Supporting Information (SI)

Self-Crosslinking All-Hydrocarbon Polyethylene Thermosets through Intrinsic Benzocyclobutene Cycloaddition

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1. General Procedures and Materials

Materials and Instrumentation. All of the following chemicals were purchased and used as received. 4-bromobenzocyclobutene, norbornadiene, and cesium carbonate were purchased from Adamas Titan. Palladium(II) acetate, triphenylphosphine, *p*-toluenesulfonyl hydrazide, and tripropylamine were purchased from Energy Chemical. Grubbs second-generation catalyst was purchased from Bidepharm.

All manipulations involving air- and moisture- sensitive compounds were carried out using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. All solvents were purified by the MBraun SPS system. NMR spectra for polymers were recorded on Bruker AV400 (^{1}H: 500 MHz, ^{13}C: 125 MHz). NMR assignments were confirmed by ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{1}H–^{1}H COSY experiments when necessary. The molecular weight (M_n) and molecular weight distribution (PDI) were measured using a TOSOH HLC-8220 GPC at 40 °C using THF as solvent (the flow rate is 0.35 mL min^{-1}) against polystyrene standards for the non-hydrogenated COPs, and a PL GPC-200 GPC at 150 °C using 1,2,4-trichlorobenzene as solvent (the flow rate is 0.35 mL min^{-1}) against polystyrene standards for the **PEa** and **PEb**. Melting points (T_m) or glass transition temperature (T_g) of polymers were measured through DSC analysis, which was carried out on a METTLER TOPEM DSC (Mettler-Toledo, Zurich, Switzerland) or a Q2000 DSC (TA Instruments, New Castle, USA) under nitrogen atmosphere at heating rate of 10 °C/min of second heating cycle. Tensile tests were conducted at room temperature using a crosshead rate of 2 mm/min. The data reported were the mean and standard deviation from at least three determinations. Thermal gravimetric analyses (TGA) were performed on a thermal analysis instrument (SDTQ600, TG instruments) from 40 °C to 700 °C under a continuous nitrogen atmosphere with a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed at a heating rate of 3 K min^{-1} in air using a Mettler Toledo DMA/SDTA861e instrument. The hydrophilicity of the film was evaluated through static contact angle measurements using a contact angle goniometer (JC2000C Contact Angle Meter, Powercat Co., Shanghai, China). The transparency of the thin film is recorded on a Shimadzu UV-3600 spectrophotometer. The refractive index of thin film samples was measured using an Abbe refractometer (DR-M4, Atago Co. Ltd., Tokyo, Japan) at 20 °C using the contact liquid. FT-IR spectra were acquired on an INVENIO-R Fourier Transform Infrared spectrometer. The elemental analysis was performed on iCAP™ TQ ICP-MS (Thermo Scientific™) (Detection mode: SQ-KED, collision gas: helium, Plasma power: 1550 W, cooling gas flow: 14.0 L/min, auxiliary gas flow: 0.8 L/min.).

A general procedure for the copolymerization of M1 and COE via ROMP: Under a nitrogen atmosphere, a quantity of M1 and 4.0 mmol COE were dissolved in a certain amount of dry, degassed dichloromethane in a 100 mL glass flask equipped with a magnetic stirrer. A certain amount of the Grubbs second-generation catalyst was dissolved in 2 mL dry, degassed dichloromethane and injected into the flask. After stirring at room temperature for 1 h, the reaction was quenched by the addition of 0.5 mL ethyl vinyl ether and stirred for another 0.5 h. Finally, the reaction solution was precipitated by pouring into ethanol (50 mL), and the precipitate was filtered and dried under vacuum at 40 °C for 24 h.

Kinetic study for the ROMP of M1 and COE with the simultaneous addition of the two monomers. Under otherwise identical conditions, the monomer solution and catalyst solution were divided into 4 parts, respectively. The ROMP of each part was conducted in polymerization time of 1 min, 15 min, 30 min, and 60 min, respectively. The ROMP was immediately quenched. According to the yield and monomer incorporation, we could obtain the monomer conversion (**Table S1**). Moreover, the molecular weight was determined by GPC analysis.

A general procedure for the hydrogenation of non-hydrogenated COPs. In a typical experiment, under a nitrogen atmosphere, non-hydrogenated COPs, *p*-toluenesulfonyl hydrazide (4 equiv, relative to the number of double bonds in the non-hydrogenated COPs) and tripropylamine (4 equiv, relative to the number of double bonds in the non-hydrogenated COPs) were dissolved in an appropriate volume of toluene solvent. The mixture was heated to reflux for 8 h and then precipitated in a large of ethanol. The precipitate was filtered and dried under a vacuum at 60 °C for 24 h.

A general procedure for the copolymerization of ethylene and M1 using Zr-Cat: In a typical experiment, a 75 mL glass pressure rector connected with a high-pressure gas line was firstly dried at 90 °C under vacuum for at least 1h. The reactor was then adjusted to the desired polymerization temperature. 8 mL of toluene and a certain amount of M1 were added to the reactor under a nitrogen atmosphere, 5.0 μmol Zr-Cat and 0.8 mL MAO cocatalyst solution (1.5 M) was mixed in another 2 mL of toluene, then the mixed solution was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and kept constant at 1 bar of ethylene. After stirring for 10 min, the reactor was vented and the polymerization was quenched by adding of 40 mL acidic ethanol (10 mol% HCl) to the reactor, the precipitate was filtered and dried under vacuum at 60 °C for 24 h.

Preparation of a free-standing cross-linked film: The polymer solution (0.1 g mL^{-1}) was prepared by dissolution in $C_2H_2Cl_4$ and dropped on the surface of a glass sheet to fabricate a film. After drying, the film was heated at 270 °C for 2 hours to cross-link fully.

Soxhlet extraction to test gel fraction: A Soxhlet extraction test was carried out by using toluene as eluting agent at 150 °C for 24 h. The gel fraction was calculated by the formula:

$$\text{gel fraction} = \frac{m_2}{m_1} \times 100\%$$

where m_1 and m_2 represented the weight of the sample before and after the Soxhlet extraction test, respectively.

Measurement of water uptake: The film was dried in vacuo until a constant weight was achieved. The sample was then placed into appropriate amount of deionized water at room temperature. After maintaining the sample at this temperature for 24 h, the sample was removed, and the residue of the water on the surface of the sample was removed using filter paper. The sample was weighed, and the water uptake was reported as the increase of the weight of the sample after immersion in the deionized water. The final data were obtained from the average of the results from 5 samples.

Zr-Cat[1] and Grubbs third-generation catalyst[2] (**G3**) were prepared according literature reports.

2. Table S1. Kinetic data in the ROMP with simultaneous addition sequence

Entry	t^a (min)	Yield (%)	$X_{M1}{}^b$ (mol %)	$X_{COE}{}^b$ (mol %)	Conv.$_{M1}{}^c$ (%)	Conv.$_{COE}{}^c$ (%)
1	1	75.0	8.8	91.2	70.3	75.9
2	15	87.5	8.4	91.6	78.9	89.1
3	30	87.5	9	91	81.3	88.6
4	60	100	8.5	91.5	100	100

[a] Polymerization time. [b] Monomer incorporation, determined by ^{1}H NMR spectroscopy. [c] Monomer conversion. [d] Determined by GPC at 40 °C in THF with polystyrene standards.

3. Table S2. ROMP of COE[a]

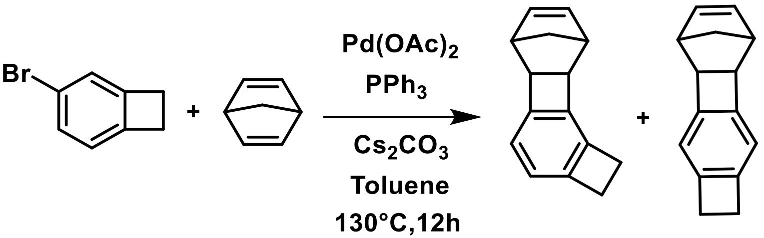
Entry	COE (mmol)	yield (%)	M_n (10^4)	PDI	T_m (°C)
1	4.0	73.0	5.4	3.3	61.1

[a] Polymerization conditions: G2 (5 μmol), DCM (10 mL), Polymerization time (15 min).

4. Table S3. Soxhlet extraction test

Sample	m_1 (mg)	m_2 (mg)	Gel fraction
P1	22	22	100%
P2	32	32	100%
Cross-linked **PEa** (Table 1, entry 1)	18	18	100%
Cross-linked **PEb** (Table 2, entry 2)	16	16	100%

5. Synthesis of Monomer



M1a **M1b**

4-bromobenzocyclobutene (5.0 g, 0.027 mol), norbornadiene (7.4 g, 0.081 mol), $Pd(OAc)_2$ (0.06 g, 0.00027 mol), PPh_3 (0.14 g, 0.00054 mol), Cs_2CO_3 (8.8 g, 0.027 mol) and 100 mL toluene were added to a 250 mL glass pressure flask. After the mixture was stirred at 130 °C for 12 h, it was cooled to room temperature and then passed through diatomite to remove inorganic salts, which was washed with DCM (3 × 10 mL). Filtered solution was concentrated and purified by silica chromatography using hexanes as the eluent to yield a colourless oil, which was a mixture of **M1a** and **M1b** isomers (4.24 g, 81.5 %) (**M1a**/**M1b**: 2.6/1).

^{1}H NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm): δ = 6.98 (q, J = 7.4 Hz, 5.2H), 6.87 (s, 2H), 6.29 (brs, 7.2H), 3.31 – 3.13 (m, 21.6H), 2.86 – 2.80 (m, 7.2H), 1.43 – 1.33 (m, 3.6H), 1.05 (d, J = 9.0 Hz, 2.6H), 0.99 (d, J = 8.9 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm): δ = 145.22, 145.17, 144.16, 144.06, 139.85, 139.13, 136.75, 136.72, 120.92, 120.23, 116.82, 48.02, 47.27, 47.11, 41.81, 41.75, 41.57, 41.45, 41.40, 30.34, 29.42, 29.40.

6. Spectra of Monomers

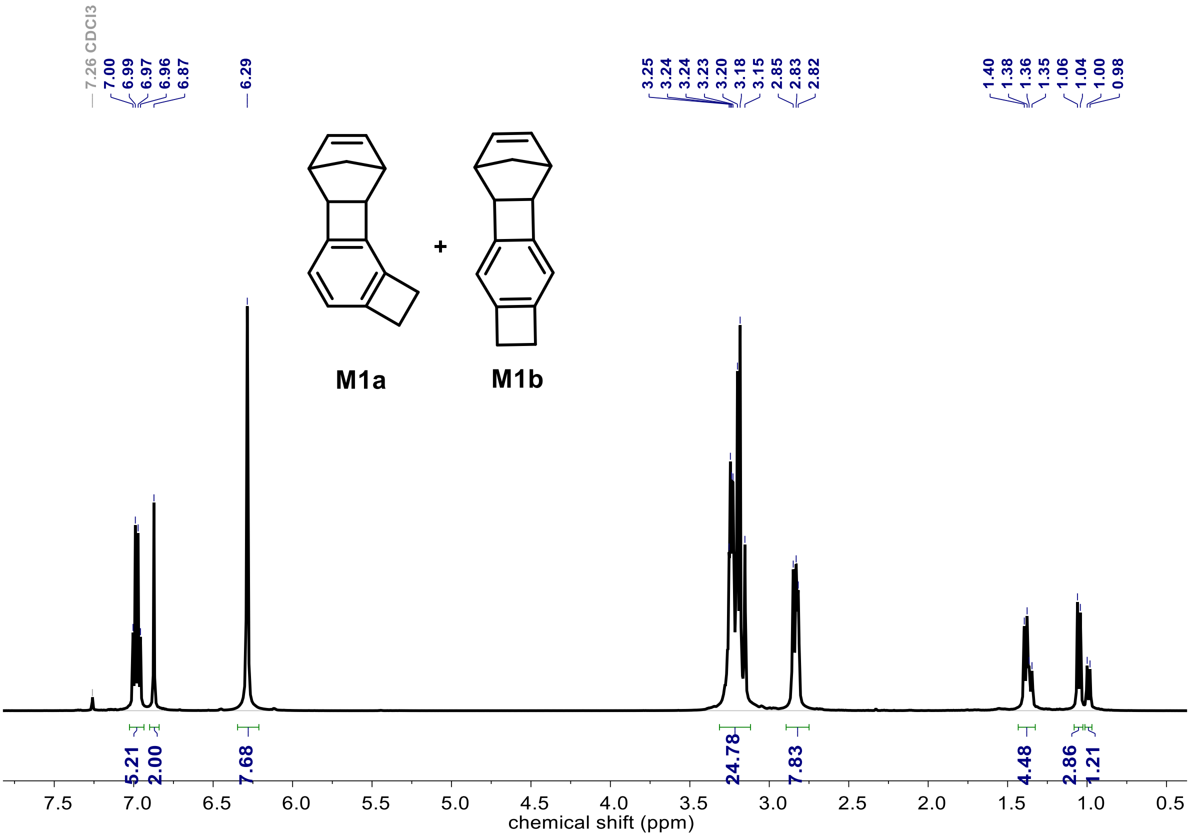


Figure S1. ^{1}H NMR spectrum of M1 in $CDCl_3$ (**M1a** / **M1b**: 2.6 / 1).

