

Foldamers as Cross-Links for Tuning the Dynamic Mechanical Property of Methacrylate Copolymers

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ABSTRACT: This paper reports a foldamer-based approach to modulating the thermal and mechanical properties of cross-linked *n*-butyl methacrylate copolymers. Intramolecularly hydrogen-bonding-induced folded aromatic amide segments were designed and prepared, which reacted with a salicylaldehyde-bearing prepolymer to form cross-linked copolymers. As a control, analogous aromatic cross-links incapable of forming discrete folded structures due to lack of specific intramolecular H-bonding were also prepared and incorporated into copolymers. From the two series of cross-linked copolymers, 18 films were prepared and characterized by dynamic mechanical analysis (DMA) as well as creep/recovery experiments. We show that, compared to the control, the discrete folded cross-links substantially improve the mechanical properties of the copolymers. We attribute this enhancement to the ability of the folded cross-links to reversibly reveal the hidden length on extension via dissipative cleavage of the intramolecular H-bonds.

Introduction

Cross-linked (co)polymers are an important family of thermoset elastomers that have a wide variety of industrial applications.¹ One strategy for preparing cross-linked polymers is to introduce cross-links between preformed linear polymers. Because crosslinking fundamentally enhances the three-dimensional networks of the polymers by preventing the flowing or slipping of the polymer chains, the resulting network can exhibit remarkably improved elastomeric properties.² Conventional cross-links consist of various covalently bonded chains. In searching for new more tunable and reversibly dissipative cross-linking modes, chemists have recently developed the biomimetic supramolecular strategy to build cross-links from dimeric segments that adopt discrete complementary noncovalent forces. In this context, electrostatic,³ metal-ligand,⁴⁻⁸ and hydrogen-bonding⁹⁻²¹ interactions have been successfully utilized for creating such reversible junctions. Concerning the hydrogen-bonding approach, quadruplehydrogen-bonded dimers have received particular attention^{15–21} due to their exceptional stability.^{22,23} Guan and co-workers have also reported a successful biomimetic design of reversibly unfolding macrocyclic cross-links in which a quadruple-hydrogenbonded dimer is incorporated.²⁴ The unfolding of the macro-cyclic cross-links can significantly enhance the mechanical properties of the cross-linked polymers.

Foldamers are synthetic oligomers that have folded conformations which are stabilized by intramolecular hydrogen bonds.²⁵ In this study, we incorporate hydrogen-bonding-driven aromatic amide-derived folding segments as the cross-links of *n*-butyl methacrylate copolymers.^{26–28} This family of foldamers has been well-established and used by us to create modular molecular tweezers and to direct the formation of several macrocyclic structures.^{28,29} It was envisioned that in the polymers the intramolecular hydrogen bonding would force the aromatic amide

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Figure 1. Schematic representation of the hydrogen-bonded foldamer cross-links in *n*-butyl methacrylate copolymers (green part). Heating or applying a stress causes the folded state (red part) to unfold or extend, while cooling or removing the stress results in the recovery of the folded state.

segments to adopt folded conformations (Figure 1). When a stress is applied to the material, the intramolecular hydrogen bonding should be broken to cause the segments to extend. Upon release of the stress, the intramolecular hydrogen bonding would be re-formed to force the segments to recover the folded conformations. Since the breaking of the hydrogen bonds are closely related to the unfolding or extending of the segments, the materials may exhibit new unique thermal and mechanical properties.²⁴ Herein we report the successful tuning of the thermal and mechanical properties of cross-linked *n*-butyl methacrylate copolymers using intramolecularly hydrogen-bonded foldamer-based cross-links. We demonstrate that this type of cross-link performs reversible folding—unfolding functions which are similar to those of intermolecularly hydrogen-bonded dimeric motifs.

Experimental Section

Methods. All reactions were carried out under a dry nitrogen atmosphere. All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials were obtained commercially and used without further

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purification. Analytical thin-layer chromatography was performed on 0.2 mm silica 60 coated on glass plates with F_{254} indicator. The NMR spectra were recorded on 300 or 400 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (¹H: chloroform: δ 7.26 ppm; DMSO: δ 2.50 ppm; ¹³C: CDCl₃: 77.2 ppm). Elemental analyses were carried out at the SIOC analytical center. Compounds **HB-1m**,³⁰ **1**,³¹ **2**,³² **4**,³³ **6**,³⁴ and **NB-3m**³⁵ were prepared according to the reported procedures.

