

Supporting Information

New Understanding on the Reaction Pathways of the Polyacrylonitrile Copolymer Fiber Pre-Oxidation: Online Tracking by Two-Dimensional Correlation FTIR Spectroscopy

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1. Theory of scaling-MW2D based on auto-correlation

$W(\nu, I)$ is a $M \times N$ spectral intensity matrix. ν and I are spectral variable (e.g., wavenumber) and perturbation variable (e.g., temperature), respectively.

$$W(\nu, I) = \begin{pmatrix} y(\nu, I_1) \\ \mathbf{M} \\ y(\nu, I_j) \\ \mathbf{M} \\ y(\nu, I_M) \end{pmatrix} \quad (1)$$

The reference spectrum and dynamic spectrum in the j th submatrix of $W(\nu, I)$:

$$\bar{y}(\nu) = \frac{1}{2m+1} \sum_{J=j-m}^{j+m} y(\nu, I_J) \quad (2)$$

$$\tilde{y}(\nu, I_J) = y(\nu, I_J) - \bar{y}(\nu) \quad (3)$$

where J corresponds to the index of rows. A mean-centered j th submatrix of $W(\nu, I)$ is obtained.

$$w_j(\nu, I) = \begin{pmatrix} \tilde{y}(\nu, I_{j-m}) \\ \mathbf{M} \\ \tilde{y}(\nu, I_j) \\ \mathbf{M} \\ \tilde{y}(\nu, I_{j+m}) \end{pmatrix} \quad (4)$$

The $w_j(\nu, I)$ has $2m+1$ rows which is called the window size. The index range of the perturbation variable I of $w_j(\nu, I)$ is from $j-m$ to $j+m$.

The generalized synchronous 2D correlation spectra is calculated from $w_j(\nu, I)$:

$$\Phi_j(\nu_1, \nu_2) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}(\nu_1, I_J) \cdot \tilde{y}(\nu_2, I_J) \quad (5)$$

For each window, the standard deviations of spectral intensities at ν_1 and ν_2 are defined as follows.

$$\sigma(\nu_1) = \sqrt{\Phi_j(\nu_1, \nu_1)} \quad (6)$$

$$\sigma(v_2) = \sqrt{\Phi_j(v_2, v_2)} \quad (7)$$

The correlation coefficient $\rho(v_1, v_2)$ is defined:

$$\rho(v_1, v_2) = \Phi_j(v_1, v_2) / [\sigma(v_1) \cdot \sigma(v_2)] \quad (8)$$

The scaled forms of the synchronous correlation spectrum in each window are defined:

$$\Phi_j(v_1, v_2)^{(Scaled)} = \Phi_j(v_1, v_2) \cdot [\sigma(v_1) \cdot \sigma(v_2)]^{-\alpha} \cdot |\rho(v_1, v_2)|^\beta \quad (9)$$

The constant α is the scaling factor, and β is correlation enhance factor. The value of α is limited to 0–1.0.

For scaling-MW2D based on auto-correlation, the each row of the correlation matrix of scaling-MW2D is directly extracted from a diagonal line of $\Phi_j^{(Scaled)}$ matrix, namely $v_1=v_2$. Thus, the auto-correlation scaling-MW2D can be described below.

$$\Phi_j(v_1, v_1)^{(Scaled)} = \Phi_j(v_1, v_1) \cdot [\sigma(v_1) \cdot \sigma(v_1)]^{-\alpha} \cdot |\rho(v_1, v_1)|^\beta \quad (10)$$

$$\rho(v_1, v_1) = \Phi_j(v_1, v_1) / [\sigma(v_1) \cdot \sigma(v_1)] = 1 \quad (11)$$

$$\Phi_j(v_1, v_1)^{(Scaled)} = [\Phi_j(v_1, v_1)]^{1-\alpha} \quad (12)$$

The auto-correlation scaling-MW2D correlation spectrum is gained *via* sliding window position from $j=l+m$ to $M-m$ and repeating calculations of equation (2)-(12) at each window. In the present study, the scaling factor was chosen as $\alpha=0.7$. The detailed theory and algorithm of scaling-MW2D can refer to the Ref.¹

