

Supplemental information for:

Acrylic triblock copolymers incorporating isosorbide for pressure sensitive adhesives

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Experimental

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. Acryloyl chloride was purified by distillation prior to use. *N*-butyl acrylate (nBA) and 2-ethylhexyl acrylate (EHA) were purified by passing through a column of basic alumina. The rosin ester tackifier Sylvalite 2E 80HP was provided by Arizona Chemical.

Characterization ^1H NMR and ^{13}C NMR spectroscopy experiments were performed on a Bruker Avance III HD 500 spectrometer at 500 MHz and 125 MHz, respectively, equipped with a 5mm Prodigy TCI cryoprobe and referenced to tetramethylsilane. FT-IR was performed using a Bruker Alpha Platinum ATR spectrometer. High-resolution mass spectrometry was performed using a Bruker Bio-TOF II in positive mode ESI. Size exclusion chromatography (SEC) was carried out in THF using three Phenomenex Phenogel-5 columns connected in series at a flow rate of 1 ml min^{-1} at $25\text{ }^\circ\text{C}$. Chromatograms were collected using a Wyatt Technology DAWN DSP MALLS detector and a Wyatt optilab EX RI detector. PAAI dn/dc was calculated from the RI signal using a known sample concentration and assuming 100% mass recovery from the

column. Copolymer dn/dc was calculated using a weighted average of homopolymer dn/dc values. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments Discovery DSC under N₂. *T_g* values were determined on the second heating at a heating rate of 10 °C min⁻¹. Small angle X-ray scattering (SAXS) was performed at the Advanced Photon Source at Argonne National Laboratories on the Sector 5-ID-D beamline maintained by DuPont-Northwestern-Dow Collaborative Access Team. Dynamic mechanical analysis (DMA) was performed on a TA Instruments ARES rheometer under N₂. Dynamic frequency sweeps were performed from 100 to 0.1 rad s⁻¹ at 1% strain. Monomer conversion values were calculated by comparing the integrations in the ¹H NMR spectra of vinyl protons to protons of the isosorbide core. *M_n* (calc) was calculated according to the formula $M_n(\text{calc}) = MW_{\text{CTA}} + [M]_0 \times MW_M \times \text{conversion} / [\text{CTA}]_0$, where $[M]_0$ and $[\text{CTA}]_0$ are the initial concentrations of monomer and CTA, respectively, and *MW_M* and *MW_{CTA}* are the molar masses of monomer and CTA, respectively. The wt% of PAAI in the triblock copolymers was determined by comparing the relative integrations from the ¹H NMR spectra of the PAAI repeat unit and that of PnBA or PEHA.

exo-acetyl isosorbide (AI). AI was prepared according to the literature.^{1,2} Briefly, isosorbide (146 g, 1.00 mol), acetic acid (78.0 ml, 1.35 mol), *p*-toluenesulfonic acid monohydrate (1.00 g, 5.26 mmol), and toluene (150 ml) were added to a 500 ml round bottom flask equipped with a Dean-Stark trap. The reaction was heated to reflux until removal of H₂O was complete. Toluene was removed under reduced pressure and KOH (3.00 g) was added. The mixture was distilled with heating through a Vigreux column at 200 mTorr. The distillate was purified by

recrystallization from methyl ethyl ketone to afford AI as a white crystalline solid (71.1g, 38% yield).

exo-acetyl-endo-acryl-isosorbide (AAI). AI (30.3 g, 0.161 mol), triethylamine (24.6 ml, 0.177 mol) and 300 ml DCM were added to a 1 L round bottom flask. The flask was immersed in an ice water bath and acryloyl chloride (13.7 ml, 0.169 mol) was added dropwise with stirring. The reaction was allowed to reach room temperature and after 18 h the triethylamine salts were filtered off. The filtrate was passed through a plug of silica (~200 g) and eluted with diethyl ether. The solvent was removed by rotary evaporation and the concentrate was passed through a plug of basic alumina (~200 g) eluting with diethyl ether. The eluent was concentrated to ~100 ml and crystallization was aided by addition of pentane to afford AAI as a clear crystalline solid after filtration and drying (22.5 g, 58% yield). ^1H NMR (500 MHz, CDCl_3) δ ppm: 6.47 (dd, $J = 17.40, 1.53$ Hz, 1 H) 6.18 (dd, $J = 17.39, 10.38$ Hz, 1 H) 5.89 (dd, $J = 10.38, 1.53$ Hz, 1 H) 5.23 (q, $J = 5.49$ Hz, 1 H) 5.19 (d, $J = 3.05$ Hz, 1 H) 4.88 (t, $J = 5.04$ Hz, 1 H) 4.51 (d, $J = 4.88$ Hz, 1 H) 3.94 - 4.01 (m, 3 H) 3.86 (dd, $J = 9.77, 5.19$ Hz, 1 H) 2.08 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3) δ ppm: 170.01, 165.36, 131.77, 127.58, 85.90, 80.80, 78.00, 74.00, 73.44, 70.32, 20.88. ATR FT-IR (neat) $\nu_{\text{cm}^{-1}}$: 2926 (C-H), 1743 (C=O), 1726 (C=O), 1637 (C=C), 1228 (C-O), 1180 (C-O), 1092 (C-O), 1076 (C-O). m.p. = 38 °C. T_g = -36 °C. MS (ESI-TOF, m/z) $[\text{M} + \text{Na}^+]$ expected = 265.0688; found: 265.0684; error 1.51 ppm.

Polymerization of AAI (PAAI). AAI (1.03 g, 4.27 mmol), AIBN (10.3 mg 0.0628 mmol), DMF (4 ml), and a stir bar were added to a 25 ml round bottom flask and sparged with Ar for 30 min. The reaction was then heated to 70 °C with stirring for 8 h. The reaction was then cooled to room temperature and exposed to air. An aliquot was taken to determine conversion by ^1H NMR. The polymer was isolated by precipitation into cold MeOH and dried in a vacuum oven at 60 °C for

24 h to give PAAI as a white solid (91% conversion by ^1H NMR spectroscopy). SEC-MALLS analysis: $M_n = 120 \text{ kg mol}^{-1}$, $\bar{D} = 4.00$, $\text{dn/dc} = 0.0959 \text{ ml g}^{-1}$, T_d (5 wt%); $N_2 = 337 \text{ }^\circ\text{C}$, air = $291 \text{ }^\circ\text{C}$, $T_g = 95 \text{ }^\circ\text{C}$.

RAFT polymerization of nBA with BTCBA (CTA-PnBA-CTA). The following is an illustrative example: nBA (10.0 g, 11.2 ml, 78.1 mmol), BTCBA (128 mg, 0.156 mmol), and AIBN (5.12 mg, 0.0312 mmol) and a stir bar were added to a 50 ml round bottom flask and sealed with a septum. After sparging with Ar for 30 min, the reaction was stirred and heated to $70 \text{ }^\circ\text{C}$ under positive Ar pressure. After 2 h, the reaction was immersed in an ice bath, exposed to air, and 20 ml DCM was added. An aliquot was taken to determine conversion by ^1H NMR. The polymer was isolated by precipitation into cold MeOH, pouring off the supernatant, and drying the polymer at $70 \text{ }^\circ\text{C}$ in a vacuum oven for 24 h to give CTA-PnBA-CTA as a yellow viscous liquid (63% conversion by ^1H NMR spectroscopy, 5.71 g, 91% yield). SEC-MALLS analysis: $M_n = 45.3 \text{ kg mol}^{-1}$, $\bar{D} = 1.03$.

RAFT polymerization of EHA with BTCBA (CTA-EHA-CTA). EHA (9.87 g, 53.6 mmol), BTCBA (191 mg, 0.233 mmol), and AIBN (7.65 mg, 0.0223 mmol) were added to a 50 ml round bottom flask, sparged with Ar for 30 min, and heated to $70 \text{ }^\circ\text{C}$ with stirring for 1 h. The reaction was then immersed in an ice bath, exposed to air, and 20 ml of toluene was added. An aliquot was taken to determine conversion by ^1H NMR. The polymer was then isolated by precipitation into cold MeOH, pouring off the supernatant and drying at $70 \text{ }^\circ\text{C}$ in a vacuum oven for 24 h to give CTA-EHA-CTA as a yellow viscous liquid (90% conversion by ^1H NMR, 6.02 g, 68% yield). SEC-MALLS analysis: $M_n = 44.7 \text{ kg mol}^{-1}$, $\bar{D} = 1.06$.

Chain extension of CTA-PnBA-CTA with AAI (PAAI-PnBA-PAAI). The following is an illustrative example: CTA-PnBA-CTA (3.94 g, 0.348 mmol), AAI (1.64 g, 6.78 mmol), AIBN

(2.8 mg, 0.017 mmol), DMF (17 ml), and a stir bar were added to a 50 ml round bottom flask. After sparging with Ar for 30 min, the reaction was heated to 70 °C with stirring under positive Ar pressure. After 2 h, the reaction was immersed in an ice bath and exposed to air. An aliquot was taken to determine conversion by ^1H NMR. The polymer was isolated by precipitating into cold MeOH, pouring off the supernatant, and drying the polymer at 70 °C in a vacuum oven for 24 h to give PAAI-PnBA-PAAI as a yellow rubbery solid (57% conversion by ^1H NMR spectroscopy, 4.43 g, 91% yield). SEC-MALLS analysis: $M_n = 60.2 \text{ kg mol}^{-1}$, $D = 1.12$). T_d (5 wt%); $N_2 = 334 \text{ °C}$, air = 304 °C. $T_g = -45 \text{ °C}$.

Chain extension of CTA-EHA-CTA with AAI (PAAI-EHA-PAAI). The following is an illustrative example: CTA-EHA-CTA (1.50 g, 0.0664 mmol), AAI (354 mg, 1.46 mmol), AIBN (1.09 mg, 6.64 μmol), toluene (4.5 ml), and a stir bar were added to a 20 ml septa capped vial. The solution was sparged with Ar for 30 min then heated to 70 °C with stirring under positive Ar pressure. After 2 h, the reaction was immersed in an ice bath and exposed to air. An aliquot was taken to determine conversion by NMR. The polymer was isolated by precipitating into cold MeOH followed by drying at 70 °C in a vacuum oven for 24 h to give PAAI-PEHA-PAAI as a yellow rubbery solid (70% conversion by ^1H NMR, 1.41 g, 81% yield). SEC-MALLS analysis: $M_n = 54.2 \text{ kg mol}^{-1}$, $D = 1.20$). T_d (5 wt%); $N_2 = 338 \text{ °C}$, air = 264 °C. $T_g = -63 \text{ °C}$.

Alcoholysis of PAAI-PnBA-PAAI. PAAI-PnBA-PAAI (360 mg) and *p*-toluenesulfonic acid monohydrate (36 mg) were added to n-butanol (5 ml) in a 15 ml pressure vessel with a stir bar. The vessel was sealed and heated to 130 °C with stirring for 48 h. The vessel was then placed in a freezer for 24 h. The supernatant was poured off and the residual polymer was dried in a vacuum oven for 24 h at 80 °C to give the product as a colorless viscous liquid.

Adhesive testing. Samples for adhesion testing were prepared by dissolving 100 mg of polymer and tackifier in 266 μl ethyl acetate (i.e. total solids content = 100 mg) to give a solution with 30 wt% solids. The solution was then solvent cast onto a 50 μm thick sheet of PETE using a wire wound rod and the films were then left to dry under ambient conditions for 24 h before adhesion testing. The targeted dry film thickness was ~ 20 μm . PSTC-grade polished stainless steel plates were used as the adherend during testing.

180° peel test. A 1.27 cm wide strip of the polymer coated PETE film was adhered to the stainless steel plate using a 500 g roller. The sample was then tested using a Shimadzu ASG-X tensile tester at a peel rate of 305 mm min^{-1} . The peel force was recorded as the maximum measure force and averaged across at least three samples.

Loop tack test. A 1.27 cm wide strip of the polymer coated PETE film was formed into a teardrop shaped loop and mounted to the upper grip of the tensile tester. The loop was then lowered onto the stainless steel plate mounted to the lower grip of the tensile tester to a total contact area of 1.27 cm x 2.54 cm. The tack force was then measured as the maximum force observed while raising the upper grip at a rate of 305 mm min^{-1} . The average of at least 3 samples is reported.

Shear test. A strip of the polymer coated PETE film was adhered to the stainless steel plate to give a contact area of 1.27 x 1.27 cm^{-1} and rolled five times with a 500 g roller. A 500 g weight was then suspended from the sample and the time to failure was recorded for 3 samples.

- (1) Stoss, P.; Merrath, P.; Schlüter, G. Regioselektive Acylierung von 1,4:3,6-Dianhydro-D-glucit. *Synthesis* **1987**, 174–176.
- (2) Stoss, P. Process for the production of isosorbide-5-nitrate. US 4371703, 1983.

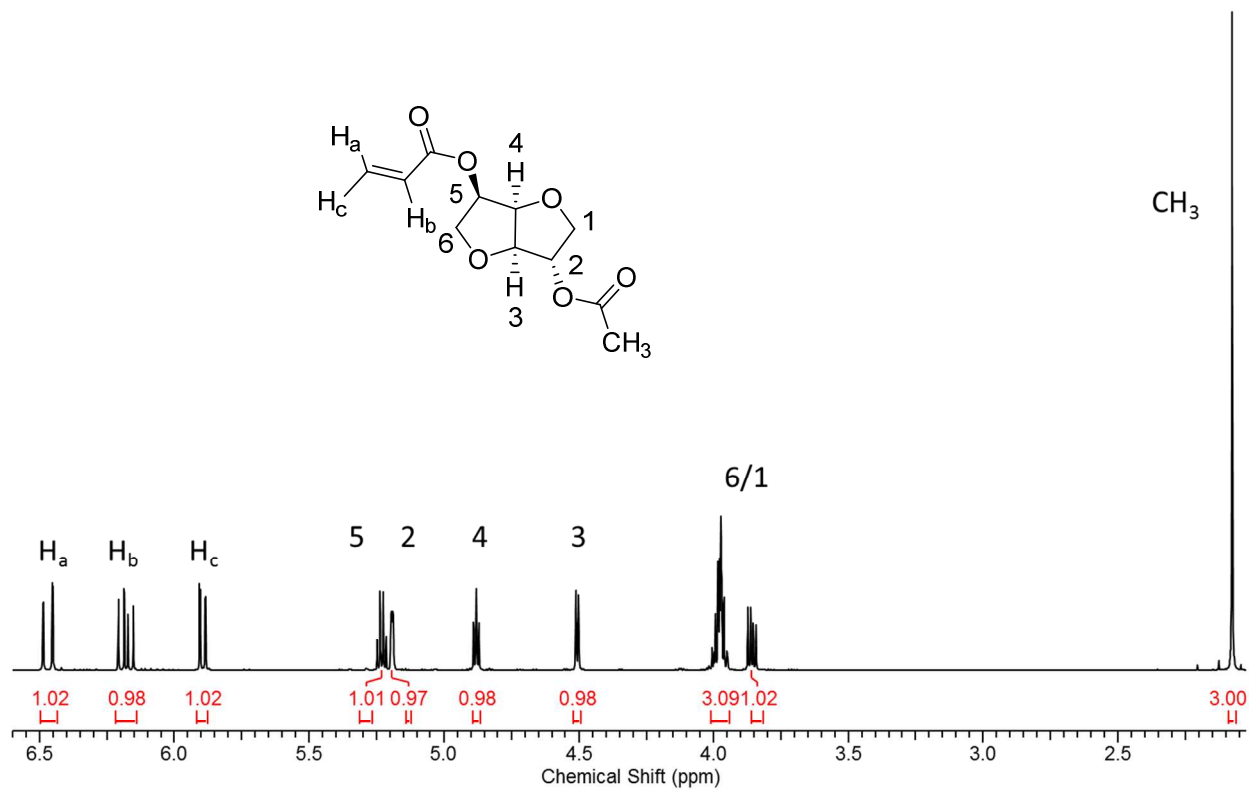


Figure S1. ^1H NMR of AAI in CDCl_3 .

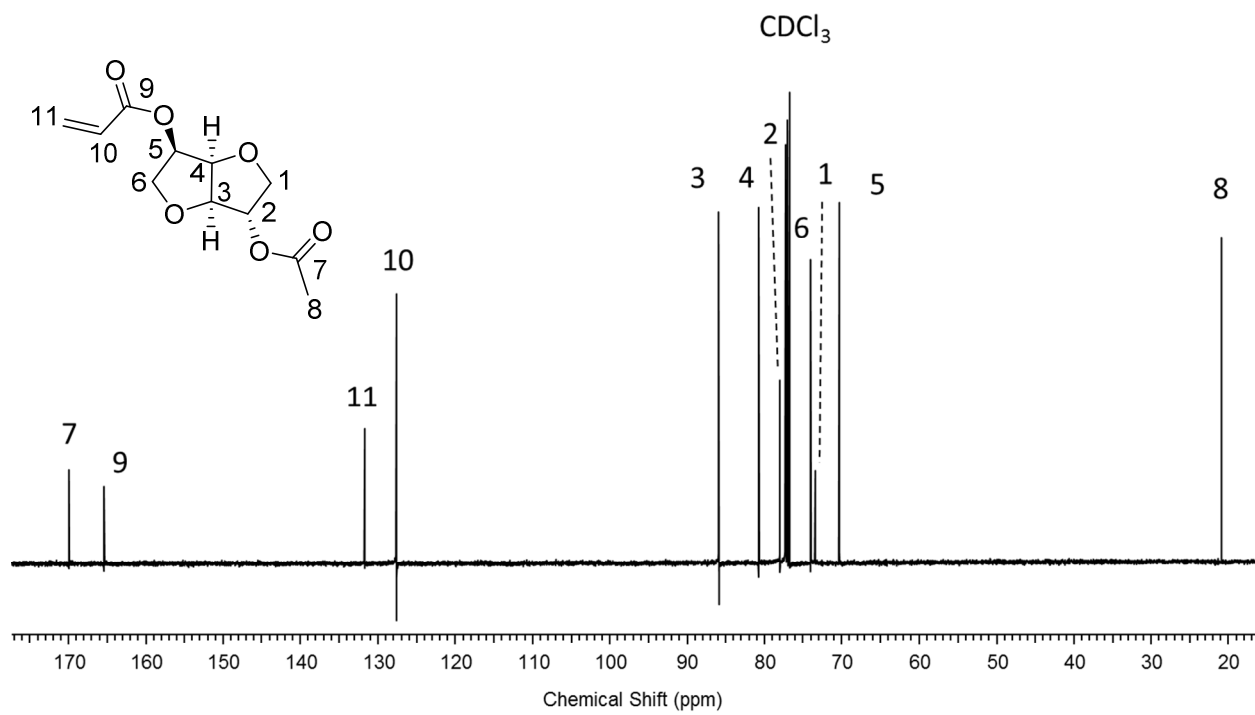


Figure S2. ¹³C NMR of AAI in CDCl₃.

