Supporting Information

Effects of Crosslink Density and Plasticizer on Thermorheological Properties of Dissociative Guanidine-based Covalent Adaptable Networks

*Adelle L. Koenig,[1] Kelsey M. Allis,[2] John S. Lehr,[2] Michael B. Larsen[1]**

*Corresponding author: mike.larsen@wwu.edu

[1]Department of Chemistry, Western Washington University, Bellingham, WA, USA 98225

[2]Department of Engineering and Design, Western Washington University, Bellingham, WA, USA 98225

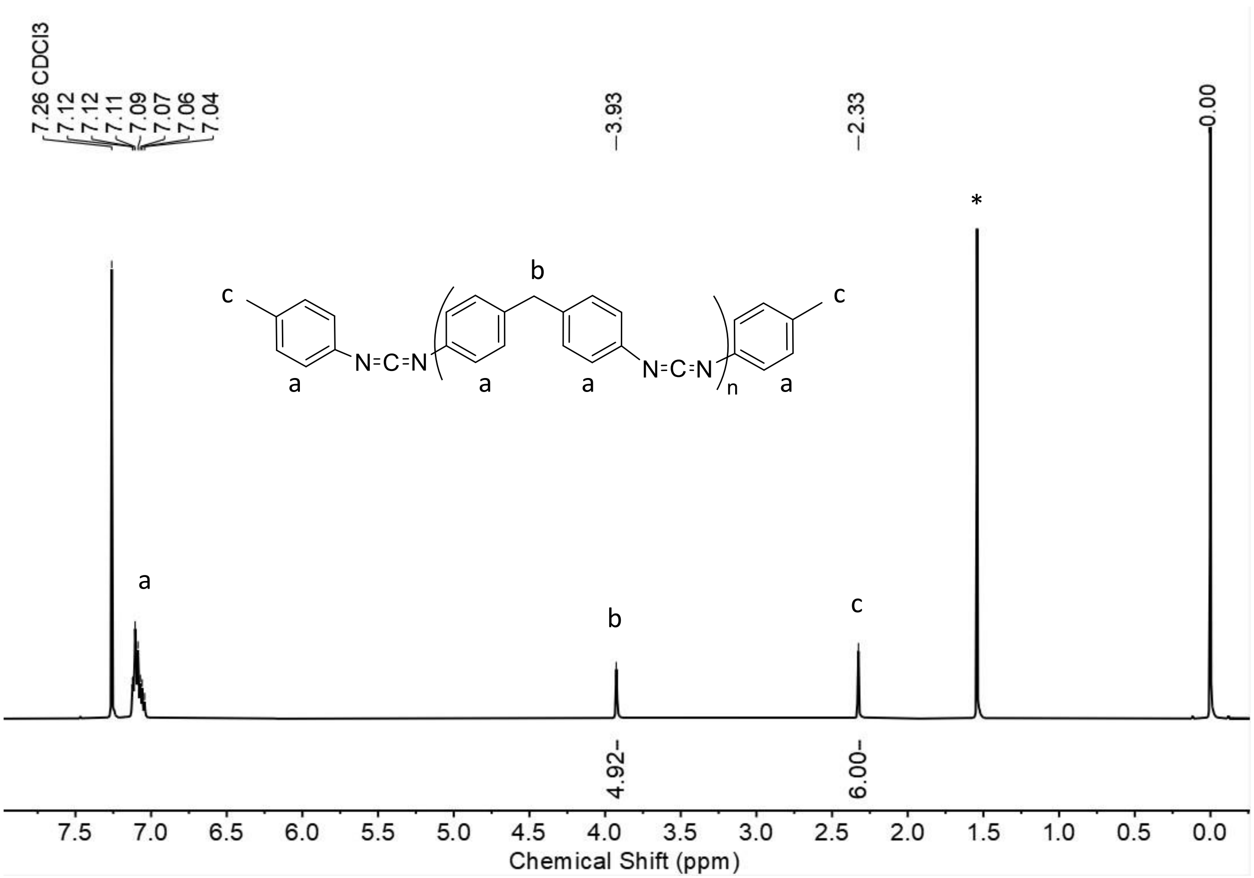


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of multifunctional carbodiimide oligomer. *H_2O from $CDCl_3$. Degree of polymerization (n) was calculated via endgroup analysis by integration of the peak at 2.33 ppm to 6.00 and division by 2 of the resultant integration of the peak at 3.93 ppm.

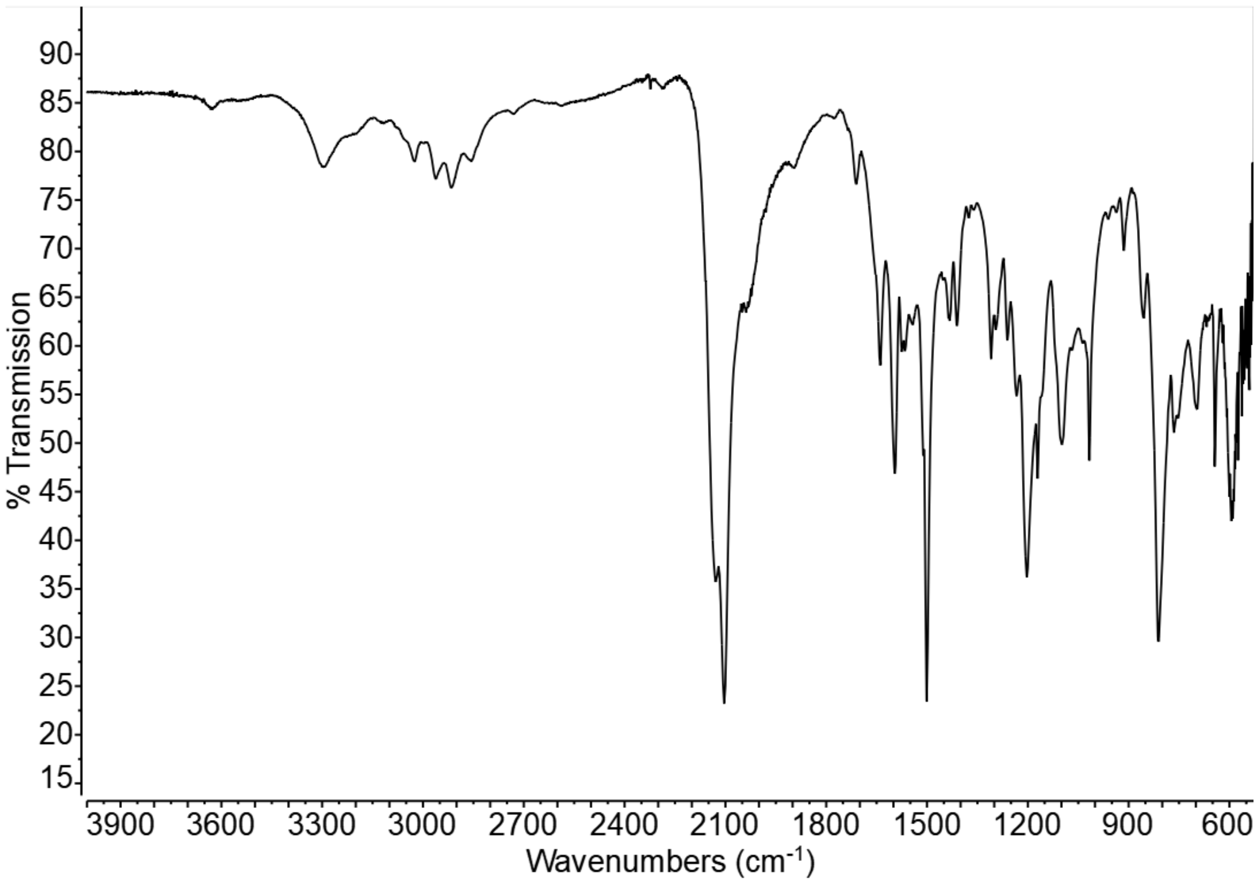


Figure S2. ATR FT-IR spectrum of multifunctional carbodiimide oligomer.

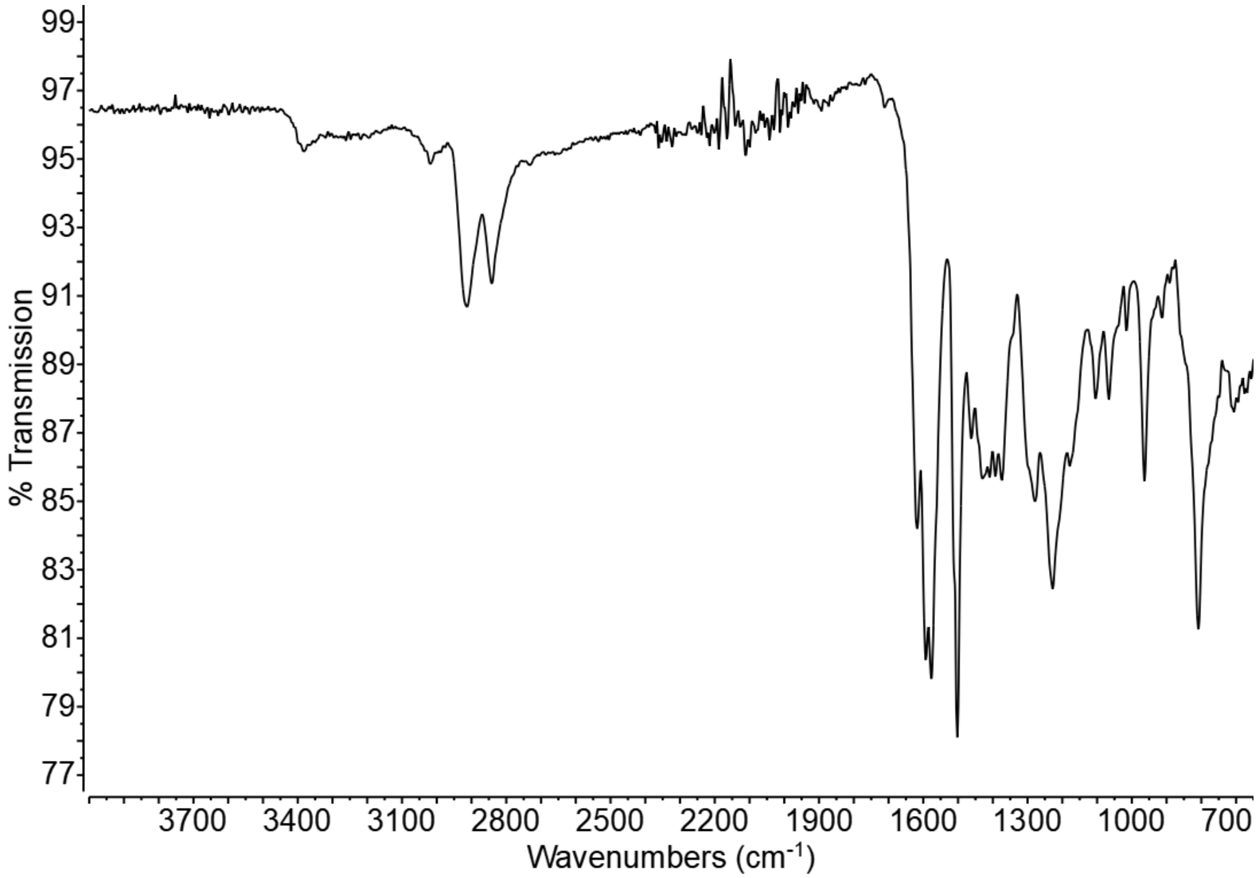


Figure S3. ATR FT-IR spectrum of CAN A_0.

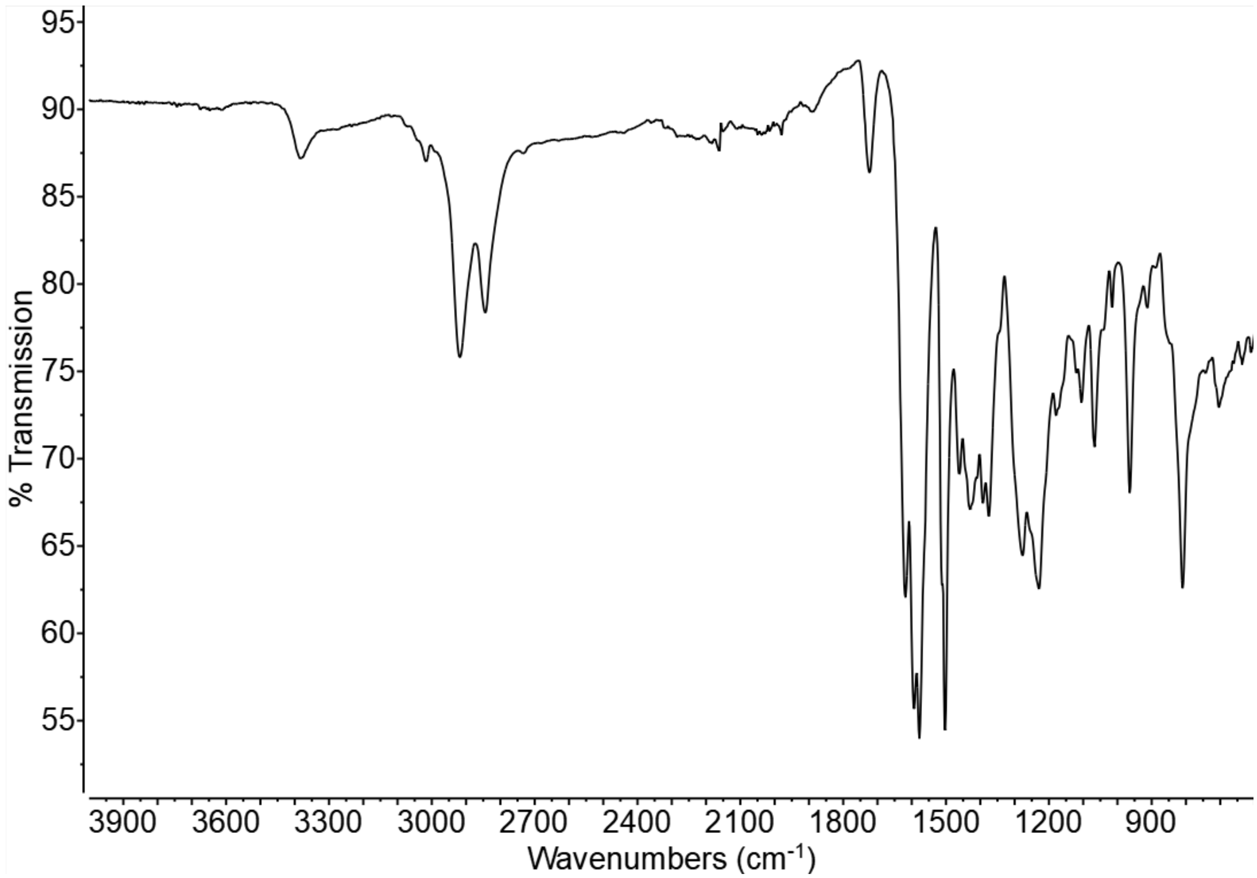


Figure S4. ATR FT-IR spectrum of CAN A_5.

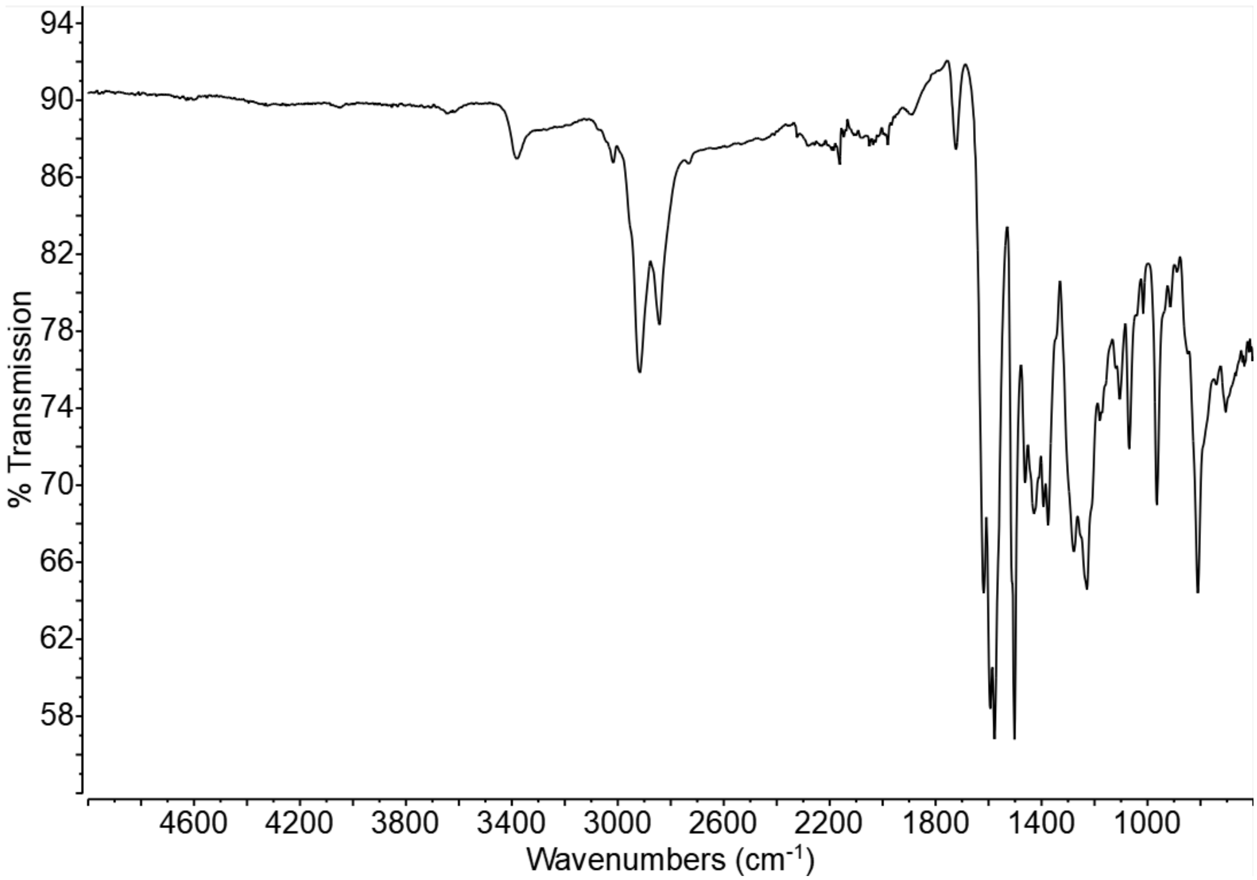


Figure S5. ATR FT-IR spectrum of CAN B_5.

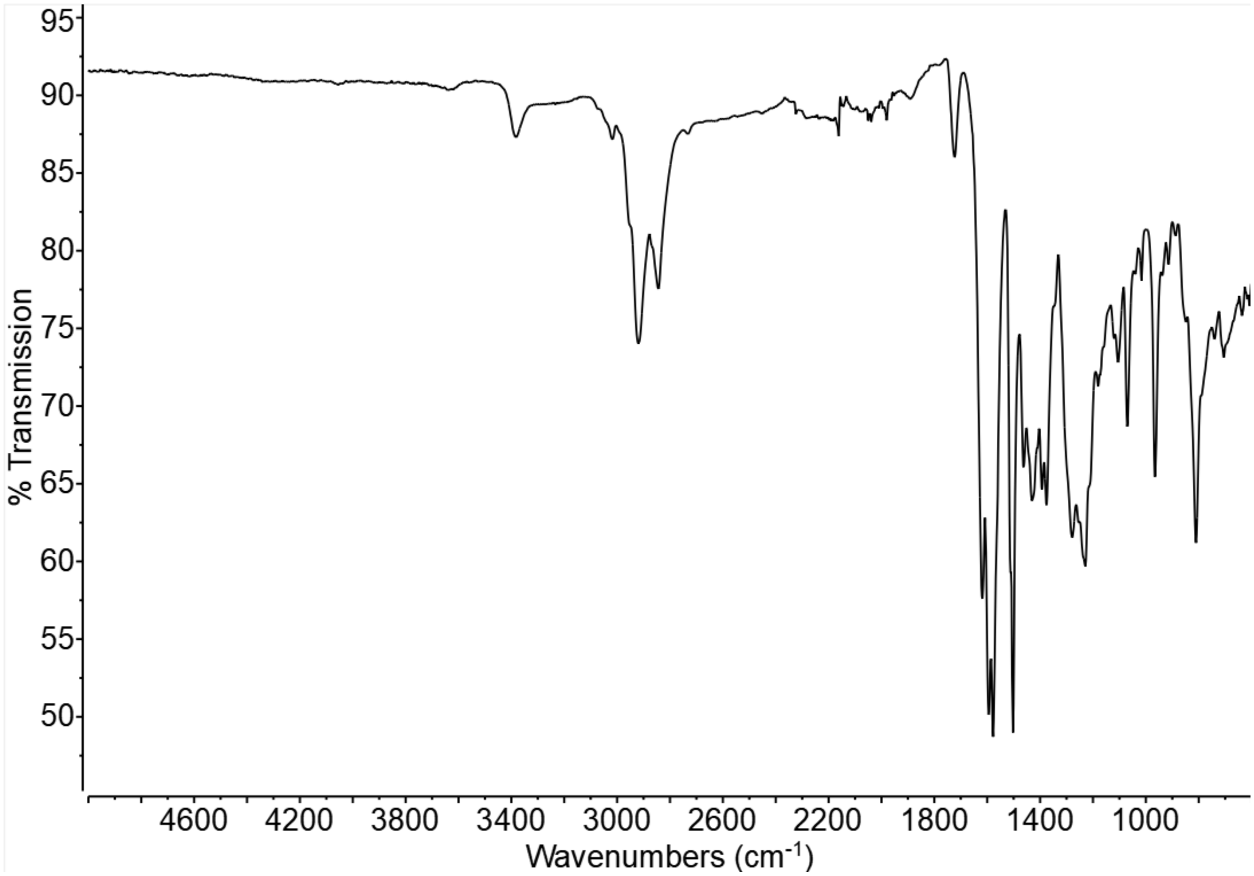


Figure S6. ATR FT-IR spectrum of CAN C_5.