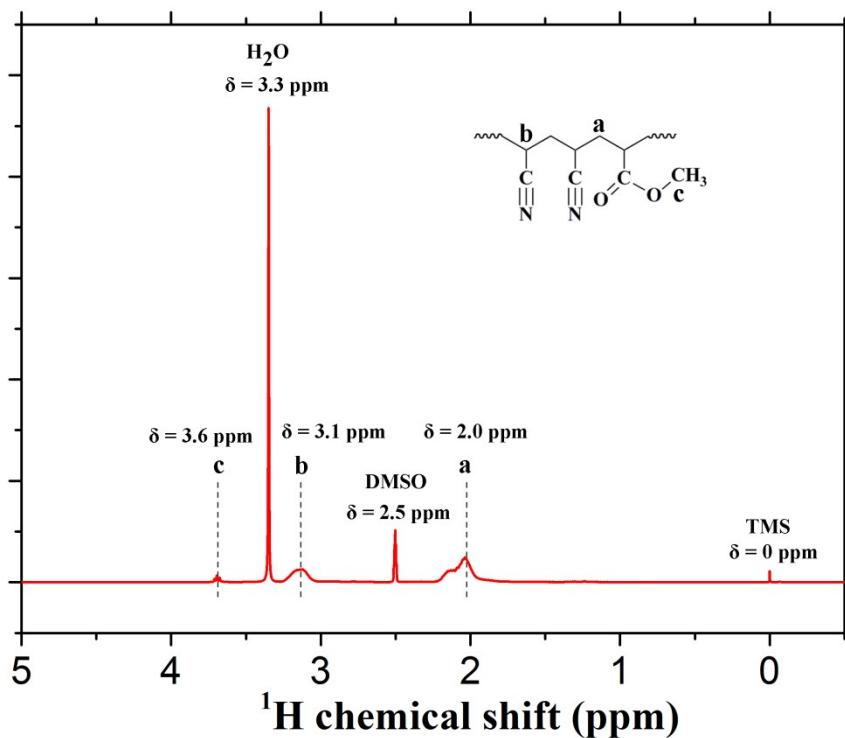


Figure S1. ^1H NMR of polyacrylonitrile (PAN) copolymer fibers.