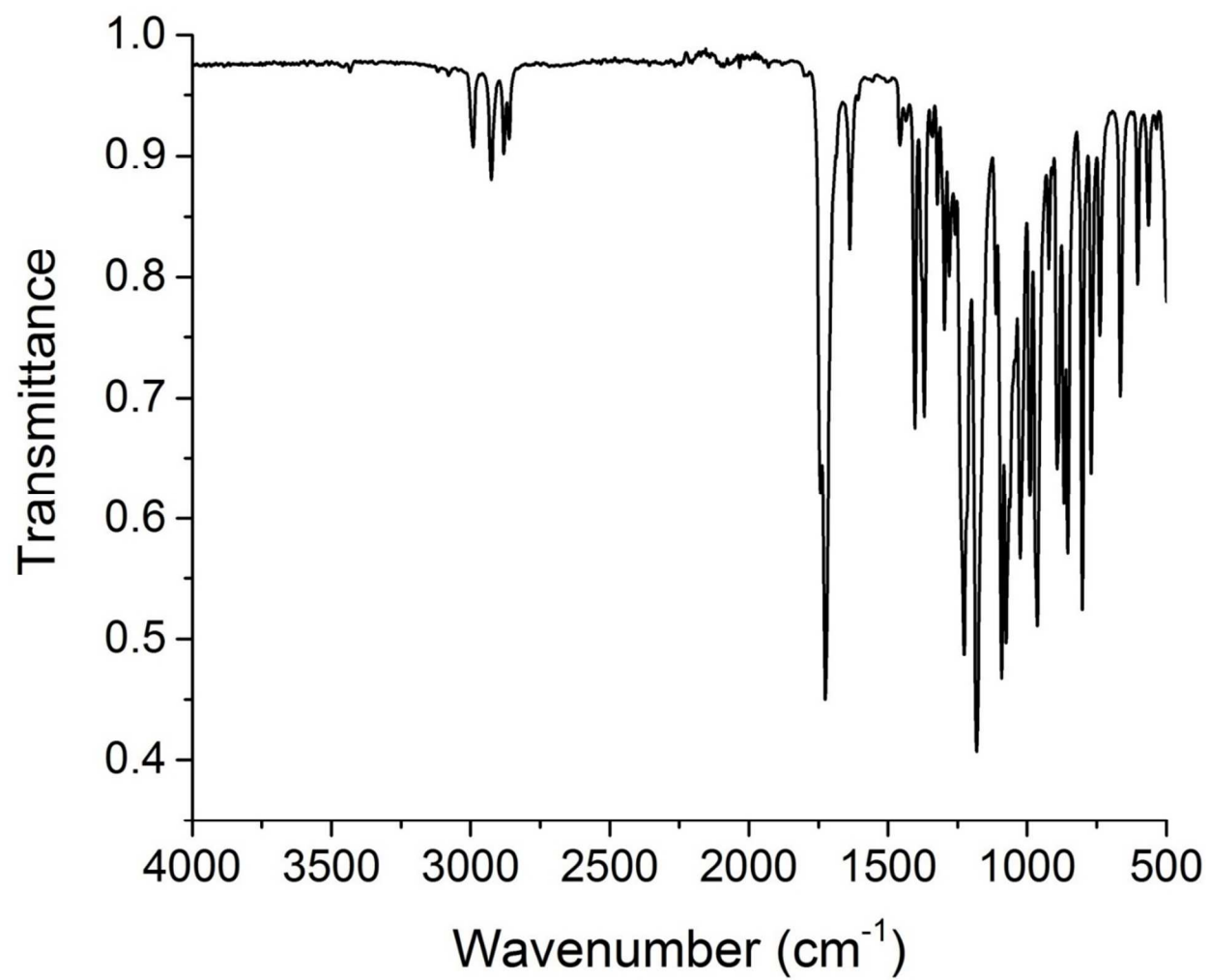


Figure S3. ATR FTIR of AAI.

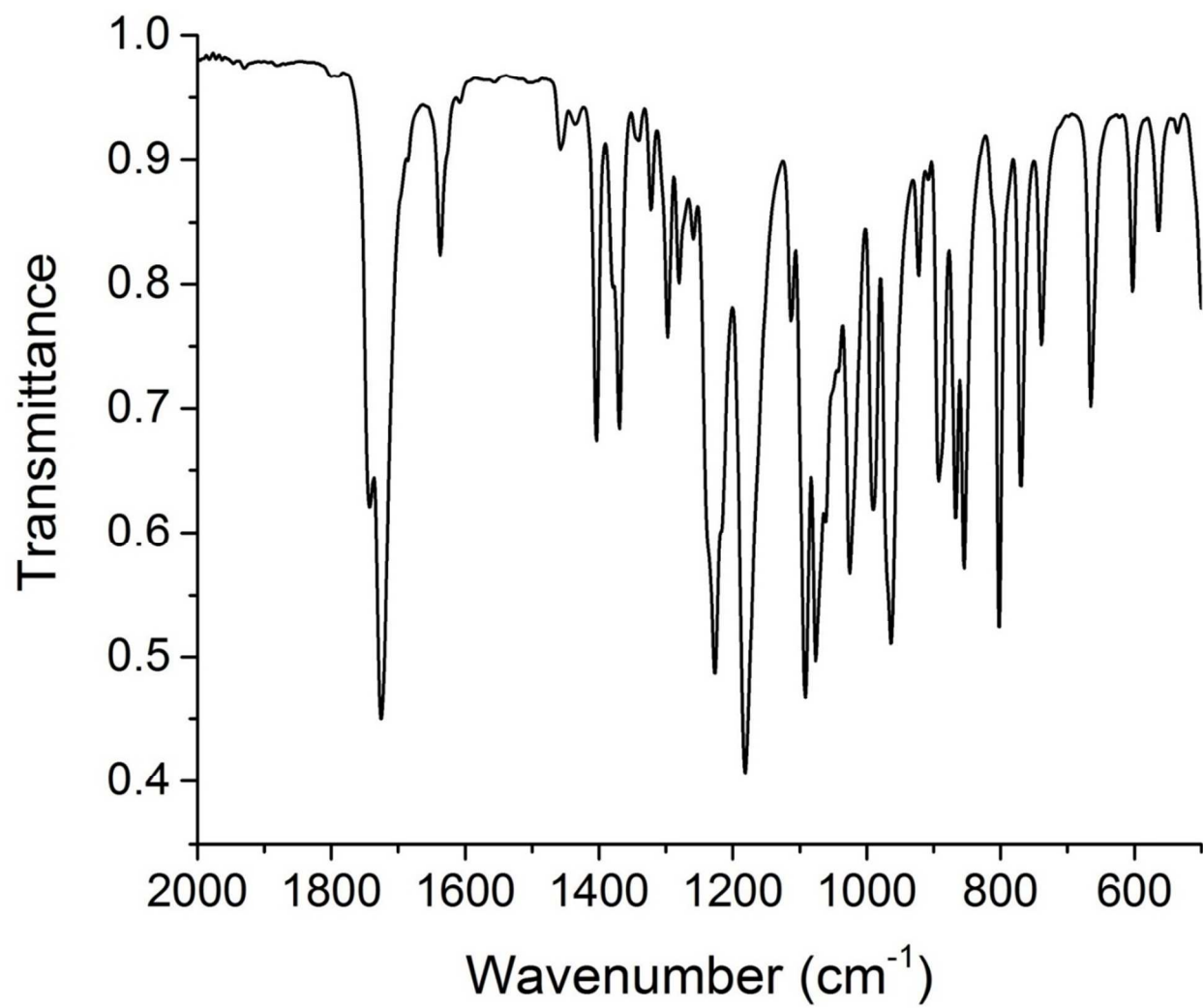


Figure S3a. ATR FTIR of AAI.

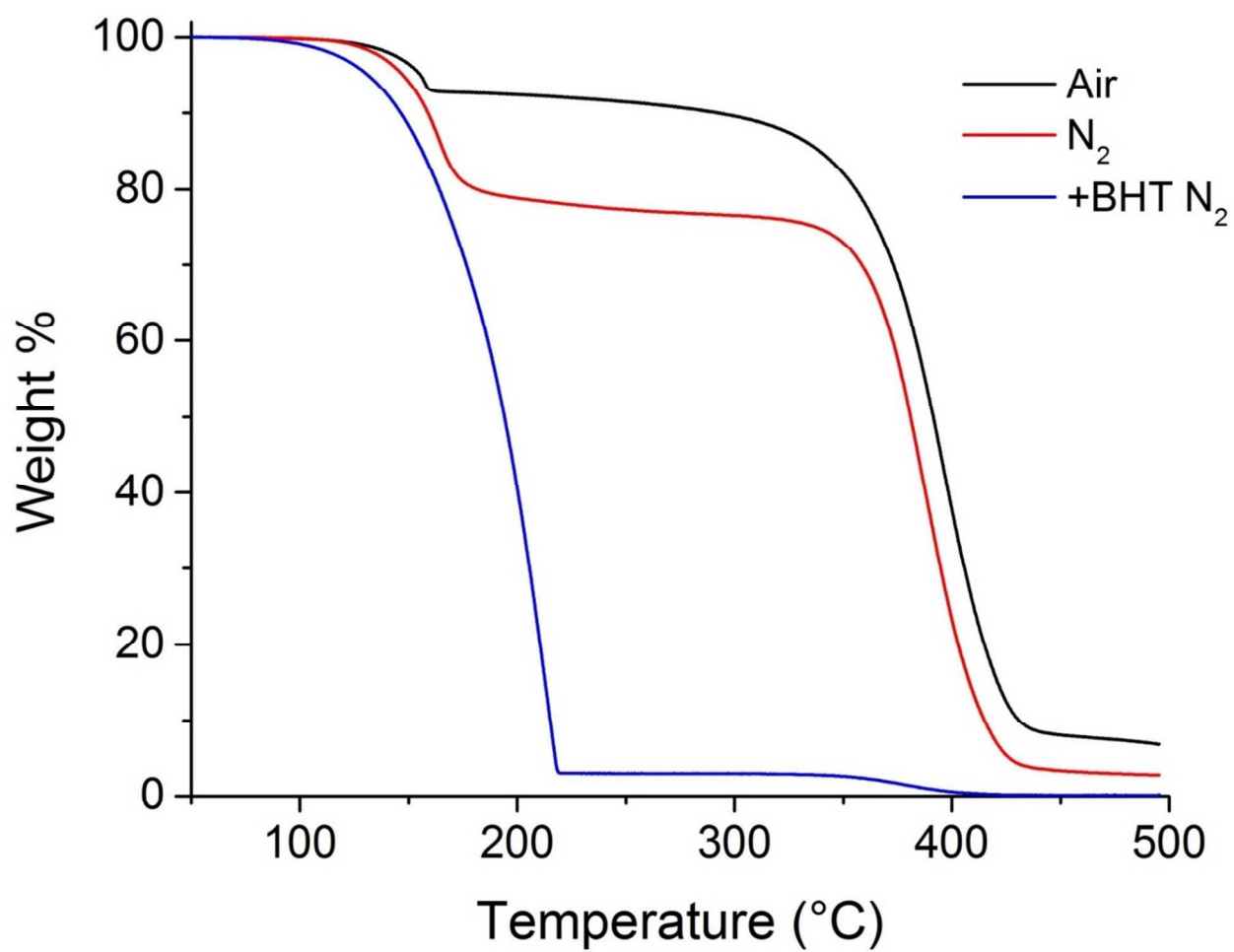
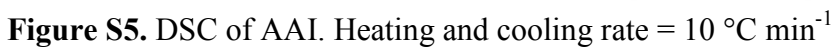
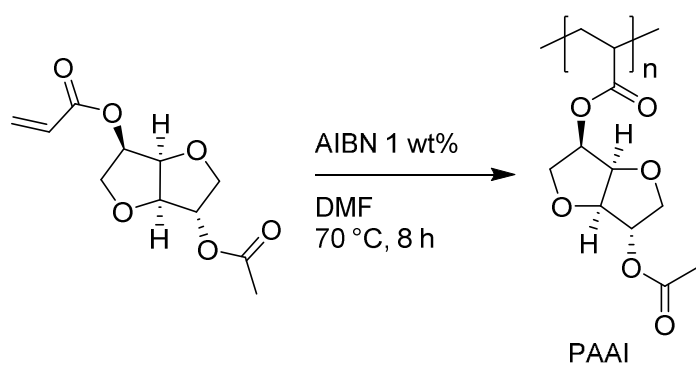


Figure S4. TGA of AAI. Heating rate = 10 °C min⁻¹.





Scheme S1. Free radical polymerization of AAI.

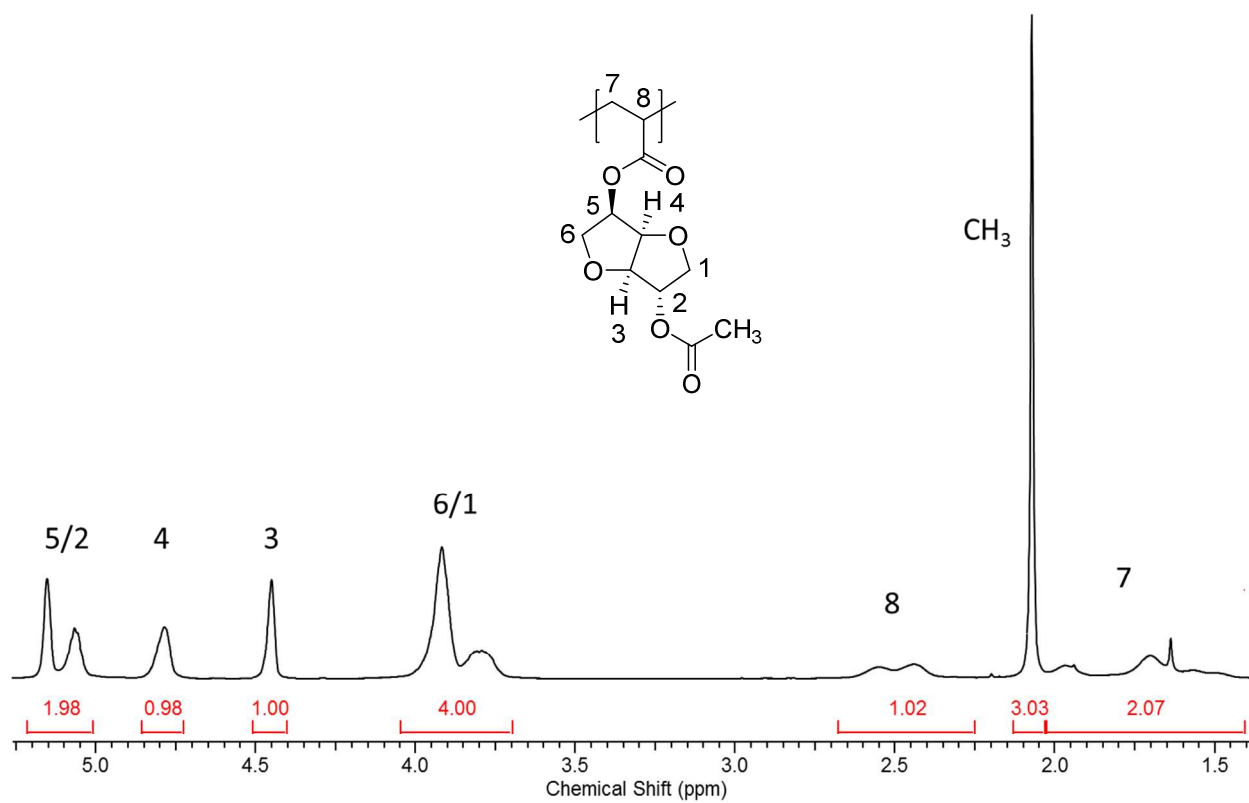


Figure S6. ^1H NMR in CDCl_3 of PAAI prepared by free radical polymerization.

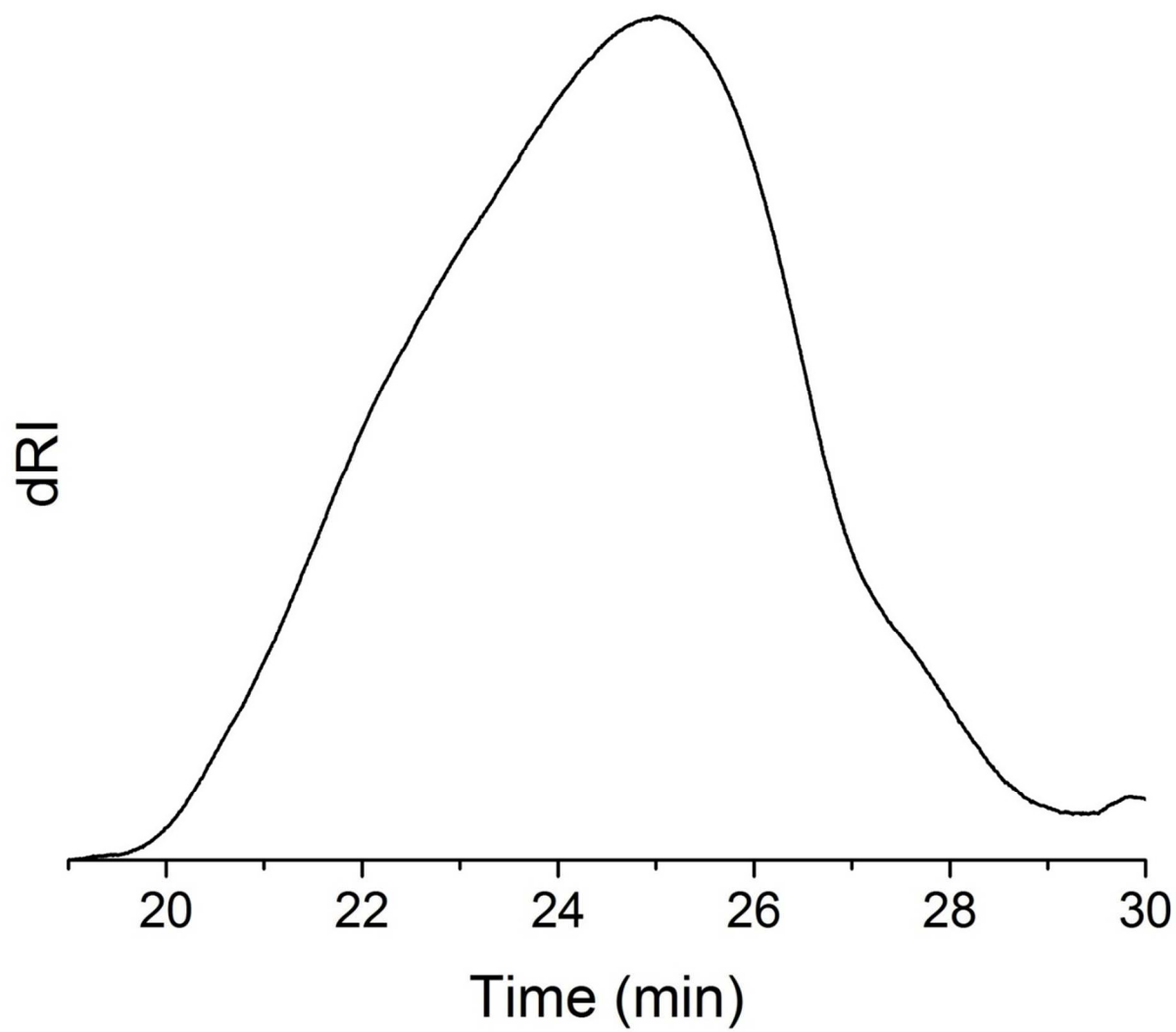


Figure S7. THF SEC of PAAI prepared by free radical polymerization

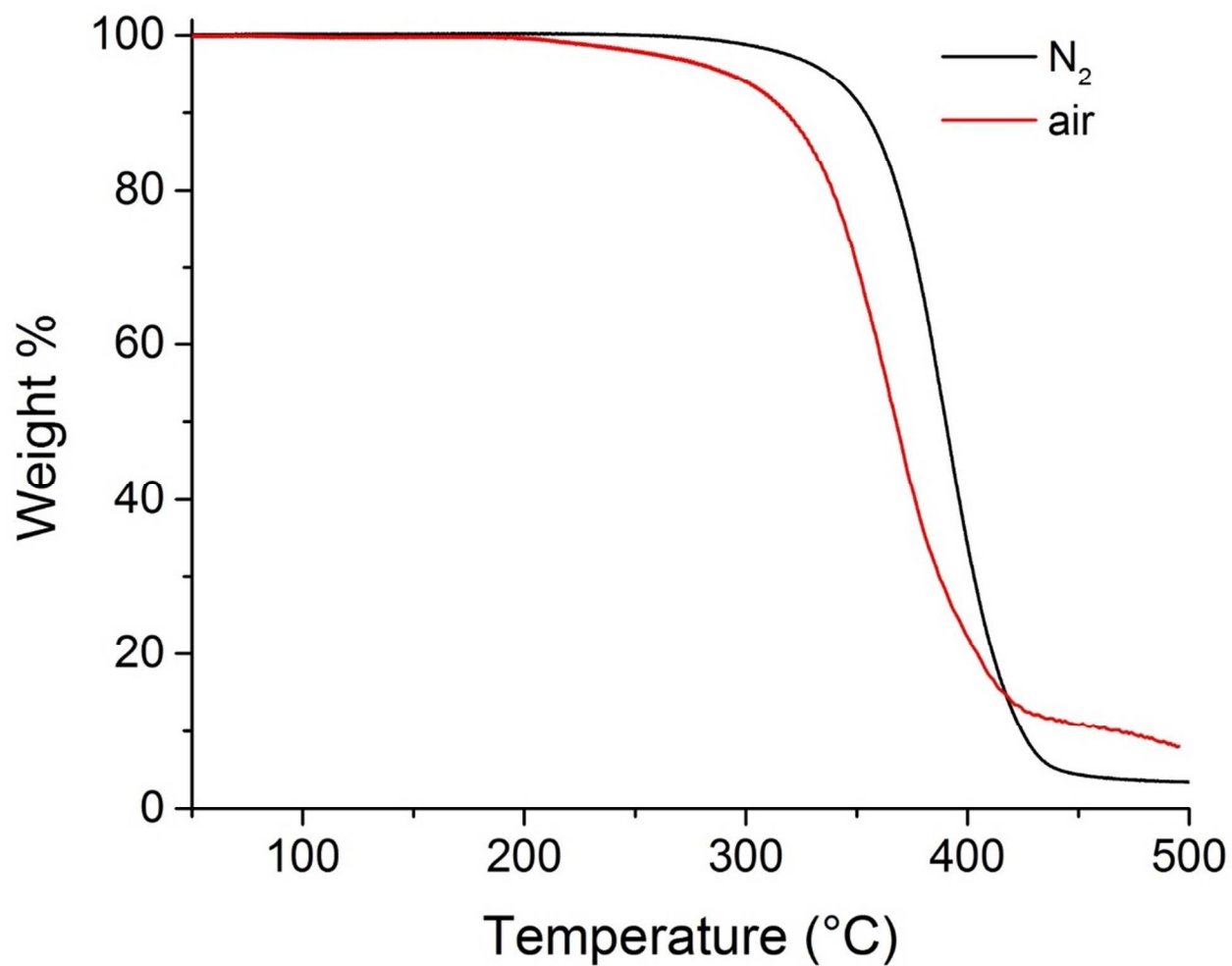


Figure S8. TGA of PAAI prepared by free radical polymerization. Heating rate = 10 °C min⁻¹

