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Supporting Information

Urea as a Monomer: Synthesis and Characterization of Semi-Aromatic Thermoplastic Non-Isocyanate Polyureas

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Detailed Methods.

SAXS/WAXS Measurements.

Small and wide-angle X-ray scattering (SAXS/WAXS) measurements were performed on a Xenocs Xeuss 3.0 (GI-)SAXS/WAXS/USAXS instrument. A GeniX3D Cu High Flux Very Long(HFVL) focus source was used to produce an 8 keV Cu K alpha collimated X-ray beam with a wavelength of 1.542 Å (generated at 50 kV and 0.6 mA). A windowless EIGER2 R 1 M DECTRIS Hybrid pixel photon counting detector was used to collect the scattering signal at the sample-to-detector distances of 50 mm, 370 mm, 900 mm, and 1800 mm (denoted as WAXS, MAXS, SAXS, and ESAXS in the Xeuss system) to cover a broad Q range between ~0.003 Å¹ and ~3.64 Å¹. A standard configuration was used for WAXS with a beam size of 0.7 mm, for MAXS with a beam size of 0.7 mm, for SAXS with a beam size of 0.5 mm, and for ESAXS with a beam size of 0.25 mm. A solid stage was used to mount the polymer samples with measuring times of 5 mins for WAXS, 10 mins for MAXS, 15 mins for SAXS, and 20 mins for ESAXS. An empty background for the same amount of time was also measured with the same configuration conditions. Each raw 2D scattering image was reduced by azimuthal averaging over 360° to produce a 1D scattering curve that considered geometrical corrections and transmitted intensity. Gaps between two detector modules, pixels near the direct beam, and invalid pixels were masked during the data reduction. Each 1D scattering curve of the sample was subtracted by the corresponding empty background signal and sample thickness for absolute intensity normalization and merged accordingly.

Atomic Force Microscopy Measurements.

Three polyurea samples with varying compositions were prepared for AFM analysis. Specimens were mounted on 12 mm diameter specimen discs using double-sided tape, with care taken to minimize air bubbles between the tape and disc surface. Samples were cut to appropriate dimensions (~12 mm) using a razor blade and secured to the tape to reduce tilt. Imaging was performed using a Bruker MM8 HR system equipped with a standard head and NanoScope V controller. Images were acquired using NanoScope Research software and processed with NanoScope Analysis. All measurements were conducted in "Soft Tapping in Air" intermittent contact mode using NuNano Scout 350 SS RAIs probes. Scan parameters are available with their respective image pairs in the results section.

DOSY Experiment.

Diffusion-ordered spectra were recorded by the pulsed-gradient stimulated-echo (PGSTE) method on a Magritek Spinsolve 80 MHz benchtop NMR spectrometer equipped with a 0.5 T m⁻¹ gradient coil. Each polymer solution and a 1.22 kDa polystyrene reference (PSS Polymer Standards Service GmbH) were prepared at 10 mg/mL in anhydrous DMSO-d₆ containing 50 mM LiBr, filtered through 0.45 µm PTFE syringe filters, and 0.60 mL portions were transferred

to 5 mm thin-wall, non-spinning tubes. The PGSTE acquisition employed eight scans with an acquisition time of 3.3 s, a 10 s recycle delay, a gradient pulse duration (δ) of 5 ms, a diffusion delay (Δ) of 100 ms, and eight gradient amplitudes spanning 2–90 % of the 0.40 T m⁻¹ maximum, corresponding to a maximum of 3.5×10^{10} s m⁻². Each experiment required approximately 11 min, after which spectra were apodised with a 0.3 Hz Lorentzian–Gaussian function, and diffusion coefficients (D) were extracted by mono-exponential fitting of the highest signal to noise backbone peaks for subsequent molecular-weight calculations.

