Electronic Supporting Information

Interplay between structure and relaxation in polyurea networks: the point of view from a novel method of cooperativity analysis of dielectric response

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Procedure for determination of the dc conductivity contribution from the electric modulus.

The complex electric modulus is defined as the inverse of the complex dielectric permittivity:

\[
M^*(\omega) = 1 / \varepsilon^*(\omega) = M'(\omega) + iM''(\omega) \tag{E1}
\]

which gives

\[
M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon^{12}(\omega) + \varepsilon'^2(\omega)}
\]

\[
M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon^{12}(\omega) + \varepsilon'^2(\omega)} \tag{E2}
\]

For pure dc-conductivity, there is no electronic conduction contribution to \( \varepsilon'(\omega) \), while \( \varepsilon''(\omega) = \sigma_0 / \omega \varepsilon_0 \). It can be demonstrated that

\[
M''(\omega) = M_\infty \frac{\omega \tau_{\text{cond}}}{1 + (\omega \tau_{\text{cond}})^2} \tag{E3}
\]

where \( \tau_{\text{cond}} = \varepsilon_0 \varepsilon_\infty / \sigma_0 \). Equation E3 is comparable to the imaginary component of a Debye relaxation process.

The electric modulus can be fitted then to

\[
M^*(\omega) = M_\infty + \frac{\Delta M_{\text{cond}}}{1 + (i\omega \tau_{\text{cond}})} + \sum_k \frac{\Delta M_k}{1 + (i\omega \tau_{M,k})^{a_{M,k}} b_{M,k}} \tag{E4}
\]

where \( \tau_{M,k} \) are the characteristic relaxation times in the modulus representation and \( \Delta M_k \) are the amplitudes for the electric modulus given by the difference between the limiting low and high frequency values of each process. Parameters \( a_{M,k} \) and \( b_{M,k} \) stand for the symmetric and asymmetric broadening of the relaxation. It should be pointed out, that the shape parameters in E4 do not correspond to those of the permittivity representation in eq. 1 of the main text. By fitting the electric modulus to expression E4, \( \sigma_0 \) can be determined as \( \varepsilon_0 \varepsilon_\infty / \tau_{\text{cond}} \). This value can then be fixed when performing the independent analysis of the complex dielectric permittivity according to equation 1 in main text. Examples of this approach are given in Figure S10.
Figure S10. Real part (empty dots) and imaginary part (empty squares) of the electric modulus (a and c) and of the dielectric permittivity (b and d) versus frequency for ED-4000 at a) and b) 20 °C and c and d) -20 °C. In the Modulus plots solid black lines represent best fit to Equation E4 (main text) and while in the permittivity plot they correspond to the results of independently fitting to equation 1 in the main text. Red and blue lines correspond to the devoncolution into the elementary modes $\alpha$ and $\alpha'$ obtained at each independent fit. Green lines correspond to the dc conductivity contribution.
Table S1. Cooperativity values ($N_\alpha$), radius of the cooperatively rearranging regions ($R_{\text{CRR}}$), soft domain average distance ($d_\alpha + d_{\alpha'}$), and thickness of the restricted mobility layer ($d_{\alpha'}$) at the temperature just above the glass transition temperature for the samples ED-2000 and ED-4000.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_\alpha$</th>
<th>$T$ (°C)</th>
<th>$R_{\text{CRR}}$ (nm)</th>
<th>SAXS $d_\alpha + d_{\alpha'}$ (nm)</th>
<th>$d_{\alpha'}$ (nm)</th>
<th>AFM $d_\alpha + d_{\alpha'}$ (nm)</th>
<th>$d_{\alpha'}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED-2000</td>
<td>84</td>
<td>-60</td>
<td>1.25</td>
<td>3.32</td>
<td>0.41</td>
<td>3.54</td>
<td>0.52</td>
</tr>
<tr>
<td>ED-4000</td>
<td>80</td>
<td>-67</td>
<td>1.23</td>
<td>5.52</td>
<td>1.53</td>
<td>5.82</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Table S2. Cooperativity values ($N_\alpha$), radius of the cooperatively rearranging regions ($R_{\text{CRR}}$), soft domain average distance ($d_\alpha + d_{\alpha'}$), and thickness of the restricted mobility layer ($d_{\alpha'}$) at -50 °C for the samples ED-2000 and ED-4000.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_\alpha$</th>
<th>$T$ (°C)</th>
<th>$R_{\text{CRR}}$ (nm)</th>
<th>SAXS $d_\alpha + d_{\alpha'}$ (nm)</th>
<th>$d_{\alpha'}$ (nm)</th>
<th>AFM $d_\alpha + d_{\alpha'}$ (nm)</th>
<th>$d_{\alpha'}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED-2000</td>
<td>71</td>
<td>-50</td>
<td>1.18</td>
<td>3.32</td>
<td>0.48</td>
<td>3.54</td>
<td>0.59</td>
</tr>
<tr>
<td>ED-4000</td>
<td>49</td>
<td>-50</td>
<td>1.05</td>
<td>5.52</td>
<td>1.71</td>
<td>5.82</td>
<td>1.86</td>
</tr>
</tbody>
</table>