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Electronic Supplementary Information

Reactive cycloalkane plasticizers covalently linked to energetic polyurethane binders *via* facile control of an *in situ* Cu-free azide-alkyne 1,3-dipolar cycloaddition reaction

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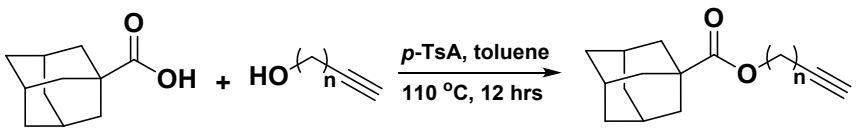
Synthesis of adamantane based RCAPs

A mixture of 1-adamantanecarboxylic acid (1.000 g, 5.548 mmol), propargyl alcohol or 3-butyn-1-ol (0.622 g or 0.778 g, 11.096 mmol), *p*-TsA (0.106 g, 0.555 mmol), and toluene (20 mL) was heated in a one-necked round bottom flask equipped with the Dean-Stark trap and condenser refluxing for 12 hrs (see Scheme S1 for synthetic route). After reaction, the toluene solution was cooled down, and extracted with 10 wt.% $NaCO_3$ solution and water, respectively. The toluene solution was then collected and dried with $MgSO_4$ overnight. After dryness, the toluene solution was filtered and toluene was removed by rotary evaporator to give the crude liquid product. The final crude product was purified by flash column chromatography to give yellow liquid (silica gel, ethyl acetate/ hexane (v/v) = 3/1).

PAC (n=1): Yield 93.2%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 ppm (m, 6H, CH–C**H**$_2$–CH), 1.87 ppm (m, 6H, CH–C**H**$_2$–C), 1.98 ppm (m, 3H, CH_2–C**H**–CH_2), 2.43 ppm (t, *J*=2.5 Hz, 1H, ≡C–**H**), 4.60 ppm (d, *J*=4.7 Hz, 2H, –C**H**$_2$–C≡). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 28.0, 36.6, 38.8, 40.8, 52.0, 74.8, 78.3, 177.0. FT-IR (neat, cm^{-1}): 3297 (≡C–H), 2905 (CH_2), 2851 (CH), 2127 (C≡C), 1729 (C=O).

BAC (n=2): Yield 95.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 ppm (m, 6H, CH–C**H**$_2$–CH), 1.83 ppm (m, 6H, CH–C**H**$_2$–C), 2.00 ppm (m, 3H, CH_2–C**H**–CH_2), 2.01 ppm (t, *J*=2.9 Hz, 1H, ≡C–**H**), 2.46 ppm (m, 2H, –C**H**$_2$–C≡), 4.09 ppm (t, *J*=4.3 Hz, 2H, O–C**H**$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 19.2, 28.1, 36.6, 38.9, 40.8, 61.8, 70.0, 80.3, 177.5. FT-IR (neat, cm^{-1}): 3304 (≡C–H), 2905 (CH_2), 2851 (CH), 2121 (C≡C), 1726 (C=O).



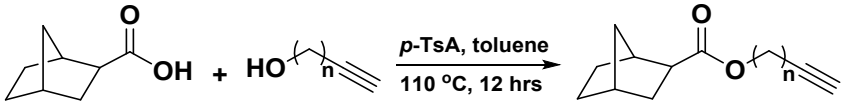
Scheme S1. Synthetic route to PAC (*n*=1) and BAC (*n*=2).

Synthesis of norbornane based RCAPs

A mixture of norbornane-2-carboxylic acid (1.000 g, 7.134 mmol), propargyl alcohol or 3-butyn-1-ol (0.799 g or 0.999 g, 14.267 mmol), *p*-TsA (0.136 g, 0.713 mmol) and toluene (20 mL) was heated in a one-necked round bottom flask equipped with the Dean-Stark trap and condenser refluxing for 12 hrs (see Scheme S2 for synthetic route). After reaction, the toluene solution was cooled down, and extracted with 10 wt.% $NaCO_3$ solution and water, respectively. The toluene solution was then collected and dried with $MgSO_4$ overnight. After dryness, the toluene solution was filtered and toluene was removed by rotary evaporator to give the crude liquid product. The final crude product was purified by flash column chromatography to give light yellow liquid (silica gel, ethyl acetate/ hexane (v/v) = 3/1).

PBCHC (n=1): Yield 94.2%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 - 1.73 ppm (m, 2H, 2H, 1H, 1H, 2H, –C–C**H**$_2$–C–, –C–C**H**$_2$–C–, –C–C**H**–C–, –C–C**H**–C–, –C–C**H**$_2$–C–), 2.24 ppm (s, 1H, –C–C**H**–COO–), 2.44 ppm (t, *J*=2.6 Hz, 1H, ≡C–**H**), 2.58 ppm (s, 1H, –C–C**H**$_2$–C–), 2.78 ppm (s, 1H, –C–C**H**$_2$–C–), 4.67 ppm (m, *J*=4.4 Hz, 2H, –C**H**$_2$–C≡). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 25.0, 29.2, 32.0, 37.1, 40.3, 40.8, 45.8, 51.9, 74.7, 78.2, 174.4. FT-IR (neat, cm^{-1}): 3299 (≡C–H), 2951 (CH_2), 2869 (CH), 2122 (C≡C), 1733 (C=O).

BBCHC (n=2): Yield 93.6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 - 1.74 ppm (m, 2H, 2H, 1H, 1H, 2H, –C–C**H**$_2$–C–, –C–C**H**$_2$–C–, –C–C**H**–C–, –C–C**H**–C–, –C–C**H**$_2$–C–), 2.00 ppm (t, *J*=2.8 Hz, 1H, ≡C–**H**), 2.24 ppm (s, 1H, –C–C**H**–C–), 2.49 - 2.54 ppm (m, 2H, 1H, –C**H**$_2$–C≡, –C–C**H**$_2$–C–), 2.78 ppm (s, 1H, –C–C**H**$_2$–C–), 4.18 ppm (m, 2H, O–C**H**$_2$). ^{13}C NMR (75MHz, $CDCl_3$, ppm) δ = 19.2, 25.0, 29.2, 32.0, 37.1, 40.3, 40.9, 46.0, 62.0, 70.0, 80.4, 175.0. FT-IR (neat, cm^{-1}): 3297 (≡C–H), 2956 (CH_2), 2873 (CH), 2122 (C≡C), 1732 (C=O).



Scheme S2. Synthetic route to the PBCHC (*n*=1) and BBCHC (*n*=2).

Preparation of GAP-based PU binders with RCAPs

GAP polyol (8.930 g, 1.62 mmol) was dried at 60 °C under vacuum for 1 hr and cooled to room temperature for 0.5 hr. The vacuum was then released and IPDI (0.504 g, 2.27 mmol) was added rapidly to GAP polyol. After stirring for 0.5 hr at room temperature, the predetermined amount of RCAPs based on the molar ratio of [acetylene group in RCAPs]/[azide group in GAP], two catalysts triphenyl bismuth (0.03 g, 20 wt.% in benzene) and 3,5-dinitro salicylic acid (0.05 g, 12.5 wt.% in benzene) was added and stirred for another 0.5 hr under vacuum. The mixture was then cast on a Teflon coated mold (5 cm × 8 cm), kept under vacuum at 30 °C for 3 hrs to remove the bubbles formed during the casting process, and then subject to curing. The curing process was carried out in an oven at 60 °C for 7 days. The control GAP-based PU binder was also prepared using the same procedure.

Cu-free 1,3-DPCA reaction between GAP and RCAPs

The azide-alkyne 1,3-DPCA reactivity of RCAPs was studied with GAP prepolymer under bulk conditions. A total of 1.0 g of the RCAP/GAP mixture ([C≡C]/[-N_3]=0.5:1) was mixed thoroughly in a vial. The mixture was then placed in an oven at 60 °C. A constant amount of sample was collected each time and dissolved in DMSO-d_6 to measure the conversion of the 1,3-DPCA reaction using a ^{1}H NMR spectrometer until the end of the 1,3-DPCA reaction.

