Supporting Information

Dynamic enamine-one bond based vitrimer via amino-yne click reaction

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Contents

1. Materials

Bisphenol A (BPA), propiolic acid, ethyl propiolate, hexylamine, 4,4'-trimethylenedipiperidine (TMPD) and trimethylolpropane (TMP) were supplied by Saan Chemical Technology (Shanghai) Co., Ltd. Ethylene carbonate, benzylamine and t-butyl acetoacetate were purchased from Tianjin heowns Biochemical Technology Co., Ltd. p-Toluenesulfonic acid (PTSA) and silicon dioxide were obtained from Shanghai Vita Chemical Reagent Co., Ltd. 1,6-Diaminohexane (HMDA) and dichloromethane (DCM) were purchased from Aladdin Reagents (Shanghai) Co., Ltd. Magnesium sulfate and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium bicarbonate and sodium carbonate were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. Tris(2-Aminoethyl) amine (TREN) was obtained from Shanghai Titan Scientific Co., Ltd. Toluene, ethyl acetate, petroleum ether and chloroform purchased from Xilong Scientific Co., Ltd. Methanol was obtained from Guangdong Guanghua Sci-Tech Co., Ltd. Silica (200-300 mesh) was purchased from Qingdao Ocean Chemical Co., Ltd. All purchased chemicals were used without any further purification.

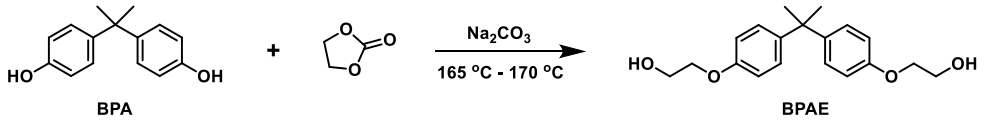
2. Characterization

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV-400 spectrometer. $CDCl_3$ was used as the solvent in each sample. The chemical shift (δ) is expressed in parts per million (ppm). The FTIR spectra were recorded on a Bruker-vertex70 spectrometer with a diamond ATR probe by 32 scans for each sample, and the scan range is from 4000 cm^{-1} to 500 cm^{-1}. Dynamic Mechanical Analysis (DMA) of sample (7 mm × 3 mm × 0.5 mm) was performed with a TA Q800 (New Castle, USA) instrument at a heating rate of 3 ℃/min from 30 ℃ to 130 ℃. Each sample was equilibrated at room temperature for 5 minutes, and the applied force was increased to 18 N at a rate of 3 N/min. Regarding the determination of the glass transition temperature (T_g), the strain control experiment was carried out under the conditions of amplitude of 10 μm and frequency of 1 Hz. The samples were heated from 30 ℃ to 150 ℃ at a rate of 3 ℃ /min, and the glass transition temperature (T_g) was determined as the peak of tan δ. Stress Relaxation Analysis (SRA) experiments were performed at the temperature range of 110 – 140 ℃. The creep-recovery experiments were conducted under constant stress (0.1 MPa) for 10 min. TA's Thermal Advantage for Q Series software were used to record the results for all DMA experiments. Thermogravimetric analysis (TGA) experiments were collected on a TA Q50 equipment at a heating rate of 10 ℃/min from 25 ℃ to 750 ℃. Differential scanning calorimetry (DSC) measurements was performed on a TA calorimeter (Q2000, TA) from −40 ℃ to 120 ℃ at a scan rate of 20 ℃/min under nitrogen flow. Acetone swelling test was performed by immersing a thin film with known weight (W_1) in an acetone bath. The acetone on the surface of the film was wiped off after soaking, and then weighted it (W_2). The acetone swelling (M %; amount of acetone absorbed by the film) of the films was calculated according to the following equation: $M (\%) = [(W_2 - W_1)/W_1] \times 100\%$. Gel content was determined by soaking in a film of known weight (W_0) (25 mm × 6 mm × 0.22 mm). The dried film was immersed in acetone for 12 h and then dehydrated at 80 ℃ for 18 h to obtain the weight of W_3. Gel content and average molecular mass between crosslinking points were calculated according to the following formula: $M (\%) = W_3/W_1 \times 100\%$. $\overline{M}_C = [(W_2 - W_3)/W_3]$ K+1; K: $\rho_{acetone} = 0.788$ g/mL (25 ℃).

3. Small-molecule study

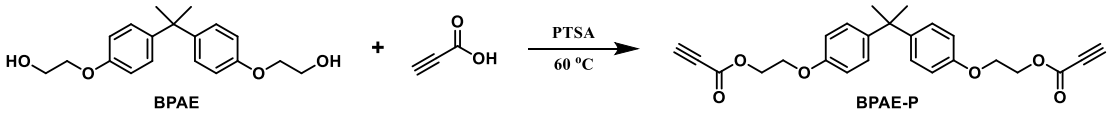
3.1 Synthetic procedures

3.1.1 Synthesis of bisphenol A diethyl alcohol ether (BPAE)



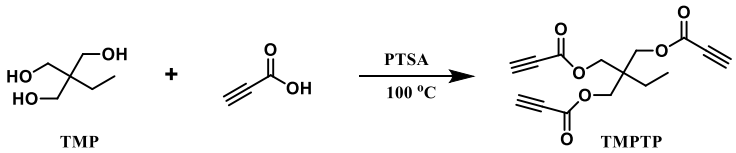
A 500 mL round-bottom flask was charged with bisphenol A (22.8 g, 0.1 mol), ethylene carbonate (17.6 g, 0.2 mol) and sodium carbonate (0.1 g) as catalyst, the mixture was heated at 165-170 °C under nitrogen flow for two hours. Then, the mixture was precipitated with water and concentrated under reduced pressure. The residual solid was recrystallized from methanol to obtain BPAE. 26.60 g, 84% of yield. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 7.17 - 7.11 (m, 4H), 6.85 - 6.79 (m, 4H), 4.09 - 4.03 (m, 4H), 3.97 - 3.92 (m, 4H), 1.66 - 1.61 (m, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 157.65, 144.81, 129.21, 115.09, 70.42, 62.86, 43.10, 32.09.

3.1.2 Synthesis of Bisphenol A diethyl ether propionate (BPAE-P)



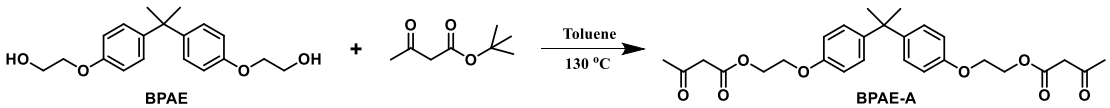
Bisphenol A diethyl alcohol ether (BPAE) (15.19 g, 48 mmol) was dissolved in $CHCl_3$ (100 mL) at room temperature, then PTSA (18.25 g, 106 mmol) and propionic acid (13.45 g, 192 mmol) were added and the mixture was refluxed for 18 hours. After that, the mixture was washed with saturated $NaHCO_3$, water and brine. The organic layer was then dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. After purification in column chromatography at CH_2Cl_2, the product was obtained as a white solid. 5.80 g, 29% of yield. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 7.21 - 7.06 (m, 4H), 6.89 - 6.74 (m, 4H), 4.59 - 4.45 (m, 4H), 4.25 - 4.10 (m, 4H), 2.98 - 2.84 (m, 2H), 1.68 - 1.60 (m, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 157.55, 153.91, 145.19, 129.15, 115.44, 76.69, 66.62, 65.79, 43.08, 32.41.

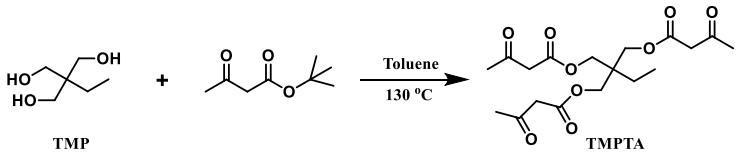
3.1.3 Synthesis of trimethylolpropane tripropiolate (TMPTP)



Trimethylolpropane (2 g, 14.9 mmol) was dissolved in 40 mL toluene, add PTSA (0.28 g, 1.6 mmol) and propionic acid (4.2 g, 59.7 mmol) to it. Heat the mixture to 100 °C for 2 days. The crude product was washed with a mixture of ethyl acetate and petroleum ether, then dried in a vacuum oven at 70 °C for 24 h. 2.94 g, 68%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 4.21 - 4.14 (m, 6H), 2.98 - 2.88 (m, 3H), 1.57 -1.51 (m, 2H), 0.94 - 0.89 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 152.15, 76.24, 74.02, 65.17, 40.65, 22.62, 7.00.

3.1.4 Synthesis of Bisphenol A diethyl ether acetoacetate (BPAE-A) and trimethylolpropane triacetoacetate (TMPTA)



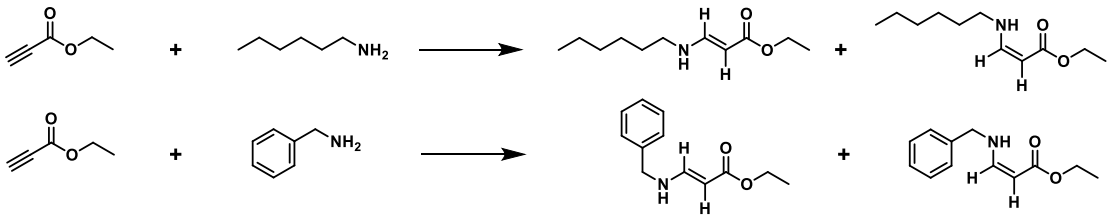


The synthesis of Bisphenol A diethyl ether acetoacetate (BPAE-A) and trimethylolpropane triacetoacetate (TMPTA) were as follow: BPAE (or trimethylolpropane) and t-butyl acetoacetate were dissolved in toluene (60 mL). The mixture was stirred at 130 °C for 18 h and the liquid of t-butanol and toluene were removed with distillation. Then, the excess t-butyl acetoacetate was removed at 140 °C under reduced pressure. Finally, a light-yellow oil was obtained.

The yield of Bisphenol A diethyl ether acetoacetate (BPAE-A) is 93%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 7.22 - 7.09 (m, 4H), 6.90 - 6.75 (m, 4H), 4.57 - 4.41 (m, 4H), 4.23 - 4.07 (m, 4H), 3.55 - 3.40 (m, 4H), 2.34 - 2.19 (m, 6H), 1.71 - 1.55 (m, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 201.77, 168.42, 157.47, 145.12, 129.14, 115.40, 66.96, 64.95, 51.21, 43.11, 32.33, 31.43.

The yield of trimethylolpropane triacetoacetate (TMPTA) is 90%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 4.16 -4.03 (m, 6H), 3.56 - 3.45 (m, 6H), 2.30 -2.24 (m, 9H), 1.74 - 1.59 (m, 2H), 0.94 - 0.86 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 200.32, 166.59, 64.23, 49.63, 40.75, 27.77, 22.61, 7.02.

3.1.5 Synthesis of ethyl 3-(benzylamino) acrylate and ethyl 3-(hexylamino) acrylate



The Ethyl 3-(benzylamino) acrylate and ethyl 3-(hexylamino) acrylate were synthesized as follows: a 1:1 ratio of benzylamine (or hexylamine) and ethyl propiolate were dissolved in CH_2Cl_2 at 0 °C and stirred for 18 hours. Then, the mixture was concentrated under reduced pressure and purified by column chromatography using CH_2Cl_2 as the eluent. The final product was dried at 40 °C under vacuum to give an orange oil.

Ethyl 3-(benzylamino) acrylate was obtained as a 1:3 mixture of *trans*- and *cis*- isomers. 90% of yield. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 8.33 - 7.88 (m, 0.75H, NH (*cis*)), 7.64 - 7.54 (m, 0.25H, =CHN (*trans*)), 7.39 - 7.18 (m, 5H), 6.74 - 6.63 (m, 0.75H, =CHN (*cis*)), 4.84 - 4.79 (m, 0.25H, CH=CHN (*trans*)), 4.77 - 4.67 (m, 0.25H, NH (*trans*)), 4.58 - 4.49 (m, 0.75H, CH=CHN (*cis*)), 4.37 - 4.31 (m, 1.50H, $NHCH_2$ (*cis*)), 4.25 - 4.17 (m, 0.50H, $NHCH_2$ (*trans*)), 4.16 - 4.07 (m, 2H), 1.29 - 1.21 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 170.60,

152.22, 138.82, 128.75, 127.44, 126.99, 82.82, 58.69, 51.99, 14.57.

Ethyl 3-(hexylamino) acrylate as a 23:77 mixture of *trans*- and *cis*- isomers. 93% of yield. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm) = 8.13 - 7.61 (m, 0.77H, NH (*cis*)), 7.60 - 7.43 (m, 0.23H, =CHN (*trans*)), 6.70 - 6.56 (m, 0.77H, =CHN (*cis*)), 4.76 - 4.68 (m, 0.23H, CH=CHN (*trans*)), 4.56 - 4.47 (m, 0.23H, NH (*trans*)), 4.46 - 4.39 (m, 0.77H, CH=CHN (*cis*)), 4.18 - 4.06 (m, 2H), 3.19 - 3.12 (m, 1.54H, $NHCH_2$ (*cis*)), 3.08 - 2.96 (m, 0.46H, $NHCH_2$ (*trans*)), 1.60 - 1.51 (m, 1.54H, $NHCH_2CH_2$ (*cis*)), 1.49 - 1.39 (m, 0.46 H, $NHCH_2CH_2$ (*trans*)), 1.34 - 1.23 (m, 9H), 0.92 - 0.85 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm) = 170.89, 152.24, 81.37, 58.50, 48.55, 31.49, 31.34, 26.27, 22.49, 14.58, 13.94.

