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Supporting Information

Difference of the Micro-Dynamics Mechanism between Aromatic Nylon and Aliphatic Nylon during Water Absorption: Spectroscopic Evidence

*Liyang Jia, Gehong Su, Qiang Yuan, Xueqian Zhang, and Tao Zhou**

State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute,

Sichuan University, Chengdu 610065, China

*Corresponding author. Tel.: +86-28-85402601; Fax: +86-28-85402465; E-mail address: zhoutaopoly@scu.edu.cn (T. Zhou)

Theory of the scaling-MW2D spectroscopy based on auto-correlation

Q(*v*, *T*) is an $M \times N$ spectral intensity matrix. The *v* and *T* are spectral variable (e.g., wavenumber) and perturbation variable (e.g., temperature), respectively.

$$Q(v,T) = \begin{pmatrix} y(v,T_1) \\ \vdots \\ y(v,T_j) \\ \vdots \\ y(v,T_M) \end{pmatrix} \tag{1}$$

The reference spectrum and dynamic spectrum in the *j*th submatrix of *Q*(*v*, *T*):

$$\bar{y}(v) = \frac{1}{2m+1} \sum_{J=j-m}^{j+m} y(v,T_J) \tag{2}$$

$$\tilde{y}(v,T_J) = y(v,T_J) - \bar{y}(v) \tag{3}$$

where *J* corresponds to the index of rows. A mean-centered *j*th submatrix of *Q*(*v*, *T*) is obtained.

$$q_j(v,T) = \begin{pmatrix} \tilde{y}(v,T_{j-m}) \\ \vdots \\ \tilde{y}(v,T_j) \\ \vdots \\ \tilde{y}(v,T_{j+m}) \end{pmatrix} \tag{4}$$

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

The generalized synchronous 2D correlation spectra is calculated from $q_j(v, T)$:

$$\Phi_j(v_1,v_2) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}(v_1,T_J) \cdot \tilde{y}(v_2,T_J) \tag{5}$$

For each window, the standard deviations of spectral intensities at v_1 and v_2 are defined as follows.

$$\sigma(v_1) = \sqrt{\Phi_j(v_1,v_1)} \tag{6}$$

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

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

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

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

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

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

For scaling-MW2D based on auto-correlation, 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.

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

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

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

The auto-correlation scaling-MW2D correlation spectrum is gained *via* sliding window position from $j=1+m$ to $M-m$ and repeating calculations of equation (2)-(12) at each window.

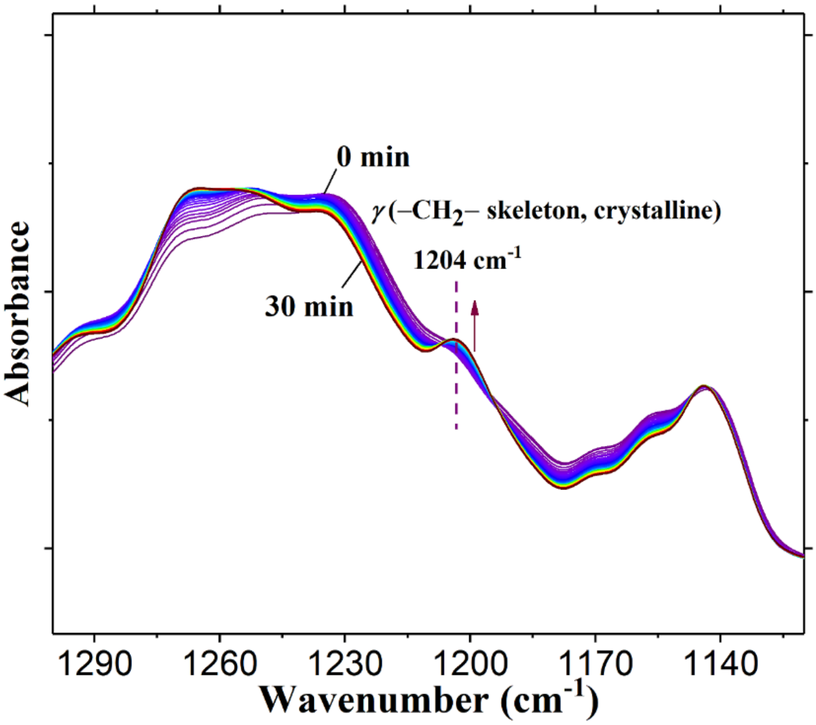

Figure S1. Time-dependent ATR FTIR spectra of the MXD6 film in the region of 1300−1120 cm^{-1} collected during ordinary water (H_2O) absorption.

