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Charge Effect of Cationic Surfactants on the Elimination of Fibre Beads in the Electrospinning of Polystyrene

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Abstract

Polystyrene nanofibres were electrospun with the inclusion of cationic surfactants, dodecyltrimethylammonium bromide (DTAB) or tetrabutylammonium chloride (TBAC), in the polymer solution. A small amount of cationic surfactant effectively stopped the formation of beaded fibres during the electrospinning. The cationic surfactants were also found to improve the solution conductivity, but had no effect on the viscosity. Only DTAB had an effect on the surface tension of the polymer solution, the surface tension decreasing slightly with an increase in the concentration of DTAB.

The formation of beaded fibres was attributed to an insufficient stretch of the filaments during the whipping of jet, due to a low charge density. Adding the cationic surfactants improved the net charge density that enhanced the whipping instability. The jet was stretched under stronger charge repulsion and at a higher speed, resulting in an exhaustion of the bead structure. In addition, a polymer/surfactant interaction was found in the polystyrene-DTAB solution system, while this interaction was not found in the polystyrene-

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TBAC system. The polymer/surfactant interaction led to the formation of thinner fibres than those formed in the absence of the interaction.

Effects of a non-ionic surfactant, Triton X-405, on the electrospun fibres were also studied. The addition of Triton X-405 did not eliminate the fibre beads, but reduced the bead numbers and changed the morphology. Triton X-405 slightly improved the solution conductivity, and had a minor effect on the surface tension, but no effect on the viscosity.

Keywords: Electrospinning, polystyrene nanofibres, beaded fibres, cationic surfactants, non-ionic surfactant, Triton X-405, charge effect.

1. Introduction

The generation of ultrafine fibres using electrospinning has been known since the 1930s[1] and has received a great deal of attention in the last few decades[2,3]. The electrospinning involves the introduction of electrostatic charges to a stream of polymer fluid in the presence of a strong electric field. When a high voltage is applied to the polymer solution, charges accumulate on the surface and the bulk of the polymer solution. A solution droplet at the tip of the nozzle gets deformed due to the electrostatic attraction of the opposite electrode, forming a so-called ‘Taylor Cone’. Increasing the strength of the electric field tends to increase the electrical attraction. When the electric field is large enough, the droplet overcomes the restriction of the surface tension to create a solution jet. This jet is further stretched into a single filament or split into multiple fibres/filaments while traveling through the electric field.

Since the electrospun nanofibres have diameters of nanometers and are usually collected as a non-woven fabric, porous structures with interconnecting pores are inherent in the electrospun fibre fabric. Such fabrics have an extremely high surface area and therefore have many potential applications in filters[4,5], protective membranes[6-8], bioengineering as scaffolds[9-13] and composite material areas[14].

Polystyrene represents a high electrical resistance polymer with a low dielectric loss. It is also stiff and brittle in nature. Electrospinning of polystyrene nanofibres has been reported by some researchers[15-18]. However, defects such as beads or necklace like fibres were often concomitant with the electrospun fibres, which adversely affected the reproducibility of the electrospinning system and the evenness of the resultant fabrics. The existence of defective fibres remains an issue of concern and has also been found in other electrospinning polymer systems[19-23].

The formation of beaded fibres has been attributed to the operating conditions and the material properties, but there has not been any unanimous agreement on the precise causes so far. Fong *et al*[19], for example, reported that the beaded fibres came from a capillary breakup of jet in the electrospinning, and that surface tension and viscoelastic properties were the key parameters for forming the beads. Lee and his co-workers[15] suggested that the beads occurred only in a low viscosity polymer solution, and emphasized that the viscosity was the main reason for the formation of beads. Jun *et al*[23] reported that the addition of an organic salt, pyridinium formate, to poly-L-lactide solution caused a significant reduction of the bead formation in the electrospinning.

Surfactants have been used in a variety of ways due to their ability to lower the surface/interfacial tension of the medium in which they are dissolved. An ionic surfactant, having an ionic hydrophilic head, also improves the conductivity of the dissolved solution. When a solution contains polymer and surfactant, if the polymer is capable of associating with the surfactants, it will have a so-called 'polymer/surfactant interaction'. The strength of the polymer/surfactant interaction depends on the polymer, the surfactant, the solvent and their relative concentrations. A strong polymer/surfactant interaction could alter the rheological properties of the polymer solution.

