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Electronic Supplementary Information for

Inverse Vulcanization of Elemental Sulfur Catalyzed by Trialkyl Amines

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Table of Contents

Experimental Section

Materials

Elemental sulfur (ES, ≥99.5%), tributylamine (TBA, 99.5%), trihexylamine (THA, 96%), trioctylamine (TOA, 98%), zinc diethyldithiocarbamate ($Zn(DEDC)_2$, 97%), ethylene glycol dimethacrylate (EGDMA, 98%), glyoxal bis(diallyl acetal) (GBDA, ≥95%), 1,3-diisopropenylbenzene (DIB, 97%), dicyclopentadiene (DCPD, ≥96%), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TVTCSi, ≥95%), pentaerythritol tetraacrylate (PETA, ≥85%), 1,6-hexanediol dimethacrylate (HDDA, ≥90%), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO, 98%), bisphenol A ethoxylate diacrylate (BPAEDA, ≥95%), bisphenol A glycerolate dimethacrylate (BPAGMA, ≥95%), 1,4-diazabicyclo[2.2.2]octane (DABCO, ≥99%), 1-methylimidazole (NMI, ≥99%), and methyl sulfoxide-d_6 (DMSO-d_6, 99.9 atom % D) from Sigma-Aldrich, were used as received. Copper(II) diethyldithiocarbamate ($Cu(DEDC)_2$, 97%) and methacrylate-polyhedral oligomeric silsesquioxane (MA-POSS, 100%) were purchased from Tokyo Chemical Industry (TCI) and Hybrid Plastics, respectively, and used as received. All other reagents and solvents were used as received from standard vendors.

Synthesis of sulfur copolymers (poly(S-r-X)s)

Sulfur copolymers synthesized via catalytic inverse vulcanization of elemental sulfur (ES) with various crosslinkers (X) are designated as poly(S-*r*-X)s, where X indicates the abbreviation of crosslinkers used for the reaction. Poly(S-*r*-X)s were synthesized from the crosslinkers in Table 1 with the same procedure as for the poly(S-*r*-EGDMA). The synthesis of the poly(S-*r*-EGDMA) is as follows. To a 20 mL glass vial equipped with a cross-shaped magnetic stirring bar was added 4.95 g of ES (19.30 mmol) with 0.1 g of tributylamine (TBA, 0.54 mmol) catalyst. The vial sealed with a septum was stirred at 200 rpm for 10 min under nitrogen (N_2) atmosphere at 130 °C to melt the crystalline sulfur completely. 4.95 g of ethylene glycol dimethacrylate (EGDMA, 24.94 mmol) was injected into the vial and reacted at a stirring rate of 900 rpm. After the reaction until vitrification, the vial with the vitrified product was immersed in liquid nitrogen to shrink the product volume. The poly(S-*r*-EGDMA) was obtained by carefully breaking the vial with a hammer. The same procedure was used for poly(S-*r*-EGDMA) synthesis using the catalysts listed in Table S1 to compare the performance of each type of catalyst. All the reactions were performed with a 1:1 weight ratio of ES and crosslinker, and the total weight was fixed at 10 g.

Kinetic study for the catalytic inverse vulcanization of ES with EGDMA

To a 20 mL glass vial equipped with a cross magnetic stir bar was added 4.95 g of ES (19.30 mmol) along with 0.1 g of a trialkyl amine catalyst. For trialkyl amines, TBA (0.54 mmol), THA (0.37 mmol), and TOA (0.28 mmol) were used. The vial sealed with septum was stirred at 200 rpm for 10 min under nitrogen (N_2) atmosphere to melt the crystalline sulfur completely. 4.95 g of ethylene glycol dimethacrylate (EGDMA, 24.94 mmol) was injected into the vial and reacted at a stirring rate of 900 rpm. Samples were quenched in liquid nitrogen by aliquots every 30 min until vitrification and dissolved in DMSO-d_6 to subject ^{1}H NMR analysis. The conversion of carbon-carbon double bonds (C=C) in EGDMA was monitored as a function of time. The integration value of proton peaks from -O–CH_2-CH_2-O-, observed at 4.36 ppm, was normalized as 4 (Fig. S2). Based on the normalized values, a relative decrease in the C=C binding peaks of EGDMA was observed at 5.67 and 6.01 ppm, respectively.

Gas capture experiment

The gas capture experiment was conducted similarly to the general method for catalytic inverse vulcanization. A 20 ml vial with a cross-shaped magnetic stirring bar, 1 wt% of catalyst, and 4.95 g of ES was heated at 135 ^oC. The catalysts used for the gas capture experiment are TBA, $Zn(DEDC)_2$, $Cu(DEDC)_2$, NMI, and DABCO. 4.95 g of EGDMA was injected into molten ES, capped with a septum, and connected to a mass cylinder and silicon tube. The mass cylinder, filled with deionized water, was placed upside down in the 1L beaker with water. While heating the capped vial to 135 ^oC for 1 h, the volume of the generated H_2S gas was measured with a mass cylinder.

Extraction of TBA catalyst from poly(S-r-EGDMA)

A chunk of poly(S-*r*-EGDMA) was immersed in liquid nitrogen and crushed into powder using a hammer. After washing the powder with D_2O and centrifugation, the supernatant was analyzed with ^{1}H NMR to confirm the extraction of TBA from poly(S-*r*-EGDMA) (Fig. S4).

Preparation of poly(S-r-X) films

Poly(S-*r*-X) films were prepared by placing the bulk poly(S-*r*-X) into a mold (40 mm (L) × 40 mm (W) × 0.2 mm (T)), made of Kapton® film and stainless spacer, and hot pressing (10 MPa at 130 ^{o}C) for 10 min (Fig. S6). Broken pieces of poly(S-*r*-X) films were gathered and reprocessed to the original form using the same procedure.

