Supporting Information

Anionic Inverse Vulcanization of 3-Methyleneazetidine for Reusable Adhesives

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1. General Information

1.1 Materials

Hydrochloric acid (36%~38%), *tert*-butyl 3-methyleneazetidine-1-carboxylate (97%), sodium hydroxide (97%), elemental sulfur (99.95%), 1,3-diisopropenylbenzene (97%, DIB), ethanol were purchased commercially and used without further purification.

1.2 Characterizations

The ^{1}H NMR spectra were measured on a JNM-ECZ500R/S1 at 25 °C using CDCl$_3$ as the solvent. The solide-state ^{13}C spectra were measured on a Bruker AVANCE III HD 600 MHz at 25 °C. Scanning electron microscopy (SEM) was performed on a Hitachi Regulus 8100 scanning electron microscope with an Xplore30 energy dispersive spectroscopy (EDS). Thermal stabilities were evaluated by performing the thermogravimetric analysis (TGA) on an STA 449 F5 Jupiter instrument under dry nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC3 calorimeter. Two scanning cycles of heating-cooling were performed in the temperature range from -15 to 130 °C with the heating rates of 10 °C/min under nitrogen. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ScientificTM K-AlphaTM+ spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W. Samples were analyzed under vacuum (P < 10^{-8} mbar) with a pass energy of 150 eV (survey scans) or 25eV (high-resolution scans). All peaks would be calibrated with C1s peak binding energy at 284.8 eV for adventitious carbon. The experimental peaks were fitted with Avantage software. FT-IR spectra were obtained on a Thermo-Fisher Nicolet 6700 spectrometer. The XRD pattern was detected by using a TD-3500XRD (Dandong Tongda Technology Co., Ltd, China) under the conditions of 40 kV and 40 mA, in the

2θ range from 5 to 80°. Organic elemental analysis (OEA) (Elementar UNICUBE, Germany) was conducted todetermine the C, H, N, S, and O content of the polymers. Raman spectra were obtained using a HORIBA Jobin Yvon micro-confocal Raman spectrometer with 785 nm laser excitation. Lap shear tests were conducted using an electronic universal tensile testing machine (Inspekt Table Blue 5 kN) at a pull rate of 30 mm/min. For each adhesive–substrate system, three replicate tests were performed. The maximum load (kN) recorded in each test was used to calculate the adhesion strength (MPa) by dividing the maximum force at fracture by the bonded overlap area. Steel and wood plates (80 × 25 mm) were used as substrates after abrasion treatment. At 130 °C, The polymer was ground into fine particles and uniformly spread on the surface of the substrate with a bonding area of 25×15 mm^2. Another substrate was then covered on top, and the resultant assembly was placed in an oven and cured at 130 °C for 6 h. After completion of curing, the bonded substrates were cooled down to room temperature and subsequently subjected to lap shear tests.