Electrospinning and the resultant nanofibres could be affected by adding a surfactant to the polymer solution, since the surfactant could have an influence on the electrostatic or rheological properties of the polymer solution. Yao *et al*[24] have reported that a small amount of non-ionic surfactant, Triton X-100, in aqueous poly(vinyl alcohol)(PVA), improved both the onset voltage and the reproducibility of electrospinning.

This paper reports on electrospinning polystyrene with the addition of a small amount of surfactants to the solution. The beaded fibres disappeared when a cationic surfactant was present in the polymer solution. Reasons as to why the cationic surfactants prevent the formation of beaded fibres in the electrospinning are discussed.

2. Experimental

Materials and Measurements

Polystyrene with an average molecular weight of 100,000(g/mol) was obtained from BDH Chemicals Ltd and used without further purification. N,N'-dimethyl formamide (DMF),

tetrahydrofuran(THF), dodecyltrimethylammonium bromide (DTAB), tetrabutylammonium chloride (TBAC) and Triton X-405 were used as received from Aldrich. The polystyrene solution used an equal-volume percentage mixture of DMF and THF as the solvent, and the concentration of polystyrene was in the range of 5~15% (w/v). The surfactants were dissolved separately into the polymer solutions, the concentration ranging from 0.03 to 30mmol/L for cationic surfactants, and from 0.001% to 1% (w/v) for Triton X-405.

The viscosities and conductivities of the polymer solution were determined by a digital rotational viscometer (D443 Rheology International) and a conductivity meter (LF330 Merck), respectively. This viscometer has 5% experimental error and good sensitivity. The surface tension was measured by the Du Nouy Ring method, using a platinum ring (Cole Parmer) and a highly precise electronic balance (AEA 160 DA ADAM). The morphology of the electrospun fibres was observed under a scanning electron microscope (SEM, LEO1530 microscope). The average diameter of the fibres was calculated based on the SEM pictures by measuring at least 50 single fibres, with the aid of computer software (ImagePro plus 4.5).

Electrospinning

The electrospinning apparatus included a high voltage power supply (ES30P, from Gamma High Voltage Research), a syringe pump (Aldrich) and some accessories, as shown in Figure 1. A high voltage was applied to the polymer solution by connecting the electrode with the metal syringe needle. A ground aluminum sheet was placed about 15 cm away from the tip of the needle. The electrospinning was conducted under the ambient

temperature, and at 1.5kV/cm of applied electric field and a polymer flow rate of 3ml/hour, except where specifically indicated.

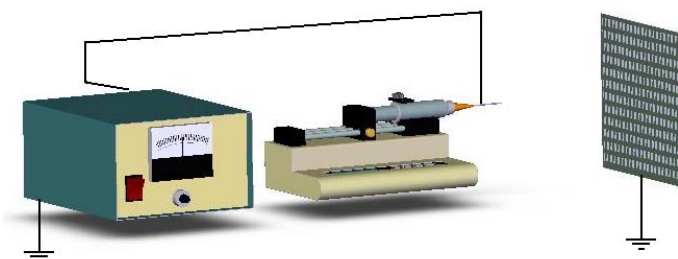


Figure 1, Apparatus for electrospinning

3. Results and discussions

Upon electrospinning a polystyrene solution without the presence of any surfactant, beads-on-string structures emerged in the spun fibres. As shown in Figure 2, the beaded fibres covered all the electrospun area. Increasing the flow rate resulted in more beads. Efforts to eliminate the beaded fibres by adjusting operating conditions and changing the polymer concentrations were unsuccessful.