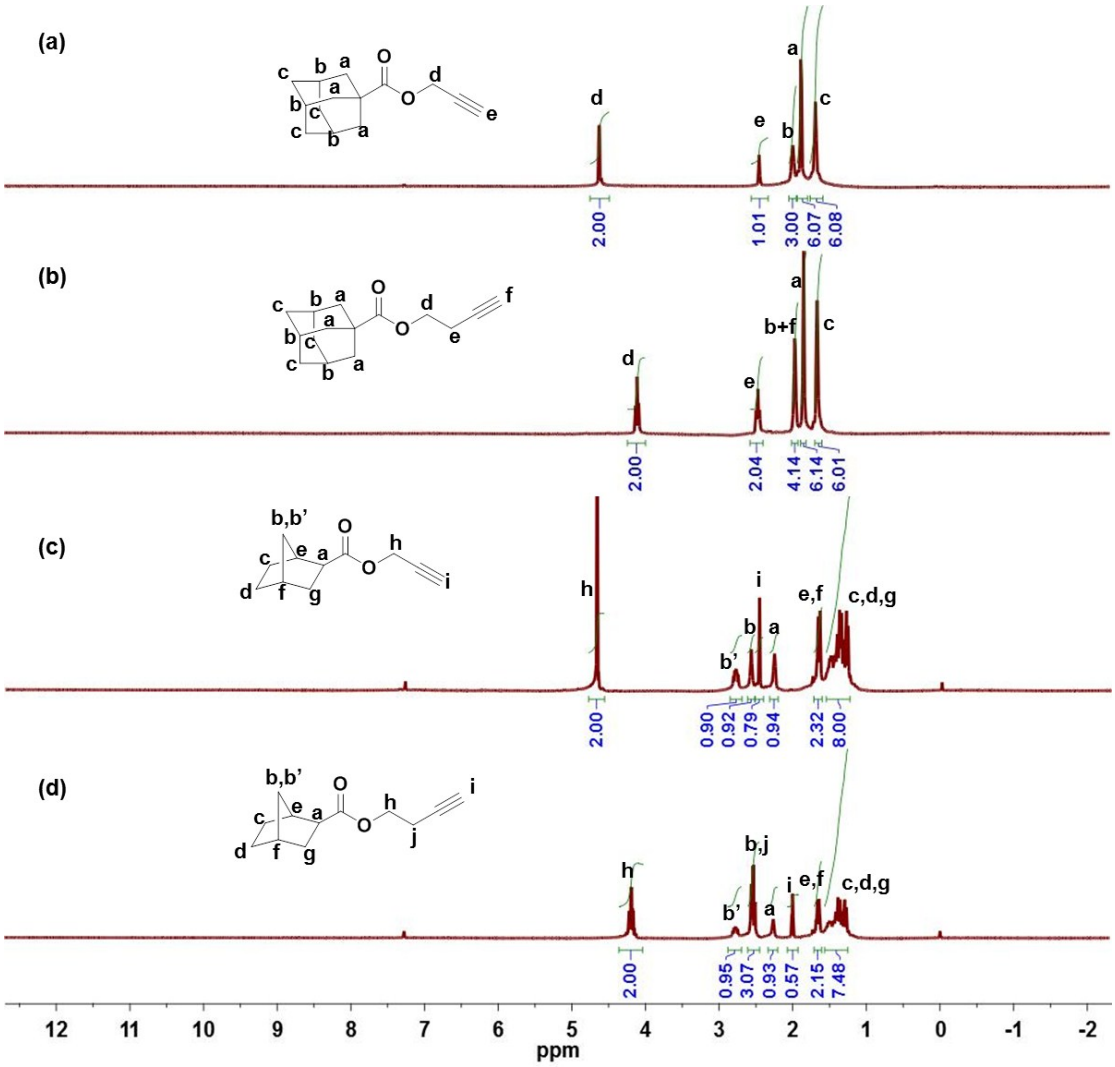


Fig. S1. ^{1}H NMR spectra of (a) PAC, (b) BAC, (c) PBCHC and (d) BBCHC.

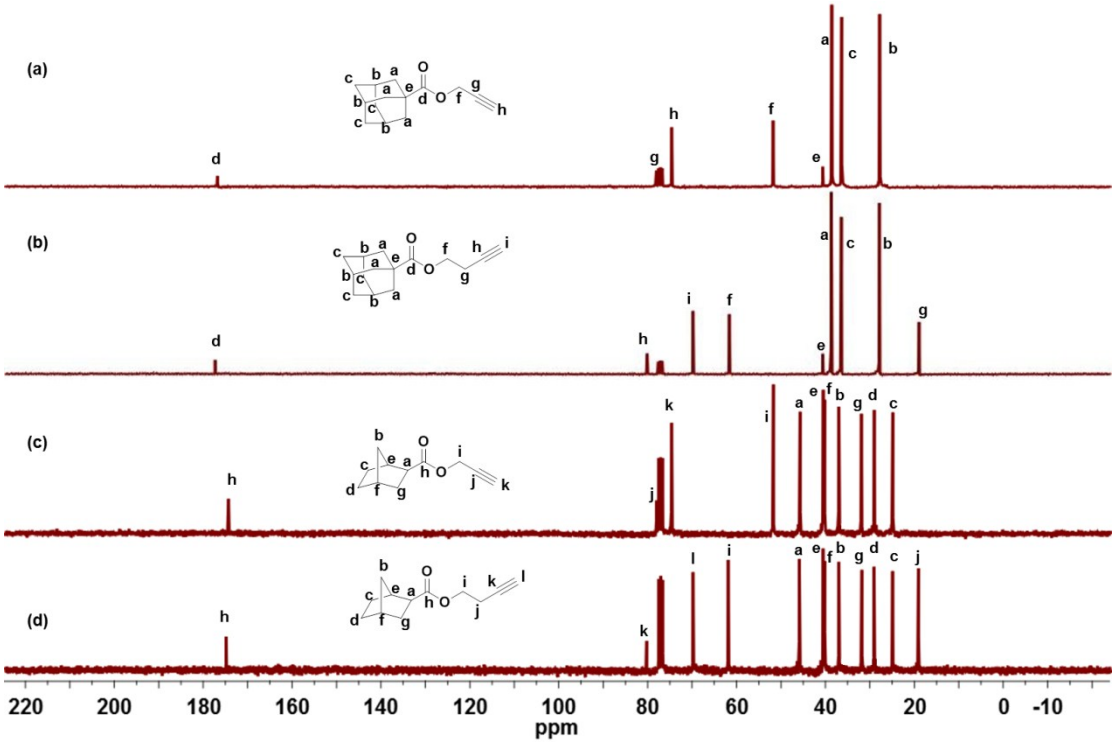


Fig. S2. ^{13}C NMR spectra of (a) PAC, (b) BAC, (c) PBCHC and (d) BBCHC.