2. Experimental Procedures
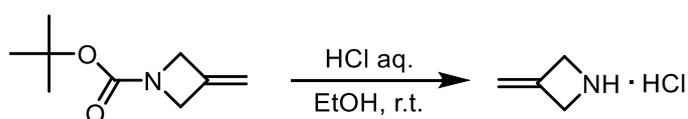
Synthesis of 3-methyleneazacyclobutane hydrochloride. Ethanol (40 mL), *tert*-butyl 3-methyleneazetidine-1-carboxylate (5.0 g, 0.03 mol, 1.0 equiv), and concentrated hydrochloric acid (5.0 mL, 0.06 mol, 2.0 equiv) were added sequentially to a 250 mL round-bottom flask. The reaction mixture was stirred at room temperature for 6 h, after which the solvent was removed under reduced pressure. The resulting residue was obtained as 3-methyleneazacyclobutane hydrochloride (2.1 g, 70% yield). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 5.14–5.13 (m, 2H), 4.75-4.72 (m, 4H).
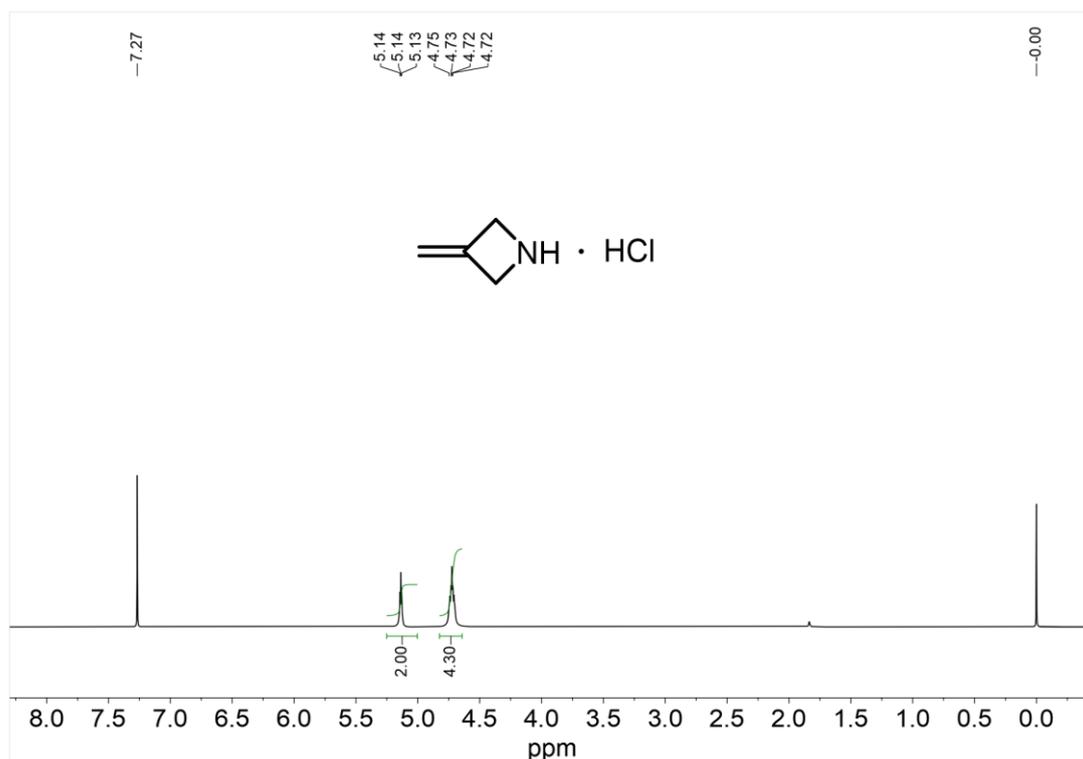
Inverse vulcanization of 3-methyleneazetidine. The synthesis of **poly(S3-*r*-Az1)** is described as a representative procedure. 3-Methyleneazetidine hydrochloride (0.275 g, 2.62 mmol, 1.0 equiv.) and an aqueous sodium hydroxide solution (0.33 mL, 2.62 mmol, 8.0 M, 1.0 equiv.) were charged into a sealed pressure bottle and stirred at room temperature for 5 min. Elemental sulfur (0.25 g, 7.81 mmol, 3.0 equiv.) was then added, and the reaction mixture was heated at 120 °C in an oil bath with stirring for 1.5 h, affording a brown solid. After cooling to room temperature, the crude product was mechanically ground and washed with distilled water under ultrasonication (three times, 10 min each) to remove inorganic salts. The resulting solid was collected and dried in an oven at 120 °C for 12 h to yield **poly(S3-*r*-Az1)**.

When 1,3-diisopropenylbenzene (DIB) was introduced as a comonomer together with elemental sulfur, the corresponding terpolymers **poly(S-*r*-Az-*r*-DIB)** were obtained. The feed ratios of all reagents are summarized in Table S1.

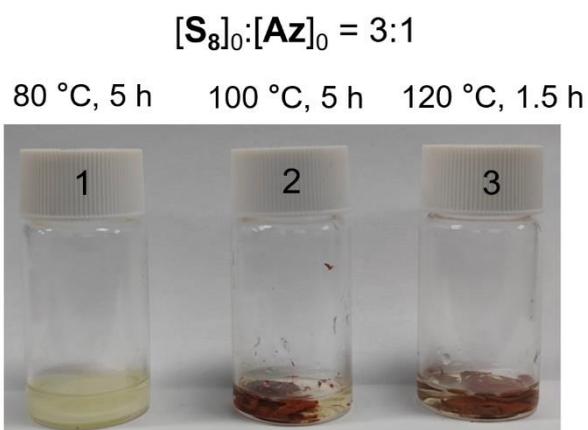# 3. Supporting Tables, Figures, and Schemes

$$[S_8]_0 : [Az]_0 = 3:1$$

80 °C, 5 h   100 °C, 5 h   120 °C, 1.5 h

Fig. S1 Photographs of the reaction mixtures obtained at 80 °C, 100 °C, and 120 °C using a feed ratio of $[S_8]_0 : [Az]_0 = 3:1$.

