Supplementary Information (SI) for Analytical Methods.
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Supporting Information for "*Identifying small molecule impurities in electrospun poly(vinyl alcohol) nanofibers with ultra-selective NMR*"

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SI.1 Modified GEMSTONE NMR pulse sequence

The GEMSTONE pulse sequence is designed to selectively excite single multiplets within a crowded spectrum. However, in very closely packed spectra, unwanted neighbouring signals are much less well filtered. This gives rise to artefacts, typically anti-phase in appearance and coincident with neighbouring signals, appearing in the GEMSTONE spectra. It was noted that the phases of the artefacts depend on the signs of the slice selective gradients, G_{slice}. Acquiring two transients, with the gradient signs switched as detailed in **Figure SI.1.1**, and taking the sum of the resulting the data sets produces the clean data presented in **Figure 6** of the main manuscript.

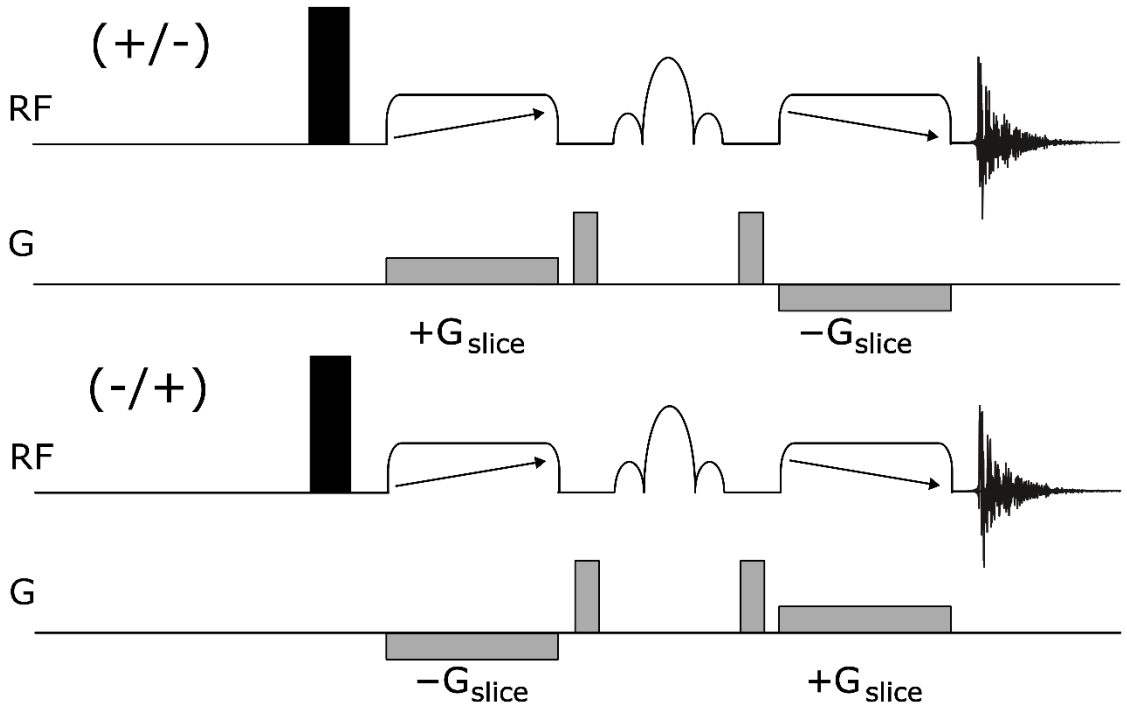

Figure SI.1.1: Pulse sequences for the revised Gradient-Enhanced Multiplet-Selective Targeted-Observation NMR Experiment (GEMSTONE) used in this work. Data from both the (+/−) and the (−/+) variants were summed for each transient, removing 'ghost' signals from very near multiplets. Closed rectangles, diagonal arrow crossed elements, and sinc shapes represent excitation, frequency-swept, and band-selective pulses,

respectively. The effective bandwidth of the frequency-swept pulses is matched to the applied gradient G_{slice}. The remaining gradient pair supports the selective 180° pulse.

SI.2 Additional proton NMR spectra

Figure SI.2.1 depicts an additional region of the 1D ^{1}H spectra of three electrospun PVA samples, focusing on the higher chemical shifts typical of the backbone signals next to the hydroxyl groups. The bottom spectrum is from sample produced by DC needle electrospinning, the middle, by DC needleless electrospinning (Nanospider™) and, the top, by AC electrospinning. As observed in **Figure 4** of the main manuscript, the broad polymer peaks are essentially the same in all three spectra, the only differences arise from the various impurity signals.

