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Modelling Small Angle Neutron Scattering Data from Electrospun Fibres

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Abstract. Electrospinning is a technique employed to produce nanoscale to microscale sized fibres by the application of a high voltage to a spinneret containing a polymer solution. Here we examine how small angle neutron scattering data can be modelled to analyse the polymer chain conformation. We prepared 1:1 blends of deuterated and hydrogenated atactic-polystyrene fibres from solutions in N, N-Dimethylformamide and Methyl Ethyl Ketone. The fibres themselves often contain pores or voiding within the internal structure on the length scales that can interfere with scattering experiments. A model to fit the scattering data in order to obtain values for the radius of gyration of the polymer molecules within the fibres has been developed, that includes in the scattering from the voids. Using this model we find that the radius of gyration is 20% larger than in the bulk state and the chains are slightly extended parallel to the fibre axis.

1. Introduction

Electrospinning is a method that can be used to produce nanoscale to microscale sized polymer fibres. This is done by the application of a high voltage to a spinneret containing a polymer solution. At the tip of the spinneret the polymer droplet deforms into a Taylor cone due to the electric field applied [1]. A polymer jet is extruded from the Taylor cone to a grounded collector. During transit the majority of solvent evaporates of the material leaving behind solid fibres which are deposited in a randomly orientated fibre mat on to the grounded collector. There are many factors that can influence fibre production that have to be taken into account. For example fibre diameters can be controlled by variations in spinneret tip to collector distance or a variation in the voltage applied, thereby altering the field strength [2]. There are also the solvent effects [3] on the spinnability along with solution viscosity [4] and the molecular weight of the polymer [5]. A polymer with a sufficiently high molecular weight is required in order for chain entanglements to occur which is crucial to the formation of fibres in the electrospinning process [4].

An understanding of the chain geometry during this electrospinning process can be developed through analysis of the chain conformations in the fibres by small angle neutron scattering. However, there are factors that have to be taken into account during data analysis. Electrospun polymer fibres have been known to contain a porous surface and an internally voided structure [6, 7]. The surface porosity is thought to be due to water vapour condensing on the fibre surface and spinodal decomposition occurring [6]. The internal void structure is a result of the fibre forming an outer skin that traps solvent within the internal structure. The solvent will subsequently evaporate off slowly leaving behind the voided structure [7]. These are important factors in data analysis of electrospun fibres as both can be on a length scale recorded using small angle neutron scattering experiments. In this paper we discuss

how we can resolve the issues caused by the voided structure of the fibres in order to analyze chain conformations in isotopically labeled fibre samples.

2. Materials and Methods

2.1. Polymers

Hydrogenated atactic-polystyrene and deuterated atactic-polystyrene with molecular weight characteristics displayed in Table 1 were used for the small angle neutron scattering experiments.

Table 1: Molecular weight characteristics of polymers used in small angle neutron scattering.

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

2.2. Electrospinning

Solutions for electrospinning were prepared in 1:1 blends of HPS-1/DPS-1 and HPS-2/DPS-2 by volume at concentrations of 0.2g/ml, 0.3g/ml and 0.4g/ml. Two different solvents were used in the electrospinning process, N, N – Dimethylformamide (DMF) and Methyl Ethyl Ketone (MEK). The polymer was weighed out in the correct proportions to the solvent and then left to dissolve on a shaker (Bühler) for 2 days.

The electrospinning equipment was set up in a horizontal configuration. Solutions were placed in a 5ml Luer lock syringe with a 22G (0.41mm inner diameter) needle attached. The syringe containing the solution was placed inside a syringe pump and set to a flow rate of 0.13ml/min. Samples were prepared at needle tip to collector distances of 20cm and 30cm and applied voltages of 10kV, 12.5kV and 15kV. Randomly orientated fibre mats were collected onto a grounded aluminium electrode and left to dry for a minimum of 24 hours to ensure that any remaining solvent had evaporated. The mass of samples varied between 100mg – 300mg, which was sufficient to enable a good signal noise ratio to be obtained in ~30 minutes during neutron scattering experiments.

Several sets of aligned samples have also been collected by electrospinning onto a grounded rotating collector with a tangential velocity of the collector surface $\sim 5\text{ms}^{-1}$. These samples were prepared at the same applied voltages and needle tip to collector distances as described above. Trial experiments determined that this rotational speed would not mechanically extend the fibres but provide sufficient levels of fibre alignment on the collector necessary for a study of the chain conformations parallel and perpendicular to the fibre axis.