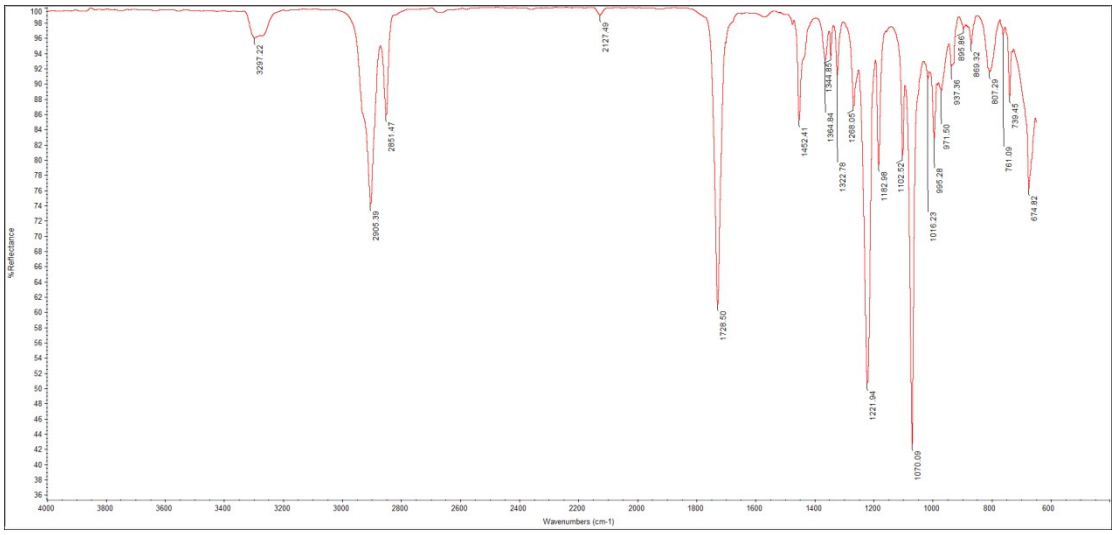


Fig. S3. FT-IR spectrum (neat) of PAC.

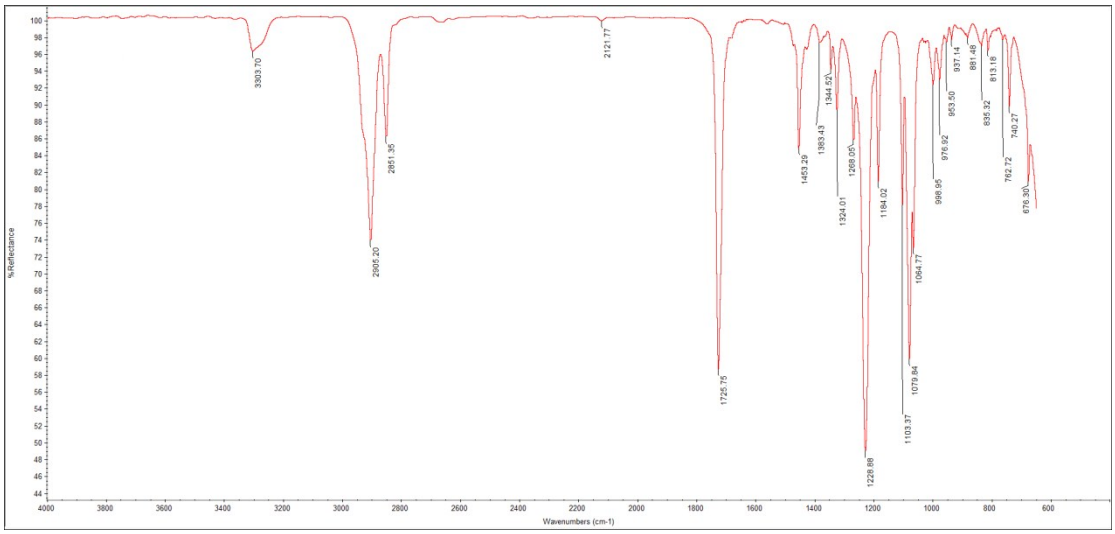


Fig. S4. FT-IR spectrum (neat) of BAC.

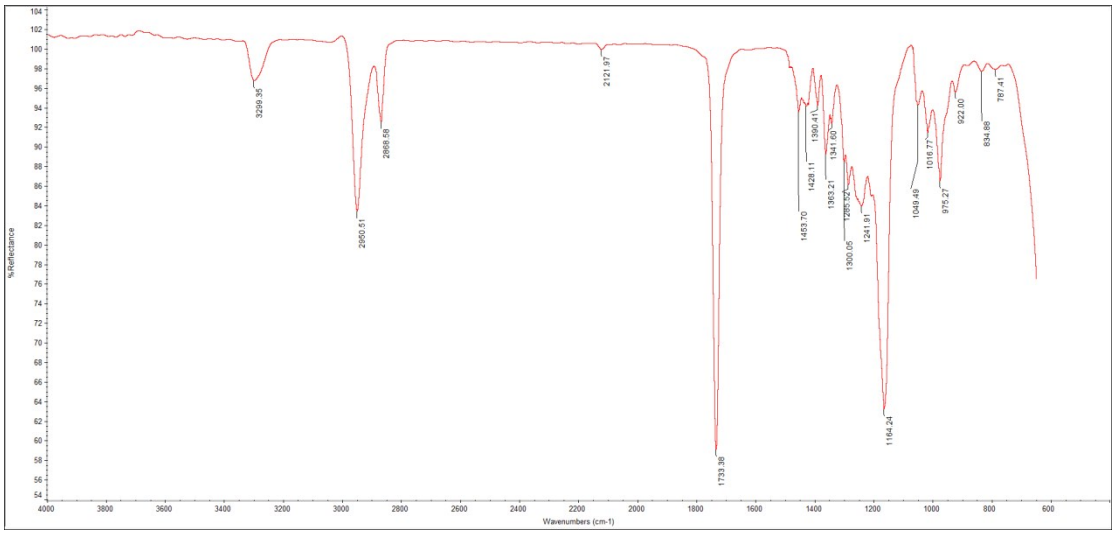


Fig. S5. FT-IR spectrum (neat) of PBCHC.

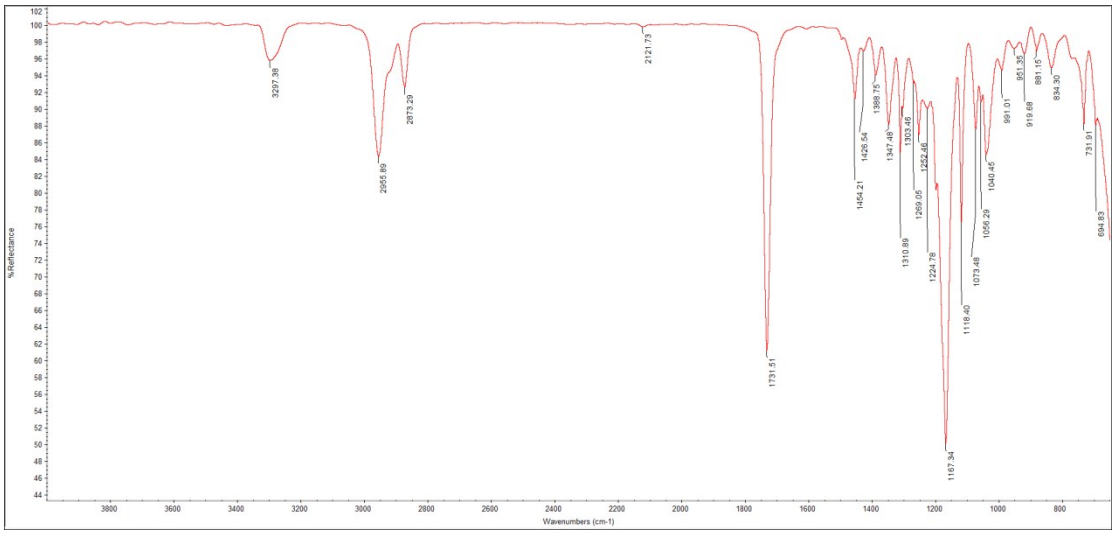


Fig. S6. FT-IR spectrum (neat) of BBCHC.

Fig. S7. Mass spectrum of PAC.