3.2 Exchange reaction

Exchange of ethyl 3-(hexylamino) acrylate with 10 eq of benzylamine at 50 °C

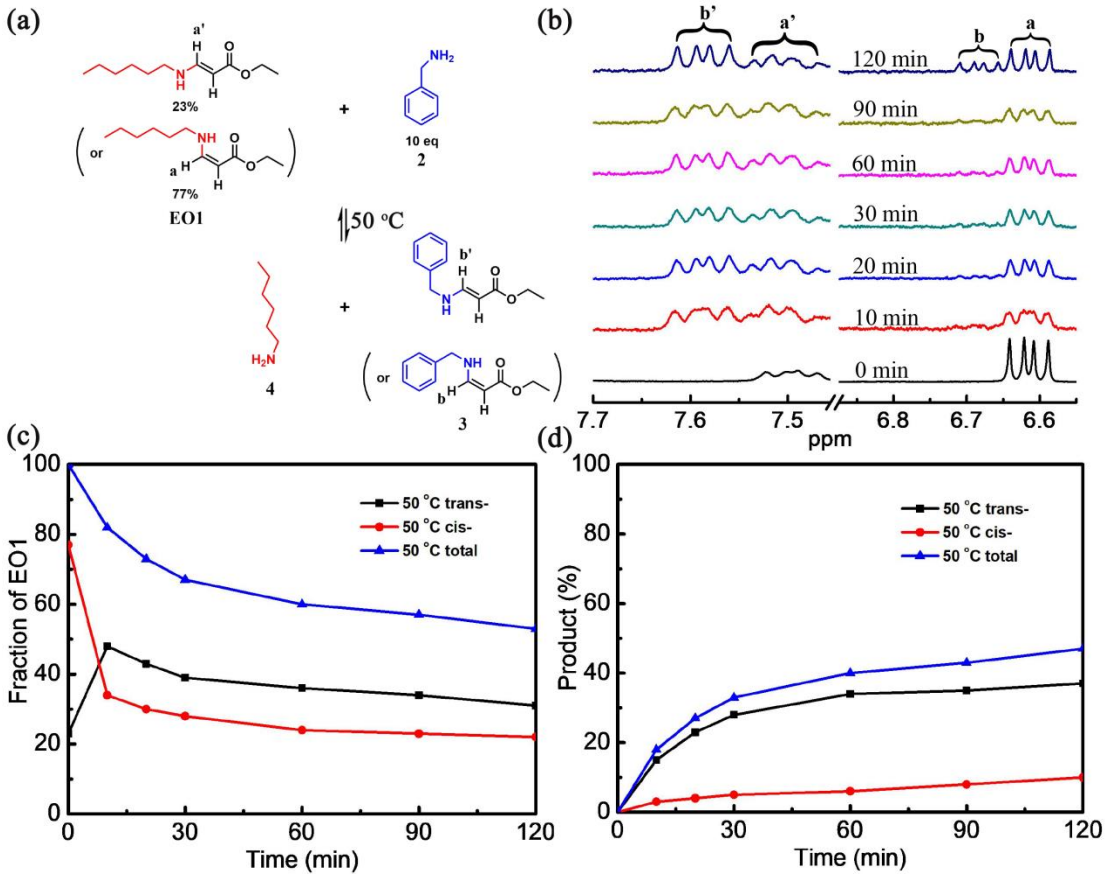


Figure S1. (a) The exchange dynamics of *cis*/*trans*-enamine-one small molecule. (b) ^{1}H NMR spectra characterization of the dynamic exchange reaction over time at 50 °C (The peaks correspond to the *cis*/*trans* alkene proton). (c) The consumption of starting materials as a function of exchange time. (d) The percentage of product 3 over exchange time.

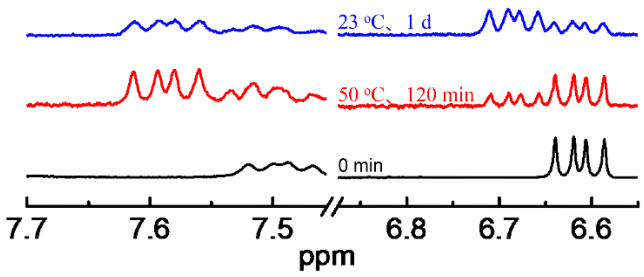


Figure S2. ^{1}H NMR characterization of the thermodynamics of *cis*/*trans*-enamine-one. Ethyl 3-(hexylamino) acrylate exchange with benzylamine at 50 ℃ for 2 hours and then set at 23 ℃ for 1 day (The peaks correspond to the *cis*/*trans* alkene proton and indicate that cis-product is more thermodynamically stable form).

Exchange of ethyl 3-(hexylamino) acrylate with 10 eq of benzylamine at 70 ℃

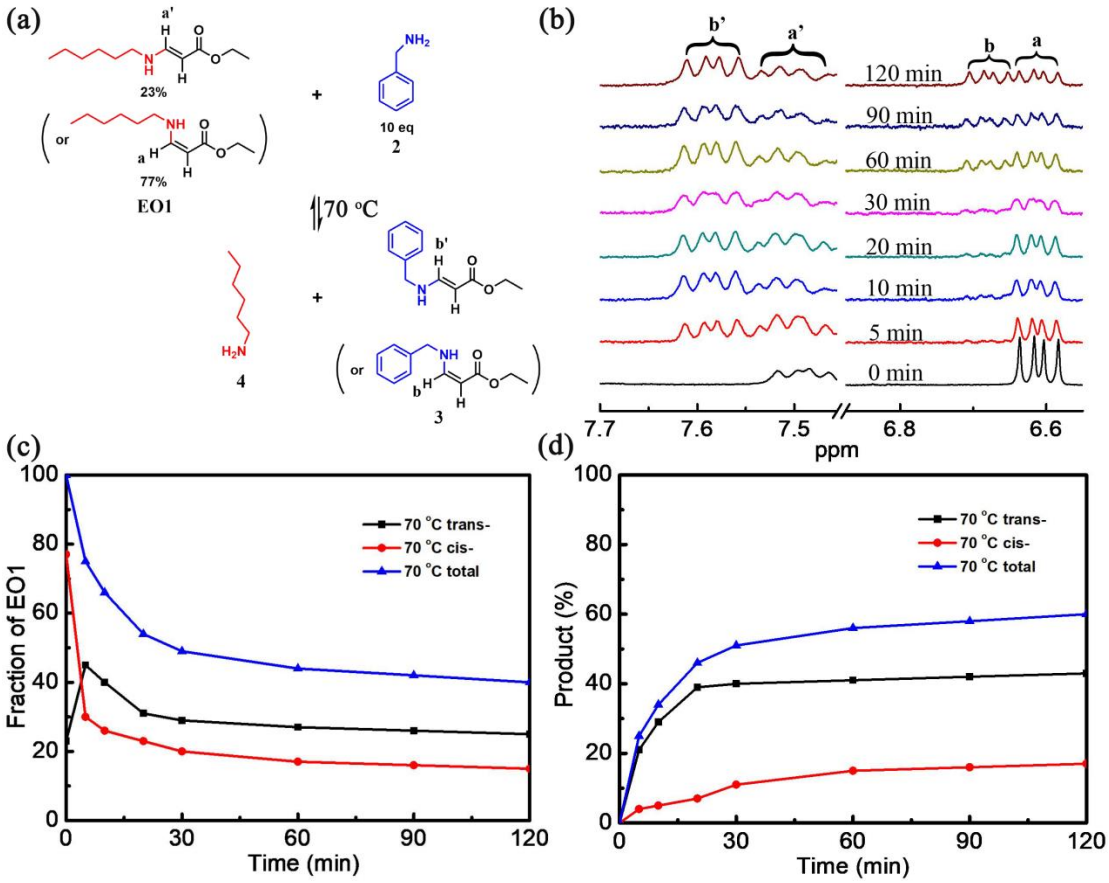


Figure S3. (a) The exchange dynamics of *cis*/*trans*-enamine-one small molecule. (b) ^{1}H NMR spectra characterization of the dynamic exchange reaction over time at 70 ℃ (The peaks correspond to the *cis*/*trans* alkene proton). (c) The consumption of starting materials as a function of exchange time. (d) The percentage of product 3 over exchange time.

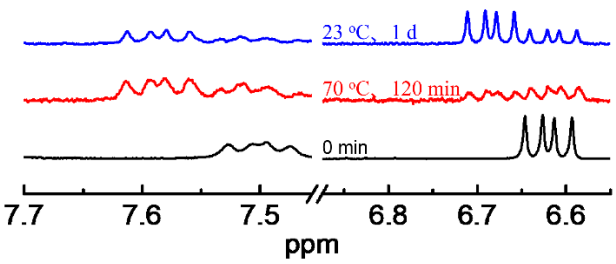


Figure S4. ^{1}H NMR characterization of the thermodynamics of *cis*/*trans*-enamine-one. Ethyl 3-(hexylamino) acrylate exchange with benzylamine at 70 °C for 2 hours and then set at 23 °C for 1 day (The peaks correspond to the *cis*/*trans* alkene proton and indicate that cis-product is more thermodynamically stable form).

Exchange of ethyl 3-(hexylamino) acrylate with 10 eq of benzylamine at 90 °C

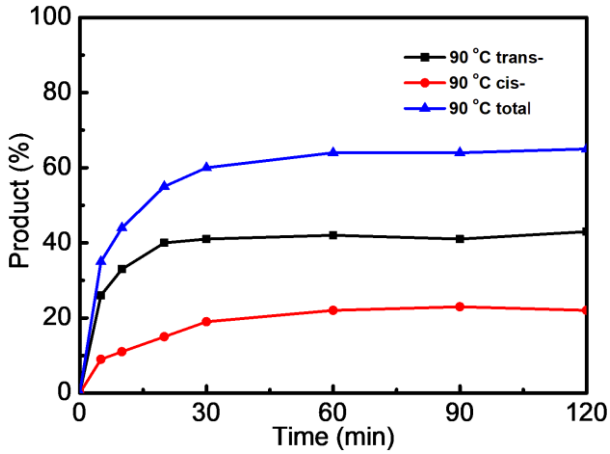


Figure S5. The evolution of product generated by the exchange of ethyl 3-(hexylamino) acrylate with benzylamine over time at 90 °C.

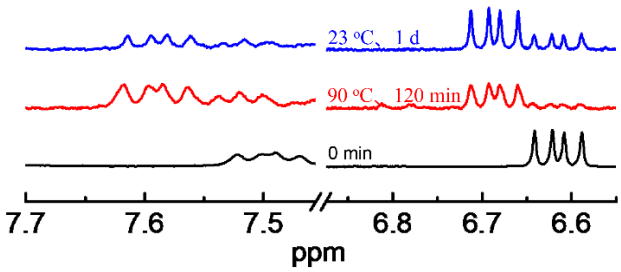


Figure S6. ^{1}H NMR characterization of the thermodynamics of *cis*/*trans*-enamine-one. Ethyl 3-(hexylamino) acrylate exchange with benzylamine at 90 °C for 2 hours and then set at 23 °C for 1 day (The peaks correspond to the *cis*/*trans* alkene proton and indicate that cis-product is more thermodynamically stable form).

