Electronic Supplementary Information For

Effect of Intramolecular Cross Links on the Mechanochemical Fragmentation of Polymers in Solution

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I. General Experimental Details

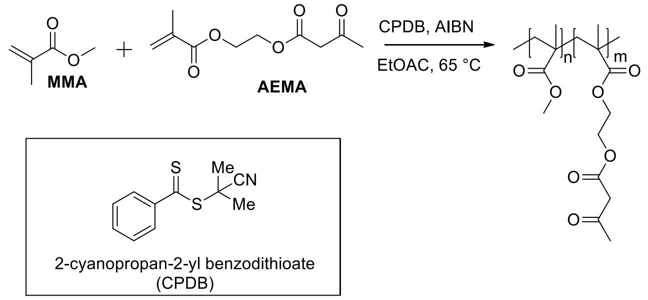
All materials, unless otherwise stated, were purchased from commercial sources and used as received. Monomers were purified by filtration through basic alumina column.

GPC analyses were done in THF at 30C using a Thermo LC system equipped with Tosoh's TSKgel Guard Column HHR-L and 4 TSKgel G4000HHR columns in sequence. Detection was obtained with a penta-detector system including Dionex DAD-3000 PDI UV-Vis Detector, Wyatt Viscostar II, Wyatt OPTILAB T-rEX, Wyatt MALS DAWN HELEOS II 8+TR and WyattQELS DLS. Wyatt's Astra 6 software was used for GPC data analysis and polymer properties calculation (Molecular weights, PDIs, Intrinsic viscosity and hydrodynamic radii). dn/dc = 0.084 mL/g was used for all polymers.

Ultrasonication was done in house-made Suslick cells using a SONICS Vibra-cell ultrasonic processor 500 Watt, tuned to 9.57 $W \cdot cm^{-2}$. UV-Vis measurements were done in a Thermo Evolution 220 Spectrophotometer. All ^1H NMR spectra were recorded using an AVANCE II 200, 300, 400 or 600 MHz Bruker spectrometer, and all ^{13}C NMR spectra were recorded using an AVANCE II 600 MHz Bruker spectrometer at the Technion NMR facilities.

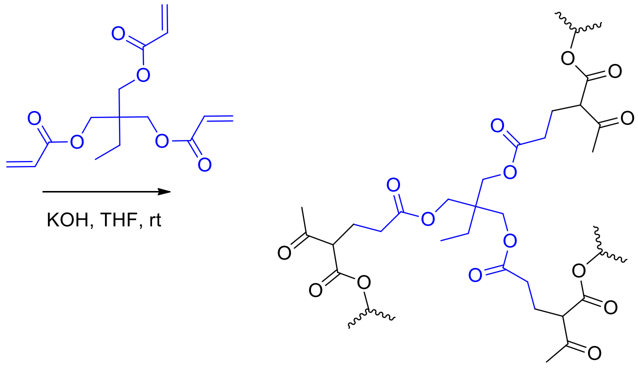
The uncertainty reported in our studies is not the full experimental uncertainty, but rather the statistical uncertainty based on noise levels of the various signals and repeated measurements.

II. Experimental Procedures



Linear p(MMA-co-AEMA) synthesis[1]

621L is used as an example. MMA (4 mL, 38 mmol), AEMA (1.28 mL, 6.6 mmol), 2-cyanoprop-2-yl-dithiobenzoate (4.68 mg, 2.2×10^{-2} mmol) and 2,2-azobis(2-methylpropionitrile) (0.7 mg, 0.4×10^{-2} mmol) were dissolved in ethyl acetate (4 mL). The reaction mixture was treated with three freeze-pump-thaw cycles, and backfilled with Argon. The reaction was carried out at 65 C for 18 h. The resulting polymer was isolated by precipitation in methanol and drying under high vacuum (52% yield). Exact AEMA composition in the copolymer was determined by ^{1}H-NMR analysis (see part III).



Procedure for Intramolecular collapse[1]

621CL is used as an example. p(MMA-*co*-AEMA) (200 mg), TMPTA (9.6 µL, 96µmol) and KOH (3 mg, 53 µmol) were dissolved in THF (200 mL) at room temperature. After three days, the reaction stopped, and few drops of 1M HCl added to neutralise the base. The mixture was concentrated and the SCPNs were isolated by precipitation in methanol and dried under high vacuum.

Sonication experiments

Polymer was dissolved in THF (1 mg/mL) and 5% BHT was added. The solution was then transferred to an oven-dried Suslick cell, which was placed into the sonicator collar and screwed onto the probe. The Suslick cell was lowered into acetone (-9 °C) bath, and N_2 was sparged for 15 min prior to ultrasound irradiation and continued throughout the experiment. Pulsed sonication (1 s on, 2 s off) was carried out using 20% amplitude (9.57 $W\cdot cm^{-2}$). Samples were extracted as required, filtered and injected to the GPC.