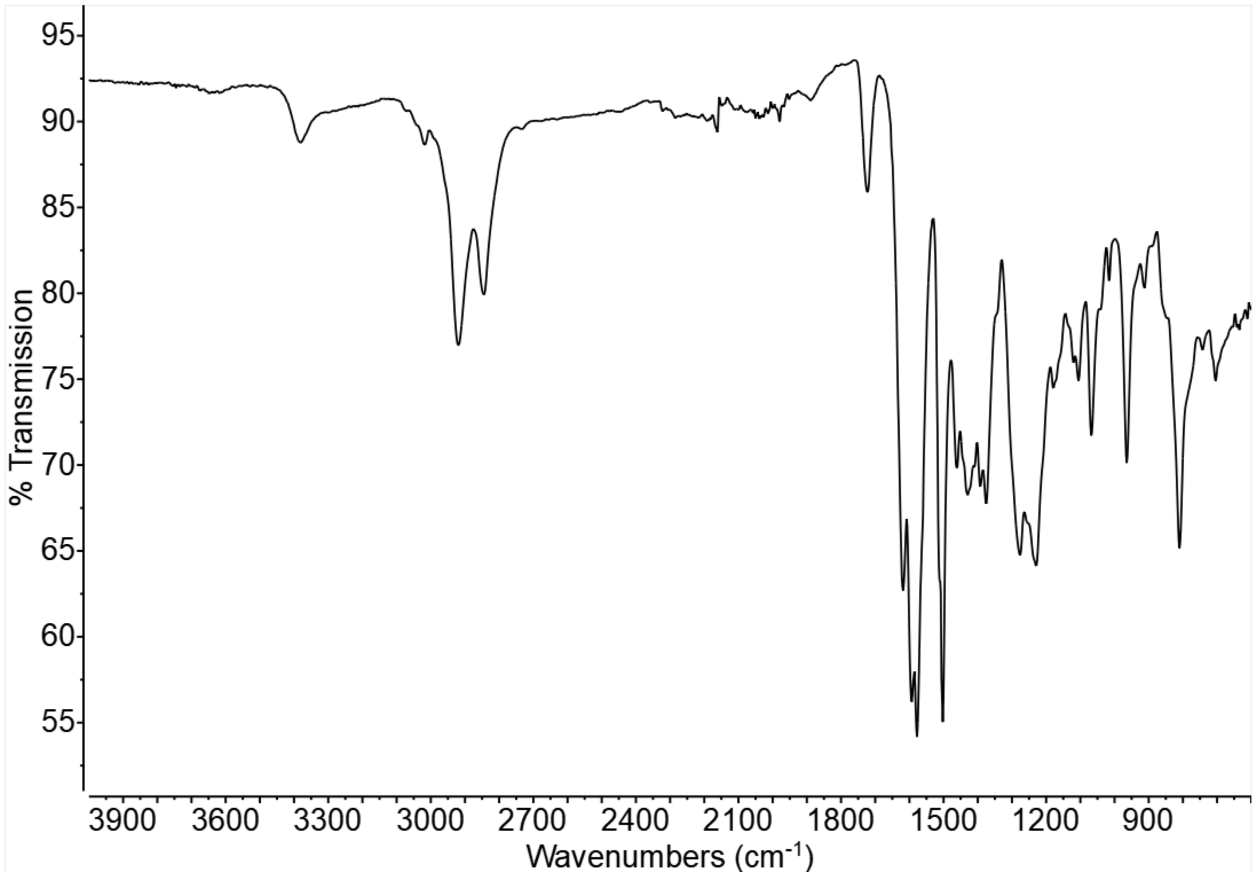


Figure S7. ATR FT-IR spectrum of CAN A_{10}.

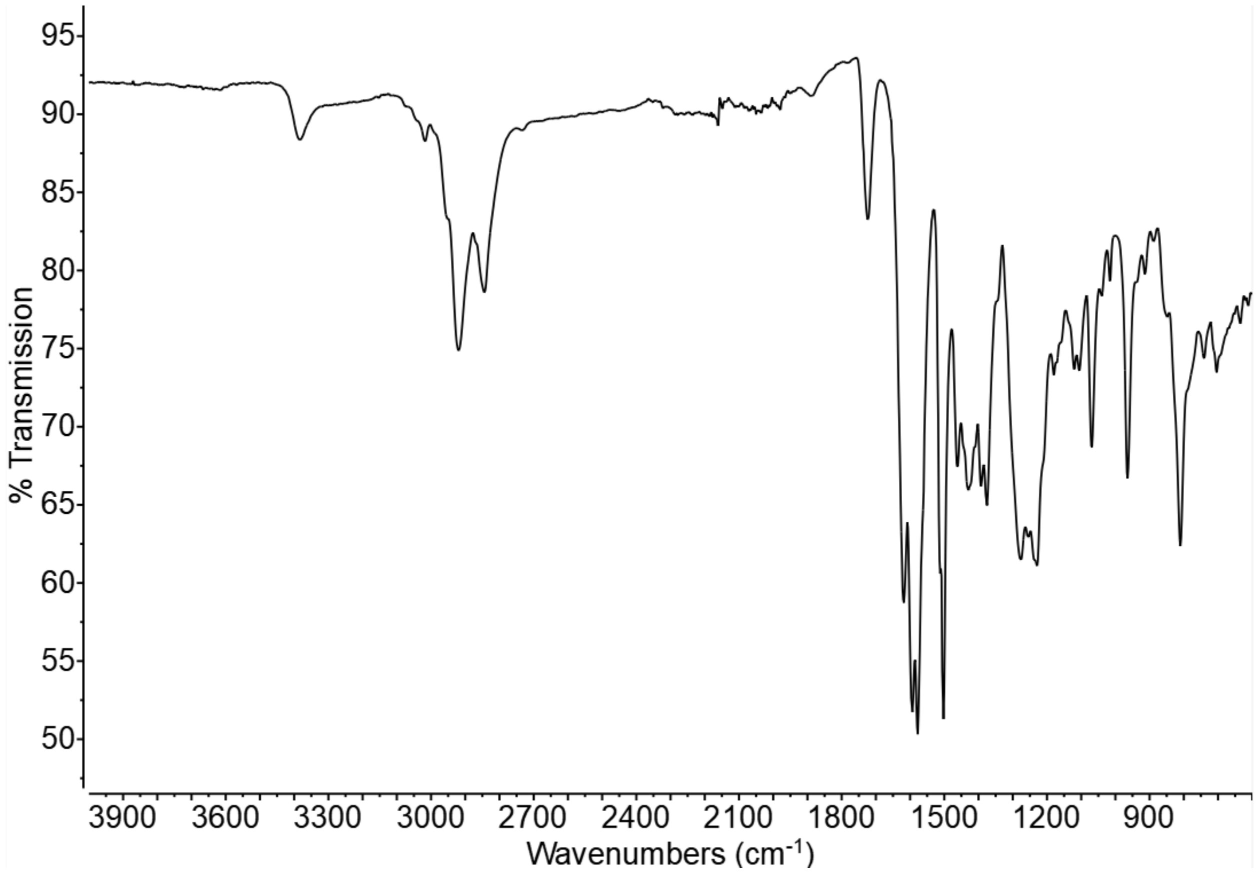


Figure S8. ATR FT-IR spectrum of CAN B_{10}.

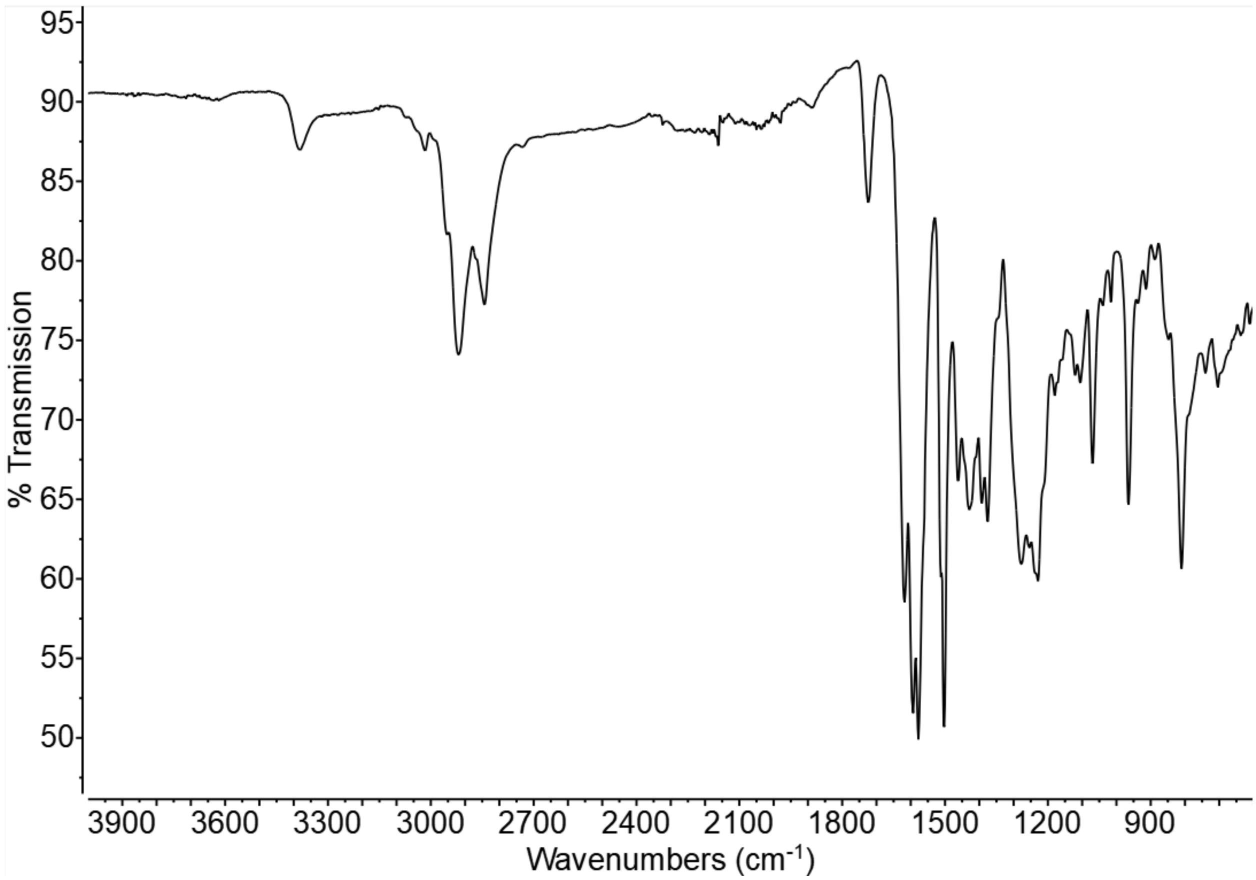


Figure S9. ATR FT-IR spectrum of CAN C_{10}.

Table S1. Mean and standard error of gel fractions for all CAN compositions.

CAN Composition	Gel Fraction
CAN A_0	99.3%
CAN A_5	94.0 ± 3.0%[a]
CAN A_{10}	88.8 ± 0.8%[b]
CAN B_5	88.9 ± 1.2%[a]
CAN B_{10}	85.0 ± 1.3%[b]
CAN C_5	74.2 ± 2.3%[a]
CAN C_{10}	77.3 ± 6.7%[b]

[a]Data from three individual samples. [b]Data from two individual samples.

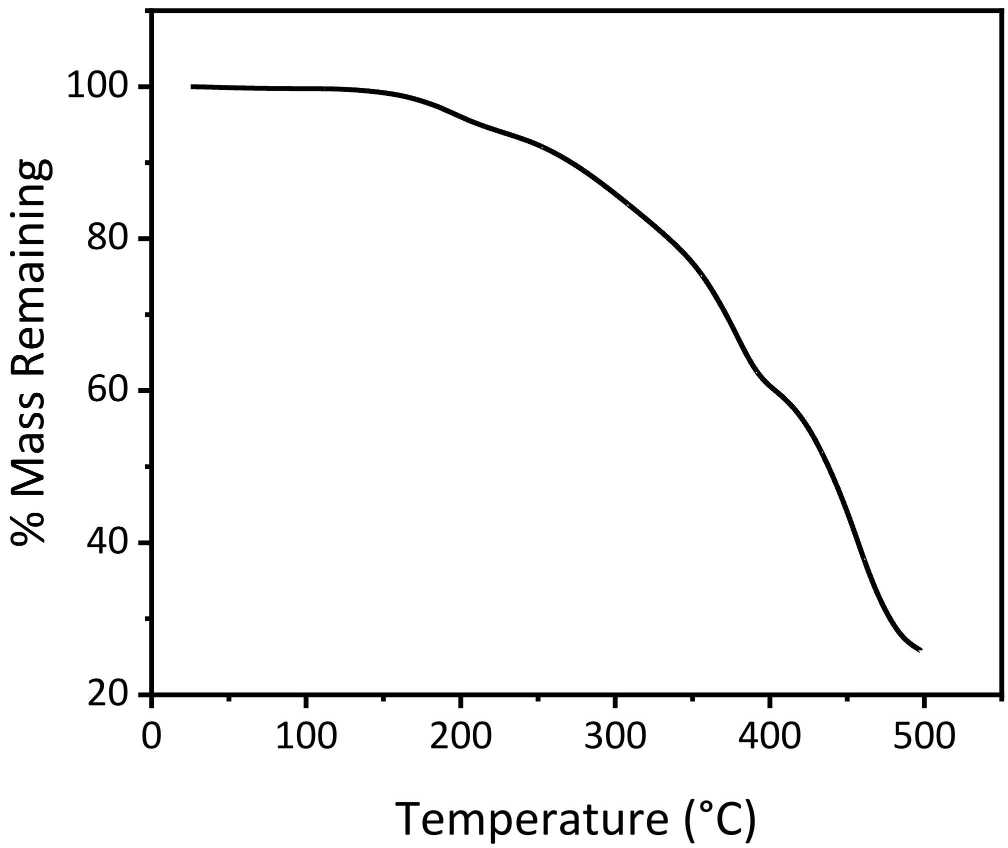


Figure S10. TGA thermogram of CAN A_0 (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 212 °C.

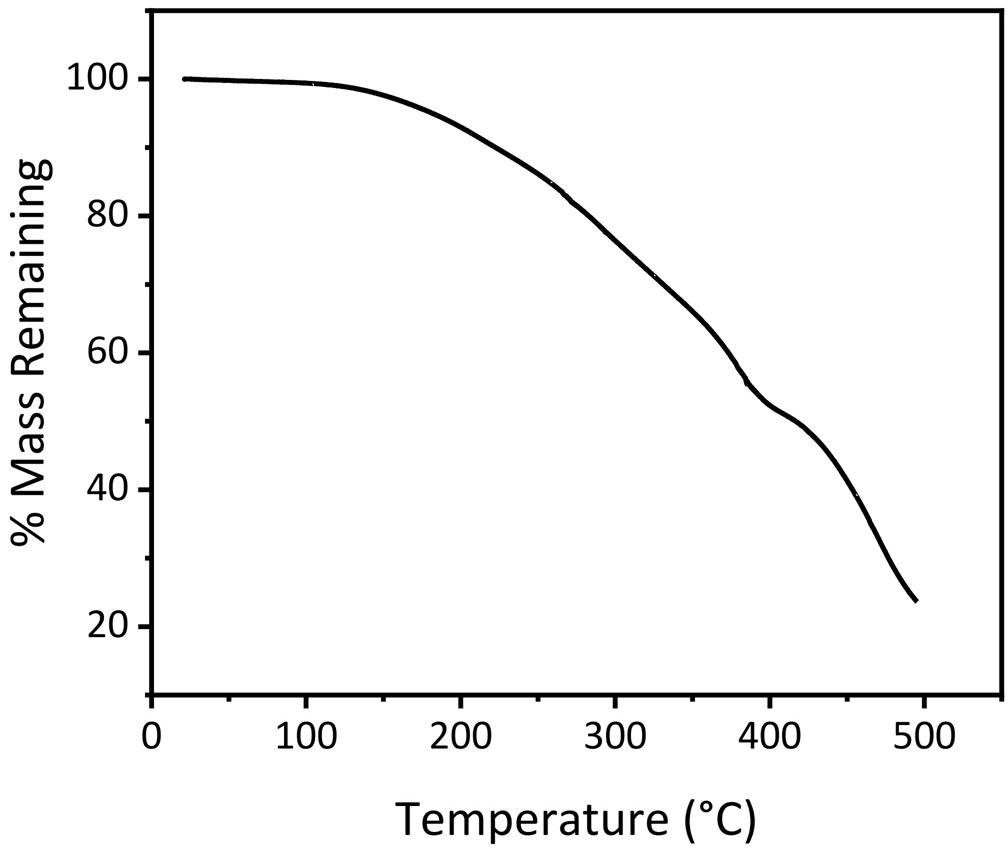


Figure S11. TGA thermogram of CAN A_5 (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 183 °C.

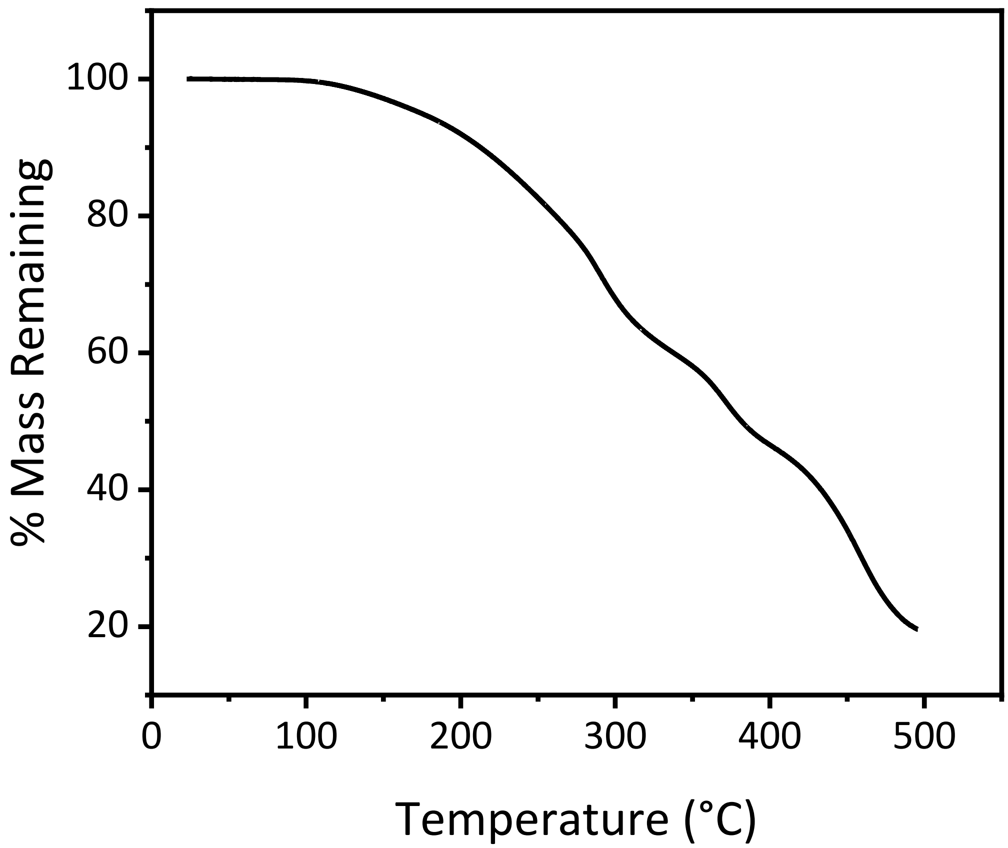


Figure S12. TGA thermogram of CAN B_5 (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 173 °C.

