Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Facile Synthesis of Hemiacetal Ester-based Dynamic Covalent Polymer Networks Combining Fast Reprocessability and High Performance

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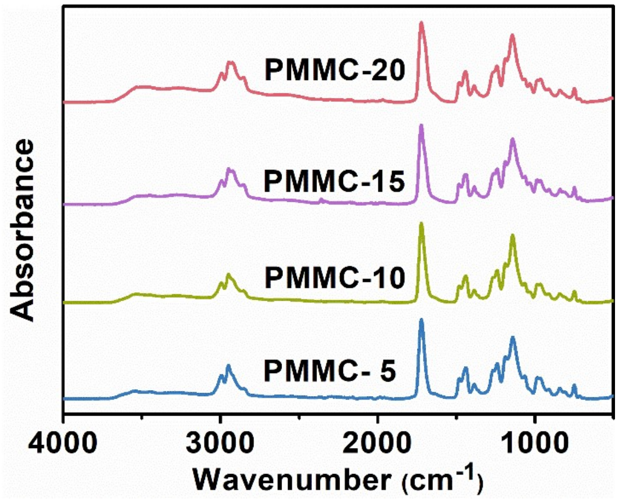


Fig. S1 FTIR spectra of PMMCs.

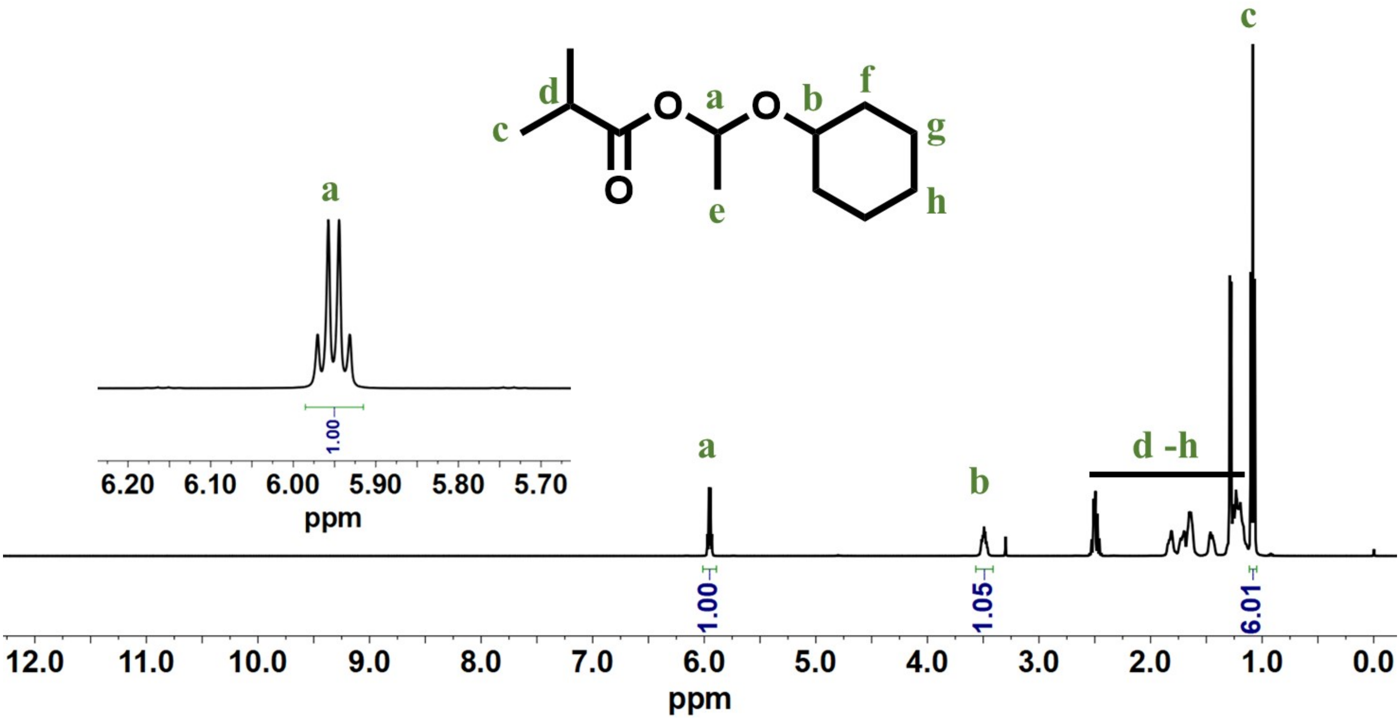


Fig. S2 ^{1}H NMR spectrum of IBA-CVE.

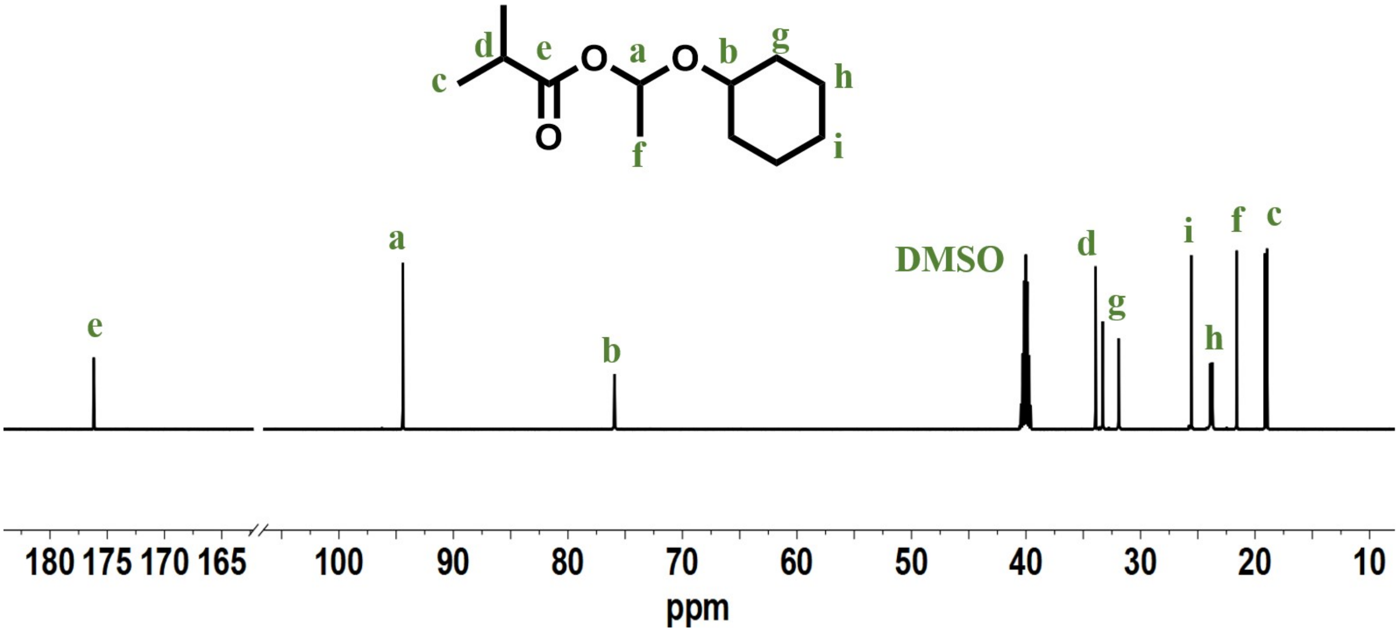


Fig. S3 ^{13}C NMR spectrum of IBA-CVE.

