Reprocessable and Chemically Recyclable Poly(Acylhydrazone-Imine) Covalent Adaptable Networks with Enhanced Mechanical Strength and Creep Resistance

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1. Experimental sections.

Materials. Trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (Tri-NH_2-PPG, M_n ~ 440 g/mol) was purchased from Sigma Aldrich. Terephthalaldehyde (TPA) was purchased from Macklin. Carbohydrazide (CHZ) was purchased from Aladdin. All the solvents used in this experiment were purchased from Beijing Chemical Reagent Company, China. Hydrochloric Acid (HCl, 36%-38%) was purchased from Beijing Chemical Reagent Company, China. All chemical compounds were used without further purification.

Characterization. ^1H NMR spectra were measured using a 400 MHz Bruker instrument. FT-IR spectra of the original and recovered monomers were taken on a SHIMANZU IRAffinity-1S FT-IR spectrometer. The FT-IR spectra of PAI$_x$-CANs were performed on a Thermo Scientific Nicolet iS20 spectrometer in ATR mode between 600 cm^{-1} and 4000 cm^{-1} at room temperature. The thermal stability analysis was determined on a Netzsch TG 209 F3 Thermogravimetric analyzer under the nitrogen atmosphere. Each sample (~10 mg) was heated from 30 to 800 °C with a rate of 10 °C/min. Dynamic thermomechanical analysis was carried out on a Dynamic Mechanical Analyzer TA Instrument Q800 using tension film mode with a frequency of 1 Hz and strain amplitude of 0.1%, and dimensions of 20 mm×0.5 mm×0.5 mm. The temperature ramp ranged from -20 to 150 °C with a heating rate of 5 °C/min. For stress relaxation experiments, the PAI$_x$-CANs samples (20 mm×0.5 mm×0.5 mm) were initially preloaded by a 1×10^{-3} N force to maintain straightness. After reaching the testing temperature, it was allowed 5 min to reach thermal equilibrium. The specimen was stretched by 2% on the DMA machine and the deformation was maintained throughout the test. The decrease of the stress was recorded. For the tensile creep test, the samples with dimensions of 20 mm × 0.5 mm × 0.5 mm were stretched by a constant force of 0.3 MPa at different temperatures for 30 min, followed by a 60 min recovery period. All the stress-strain curves were performed on a UTM4103 Tension Instrument (Shenzhen SUNS Technology Co. LDT, China) with a stretching speed of 10 mm/min at a temperature of 20 °C and relative humidity of ~20%. For the tensile test, the PAI$_x$-CANs samples were cut into dumbbell shape (12 mm×2 mm×0.4 mm). Young's modulus values were determined by the slope of the stress-strain curve in the initial linear region within the strain of 5%.

Synthesis of PAI$_x$-CANs. The synthesis route of PAI$_x$-CANs was shown in Figure 1a(i). Taking the synthesis of PAI$_1$-CAN as an example, First, Tri-NH$_2$-PPG (2.20 g, 5 mmol) and DMF (5 ml) was added to a round-bottom flask. TPA (2.01 g, 12 mmol) was dissolved in DMF (15 ml), and this solution was dropped added into the above solution under an ice-water bath. After stirring for 2 h, the reacting mixture was transferred to a 60 °C oil bath. Then, CHZ (0.68 g, 7.5 mmol) was added into the above solution. The mixture was further stirred until a yellow gel formed. Finally, the gelation product was broken into pieces and put into a silica mold. This product was dried at 80 °C for 24 h to remove most solvent followed by vacuum drying at 80 °C for 48 h to obtain the final product of PAI$_1$-CAN. PAI$_{1.5}$-CAN and PAI$_3$-CAN were prepared with the same procedure.

