Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary information:

Inverse vulcanization below the melting point of sulfur

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Materials. Cyclohexanedimethanol divinyl ether (CDE, 98%, Sigma Aldrich), Poly(methyl methacrylate) (PMMA, Sigma Aldrich), and Chloroform-d (99.8 atom % D, Sigma Aldrich), hexane (≥95%, Sigma Aldrich)

Powder X-ray Diffraction (PXRD). Data were measured using a PANalytical X'Pert PRO diffractometer with Cu- Kα radiation, operating in transmission geometry. And all data were measured over the range 5-50° 2Θ in 0.013° steps over 60 minutes.

Differential Scanning Calorimetry (DSC). DSC were performed on a TA Instruments Q200 DSC, under nitrogen flow, and with heating and cooling rates of 5 °C min^{-1} from -50 to 150°C in 'heat-cool-heat' program.

Nuclear magnetic resonance (NMR). The reactions were monitor by solution NMR in deuterated chloroform, and recrystallized catalysts were performed by solution NMR in D_2O, using a Bruker Advance DRX (400 MHz) spectrometer.

Attenuated total reflection fourier transform infra-red (ATR-FTIR).

Fourier Transform Infrared (FTIR) spectra were measured between 4000 and 500 cm^{-1} on a Bruker Vertex 70 spectrometer, with a Platinum ATR module.

Elemental Analysis. CHNS elemental analysis was conducted on a Thermo Flash EA 1112.

Gel permeation chromatography (GPC): The molecular weight of the soluble fraction of the polymers was determined by gel permeation chromatography (GPC) using a Viscotek system comprising a GPCmax (degasser, eluent and sample delivery system), and a TDA302 detector array, using THF as eluent

Thin layer chromatography (TLC). 10 mg polymer or sulfur was added into 10 mL dichloromethane (DCM), and 1 mL DIB was dissolved into 10 mL DCM. Solutions were spotted individually on the traditional □silica TLC plates with hexane eluent.

Poly(S-CDE): 5 g sulfur, 5 g CDE, and 10% NaDTC were mixed in 40 mL volume glass vials by vortex, before being heated at 110 °C in aluminium blocks and stirred by magnetic stirrer bars for polymerisations for 1 hour. Reaction absence of catalyst in same scale and same conditions was conducted as well.

Table S1 Elemental analysis of sulfur polymers with different component and prepared under different conditions.

	Calc %			Analysis %		
	% C	% H	% S	% C	% H	% S
SEGDMAC1T100	30.75	3.61	50.48	30.18	3.56	50.91
SEGDMAC1T110	30.75	3.61	50.48	30.51	3.61	50.43
SDIBC1T110	44.45	5.57	49.98	39.25	3.90	55.48
SDIBC5T110	46.22	5.87	51.87	42.17	4.15	52.74
SDIBC10T110	48.44	6.23	54.24	43.20	4.36	50.43
SDIBC0T180	44.44	5.56	50.00	45.34	4.44	51.02

Fig S1. It can be observed that sample SDIB30C1T110 is inhomogeneous with bubbles, which is because of low mobility of the system followed by triggering autoacceleration.

