

Supplementary information:

## A ternary system for delayed curing inverse vulcanisation

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**Materials:** Sulfur (S<sub>8</sub>, sublimed powder, reagent grade,  $\geq 99.5\%$ , Brenntag UK & Ireland. Purchased in 25 kg bags), ethylene glycol dimethylacrylate (EGDMA, 98%, Alfa Aesar), ethylene glycol diacetate (EGDA, 99% SigmaAldrich), dicyclopentadiene (DCPD  $>95\%$ , TCI), chloroform-d (CDCl<sub>3</sub>, Cambridge Isotope Laboratories Inc.)

### Characterisation methods

**Powder X-ray Diffraction (PXRD).** Data was measured using a PANalytical X'Pert PRO diffractometer with Cu-K $\alpha$  radiation, operating in transmission geometry.

**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<sup>-1</sup>.

**Nuclear magnetic resonance (NMR).** The reactions were monitored by solution NMR in deuterated chloroform, and recrystallized catalysts were performed by solution NMR in CDCl<sub>3</sub>, using a Bruker Advance DRX (400 MHz) spectrometer.

**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.

**Thermal gravimetric analysis (TGA):** TGA was carried out in platinum pans using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 10 °C min<sup>-1</sup> to 950 °C under nitrogen.

Table S1 Elemental analysis of delayed curing polymers

	Calc %			Analysis		
	% C	% H	% S	% C	% H	% S
S-D-E-7	37.80	4.00	50.00	36.25	3.93	53.90
S-D-E-14	37.80	4.00	50.00	36.34	3.91	53.46
S-D-E-21	37.80	4.00	50.00	36.45	3.94	53.30
S-D-E-28	37.80	4.00	50.00	36.25	3.90	53.55

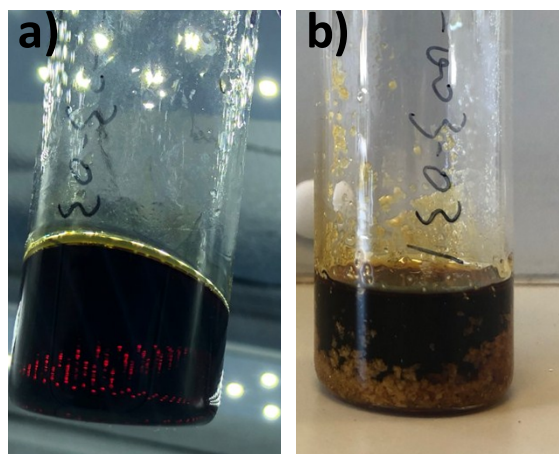


Figure S1. (a) Incomplete inverse vulcanisation of sulfur and DCPD taken directly from the heated and stirred reaction. The solution is homogeneous. (b) After cooling for  $\sim 1$  hour a solid yellow precipitate can be seen.