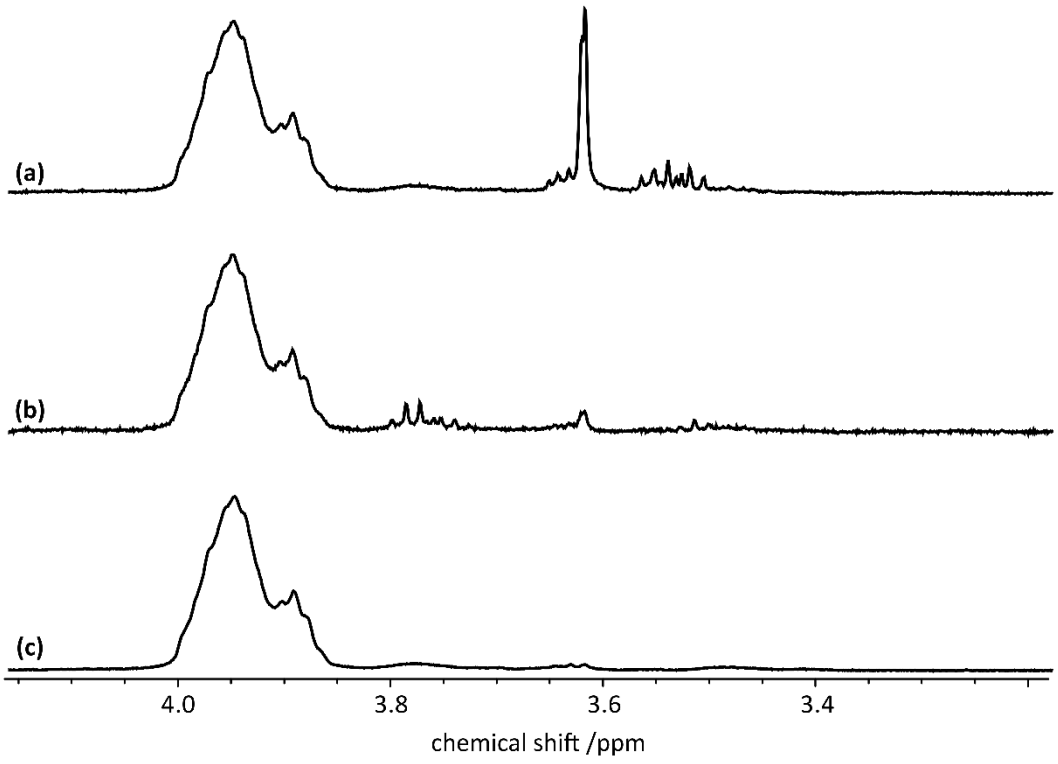

Figure SI.2.1: Sections of 1D ^{1}H NMR spectra of three electrospun PVA samples, dissolved in D_2O. Chemical shifts between 3.2 and 4.2 ppm shown. Bottom spectrum, sample prepared by DC needle electrospinning; middle spectrum, sample prepared by

DC needleless electrospinning (Nanospider^{TM}) and sample (c), top spectrum, by AC electrospinning.

SI.3 Discussion of Possible Small-Molecule Impurities

The synthesis of PVA from PVAc produces one major side product, sodium acetate, as well as potentially leaving solvents and reagents, such as methanol and sodium hydroxide, in the polymer samples. To further support our assignments and argument, **Figure SI.3.1** is reproduced from Reference 53 and **Figure SI.3.2** depicts 1D ^{1}H NMR spectrum of 20 mg mL^{-1} stock PVA in D_2O. **Figure SI.3.2** has been labelled according to scheme of **Figure SI.3.1** and an additional label for methanol.

