Supporting Information

Exploring the effect of dynamic bond placement in liquid crystal elastomers

*Charlie A. Lindberg, Elina Ghimire, Chuqiao Chen, Sean Lee, Neil D. Dolinski, Joseph M. Dennis, Sihong Wang, Juan J. de Pablo, Stuart J. Rowan**

C. A. Lindberg, E. Ghimire, C. Chen, Dr. N. D. Dolinski, Prof. S. Wang, Prof. J. J. de Pablo, Prof. S. J. Rowan
Pritzker School of Molecular Engineering, University of Chicago
5640 S. Ellis Ave., Chicago, Illinois 60637, USA

S. Lee, Prof. S. J. Rowan
Department of Chemistry, University of Chicago
5735 S. Ellis Ave., Chicago, Illinois 60637, USA

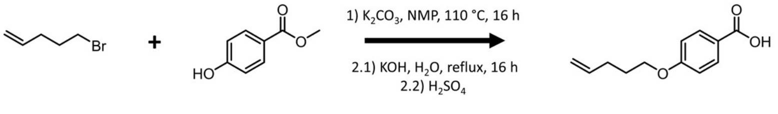
Dr. J. M. Dennis
Sciences of Extreme Materials Division, Polymers Branch,
U.S. DEVCOM Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

Prof. J. J. de Pablo, Prof. S. J. Rowan
Center for Molecular Engineering, Argonne National Lab
9700 S. Cass Ave., Lemont, Illinois 60439, USA
E-mail: stuartrowan@uchicago.edu

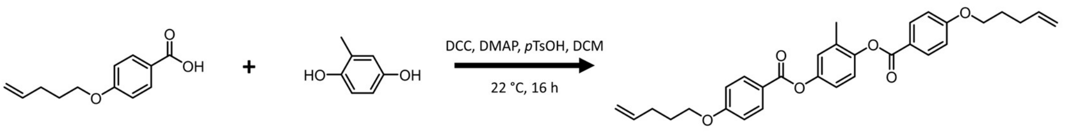
Table of contents:

Materials and Methods:

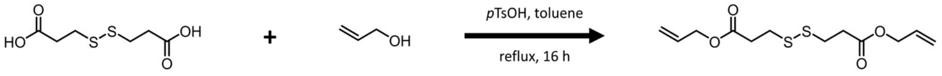
Potassium carbonate was purchased from Fisher Scientific. 5-Bromo-1-pentene was purchased from Combi-Blocks. All other chemicals were purchased from Millipore-Sigma and were used as received unless noted otherwise. All solvents were purchased from Fisher Scientific and were used as received unless noted otherwise.



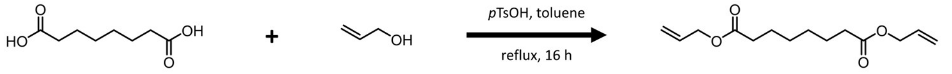
4′-(Pent-1-enyloxy)benzoic acid: 4′-(Pent-1-enyloxy)benzoic acid was synthesized using a modified version of previously published procedures.[1,2] 5-bromo-1-pentene (50 g, 0.336 mol, 1 eq), methyl-4-hyroxybenzoate (52.145 g, 0.342 mol, 1.02 eq), potassium carbonate (50.172 g, 0.362 mol, 1.08 eq) were all added to a flask containing N-methyl-2-pyrrolidone (150 mL, 3 vol). The flask was equipped with a condenser, and the reaction mixture was heated to 80°C while stirring. After observing an exotherm in the form of vigorous bubbling the temperature was raised to 110°C where the reaction was allowed to proceed for 16 h. The reaction mixture was then cooled to room temperature and added to a separatory funnel with toluene (300 mL) and water (100 mL). The organic layer was washed three times with water whereafter the solvent was removed under vacuum. To the resulting oil was added 300 mL of 10 wt% aqueous potassium hydroxide solution. The reaction mixture was then heated to 110 °C and allowed to proceed for 16 h with stirring. After cooling to room temperature, the reaction mixture was extracted with ethyl ether (50 mL) three times. The aqueous layer was then diluted with water to a volume of 2 L while stirring whereupon concentrated sulfuric acid (25 mL) was added to adjust the solution to a pH of about 2. As the sulfuric acid is added, white solid began to precipitate from solution until the reaction mixture became a slurry that was difficult to stir magnetically. The solid was removed from the aqueous solution using a Buchner funnel and recrystallized three times in hot ethanol yielding white crystals. (61 g, 88% yield) ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 – 7.97 (m, 2H), 7.00 – 6.88 (m, 2H), 5.98 – 5.74 (m, 1H), 5.17 – 4.94 (m, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.25 (qd, J = 7.4, 1.4 Hz, 2H), 2.03 – 1.82 (m, 2H).



