**[Quadruple hydrogen bond-containing A-AB-A triblock copolymers: Probing the influence of hydrogen bonding in the central block](https://acs.digitellinc.com/acs/live/22/page/677/5?eventSearchInput=&eventSearchDateTimeStart=&eventSearchDateTimeEnd=&eventSearchTrack%5b%5d=201" \l "sessionCollapse394071)**

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This work reveals the influence of pendant hydrogen bonding strength and distribution on self-assembly and the resulting thermomechanical properties of A-AB-A triblock copolymers. Inspired by complementary hydrogen bonding interactions between nucleobase pairs in DNA, we prepared cytosine acrylate (CyA) and ureidocytosine acrylate (UCyA)-functionalized A-AB-A triblock copolymers using reversible addition-fragmentation chain transfer (RAFT) polymerization. Thermal, thermomechanical, and morphological analysis revealed the microphase-separated structures of the triblock copolymers. CyA triblock copolymers exhibited a cylindrical microphase-separated morphology according to small-angle X-ray scattering. UCyA triblock copolymers bearing highly oriented quadruple hydrogen bonds promoted the central-external block interactions resulting in a more phase mixed structure than the CyA copolymers. Stronger physical crosslinks within UCyA copolymers extend the plateau modulus nearly 150 °C. Controlled microstructures resulted in A-AB-A UCyA triblock copolymers with superior tensile strength, extensibility, and toughness compared to the AB random copolymer and ABA triblock copolymer analogs. These experiments provided fundamental structure-property-processing relationships of the A-AB-A triblock copolymer tailoring of the self-association constants of the A unit and concentration of A unit in the central block. Balancing the design parameters as mentioned above offers a strategy of tuning thermomechanical and morphological properties of block copolymers.

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