Instrumentation and Characterization Techniques

^{1}H nuclear magnetic resonance (NMR) data were acquired on a Bruker Ascend 400 MHz NMR spectrometer. Differential scanning calorimetry (DSC) was run using a TA Instruments DSC Q1000 under a nitrogen atmosphere. Samples with a typical mass of 5–10 mg were encapsulated in sealed aluminum pans. They were first heated from –40 ^{o}C to 150 ^{o}C and then cooled down to –40 ^{o}C, which were followed by second heating to 150 ^{o}C at a constant rate of 10 ^{0}C min^{-1}. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Alpha II FTIR spectrometer using attenuated total reflectance (ATR) equipment. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IVX-ray diffractometer with Cu-Kα radiation using 40 kV/40 mA as accelerating voltage/tube current. The sample powders were mounted on an aluminum holder and scanned from 5^{o} to 90^{o}. Solvent extraction experiment was performed by placing a small piece (ca. 20 mg) of sulfur copolymer films into a 20 mL vial filled with toluene. After being stored in an oven at 25 ^{o}C for 24 h, the film was recovered and dried at 70 ^{o}C under vacuum for 18 h. Gel fraction (f_g) was calculated as

$$f_g = W_a / W_d \tag{1}$$

where W_d and W_a are the weights of the dried film before and after the toluene solvent extraction.

Synthesis and Characterization of TAA-catalyzed poly(S-*r*-EGDMA)

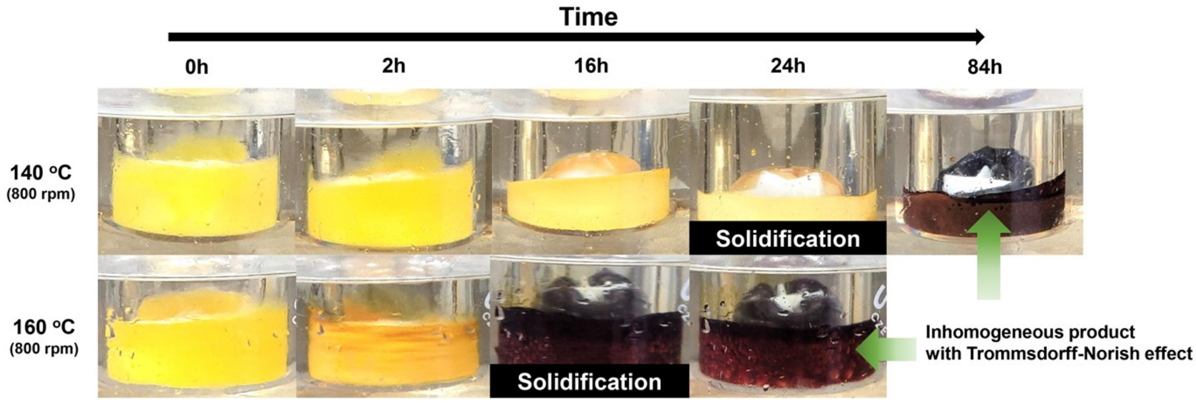

Fig. S1 Inverse vulcanization process of ES via EGDMA under non-catalytic conditions.

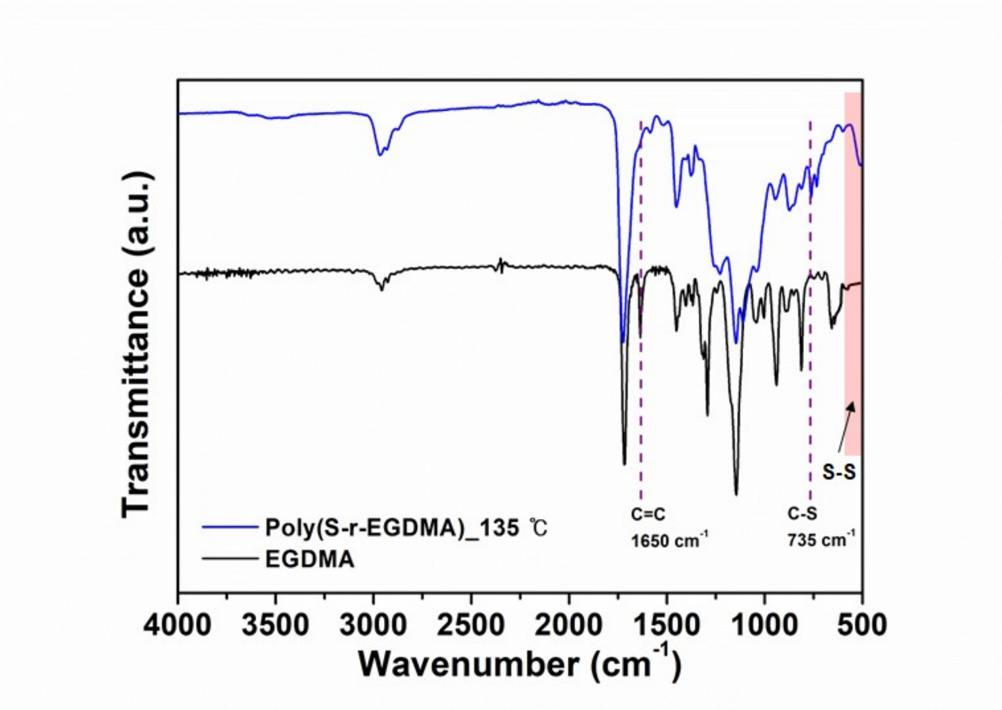

Fig. S2 FT-IR spectra of EGDMA and Poly(S-*r*-EGDMA) prepared via TBA-catalyzed inverse vulcanization at 135 °C.