Weight-average molecular weights (M_w) were obtained by comparing the diffusion coefficient of each polymer to that of the polystyrene reference according to:

$$M_{w(poly)} = M_{w(std)} \times \left(D_{std}/D_{poly}\right)^{(1/0.55)}$$

where $M_{w(poly)}$ is the weight-average molar mass of the polymer, $M_{w(std)}$ is the weight-average molar mass of the polystyrene standard (1.22 kDa), D_{poly} and D_{std} are the self-diffusion coefficients of the polymer and standard, respectively, and 0.55 is the Flory–Fox exponent for flexible coils.

Supplementary Figures.



Figure S1. Representative tensile stress-strain curves (5 runs per sample) for poly(EBA)-co-poly(PPD) copolymers. (a) 5 wt.% PPD synthesized without TBD catalyst. (b) 5 wt.% PPD synthesized with TBD catalyst. (c) 10 wt.% PPD synthesized with TBD catalyst. (d) 20 wt.% PPD synthesized with TBD catalyst. Tests were conducted at a crosshead speed of 10 mm/min according to ASTM D638 Type V. The comparison between (a) and (b) highlights the significant improvement in mechanical properties upon addition of the TBD catalyst.



Figure S2. Normalized ATR-FTIR spectra (fingerprint region, 1800-1000 cm⁻¹) of poly(EBA)-copoly(PPD) copolymers containing 5 wt.% (yellow), 10 wt.% (maroon), and 20 wt.% (grey) pphenylenediamine (PPD). Characteristic peaks include the urea C=O stretch (Amide I, ~1630 cm⁻¹), N-H bending/C-N stretching (Amide II, ~1540 cm⁻¹), and aromatic C=C-C stretching (~1457 cm⁻¹).



Figure S3. Dynamic Mechanical Analysis (DMA) thermograms for poly(EBA)-co-poly(PPD) copolymers showing Storage Modulus (G', yellow), Loss Modulus (G'', maroon), and Tan Delta (tan δ , grey) as a function of temperature for samples containing: (a) 5 wt.% PPD, (b) 10 wt.% PPD, and (c) 20 wt.% PPD. Experiments were conducted at 1 Hz, 0.1% strain, with a heating rate of 3°C/min. The primary relaxation (peak in tan δ) corresponds to the glass transition (T_g).



Figure S5. Two-dimensional SAXS/WAXS patterns of poly(EBA)-*co*-poly(PPD) films recorded at room temperature ($\lambda = 1.542$ Å, Cu Ka; sample-detector distance = 900 mm). (a) 5 wt % PPD, (b) 10 wt % PPD, (c) 20 wt % PPD. All three samples display isotropic diffuse halos with no Bragg reflections or azimuthal anisotropy, confirming the absence of long-range crystalline order or oriented hard-segment domains in these copolymers.



Figure S6. Small-angle and wide-angle X-ray scattering analysis of poly(EBA)-co-poly(PPD) copolymers with varying PPD content presented as individual plots. Top panels (a-c) show Lorentz-corrected SAXS data (I·q² vs. q) for samples containing 5 wt.%, 10 wt.%, and 20 wt.% PPD, respectively, to enhance structural features and probe for potential microphase separation. Bottom panels (d-f) display corresponding WAXS profiles (intensity vs. q) for the same samples showing the characteristic amorphous halo. The Lorentz-corrected SAXS data reveal no distinct peaks or pronounced features that would indicate nanoscale phase separation, while the WAXS profiles confirm the predominantly amorphous nature of all compositions with the main peak around q ≈ 1.5 Å⁻¹ corresponding to average interchain spacing. The absence of characteristic correlation peaks in the SAXS region (typically d $\approx 100-300$ Å for microphase-separated domains) provides strong evidence for homogeneous morphology regardless of PPD content.



Figure S7. Photographs of each of the polymer films a) 5 wt. % PPD b) 10 wt. % PPD and c) 20 wt. % PPD. As PPD content increases the films become more yellow/orange, however, all are transparent.