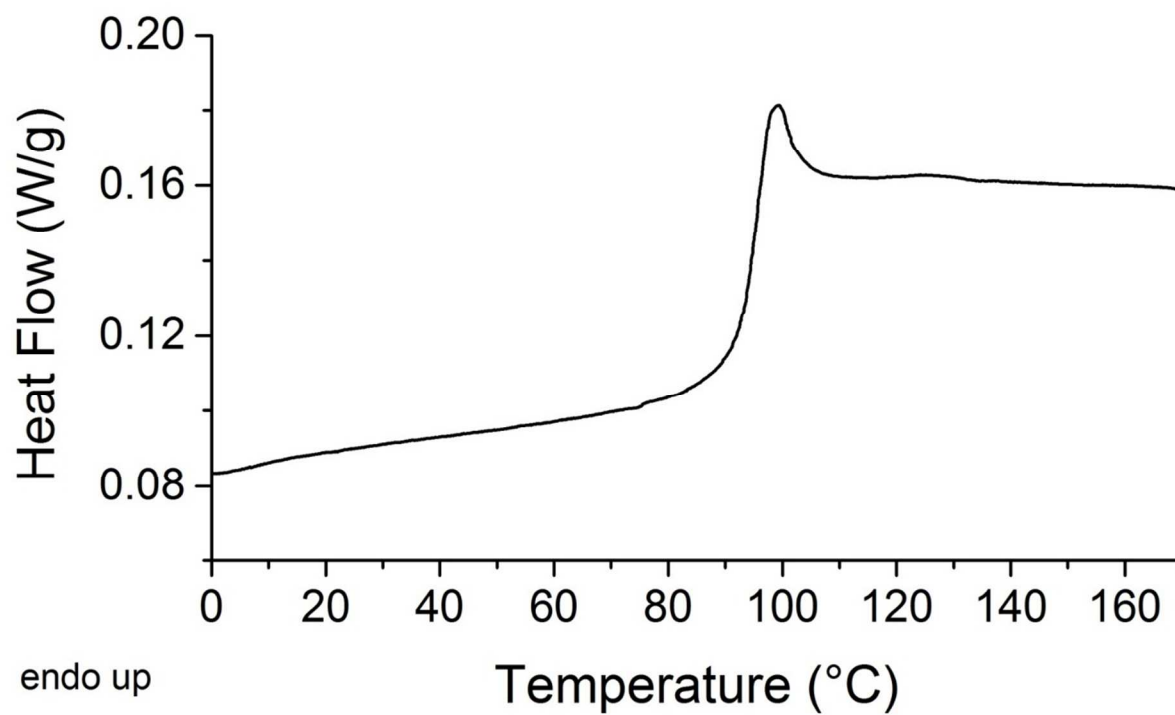
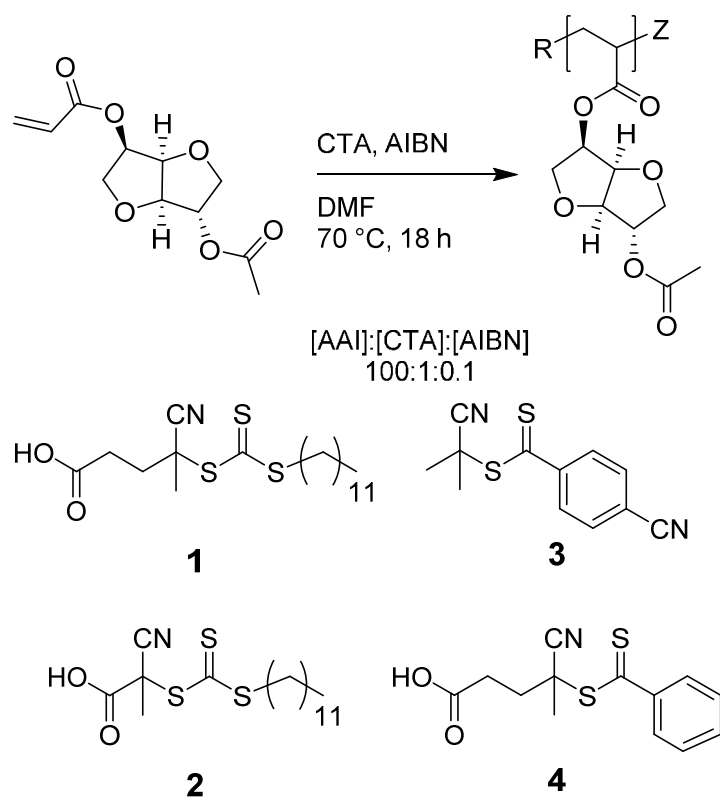


Figure S9. DSC of PAAI prepared by free radical polymerization. Ramp rate = 10 °C min⁻¹. Second heat.

Table S1. Screening RAFT agents for PAAI polymerization

CTA	% conv. ^a	M_n (calc) ^b (kg mol ⁻¹)	M_n (SEC) ^c (kg mol ⁻¹)	\bar{D}^c
1	77	18.6	18.5	1.20
2	56	13.6	13.0	1.15
3	<5	-	-	-
4	<5	-	-	-

^aFrom ¹H NMR; ^bAssuming 1 CTA per chain; ^cSEC-MALLS in THF



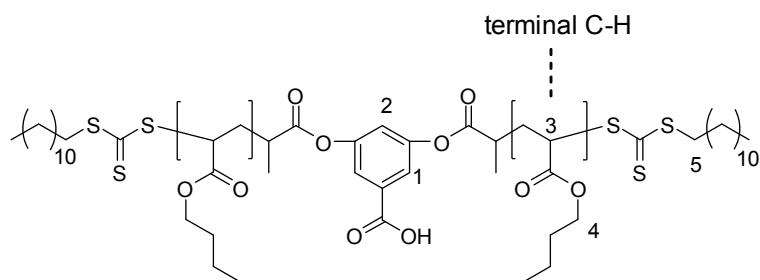
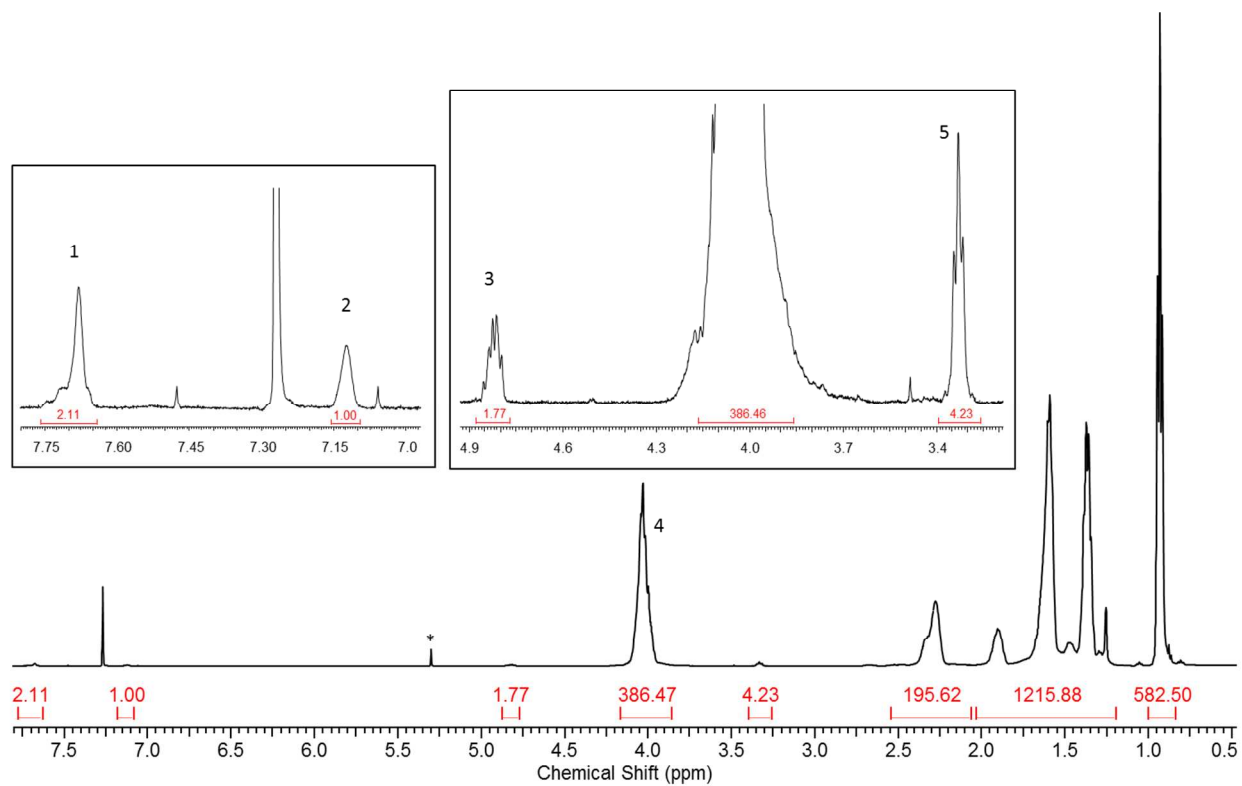


Figure S10. ^1H NMR of PnBA 27k in CDCl_3 . End group resonances in insert. * = residual CH_2Cl_2 .

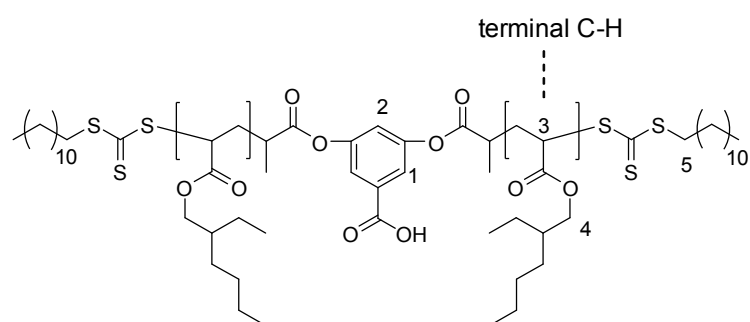
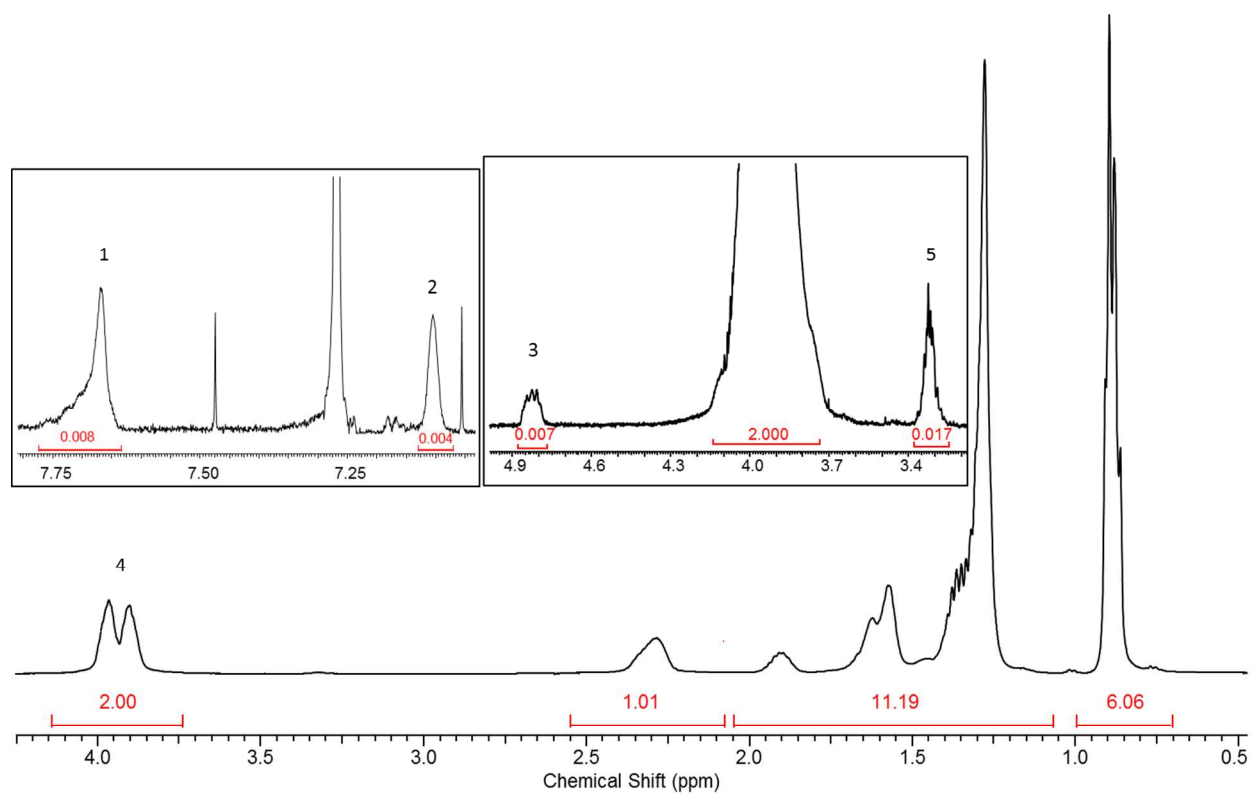


Figure S11. ^1H NMR of PEHA 45k in CDCl_3 . End group resonances in insert.

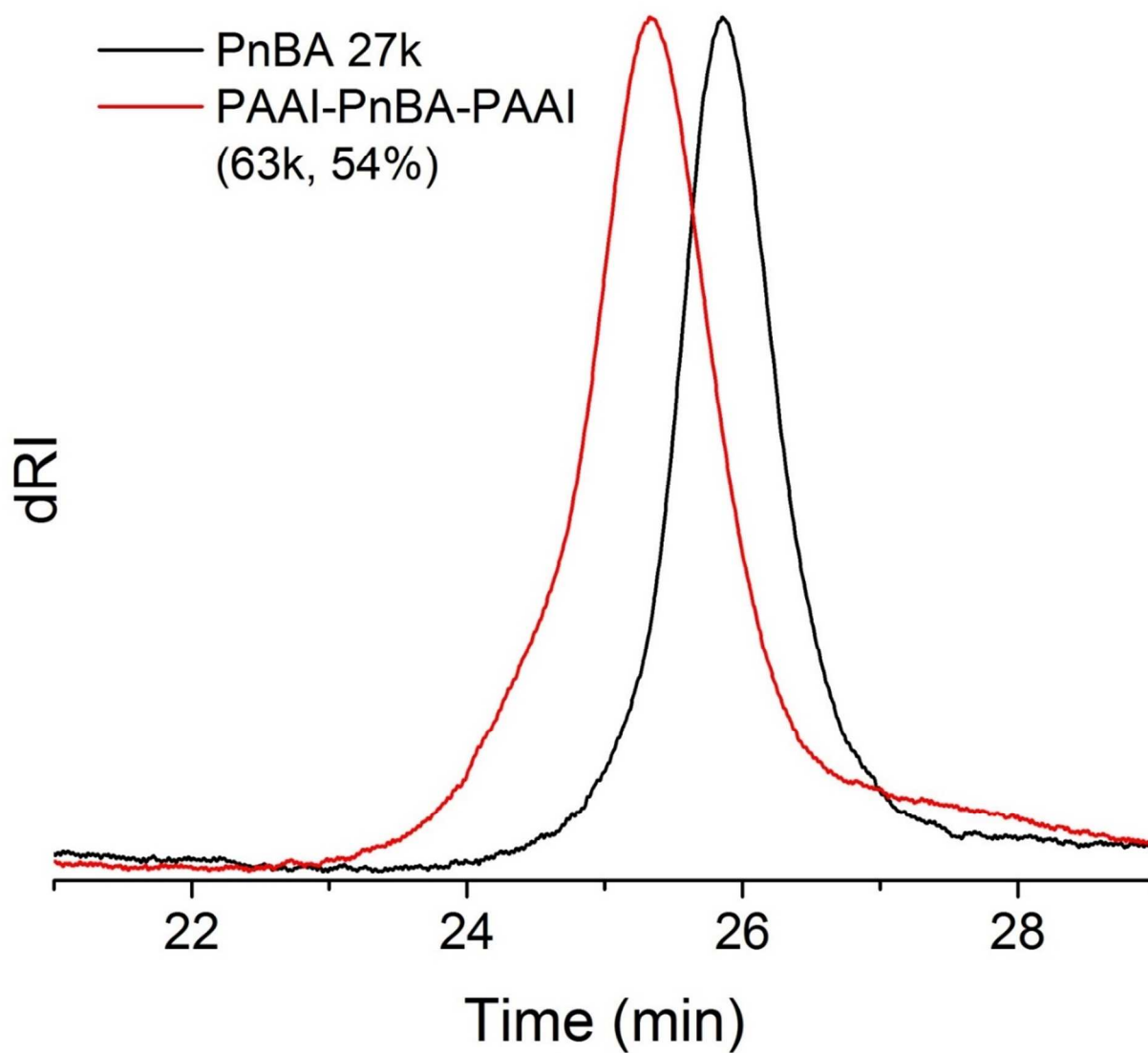


Figure S12. THF SEC of PnBA 27k macro-CTA and PAAI-PnBA-PAAI (63k, 54%).

