Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Macrocycle-based Topological Azo-Polymers: Facile Synthesis and Unusual Photoresponsive Properties

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Content

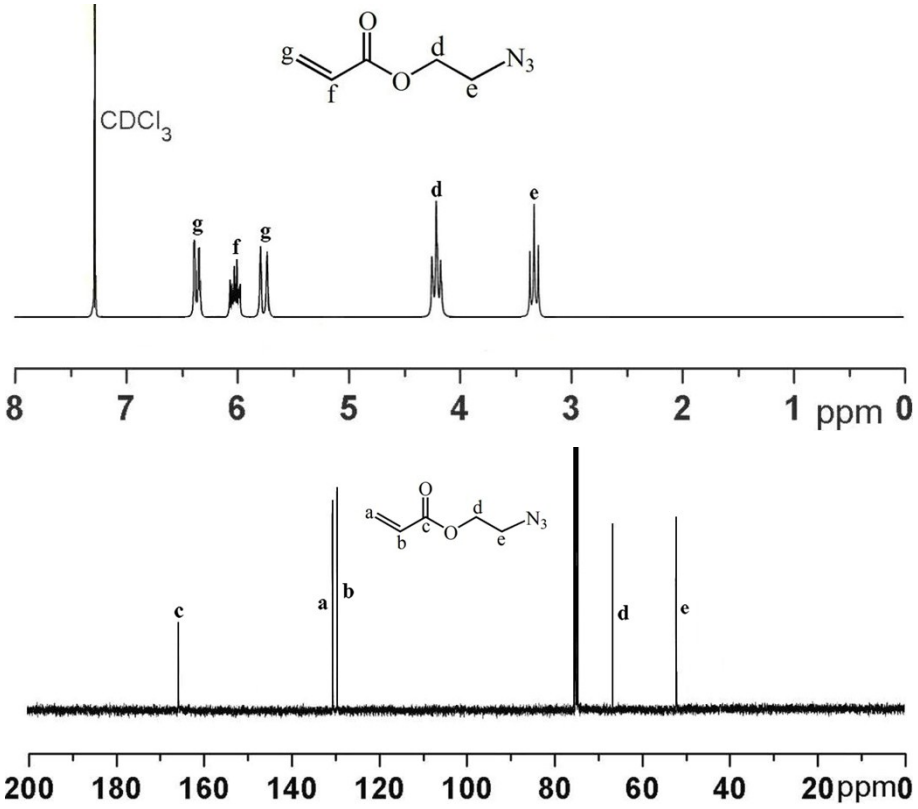

Fig. S1 ^{1}H NMR and ^{13}C NMR spectra for 2-azidoethyl acrylate.

