text{S}/\text{cm}$ ), *DMF-Fluka998* solutions (0.7  $\mu\text{S}/\text{cm}$ ) and *DMF-Fluka98* solutions

(0.5–0.4  $\mu\text{S}/\text{cm}$ ). This observation is consistent with the literature in which the conductivity of pure DMF and its PS solutions has been reported to be in the range of 0.06–10.9  $\mu\text{S}/\text{cm}$  ([14,16,18,23]), confirming that DMF solvents have different conductivities depending on the grades and/or suppliers.

The solution conductivity is one of the main parameters in the electrospinning process since the viscous polymer solution is being stretched due to the repulsion of the charges present on its surface, and more charges can be carried at higher solution conductivity. Often, polymer solutions are prepared using solvents that have a higher conductivity or salts are added to solution to increase the conductivity. The increase in the conductivity of solution results in production of bead-free uniform and thinner fibers since the polymer solution is subjected to more stretching under the high electrical field [16–18]. From the results depicted above we have revealed that the difference in conductivity of DMF solutions has a significant effect on the morphology of the electrospun PS fibers (see Figs. 2–5) obtained at the same polymer concentrations when the electrospinning parameters are kept constant. When *DMF1-Aldrich99* was used as a solvent, a smaller number of beads were obtained with 10% (w/v) PS solution when compared to the results of the other polymer solutions (Fig. 2). When the PS concentration is increased to 15% (w/v), the number of beads decreased for all the systems studied (Fig. 3) due to the viscosity increase, and nanofibers along with a very limited number of elongated beads were obtained only for *DMF1-Aldrich99* solution (Fig. 3e). The difference in fiber morphology was much more distinct in the case of electrospun PS fibers from a 20% (w/v) (Fig. 4). *DMF1-Aldrich99* solution yielded bead-free uniform fibers at a PS concentration of 20% (w/v) whereas all the other four solutions yielded beaded fibers. The only difference is that the *DMF1-Aldrich99* solution has a higher conductivity, further proving that the conductivity plays a key factor in obtaining uniform electrospun PS fibers. Once the polymer concentration is increased to above 25% w/v, bead-free PS fibers were obtained in the case of *DMF2-Aldrich99* and *DMF-Sigma998* solutions (Fig. 5a and b), and beads still were observed from

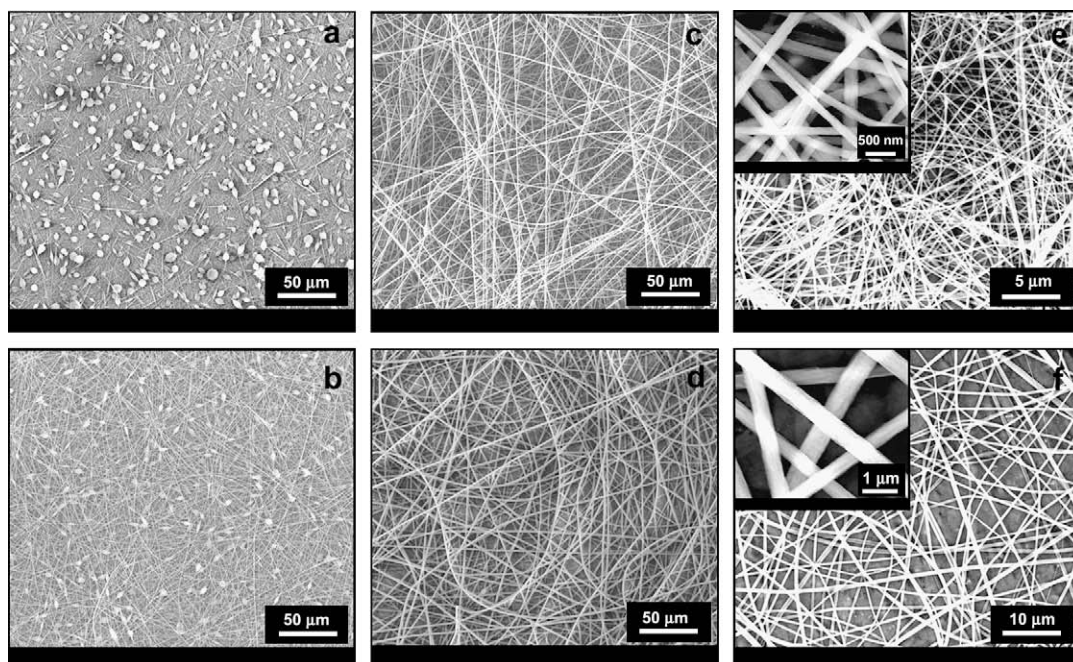


Fig. 8. SEM images of electrospun PS nanofibers obtained from different concentrations of PS solution in DMF (Fluka 98%) with addition of 0.003% TBAB (w/w, with respect to DMF) (a) 10% PS, (b) 15% PS, (c) 20% PS and (d) 25% PS. SEM images of electrospun PS nanofibers obtained from DMF (Sigma 99%) with addition of 1% TBAB (w/w, with respect to PS) (a) 10% (w/v) PS (b) 15% (w/v).

