

**CHAPTER IV**  
**FUNDAMENTALS OF ELECTROSPINNING**  
**EFFECT OF SOLVENTS**

**ABSTRACT**

The effects of solvents and their properties on electro-spinnability of the as-prepared polystyrene (PS) solutions and morphological appearance of the as-spun PS fibers were qualitatively investigated by means of a scanning electron microscope (SEM). The eighteen solvents used were benzene, *t*-butylacetate, carbontetrachloride, chlorobenzene, chloroform, cyclohexane, decahydronaphthalene (decalin), 1,2-dichloroethane, dimethylformamide (DMF), 1,4-dioxane, ethylacetate, ethylbenzene, hexane, methylethylketone (MEK), nitrobenzene, tetrahydrofuran (THF), 1,2,3,4-tetrahydronaphthalene (tetralin), and toluene. Only the PS solutions in 1,2-dichloroethane, DMF, ethylacetate, MEK, and THF could produce fibers with high productivity.

**(Key Words:** Electrospinning, Polystyrene)

## 1. INTRODUCTION

Electrospinning is an interesting process for producing non-woven fibers with the average diameters in the range of micro- to nanometers. In this process, a continuous filament is drawn from a polymer solution or a melt through a spinneret by high electrostatic forces to deposit on a grounded-metal collective screen [1]. The appearance of the collected fibers depends on many factors: a) viscoelastic force which has been found to depend on solution concentration [2-5], molecular weight average of the polymer [3], and viscosity of the solution [5-7]; b) surface tension which has been found to depend on solution concentration, molecular weight average of the polymer, and surface tension of the solvent [6]; c) gravitational force which is dependent on solution density; and d) electrostatic force which has been found to depend on the applied electrostatic field (i.e. an applied electrostatic potential divided by a collection distance) and the conductivity of the solution [5-6].

In the electrospinning process of polymer solution, solvent is one of the main contributor for solution properties, e.g. conductivity. Water, a good solvent for poly(ethylene oxide) (PEO), has been successfully used in the electrospinning process of PEO [6,8-9]. When ethanol was added to water to attain mixed solvent systems, the diameters of the electrospun PEO fibers became bigger and the beaded fibers earlier observed disappeared [6]. The reason was claimed to the reduction of charge density carried by a charged jet and the increase in viscosity and evaporation rate of the mixed solvent, respectively. Dimethylformamide (DMF) was successfully used as a solvent for the electrospinning of polyacrylonitrile [10] and polyurethaneurea copolymer [4]; whereas, for biodegradable poly(*p*-dioxanone-*co*-L-lactide)-block-poly(ethylene glycol) copolymer, a mixed solvent of dichloromethane and DMF had to be employed [11]. Solvents with high vapor pressures, e.g. carbondisulfide (CS<sub>2</sub>), have been discussed as the cause of the observed nanoporous morphology of electrospun polystyrene (PS) fibers [12]. Trichloromethane or chloroform (CHCl<sub>3</sub>) was found to be the best solvent for producing highly textured poly(methyl methacrylate) (PMMA) fibers [12].

In a recent preliminary report [13], six solvents (i.e. acetic acid, acetonitrile, *m*-cresol, toluene, THF, and DMF) with different properties (e.g. density, boiling point, solubility parameter, dipole moment, and dielectric constant) were used to

prepare electrospun polystyrene (PS) fibers. Fiber diameters were found to decrease with increasing density and boiling point of the solvents. A large difference between the solubility parameters of PS and a solvent was responsible for the bead-on-string morphology observed. Productivity of the fibers (the numbers of fiber webs per unit area per unit time) was found to increase with increasing dielectric constant and dipole moment of the solvents. Among the solvents investigated, DMF was the best solvent that provided PS fibers with highest productivity and optimal morphological characteristics. The beadless, well-aligned PS fibers with a diameter of ca. 0.7  $\mu\text{m}$  were produced from 10% (w/v) PS solution in DMF at an applied electrostatic field of 15 kV/10 cm, a  $\text{N}_2$  flow rate of 101 ml/min, and a rotational speed of the collector of 1500 rpm.

In the present contribution, solutions of PS in eighteen different solvents were prepared in three different concentrations [i.e. 10, 20, and 30% (w/v), respectively]. These solutions were tested for some basic properties, i.e. viscosity, surface tension, and conductivity. The effects of solvents and their properties on electro-spinnability of the as-prepared PS solutions and morphological appearance of the obtained PS fibers were qualitatively observed by means of a scanning electron microscope (SEM).

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

The polystyrene (PS) resin used in this work was a general purpose grade (685D, Dow Plastics, USA). Molecular weight characteristics of the resin was investigated using a Waters 150CV size-exclusion chromatograph. The operating conditions were: diluent = tetrahydrofuran (THF), injection flowrate = 1.0 ml/min, injection volume = 100  $\mu\text{l}$ , and temperature = 30°C. The result showed the molecular characteristics as follows:  $M_w = 2.99 \times 10^5$  Da,  $M_n = 1.19 \times 10^5$  Da, and polydispersity = 2.51.

The eighteen solvents used in this work were benzene [Labscan (Asia), Thailand], *t*-butylacetate [Labscan (Asia), Thailand], carbontetrachloride (Ajax

Chemicals, Australia), chlorobenzene [Labsan (Asia), Thailand], chloroform [Labsan (Asia), Thailand], cyclohexane [Labsan (Asia), Thailand], decahydronaphthalene (decalin; Fluka, Switzerland), 1,2-dichloroethane [Labsan (Asia), Thailand], dimethylformamide [DMF; Labsan (Asia), Thailand], 1,4-dioxane [Labsan (Asia), Thailand], ethylacetate (Carlo Erba, Italy), ethylbenzene [Labsan (Asia), Thailand], hexane (Carlo Erba, Italy), methylethylketone [MEK; Labsan (Asia), Thailand], nitrobenzene (Carlo Erba, Italy), tetrahydrofuran (THF; J.T.Baker, USA), 1,2,3,4-tetrahydronaphthalene (tetralin; Labsan (Asia), Thailand), and toluene [Labsan (Asia), Thailand]. All of these solvents were analytical research grade and used without further purification. Some basic properties of these solutions (i.e. chemical formula, molecular weight, boiling point, density, dipole moment, solubility parameter, and surface tension) are summarized in Table 1.