Table S1. Summary of the fraction of product over exchange time at 50 °C, 70 °C, and 90 °C

Temperature	Code	5 min	10 min	20 min	30 min	60 min	90 min	120 min
50 °C	cis-	—	3%	4%	5%	6%	8%	10%
	trans-	—	15%	23%	28%	34%	35%	37%

	total	—	18%	27%	33%	40%	43%	47%
70 °C	cis-	4%	5%	7%	11%	15%	16%	17%
	trans-	21%	29%	39%	40%	41%	42%	43%
	total	25%	34%	46%	51%	56%	58%	60%
90 °C	cis-	9%	11%	15%	19%	22%	23%	22%
	trans-	26%	33%	40%	41%	42%	41%	43%
	total	35%	44%	55%	60%	64%	64%	65%

Table S2. Summary of the fraction of reactant over exchange time at 50 °C, 70 °C, and 90 °C

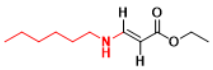
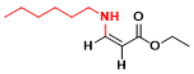
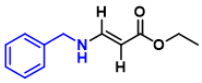
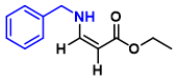
Temperature	Code	0 min	5 min	10 min	20 min	30 min	60 min	90 min	120 min
50 °C	cis-	77%	—	34%	30%	28%	24%	23%	22%
	trans-	23%	—	48%	43%	39%	36%	34%	31%
	total	100%	—	82%	73%	67%	60%	57%	53%
70 °C	cis-	77%	30%	26%	23%	20%	17%	16%	15%
	trans-	23%	45%	40%	31%	29%	27%	26%	25%
	total	100%	75%	66%	54%	49%	44%	42%	40%
90 °C	cis-	77%	27%	21%	18%	14%	11%	11%	9%
	trans-	23%	38%	35%	27%	26%	25%	25%	26%
	total	100%	65%	56%	45%	40%	36%	36%	35%

Table S3. Summarized retention of reactants over exchange time at 50 °C, 70 °C and 90 °C

Temperature	Trial	0 min	5 min	10 min	20 min	30 min	60 min	90 min	120 min
50 °C	1	100%	—	82%	73%	67%	60%	57%	53%
	2	100%	—	80%	70%	66%	63%	60%	56%
	3	100%	—	78%	69%	67%	65%	62%	54%
70 °C	1	100%	75%	66%	54%	49%	44%	42%	40%

	2	100%	73%	68%	64%	61%	58%	56%	51%
	3	100%	73%	65%	61%	58%	54%	49%	45%
90 °C	1	100%	65%	56%	45%	40%	36%	36%	35%
	2	100%	57%	55%	46%	40%	36%	37%	35%
	3	100%	56%	53%	42%	39%	36%	36%	35%

Table S4. Summary of each substances content at three temperatures

Temperature	Time				
50 °C	2 h	31%	22%	37%	10%
	a	17%	17%	27%	39%
70 °C	2 h	25%	15%	43%	17%
	b	18%	18%	26%	38%
90 °C	2 h	26%	9%	43%	22%
	c	19%	17%	26%	38%

a, b, c: Exchange reaction at 50 °C / 70 °C / 90 °C for two hours, then set at 23 °C for 1 day.

3.3 Thermal dynamics of cis/trans enamine-one

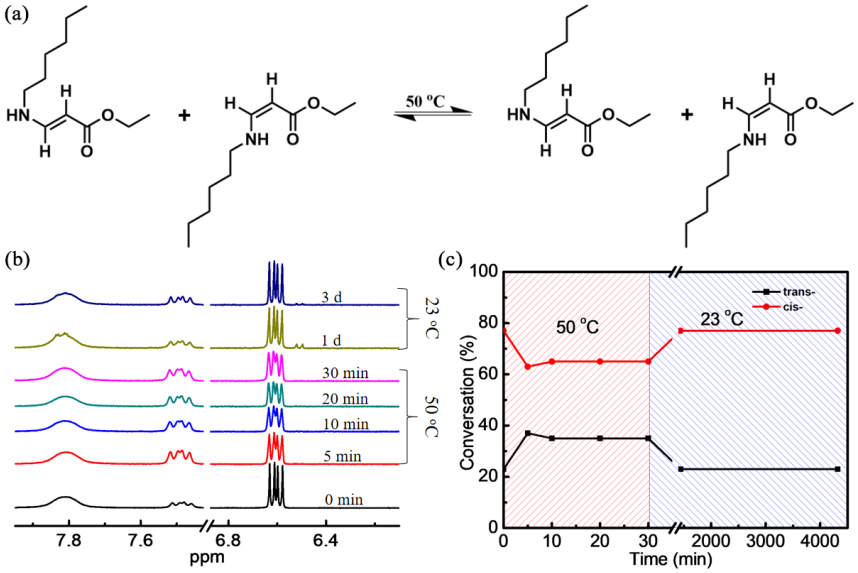


Figure S7. (a) Scheme and (b) ^{1}H NMR characterization for thermodynamics study of ethyl 3-(hexylamino) acrylate at 50 °C. (c) Fraction of *cis*/*trans* ethyl 3-(hexylamino) acrylate over time.

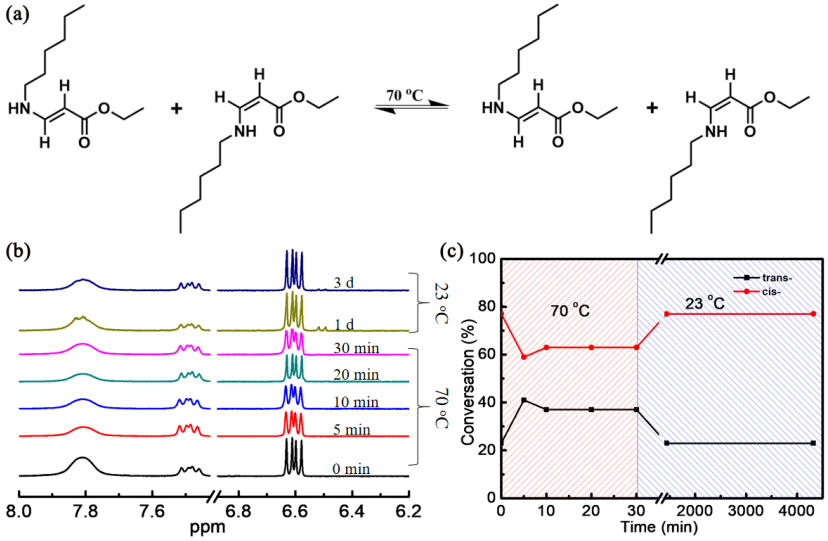


Figure S8. (a) Scheme and (b) ^{1}H NMR characterization for thermodynamics study of ethyl 3-(hexylamino) acrylate at 70 °C. (c) Fraction of *cis*/*trans* ethyl 3-(hexylamino) acrylate over time.

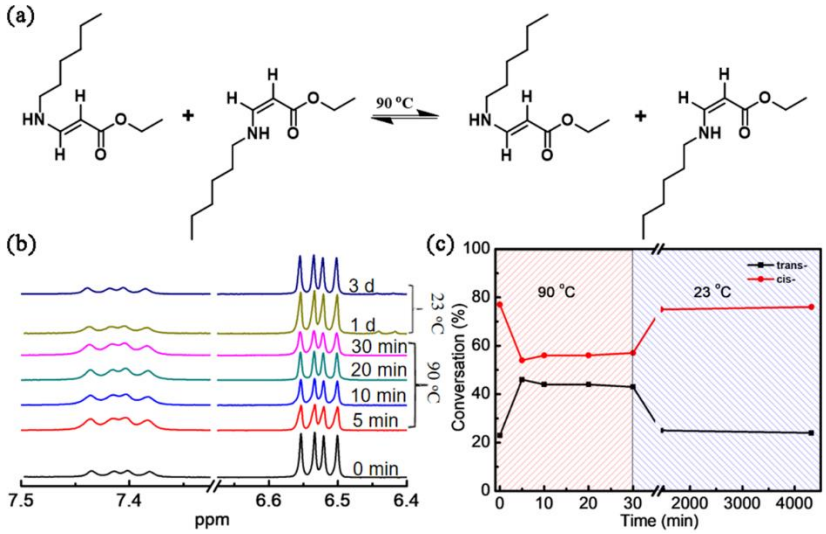


Figure S9. (a) Scheme and (b) ^{1}H NMR characterization for thermodynamics study of ethyl 3-(hexylamino) acrylate at 90 °C. (c) Fraction of *cis*/*trans* ethyl 3-(hexylamino) acrylate over time.

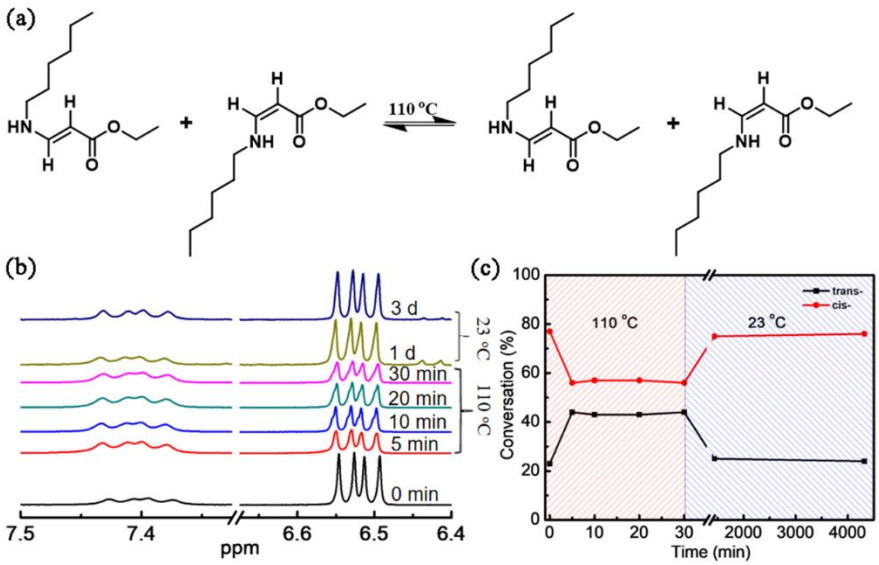


Figure S10. (a) Scheme and (b) ^{1}H NMR characterization for thermodynamics study of ethyl 3-(hexylamino) acrylate at 110 °C. (c) Fraction of *cis*/*trans* ethyl 3-(hexylamino) acrylate over time.

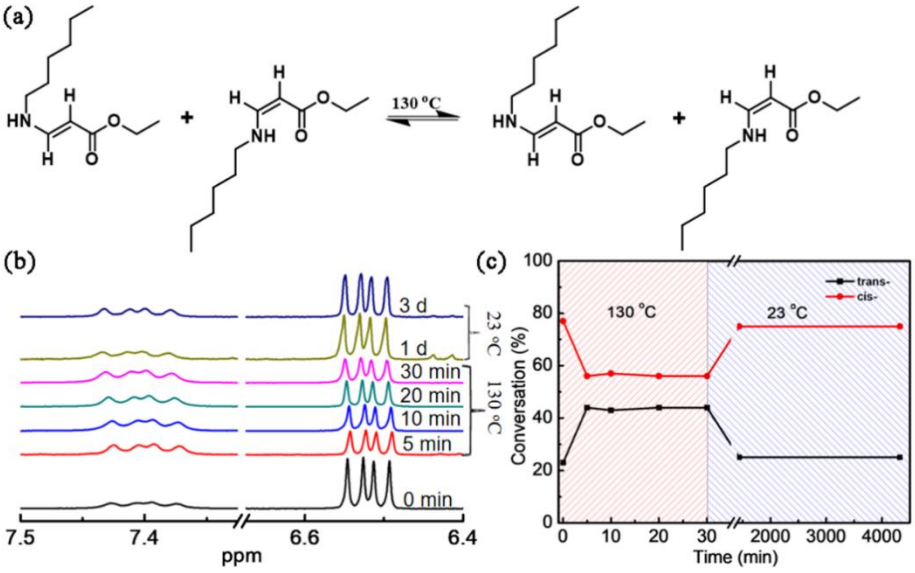


Figure S11. (a) Scheme and (b) ^{1}H NMR characterization for thermodynamics study of ethyl 3-(hexylamino) acrylate at 130 °C. (c) Fraction of *cis*/*trans* ethyl 3-(hexylamino) acrylate over time.

3.4 Calculation of the activation energy

The activation energy can be calculated by plotting ln(k) versus 1000/T. The k values are extracted from exponential fits of kinetic curves according to the following function.

$$x(t) = x_0 exp^{-k(t-t_0)} + C$$

Then, E_a is calculated from the slope of the following function:

$$ln\ k = -\frac{E_a}{RT}$$

Table S5. Summary of *k* (rate constant) values retrieved at three different temperatures

Temperature	k (rate constant)	$\bar{k}$ (rate constant)	E_a
50 °C	3.28×10^{-4} s^{-1}	4.06×10^{-4} s^{-1}	35 ± 3 kJ/mol
	4.62×10^{-4} s^{-1}		
	4.27×10^{-4} s^{-1}		
70 °C	8.14×10^{-4} s^{-1}	9.8×10^{-4} s^{-1}	
	1.04×10^{-3} s^{-1}		
	9.30×10^{-4} s^{-1}		
90 °C	1.33×10^{-3} s^{-1}	1.66×10^{-3} s^{-1}	
	1.92×10^{-3} s^{-1}		
	1.73×10^{-3} s^{-1}		

3.5 Control experiment

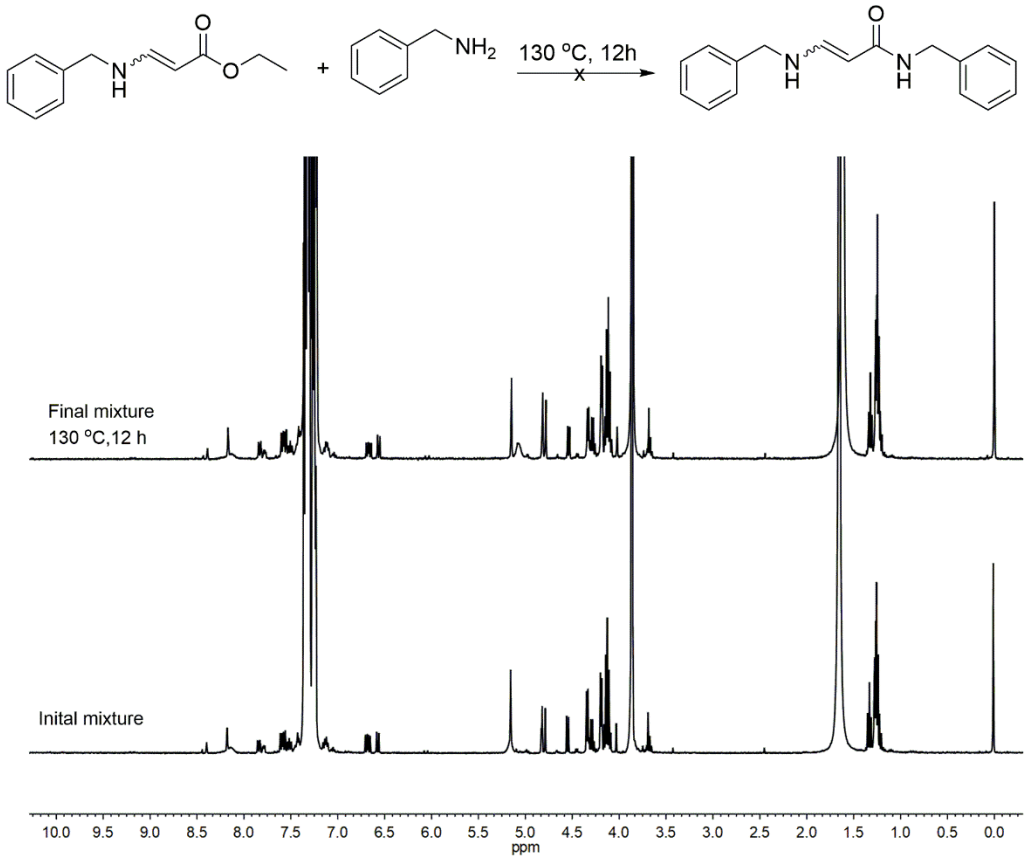


Figure S12. ^{1}H NMR study of potential transesterification during the dynamic exchange. The result indicated no observable transesterification after heating at 130 °C for 12h.

