Electrospinning atactic polystyrene: a neutron scattering study

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Abstract. Electrospinning is a method used to produce nanoscale to microscale sized polymer fibres. In this study we electrospin 1:1 blends of deuterated and hydrogenated atactic-Polystyrene from N,N-Dimethylformamide for small angle neutron scattering experiments in order to analyse the chain conformation in the electrospun fibres. Small angle neutron scattering was carried out on randomly orientated fibre mats obtained using applied voltages of 10kV-15kV and needle tip to collector distances of 20cm and 30cm. Fibre diameters varied from 3µm – 20µm. Neutron scattering data from fibre samples were compared with bulk samples of the same polymer blend. The scattering data indicates that there are pores and nanovoiding present in the fibres; this was confirmed by scanning electron microscopy. A model that combines the scattering from the pores and the labelled polymer chains was used to extract values for the radius of gyration. The radius of gyration in the fibres is found to vary little with the applied voltage, but varies with the initial solution concentration and fibre diameter. The values for the radius of gyration in the fibres are broadly equivalent to that of the bulk state.

1. Introduction
Electrospinning is a technique used to produce polymer fibres varying from nanoscale to microscale diameters. A polymer is dissolved in a suitable solvent, preferably one with a high dielectric constant. This solution is then placed into a spinneret where a high voltage is applied to the spinneret tip. The applied field causes the droplet at the tip of the spinneret to form into a Taylor cone [1]; a jet is then pulled from the Taylor Cone to a grounded collector. As the jet travels through the air the solvent evaporates, and the polymer fibre is deposited onto the grounded collector. Many factors affect the fibre diameter, such as the applied voltage, the distance between the collector and spinneret tip, and the solution concentration. In the electrospinning process, chain entanglements play a critical role in the formation of fibres [1]. We have used small angle neutron scattering to obtain values of the dimensions of the chain trajectories in fibres prepared by electrospinning as part of a program to understand the molecular behaviour during the electrospinning process.

Small angle neutron scattering (SANS) is a technique that can be utilised to analyse polymer chains, in particular the polymer-chain trajectory, at lengths scales of between 10 and 100nm. The technique requires isotopic labelling to gain a contrast, but by utilising polymers selectively substituted with deuterium rather than hydrogen the technique remains a powerful analytical tool for the determination of polymer chain dimensions, both in the bulk state and in solution. [2].

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In this study we prepare fibres in 1:1 blends of hydrogenated and deuterated atactic-Polystyrene (a-PS) spun from the solvent N,N-Dimethylformamide (DMF), which is known to be an effective solvent for electrospinning polystyrene fibres [3]. The contrast between the deuterated and hydrogenated polymer chains allows for the study of how the electrospinning process affects the chain conformation.

2. Materials and Methods

2.1 Polystyrene

We have used hydrogenated and deuterated atactic-polystyrene with molecular weights shown in Table 1 as measured by GPC.

2.2 Solutions

For electrospinning 1:1 blends of HPS-1/DPS-1 and HPS-2/DPS-2 in DMF at 0.2, 0.3 and 0.4 g/mL of solvent were prepared. High concentrations were used so that smooth fibres were formed without beading [1].

2.3 Electrospinning

The electrospinning equipment is arranged in a horizontal set up. The syringe pump equipped with a needle gauge of 22G (0.41mm inner diameter) provided a flow rate of 0.13ml/min. Voltages of 10 kV, 12.5 kV and 15 kV were applied at distances from tip of the needle to grounded collector of 20 cm and 30 cm. The grounded collector was a sheet of aluminium foil and the fibres were collected as randomly orientated fibre mats. NMR analysis on fibres immediately after spinning showed small levels of solvents. These were eliminated by standing at room temperature for 24 hours after spinning and all samples for neutron scattering measurements were prepared in this manner.