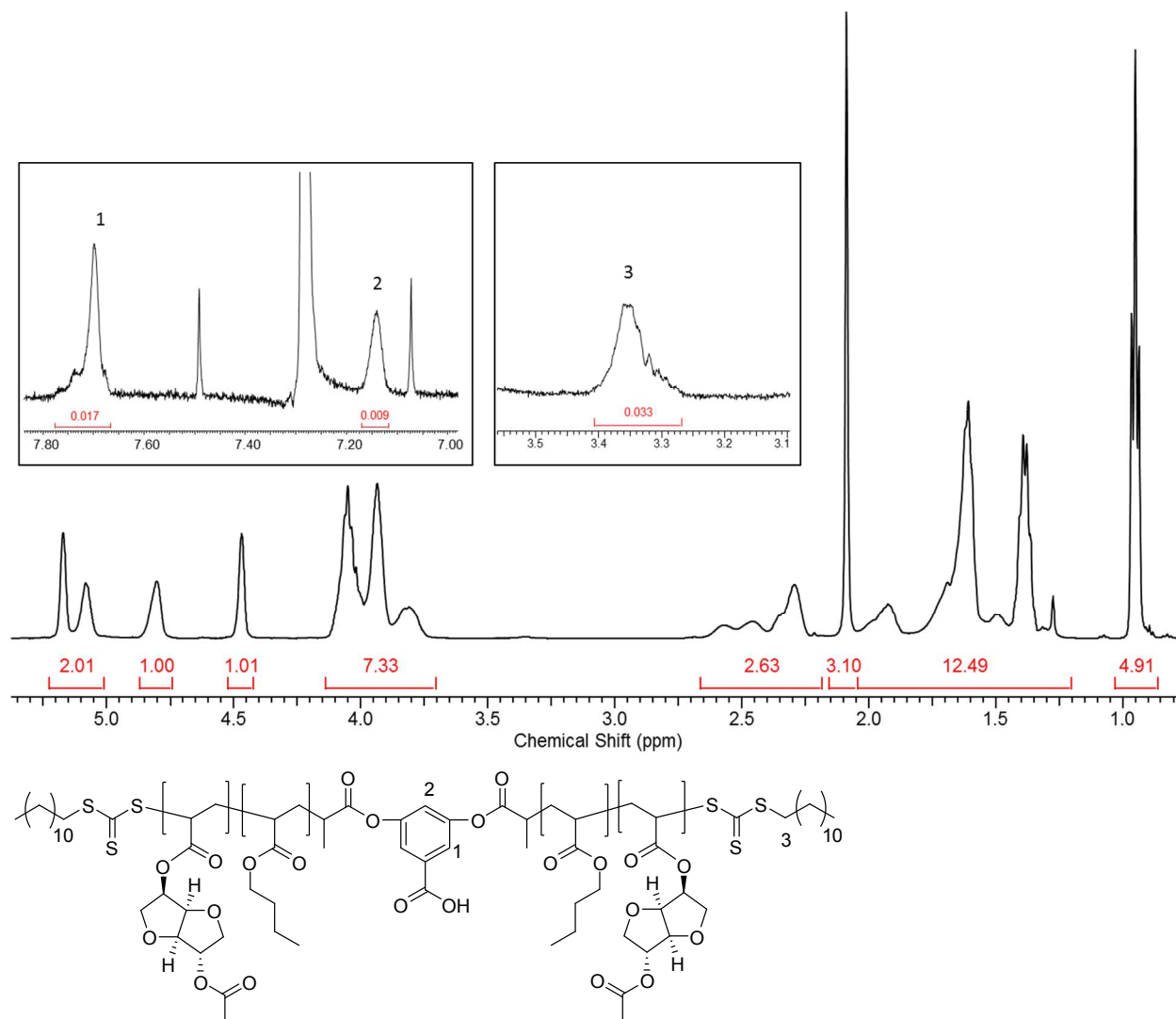
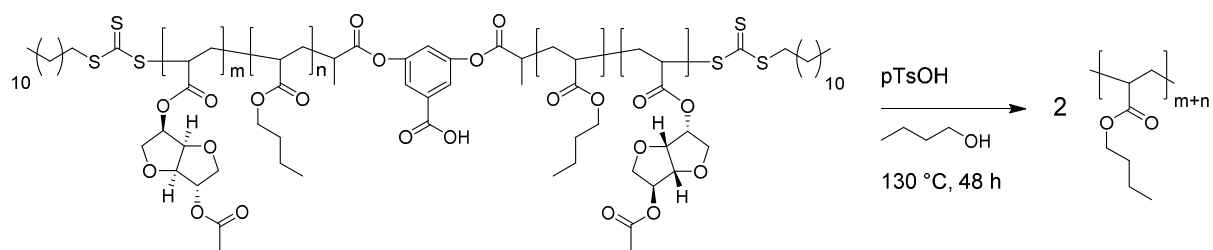


Figure S13. ^1H NMR of PAAI-PnBA-PAAI (63k, 54%) in CDCl_3 . End group resonances in insert.



Scheme S2. Alcoholysis of PAAI-PnBA-PAAI (60k, 17%).

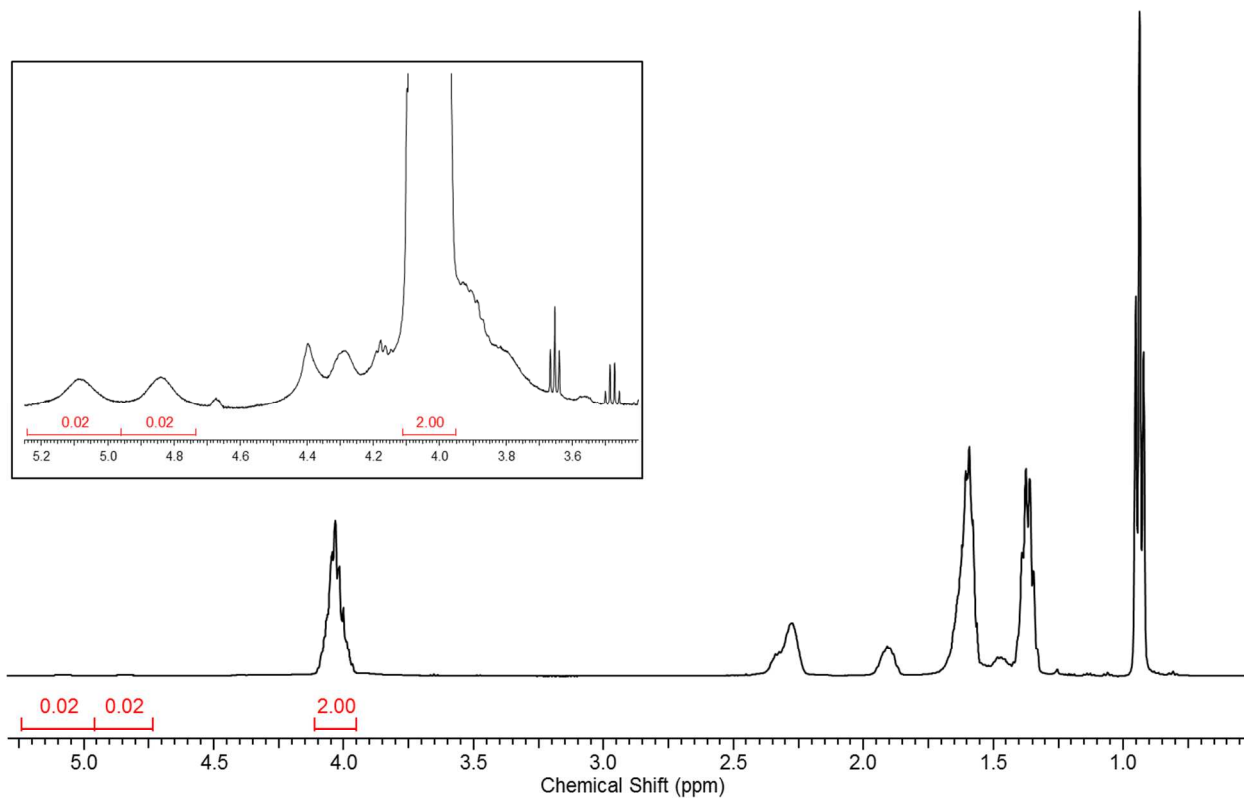


Figure S14. ^1H NMR in CDCl_3 of PAAI-PnBA-PAAI (60k, 17%) after alcoholysis.

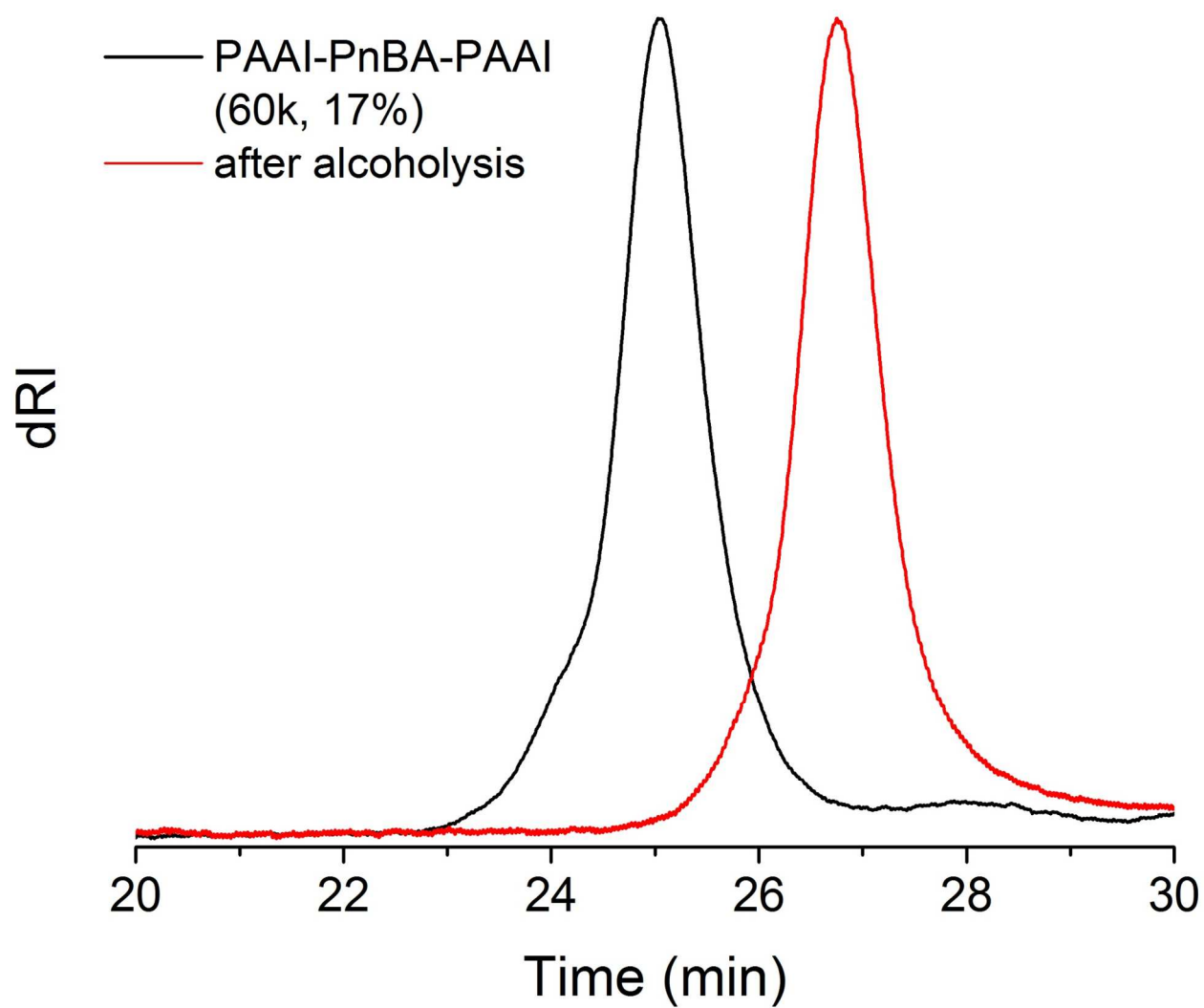


Figure S15. THF SEC of PAAI-PnBA-PAAI (60k, 17%) before and after alcoholysis.

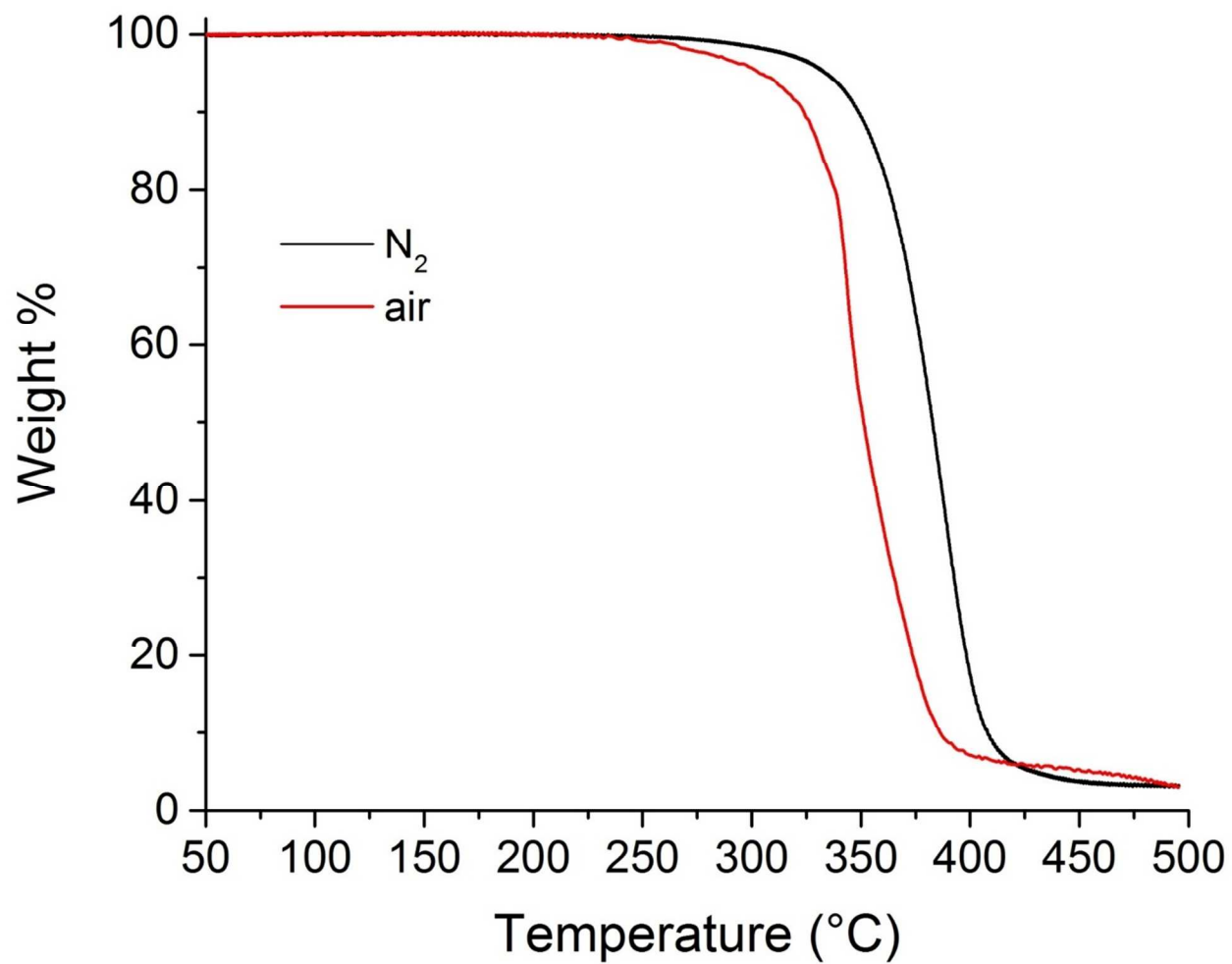


Figure S16. TGA of PAAI-PnBA-PAAI (60k, 17%). Heating rate = 10 °C min⁻¹.

