Supporting Information

Impact of dynamic covalent chemistry and precise linker length on crystallization kinetics and morphology in ethylene vitrimers

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Experimental Section

Materials: Boric acid ($B(OH)_{3,}$ ≥ 99.5%), 1,8 octanediol (C_8, 98%), 1,10 decanediol (C_{10}, 98%), 1,12 dodecanediol (C_{12}, 99%), N-Hydroxysuccinimide (98%), dodecanedioyl dichloride (98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), tris(2-aminoethyl)amine (96%), anhydrous dimethyl sulfoxide (DMSO, >99.9%) were purchased from Sigma-Aldrich without further purification. 2,2'-Diamino-N-methyldiethylamine (>98%) and dimethyl dodecanedioate (98.0+%) were purchased from TCI and was used without purification. Dichloromethane (HPLC), methanol, triethylamine was purchased from Sigma-Aldrich and stored with activated molecular sieves to remove moisture.

Ethylene dynamic network synthesis: Carefully weighed amounts of monomer were mixed together in a glass vial with stoichiometry of 1.0 mol boric acid to 1.5 mol diol. The mixture was heated and stirred continuously overnight at 120 ˚C on a hotplate. A viscous transparent gel was obtained. The vial was then transferred to a vacuum oven, held at 60˚C overnight under vacuum to drive water off and then immediately brought into an argon glovebox maintained at < 0.5 ppm O_2 and < 0.1 ppm H_2O. No solvent was used in the synthesis.

Synthesis of C_{10} diNHS linker: In a 200 mL oven dried round bottom flask charged with stir bar and N2, n-Hydroxysuccinimide (1.89 g, 16.4 mmol) and triethylamine (3.24 g, 32.0 mmol) was dissolved into 55 mL dry DCM. The reaction flask was cooled in water bath while dodecanedioyl dichloride (2.14 g, 8.0 mmol) was added dropwise via. a syringe. The reaction was then stirred overnight under N2 environment and the completion was confirmed by TLC. The reaction solution was then transferred into a separatory funnel with an additional 100 mL DCM. The organic phase was washed with deionized (DI) water 3 times followed by saturated NaCl solution. The organic solution was then dried with NasSO4 and concentrated with rotary evaporator. A white crystalline solid (1.7g, 52% yield) was obtained after the recrystallization of the crude product with DCM. 1H NMR (500 MHz, CDCl3) □ (ppm): 2.83(s, 8H, -CH2¬¬-CON-), 2.60(t, 4H, -OCO-CH2-), 1.73(q, 4H,-CH2-CH2-), 1.43-1.27(m, 12H, -CH2-CH2-). Crystal was dried before further use.

Synthesis of C_{10} permanent amide network: A solution of triazabicyclodecene (24.6 mg, 0.17 mmol), dimethyl dodecanedioate (224.3 mg, 0.86 mmol), tris(2-aminoethyl)amine (88.2 mg, 0.58 mmol) and 109 µL CH3CN was transferred on top of a glass slide that has a layer of Kapton tape as a spacer. Another glass slide was placed on top to seal the reaction container. The reaction mixture was heated to 80 °C and allowed to cure for 24 h. The crosslinked polyamide network was then further cured at 100 °C, overnight, under vacuum (with the top glass slide removed) to push the completion of the aminolysis reaction. After the network has formed, TBD calaytst was removed by excessive washing with MeOH and water mixtures. The final network is a transparent polymer sheet.

Synthesis of C_{10} amide linear polymer: An oven-dried round bottom flash was filled with N_2, 400 mg (0.94 mmol) of C_{10} diNHS, and 1.5 mL DMSO at 80 °C. Diamino-N-methyldiethylamine (112.70 mg, 0.94 mmol) was then added via syringe. The polymerization was allowed to proceed at 80 °C for 18 hours with continuous stirring. A white precipitate formed during the reaction. After the reaction was completed, MeOH was added to re-dissolve the reaction mixture. Polyamide was then precipitated by dropwise addition of the reaction mixture to 200 mL DI water with strong agitation. The polymer was collected by centrifuge and further washed in a dialysis bag for two days followed by drying in the vacuum oven. The final polymer was a light brown powder (yield 58 %).

ATR-FTIR: IR spectra of the samples were collected using a Bruker ALPHA FTIR spectrometer with a platinum-ATR QuickSnap sampling module. All measurements were made at 80 °C by scanning from 400 cm^{-1} to 4000 cm^{-1} with 16 total scans. Solid samples (networks) were clamped down to the diamond ATR crystal to ensure sufficient contact, while liquid samples (monomers) were left undisturbed.