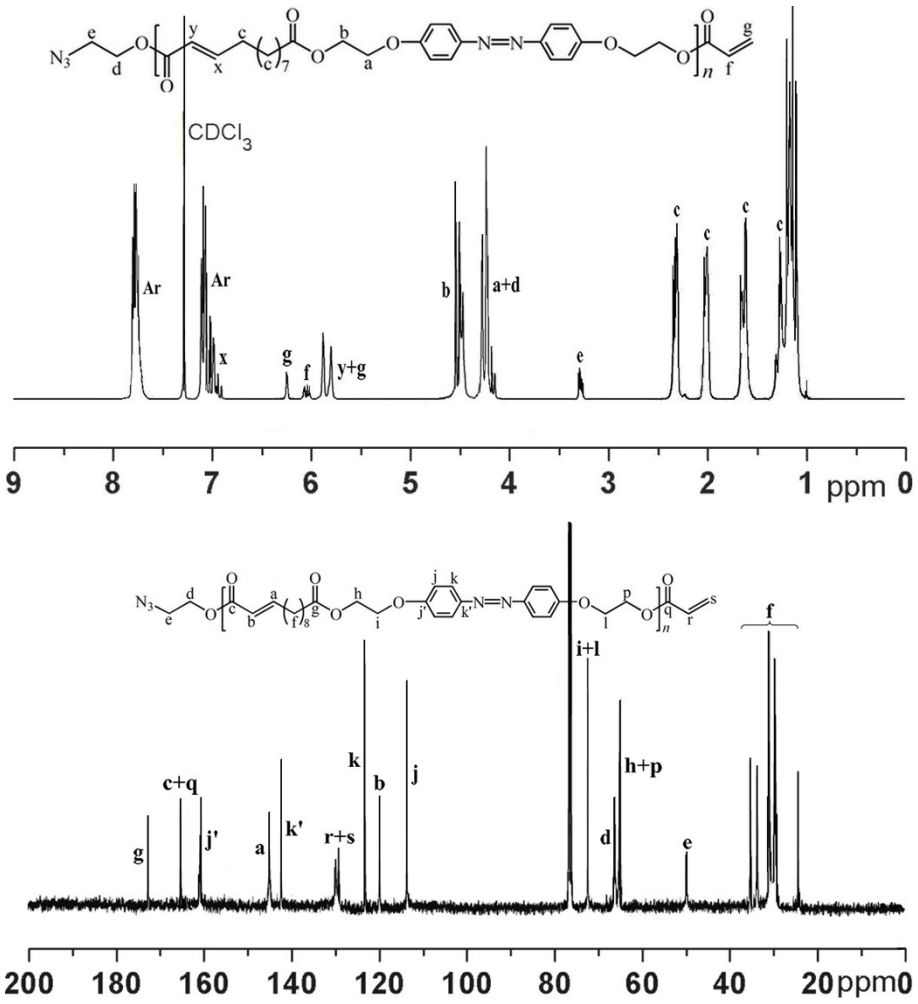

Fig. S2 ^{1}H NMR and ^{13}C NMR spectra for linear azo-polymer, **1**.

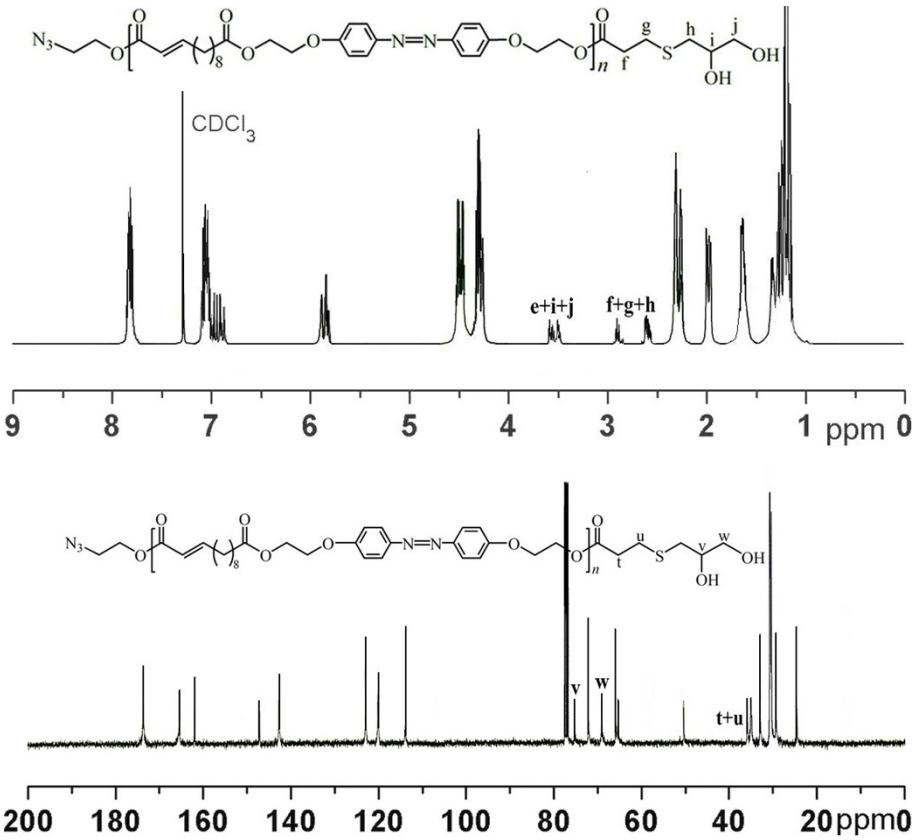

Fig. S3 ^{1}H NMR and ^{13}C NMR spectra for linear azo-polymer, **2**.