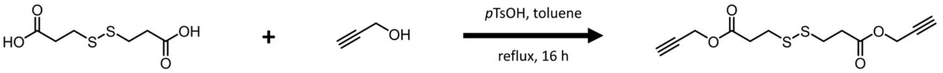
Liquid crystal monomer (1): Liquid crystal monomer (**1**) was prepared using a previously reported procedure.[3] 4′-(Pent-1-enyloxy)benzoic acid (24.3 g, 0.118 mol, 1.95 eq), methylhydroquinone (7.5 g, 0.060 mol, 1 eq), dicyclohexylcarbodiimide (28.692g, 0.139 mol, 2.4 eq), 4-dimethylaminopyridine (14.050g, 0.115 mol, 1.9 eq), and *p*-toluenesulfonic acid monohydrate (21.875 g, 0.115 mol, 1.9 eq) were added to a flask containing 400 mL of dichloromethane. The reaction mixture was stirred at room temperature (22 °C) for 16 hours. A solid white urea byproduct was then filtered out of the reaction mixture, and the solvent was then removed from the filtrate under vacuum. The remaining solid was then recrystallized three times in hot ethanol to afford white powdery crystals. (44.25 g, 75% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.04 (m, 4H), 7.22 – 7.04 (m, 3H), 7.04 – 6.92 (m, 4H), 5.96 – 5.77 (m, 2H), 5.17 – 4.97 (m, 4H), 4.07 (td, J = 6.4, 2.0 Hz, 4H), 2.35 – 2.20 (m, 7H), 2.01 – 1.87 (m, 4H).



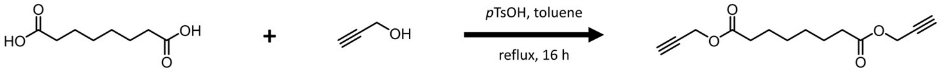
Dynamic monomer (2D): Dynamic monomer (**2D**) was prepared using a modified version of a previously reported procedure.[4] 3,3′-Dithiodipropionic acid (10 g, 0.048 mol, 1 eq), allyl alcohol (6.911 g, 0.119 mol, 2.5 eq), and *p*-toluenesulfonic acid (0.913 g, 0.005 mol, 0.1 eq) were added to a flask containing 200 mL of toluene. The flask was equipped with a Dean-Stark apparatus, and the reaction mixture was stirred under reflux for 16 h. Upon cooling to room temperature, the reaction mixture was transferred to a separatory funnel and washed with an aqueous solution saturated with sodium bicarbonate three times and then water three times. The organic layer was isolated and had the solvent removed from it under vacuum. The resulting product was a yellow oil. (12.824 g, 92% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddt, J = 17.1, 10.4, 5.8 Hz, 2H), 5.40 – 5.20 (m, 4H), 4.61 (dt, J = 5.8, 1.4 Hz, 4H), 2.94 (td, J = 7.2, 0.7 Hz, 4H), 2.77 (td, J = 7.1, 0.7 Hz, 4H).



Covalent monomer (2C): Covalent monomer (**2C**) was prepared using a modified version of a previously reported procedure.[4] Suberic acid (10 g, 0.057 mol, 1 eq), allyl alcohol (8.305 g, 0.143 mol, 2.5 eq), and *p*-toluenesulfonic acid (1.141 g, 0.006 mol, 0.1 eq) were added to a flask containing 200 mL of toluene. The flask was equipped with a Dean-Stark apparatus, and the reaction mixture was stirred under reflux for 16 h. Upon cooling to room temperature, the reaction mixture was transferred to a separatory funnel and washed with an aqueous solution saturated with sodium bicarbonate three times and then water three times. The organic layer was isolated and had the solvent removed from it under vacuum. The resulting product was a yellow oil. (12.322 g, 85% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddt, J = 17.2, 10.4, 5.7 Hz, 2H), 5.37 – 5.15 (m, 4H), 4.57 (dt, J = 5.8, 1.4 Hz, 4H), 2.33 (t, J = 7.5 Hz, 4H), 1.73 – 1.54 (m, 4H), 1.43 – 1.28 (m, 4H).