III. Characterisation & Results

NMR Spectra of polymers

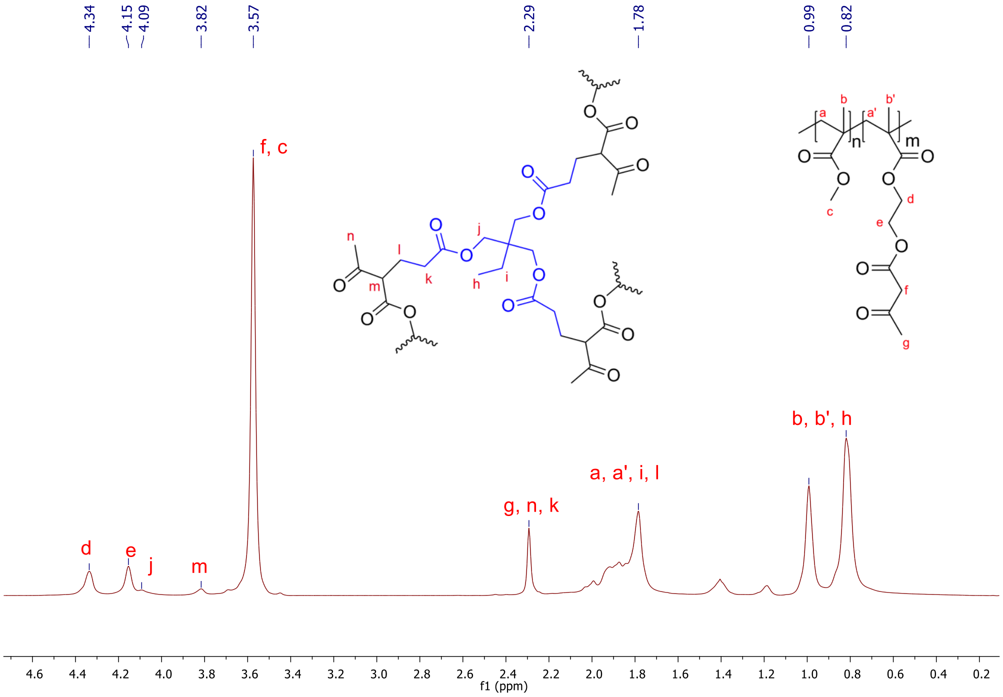


Figure S1. ^{1}**H-NMR spectrum of 1528CL polymer.**

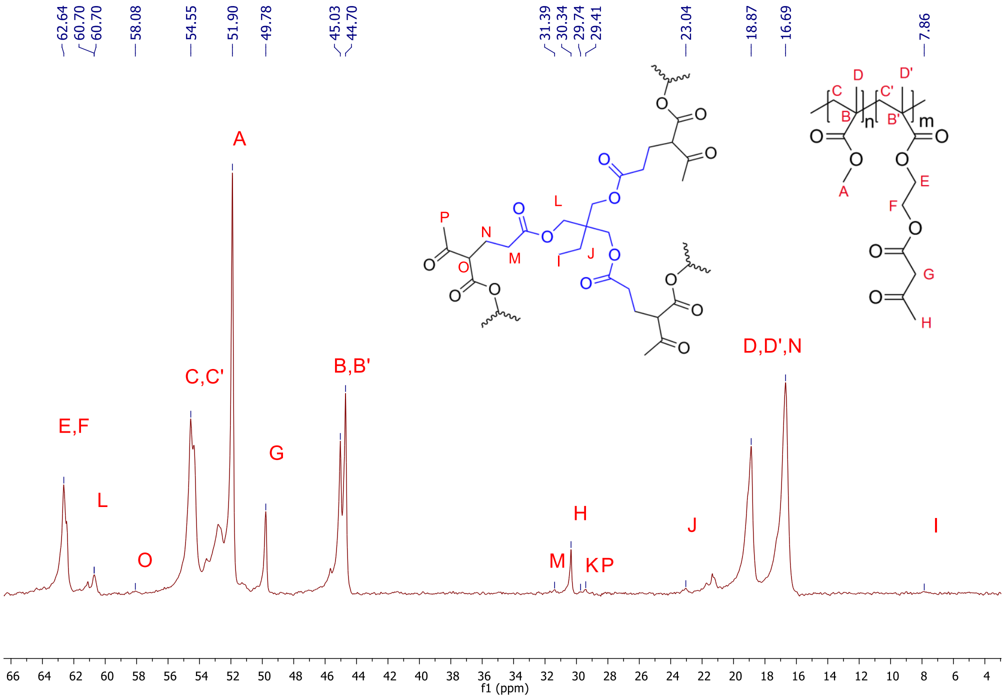


Figure S2. ^{13}**C-NMR spectrum of 1528CL polymer.**

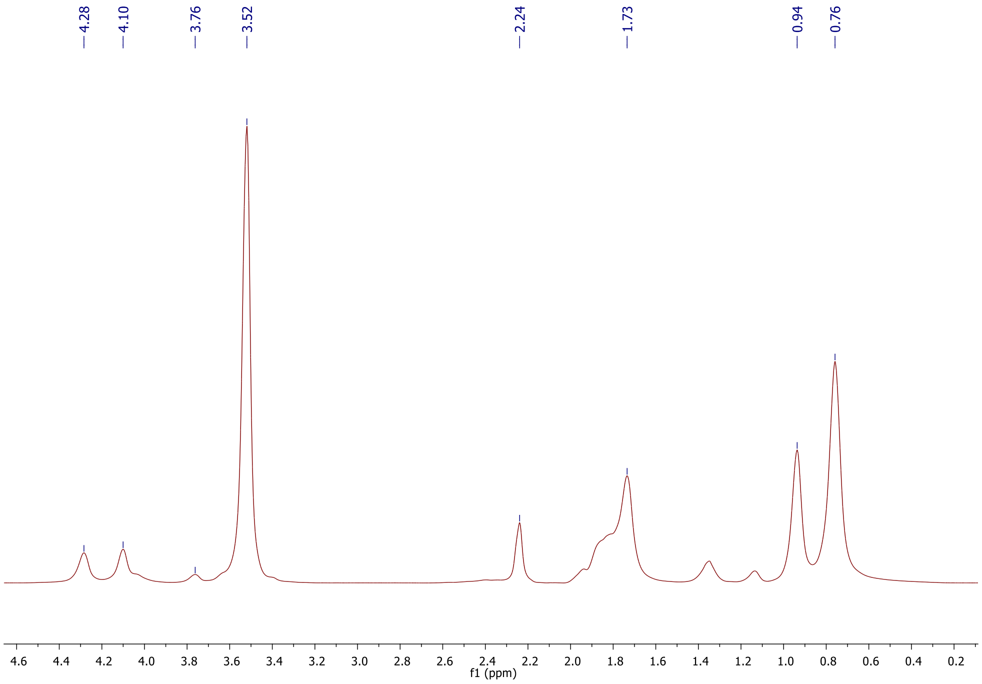


Figure S3. ^{1}H-NMR spectrum of 1344CL polymer.

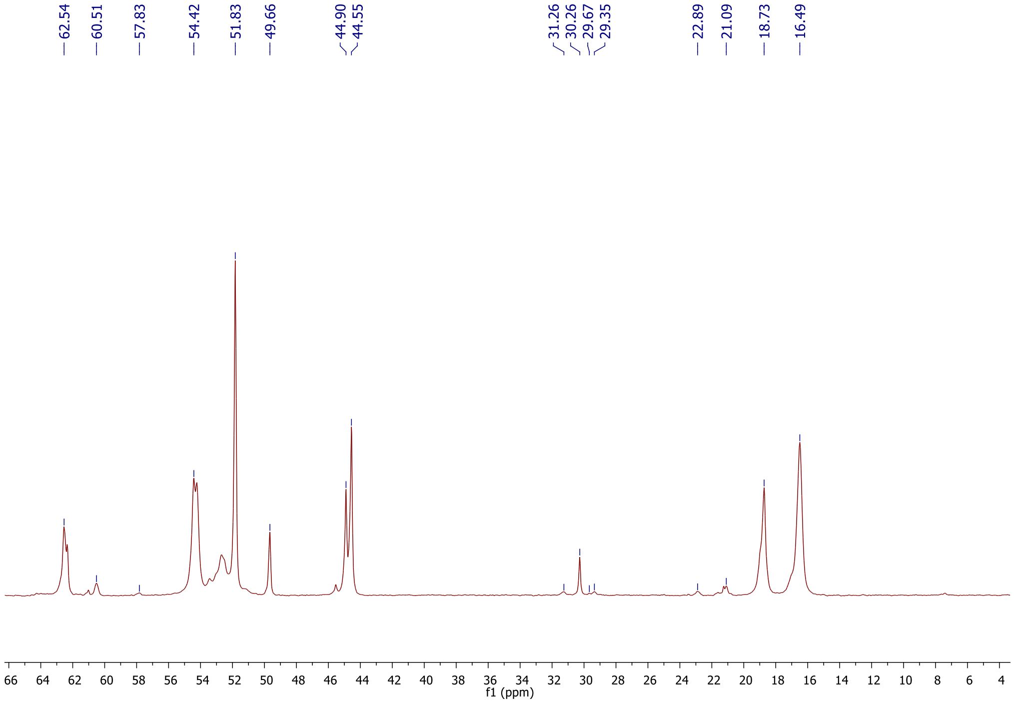


Figure S4. ^{13}C-NMR spectrum of 1344CL polymer.

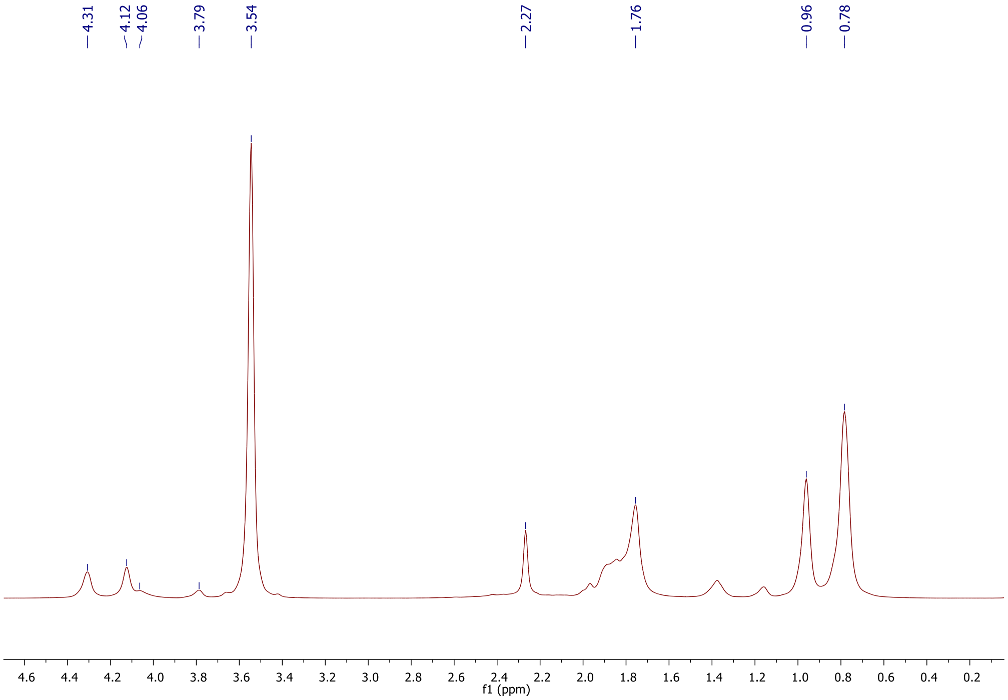


Figure S5. ^{1}H-NMR spectrum of 1156CL polymer.

