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Supramolecular polymer-assisted manipulation of triblock copolymers: Understanding the relationships between microphase structures and mechanical properties

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Materials and general methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Monomers A and B were synthesized according to our previous published work.[S1-S4]

Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H NMR chemical shifts are reported relative to residual solvent signals.

Gel permeation chromatograph (GPC) was obtained on a HLC-8320GPC (TOSOH, Japan) instrument using dimethylformamide (DMF) as eluent with polystyrene standards.

The thermal stability of materials was measured using a TA Instruments Q500 thermogravimetric analyzer (TGA) under the nitrogen. Each sample (5 ~10 mg) was heated from 50 to 800 ℃ with a rate of 20 ℃/min.

Transition temperatures of materials were determined by a TA modulated differential scanning calorimetry Q2000 (DSC) under the nitrogen in heat flow endo up (mW) mode. Each sample (15 ~20 mg) was heated from –70 to 100 ℃ with a rate of 20 ℃/min.

Dynamic mechanical analyses (DMA) were conducted on a Discovery DMA 850 apparatus (Germany) in a tensile mode. Temperature ramp measurements (–50 to 100 ℃) at a heating rate of 5 ℃/min were carried out with an oscillation frequency of 1.0 Hz, and oscillation amplitude of 0.5%. Frequency sweep measurements at different temperatures were carried out from 0.08 to 100 Hz within the linear viscoelastic oscillating region. Creep and creep recovery tests were carried out at 0 ℃ with a stress at 0.1 MPa for 10 minutes and recovery for 20 minutes.

Fourier transform infrared (FT-IR) spectrometer was performed on a Thermoscientific Nicolet 6700 FT-IR spectrometer at room temperature in the range of 550~4000 cm^{-1} by attenuated total reflectance (ATR) technology.

Atomic force microscope (AFM) nanomechanical measurements on a Bruker Bio-FastScan AFM in a PeakForce QNM (Quantitative Nano-Mechanics) were performed to characterize the microstructures of the films. The examined samples were prepared by frozen section through Leica EM UC7 Cryo-ultramicrotome at about –50~–80 ℃. The moduli and adhesion forces were measured by approaching the tip to the samples and then retracting the tip. The oscillation frequency of the Z-piezo was 2.0 kHz, scan rate was 1.0 Hz and the peak force amplitude was set at 50 nm. The samples were scanned using OMCL-AC240TS-R3 cantilevers (Olympus) with a normal spring constant of 2.0 N/m.

Transmission electron microscope (TEM) measurements were conducted on a Tecnai G2 SpiritBio TWIN. The accelerating voltage range is 20 KV~120 KV. The samples were prepared by frozen section through Leica EM UC7 Cryo-ultramicrotome at about −50~−80 ℃ and loaded onto the copper wire mash.

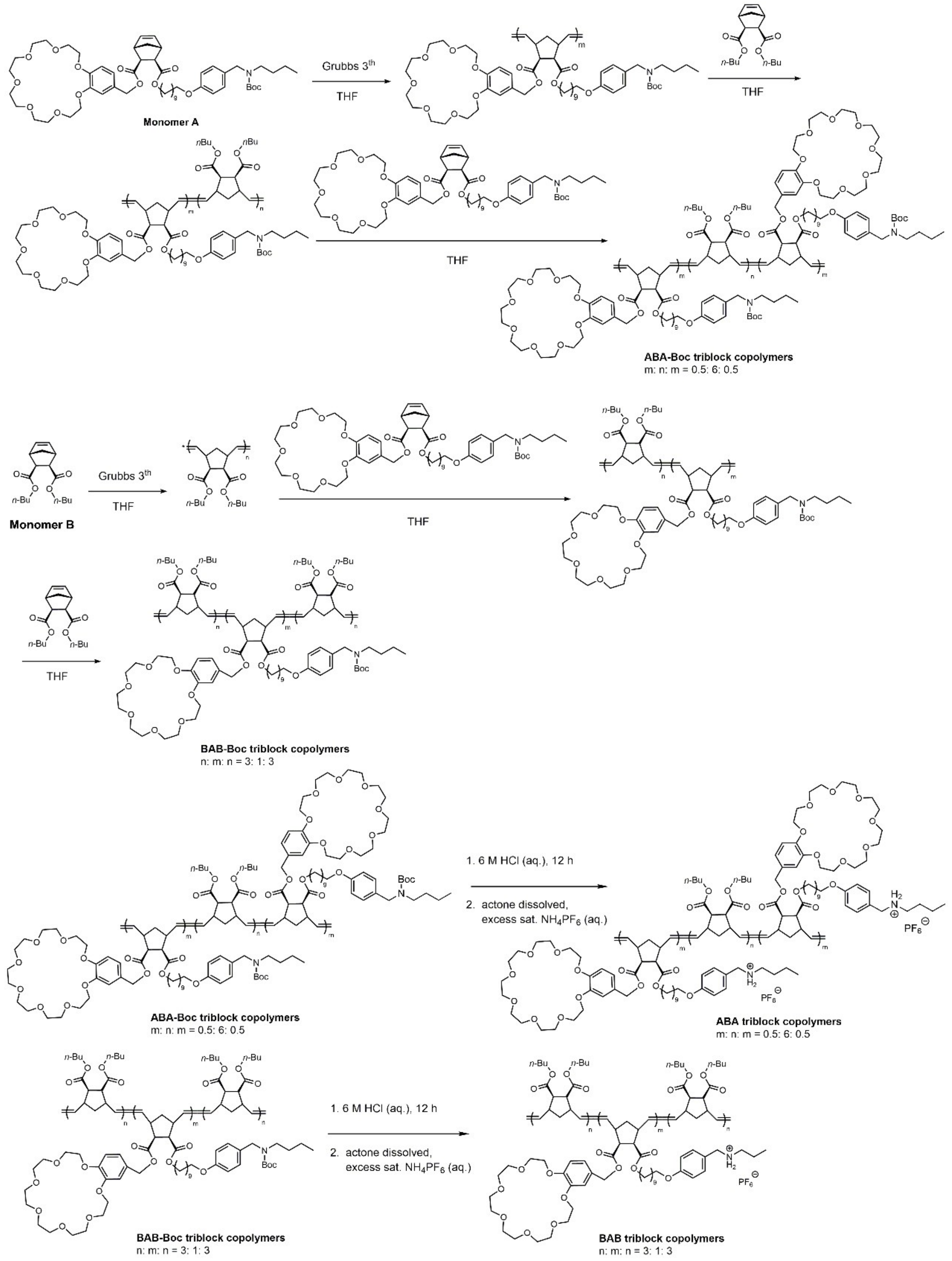
Mechanical tests**:** The mechanical properties of the polymers were tested on an Instron 3343 machine in standard stress/strain experiments. Samples were prepared by hot-pressing into rectangle teflon moulds, and the renewable processing was also conducted based on this method. Young's modulus was calculated from the initial slope of the stress-strain curve. Toughness was obtained by integrating the area under stress-strain curve. Hysteresis was calculated by integrating the closed area of tensile cycle curve. Stress relaxation was conducted to 50% strain, deformation rate: 300%/min, and the stress development with time was recorded till almost no decrease.