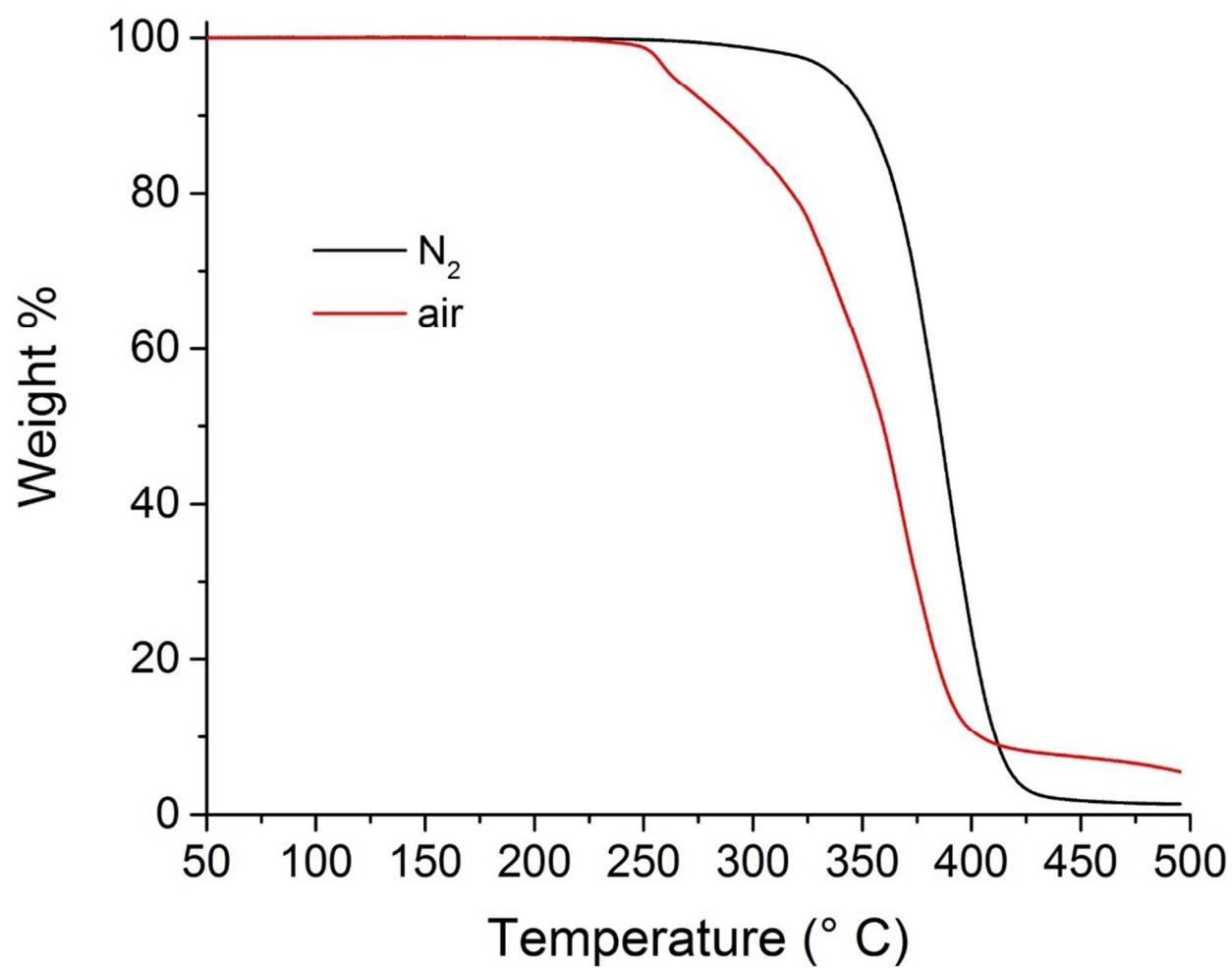


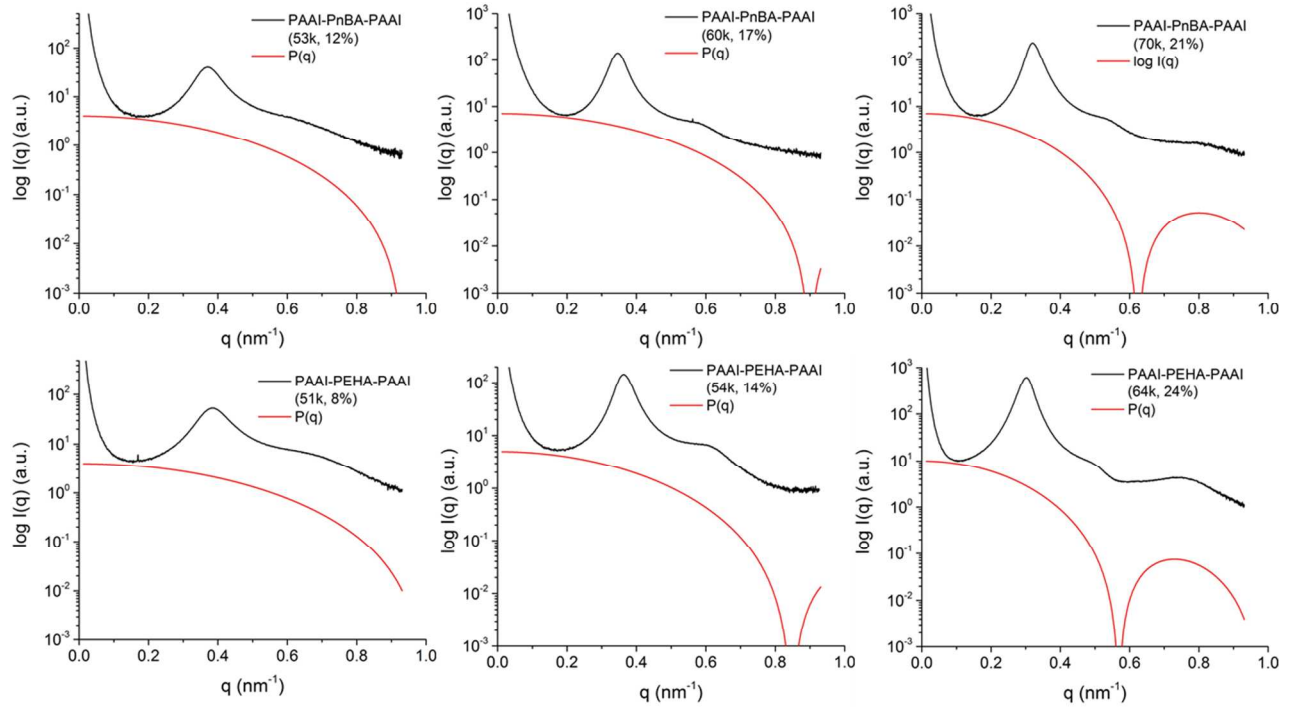
Figure S17. TGA of PAAI-PEHA-PAAI (54k, 14%). Heating rate = 10 °C min⁻¹.

Table S2. q^* and D^* for PAAI-PnBA-PAAI and PAAI-PEHA-PAAI triblock copolymers obtained from SAXS.

Polymer	q^* (nm^{-1})	D^* (nm)	R_s^a (nm)
PAAI-PnBA-PAAI (63k, 54%)	0.296	21.2	
PAAI-PnBA-PAAI (53k, 12%)	0.372	16.9	4.9
PAAI-PnBA-PAAI (60k, 17%)	0.347	18.1	5.3
PAAI-PnBA-PAAI (70k, 21%)	0.320	19.7	7.2
PAAI-PEHA-PAAI (51k, 8%)	0.385	16.3	4.5
PAAI-PEHA-PAAI (54k, 14%)	0.363	17.3	5.3
PAAI-PnBA-PAAI (64k, 24%)	0.302	20.8	7.9

^aEstimated sphere radius from fitting the spherical form factor to SAXS scattering patterns.

$$P(q) = \left(\frac{3}{(qR_s)^3} \right)^2 (\sin qR_s - qR_s \cos qR_s)^2$$



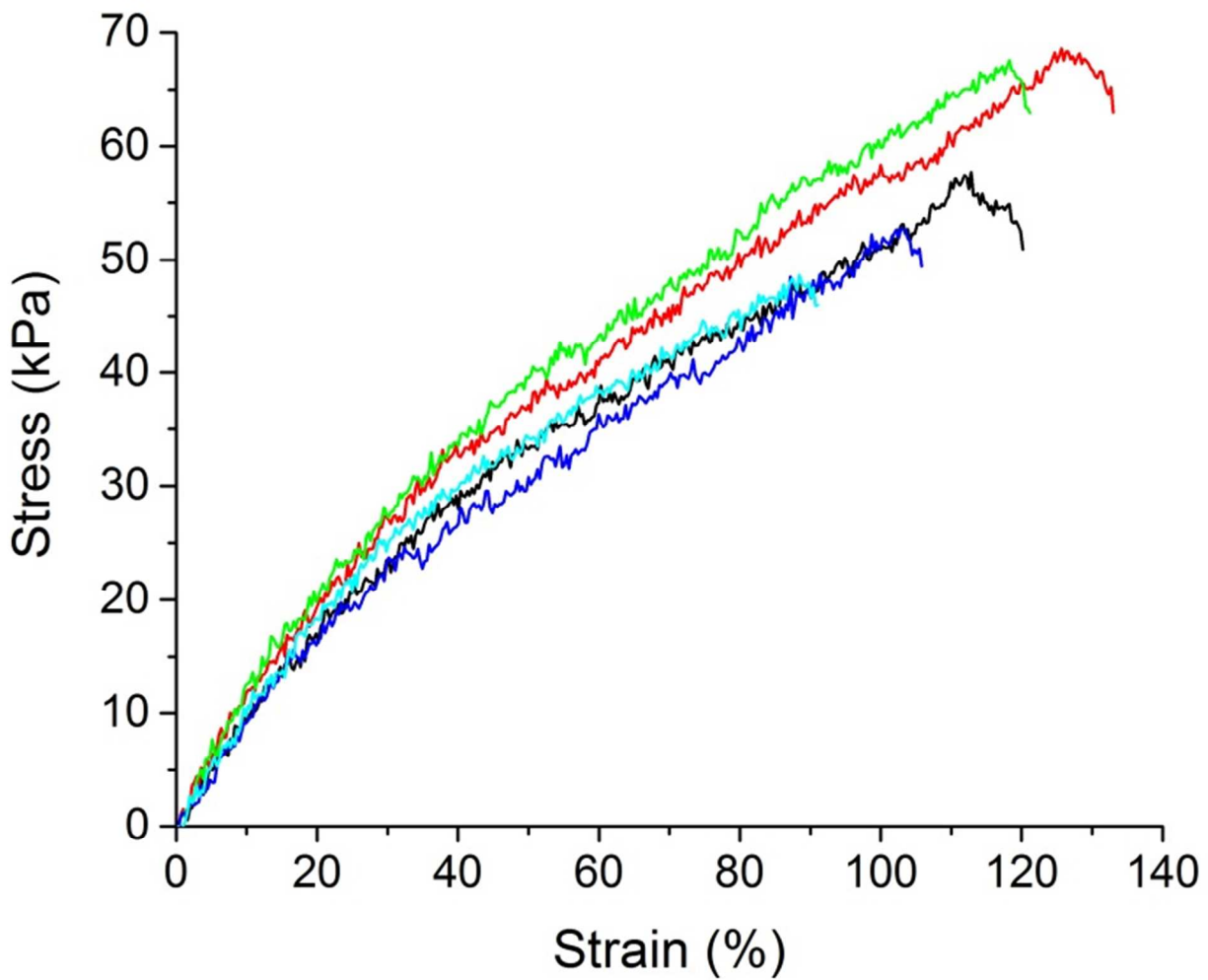


Figure S18. Tensile testing of PAAI-PnBA-PAAI (60k, 17%).

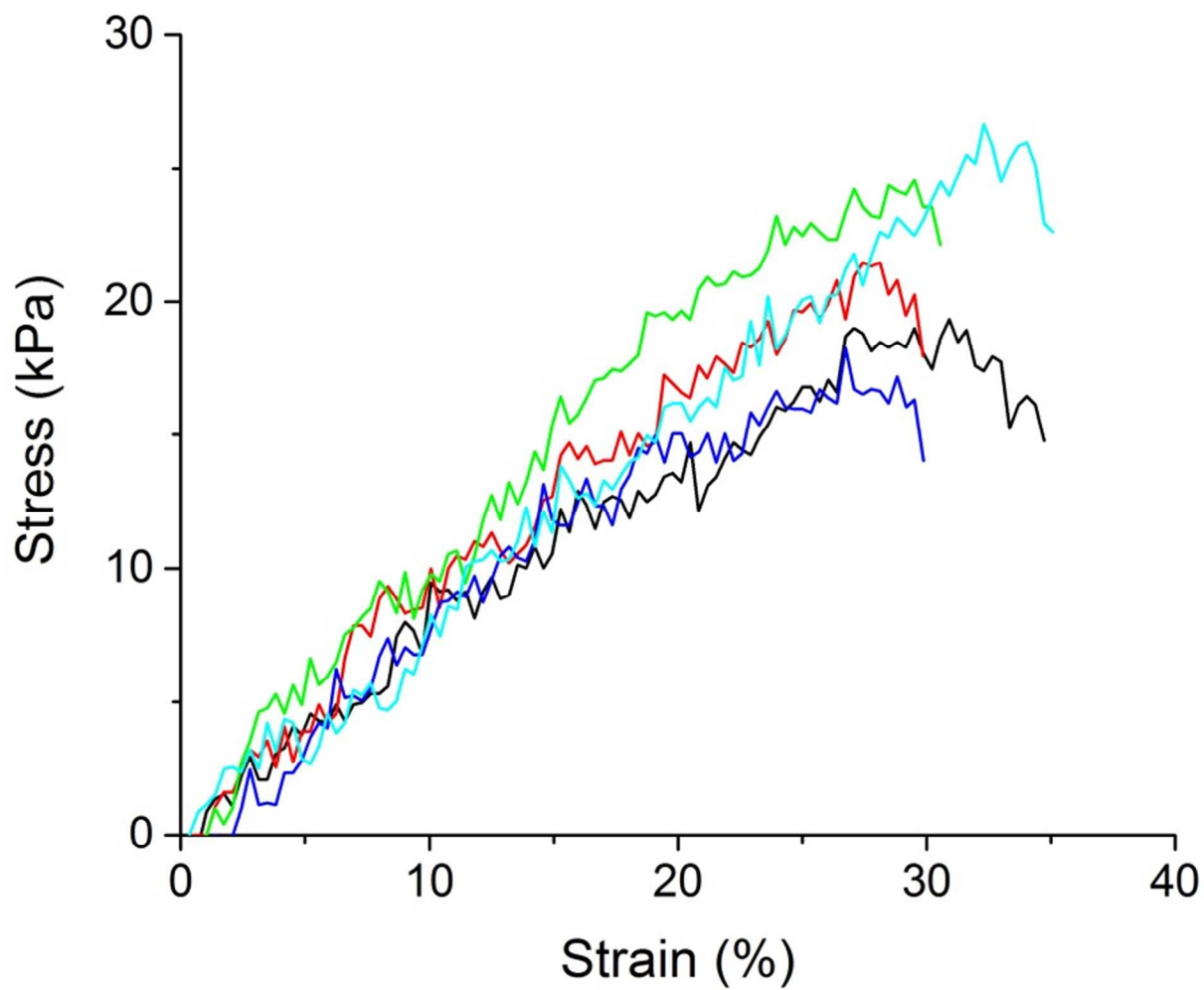


Figure S19. Tensile testing of PAAI-PEHA-PAAI (54k, 14%).

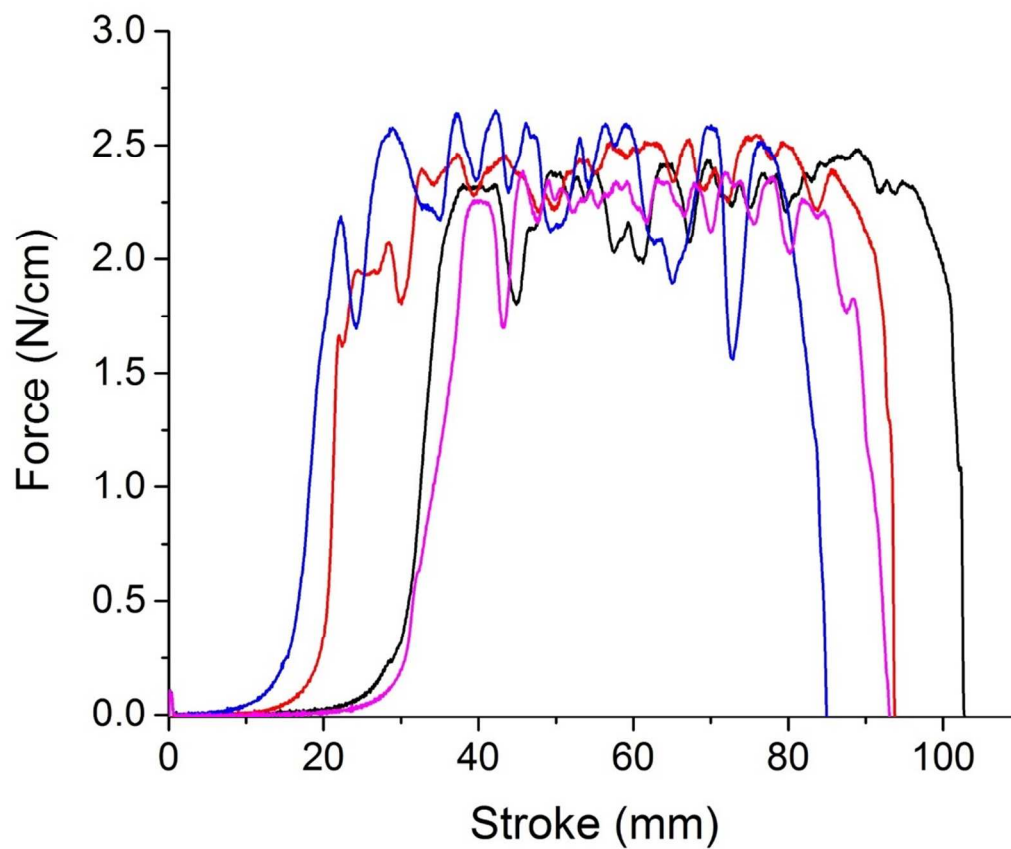


Figure S20. 180° peel test of PAAI-PnBA-PAAI (53k, 12%).

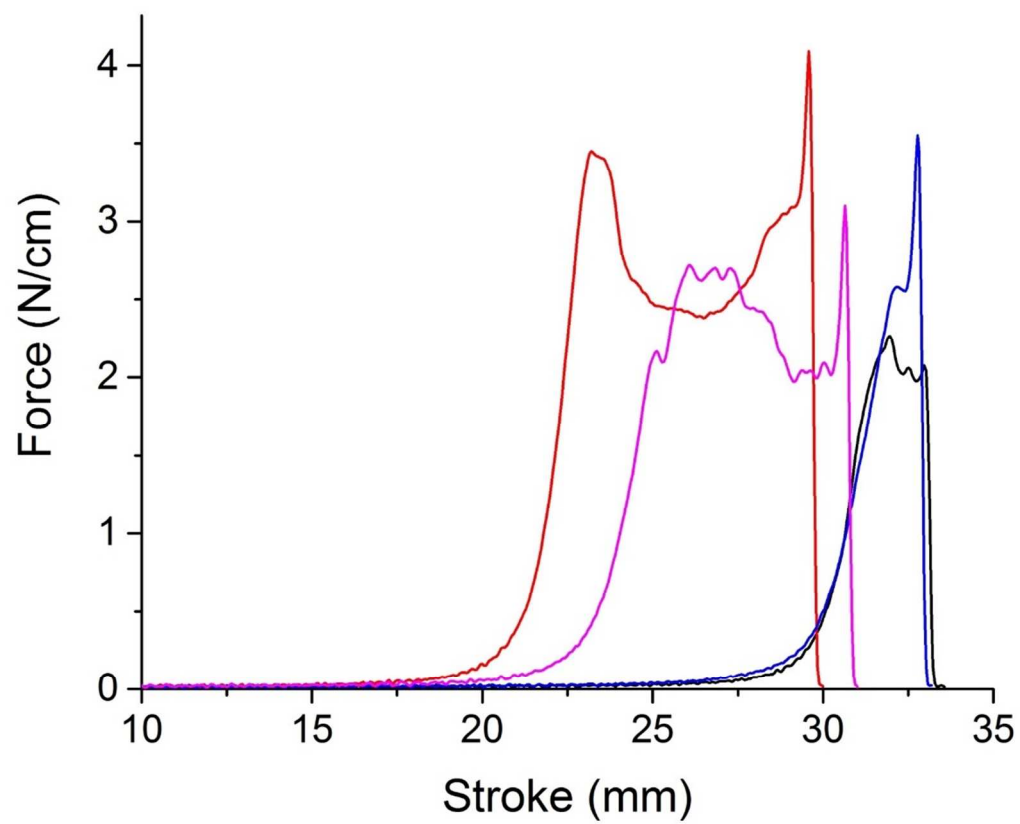


Figure S21. Loop tack test of PAAI-PnBA-PAAI (53k, 12%).

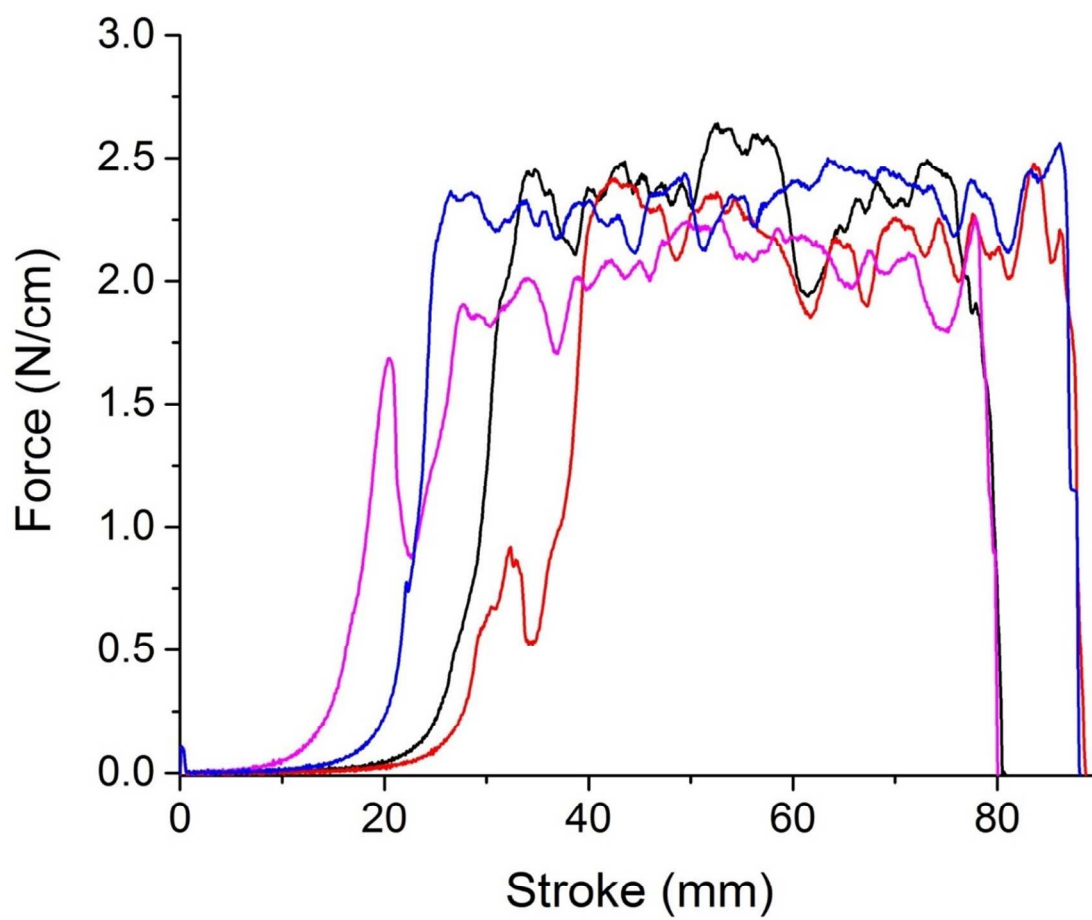


Figure S22. 180° peel test of PAAI-PnBA-PAAI (60k, 17%).