Table S1 Feed amounts of reagents used for inverse vulcanization.

Polymer	Az (g)	S_8 (g)	DIB (g)	8.0 M NaOH a.q. (mL)
poly(S3-*r*-Az1)	0.275	0.250	/	0.33
poly(S5-*r*-Az1)	0.275	0.420	/	0.33
poly(S7-*r*-Az1-*r*-DIB1)	0.275	0.583	0.412	0.33
poly(S7-*r*-Az3-*r*-DIB1)	0.316	0.224	0.158	0.37
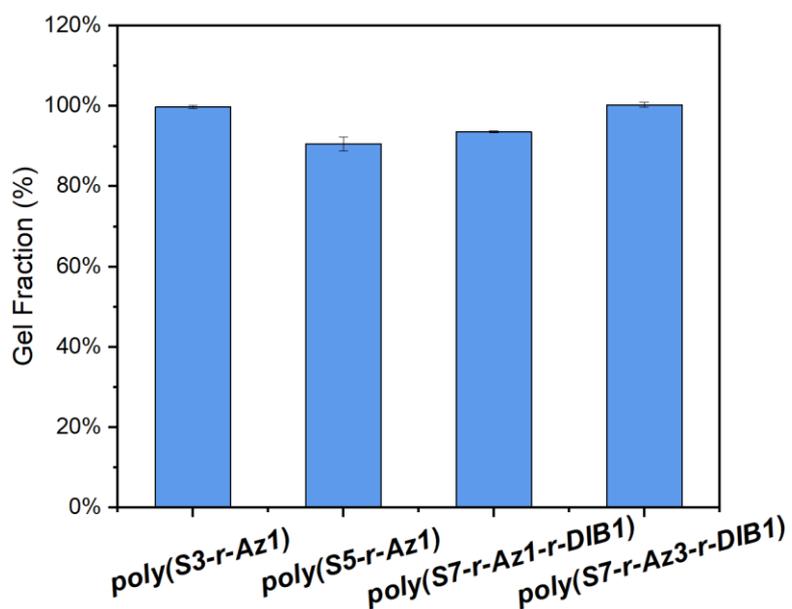
Fig. S2 Gel fractions of **poly(S3-*r*-Az1)**, **poly(S5-*r*-Az1)**, **poly(S7-*r*-Az1-*r*-DIB1)** and **poly(S7-*r*-Az3-*r*-DIB1)** after immersion in toluene for 24 h at room temperature.