4. Material study

4.1 Network synthesis

Preparation of vitrimer network.

The polymer network was prepared with a 1:1.05 ratio of alkyne/acetoacetate: amine group. A mixture of BPAE-P (or BPAE-A), TREN and HMDA were dissolved in 3 mL DCM, and the mixture was poured into a polytetrafluoroethylene (PTFE) mold (8 cm* 8 cm* 1.5 cm). The final polymer network was cured at room temperature for 48 hours.

Table S6. Contents of starting materials for films curing in this study

Sample code	BPAE-P (mmol)	BPAE-A (mmol)	TREN (mmol)	HMDA (mmol)	alkyne/acetoacetate : amine ratio
BPAE-PTH	4.8	-	1.68	2.52	1 : 1.05
BPAE-ATH	-	4.8	1.68	2.52	1 : 1.05

4.2 FTIR spectra

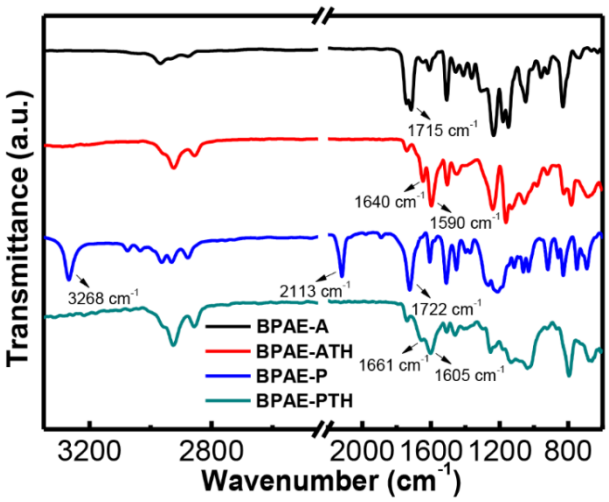


Figure S13. FTIR spectra of BPAE-A, BPAE-P, and vitrimer networks (BPAE-ATH and BPAE-PTH).

4.3 Hot press recycling

The reprocessing test was performed using a hot press (RYJ-600C, Shanghai Xinuo Instrument Equipment Co., Ltd., China). The polymer film (about 1 g) was cut into pieces (~ 2 mm * 2 mm) and remodeled under 10 MPa pressure at 130 °C for 60 minutes.

4.4 FTIR spectra of film after hot pressing cycles

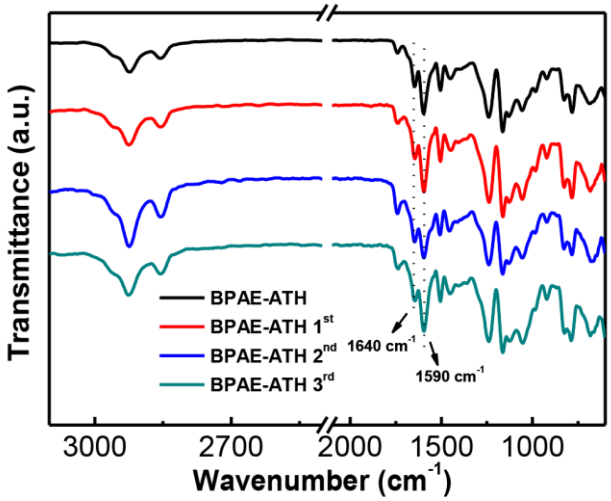


Figure S14. FTIR spectra of pristine and remodeled BPAE-ATH.

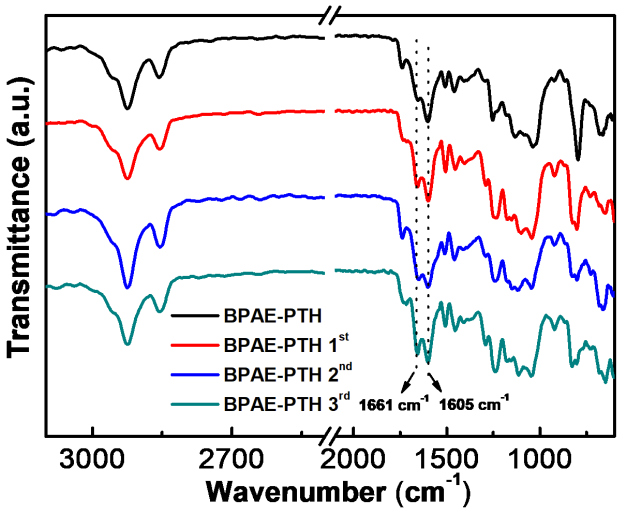


Figure S15. FTIR spectra of pristine and remodeled BPAE-PTH.

4.5 Creep - recovery analysis

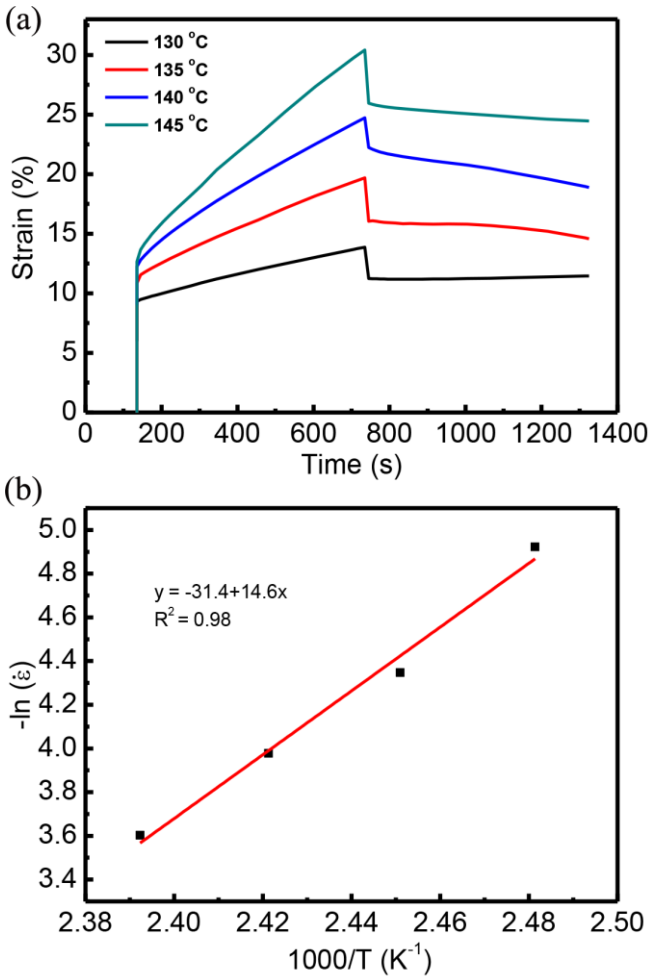


Figure S16. (a) Overlay of BPAE-ATH creep-recovery curves at different temperatures. (b) Arrhenius plot of creep rate over inversed temperature. E_a = 121 kJ/mol

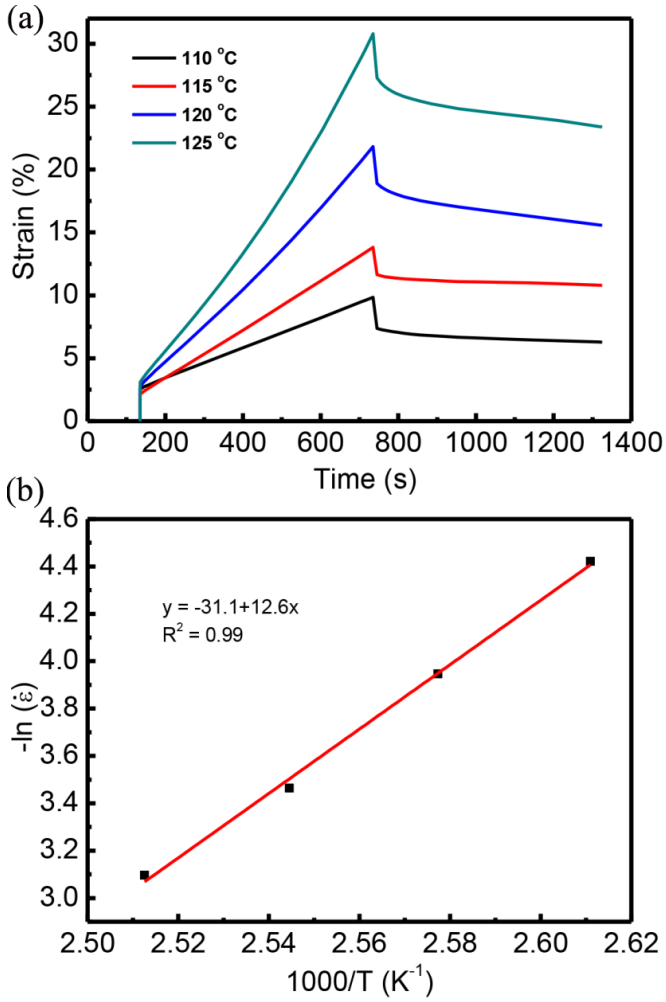


Figure S17. (a) Overlay of BPAE-PTH creep-recovery curves at different temperatures. (b) Arrhenius plot of creep rate over inversed temperature. E_a = 105 kJ/mol

4.6 Thermogravimetric analysis (TGA)

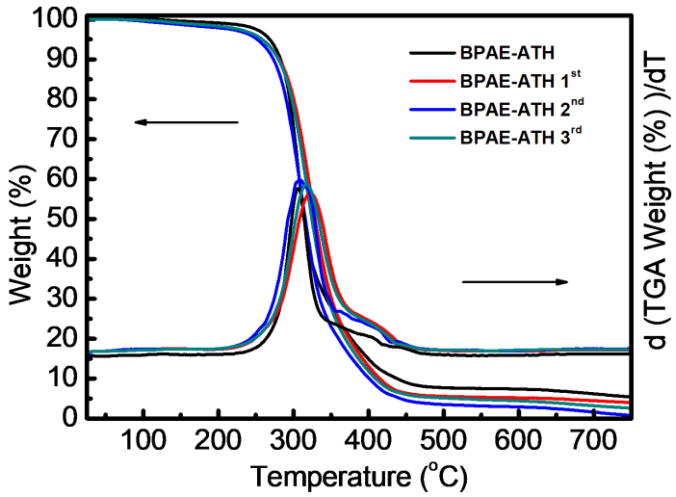


Figure S18. TGA analysis of pristine and remodeled BPAE-ATH

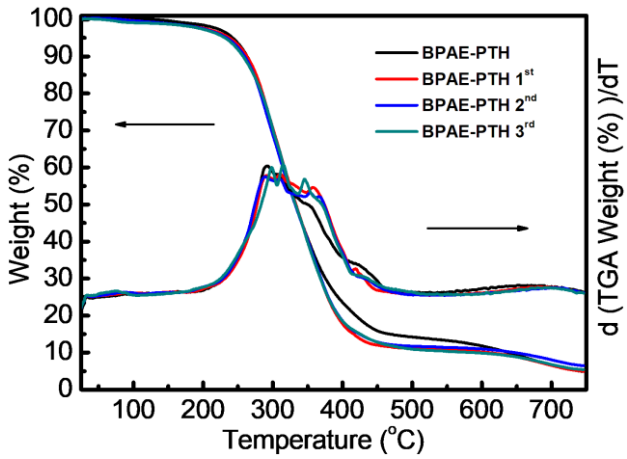


Figure S19. TGA analysis of pristine and remodeled BPAE-PTH

Table S7. Summary of thermal properties of original and reprocessed vitrimer networks