## 2.2. Preparation and characterization of PS solutions

PS solutions were prepared by dissolving a measured amount of PS pellets in each of the eighteen solvents at room temperature (i.e. ca.  $26 \pm 2^\circ\text{C}$ ). Three concentrations were prepared: 10, 20, and 30% (w/v). These solutions were characterized for their viscosity using a Brookfield DV-III programmable viscometer, surface tension using a Krüss DSA10 Mk2 drop shape analyzer, and conductivity using an Orion 160 conductivity meter. The values of the viscosity, surface tension, and conductivity of the as-prepared solutions are summarized in Tables 2, 3, and 4, respectively.

## 2.3. Electrospinning set-up

In the electrospinning set-up (see Figure 1), each of the as-prepared solutions was stocked in a glass syringe. A 1-cm long, stainless steel needle with a flat tip, a cone angle of  $90^\circ$ , and 0.45 mm inner diameter was used as a spinneret. The tilt angle of the syringe was  $45^\circ$  from a horizontal baseline. The angle of  $45^\circ$  was to maintain constant presence of a droplet at the spinneret tip during an experiment. Besides the effects of solvent and its properties on electro-spinnability of the as-prepared PS solutions and morphological appearance of the obtained PS fibers, the effects of applied potential and collection distance (i.e. the distance measuring

between the spinneret tip and a grounded aluminum foil) on the morphological appearance of the as-spun fibers were also investigated. To observe the effect of the applied potential, an applied potential of 15, 20, or 25 kV was applied across a fixed collection distance of 10 cm, while, to observe the effect of the collection distance, a fixed applied potential of 20 kV was applied across a collection distance of 7, 10, or 15 cm, respectively. In order to compare the results obtained from these experimental conditions, the collection time for each spinning condition was fixed at around 3 minutes.

#### **2.4. Morphological observation**

The density and morphological appearance of the as-spun PS fibers were visually investigated from scanning electron micrographs obtained using a JEOL JSM-5200 scanning electron microscope (SEM). Each sample was coated with thin film of gold using a JEOL JFC-1100E ion sputtering device.

### **3. RESULTS AND DISCUSSION**

#### **3.1. Benzene**

Benzene was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in benzene were found to increase from that of the pure solvent (i.e. 0.56 cp) to be 46, 298, and 1292 cp (see Table 2), while the surface tensions were found to increase very slightly from that of the pure benzene (i.e. 27.6 mN/m, see Table 3) to be 30.9, 30.9, and 32.4 mN/m (see Table 3). At 10% (w/v), discrete droplets were sprayed out to form globs of PS solution on the collective screen. At 20% (w/v), among the electrospayed droplets, very small amount of electrospun fibers were occasionally observed. It should be noted that for both 10 and 20% solutions, the large amount of electrospayed droplets formed globs of PS solution on the collective target. With increasing concentration of the solution to 30% (w/v), not even droplets were obtained. It is believed that the combination of the relatively high viscosity of the solution and the low boiling point of the solvent (i.e. 80.1°C, see Table 1) made the droplets dried out at the tip of the spinneret.

### 3.2. t-Butylacetate

t-Butylacetate was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in t-butylacetate were found to increase from that of the pure solvent (i.e. 0.53 cp) to be 27, 290, and 1936 cp (see Table 2), while the surface tensions were found to increase very slightly from that of the pure solvent (i.e. 21.1 mN/m, see Table 3) to be 22.6, 23.4, and 27.3 mN/m (see Table 3). At 10% (w/v), the viscosity of the solution was not high, causing droplets to be sprayed out. Even at such a low viscosity, trace amount of as-spun fibers with the bead-on-string morphology was observed. In comparison with benzene, the fact that t-butylacetate has a dipole moment of 1.9 Debye (see Table 1) as compared with none for benzene (see Table 1) may be responsible for the better electro-spinnability of the resulting solution. With a further increase in the concentration of the solution to 20% (w/v), smooth fibers without the presence of beads were obtained. At 30% (w/v), clogging at the tip of the spinneret was observed, which was likely due to the combination of the relatively high viscosity of the solution and the low boiling point of the solvent (i.e. ca. 95°C, see Table 1). The cross-sectional geometry of the as-spun fibers was a combination between round and c-shaped. The formation of the c-shaped cross-sectional fibers could be a result of the collapsing of the fibers upon evaporation of the solvent.

### 3.3. Carbontetrachloride

Carbontetrachloride was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in carbontetrachloride were found to increase from that of the pure solvent (i.e. 0.84 cp) to be 59, 516, and 2830 cp (see Table 2), while the surface tensions were found to decrease from that of the pure solvent (i.e. 25.7 mN/m, see Table 3) to be 16.2, 17.6, and 19.4 mN/m (see Table 3). At 10% (w/v), the solution was easy to be spun, with the products being a combination of ultrafine fibers and relatively large beads. The electro-spinnability became more difficult with increasing concentration to 20 and 30% (w/v), most likely a result of the combination of the relatively high viscosity of the solutions and the low boiling point of the solvent (i.e. 76.8°C, see Table 1).

Again, the geometry of the fiber cross-section was a combination between round and c-shaped.