2.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on using an FEI Quanta 600 SEM equipped with a field emission gun and a Cambridge Instrument SEM 360. All samples were coated with gold prior to examination. Fibre diameters were measured from images obtained using the Scandium software. A grid was overlaid over the image and measurements made on several fibres in each grid square to ensure unbiased sampling.

2.4. Small Angle Neutron Scattering

Small Angle Neutron Scattering (SANS) was performed using the LOQ instrument at the STFC ISIS facility, UK. A wavelength, λ , range of $2.2\text{\AA} - 10\text{\AA}$ was used giving a scattering vector range $|Q|(\text{\AA}^{-1})$ range of $0.006\text{\AA}^{-1} - 0.27\text{\AA}^{-1}$ where:

$$|Q| = 4\pi \sin \theta / \lambda \quad (1)$$

and 2θ is the scattering angle.

Fibres were easily removed from the aluminium electrode and placed into an open ended cylindrical shaped sample holder. The sample holder was covered with aluminium foil to hold the sample in place and the whole assembly was placed inside the sample holder rack on the LOQ instrument.

Scattering experiments were run for ~30 minutes on each sample. All scattering experiments were carried out at 25°C. Data was collected onto the two dimensional ORDELA area detector. The data was converted to an absolute scale by measurements of known polystyrene blends. An empty sample holder was prepared in a similar fashion to that described above and the measured scattering was subtracted as a background. The incoherent background was incorporated into the data fitting method. Data were radially averaged and reduced to a one dimensional differential scattering cross section as a function of the scattering vector. Data analysis was performed using the non-linear least squares data fitting program FISH [8].

3. Results and Discussion

3.1. SEM of fibres

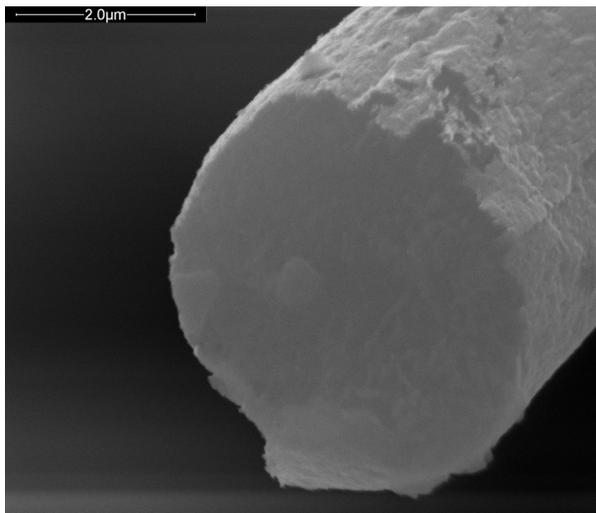


Figure 1a: Cross section of a fibre prepared from a solution of 0.2g/ml HPS-1/DPS-1 in DMF at a collector distance of 20cm with an applied voltage of 15kV

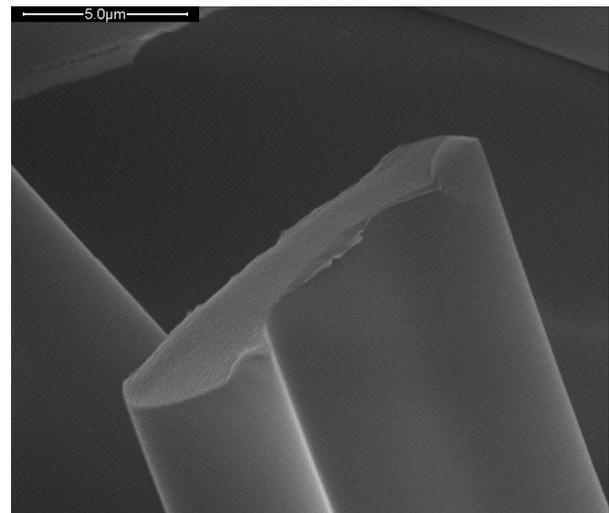


Figure 1b: Cross section of a fibre prepared from a solution of 0.2g/ml HPS-1/DPS-1 in MEK at a collector distance of 20cm with an applied voltage of 15kV

Images of fibres prepared from DMF and MEK obtained using SEM are shown in Figure 1. Fibres that have been prepared from DMF (Figure 1a) have a cylindrical shape, whereas those prepared from MEK (Figure 1b) show a more ribbon like structure. This ribbon like structure is thought to be due to the collapse of the fibre during the electrospinning process itself [2].