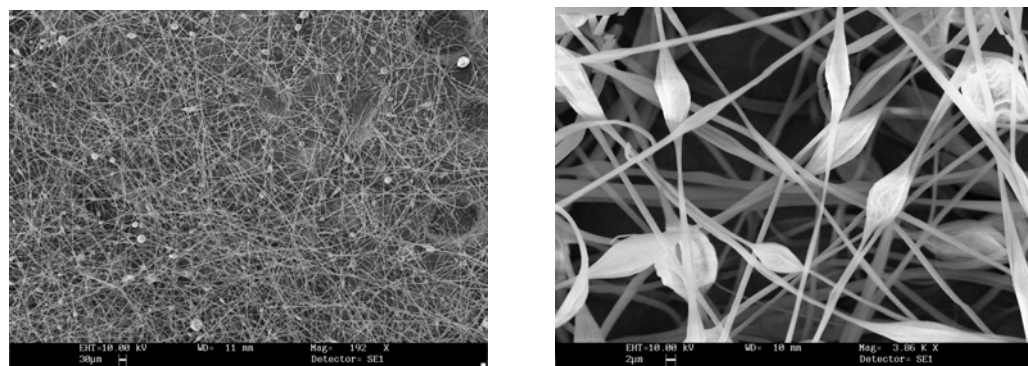


Figure 2, Polystyrene nanofibres electrospun from a 10% polystyrene solution (w/v, DMF/THF 1:1 v/v).

When a small amount of TBAC or DTAB was added in the polymer solution, the same electrospinning process produced non-beaded fibres. SEM images in Figure 3 revealed that the addition of the surfactants led to bead-free and homogeneous fibres. No isolated beads and beads-on-string structures were found. The surfactant was so effective that a concentration as low as 10^{-6} mol/L was enough to prevent the formation of the beaded fibres.

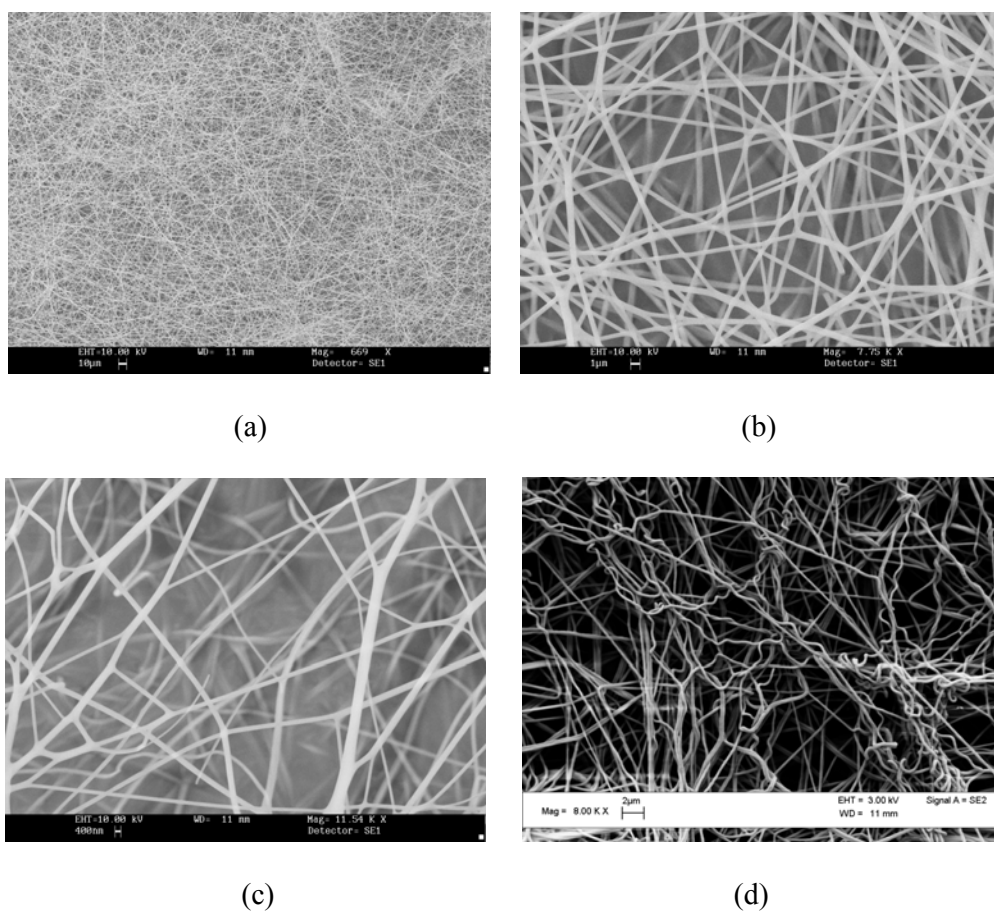


Figure 3, Polystyrene nanofibres electrospun with the cationic surfactants in the polystyrene solution. In (a) and (b) TBAC 0.1mmol/L, (c) TBAC 10mmol/L, (d) DTAB 10mmol/L.

