Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for:

Effect of precise linker length, bond density, and broad temperature window on the rheological properties of polyethylene vitrimers

Bhaskar Soman,[1,2] and Christopher M. Evans[1,2,]

[1]Department of Materials Science and Engineering and [2]Frederick Seitz Materials Research Laboratory University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States.

Experimental Section

Materials: Boric acid ($B(OH)_3$, ≥ 99.5%), 1,4 butanediol (C_4, ≥ 99%), 1,6 hexanediol (C_6, 99%), 1,8 octanediol (C_8, 98%), 1,10 decanediol (C_{10}, 98%) and 1,12 dodecanediol (C_{12}, 99%), were purchased from Sigma-Aldrich and used without further purification.

Vitrimer 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 drier, 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.

Vitrimer Rheology: Rheological 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. Samples 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 -10 ˚C at 10 ˚C intervals with an applied stress of 1000 Pa. Viscosity of the networks was calculated by measuring the slope of the loss modulus vs frequency curve in the low frequency limit. Viscosity of the networks was plotted against inverse temperature and a characteristic Arrhenius behavior is observed as expected for vitrimers. Time temperature superposition master curves were generated using the TRIOS (TA Instruments) software with a reference temperature of 140 ˚C with no vertical shifting.

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 ℃ 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.

Differential Scanning Calorimetry (DSC): Samples with average weight between 3-6 mg were crimped in Tzero hermetic aluminum pans inside the glovebox. A TA Instruments DSC 25 with a RCS 120 cooling accessory was used to take all measurements. The glass transition temperature (T_g) for each sample was obtained by first heating the samples to 150 ℃ followed by quenching to -80 ℃ and then ramping to 120 ℃ at 20 ℃ / min. The DSC quench rate is the fastest allowed by the instrument, and varies depending on the temperature range from 50 °C/min (down to -30 °C) to 5 °C/min (when approaching -75 °C). The T_g is obtained from analysis of the heating profile using the ½ ΔCp criterion.

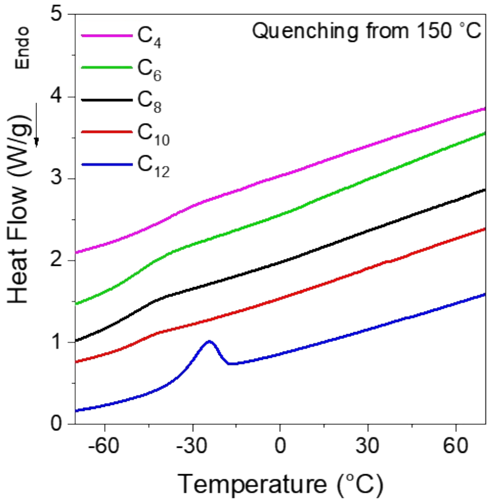

Figure S1. Quenching cycle of the DSC scan. An exothermic crystallization peak can be seen for C_{12}. The other networks do not crystallize during quenching.

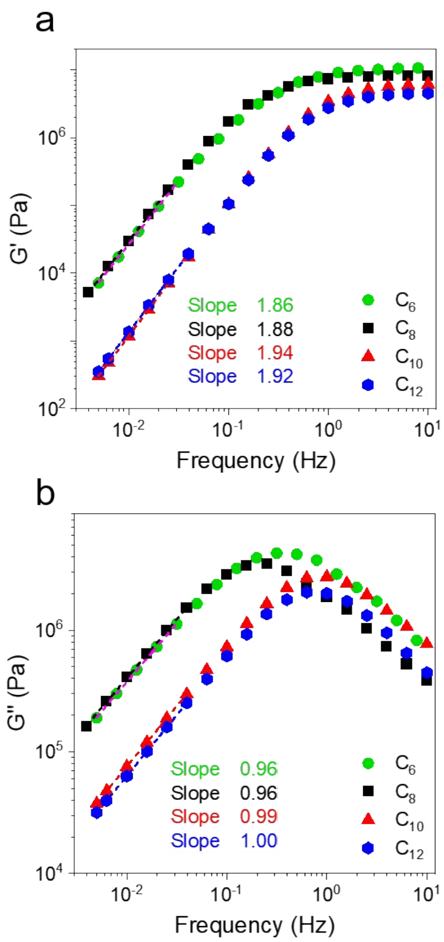

Figure S2. (a) Storage - G’ and (b) Loss - G’’ modulus of the PE vitrimers at 40 C. A high frequency rubbery plateau modulus monotonically increasing with crosslink density observed. The terminal relaxation at low frequency is confirmed by observation of characteristic slopes of ~ 1 for G’’ and ~2 for G’.