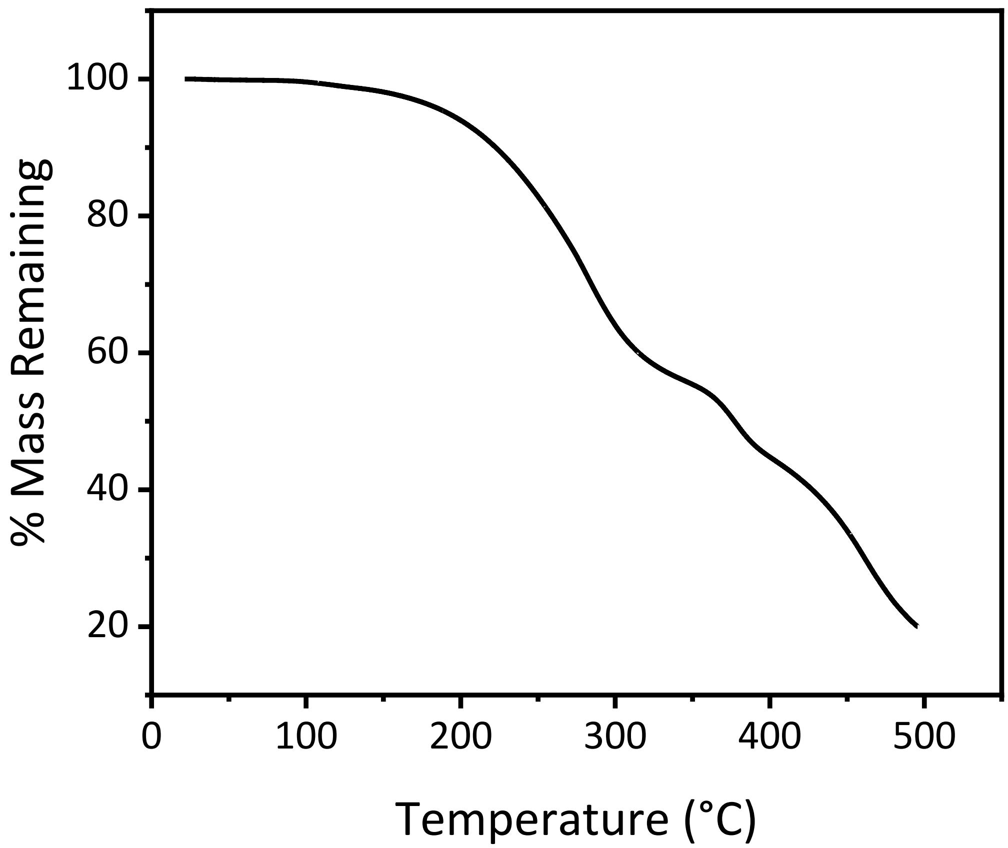


Figure S13. TGA thermogram of CAN C_5 (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 191 °C.

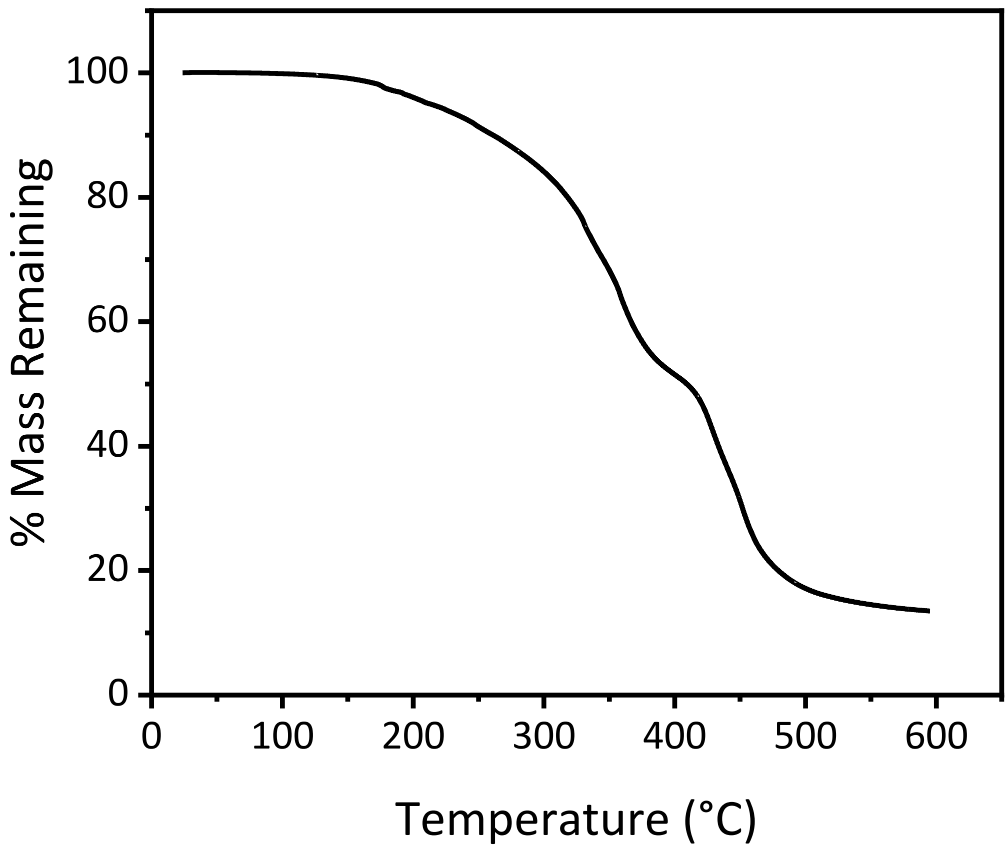


Figure S14. TGA thermogram of CAN A_{10} (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 212 °C.

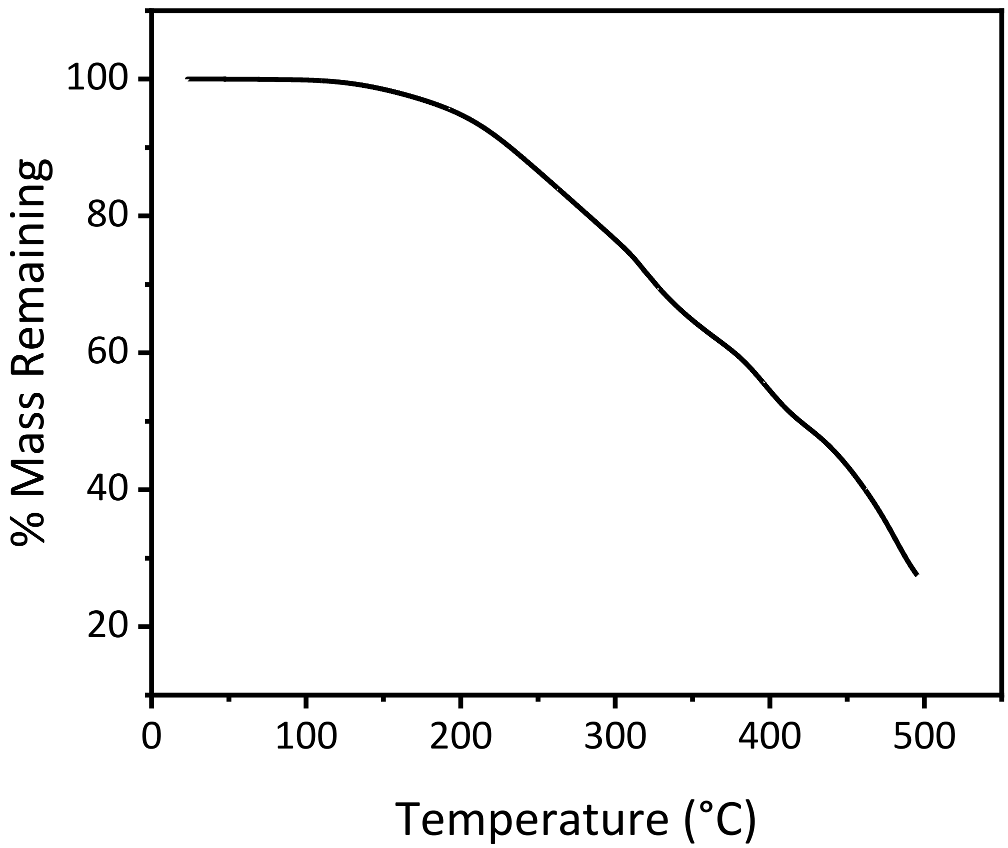


Figure S15. TGA thermogram of CAN B_{10} (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 198 °C.

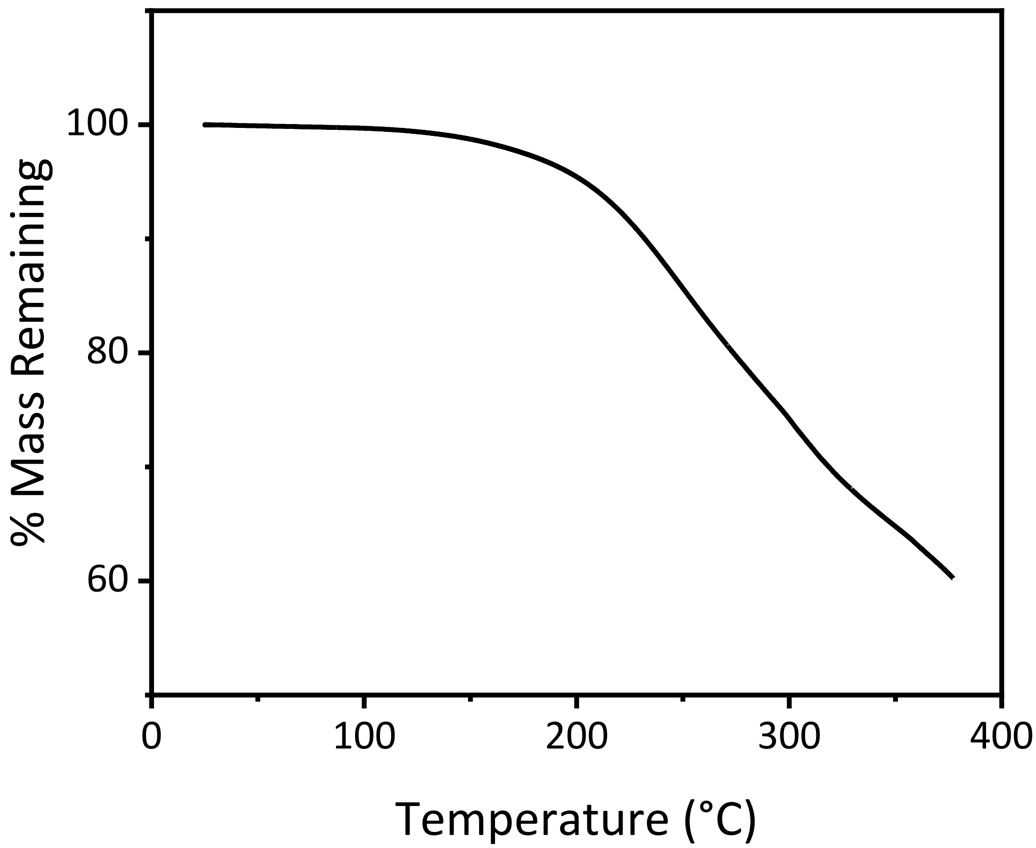


Figure S16. TGA thermogram of CAN C_{10} (10 °C/min, N_2 atmosphere). $T_{d,5\%}$ = 204 °C.

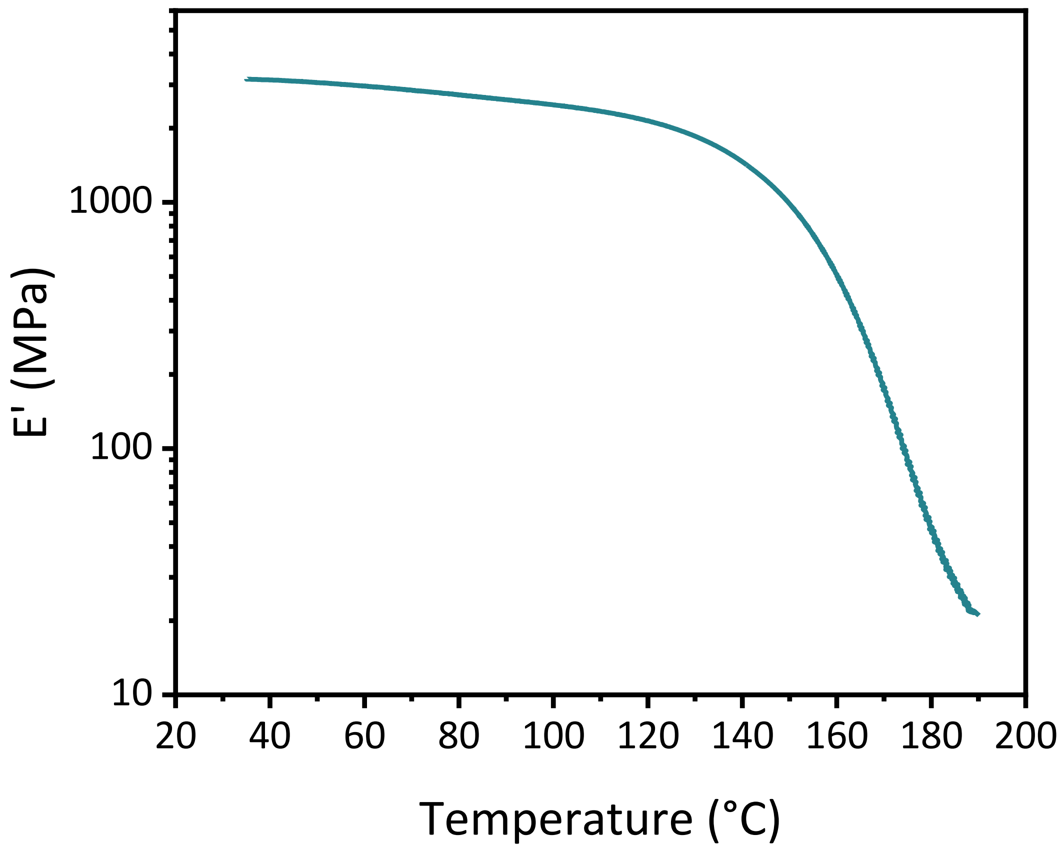


Figure S17. DMA thermogram of storage modulus versus temperature for representative sample of CAN A_0.

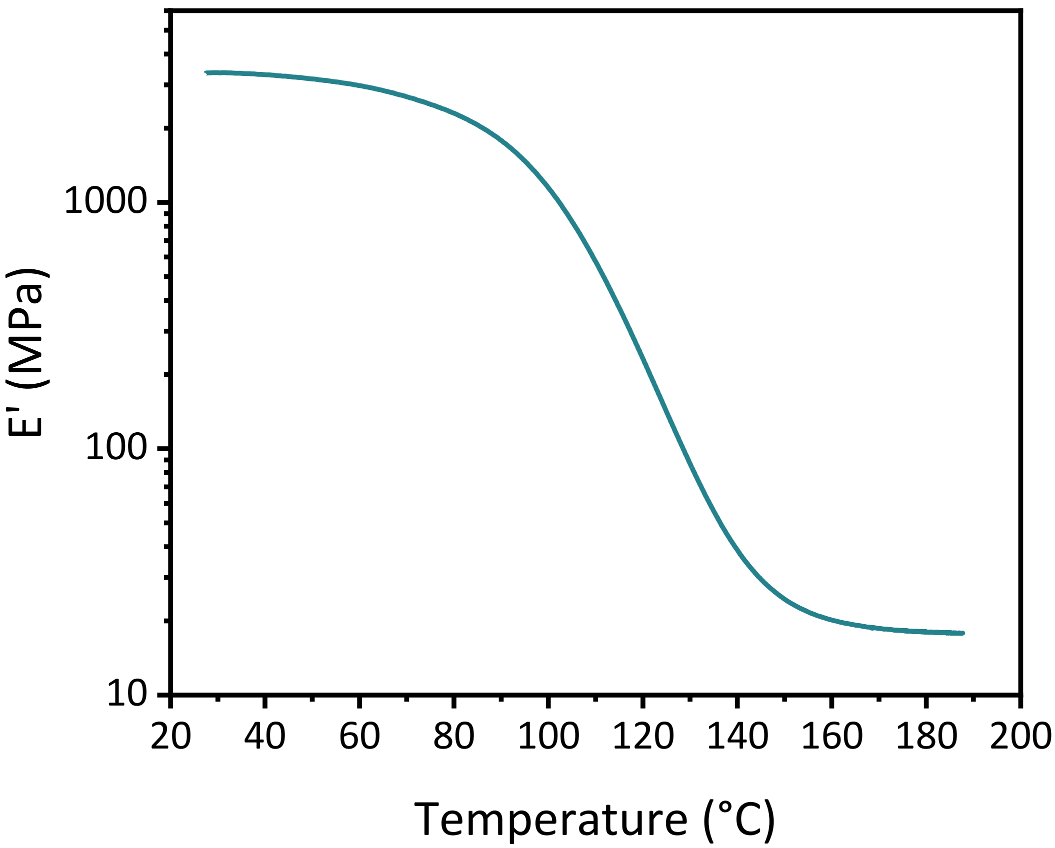


Figure S18. DMA thermogram of storage modulus versus temperature for representative sample of CAN A_5.

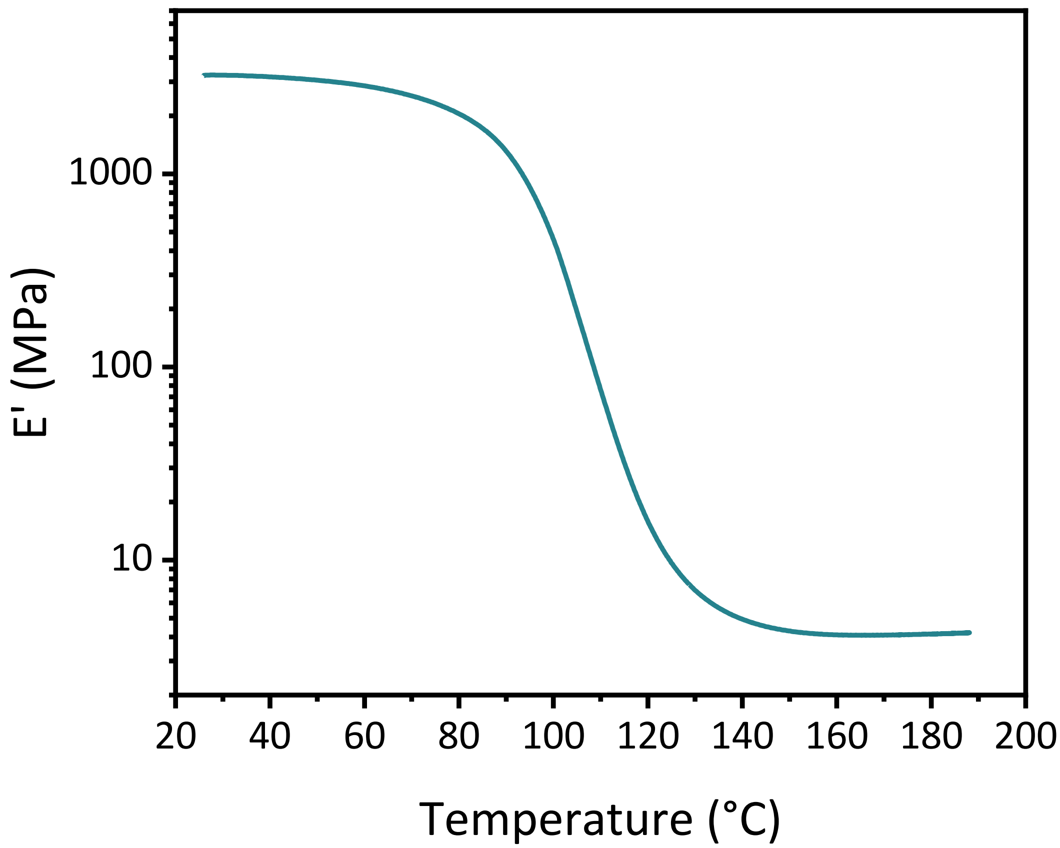


Figure S19. DMA thermogram of storage modulus versus temperature for representative sample of CAN B_5.

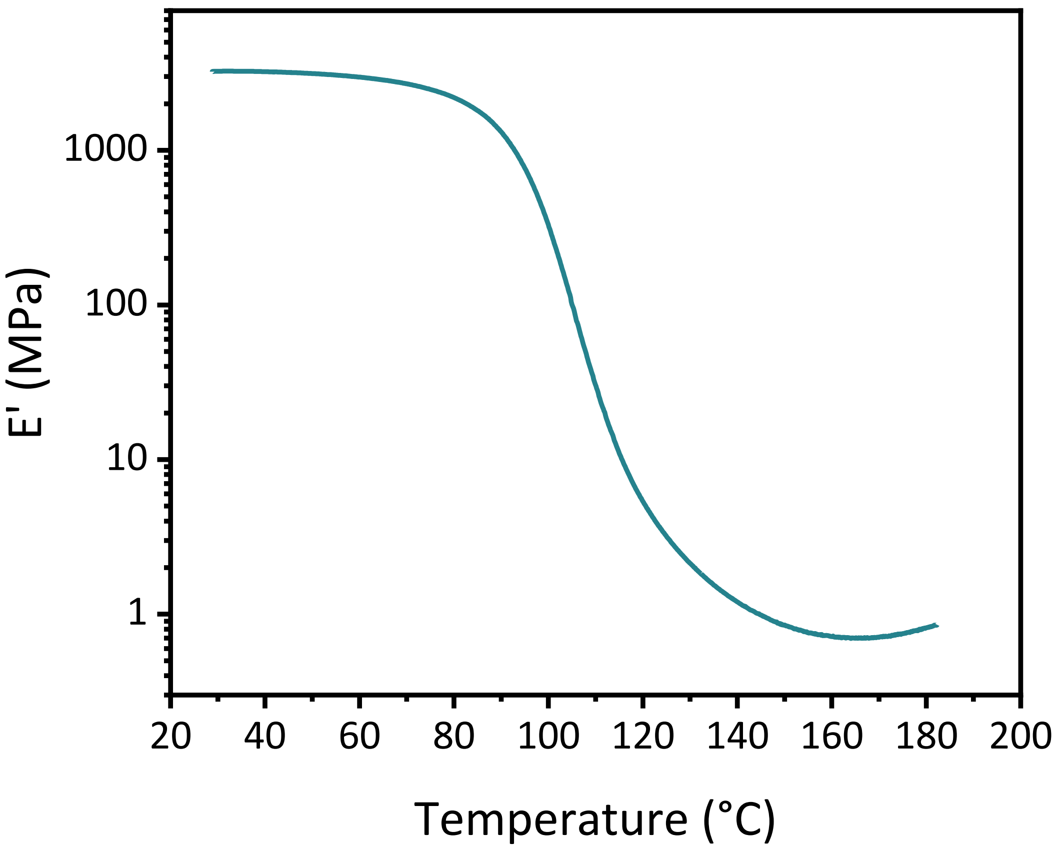


Figure S20. DMA thermogram of storage modulus versus temperature for representative sample of CAN C_5.