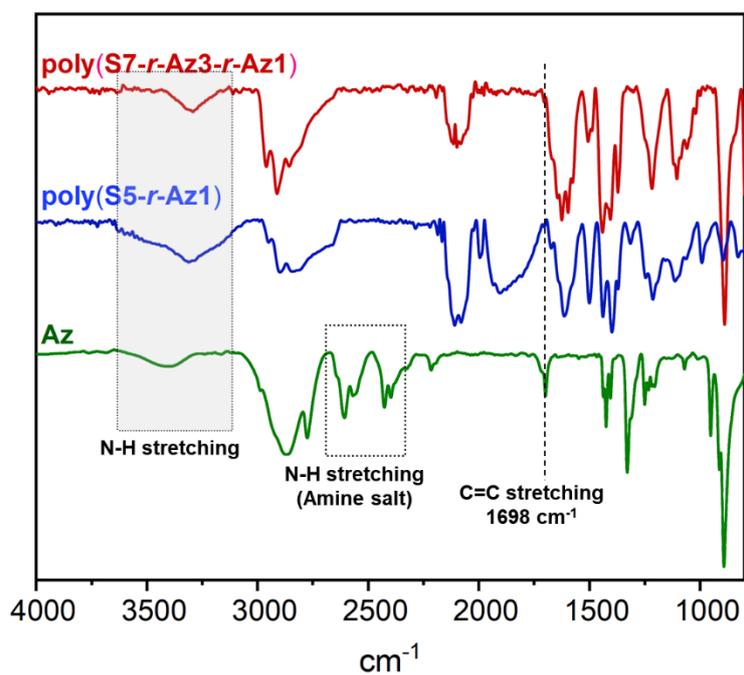
Fig. S3 FT-IR spectra of **poly(S5-*r*-Az1)**, **poly(S7-*r*-Az3-*r*-DIB1)** and 3-methyleneazacyclobutane hydrochloride.
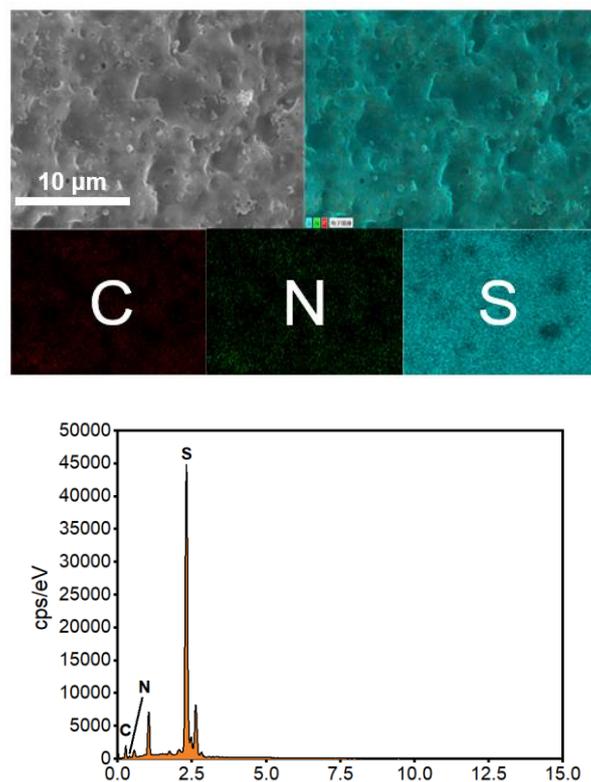
Fig. S4 SEM–EDS analysis and corresponding elemental mapping images of **poly(S3-r-Az1)**.
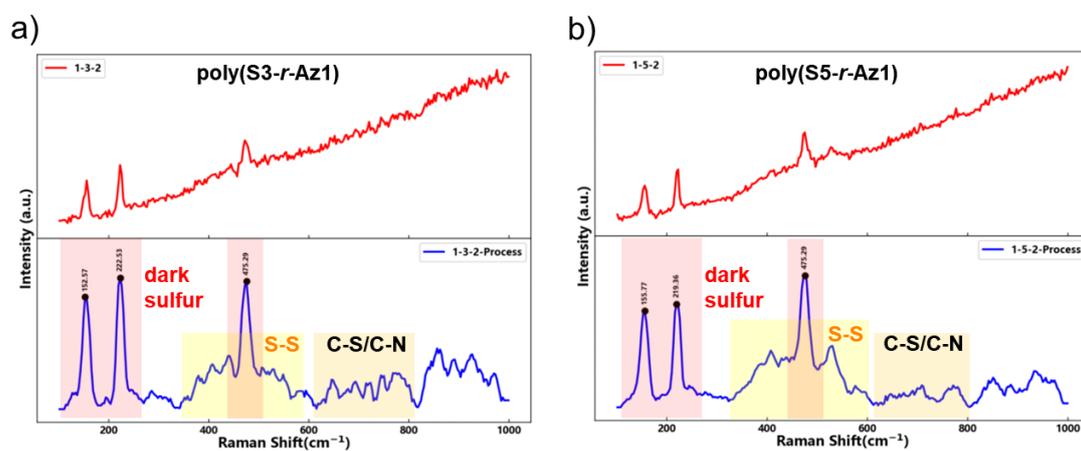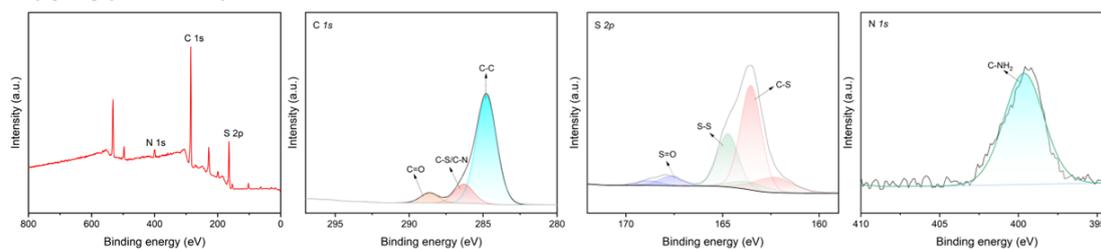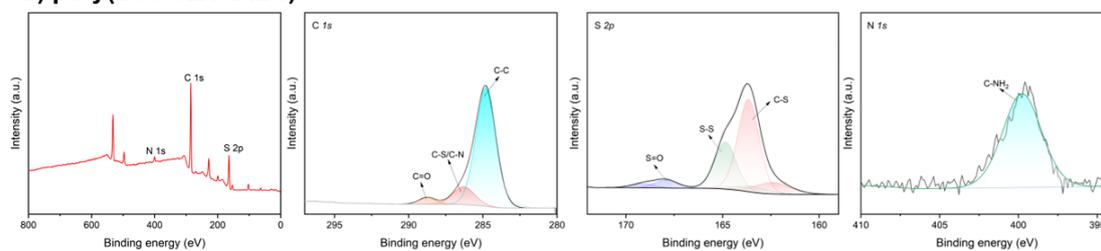