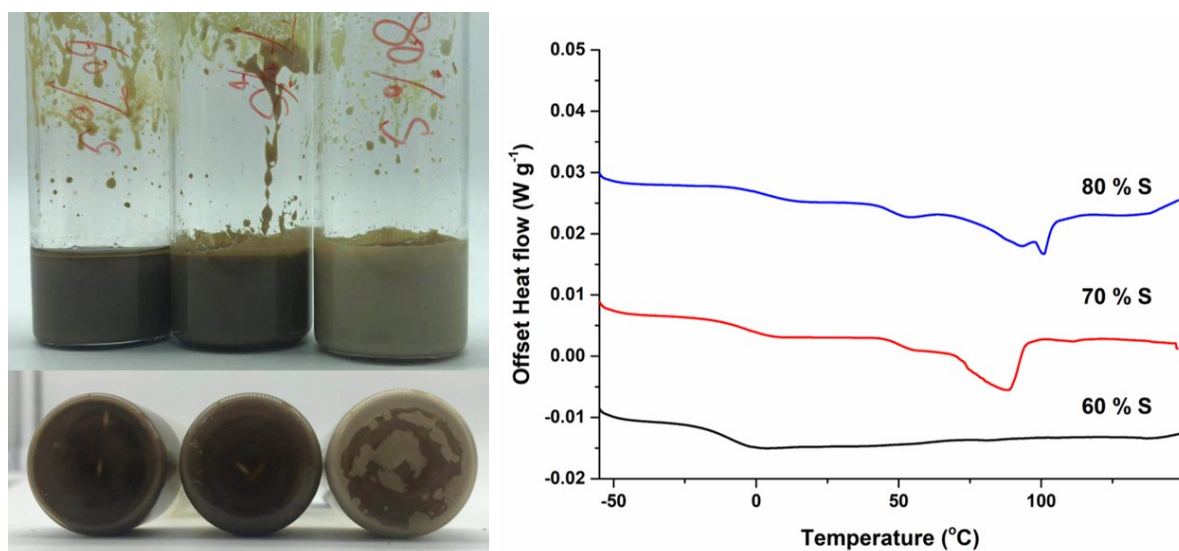


Figure S2. Left, photographs of vials of prepolymer: From left to right, prepolymers with 60 wt.%, 70 wt.%, and 80 wt.% sulfur respectively were preserved in room temperature for 7 days. Visibly, phase separation could be observed from the prepolymer with 80% sulfur. Right, DSC traces of these prepolymers. A first order transition could also be detected from 70 and 80 wt.% sulfur content prepolymers. At 60 wt.% S content the prepolymer has a clear  $T_g$  but no other transition.

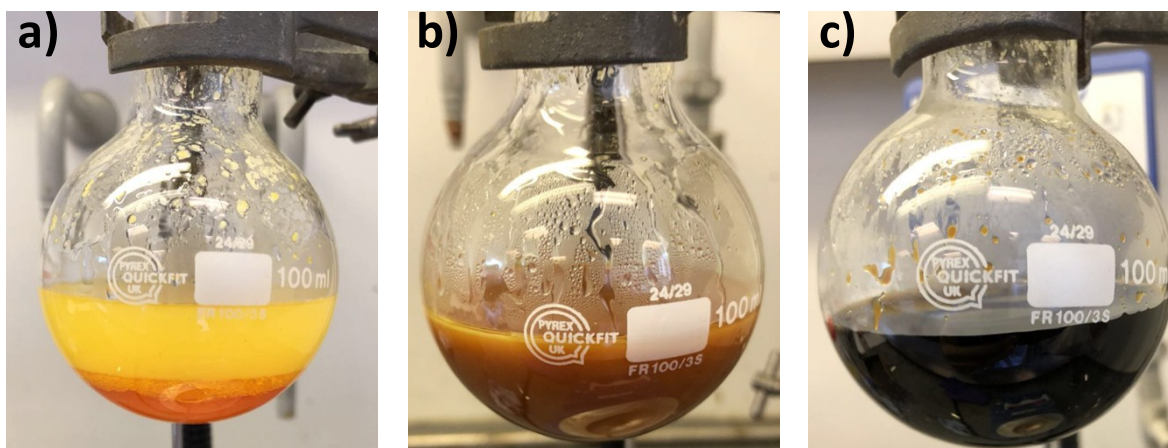


Figure S3. (a) Reaction at 3 minutes. (b) Reaction at 5 minutes. (c) Reaction at 8 minutes. The reaction was initially two phases, but transitted to homogeneous after 8 minutes and the coulour of product changed to black.