Yarin et al[25] have simulated the formation of a beads-on-string structure during a free polymer fluid jet propagating in air. They suggested that an elongational flow arising in the

thin section of the jet transformed the thin section into thread where the polymer jet was hyper-stabilized due to the orientation and appreciable stretching of the polymer macromolecules. This would strengthen the liquid into a filament and make it thinner. Its outflow into droplets under the action of surface tension was decelerated abruptly, preventing rapid breakup.

A theoretical description of an electrospinning mechanism showed that under the action of the electric field the jet involved a whipping instability process during its propagation in air [26-28]. Charges repulsing in the jet resulted in bending the jet and stretching it thinner. The whipping instability mainly depended on two reversed actions, surface tension and charge repulsion. The surface tension tended to stabilize the jet and minimize its surface, while the charge repulsion tended to unstabilize the jet. When charge repulsion dominated, the perturbation to the jet centerline grew, and the jet became bent. As the jet thinned away from the nozzle, the charge density grew until charge repulsion overcame surface tension, after which the jet whipping began. The whipping instability resulted in stretching the jet thinner, until it exactly balanced the surface tension.

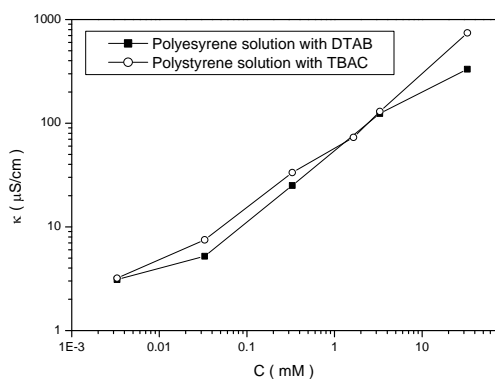
During the whipping, the jet was stretched under the action of axisymmetric and non-axisymmetric instabilities due to the perturbations of surface charges. The axisymmetric instability came from the perturbations of the surface charges along the jet axis. Different sections were affected by different strengths of force that resulted in an uneven jet. However, the non-axisymmetric instability came from the perturbations of surface charges around the circumference of the jet. It led to a localized torque and accounts for the whipping motion of the jet. Under the action of the non-axisymmetric instability, the jet tended to be uniform. The formation of beads-on-string structures could be related to a

strong axisymmetric instability, especially when the net charge density was low. The jet stretched under weak non-axisymmetric instabilities and strong axisymmetric instabilities could lead to the formation of beads.

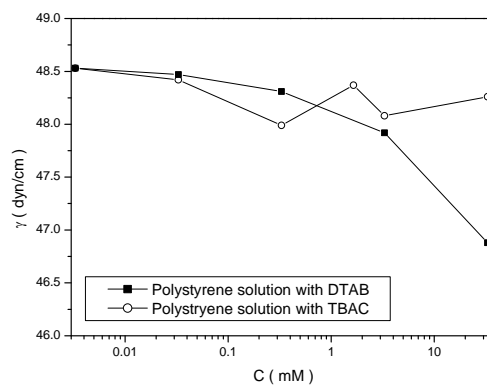
Solvent evaporation is another important factor in the formation of beads. The stretched liquid threads solidified rapidly due to the evaporation of solvent in the whipping. The solid fibres lost their mobility and were not deformed under the action of the surface tension. The beads-on-string structures could also be formed if the jet was not stretched to a uniform thread before solidification.

Therefore, the formation of beads is related to the strength of the whipping instability, the stretching velocity, the viscosity and the surface tension of the polymer solution, as well as the solvent properties. Increasing the whipping instability led to stronger stretching forces that resulted in the formation of uniform threads.