Rheology of polymer networks: Oscillatory shear measurements were made on a TA Instruments DHR-2 rheometer using a parallel plate geometry. Samples were pressed into an 8 mm disc under ambient conditions and then loaded on to the rheometer at 40 ˚C. The dynamic networks were heated and held at 140 ˚C for 30 min to remove any water absorbed during sample loading. Sample thickness of approximately 800 µm was used for all measurements. Frequency sweeps were conducted at isothermal temperatures from 140 ˚C to 40 ˚C at 10 ˚C intervals with an applied stress of 1000 Pa. The viscosity of the networks was calculated by measuring the slope of the loss modulus vs frequency curve in the low frequency limit, and a characteristic Arrhenius behavior is observed as expected.

Differential Scanning Calorimetry (DSC): Samples with a mass between 3-6 mg were crimped in Tzero hermetic aluminum pans inside a glovebox. A TA Instruments DSC 25 was used to take all measurements. The glass transition temperature for each sample was measured by rapidly quenching from 150 °C to -80 °C and then heating at 20 °C/min. T_g is obtained from analysis of the heating profile using the ½ ΔC_p criterion. For measurement of the melting temperature after room temperature crystallization, samples were equilibrated to 20 °C and ramped at 20 °C /min to 120 °C. (All graphs are plotted with "endothermic down" convention.)

X-ray scattering: Scattering patterns were first collected on a Siemens Kristalloflex (Diffractometer D5000) in the reflection geometry. Thin films of C_{10} and C_{12} were prepared by mechanical pressing at 60 °C. Films were heated at 120 °C for 12 hours to erase any thermal history and any possible effects of mechanical pressing. The films were cooled under ambient conditions and WAXS spectra were systematically collected at 12 hr time steps under ambient conditions. Next, a separate set of samples were crystallized in the glovebox and sealed between Kapton prior to being taken to the beamline. These sealed samples were analyzed with a Xenocs GeniX3D Cu Kα X-ray source (1.54 Å) and a Pilatus 2D detector (1M pixels). The sample-to-detector distance was calibrated with silver behenate powder, and scattering patterns were collected with a 10-minute exposure. The 2D diffraction data were radially averaged using FIT2D software or MATLAB-based GIXSGUI package and the intensity was plotted as a function of scattering vector q.

Optical Microscopy: Micrographs were collected using a Zeiss Axioscope A1 microscope. Thin films were prepared in a similar fashion as for X-ray diffraction and imaged under 10x, 20x and 50x magnification in reflection mode.

NMR spectroscopy**:** Solution state 1H NMR was done using a Varian UI500NB (500-MHz) at 23 degree Celsius. Solid state 13C NMR was done using Varian Unity Inova instrument (UI300WB, 300 MHz) via direct polarization magic angle spinning (DPMAS) method at 10 kHz spanning frequency with 5600 scan, and 5 s cycle delays (d1 = 5 s). A pseudo T1 measurement was done with d1 = 1, 5, 10 and 20 s to ensure 5 s is sufficient for all 13C nuclei to relax.

Recycling of ethylene dynamic networks: Approximately 0.1 g of the vitrimer network is added to 5ml of ethanol and heated to 80 °C with continuous stirring. It was observed that white crystalline chunks of the C_{10} and C_{12} networks take longer to dissolve as compared to the amorphous C_8. Ethylene vitrimers are recovered by evaporating the ethanol at 80 °C followed by vacuum drying at 60 °C to remove any residual solvent.

Results and Discussion.

The networks were synthesized and characterized by FTIR which indicated high conversion of the reaction (**Fig. S1a**). Rapid quenching showed no crystallization in the cooling curves of C_8 or C_{10}, while a peak was observed for C_{12} and linear polyethylene (**Fig. S1b-c**). Rheology reveals the dynamic nature of these networks with a rubbery plateau and a flow regime (**Figure S1d**).