Synthesis of PI-CAN. The synthesis route of PI-CAN was shown in Figure 1a(i). First, TPA (1.21 g, 9 mmol) was dissolved in DMF (10 ml) in a round-bottom flask. Then, Tri-NH$_2$-PPG (2.64 g, 6 mmol) was dissolved in DMF (5 ml) and the solution was dropped added to the above solution under an ice-water bath. After that, the mixture was heated at 60 °C until a yellow gel formed. Finally, the gelation product was broken into pieces and put into a silica mold. This product was dried at 80 °C for 24 h to remove most solvent followed by vacuum drying at 80 °C for 48 h to obtain the final product of PI-CAN.

Reprocessing of PAI$_x$-CANs and PI-CAN. The reprocessing process of PAI$_x$-CANs was carried out by the hot-pressing method. The detailed procedures as follows: the pre-dried PAI$_x$-CANs samples were cut into small pieces and the small pieces were placed into the tailor-made molds between two polyimide films. After hot-pressing in a hot-pressing machine under 10 MPa at 140 °C for 20 min, various shaped PAI$_x$-CANs samples were prepared. The reprocessing procedure of PI-CAN was similarly to that of PAI$_x$-CANs. However, due to the fast dynamic reversibility of imine bonds in their polymer networks, the hot-pressing temperature need to be reduced to 90 ^{o}C.

Chemical recycling of PAI$_x$-CANs. In a typical experiment, the PAI$_1$-CAN film was cut into small pieces and then immersed in a 1 M HCl/H_2O solution. After stirring for 24 h at room temperature, the PAI$_1$-CAN can be fully decomposed and TPA were precipitated as powders. After filtering, the acid solution was further extracted by ethyl acetate to further extract the unprecipitated TPA. Then, the aqueous solution containing hydrochloride of Tri-NH_2-PPG and CHZ was freeze drying to obtain the crude Tri-NH_2-PPG and CHZ. Then, the mixture of Tri-NH_2-PPG and CHZ was dissolved in THF and neutralized with KOH. After filtering, THF was removed under reduced pressure and the pure Tri-NH_2-PPG was obtained.

Calculation of the activation energies (E_a) of the polymer networks. The activation energies (E_a) of the polymer network were calculated via the Arrhenius equation:

$$\tau^*(T) = \tau_0 exp(E_a/RT)$$

where the relaxation time τ^* was determined via modulus relaxation to 1/e. τ_0 is the characteristic relaxation time, T is the experimental temperature, and R is the gas constant.

2. Supporting Tables and Figures

Table S1. Feed compositions of PAI$_x$-CANs and PI-CAN.

	Tri-NH$_2$-PPG (mmol)	TPA (mmol)	Carbohydrazide (mmol)	Molar ratio between imine bonds and acylhydrazone bonds
PAI$_1$-CAN	5	15	7.5	1
PAI$_{1.5}$-CAN	5	12.5	5	1.5
PAI$_3$-CAN	5	10	2.5	3
PI-CAN	6	9	0	--

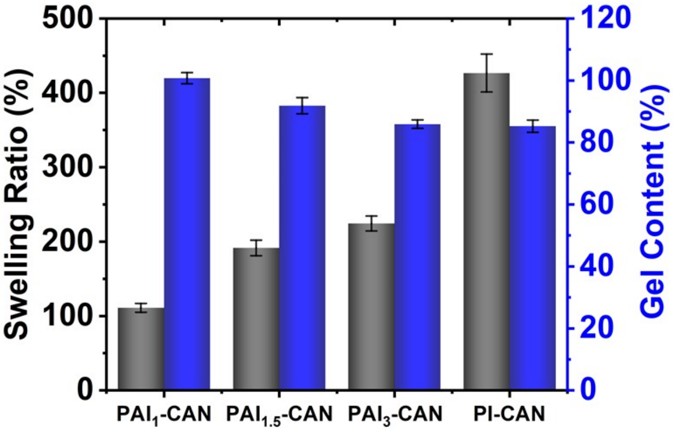

Figure S1. Swelling ratios and gel contents of PAI$_x$-CANs and PI-CAN immersing in THF at room temperature after 72 h.