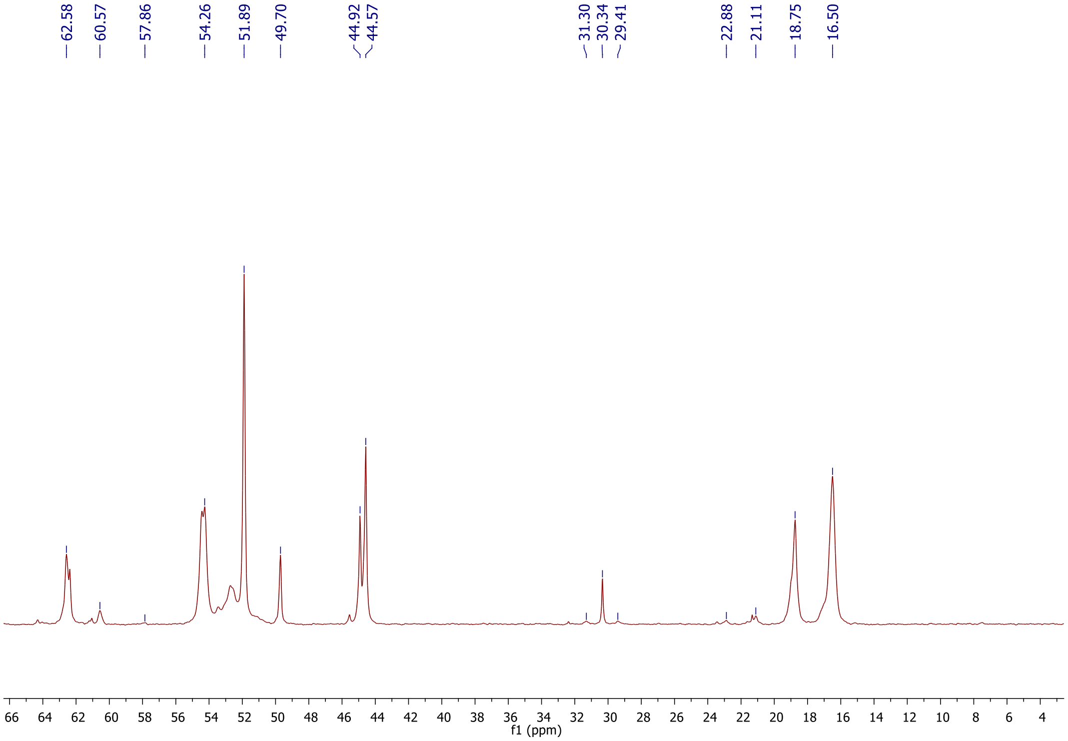


Figure S6. ^{13}C-NMR spectrum of 1156CL polymer.

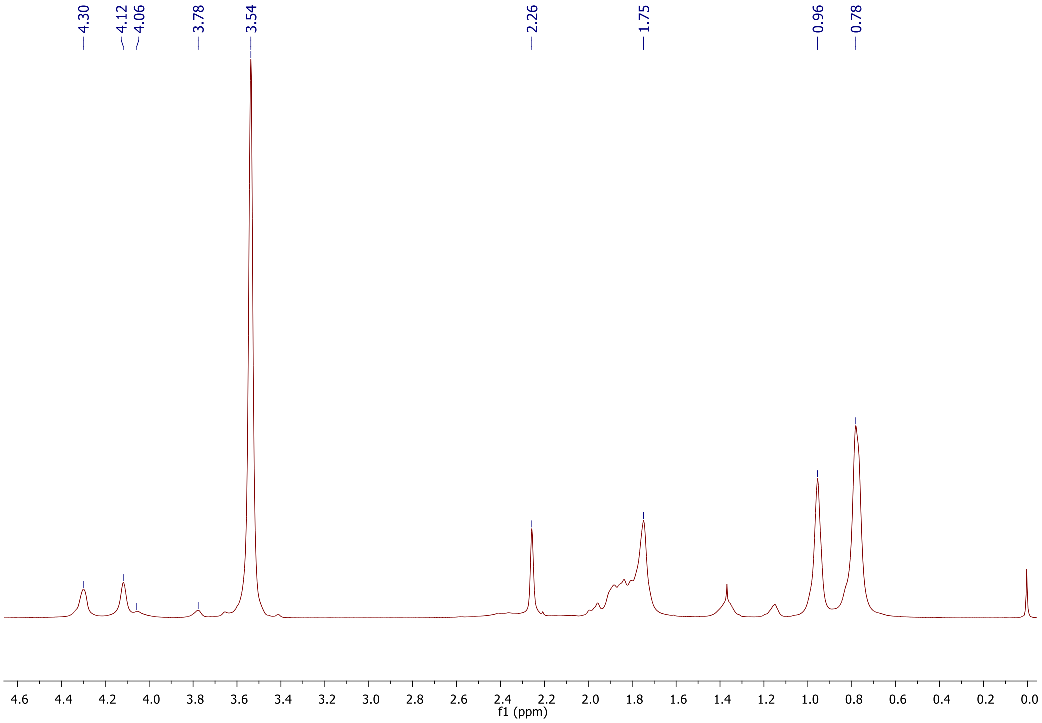


Figure S7. ^{1}H-NMR spectrum of 1000CL polymer.

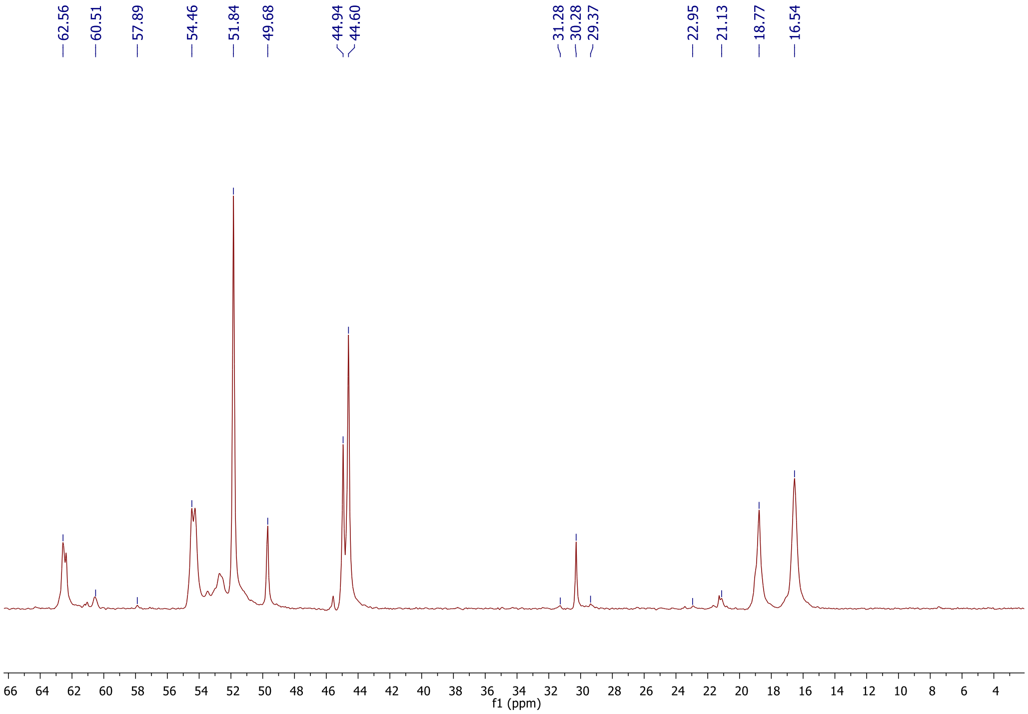


Figure S8. ^{13}C-NMR spectrum of 1000CL polymer.