Syntheses of ABA and BAB triblock copolymers

The syntheses of the two triblock copolymers were analogous except for the different feeding sequence of the two monomers. Hence, taking the synthesis of ABA as an example, the synthetic procedure of the two copolymers could be described as follow. Firstly, Boc-protected block copolymers were prepared by ring opening metathesis polymerization (ROMP). Three oven-dried vials were charged with monomer A (0.53 g, 0.547 mmol), monomer B (0.97 g, 3.30 mmol) and Grubbs 3th catalyst (15 mg, 0.0176 mmol), respectively. The vials were then degassed, and 10 mL, 20 mL, and 2.0 mL of degassed anhydrous THF was added via a syringe under a nitrogen atmosphere to dissolve the two monomers and catalyst, respectively. Half of the monomer A solution was extracted and injected to the Ru catalyst solution to initiate polymerization. The solution was stirred for 30 min at room temperature. After monomer A was run out, monomer B solution was added into the vial through the syringe to continue copolymerization. After monomer B was run out, the rest of monomer A solution was extracted and injected into the vial again for about 30 minutes. Then the mixture was quenched and end-capped by the addition of 0.20 mL neat ethyl vinyl ether. After 15 minutes, the polymerization was stopped and the mixture was added dropwise to 600 mL stirring methanol and a white precipitate formed immediately. The suspension was then centrifuged and collected to afford the ABA-Boc triblock copolymer (1.3 g, 87%).

Secondly, the ABA-Boc triblock copolymer were dissolved in dichloromethane and 6 M HCl was added dropwise until the solution turned cloudy. The solution was stirred for further 12 h, then the solution was centrifuged and the sediment was dissolved in acetone. A saturated aqueous solution of NH_4PF_6 was added, and the precipitate was formed and collected to generate ABA triblock copolymer as a solid (1.2 g, 92%).

The ^1H NMR spectra of Boc-protected and the post-processing triblock copolymers were shown in Fig. S1. The SEC curves of ABA-Boc and BAB-Boc triblock copolymers were shown in Fig. S3.



Scheme S1. Synthetic routes of the ABA and BAB triblock copolymers.

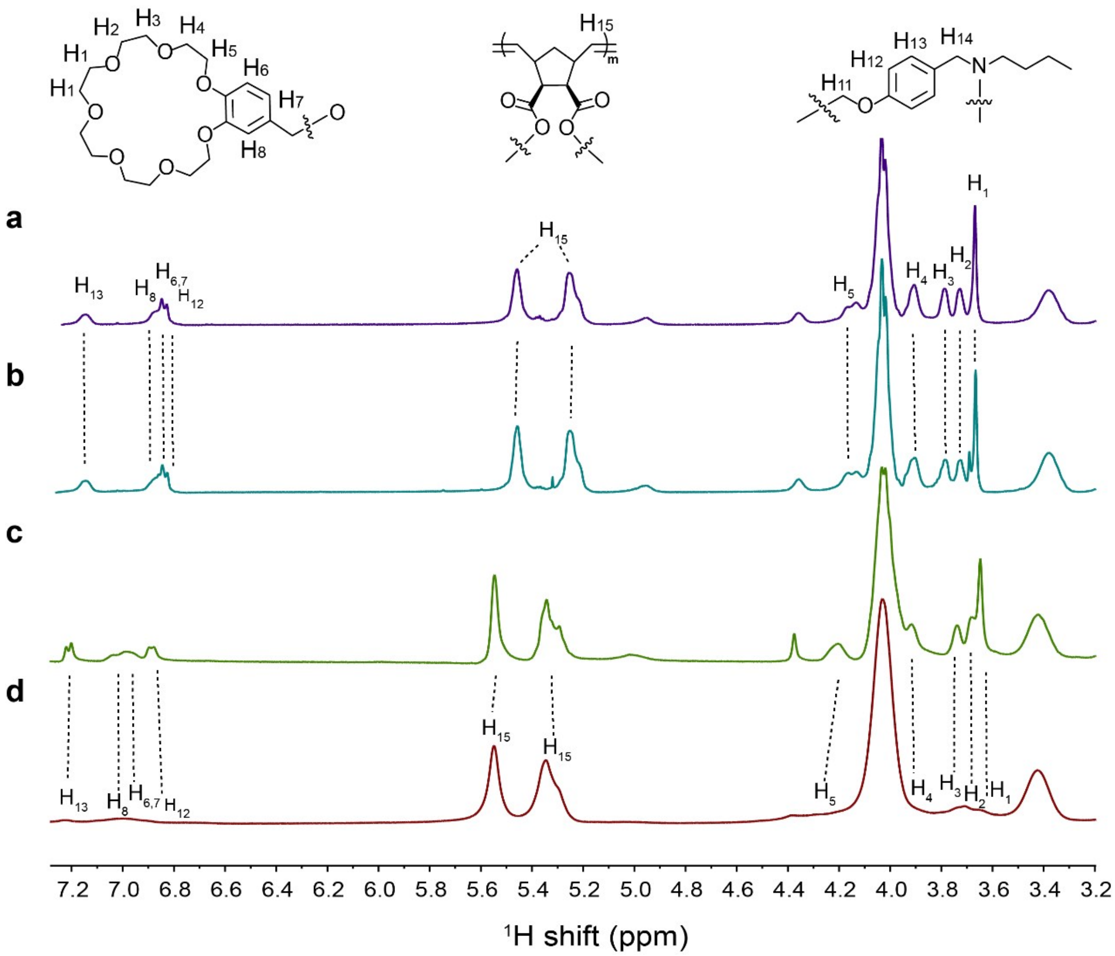


Fig. S1 Partial ^1H NMR spectra (400 MHz, room temperature) of the two types of copolymers. ABA-Boc (a) and BAB-Boc (b) triblock copolymers in $CDCl_3$, and ABA (c) and BAB (d) triblock copolymers in acetone-d_6.

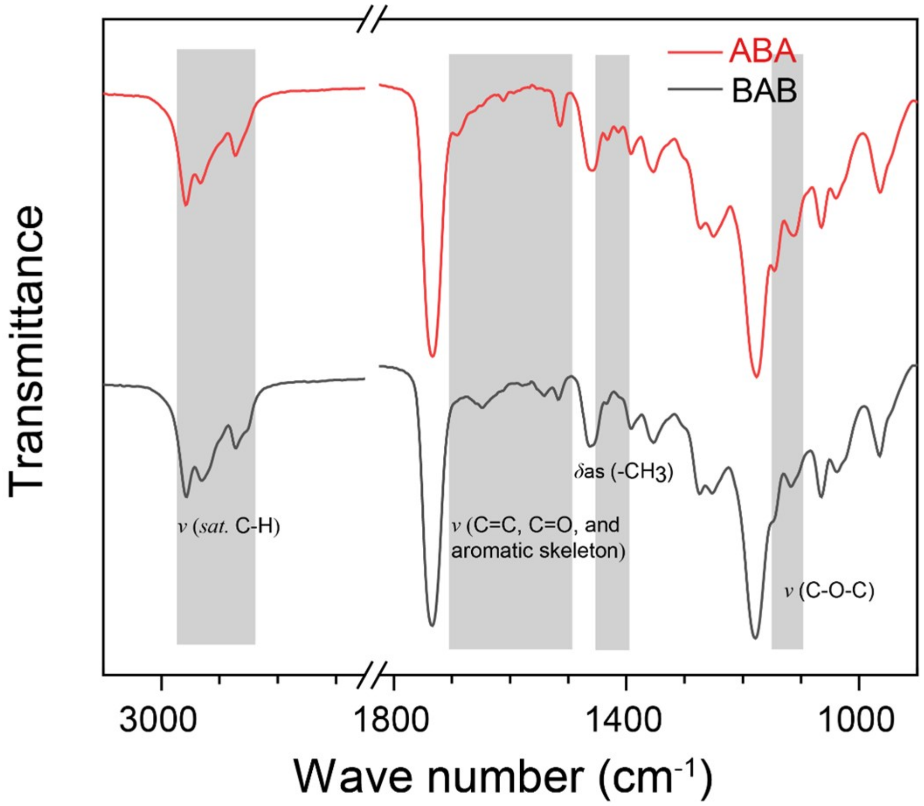


Fig. S2. Partial ATR-FTIR spectra of ABA and BAB triblock copolymers.