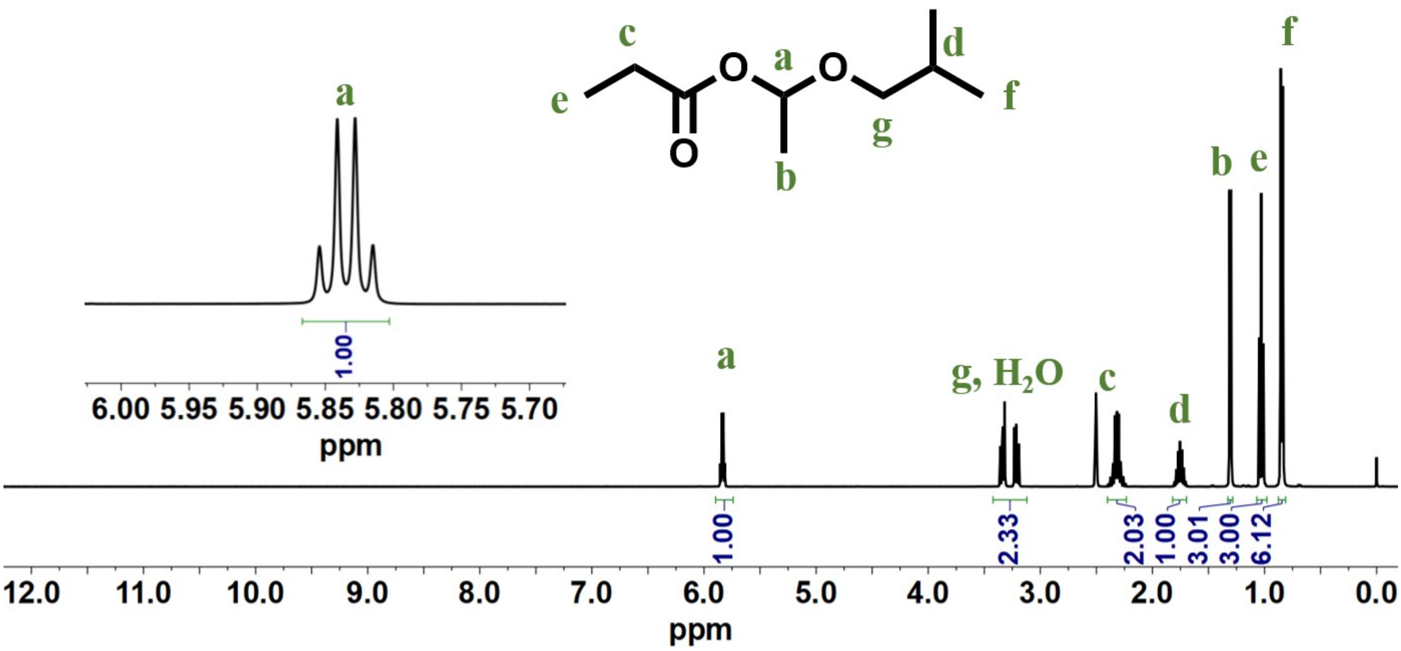


Fig. S4 ^{1}H NMR spectrum of PPA-IVE.

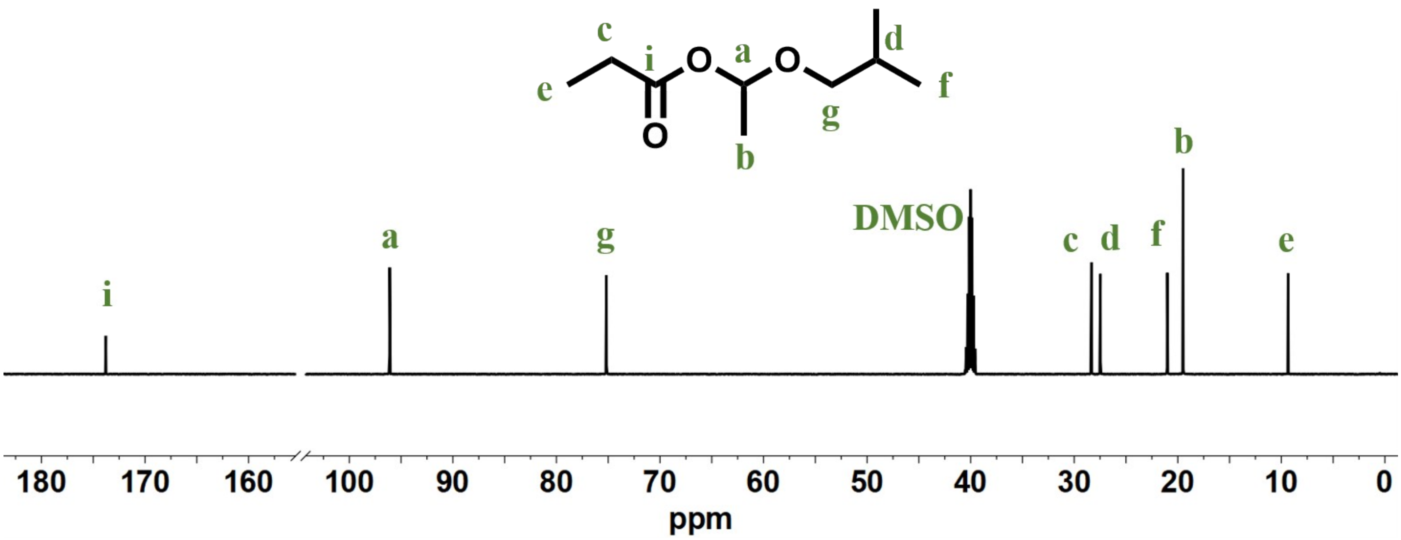


Fig. S5 ^{13}C NMR spectrum of PPA-IVE.