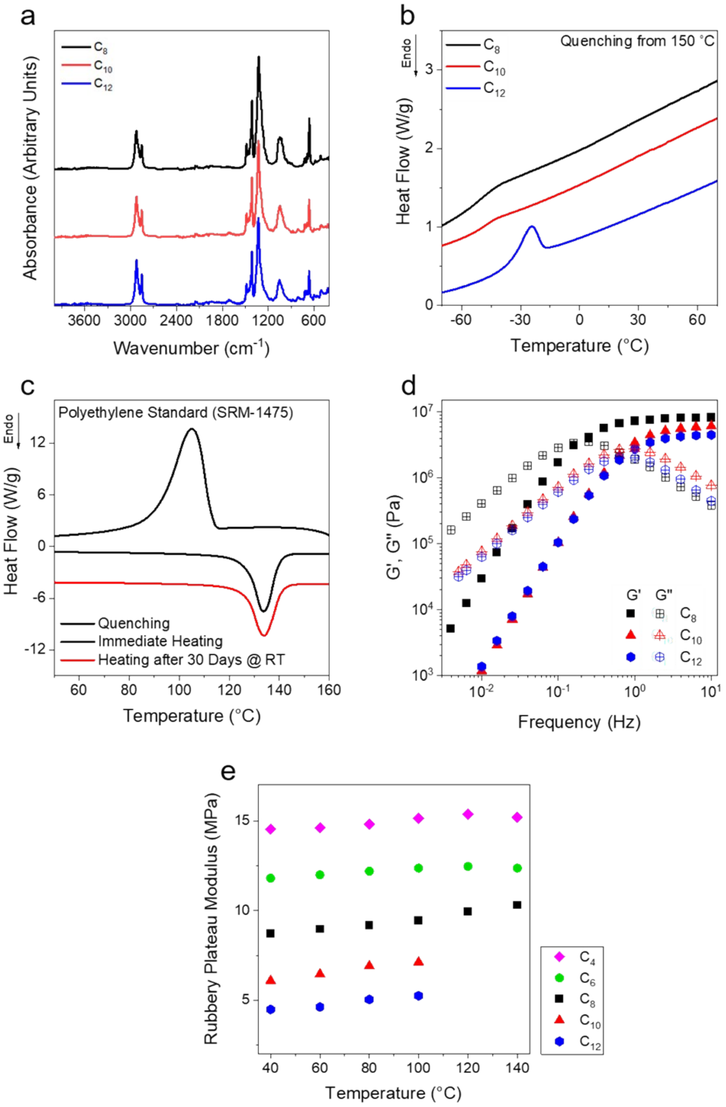


Figure S1. (a) FTIR of C_8, C_{10} and C_{12} networks confirms the absence of OH peak due to unreacted diol or water. The sharp peak at ~1300 cm^{-1} is characteristic of the boronic ester bond. (b) DSC cooling curves show no crystallization for C_8 and C_{10} networks quenched from 150 °C to -80 °C, while C_{12} reveals a weak peak. (c) DSC of linear PE standard (SRM 1475) shows no change in T_m even after 43200 min at room temperature. (d) Frequency sweep of ethylene vitrimers measured at 40 °C. A high frequency rubbery plateau and a low frequency terminal relaxation are observed for all dynamic networks. (e) The rubbery plateau modulus as a function of temperature. Modulus scales proportionally to crosslink density.

A separate set of samples was quenched directly to room temperature to probe the initial 300 min of crystallization (**Fig. S2**).

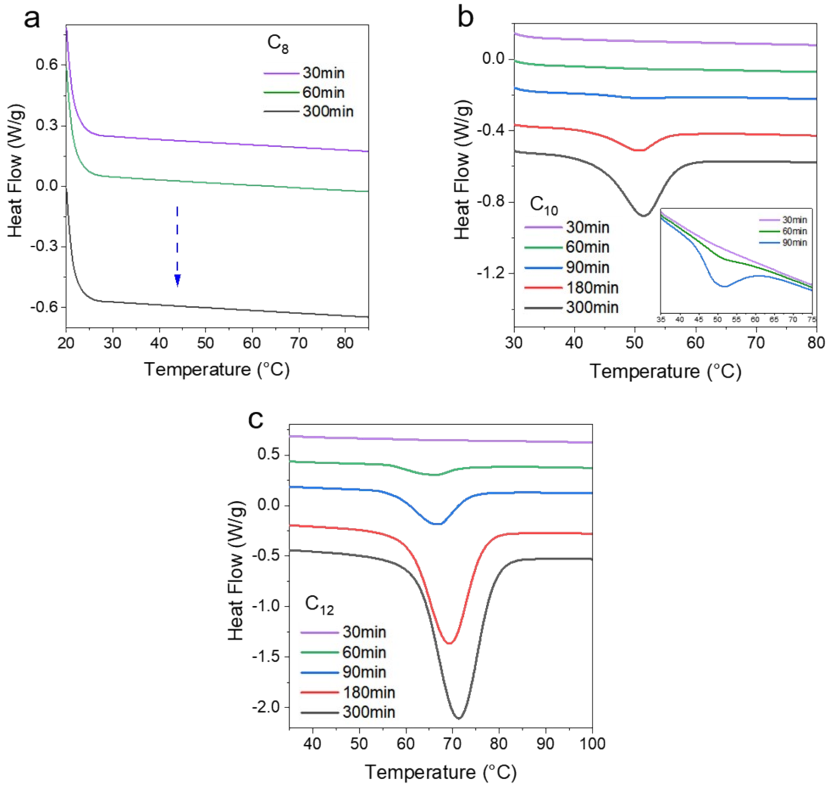


Figure S2. DSC curves show the evolution of T_m following a quench to 20 °C for a 300 min isothermal crystallization (a) C_8 shows no T_m while (b) C_{10} and (c) C_{12} show a continual growth of a melting peak which shifts to higher temperature.