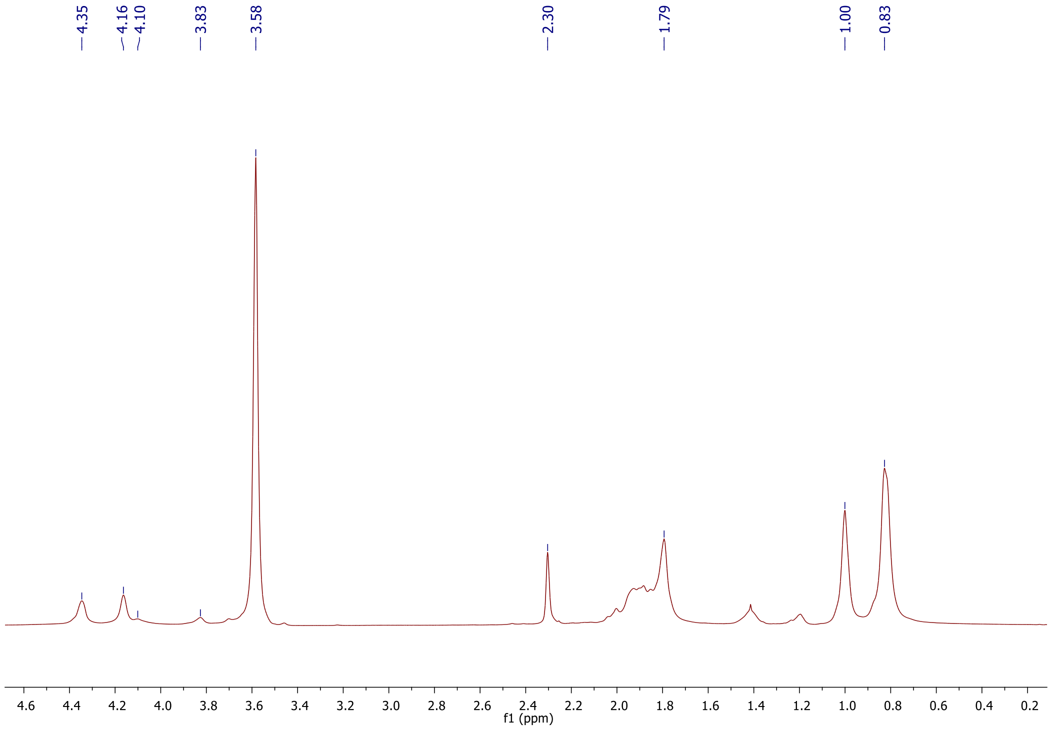


Figure S9. ^{1}H-NMR spectrum of 859CL polymer.

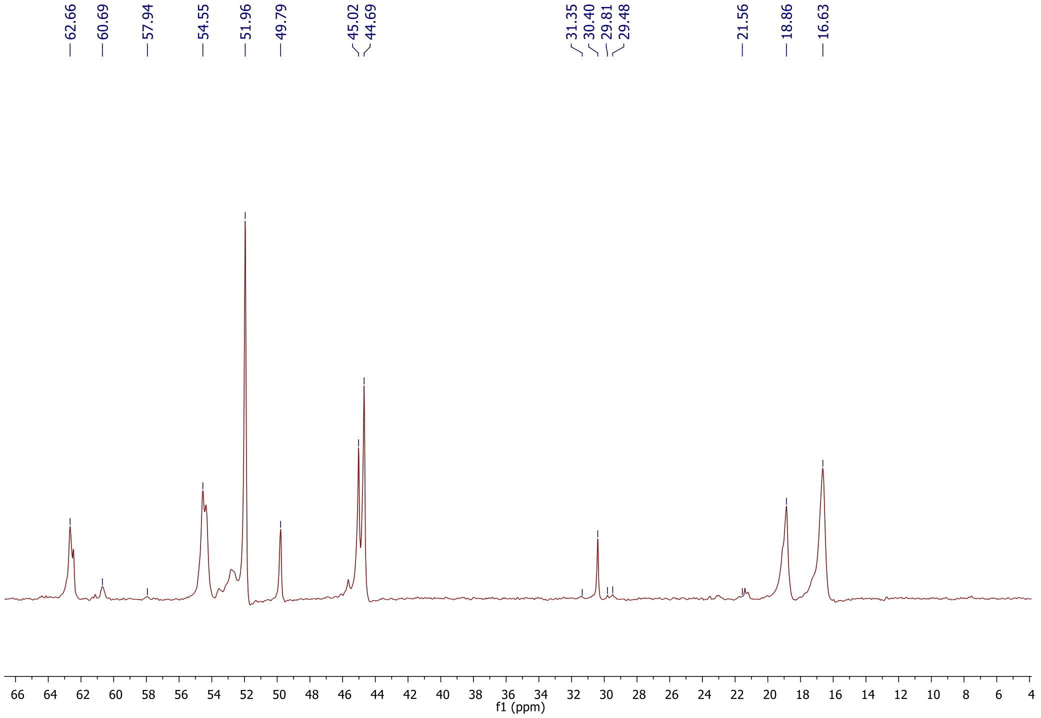


Figure S10. ^{13}C-NMR spectrum of 859CL polymer.

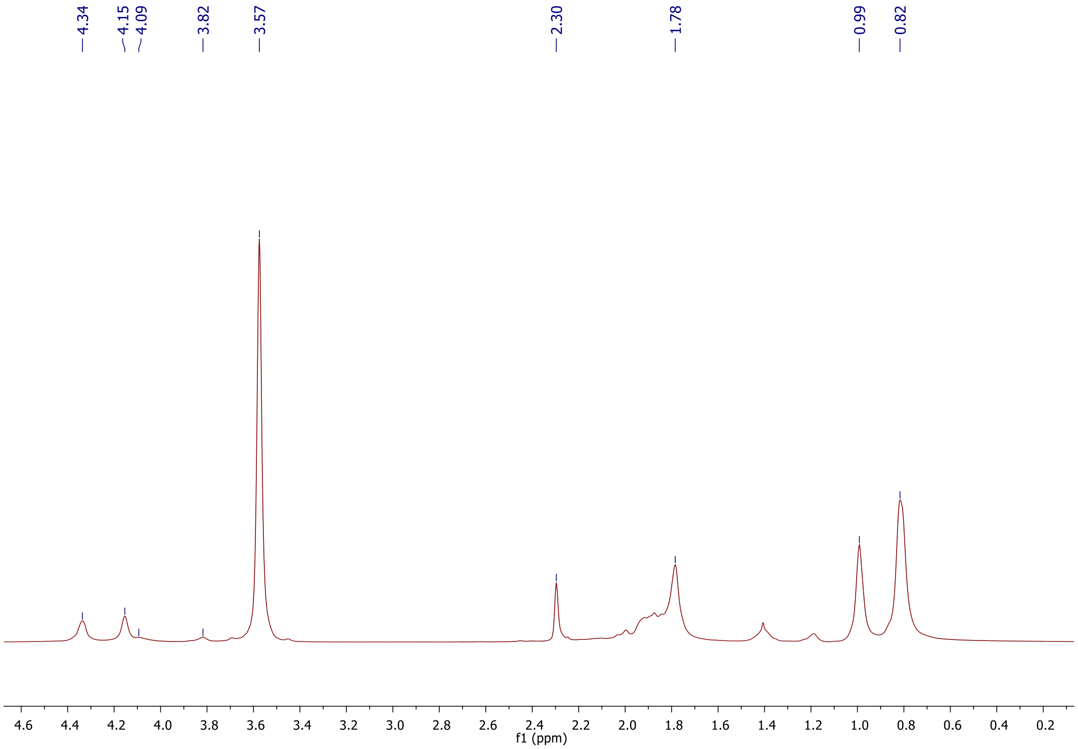


Figure S11. ^{1}H-NMR spectrum of 621CL polymer.