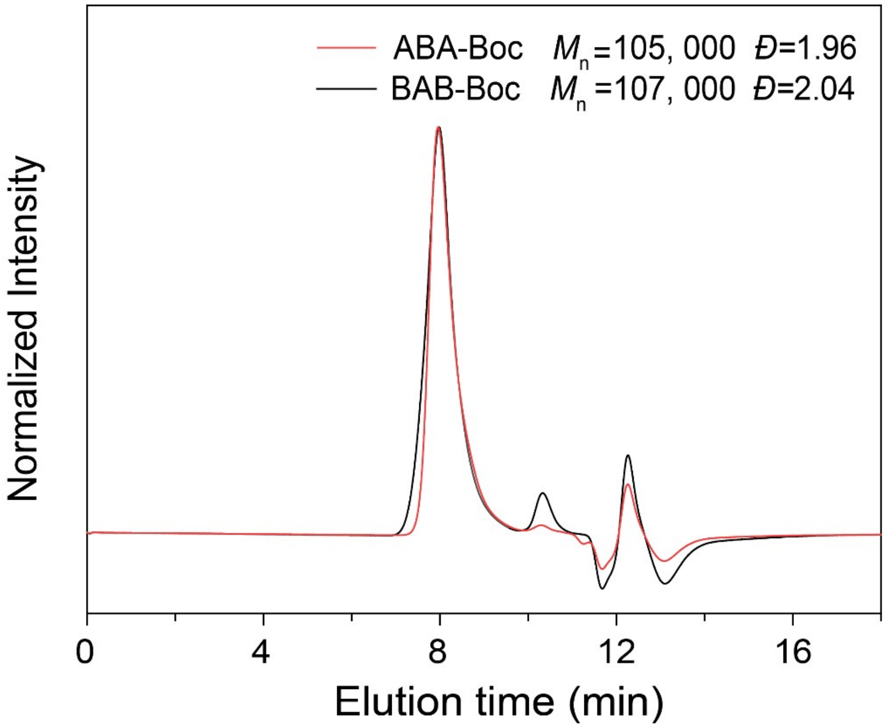


Fig. S3 The GPC elution curves of ABA-Boc and BAB-Boc triblock copolymers with DMF as the eluent and PS as the standard.

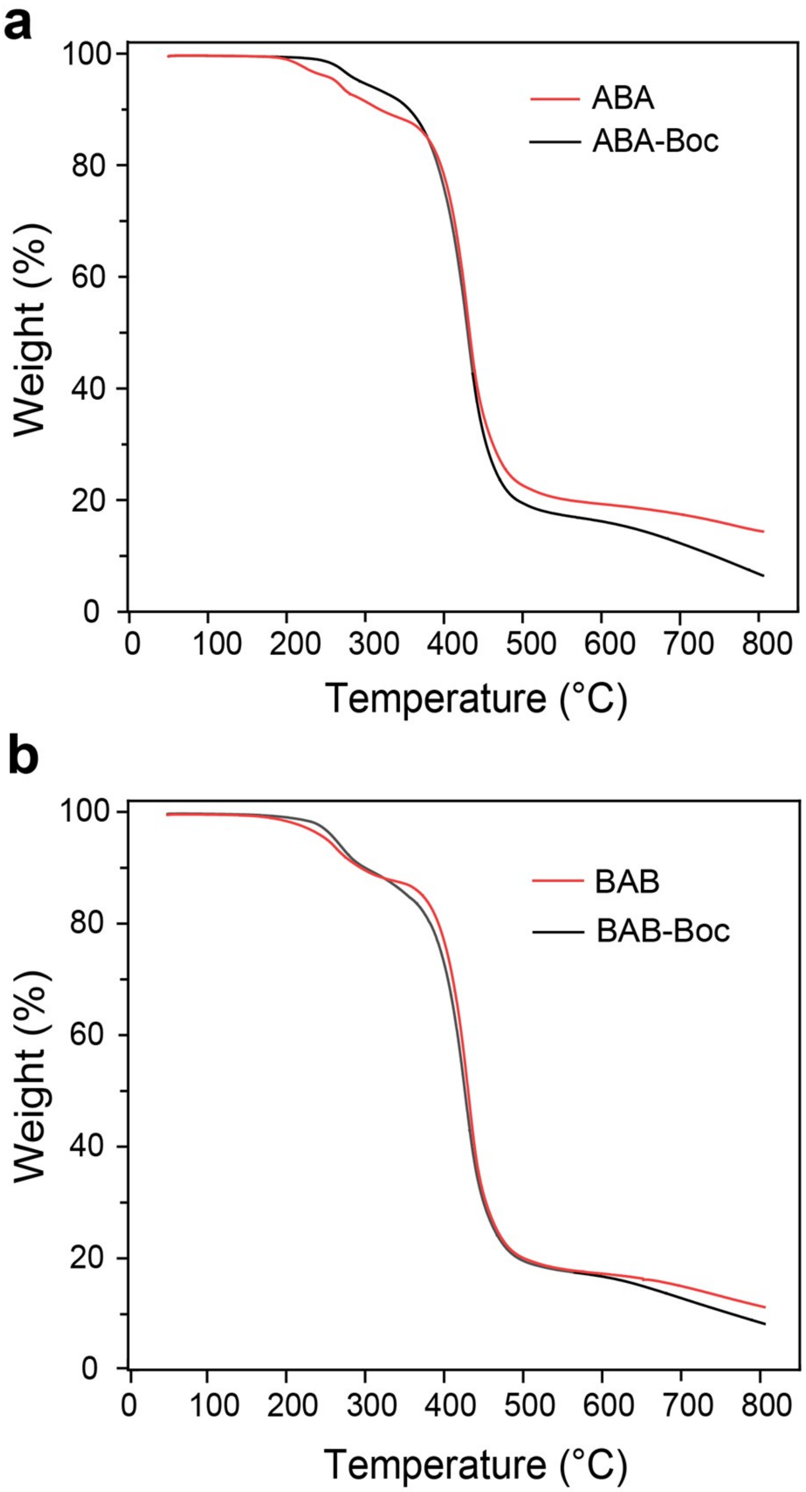


Fig. S4 The TGA curves of ABA-Boc and ABA triblock copolymers (a), and BAB-Boc and BAB triblock copolymers (b) recorded under N_2 flow (50 mL/min) with a heating rate of 20 ºC/min.