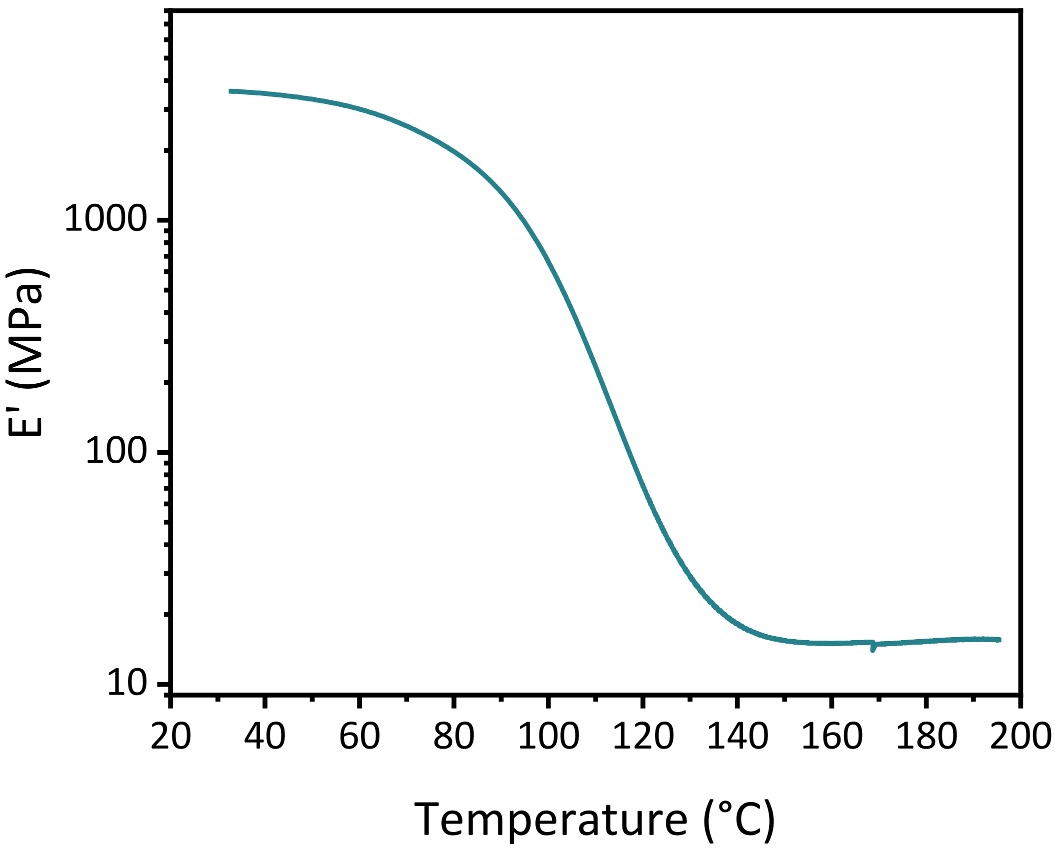


Figure S21. DMA thermogram of storage modulus versus temperature for representative sample of CAN A_{10}.

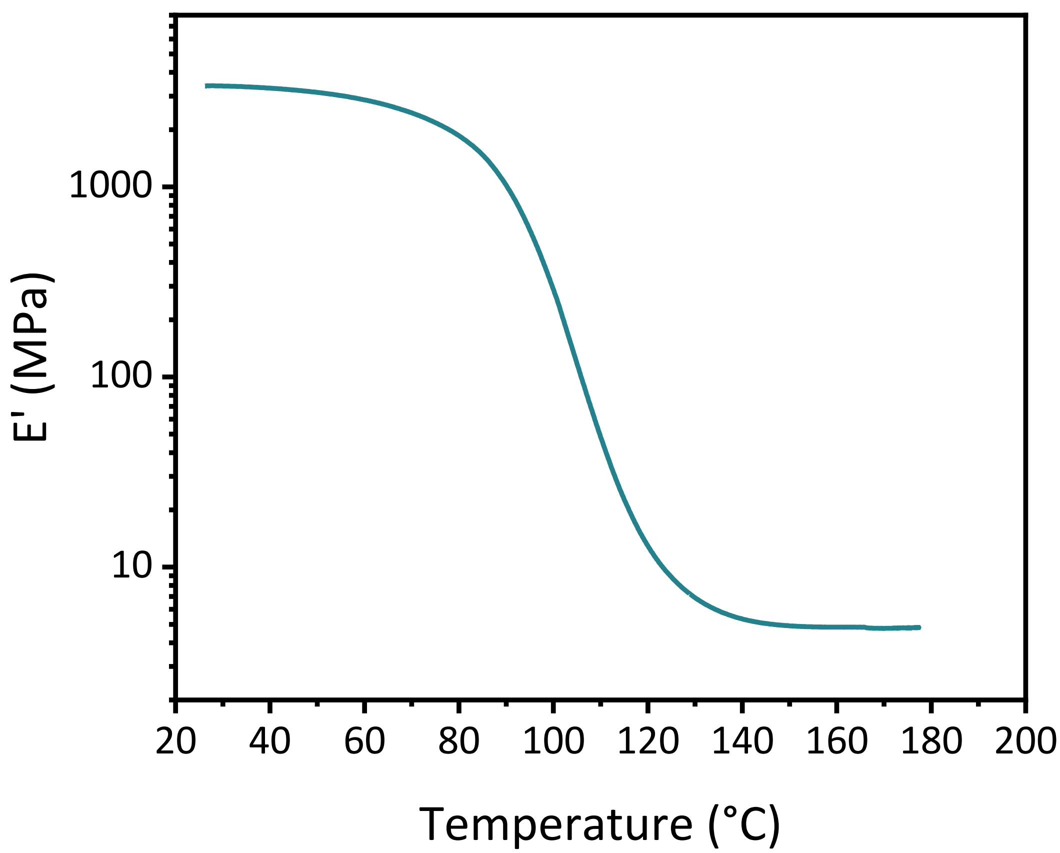


Figure S22. DMA thermogram of storage modulus versus temperature for representative sample of CAN B_{10}.

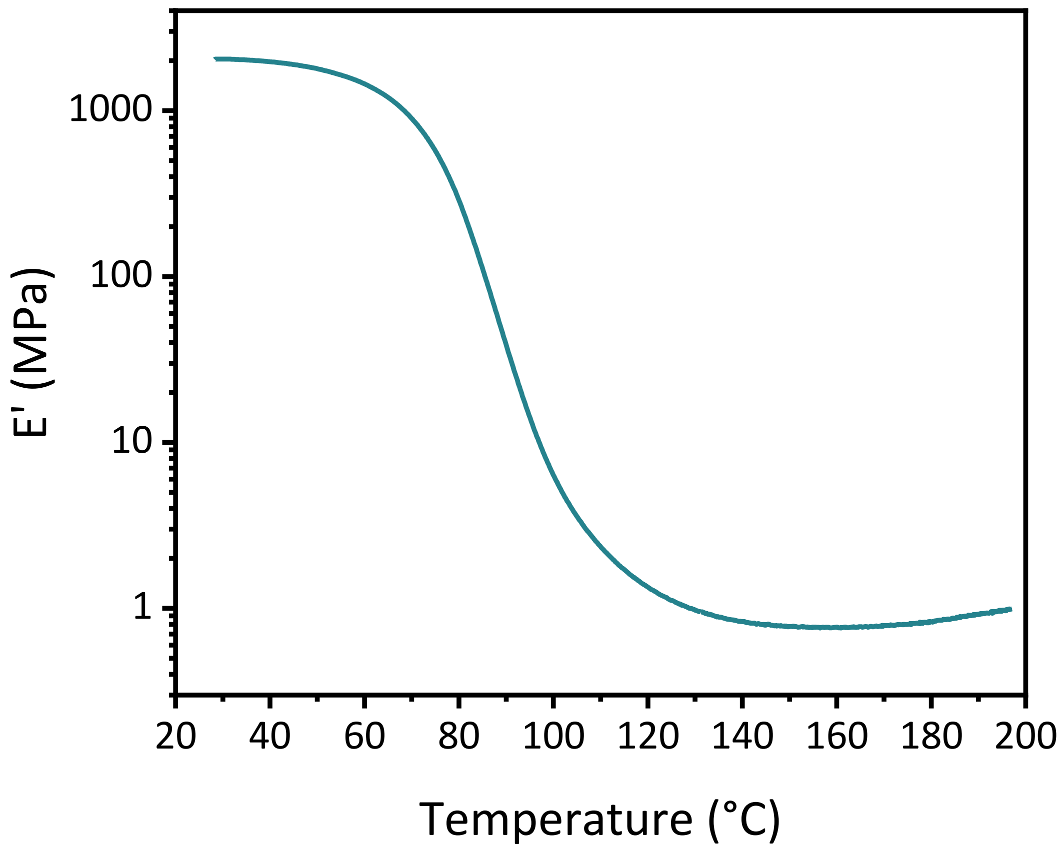


Figure S23. DMA thermogram of storage modulus versus temperature for representative sample of CAN C_{10}.

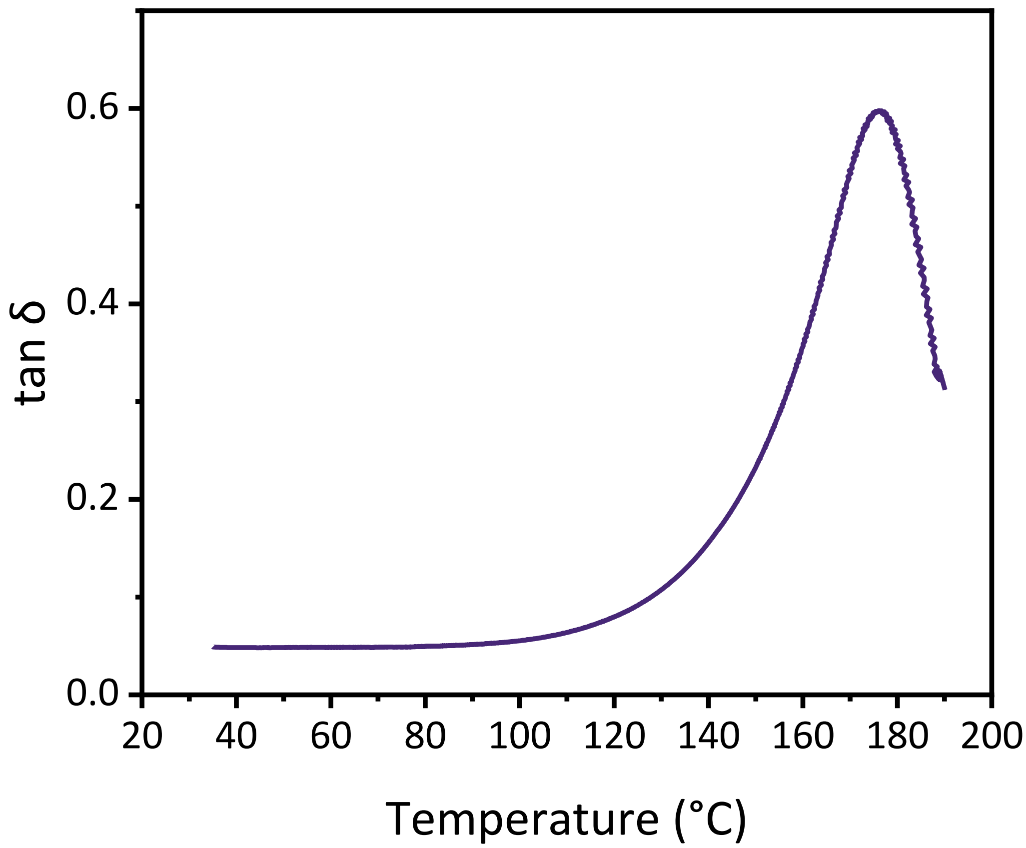


Figure S24. DMA thermogram of tan δ versus temperature for representative sample of CAN A_0. T_g is taken as the peak of tan δ; T_g = 176 °C.

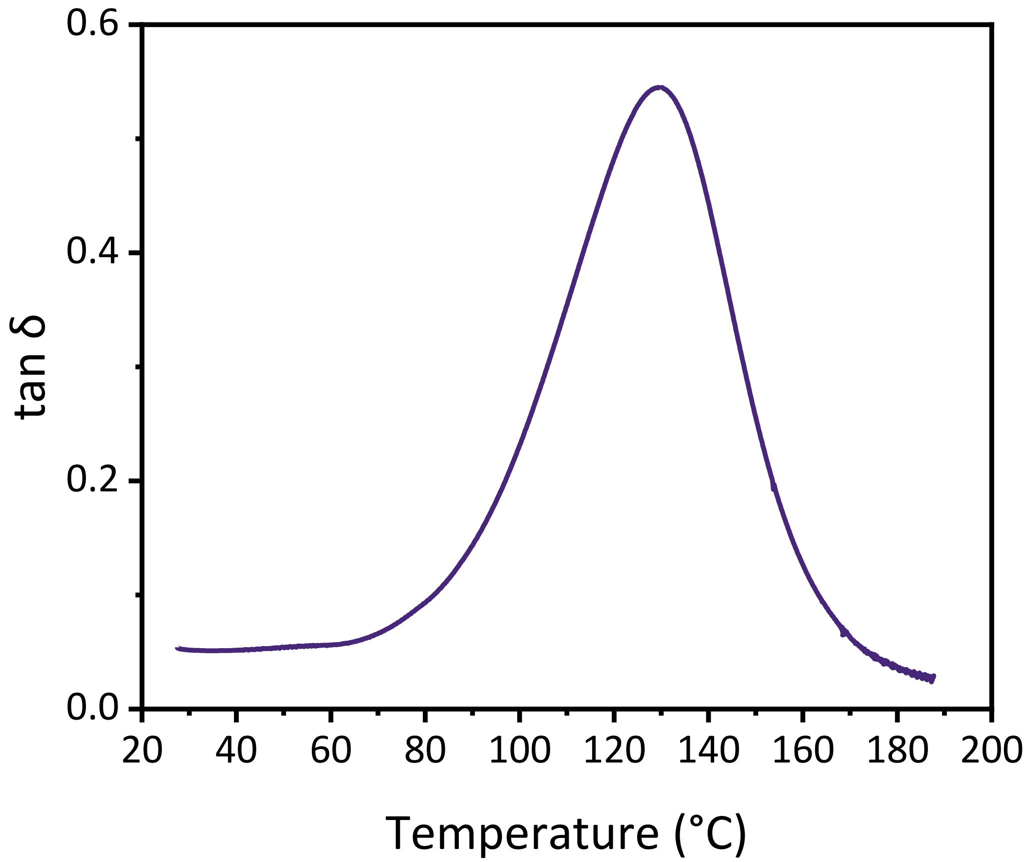


Figure S25. DMA thermogram of tan δ versus temperature for representative sample of CAN A_5. T_g is taken as the peak of tan δ; T_g = 130 °C.

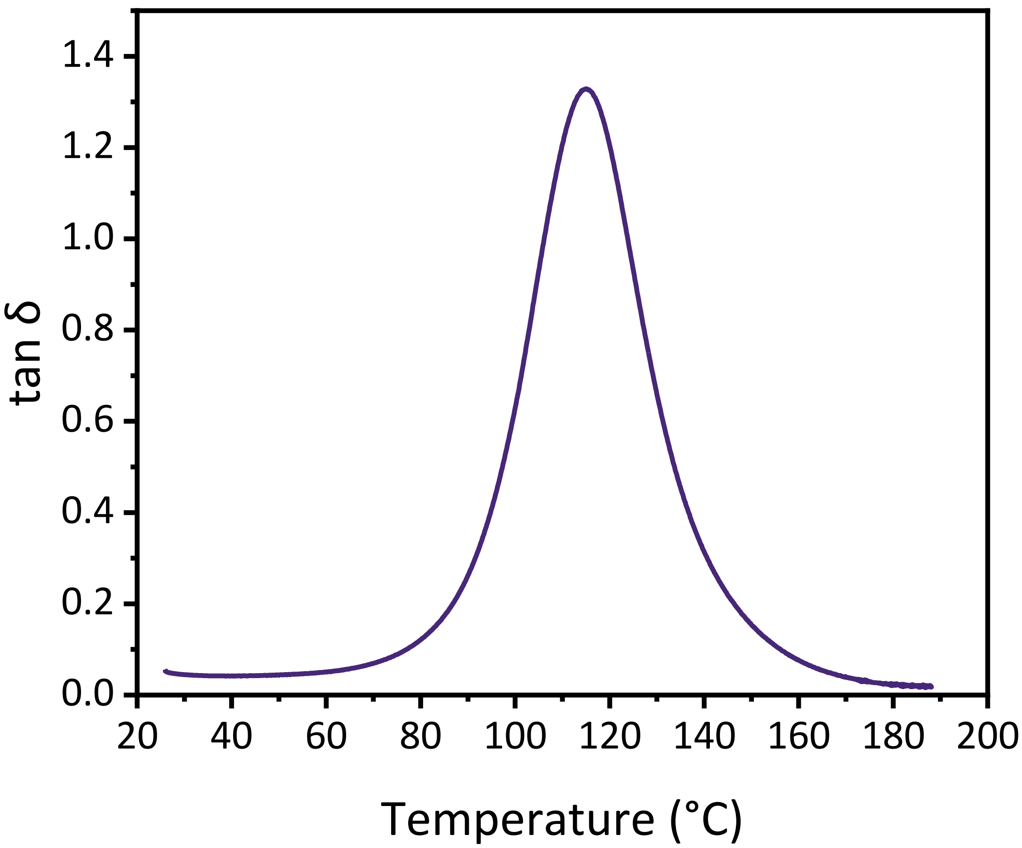


Figure S26. DMA thermogram of tan δ versus temperature for representative sample of CAN B_5. T_g is taken as the peak of tan δ; T_g = 116 °C.

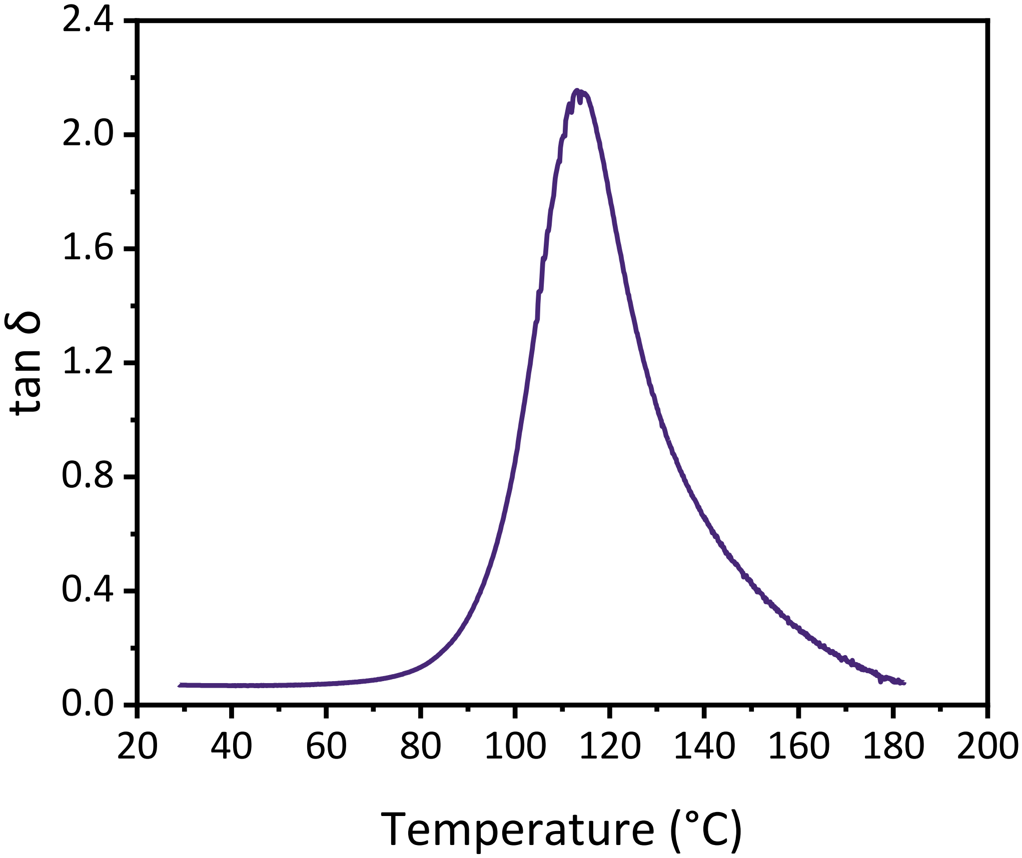


Figure S27. DMA thermogram of tan δ versus temperature for representative sample of CAN C_5. T_g is taken as the peak of tan δ; T_g = 114 °C.