Gel Permeation Chromatography (GPC). GPC analyses were carried out with Waters 1515 Isocratic HPLC pump and Waters 2487 dual absorbance detector. The flow rate was 1 mL/min in THF and 45 min per sample. The molecular weights were calculated relative to polystyrene.

Polarized Optical Microscopy (POM). POM images were obtained on an Olympus BX51 polarizing microscope equipped with a Linkam LTS350 hot stage. The heating rate was 5 $^{\circ}C/$ min. The temperature ranged from 25 to 150 $^{\circ}C$.

Wide-Angle X-ray Scattering (WAXS) Analysis. The WAXS data were collected on a Bruker Avance D8 X-ray diffractometer with a range from 2° to 40° for 20 min. The samples were about $15 \times 5 \times 0.1 \text{ mm}^3$ in size.

Dynamic Mechanical Analysis (DMA). DMA analyses were performed in the tensile mode on a TA Instruments Q800 Series DMA under a nitrogen atmosphere with a gas-cooling accessory. The dimensions of the films tested were usually $15 \times 5 \times 0.1 \text{ mm}^3$. The dynamic tests for the determination of T_g values were performed at a heating rate of 3 °C/min and a frequency of 1 Hz. The T_g values were reported by the peaks on the loss modulus curves. The temperature range was from -10 to 80 °C. Each measurement was performed at 40 °C and at a stress of 0.25 or 1.0 MPa and a creep time of 10, 20, or 40 min, followed by a recovery time of 20-40 min. Each measurement was performed three times.

Compound HB-3m. To a stirred solution of diacid 1 (1.57 g, 8.00 mmol) in dichloromethane (50 mL) in a round flask, cooled in an ice bath, were added dropwise oxalyl chloride (3.50 mL, 40.0 mmol) and DMF (0.05 mL). After stirring for 2 h, the solution was concentrated under reduced pressure. The obtained residue was dissolved in dichloromethane (50 mL), and the solution was added dropwise to a stirred solution of compound **HB-1m** (4.11 g, 18.4 mmol) in triethylamine (22 L, 0.15 mol) at 0 °C. The mixture was stirred for 12 h and then concentrated with a rotavapor. The resulting residue was dissolved in dichloromethane (50 mL), and the solution was washed with a saturated sodium bicarbonate solution (25 mL), water (25 mL \times 2), and brine (25 mL) and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the crude product was purified by column chromatography (AcOEt/CH₂Cl₂/petroleum ether 1:3:3 v/v/v) to give compound **HB-3m** as a white solid (2.47 g, 53%). ¹H NMR (400 MHz, CDCl₃): δ 9.94 (s, 2H), 8.30 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 0.8 Hz, 2H), 7.45 (t, J = 8.0 Hz, 1H), 6.40 (d, J = 0.8Hz, 2H), 4.04 (s, 3H), 3.84 (s, 6H), 3.75 (br, 4H), 2.30 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 162.4, 155.7, 138.9, 135.3, 135.1, 134.3, 131.5, 128.1, 125.7, 112.7, 111.3, 64.5, 59.6, 21.5. MS (ESI) m/z: 465.1 [M + H]⁺. HRMS (MALDI-FT): Calcd for C₂₆H₃₀- $N_3O_5 [M + H]^+$: 464.2186. Found: 464.2129.

Compound 3. To a stirred solution of compound 2(1.31 g, 4.45 mmol) in dichloromethane (25 mL) in a round flack, cooled in an ice bath, were add oxalyl chloride (0.85 mL, 9.75 mmol) and DMF (0.1 mL). The mixture was stirred for 1 h and then concentrated under reduced pressure. The resulting residue was dissolved in THF (30 mL), and the solution was slowly added to a solution of compound **HB-3m** (1.03 g, 2.22 mmol) in triethylamine (1 mL) and THF (30 mL). The solution was stirred for 12 h, and then the solvent was removed with a rotavapor. The resulting residue was dissolved in dichlromethane (50 mL). After work-up, the crude product was subjected to column

