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.

\[
Q(v, T) = \begin{pmatrix}
  y(v, T_1) \\
  \vdots \\
  y(v, T_j) \\
  \vdots \\
  y(v, T_M)
\end{pmatrix}
\]  

(1)

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

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

(2)

\[
\bar{y}(v, T_J) = y(v, T_J) - \bar{y}(v)
\]  

(3)

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

\[
q_j(v, T) = \begin{pmatrix}
  \bar{y}(v, T_{j-m}) \\
  \vdots \\
  \bar{y}(v, T_j) \\
  \vdots \\
  \bar{y}(v, T_{j+m})
\end{pmatrix}
\]  

(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 \( q_j(v, T) \):

\[
\Phi_j(v_1, v_2) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \bar{y}(v_1, T_J) \bar{y}(v_2, T_J)
\]  

(5)

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

\[
\sigma(v_1) = \sqrt{\Phi_j(v_1, v_1)}
\]  

(6)

\[
\sigma(v_2) = \sqrt{\Phi_j(v_2, v_2)}
\]  

(7)
The correlation coefficient $\rho(v_1, v_2)$ is defined:

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

(8)

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

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

(9)

The constant $\alpha$ is the scaling factor, and $\beta$ is a correlation enhance factor. The value of $\alpha$ 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.

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

(10)

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

(11)

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

(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\(_2\)O) absorption.

Figure S2. Spectral intensity changes extracted from the time-dependent ATR FTIR spectra of MXD6 during D\(_2\)O 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$_2$O 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 D₂O 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.

<table>
<thead>
<tr>
<th>Cross correlation peaks (cm⁻¹, cm⁻¹)</th>
<th>Sign in synchronous spectra</th>
<th>Sign in asynchronous spectra</th>
<th>Sequential order</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1632, 1537)</td>
<td>+</td>
<td>-</td>
<td>1632←1537</td>
</tr>
<tr>
<td>(1632, 1463)</td>
<td>+</td>
<td>+</td>
<td>1632→1463</td>
</tr>
<tr>
<td>(1632, 1421)</td>
<td>+</td>
<td>+</td>
<td>1632→1421</td>
</tr>
<tr>
<td>(1632, 700)</td>
<td>+</td>
<td>+</td>
<td>1632→700</td>
</tr>
<tr>
<td>(1537, 1463)</td>
<td>+</td>
<td>+</td>
<td>1537→1463</td>
</tr>
<tr>
<td>(1537, 1421)</td>
<td>+</td>
<td>+</td>
<td>1537→1421</td>
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<td>+</td>
<td>+</td>
<td>1463→1421</td>
</tr>
<tr>
<td>(1463, 700)</td>
<td>+</td>
<td>+</td>
<td>1463→700</td>
</tr>
<tr>
<td>(1421, 700)</td>
<td>+</td>
<td>+</td>
<td>1421→700</td>
</tr>
<tr>
<td>(1632, 1204)</td>
<td>+</td>
<td>+</td>
<td>1632→1204</td>
</tr>
<tr>
<td>(1463, 1204)</td>
<td>+</td>
<td>0</td>
<td>1463=1204</td>
</tr>
<tr>
<td>(1421, 1204)</td>
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<td>0</td>
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</tr>
<tr>
<td>(1204, 700)</td>
<td>+</td>
<td>-</td>
<td>1204←700</td>
</tr>
</tbody>
</table>

δ(N−H, bonded) → ν(C=O, bonded) → δ(C−H, −CH₂−NH−) → δ(C−H, −CH₂−CO−) → δ(−CH₂− benzene ring) → γ(−CH₂− skeleton, crystalline)

1537 cm⁻¹→1632 cm⁻¹→1463 cm⁻¹→1421 cm⁻¹→700 cm⁻¹→1204 cm⁻¹

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.

<table>
<thead>
<tr>
<th>Cross correlation peaks (cm⁻¹, cm⁻¹)</th>
<th>Sign in synchronous spectra</th>
<th>Sign in asynchronous spectra</th>
<th>Sequential order</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1632, 1463)</td>
<td>+</td>
<td>+</td>
<td>1632→1463</td>
</tr>
<tr>
<td>(1632, 1421)</td>
<td>+</td>
<td>+</td>
<td>1632→1421</td>
</tr>
<tr>
<td>(1632, 700)</td>
<td>+</td>
<td>0</td>
<td>1463→1421</td>
</tr>
<tr>
<td>(1463, 1421)</td>
<td>+</td>
<td>-</td>
<td>1421←700</td>
</tr>
<tr>
<td>(1463, 700)</td>
<td>+</td>
<td>+</td>
<td>1463=700</td>
</tr>
<tr>
<td>(1204, 700)</td>
<td>+</td>
<td>+</td>
<td>1204←700</td>
</tr>
</tbody>
</table>

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, −CH₂−NH−) = δ(C−H, −CH₂−CO−) = γ(−CH₂− 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.

<table>
<thead>
<tr>
<th>Cross correlation peaks (cm⁻¹, cm⁻¹)</th>
<th>Sign in synchronous spectra</th>
<th>Sign in asynchronous spectra</th>
<th>Sequential order</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1633, 1540)</td>
<td>+</td>
<td>-</td>
<td>1633←1540</td>
</tr>
<tr>
<td>(1633, 1476)</td>
<td>+</td>
<td>+</td>
<td>1633→1476</td>
</tr>
<tr>
<td>(1633, 1417)</td>
<td>+</td>
<td>+</td>
<td>1633→1417</td>
</tr>
<tr>
<td>(1540, 1476)</td>
<td>+</td>
<td>+</td>
<td>1540→1476</td>
</tr>
<tr>
<td>(1540, 1417)</td>
<td>+</td>
<td>+</td>
<td>1540→1417</td>
</tr>
<tr>
<td>(1476, 1417)</td>
<td>+</td>
<td>-</td>
<td>1476←1417</td>
</tr>
</tbody>
</table>

1540 cm⁻¹→1633 cm⁻¹→1417 cm⁻¹→1476 cm⁻¹

δ(N−H, bonded) → ν(C=O, bonded) → δ(C−H, −CH₂−CO−) → δ(C−H, −CH₂−NH−)