### **3.4. Chlorobenzene**

Chlorobenzene was able to dissolve PS pellets to form a clear solution within two days. The viscosities of 10, 20, and 30% (w/v) PS solutions in chlorobenzene were found to increase from that of the pure solvent (i.e. 0.69 cp) to be 47, 283, and 1172 cp which were very comparable to the PS solutions in benzene (see Table 2), while the surface tensions were found to decrease slightly from that of the pure solvent (i.e. 32.3 mN/m, see Table 3) to be 28.8, 30.2, and 30.4 mN/m (see Table 3). In comparison with benzene, the higher value of the dipole moment that chlorobenzene exhibits (i.e. 1.7 Debye, see Table 1) in comparison with none for benzene (see Table 1) should render the solutions of PS in chlorobenzene to be more spinnable than those in benzene. At 10 and 20% (w/v), only electrospayed droplets were observed. With increasing concentration to 30% (w/v), relatively large amount of smooth, round fibers were observed. Interestingly, for a fixed applied potential of 20 kV, both the density and the diameters of the as-spun fibers were found to decrease with increasing collection distance. On the contrary, for a fixed collection distance of 10 cm, both the density and the diameters of the obtained fibers were found to increase with increasing applied potential.

### **3.5. Chloroform**

Chloroform was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in chloroform were found to increase from that of the pure solvent (i.e. 0.51 cp) to be 38, 239, and 1210 cp (see Table 2), while the surface tensions were found to decrease from that of the pure solvent (i.e. 26.0 mN/m, see Table 3) to be 19.5, 20.0, and 20.8 mN/m (see Table 3). The spinning of the PS solutions in chloroform was relatively easy. At 10% (w/v), very small amount of as-spun PS fibers was observed, with the majority being globs of electrospayed droplets on the collecting screen. At 20% (w/v), the presence of globs of PS solutions was still evident, but larger amount of as-spun fibers with occasional presence of beads was obtained. With further increasing

concentration to 30% (w/v), globs of PS solution on the collective screen were absent, leaving only as-spun fibers on the screen. A closer examination of the obtained fibers with higher magnifications revealed that the surface of the fibers was rather rough and the cross-sectional geometry was quite round. The rough surface of the fibers obtained may be a result of the very low boiling point that chloroform exhibits (i.e. 61.2°C, see Table 1).

### **3.6. Cyclohexane**

Cyclohexane was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in cyclohexane were found to increase from that of the pure solvent (i.e. 0.84 cp) to be 37, 562, and 4491 cp, while the surface tensions were found to decrease from that of the pure solvent (i.e. 24.1 mN/m, see Table 3) to be 21.9, 22.0, and 22.2 mN/m (see Table 3). PS solutions in cyclohexane were not spinnable in every concentration prepared, which could be a result of the very high viscosity as well as the zero conductivity (see Table 4) that these solutions exhibited.

### **3.7. Decahydronaphthalene (Decalin)**

Decalin was able to dissolve PS pellets to form a clear solution within four days, while the 30% PS solution required at least 7 days to become homogeneous. Due to the highly viscous nature of the resulting solutions, only the viscosities of 10 and 20% (w/v) PS solutions in decalin could be measured. The viscosity values were found to markedly increase from that of the pure solvent (i.e. 2.91 cp) to be 80.2 and 969 cp (see Table 3). Due to the zero dipole moment of the solvent (see Table 1), the relatively high surface tension of the solvent (i.e. 31.2 mN/m, see Table 3), and the zero conductivity of the solvent and the resulting solutions (see Table 4), the PS solutions in decalin were not spinnable.

### **3.8. 1,2-Dichloroethane**

1,2-Dichloroethane was able to dissolve PS pellets to form a clear solution within two days. The viscosities of 10, 20, and 30% (w/v) PS solutions in 1,2-dichloroethane were found to increase from that of the pure solvent (i.e. 0.72 cp) to



be 82, 398, and 1610 cp (see Table 2), while the surface tensions were found to decrease from that of the pure solvent (i.e. 31.6 mN/m, see Table 3) to be 24.9, 24.9, and 25.2 mN/m (see Table 3). The spinning of the PS solutions in 1,2-dichloroethane was very easy, most likely due to the relatively high dipole moment that the solvent exhibits (i.e. 2.9 Debye, see Table 1) and the fair conductivity value of the solvent (i.e. 0.34  $\mu\text{S}/\text{cm}$ , see Table 4). At both 10 and 20% (w/v), a large amount of smooth fibers and beaded fibers was obtained. Interestingly, for a fixed applied potential of 20 kV, both the fiber and bead density observed were found to increase with increasing collection distance, and, for a fixed collection distance of 10 cm, both the fiber and bead density were found to decrease with increasing applied potential. With further increasing concentration of the solution to 30% (w/v), only smooth, bead-less fibers were obtained. In a similar manner, for a fixed applied potential of 20 kV, the density of the fibers was found to increase with increasing collection distance, and, for a fixed collection distance of 10 cm, the density of the fibers was found to decrease with increasing applied potential. Observation under higher magnifications revealed that the cross-sectional geometry of the obtained fibers was c-shape, likely a result of the collapsing of the fibers upon evaporation of the solvent.

### 3.9. Dimethylformamide (DMF)

DMF was able to dissolve PS pellets to form a clear solution within only 6 hours. The viscosities of 10, 20, and 30% (w/v) PS solutions in chloroform were found to increase from that of the pure solvent (i.e. 0.79 cp) to be 24, 210, and 924 cp (see Table 2), while the surface tensions were found to increase from that of the pure solvent (i.e. 24.4 mN/m, see Table 3) to be 36.8, 36.5, and 36.2 mN/m (see Table 3). The spinning of the PS solutions in DMF was extremely easy, due possibly to the relatively high dipole moment value of 3.8 Debye and the relatively high conductivity value of ca. 10.9  $\mu\text{S}/\text{cm}$  of the solvent. At 10% (w/v), very large amount of smooth and beaded fibers was observed. Interestingly, for the spinning condition where the applied potential was 20 kV and the collection distance was 7 cm, the obtained fibers were fused to adjacent fibers. This could be explained based on the fact that since the boiling point of DMF is relatively high (i.e. 153°C, see

Table 1), there was not enough time for the solvent in the charged jet to evaporate before “dried” fibers could deposit on the collective target. Apparently, for a fixed applied potential of 20 kV, the size of the beads was found to increase with increasing collection distance. For a fixed collection distance of 10 cm, the size of the beads was instead found to decrease with increasing applied potential. With increasing the concentration of the solution to 20% (w/v), very small amount of beads was present. Obviously, for a fixed collection distance of 10 cm, the amount of beads was found to decrease with increasing the applied potential from 15 to 25 kV. At 30% (w/v), only smooth as-spun fibers were observed. Observation of these results at higher magnifications revealed that the fibers obtained for any spinning condition were smooth and cross-sectionally round.