$$\mathrm{M1}a\ /\ \mathrm{M1}b = I_{6.93-7.03}/I_{6.84-6.89} = 5.21/2 = 2.6/1$$

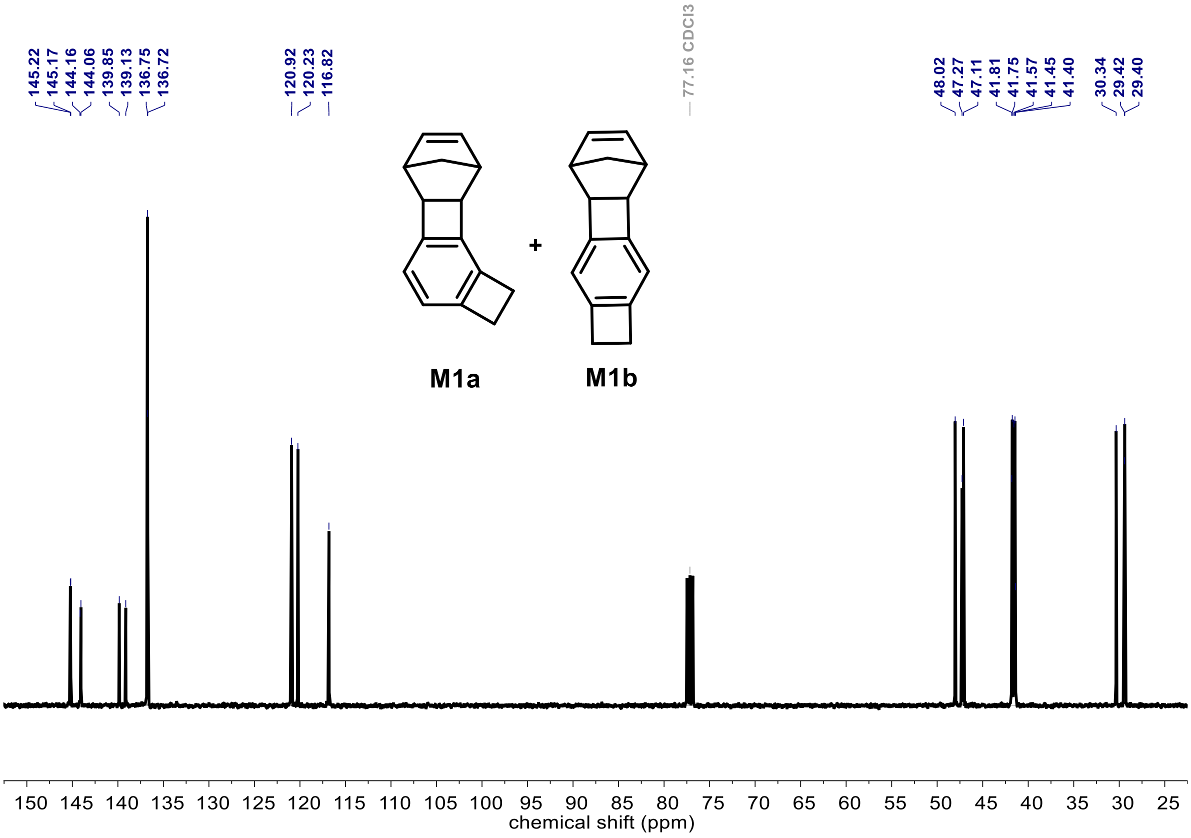


Figure S2. ^{13}C NMR spectrum of M1 in $CDCl_3$ (**M1a** / **M1b**: 2.6 / 1).

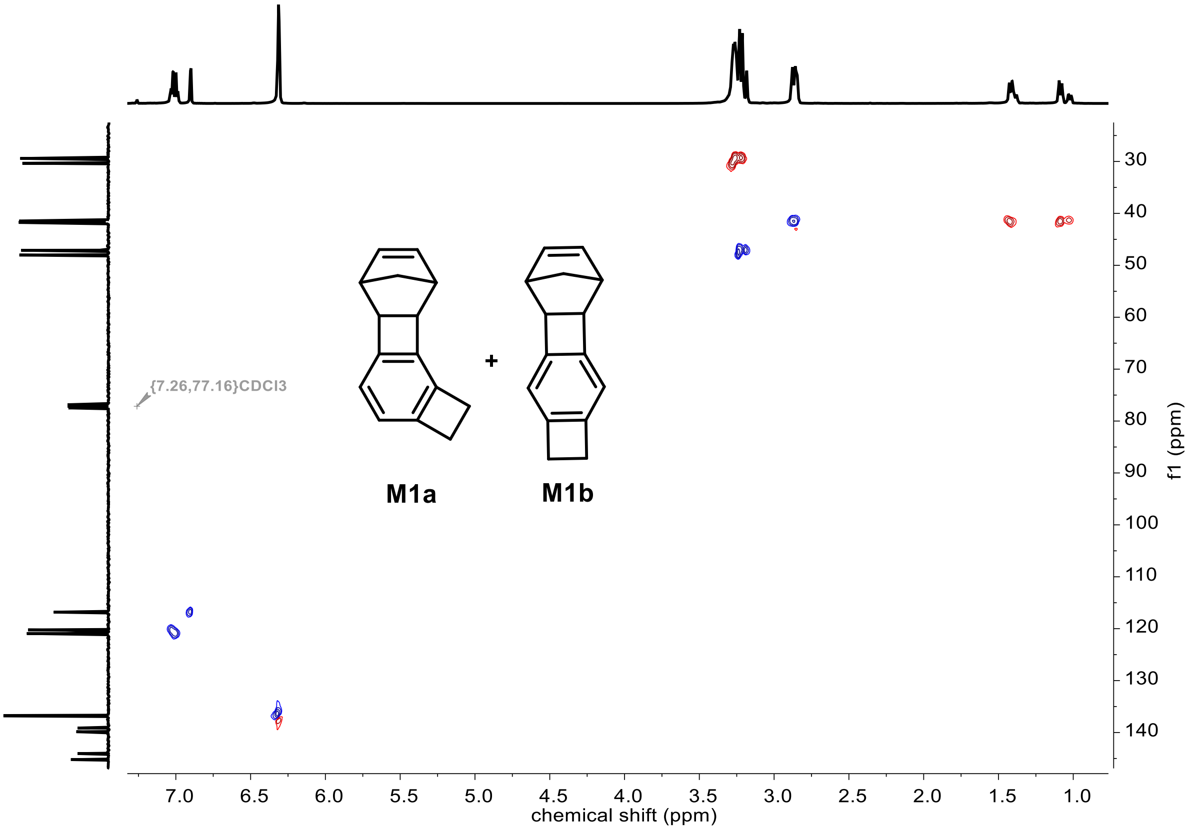


Figure S3. ^{1}H-^{13}C HSQC spectrum of M1 in $CDCl_3$ (**M1a** / **M1b**: 2.6 / 1).

7. NMR Figures of Polymers

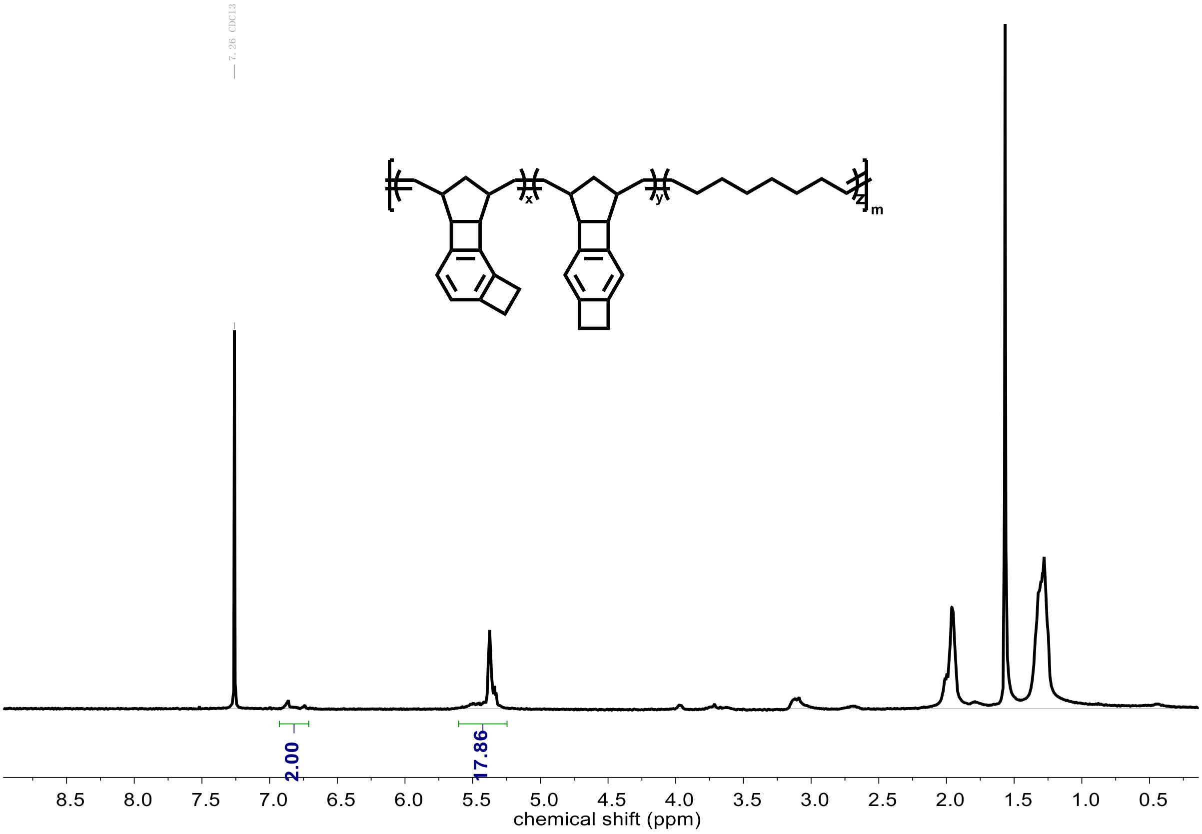


Figure S4. ^{1}H NMR spectrum of Pre-**PEa** from table 1, entry 1 in $CDCl_3$.

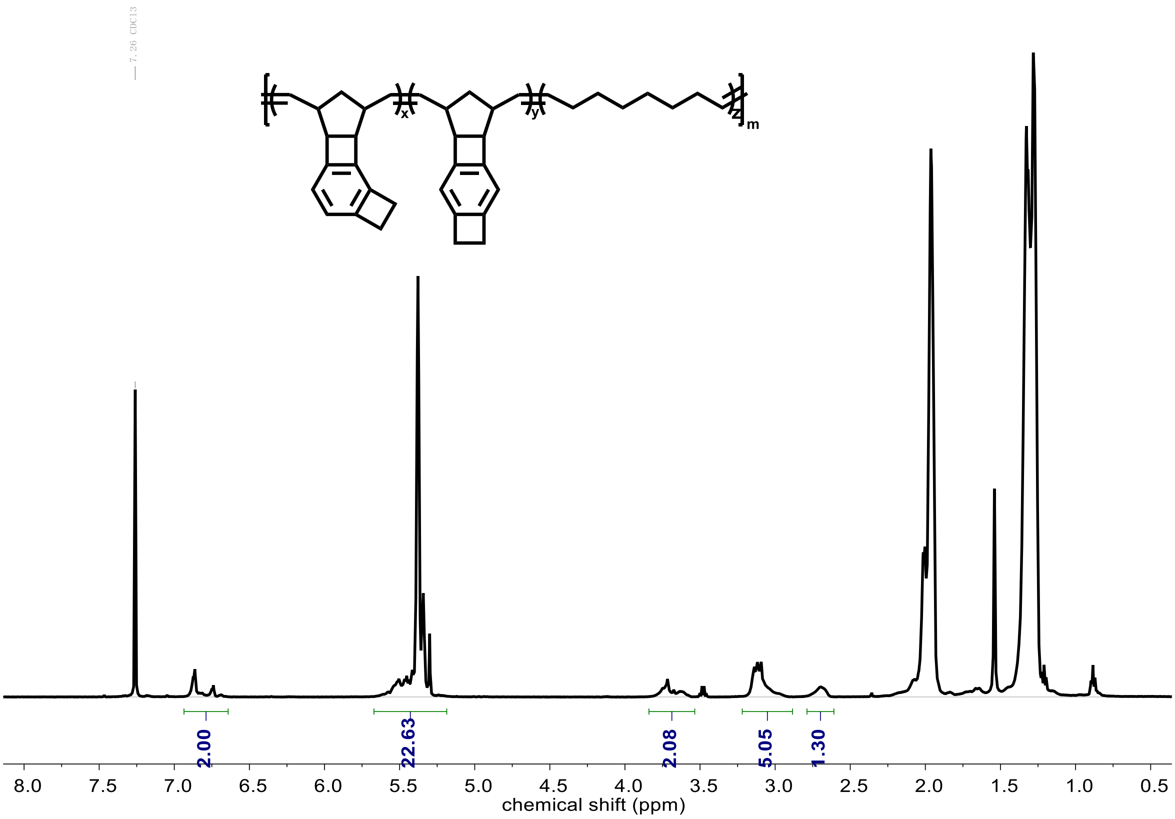


Figure S5. ^{1}H NMR spectrum of Pre-**PEa** from table 1, entry 2 in $CDCl_3$.