Kinetic Analysis and Mechanisms of the TAA Catalytic Inverse Vulcanization

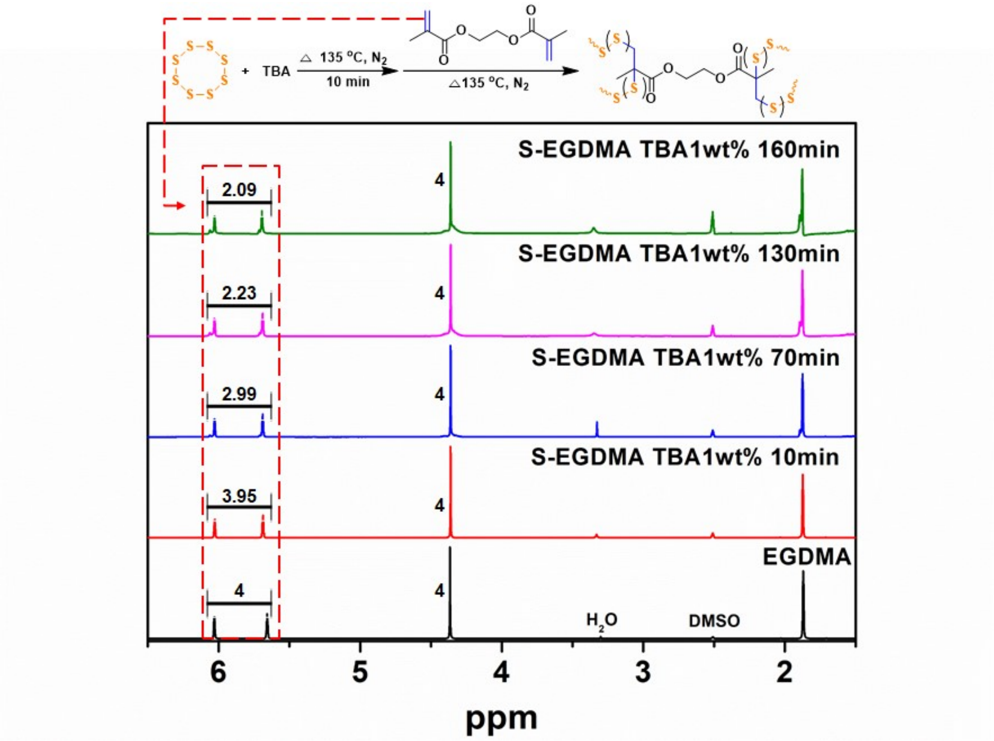

Fig. S3 ^{1}H NMR spectra for the reaction between ES and EGDMA in the presence of 1 wt % TBA catalyst at different reaction time.

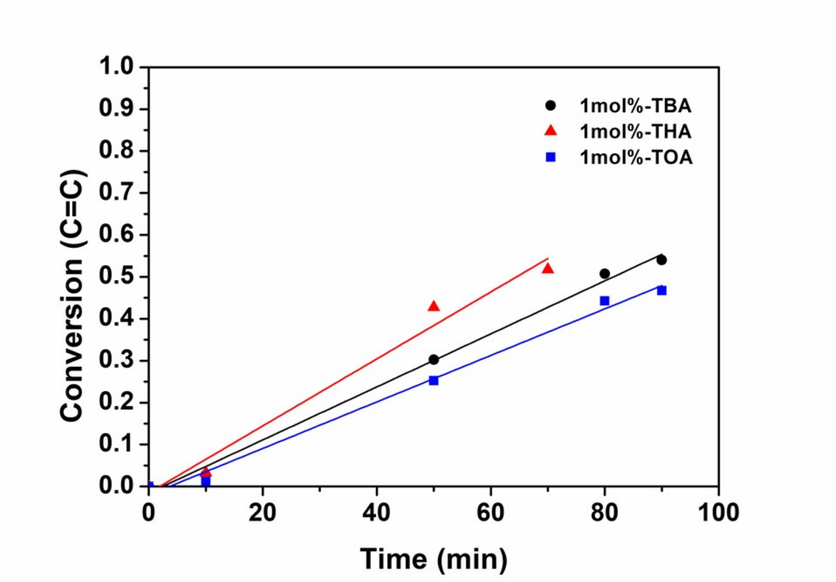

Fig. S4 A plot of C=C double bond conversion vs. reaction time (before vitrification) for the inverse vulcanization catalyzed by 1 mol % of trialkyl amine catalyst.

Table S1 Summary of catalytic inverse vulcanization of elemental sulfur with EGDMA crosslinker under different content of TBA.[a]

Catalyst (wt%)	Reaction Temp. (°C)	Vitrification Time[b]	Residual Sulfur	T_g^c (°C)	f_g^d	Yield (%)	Color
TBA (1 wt %)	*135*	*2 h 40 min*	-[e]	*23.3*	*0.97*	97.4	*Dark brown*
TBA (3 wt %)	*135*	*1 h 10 min*	-[e]	*15.6*	*0.97*	97.5	*Dark brown*
TBA (5 wt %)	*135*	*40 min*	-[e]	*5.71*	*0.96*	93.8	*Dark brown*

[a] Performed with 1:1 weight ratio of ES and EGDMA. [b] Time passed until the magnetic stirring bar stops rotating. [c] Glass transition temperature, determined by DSC. [d] Gel fraction, obtained by $f_g = W_a/W_d$, where W_d and W_a are the weights of the dried sample before and after toluene solvent extraction. [e] Not detected from DSC and XRD analyses.

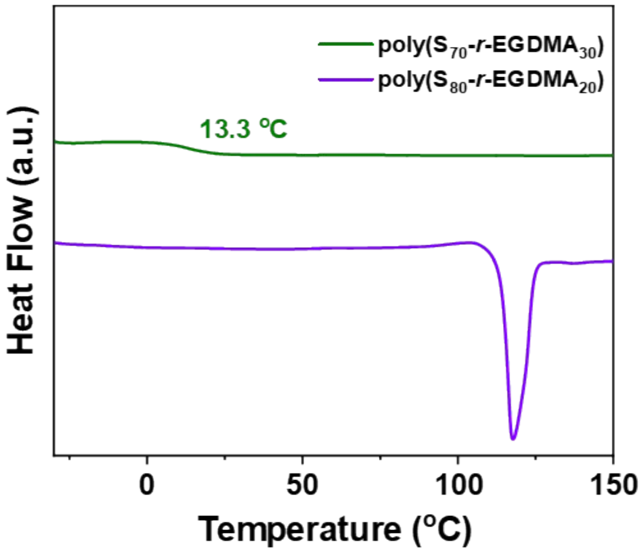

Fig. S5 DSC thermograms of poly(S-*r*-EGDMA) by different sulfur contents.