### **3.10. 1,4-Dioxane**

1,4-Dioxane was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in 1,4-dioxane were found to increase from that of the pure solvent (i.e. 1.10 cp) to be 56, 352, and 1410 cp (see Table 2), while the surface tensions were found to be very close (i.e. 31.4, 31.7, and 32.7 mN/m, see Table 3) to that of the pure solvent (i.e. 32.2 mN/m, see Table 3). Due possibly to the extremely low values of the dipole moment of the solvent and of the conductivity of the solutions, the PS solutions in 1,4-dioxane were very difficult to be spun. Observations under SEM revealed that some smooth and beaded fibers with rough surface were occasionally observed.

### **3.11. Ethylacetate**

Ethylacetate was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in ethylacetate were found to increase from that of the pure solvent (i.e. 0.40 cp) to be 17, 138, and 690 cp (see Table 2), while the surface tensions were found to decrease from that of the pure solvent (i.e. 22.7 mN/m, see Table 3) to be 18.8, 18.9, and 19.0 mN/m (see Table 3). Judging from the fair dipole moment value of 1.8 Debye and the fair conductivity value of ca. 0.3  $\mu\text{S}/\text{cm}$  of the solvent, PS solutions in ethylacetate should be fairly easy to be spun. Evidently, both smooth and beaded fibers were

observed for 10% (w/v) PS solution. Observation under higher magnifications revealed that the appearance of the beads was flattened spindle-like, while that of the fiber was c-shaped ribbon-like. The occurrence of such appearance was believed to be a result of the very low boiling point of the solvent (i.e. 77.1°C, see Table 1). With further increasing the concentration of the solution to 20 and 30% (w/v), smaller amount of large, c-shaped ribbon-like fibers was observed. The smaller amount of the fibers obtained was likely a result of the fast evaporation of the solvent (viz. a directly result of the low boiling point of the solvent) from the droplets at the tip of the spinneret, causing the partial clogging at the tip of the spinneret.

### **3.12. Ethylbenzene**

Ethylbenzene was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in ethylacetate were found to increase from that of the pure solvent (i.e. 0.60 cp) to be 35, 269, and 1162 cp (see Table 2), while the surface tensions were found to be very close (i.e. 26.5, 30.0, and 31.2 mN/m, see Table 3) to that of the pure solvent (i.e. 28.0 mN/m, see Table 3). The PS solutions in ethylbenzene were not spinnable in every concentration prepared, possibly due to the zero conductivity that the solvent and the resulting solutions exhibited (see Table 4).

### **3.13. Hexane**

Hexane was not able to dissolve PS pellets to form a clear solution even after seven days.

### **3.14. Methyleneethylketone (MEK)**

MEK was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in MEK were found to increase from that of the pure solvent (i.e. 0.38 cp) to be 14, 142, and 562 cp (see Table 2), while the surface tensions were found to increase from that of the pure solvent (i.e. 23.4 mN/m, see Table 3) to be 25.8, 26.9, and 28.0 mN/m (see Table 3). Judging from the values of the dipole moment (i.e. 2.8 Debye, see Table 1) and the conductivity (i.e. 4.4  $\mu\text{S}/\text{cm}$ , see Table 4) of the solvent, the PS solutions in MEK

should be fairly easy to be spun. Large amount of regular flat ribbon-like or c-shaped ribbon-like fibers with occasional beads were obtained from the spinning of 10% (w/v) PS solution. The beads were completely disappeared when the concentration of the solution increased to 20 and 30% (w/v). At such concentrations, only large amount of flat ribbon-like or c-shaped ribbon-like fibers were observed. At 30%, the amount of the as-spun fibers was not as high as that obtained at 20%. The reason could be that, at 30%, the emission of charged jets was intermittent, a direct result of the drying-out of the pending droplets at the spinneret tip (cf. the low boiling point of MEK of 79.6°C, see Table 1).

### 3.15. Nitrobenzene

Nitrobenzene was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in nitrobenzene were found to increase from that of the pure solvent (i.e. 1.73 cp) to be 58, 282, and 1579 cp (see Table 2), while the surface tensions were found to markedly decrease from that of the pure solvent (i.e. 42.7 mN/m, see Table 3) to be 22.8, 22.1, and 20.6 mN/m (see Table 3). Judging from the very high dipole moment value (i.e. 4.2 Debye, see Table 1) and the fair conductivity value (i.e. 3.3  $\mu\text{S}/\text{cm}$ , see Table 4) of the solvent, the PS solutions in nitrobenzene should be readily spinnable, but this was not the case. It was observed that, upon spinning, the solutions were jet out rather easily, but the ejected streams of the solutions did not form into fibers. The most likely explanation might be a result of the extremely high boiling point of nitrobenzene (i.e. 210.8°C, see Table 1) which caused the ejected streams to stay in the liquid form even after being collected on a collective target. Spinning of these solutions at elevated temperatures and/or reduced pressure should facilitate evaporation of the solvent, hence an increased tendency for the ejected streams of solutions to finally become fibers.