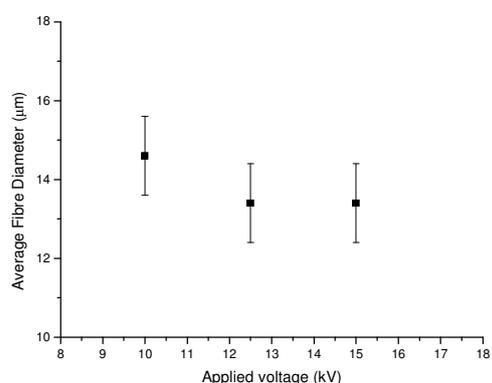


Figure 2a: Variation in average fibre diameter as a function of applied voltage for 0.3g/ml solution of HPS-1/DPS-1

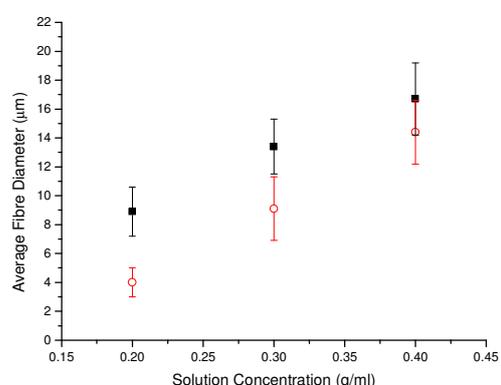


Figure 2b: Variation in average fibre diameter with solution concentration they were prepared from. Samples were electrospun at 10kV with a collector distance of 30cm □ HPS-1/DPS-1 and ○ HPS-2/DPS-2.

Samples were prepared under different spinning conditions with variations in the collector distance, applied voltage and solution concentration. By increasing the applied voltage in the electrospinning process, fibres are produced with smaller diameters (Figure 2a), as there is a greater acceleration to the grounded collector, causing more stretching [2]. Figure 2b shows that the fibre diameter increases with solution concentration. Figure 2b also shows that the higher the molecular weight polymer produces larger diameter fibres, due to an increase in viscosity [4]. SEM analysis of fibre cross sections reveal an internal structure with voids present as shown in Figure 3. The voids vary in shape and size from fibre to fibre, in sizes from several hundred nanometres to tens of nanometres. The latter are small enough to be detected in SANS.

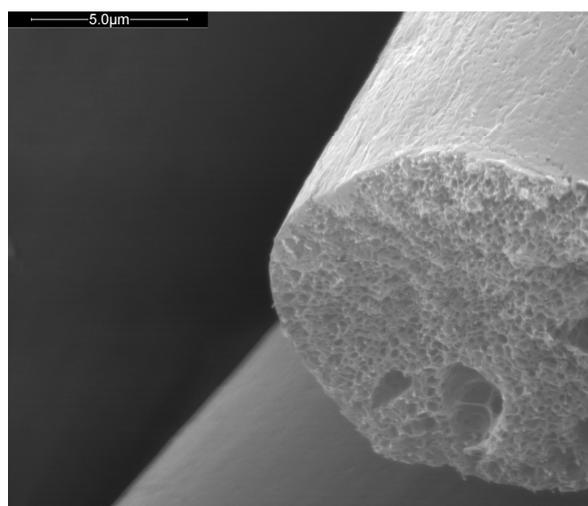


Figure 3: Cross section of a fibre prepared from a 0.4g/ml solution of HPS-2/DPS-2 in DMF at collector distance of 30cm and an applied voltage of 10kV.

3.2. SANS of Fibres

In order to analyse the chain conformation in these polymer fibres, a model that takes the voids into account has been developed so that a value for the radius of gyration can be extracted. Firstly, fibres were prepared using only deuterated polymers from both solvents so that the contrast arises only from the voids themselves and other inhomogenieties present in the fibres. Fitting a model, $I(Q) = kQ^{-N}$, where k is scaling factor, to the scattering data from the purely deuterated fibres prepared from both solvents gave a value for N of 4, as shown in Figure 4a and 4b for fibres spun from DMF and MEK respectively. A value of $N = 4$ is consistent with scattering arising from the sharp interfaces of the voids [9]. Both sets of deuterated fibres prepared from different solvents display a scaling of Q^{-4} although the level of scattering from the fibres prepared from MEK is much lower than those prepared from DMF. Fibres prepared from DMF display higher levels of voiding in the internal structure than those prepared from MEK explaining this higher level of scattering. Attempts to include a contribution from the surface porosity did not lead to an improved fit and we concluded that the majority of the scattering arises from the internal structure rather than any surface features.