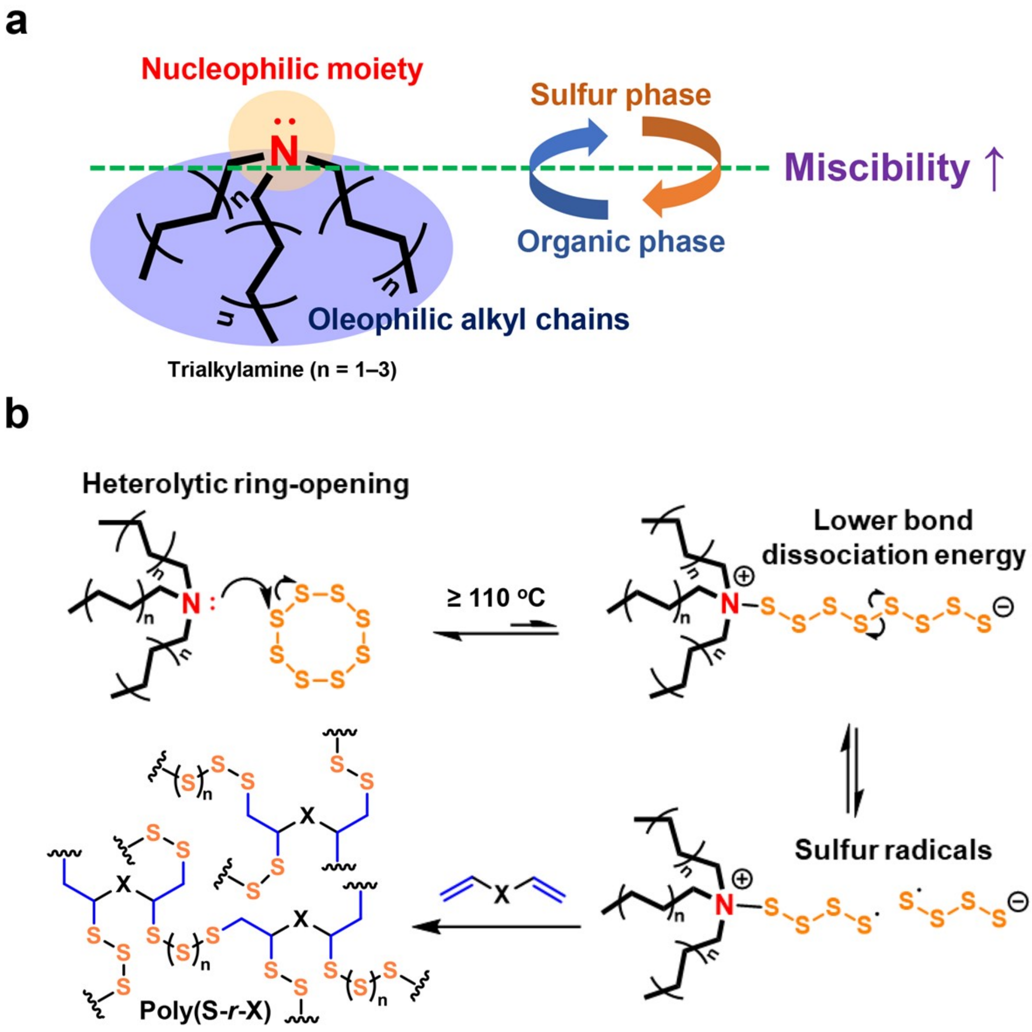

Fig. S6 Schematic illustrations for the proposed TAA-catalyzed inverse vulcanization of ES. (a) Schematic illustrations of TAAs with nucleophilic moiety and oleophilic alkyl chains. (b) Proposed mechanism of inverse vulcanization processes under TAA catalysis.

Trialkylamine (TAA) is a tertiary amine with high nucleophilicity similar to the N-methylimidazole (NMI) with high nucleophilicity,[1] which can be used as a catalytic activator to induce heterolytic fission of S_8. Due to the lowered bond dissociation energy of the polysulfides above the floor temperature (110 ^{o}C),[1] sulfur radicals are generated and react with the C=C bond of the crosslinker to produce poly(S-*r*-X). In addition, TAA has oleophilic alkyl chains, which can act as a phase transfer agent similar to the diethyl dithiocarbamate (DEDC).[2] Therefore, TAA is presumed to facilitate the transfer between sulfur and organic phases due to the nucleophilic moiety and oleophilic alkyl chains. Based on the advantages above, the TAA catalyst is assumed to induce rapid and facile inverse vulcanization of ES using unreactive crosslinkers.

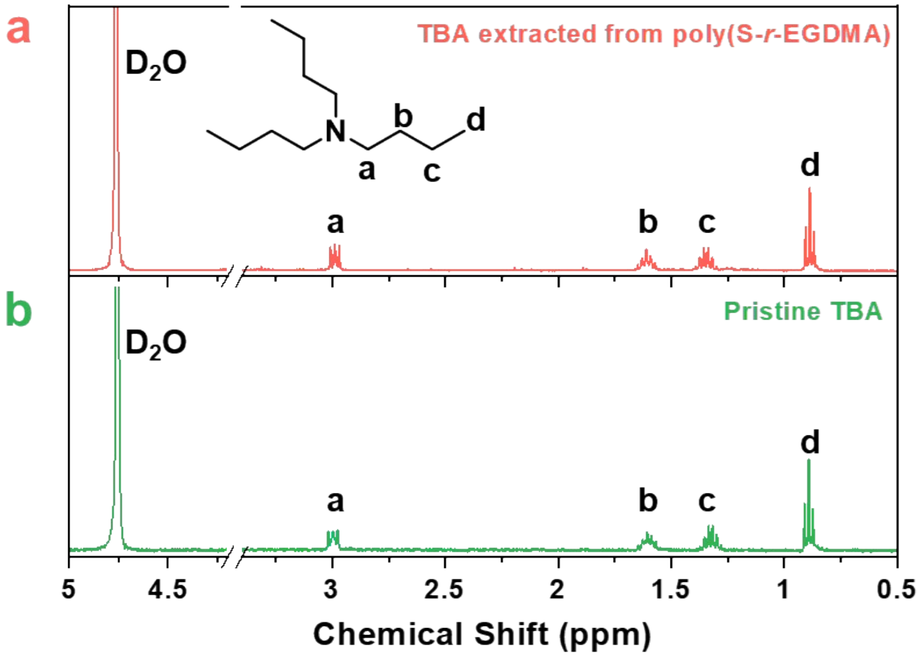

Fig. S7 ^{1}H NMR spectra of (a) extracted TBA from poly(S-*r*-EGDMA) and (b) pristine TBA with the D_2O NMR solvent.