Sample	Molding step	TGA in nitrogen (°C)			T_g by DSC (°C)
		T_{10}	T_{50}	T_{max}	
BPAE-PTH	origin	263 °C	333 °C	750 °C	79
	1st	263 °C	332 °C	750 °C	79
	2nd	260 °C	332 °C	750 °C	79
	3rd	258 °C	333 °C	750 °C	79
BPAE-ATH	origin	283 °C	314 °C	750 °C	44
	1st	281 °C	328 °C	750 °C	45
	2nd	274 °C	315 °C	750 °C	45
	3rd	280 °C	324 °C	750 °C	45

4.7 Chemical recycling of BPAE-ATH and BPAE-PTH.

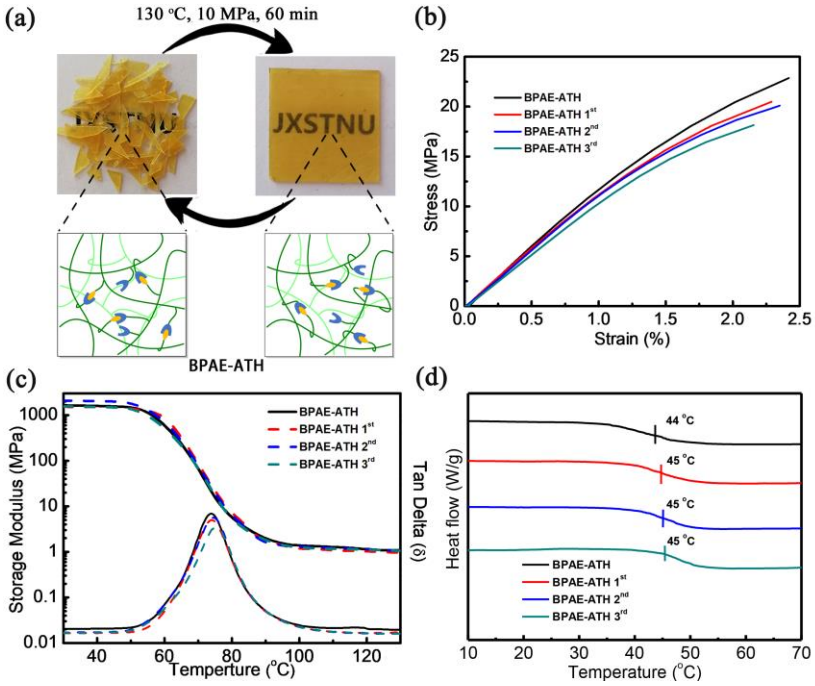


Figure S20. (a) Representative image of hot-press reprocessing of BPAE-ATH pieces into a film, (b) stress−strain curves of the reprocessed BPAE-ATH, (c) DMA curves of the reprocessed BPAE-ATH, (d) DSC curves of remold BPAE-ATH.

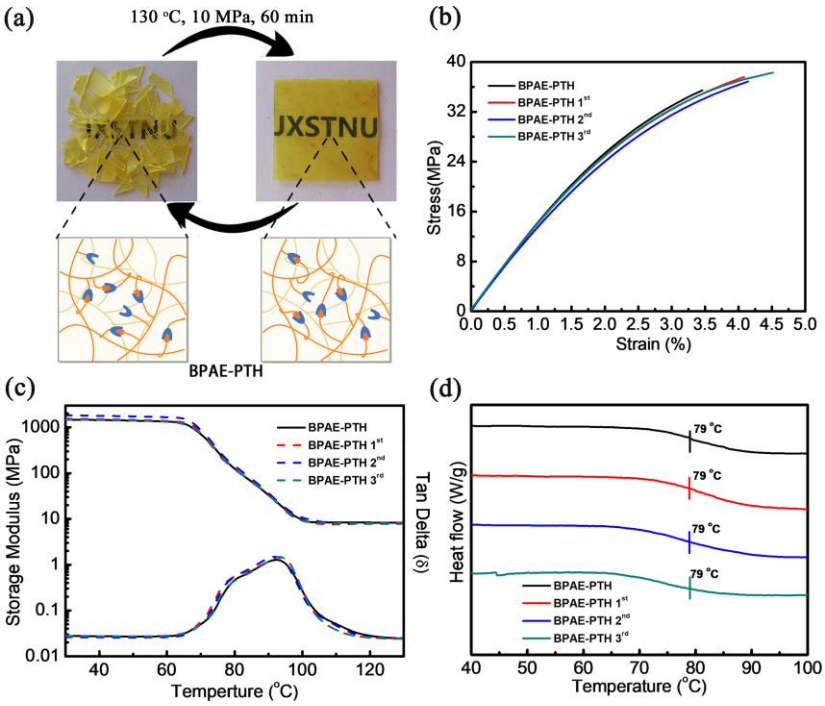


Figure S21. (a) Representative image of hot-press reprocessing of BPAE-PTH pieces into a film, (b) stress−strain curves of the reprocessed BPAE-PTH, (c) DMA curves of the reprocessed BPAE-PTH, (d) DSC curves of remold BPAE-PTH.

Table S8. Summary of tensile test results for the initial and remolded vitrimer networks.

Sample	Molding step	Young's	Stress at	Elongation at

		Modulus (MPa)	breaks (MPa)	breaks (%)
BPAE-PTH	Origin	1501 ± 6	36 ± 3	3.5 ± 0.5
	1st	1520 ± 1	38 ± 4	4.1 ± 0.4
	2nd	1455 ± 8	37 ± 4	4.2 ±0.4
	3rd	1477 ± 13	38 ± 2	4.5 ± 0.5
BPAE-ATH	Origin	1245 ± 23	23 ± 4	2.4 ± 0.4
	1st	1188 ± 10	21 ± 2	2.3 ± 0.2
	2nd	1119 ± 10	20 ± 3	2.4 ± 0.3
	3rd	1046 ± 20	18 ± 5	2.2 ± 0.4

4.8 DMA curves

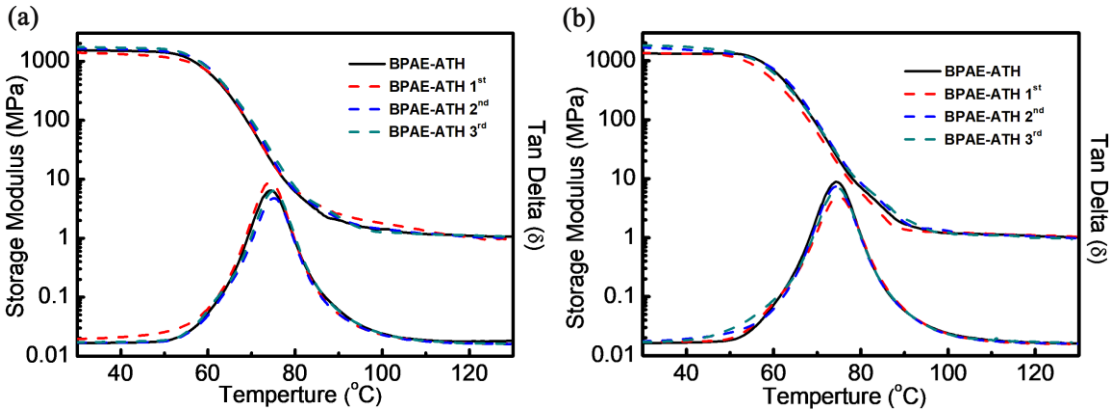


Figure S22. DMA curves of the reprocessed BPAE-ATH.

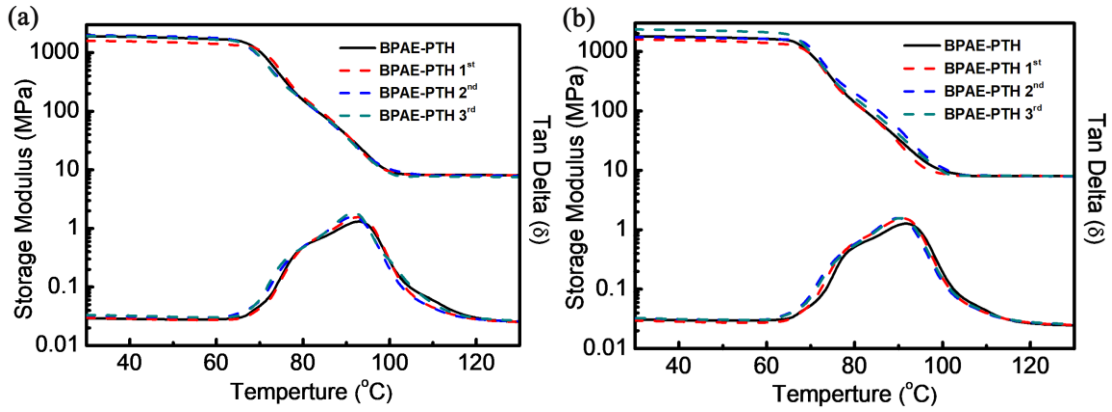


Figure S23. DMA curves of the reprocessed BPAE-PTH.

Table S9. Summary of DMA results for the initial and remolded vitrimer networks

Sample	Molding step	T_g (Tan δ) (°C)	E' at T_g + 50 °C (MPa)	Crosslinking (ν_e) (mol m^{-3})	Average crosslinking (ν_e) (mol m^{-3})
BPAE-ATH	Origin	74	1.12	113	111
		75	1.07	108	
		74	1.10	111	
	1st	75	0.94	110	103

		75	0.95	96	
		76	1.03	103	
	2nd	75	0.99	100	101
		75	1.04	105	
		74	0.97	98	
	3rd	74	1.00	101	97
		74	0.93	93	
		75	0.95	96	
BPAE-PTH	Origin	93	8.00	771	771
		93	8.05	776	
		92	7.92	765	
	1st	92	8.00	770	764
		93	7.92	763	
		93	7.98	769	
	2nd	92	7.94	767	766
		93	7.90	763	
		92	7.95	768	
	3rd	92	7.96	769	766
		92	7.90	763	
		92	7.93	765	

4.9 DSC analysis

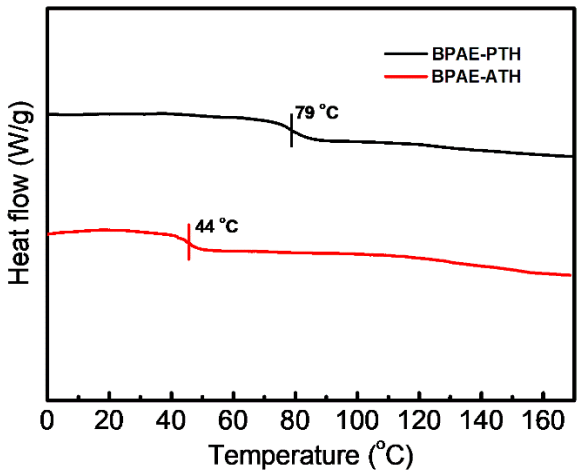


Figure S24. DSC curves BPAE-PTH and BPAE-ATH of vitrimer networks.

4.10 Solvent swelling

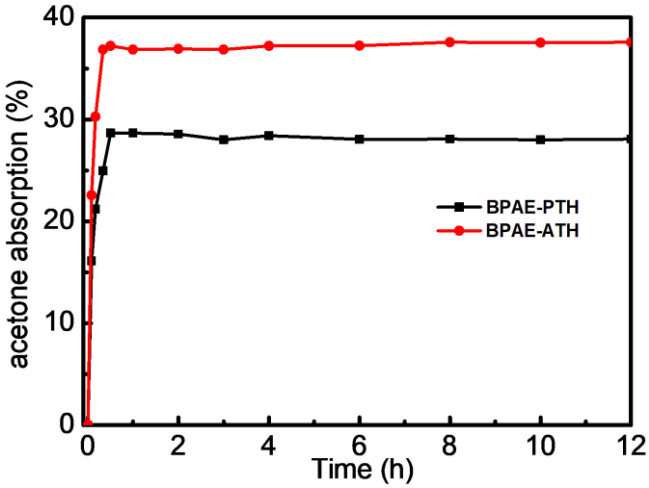


Figure S25. Solvent swelling (acetone absorption-time diagram) of BPAE-PTH and BPAE-ATH.

Table S10. Summary of solvent swelling of vitrimer networks

Sample	Swelling ratio	Gel content	$\overline{M}_C$
BPAE-PTH	28%	94%	1.29 g/mol
BPAE-ATH	37%	87%	1.45 g/mol

5. Studies of network curing using secondary amine substrate

The resin was prepared with a 1:1.05 ratio of alkyne group (or acetoacetyl group): amine group. A mixture of BPAE-P (or BPAE-A), TMPTP (or TMPTA) and 4,4'-trimethylenedipiperidine (TMPD) were dissolved in 3 mL DCM. Then, the mixture was poured into a polytetrafluoroethylene (PTFE) mold (8 cm* 8 cm* 1.5 cm) and dried for 48 hours at room temperature, yielding final TMPTP-H or TMPTA-H network.