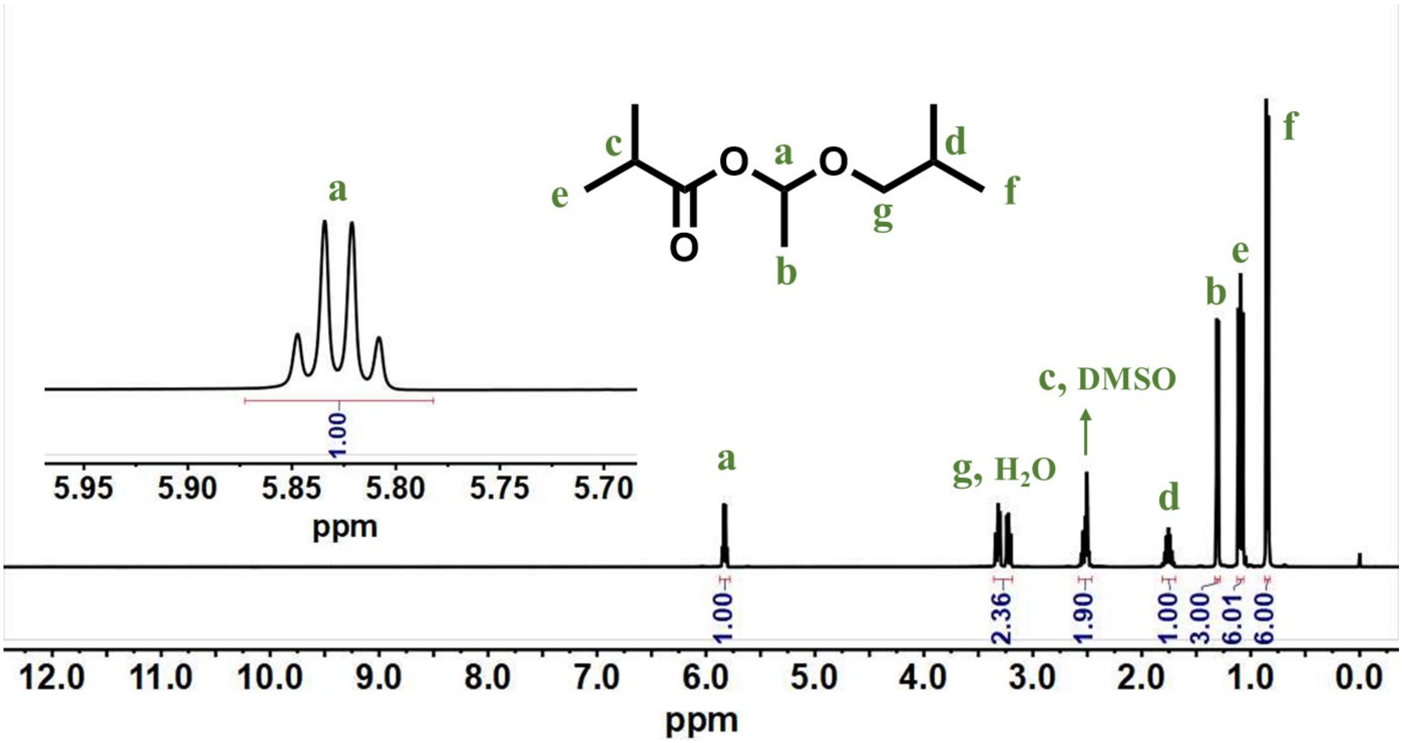


Fig. S6 ^{1}H NMR spectrum of IBA-IVE.

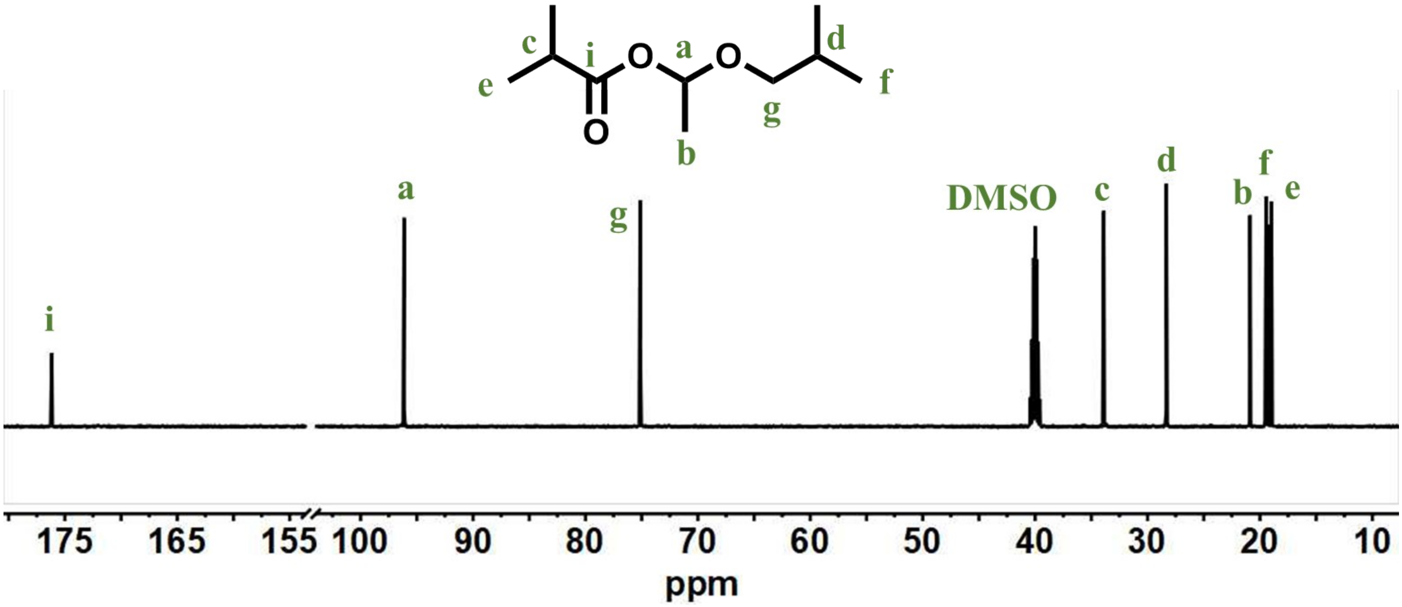


Fig. S7 ^{13}C NMR spectrum of IBA-IVE.

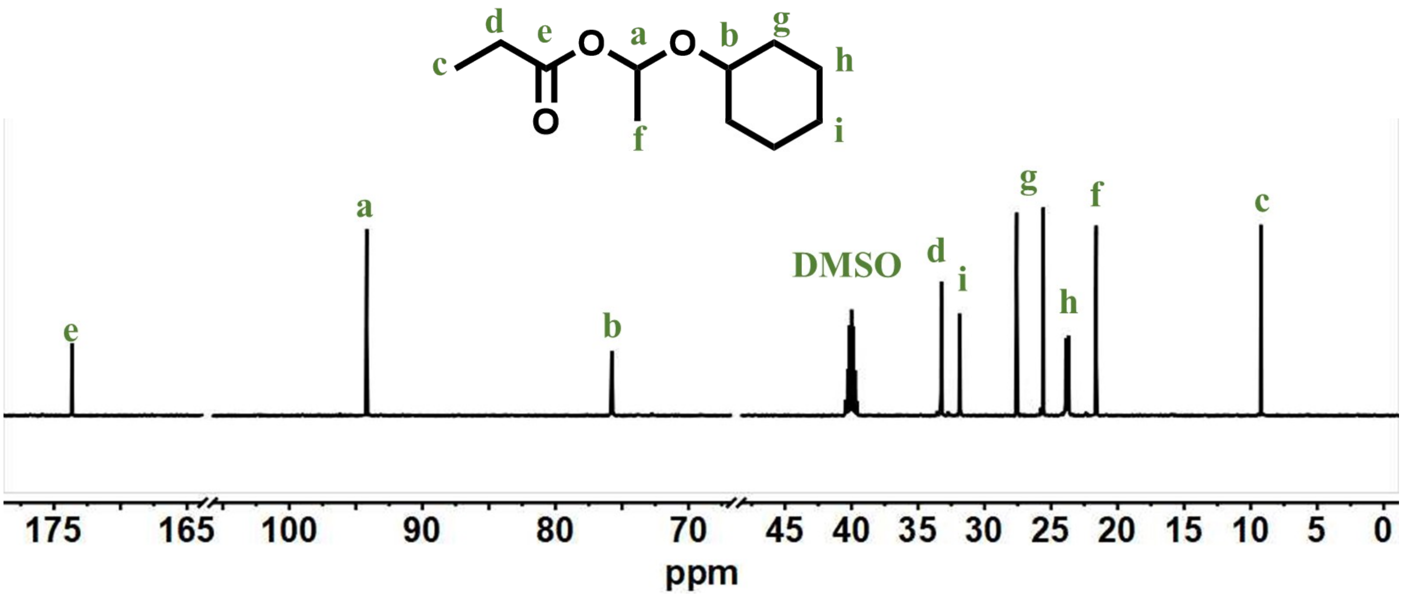


Fig. S8 ^{1}H NMR spectrum of PPA-CVE.