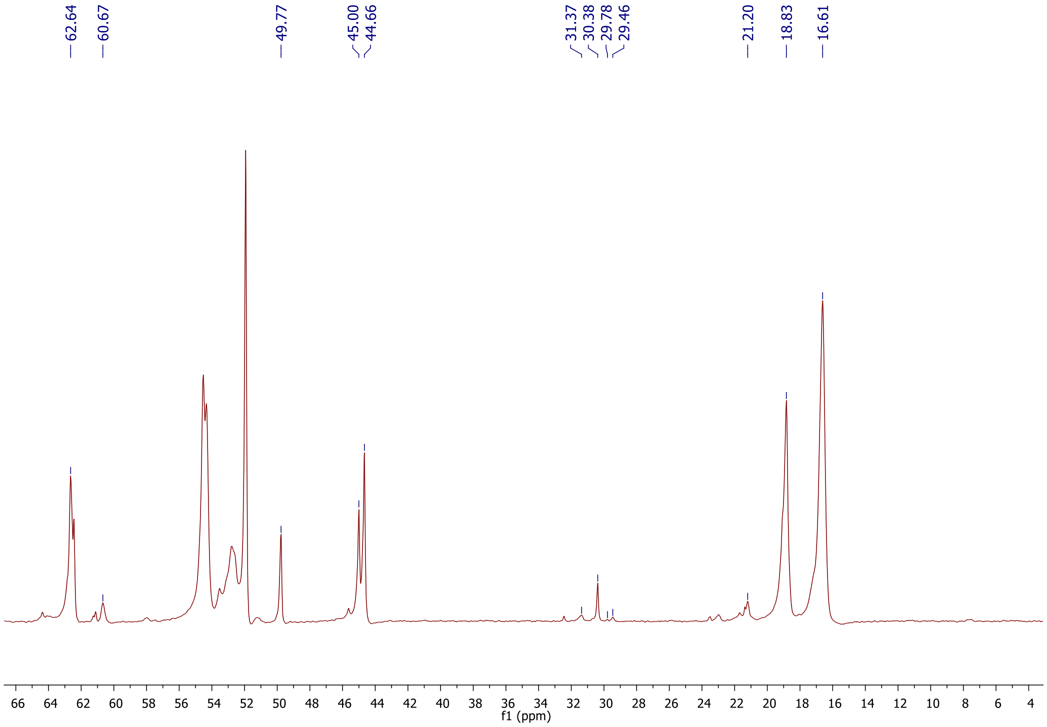


Figure S12. ^{13}C-NMR spectrum of 621CL polymer.

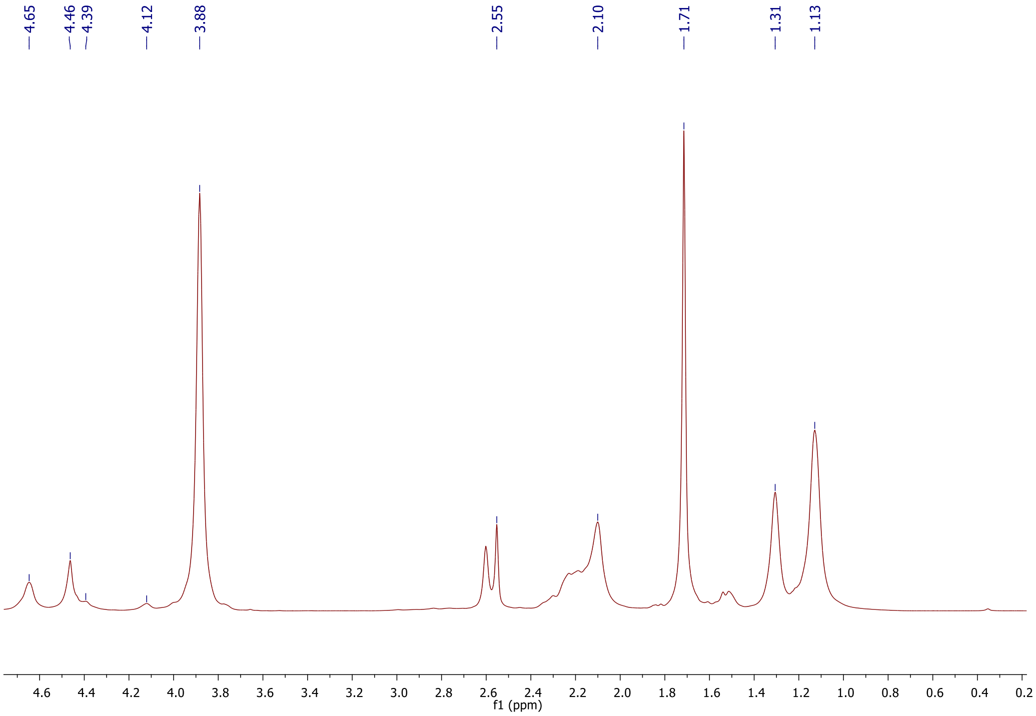


Figure S13. ^{1}H-NMR spectrum of 290CL polymer.

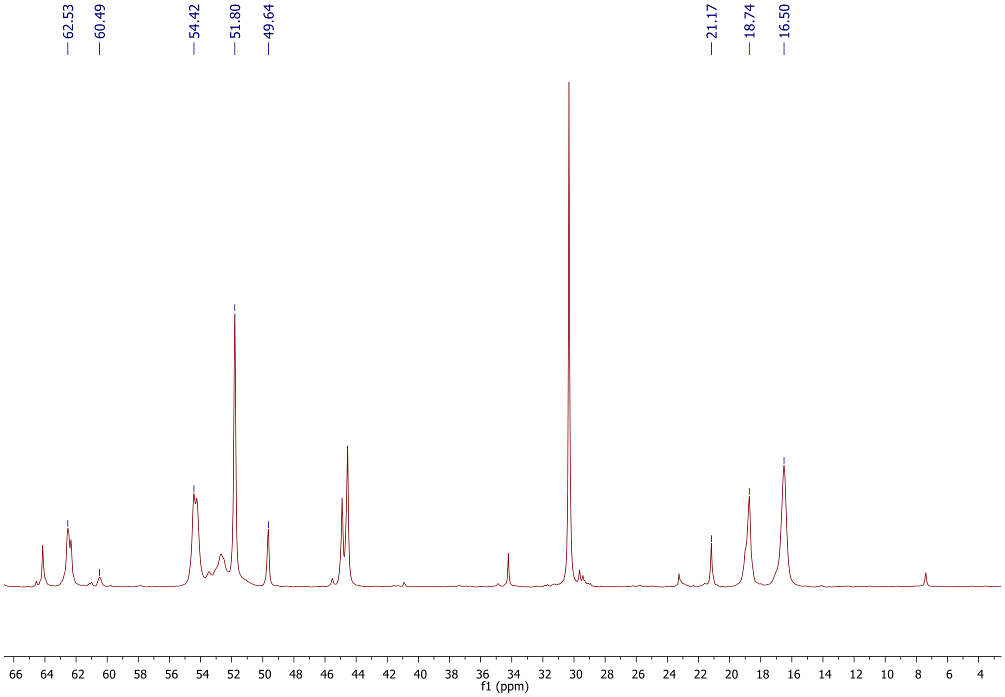


Figure S14. ^{13}C-NMR spectrum of 290CL polymer.