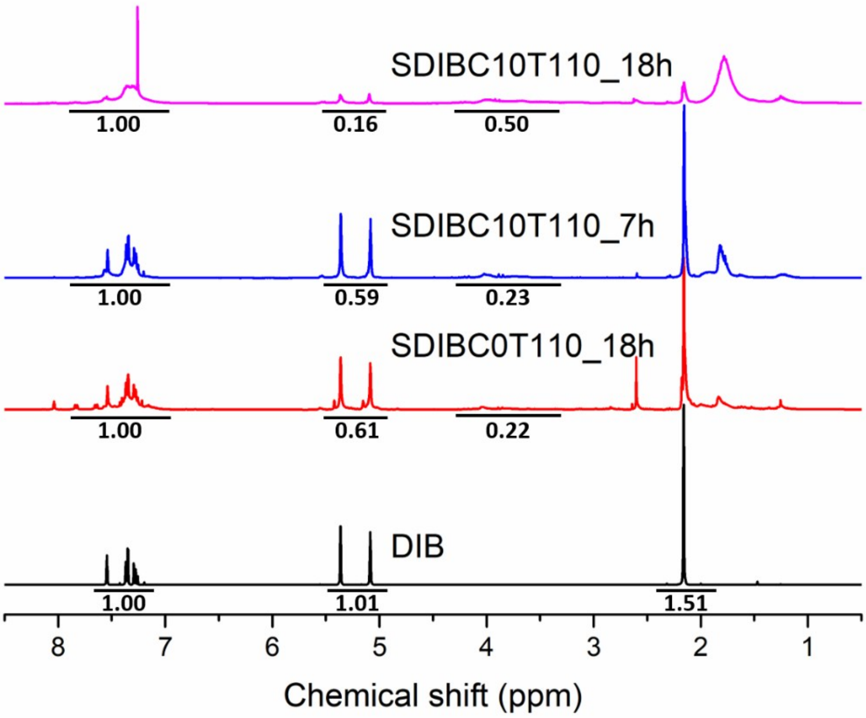

Fig S2. ^1H NMR spectra for SDIBC0T110 followed at 18 hours, SDIBC10T110 followed at 7 hours and 18 hours, and DIB standard. For SDIBC0T110, clearly, compared with pure DIB, the integral ratio of the peaks at 7.0 to 7.5 to the peak at 5.0 to 5.5 decreased, demonstrating the reduction of C=C bonds. And new peaks at 3.0 to 4.0 suggested the apparence of S-C-H generatted. For SDIBC10T110, followed at 7 hours, the integral of the peaks at this stage is similar to that of SDIBC0T110 at 18 hours, indicating that the degree of reactions is similar. After 18 hours, spectra of SDIBC10T110 was performed from the dissolved part of sulfur polymers. Only a small signal of C=C bonds remains compared with the reaction without catalyst assuming same time. The peaks are also broader, indicative of polymerisation.

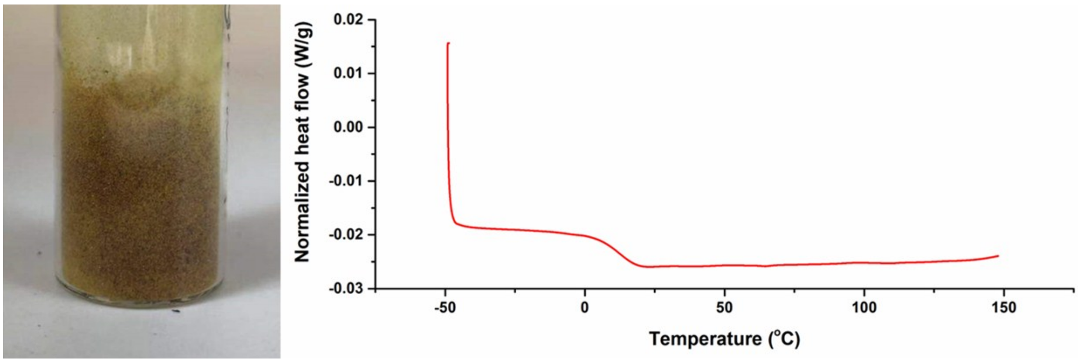

Fig S3. Left is ground SDIBC0T110 samples and the right is DCS trace of SDIBC0T110, showing that T_g is around 10 °C and no peaks of melting sulfur.

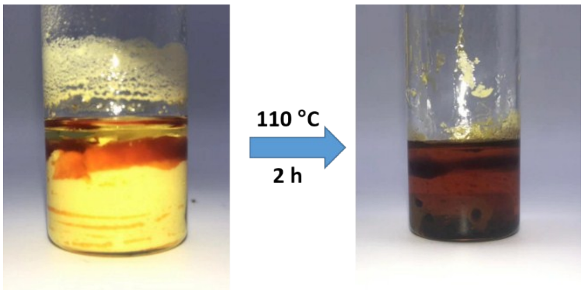

Fig S4. Images of reaction of SDIBC10T110: left is the beginning of the reaction with solid sulfur, and right is, after 2 hours, the two phases of reaction but no solid sulfur observed.