chromatography (AcOEt/CH₂Cl₂ 1:20 v/v) to give compound **3** as a white solid (1.62 g, 70%). ¹H NMR (300 MHz, CDCl₃): δ 10.00 (s, 2H), 9.49 (s, 2H), 9.21 (d, J = 6.0 Hz, 2H), 8.38 (dd, $J_1 = 9.0$ Hz, $J_2 = 1.8$ Hz, 2H), 8.22 (s, 1H), 8.20 (s, 3H), 8.08 (s, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 9.0 Hz, 2H), 4.33 (t, J = 6.9 Hz, 4H), 4.13 (s, 3H), 3.83 (s, 6H), 2.44 (s, 6H), 1.96–1.90 (m, 4H), 1.46–1.41 (m, 4H), 1.33–1.07 (m, 16H), 0.77 (t, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 163.2, 161.2 (d), 156.0, 142.2, 137.7, 135.8, 134.9, 131.1, 130.7, 129.0, 128.8, 128.7, 125.8, 122.9, 119.0, 118.0, 113.2, 71.2, 64.5, 61.3, 31.8, 29.4, 29.3, 28.9, 26.0, 22.7, 22.1, 14.2. MS (MALDI-TOF): m/z 1041.4 [M + Na]⁺. Anal. Calcd for C₅₅H₆₆N₆O₁₃: C, 64.82; H, 6.53; N, 8.25. Found: C, 65.30; H, 6.73; N, 7.75.

Compound 5 was prepared as a pale yellow solid from the reaction of compounds **NB-3m** and **4** in 78% yield by using a procedure similar to that described for compound **3**. ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.67 (s, 2H), 10.53 (s, 2H), 8.82 (s, 2H), 8.57 (s, 1H), 8.44 (s, 3H), 8.40 (s, 2H), 8.17 (d, *J* = 6.9 Hz, 2H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.73 (t, *J* = 1.8 Hz, 2H), 7.55 (s, 3H), 7.36 (t, *J* = 6.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 165.5, 163.7, 148.0, 139.6, 139.2, 136.6, 135.4, 134.5, 131.1, 130.5, 129.1, 128.9, 127.4, 126.5, 122.8, 116.7, 116.6, 113.3. MS (MALDI-TOF): *m*/*z* 666.2 [M + Na]⁺. HRMS (MALDI-FT): Calcd for C₃₄H₂₄N₆O₈Na [M + Na]⁺: 667.1553. Found: 667.1551.

Compound HB-5m. A suspension of compound 3 (2.12 g, 2.08 mmol) and Raney nickel (0.50 g, 25% w/w) in THF (200 mL) was stirred under 40 atm of hydrogen gas at 60 °C for 20 h and then cooled to room temperature. The solid was filtrated off (caution! the solid may spontaneously ignite), and the filtrate was concentrated with a rotavapor. The resulting residue was recrystallized from methanol to give compound HB-5m as a white solid (1.99 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ 10.41 (s, 2H), 9.68 (s, 2H), 8.26 (d, J = 7.6 Hz, 2H), 8.19 (s, 2H), 8.05(s, 2H), 7.67 (d, J = 2.7 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 6.89 -6.81 (s, 4H), 4.17-4.10 (m, 6H), 3.83 (s, 6H), 3.75 (s, 3H), 3.70 (s, 3H) 2.41 (s, 6H), 1.85-1.80 (m, 4H), 1.38-1.05 (m, 20H), 0.76 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 174.3, 166.4, 165.8, 158.8, 154.0, 141.5, 140.5, 138.3, 138.2, 134.2, 134.1, 131.2, 128.8, 125.3, 124.5, 122.5, 121.7, 120.1, 117.9, 73.59, 67.4, 64.1, 63.6, 34.7, 32.3, 32.2, 32.1, 29.0, 25.6, 25.0, 24.33, 17.4, 17.2. MS (MALDI-TOF): *m*/*z* 981.7 [M + Na⁺]. HRMS (MALDI-FT): Calcd for $C_{55}H_{70}N_6O_9Na[M + Na]^+$: 981.5102. Found: 981.5101.

Compound NB-5m. A suspension of compound **5** (0.10 g, 0.16 mmol), ammonium formate (0.14 g, 2.05 mmol), and Pd-C (10 mg, 10%) in N,N-dimethylacetamide (25 mL) was stirred at 50 °C for 12 h and then cooled to room temperature. The solid was filtrated off, and the filtrate was concentrated with a rotavapor. The resulting residue was recrystallized from methanol and chloroform (1:1) to give compound NB-5m as a white solid (70 mg, 77%). ¹H NMR (300 MHz, DMSO- d_6): δ 10.48 (s, 2H), 10.15 (s, 2H), 8.55 (s, 1H), 8.32 (s, 2H), 8.15 (d, J = 7.5 Hz, 3H),7.70 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 6.3 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 8.4 Hz, 2H), 6.76 (d, J = 7.5 Hz, 2H), 5.50 (br, 3H). ¹³C NMR (100 MHz, DMSO- d_6): δ 165.5, 163.7, 148.0, 139.6, 139.2, 136.6, 135.4, 134.5, 131.1, 130.5, 129.1, 128.9, 127.4, 126.5, 122.8, 116.7, 116.6, 113.3. MS (MALDI-FT): m/z 585.2 [M + H]⁺. HRMS (MALDI-FT): Calcd for $C_{34}H_{29}N_6O_4$ [M + H]⁺: 585.2250. Found: 585.2259.