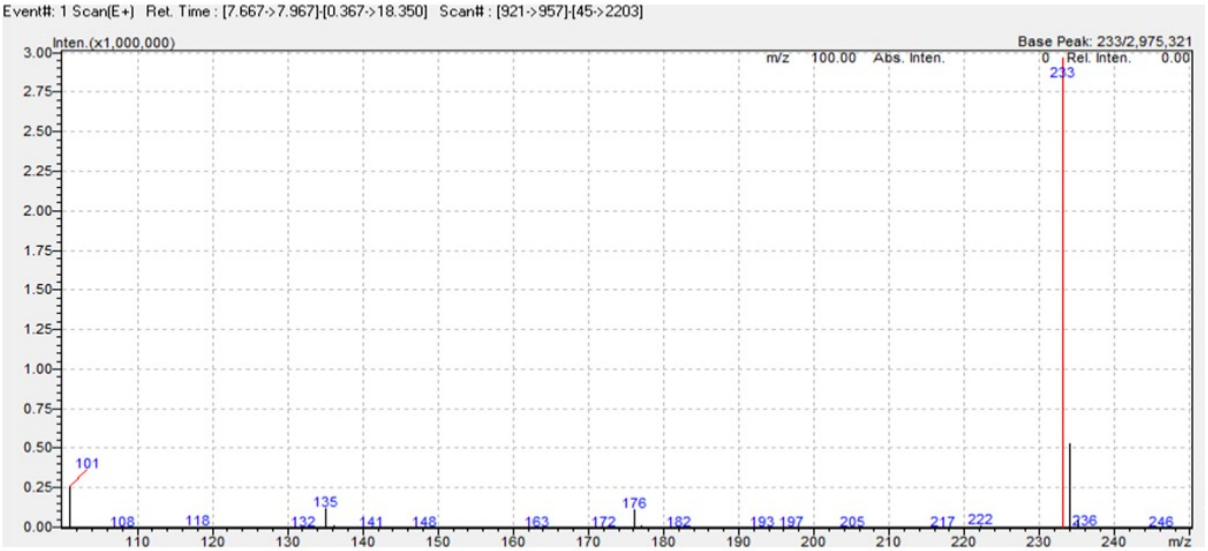


Fig. S8. Mass spectrum of BAC.

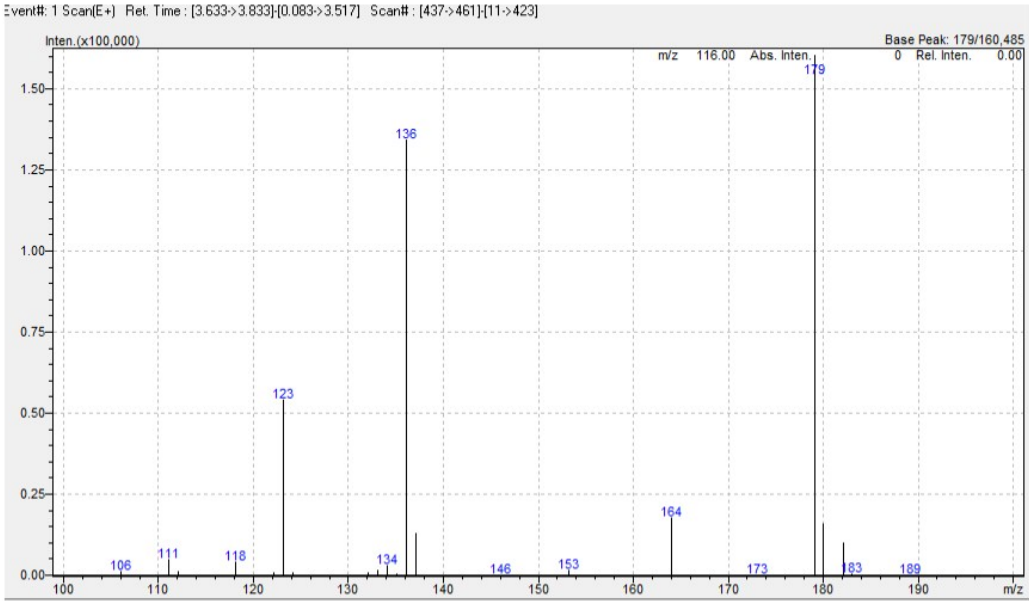


Fig. S9. Mass spectrum of PBCHC.

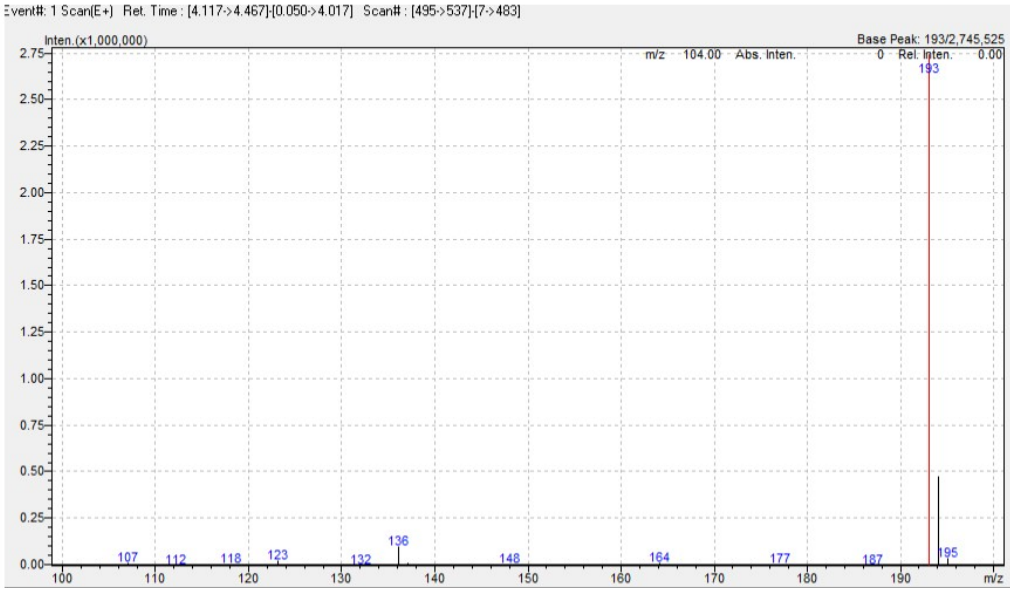


Fig. S10. Mass spectrum of BBCHC.

B3LYP/6-31G* Total Energies in hartrees.

Cartesian coordinates in Å.

All structures have zero imaginary frequencies.

The second column refers to the atom type: 1=hydrogen, 6=carbon, etc.

PAC

E(RB+HF-LYP) = -694.7332802

Sum of electronic and zero-point Energies= -694.437078

1	6	0	-0.973134	0.283025	-1.246789
2	1	0	0.146652	0.283025	-1.246789
3	1	0	-1.319425	1.347909	-1.246789
4	6	0	-1.489796	-0.428571	0.000000
5	6	0	-1.490091	-0.428747	-2.493341
6	1	0	-1.109525	0.095468	-3.409730
7	6	0	-1.000356	-1.873710	-2.491914
8	1	0	0.119164	-1.894878	-2.504445
9	1	0	-1.366850	-2.399437	-3.410169
10	6	0	-1.000007	-1.873521	-0.001406
11	1	0	-1.366209	-2.399141	0.917029
12	1	0	0.119516	-1.894641	0.010782
13	6	0	-1.516946	-2.587812	-1.246533
14	1	0	-1.156129	-3.650451	-1.246504
15	6	0	-3.042497	-2.567072	-1.246345
16	1	0	-3.429299	-3.099714	-2.152209
17	1	0	-3.429036	-3.099570	-0.340284
18	6	0	-3.015378	-0.410356	-0.001219
19	1	0	-3.382164	0.647575	0.011199
20	1	0	-3.401612	-0.921501	0.917194
21	6	0	-3.015677	-0.410431	-2.491696
22	1	0	-3.382376	0.647537	-2.503983
23	1	0	-3.402224	-0.921498	-3.410012
24	6	0	-3.534598	-1.122913	-1.246379
25	1	0	-4.656735	-1.108873	-1.246230
26	6	0	-0.967287	0.291004	1.257297
27	8	0	-0.264700	-0.128957	2.175756
28	8	0	-1.371304	1.585160	1.315082
29	6	0	-0.866935	2.217722	2.494225
30	1	0	0.202628	2.188610	2.484890
31	1	0	-1.230231	1.702305	3.358668
32	6	0	-1.340264	3.682655	2.533354
33	6	0	-1.707555	4.819404	2.563717
34	1	0	-2.033661	5.828686	2.590676