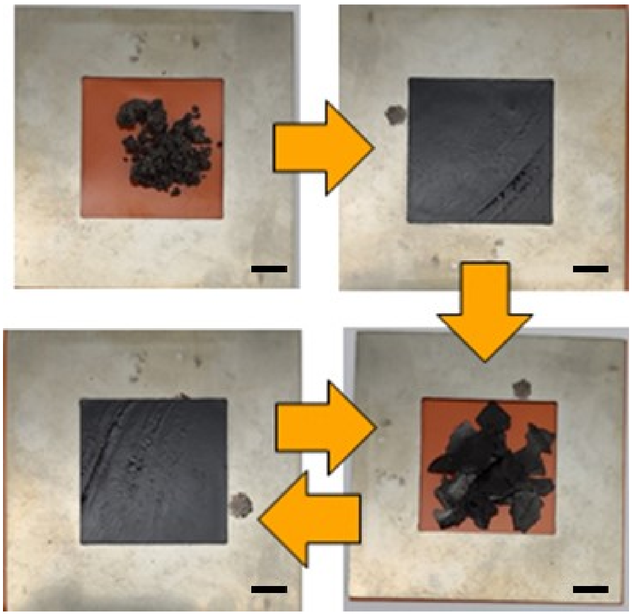

Fig. S8 Photographs for the preparation and reprocessing of poly(S-*r*-EGDMA) film after the extraction of TBA catalyst via hot pressing (scale bar = 1 cm).

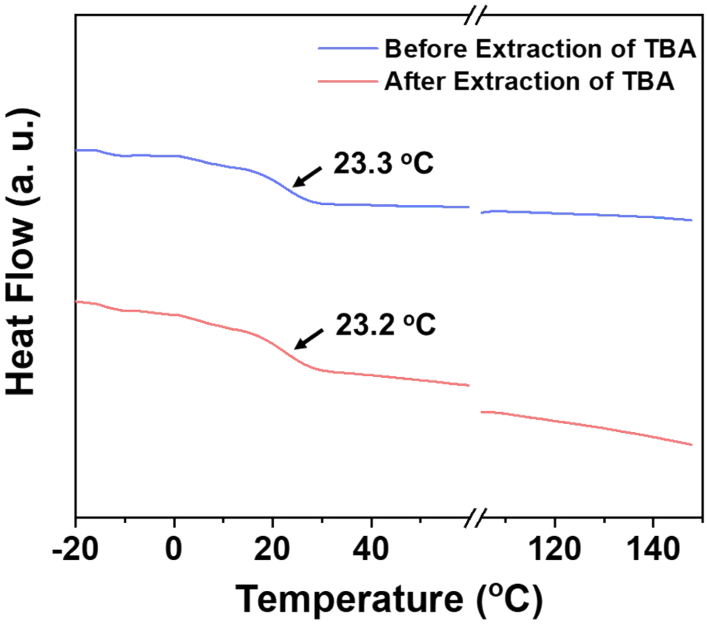

Fig. S9 DSC thermograms of poly(S_{50}-*r*-$EGDMA_{50}$)s before and after the extraction of TBA catalyst.

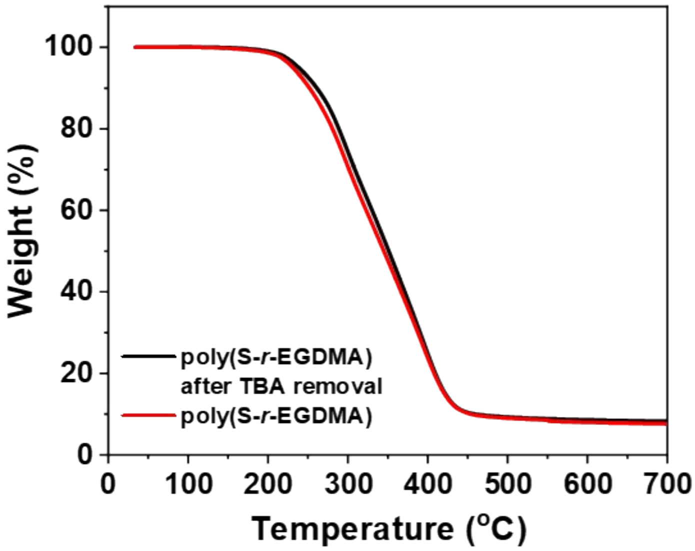

Fig. S10 TGA curves of poly(S_{50}-*r*-$EGDMA_{50}$)s before and after the extraction of TBA catalyst.

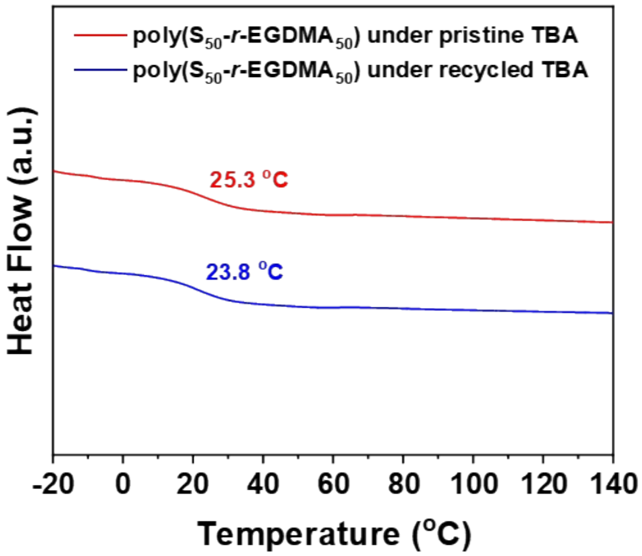

Fig. S11 DSC thermograms of inverse vulcanized poly(S_{50}-*r*-$EGDMA_{50}$)s using pristine and recycled TBA catalysts.

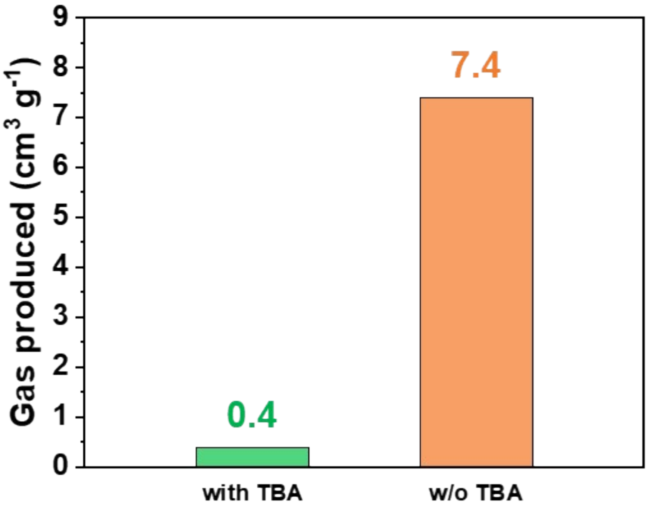

Fig. S12 Comparison of H_2S gas generation during inverse vulcanization using DIB with and without TBA at 160 °C.