Table S11. Contents of alkyne and secondary amine for network curing

Sample code	BPAE-P (mmol)	TMPTP (mmol)	BPAE-A (mmol)	TMPTA (mmol)	TMPD (mmol)	alkyne/acetoacetate : amine ratio
TMPTP-H	6.0	1.0	-	-	7.9	1 : 1.05
TMPTA-H	-	-	6.0	1.0	7.9	1 : 1.05

6. ^{1}H and ^{13}C NMR Spectra

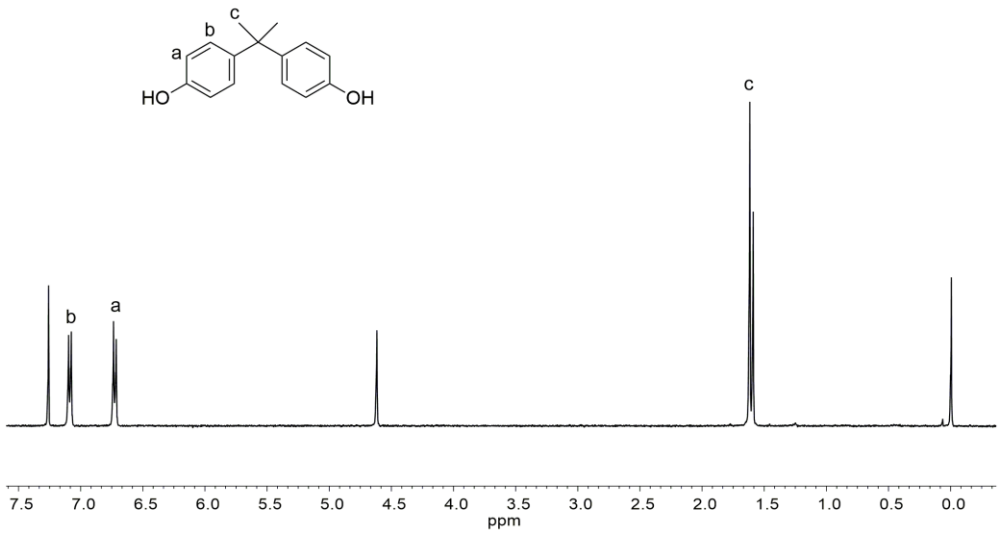


Figure S26. ^{1}H NMR Spectrum of Bisphenol A (BPA) (400 MHz, $CDCl_3$, 7.26 ppm)

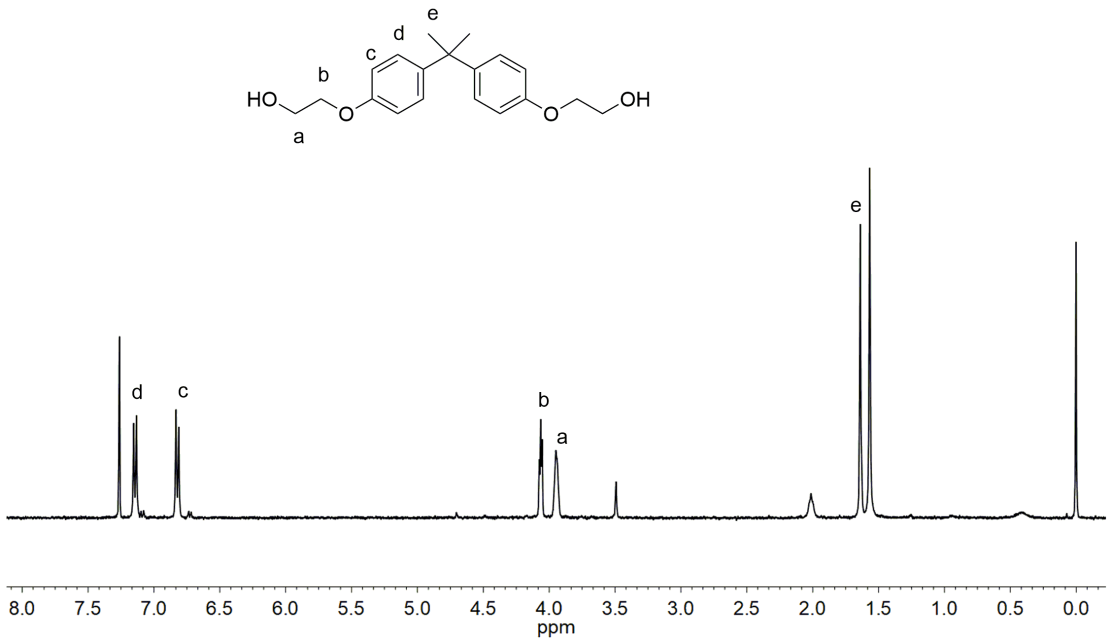


Figure S27. ^{1}H NMR Spectrum of Bisphenol A diethyl alcohol ether (BPAE) (400 MHz, $CDCl_3$, 7.26 ppm)

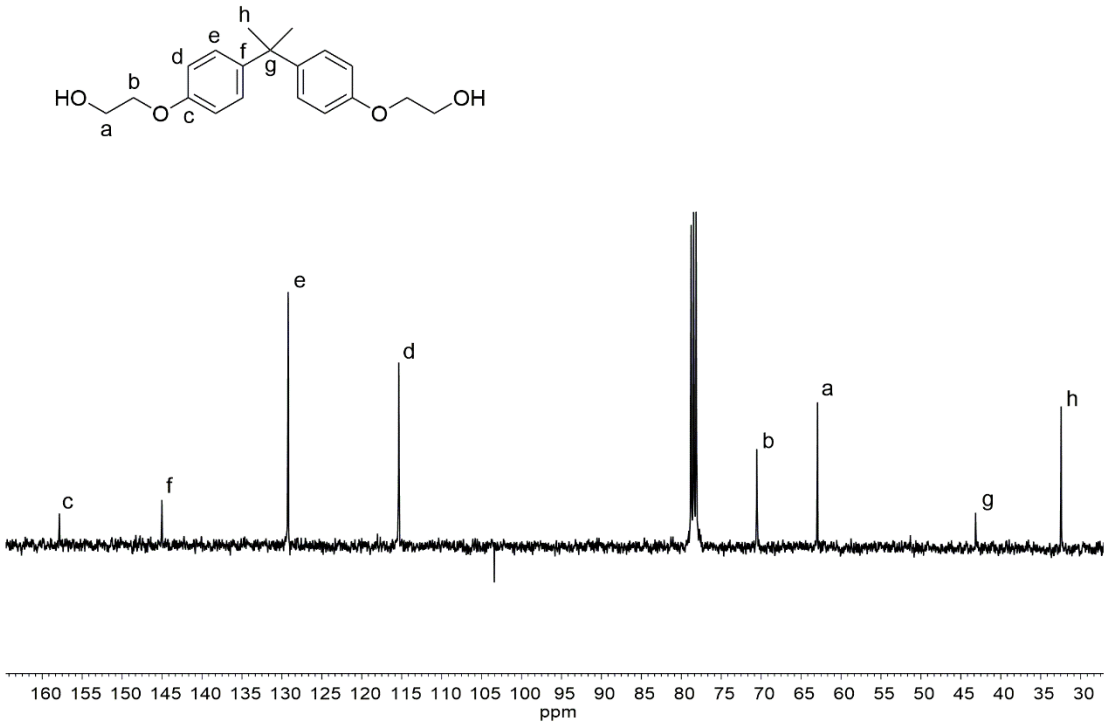


Figure S28. ^{13}C NMR Spectrum of Bisphenol A diethyl alcohol ether (BPAE) (100 MHz, $CDCl_3$, 77 ppm)

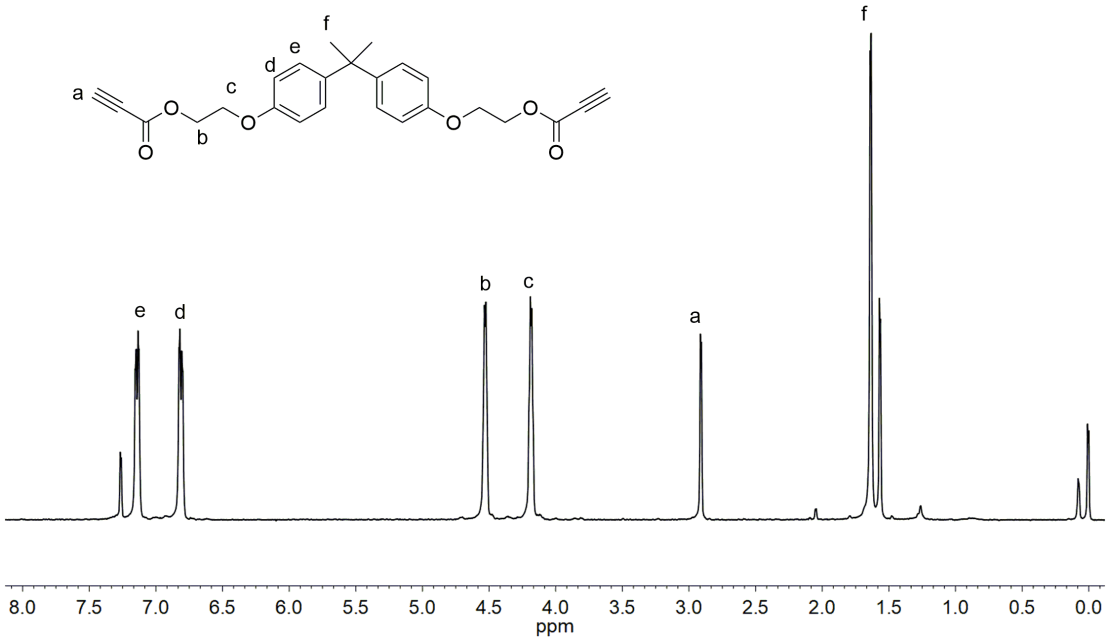


Figure S29. ^{1}H NMR Spectrum of Bisphenol A diethyl ether propionate (BPAE-P) (400 MHz, $CDCl_3$, 7.26 ppm)

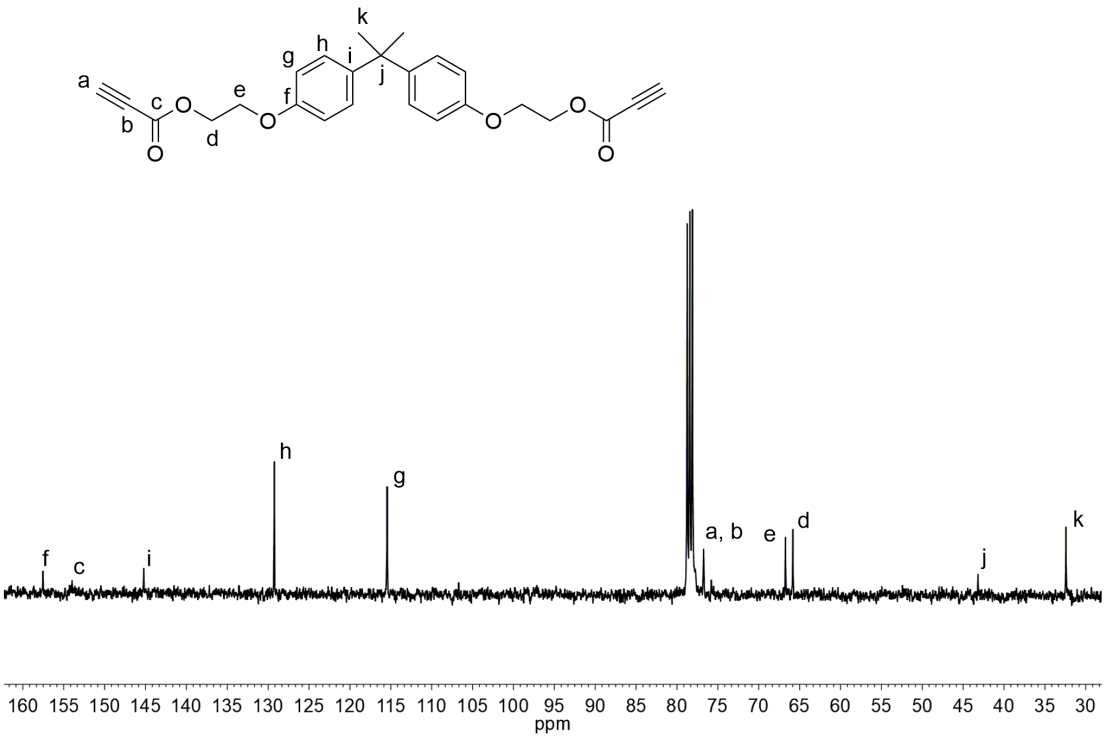


Figure S30. ^{13}C NMR Spectrum of Bisphenol A diethyl ether propionate (BPAE-P) (100 MHz, $CDCl_3$, 77 ppm)