Over a longer time period of 30 days, the T_m continues to evolve as does the area under the DSC melting peaks (**Fig. S3a**). After 150 days, the melting temperature stabilize and no free OH groups are detectable, indicating that the boronic ester is preserved and incorporated into the polymer crystal (**Fig. S3b and d**).

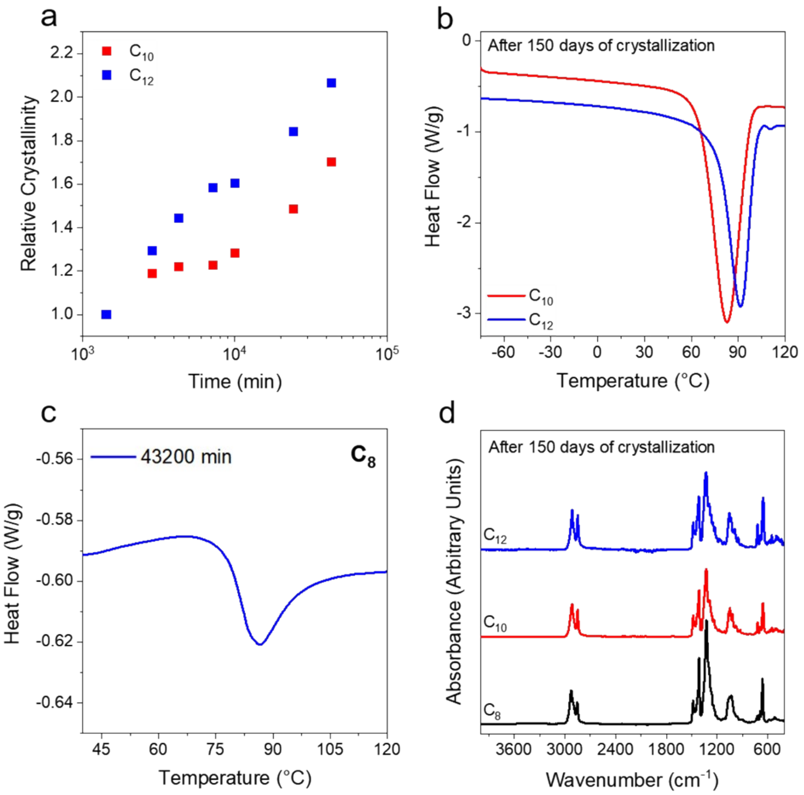
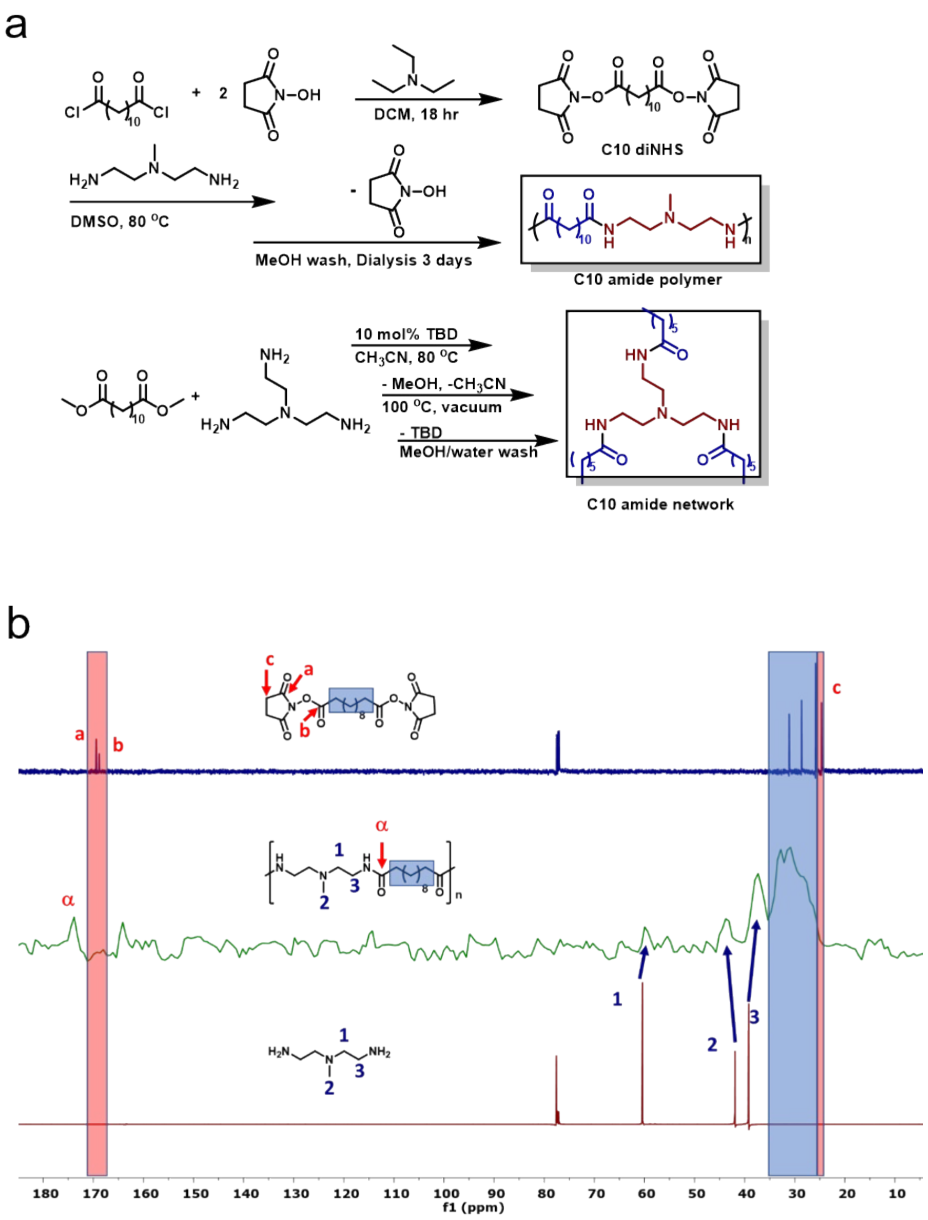