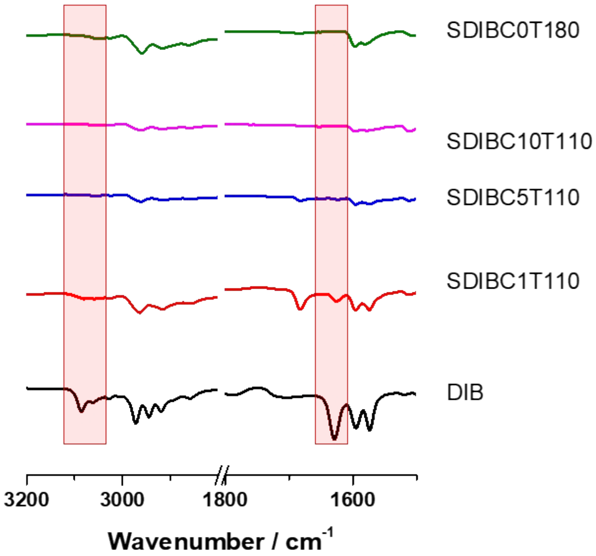

Fig S5. Specific regions of the ATR-FTIR patterns, of Poly(S-DIB) further confirmed this assumption. As the amount of catalyst is increased, reductions of signals were seen at 3080, 3041, and 1640 cm^{-1}, corresponding to the stretching and symmetric stretching vibrations of C=C-H and stretching vibration of C=C respectively.

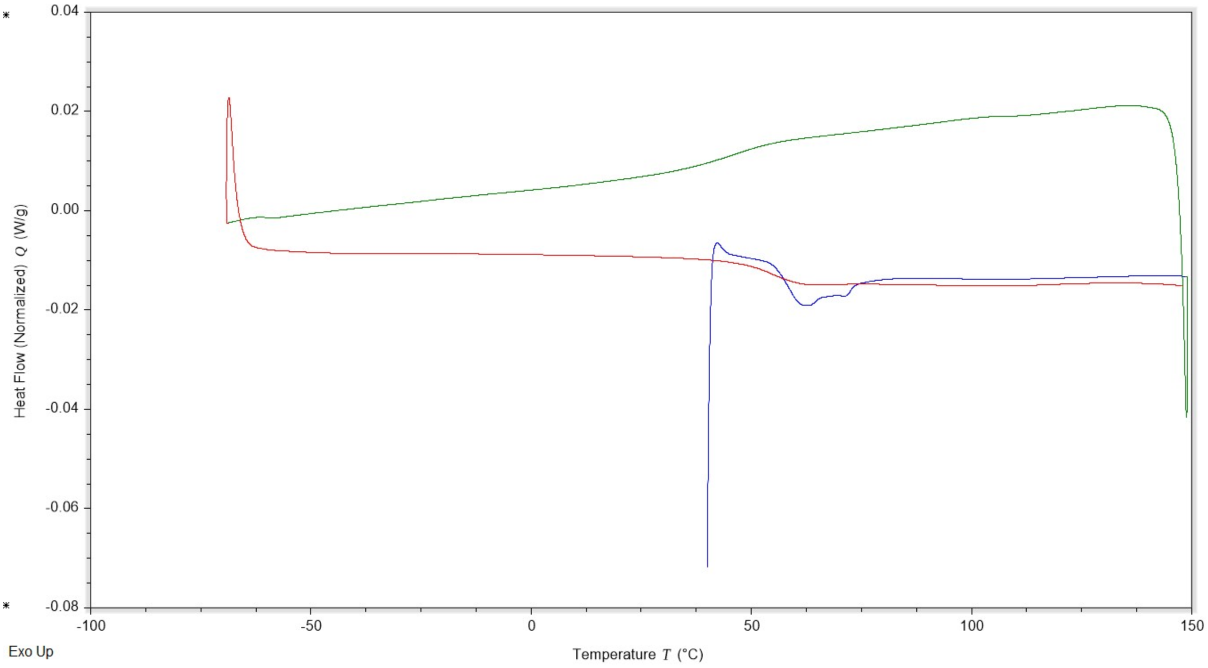

Fig S6. Full DSC traces of SDIBC10T110 scanned by heating-cooling-heating program showed no sulfur crystals remain and there is a glass transition temperature of 53 °C.