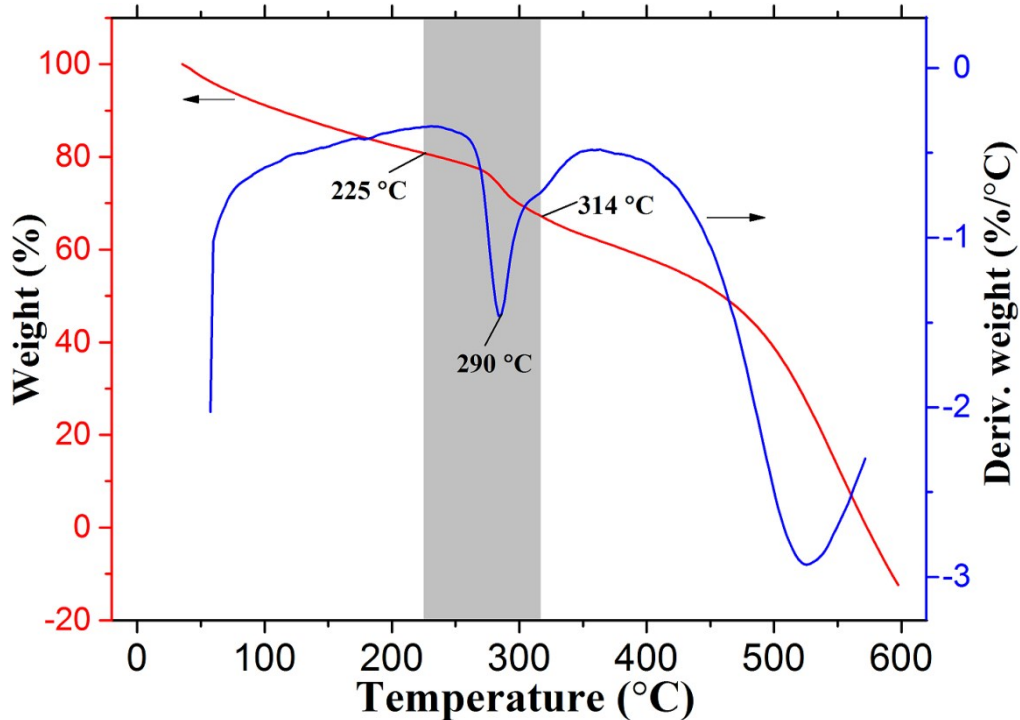


Figure S2. TGA and DTG curves of PAN copolymer fibers at $5^{\circ}\text{C}/\text{min}$ upon heating from 40°C to 600°C under air atmosphere.

Table S1. GPC results of PAN copolymer fibers

M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	M_z (g/mol)	M_{z+1} (g/mol)	Polydispersity (M_w/M_n)
686293	1341401	2850697	1842718	2162305	1.954560

Table S2. The bands assignments of FTIR spectra for PAN copolymer fibers and pre-oxidized PAN copolymer fibers.

Wavenumber (cm ⁻¹)	Assignments	Explanations	References
3371	$\nu(\text{O-H})$	O-H stretching of O-H groups	2, 3
3224	$\nu(\text{N-H})$	N-H stretching of N-H groups	2-4
2940	$\nu_{as}(-\text{CH}_2-)$	C-H asymmetrical stretching of $-\text{CH}_2-$ groups	5-7
2243	$\nu(\text{C}\equiv\text{N})$	C \equiv N stretching of $-\text{C}\equiv\text{N}$ groups	2, 8-10
2195	$\nu(\text{C}\equiv\text{N}, \beta\text{-amino})$	C \equiv N stretching of $-\text{C}\equiv\text{N}$ groups in β -amino nitrile	11, 12
1733	$\nu(\text{C}=\text{O}, \text{MMA})$	C=O stretching of carbonyl groups originated from methyl methacrylate (MMA)	2, 13-15
1650	$\nu(\text{C}=\text{O}, \text{cyclic})$	C=O stretching on the cyclic structure	16, 17
1626	$\delta(\text{O-H}, \text{absorbed water})$	O-H bending of the absorbed water	18
1610	$\nu(\text{C}=\text{C}, \text{cyclic})$	C=C stretching on the cyclic structure	16, 17
1580	$\nu(\text{C}=\text{N}, \text{cyclic})$	C=N stretching on the cyclic structure	16, 17
1454	$\delta(-\text{CH}_2-)$	C-H bending of $-\text{CH}_2-$ groups	2, 5
1380	$\delta(\text{C-H}, \text{rings})+$ $\delta(\text{N-H}, \text{rings})+$ $\delta(\text{O-H}, \text{rings})$	C-H, N-H, and O-H bending in rings	2, 17
1358	$\delta(\text{CH})+\omega(-\text{CH}_2-)$	C-H bending of CH groups + C-H wagging of $-\text{CH}_2-$ groups	19, 20
1250	$\omega(\text{CH})$	C-H wagging of CH groups	19, 21
1232	$\nu(\text{C-C})+$ $\nu(\text{C-N})+$ $\nu(\text{C-O})$	C-C, C-N, and C-O stretching	22, 23
1150	$\nu(\text{C-O-C})$	C-O-C stretching	2, 24
1073	$\nu_s(\text{C-CN})$	C-C symmetrical stretching of C-CN	17, 25

Table S3. Sequential order of the bands of absorbed water, C=O groups in MMA, and C≡N groups in AN obtained from **Figure 6**.