Table S2 Summary of catalytic inverse vulcanization of elemental sulfur with EGDMA crosslinker under different catalysts and conditions.[a]

Catalyst (wt%)	Reaction Temp. (°C)	Vitrification Time[b]	Residual Sulfur	T_g[c] (°C)	f_g[d]	Yield (%)	Color
TBA (1 wt %)	*135*	*2 h 40 min*	-[e]	*23.3 ± 0.1*	*0.97 ± 0.01*	97.4 ± *0.5*	*Dark brown*
Zn(DEDC)$_2$ (1 wt %)	*135*	*4 h 40 min*	-[e]	*22.7 ± 0.2*	*0.96 ± 0.01*	96.1 ± *0.8*	*Dark red*
Cu(DEDC)$_2$ (1 wt %)	*135*	*4 h 50min*	-[e]	*23.3 ± 0.4*	*0.96 ± 0.03*	95.1 ± *0.3*	*Dark brown*
NMI (1 wt %)	*135*	*3 h 40 min*	-[e]	*26.2 ± 0.2*	*0.98 ± 0.01*	96.8 ± *0.2*	*Dark red*
DABCO (1 wt %)	*135*	*3 h*	-[e]	*21.8 ± 0.3*	*0.93 ± 0.01*	95.2 ± *0.3*	*Red*

[a] Performed with 1:1 weight ratio of ES and EGDMA. [b] Time passed until the magnetic stirring bar stops rotating. [c] Glass transition temperature, determined by DSC. [d] Gel fraction, obtained by $f_g = W_a/W_d$, where W_d and W_a are the weights of the dried sample before and after toluene solvent extraction. [e] Not detected from DSC and XRD analyses.

Table S3 Summary of catalytic inverse vulcanization of elemental sulfur with EGDMA crosslinker via TBA catalyst under different temperatures.[a]

Catalyst (wt%)	Reaction Temp. (°C)	Vitrification Time[b]	Residual Sulfur	T_g[c] (°C)	f_g[d]	Yield (%)	Color
TBA (1 wt %)	*135*	*2 h 40 min*	-[e]	*23.3*	*0.97*	97.4	*Dark brown*
TBA (1 wt %)	*130*	*6 h*	-[e]	*21.3*	*0.99*	94.8	*Dark brown*
TBA (1 wt%)	*120*	*8 h*	-[e]	*20.5*	*0.94*	93.9	*Dark brown*
TBA (1 wt %)	*110*	*>12 h, <24 h*	-[e]	*20.0*	*0.93*	93.2	*Dark brown*

[a] Performed with 1:1 weight ratio of ES and EGDMA. [b] Time passed until the magnetic stirring bar stops rotating. [c] Glass transition temperature, determined by DSC. [d] Gel fraction, obtained by $f_g = W_a/W_d$, where W_d and W_a are the weights of the dried sample before and after toluene solvent extraction. [e] Not detected from DSC and XRD analyses.