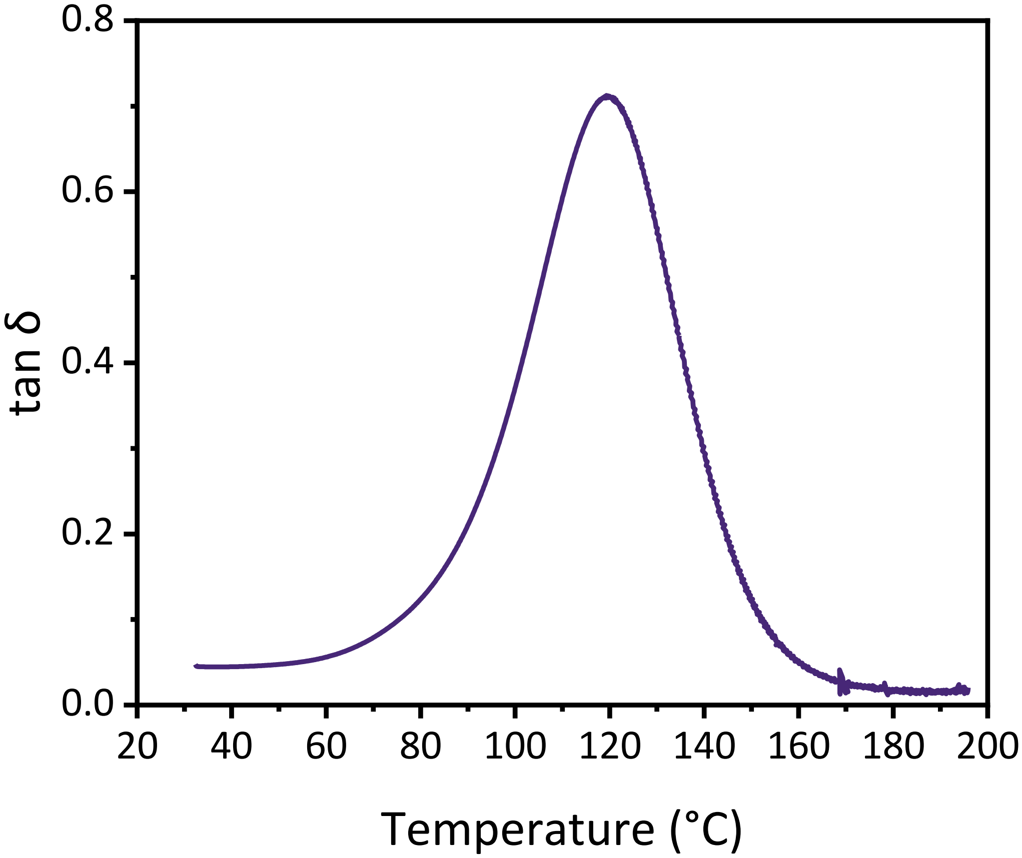


Figure S28. DMA thermogram of tan δ versus temperature for representative sample of CAN A_{10}. T_g is taken as the peak of tan δ; T_g = 120 °C.

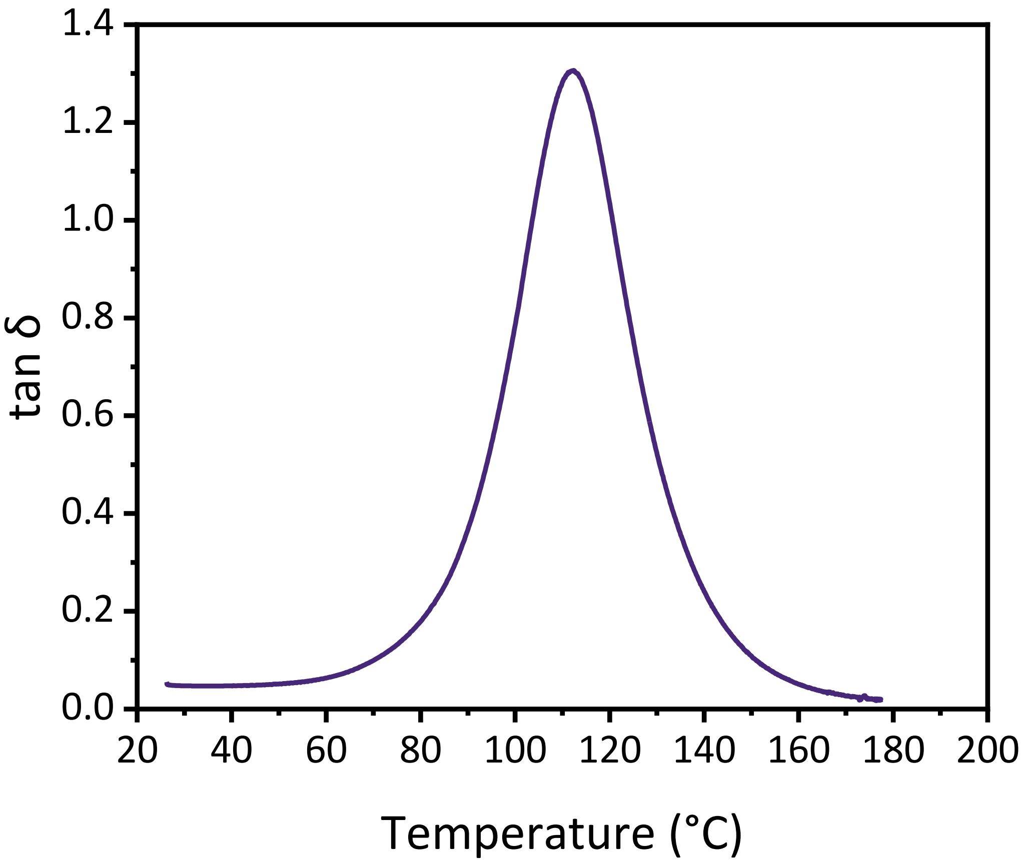


Figure S29. DMA thermogram of tan δ versus temperature for representative sample of CAN B_{10}. T_g is taken as the peak of tan δ; T_g = 112 °C.

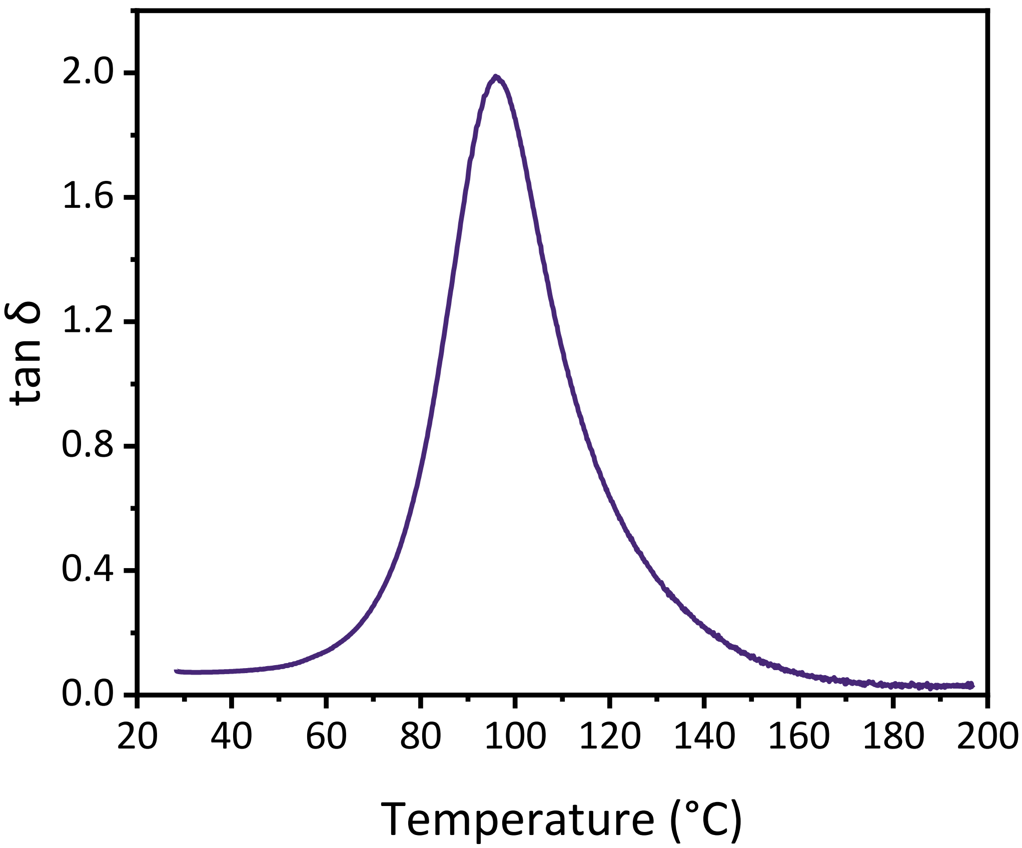


Figure S30. DMA thermogram of tan δ versus temperature for representative sample of CAN C_{10}. T_g is taken as the peak of tan δ; T_g = 96 °C.

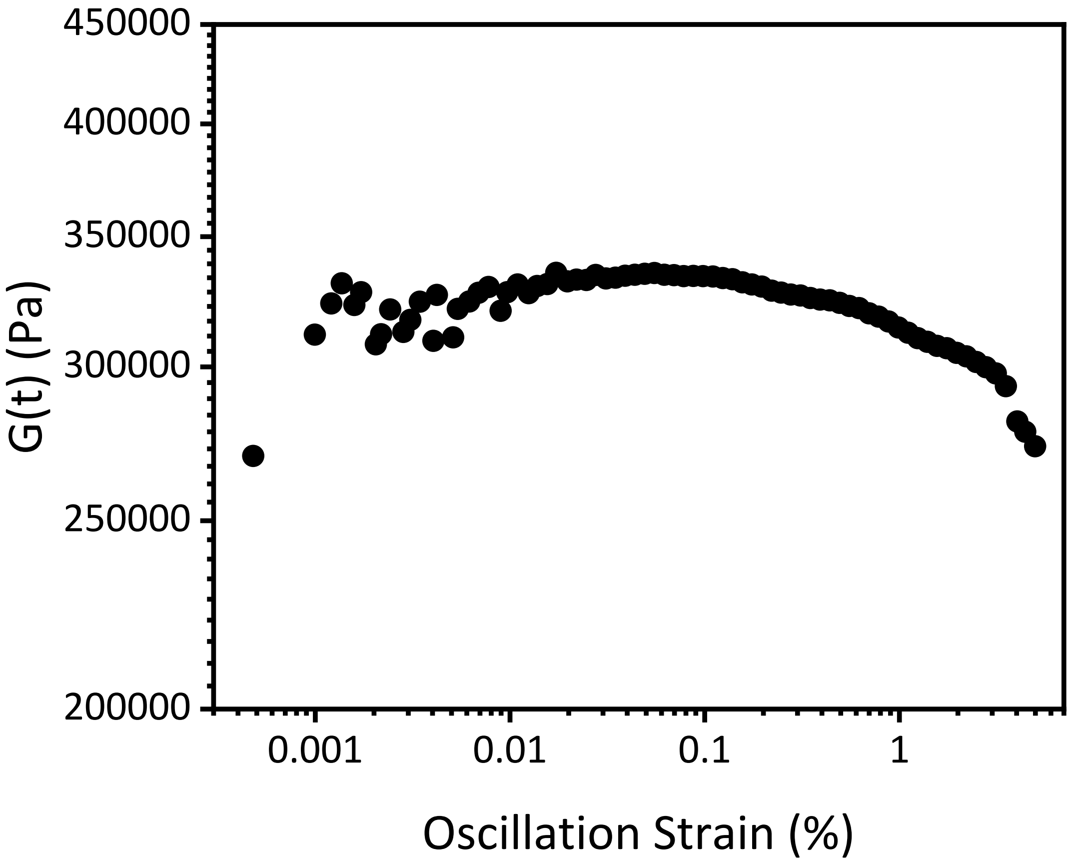


Figure S31. Strain sweep data for a representative sample of CAN A_5.

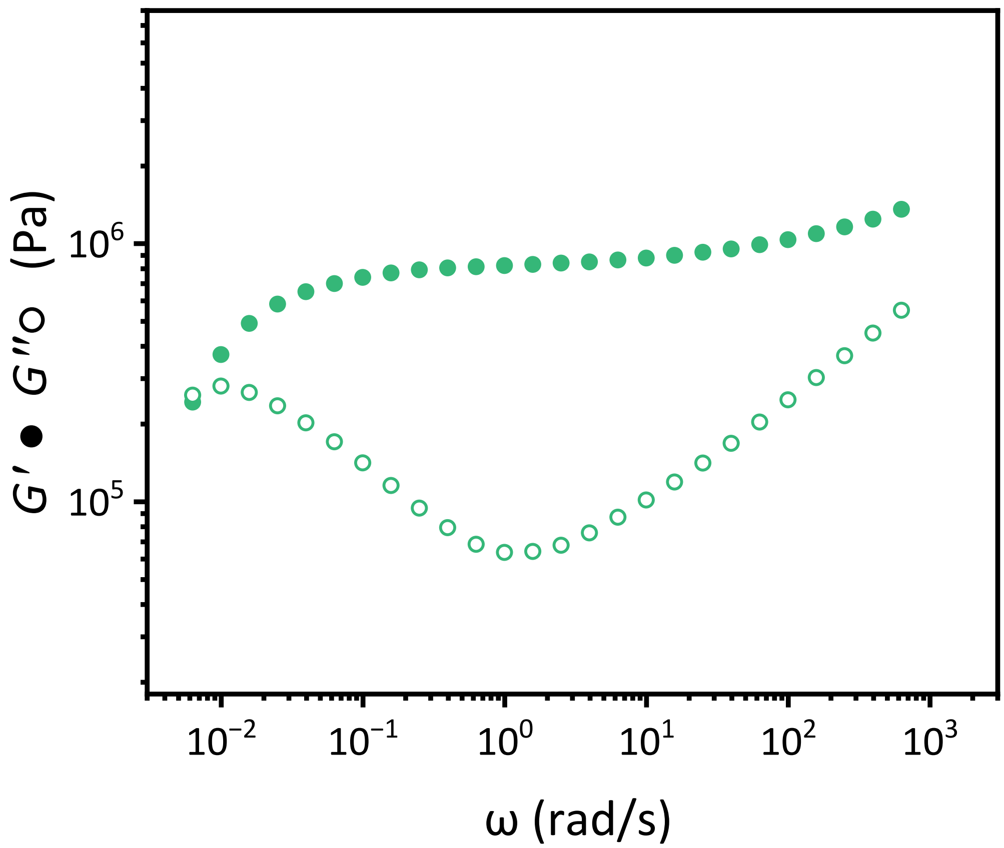


Figure S32. Frequency sweep performed at 175 °C for a representative sample of CAN A_5. τ^*_{cross} = 146 s.

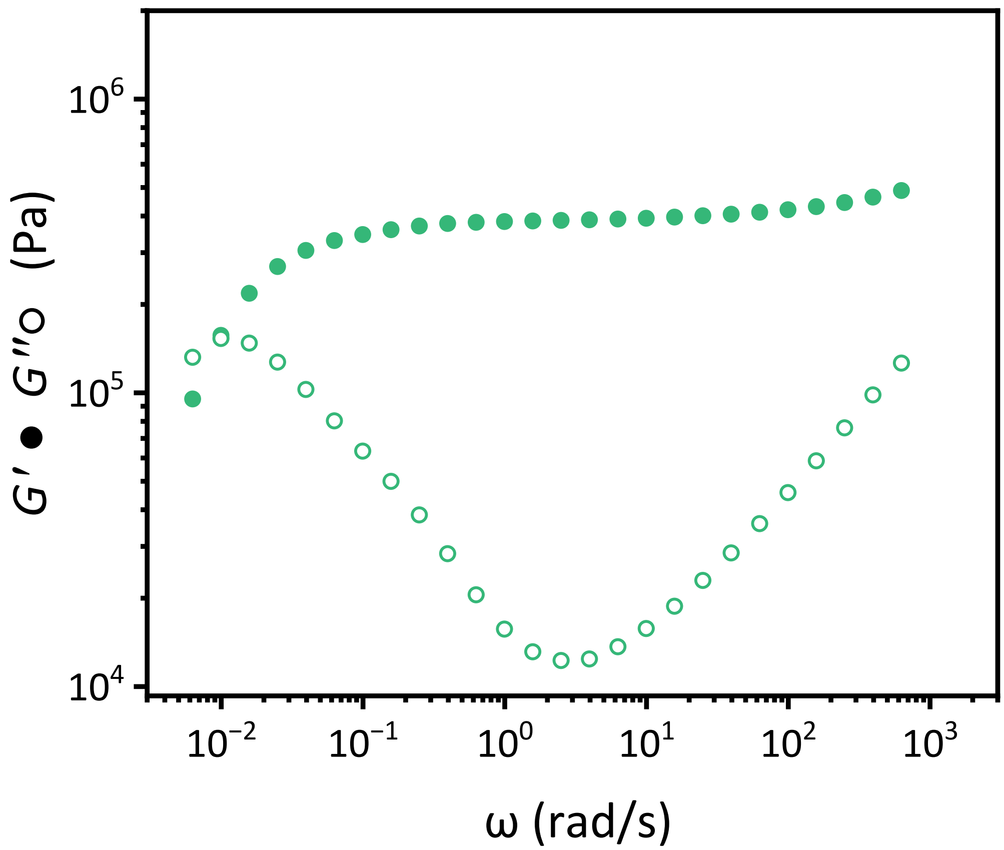


Figure S33. Frequency sweep performed at 175 °C for a representative sample of CAN B_5. τ^*_{cross} = 104 s.

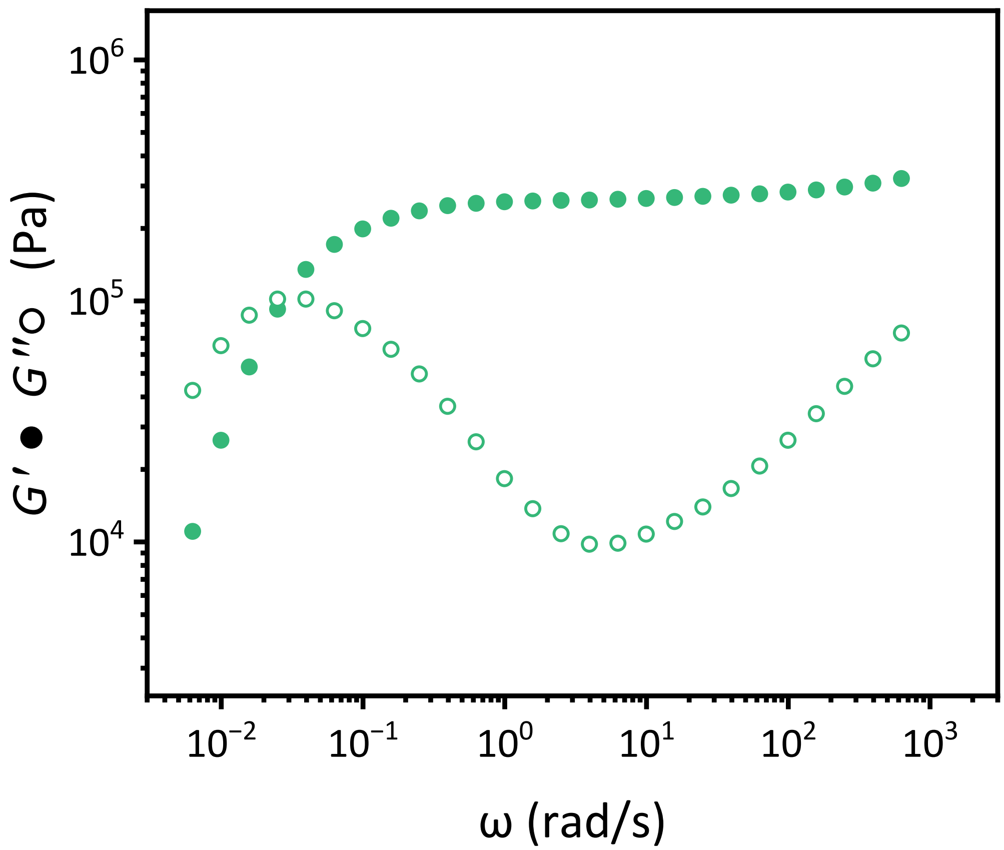


Figure S34. Frequency sweep performed at 175 °C for a representative sample of CAN C_5. τ^*_{cross} = 36 s.