### 3.16. Tetrahydrofuran (THF)

THF was able to dissolve PS pellets to form a clear solution within one day. The viscosities of 10, 20, and 30% (w/v) PS solutions in THF were found to increase

from that of the pure solvent (i.e. 0.44 cp) to be 37, 297, and 2069 cp (see Table 2), while the surface tensions were found to slightly decrease from that of the pure solvent (i.e. 24.4 mN/m, see Table 3) to be 22.8, 22.6, and 22.3 mN/m (see Table 3). The electrospinning of the 10 and 20% (w/v) PS solutions in THF was very easy, while that of the 30% solution was difficult due to the rather high viscosity of the solution and the clogging of the spinneret at the tip due to the fast evaporation of the hanging droplets (cf. the very low boiling point of THF of 66°C, see Table 1). At 10% (w/v), a large amount of smooth fibers and beaded fibers was observed. The appearance of both the fibers and the beads, observed under higher magnifications, revealed irregularly c-shaped ribbon-like fibers in combination with irregularly round fibers and flattened beads. With further increasing concentration of the solution to 20% (w/v), the fiber density decreased appreciably, due possibly to the increased viscosity and the fast evaporation of the solvent which resulted in the drying-out of the hanging droplets. At this concentration, the as-spun fibers were bead-free and exhibited irregularly c-shaped ribbon-like morphology.

### **3.17. 1,2,3,4-Tetrahydronaphthalene (Tetralin)**

Tetralin was able to dissolve PS pellets to form a clear solution within three days. The viscosities of 10, 20, and 30% (w/v) PS solutions in tetralin were found to increase from that of the pure solvent (i.e. 1.85 cp) to be 110, 831, and 3769 cp (see Table 2), while the surface tensions were found to be very close (i.e. 32.3, 31.7, and 31.3 mN/m, see Table 3) to that of the pure solvent (i.e. 32.7 mN/m, see Table 3). The PS solutions in tetralin were not spinnable at all concentrations investigated, possibly a result of the relatively high viscosity and the zero conductivity (see Table 4) that these solutions exhibited.

### **3.18. Toluene**

Toluene was able to dissolve PS pellets to form a clear solution within two days. The viscosities of 10, 20, and 30% (w/v) PS solutions in toluene were found to increase from that of the pure solvent (i.e. 0.52 cp) to be 33, 236, and 1098 cp (see Table 2), while the surface tensions were found to increase from that of the pure solvent (i.e. 27.4 mN/m, see Table 3) to be 30.2, 30.0, and 29.9 mN/m (see Table 3).

At 10% (w/v), droplets were sprayed out from the spinneret to form globs of PS solution on the collective target. With increasing concentration of the solution to 20 and 30% (w/v), extremely small amount of smooth fibers with round and c-shaped ribbon-like fibers was observed.

#### 4. FURTHER DISCUSSION

Among the eighteen solvents investigated in this work, the solutions of PS in only five of them (i.e. 1,2-dichloroethane, DMF, ethylacetate, MEK, and THF) were found to be highly spinnable. Very interestingly, these five solvents have reasonably high value of dipole moment (see Table 1), which can be ranked in a descending order as follows: DMF (3.8 Debye) > 1,2-dichloroethane (2.9 Debye) > MEK (2.8 Debye) > ethylacetate (1.8 Debye) > THF (1.6 Debye). In addition, the PS solutions in these solvents exhibited reasonably fair conductivity value (see Table 4), which can be ranked in a descending order according to each concentration investigated as follows: for 10% (w/v), MEK (3.7  $\mu\text{S/cm}$ ) > DMF (0.8  $\mu\text{S/cm}$ ) > ethylacetate (0.3  $\mu\text{S/cm}$ )  $\approx$  1,2-dichloroethane (0.3  $\mu\text{S/cm}$ ) > THF (0  $\mu\text{S/cm}$ ); for 20% (w/v), MEK (3.5  $\mu\text{S/cm}$ ) > DMF (0.6  $\mu\text{S/cm}$ ) > 1,2-dichloroethane (0.5  $\mu\text{S/cm}$ ) > ethylacetate (0.4  $\mu\text{S/cm}$ ) > THF (0  $\mu\text{S/cm}$ ); and for 30% (w/v), MEK (2.2  $\mu\text{S/cm}$ ) > DMF (0.6  $\mu\text{S/cm}$ ) > 1,2-dichloroethane (0.3  $\mu\text{S/cm}$ ) > ethylacetate (0.1  $\mu\text{S/cm}$ ) > THF (0  $\mu\text{S/cm}$ ). Based on the results observed, the values of the dipole moment of the solvent and the conductivity of the resulting solutions were the factors determining the electro-spinnability of the solutions.

Tables 5 and 6 shows some scanning electron micrographs (at the magnifications of 200 $\times$  and 2000 $\times$ , respectively) of PS fibers from solutions of PS in 1,2-dichloroethane, DMF, ethylacetate, MEK, and THF. These PS fibers were spun from an applied potential of 20 kV and a collection distance of 10 cm. From the micrographs shown in these tables, marked difference in the “productivity” (e.g. the number density of the as-spun fibers per unit area per unit time) and the morphological appearance of the as-spun fibers is evident. Since the main objective of the present contribution is to qualitatively observe the effects of solvents and their properties on electro-spinnability of the as-prepared PS solutions and morphological appearance of the obtained PS fibers, the issue regarding the effect of solution

properties on “productivity” of the as-spun fibers will be the main objective for a future contribution [14].

Two important aspects can be drawn by careful observation of the micrographs shown in Tables 5 and 6. First, beaded PS fibers only resulted from the solutions of “low” concentrations and the tendency for bead formation was less observed when the concentration of the solution was “high” enough. Second, for most cases, the diameters (for round fibers) or widths (for ribbon-like fibers) of the as-spun fibers were found to increase with increasing solution concentration. For the formation of beads, Fong *et al.* [6] attributed the formation of beads to the “low” viscosity and “high” surface tension of the solutions and to the “high” boiling point of the solvent. To a first approximation, such a postulation seems very reasonable in explaining the occurrence of beads on as-spun fibers from a polymer solution, but problems remain as to how “low” or how “high” the related property values should be. By referring to the related property values of the PS solutions which resulted in beaded fibers (i.e. PS solutions in 1,2-dichloroethane, DMF, ethylacetate, MEK, and THF), the above postulation failed to comparatively describe the formation of beads on the resulting fibers from these solutions.