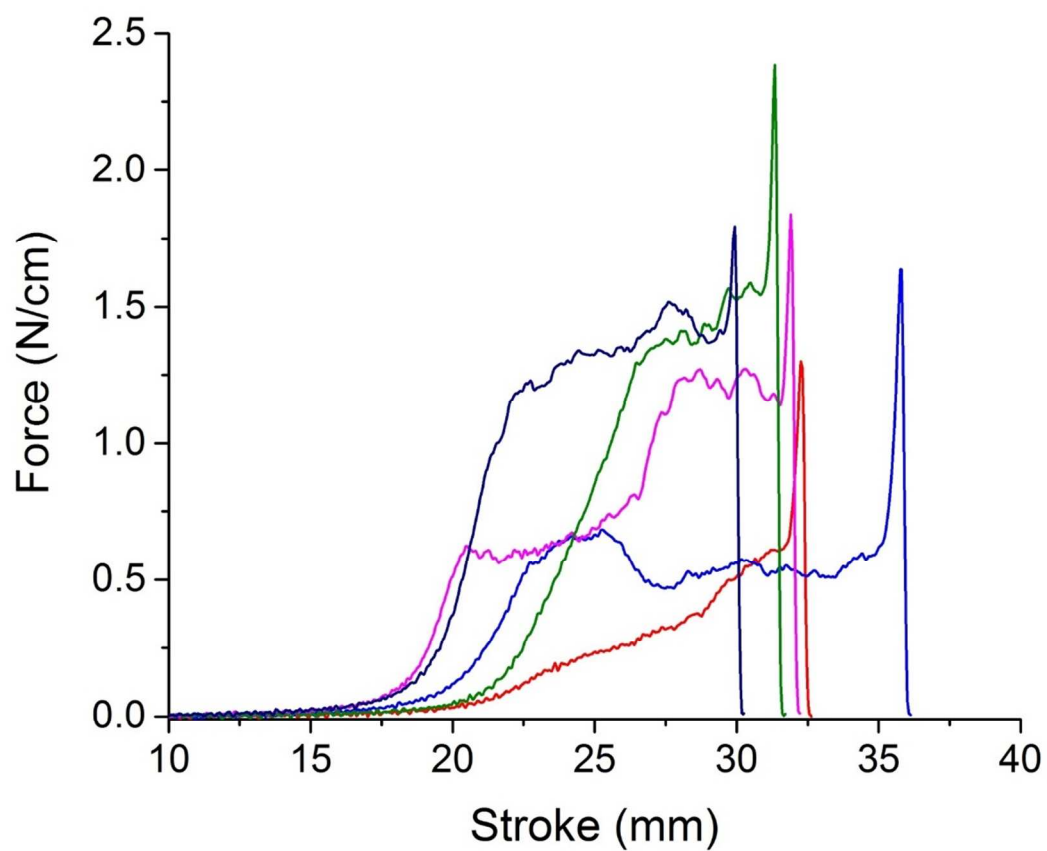


Figure S23. Loop tack test of PAAI-PnBA-PAAI (60k, 17%).

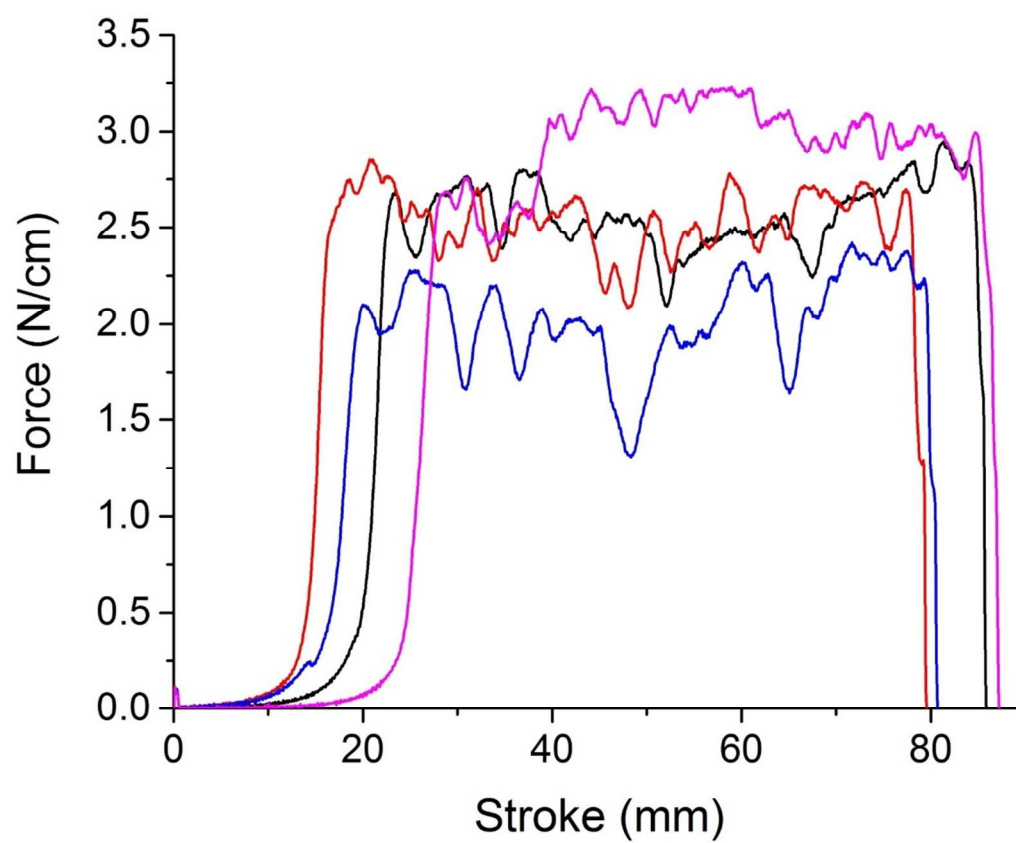


Figure S24. 180° peel test of PAAI-PnBA-PAAI (70k, 21%).

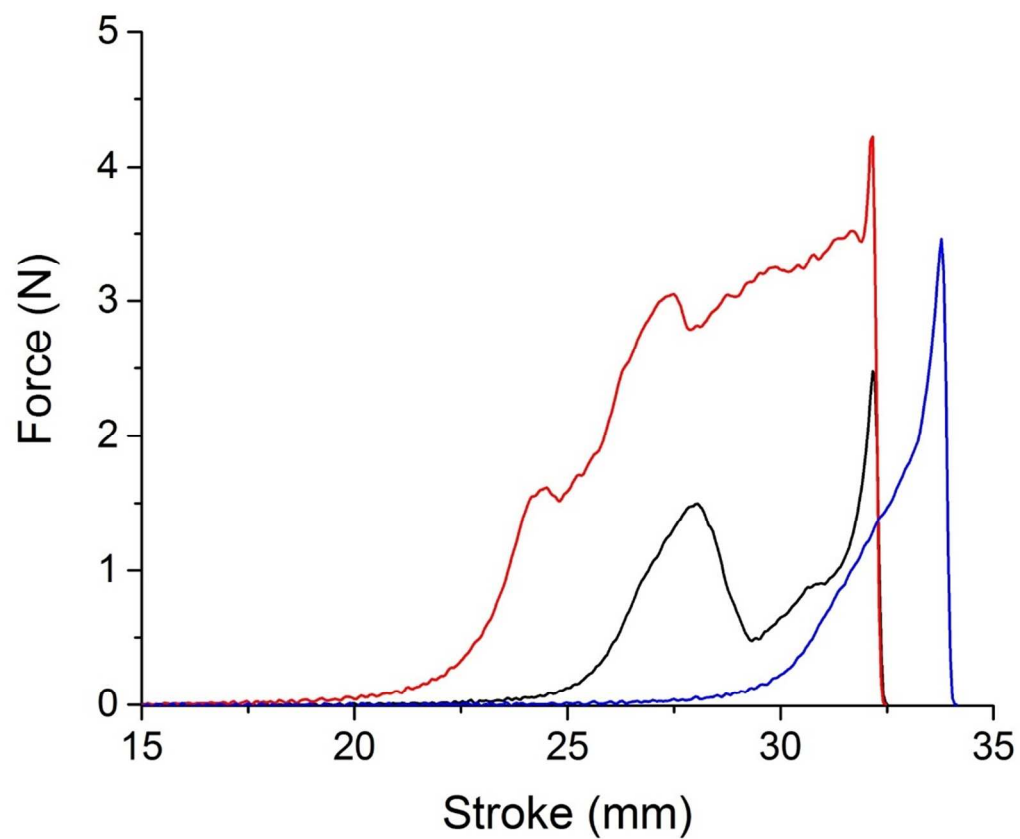


Figure S25. Loop tack test of PAAI-PnBA-PAAI (70k, 21%).

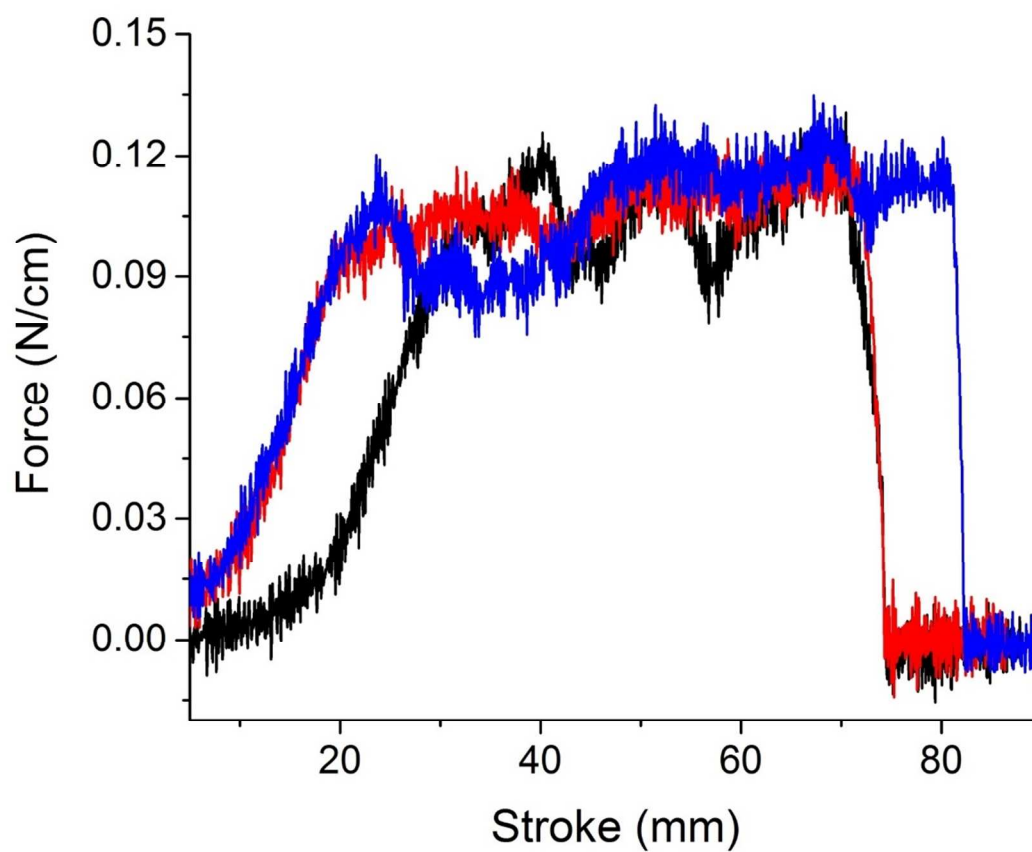


Figure S26. 180° peel test of PAAI-PEHA-PAAI (64k, 24%).

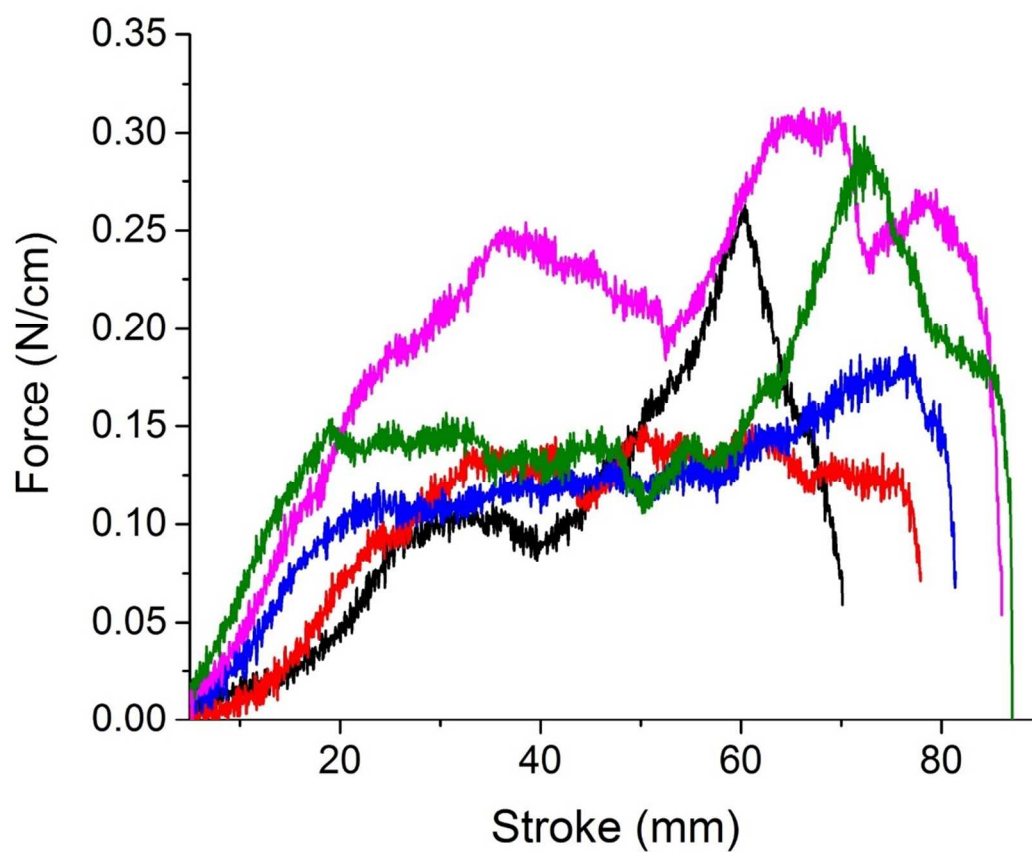


Figure S27. 180° peel test of PAAI-PEHA-PAAI (54k, 14%).

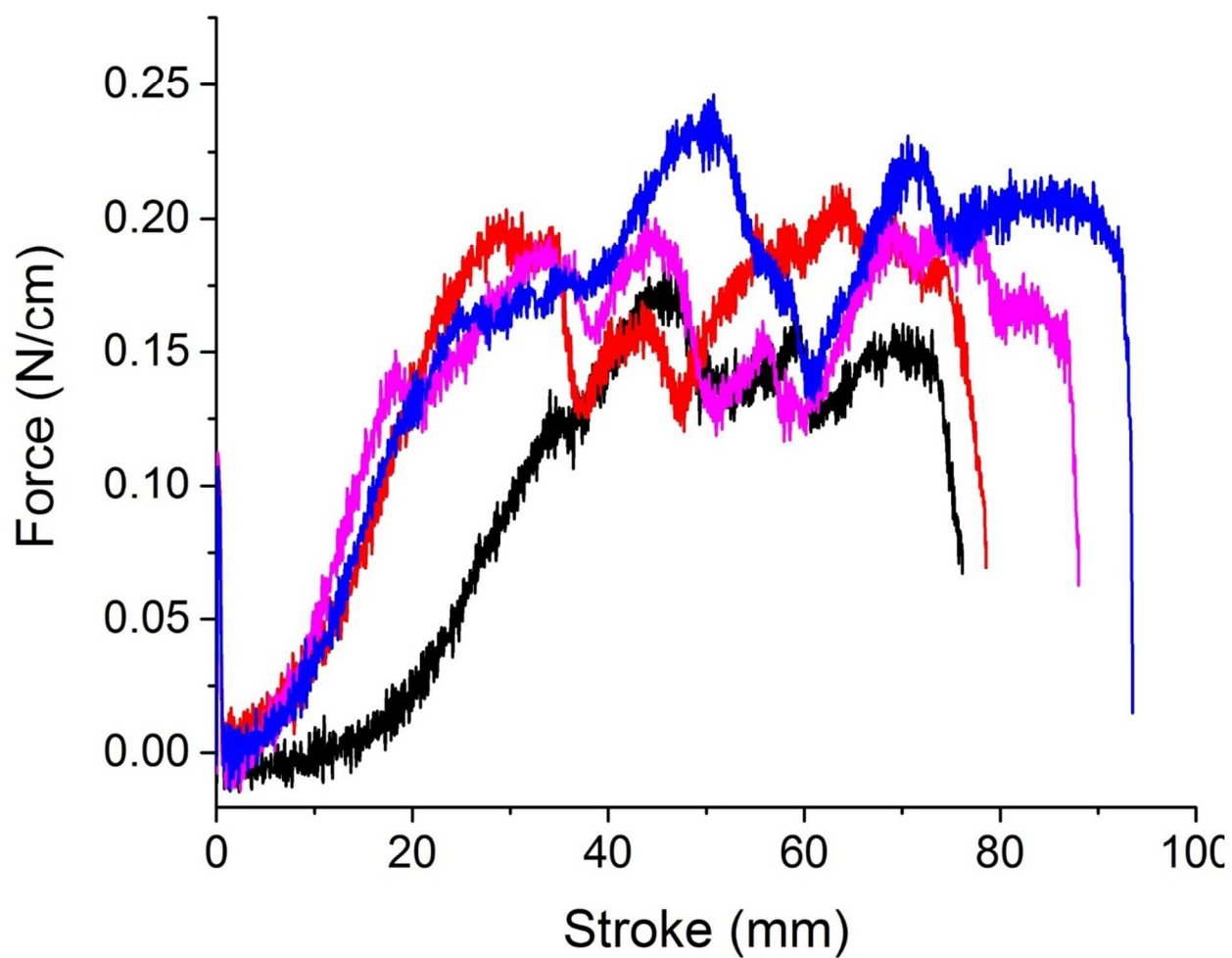


Figure S28. 180° peel test of PAAI-PEHA-PAAI (51k, 8%).