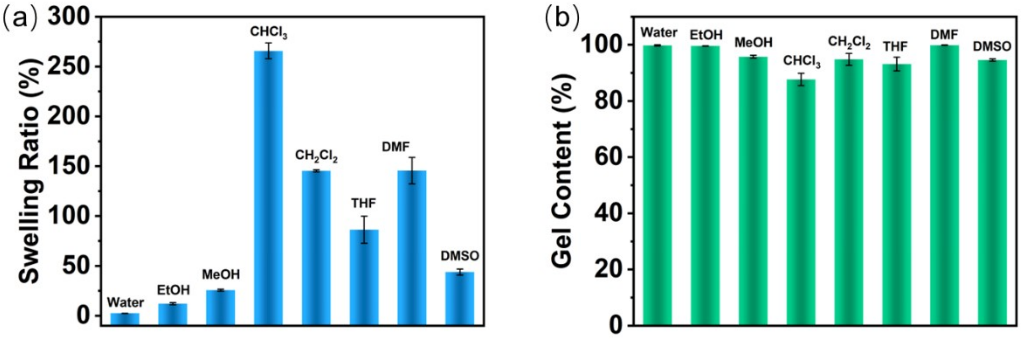

Figure S2. (a) Swelling ratios and (b) gel contents of PAI$_1$-CAN in various solvents at room temperature after 72 h.

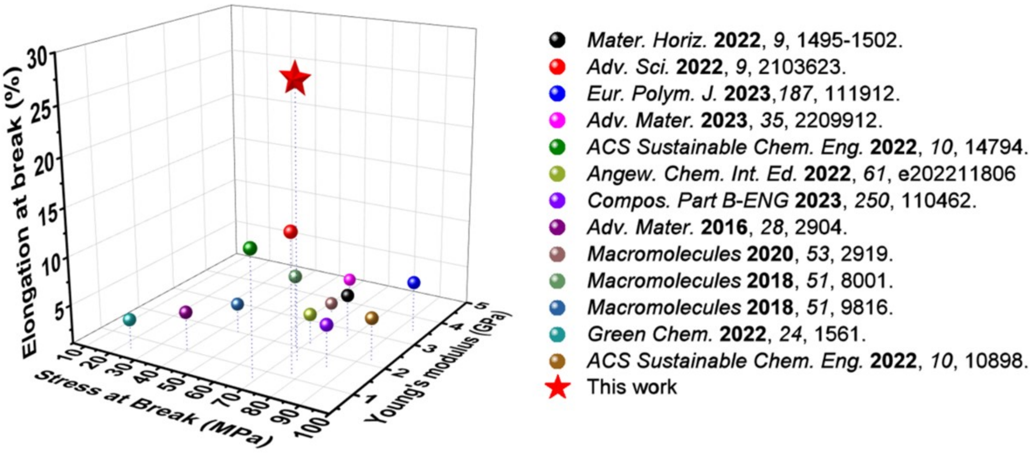

Figure S3. Comparison of elongation at break, stress at break, and Young's modulus of PAI$_x$-CANs and other reported polyimine-based CANs.

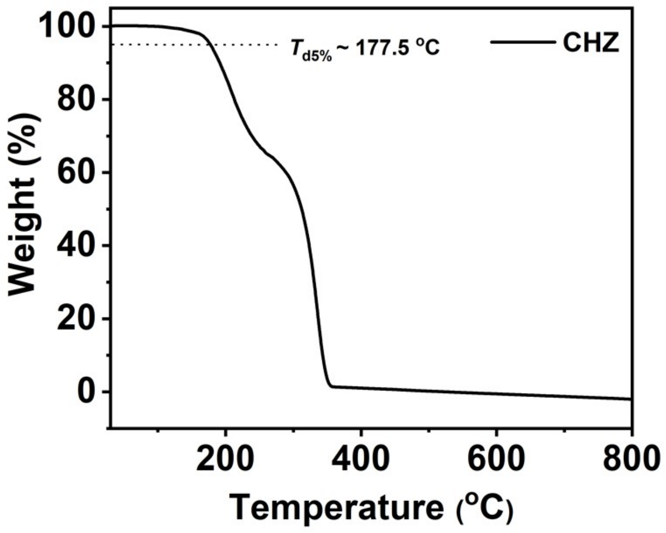

Figure S4. TGA curve of CHZ.

