Supporting Information for “Model transient networks from strongly hydrogen bonded polymers”

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Figure 1 shows ¹H NMR characterization of the precursor (P(nBA-*r*-boc-AHA) and P(nBA-*r*-AHA) (TFA salt)) and MHB random copolymers (P(nBA-*r*-UPyA)), confirming boc deprotection and UPy functionalization. Additionally, FTIR analysis (Figure 2) shows a characteristic peak at 1698 cm⁻¹ attributed to the keto UPy tautomer. Wide angle x-ray scattering confirms the absence of stacking or crystallization of the UPy side chains.

Several possible methods for measuring τ_b^* , the effective bond lifetime in the reversible network, have been compared. Values presented in the main text were measured as the inverse of the frequency at which G' fell to 90% of its plateau value, since this is the timescale at which the reversible crosslinks begin to break. Alternatively, the G'/G''

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Figure 1: ^1H NMR characterization of UPy-based random copolymers (a: $\text{P}(\text{nBA-}r\text{-boc-AHA})$, b: $\text{P}(\text{nBA-}r\text{-AHA})$ (TFA salt), c: $\text{P}(\text{nBA-}r\text{-UPyA})$). The degree of incorporation of boc-AHA is calculated by comparing integration of peaks A and B in Figure 1a, full deprotection and TFA removal verified in Figure 1b, and extent of functionalization calculated by comparing integration of peaks A and L in Figure 1c.

Figure 2: FTIR characterization of UPy-based random copolymers. The peak at 1698 cm^{-1} present in P(nBA-*r*-UPyA) is characteristic of the keto UPy tautomer.¹

Figure 3: Wide angle x-ray scattering data for UPy containing random copolymers and high molecular weight (150 kg/mol) PnBA homopolymer. All materials show only two broad peaks due to amorphous scattering, confirming that no UPy stacks exist in these materials.

crossover frequency corresponds to the lifetime of the reversible network strands; this timescale is longer and reflects the final breaking of the strand. A comparison of the two measurements is shown in Figure 4. From the plot it appears that $\tau_b^*(\text{plateau falloff}) \sim \tau_b^*(\text{crossover})^{1/3}$.

Figure 4: Comparison of effective bond lifetime measured from the crossover of G' and G'' and the falloff of the plateau.

References

- (1) Hirschberg, J. H. K. K.; Beijer, F. H.; van Aert, H. A.; Magusin, P. C. M. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **1999**, 32, 2696–2705.