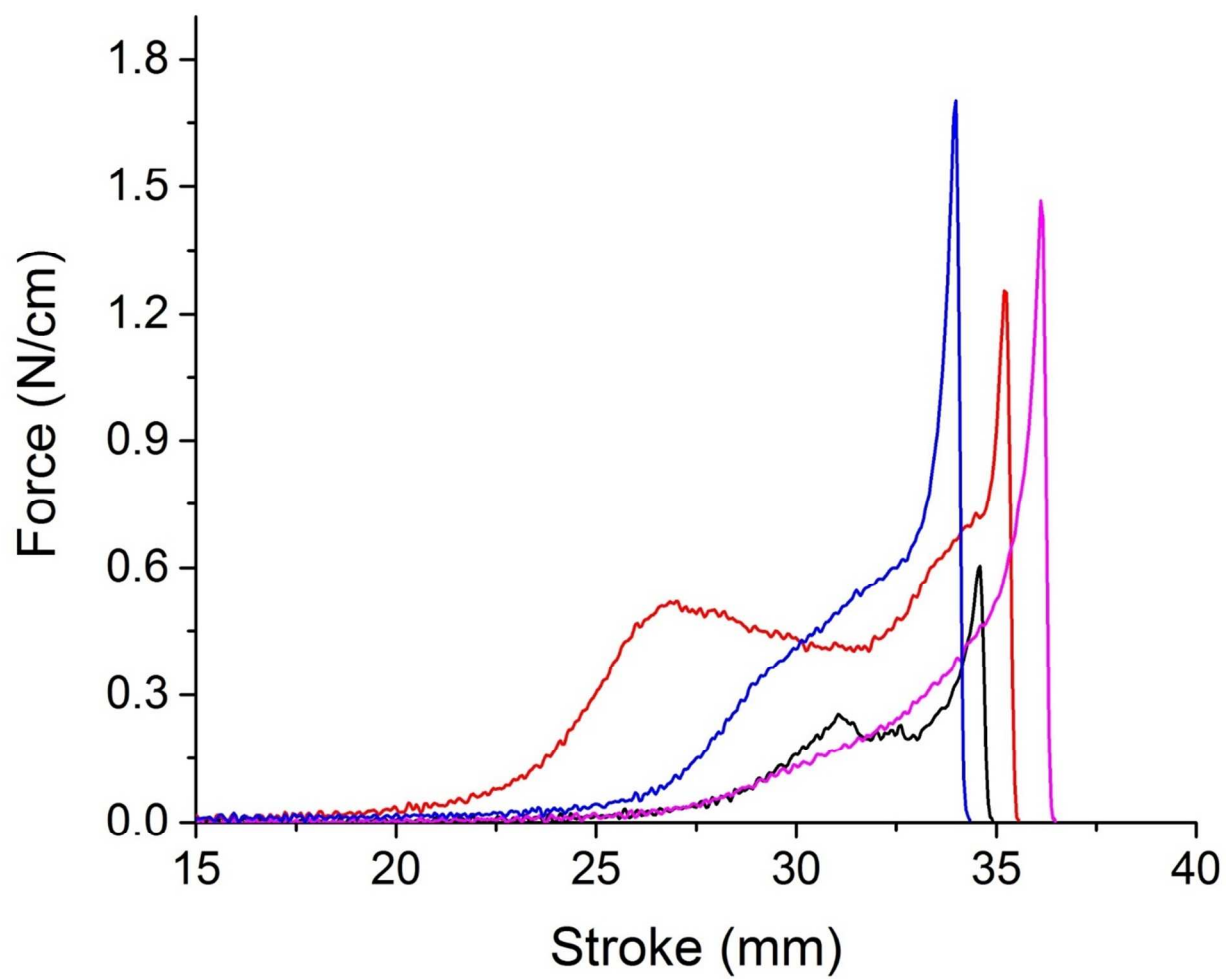


Figure S29. Loop tack test of PAAI-PEHA-PAAI (51k, 8%).

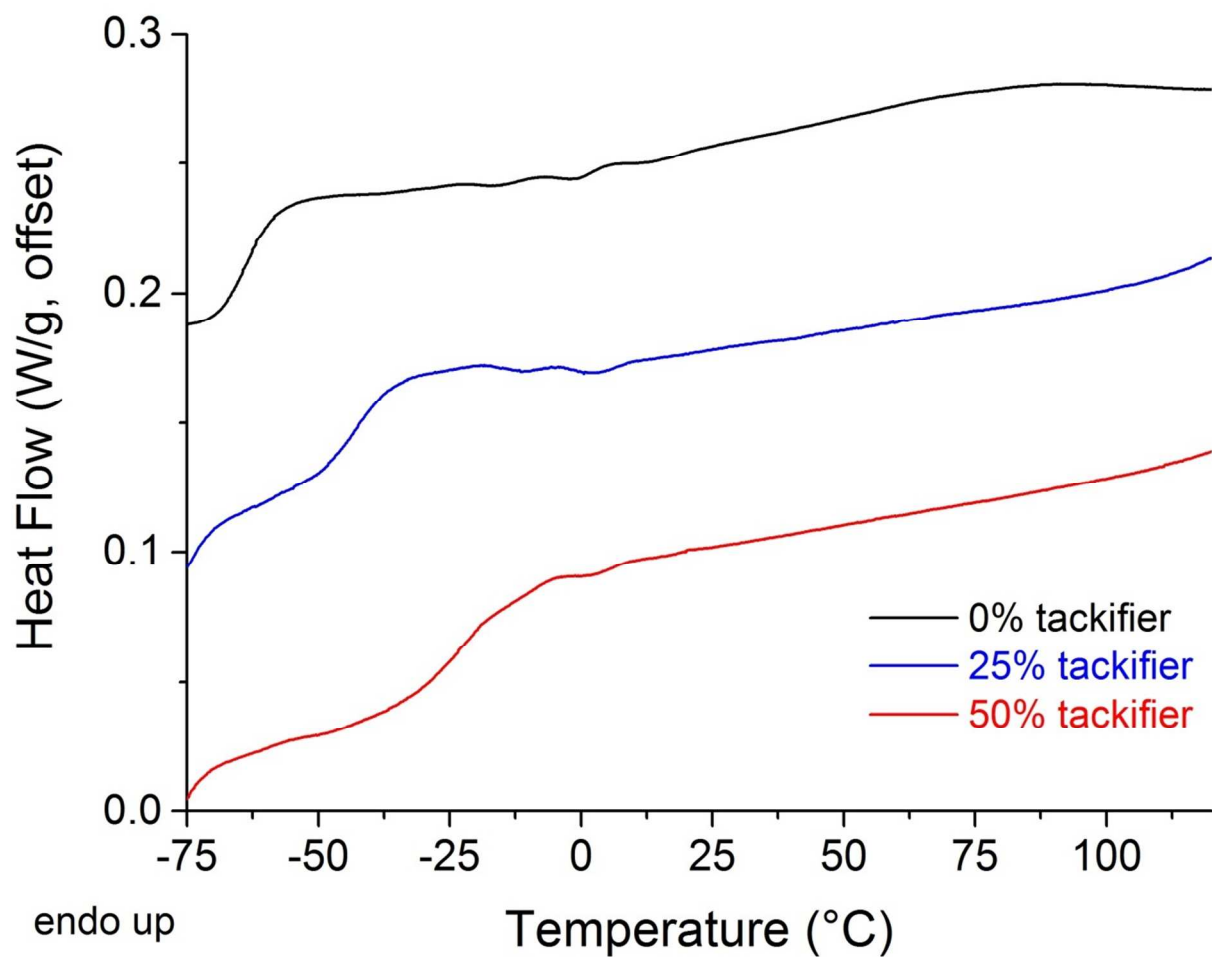


Figure S30. DSC of PAAI-PEHA-PAAI (54k, 14%) with rosin ester tackifier. Ramp rate = 10 °C min⁻¹. Second heat.

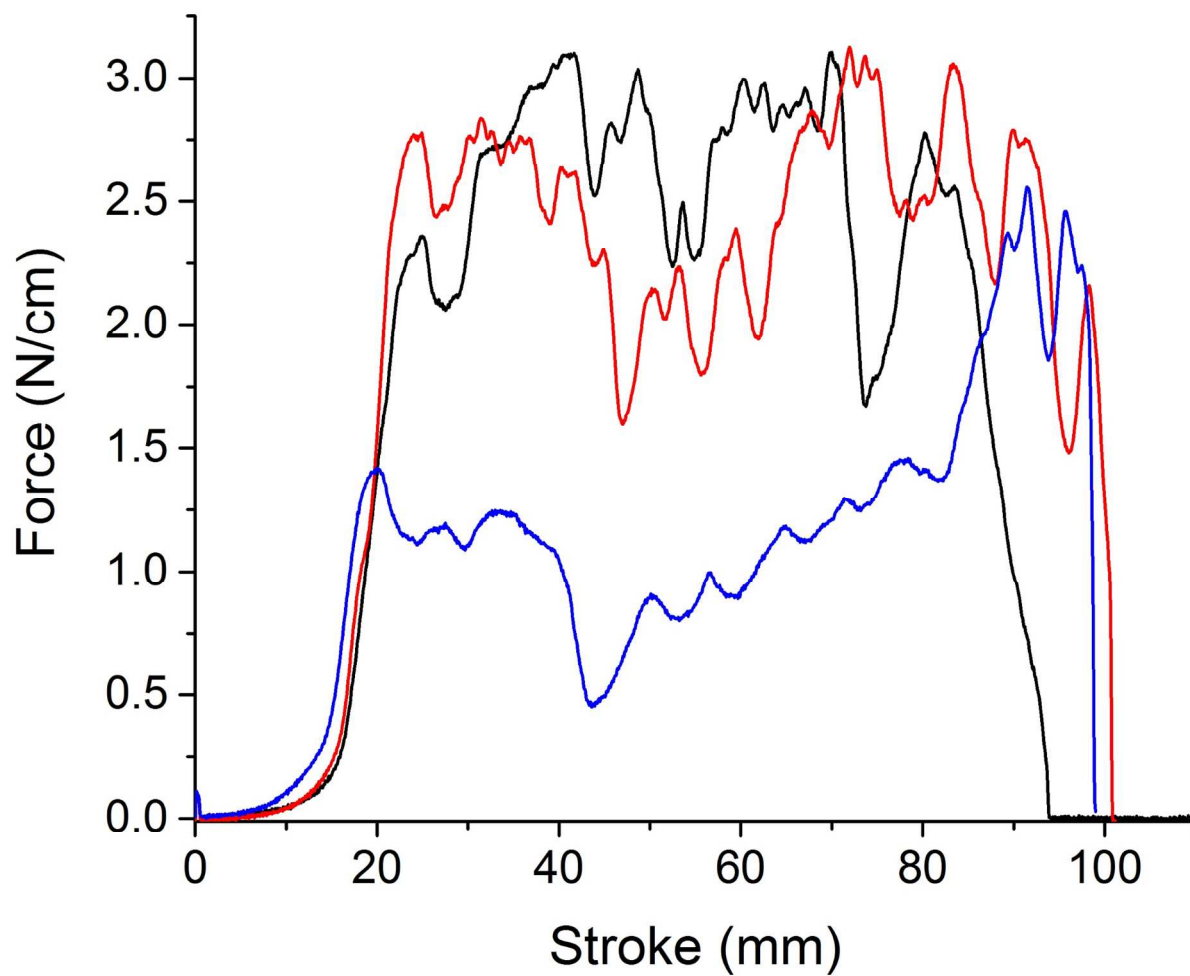


Figure S31. 180° peel test of PAAI-PEHA-PAAI (54k, 14%) with 25 wt% rosin tackifier.

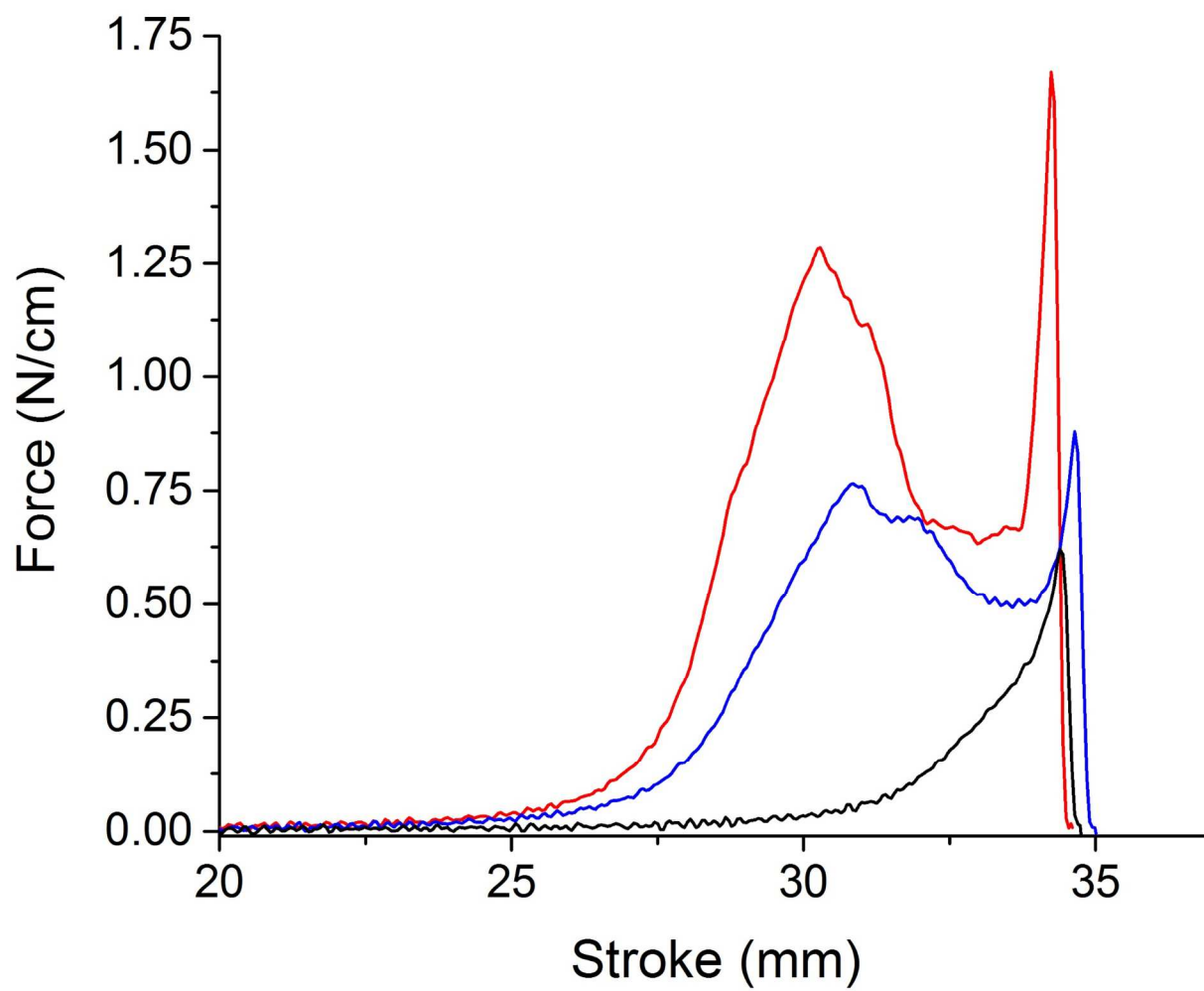


Figure S32. Loop tack test of PAAI-PEHA-PAAI (54k, 14%) with 25 wt% rosin tackifier.

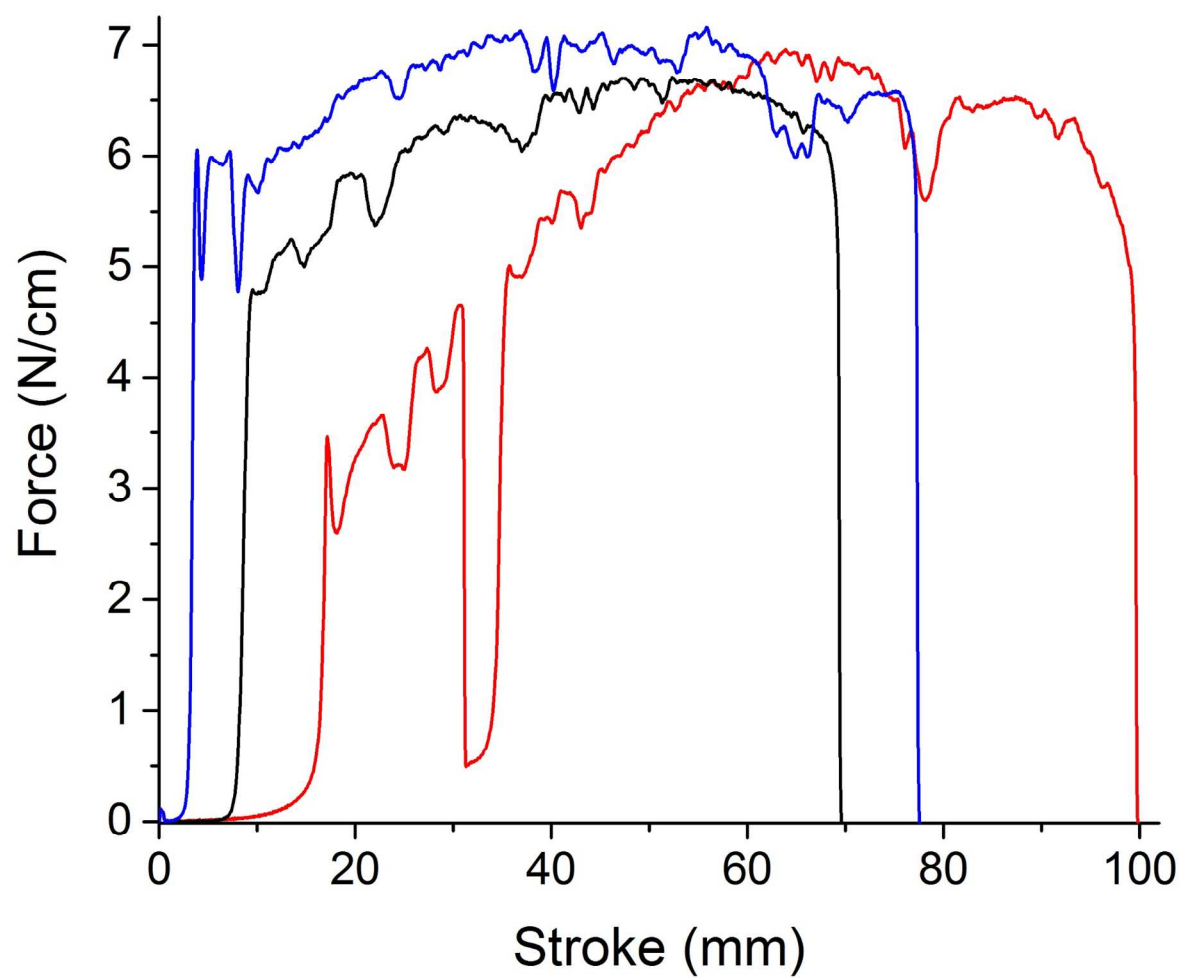


Figure S33. 180° peel test of PAAI-PEHA-PAAI (54k, 14%) with 50 wt% rosin tackifier.