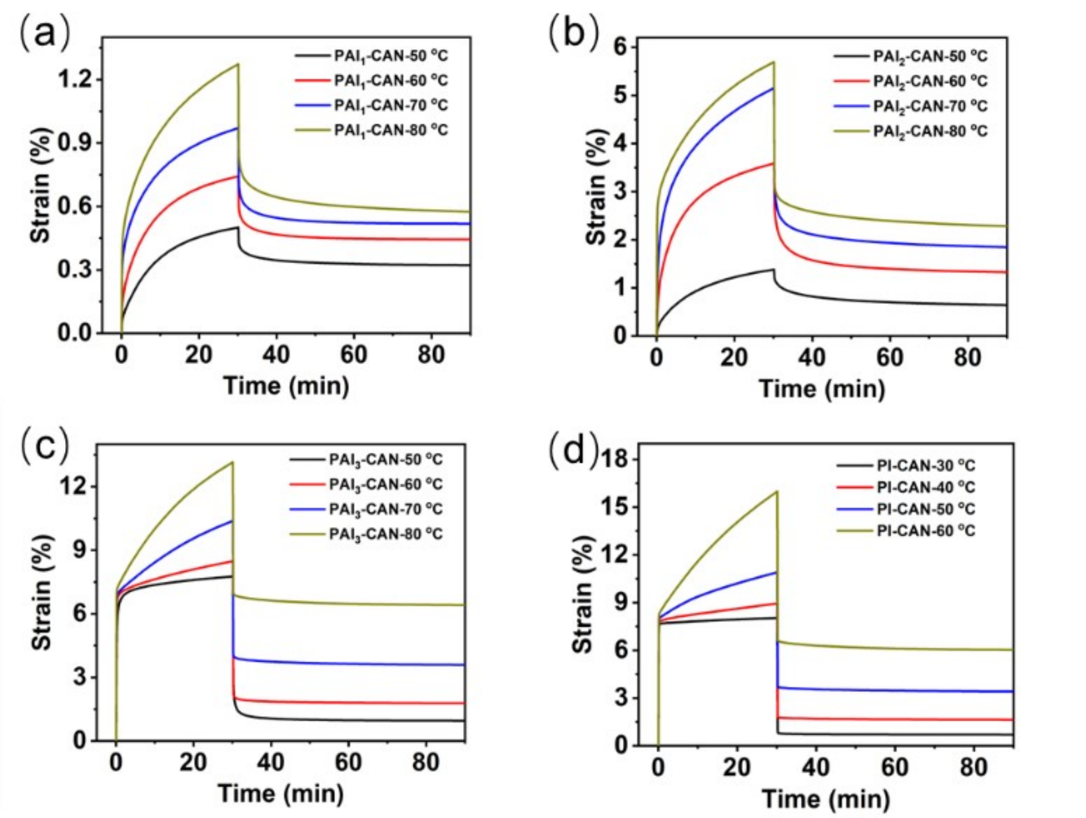

Figure S5. Creep behaviors of (a) PAI$_1$-CAN, (b) PAI$_{1.5}$-CAN, (c) PAI$_3$-CAN, and (d) PI-CAN.