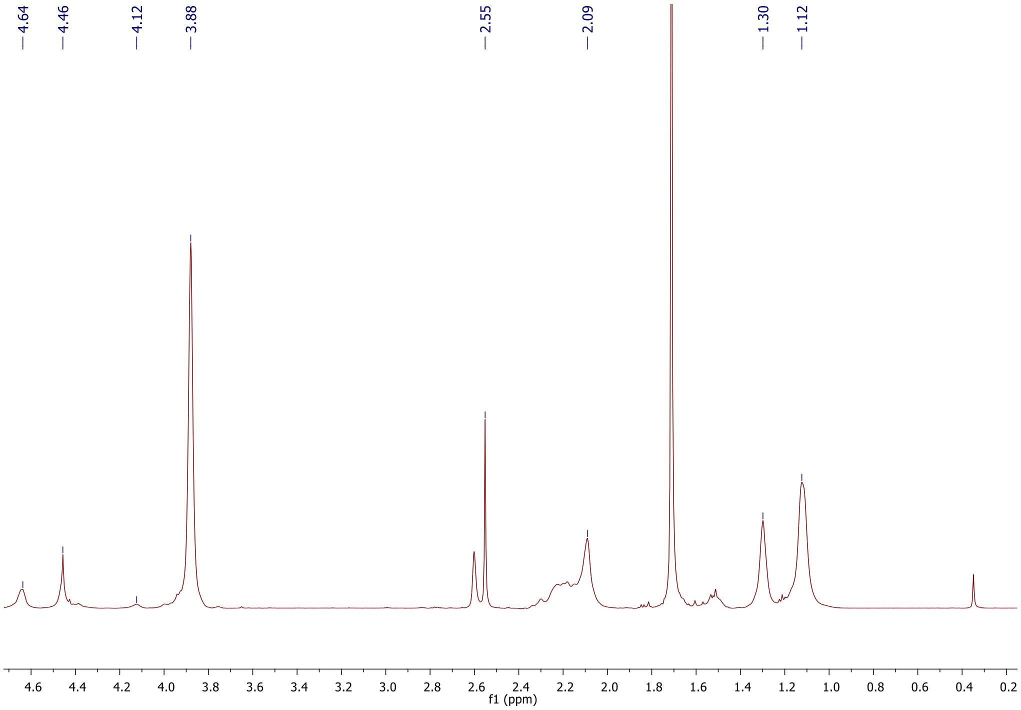


Figure S15. ^{1}H-NMR spectrum of 168CL polymer.

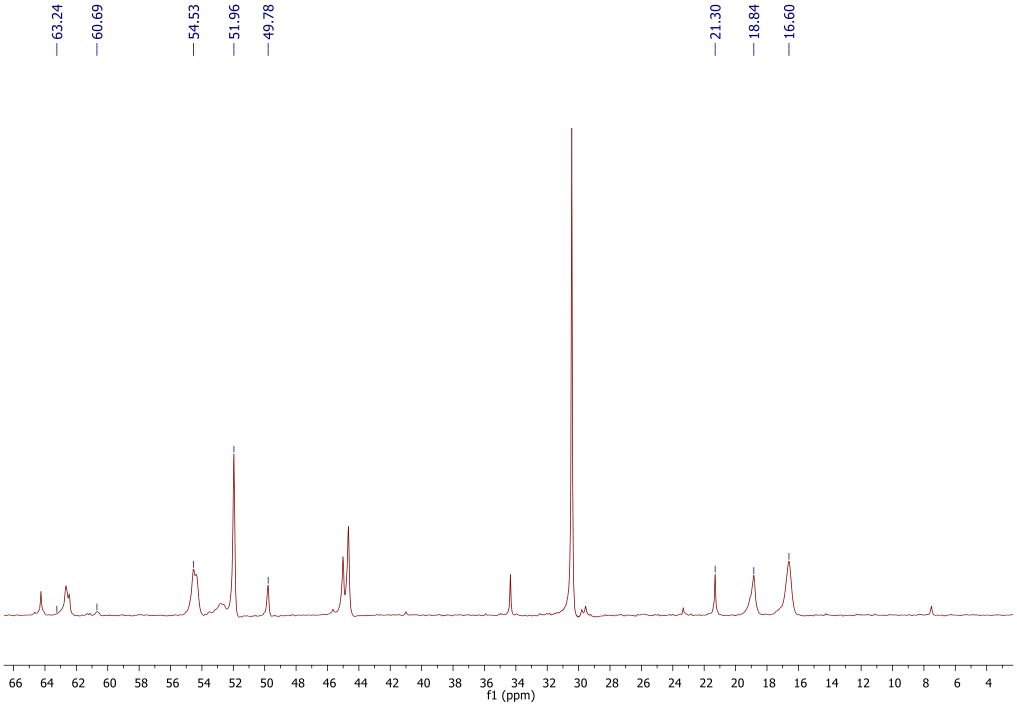


Figure S16. ^{13}C-NMR spectrum of 168CL polymer.

Monomer composition in copolymer

Determination of exact monomer composition in copolymer was obtained from ^{1}H-NMR spectrum according to the peak assignment reported in the literature.[2]

Using peaks integration and assigning them to the equation:

$$\%n(AEMA) = \frac{I_d/2}{I_d/2 + \frac{(I_{f,c} - I_d)}{3}} \times 100$$

Will result in the molar percentage of AEMA monomer in the copolymer. For example, the molar percentage of the co-monomer AEMA in **1528CL** polymer is 14% as the integration of peak d and f/c is 0.1 and 1 respectively:

$$\%n(AEMA) = \frac{0.1/2}{0.1/2 + \frac{(1 - 0.1)}{3}} \times 100 = 14\%$$

Cross-links density calculation

Determination of the molar cross-links density was obtained from ^{13}C-NMR spectrum according to the peak assignment reported previously.[3] Comparable integration obtained only for the same carbon type. Here, we compare the integration of the methylene peaks of the free AEMA co-monomer and the TMTPTA (peak F and L in **Figure S2** respectively) to obtained the ratio of AEMA co-monomer which underwent Michael addition. When this is multiplied by the molar AEMA composition, the cross-links density is determined:

$$CL\ density = \frac{I_L}{I_L + I_F} \times \%n(AEMA)$$

For example, the cross-links density in **1528CL** polymer is 2.98% as the integration of peak L and F is 0.28 and 1 respectively:

$$CL\ density = \frac{0.28}{1 + 0.28} \times 14\% = 2.98\%$$

Sonication results

The average results of three sonication experiments for every polymer are presented in **Tables S1-8**.

Table S1. Mn values during sonication of 1528 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
1528L	0	178.5 ± 5.4	**1528CL**	0	212.6 ± 24.4
	15	137.2 ± 2.3		15	191.5 ± 19.8
	30	115.7 ± 7.2		30	162.8 ± 13.0
	45	102.4 ± 6.2		45	149.8 ± 17.4
	60	91.9 ± 2.1		60	139.1 ± 12.4
	75	87.8 ± 5.2		75	125.3 ± 4.0
	90	77.3 ± 1.6		90	120.4 ± 2.2
	105	74.0 ± 1.8		105	114.4 ± 5.3
	120	65.8 ± 2.5		120	110.0 ± 7.2

Table S2. Mn values during sonication of 1344 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
1344L	0	158.5 ± 4.4	**1344CL**	0	182.0 ± 7.3
	15	135.9 ± 7.8		15	159.6 ± 14.9
	30	120.8 ± 1.8		30	151.9 ± 14.4
	45	111.5 ± 0.3		45	142.5 ± 4.1
	60	105.4 ± 2.3		60	134.8 ± 8.8
	75	93.7 ± 1.1		75	120.0 ± 7.8
	90	86.3 ± 2.7		90	112.9 ± 5.0
	105	77.4 ± 0.4		105	107.7 ± 3.3
	120	70.2 ± 1.3		120	100.3 ± 6.8