**Table 2**  
The characteristics of PS solutions with the addition of TBAB and the resulting electrospun PS fibers

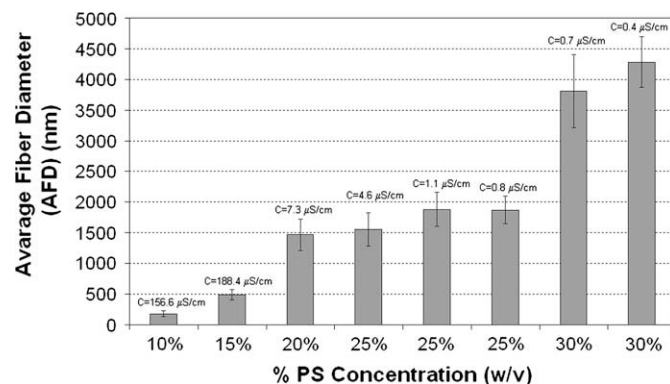
Name	DMF grade	% PS (w/v)	% TBAB (w/v)	Fiber morphology	Fiber diameter (nm)	Bead size (l/w) (micron)	Bead aspect ratio (micron)	Conductivity ( $\mu\text{S}/\text{cm}$ )
DMF-Fluka98-TBAB	Fluka, 98%	–	0.003	–	–	–	–	11.0
DMF-F98-TBAB-PS10	Fluka, 98%	10	0.003	Nano-fibers, many beads	$191 \pm 35$	$7.63 \pm 1.51/3.75 \pm 0.75$	$2.08 \pm 0.45$	7.5
DMF-F98-TBAB-PS15	Fluka, 98%	15	0.003	Nano-fibers with beads	$443 \pm 86$	$8.29 \pm 0.50/3.26 \pm 0.42$	$2.58 \pm 0.35$	6.1
DMF-F98-TBAB-PS20	Fluka, 98%	20	0.003	Micro-fibers, very few beads	$1017 \pm 173$	$9.78 \pm 1.20/3.97 \pm 0.77$	$2.52 \pm 0.41$	5.2
DMF-F98-TBAB-PS25	Fluka, 98%	25	0.003	Micro-fibers only	$1552 \pm 273$	–	–	4.6
DMF2-Aldrich99-TBAB	Aldrich, 99%	–	0.1	–	–	–	–	224.0
DMF2-A99-TBAB-PS10	Aldrich, 99%	10	0.1	Nano-fibers only	$181 \pm 46$	–	–	156.6
DMF2-A99-TBAB-PS15	Aldrich, 99%	15	0.15	Nano-fibers only	$490 \pm 83$	–	–	188.4

DMF-Fluka98 and DMF-Fluka998 solutions (Fig. 5c and d). In this connection, it should also be noted that the DMF-Fluka98 and DMF-Fluka998 solutions have a lower solution conductivity, and therefore the beads were only eliminated totally at 30% (w/v) PS concentration (Fig. 5e and f). To summarize, uniform electrospun fibers are obtained at a PS concentration of 20% (w/v) in a DMF1-Aldrich99 solution due to its high conductivity whereas a PS concentration of 25% (w/v) or above is required to obtain bead-free PS fibers for the other DMF solutions due to the low solvent conductivity.