Compound 7. A solution of compound **6** (1.46 g, 4.45 mmol), methacrylic acid (2 mL, 23.5 mmol), 1,4-hydroquinone (0.20 g), and *p*-toluenesulfonic acid (0.20 g) in toluene (150 mL) was refluxed azeotropically for 6 h and then cooled to room temperature. The solution was washed with saturated sodium bicarbonate solution (100 mL × 2), water (100 mL), and brine (100 mL) and dried over sodium sulfate. The solvent was then removed with a rotavapor to give compound 7 as an oily solid (1.65 g, 97%). ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.13 (t, *J* = 6.6 Hz, 2H),

Chart 1. Structures of Precursors and Polymers



4.03 (t, J = 6.6 Hz, 2H), 2.45 (s, 3H), 1.94 (s, 3H), 1.65–1.60 (m, 4H), 1.27–1.20 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 144.2, 136.1, 132.8, 129.4, 127.4, 124.7, 70.2, 64.3, 28.9, 28.8, 28.7, 28.4 (d), 28.1, 25.5, 24.9, 21.2, 17.9. MS (EI): m/z 396 [M]⁺. Anal. Calcd for C₂₁H₃₂O₅S: C, 63.61; H, 8.13. Found: C, 63.94; H, 8.22.

Compound 9. A suspension of compounds 7 (1.10 g, 2.87 mmol), 8 (0.44 g, 3.15 mmol), potassium bicarbonate (0.32 g, 3.15 mmol), and potassium iodide (0.50 g, 3.01 mmol) in dried acetone (50 mL) was refluxed for 48 h and then concentrated with a rotavapor. The resulting slurry was triturated with ethyl acetate (150 mL). The organic phase was washed with saturated sodium bicarbonate solution (50 mL), water (50 mL), and brine (50 mL) and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the resulting residue was subjected to column chromatography to give compound 9 as a white solid (0.87 g, 84%). ¹H NMR (300 MHz, CDCl₃): δ 11.49 (s, 1H), 9.71 (s, 1H), 7.42 (d, J = 8.7 Hz, 1H), 6.52 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.7$ Hz, 1H), 6.41 (d, J = 2.7 Hz, 1H), 6.10 (s, 1H), 5.55 (s, 1H), 4.13 (t, J = 6.6 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 1.94 (s, 3H), 1.64-1.58 (m, 2H), 1.55–1.50 (m, 2H), 1.27–1.20 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 193.8, 167.0, 166.0, 164.0, 136.1, 134.7, 124.7, 114.5, 108.2, 100.6, 68.1, 64.3, 28.9, 28.8, 28.7, 28.4, 28.1, 25.5, 25.4, 17.9. MS (EI): m/z 362 [M]⁺. Anal. Calcd for C₂₁H₃₀O₅: C, 69.59; H, 8.34. Found: C, 69.87; H, 8.06.

Prepolymer PP. A solution of *n*-butyl methacrylate (3.49 g, 25.0 mmol), compound **9** (0.36 g, 1.00 mmol), and AIBN (4.1 mg, 0.025 mmol) in THF (7.5 mL) was refluxed for 60 h and then concentrated with a rotavapor to about 3 mL. The polymer was precipitated into methanol (25 mL). The precipitate was filtrated and rinsed with methanol and then dried in vacuo to give **PP** as a white solid (3.46 g, 88%). GPC (THF): M_w 1.4 × 10⁵, M_n 0.9 × 10⁵, MWD = 1.53. ¹H NMR (400 MHz, CDCl₃): δ 11.47 (s, 4H), 9.71 (s, 4H), 7.40 (s, 4H), 6.53 (s, 4H), 6.40 (s, 4H), 6.09 (s, 1H), 5.54 (s, 1H), 3.95 (s, 198H), 1.93 (s, 81H), 1.81 (s, 80H), 1.61 (s, 200H), 1.40 (s, 259H), 0.95 (s, 546H). ¹³C NMR (101 MHz, CDCl₃): δ 194.2, 178.1, 177.7, 177.4, 176.6, 175.9, 166.3, 164.4, 136.4, 135.1, 125.0, 114.9, 108.6, 100.9, 68.4, 64.6, 54.2, 52.2, 45.0, 44.6, 30.2, 30.1, 29.3, 29.1, 28.8, 28.5, 28.0, 25.8, 19.2, 18.3, 16.4, 13.6. IR (KBr): 1727 and 1630 cm⁻¹.