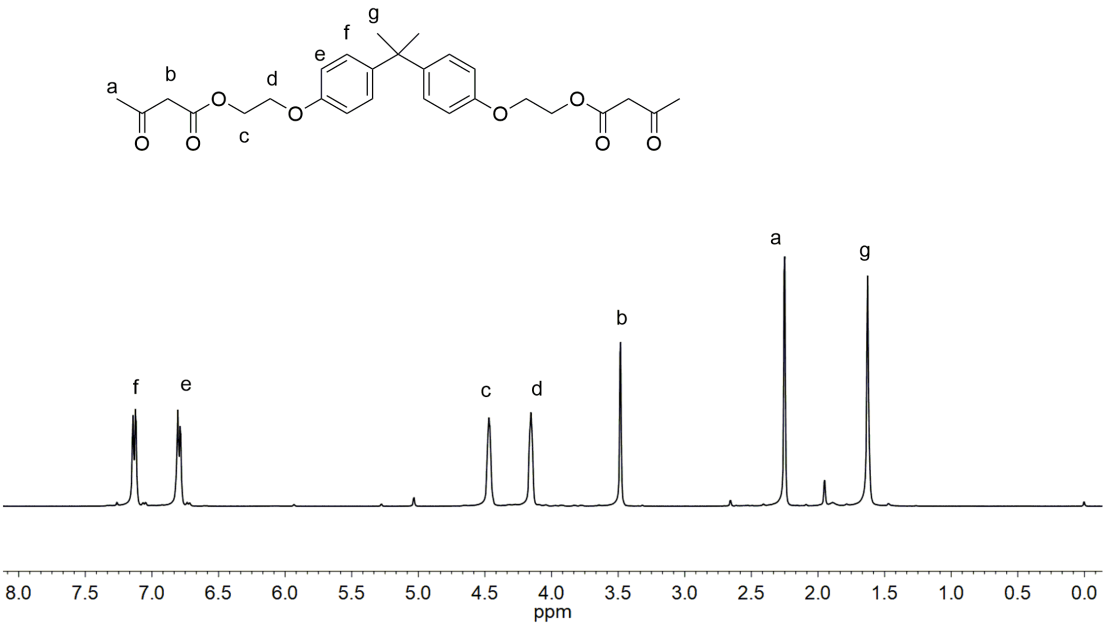


Figure S31. ^{1}H NMR Spectrum of Bisphenol A diethyl ether acetoacetate (BPAE-A) (400 MHz, $CDCl_3$, 7.26 ppm)

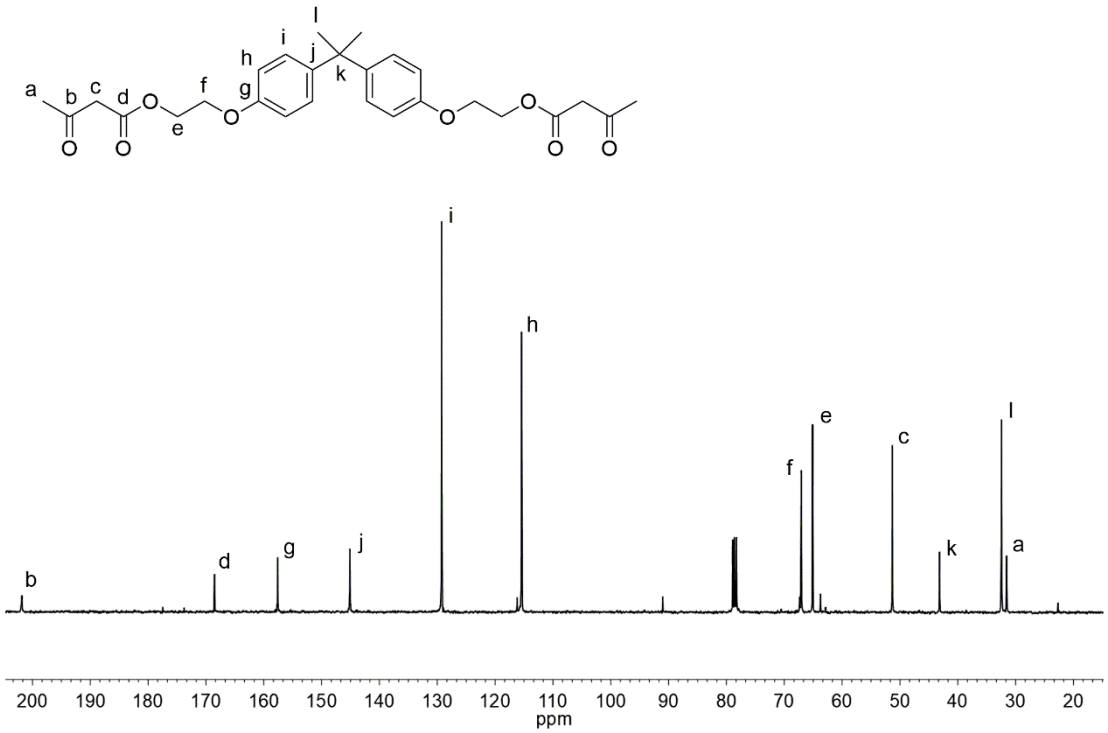


Figure S32. ^{13}C NMR Spectrum of Bisphenol A diethyl ether acetoacetate (BPAE-A) (100 MHz, $CDCl_3$, 77 ppm)

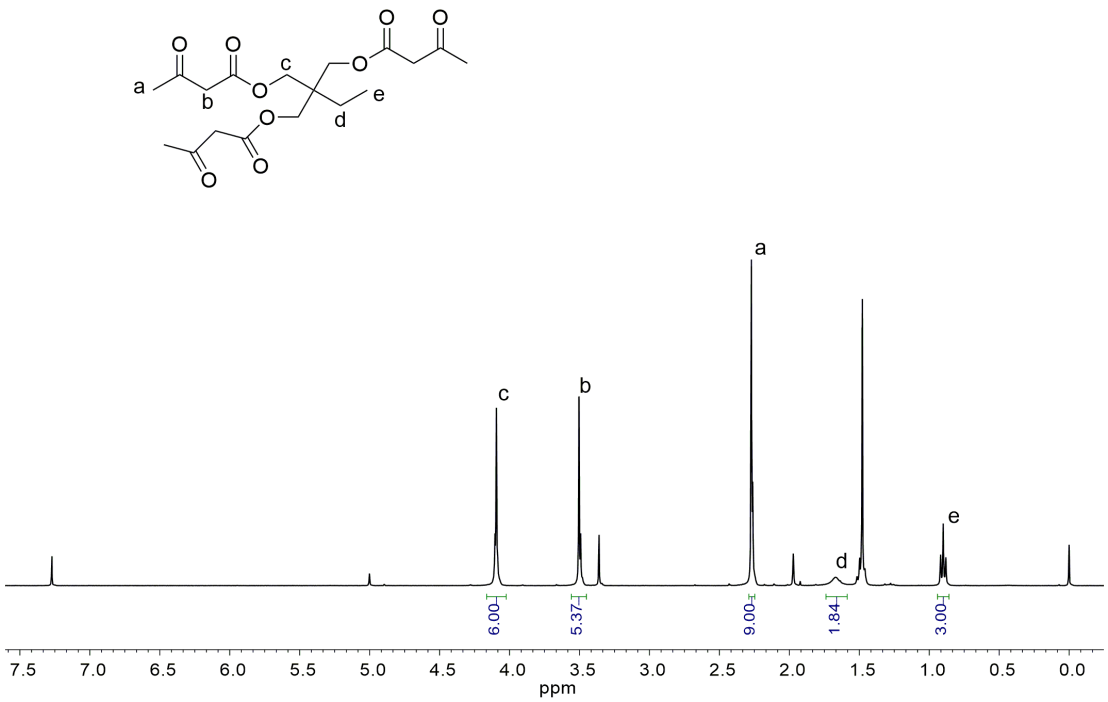


Figure S33. ^{1}H NMR Spectrum of trimethylolpropane triacetoacetate (TMPTA) (400 MHz, $CDCl_3$, 7.26 ppm)

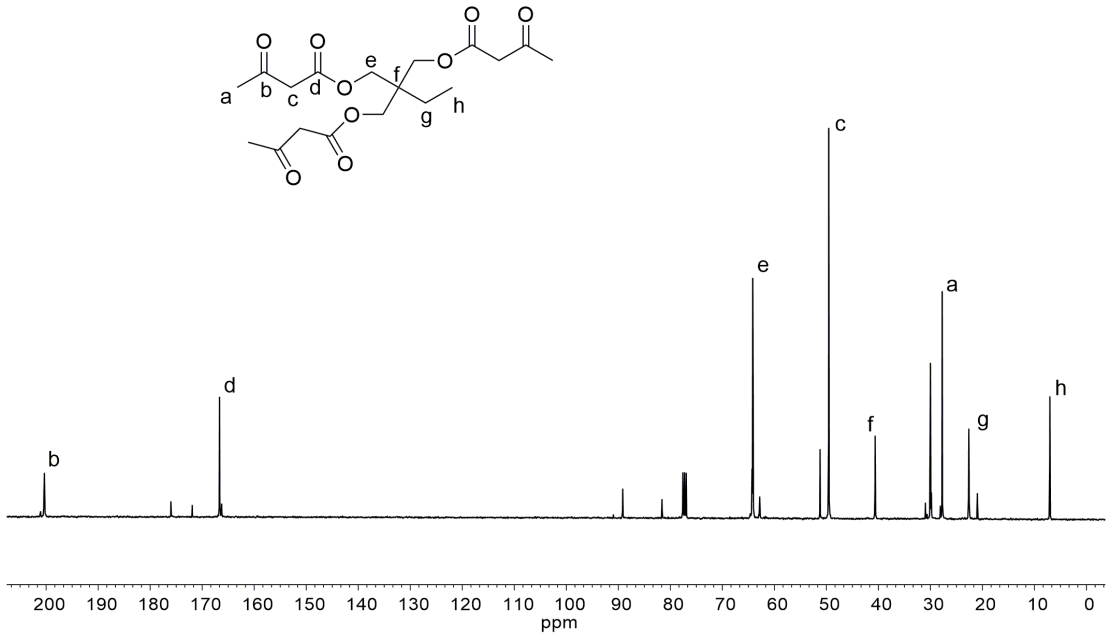


Figure S34. ^{13}C NMR Spectrum of trimethylolpropane triacetoacetate (TMPTA) (100 MHz, $CDCl_3$, 77 ppm)

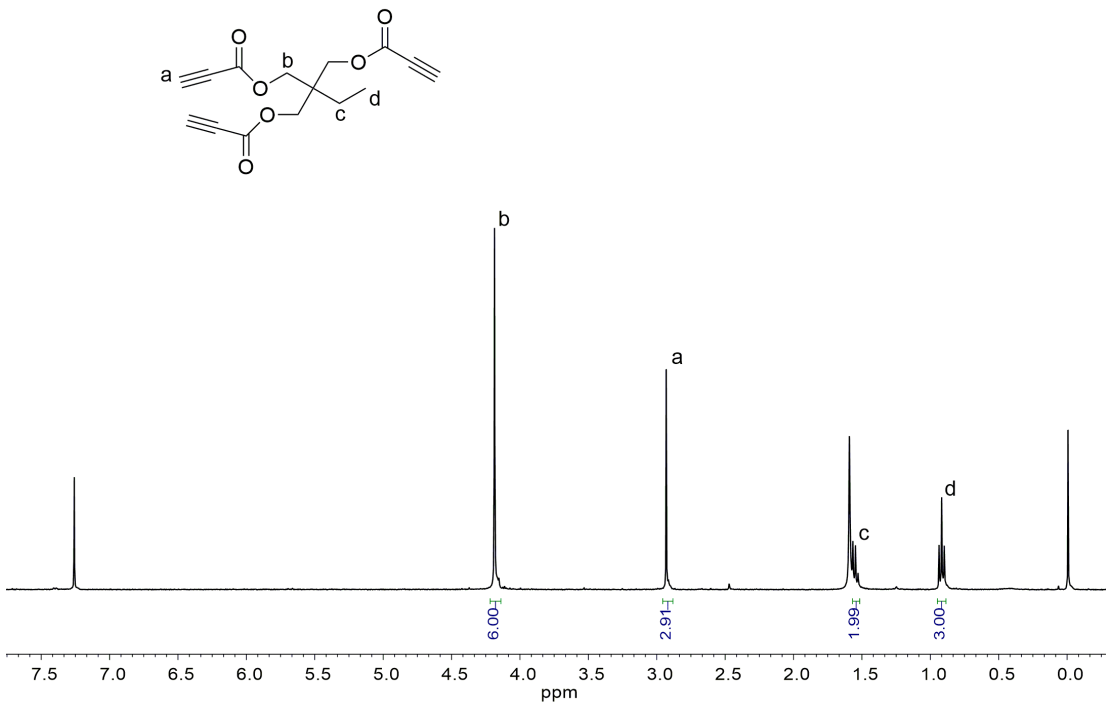


Figure S35. ^{1}H NMR Spectrum of trimethylolpropane tripropiolate (TMPTP) (400 MHz, $CDCl_3$, 7.26 ppm)