Fig. S5 Raman spectra of a) **poly(S3-r-Az1)**, and b) **poly(S5-r-Az1)**. The upper traces show the raw spectra, while the lower traces present the background-subtracted spectra.

a) poly(S5-*r*-Az1)

b) poly(S7-*r*-Az1-DIB1)

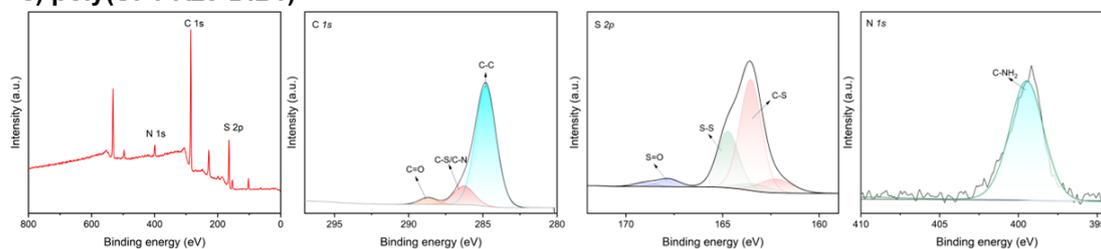**c) poly(S7-*r*-Az3-DIB1)**

Fig. S6 XPS spectra of a) **poly(S5-*r*-Az1)**, b) **poly(S7-*r*-Az1-*r*-DIB1)**,c) **poly(S7-*r*-Az 3-*r*-DIB1)**, including survey scans and high-resolution C 1*s*, S 2*p*, and N 1*s* spectra.
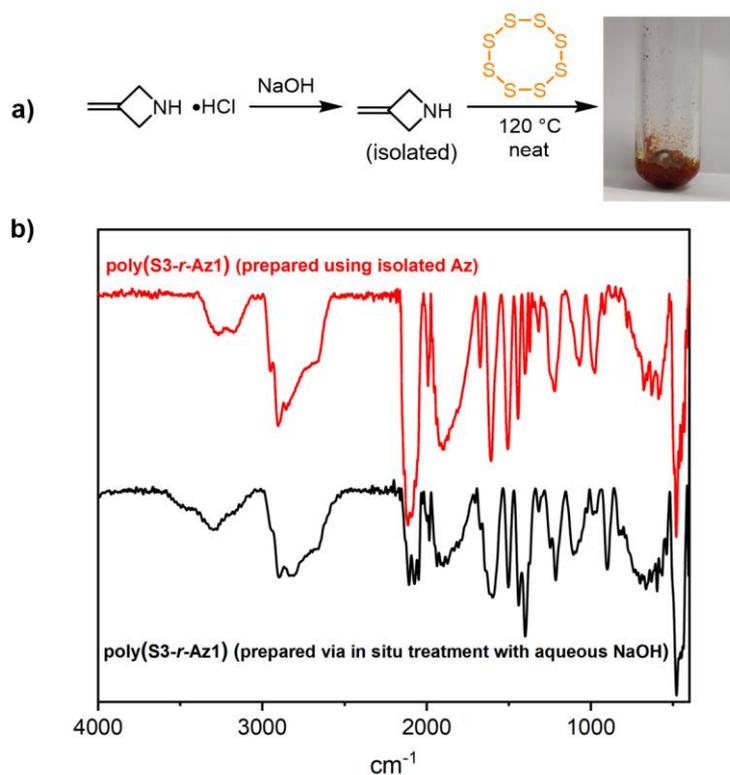
Fig. S7 a) Synthetic procedure for **poly(S3-*r*-Az1)** using isolated 3-methyleneazetidine;

(b) FT-IR spectra of **poly(S3-*r*-Az1)**s synthesized using isolated 3-methyleneazetidine