BAC

E(RB+HF-LYP) = -734.0530006

Sum of electronic and zero-point Energies= -733.727944

1	6	0	-0.888158	1.924342	0.000000
2	1	0	0.231628	1.924342	0.000000
3	1	0	-1.234449	2.989226	0.000000
4	6	0	-1.404820	1.212746	1.246789
5	6	0	-1.405115	1.212570	-1.246552
6	1	0	-1.024549	1.736785	-2.162941
7	6	0	-0.915380	-0.232393	-1.245125
8	1	0	0.204140	-0.253561	-1.257656
9	1	0	-1.281874	-0.758120	-2.163380
10	6	0	-0.915031	-0.232204	1.245383
11	1	0	-1.281233	-0.757824	2.163818
12	1	0	0.204492	-0.253324	1.257571
13	6	0	-1.431970	-0.946495	0.000256
14	1	0	-1.071153	-2.009134	0.000285
15	6	0	-2.957521	-0.925755	0.000444
16	1	0	-3.344323	-1.458397	-0.905420
17	1	0	-3.344060	-1.458253	0.906505
18	6	0	-2.930402	1.230961	1.245570
19	1	0	-3.297188	2.288892	1.257988
20	1	0	-3.316636	0.719816	2.163983
21	6	0	-2.930701	1.230886	-1.244907
22	1	0	-3.297400	2.288854	-1.257194
23	1	0	-3.317248	0.719819	-2.163223
24	6	0	-3.449622	0.518404	0.000410
25	1	0	-4.571759	0.532444	0.000559
26	6	0	-0.882311	1.932321	2.504086
27	8	0	-0.179724	1.512360	3.422545
28	8	0	-1.286328	3.226478	2.561871
29	6	0	-0.781959	3.859039	3.741014
30	1	0	0.287604	3.829927	3.731679
31	1	0	-1.145255	3.343623	4.605457
32	6	0	-1.255288	5.323972	3.780143
33	1	0	-2.324865	5.353129	3.787600
34	1	0	-0.890437	5.839866	2.916640
35	6	0	-0.714339	6.004439	5.051339
36	6	0	-0.294577	6.532464	6.037754
37	1	0	0.078116	7.001279	6.913558

PBCHC

E(RB+HF-LYP) = -577.9777013

Sum of electronic and zero-point Energies= -577.747599

1	6	0	-2.814323	-1.148988	1.389192
2	6	0	-1.272613	-1.148988	1.389192
3	6	0	-1.813728	1.060012	1.389192
4	6	0	-3.180894	0.347501	1.389380
5	1	0	-3.222727	-1.672810	0.493680
6	1	0	-3.205949	-1.656877	2.302370
7	1	0	-3.785417	0.623448	0.494088
8	1	0	-3.762577	0.616617	2.302891
9	6	0	-0.969987	0.095915	2.262705
10	1	0	0.109219	0.360309	2.282942
11	1	0	-1.354614	0.001716	3.301054
12	6	0	-0.816949	-0.659759	0.000131
13	1	0	0.282943	-0.801939	-0.123748
14	1	0	-1.336667	-1.211102	-0.817842
15	6	0	-1.183673	0.836735	0.000000
16	1	0	-1.899491	1.085050	-0.817990
17	1	0	-0.812337	-2.099481	1.716279
18	1	0	-1.844852	2.115596	1.716406
19	6	0	0.071447	1.712495	-0.171221
20	8	0	1.111136	1.743607	0.485773
21	8	0	-0.034731	2.564478	-1.222060
22	6	0	1.147855	3.358590	-1.347665
23	1	0	1.290355	3.929954	-0.454280
24	1	0	1.992154	2.719334	-1.500676
25	6	0	1.001157	4.311499	-2.548516
26	6	0	0.887323	5.050932	-3.480345
27	1	0	0.786253	5.707449	-4.307685

BBCHC

E(RB+HF-LYP) = -617.2976076

Sum of electronic and zero-point Energies= -617.038594

1	6	0	0.193929	0.059022	0.000000
2	6	0	1.735639	0.059022	0.000000
3	6	0	1.194524	2.268022	0.000000
4	6	0	-0.172642	1.555511	0.000188
5	1	0	-0.214475	-0.464800	-0.895512
6	1	0	-0.197697	-0.448867	0.913178
7	1	0	-0.777165	1.831458	-0.895104
8	1	0	-0.754325	1.824627	0.913699
9	6	0	2.038265	1.303925	0.873513
10	1	0	3.117471	1.568319	0.893750
11	1	0	1.653638	1.209726	1.911862
12	6	0	2.191303	0.548251	-1.389061
13	1	0	3.291195	0.406071	-1.512940
14	1	0	1.671585	-0.003092	-2.207034
15	6	0	1.824579	2.044745	-1.389192
16	1	0	1.108761	2.293060	-2.207182
17	1	0	2.195915	-0.891471	0.327087
18	1	0	1.163400	3.323606	0.327214
19	6	0	3.079699	2.920506	-1.560413
20	8	0	4.119388	2.951617	-0.903419
21	8	0	2.973522	3.772488	-2.611252
22	6	0	4.156108	4.566600	-2.736857
23	1	0	4.298608	5.137965	-1.843472
24	1	0	5.000406	3.927344	-2.889868
25	6	0	4.009410	5.519509	-3.937708
26	1	0	3.856568	4.948456	-4.829581
27	1	0	3.171302	6.165717	-3.779937
28	6	0	5.288936	6.364252	-4.082001
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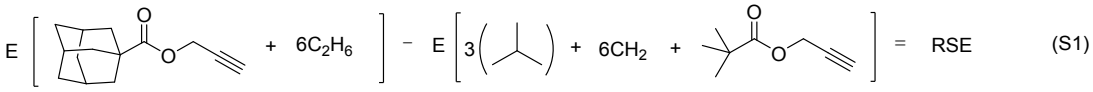
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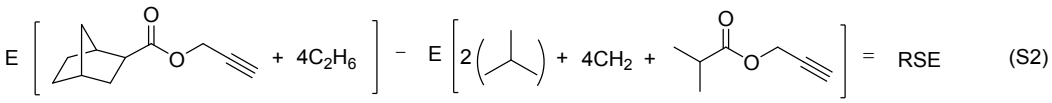
+ 6C2H6
E
3
+ 6CH2 +
= RSE (S1)


E
+ 4C2H6
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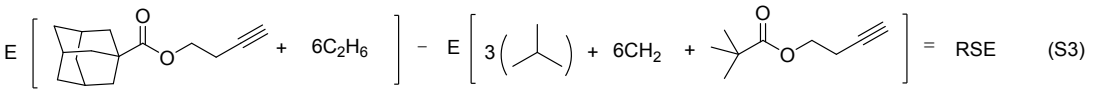
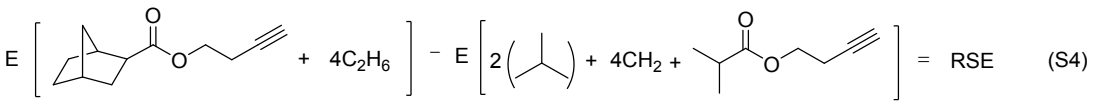
2
+ 4CH2 +
= RSE (S2)


E
+ 6C2H6
E
3
+ 6CH2 +
= RSE (S3)


E
+ 4C2H6
E
2
+ 4CH2 +
= RSE (S4)