$$X_{\mathrm{M1}}=\frac{1}{1+\frac{I_{5.19-5.67}-2}{2}}\times 100\%=\frac{1}{1+\frac{22.63-2}{2}}\times 100\%=8.8\%$$

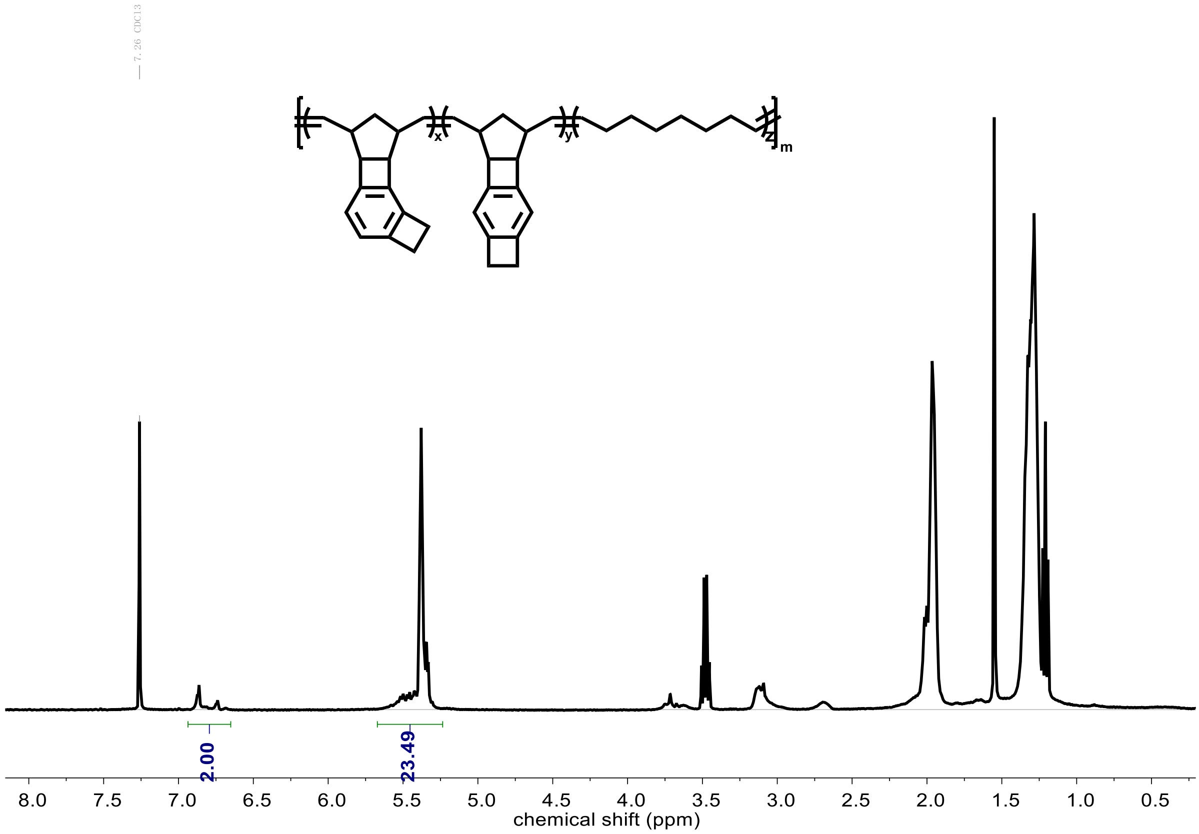


Figure S6. ^{1}H NMR spectrum of Pre-**PEa** from table 1, entry 3 in $CDCl_3$.

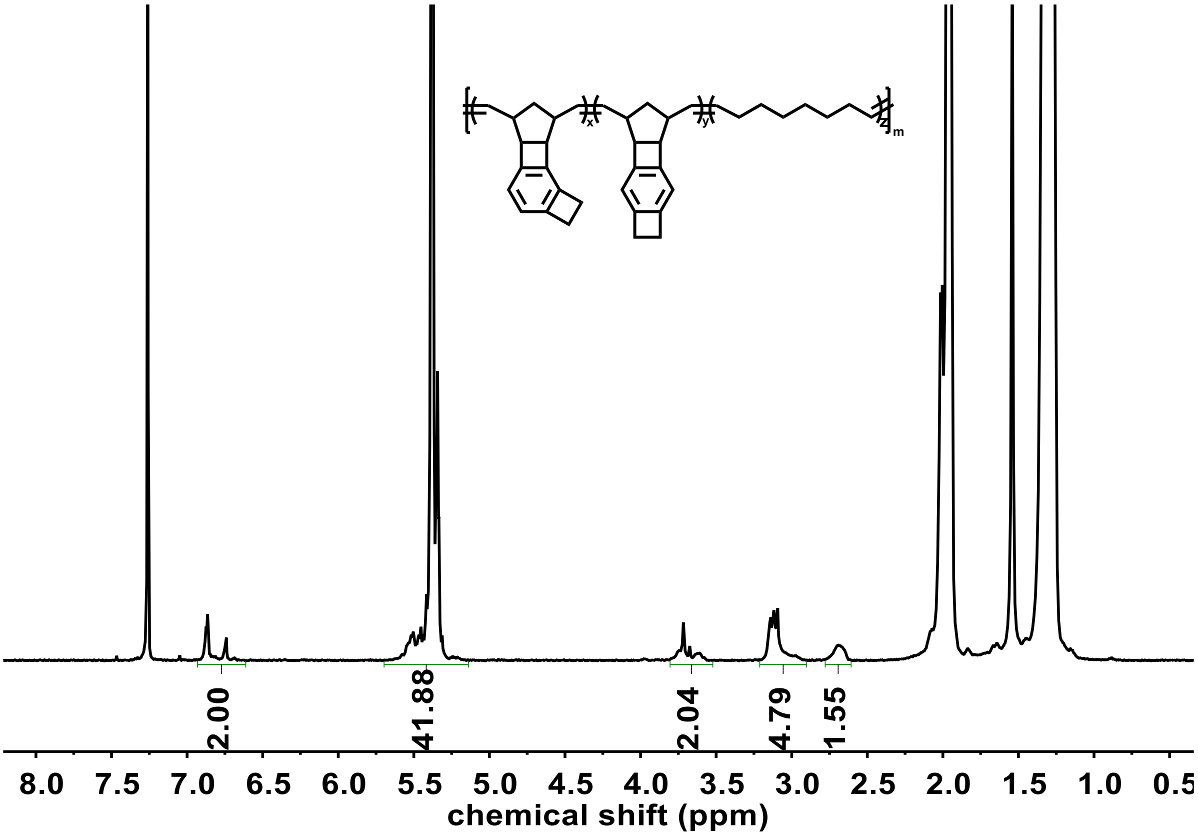


Figure S7. ^{1}H NMR spectrum of Pre-**PEa** from table 1, entry 4 in $CDCl_3$.

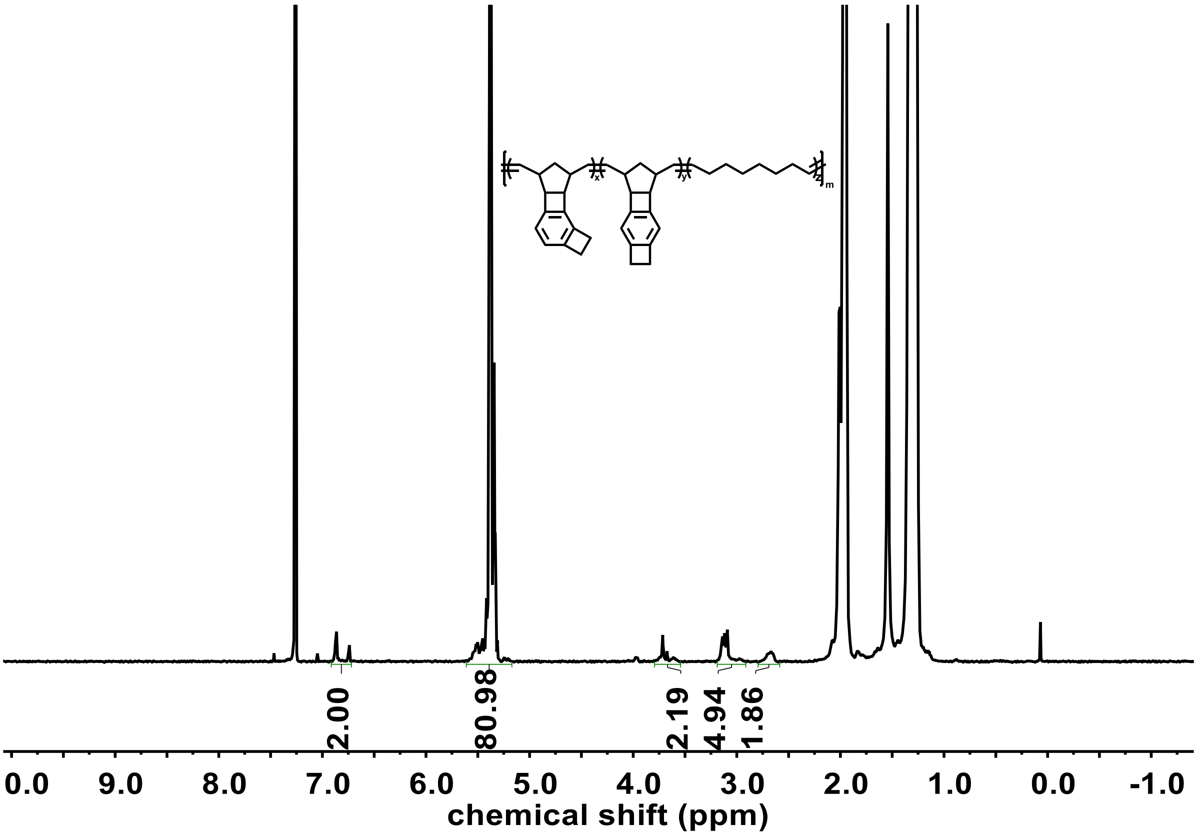


Figure S8. ^{1}H NMR spectrum of Pre-**PEa** from table 1, entry 5 in $CDCl_3$.