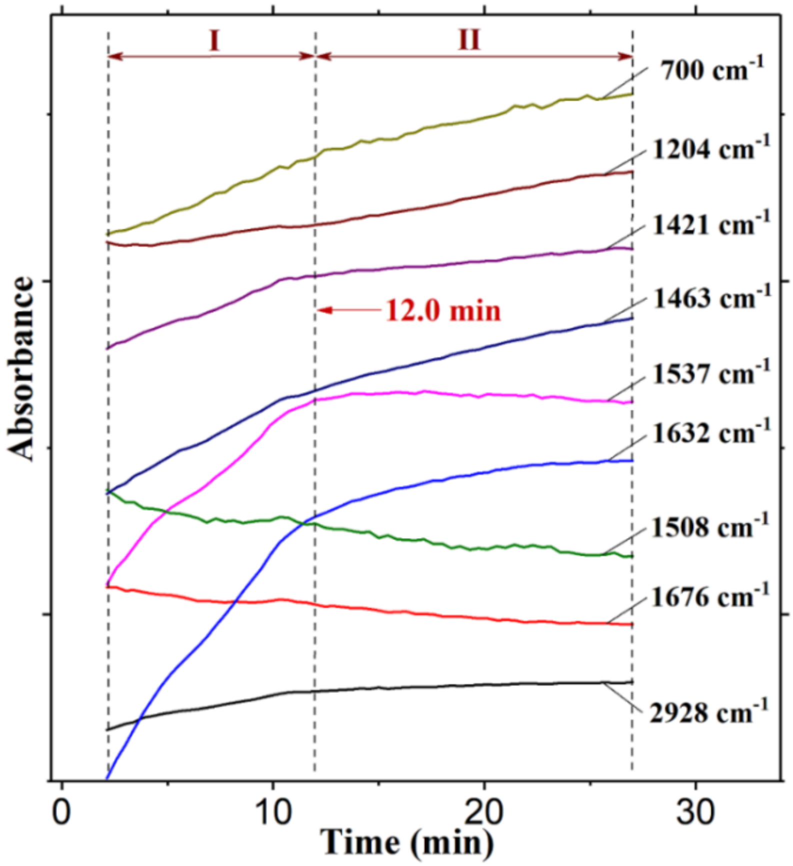

Figure S2. Spectral intensity changes extracted from the time-dependent ATR FTIR spectra of MXD6 during D_2O absorption from 2.0 min to 27.0 min.

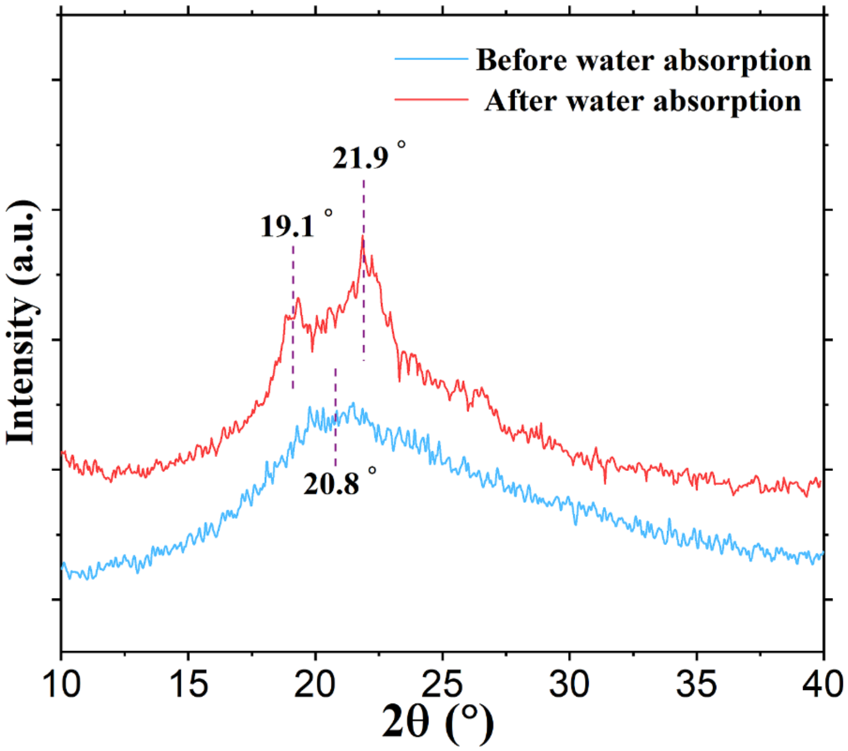

Figure S3. WAXD spectra of MXD6 films before and after water absorption.