Table S3. Mn values during sonication of 1156 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
1156L	0	136.4 ± 1.6	**1156CL**	0	155.7 ± 0.4
	15	123.8 ± 2.0		15	151.7 ± 5.7
	30	114.7 ± 2.1		30	140.7 ± 3.7
	45	102.1 ± 3.3		45	131.2 ± 5.3
	60	91.7 ± 0.5		60	128.1 ± 3.8
	75	88.8 ± 0.1		75	117.7 ± 2.1
	90	83.8 ± 2.5		90	105.9 ± 1.4
	105	77.5 ± 0.7		105	100.9 ± 3.1
	120	71.9 ± 2.2		120	97.0 ± 1.8

Table S4. Mn values during sonication of 1000 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
1000L	0	117.9 ± 0.4	**1000CL**	0	126.7 ± 4.7
	15	108.5 ± 0.5		15	127.8 ± 2.0
	30	100.2 ± 0.9		30	106.8 ± 3.7
	45	95.2 ± 0.5		45	112.4 ± 8.0
	60	89.8 ± 0.3		60	103.2 ± 1.2
	75	85.2 ± 0.6		75	100.0 ± 3.3
	90	79.9 ± 0.4		90	94.0 ± 0.4
	105	74.3 ± 1.1		105	88.5 ± 1.2
	120	70.2 ± 0.1		120	83.4 ± 2.9

Table S5. Mn values during sonication of 859 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
859L	0	101.5 ± 2.1	**859CL**	0	115.4 ± 1.6
	15	96.1 ± 1.1		15	111.7 ± 2.6
	30	90.8 ± 2.2		30	108.5 ± 2.8
	45	86.8 ± 2.0		45	104.9 ± 0.7
	60	81.4 ± 2.0		60	104.3 ± 1.6
	75	78.1 ± 1.1		75	103.8 ± 0.8
	90	75.8 ± 0.4		90	97.3 ± 2.9
	105	72.4 ± 0.7		105	93.3 ± 0.9
	120	69.8 ± 0.5		120	90.5 ± 1.3

Table S6. Mn values during sonication of 621 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
621L	0	74.7 ± 1.2	**621CL**	0	85.3 ± 1.4
	15	73.1 ± 0.7		15	84.8 ± 1.7
	30	71.7 ± 0.3		30	85.3 ± 0.9
	45	68.6 ± 0.4		45	83.8 ± 1.7
	60	66.6 ± 0.4		60	82.8 ± 0.9
	75	64.5 ± 0.4		75	81.7 ± 1.7
	90	63.2 ± 0.3		90	81.2 ± 1.0
	105	62.3 ± 0.4		105	79.8 ± 0.8
	120	69.8 ± 0.5		120	90.5 ± 1.8

Table S7. Mn values during sonication of 290 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
290L	0	35.0 ± 0.1	**290CL**	0	36.6 ± 1.1
	15	34.8 ± 0.1		15	37.5 ± 2.5
	30	34.6 ± 0.1		30	36.5 ± 1.2
	45	34.4 ± 0.1		45	36.4 ± 1.8
	60	34.2 ± 0.1		60	35.9 ± 1.6
	75	34.0 ± 0.1		75	35.7 ± 1.7
	90	33.9 ± 0.1		90	36.3 ± 1.5
	105	33.8 ± 0.1		105	36.5 ± 0.3
	120	33.7 ± 0.1		120	37.8 ± 3.6

Table S8. Mn values during sonication of 168 polymer.

	Time [min]	Mn [kDa]		Time [min]	M_n [kDa]
168L	0	18.6 ± 0.6	**168CL**	0	20.3 ± 0.6
	15	18.8 ± 0.9		15	20.4 ± 0.5
	30	18.2 ± 0.6		30	20.2 ± 0.3
	45	18.7 ± 0.6		45	20.3 ± 0.5
	60	18.5 ± 0.6		60	21.1 ± 1.6
	75	18.4 ± 0.6		75	20.4 ± 0.1
	90	18.5 ± 0.3		90	21.1 ± 0.8
	105	18.5 ± 0.2		105	21.3 ± 1.0
	120	18.6 ± 0.4		120	20.6 ± 0.4

GPCs

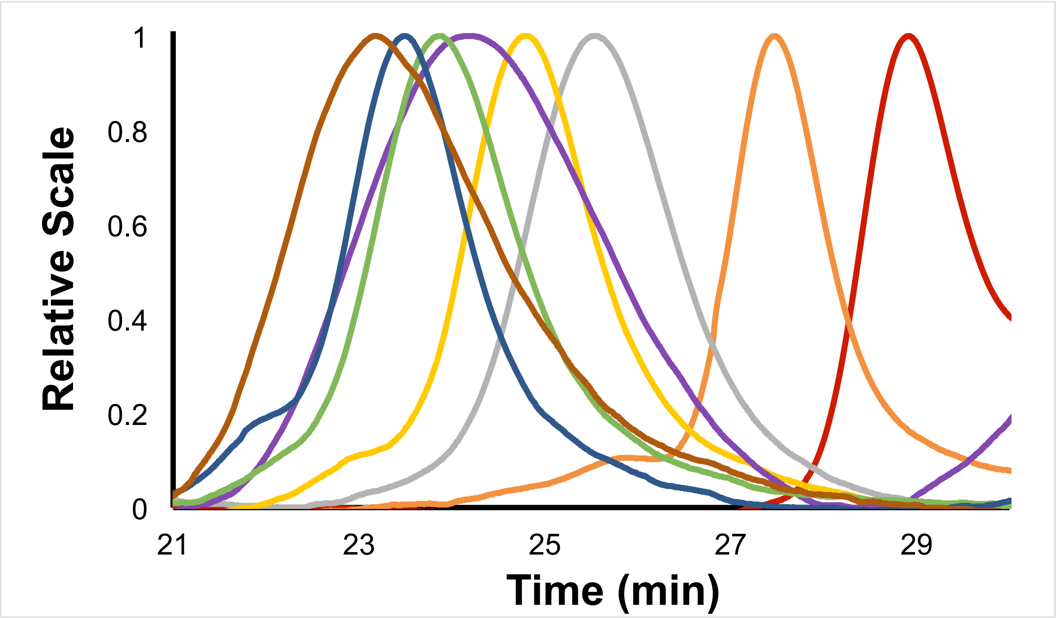


Figure S17. GPCs overlay chromatogram of linear polymers (signals from RI detector). Red (**168L**), orange (**290L**), grey (**621L**), yellow (**859L**), purple (**1000L**), green (**1156L**), blue (**1344L**), brown (**1528L**).

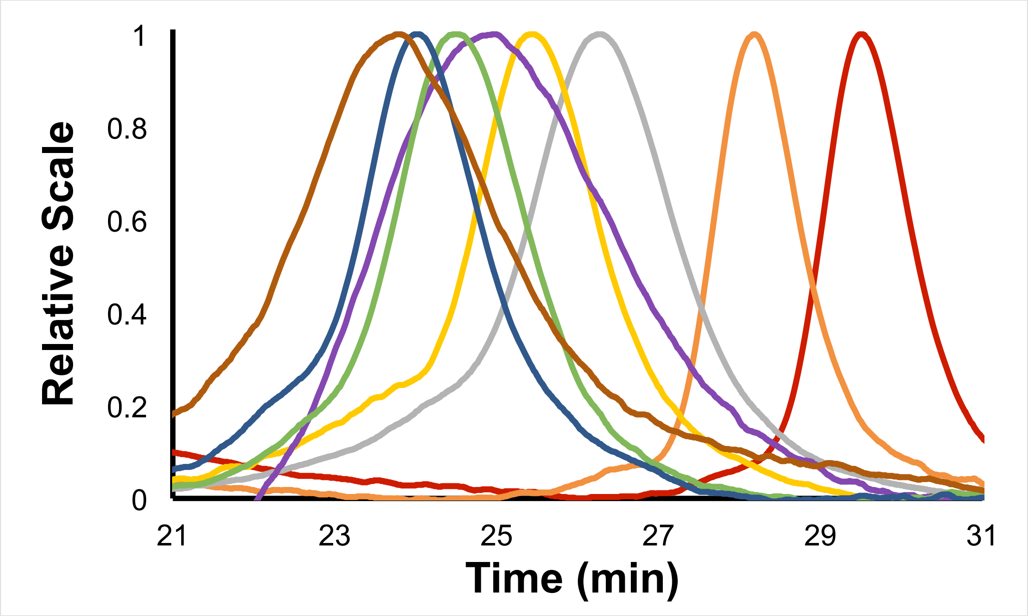


Figure S18. GPCs overlay chromatogram of intra-molecular cross-linked polymers (signals from RI detector). Red (**168CL**), orange (**290CL**), grey (**621CL**), yellow (**859CL**), purple (**1000CL**), green (**1156CL**), blue (**1344CL**), brown (**1528CL**).