Dynamic crosslinker (3D): Dynamic crosslinker (**3D**) was prepared using a modified version of a previously reported procedure.[4] 3,3′-Dithiodipropionic acid (10 g, 0.048 mol, 1 eq), propargyl alcohol (6.671 g, 0.143 mol, 2.5 eq), and *p*-toluenesulfonic acid (0.913 g, 0.005 mol, 0.1 eq) were added to a flask containing 200 mL of toluene. The flask was equipped with a Dean-Stark apparatus, and the reaction mixture was stirred under reflux for 16 h. Upon cooling to room temperature, the reaction mixture was transferred to a separatory funnel and washed with an aqueous solution saturated with sodium bicarbonate three times and then water three times. The organic layer was isolated and had the solvent removed from it under vacuum. The resulting product was a pale-yellow oil. (11.958 g, 87% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, J = 2.5 Hz, 4H), 2.94 (td, J = 7.1, 0.9 Hz, 4H), 2.80 (td, J = 7.1, 0.9 Hz, 4H), 2.49 (t, J = 2.5 Hz, 2H).



Covalent crosslinker (3C): Covalent crosslinker (**3C**) was prepared using a modified version of a previously reported procedure.[4] Suberic acid (10 g, 0.048 mol, 1 eq), propargyl alcohol (8.017 g, 0.143 mol, 2.5 eq), and *p*-toluenesulfonic acid (1.141 g, 0.006 mol, 0.1 eq) were added to a flask containing 200 mL of toluene. The flask was equipped with a Dean-Stark apparatus, and the reaction mixture was stirred under reflux for 16 h. Upon cooling to room temperature, the reaction mixture was transferred to a separatory funnel and washed with an aqueous solution saturated with sodium bicarbonate three times and then water three times. The organic layer was isolated and had the solvent removed from it under vacuum. The resulting product was a pale-yellow oil. (10.211 g, 85% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, J = 2.5 Hz, 4H), 2.46 (t, J = 2.5 Hz, 2H), 2.35 (t, J = 7.5 Hz, 4H), 1.72 – 1.59 (m, 4H), 1.42 – 1.29 (m, 4H).

Dynamic LCE Network Preparation (4B, 4BX, 4X): Dynamic LCE networks were prepared as follows utilizing a 1:1 ratio of thiol:(alkene + (alkyne/2)) to ensure a stoichiometric amount of functionalities. For example, synthesis of **4B** consisted of adding **1** (2.25 g, 0.005 mol), **HDT** (0.700 g, 0.005 mol), **PDT** (0.849 g, 0.005 mol), **2D** (0.436 g, 0.002 mol), **3C** (0.415 g, 0.002 mol), and a catalytic amount of photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (0.092 g, 0.0004 mol) to a vial containing tetrahydrofuran (4 mL). The reaction mixture was thoroughly mixed and sonicated until all components were well dissolved in solution. The reaction mixture was then transferred to a Teflon dish where it was exposed to UV light (320-390 nm, 2 x 30 s, 50 mW cm^{-2}) to initiate the polymerization and form a solid LCE film.

Nondynamic LCE Network Preparation (4N): Nondynamic LCE network (4N) was prepared as follows utilizing a 1:1 ratio of thiol:(alkene + alkyne/2) to ensure a stoichiometric amount of functionalities. Synthesis of **4N** consisted of adding **1** (2.25 g, 0.005 mol), **HDT** (0.700 g, 0.005 mol), **PDT** (0.849 g, 0.005 mol), **2C** (0.381 g, 0.002 mol), **3C** (0.415 g, 0.002 mol), and a catalytic amount of photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (0.092 g, 0.0004 mol) to a vial containing tetrahydrofuran (4 mL). The reaction mixture was thoroughly mixed and sonicated until all components were well dissolved in solution. The reaction mixture was then transferred to a Teflon dish where it was exposed to UV light (320-390 nm, 2 x 30 s, 50 mW cm^{-2}) to initiate the polymerization and form a solid LCE film.