As shown in Figure 4, the conductivity of the polymer solution was largely improved with increase in the concentration of DTAB. The conductivity value was increased by $330\mu\text{S}/\text{cm}$, when the concentration of DTAB was changed from 0.003mM to 30mM . A similar result was found for TBAC. When the concentration was larger than $10\text{mmol}/\text{L}$, TBAC led to a higher conductivity value than DTAB. Increasing the solution conductivity suggested that the net charge density of the jet was increased [29]. The whipping instability was thus enhanced and the jet was stretched under the stronger force, resulting in the exhaustion of any bead like fluid in the whipping process.



(a)



(b)

Figure 4, Conductivity and surface tension change with the concentration of cationic surfactants. The polymer solutions contain 10% polystyrene (w/v in DMF/THF).

Further increasing the concentration of surfactant led to a larger charge repulsion that could result in stretching the thread thinner. As shown in Figure 5(a), the average diameter of the electrospun fibres decreased slightly with the increase in the concentration of TBAC. This result confirmed that the effect of cationic surfactants on the whipping process came from the ionic nature.

When the concentration of surfactant was larger than 10mmol/L, the conductivity of the polymer solution reached a very high value. Long and branched fibres were observed for the TBAC involved fibres (in Figure 3c), indicating a split of the single fibre in the electrospinning. However, such branched fibres did not appear when the solution contained the same concentration of DTAB (Figure 3d).

The polymer/surfactant interaction in the aqueous system has been studied intensively[30,31]. This interaction occurs when a non-ionic polymer associates with ionic

surfactants by wrapping the individual polymer chain around the surfactant molecules. It makes the polymer/surfactant behave like a polyanion of the absorbed species. The absorbed surfactant increases charges and maintains the polymer chain in a more expanded structure than in the presence of an equivalent amount of salt, such as NaCl [32].

For a system with a polymer/surfactant interaction, it is generally observed that the surfactant self-associates cooperatively, i.e., in the form of aggregations, at a so-called critical aggregation concentration (*cac*). This *cac* value is usually lower than the critical micelle concentration (*cmc*) of the surfactant by a factor of say between 1 and 10. The strength of the interaction between a polymer and a surfactant can be characterized by the ratio of *cac/cmc*[33,34]. The *cac/cmc* for the studied polymer-surfactant-solvent systems was determined according to the reported method[34]. The *cac/cmc* value for the polystyrene-DTAB system is about 0.8(*cac* 1.68mmol/L and *cmc* 2.10mmol/L), indicating that a polymer/surfactant interaction occurs between polystyrene and DTAB. However, the *cac/cmc* value for the polystyrene-TBAC system is about 0.97(*cac* 1.75mmol/L and *cmc* 1.81mmol/L), which indicates that *cac* and *cmc* are too close to have the polymer/surfactant interaction in the system.