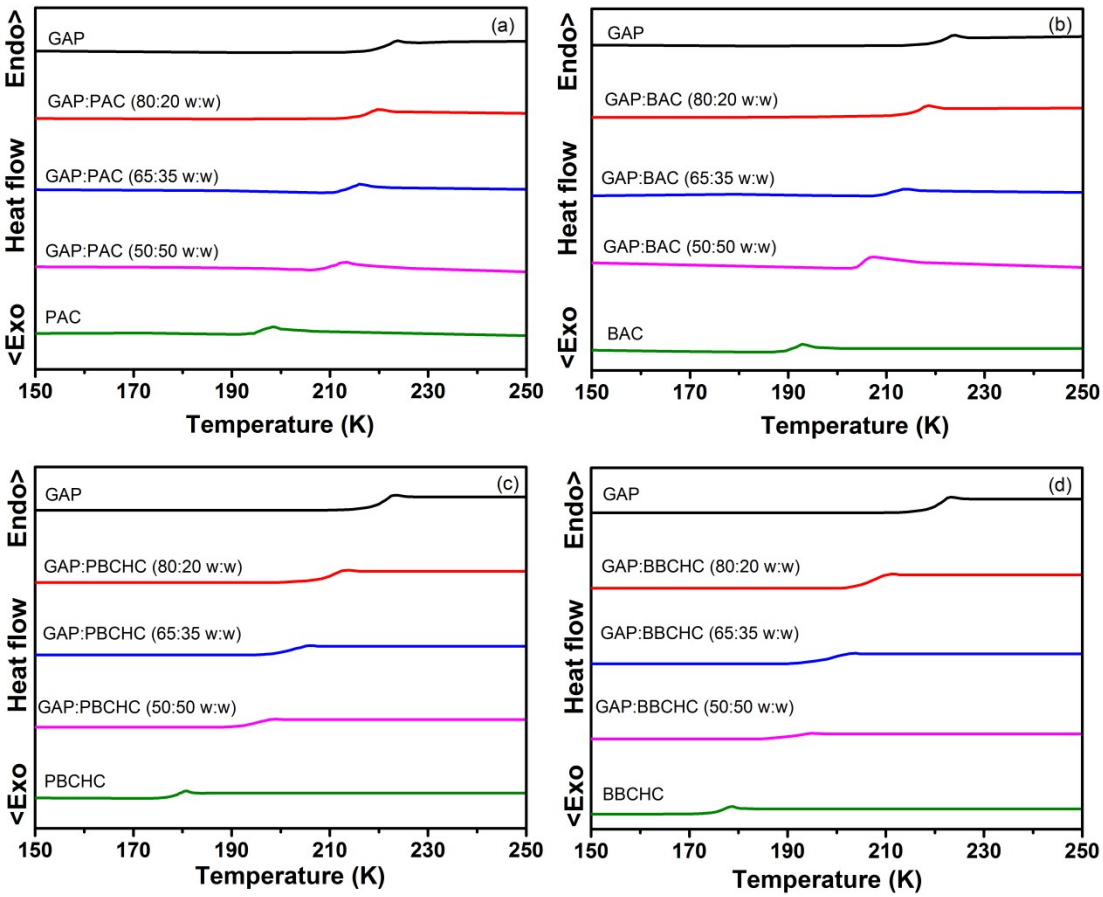


Fig. S11. DSC thermograms of (a) GAP:PAC; (b) GAP:BAC; (c) GAP:PBCHC; (d) GAP: BBCHC.

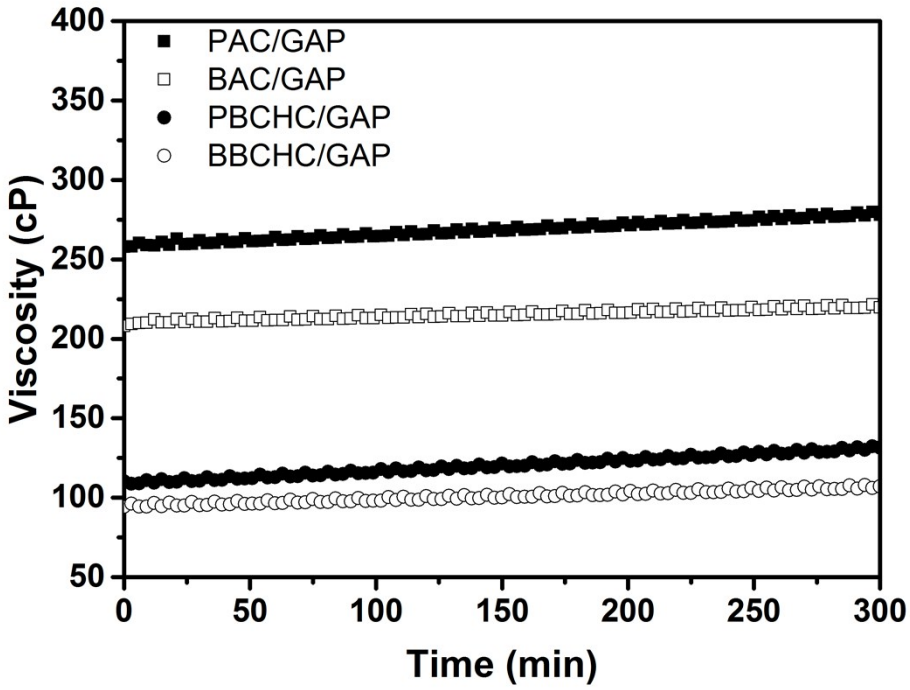


Fig. S12. Viscosity vs. time for binary mixtures of RCAPs/GAP prepolymer (50/50 w/w) isothermally at 30 ^{o}C.

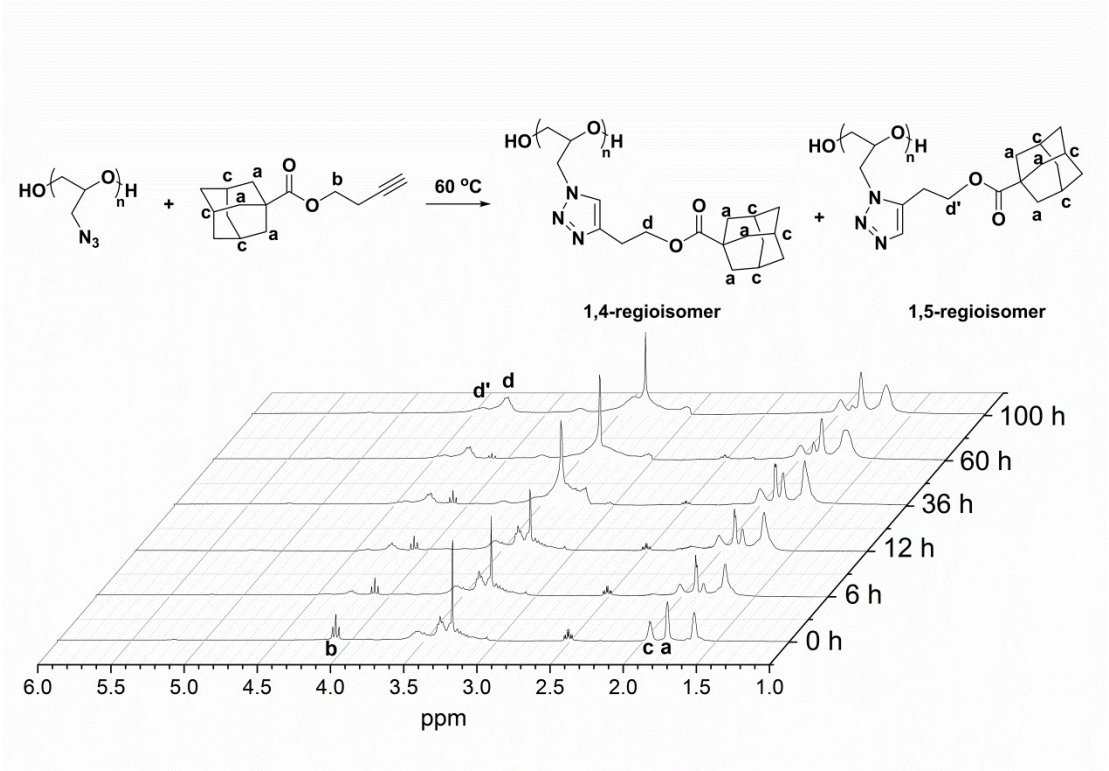


Fig. S13. ^{1}H NMR spectra as a function of reaction time of Cu-free azide-alkyne 1,3-DPCA reaction of BAC (n=2) and GAP prepolymer carried out in bulk condition at 60 ^{o}C.