Figure S3. (a) The increasing melting temperature of C_{10} and C_{12} is accompanied by an increase in the ethalpy of fusion. The relative crystallinity approximately doubles for C_{12} and increases by ~70% for C_{10} networks. Relative crystallinity of the samples was determined by normalizing to the enthalpy value at 1440 min. (b) After 150 days of isothermal crystallization, the T_g is not observed and T_m stops shifting. (c) An extremely weak melting transition is seen for C_8 networks even after 43200 min of isothermal crystallization at room temperature. (d) FTIR collected after 150 days of crystallization. Measurements were made in a glovebox, and the absence of the OH peak indicates that the crosslink density is conserved even after crystallization.

A permanent ethylene network (C_{10} amide network) and a linear permanent network (C_{10} amide polymer) were synthesized to provide a control to the dynamic system, and the synthesis is shown in **Fig. S4**. DSC of the network confirms the absence of crystallization, whereas the linear amide polymer shows a distinct melting peak (**Fig. S5**).



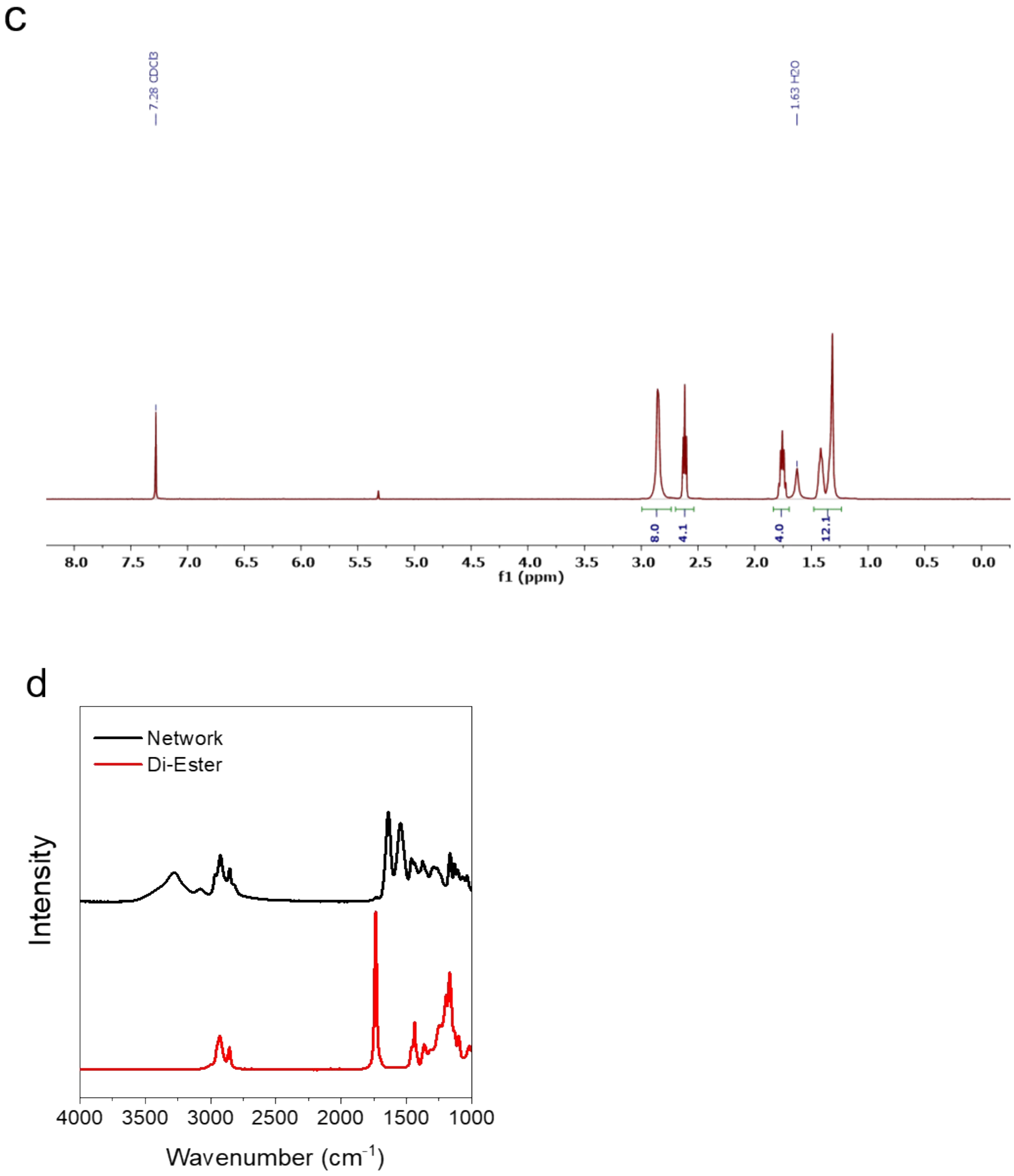


Figure S4. (a) Synthesis routes for the C_{10} amide polymer and C_{10} amide network. The use of NHS functionality ensures controllable network formation as the reaction between acid chloride and amine is too fast. (b) ^{13}C Solid-state NMR (green trace) of C_{10} amide linear polymer with diNHS (blue) and diamine (red) starting