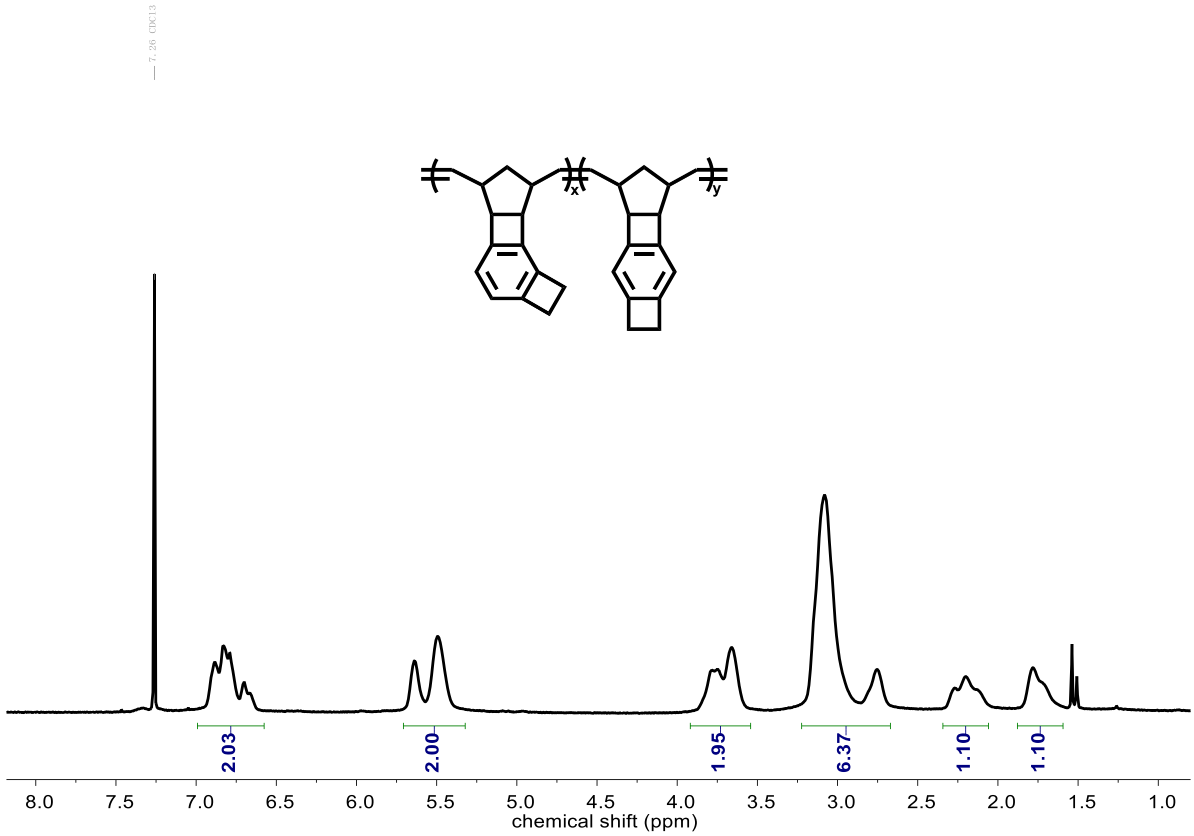


Figure S9. ^{1}H NMR spectrum of PM1 from table 1, entry 6 in $CDCl_3$.

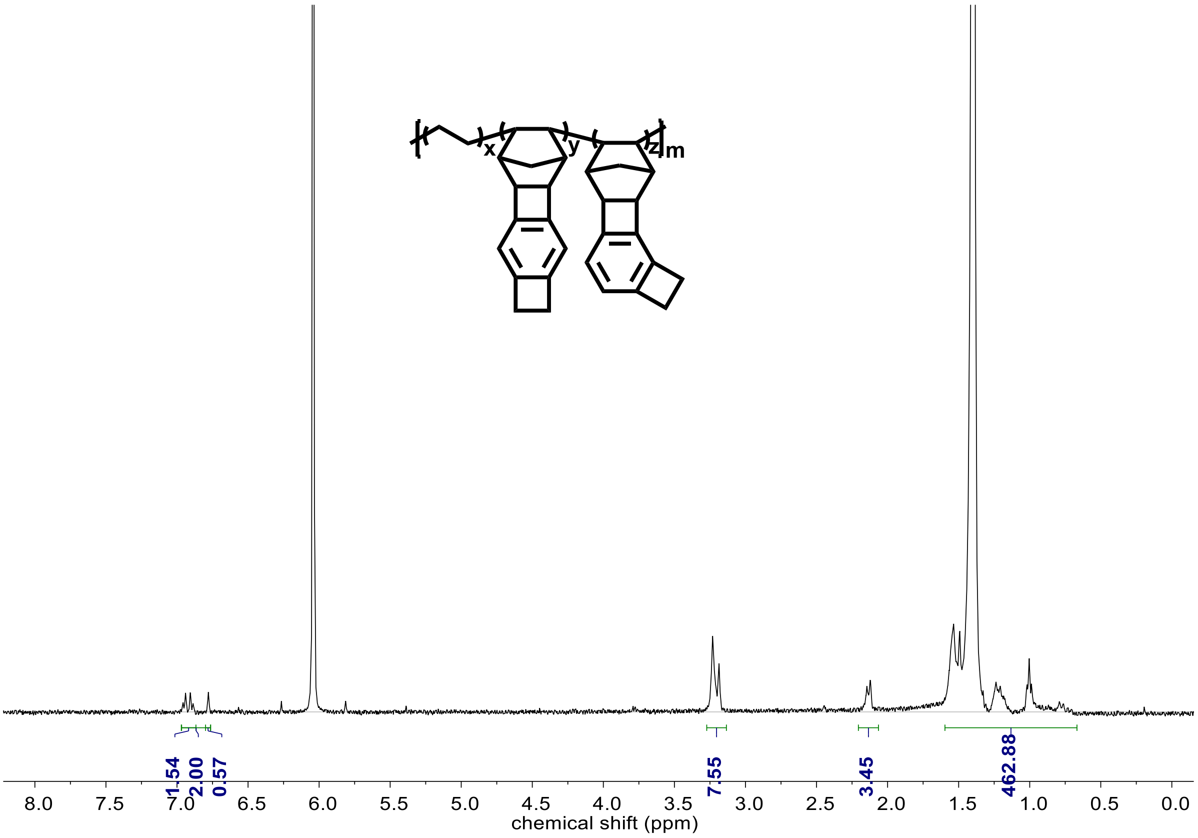


Figure S10. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of **PEb** from table 2, entry 1.

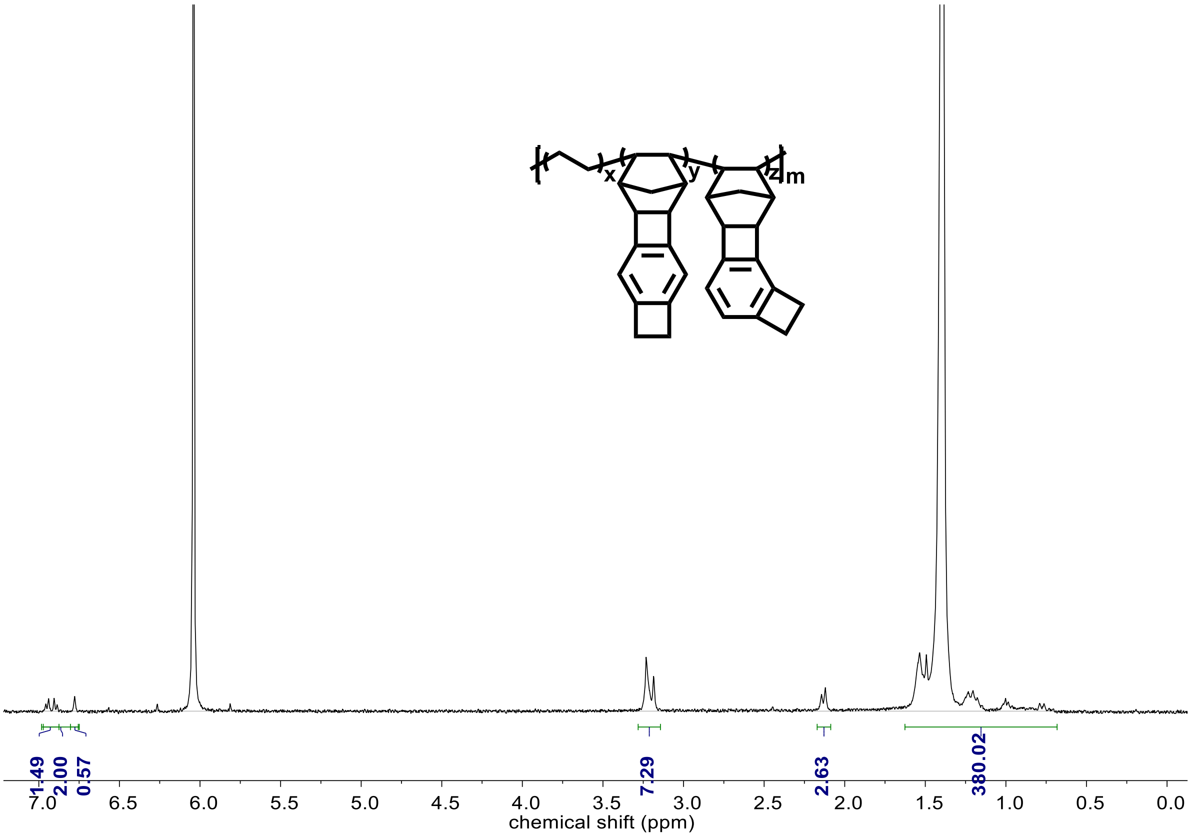


Figure S11. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of **PEb** from table 2, entry 2.

$$X_{\mathrm{M1}} = \frac{1}{1+\frac{I_{0.66-1.59}-4}{4}} \times 100\% = \frac{1}{1+\frac{380.02-4}{4}} \times 100\% = 1.05\%$$

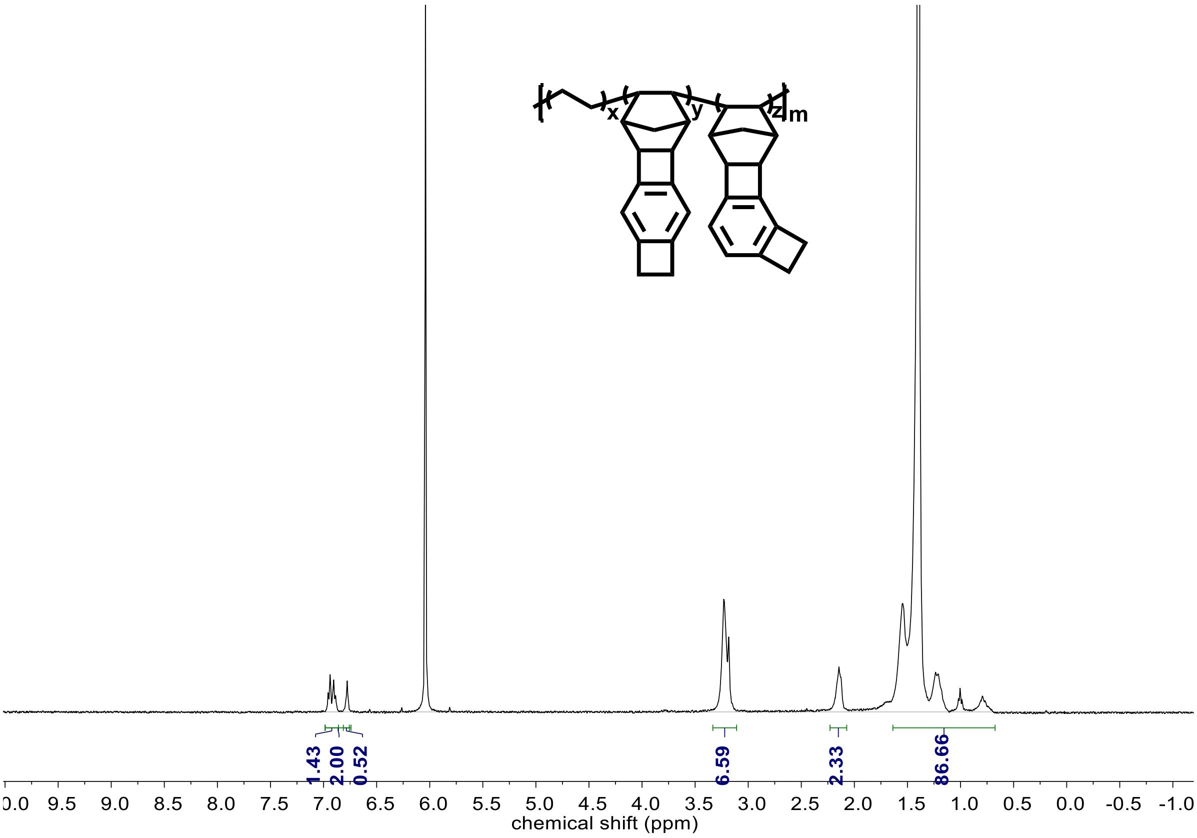


Figure S12. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of **PEb** from table 2, entry 3.