Calculation of kinetic rate constant of Mw degradation during sonication

Rate constants were measured according to the method reported by Malhotra and co-workers[4] using the equation $\frac{1}{M_t} - \frac{1}{M_0} = k' \cdot t$, $k' = \frac{k}{m_0}$. Where M_0 is the initial number molecular weight of the polymer, Mt is the average number molecular weight of an aliquot from three different sonication experiments and t is the time of aliquot sonication.

Table S9. Rate constants and Mw of the repeating unit. [a] L=linear, CL= Intramolecular cross-linked polymer.

DP	Architecture[a]	m_0 (g·mol)	K'(10^{-8} g·mol^{-1}·min^{-1})	K (10^{-6} min^{-1})
168	L	117.1	0	0
	CL	118.3	0	0
290	L	117.1	0.94 ± 0.04	1.10 ± 0.05
	CL	121.7	0	0
621	L	115.7	2.67 ± 0.10	3.09 ± 0.12
	CL	118.2	0.63 ± 0.08	0.75 ± 0.09
859	L	115.7	3.75 ± 0.07	4.34 ± 0.08
	CL	119.4	1.79 ± 0.19	2.14 ± 0.23
1000	L	115.7	4.67 ± 0.13	5.41 ± 0.15
	CL	116.0	3.38 ± 0.30	3.93 ± 0.35
1156	L	114.3	5.41 ± 0.17	6.18 ± 0.19
	CL	115.9	3.45 ± 0.20	4.00 ± 0.23
1344	L	114.3	6.31 ± 0.28	7.21 ± 0.32
	CL	115.8	3.65 ± 0.13	4.22 ± 0.15
1528	L	115.7	7.48 ± 0.30	8.65 ± 0.35
	CL	117.8	3.75 ± 0.18	4.42 ± 0.16

The molecular weight of the repeating unit is calculated from the changes of the molecular weight between the linear polymer and the SCPN, since the degree of polymerisation is not changed after the chain collapse reaction and the added Mw is originating from the cross linker. For example, the calculation of m_0 of the **1528L** linear polymer and **1528CL** SCPN is presented:

$$m_{0\,linear} = \%n(AEMA)\times Mw_{AEMA} + [1 - \%n(AEMA)]\times Mw_{MMA}$$

$$m_{0\,linear} = 0.14\times 214.22 g\cdot mol^{-1} + 0.86\times 100.1 g\cdot mol^{-1} = 115.7 g\cdot mol^{-1}$$

$$m_{0\,linear} = 115.7 g\cdot mol^{-1}$$

$$m_{0\,SCPN} = \frac{m_{0\,linear}\times M_{n\,SCPN}}{M_{n\,linear}} = \frac{115.7 g\cdot mol^{-1}\times(180.0\times 10^3 g\cdot mol^{-1})}{176.7\times 10^3 g\cdot mol^{-1}}$$

$$m_{0\,SCPN} = 117.8 g\cdot mol^{-1}$$

Rate of mechanochemistry of SCPNs

Rate constants of total mechanochemistry were measured using a pyrone spin trap[5] according to the procedure reported by our group previously.[3]

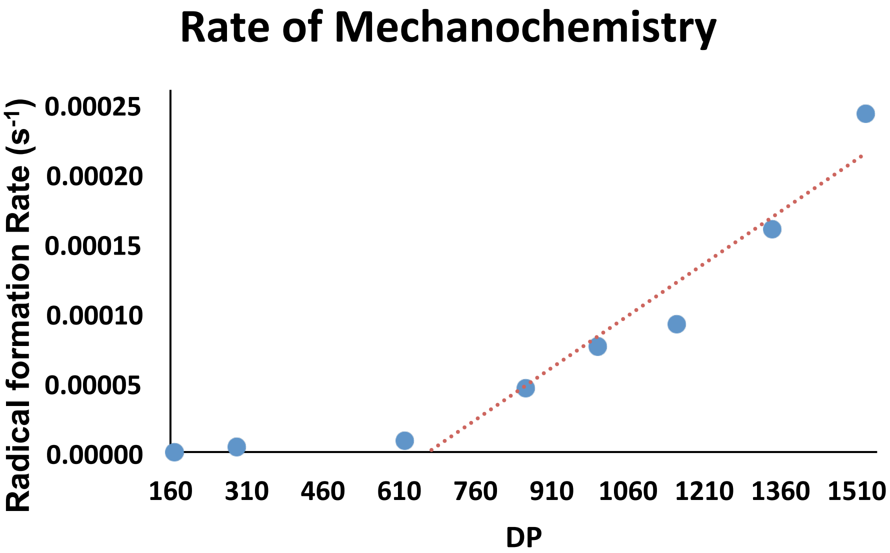


Figure S19. Rate of total mechanochemical events (decrease in UV absorbance) vs. DP in polymers **168CL-1528CL**

Rate of fragmentation vs. Rh

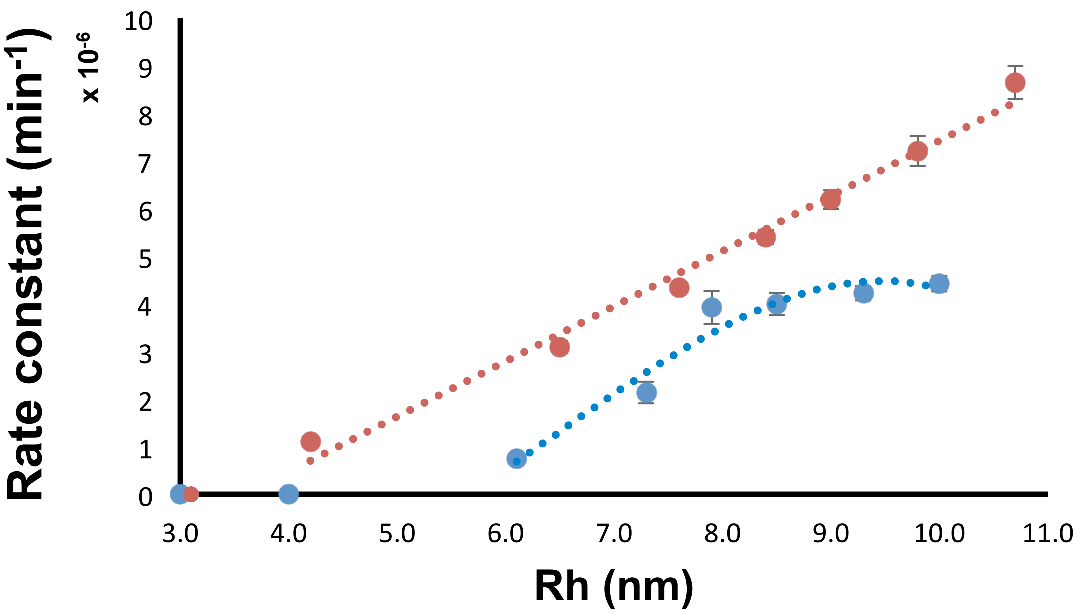


Figure S20. Experimental rate constants of mechanochemical fragmentation of linear polymers (red dots) fitted to linear equation (dashed red line) and the corresponding SCPNs (blue dots) fitted to 3rd degree polynomial equation (dashed blue line).

IV. References

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2. A. Sanchez-Sanchez, D. A. Fulton and J. A. Pomposo, *Chem. Commun.*, 2014, **50**, 1871-1874.
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