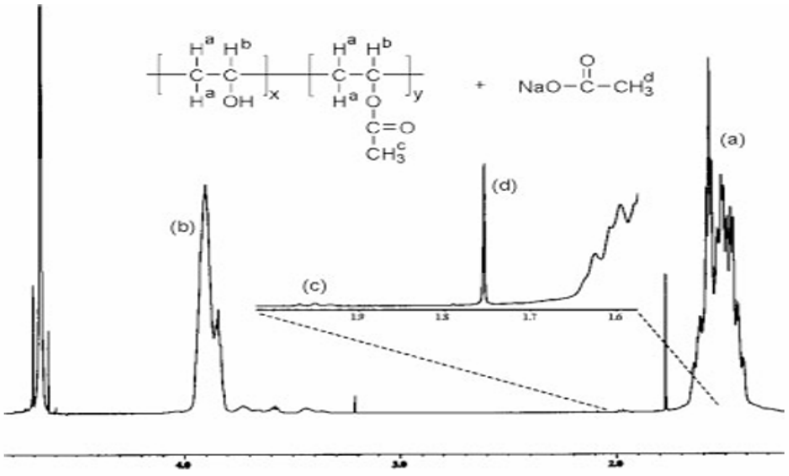

Figure SI.3.1. A typical ^{1}H NMR spectrum of PVA in D_2O. Reproduced from Reference 53, J. Shin, Y. Kim, Y. M. Lim, Y. C. Nho, *J. Appl. Polym. Sci.* 2008, 107, 3179-3183.

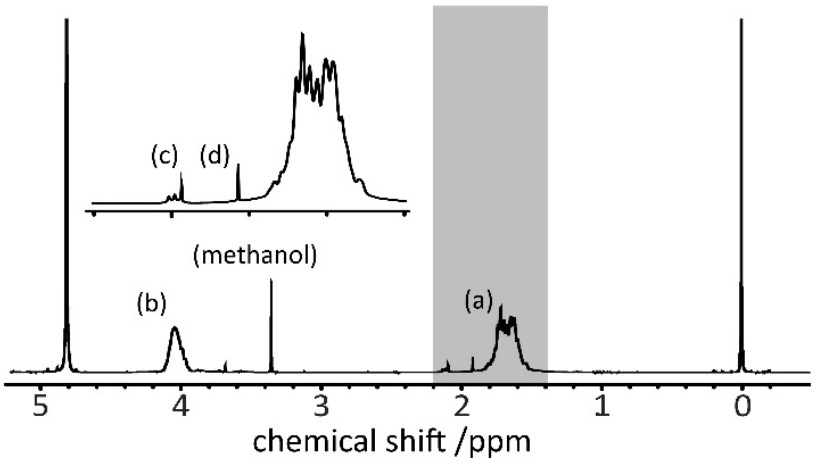

Figure SI.3.2. Recently acquired ^{1}H NMR spectrum of stock PVA in D_2O, labelled according to Figure SI.6.1.

Note that there are no peaks at *ca*. 1 ppm, where the distinctive multiplets of the small molecule impurities are observed in 1D ^{1}H NMR spectra of both AC and DC needleless electrospun samples.

In addition, all DC electrospinning experiments were performed by using PVA dissolved in 9:1 water:ethanol solution. To demonstrate that ethanol is not present in the final electrospun samples, **Figure SI.3.3** reproduces the COSY spectra of DC Needleless electrospun PVA from **Figure 5** in the main manuscript but with the likely position of ethanol chemical shifts highlighted by a square with vertices at 1.2 and 3.3 ppm. Neither diagonal nor cross peaks can be observed at these points in the spectrum.

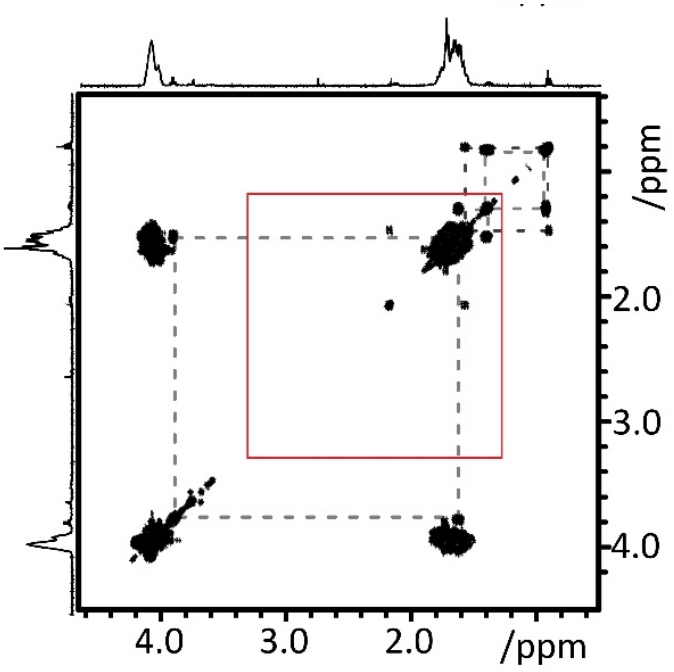

Figure SI.3.3. COSY spectra of DC needleless NanospiderTM electrospun PVA samples, acquired on a 500 MHz spectrometer. Dashed lines have been added to highlight correlations between signals. Red square added to highlight where ethanol signals would be expected to be observed.