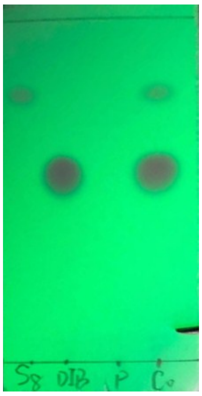

Fig S7. Detection of elemental sulfur by TLC. Spots on the baseline from left to right are elemental sulfur, DIB, poly(S-DIB), and mixture of sulfur, DIB, and poly(S-DIB). Neither sulfur or DIB was detected in the polymer after 3 months since being synthesized, proving the high completion of reaction and good stability of the final product.

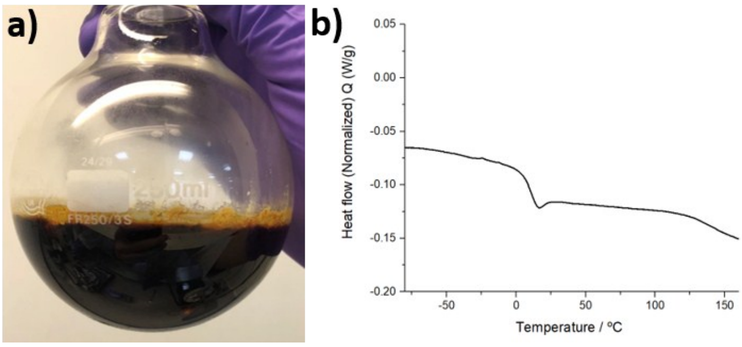

Fig S8. a) Scale up testing of reaction of sulfur and DIB from 10 g to 100 g. b) DCS trace of large-scale products, showing comparable T_g to SDIBC10T110.

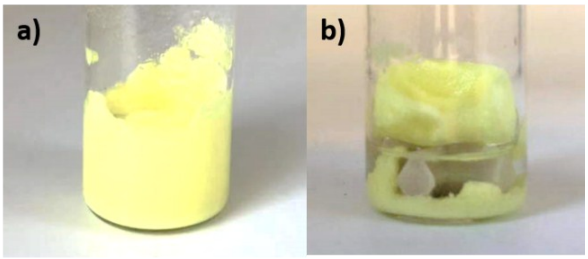

Fig S9. a) The reaction of SEGDMAC0T110, b) the reaction of SMMAC0T95

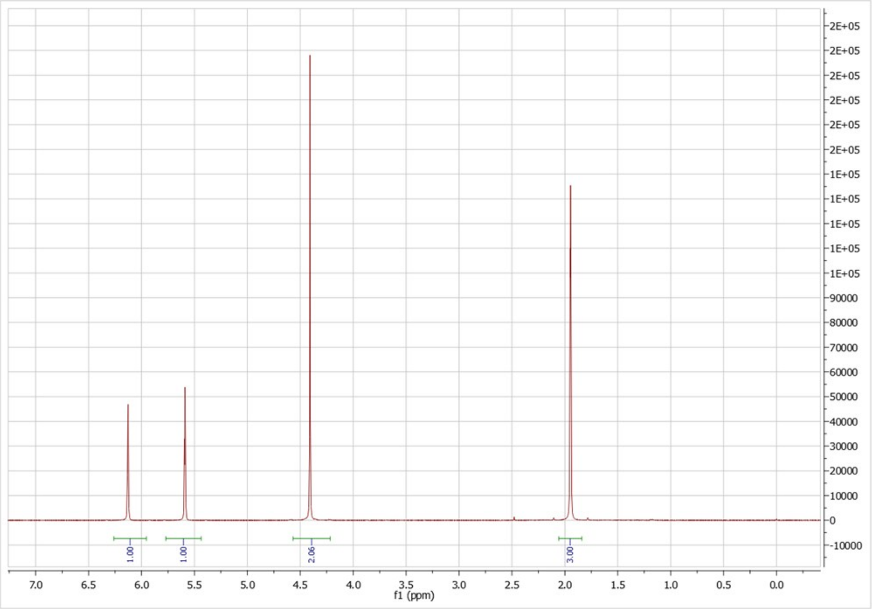

Fig S10. ^{1}H NMR spectra for SEGDMAC0T110. Apparently, C=C bonds in EGDMA were not reacted.