2.4 Small Angle Neutron Scattering (SANS)

SANS data is given in the form of the differential scattering cross section \((d\Sigma/d\Omega)(Q) (\text{cm}^{-1})\), as a function of the scattering vector \((Q (\text{Å}^{-1}))\). The differential scattering cross section contains all the information on the size, shape and interaction between the scattering centres within the sample [2]. SANS was performed using LOQ at the STFC ISIS Facility in the UK. A wavelength range of 2.2 Å to 10 Å was employed giving a scattering vector range \(|Q| (\text{Å}^{-1})\) range of 0.006 Å^{-1} – 0.27 Å^{-1} where \(|Q|\) is given by (1) and 20 is the scattering angle. The data was collected on a 2 dimensional detector which was radially averaged to give \((d\Sigma/d\Omega)(Q) (\text{cm}^{-1})\) as a function of \(|Q| (\text{Å}^{-1})\).

\[ |Q| = \frac{4\pi \sin \theta}{\lambda} \quad (1) \]

3. Results and Discussion

3.1 SANS on Fibres

Scattering from the randomly orientated fibre mats shows a strong component from pores and nanovoids. Thus, scattering from purely deuterated fibres shows that \((d\Sigma/d\Omega)(Q)\) varied as \(Q^{-4}\) which indicates sharp interfaces are present within the material. This is confirmed by analysis of fibres in a scanning electron microscope. The fibre surfaces show varying amounts of porosity and fractured

Table 1. Characteristics of Polymers

| Polymer          | Label | Molecular Weight (g/mol) | Mw/Mn |
|------------------|-------|--------------------------|-------|
| Hydrogenated Polystyrene | HPS-1 | 241,000                  | 4.8   |
| Hydrogenated Polystyrene | HPS-2 | 136,000                  | 4.4   |
| Deuterated Polystyrene     | DPS-1 | 205,000                  | 3.8   |
| Deuterated Polystyrene     | DPS-2 | 128,000                  | 3.8   |
fibres show voiding present inside, with pores varying from 20nm-120nm in diameter. Fibre mats exhibit a distribution of fibre diameters and in order to get a statistical representation for the mean average diameter a grid is overlaid over the image, and fibres are randomly selected in each square of the grid. Figure 3 shows the diameter distribution of fibres obtained in this way for fibres prepared from a 0.2 g/mL solution.

The amount of porosity varies between samples. Figure 2 is a case in which a high surface porosity is present on the fibres. The relative humidity level is thought to contribute to porosity in electrospun fibres [4], in this case samples were prepared at humidities of between 47%-50%. Voiding is caused by the high concentration of the polymer and the large fibre diameter trapping solvent into the fibre [5]. The results indicate that with increasing solution concentration there is an increase in fibre diameter.

We have modelled the scattering from fibres using the Debye Gaussian Coil plus the scattering component from the pores and this can be described by Equation (2), where \( A = x (1-x)V(\Delta \rho)^2 \), \( x \) is the concentration of the labelled polymer, \( V \) is the volume, \( \Delta \rho \) is the difference in the scattering length and \( B \) is a scaling factor relating to the fraction of the voids [6].
\[ I(Q) = \frac{2A}{(QR_g)^2} \left\{ (QR_g)^2 - 1 + e^{-[QR_g]^2} \right\} + BQ^{-N} \]  

(2)

Using this model with the scattering data we are able to extract values for the radius of gyration \( (R_g) \). Optimisation of the model to the data was achieved using the data-fitting program FISH [6]. The radius of gyration of the polymer chains in the fibres was found to decrease with increasing initial solution concentration as shown in Figure 5, and replotted in Figure 6, which shows that there is an increase in the \( R_g \) of the polymer chains in the fibre with decreasing fibre diameter. We expect that this is related to the different solution concentrations rather than a direct consequence of the fibre diameter. No variation in \( R_g \) was found with other changes to the preparation conditions, such as the applied voltage and the collector distances. The values of the radius of gyration obtained for the fibres are broadly equivalent to those of the bulk state \( (R_g \sim 90\text{Å}) \) suggesting that the chains have largely reached an equilibrium state.

**Figure 5.** Radius of gyration for fibre samples versus the initial solution concentration. (Solid line acts as a visual guide)

**Figure 6.** Variation of the fibre diameter with radius of gyration of the polymer chains. (Solid line acts as a visual guide)

4. Conclusions

Electrospun fibres of isotopically labelled polystyrene were successfully studied by SANS and the conformation compared to that of the solution state. The scattering from the fibres indicates high porosity and nanovoids, which was also confirmed with scanning electron microscopy. A model was successfully applied to describe the scattering from the pores and the labelled chains allowing for a value for the radius of gyration to be extracted from the scattering data. It was found that there is little variation in the radius of gyration given the voltages and distance that were utilised in this case. The radius of gyration decreases in the fibre with increasing fibre diameter as the solution concentration increases. The radius of gyration for the fibres approaches that of the bulk state.

5. References:

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