Effect of Thermal History on the Microstructure of a Poly(tetramethylene oxide) Based Polyurea

Alicia M. Castagna, [‡,†] Autchara Pangon,[‡] Gregory P. Dillon,[§] and James Runt*[,‡]

[‡]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

[§]Applied Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

* To whom correspondence should be addressed; Tel.: +1-814-863-2749; E-mail:

runt@matse.psu.edu (J. Runt).

[†]Present address: DuPont Central Research and Development, Wilmington, DE 19880, USA

Supporting Information

I. ATR-FTIR: Determination of chemical stability of the polyurea treated at different temperatures

Unannealed P1000 films were heated in an oven at ambient atmosphere to selected temperatures, and cooled naturally to room temperature. ATR-FTIR measurements were then conducted at room temperature using 200 scans and resolution of 2 cm^{-1}. ATR-FTIR spectra of the thermally treated samples are displayed in Figure S1.
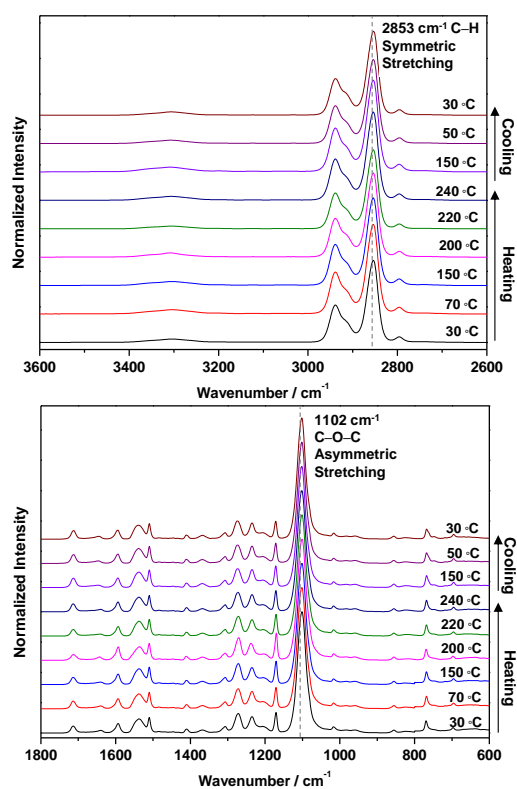

Figure S1. ATR-FTIR spectra of the mMDI − P1000 polyurea treated at different heating and cooling temperatures.

Average integral ratios of A_{C-O-C}/A_{CH2} were evaluated by curve fitting the FTIR spectra in Figure S1. A plot of A_{C-O-C}/A_{CH2} as a function of treatment temperature is displayed in Figure

S2. Taking into consideration experimental uncertainties associated with the curve fitting, we estimate the uncertainty of the points in Figure S2 to be ~12% of the reported values.
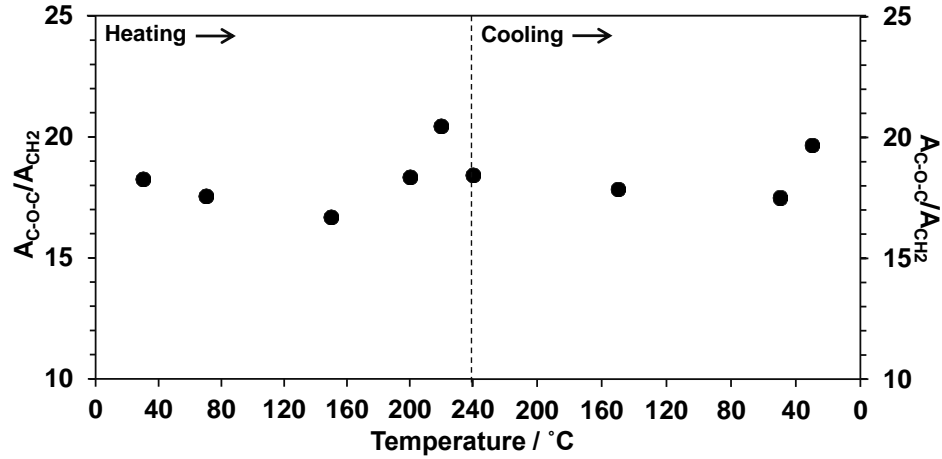

Figure S2. Plot of A_{C-O-C}/A_{CH2} as a function of treatment temperature on heating and cooling.

II. SAXS: Calculation of boundary and intermixing effects

The contribution of interface boundary diffuseness and unlike segment mixing is determined from absolute SAXS intensity. Assuming a sigmoidal-gradient profile for the interfacial boundary, the background corrected scattering intensity can be written, at large q:[43,44]

$$I_{obs}(q) = I(q) - I_b(q) = I_{id}(q)H^2(q) = I_{id}(q)\exp(-\sigma^2 q^2) = I_{id}(q)(1 - \sigma^2 q^2) \quad (S1)$$

where $I_{id}(q)$ is the ideal scattering intensity, $H(q)$ is the Fourier transform of a smoothing function characterizing the shape and size of the diffuse boundaries, and σ is the width of the boundary layer. From Porod's Law,[43] eqn (S1) can be written as:

$$I_{obs}(q) = \frac{K}{q^4}(1 - \sigma^2 q^2) \quad (S2)$$

where K and σ are estimated from intercept and slope the of plot between $I(q)q^4$ and q^2 at large q.[45]

An additional electron density variance ($\overline{\Delta\eta^{2''}}$) can also be determined, which removes the scattering contribution from diffuse interfacial boundaries:[9,12]

$$\overline{\Delta\eta^{2''}} = c\int_0^\infty \frac{[I(q)-I_b(q)]q^2}{H^2(q)}dq, \tag{S3}$$

where $H(q) = \exp(-\frac{\sigma^2 q^2}{2})$. It follows that $\left|\overline{\Delta\eta^{2'}}-\overline{\Delta\eta^{2''}}\right|/\overline{\Delta\eta_c^2}$ represents the scattering contribution from boundary diffuseness, and $\left|\overline{\Delta\eta^{2''}}-\overline{\Delta\eta_c^2}\right|/\overline{\Delta\eta_c^2}$ is a measure of the influence of intermixed segments on overall phase separation. The electron density variance $\overline{\Delta\eta^{2''}}$, boundary effect, and intermixing contribution to the experimental scattering at different annealing temperatures are summarized in Table S1.

Table S1

$\overline{\Delta\eta^{2"}}$, boundary effect, and intermixing contribution for mMDI – P1000 polyureas before and after annealing

P1000 Polyurea	$\overline{\Delta\eta^{2"}}$ x10^{-3}	Boundary effect $\left\|\overline{\Delta\eta^{2'}}-\overline{\Delta\eta^{2"}}\right\|/\overline{\Delta\eta_c^2}\times100$ (%)	Intermixing effect $\left\|\overline{\Delta\eta^{2"}}-\overline{\Delta\eta_c^2}\right\|/\overline{\Delta\eta_c^2}\times100$ (%)
Unannnealed	3.36	21	40
Annealed at 120 ˚C	3.08	16	45
Annealed at 150 ˚C	3.45	17	38
Annealed at 170 ˚C	2.94	13	48

*The units of electron density variances are (mol e$^-$ cc^{-1})^2 and the ideal electron density variance

($\overline{\Delta\eta_c^2}$) is 5.6 x 10^3 (mol e$^-$ cc^{-1})^2 for all materials.