Dynamic LCE Network Processing: Freshly cured dynamic LCE networks were cut into pieces and washed in a Soxhlet extractor apparatus using a 50/50 mixture of tetrahydrofuran and methanol for 16 h. The washed LCE pieces were then dried under vacuum at 60 °C for 16 h. 0.5 mm thick Teflon was cut into 5 cm x 5 cm molds and used to set the thickness of the LCE films. Pieces of the washed and dried LCE were then thermally processed in the molds to make uniform films using a hot melt press at 180 °C for 1 h under 4 tons of pressure. The as-pressed films were then used as is for subsequent characterization.

Nondynamic LCE Network Processing: Freshly cured nondynamic LCE network was washed by allowing the as-cured film to swell in a gently stirring mixture of tetrahydrofuran and methanol that was changed once every hour for 6 hours. The film was then dried in a vacuum oven at 60 °C under vacuum for 16 h. The washed and dried film was then used for subsequent characterization.

Instrumentation:

All nuclear magnetic resonance (NMR) spectra were collected on a Bruker Avance III HD nanobay 400 MHz spectrometer.

All differential scanning calorimetry (DSC) thermograms were collected on a TA Instruments Discovery 2500 differential scanning calorimeter. Experiments were run following a (22/200/-90/200) ramp using heating and cooling rates of 10 °C min^{-1}. All curves shown are from the second heating.

All shear mechanical testing including dynamic temperature ramps and stress relaxation data were collected on TA Instruments ARES-G2 shear rheometer. Shear rheology experiments were performed on discs (diameter = 8 mm, thickness = 0.43 mm)

All tensile mechanical testing were collected on films (~ 5mm x 0.45mm x 10mm) using a Zwick-Roell zwickiLine Z0.5 materials testing instrument. Tensile tests were performed on at 22 °C at a strain rate of 5 mm/min until failure.

All wide-angle x-ray scattering (WAXS) data were collected on a SAXSLAB GANESHA 300XL utilizing a Cu Kα source ($\lambda = 0.154$ nm) at a voltage and power of 40 kV and 40 mA, respectively. Films were affixed to a stage with Kapton tape and shot directly and measured for 5 min at $q = 0.05 – 0.25$.

WAXS Data Processing

To capture the whole 2D scattering pattern, four individual WAXS patterns are acquired with shifted detector location. Polar transformation is performed to align and average the four scattering patterns. The final scattering pattern is computed by the inverse transformation of the averaged plot. The samples show peak intensity around $q = 1.45 \sim 1.5 \text{Å}^{-1}$, indicating an average spacing of $d = 4.27$ Å between the mesogens. To compute the order parameter, the 1D azimuthal data is calculated by integrating the 2D data between $q = 0.97 \text{ Å}^{-1}$ and $q = 1.90 \text{ Å}^{-1}$. The background is subtracted by a linear fit and the order parameter is calculated by the Kratky method as described previously.[5]

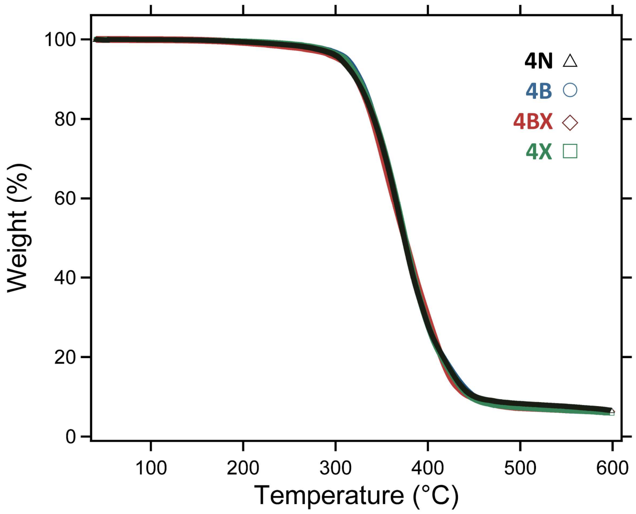


Figure S1: Stacked thermal degradation profiles for **4N, 4B**, **4BX**, and **4X**.