Typical Procedure for the Film Casting of the Cross-Linked Copolymers. Prepolymer PP (1.00 g) and the corresponding diamine (1.00 mmol) were dissolved in THF (10 mL). The

solution was added in a Teflon mold (200 mm \times 50 mm \times 2 mm). After the solvent was evaporated, the mold was gradually heated to 80 °C and kept at this temperature for 48 h and then at 50 °C for another 12 h in vacuum. After cooling to room temperature, the obtained cross-linked film was easily detached from the mold. The film thickness was about 0.1 mm. An extraction experiment (see Supporting Information) was performed in chloroform, which showed that most of the diamine (>95%) was consumed.

Results and Discussion

Design and Synthesis. Two series of diamines, that is, **HB**-*n***m** and **NB**-*n***m** (n = 1, 3, 5): the number of the benzene rings; HB: hydrogen bonding, NB: non-hydrogen bonding, m: monomer), were designed and synthesized (Chart 1). Their reactions with prepolymer (PP) produced cross-linked polymers **HB**-*n***p** and **NB**-*n***p** (n = 1, 3, 5, p: polymer) via the formation of two imine bonds. n-Butyl methacrylate was chosen as the primary monomer in the random copolymers due to its low glass transition temperature ($T_g = \sim 20$ °C).³⁶ The salicylaldehyde unit was chosen for cross-linking because its hydroxyl group would substantially stabilize the imine linkage due to the formation of a six-membered $O-H \cdots N(=C)$ hydrogen bond.³⁷ HB-3m and HB-5m could form four and eight intramolecular hydrogen bonds, respectively. Because they are all located toward the internal cavity of the aromatic backbones, we envisioned that these hydrogen bonds should exist in the designed polymers and induce them to adopt folded conformations. In contrast, compounds NB-3m and NB-5m do not form similar hydrogen bonds and thus were expected to have random conformations. A comparison of their thermal and mechanical properties would reveal the functions of the hydrogen-bonded folded segments in the first series of polymers.

The synthetic routes for the precursors and polymers are summarized in Scheme 1. **HB-3m** was first prepared from diacid 1 and **HB-1m** in 53% yield. The trimer was then further coupled with acid 2 to give 3 in 53% yield. Intermediate 3 underwent Raney nickel-catalyzed hydrogenation to produce **HB-5m** in nearly quantitative yield. The two *n*-octyl chains enabled a good solubility for 3 and **HB-5m**.



Scheme 1. Synthesis of HB-3m, HB-5m, NB-5m, Prepolymer PP, and Cross-Linked Polymers HB-nP and NB-np

We initially performed the reaction of **HB-3m** with the methoxyl analogue of **2** to prepare an intermediate that was similar to **3**. The resulting product was found to have a very poor solubility and thus could not be used for the next reaction. For the preparation of **NB-5m**, pentamer **5** was first obtained from the reaction of **NB-3m** with **4**. Reduction of **5** with ammonium formate was performed under the catalysis of Pd-C, which gave **NB-5m** in 90% yield. For the preparation of **PP**, methacrylic acid was first condensed with **4** to give ester **7** in nearly quantitative yield. The latter was reacted with **8** to selectively produce intermediate **9**.³⁸ Using azobis(isobutyronitrile) (AIBN) as the initiator, *n*-butyl methacrylate and **9** (molar ratio = 25:1) underwent statistical free radical copolymerization in THF to give **PP** in 88% yield.

The test films of the target polymers were prepared by curing the prepolymer **PP** with one of the diamines (**HB-nm** and **NB-nm**) in THF in a rectangular Teflon mold heated in an oven at 80 °C for 48 h. For all the reactions, 1.00 g of PP was used, which corresponded to a reaction concentration of 0.38 mM for the appended salicylaldehyde unit. In all cases, less than stoichiometric amounts of diamines were used to ensure their maximum incorporation as cross-linking bridges. Eighteen cross-linked copolymer films were prepared, with the concentrations of the reacted diamines being 0.025, 0.050, and 0.10 mmol (Table 1). The resulting films were pale yellow due to the formation of the aromatic imines. The thickness of the dried films was estimated to be about 0.1 mm. FTIR spectra showed that the strength of the imine stretching peak at around 1680 cm⁻¹ was no longer increased after 5 h. The films were further cured for 43 h at 80 °C.