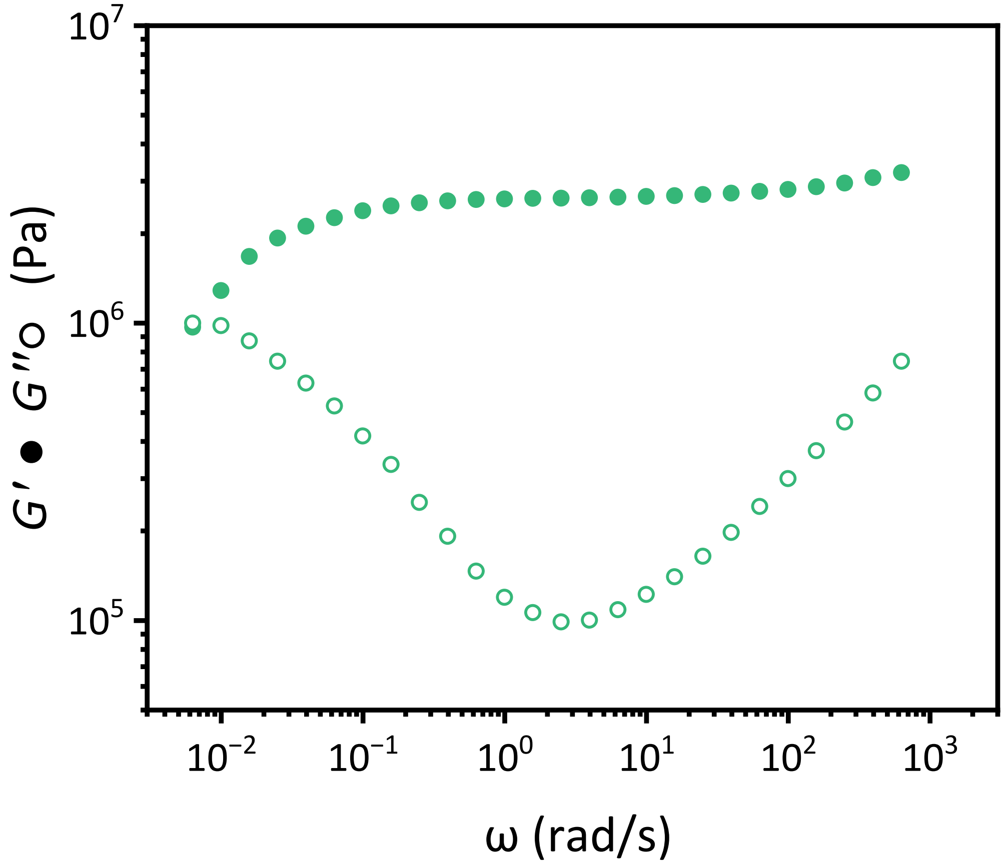


Figure S35. Frequency sweep performed at 175 °C for a representative sample of CAN A_{10}. τ^*_{cross} = 152 s.

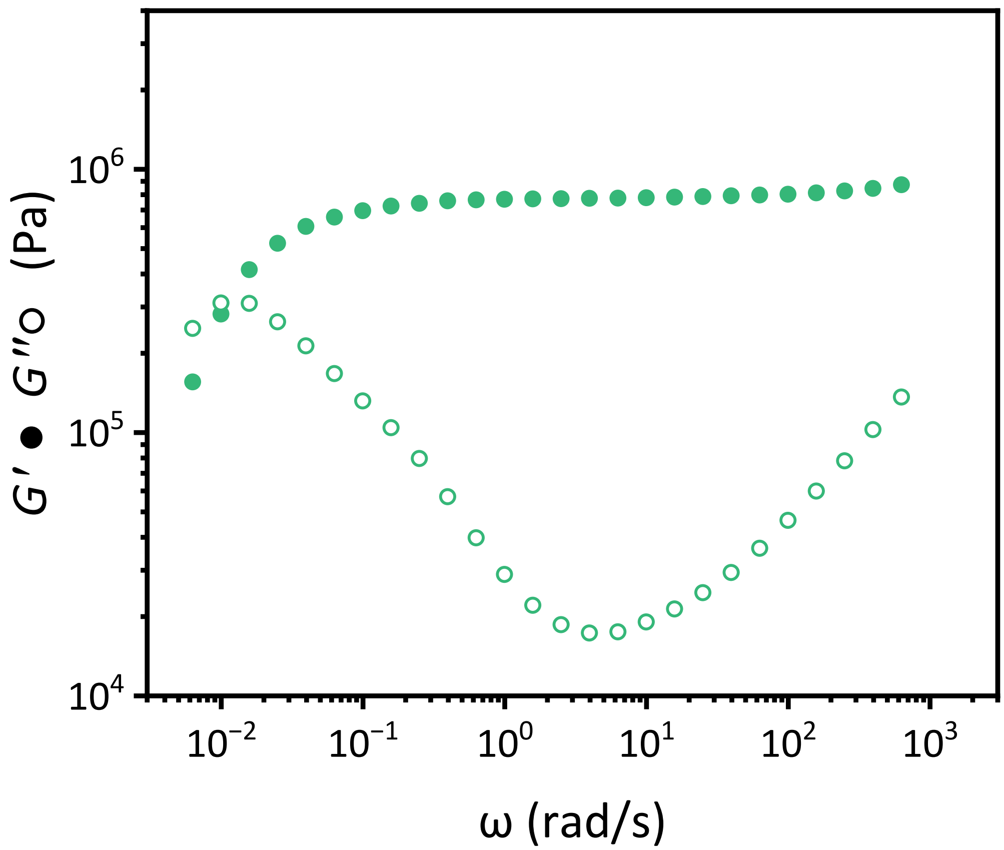


Figure S36. Frequency sweep performed at 175 °C for a representative sample of CAN B_{10}. τ^*_{cross} = 90 s.

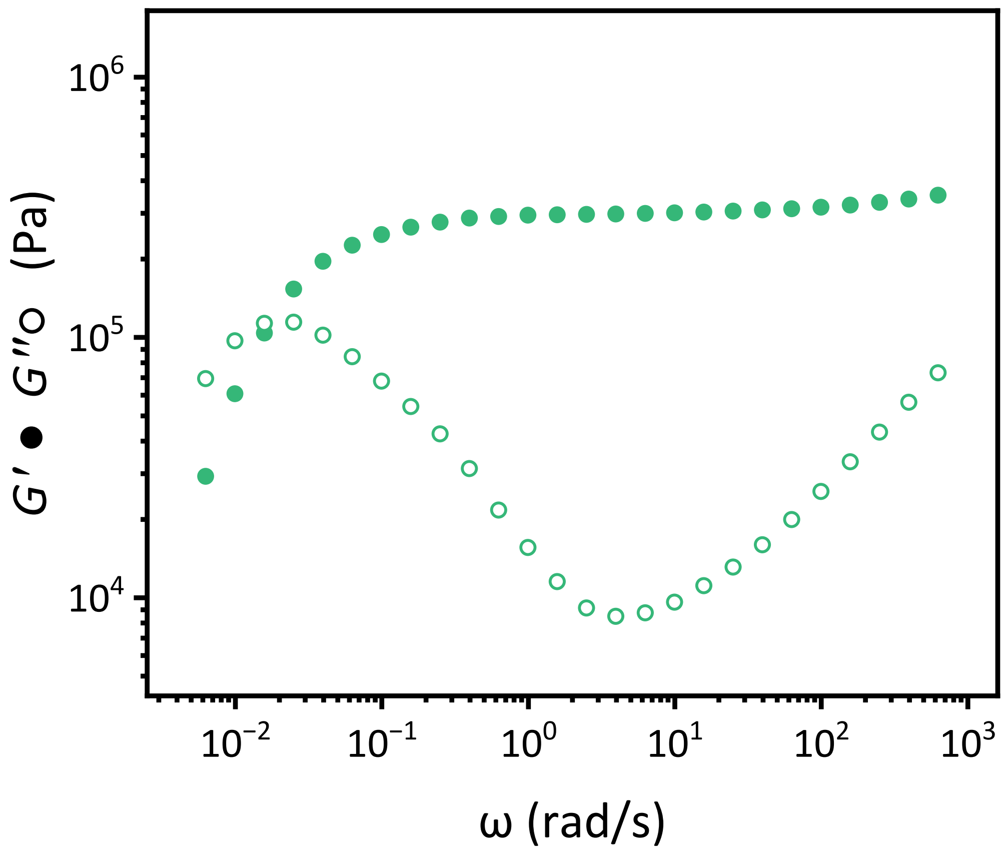


Figure S37. Frequency sweep performed at 175 °C for a representative sample of CAN C_{10}. τ^*_{cross} = 57 s.

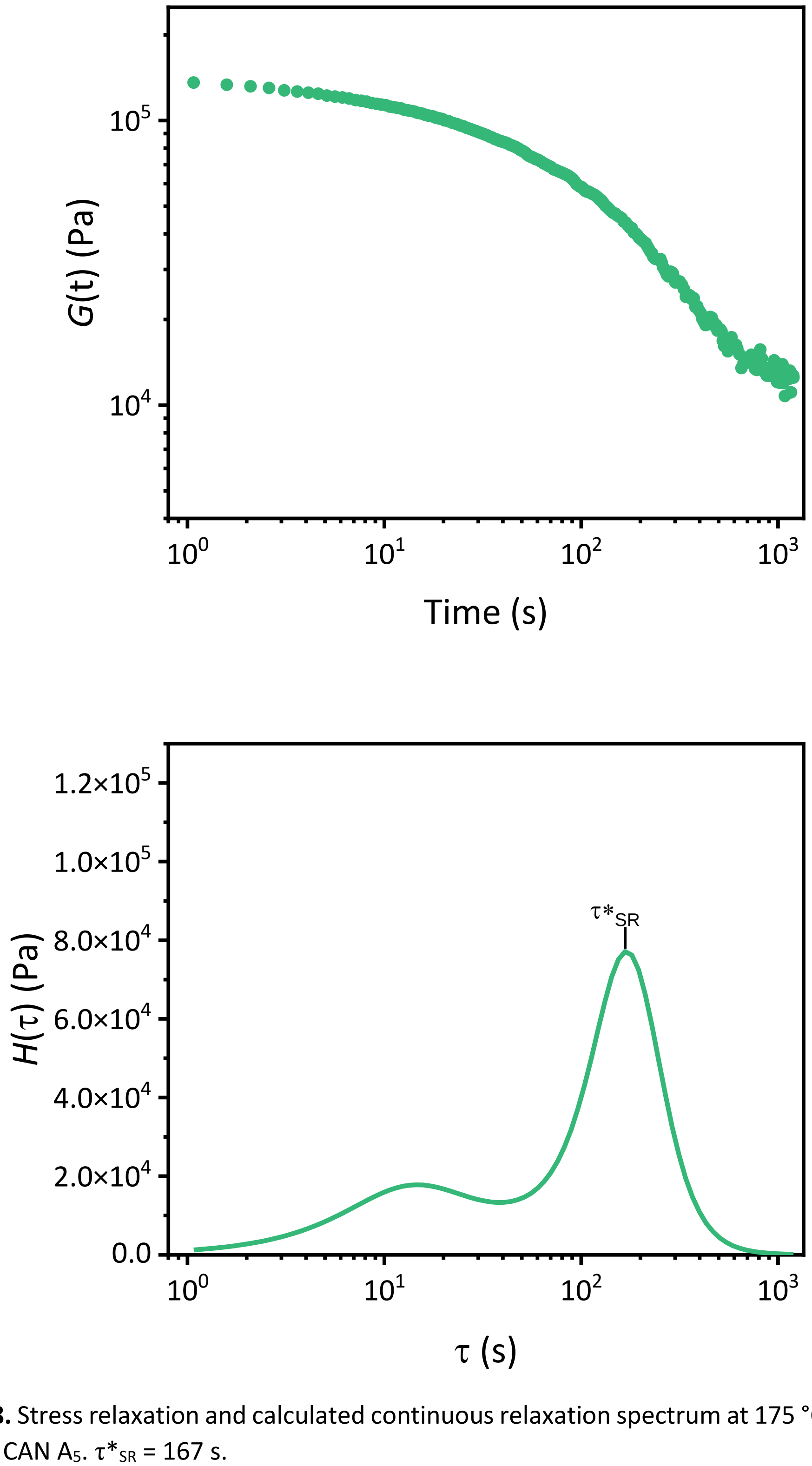
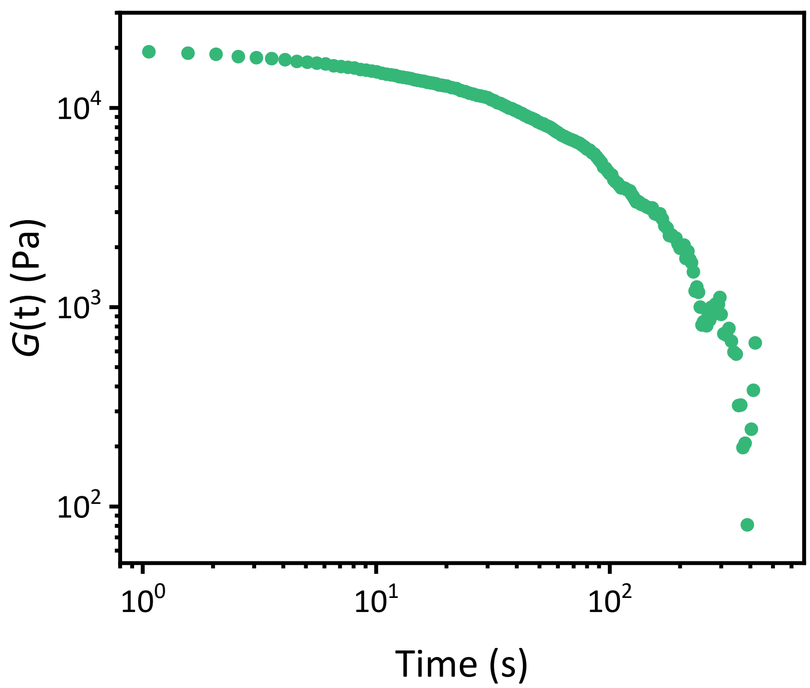


Figure S38. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN A_5. τ^*_{SR} = 167 s.



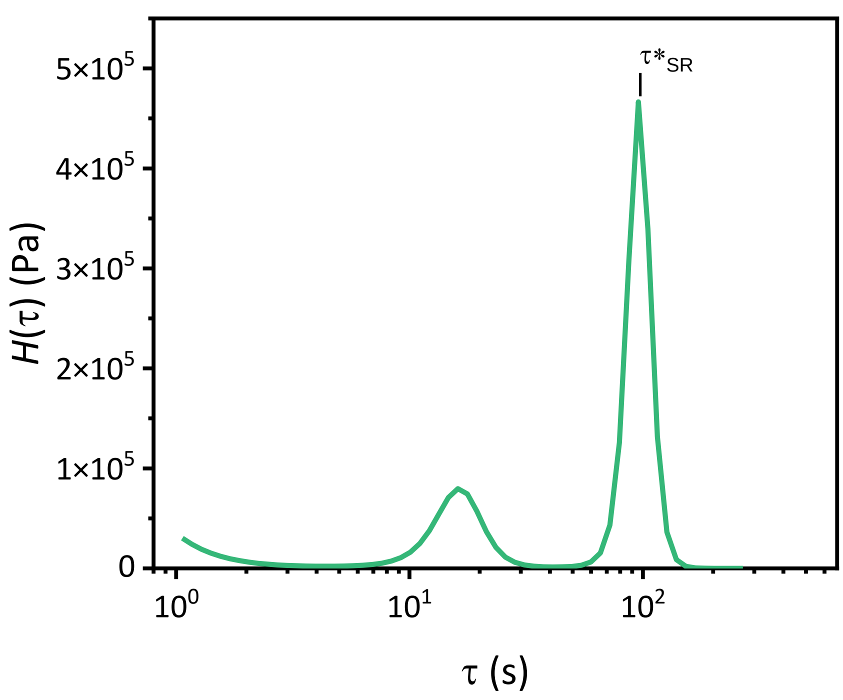


Figure S39. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN B_5. τ^*_{SR} = 96 s.

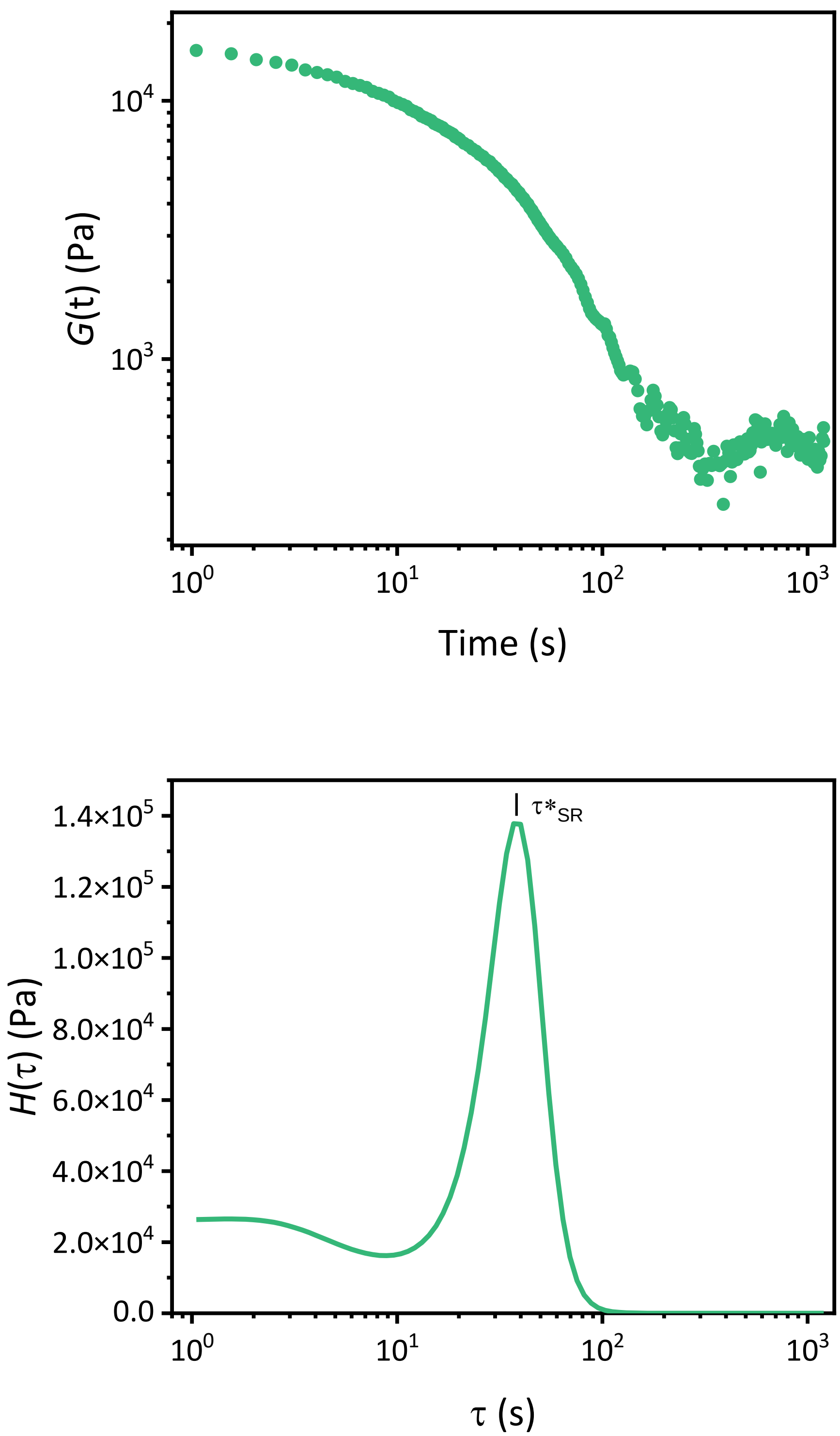


Figure S40. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN C_5. τ^*_{SR} = 40 s.