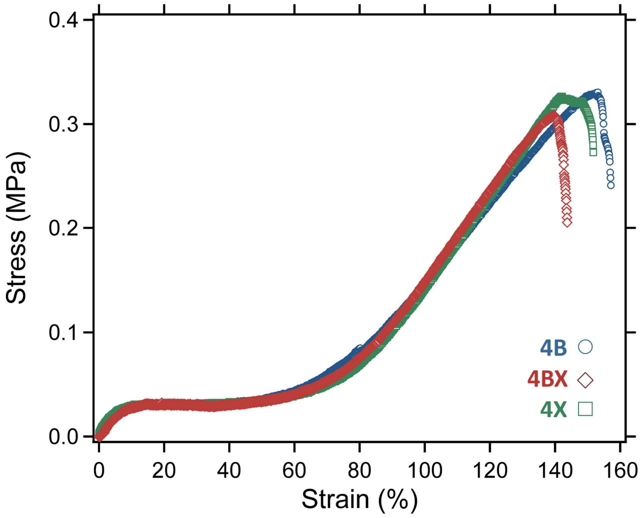


Figure S2: Stacked stress-strain profiles for the representative tensile curves for **4B**, **4BX**, and **4X**.

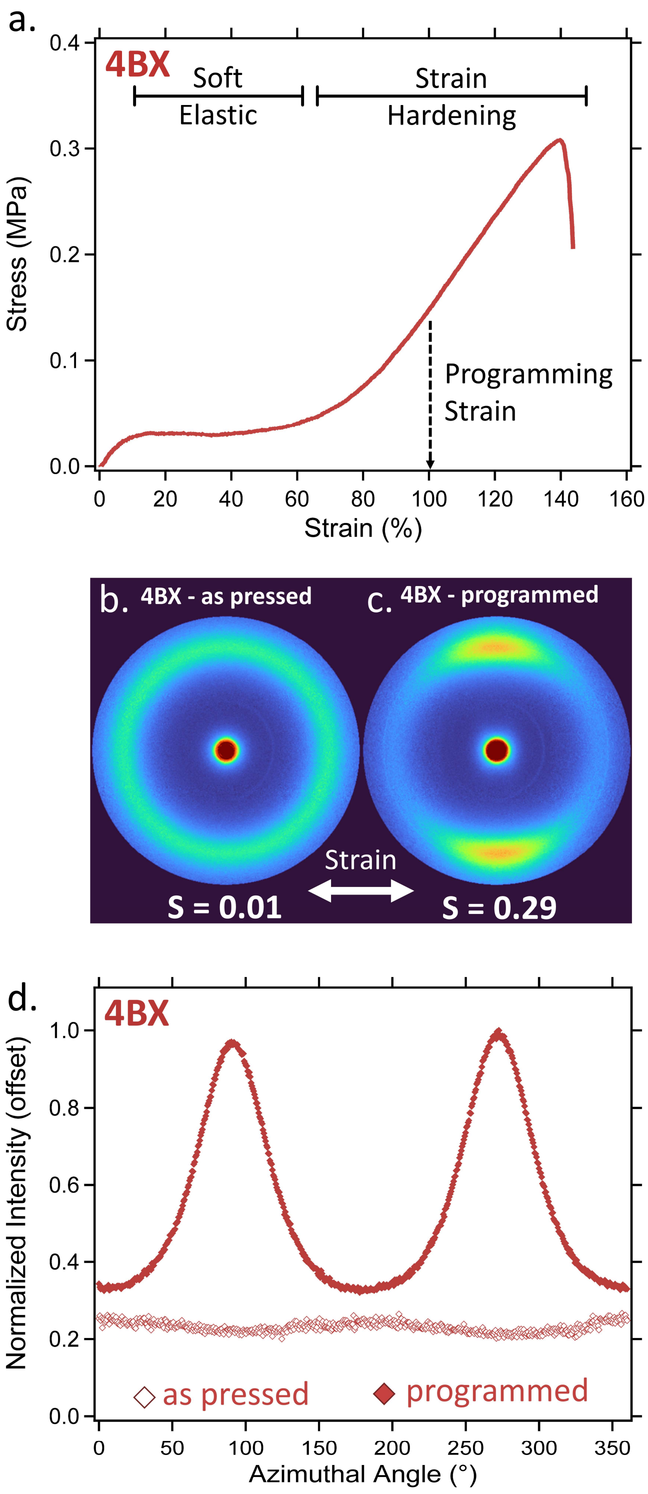


Figure S3: a. Stress-strain profile of an as pressed sample of **4BX**; b. 2D WAXS image of an as pressed film of **4BX**; c. 2D WAXS image of an aligned programmed; d. Plots of normalized intensity as a function of angle for both an as-pressed and aligned programmed film of **4BX**.