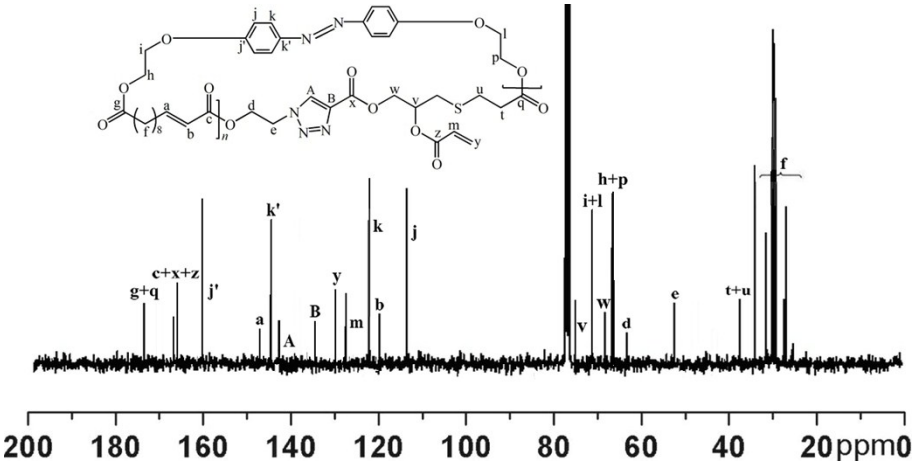

Fig. S4 ^{13}C NMR spectra for cyclic azo-polymer with acrylate.

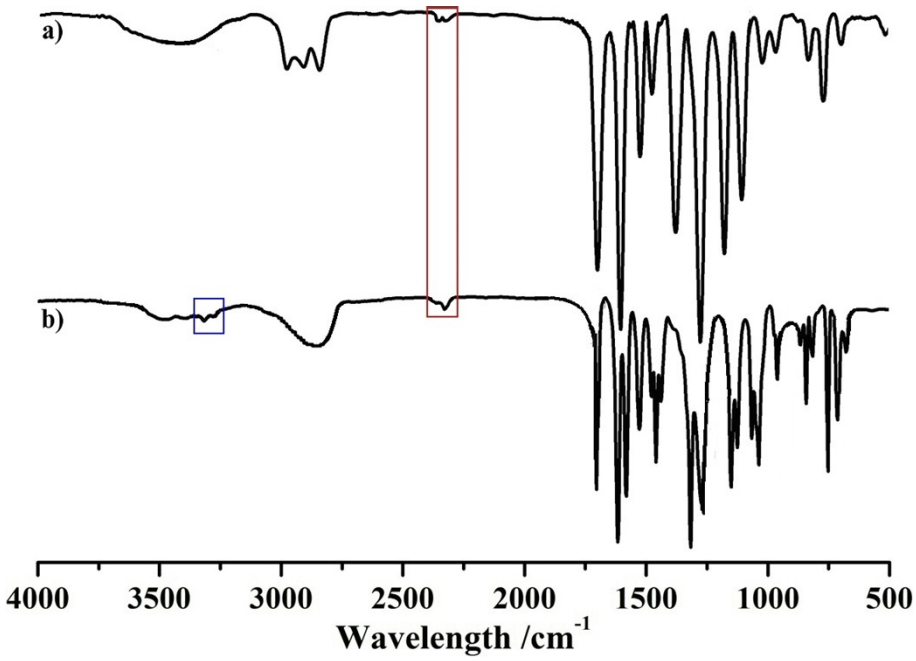

Fig. S5 ATR–IR spectra for (a) linear azo-polymer, **2** and (b) linear azo-polymer precursor, **3.**