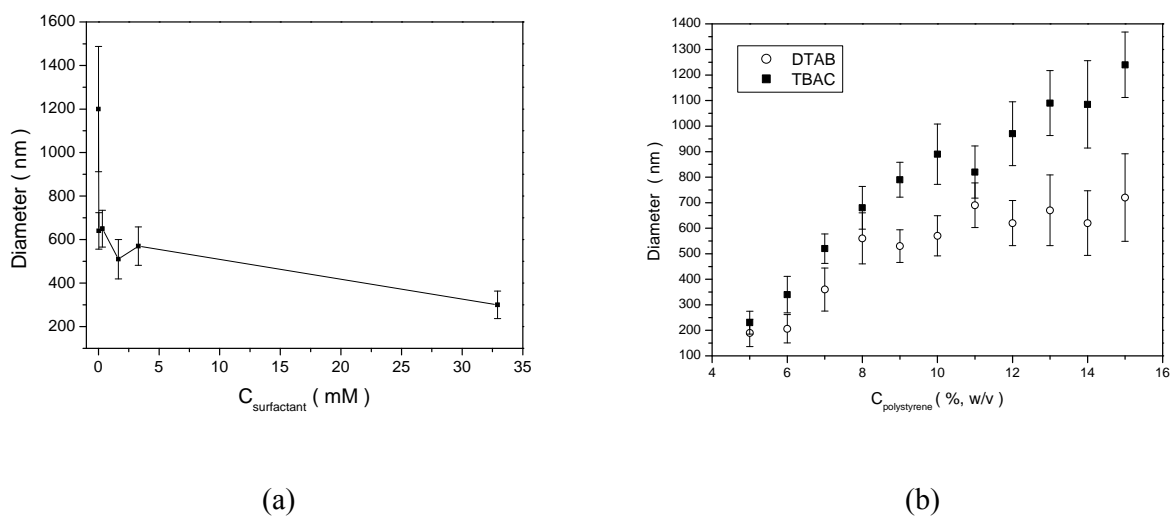


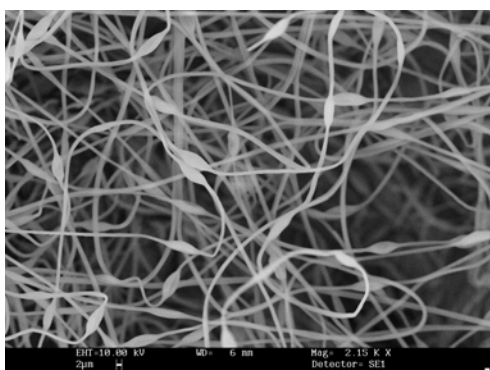
Figure 5. Average fibre diameters change with the solution concentrations. (a) The solutions contain 10% polystyrene and different concentrations of TBAC; (b) the solutions contain different concentrations of polystyrene, while keeping the ratio of polystyrene/surfactant (w/mol) constant (100g/0.715mmol).

Similar to other polymer systems, the concentration of polymer depends on the average fibre diameters. It was observed that the average fibre diameters increased with the concentration of polystyrene for both of the two surfactants, as shown in Figure 5(b). However, it was interesting to note that the same concentration of DTAB led to thinner fibres than with TBAC, which suggested that thinner fibres were electrospun in the system involving a polymer/surfactant interaction.

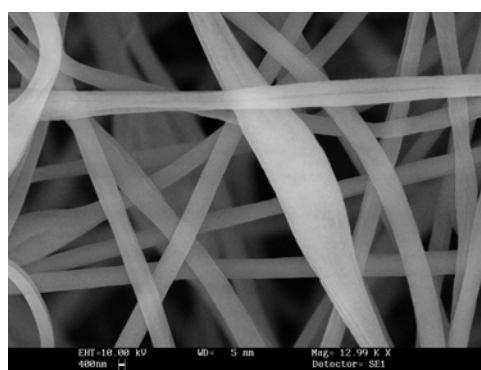
Effects of the surfactants on the solution viscosity and the surface tension were also studied. It was found that the addition of cationic surfactants did not affect the solution viscosity. For a 10% polystyrene solution, the viscosity value was about 14.24 centipoises (cp). This value only fluctuated within the range of experimental error when the concentration of

TBAC was changed within 0.003~30mM. A similar result was found for DTAB. The effect of the surfactant on the surface tension is shown in Figure 4(b). DTAB led to a slight decrease in the surface tension, by 2dyn/cm, when its concentration was increased from 0.003mM to 30mM. However, in the same range of concentration, TBAC showed no influence on the surface tension.

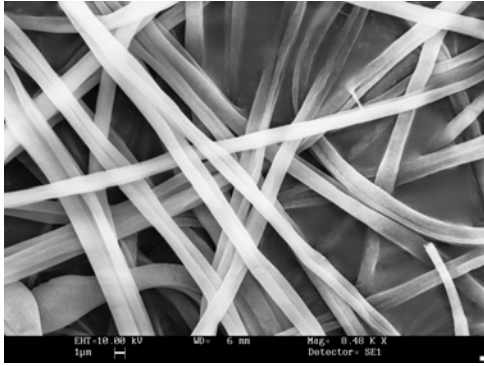
In order to confirm the charge effect of cationic surfactants on the elimination of beaded fibres, a similar electrospinning process was also conducted by replacing the cationic surfactant with a non-ionic surfactant, Triton X-405. Figure 6 shows the SEM images of fibres electrospun with the presence of different concentrations of Triton X-405. Obviously, the addition of a non-ionic surfactant did not stop, but largely reduced, the formation of beaded fibres. The beads showed a long elongated ellipsoid structure; the morphology being different to those that were electrospun with the absence of any surfactants (in Figure 2b). Increasing the concentration of the Triton tended to elongate the beads.