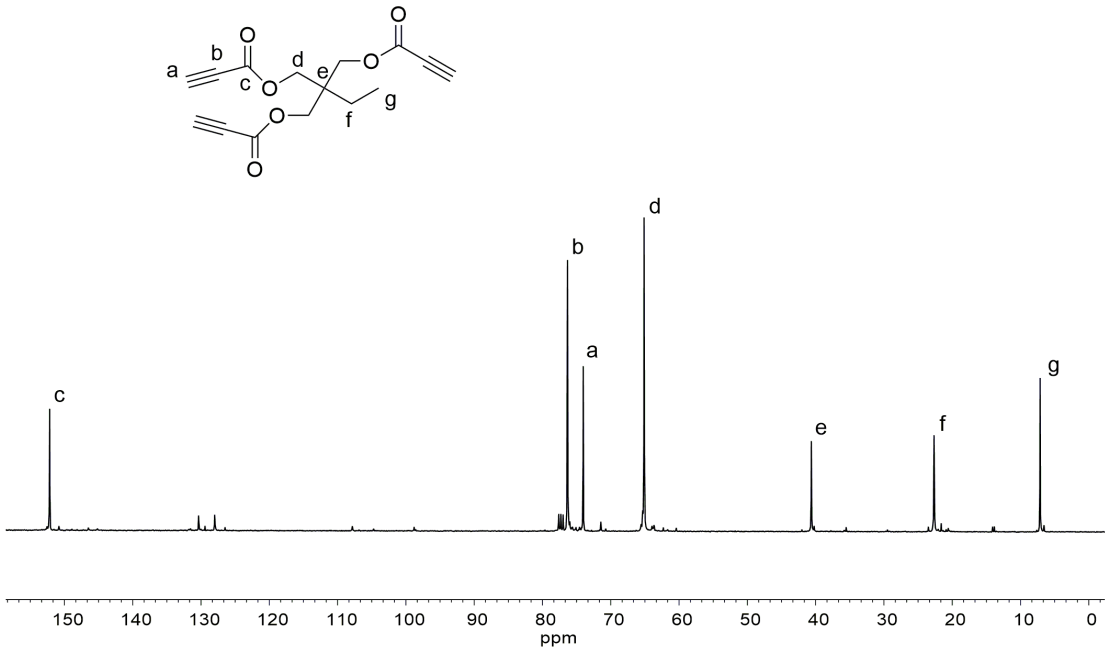


Figure S36. ^{13}C NMR Spectrum of trimethylolpropane tripropiolate (TMPTP) (100 MHz, $CDCl_3$, 77 ppm)

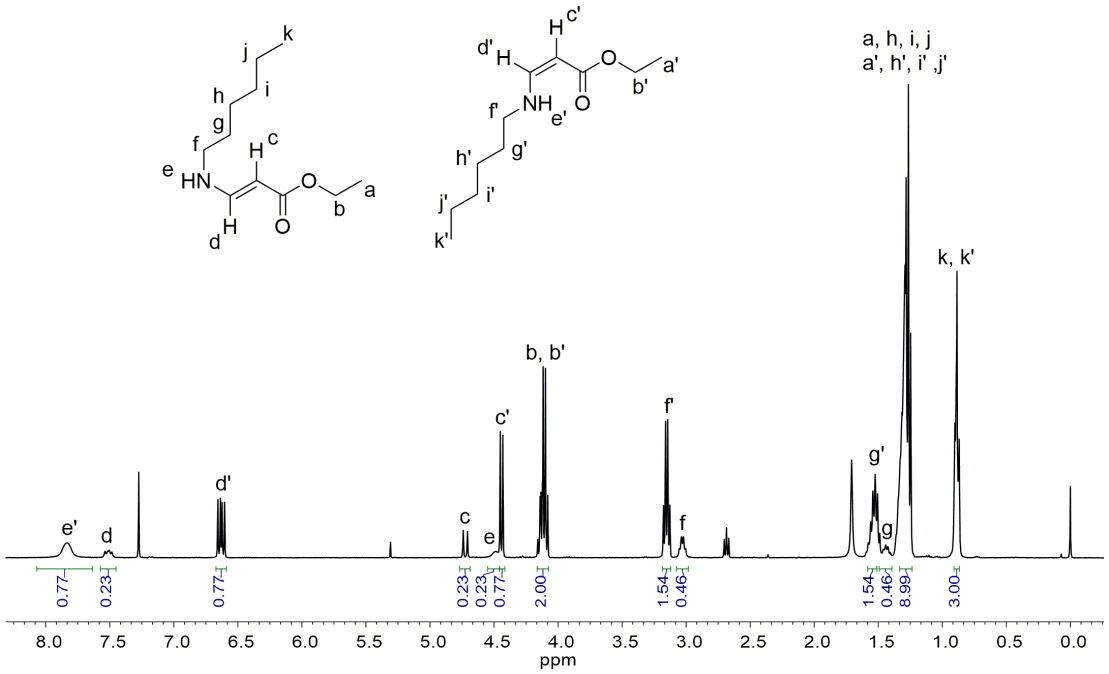


Figure S37. ^{1}H NMR Spectrum of ethyl (E)-3-(hexylamino)acrylate and ethyl (Z)-3-(hexylamino) acrylate (400 MHz, $CDCl_3$, 7.26 ppm)

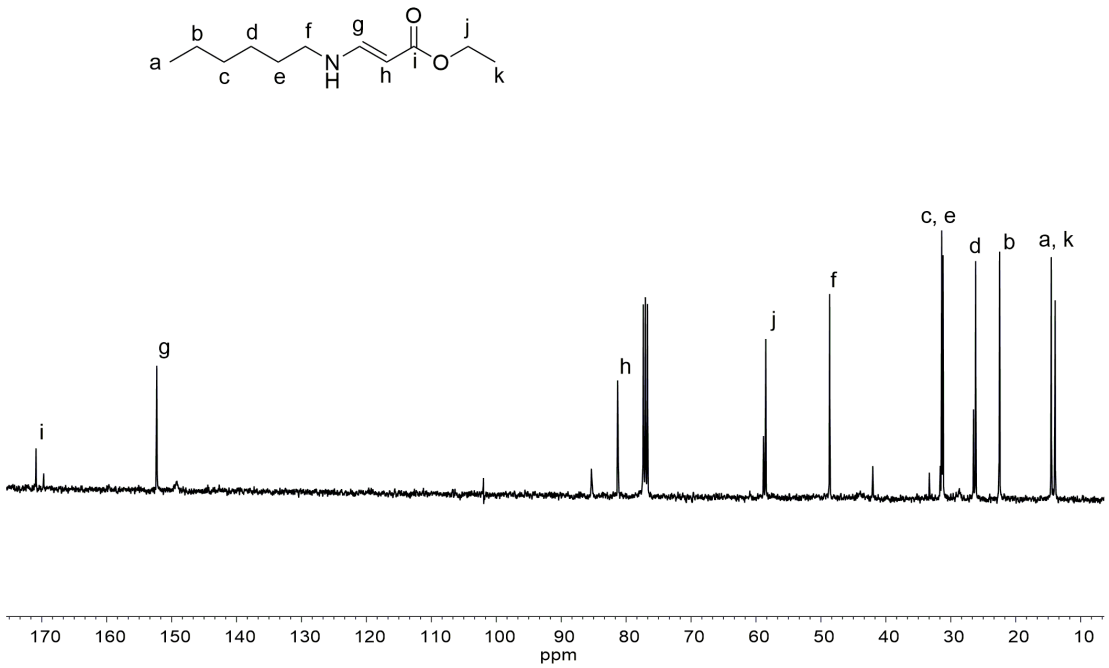


Figure S38. ^{13}C NMR Spectrum of ethyl (E)-3-(hexylamino)acrylate and ethyl (Z)-3-(hexylamino) acrylate (100 MHz, $CDCl_3$, 77 ppm)

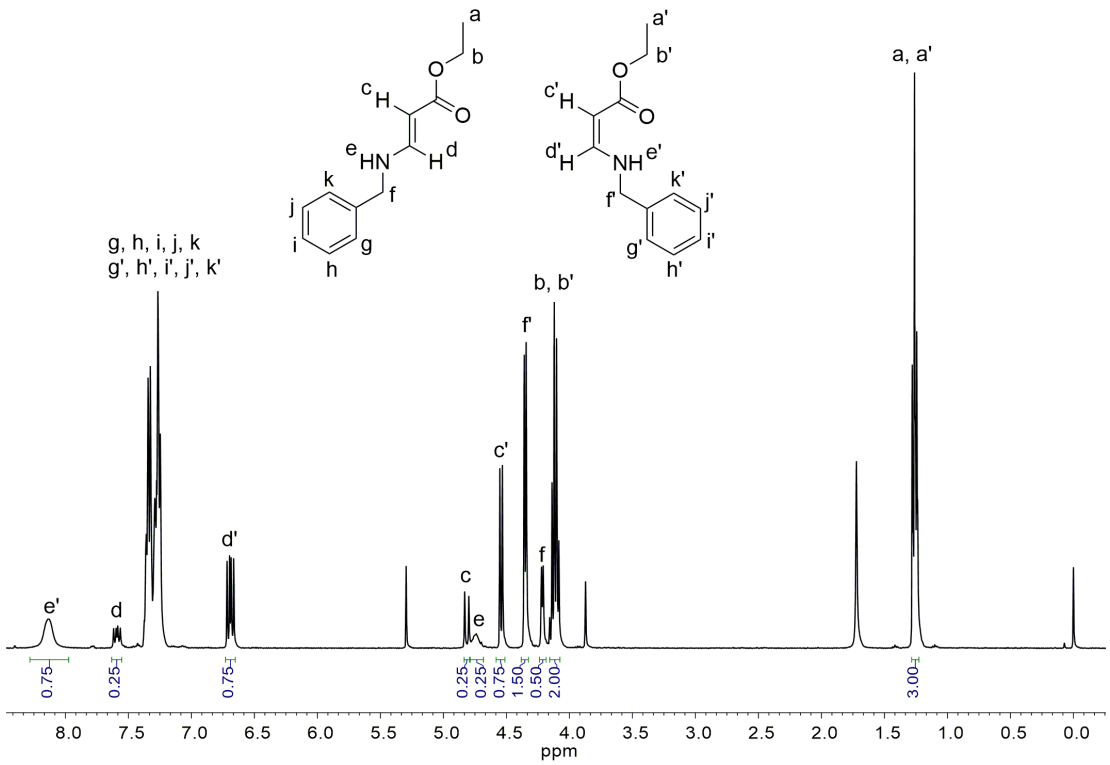


Figure S39. ^{1}H NMR Spectrum of ethyl (Z)-3-(benzylamino) acrylate and ethyl (E)-3-(benzylamino) acrylate (400 MHz, $CDCl_3$, 7.26 ppm)

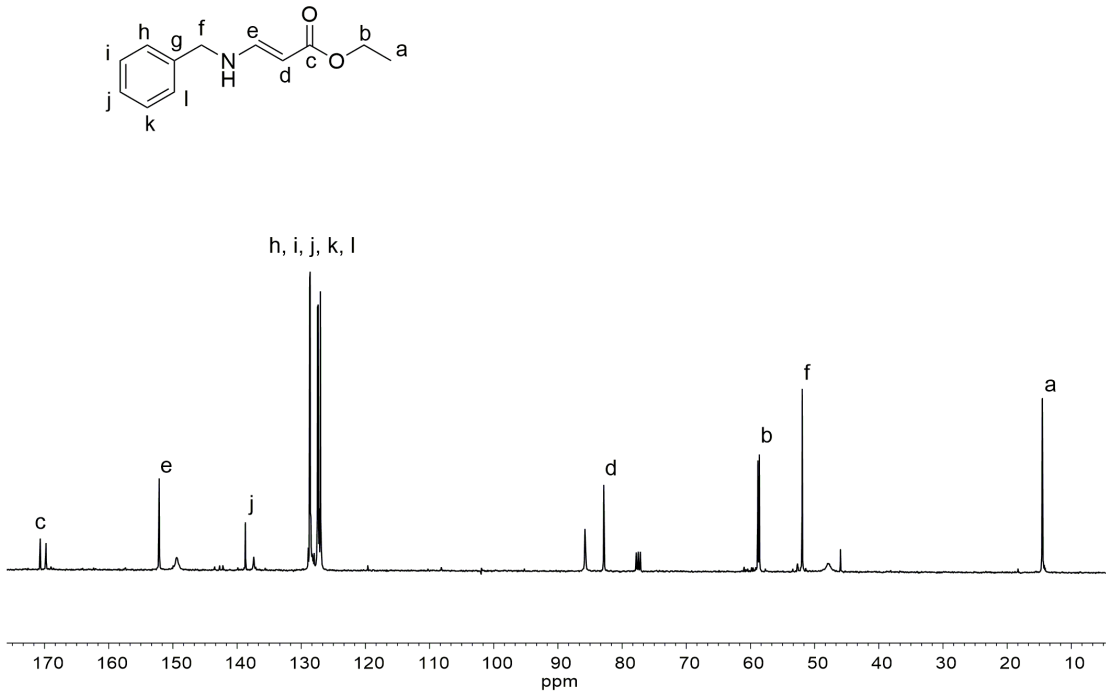


Figure S40. ^{13}C NMR Spectrum of ethyl (Z)-3-(benzylamino) acrylate and ethyl (E)-3-(benzylamino) acrylate (100 MHz, $CDCl_3$, 77 ppm)