## **Supplementary Information**

#### **Solutions**

PEO was selected on account of its good solubility in a range of polar solvents, and it availability in well-defined high molecular weights at low cost compared to other polymers. The PEO/ACN solution had a low conductivity and, due to the high molecular weight (2M) of the polymer, was highly viscous (Table 1). Addition of AB increased the conductivity and lowered the viscosity. While many solutions can only be spun using well-defined experiment specific conditions, here the PEO afforded the necessary stability for the high conductivity of dissolved AB. All of the solutions could be spun stably under a range of conditions. In this work constant process parameters were used for simplicity. Additionally, the 2M polymer chain length provided the required entanglement to support the high loadings of AB. The capability to spin AB-PEO materials with such different solution properties using the same parameters highlights might be beneficial for scale-up of materials production.

During the preparation of the samples it was noted that small bubbles formed in the solutions following the addition of AB. This is possibly the result of a reaction with ACN <sup>1</sup>. As a result of these possible reactions, the stirring time following the addition of the AB was kept as short as possible and spinning commenced as soon as the stirring process was complete. No DADB was observed in the <sup>11</sup>B NMR of the as-spun materials showing that this control was appropriate.

Table 1: The viscosity and conductivity of the AB and PEO in ACN solutions. Addition of AB increases the conductivity and lowers the viscosity.

AB content	Conductivity µSv/cm	Viscosity at high shear, cP
0	1.1±0.1	780
25	2.2±0.2	360
50	7±2.0	350
75	25±5.0	240

Electrospinning has a slow sample production rate but this can be scaled by the use of a multi nozzle system <sup>2</sup>. In this case the PEO-AB solutions in ACN can be spun thorough a multi-needle head, where 10 needles are arranged in around a circle of 10 cm diameter. The spinning conditions most favourable with this arrangement where, a flow of 0.5 ml/h per nozzle, a potential difference of 12-30 keV, a tip to nozzle distance of 30cm and an internal needle diameter of ~0.5mm. Depending on humidity and temperature some adjustments may have to be made.

## Total mass loss from composites under ramp heating.

Under ramp heating the composite fibres total mass loss increases successively as the AB content increases see Fig. 1. As no mass is lost from the PEO we can assume that the mass losses observed are due to the dehydrogenation of AB.



Fig. 1 Mass loss of samples normalised to the total sample mass of pristine AB (black), PEO (grey) and the AB-PEO electrospun fibres; 25AB-75PEO (green), 50AB-50PEO (blue) and 75AB-25PEO (pink). As the AB content is raised the mass loss observed is greater.

### FTIR peak determination

The positions of overlapping peaks in the FTIR data were determined by fitting with Gaussian curves using OriginPro see Fig. 2. The positions of the peaks are recorded in Table 1.



Fig. 2 The central portion of the fingerprint region of the AB, PEO and AB50 fibres FTIR spectrum. The graphs have been deconvoluted with multiple Gaussians to assist the positioning of the new peaks. Those highlighted with grey show a blue-shift indicating a shortening of the B-H bonds in AB. The peaks marked with a dashed line indicate splitting of the PEO C-O stretch.

Table 2: FTIR stretches observed

AB 3-6	5	PEO <sup>7,8</sup>		New peaks in AB-PEO fibres at 85°C 9-11	
Peak cm <sup>-1</sup>	Description	Peak cm <sup>-1</sup>	Description	Peak cm <sup>-1</sup>	Description
3306	N-H stretch asym.	2878	CH stretch	1635	NH scissor - shorter N-H bond
3250	N-H stretch sym.	1467	CH scissor	1402	$\mathrm{NH}_3$ scissor – shorter N-H bonds
2360	B-H stretch asym.	1341 & 1359	CH wagging	1285 & 1287	C-H twist – split peak
2283	B-H stretch sym.	1279 & 1241	CH twist	1187 & 1165	BH <sub>3</sub> scissor deformation – shorter B-H bond
1599	NH <sub>3</sub> scissor deformation asym.	1146, 1097 & 1060	C-O stretch	1105 & 1093	C-O stretch -split
1374	NH <sub>3</sub> scissor deformation sym.	961 & 947	C-O-C vibration, and $CH_2$ rocking	1077	H-wagging, NBH rocking – shorter intermolecular AB bonds
1154	BH <sub>3</sub> scissor deformation	841	CH <sub>2</sub> rocking	1024	B-O Interaction
1055	H-wagging, NBH rocking	549 & 509	C-O-C bending	924, 807 & 879	B-O Symmetric stretch
783	NBH stretch			753 & 738	-
726	H-wagging			696 & 665	B-O out of plane bend

## **Raman Peak Positions**

Table 2: NMR peak assignments.			
Signal (ppm)	Group		
-38	BH <sub>4</sub> (DADB) <sup>12</sup>		
-25 & -28	BH <sub>3</sub> (AB) <sup>12</sup>		
-23	BH <sub>3</sub> (AB*) $^{12}$ or end group $^{13}$		
-21.7	$BH_3$ (end group, linear dimer) $^{12}$		
-13.5	BH <sub>2</sub> (DADB) <sup>12</sup>		
-12.5	BH <sub>2</sub> (linear dimer) <sup>12</sup>		
-11.2	BH <sub>2</sub> <sup>12</sup> (PAB) <sup>13</sup>		
-9.9	BH <sub>2</sub> (PAB) <sup>13</sup>		
-7	BH (PIB or branched PAB) <sup>13</sup>		
12	BO interaction <sup>10</sup>		

#### Structure and Crystalinity

During dehydrogenation the samples melt and the initial crystallinity is destroyed leaving an amorphous mix behind. An example of the 50AB sample as-produced and after an hour of heating at 120 °C is shown in Fig. 3. Some small holes are present in the dehydrogenated AB50 which are likely to be gas release pathways.



Fig. 3 The x-ray diffractogram of the AB50 sample before and after dehydrogenation at 85 °C for 1 hour. The sample melts and the initial crystallinity is destroyed.

# References

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