 Table 1. Cross-Linked Copolymers HB-np and NB-np and Their Properties^a

sample ^b	diamine-to-PP weight ratio (% w/w)	T_{g} (°C) ^c	activation energy (E_a) (kJ/mol) ^c
РР		13	217
HB-1p-0.025	0.038	21	346
HB-1p-0.05	0.075	23	354
HB-1p-0.10	0.15	23	393
HB-3p-0.025	0.12	22	347
HB-3p-0.05	0.23	28	393
HB-3p-0.10	0.46	30	415
HB-5p-0.025	0.24	18	375
HB-5p-0.05	0.48	32	403
HB-5p-0.10	0.96	38	432
NB-1p-0.025	0.028	19	489
NB-1p-0.05	0.055	24	441
NB-1p-0.10	0.11	24	387
NB-3p-0.025	0.09	18	519
NB-3p-0.05	0.18	28	402
NB-3p-0.10	0.35	26	350
NB-5p-0.025	0.15	23	528
NB-5p-0.05	0.29	24	393
NB-5p-0.10	0.58	24	317

^{*a*} The concentration of the appended salicylaldehyde unit was kept at 0.38 mM. ^{*b*} The number at the end represents the millimolar concentration of the diamines for the cross-linking reactions. ^{*c*} Obtained by DMA (the peak on the loss modulus curves).

Physical Characterizations of the Cross-Linked Copolymers. Small-angle X-ray scattering (SAXS) studies revealed that the prepolymer **PP** exhibited two scattering peaks at d =0.49 and 1.2 nm (Figure 2). The first peak may be ascribed to the loose stacking of the salicylaldehede unit,³⁹ while the second one should primarily arise from the correlation hole



Figure 2. Small-angle X-ray scattering (SAXS) diagrams of PP, HB-1p-0.05, HB-3p-0.05, and HB-5p-0.05 at room temperature. Traces are vertically shifted for clarity.

scattering in the disordered state.^{18a,40} Cross-linked polymers **HB-1p-0.05**, **HB-3p-0.05**, **HB-5p-0.05**, **NB-1p-0.05**, **NB-3p-0.05**, and **NB-5p-0.05** all exhibited two similar scattering peaks (Figure 2 for HB series and Figure S1 in Supporting Information for the **NB** series). These results indicated that the introduction of the aromatic amide cross-links into the polymers did not cause an observable new phase separation or aromatic aggregation.

Polarized optical microscopy (POM) was used to further investigate if any crystallization of the aromatic amide units occurred in the cross-linked polymers.⁴¹ The POM pictures of **HB-1p-0.10**, **HB-3p-0.10**, **HB-5p-0.10**, **NB-1p-0.10**, **NB-3p-0.10**, and **NB-5p-0.10** were recorded with a 1000-fold magnification, which all exhibited no crystalline phases from 25 to 150 °C (see Figure S2 in Supporting Information). In addition, no melting transition was observed for all the samples. In contrast, the POM image of prepolymer **PP** showed that it melted at 140 °C. These observations supported that amorphous cross-linked 3D networks were formed for all the copolymers.

Thermal and Mechanical Characterizations of the Cross-Linked Copolymers. The hydrogen-bonding interactions in copolymers manifested themselves in the solid through changes in glass transition temperature and modulus. The glass transition temperatures (T_g) were measured by the DMA method and are shown in Table 1. For both series of cross-linked copolymers, no melting transition was observed, which is consistent with the POM studies. Compared with that of prepolymer PP, which was determined to be 13 °C, the T_g of all the cross-linked copolymers was increased. For the HB-3p and HB-5p series, T_g was increased notably with the increase of the diamine content. Two factors might be proposed to account for this increase. The first one is the intramolecular hydrogen bonds formed in the cross-links. Breaking these hydrogen bonds needs additional energy, as observed for intermolecular hydrogen-bonding-induced dimeric cross-linking systems.^{18a,19} The second is the conformational change of the cross-links. The breaking of the intramolecular hydrogen bonds would increase the flexibility of the backbones, which forces the neighboring polymer chains to reshape or move to a larger extension and thus consumes more energy. Both HB-1p and NB-1p have no intramolecular hydrogen bonds and thus exhibited a similar $T_{\rm g}$ changing tendency. The $T_{\rm g}$ values of the **HB** series were also measured by using the DSC method (see Supporting Information). The values were generally lower than the related ones obtained by the DMA method.¹⁹ For the HB-3p and HB-5p series, the values were also increased with the increase of the concentration of the foldamer segments.