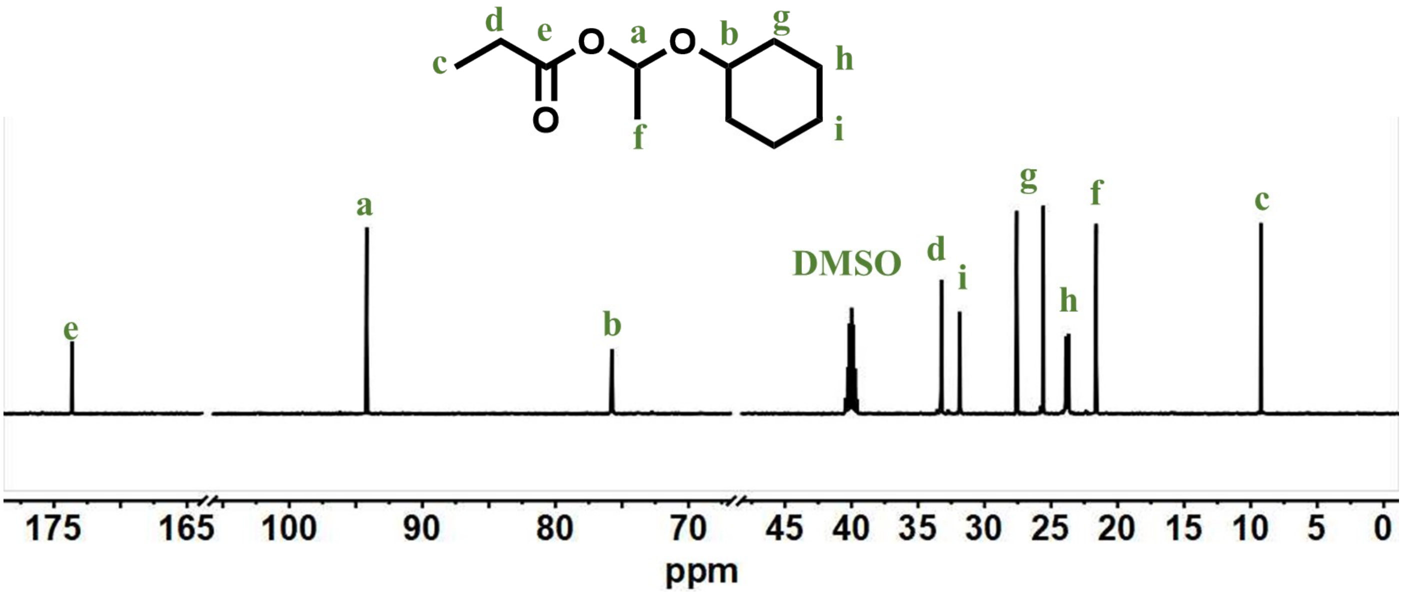


Fig. S9 [13]C NMR spectrum of PPA-CVE.

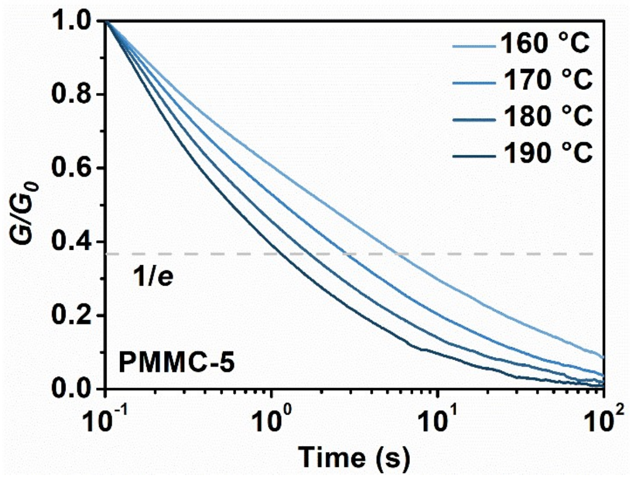


Fig. S10 Stress relaxation curves of PMMC-5 at different temperatures.

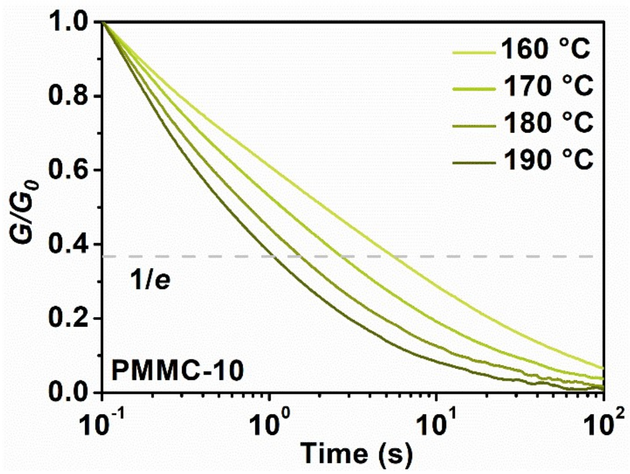


Fig. S11 Stress relaxation curves of PMMC-10 at different temperatures.

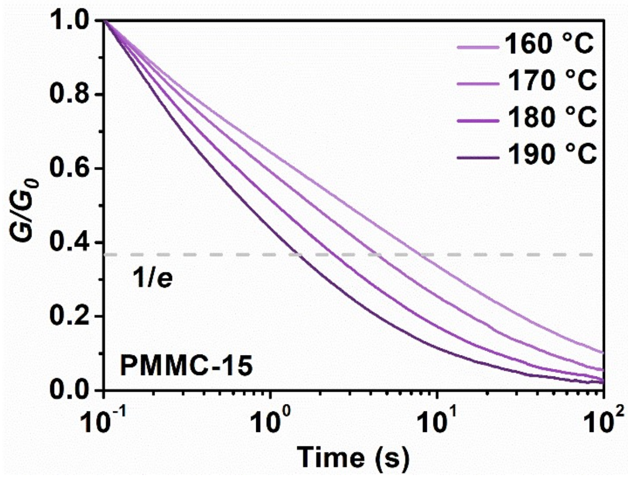


Fig. S12 Stress relaxation curves of PMMC-15 at different temperatures.

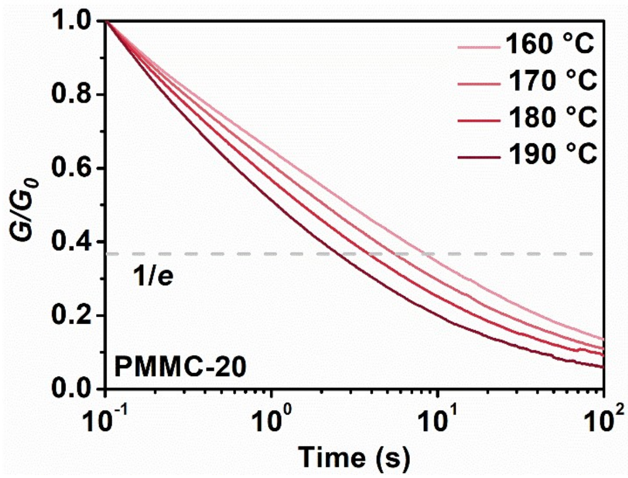


Fig. S13 Stress relaxation curves of PMMC-20 at different temperatures.