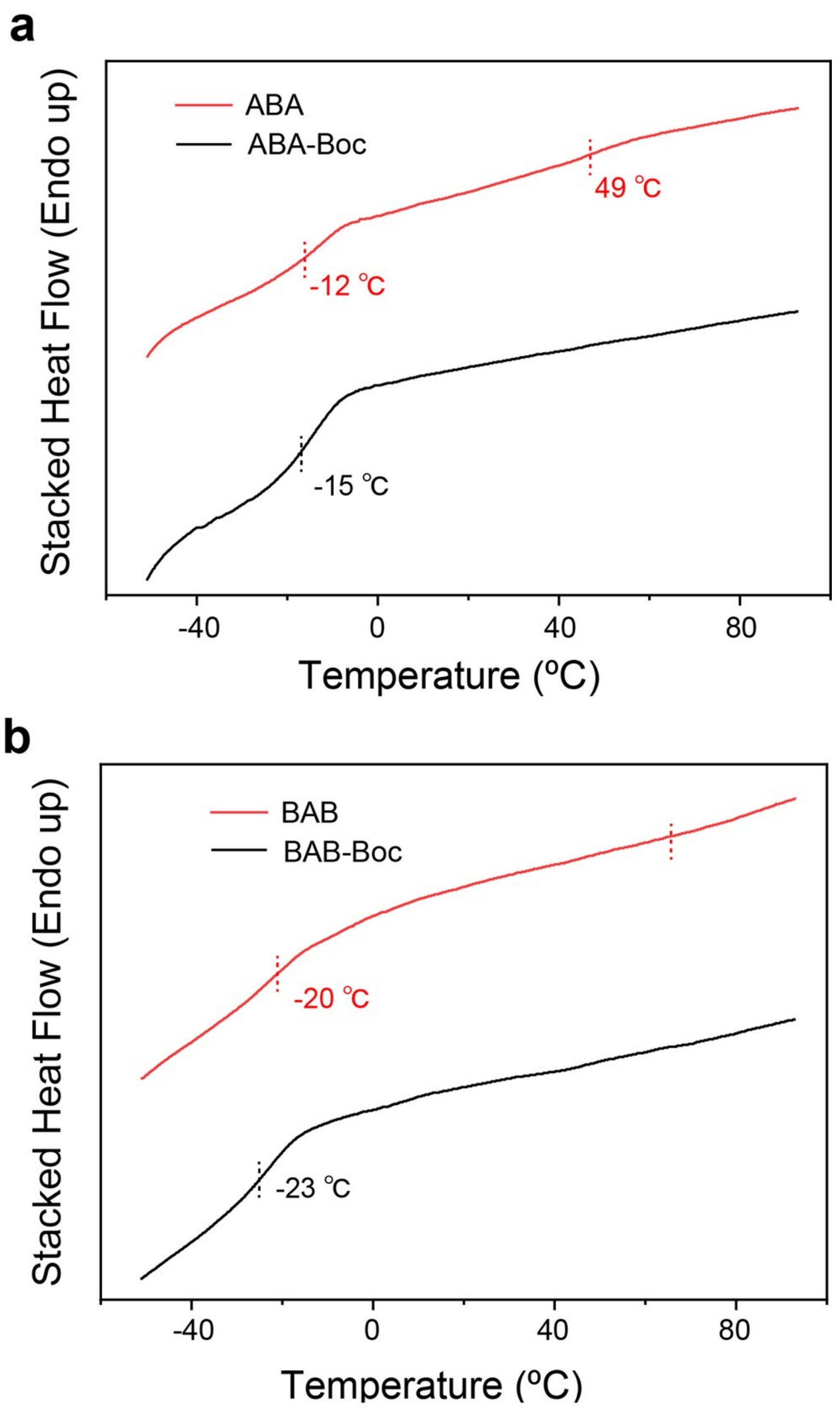


Fig. S5 The DSC curves of ABA-Boc and ABA triblock copolymers (a), and BAB-Boc and BAB triblock copolymers (b) recorded by the second heating scan from –50 to 100 ºC with a heating rate of 20 ºC/min.

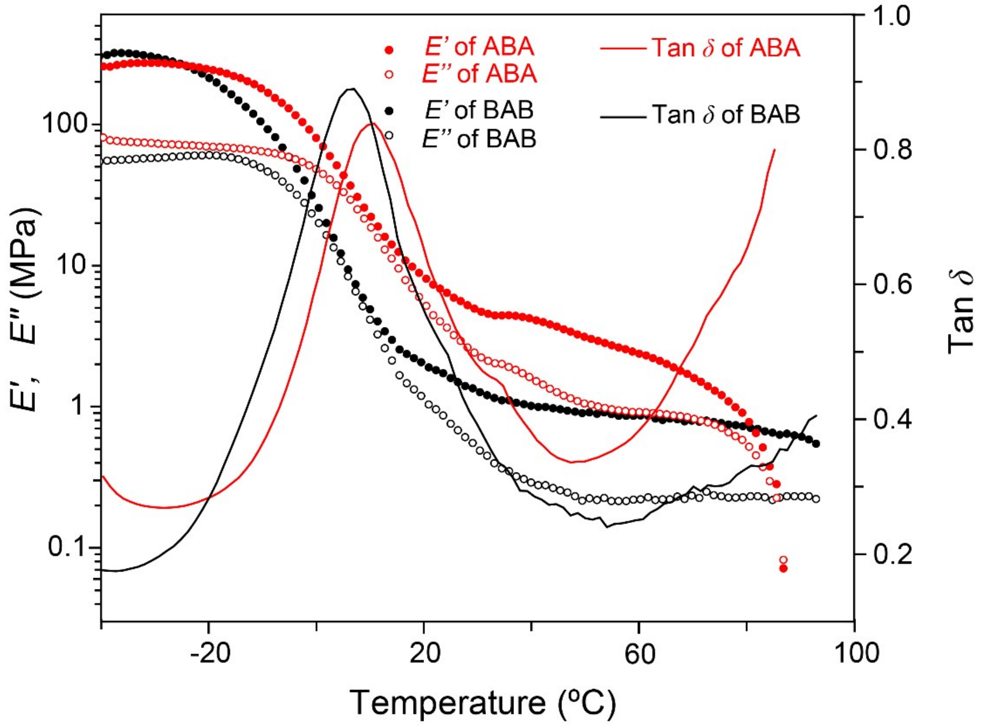


Fig. S6 DMA temperature sweeps of ABA and BAB triblock copolymers.

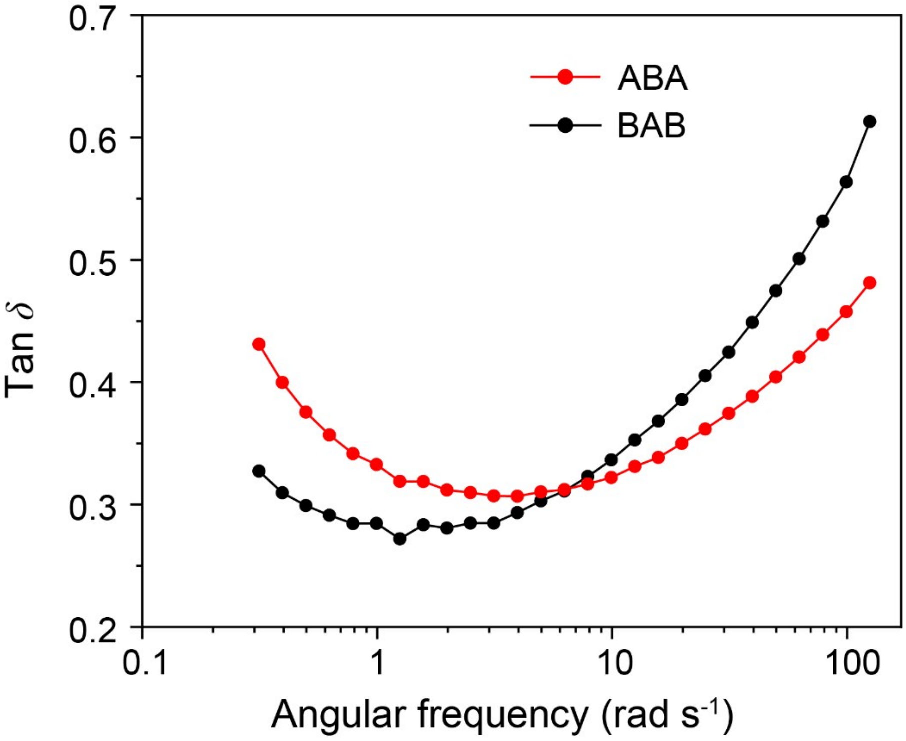


Fig. S7 Tan δ curves in DMA frequency sweeps of ABA and BAB triblock copolymers.