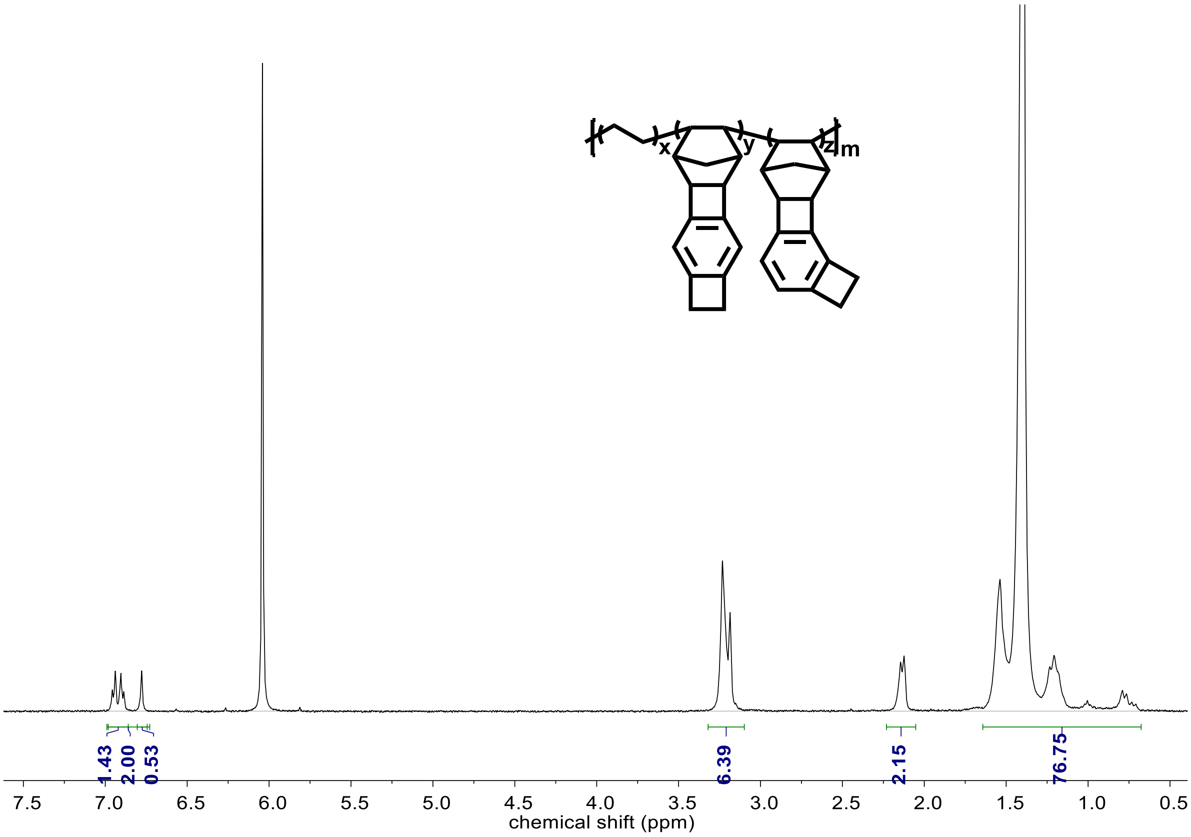


Figure S13. ^1H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of **PEb** from table 2, entry 4.

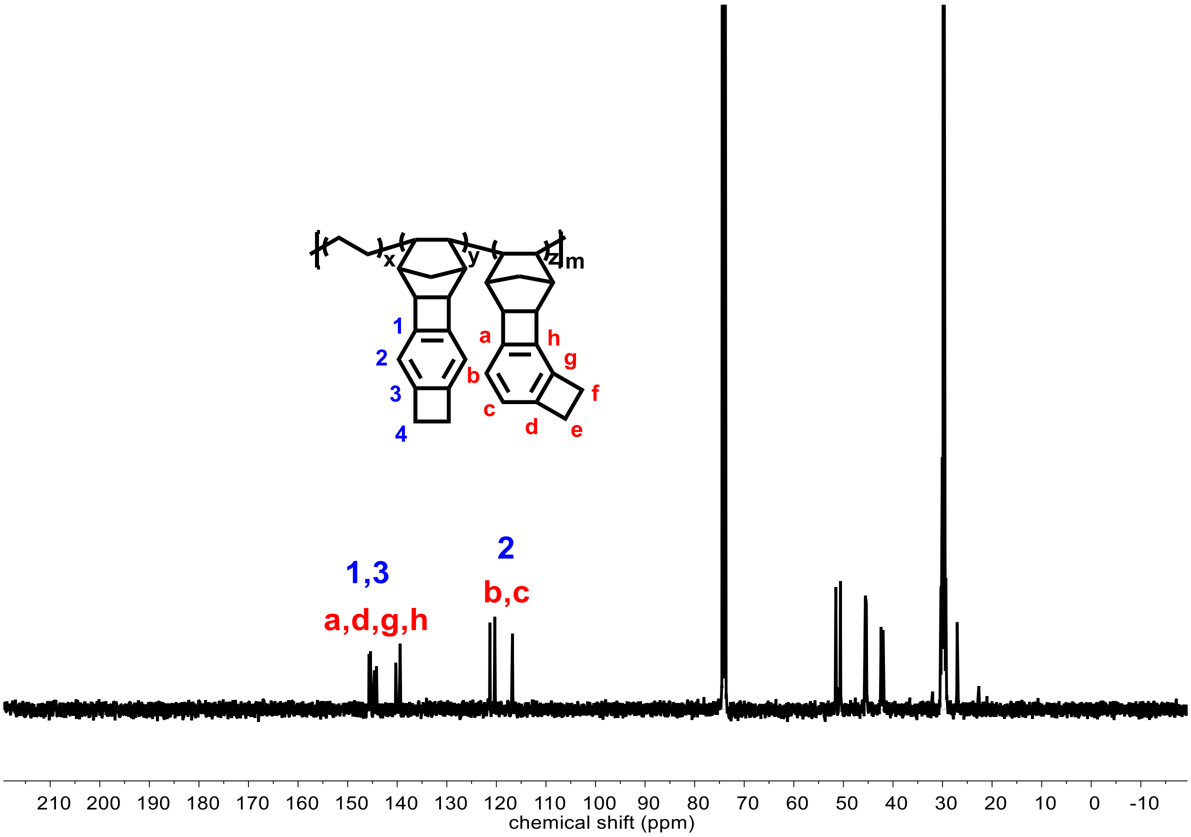
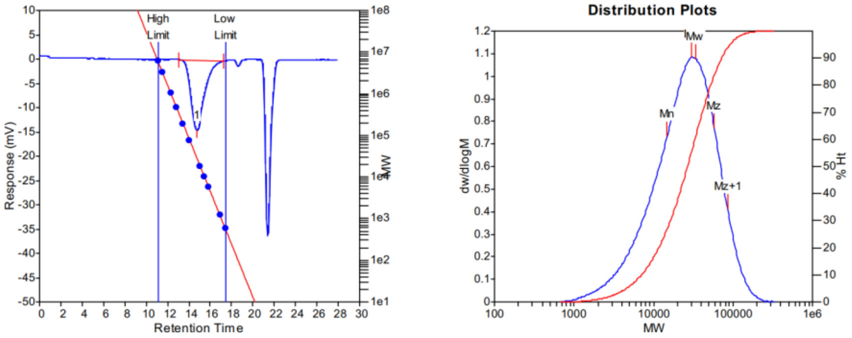


Figure S14. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 110 °C) of **PEb** from table 2, entry 4.

8. GPC Figures of Polymers



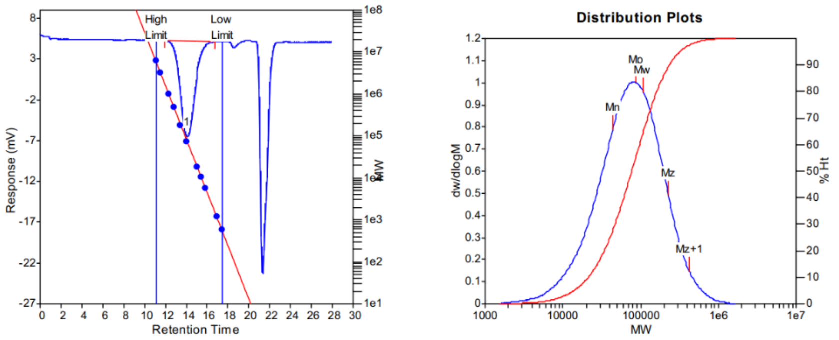
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30003	14899	34150	58424	85547	30749	2.2921

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.08	14.72	17.30	-14.3486	100	1247.85	100

Figure S15. GPC trace of **PEb** from table 2, entry 1. (TCB, 150 °C)



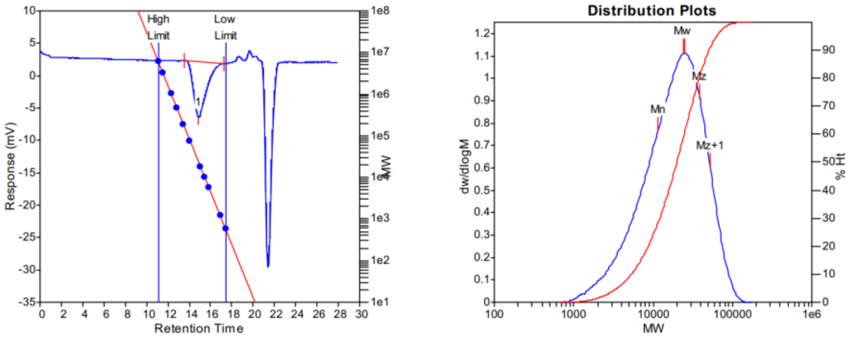
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	85824	43590	109641	228791	421317	96207	2.51528

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.98	14.00	16.73	-11.7407	100	1101.16	100

Figure S16. GPC trace of **PEb** from table 2, entry 2. (TCB, 150 °C)



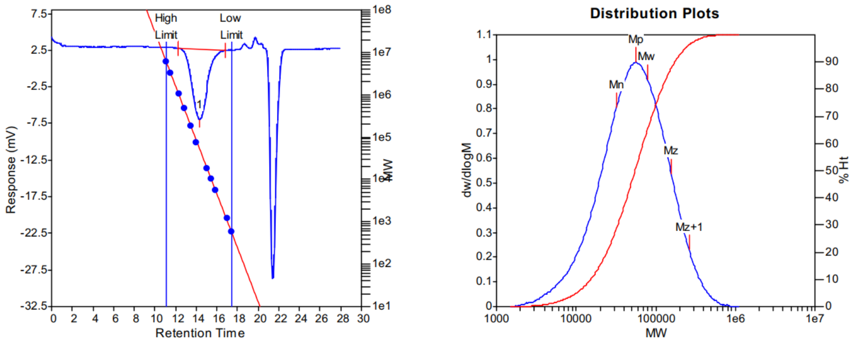
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25285	11452	24437	39038	52668	22225	2.13386

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.50	14.83	17.30	-8.58145	100	727.014	100

Figure S17. GPC trace of **PEb** from table 2, entry 3. (TCB, 150 °C)



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56644	32024	78798	157450	262677	69293	2.46059

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.27	14.28	16.77	-9.60272	100	914.892	100

Figure S18. GPC trace of **PEb** from table 2, entry 4. (TCB, 150 °C)

9. DSC Figures of Polymers

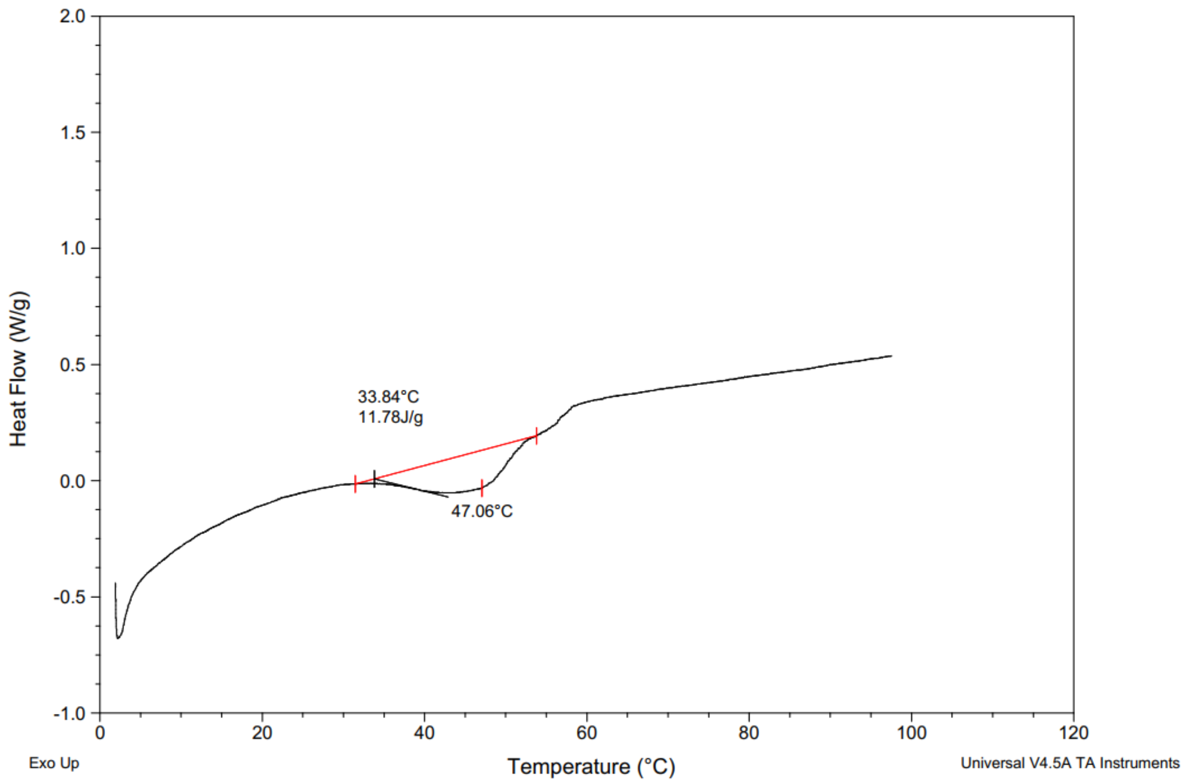


Figure S19. DSC data of Pre-**PEa** from table 1, entry 1.