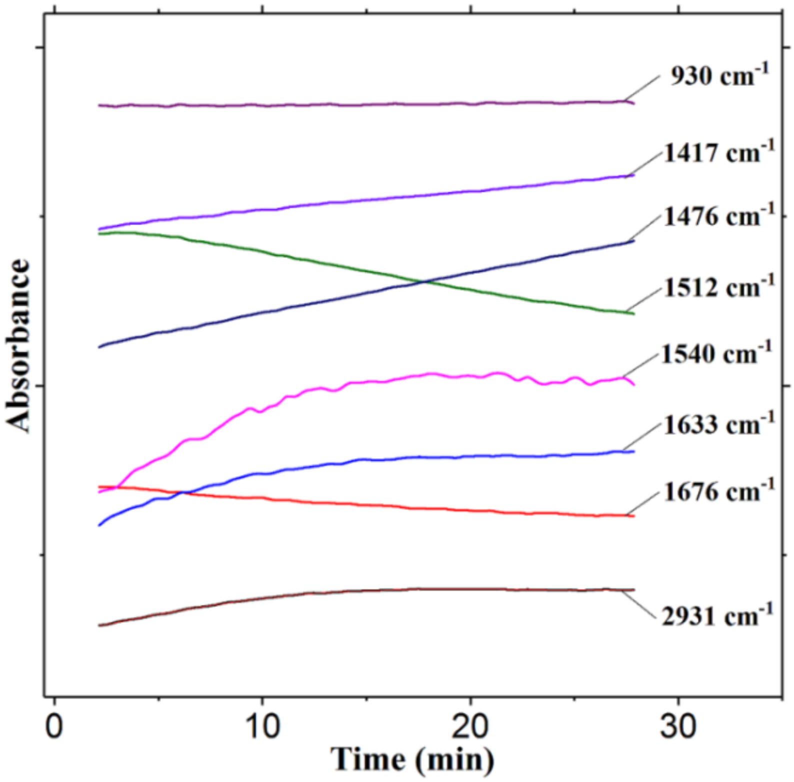

Figure S4. Spectral intensity changes extracted from the time-dependent ATR FTIR spectra of the PA6 film during D_2O absorption from 2.0 min to 27.0 min.