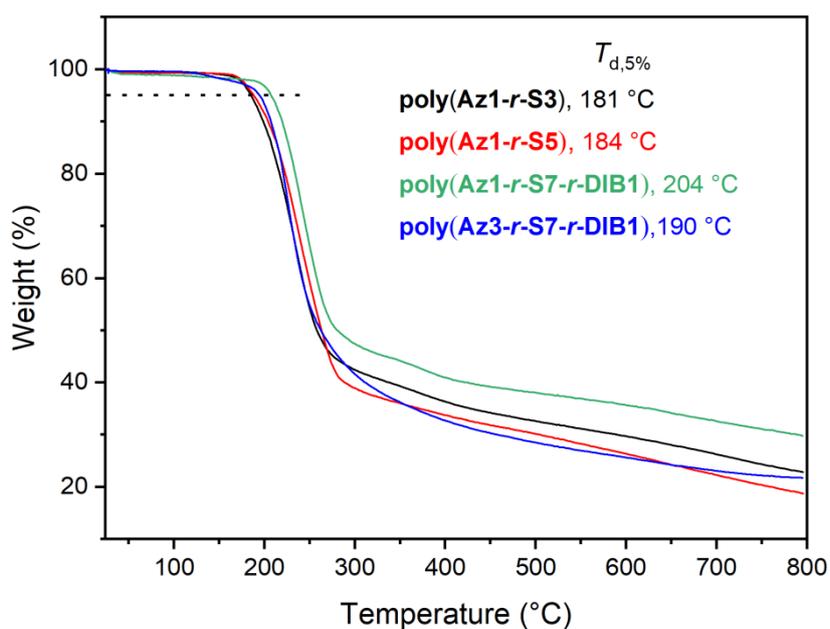and via in situ treatment with aqueous NaOH.

Fig. S8 Thermogravimetric analysis (TGA) curves of **poly(Az-*r*-S)** and **poly(S-*r*-Az-*r*-DIB)**, measured at a heating rate of 10 °C min^{-1} under nitrogen.
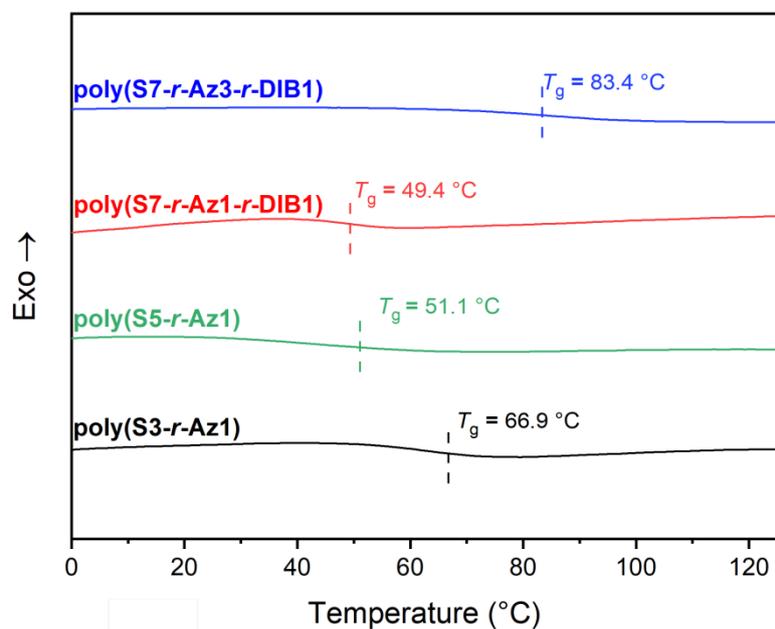
Fig. S9 Differential scanning calorimetry (DSC) thermograms of **poly(Az-*r*-S)** and **poly(S-*r*-Az-*r*-DIB)**, recorded at a heating rate of 10 °C min^{-1}.
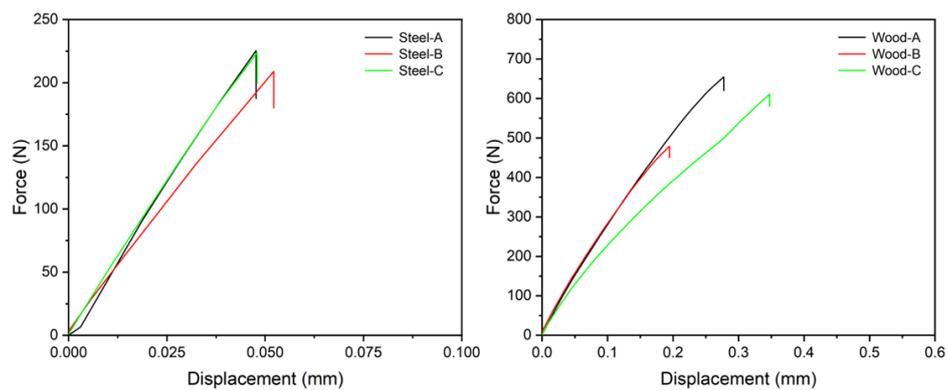