Dynamic mechanical analysis (DMA) was utilized to examine the effects of the aromatic amide cross-links on the thermomechanical properties of the cross-linked copolymers.42,43 Modulus versus temperature plots were recorded from 0 to 150 °C at a constant frequency (1 Hz) (heating rate = 3 °C/ min). Figure 3 shows the storage moduli (E')-temperature plots of the cross-linked copolymers. For all the specimens, the moduli were close to zero at above 70 °C, above which the films yielded and lost the elasticity. Below 0 °C, the films were brittle. Through the temperature range investigated, no plateau zone or abrupt drop was observed, and the moduli were decreased gradually with the increase of temperature. For the HB-1p and NB-1p series (Figure 3a,d), the increase of the cross-links produced a similar increase of the moduli, which was in agreement with the fact that their cross-links have no intra- or intermolecular hydrogen bonds. The moduli of HN-3p and HB-5p (Figure 3b,c) were all higher than those of their NB counterparts (Figure 3e,f) when the concentration of the diamines was increased (0.05 and 0.10 mM). The difference was more conspicuous between the two films containing 0.10 mM cross-links, reflecting the importance of the intramolecular hydrogen bonds in consuming or absorbing energy for breaking and reshaping the folded conformations. A recent work by Sijbesma et al. showed that intermolecular hydrogen-bonding-driven dimeric crosslinking systems in ε -caprolactone and L-lactic acid-derived copolymers caused a quick drop of their storage modulus around the T_g temperature.¹⁹ The present result reasonably reflects the feature of the covalently bonded, folded crosslinks. That is, their intramolecular hydrogen bonds were broken gradually, depending on the unfolding extent of the whole segment.

Figure 4 shows the loss moduli (E')—temperature plots of the cross-linked copolymers. All the specimens showed a broad peak, from which the DMA T_g 's were estimated (Table 1). Notably, the values of **HB-5p-0.05** and **HB-5p-0.10** were all higher than those of **NB-5p-0.05** and **NB-5p-0.10**, which appears also to support that the folded segments in the **HB** series more efficiently strengthened the threedimensional network structures. The films were also prepared from **PP** and amino-free compound **3** (0.025, 0.05, and 0.1 mM). As expected, the storage and loss modulus versus temperature plots of the films revealed no important changes with the increase of compound **3** (see Supporting Information).

Multifrequency analysis also permitted determination of the apparent activation energy (E_a) of the glass transition for all the copolymer films. In the relaxation range, master curves were built by following the frequency dependence of the temperature maximum, assuming an Arrhenius dependence of the transition (see Supporting Information).⁴⁴ The results are provided in Table 1. For the **HB** series, the values were increased with the increase of the content of the cross-links due to the rise of the density of the intramolecular hydrogen bonds. In contrast, the **NB** series displayed an opposite trend, presumably as a result of the increased incompatibility of the polar amide segments and the less polar polymer backbones.

To obtain deeper insight into the effect of the hydrogen bonded cross-links on the mechanical properties of the resulting copolymers, creep/stress relaxation experiments were further performed. The measurements were first performed for **HB-1p-0.10**, **HB-3p-0.10**, and **HB-5p-0.10** at 0.25 MPa at 40 °C (Figure 5a). This temperature is higher than their T_g , and the moduli obtained at this temperature are still relatively high. The stress was kept for 10 min and then removed. The films were allowed to recover for



Figure 3. Temperature dependence of the storage modulus (E') of the aromatic amide cross-linked copolymers: (a) HB-1p, (b) HP-3p, (c) HB-5p, (d) NB-1p, (e) NB-3p, and (f) NB-5p.



Figure 4. Temperature dependence of the loss modulus (E') of the aromatic amide cross-linked copolymers: (a) HB-1p, (b) HP-3p, (c) HB-5p, (d) NB-1p, (e) NB-3p, and (f) NB-5p.

another 20 min. After 10 min, the three films showed 78%, 43%, and 16% final strains, respectively. The value was significantly smaller for **HB-5p-0.10**. After the stress was removed, **HB-1p-0.10** recovered quickly, taking only 1 min to recover $\sim 80\%$. This recovering extent (*re*) was chosen for

comparison throughout the studies. In contrast, to reach this *re*, **HB-3p-0.10** and **HB-5p-0.10** used 6 and 10 min, respectively. Under the same conditions, the creep/stress relaxations of **NB-1p-0.10**, **NB-3p-0.10**, and **NB-5p-0.10** were also measured (Figure 5b), which revealed 33%, 15%, and 83%



Figure 5. Creep and recovery behavior of the cross-linked HB (a) and NB (b) copolymers at a constant stress of 0.25 MPa at 40 °C.