(a)



(b)



(c)

Figure 6, Polystyrene nanofibres electrospun with the presence of Triton X-405. In (a), (b) and (c), the concentrations of Triton X-405 are 0.01%, 0.1% and 1% (w/v) respectively.

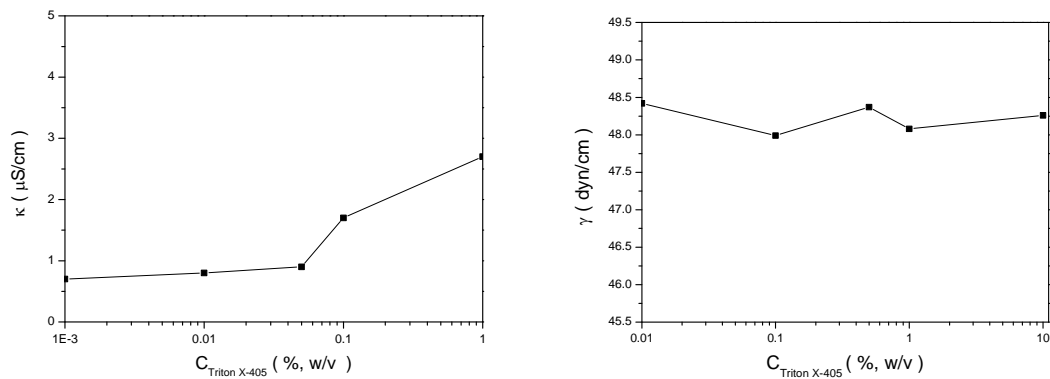
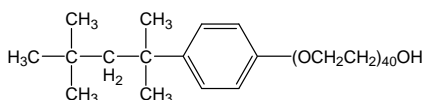


Figure 7, Conductivity and surface tension change with the concentration of TritonX-405. The polymer solutions contain 10% polystyrene (w/v, in DMF/THF).

The addition of the Triton led to a minor decrease in the surface tension but had no effect on the solution viscosity. Although Triton X-405 is a non-ionic surfactant, it made the solution conductivity increase slightly, from 0.7 to 2.7μS/cm when the concentration changed from zero to 1% (w/v). The improvement in the conductivity could be attributed to the weak conductivity of the Triton, due to the existence of polarity groups, such as the hydroxyl group and ethylene oxide units, in the molecule. However, the improvement is

very limited, because even for the pure Triton X-405, the conductivity is as low as 19.8 μ S/cm. The small improvement in the conductivity accounted for the reduction of beads in the electrospinning.



Scheme 1, The chemical structure of Triton X-405.

In addition, the fibre morphology was different from those that were electrospun with the presence of a cationic surfactant. Electrospinning the polymer solution containing 1% Triton (the conductivity 2.7 μ S/cm) produced fibres with an average diameter larger than 1 μ m. However, the fibres electrospun from a TBAC involved solution, having the same level of conductivity, showed an average diameter of 0.61 μ m. Furthermore, the addition of the Triton resulted in irregular cross-sections and sharp edges on the fibre surface.

4. Conclusion

Results from this study suggest that the formation of beaded fibres in the electrospinning comes from a low strength of whipping instability caused by weak charge repulsion in the jet. Under the weak forces, the polymer jet cannot be fully stretched into even filaments. Adding cationic surfactants improves the net charge density considerably, which enhances the jet whipping instability. The jet is thus stretched under stronger forces, preventing the formation of beads-on-string structures on the filaments. Increasing the concentration of cationic surfactant leads to thinner fibres. However, the presence of a non-ionic surfactant cannot stop the formation of bead fibres, but reduces the bead numbers and changes the fibre morphology.

The polymer/surfactant interaction occurs between the polystyrene and DTAB. Such an interaction tends to produce thinner fibres than a system without a polymer/surfactant interaction. It is expected that a strong polymer/surfactant interaction between a non-ionic polymer and an ionic surfactant can be used to tune the diameter of the electrospun fibres.

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