To support the effect of solution conductivity, a study in which a salt, tetrabutylammonium bromide (TBAB), was used to increase the conductivity of the DMF-Fluka98 solvent was carried out. When 0.003% (w/v) of TBAB was added to the DMF-Fluka98 solution, the conductivity was increased to  $11.0 \mu\text{S}/\text{cm}$ , which is comparable to the conductivity ( $15.9 \mu\text{S}/\text{cm}$ ) of the DMF1-Aldrich99. Solutions with PS concentrations from 10% (w/v) to 25% (w/v) were prepared from this solvent (DMF-Fluka98-TBAB) and fibers were subsequently electrospun. In Fig. 8 is depicted the SEM images of electrospun PS fibers, and Table 2 summarizes the characteristics of the polymer solutions and the fibers when the salt TBAB was added. Distinct changes were observed with the addition of salt, TBAB, when these results are compared to the DMF-Fluka98 solvent system with no salt added. The number and the size of the beads are greatly reduced for fibers electrospun from solutions with the PS concentration varying between 10 and 20% (w/v) PS and bead-free uniform fibers are indeed obtained from 25% (w/v) PS solutions (Fig. 8a–d). In an additional study we increased the salt content to 1% (w/w) (with respect to polymer) for the DMF2-Aldrich99 solutions with PS concentrations of 10% (w/v) and 15% (w/v). The viscosity of the 10% (w/v) and 15% (w/v) PS solutions with 1% (w/w) TBAB was measured to be  $20.4 \pm 0.1$  cP and  $55.9 \pm 0.2$  cP, respectively, which shows that the addition of the salt has almost no effect on the viscosity of the PS solutions, but however; the conductivity of the solutions was increased drastically to  $156.6 \mu\text{S}/\text{cm}$  and  $188.4 \mu\text{S}/\text{cm}$ , respectively. As depicted in Fig. 8e and f uniform bead-free PS electrospun nanofibers were subsequently obtained from the solutions with 10% w/v and 15% w/v PS concentrations with the addition of salt and the fiber diameter was determined to be  $181 \pm 46$  nm and  $490 \pm 83$  nm, respectively (Table 2). This finding shows that the addition of salt leads to an extreme change in the fiber morphology since 10% (w/v) and 15% (w/v) PS solutions with no salt added, yielded fibers with a large number of beads (Figs. 2 and 3). The addition of salt increases the charge density of the polymer solution, which causes a greater repulsion and a greater bending instability during electrospinning, and therefore the fibers are stretched into thinner fibers with a smaller diameter and the beads are totally eliminated [16–18]. As discussed above, similar behavior was observed when DMF with higher conductivity (DMF1-Aldrich99) was used as a solvent. In conclusion, we have clearly demonstrated that the conductivity of the solution is a very

critical parameter for the formation of bead-free fibers especially when low polymer concentrations are used.

In Tables 1 and 2 we have summarized the results for the average fiber diameter (AFD), the bead size and bead aspect ratio as determined from the SEM images of electrospun PS fibers. The AFD was observed to be the largest when solutions with the highest concentration of polymers were used for electrospinning. As the polymer concentration increases, the viscosity of the solution increases, therefore, the fibers get thicker, consistent with previous electrospinning results from polymer solutions [15,18,20,22]. More polymer chain entanglements are present at higher polymer concentrations and continuous fibers will be stretched without breaking the jet during the electrospinning process and the number of beads is reduced significantly. The increase in fiber diameter is due to a greater resistance of the viscous solution to stretching and elongation. Additionally, the jet path is reduced since the bending instability will be smaller at higher viscosity. The SEM images also reveal that the number of the beads is reduced significantly and the aspect ratio of beads is increased for fibers electrospun from solutions with higher polymer concentrations. In cases when the polymer concentration is kept constant but the conductivity of the solution is higher, the AFD is significantly reduced, resulting in thinner fibers and the beads have a higher aspect ratio since the fibers were subjected to more stretching during electrospinning. In Fig. 9 we show the average fiber diameter (AFD) of the PS fibers electrospun from different polymer solutions which only resulted in uniform and bead-free fibers. It is evident that the polymer solutions which have the highest conductivity and lowest polymer concentration yielded the thinnest fibers; correspondingly the higher solution



**Fig. 9.** Average fiber diameter (AFD) of PS fibers obtained from electrospinning of different PS solutions which only yielded uniform bead-free fibers. From left to right, the electrospun PS solutions having different conductivities are: 1.) DMF2-A99-TBAB-PS10, 2.) DMF2-A99-TBAB-PS15, 3.) DMF1-PS20, 4.) DMF-F98-TBAB-PS25, 5.) DMF2-A99-PS25, 6.) DMF-S998-PS25, 7.) DMF-F998-PS30 and 8.) DMF-F98-PS30.

conductivity facilitates the production of bead-free fibers from the lower polymer concentrations.

#### 4. Conclusion

We have carried out a thorough and systematic study of the influence of the solution conductivity on the electrospinning of polystyrene (PS) fibers using dimethylformamide (DMF) as a solvent. It is revealed that different grades of as-received solvent (DMF) from various suppliers have slightly different solution conductivities. Consequently, the polymer solutions prepared with the same PS concentration have different conductivities, which are shown to influence the morphology of the PS fibers obtained under otherwise identical electrospinning conditions. For instance, 20% (w/v) PS solution corresponding to a polymer solution conductivity of 7.3  $\mu\text{S}/\text{cm}$  prepared from DMF, results in bead-free electrospun fibers whereas a 30% (w/v) PS solution (polymer solution conductivity = 0.4  $\mu\text{S}/\text{cm}$ ) was required to produce bead-free fibers when the used DMF solvent has a lower conductivity under the same electrospinning conditions. In general it was observed that solutions with a higher conductivity yielded bead-free fibers from lower polymer concentrations, which demonstrates that the solution conductivity plays a very significant role in producing uniform PS fibers. Our findings show that any slight changes in solution conductivity result in significant morphological variations for electrospun PS fibers when DMF is used as a solvent, and therefore, the reproducibility of uniform polystyrene fibers by electrospinning is very much dependent on the solution conductivity.

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