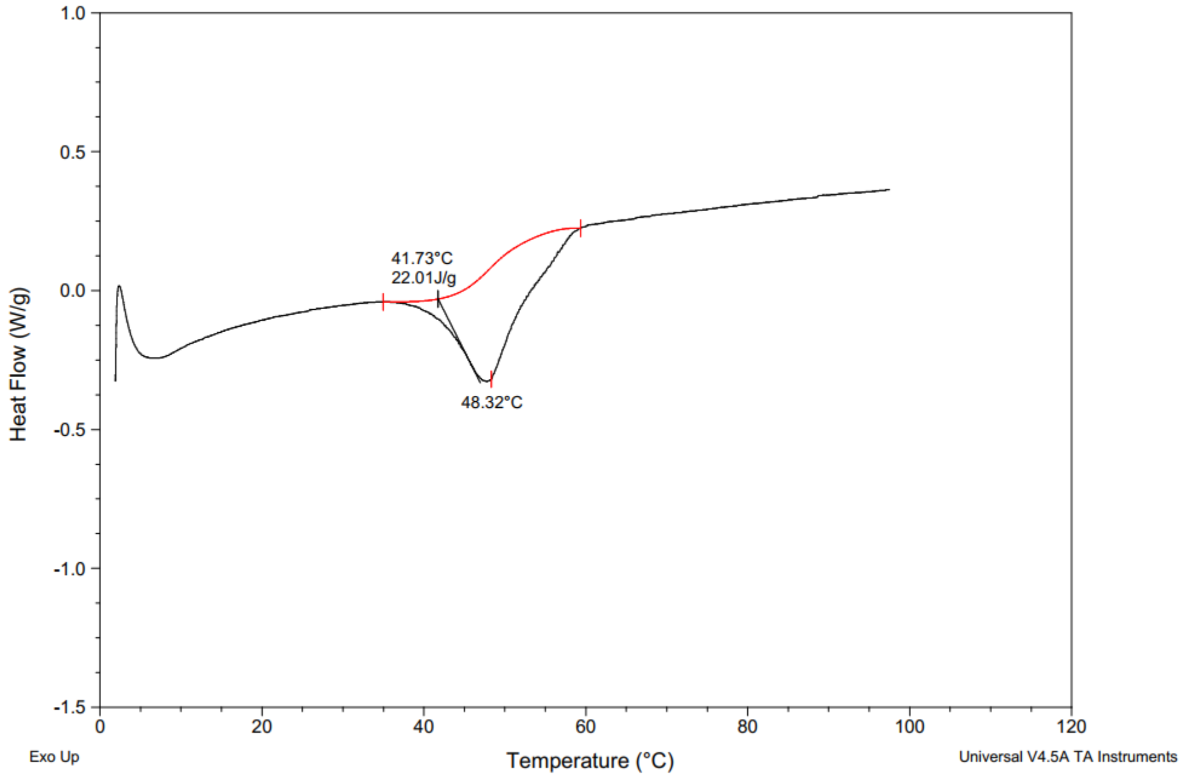


Figure S20. DSC data of Pre-**PEa** from table 1, entry 2.

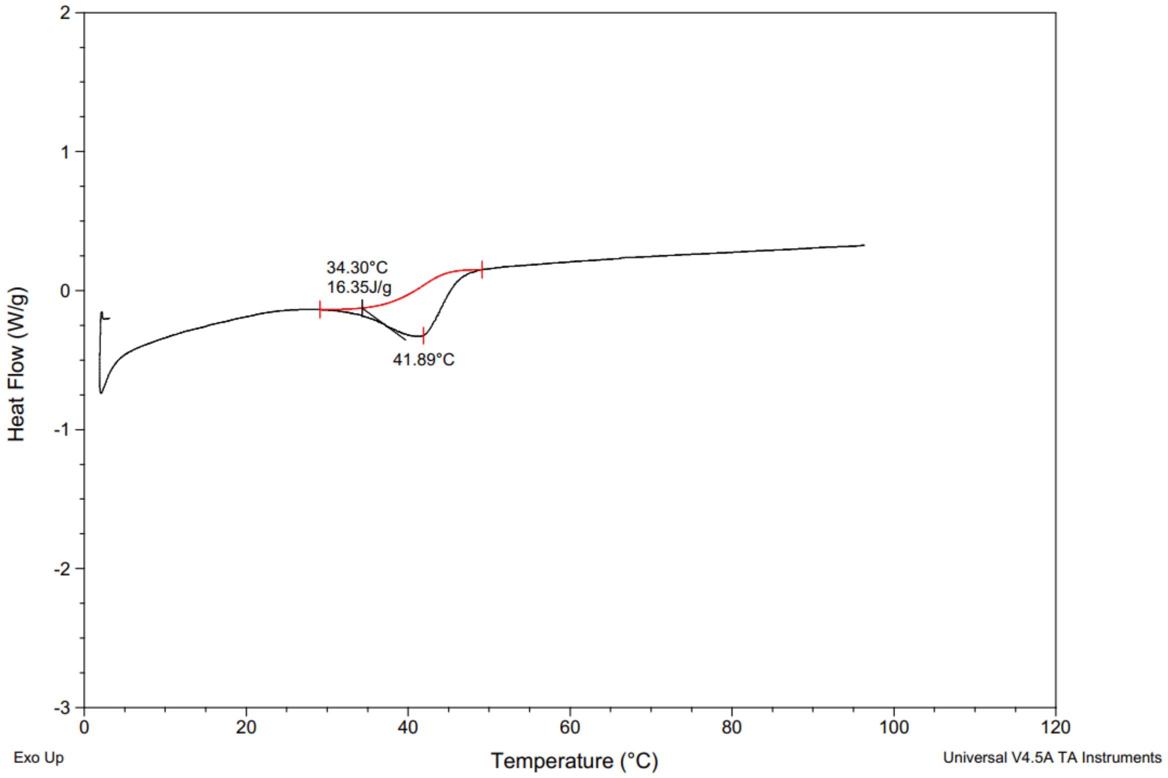


Figure S21. DSC data of Pre-**PEa** from table 1, entry 3.

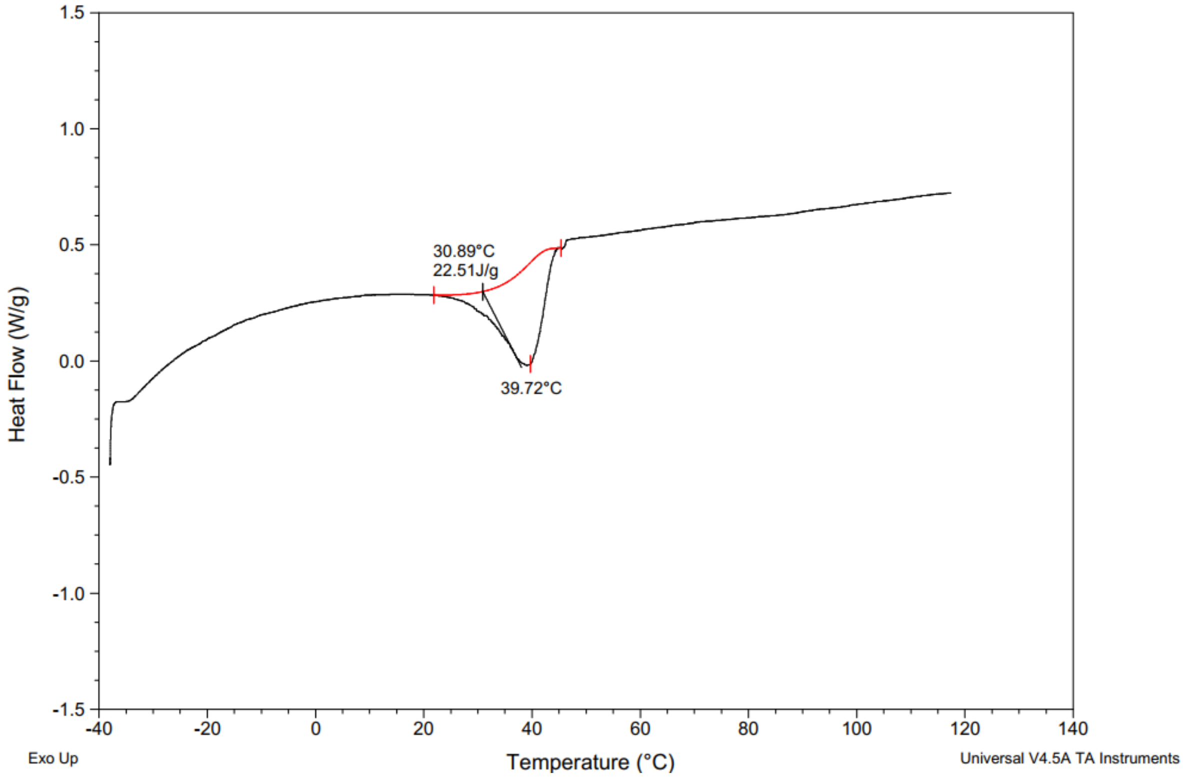


Figure S22. DSC data of Pre-**PEa** from table 1, entry 4.

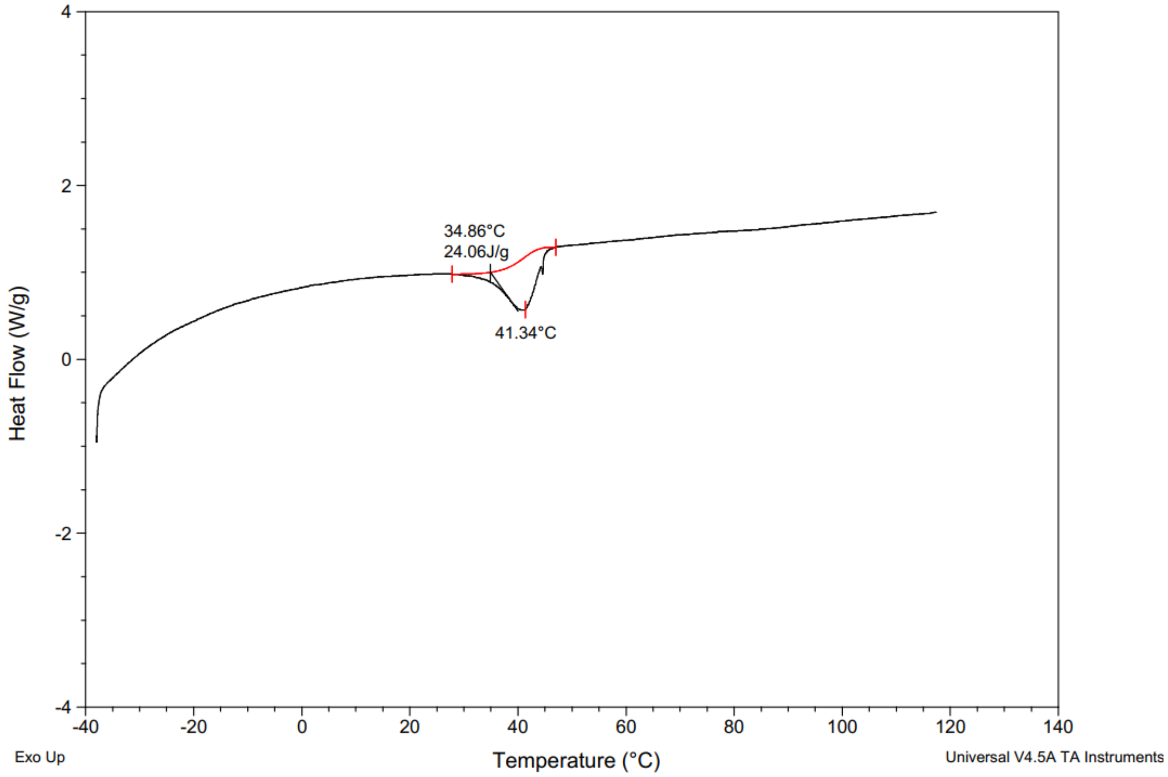


Figure S23. DSC data of Pre-**PEa** from table 1, entry 5.