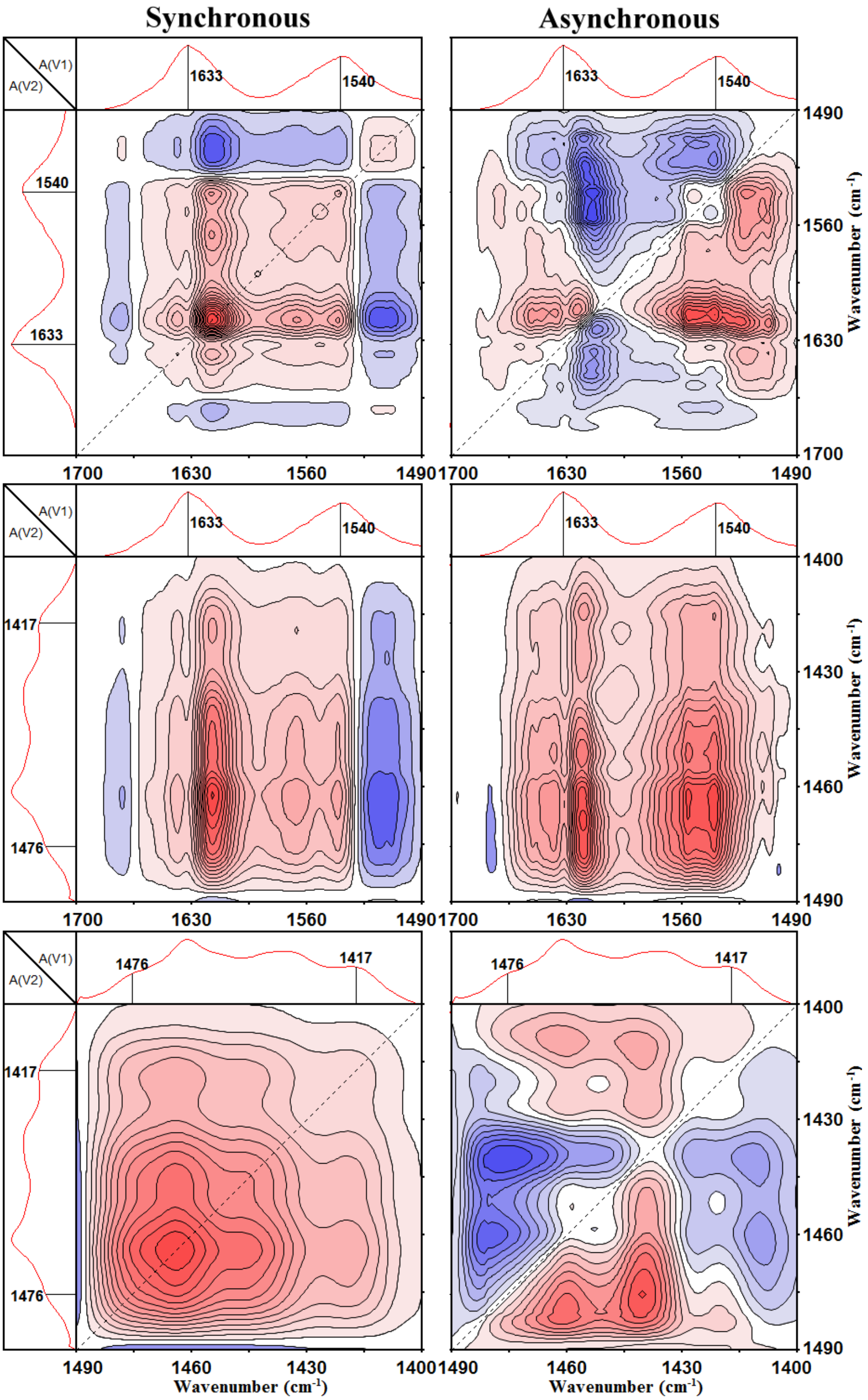

Figure S5. Synchronous (left) and asynchronous (right) generalized 2D correlation ATR FTIR spectra calculated from time-dependent ATR FTIR spectra of the PA6 film during D_2O absorption within 2.0–27.0 min in the regions of 1700–1490 cm^{-1}, 1700–1490 cm^{-1} *vs* 1490–1400 cm^{-1}, and 1490–1400 cm^{-1}.

Table S1. Sequential orders of the process I (2.0−12.0 min) for MXD6 obtained from the synchronous and asynchronous 2D correlation ATR-FTIR spectra in **Figure 6.**

Cross correlation peaks (cm^{-1}, cm^{-1})	**Sign in synchronous spectra**	**Sign in asynchronous spectra**	**Sequential order**
(1632, 1537)	+	-	1632←1537
(1632, 1463)	+	+	1632→1463
(1632, 1421)	+	+	1632→1421
(1632, 700)	+	+	1632→700
(1537, 1463)	+	+	1537→1463
(1537, 1421)	+	+	1537→1421
(1537, 700)	+	+	1537→700
(1463, 1421)	+	+	1463→1421
(1463, 700)	+	+	1463→700
(1421, 700)	+	+	1421→700
(1632, 1204)	+	+	1632→1204
(1537, 1204)	+	+	1537→1204
(1463, 1204)	+	+	1463→1204
(1421, 1204)	+	+	1421→1204
(1204, 700)	+	-	1204←700
1537 cm^{-1}→1632 cm^{-1}→1463 cm^{-1}→1421 cm^{-1}→700 cm^{-1}→1204 cm^{-1}			
δ(N−H, bonded) → ν(C=O, bonded) → δ(C−H, $-CH_2-NH-$) → δ(C−H, $-CH_2-CO-$) → δ(=C−H, benzene ring) → γ($-CH_2-$ skeleton, crystalline)			

Table S2. Sequential orders of the process II (12.0−27.0 min) for MXD6 obtained from the synchronous and asynchronous 2D correlation ATR-FTIR spectra in **Figure 7.**

Cross correlation peaks (cm^{-1}, cm^{-1})	**Sign in synchronous spectra**	**Sign in asynchronous spectra**	**Sequential order**
(1632, 1463)	+	+	1632→1463
(1632, 1421)	+	+	1632→1421
(1632, 700)	+	+	1632→700
(1463, 1421)	+	0	1463=1421
(1463, 700)	+	-	1463←700
(1421, 700)	+	-	1421←700
(1632, 1204)	+	+	1632→1204
(1463, 1204)	+	0	1463=1204
(1421, 1204)	+	0	1421=1204
(1204, 700)	+	-	1204←700
1632 cm^{-1}→700 cm^{-1}→1463 cm^{-1}=1421 cm^{-1}=1204 cm^{-1}			
ν(C=O, bonded) → δ(=C−H, benzene ring) → δ(C−H, $-CH_2-NH-$) = δ(C−H, $-CH_2-CO-$) = γ($-CH_2-$ skeleton, crystalline)			

Table S3. Sequential orders of PA6 (2.0−27.0 min) obtained from the synchronous and asynchronous 2D correlation ATR-FTIR spectra in **Figure S5.**

Cross correlation peaks (cm^{-1}, cm^{-1})	**Sign in synchronous spectra**	**Sign in asynchronous spectra**	**Sequential order**
(1633, 1540)	+	-	1633←1540
(1633, 1476)	+	+	1633→1476
(1633, 1417)	+	+	1633→1417
(1540, 1476)	+	+	1540→1476
(1540, 1417)	+	+	1540→1417
(1476, 1417)	+	-	1476←1417
1540 cm^{-1}→1633 cm^{-1}→1417cm^{-1}→1476 cm^{-1}			
δ(N−H, bonded) → v(C=O, bonded) → δ(C−H, −CH$_2$−CO−) → δ(C−H, −CH$_2$−NH−)			