materials. The disappearance of signal a,b and c from the NHS moieties of the C_{10} small molecule and the appearance of α (new amide C=O) indicates a high functional group conversion. Carbon signals from the diamine molecule (1,2 and 3) along with methylene signal from C_{10} linker (in diNHS) are also in agreement of the proposed C_{10} polyamide structure. (c) ^{1}H NMR of C_{10} diNHS linker. (d) FTIR trace of C_{10} amide network with the reference of the C_{10} di ester monomer. Ester C=O stretch (1635 and 1542 cm^{-1}) completely disappeared and new amide C=O stretch appears (1734 cm^{-1}). FTIR gives strong evidence of high reaction conversion

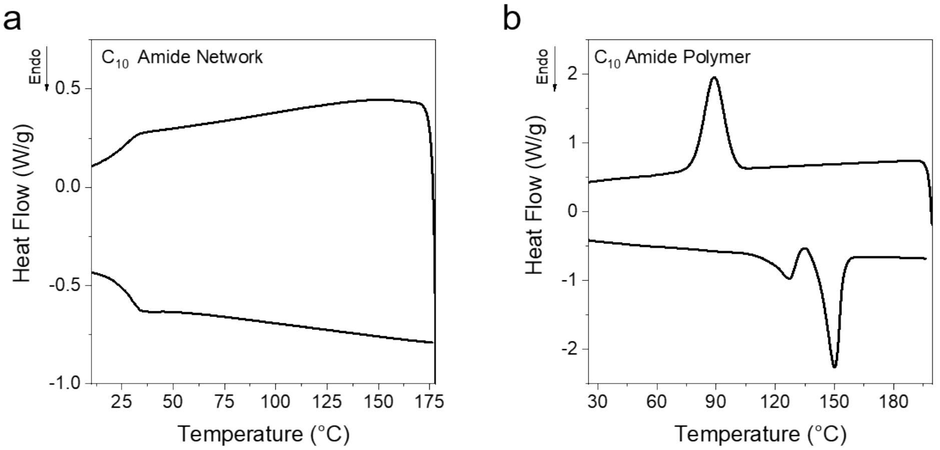


Figure S5. (a) DSC of the C_{10} amide network shows a T_g of 34°C and no crystallization. (b) In comparison the DSC of the linear counterpart, the C_{10} amide polymer crystallizes and shows a broad high temperature melting peak. This provides evidence that it is the network architecture and not the chemistry of the crosslink junction that is restricting the crystallization of the permanent network.

Wide-angle diffraction was measured on a benchtop system under ambient conditions (**Fig. S6**). This is in support of the patterns collected using sealed samples which crystallized entirely in a glove box (**Fig. 5**). Both samples show the transition from 1 to 2 dominant peaks in the C_{10} system, while the C_{12} system showed 2 peaks after higher temperature annealing.