SI.4: Summary of PROJECT NMR experiments

PROJECT (Periodic Refocusing of J Evolution by Coherence Transfer) is a perfect-echo NMR pulse sequence. A spin echo consists of a 90-τ-180-τ pulse sequence but leads to distortions of the signals as both coupling and chemical shift evolve during the delays. By expanding to 90_x-τ-180-τ-90_y-τ-180-τ, as in **Figure SI.4.1**, the resulting signals are not distorted and can be phased just like conventional ^{1}H spectra[22].

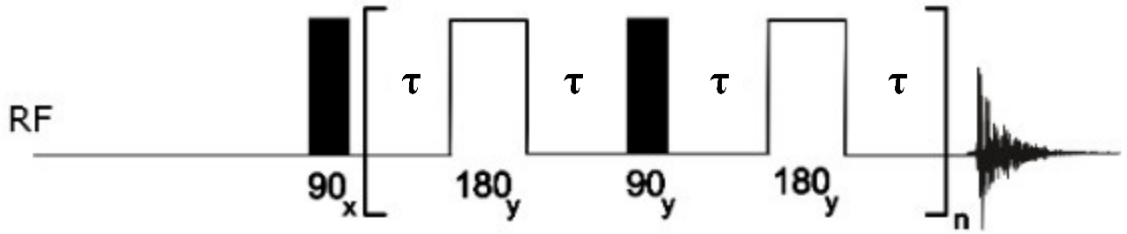

Figure SI.4.1: Pulse sequence for the PROJECT experiment.

This pulse sequence can also be used to filter spectra. In each of the delays, τ, the signals decay according to their transverse relaxation time, T_2. Bigger species, such as polymers, have shorter values of T_2 and their signals decay faster as the number of loops increases. The effect on the NMR spectrum of the samples studied here is shown in **Figure SI.4.2**. The PROJECT experiment here used a total delay time of 1 ms and increased the number of loops of the PROJECT element from 32 to 2048 in two-fold jumps. Each individual PROJECT experiment consisted of 16 transients and 1 dummy scan. This series of data indicates how an optimum filtration time can be determined by acquiring a series of experiments with increasing number of loops of the filter. Note that in **Figure SI.4.2**, both the polymer and the impurity signals decrease, albeit at different rates.