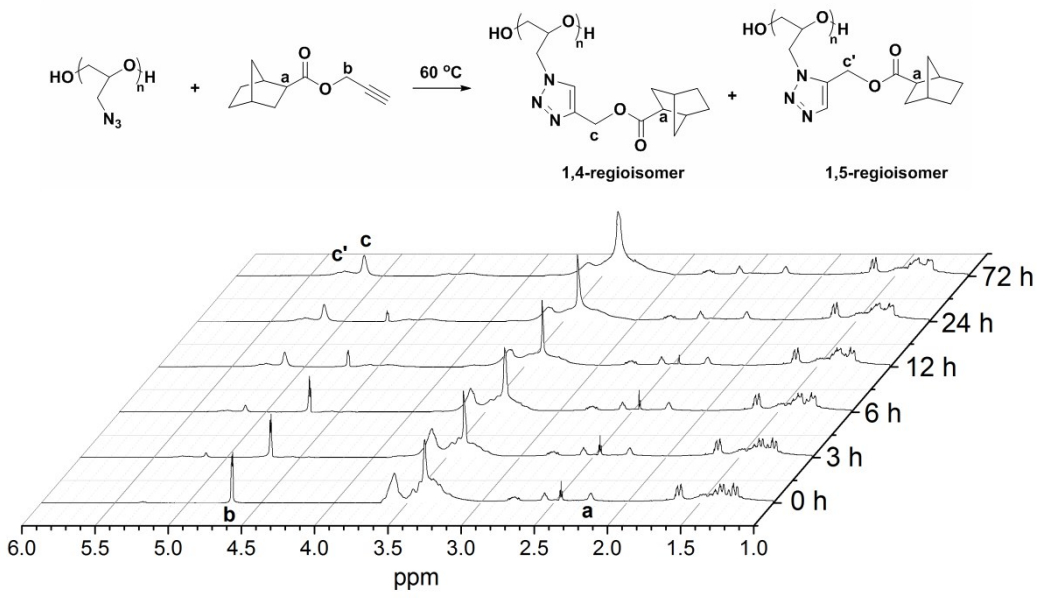


Fig. S14. ^{1}H NMR spectra as a function of reaction time of Cu-free azide-alkyne 1,3-DPCA reaction of PBCHC (*n*=1) and GAP prepolymer carried out in bulk condition at 60 ^{o}C.

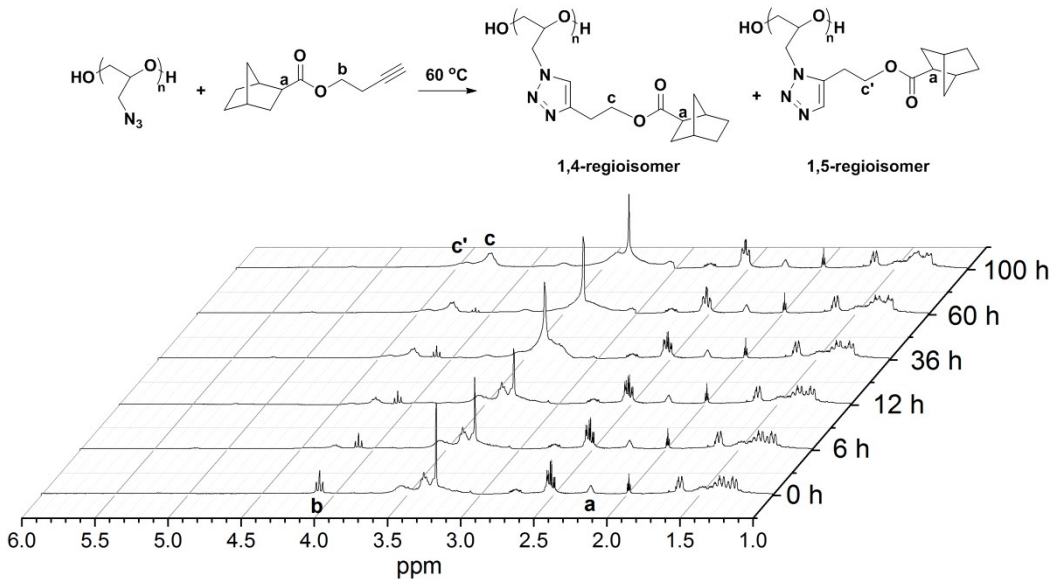


Fig. S15. ^{1}H NMR spectra as a function of reaction time of Cu-free azide-alkyne 1,3-DPCA reaction of BBCHC (*n*=2) and GAP prepolymer carried out in bulk condition at 60 ^{o}C.

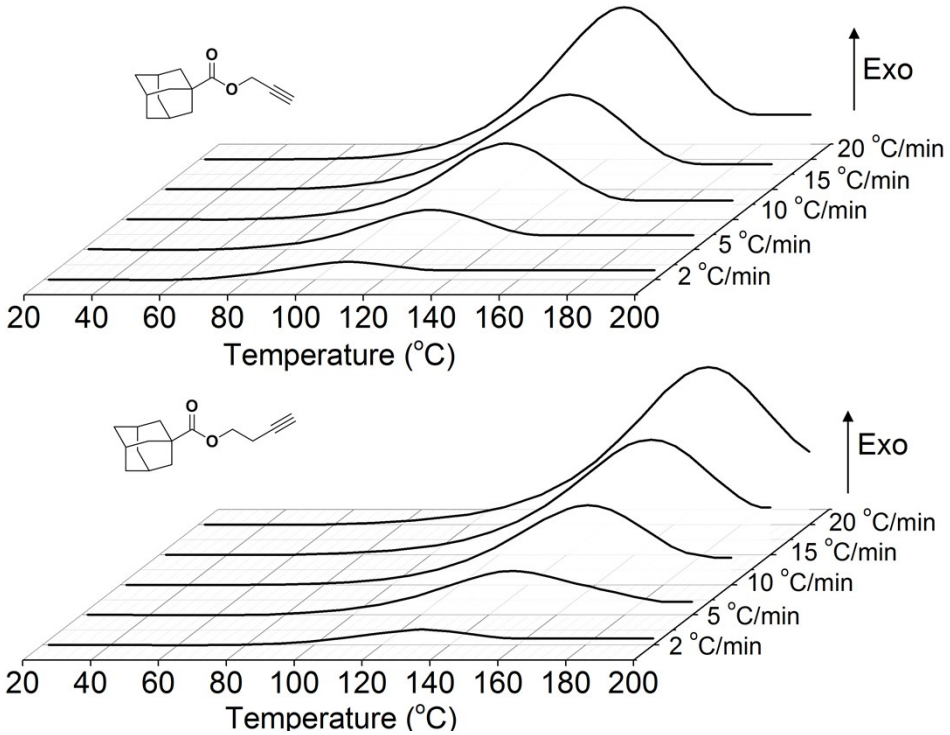


Fig. S16. Dynamic DSC curves of PAC (*n*=1)/GAP (top) and BAC (*n*=2)/GAP (bottom) mixtures at different heating rates.