Figure S8. Solvent screening at 50 °C for 24 h in 1 mL of each respective solvent on the 5 wt. %, 10 wt.%, and 20 wt. % PPD films, from left to right. From left to right the solvents are THF, DMF with 0.1 M LiBr, NMP, DMSO with 1 M LiBr, and HFIP. The top panels a-c show the films in solvent immediately after addition and the bottom panels d-f show the film pieces after 24h at 50 °C. In all cases, HFIP and 1M LiBr in DMSO swelled the films by the largest margin, however, none dissolved. All other solvents swelled the polymers minimally.



Figure S9. Identifiable structural units present in the prepolymerization products as determined by ¹H NMR analysis with marron circles representing continuation of the polymer chain.



Figure S10. ¹H NMR spectrum (500 MHz, DMSO-d₆) of oligomeric products obtained from the TBDcatalyzed prepolymerization reaction containing 5 wt.% PPD after heating at 170°C for 1 h under nitrogen. The spectrum reveals three distinct product types: two different polymer sections with varying chain lengths and compositions, and a small molecule identified as the mono urea PPD compound. Peak assignments are indicated by colored symbols corresponding to the structural diagram. ¹H NMR (500 MHz, DMSO-d₆) δ 8.37 (s, 0.06H), 8.02 (s, 0.04H), 7.22 (s, 0.12H), 6.99 (d, J = 8.2 Hz, 0.08H), 6.46 (d, J = 8.3 Hz, 0.08H), 6.02 (t, J = 5.7 Hz, 2.21H), 5.50 (s, 0.36H), 4.66 (s, 0.08H), 3.50 (s, 4.00H), 3.38 (t, J = 5.7 Hz, 4.00H), 3.14 (q, J = 5.7 Hz, 4.01H). Integration analysis confirms that the total PPD content distributed between the small molecule and polymer fractions equals the theoretical 7 mol% added to the reaction, with approximately 3 mol% incorporated into the polymer network, demonstrating quantitative retention of the aromatic diamine during the prepolymerization stage.



Figure S11. ¹³C NMR spectrum (126 MHz, DMSO-d₆) of TBD-catalyzed prepolymerization products. ¹³C NMR (126 MHz, DMSO-d₆) δ 159.19, 158.48, 156.17, 155.82, 134.75, 130.00, 120.70, 118.85, 114.62, 72.82, 70.59, 70.46, 70.36, 70.03, 60.70, 46.73, 39.95, 38.06, 20.74 ppm. The spectrum confirms the presence of multiple urea carbonyl environments (155-159 ppm), aromatic carbons from incorporated PPD units (114-135 ppm), and aliphatic carbons from EBA segments (38-73 ppm), supporting the structural diversity observed in the corresponding ¹H NMR analysis.



Figure S12. ¹H NMR spectrum (500 MHz, DMSO-d₆) of uncatalyzed prepolymerization products showing reduced oligomer formation compared to TBD-catalyzed reaction. The spectrum reveals the same three structural types as the catalyzed reaction but with altered distributions. Peak assignments are indicated by colored symbols corresponding to the structural diagram. ¹H NMR (500 MHz, DMSO-d₆) δ 8.35 (s, 0.02H), 8.00 (s, 0.04H), 7.22 (s, 0.04H), 6.99 (d, J = 8.6 Hz, 0.08H), 6.46 (d, J = 8.7 Hz, 0.08H), 6.01 (t, J = 5.7 Hz, 2.07H), 5.49 (s, 0.25H), 4.66 (s, 0.08H), 3.50 (s, 4.00H), 3.37 (t, J = 5.7 Hz, 4.00H), 3.14 (q, J = 5.7 Hz, 4.00H). Integration analysis indicates only approximately 1 mol% PPD incorporation into the polymer network with 4 mol% present as mono urea PPD compound, leaving 2 mol% unaccounted for, likely due to volatilization during heating, demonstrating reduced PPD retention and network incorporation compared to the TBD-catalyzed reaction.