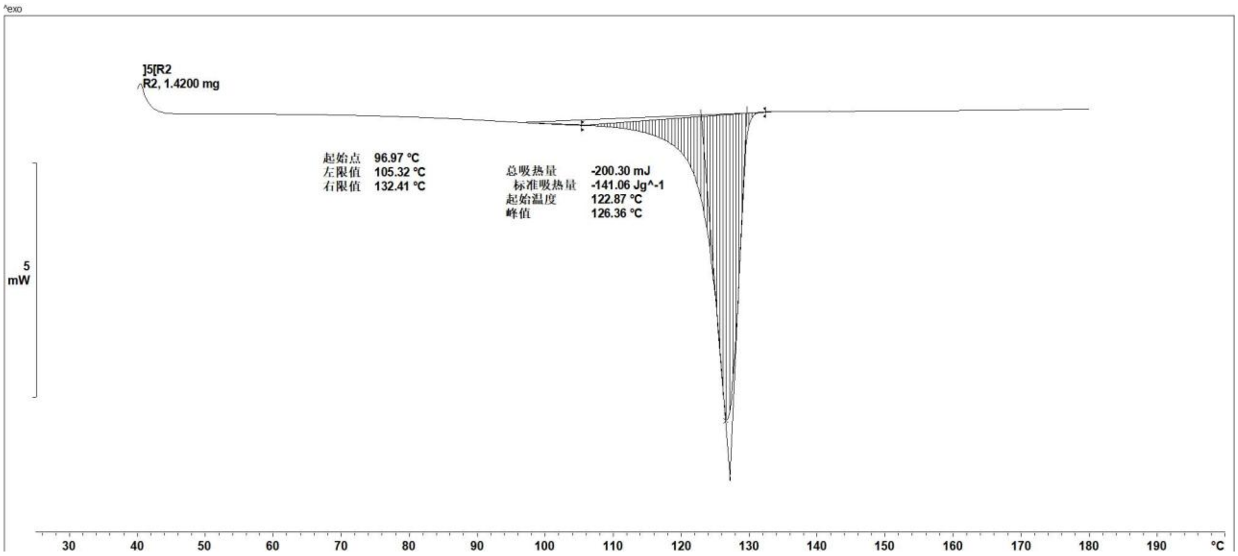


Figure S24. DSC data (second heating) of **PEb** from table 2, entry 1.

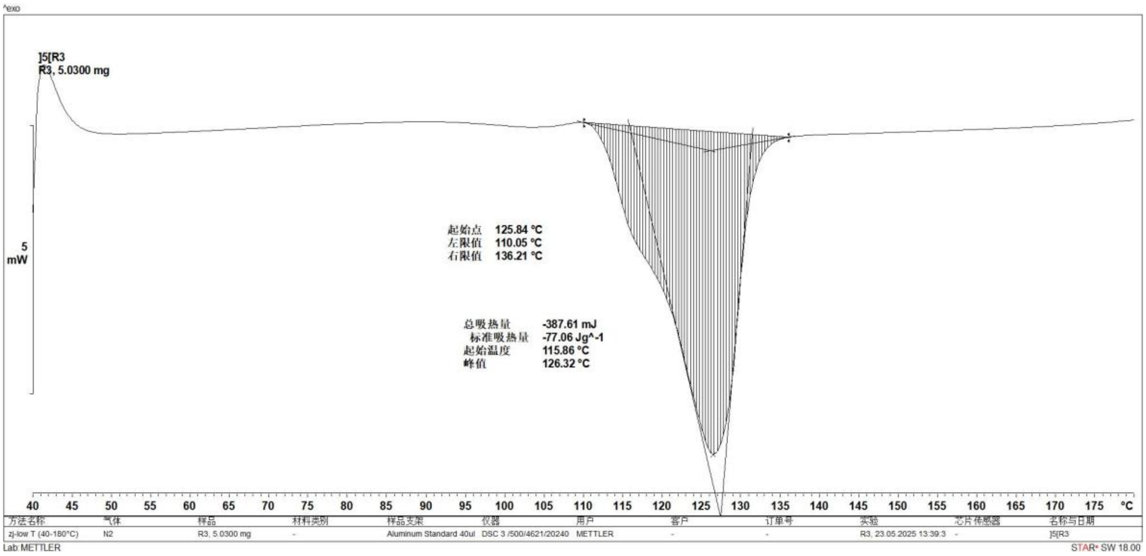


Figure S25. DSC data (second heating) of **PEb** from table 2, entry 2.

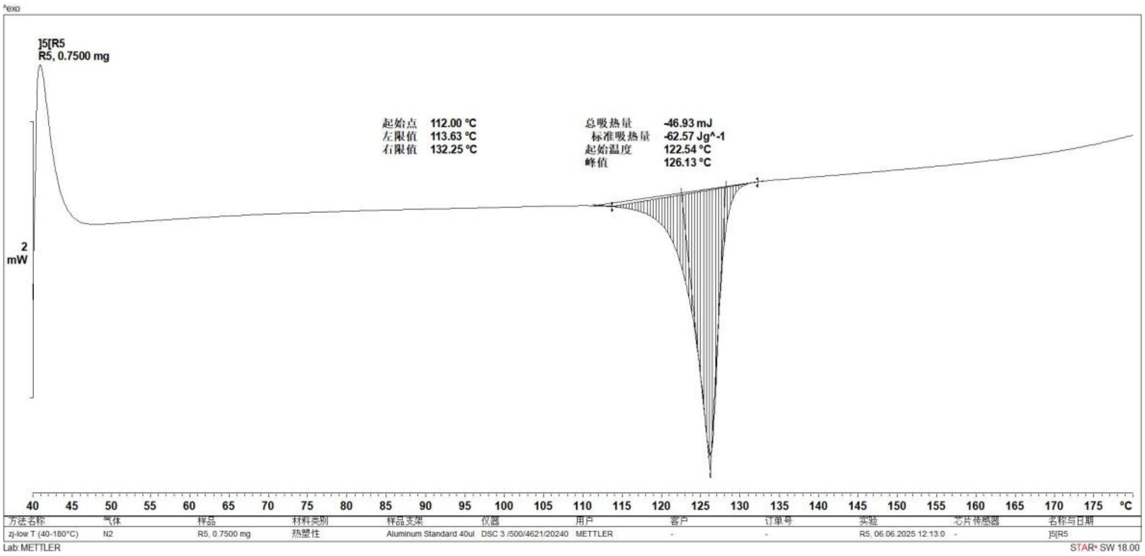


Figure S26. DSC data (second heating) of **PEb** from table 2, entry 3.

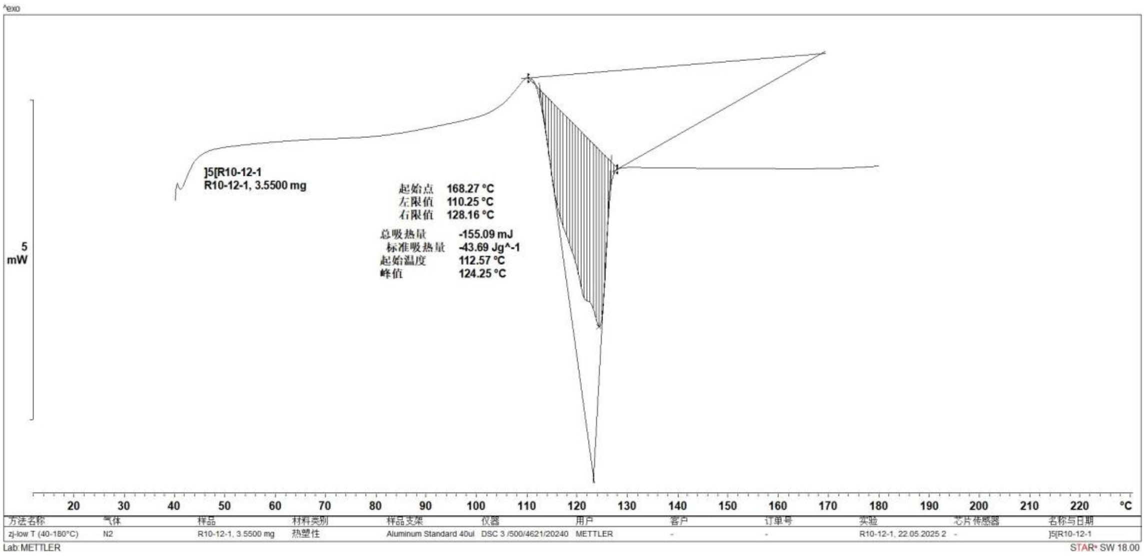


Figure S27. DSC data of **PEb (**second heating**)** from table 2, entry 4.

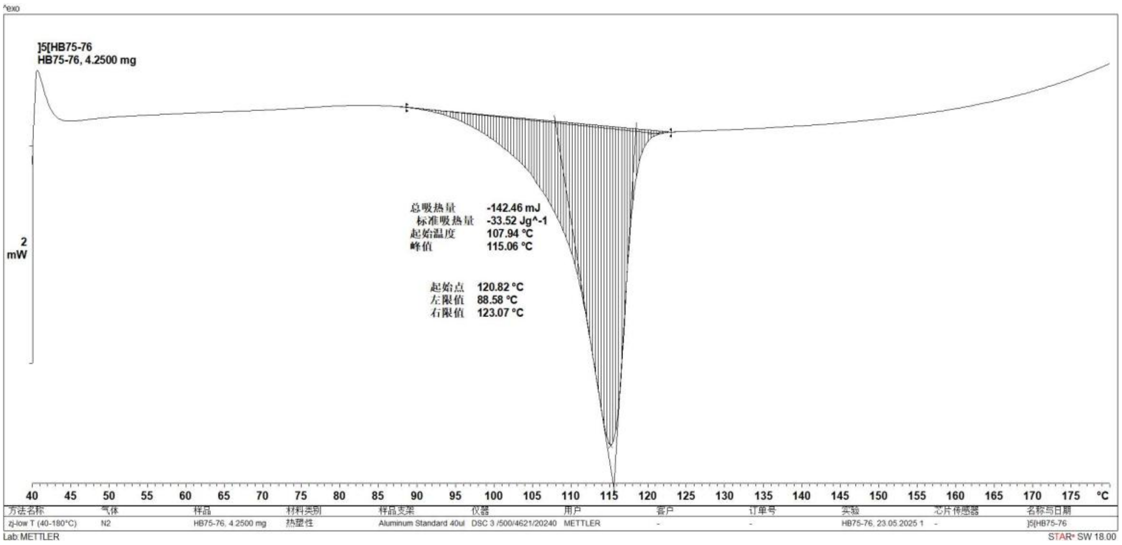


Figure S28. DSC data (second heating) of **PEa** from table 1, entry 1.

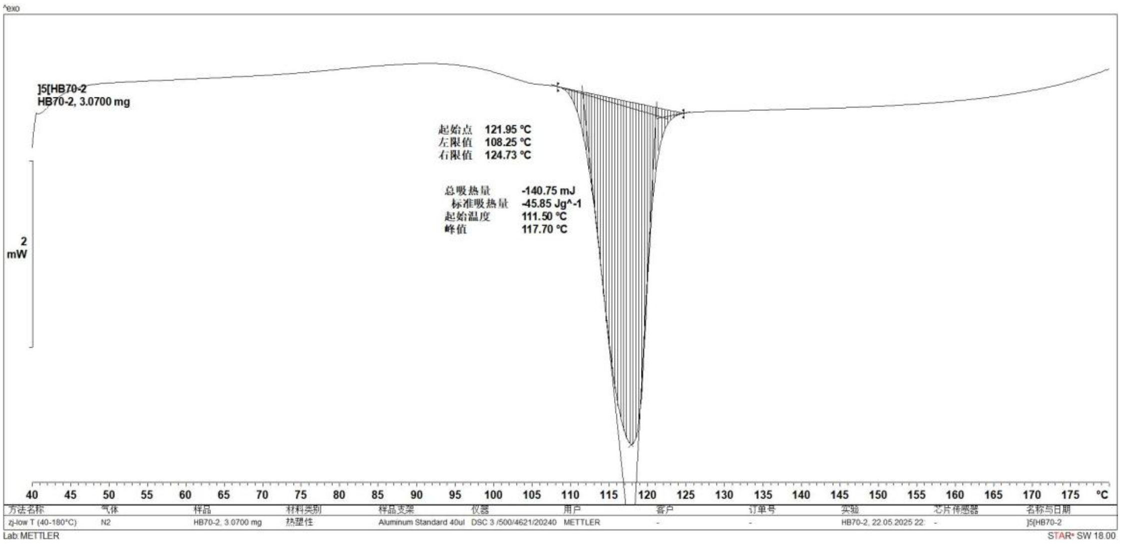


Figure S29. DSC data (second heating) of **PEa** from table 1, entry 2.