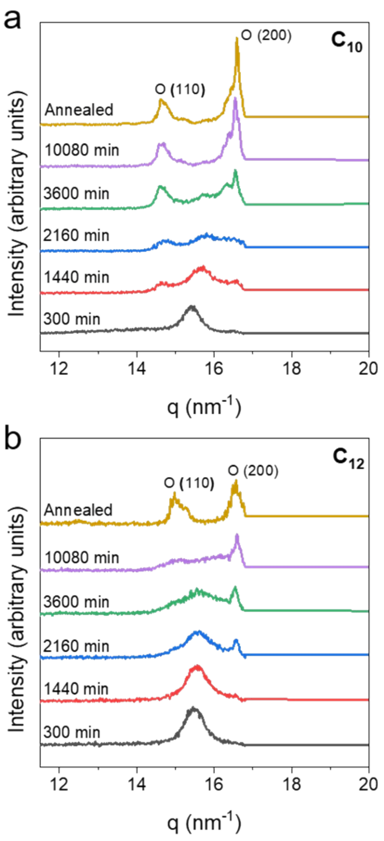


Figure S6. Benchtop X-ray scttering patterns for C_{10} and C_{12} under ambient conditions. The transition from hexagonal to orthorhombic is preserved in the C_{10} networks, while the C_{12} network partially transforms to orthorhombic prior to annealing. This is attributed to atmospheric water which can hydrolyse the boronic ester. In contrast, sample in **Figure 5** were crystallized in a glove box and rigorously dried.

Linear polyethylene instantly crystallized into the orthorhombic phase upon cooling to room temperature (**Fig. S7**).

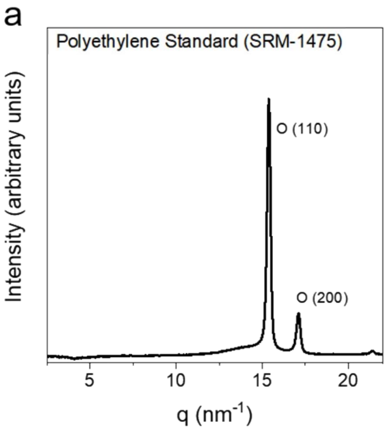


Figure S7. (a) WAXS for PE standard. The canonical orthorhombic phase is predominant in the linear polyethylene.

Optical microscopy was used to visually track the crystals, and for C_{12} networks was substantially different from the C_{10} crystals (**Figure S8**).