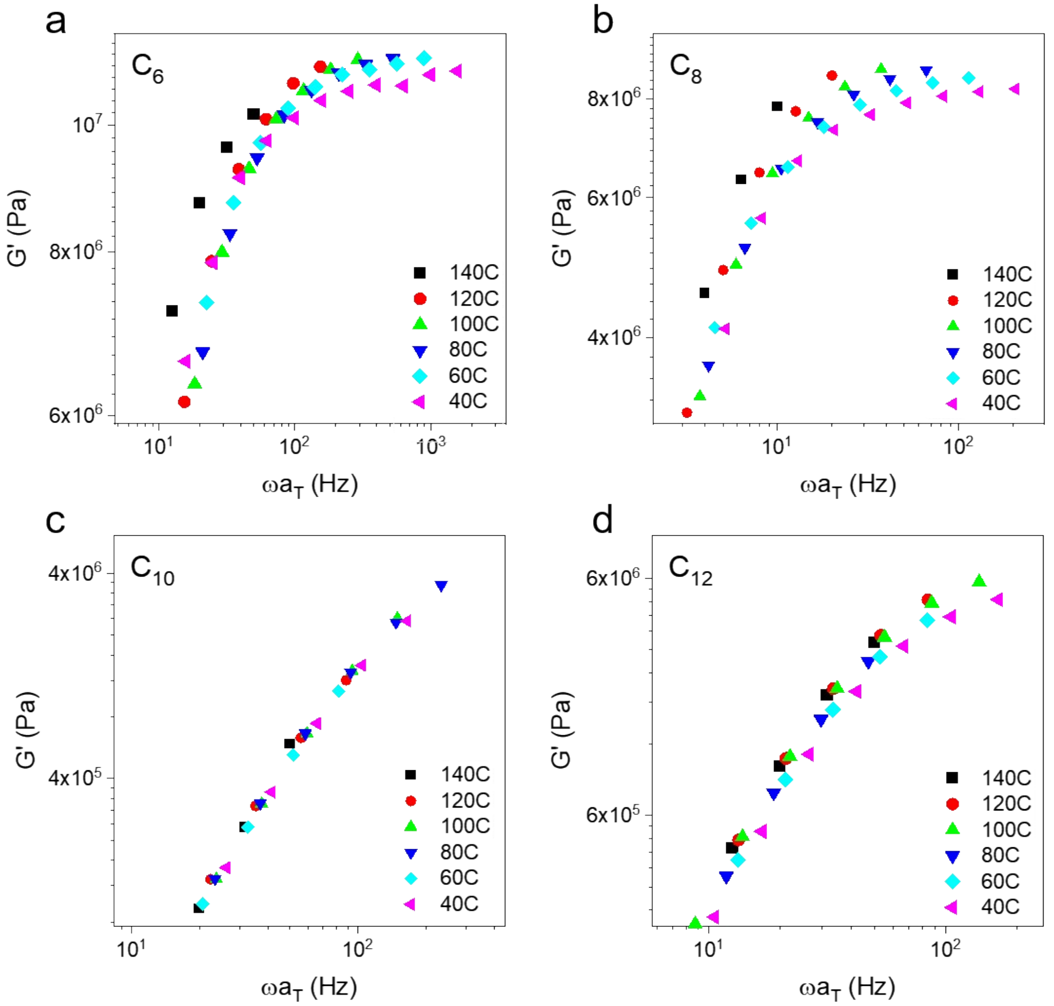

Figure S3. A zoomed in image of the high frequency region of the TTS plots from Figure 3. In all cases, the plateau modulus shows a slight increase with temperature.

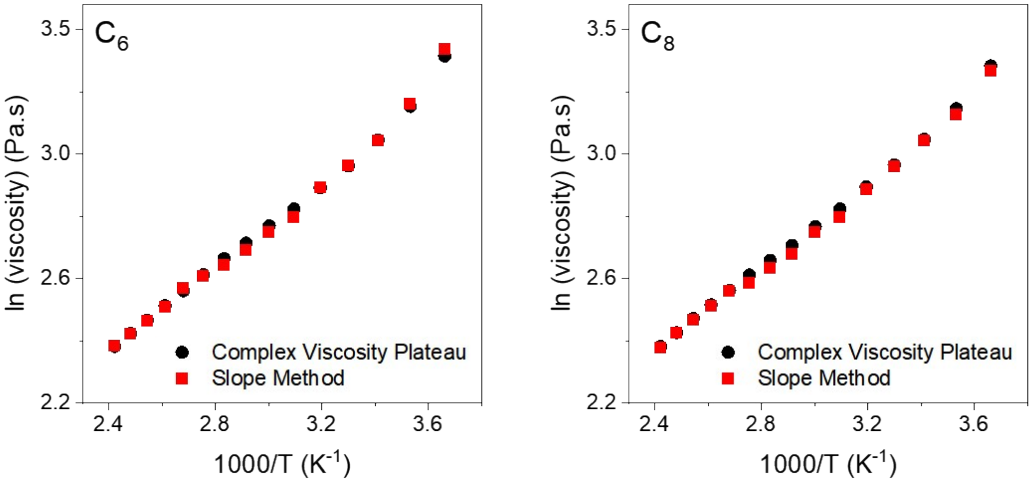

Figure S4. A comparison between viscosities obtained from the low frequency slope of G" compared to the complex viscosity. The values are the same within error.