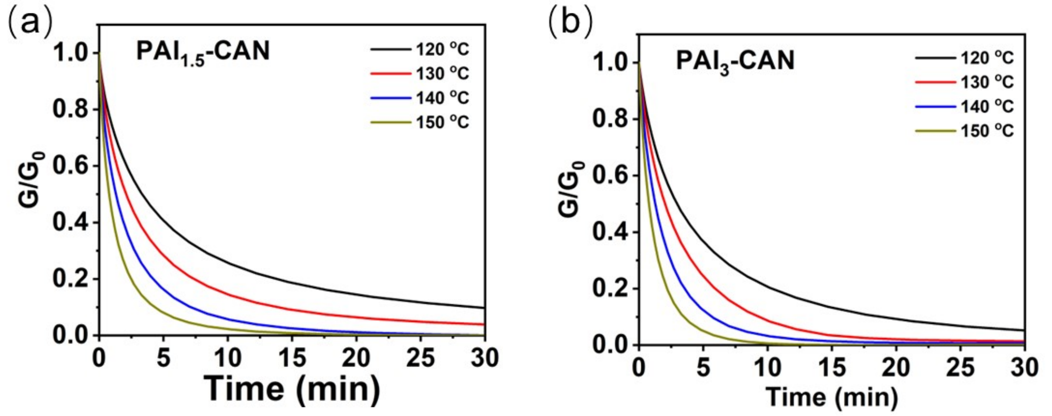

Figure S6. Stress relaxation at different temperatures of (a) PAI$_{1.5}$-CAN and (b) PAI$_3$-CAN.

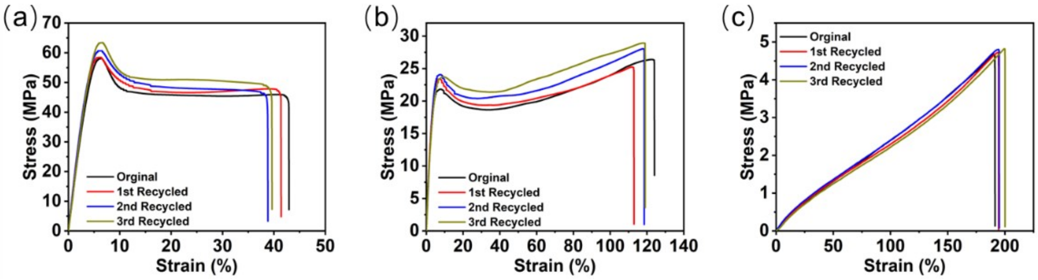

Figure S7. Tensile stress-strain curves of original and reprocessed (a) $PAI_{1.5}$-CAN, (b) PAI_3-CAN, and (c) PI-CAN.

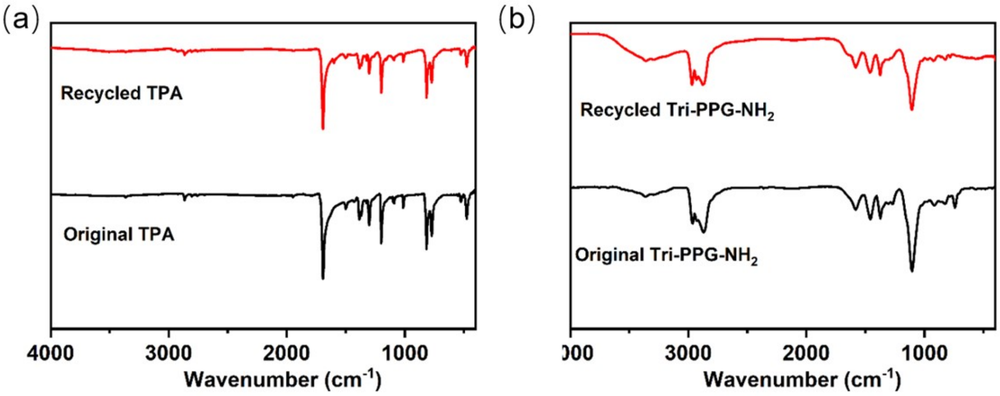

Figure S8. (a) FT-IR spectra of original and recycled TPA. (b) FT-IR spectra of pristine and original Tri-NH_2-PPG.