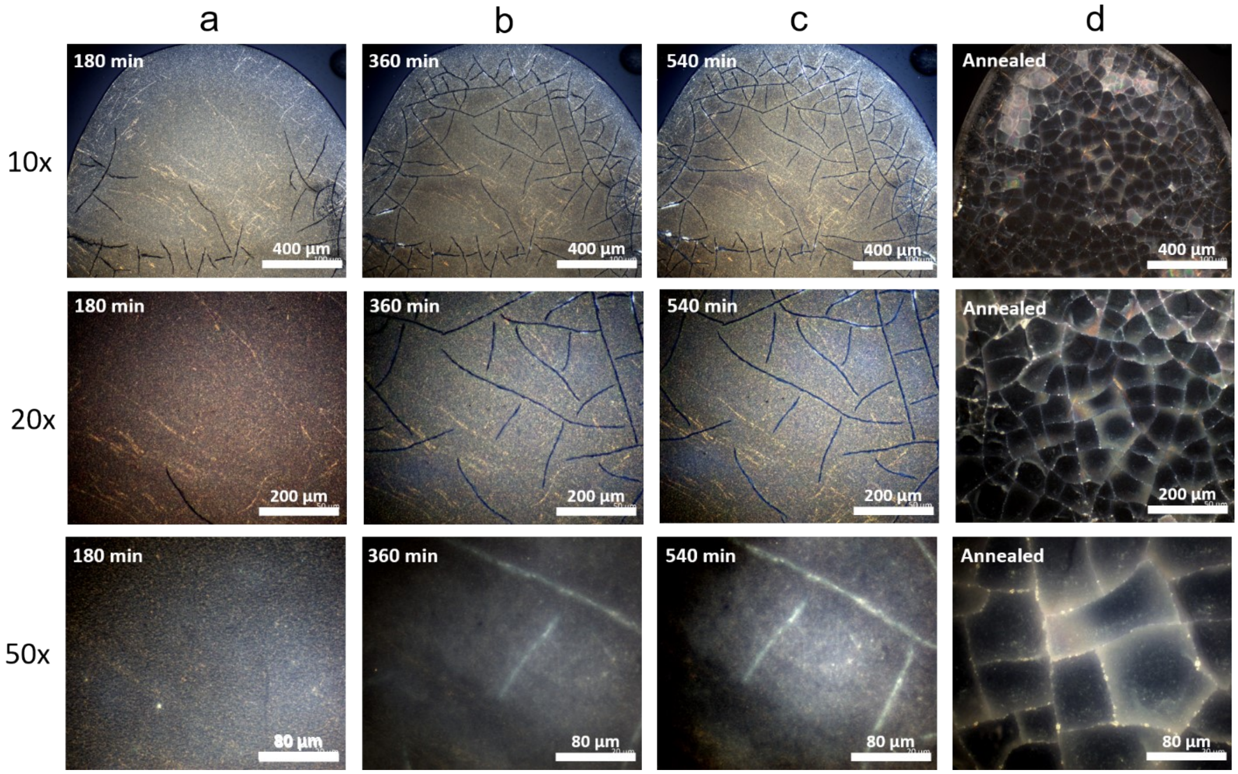


Figure S8. Optical microscopy of C_{12} vitrimer, crystallization at room temperature after (a) 180, (b) 360 and (c) 540 min of crystallization time, (d) Sample annealed at 65 °C for 2880 min after 10080 min of room temperature crystallization. Over time the grains shrink and collide. No dendritic structures are observed, consistent with the absence of a second melting peak in DSC.

The final vitrimer T_m exceeded that of the alkane diol, and the diffraction patterns are substantially different indicating the diols are not being expelled from the network and independently crystallizing (**Fig. S9**). The diols peaks were indexed and are a good match with literature.[1-3]

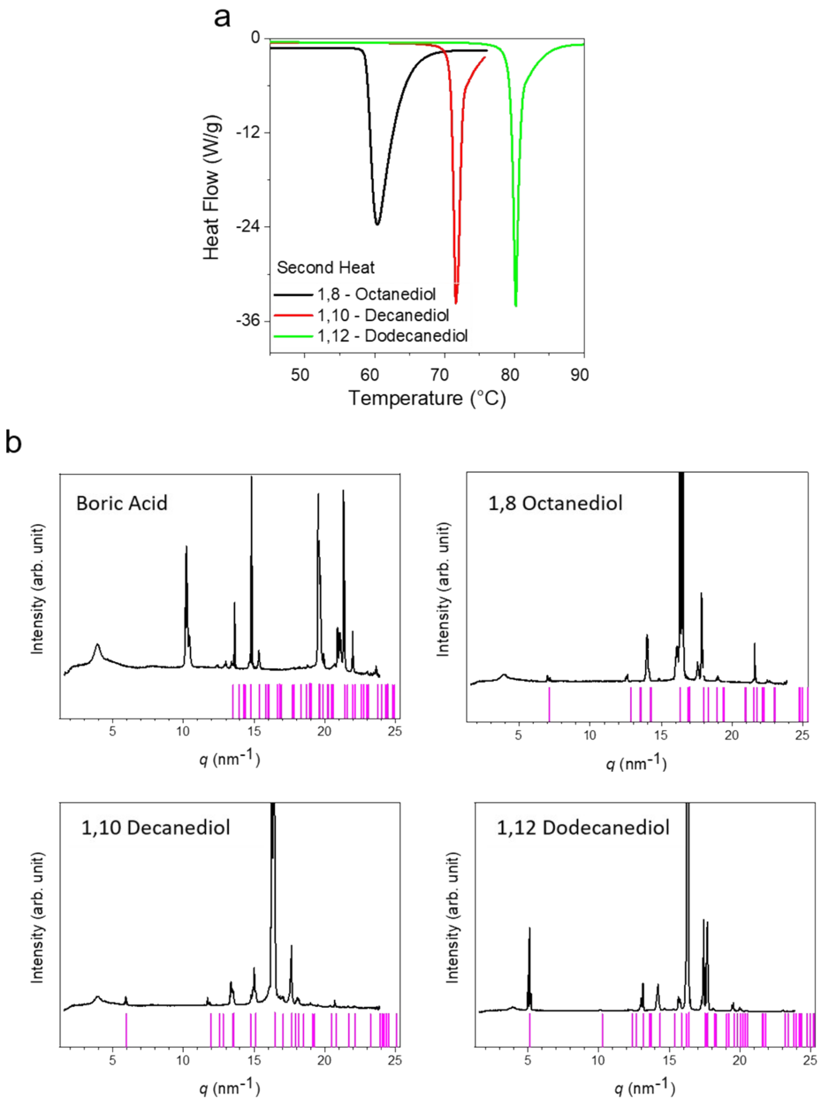


Figure S9. (a) Melting curves of the diol monomers show a sharp melting transition. (b) WAXS patterns of the diol monomers and boric acid crosslinker overlaid with simulated powder diffraction peaks shown as pink lines (VESTA software was used for the simulation).

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