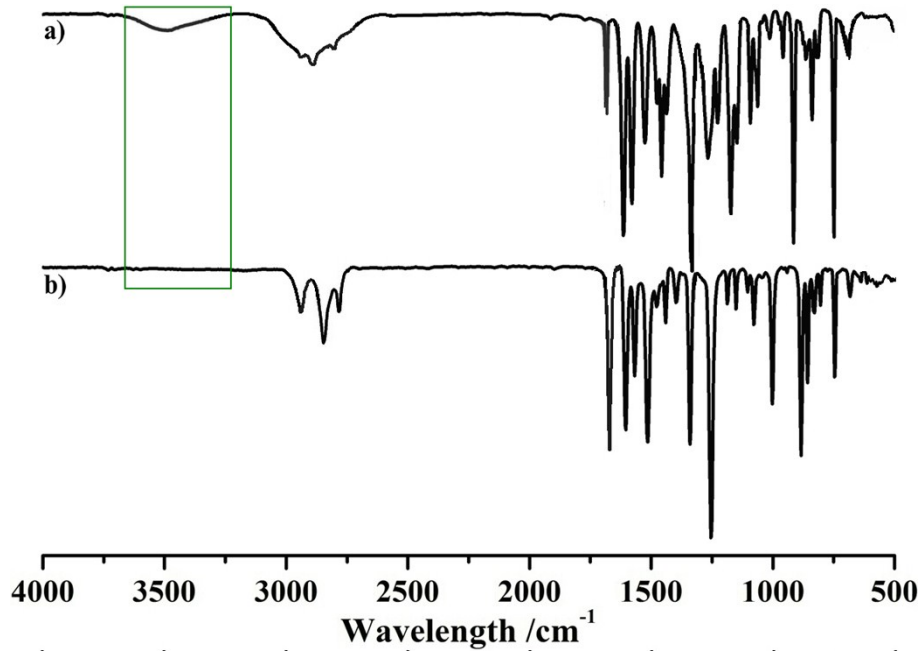

Fig. S6 ATR–IR spectra for (a) cyclic azo-polymer with a hydroxyl group and (b) cyclic azo-polymer with acrylate.