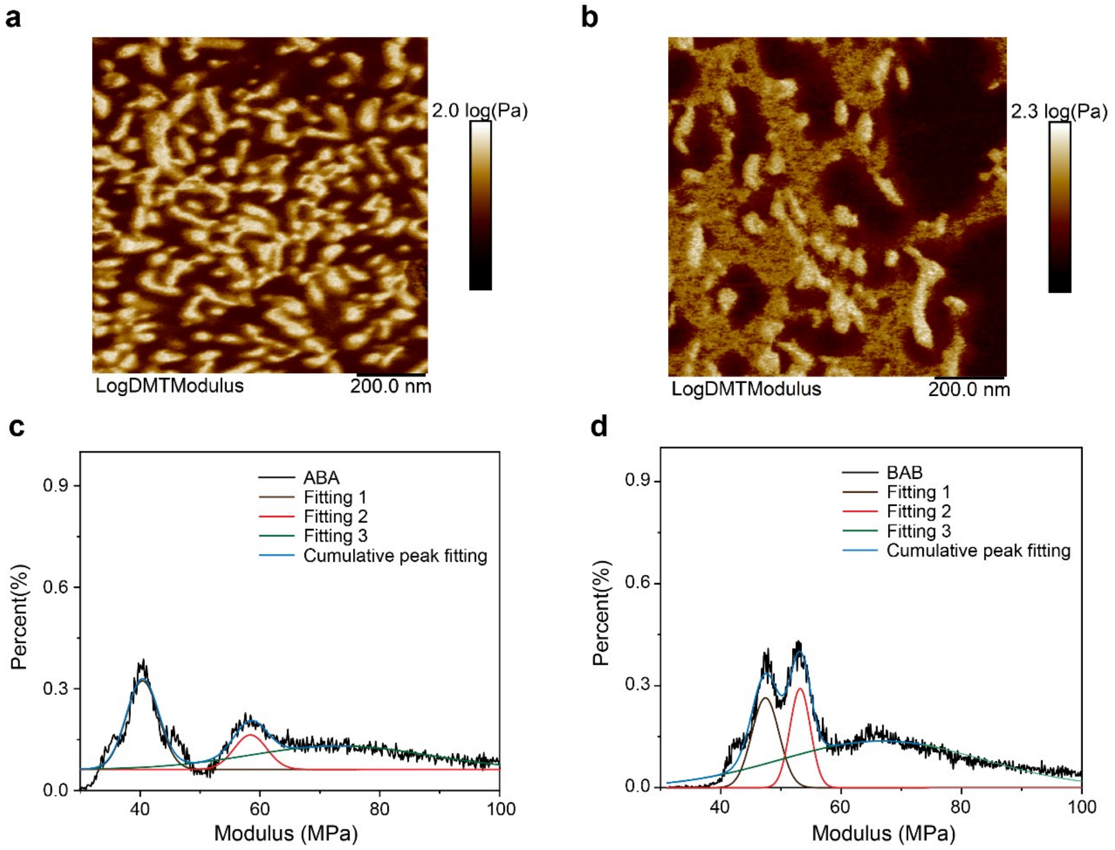


Fig. S8 The Log DMTModulus images of ABA (a) and BAB (b) triblock copolymers obtained by nanomechanical mapping through AFM, as well as their modulus distribution analysis made by Gauss fitting functions for ABA (c) and BAB (d) triblock copolymers.[S5] The sample sheet was sectioned at −50 ºC.

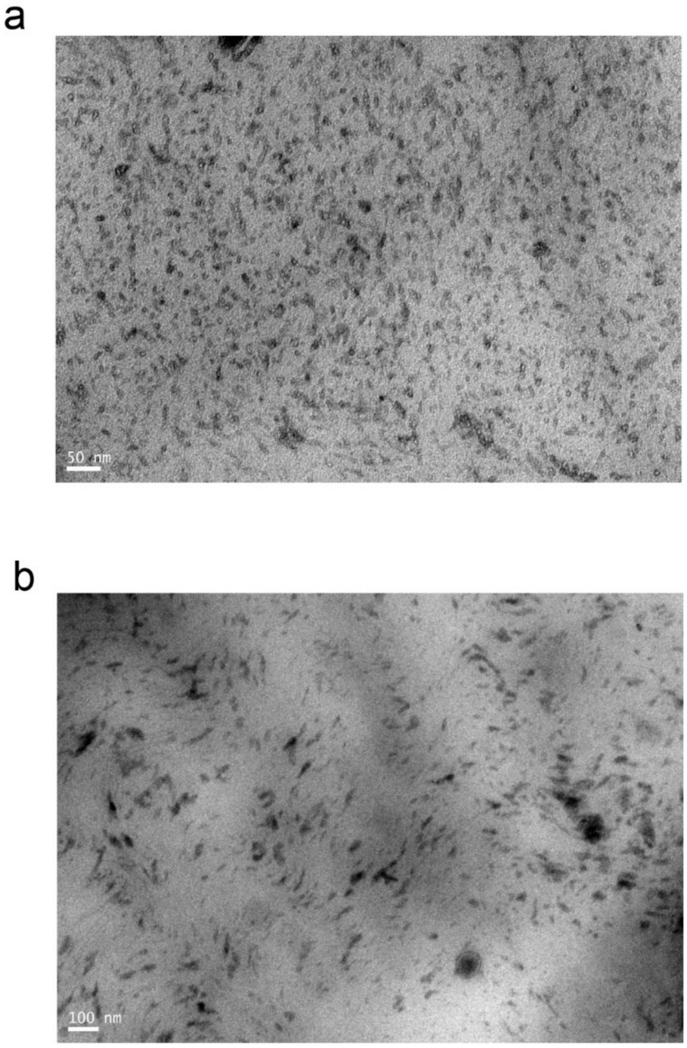


Fig. S9 TEM images of ABA (a) and BAB (b) triblock copolymers. Similar to the AFM results, ABA triblock copolymers showed small and regular distribution of hard domains, and BAB triblock copolymers exhibited not only hard domains but also continuous secondary hard domains (grey shaded area).