In order to explain the effect of solution concentration on the diameters or widths of the as-spun fibers, analysis of all forces acting on a small segment of a charged jet is necessary. Six types of force may be considered; they are 1) body or gravitational force, 2) electrostatic force which carries the charged jet from the spinneret to the target, 3) Coulombic force which tries to push apart adjacent charged carriers being present within the jet segment and is responsible for the stretching of the charged jet during its flight to the target, 4) viscoelastic force which tries to prevent the charged jet from stretching, 5) surface tension which also acts against the stretching of the surface of the charged jet, and 6) drag force from the friction between the charged jet and the surrounding air.

According to Table 2, an increase in the solution concentration markedly increased the viscosity value of the solution, while it did not affect much the value of the surface tension (see Table 3). For a given solution system, an increase in the solution concentration resulted in an increase in the solution viscosity, hence an increase in the viscoelastic force. Since the applied electrostatic field used to

obtained PS fibers shown in Tables 5 and 6 was fixed (i.e. 20 kV/10 cm), the electrostatic force acting on a jet segment should depend significantly on the amount of charge carriers being present in the jet segment. The amount of charge carriers can either increase or decrease with increasing solution concentration, depending on the nature of charge carriers and the electro-chemical characteristics of the polymer and solvent molecules.

If, regardless of the solution concentration, the amount of charge carriers is constant, both the electrostatic force and the Coulombic force will be constant as well. With increasing solution concentration, the increased viscoelastic force should prevent the jet segment from being stretched by the Coulombic force, resulting in fibers of larger diameters or widths. If the amount of charge carriers increases, the electrostatic force will increase and the Coulombic force will be likely to increase with increasing solution concentration. The increased electrostatic force could be responsible for an increase in the mass throughput from the spinneret. Both an increase in the mass throughput and the viscoelastic force with increasing solution concentration should result in an increase in the diameters or widths of the obtained fibers, despite an increase in the Coulombic force as well.

## 5. CONCLUSIONS

In the present contribution, the effects of solvents and their properties on electro-spinnability of the as-prepared polystyrene (PS) solutions morphological appearance of the as-spun PS fibers were qualitatively investigated by means of a scanning electron microscope (SEM). The eighteen solvents used were benzene, *t*-butylacetate, carbontetrachloride, chlorobenzene, chloroform, cyclohexane, decahydronaphthalene (decalin), 1,2-dichloroethane, dimethylformamide (DMF), 1,4-dioxane, ethylacetate, ethylbenzene, hexane, methylethylketone (MEK), nitrobenzene, tetrahydrofuran (THF), 1,2,3,4-tetrahydronaphthalene (tetralin), and toluene. Only the PS solutions in 1,2-dichloroethane, DMF, ethylacetate, MEK, and THF could produce fibers with high productivity. The electro-spinnability of the solutions from these five solvents was most likely a result of the high value of dipole moment that these solvents exhibit and the reasonably fair conductivity value that the resulting solutions exhibited.



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Solvent	Chemical formula	Molecular weight (g/mol)	Boiling point (°C)	Density (g/cm <sup>3</sup> )	Dipole moment (Debye)	Solubility parameter (MPa) <sup>1/2</sup>
Benzene	C <sub>6</sub> H <sub>6</sub>	78.1	80.1	0.868	-	18.7
t-Butyl acetate	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub>	116.2	94 - 96	0.857	1.91	16.0
Carbontetrachloride	CCl <sub>4</sub>	153.8	76.8	1.574	-	17.6
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	112.6	131.7	1.096	1.69	19.3
Chloroform	CHCl <sub>3</sub>	119.4	61.2	1.470	1.01	19.0
Cyclohexane	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub>	84.2	80.7	0.769	0.61	16.7
Decahydronaphthalene (Decalin)	C <sub>10</sub> H <sub>18</sub>	138.3	189 - 191	0.891	-	17.6
1,2-Dichloroethane	ClCH <sub>2</sub> CH <sub>2</sub> Cl	99.0	83.5	1.239	2.94	20.2
Dimethylformamide (DMF)	(CH <sub>3</sub> ) <sub>2</sub> NCHO	73.1	153.0	0.940	3.82	24.0
1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.1	101.3	1.023	-	20.1
Ethylacetate	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	88.1	77.1	0.888	1.78	18.3
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106.2	134 - 137	0.861	0.59	18.0
Hexane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	86.2	68.7	0.652	-	15.0
Methylethylketone (MEK)	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	72.1	79.6	0.794	2.76	18.8
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	123.1	210.8	1.194	4.22	22.6
Tetrahydrofuran (THF)	C <sub>4</sub> H <sub>8</sub> O	72.1	66.0	0.875	1.63	19.1
1,2,3,4-Tetrahydronaphthalene (Tetralin)	C <sub>10</sub> H <sub>12</sub>	132.2	204 - 207	0.964	0.22	19.5
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92.1	110.6	0.820	0.36	18.3

Table 1. Properties of solvents used in this work.