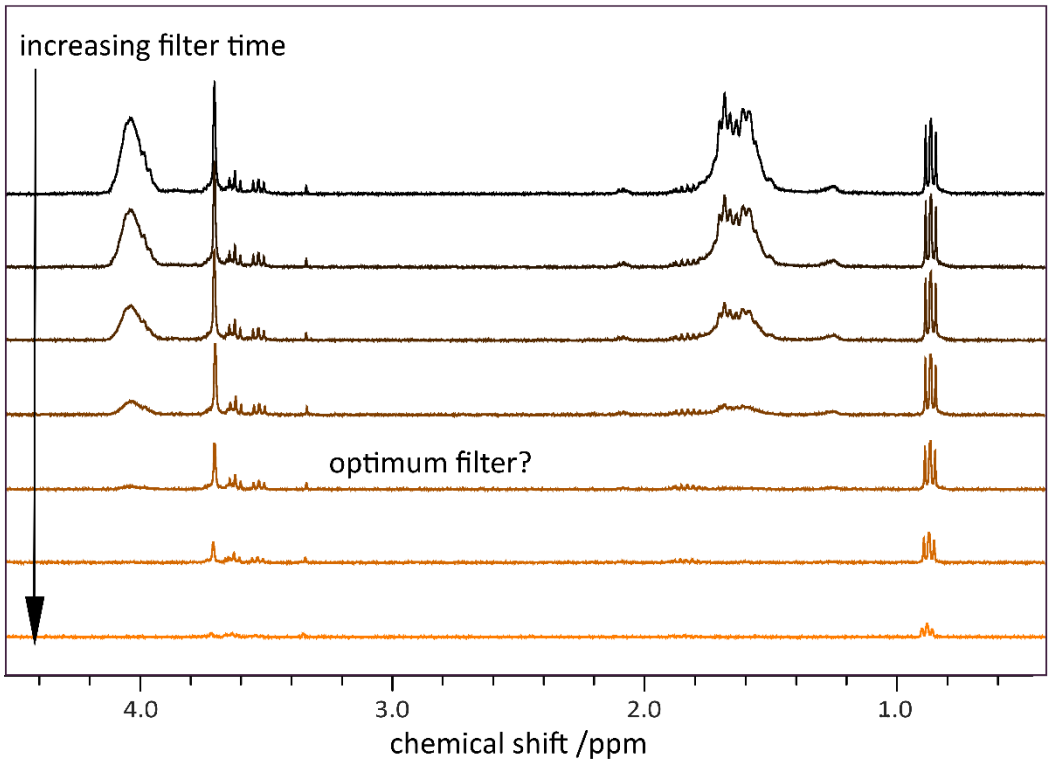

Figure SI.4.2: Series of PROJECT experiments with number of loops of PROJECT element increasing from 32 through to 2048. Each loop corresponds to an echo time of *ca.* 1 ms. Optimum filter indicated corresponds to an experiment with 512 loops of the PROJECT element.

A T_2-filtered DOSY experiment was written by prepending a Oneshot experiment with a looped PROJECT filter, based on the pulse sequences described in Reference 26, depicted by **Figure SI.4.1** and also by Reference 50. Initial experiments indicated that the experiment was highly susceptible to instabilities during the experiment. These are most likely temperature changes within the sample as a result of the rapid RF pulsing during the PROJECT part of the sequence. Chemical shifts moved by as much as 1.5 Hz, rendering the experimental data useless. Even with careful temperature regulation, the increased experiment duration and significant increase in number of pulses means that there were observed increases in the linewidths of the peaks, between 0.2 to 0.4 Hz. These factors combined to make the PROJECT-DOSY less useful than hoped. As **Figure 7** in the main manuscript shows, processing of the

diffusion NMR data can focus on a limited region of the spectrum. The 1D PROJECT inferred connectivity between the various peaks left unfiltered, something firmly confirmed by the GEMSTONE-TOCSY experiments described in the main text.

A PROJECT-COSY experiment was considered, prepending a double-quantum filtered COSY with the optimum filter. However, the optimum PROJECT element indicated in **Figure SI.4.2** was 512 loops of a PROJECT element of duration *ca*. 1 ms for a total duration of *ca*. 0.5 s. For a 'standard' COSY experiment consisting of 128 increments, each of 128 transients and 4 dummy scans, this would add over 2 hours to the experiment time. In addition, preliminary experimental results did not give much additional clarity for the increased duration. As **Figure 5** indicates, the diagonal peaks are typically far enough from the large polymer peaks to indicate coupling. It is clear from the data that a different NMR methodology is required to unravel the chemistry of this system.

SI.5 GEMSTONE-TOCSY experiments

The combined GEMSTONE-TOCSY spectrum in **Figure 6** was produced by adding two separate GEMSTONE-TOCSY experiments together, as depicted in **Figure SI.5.1**. The vertical scales of both GEMSTONE-TOCSY spectra are increased four-fold. The target offsets of the two experiments are indicated by text in the figure. Full experimental details are reported in the main text.