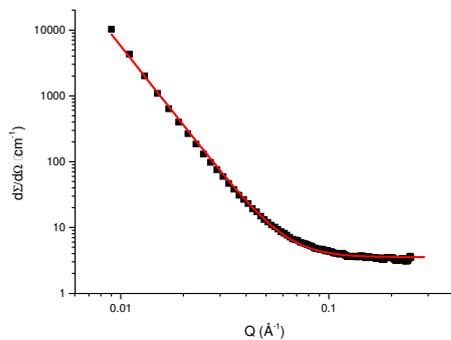


Figure 4a: Log-log plot of scattering data and data fit for the Q^{-N} model to a purely deuterated polystyrene fibre spun from DMF. Fibres were prepared from 0.3g/ml solution of DPS-1 in DMF at an applied voltage of 10kV and collector distance of 20cm. \blacksquare is the scattered data, solid line is the model fit.

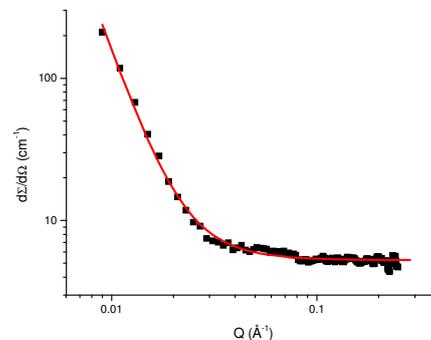


Figure 4b: Log-log plot of scattering data and data fit for the Q^{-N} model to a purely deuterated polystyrene fibre spun from MEK. Fibres were prepared from 0.3g/ml solution of DPS-1 in MEK at an applied voltage of 10kV and collector distance of 20cm. \blacksquare is the scattered data, solid line is the model fit.

Further analysis was performed on the deuterated fibres by an application of the Shultz polydisperse sphere model. The distribution function for the model is defined in Equation 2 [8]:

$$f(R) = \left[\frac{z+1}{\bar{R}} \right]^{z+1} R^z \exp \left[- \left(\frac{z+1}{\bar{R}} R \right) \right] \frac{1}{\Gamma(z+1)} \quad (2)$$

Where \bar{R} is the mean sphere radius, z is the parameter related to the width of the distribution.

We have taken the voids to be spherical in nature as observed in the SEM images and we have applied the model to the scattering from the deuterated fibres. Figure 5 shows a polydisperse sphere model fit to the deuterated fibres. A mean void size of approximately $21\text{nm} \pm 2\text{nm}$ for fibres prepared from DMF and fibres prepared from MEK show a higher mean void size at $25\text{nm} \pm 2\text{nm}$. These values are in broad agreement with those obtained from the image analysis of the SEM micrographs. Void sizes measured in the SEM analysis vary between 20nm to several hundred nanometres in fibres

prepared from DMF, with a mean void size of 19.5nm. Fibres prepared from MEK show a smaller variation in void sizes ranging from 20nm-140nm with a mean size of 35nm.

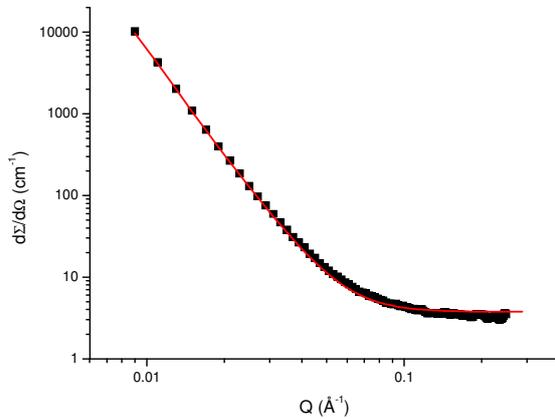


Figure 5: Log-log plot of scattering data and data fit for the Shultz Polydisperse Sphere model to a purely deuterated polystyrene fibre spun from DMF. \blacksquare is the scattered data, solid line is the model fit.

The previous section shows that $I(Q) = kQ^{-4}$ provides a good fit to the void scattering. We use a Shultz Polydisperse Gaussian coil model combined with this Q^{-4} model to fit the complete scattering from fibres prepared using isotopically labelled mixtures. This model is defined in equation 3 [8]:

$$I(Q) = \frac{A}{((1+U)y^2)} \left\{ y - 1 + (1+Uy)^{-1/U} \right\} + BQ^{-4} \quad (3)$$

Where $A = 2x(1-x)V(\Delta\rho)^2$ x is the concentration of the labelled polymer, V is the volume, $\Delta\rho$ is the difference in the scattering length, $y = (QRg)^2/(1+2U)$ and $U = 1 - M_w/M_n$, R_g is the radius of gyration and B is a scaling constant. In this model, values are fixed by the molecular weight characteristics of the polymer apart from R_g and B which are allowed to vary. R_g was initially set to that of the bulk state material and B started at 0.