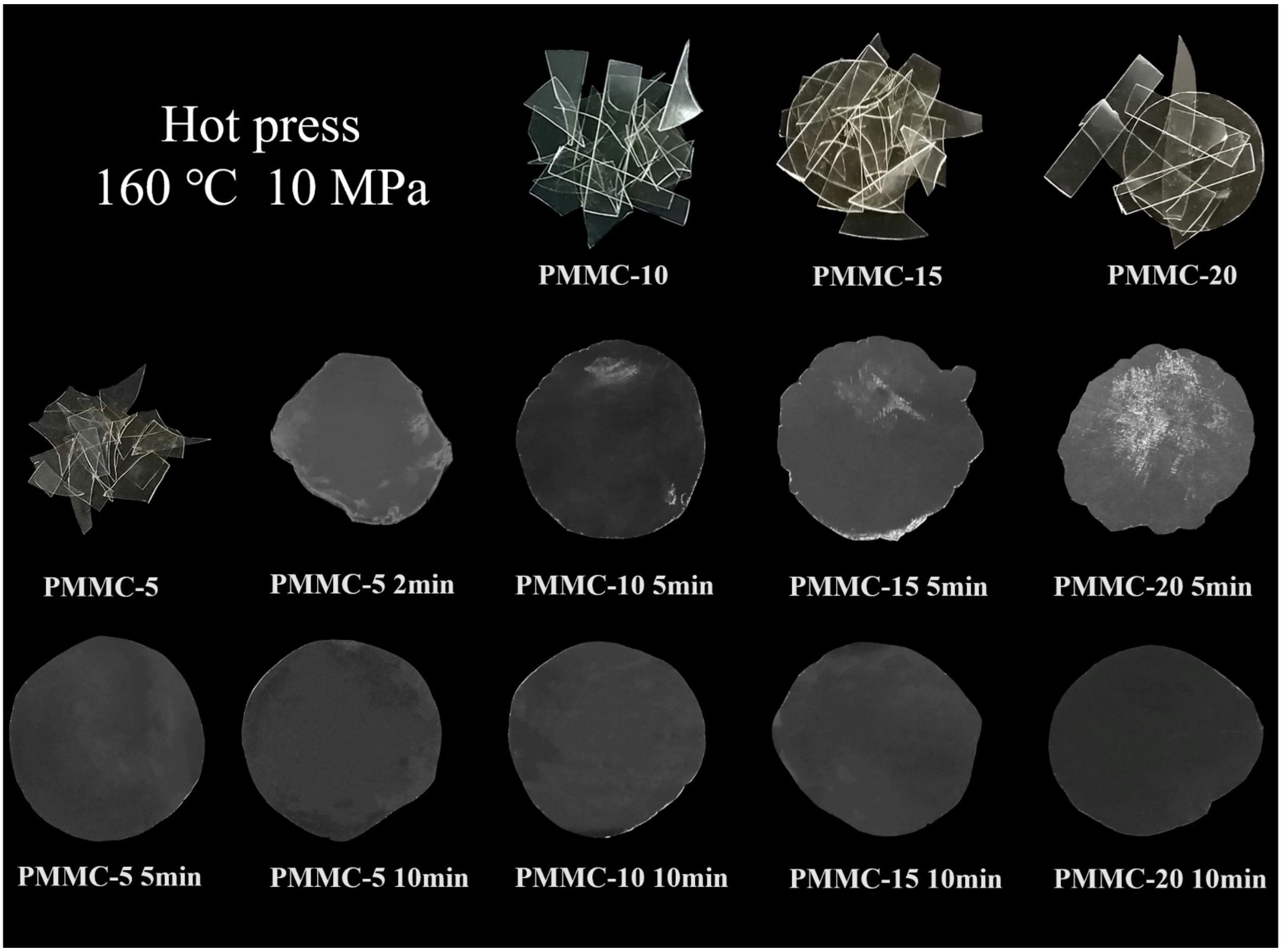


Fig. S14 Reprocess recycling through hot press with different time.

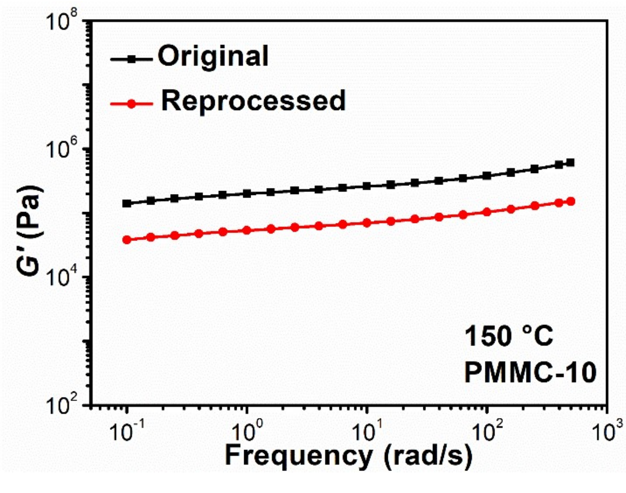


Fig. S15 Frequency sweep measurements at 150 °C of the original and reprocessed (compression remolded) PMMC-10.

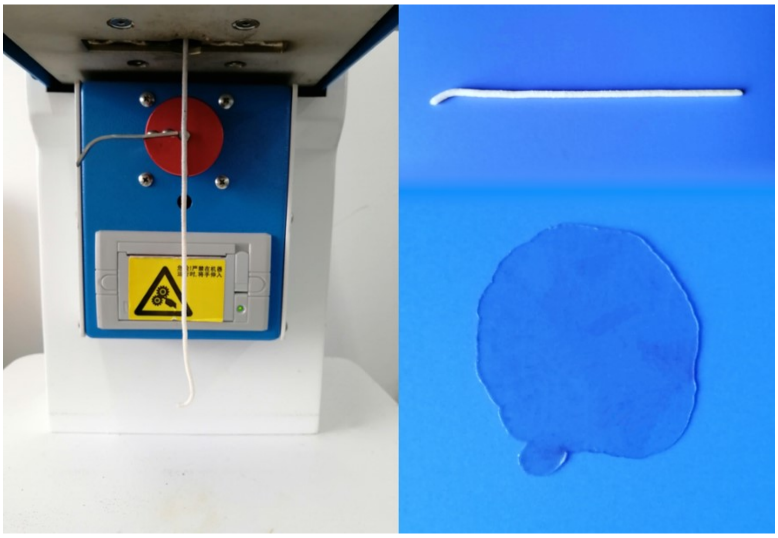


Fig. S16 Reprocess recycling through extrusion plastometer and hot press at 160 °C for 10 min.