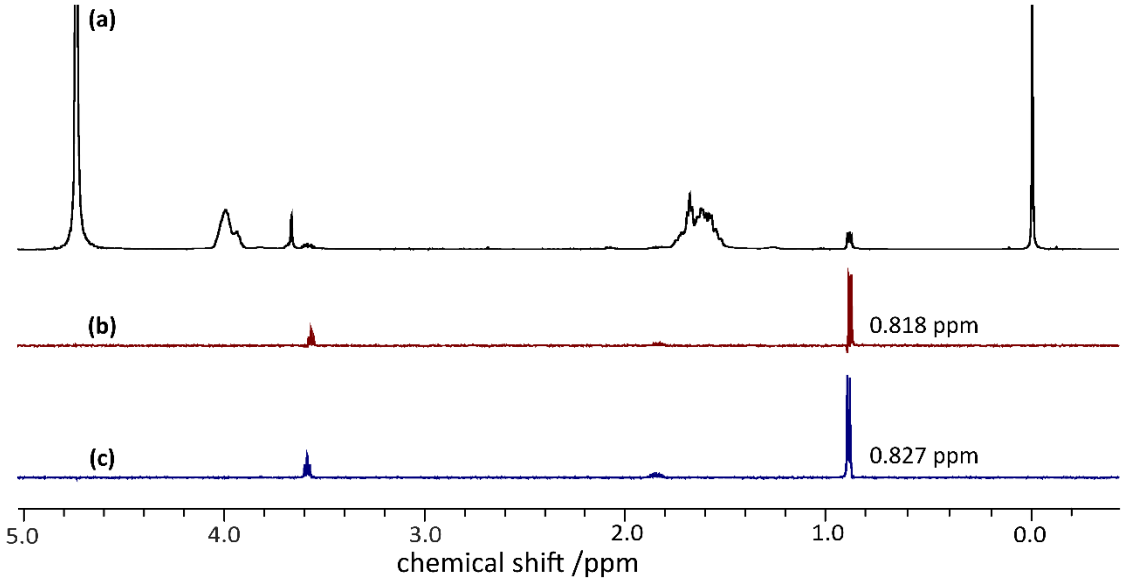

Figure SI.5.1: Summary of GEMSTONE-TOCSY NMR spectra of the AC electrospun PVA sample. Top major spectrum (a) reproduces the full proton spectrum of the AC electrospun sample from Figure 4. The bottom spectra (b) and (c) depict GEMSTONE-TOCSY experiments on the same sample, with offsets of selective pulses indicated as inset text in the Figure.

SI.6 Diffusion-Ordered Spectroscopy

To complement the diffusion NMR experiment presented in the main text, **Figure SI.6.1** is presented, showing the DOSY spectrum of the full range of relevant chemical shifts in the sample.

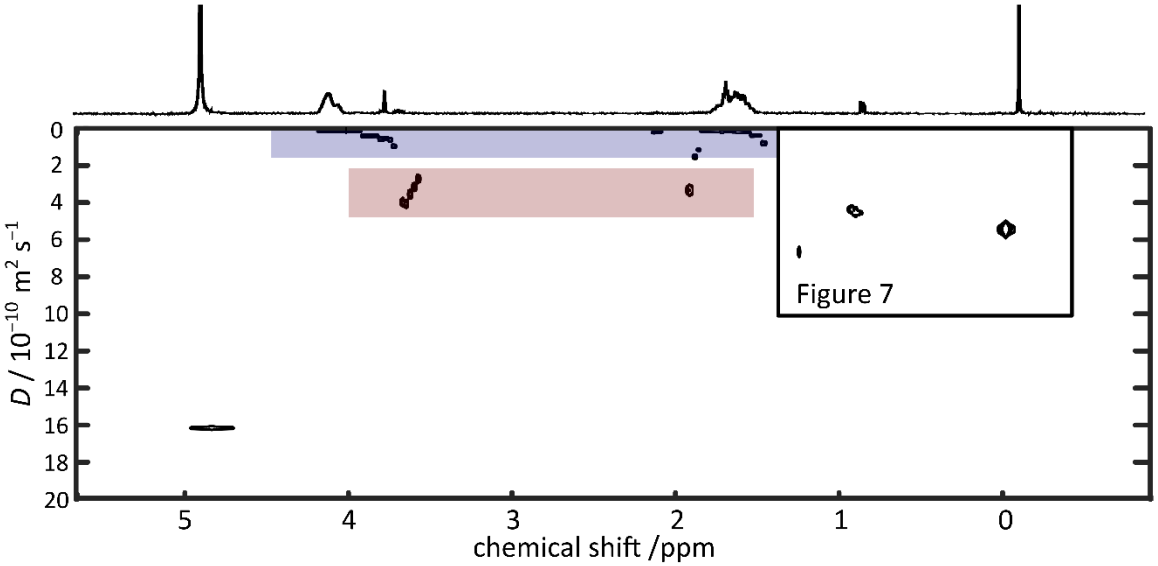

Figure SI.6.1: ^{1}H DOSY NMR spectrum of the AC electrospun PVA sample, dissolved in D_2O, processed with 2 Hz of line-broadening applied. Insert highlights region between −0.3 and 1.3 ppm, reproduced as Figure 7 in the main text. Blue shaded region highlights polymer signals. Red shaded region highlights impurity signals overlapped with polymer peaks and other species.

Additional References

All additional references introduced in this **Supporting Information** are listed at the end of the **References** section in the main manuscript.