Cross correlation peak (cm ⁻¹ , cm ⁻¹)	Sign in synchronous spectra	Sign in asynchronous spectra	Sequential order
(1733, 1626)	+	-	1733←1626
(1733, 2243)	+	+	1733→2243
(1626, 2243)	+	+	1626→2243
1626 cm ⁻¹ →1733 cm ⁻¹ →2243 cm ⁻¹			
$\delta(\text{O-H, absorbed water}) \rightarrow \nu(\text{C=O, MMA}) \rightarrow \nu(\text{C}\equiv\text{N})$			

Table S4. Sequential order of the bands of functional groups involved in the main process of the PAN fibers pre-oxidation.

Cross correlation peak (cm ⁻¹ , cm ⁻¹)	Sign in synchronous spectra	Sign in asynchronous spectra	Sequential order
(3371, 3224)	+	0	3371=3224
(3371, 2940)	-	-	3371→2940
(3371, 2243)	-	-	3371→2243
(3371, 2195)	+	+	3371→2195
(3371, 1733)	-	+	3371←1733
(3371, 1650)	+	+	3371→1650
(3371, 1610)	+	-	3371←1610
(3371, 1580)	+	-	3371←1580
(3371, 1150)	+	+	3371→1150
(3224, 2940)	-	-	3224→2940
(3224, 2243)	-	-	3224→2243
(3224, 2195)	+	+	3224→2195
(3224, 1733)	-	+	3224←1733
(3224, 1650)	+	+	3224→1650
(3224, 1610)	+	-	3224←1610
(3224, 1580)	+	-	3224←1580
(3224, 1150)	+	+	3224→1150
(2940, 2243)	+	-	2940←2243
(2940, 2195)	-	+	2940←2195
(2940, 1733)	+	-	2940←1733
(2940, 1650)	-	+	2940←1650
(2940, 1610)	-	+	2940←1610
(2940, 1580)	-	+	2940←1580
(2940, 1150)	-	+	2940←1150
(2243, 2195)	-	-	2243→2195

(2243, 1733)	+	-	2243←1733
(2243, 1650)	-	+	2243←1650
(2243, 1610)	-	+	2243←1610
(2243, 1580)	-	+	2243←1580
(2243, 1150)	-	+	2243←1150
(2195, 1733)	-	+	2195←1733
(2195, 1650)	+	-	2195←1650
(2195, 1610)	+	-	2195←1610
(2195, 1580)	+	-	2195←1580
(2195, 1380)	+	-	2195←1380
(2195, 1232)	+	-	2195←1232
(2195, 1150)	+	-	2195←1150
(1733,1650)	-	-	1733→1650
(1733,1610)	-	-	1733→1610
(1733,1580)	-	-	1733→1580
(1733,1150)	-	-	1733→1150
(1650,1610)	+	-	1650←1610
(1650,1580)	+	-	1650←1580
(1650,1150)	+	+	1650→1150
(1610,1580)	+	-	1610←1580
(1610,1150)	+	+	1610→1150
(1580,1150)	+	+	1580→1150
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1733 cm ⁻¹ →1580 cm ⁻¹ →1610 cm ⁻¹ →3371 cm ⁻¹ =3224 cm ⁻¹ →1650 cm ⁻¹ →1150 cm ⁻¹ →			
2243 cm ⁻¹ →2190 cm ⁻¹ →2940 cm ⁻¹			
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ν(C=O, MMA)→ν(C=N, cyclic)→ν(C=C, cyclic)→ν(O-H)=ν(N-H)→ν(C=O, cyclic)→ν(C-O-C)→ν(C≡N)→ν(C≡N, β-amino)→ν _{as} (-CH ₂ -)			
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