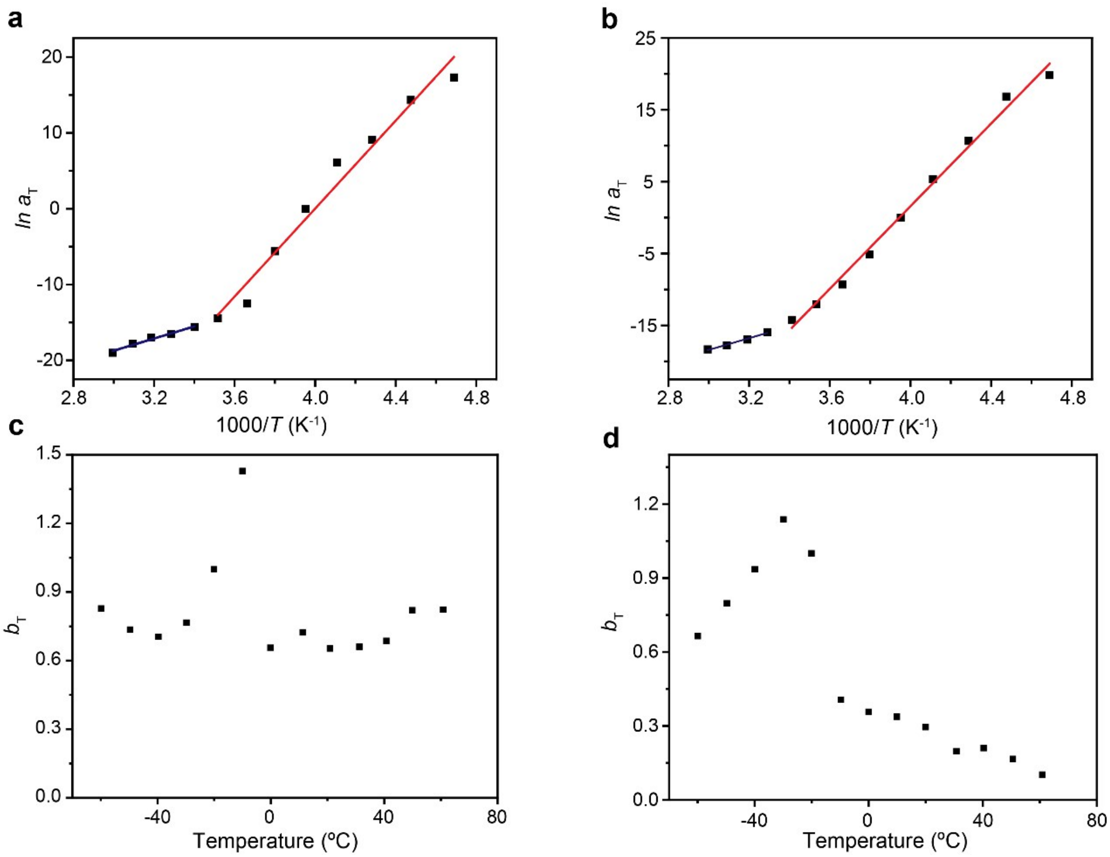


Fig. S10 Temperature dependence of horizontal shift factors a_T of the master curves of ABA (a) and BAB (b) triblock copolymers, and the partitioned activation energy for glass transition and supramolecular dissociation. Vertical shift factors b_T of the master curves of ABA (c) and BAB (d) triblock copolymers.

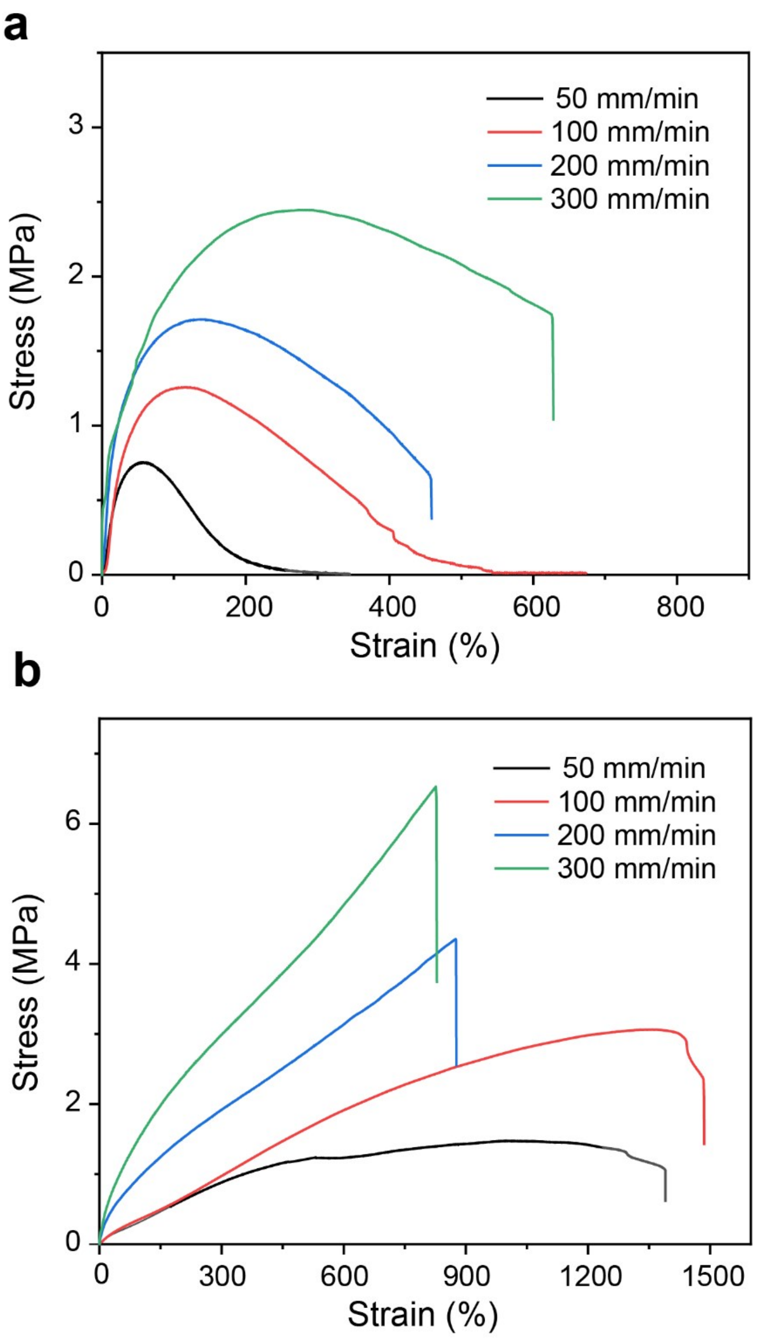


Fig. S11 The stress-strain curves of ABA (a) and BAB (b) triblock copolymers at different tensile rates.