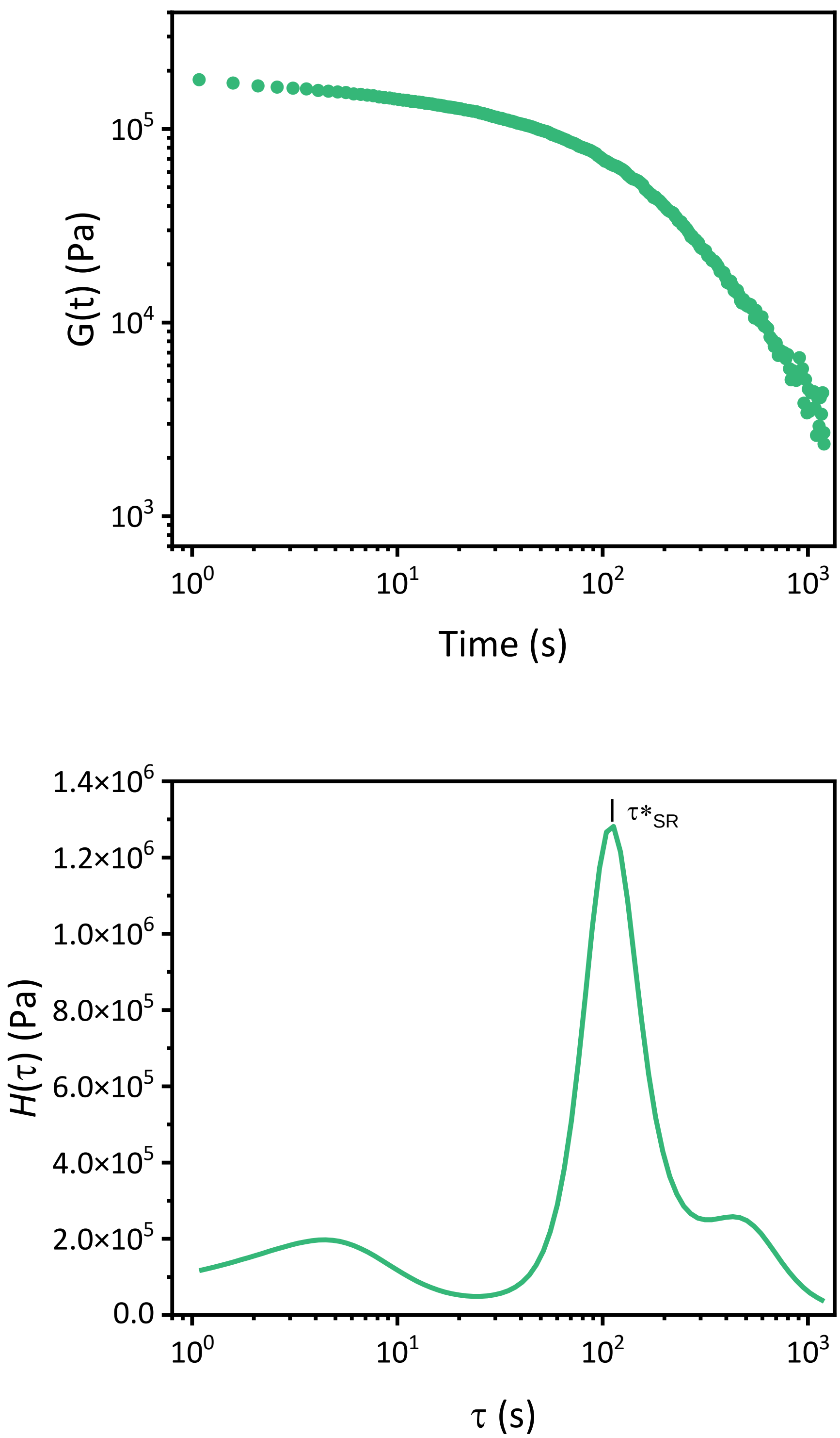
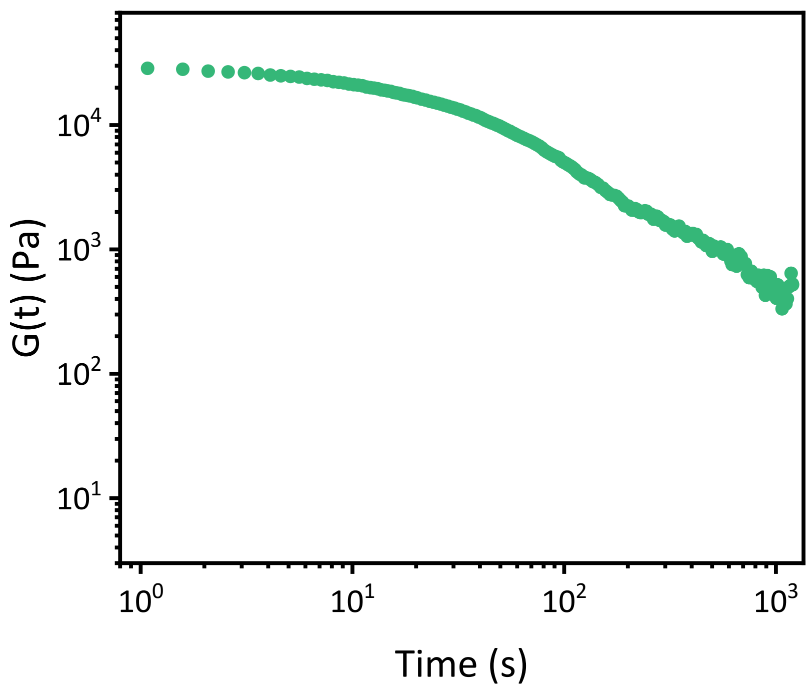


Figure S41. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN A_{10}. τ^*_{SR} = 113 s.



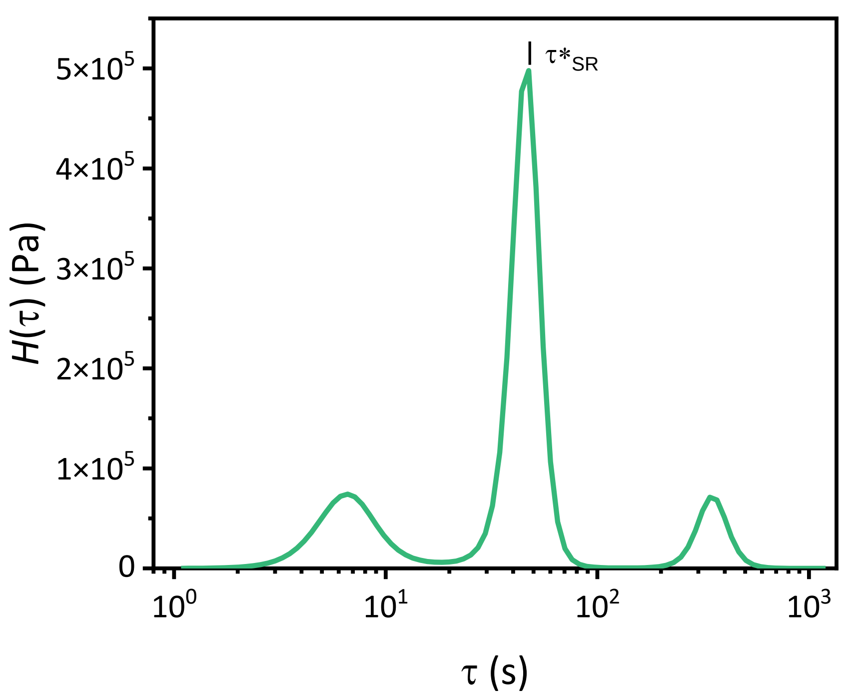


Figure S42. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN B_{10}. τ^*_{SR} = 48 s.

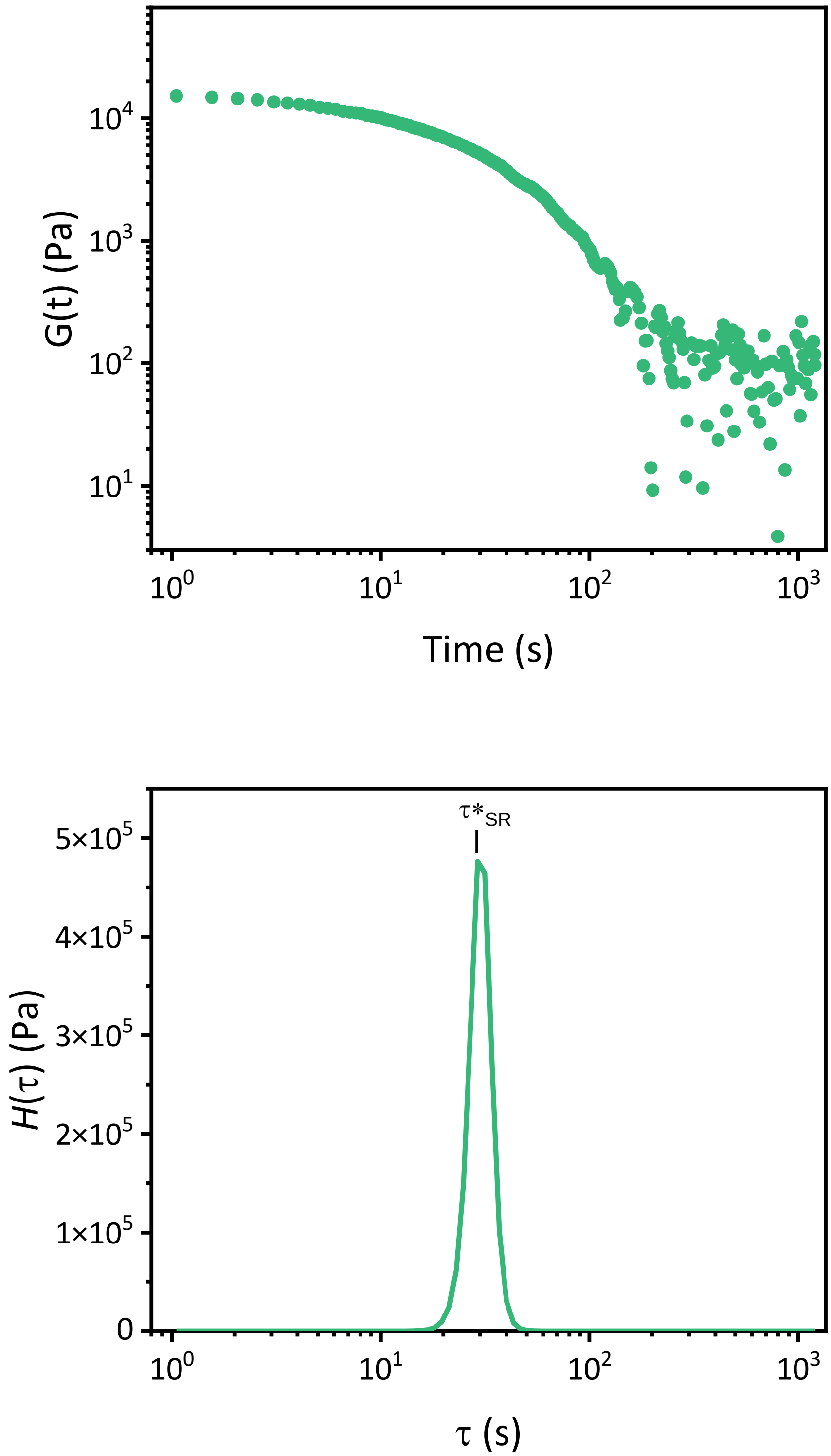


Figure S43. Stress relaxation and calculated continuous relaxation spectrum at 175 °C for a representative sample of CAN C_{10}. τ^*_{SR} = 29 s.

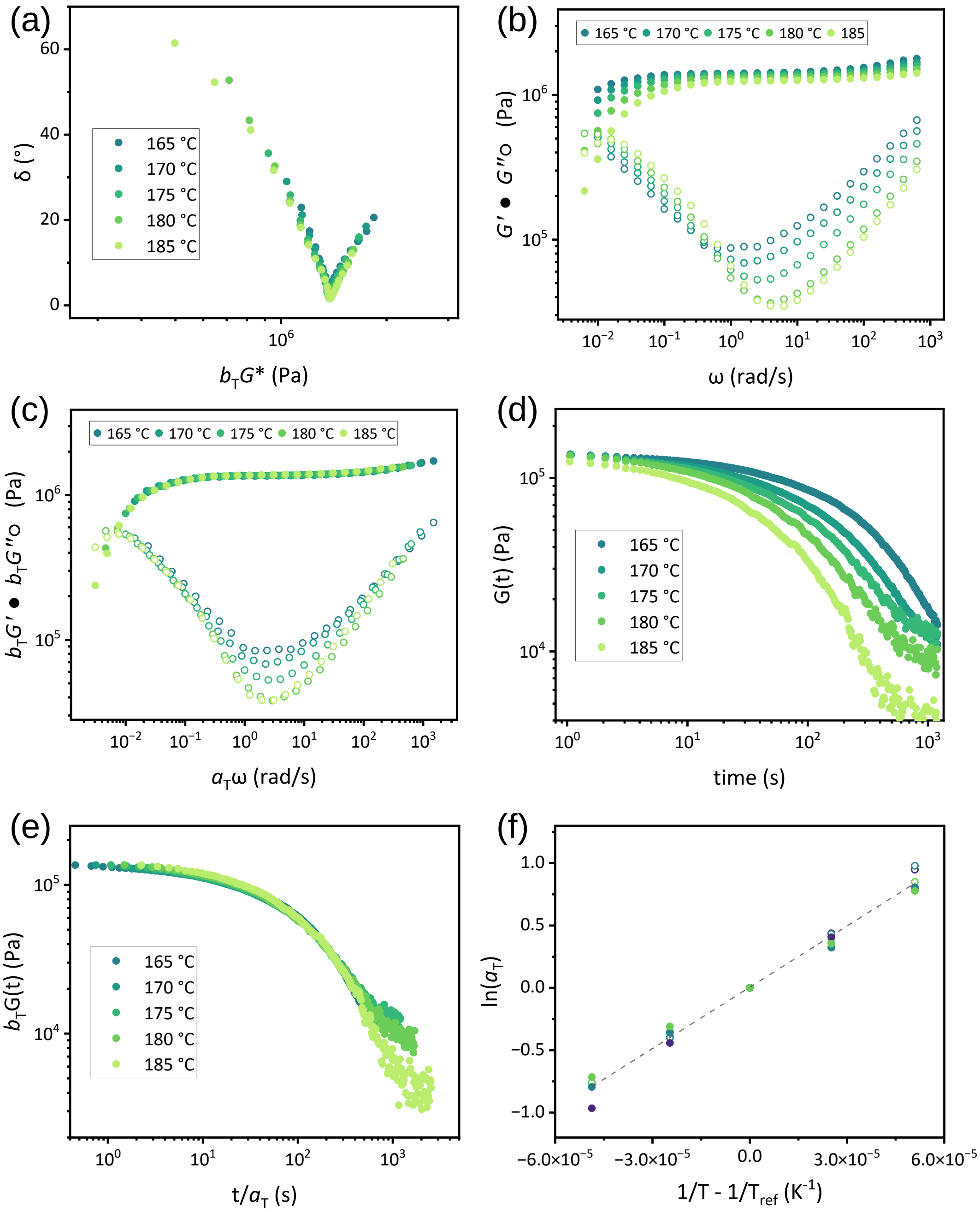


Figure S44. (a) Reduced van Gurp-Palmen plot of a sample of CAN A_5. (b) Unshifted frequency sweep data of a sample of CAN A_5. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN A_5. (d) Unshifted stress relaxation data of a sample of CAN A5. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN A_5. (f) Arrhenius analysis of horizontal shift factors for all CAN A_5 samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses.

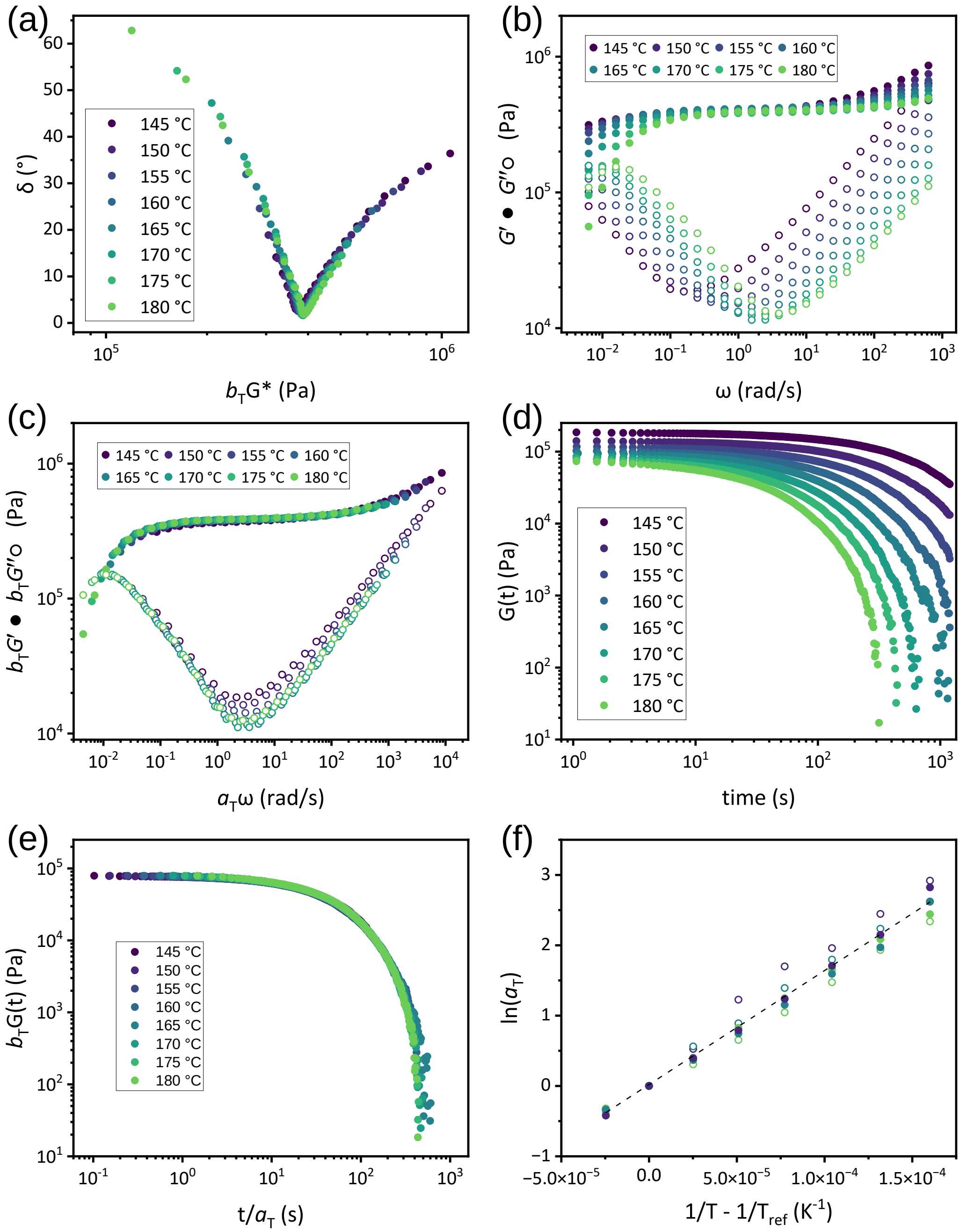


Figure S45. (a) Reduced van Gurp-Palmen plot of a sample of CAN B_5. (b) Unshifted frequency sweep data of a sample of CAN B_5. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN B_5. (d) Unshifted stress relaxation data of a sample of CAN B_5. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN B_5. (f) Arrhenius analysis of horizontal shift factors for all CAN B_5 samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses.

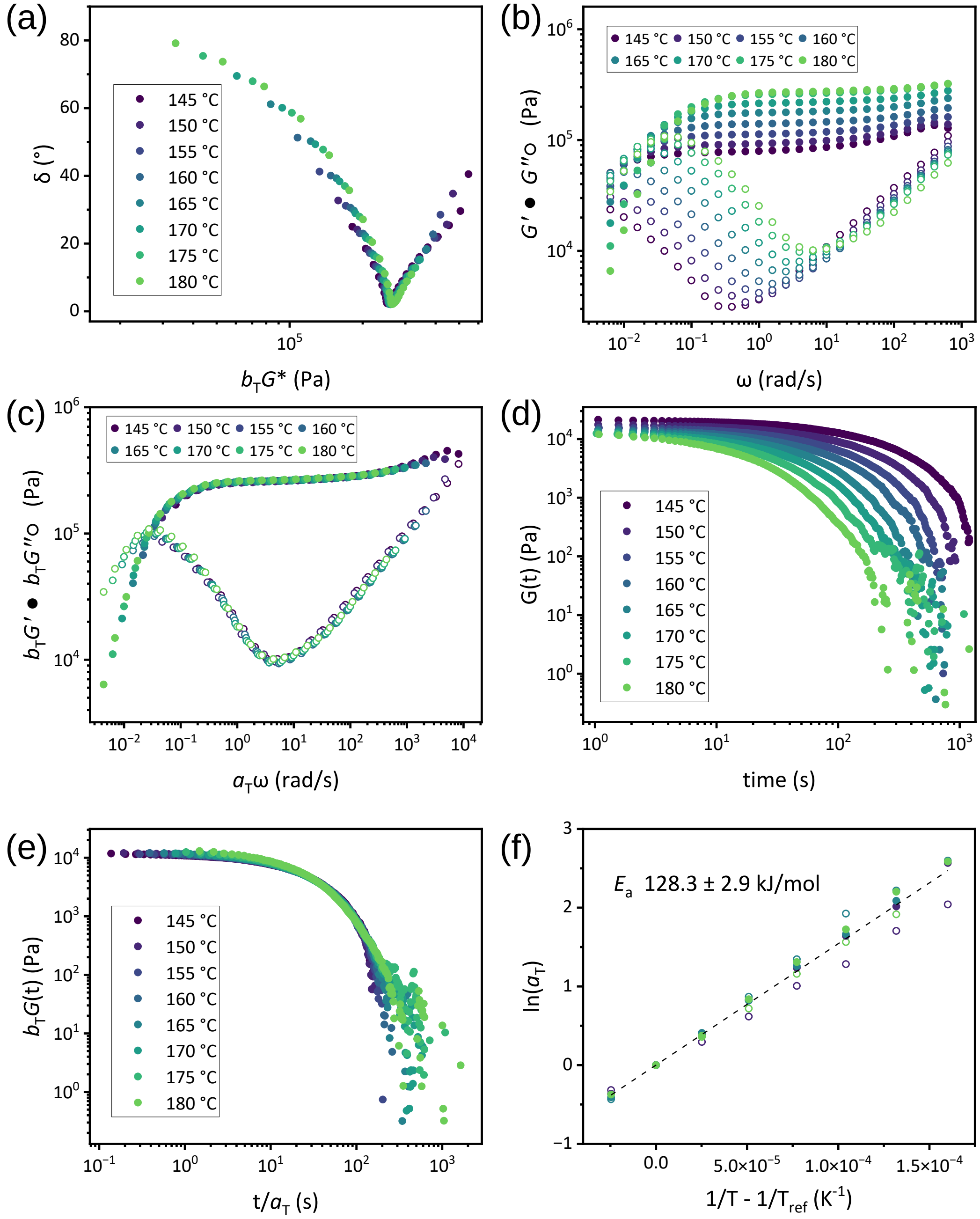


Figure S46. (a) Reduced van Gurp-Palmen plot of a sample of CAN C_5. (b) Unshifted frequency sweep data of a sample of CAN C_5. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN C_5. (d) Unshifted stress relaxation data of a sample of CAN C_5. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN C_5. (f) Arrhenius analysis of horizontal shift factors for all CAN C_5 samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses. Figures a, c, e, and f are identical to main text Figure 4.