Fig. S10 Lap shear stress–strain curves of **poly(S3-*r*-Az1)** bonded to steel and wood substrates at room temperature.
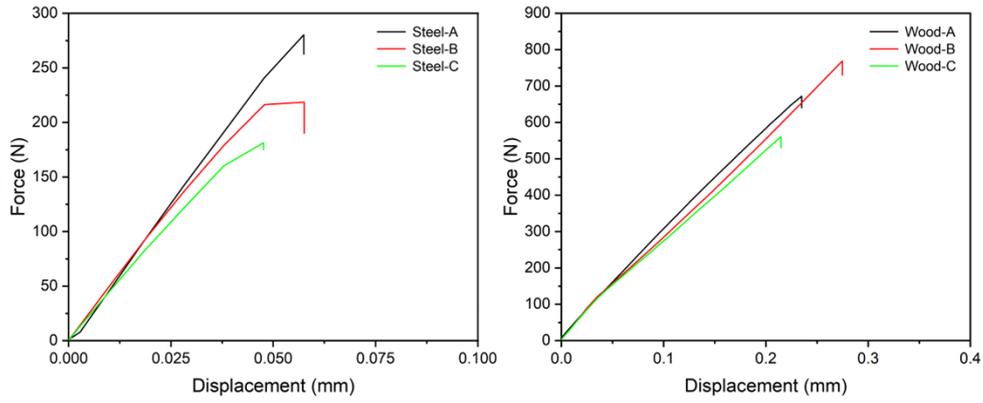
Fig. S11 Lap shear stress–strain curves of **poly(S5-*r*-Az1)** bonded to steel and wood substrates at room temperature.
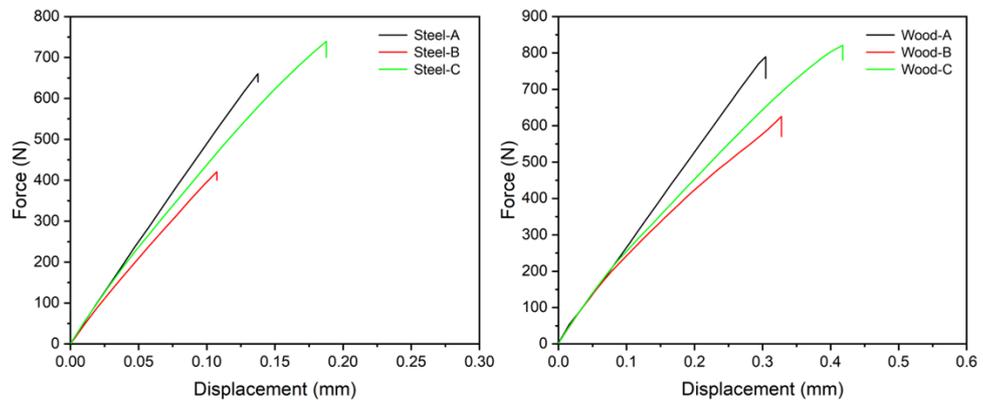

Fig. S12 Lap shear stress–strain curves of **poly(S7-*r*-Az1-*r*-DIB1)** bonded to steel and wood substrates at room temperature.
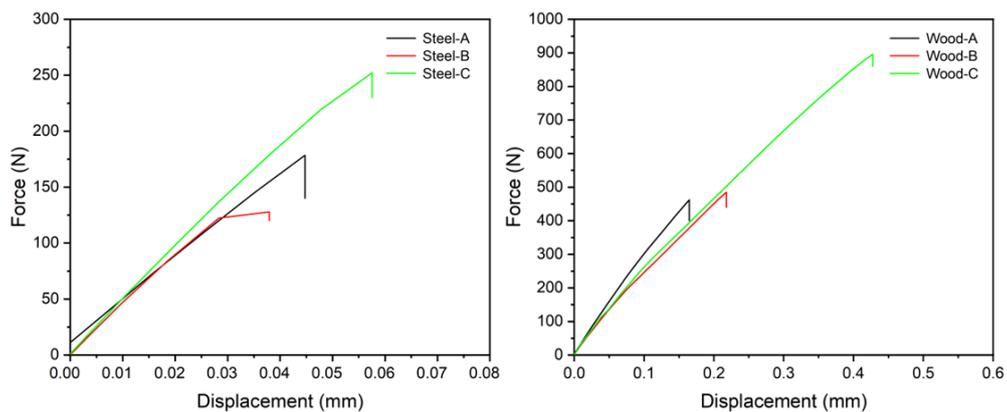

Fig. S13 Lap shear stress–strain curves of **poly(S7-*r*-Az3-*r*-DIB1)** bonded to steel and wood substrates at room temperature.