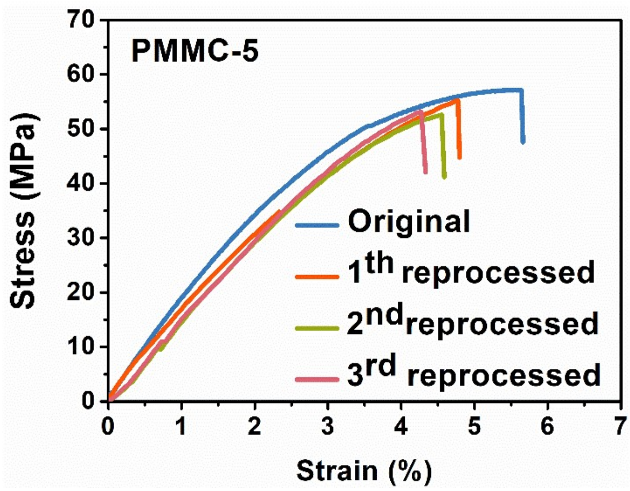


Fig. S17 Representative tensile stress-strain curves of the original and reprocessed PMMC-5.

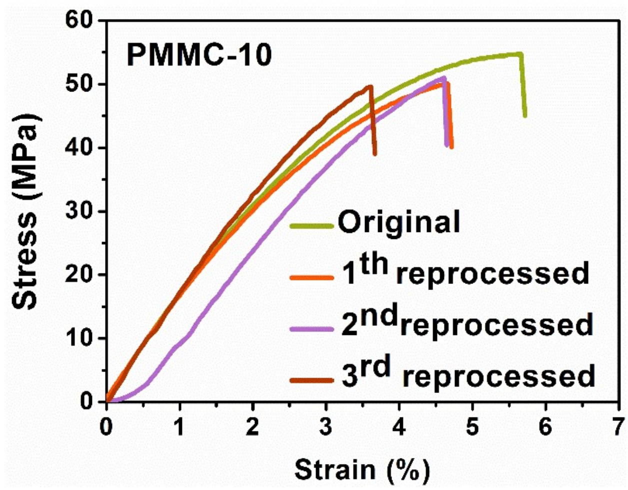


Fig. S18 Representative tensile stress-strain curves of the original and reprocessed PMMC-10.

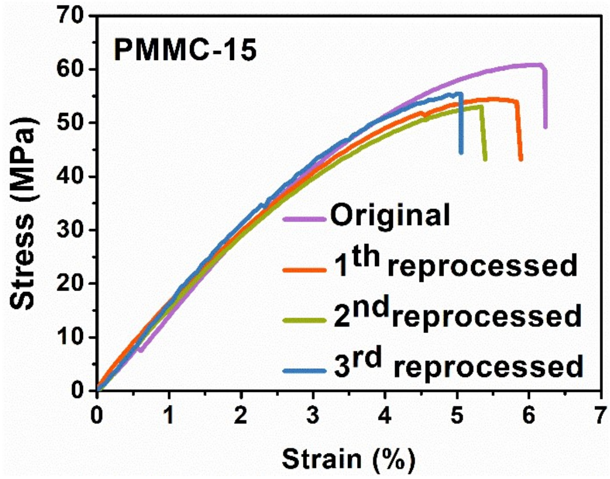


Fig. S19 Representative tensile stress-strain curves of the original and reprocessed PMMC-15.

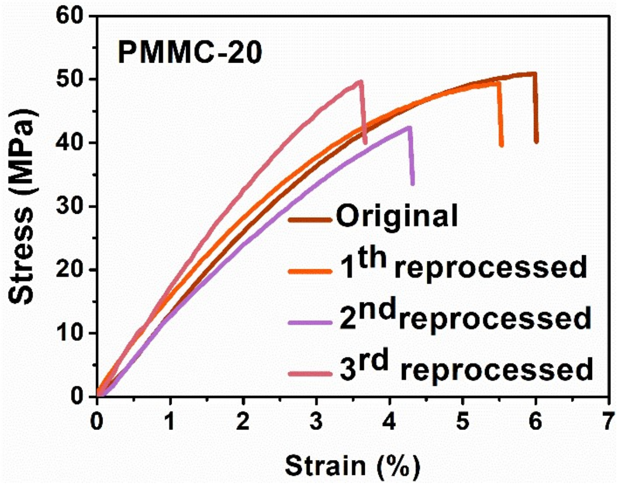


Fig. S20 Representative tensile stress-strain curves of the original and reprocessed PMMC-20.

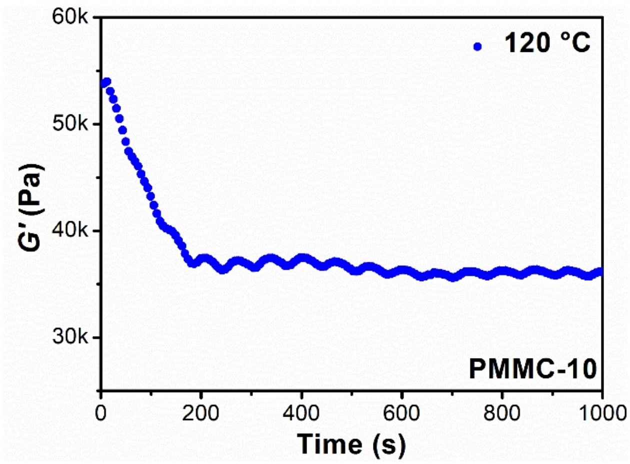


Fig. S21 Time sweep measurement at 120 ℃ of the PMMC-10.