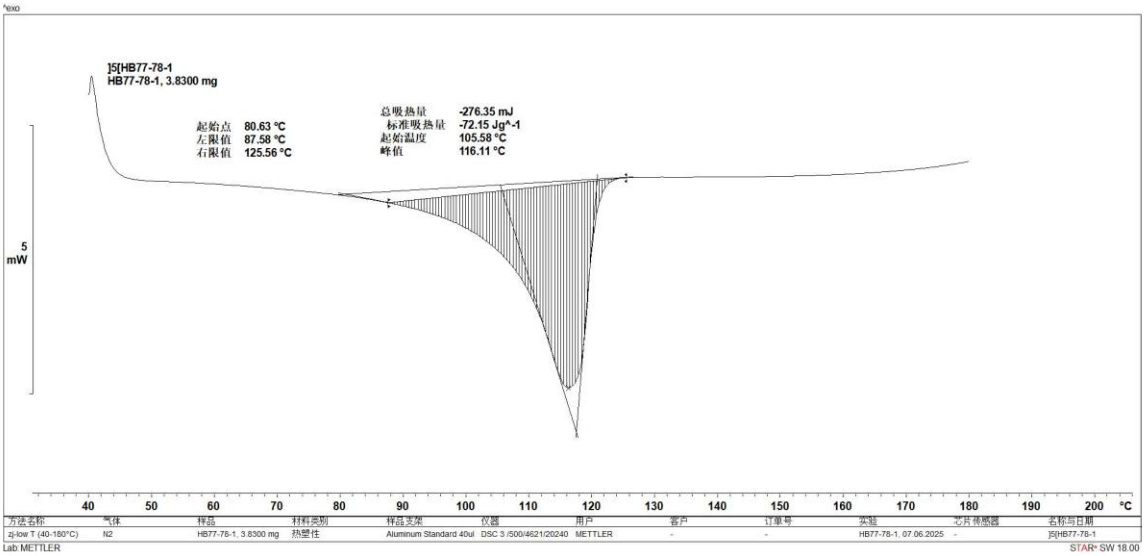


Figure S30. DSC data (second heating) of **PEa** from table 1, entry 3.

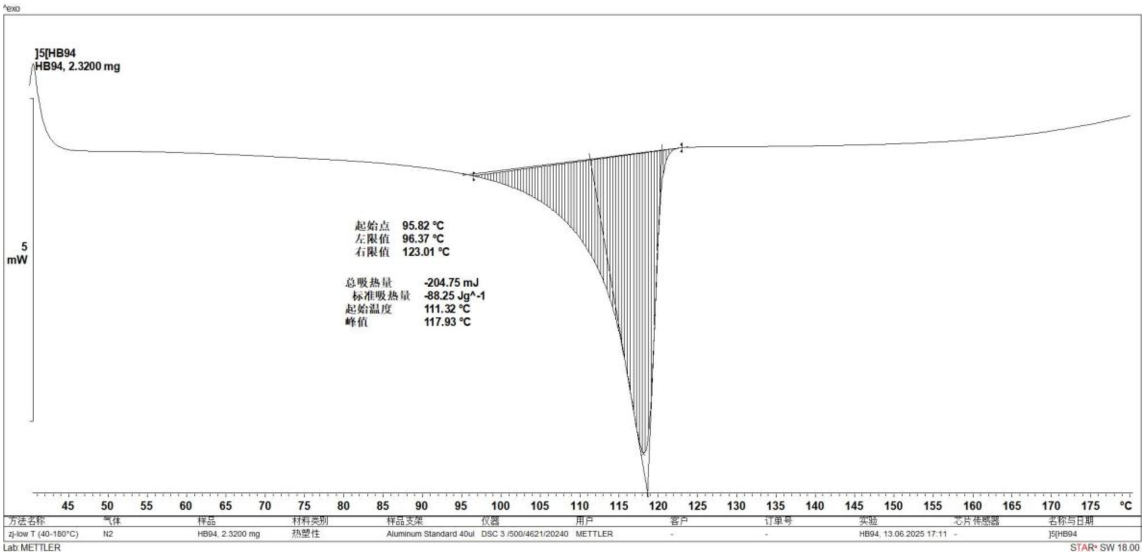


Figure S31. DSC data (second heating) of **PEa** from table 1, entry 4.

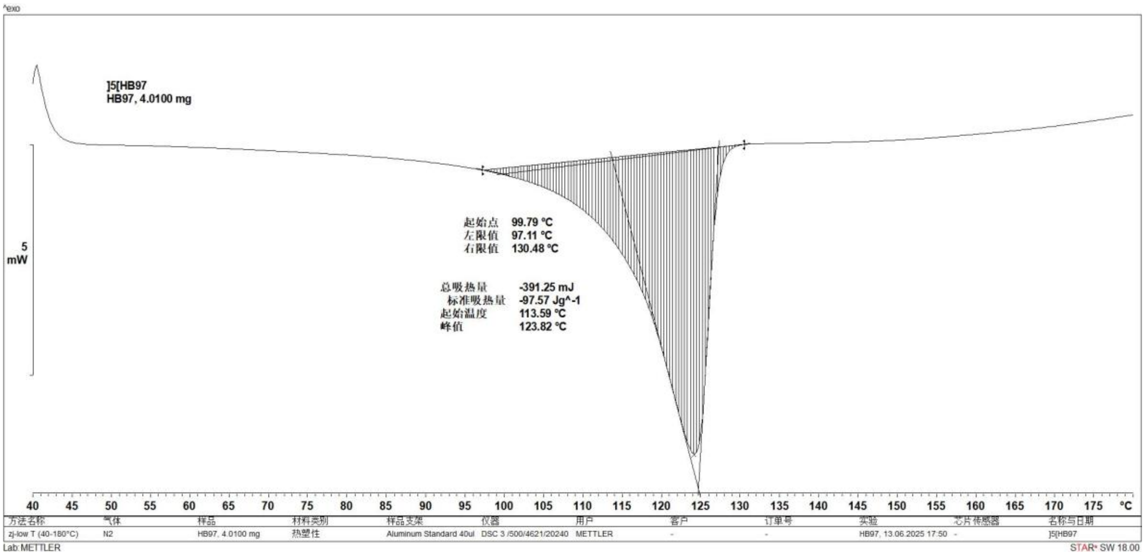


Figure S32. DSC data (second heating) of **PEa** from table 1, entry 5.

10. FT-IR spectra of polymers before and after cross-linking

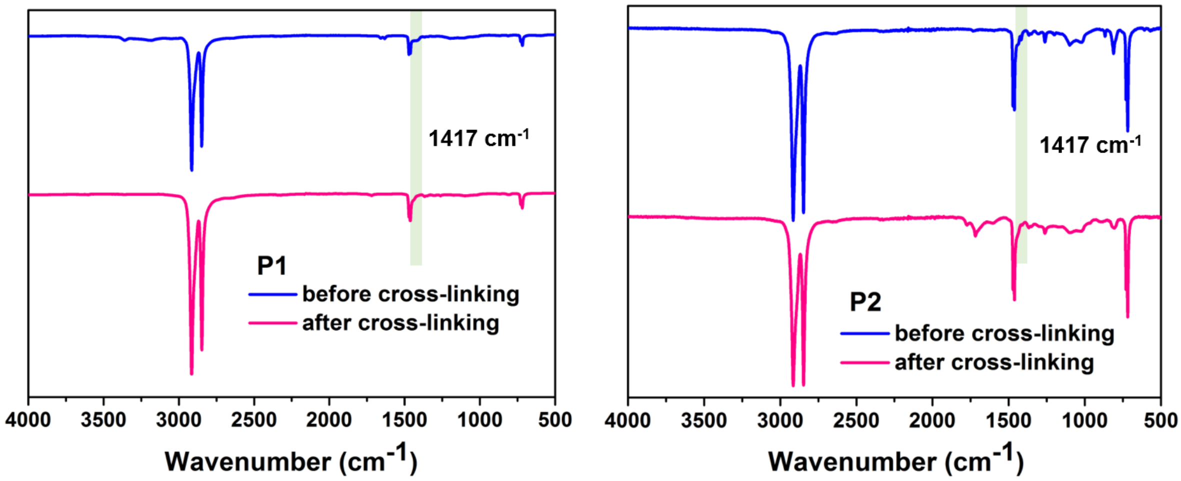


Figure S33. FT-IR spectra of **P1** and **P2** before and after cross-linking.

11. Optical properties of cross-linked polymers

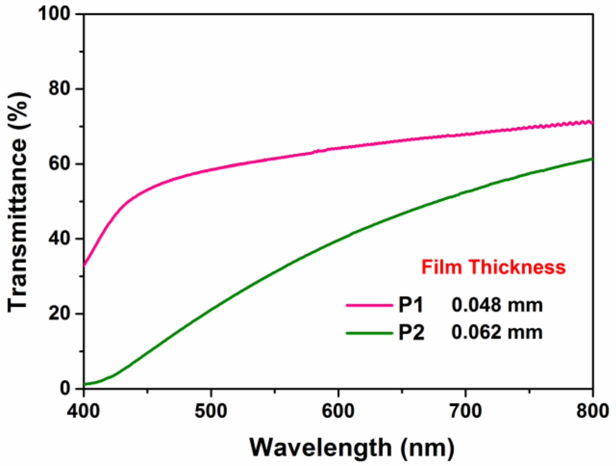


Figure S34. Optical transmittance of **P1** and **P2** at the range of 400-800 nm.

Table S4. Optical properties of **P1** and **P2**

Sample	Transmittance[a] (800 nm, %)	n_D[b] (589 nm)	n_F[b] (486 nm)	n_C[b] (656 nm)	Abbe number[b]
P1	71	1.5397	1.5442	1.5347	56.8
P2	61	1.5557	1.5645	1.5523	45.5

[a] Transmittance at 800 nm. [b] Determined by Abbe refractometer.

12. Table S5. Metal residue and dielectric properties of P1 and P2

Sample	Metal residue	BCB content (mol%)	D_k[a]	D_f[a]
P1	Ru (2.6 ppm)	2.1	2.27	0.0017
P2	Zr (3.6 ppm), Al (20.5 ppm)	5.2	2.40	0.0014

[a] Dielectric properties at a frequency of 10GHz.

13. Stress-strain curves of polymers

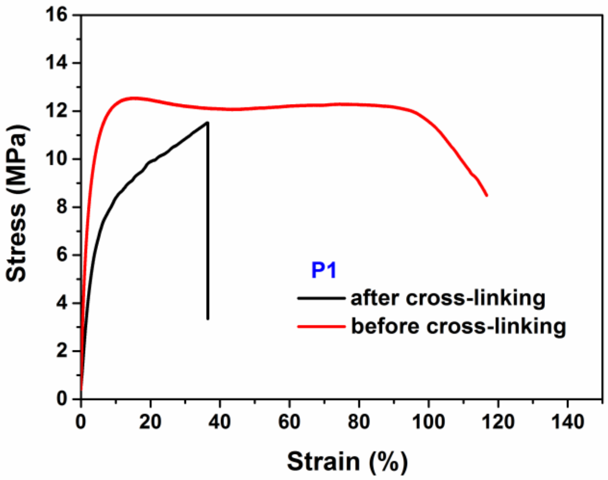


Figure S35. Stress-strain curves of **P1** before and after cross-linking

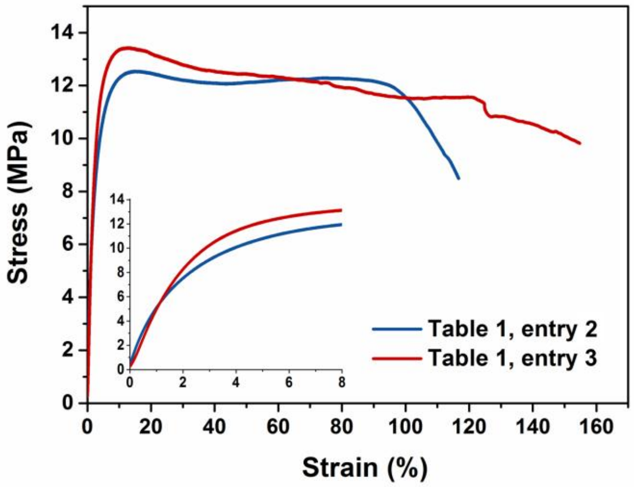


Figure S36. Stress-strain curves of copolymers in table 1, entries 2-3.

14. References

(1) L. Stieglitz, D. Henschel, T. Pehl and B. Rieger, *Organometallics*, 2021, **40**, 4055-4065.

(2) Walsh, D. J.; Lau, S. H.; Hyatt, M. G.; Guironnet, D., *J. Am. Chem. Soc.* 2017, **139**, 13644-13647.