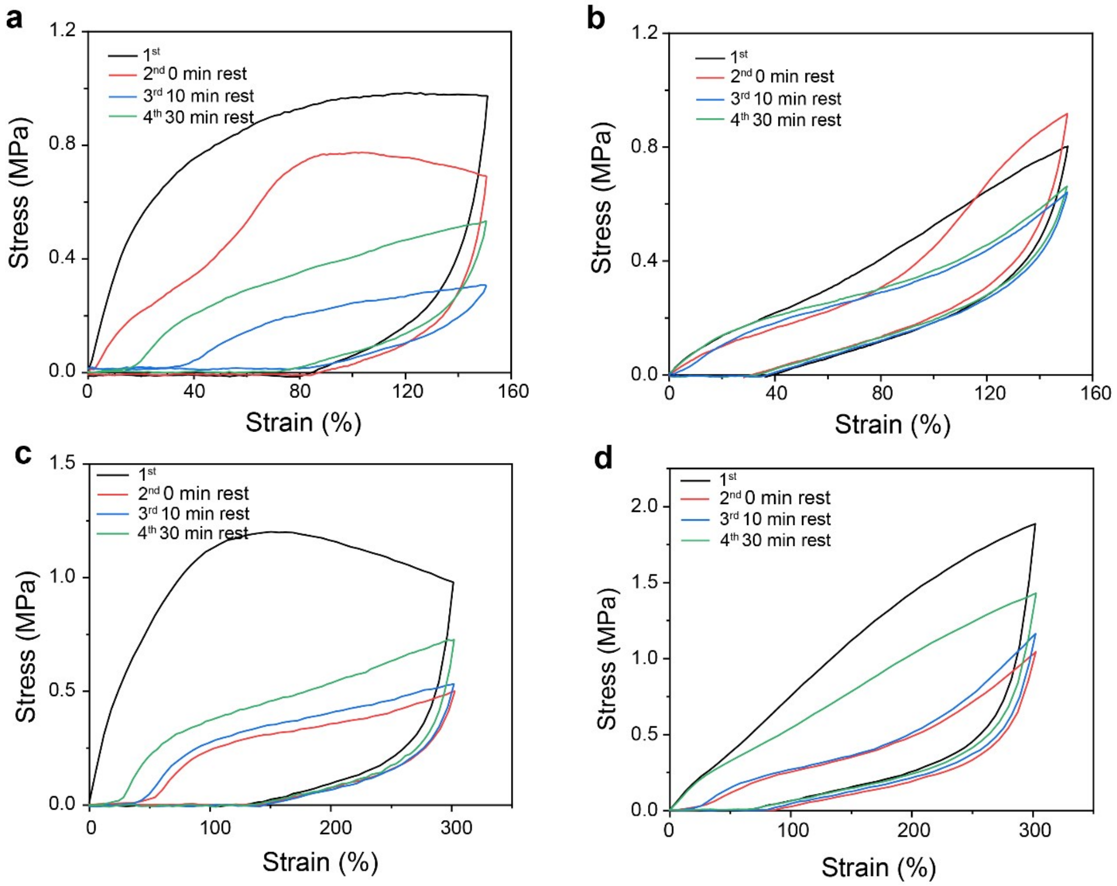


Fig. S12 Repeatedly loading-unloading curves of ABA (a) and BAB (b) triblock copolymers with different rest time at a strain of 150%. Repeatedly loading-unloading curves of ABA (c) and BAB (d) triblock copolymers at a strain of 300%. Deformation rate: 100 mm/min.

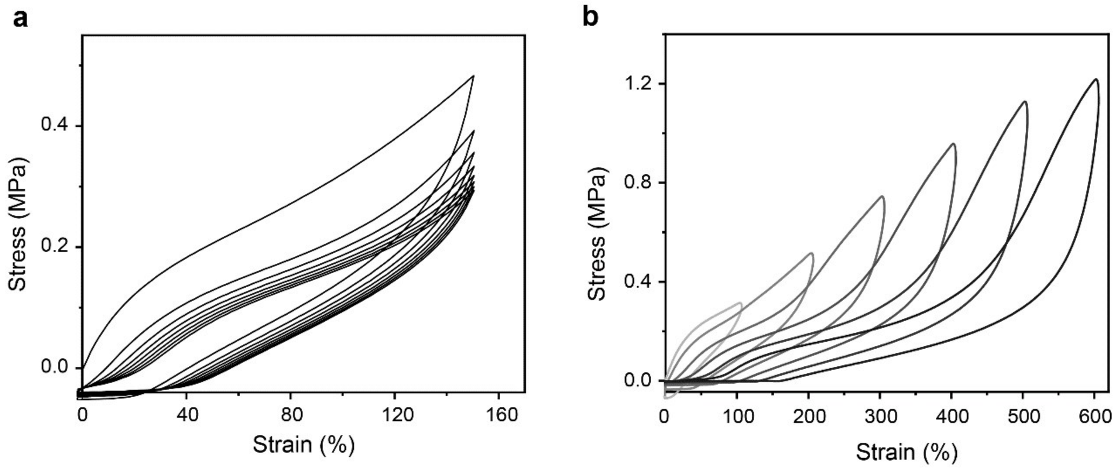


Fig. S13 Continuous loading-unloading curves of BAB triblock copolymer. (a) Ten times tensile cyclic tests for 10 s rest. Deformation rate: 50 mm/min. (b) Different strain cyclic tests from 100% to 600%. Deformation rate: 50 mm/min.

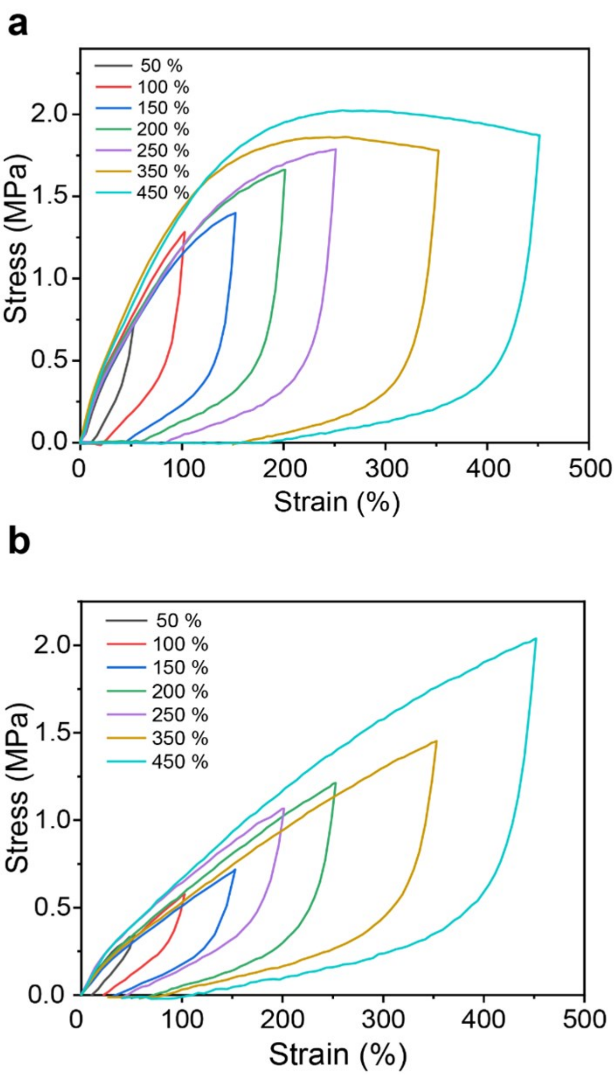


Fig. S14 Cyclic tensile test curves of ABA (a) and BAB (b) triblock copolymers at different strains. Deformation rate: 100 mm/min.

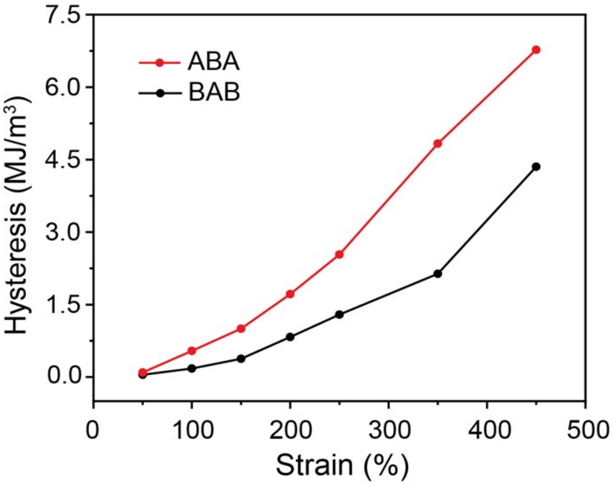


Fig. S15 Hysteresis area of ABA (a) and BAB (b) triblock copolymers for each circle of the cyclic tensile test curves in Fig. S14. The results showed that the two copolymers had different energy dissipation behaviors in the strain ranging from 50% to 450%. At same strain, ABA could dissipate more energy than that of BAB. Moreover, in the range of 50%□350%, the increment rate of hysteresis area for ABA was much higher than that of BAB.