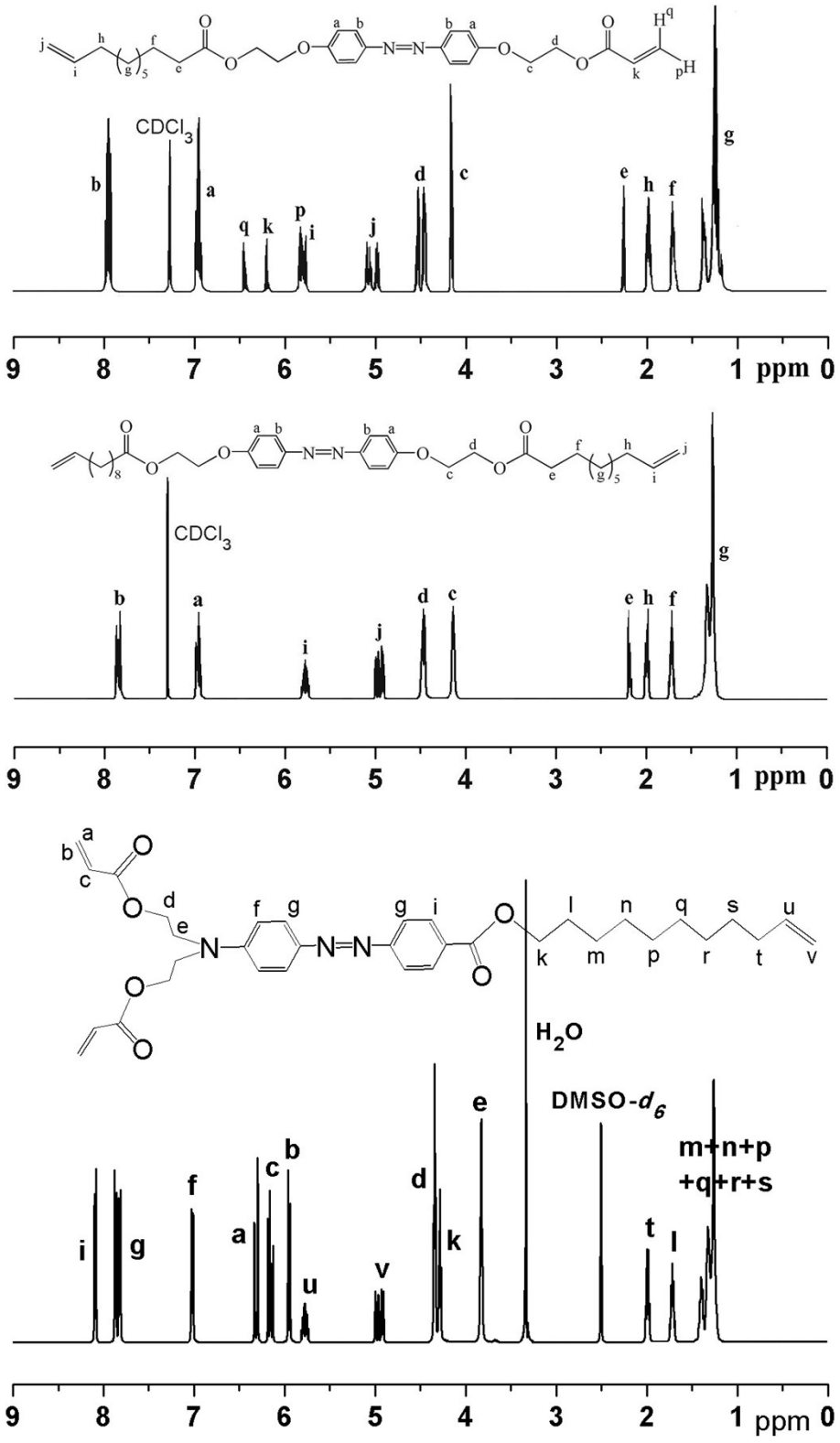

Fig. S7 ^{1}H NMR spectra for monomer **M1**, **M2**, and **M3**.

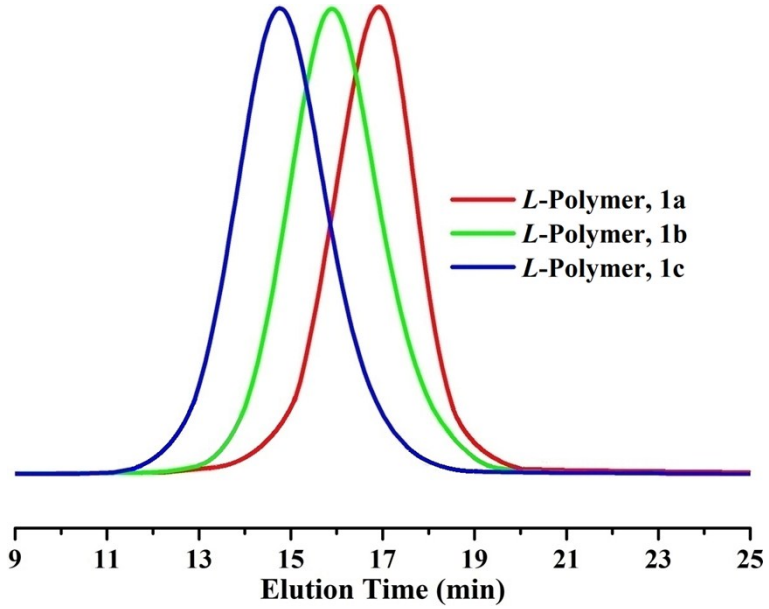

Fig. S8 GPC traces for linear azo-polymers, **1** showing the different molecular weights correlated to different amounts of chain stopper.