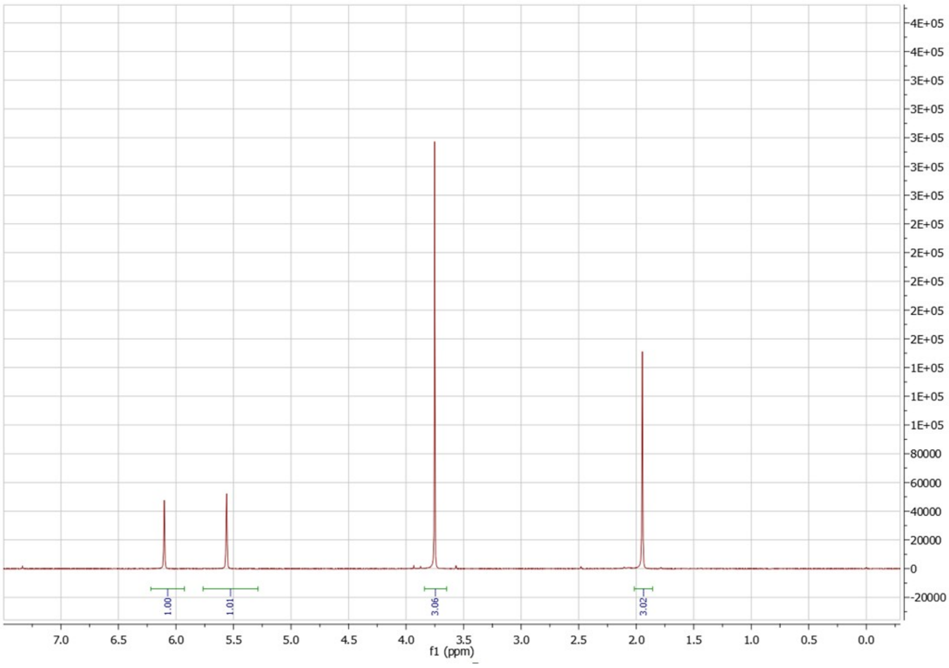

Fig S11. ^{1}H NMR spectra for SMMAC0T95. Same with the reaction of SEGDMAC0T110, without NaDTC, MMA cannot react with sulfur.

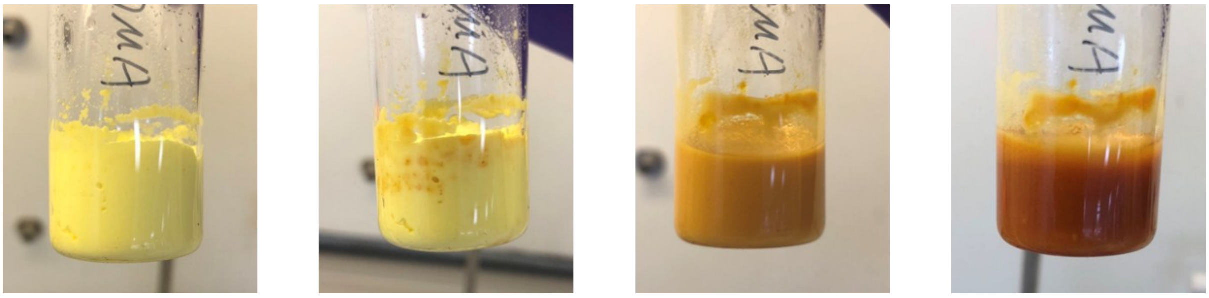

Fig S12. Images of processing to produce Poly(S-EGDMA) at 110 °C, showing heterogeneity initially and homogeneity as time progresses.