Figure 6. Creep and recovery behavior of the cross-linked HB (a) and NB (b) copolymers at a constant stress of 1.0 MPa at 40 °C.

final strains after 10 min. The times for reaching 80% of re were 1, 17, and 5 min, respectively. The creep and recovery behavior of the film prepared from **PP** and compound **3** (0.1 mM) was also investigated. The film displayed a much larger strain (186%) after 10 min but could not recover completely (see Supporting Information). The measurements were also performed at 10 °C above T_g for the samples prepared from 0.1 mM of cross-linkers (see Supporting Information), which revealed a changing tendency that was similar to that observed for the same series of samples performed at 40 °C.

The creep/stress relaxation plots at longer stress times were also obtained (see Supporting Information). When the stress time was extended to 20 min, the **HB** series of films displayed 92%, 64%, and 22% final strains and, after removal of the stress, took 7, 20, and 39 min, respectively, to reach 80% *re*. When the stress time was further extended to 40 min, they reached 111%, 79%, and 29% final strains and recovered to 80% of *re* after 11, 12, and 40 min, respectively. After stressing for 20 min, the three **NB** films reached the 37%, 22%, and 98% final strains. The films of **NB-1p-0.10** and **NB-3p-0.10** could recover gradually, while that of **NB-5p-0.10** lost the elasticity completely. When the stress time was further increased to 40 min, the film of **NB-3p-0.10** also lost the elasticity.

When the constant stress was increased to 1.0 MPa, **HB-1p-0.10**, **HB-3p-0.10**, and **HB-5p-0.10** also exhibited a tendency similar to that at 0.25 MPa (Figure 6a). After 10 min of stress, the three films produced 340%, 300%, and 89% final strains and took 0.1, 0.6, and 8 min, respectively, to reach 80% *re* after the stress was removed. The rates of creep of **HB-5p-0.10** at both 0.25 and 1.0 MPa stresses were much lower than those of the other two **HB** samples, clearly showing the effect of its folded cross-link on the mechanical

properties. Presumably, the more stored energy in the HB-**5p-0.10** system helped to delay or retard the creep and relaxation processes and to increase the toughness of the films, through producing large conformational changes. At 1.0 MPa, the NB series displayed a similar tendency in the early stage, and NB-1p-0.10 and NB-3p-0.10 reached 178% and 88% final strains after 10 min (Figure 6b). However, NB-5p-0.10 was broken when it reached the 260% maximum strain after about 1 min. It is also noteworthy that the creep property of this series of films did not exhibit a linear change with the contents of the cross-links in the copolymers. For all the studies, NB-3p-0.10 always exhibited the lowest strains, although the reason is not clear. However, whatever it is, the above results indicated that the cross-link formed by NB-5m did not exhibit the capacity of tuning the mechanical properties of the copolymers, as revealed by **HB-5m**.

Conclusions

We have developed a new strategy for modulating the thermal and mechanical properties of polymers by creating new intramolecularly hydrogen-bonded oligoamide folded cross-links. The main chains of the cross-links are fully covalent but can undergo large conformational changes due to the breaking and re-formation of the intramolecular hydrogen bonding. Such a process itself consumes energy and also causes large movements or conformational changes of the neighboring polymer chains. As a result, intramolecularly hydrogen-bonded folded cross-links have a significant effect on the glass transition temperatures as well as thermal and dynamic mechanical behaviors of the resulting copolymers. This effect is unique in that the breaking and reformation of the intramolecular hydrogen bonds need great rearrangements of related segments or chains. Therefore, both processes are gradual and consequently lead to slow creep and relaxation of the copolymer films.

Since the side chains of the folded cross-links may have important effects on the conformational change of the folded segment, one future work concerns the utility of the $F-H\cdots N$ hydrogen-bonding-driven similar aromatic amide segments for preparing the cross-linked copolymers.⁴⁵ In this way, the functions of both the intra- and intermolecular hydrogen bonds can be investigated more accurately because the sizes of the corresponding folded segments, if without additional substituents, are very close to their intramolecular hydrogen-bonding-free counterparts. It may also be possible to incorporate the folded segment into the main chains of polymers. The corresponding polymers should display new interesting mechanical properties due to the reversible unfolding and refolding, as already revealed by the intermolecular hydrogen-bonding-driven supramolecular polymers.

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Supporting Information Available: Additional SAXS diagrams, POM images, the method for determining the apparent activation energy of T_g , T_g data obtained by DSC, creep, and recovery plots, storage and loss modulus experiments, and ¹H and ¹³C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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