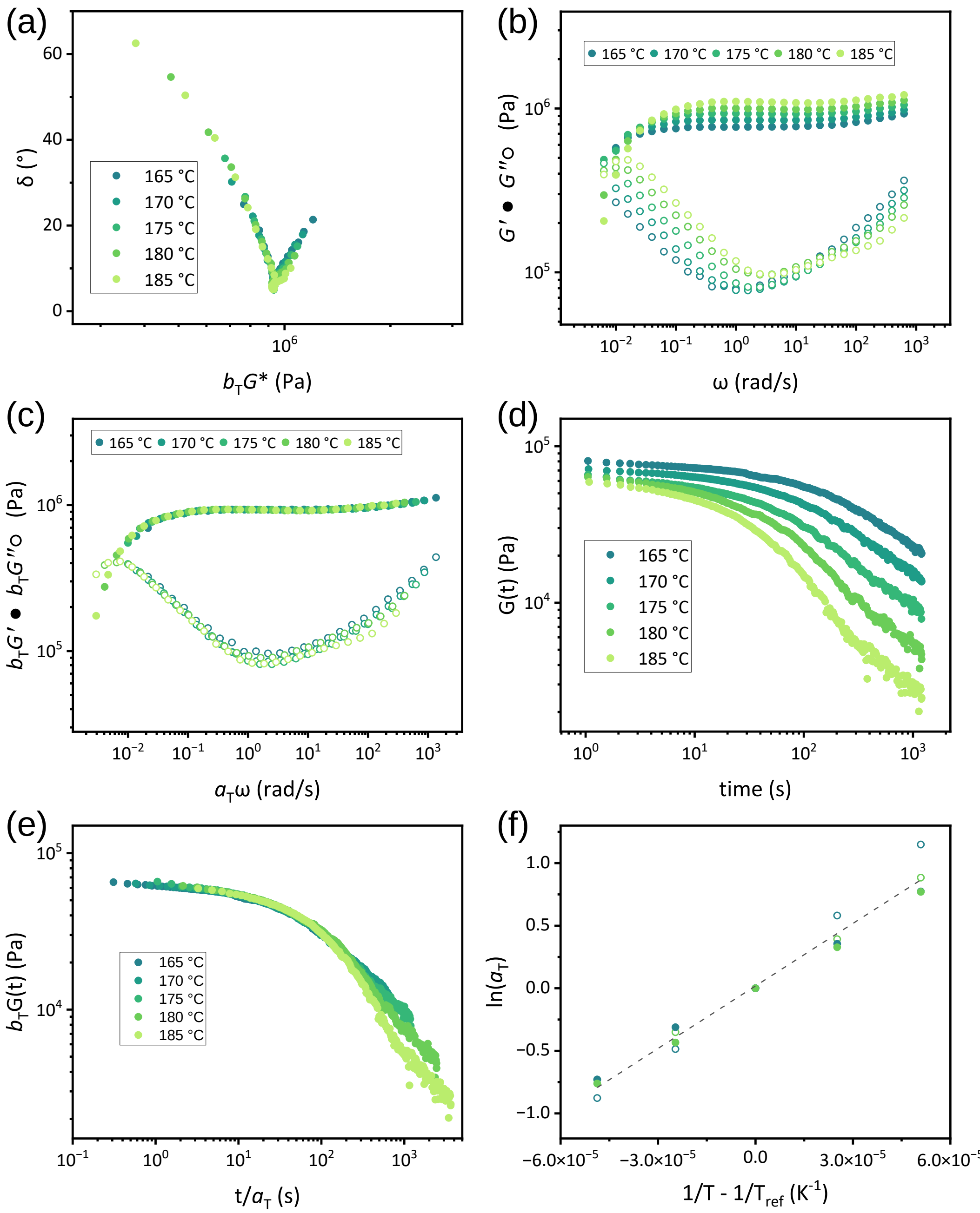


Figure S47. (a) Reduced van Gurp-Palmen plot of a sample of CAN A_{10}. (b) Unshifted frequency sweep data of a sample of CAN A_{10}. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN A_{10}. (d) Unshifted stress relaxation data of a sample of CAN A_{10}. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN A_{10}. (f) Arrhenius analysis of horizontal shift factors for all CAN A_{10} samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses.

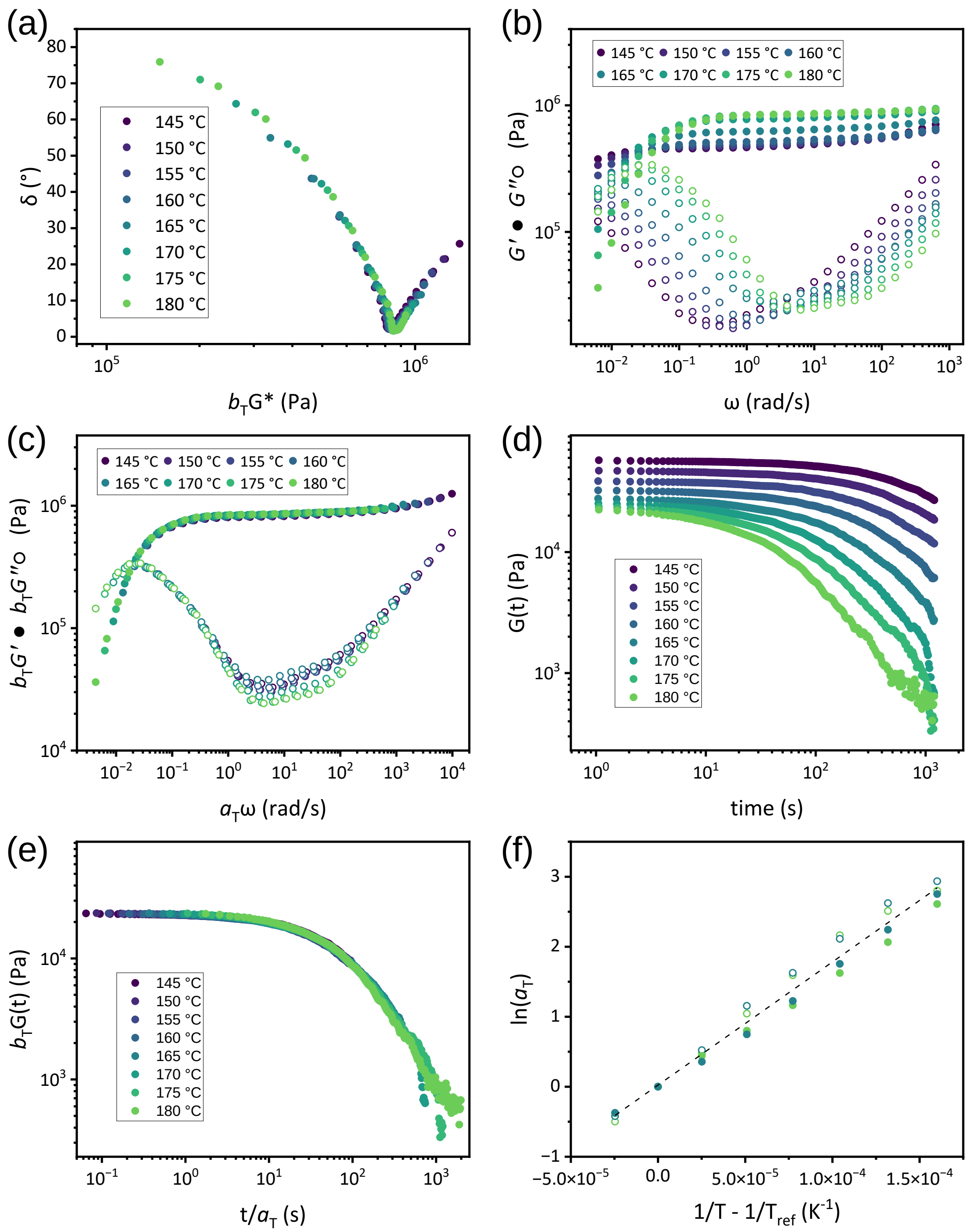


Figure S48. (a) Reduced van Gurp-Palmen plot of a sample of CAN B_{10}. (b) Unshifted frequency sweep data of a sample of CAN B_{10}. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN B_{10}. (d) Unshifted stress relaxation data of a sample of CAN B_{10}. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN B_{10}. (f) Arrhenius analysis of horizontal shift factors for all CAN B_{10} samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses.

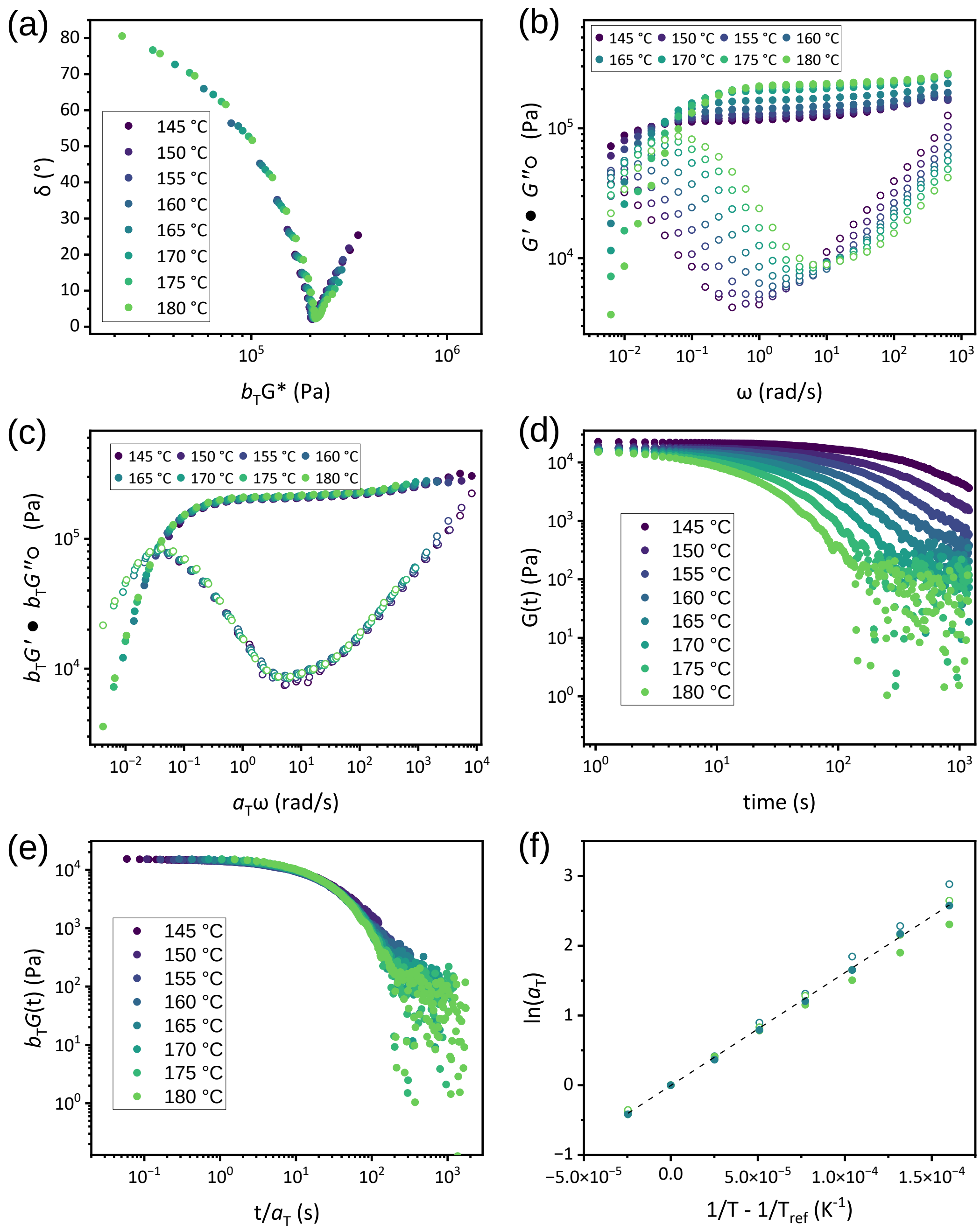


Figure S49. (a) Reduced van Gurp-Palmen plot of a sample of CAN C_{10}. (b) Unshifted frequency sweep data of a sample of CAN C_{10}. (c) Master curve of frequency sweep data constructed via TTS of a sample of CAN C_{10}. (d) Unshifted stress relaxation data of a sample of CAN C_{10}. (e) Master curve of stress relaxation constructed from TTS of a sample of CAN C_{10}. (f) Arrhenius analysis of horizontal shift factors for all CAN C_{10} samples. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. Dashed line is line of best fit. T_{ref} = 175 °C for all analyses.

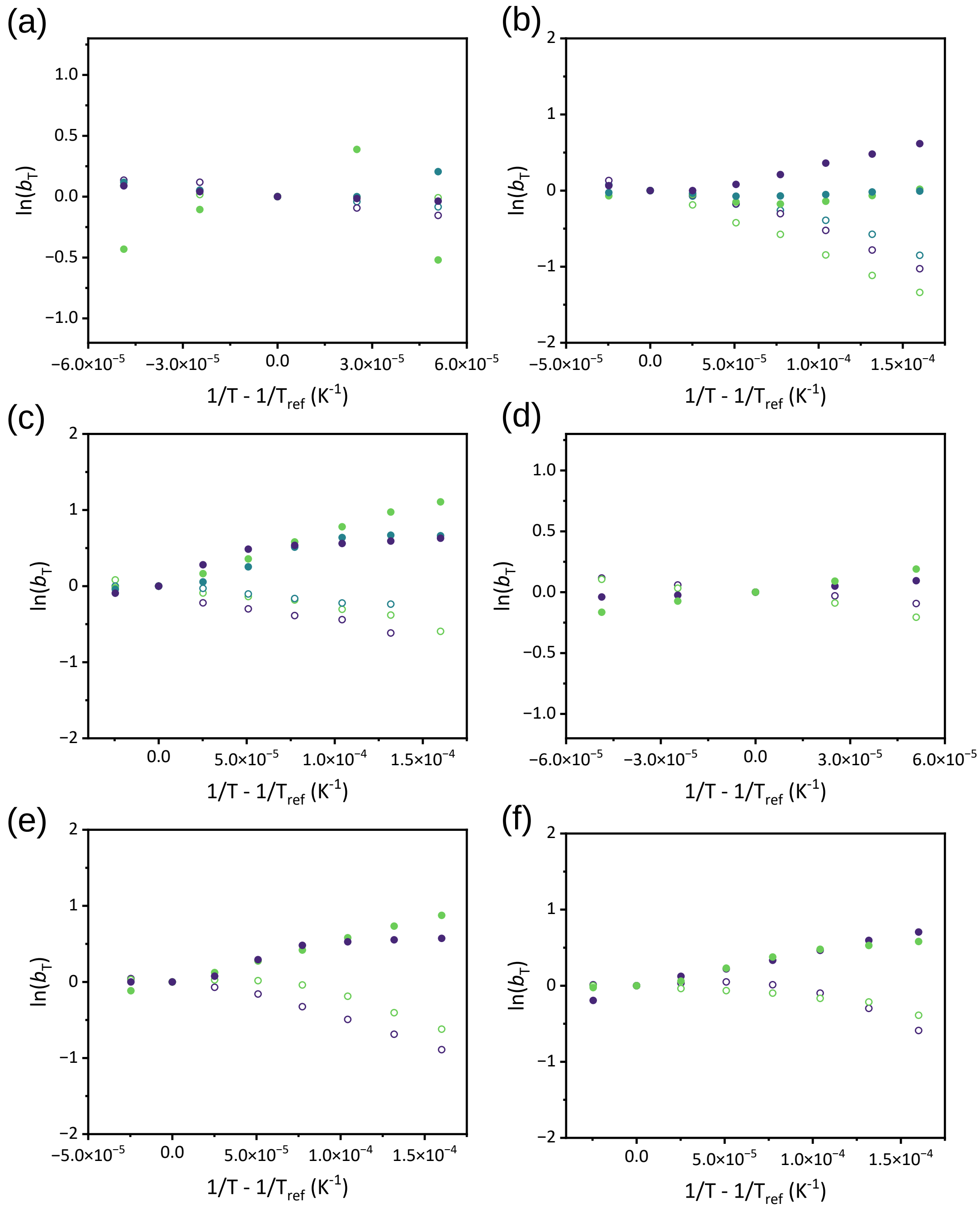


Figure S50. Arrhenius analysis of vertical shift factors for CAN samples. (a) CAN A_5; (b) CAN B_5; (c) CAN C_5; (d) CAN A_{10}; (e) CANB$_{10}$; (f) CAN C_{10}. Filled circles are from frequency sweep data and empty circles from stress relaxation; each color is a single sample. T_{ref} = 175 °C for all analyses.

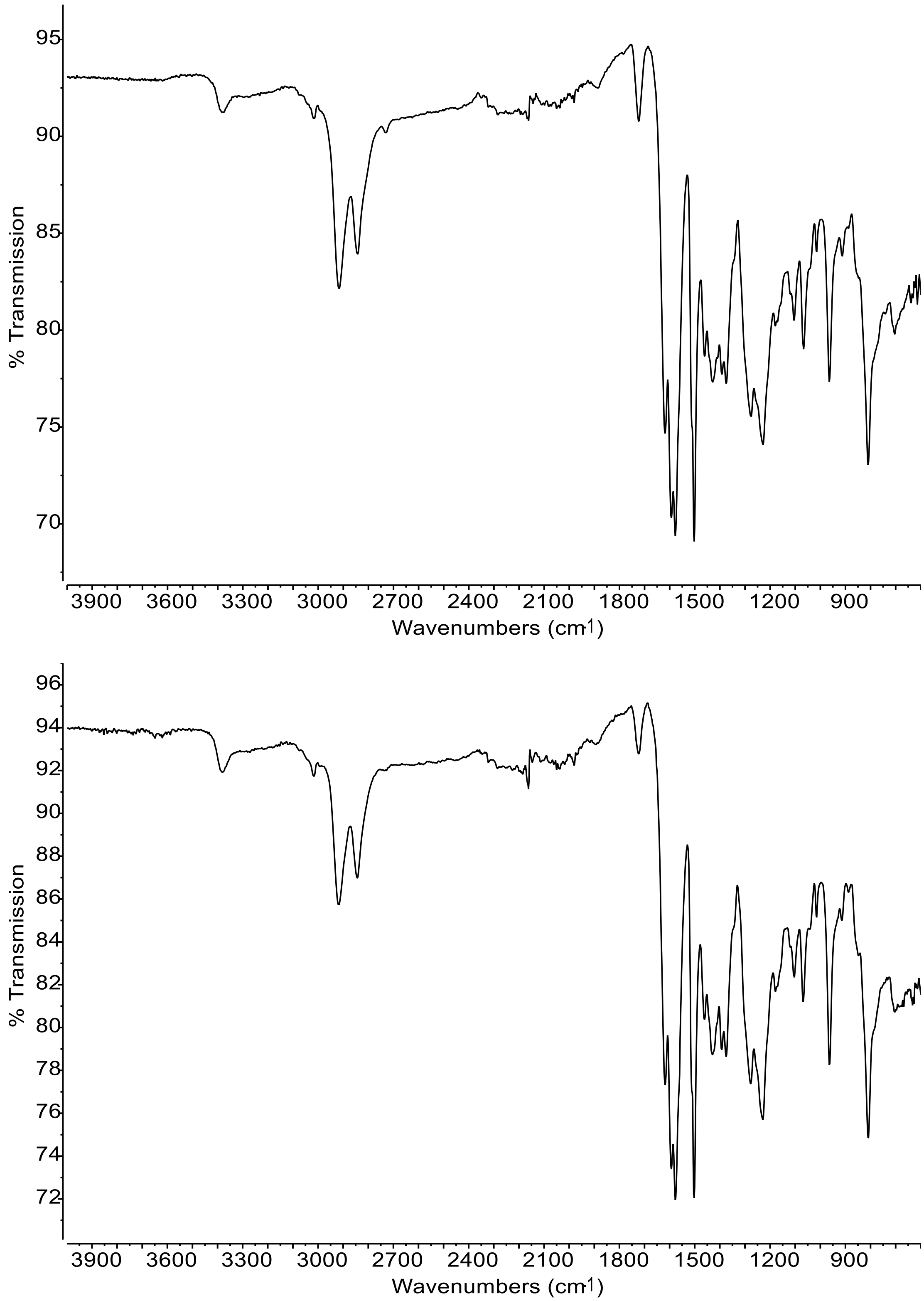


Figure S51. ATR FT-IR spectra of a sample of CAN A_5 before (top) and after (bottom) rheological analysis.

Discussion of the sticky Rouse model for unentangled CANs. The terminal relaxation time (τ_{term}) in this model is expressed as

$$\tau_{term} = \tau_{xl} N_{xl}^2$$

where τ_{xl} is the crosslink lifetime and N_{xl} is the number of crosslinks per chain. While our systems do not achieve terminal relaxation in the experimental conditions, the longest relaxation times we observe (i.e., τ^*) still follow this trend. τ_{xl} can be further described as

$$\tau_{xl} = \sigma \tau_0 \exp\left(\frac{E_a^{sm}}{RT}\right)$$

where σ describes the mobility of the exchanging functional group, τ_0 is the Rouse segmental relaxation time, and E_a^{sm} is the activation energy of the crosslink exchange reaction. Thus, if σ is relatively constant under the experimental conditions, the temperature dependence of τ_{xl} (i.e., the flow E_a measured by rheometry) will only be dependent on E_a^{sm} and τ_0. For additional discussion and comparison to other models of CAN dynamics, see main text refs. 52 and 54.