Solvent	Viscosity (cp)			
	Pure solvent	10% (w/v)	20% (w/v)	30% (w/v)
Benzene	0.56	46	298	1292
t-Butyl acetate	0.53	27	290	1936
Carbontetrachloride	0.84	59	516	2830
Chlorobenzene	0.69	47	283	1172
Chloroform	0.51	38	239	1210
Cyclohexane	0.84	37	562	4491
Decahydronaphthalene (Decalin)	2.92	80	969	-
1,2-Dichloroethane	0.72	82	398	1610
Dimethylformamide (DMF)	0.79	24	210	924
1,4-Dioxane	1.10	56	352	1410
Ethylacetate	0.40	17	138	690
Ethylbenzene	0.60	35	269	1162
Hexane	0.28	-	-	-
Methylethylketone (MEK)	0.38	14	142	562
Nitrobenzene	1.73	58	282	1579
Tetrahydrofuran (THF)	0.44	37	297	2069
1,2,3,4-Tetrahydronaphthalene (Tetralin)	1.85	110	831	3769
Toluene	0.52	33	236	1098

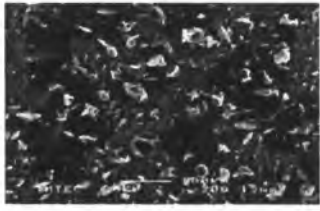
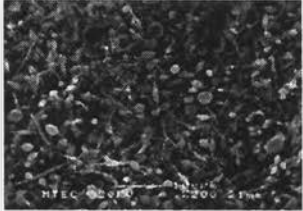
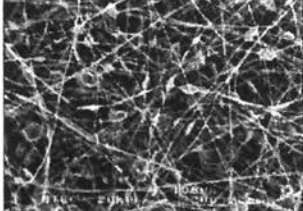
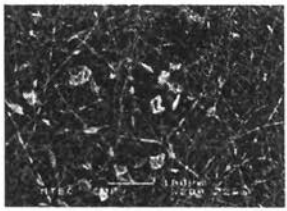
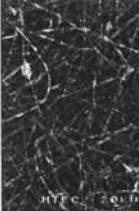
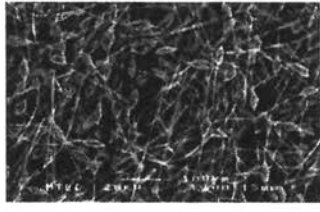
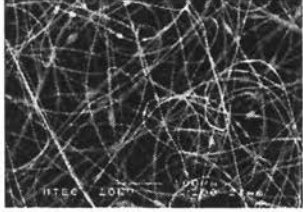
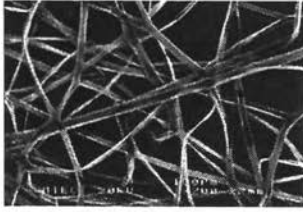
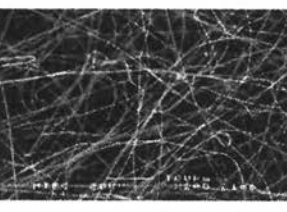
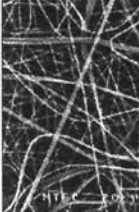
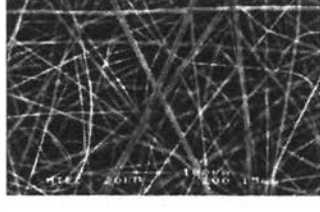
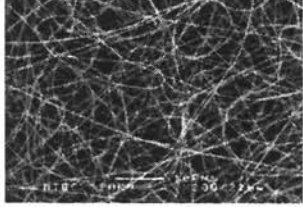
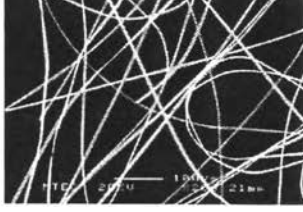
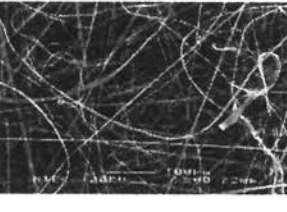

**Table 2.** Viscosity of solvents and as-prepared polystyrene solutions.

Solvent	Surface tension (mN/m)			
	Pure solvent	10% (w/v)	20% (w/v)	30% (w/v)
Benzene	27.6	30.9	30.9	32.4
t-Butyl acetate	21.1	22.6	23.4	27.3
Carbontetrachloride	25.7	16.2	17.6	19.4
Chlorobenzene	32.3	28.8	30.2	30.4
Chloroform	26.0	19.5	20.0	20.8
Cyclohexane	24.1	21.9	22.0	22.2
Decahydronaphthalene (Decalin)	31.2	-	-	-
1,2-Dichloroethane	31.6	24.9	24.9	25.2
Dimethylformamide (DMF)	33.9	36.8	36.5	36.2
1,4-Dioxane	32.2	31.4	31.7	32.7
Ethylacetate	22.7	18.8	18.9	19.0
Ethylbenzene	28.0	26.5	30.0	31.2
Hexane	17.4	-	-	-
Methylethylketone (MEK)	23.4	25.8	26.9	28.0
Nitrobenzene	42.7	22.8	22.1	20.6
Tetrahydrofuran (THF)	24.4	22.8	22.6	22.3
1,2,3,4-Tetrahydronaphthalene (Tetralin)	32.7	32.3	31.7	31.3
Toluene	27.4	30.2	30.0	29.9

**Table 3.** Surface tension of solvents and as-prepared polystyrene solutions.

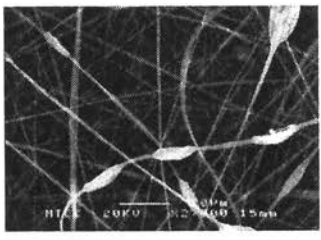
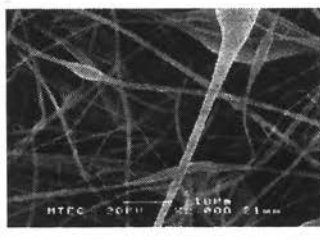
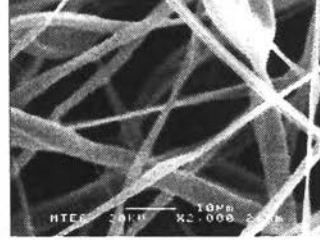
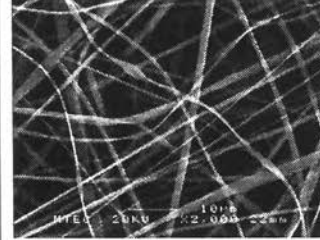