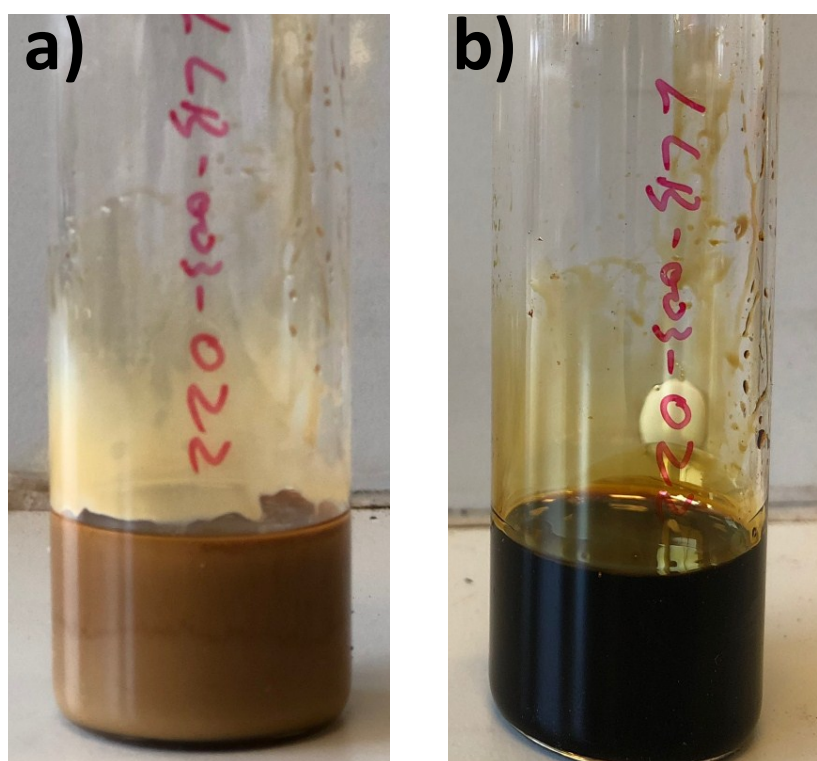


Figure S4. (a) Reserved pre-polymer Pre-S-D-E-14. (b) Reheated prepolymer Pre-S-D-E-14.

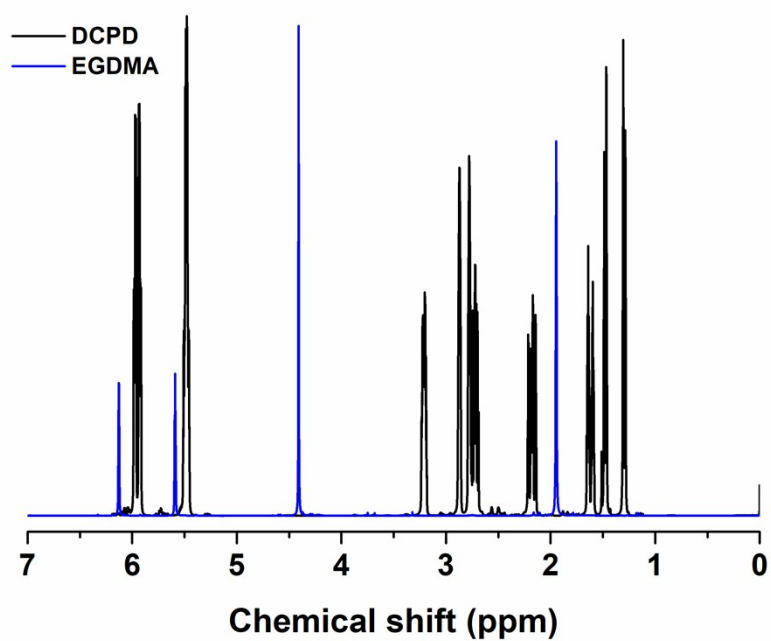


Figure S5.  $^1\text{H}$  NMR spectrum of standard DCPD and EGDMA.