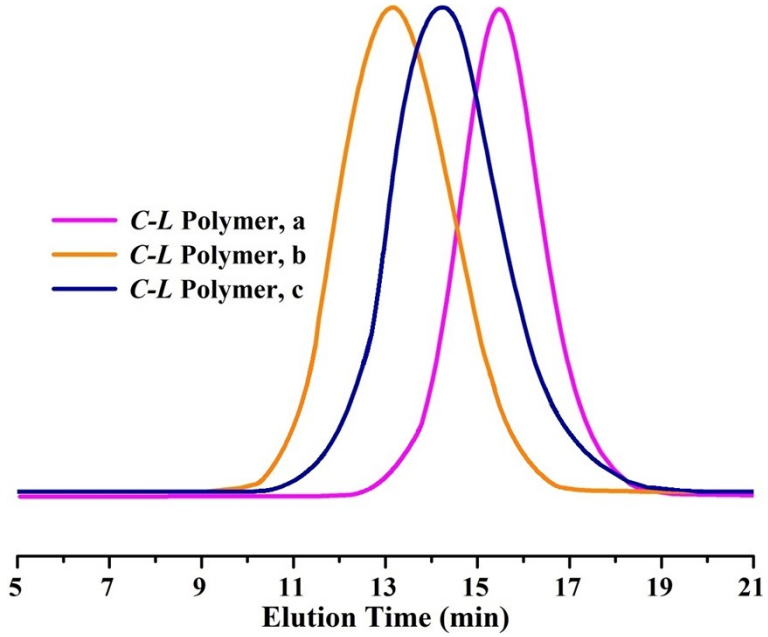

Fig. S9 GPC traces for cyclic-linear azo-polymers showing the different molecular weights correlated to different amounts of chain stopper.

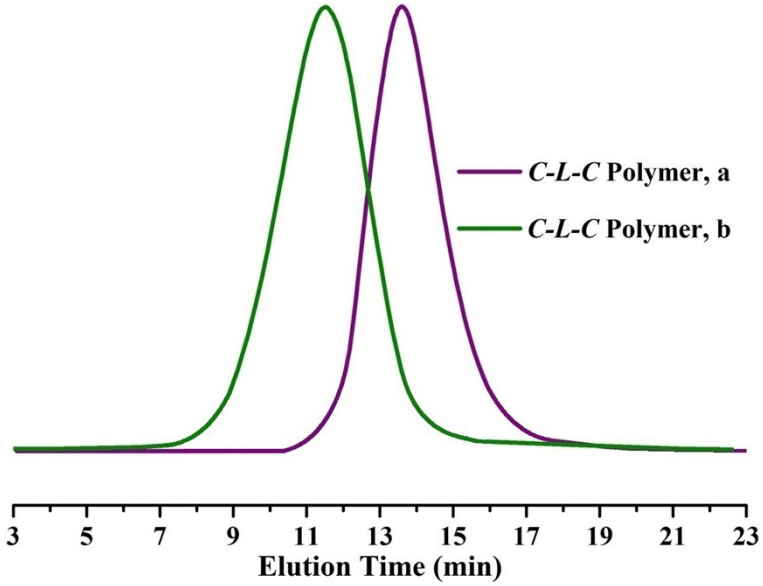

Fig. S10 GPC traces for cyclic-linear-cyclic azo-polymers showing the different molecular weights correlated to different amounts of chain stopper.