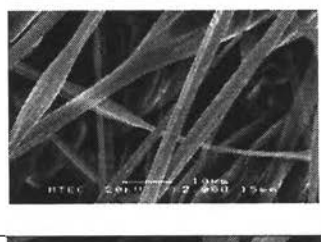
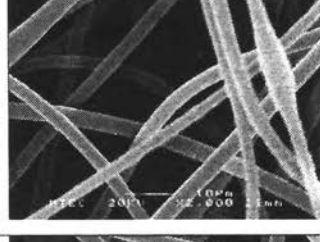
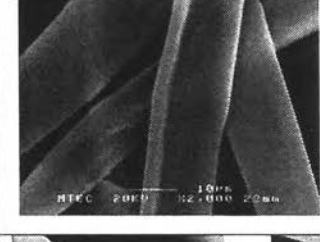
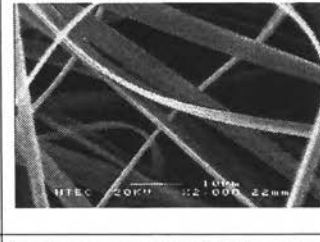
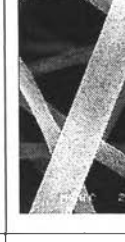
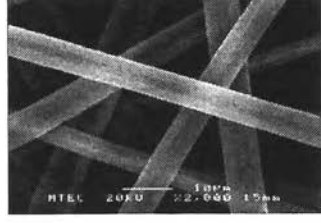
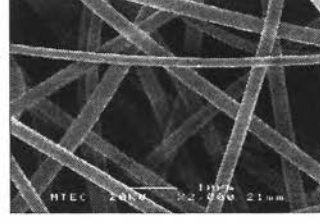
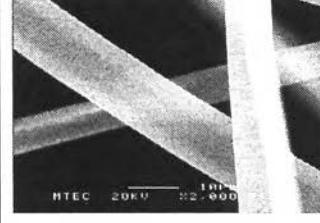
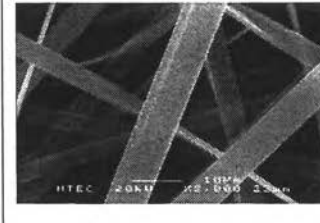

Solvent	Conductivity ( $\mu\text{S}/\text{cm}$ )			
	Pure solvent	10% (w/v)	20%(w/v)	30% (w/v)
Benzene	-	-	-	-
t-Butyl acetate	-	-	-	-
Carbontetrachloride	-	-	-	-
Chlorobenzene	-	-	-	-
Chloroform	-	-	-	-
Cyclohexane	-	-	-	-
Decahydronaphthalene (Decalin)	-	-	-	-
1,2-Dichloroethane	0.34	0.39	0.47	0.27
Dimethylformamide (DMF)	10.90	0.80	0.60	0.58
1,4-Dioxane	-	-	-	-
Ethylacetate	0.29	0.66	0.36	0.12
Ethylbenzene	-	-	-	-
Hexane	8.40	-	-	-
Methylethylketone (MEK)	4.41	3.70	3.50	2.19
Nitrobenzene	3.31	1.56	1.16	0.79
Tetrahydrofuran (THF)	-	-	-	-
1,2,3,4-Tetrahydronaphthalene (Tetralin)	-	-	-	-
Toluene	-	-	-	-

**Table 4.** Conductivity of solvents and as-prepared polystyrene solutions.

Solution	Solvent				
	1,2-Dichloroethane	DMF	Ethylacetate	MEK	THF
1% (w/v)					
2% (w/v)					
3% (w/v)					

Remark: the applied potential and the collection distance were 20 kV and 10 cm and the scale bar in each micrograph is for 100  $\mu$ m.

**Table 5.** Some scanning electron micrographs (at 200 $\times$ ) of as-spun polystyrene fibers from solutions of polystyrene in 1,2-dichloroethane, dimethylformamide (DMF), ethylacetate, methylethylketone (MEK), and tetrahydrofuran (THF).

Solution	Solvent				
	1,2-Dichloroethane	DMF	Ethylacetate	MEK	THF
(w/v)					
(w/v)					
(w/v)					

Remark: the applied potential and the collection distance were 20 kV and 10 cm and the scale bar in each micrograph is for 10 μm.

Table 6. Some scanning electron micrographs (at 2000×) of as-spun polystyrene fibers from solutions of polystyrene in 1,2-dichloroethane, dimethylformamide (DMF), ethylacetate, methylethylketone (MEK), and tetrahydrofuran (THF). The applied potential and the collection distance were 20 kV and 10 cm.



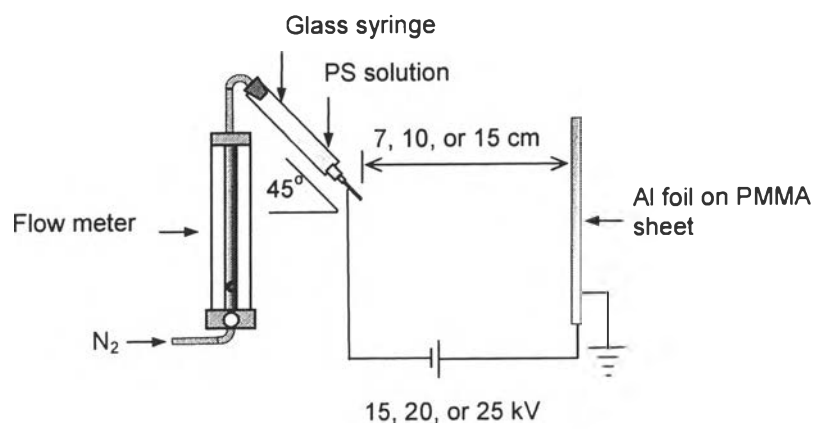


Figure 1 Basic scheme of apparatus for the electrospinning process