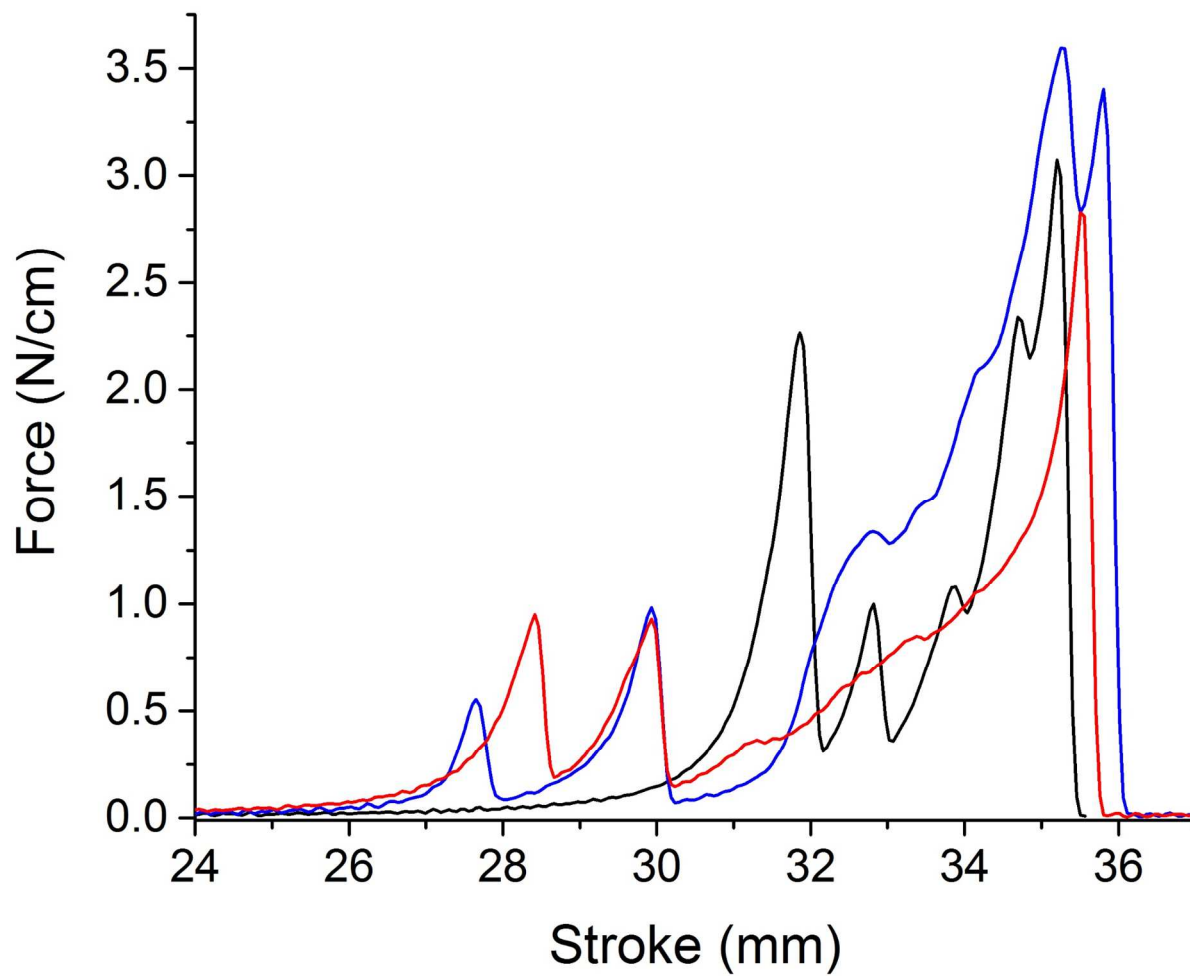


Figure S34. Loop tack test of PAAI-PEHA-PAAI (54k, 14%) with 50 wt% rosin tackifier.

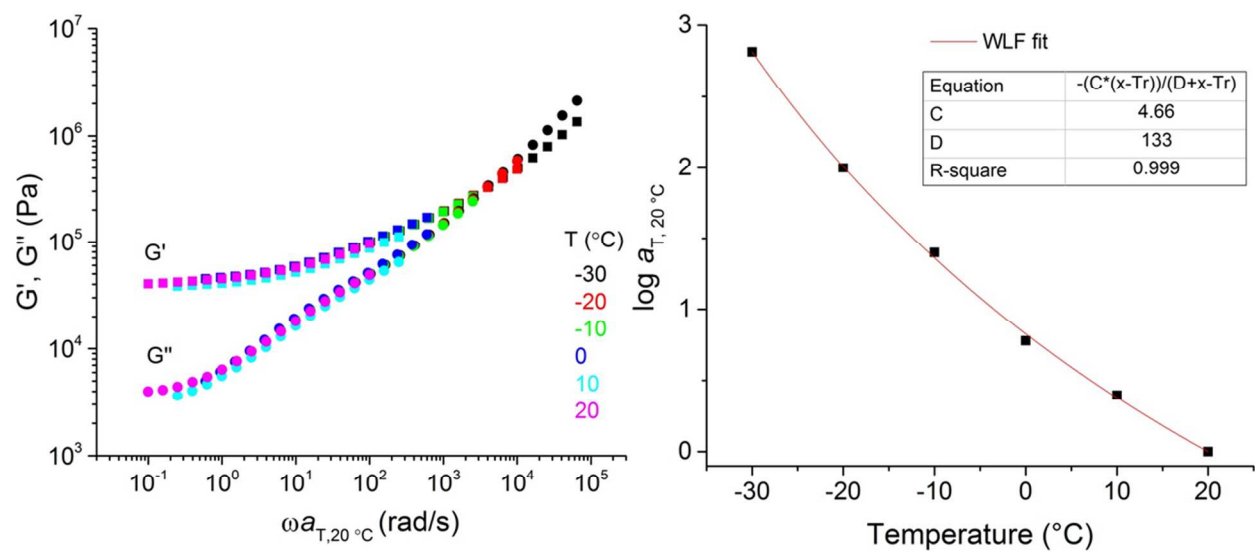


Figure S35. Time temperature superposition and William–Landel–Ferry fit for DMA of PAAI-PEHA-PAAI (54k, 14%).

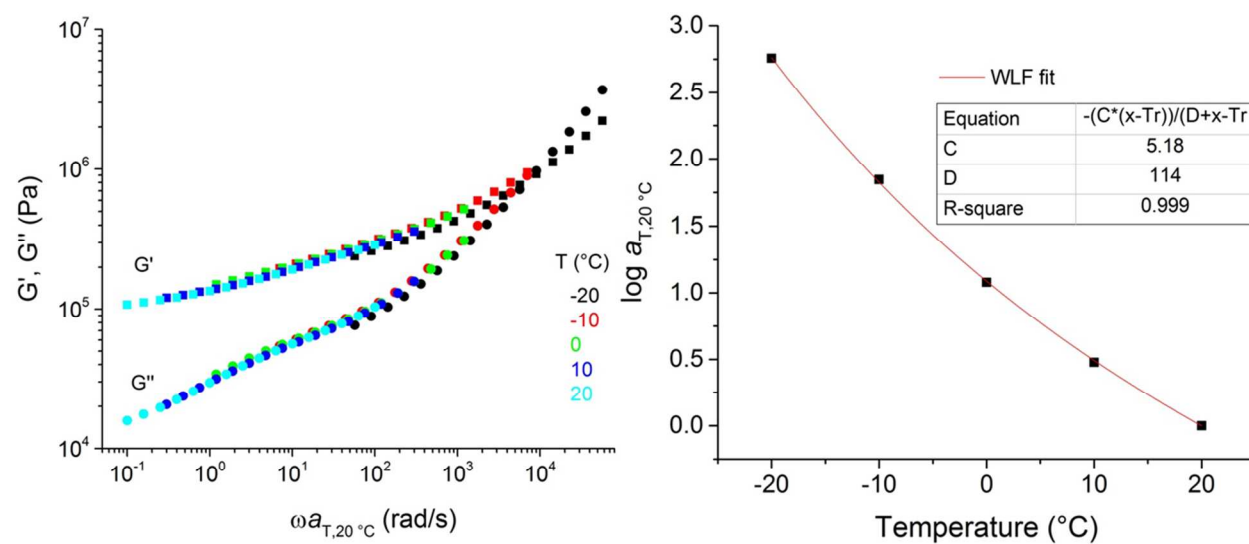


Figure S36. Time temperature superposition and William–Landel–Ferry fit for DMA of PAAI-PnBA-PAAI (60k, 17%).

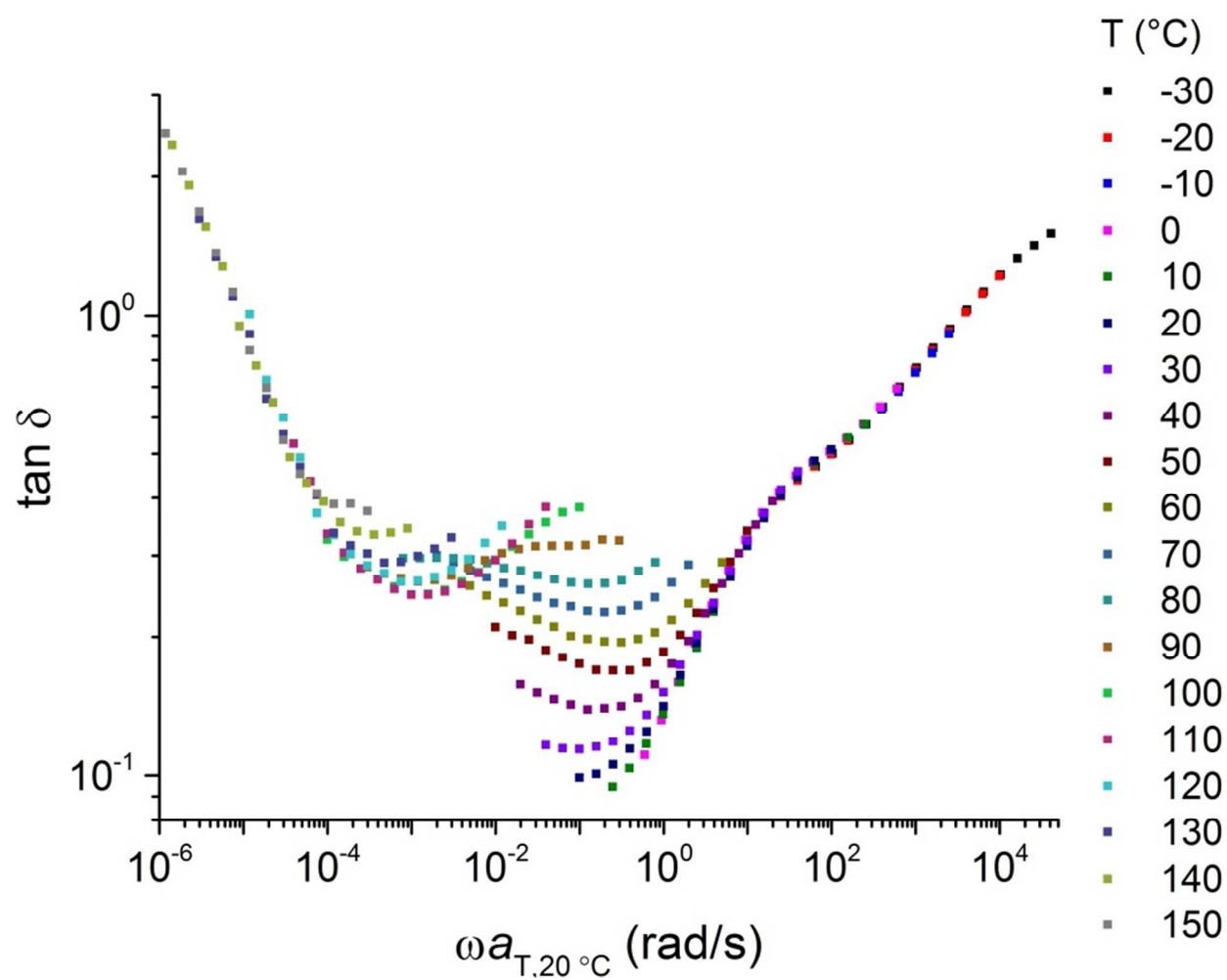


Figure S37. Attempted time temperature superposition for DMA of PAAI-PEHA-PAAI (54k, 14%).

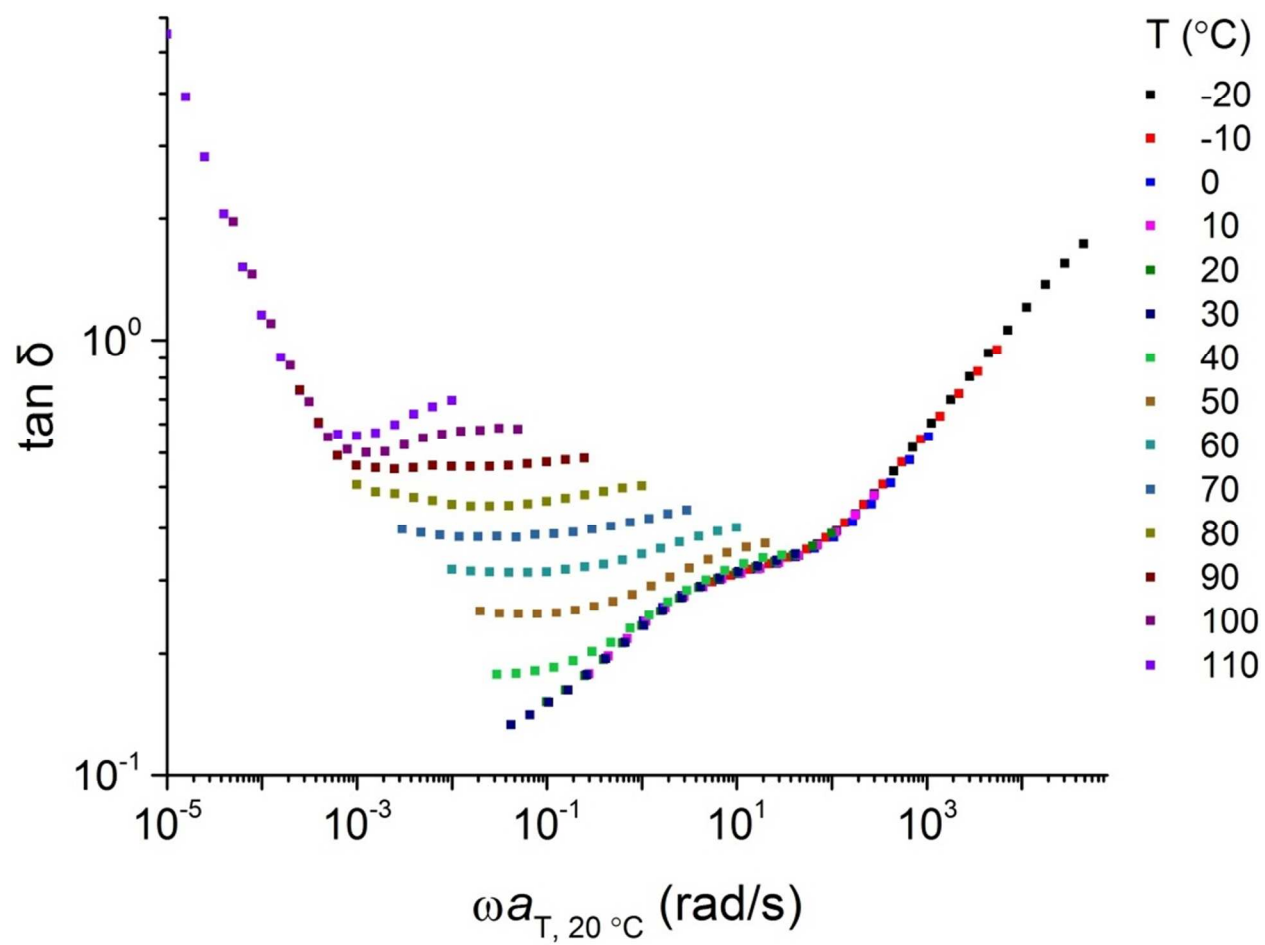


Figure S38. Attempted time temperature superposition for DMA of PAAI-PnBA-PAAI (60k, 17%).

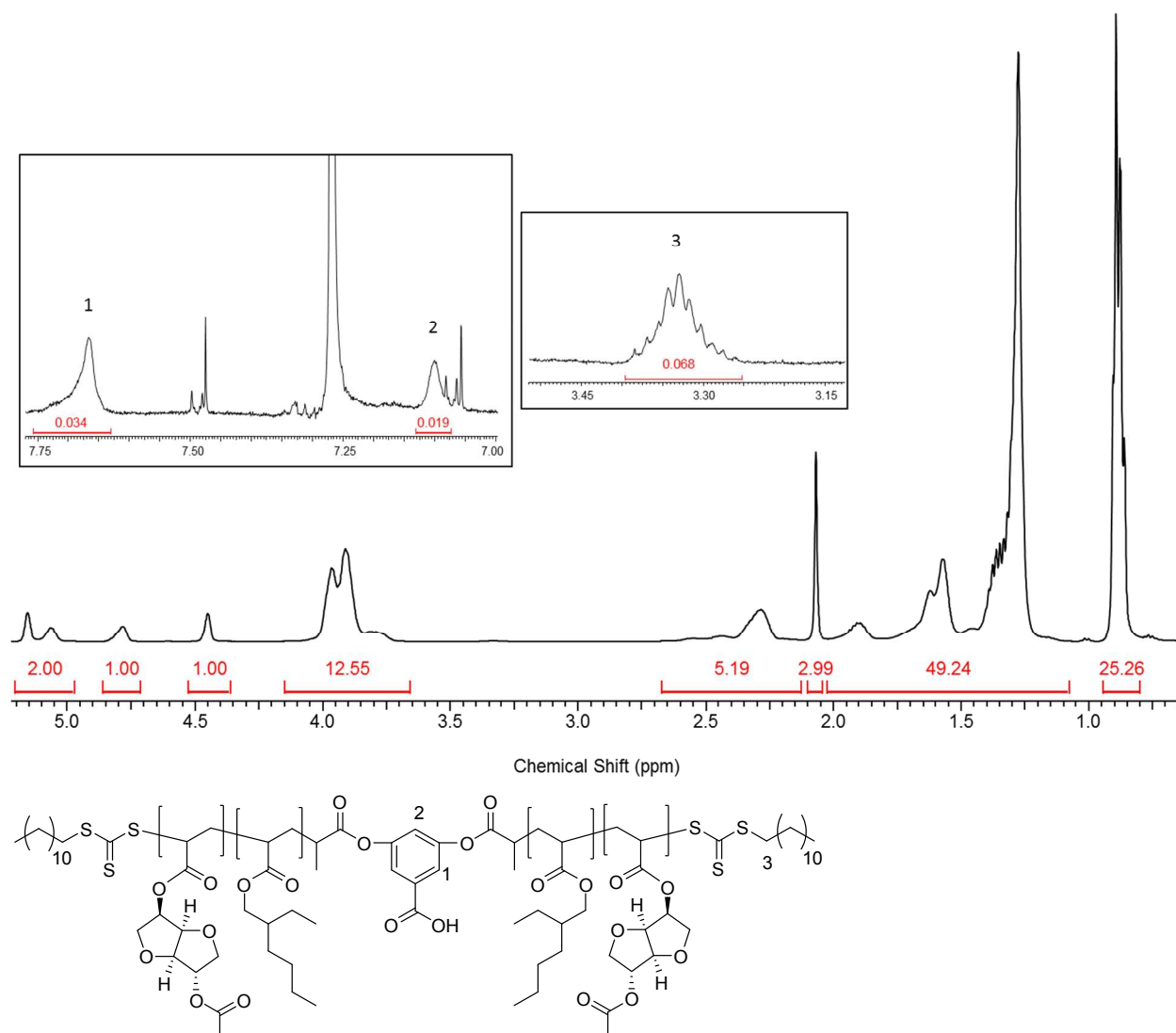


Figure S39. ¹H NMR of PAAI-PEHA-PAAI (64k, 24%) in CDCl₃. End group resonances in insert.