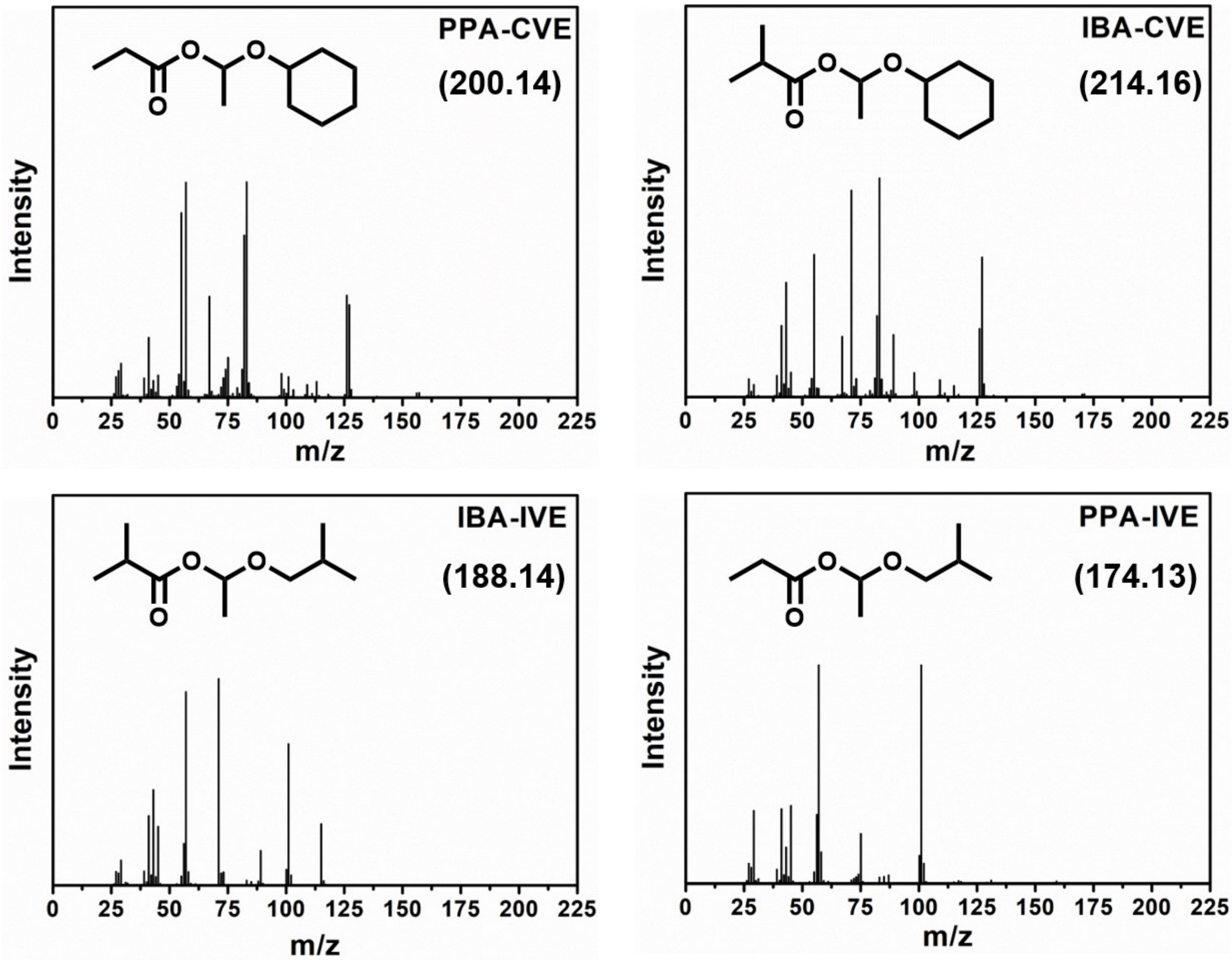


Fig. S22 Mass spectra of PPA-IVE, IBA-CVE, IBA-IVE, PPA-CVE.

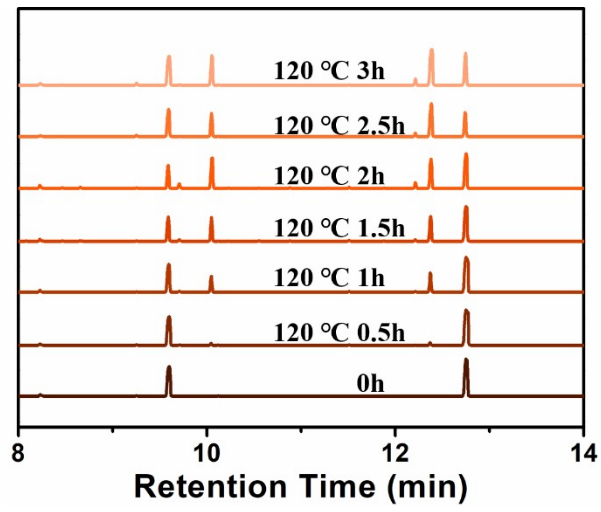


Fig. S23 Gas chromatograms of metathesis without PPA at 120 °C for different time.

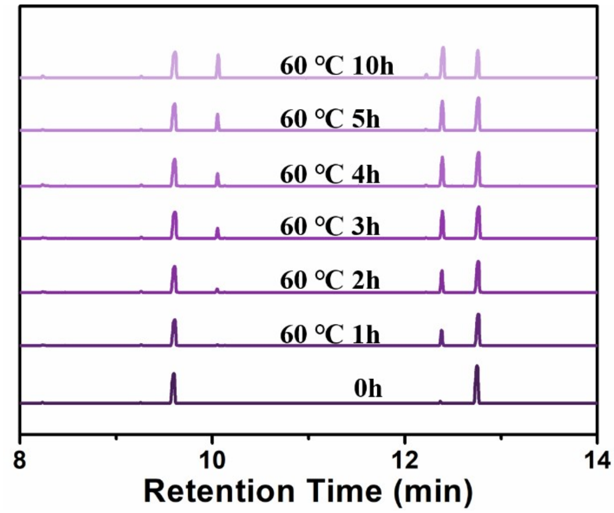


Fig. S24 Gas chromatograms of metathesis with PPA at 60 °C for different time.

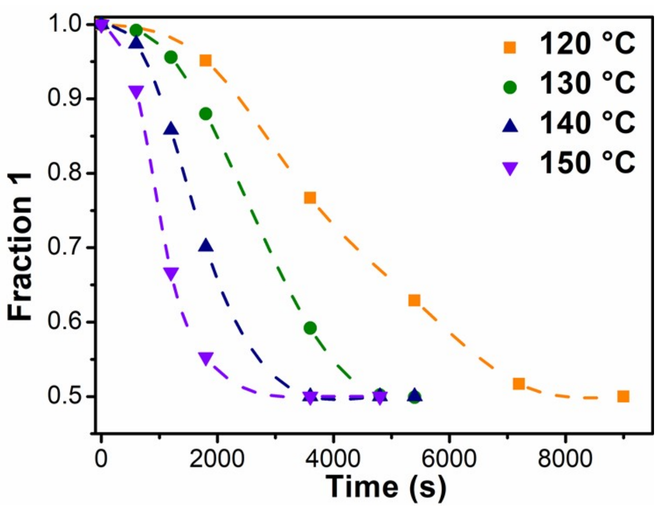


Fig. S25 Fraction of 1 as a function of time during the exchange experiment at different temperatures.

As shown in the main text, this reaction can be described in terms of second-order kinetics (eq (1)). In addition, considering a vast excess of PPA-IVE, eq (1) can be transformed into eq (2). Small molecule IBA-CVE = **1**, PPA-IVE =**2**.

$$\frac{d[1]}{dt} = -k[1][2] \qquad (1)$$

$$= -k_{exp}[1] \qquad (2)$$

k: rate constant, k_{exp}: experimental rate constant

If the initial concentration of **1** is described as $[1]_0$, eq (2) can be transformed to eq (3) [1].

$$ln\left(\frac{[1]}{[1]_0}\right) = -k_{exp}\,t \qquad (3)$$

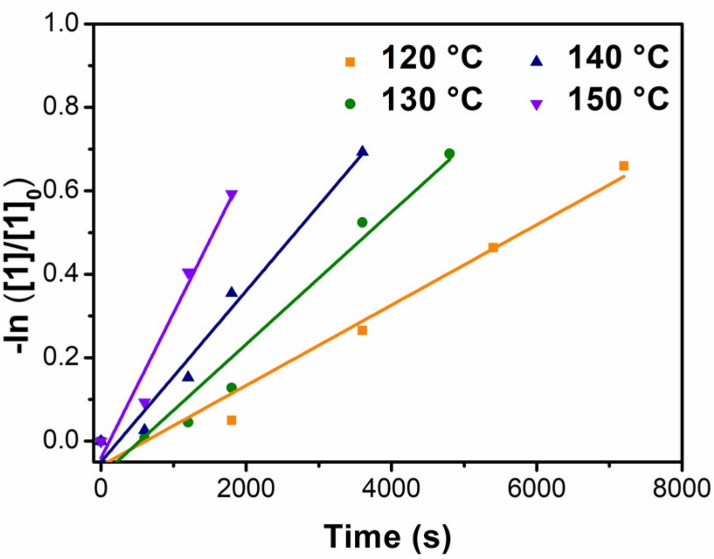


Fig. S26 Plot of -ln ([1] [1]$_0$) versus t for the small molecule 1. k_{exp} at each temperature was determined by its slope value.