Processing of Poly(S-*r*-X)s

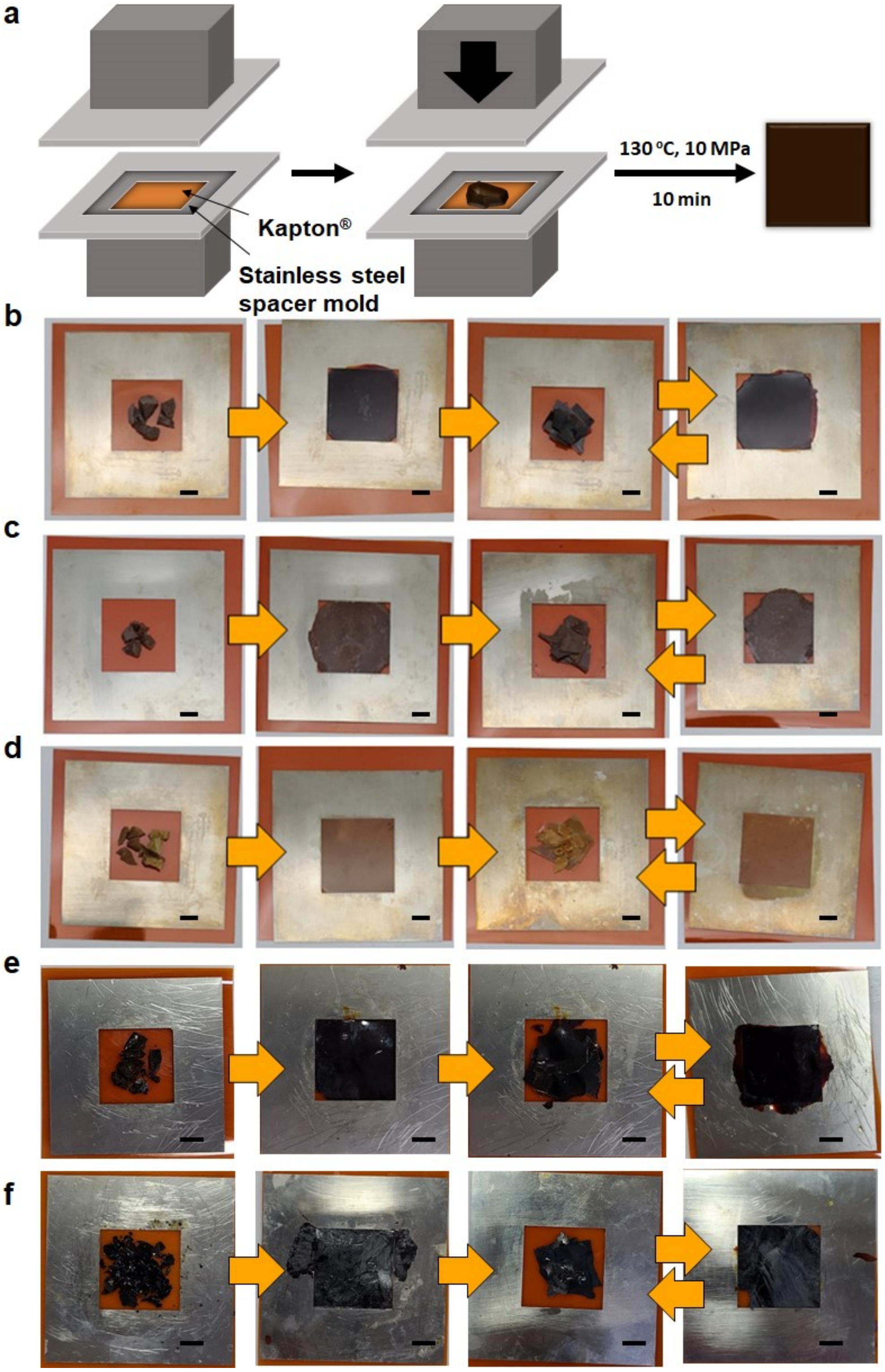

Fig. S13 (a) Schematic illustration for the preparation of poly(S-*r*-X) films via hot pressing. Photographs of (b) poly(S-*r*-HDDA), (c) poly(S-*r*-BPAGMA), (d) poly(S-*r*-BPAEDA), (e) poly(S-*r*-TATATO), and (f) poly(S-*r*-MA-POSS) films, which can be reprocessed several times (scale bar = 1 cm).

Table S4. Summary of the catalytic inverse vulcanization of ES with various crosslinkers

Catalyst	Crosslinker	Crosslinker content (wt %)	Reaction Temp. (°C)	vitrification time[a]	Residual sulfur	T_g[b] (°C)	yield[c] (%)	H_2S gas generation (cm^3/g)	Reference
Zn(DEDC)$_2$	EGDMA	50	135	>12, <24 h (1 wt %), >12, <24 h (5 wt %)	X	19.3 ~ 23.9	99	-[d]	2
Zn(DEDC)$_2$	EGDMA	50	135	4 h 40 min (1 wt %)	X	22.7 ± 0.2	96.1 ± 0.8	0.4	This work
Zn(DEDC)$_2$	DIB	50	135	6.5 h (1 wt %), 1 h (5 wt %)	X	36 ~ 50	-[d]	< 0.5	2
Zn(DEDC)$_2$	DIB	50	165	20 min (1 wt %), 10 min (5 wt %)	-[d]	-[d]	-[d]	-[d]	2
Zn(DEDC)$_2$	DIB	50	160	16 ± 0.0 min (1 wt %)	-[d]	2.30 ± 1.17	92.5 ± 0.1	-[d]	3
Zn(DEDC)$_2$	DVB	50	135	1.5 h (1 wt %), 0.85 h (5 wt %)	X	103 ~ 107	-[d]	< 0.5	2
Zn(DEDC)$_2$	DVB	50	135	40.3 ± 0.5 min (1 wt %)	-[d]	94.4 ± 1.0	94.1 ± 0.7	-[d]	3
Zn(DEDC)$_2$	DVB	30	135	21.7 ± 0.5 min (1 wt %)	-[d]	34.8 ± 0.3	95.3 ± 0.1	-[d]	3
Zn(DEDC)$_2$	DVB	70	135	98.0 ± 0.8 min (1 wt %)	-[d]	82.4 ± 0.7	84.7 ± 0.5	-[d]	3
Zn(DEDC)$_2$	Limonene	50	135	8.5 h (1 wt %), 1 h (5 w t%)	X	-[d]	-[d]	1	2
Zn(DEDC)$_2$	DCPD	50	135	1.6 h (1 wt %), 0.4 h (5 wt %)	X	70 ~ 90	-[d]	0.35	2
Zn(DEDC)$_2$	squalene	50	135	>12 (<24) h (1 wt %), 1.5 h (5 wt %)	O (5 wt % Zn(DEDC$_2$))	-[d]	-[d]	-[d]	2
Zn(DEDC)$_2$	sunflower oil	50	135	>12 (<24) h (1 wt %), <2 h (5 wt %)	O	-[d]	-[d]	-[d]	2
Zn(DEDC)$_2$	linseed	50	135	4 h (1 wt %), 2.5 h (5 wt %)	O (5 wt % Zn(DEDC$_2$))	- 26 ~ - 23	-[d]	-[d]	2
Zn(DEDC)$_2$	VNB	50	135	>4, <6 h (1 wt %), 2 h (5 wt %)	X	100 ~ 113	-[d]	-[d]	2
Zn(DEDC)$_2$	CDDT	50	135	6 h (1 wt %), 3 h (5 w t%)	X	35.1 ± 0.9	-[d]	-[d]	2
Zn(DEDC)$_2$	TVCH	50	135	6 h (1 wt %), 2 h (5 wt %)	X	21.5 ~ 39.7	-[d]	-[d]	2
Zn(DEDC)$_2$	TVTCSi	50	135	-[d]	O	-[d]	-[d]	-[d]	2
Zn(DEDC)$_2$	TVTCSi	50	160	>12, <24 h (1 w t%), >12, <24 h (5 wt %)	O (5 wt % Zn(DEDC$_2$))	-[d]	-[d]	-[d]	2
Zn(DEDC)$_2$	GBDA	50	135	>12, <24 h (1 wt %), 2.5 h (5 wt %)	X	-[d]	-[d]	-[d]	2
Zn(DMDC)$_2$	DIB	50	135	70 min (1 wt %)	-[d]	26.6	85.1	-[d]	3
Zn(DMDC)$_2$	DCPD	50	135	58 min (1 wt %)	-[d]	111.6	94.7	-[d]	3
Zn(DMDC)$_2$	EGDMA	50	160	74 min (1 wt %)	-[d]	10.6	90.1	-[d]	3
Na(DEDC)	EGDMA	50	100	20 min (1 wt %)	-[d]	-[d]	-[d]	-[d]	4
Na(DEDC)	EGDMA	50	110	10 min (1 wt %)	-[d]	-[d]	-[d]	-[d]	4
Na(DEDC)	EGDMA	50	160	103 min (1 wt %)	-[d]	5.5	86.9	-[d]	3
Na(DEDC)	DIB	30	110	-[d]	O	-[d]	-[d]	-[d]	4
Na(DEDC)	DIB	50	110	>12 h, <24 h (1 wt %)	-[d]	-[d]	-[d]	-[d]	4
Na(DEDC)	DIB	50	110	>12 h, <24 h (5 wt %)	-[d]	-[d]	-[d]	-[d]	4
Na(DEDC)	DIB	50	110	12 h (10 wt %)	-[d]	53	-[d]	-[d]	4
Na(DEDC)	DIB	50	135	126 min (1 wt %)	-[d]	14.9	77.9	-[d]	3
Na(DEDC)	DCPD	50	135	155 min (1 wt %)	-[d]	79.2	88.7	-[d]	3
Na(DEDC)	MMA	50	95	>12 h, <24 h (10 wt %)	-[d]	-[d]	-[d]	-[d]	4
Fe(DEDC)$_2$	EGDMA	50	135	10 h (1 wt %)	-[d]	22	-[d]	-[d]	2
Co(DEDC)$_2$	EGDMA	50	135	10 h (1 wt %)	-[d]	18	-[d]	-[d]	2
Cu(DEDC)$_2$	EGDMA	50	135	10 h (1 wt %)	-[d]	24	-[d]	-[d]	2
Cu(DEDC)$_2$	EGDMA	50	135	10 h (1 wt %)	X	23.3 ± 0.4	95.1 ± 0.3	0.475	This work
Ni(DEDC)$_2$	EGDMA	50	135	10 h (1 wt %)	-[d]	18	-[d]	-[d]	2