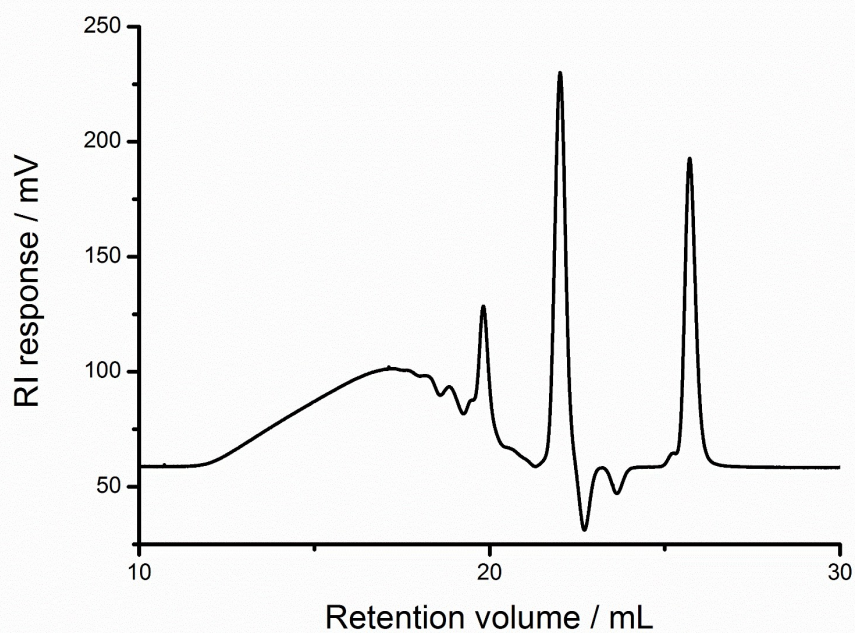


Figure S6. GPC trace for prepolymer Pre-S-D-E in THF. Oligomers could be observed with low molecular weight and broad polydispersity.

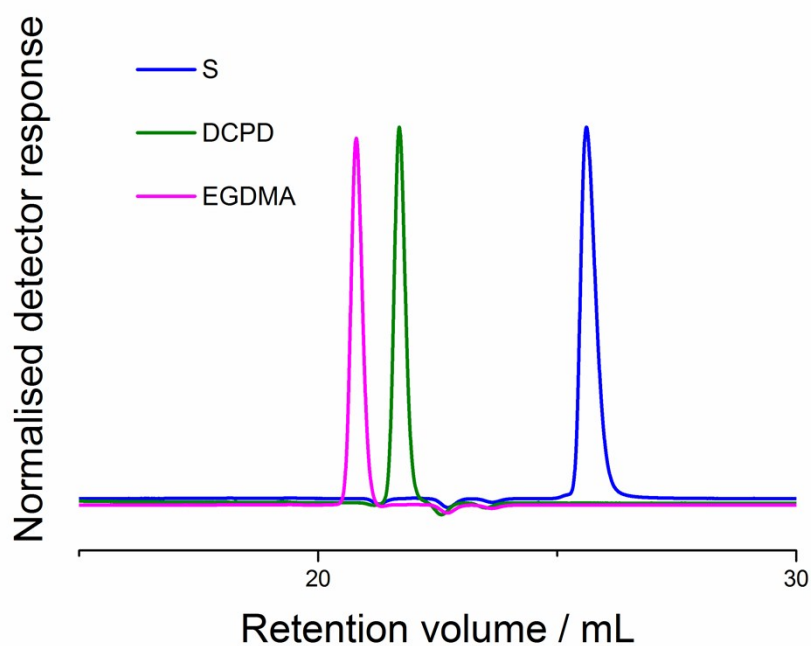


Figure S7. Crosslinkers and elemental sulfur were also tested through GPC to compare to the trace of the prepolymer. The organic crosslinker peaks do not directly match any of the peaks observed for the pre-polymer (Figure S6), though they could be slightly shifted due to the presence of the polymer. In comparison, the NMR shows no DCPD, but does show remaining EGDMA, therefore the sharp peaks in the GPC shown in figure S6 could be due to unreacted crosslinkers or low molecular weight oligomers. The sulfur peak could be matched with the peak from prepolymer, suggesting that sulfur may precipitate from the THF solution due to back-biting of dangling sulfur chains.





Figure S8. EGDMA was substituted by EGDA to test the role of plasticizers. From the testing, we found that no sulfur was precipitated and there was no autoacceleration during the reaction. However, a lower miscibility of the EGDA resulted in its separation out to a lighter surface layer.