Figure S13. ¹³C NMR spectrum (126 MHz, DMSO-d₆) of uncatalyzed prepolymerization products. ¹³C NMR (126 MHz, DMSO-d₆) δ 159.17, 158.47, 156.16, 155.81, 143.88, 129.99, 120.70, 118.85, 115.88, 114.62, 72.82, 70.59, 70.47, 70.36, 70.21, 70.03, 60.70, 39.96 ppm. The spectrum confirms the presence of multiple urea carbonyl environments (155-159 ppm), aromatic carbons from PPD units (114-144 ppm), and aliphatic carbons from EBA segments (39-73 ppm), consistent with the reduced oligomerization observed in the corresponding ¹H NMR analysis.



Figure S14. Diffusion-ordered ¹H NMR spectroscopy (DOSY) analysis of prepolymerization products for molecular weight determination. Left panels show DOSY spectra with diffusion-encoded regions highlighted, and right panels display corresponding diffusion coefficient plots with two different integration regions per sample. (a,b) Polystyrene reference standard (1.22 kDa) with diffusion coefficient D = 1.213×10^{-10} m²/s. (c,d) TBD-catalyzed oligomers (M_w = 4200 g/mol) with diffusion coefficients D = 6.142×10^{-11} m²/s (green) and D = 6.011×10^{-11} m²/s (red). (e,f) Uncatalyzed oligomers (M_w = 5000 g/mol) with diffusion coefficients D = 5.589×10^{-11} m²/s (green) and D = 5.736×10^{-11} m²/s (red). The two integration regions represent different peaks from the same polymer chains and should theoretically be identical but show slight differences likely due to signal-to-noise variations. The lower molecular weight of TBD-catalyzed oligomers likely results from the increased incorporation of less nucleophilic aromatic amines, which slows chain growth compared to the uncatalyzed system.



Figure S15. ¹H NMR spectrum of urea (Bruker Avance NEO 500 MHz, DMSO-d₆, 298 K). δ 5.58 ppm (s, 2 H, NH₂); residual solvent DMSO-d₆ at 2.54 ppm (s, 1 H).



Figure S16. ¹³C NMR spectrum of urea (Bruker Avance NEO 500 MHz, DMSOd₆, 298 K). δ 160.1 ppm (C=O); residual solvent DMSO-d₆ at 39.5 ppm.



Figure S17. ¹H NMR spectrum of 1,2-bis(2-aminoethoxy)ethane (Bruker Avance NEO 500 MHz, DMSO-d₆, 298 K) δ 3.50 ppm (s, 4 H, O–CH₂), 3.35 ppm (t, J = 5.8 Hz, 4 H, O–CH₂–CH₂), 2.64 ppm (t, J = 5.9 Hz, 4 H, CH₂–NH₂), 1.26 ppm (s, 4 H, NH₂); residual DMSO-d₆ at 2.50 ppm (s, 1 H).



Figure S18. ¹³C NMR spectrum of 1,2-bis(2-aminoethoxy)ethane (Bruker Avance NEO 500 MHz, DMSO-d₆, 298 K) δ 73.18 ppm (O–CH₂–CH₂–O), 69.59 ppm (O–CH₂–CH₂–NH₂), 41.41 ppm (CH₂–NH₂); residual DMSO-d₆ at 39.52 ppm.



Figure S19. ¹H NMR spectrum of p-phenylenediamine (Bruker Avance NEO 500 MHz, DMSO-d₆, 298 K) δ 6.40 ppm (s, 4 H, Ar–CH), 4.15 ppm (s, 4 H, NH₂); residual DMSO-d₆ at 2.54 ppm (s, 1 H).



Figure S20. ¹³C NMR spectrum of p-phenylenediamine (Bruker Avance NEO 500 MHz, DMSO-d₆, 298 K) δ 138.91 ppm (C–NH₂), 115.43 ppm (Ar–CH); residual DMSO-d₆ at 39.52 ppm.