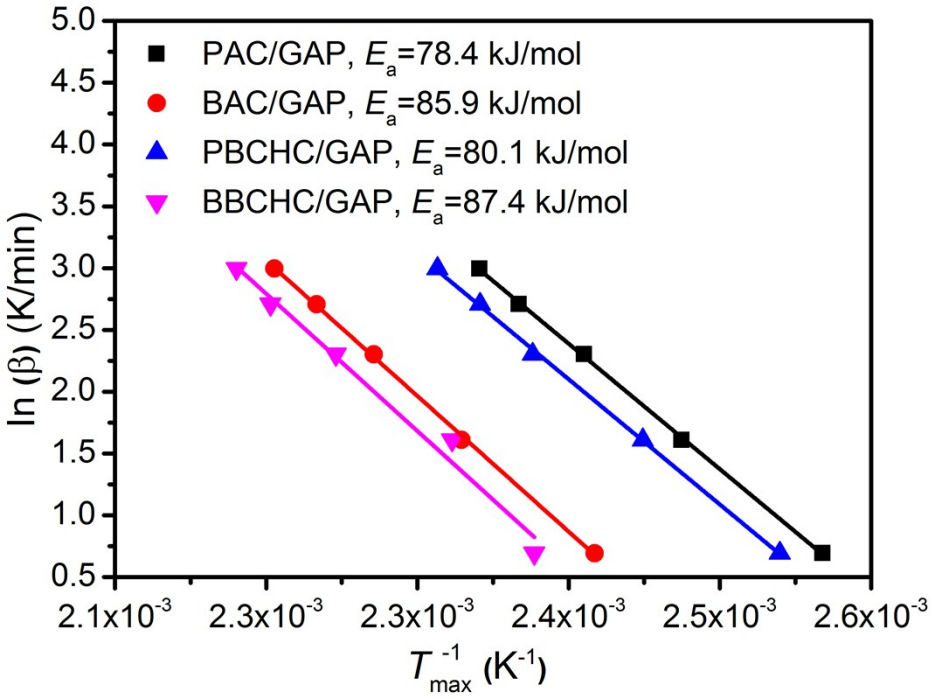


Fig. S17. Arrhenius plots of ln(β) versus $T-1$ *max*. For all samples, the linear fitting coefficient of determination (R^2) was greater than 0.99. Activation energy, E_a was determined by plotting ln(β) against $T-1$ *max*.

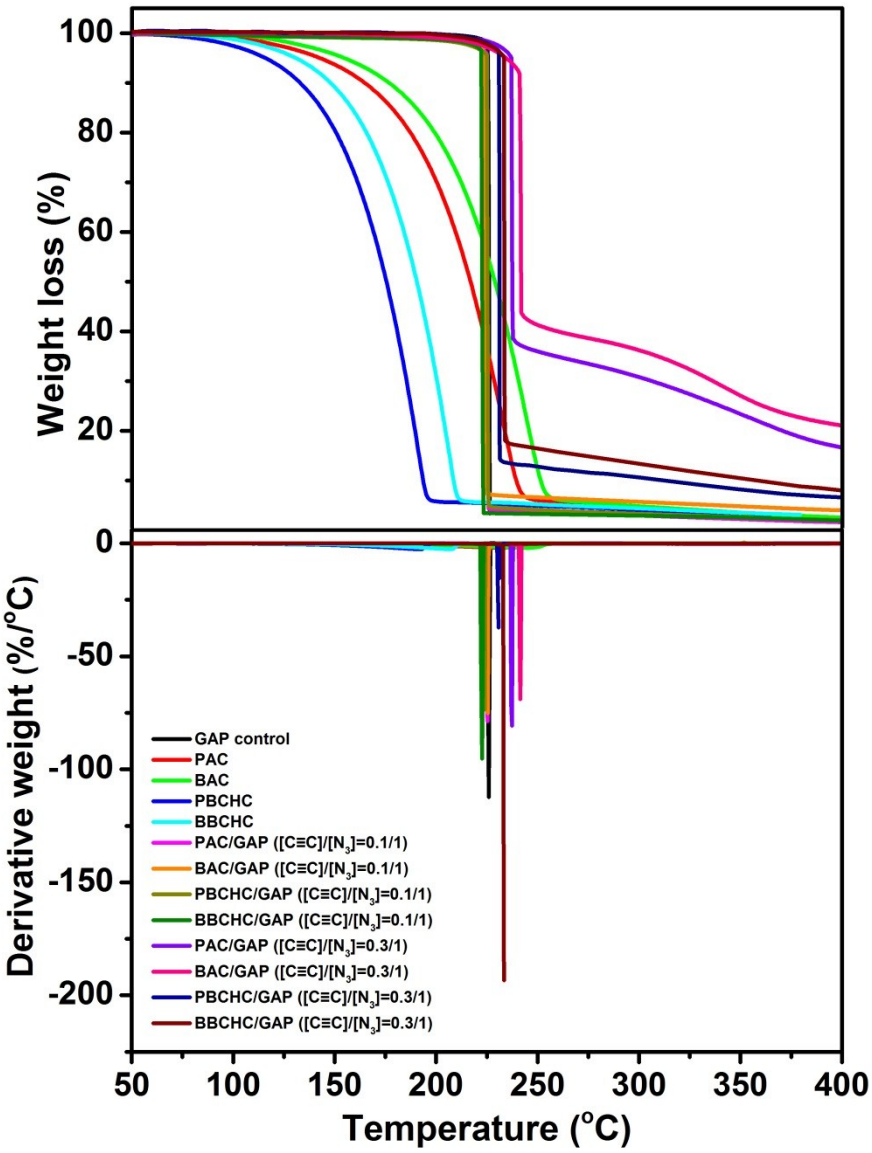
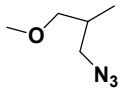
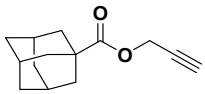
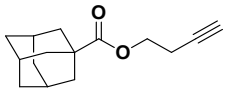
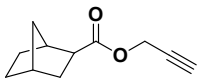
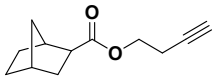


Fig. S18. TGA (top) and DTG (bottom) curves of the RCAPs and RCAPs/GAP-based PUs.

Table S1. Computational results of orbital energies at the B3LYP/6-31G* level of theory (eV).

Dipole	HOMO	LUMO
	-6.734	-0.776
Dipolarophile	**HOMO**	**LUMO**
	-7.071	0.265
	-7.074	0.331
	-7.245	0.182
	-7.256	0.251

1-Azido-3-methoxy-2-methylpropane

Alpha occ. eigenvalues -- -0.24749

Alpha virt. eigenvalues -- -0.02851 0.01165 0.08848 0.10733 0.11392

PAC

Alpha occ. eigenvalues -- -0.25988

Alpha virt. eigenvalues -- 0.00973 0.02403 0.04939 0.06827 0.11372

BAC

Alpha occ. eigenvalues -- -0.25998

Alpha virt. eigenvalues -- 0.01218 0.04736 0.05478 0.06574 0.10426

PBCHC

Alpha occ. eigenvalues -- -0.26627

Alpha virt. eigenvalues -- 0.00668 0.02416 0.04904 0.08140 0.10440

BBCHC

Alpha occ. eigenvalues -- -0.26668

Alpha virt. eigenvalues -- 0.00923 0.04727 0.05470 0.08036 0.09919

Table S2. Percentage of carbon (C), hydrogen (H), oxygen (O) and nitrogen (N), and empirical formula for GAP and respective RCAP/GAP polymers.

PU[a]	Elemental analysis (wt.%)				Experimental formula for 100 g
	C ±0.6	H ±0.4	O ±1.1	N ±0.4	
GAP	38.5	5.3	17.0	39.2	$C_{3.20}H_{5.27}O_{1.06}N_{2.80}$
PAC/GAP	52.6	6.5	15.8	25.1	$C_{4.38}H_{6.44}O_{0.99}N_{1.79}$
BAC/GAP	53.5	6.6	15.4	24.5	$C_{4.46}H_{6.49}O_{0.97}N_{1.75}$
PBCHC/GAP	49.1	6.1	17.9	26.9	$C_{4.09}H_{6.02}O_{1.12}N_{1.92}$
BBCHC/GAP	50.6	6.3	16.9	26.2	$C_{4.21}H_{6.22}O_{1.05}N_{1.88}$

[a]Mole ratio of $[C\equiv C]/[N_3]= 0.3/1$