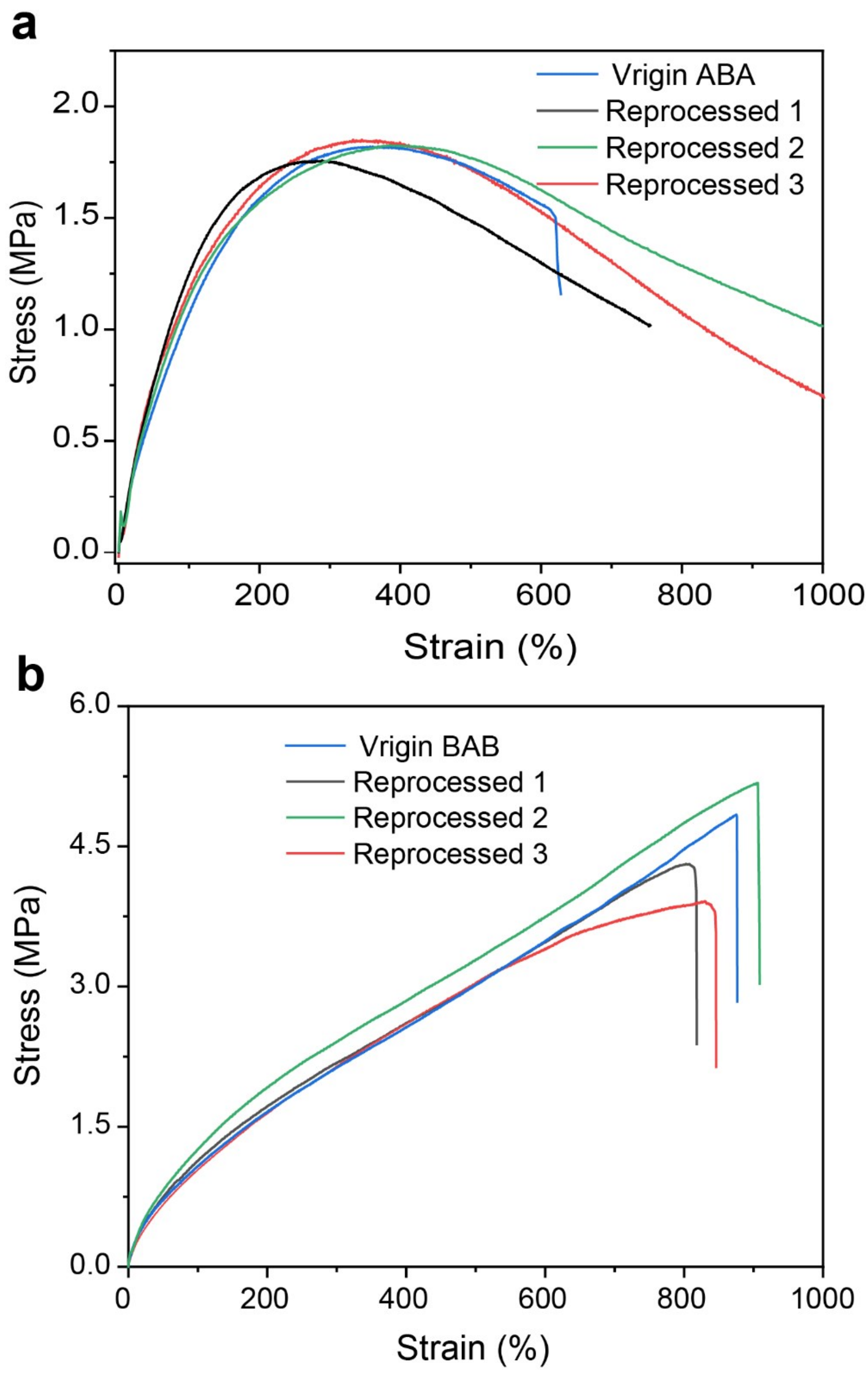


Fig. S16 Stress-strain curves of ABA (a) and BAB (b) triblock copolymers after multiple cycles of recycle. Deformation rate: 200 mm/min. Both of the samples showed good reprocessability.

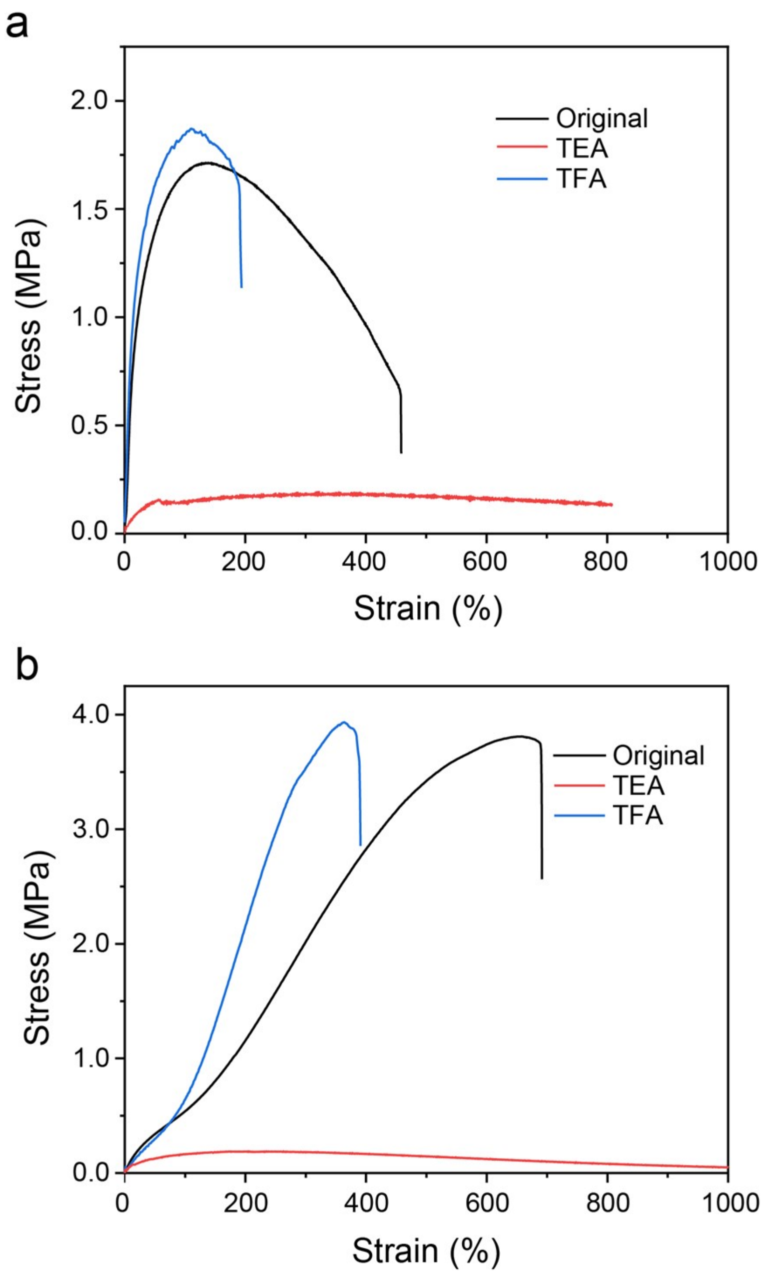


Fig. S17 Stress-strain curves of the initial samples and those after being treated with TEA and TFA for ABA (a) and BAB (b). For the two samples, the mechanical properties of TEA-treated samples decreased largely in terms of stiffness, stress, and toughness. TEA treatment could neutralize the secondary ammonium salt and thus destroy the host–guest recognition. Hence, these results indicated the important role of supramolecular polymer in the mechanical properties of the two copolymers. In addition, the samples were further acidized by TFA and then treated with NH_4PF_6 to exchange the counter anion to PF_6^-. The mechanical properties of the copolymers recovered basically, and the difference between the curves for the initial sample and that of the base/acid-treated one might be due to the changed microenvironment of the samples.

References

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