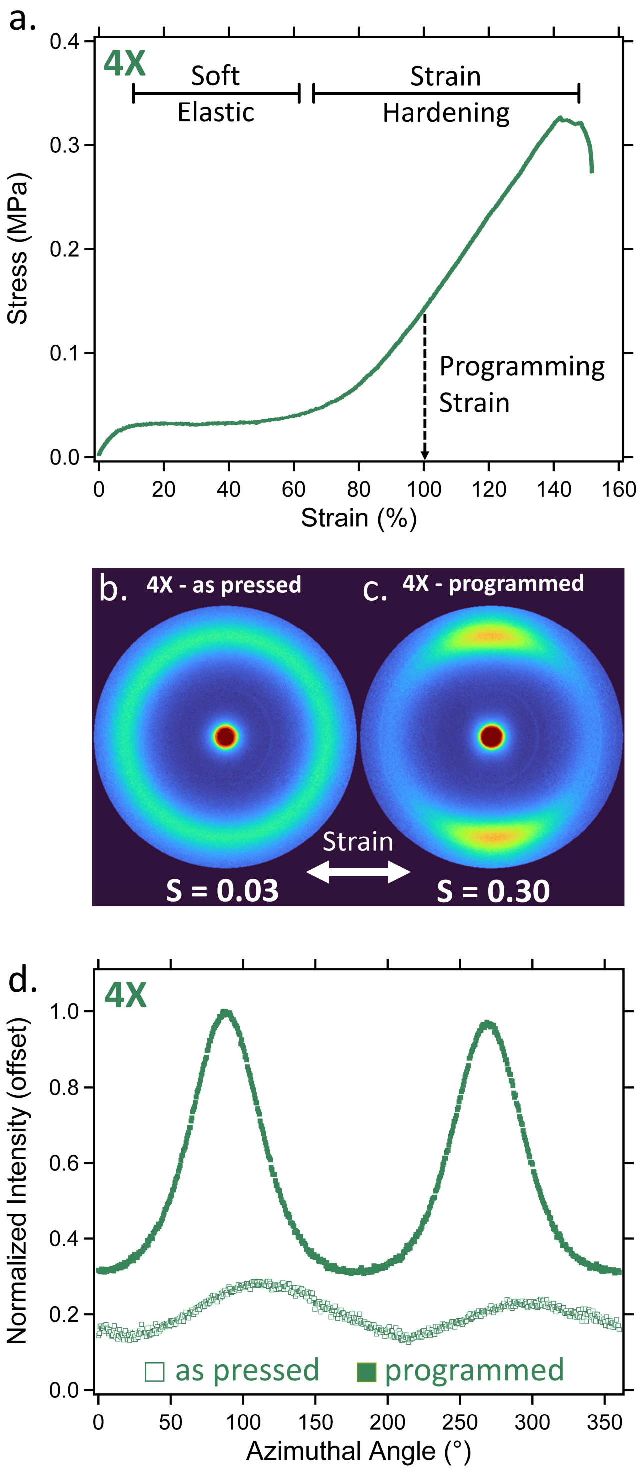


Figure S4: a. Stress-strain profile of an as pressed sample of **4X**; b. 2D WAXS image of an as pressed film of **4X**; c. 2D WAXS image of an aligned programmed; d. Plots of normalized intensity as a function of angle for both an as-pressed and aligned programmed film of **4X**.

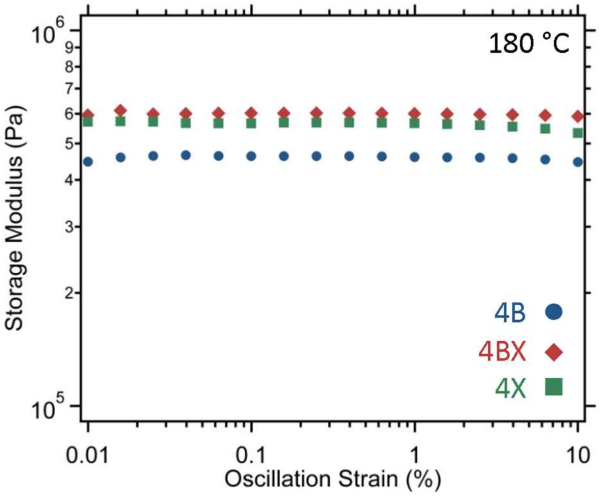


Figure S5: Amplitude sweeps showing storage modulus versus oscillation strain at 180 °C for **4B**, **4BX**, and **4X** to illustrate the linear viscoelastic regime for these materials.