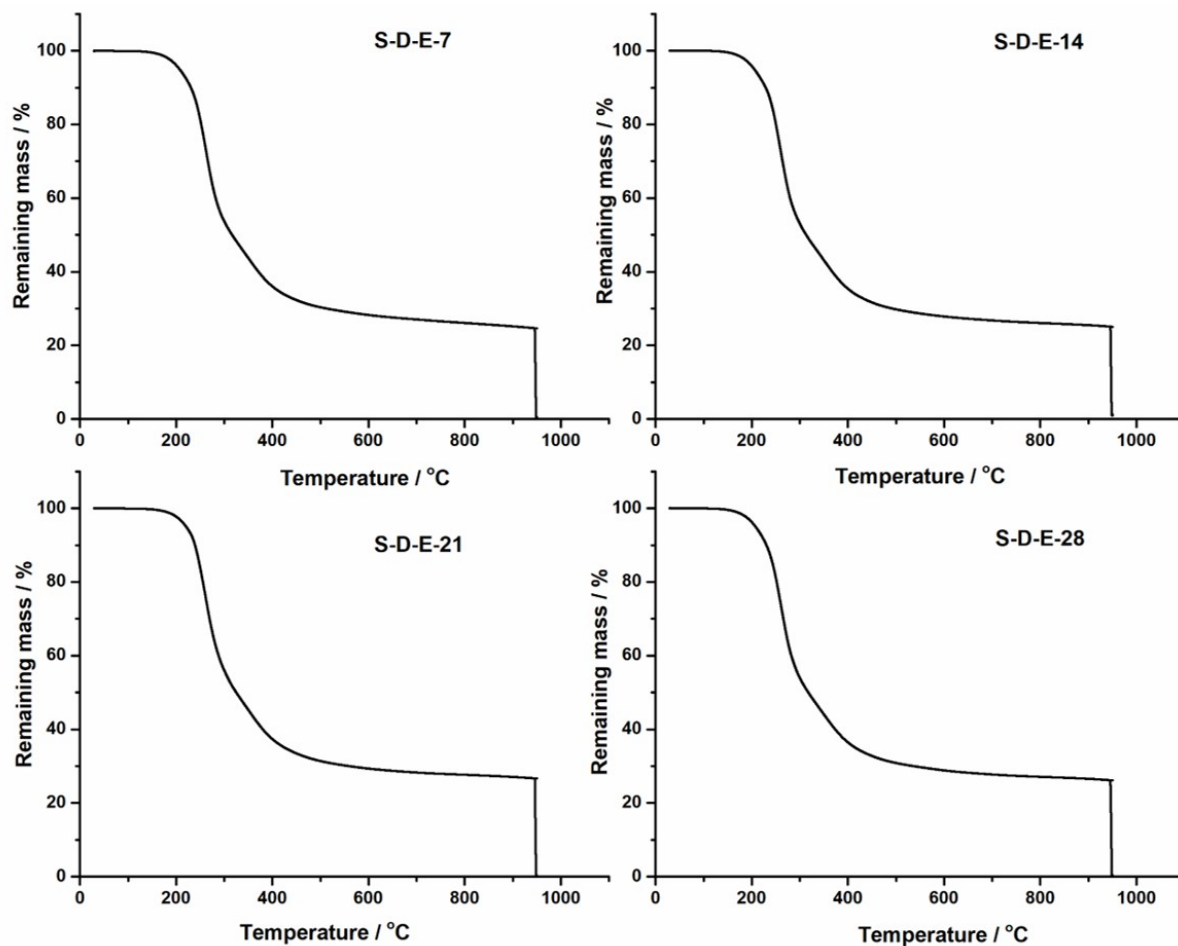


Figure S9. Thermogravimetric analysis of inverse vulcanisation polymers cured from corresponding pre-polymers. TGA thermograms showed all polymers had similar decomposition temperature and char mass remaining.