120 °C	y= 0.0000962963x -0.059	$R^2 = 0.96$
130 °C	y= 0.000158194x -0.08401	$R^2 = 0.95$
120 °C	y= 0.000205213x -0.05006	$R^2 = 0.97$
120 °C	y= 0.000348328x -0.04085	$R^2 = 0.95$

To calculate the activation energy for each reaction, the Arrhenius plots were made using k_{exp}.

k = A exp(- Ea/RT) (A : pre-exponential factor, Ea : activation energy, R : universal gas constant)

R = 8.314 J K^{-1} mol^{-1} was used to calculate the activation energies from the slope values.

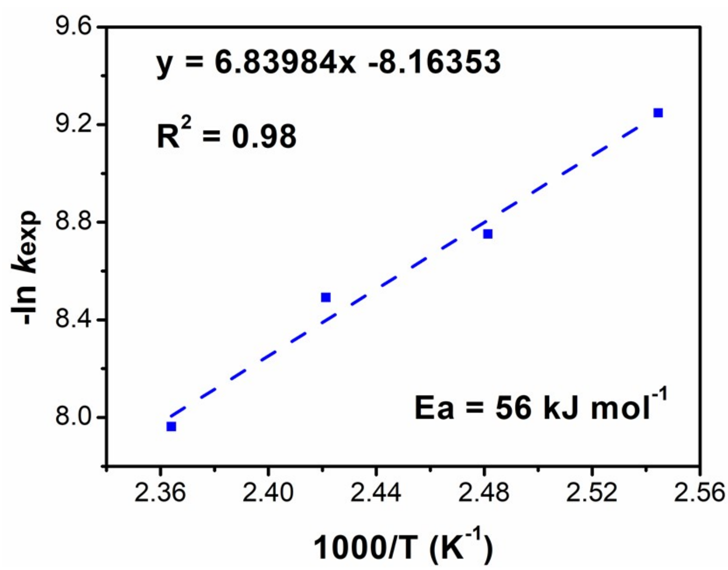


Fig. S27 Arrhenius analysis of the rate constant k_{exp} versus T for 1 and 2 exchange.

Table S1 Thermo-physical properties of different samples

Sample	T_g (°C)	v_e(mol cm^{-3})	$T_{d5\%}$ (°C)	$T_{d30\%}$ (°C)	T_s (°C)
PMMC-5	126	154	238	379	158
PMMC-10	124	130	227	386	158
PMMC-15	117	114	217	388	157
PMMC-20	113	164	218	387	157

$$T_s = 0.49\left[T_{d5\%} + 0.6\left(T_{d30\%} - T_{d5\%}\right)\right]$$

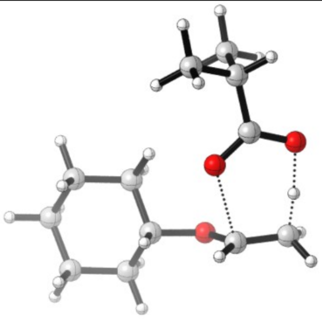
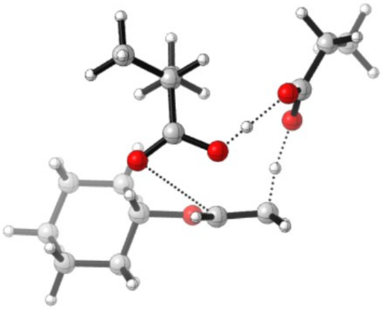
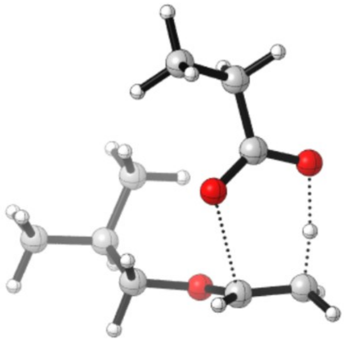
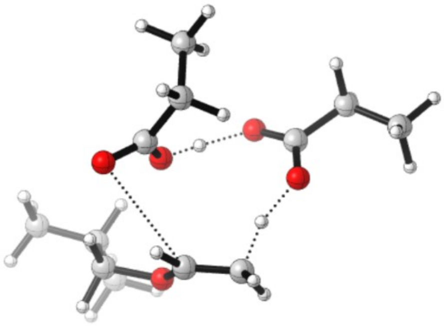
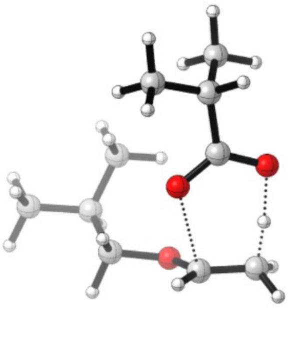
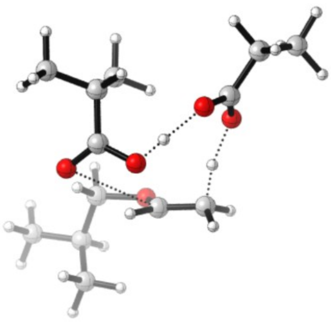
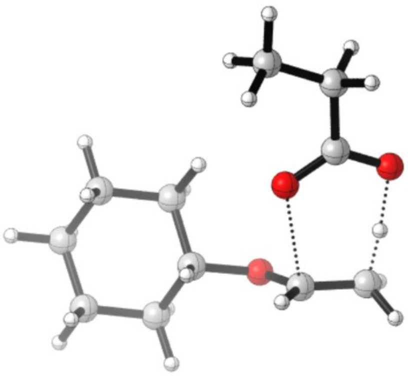
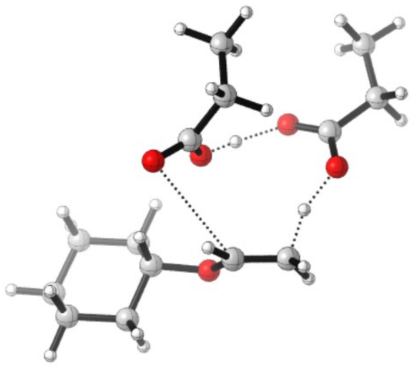
Table S2 Mechanical properties of different samples

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PMMC-5	1967±43	57±5	5.63±0.37
PMMC-10	1906±34	54±6	5.66±0.18
PMMC-15	1864±55	53±4	5.83±0.27
PMMC-20	1773±47	52±9	5.49±0.32

Table S3 Mechanical properties of the original and reprocessed PMMC-5

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Original	1967±43	57±5	5.43±0.32
Hot press	1827±60	55±8	4.79±0.45
Melt flow	1760±72	53±6	4.40±0.54
Extrude	1810±48	56±4	4.37±0.27

Table S4 Transition state geometry

	
TS1	TS1_HA
	
TS2	TS2_HA
	
TS3	TS3_HA
	
TS4	TS4_HA

References

1 Q. Li, S. Ma, P. Li, B. Wang, H. Feng, N. Lu, S. Wang, Y. Liu, X. Xu, J. Zhu, *Macromolecules,* 2021, **54**, 1742-1753.