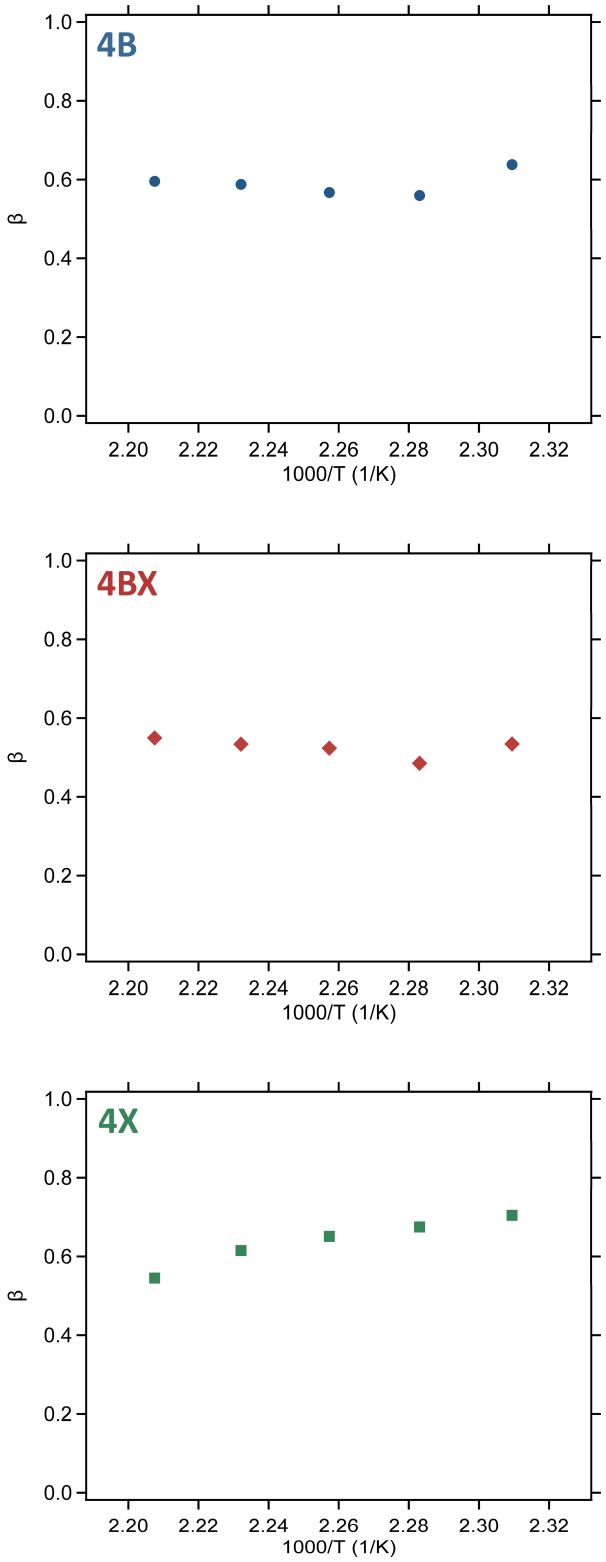


Figure S6: Plots of β parameters as a function of temperature for stretched exponential fits of stress relaxation measurements.

References

[1] M. C. Wilkinson, M. Higson, *Org. Process Res. Dev.* **2017**, *21*, 75.

[2] Y. Barre, M. Simon, R. Neige, R. Duval (Commissariat a l'Energir Atomique), U.S. 7230123B2. **2007**.

[3] S. V. Arehart, C. Pugh, *J. Am. Chem. Soc.* **1997**, *119*, 3027.

[4] Y.-K. Lee, K. Onimura, H. Tsutsumi, T. Oishi, *Polym. J.* **2000**, *32*, 395.

[5] M. T. Sims, L. C. Abbott, R. M. Richardson, J. W. Goodby, J. N. Moore, *Liq. Cryst.* **2019**, *46*, 11.