Table S4 (Continued).

ZnO	EGDMA	50	135	(1 wt %)	O	-[d]	97	-[d]	2
Zinc	EGDMA	50	135	(1 wt %)	O	-[d]	93	-[d]	2
$ZnCl_2$	EGDMA	50	135	(1 wt %)	O	-[d]	95	-[d]	2
$FeCl_2$	EGDMA	50	135	(1 wt %)	O	-[d]	93	-[d]	2
CuO	EGDMA	50	135	(1 wt %)	O	-[d]	90	-[d]	2
$CuCl_2$	EGDMA	50	135	(1 wt %)	O	-[d]	93	-[d]	2
Zn-STR	EGDMA	50	135	(1 wt %)	O	-[d]	93	-[d]	2
KEtX	EGDMA	50	160	94 min (1 wt %)	-[d]	5.5	84.6	-[d]	3
KEtX	DIB	50	135	129 min (1 wt %)	-[d]	18.6	75.4	-[d]	3
KEtX	DCPD	50	135	175 min (1 wt %)	-[d]	57	66.2	-[d]	3
2-MBT	EGDMA	50	160	135 min (1 wt %)	-[d]	7.6	82.3	-[d]	3
2-MBT	DIB	50	135	154 min (1 wt %)	-[d]	29.3	82.6	-[d]	3
2-MBT	DCPD	50	135	194 min (1 wt %)	-[d]	68.3	68.9	-[d]	3
Dioctylamine	EGDMA	50	160	121 min (1 wt %)	-[d]	6.9	81.7	-[d]	3
Dioctylamine	DIB	50	135	146 min (1 wt %)	-[d]	29.4	86.4	-[d]	3
Dioctylamine	DCPD	50	135	164 min (1 wt %)	-[d]	77.4	76.3	-[d]	3
NMI	EGDMA	50	135	3 h 40 min (1 wt %)	X	26.2 ± 0.2	96.8 ± 0.2	0.5	This work
DABCO	EGDMA	50	135	3 h (1 wt %)	X	21.8 ± 0.3	95.2 ± 0.3	0.53	This work
TBA	EGDMA	50	135	2 h 40 min (1 wt %)	X	23.3 ± 0.4	97.4 ± 0.5	0.395	This work
TBA	EGDMA	50	135	1 h 10 min (3 wt %)	X	15.6	97.5	-[d]	This work
TBA	EGDMA	50	135	40 min (5 wt %)	X	5.71	93.8	-[d]	This work
TBA	EGDMA	50	130	6 h (1 wt %)	X	21.3	94.8	-[d]	This work
TBA	EGDMA	50	120	8 h (1 wt %)	X	20.5	93.9	-[d]	This work
TBA	EGDMA	50	110	> 12 h, < 24 h (1 wt %)	X	20	93.2	-[d]	This work
TBA	DIB	50	135	2 h (1 wt %)	X	49.9	93.5	-[d]	This work
TBA	DCPD	50	135	3 h (1 wt %)	X	5.9	99	-[d]	This work
TBA	TVTCSi	50	135	> 12 h, < 24 h (1 wt %)	X	6.3	94.5	-[d]	This work
TBA	GBDA	50	135	2 h (1 wt %)	X	6.7	93	-[d]	This work
TBA	HDDA	50	135	2 h (1 wt %)	X	0.5	97.3	-[d]	This work
TBA	BPAGMA	50	135	2 h 10 min (1 wt %)	X	46.6	91.2	-[d]	This work
TBA	BPAEDA	50	135	2 h 30 min (1 wt %)	X	6	96.9	-[d]	This work
TBA	TATATO	50	135	< 12 h (1 wt %)	X	5.9	95.7	-[d]	This work
TBA	MA-POSS	50	135	1 h 30 min (1 wt %)	X	X	99.3	-[d]	This work

[a] Time passed until the magnetic stirring bar stops rotating and weight percentage (wt %) of catalyst. [b] Glass transition temperature, determined by DSC. [c] Calculated weight percentage (wt %) of the product obtained compared to the weight before the reaction. [d] Not stated in literatures

Due to the different experimental conditions (crosslinker content, reaction temperature, catalyst wt %), it was difficult to compare all data directly. However, overall, it was observed that the higher the catalyst content, the faster the vitrification time, but the lower the T_g. In addition, it was possible to compare some of the data and showed the following tendencies. As shown in Table S4, (meth)acryl-functionalized crosslinkers tended to have faster vitrification times and higher T_g under tertiary amine catalysts than metal complexes. On the contrary, vinyl and isopropenyl functionalized crosslinkers showed faster vitrification times under metal complex catalysis than tertiary amine catalysis.

References for Electronic Supporting Information

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