This model was successfully applied to the electrospun fibres prepared from isotopically labelled mixtures of polystyrene. This is demonstrated for fibres prepared from a 0.2g/ml solution prepared at 10kV with needle tip to collector distance of 20cm for HPS-1/DPS-1 in DMF (Figure 6a) and MEK (Figure 6b).

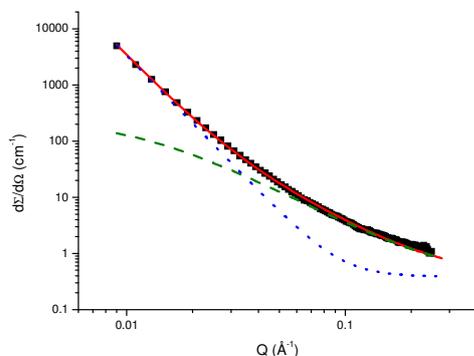


Figure 6a: Log-log plot of scattering data and data fits for a fibre spun from 0.2g/ml HPS-1/DPS-1 in DMF at a voltage of 10kV and collector distance 20cm. \blacksquare is the scattered data, solid line is the combined model fit, dashed line is the polydisperse Gaussian coil fit and the dotted line is the Q^{-4} fit.

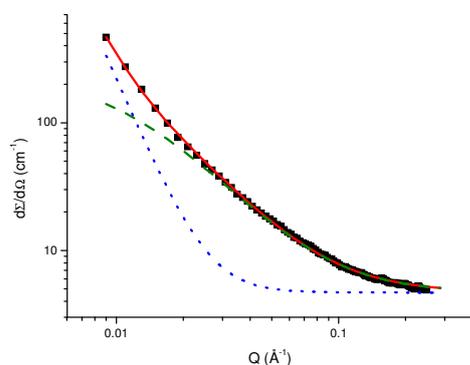


Figure 6b: Log-log plot of scattering data and data fits for a fibre spun from 0.2g/ml HPS-1/DPS-1 in MEK at a voltage of 10kV and collector distance 20cm. \blacksquare is the scattered data, solid line is the combined model fit, dashed line is the polydisperse Gaussian coil fit and the dotted line is the Q^{-N} fit.

Figure 6a and 6b shows that the contribution of the scattering from the voids dominates at low Q . The scattering from the voids is less in fibres that have been prepared from MEK. This is possibly due to the collapsed structure of the fibre reducing the trapped solvent present. Values of the radius of gyration extracted using this approach for the samples referred to in Figure 6 are $157\text{\AA} \pm 10\text{\AA}$ for the fibre prepared from DMF and $156\text{\AA} \pm 10\text{\AA}$ for the fibre prepared from MEK. These values are $\sim 20\%$ above that found in the bulk state material (130\AA) as is expected from a good solvent which suggests that little rearrangement of the chains has taken place during what can be considered to be flash drying during the electrospinning process.

The data recorded for samples with a macroscopic alignment of the electrospun fibres were subjected to a similar analysis but using sections taken from the 2-d data between 60° and 120° and -30° to 30° where 90° corresponds to the fibre axis. Application of the model defined in Equation 3 was used to measure the radius of gyration for the isotopically labelled aligned samples for each data set at 60° to 120° (parallel to fibre axis) and -30° to 30° (perpendicular to fibre axis). In the aligned samples there is a larger radius of gyration value parallel to the fibre axis when compared to the perpendicular component showing an extension of the chain conformation. The largest difference observed was an extension of $\sim 10\%$ parallel to the fibre axis. The fibres are not perfectly aligned with respect to the main axis of rotation of the collector. There is an angular distribution of fibres, therefore the scattering observed is a convolution of the angular distribution of the fibres from the main axis of rotation for the collector and the scattering for an individual fibre. The angular variation of the fibres varies between samples and work is currently underway to include this deconvolution process in the analysis procedure.

4. Conclusions

SANS from electrospun fibres indicates that there is a high level of voiding within samples prepared from DMF, as confirmed by SEM analysis. A model has been developed and successfully applied to extract the values for the radius of gyration of the polymer chains within the fibres. This analysis shows that the radius of gyration in the fibres is $\sim 20\%$ greater than that of the bulk state as expected for a good solvent system. Similar values were recorded for samples prepared using MEK as the solvent. This analysis was extended to analyse the anisotropy of the chain conformations, by comparing the dimensions parallel and perpendicular to the fibre axis. This revealed anisotropy in the radius of gyration which was up to 10% greater in the direct parallel to the fibre axis.

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