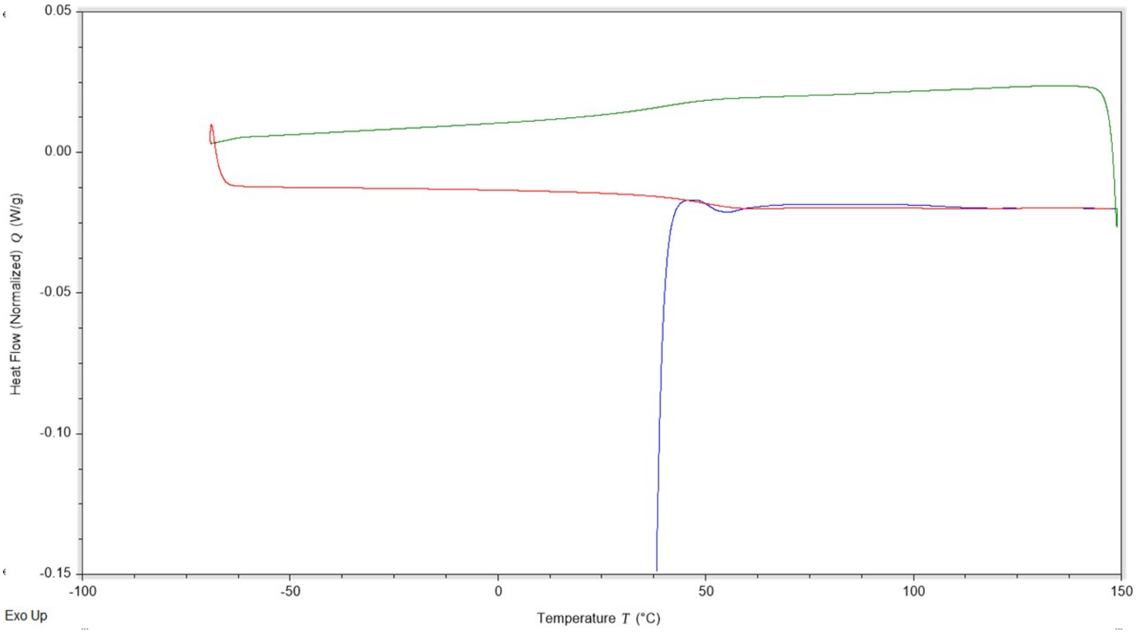

Fig S13. Full DSC traces of SEGDMAC1T110 scanned by heating-cooling-heating program showed no sulfur crystals remaining and a glass transition temperature of 57 °C.

Fig S14. 5% NaDTC led to Trommsdorff-Norrish effect driven auto-acceleration in the reaction of sulfur and EGDMA, resulting in heterogeneity.

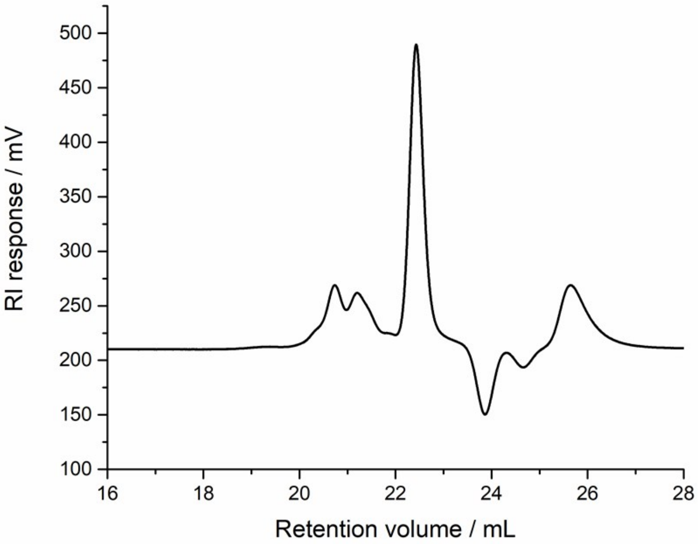

Figure S15. GPC trace for SMMAC10T95 in THF. Oligomers could be observed with low molecular weight and broad polydispersity.