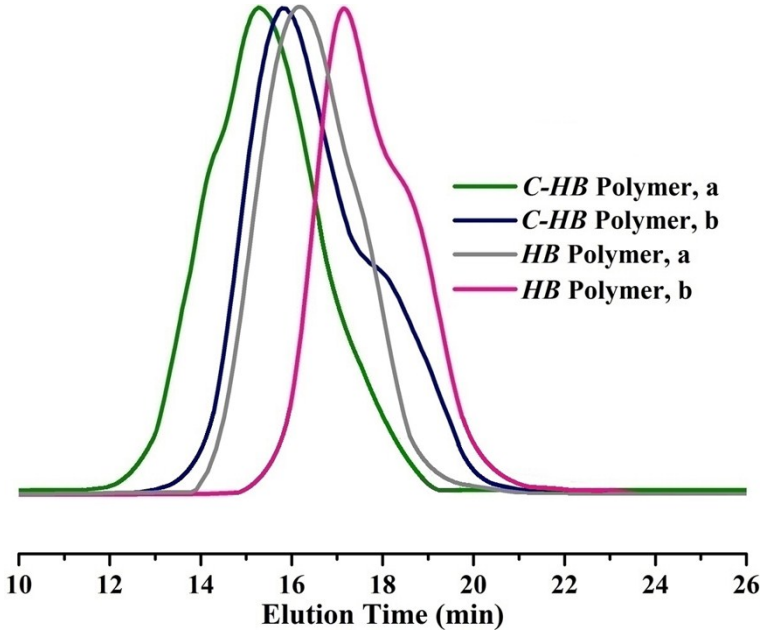

Fig. S11 GPC traces for hyperbranched and cyclic-hyperbranched azo-polymers showing the different molecular weights correlated to different polymerization times.

Table S1 Characteristic molecular weight data of prepared azo-polymers with different amounts of selective chain stoppers via ADMET polymerization[a]

Polymer	Yield (%)[b]	[M]/[CS]	$M_{n,GPC}$[c]	M_w/M_n[c]	$M_{n,theo}$[d]
***L*-1**	93	10: 1	6500	1.54	5100
	94	20: 1	11800	1.56	9900
	91	30: 1	16900	1.54	14400
C-L	92	10: 1	13900	1.62	11300
	87	20: 1	17700	1.66	14200
	90	30: 1	22300	1.65	19100
C-L-C	88	10: 1	22800	1.71	15700
	92	20: 1	30100	1.79	21800

[a] ADMET polymerization reaction conditions for preparation azo-polymers with diverse structures: polymerization temperature = 50 ºC, polymerization time = 24 h, [Monomer] = 2.0 mol/L, [Monomer]: [Chain Stopper] = 10: 1 ~ 30: 1;

[b] Obtained gravimetrically from the dried polymer;

[c] Determined by GPC in THF relative to monodispersed polystyrene standards;

d For ***L*-1** polymers, $M_{n,theo} = ([\mathbf{M1}]/[\mathbf{CS}]) \times \text{yield}\% \times M_{(\mathbf{M1})} + M_{(\mathbf{CS})} - M_{(\mathbf{ethylene})}$; for ***C-L*** polymers, $M_{n,theo} = ([\mathbf{M1}]/[\mathbf{CS}]) \times \text{yield}\% \times M_{(\mathbf{M1})} + M_{(\boldsymbol{C}\textbf{-Acrylate})} - M_{(\mathbf{ethylene})}$; and for ***C-L-C*** polymers, $M_{n,theo} = ([\mathbf{M2}]/[\mathbf{CS}]) \times \text{yield}\% \times M_{(\mathbf{M2})} + 2 \times M_{(\boldsymbol{C}\textbf{-Acrylate})} - 2 \times M_{(\mathbf{ethylene})}$, where $M_{(\mathbf{M1})} = 523$, $M_{(\mathbf{M2})} = 634$, $M_{(\mathbf{CS})} = 141$, and $M_{(\mathbf{ethylene})} = 28$.

Table S2 Characteristic molecular weight data of hyperbranched and cyclic-hyperbranched azo-polymers via ADMET polymerization in different reaction times

Polymer	Yield (%)[a]	Time (h)	$M_{n,GPC}$[b]	M_w/M_n[b]
HB	76	24	3400	1.95
	84	48	8600	1.93
C-HB	87	24	9700	1.91
	82	48	14600	1.89

[a] Obtained gravimetrically from the dried polymer;

[b] Determined by GPC in THF relative to monodispersed polystyrene standards.