Table S2 Summary of lap-shear test results for **poly(S3-*r*-Az1)**, **poly(S5-*r*-Az1)**, **poly(S7-*r*-Az1-*r*-DIB1)** and **poly(S7-*r*-Az3-*r*-DIB1)** on steel and wood substrates at room temperature.

Substrate board	Sample	LSS [MPa] trial A	LSS [MPa] trial B	LSS [MPa] trial C	Mean value [MPa]	Standard deviation [MPa]
	poly(S3-*r*-Az1)	0.60097	0.55747	0.59696	0.58513	0.02404
	poly(S5-*r*-Az1)	0.74781	0.58296	0.4838	0.60486	0.13336
Steel	**poly(S7-*r*-Az1-*r*-DIB1)**	1.76135	1.1228	1.97304	1.61906	0.44262
	poly(S7-*r*-Az3-*r*-DIB1)	0.47575	0.34123	0.67253	0.4965	0.16663
	poly(S3-*r*-Az1)	1.74511	1.27759	1.62892	1.55054	0.24342
	poly(S5-*r*-Az1)	1.79192	2.05083	1.49593	1.77956	0.27765
Wood	**poly(S7-*r*-Az1-*r*-DIB1)**	2.105	1.66725	2.18948	1.95224	0.26437
	poly(S7-*r*-Az3-*r*-DIB1)	1.16897	1.29371	2.3896	1.6391	0.65064

Table S3 Summary of cyclic lap shear test results for **poly(S7-*r*-Az3-*r*-DIB1)** on wood substrates at room temperature.

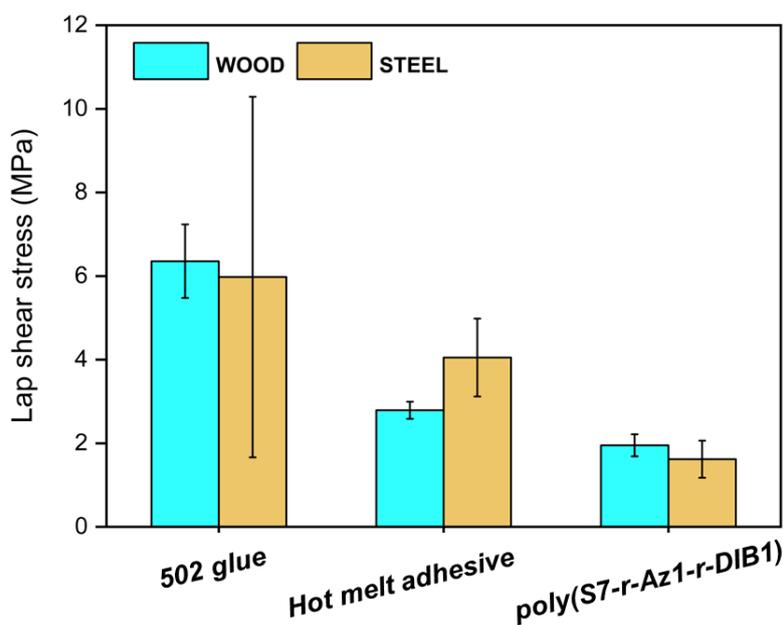| Sample	Sample	LSS [MPa] trial A	LSS [MPa] trial B	LSS [MPa] trial C	Mean value [MPa]	Standard deviation [MPa]
poly(S7-*r*-Az1-*r*-DIB1)	1	2.16253	2.79017	3.08492	2.67921	0.4711
	2	2.47675	2.38848	2.53788	2.4677	0.07511
	3	1.42136	2.39075	2.45899	2.09036	0.58038
	4	1.8828	1.92233	2.18837	1.99784	0.16619
	5	2.11819	2.0668	2.69931	2.29476	0.35128

Fig. S14 Comparison of the lap-shear strengths of **poly(S7-*r*-Az1-*r*-DIB1)**, 502 glue, and a commercial hot-melt adhesive on wood and steel substrates.