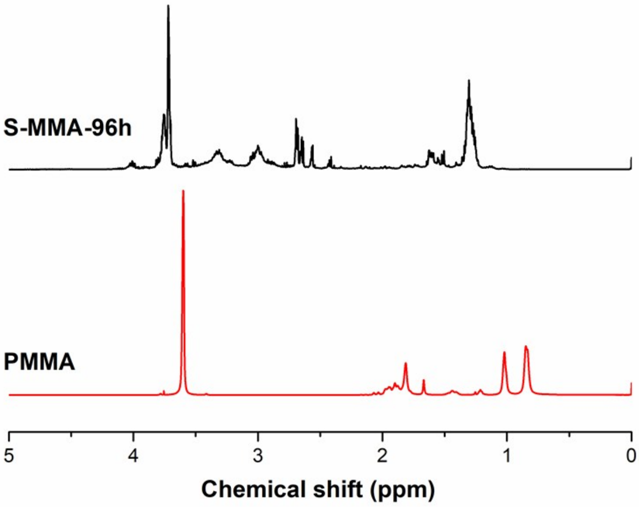

Fig S16 ^{1}H NMR spectra for S-MMA-96h and PMMA. Chemical shifts of main peaks of PMMA and those of S-MMA-96h are different, suggesting the reaction is mainly copolymerisation of sulfur and MMA instead of homopolymer of MMA.

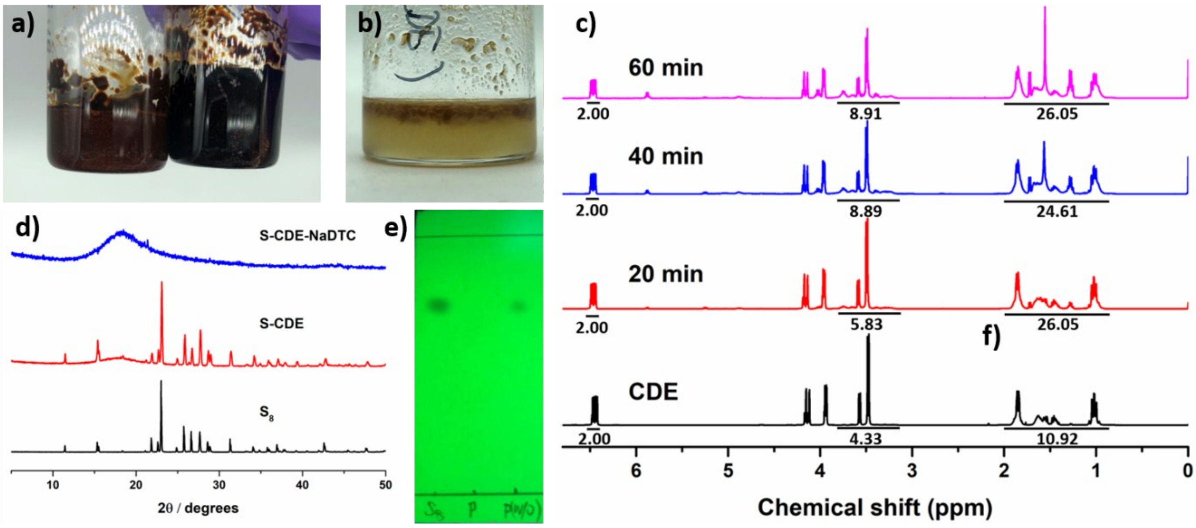

Fig S17. Like DIB, CDE surprisingly could react sparingly with sulfur at 110 °C, but free sulfur, either crystal or amorphous, could still be detected from the products. However, no sulfur could be detected from poly(S-CDE) made involving catalyst. NMR was conducted to screen the reaction, suggesting the large reduction of C=C bonds. a) left sample is the product without catalyst (lighter in colour) and right one is poly(S-CDE) made adding 10% NaDTC (darker). b) Final poly(S-CDE) is insoluble in $CDCl_3$, suggesting the polymer crosslinked and only the low molecular weight oligomer was tested in NMR. c) Kinetic studies for the S-CDE proved reactions between sulfur and C=C bonds, because of the decrease of the integral of vinyl protons, and new peaks appeared at 4, and between 5 and 6. d) from top to bottom, PXRD patterns of poly(S-CDE), the product made absence catalyst, and elemental sulfur. Apparently, sulfur crystals still could be detected from the product prepared without catalyst, however, poly(S-CDE) is amorphous. e) TLC results showing no detectable sulfur in poly(S-CDE). Spots on baseline are sulfur, poly(S-CDE), and the product made absence catalyst.

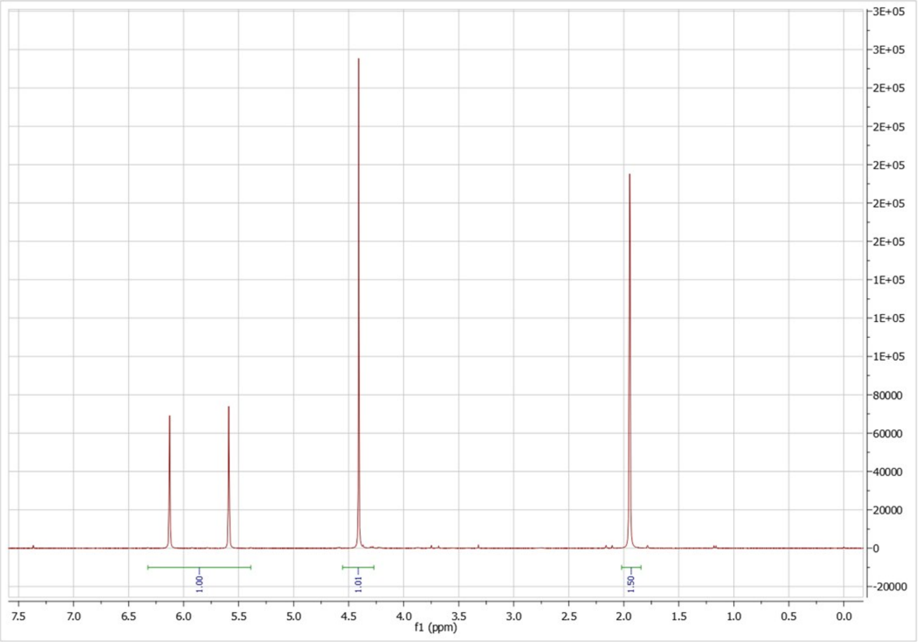

Fig S18. ^1H NMR spectra for standard EGDMA

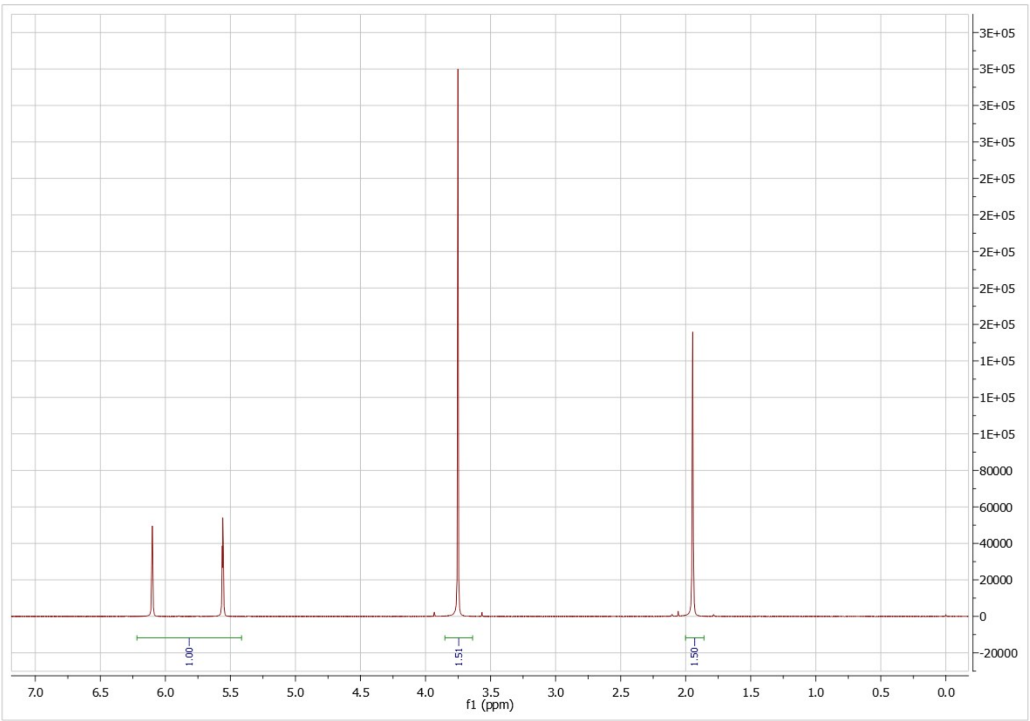

Fig S19. ^{1}H NMR spectra for standard MMA