Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Aluminium-Catalyzed Terpolymerization of Furfuryl Glycidyl Ether with Epichlorohydrin and Ethylene Oxide: Synthesis of Thermoreversible Polyepichlorohydrin Elastomers with Furan/Maleimide Covalent Crosslinks

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Content

Table. S1 Copolymerization of ethylene oxide (EO) and epichlorohydrin (ECH) by *i*-Bu_3Al/H_3PO_4/DBU[a]

run	H_3PO_4[b]	DBU[b]	ECH[b]	EO[b]	FGE[b]	yield (%)	composition[c](mol%)			M_n[d] (×10^4)	M_w/M_n[d]	T_g[e] (ºC)	T_m[e] (ºC)
							ECH	EO	FGE				
1	0.35	0.26	32	8	0	100	80	20	0	11.4	1.64	-28	–
2	0.35	0.26	24	16	0	100	60	40	0	10.1	1.52	-36	–
3	0.35	0.26	16	24	0	100	40	60	0	8.7	1.54	-42	–
4	0.35	0.26	8	32	0	100	20	80	0	7.4	1.56	-46	47

[a] Reaction condition: *i*-Bu_3Al, 0.5 mmol; monomer concentration, 2 mol/L in toluene; reaction time, 0.5 h; 25 ºC. [b] Molar ratio of *i*-Bu_3Al. [c] Determined by ^{13}C-NMR. [d] Determined by GPC in 1,2,4 trichlorobenzene at 135 ºC against polystyrene standard. [e] Determined by DSC.

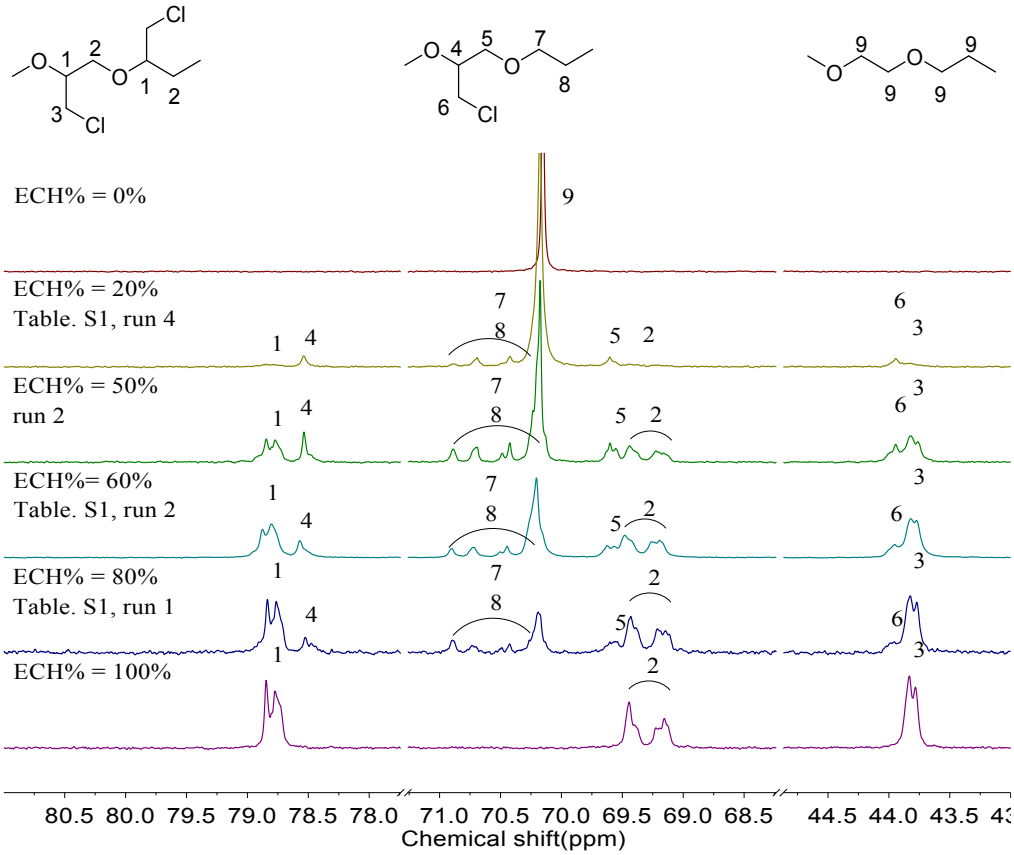

Fig. S1 ^{13}C-NMR spectra (100 MHz, $C_2D_2Cl_4$, r.t.) of a EO homopolymer, a ECH homopolymer and ECH/EO copolymers having different ECH contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, run 2, Table. S1, runs 1, 2, 4).

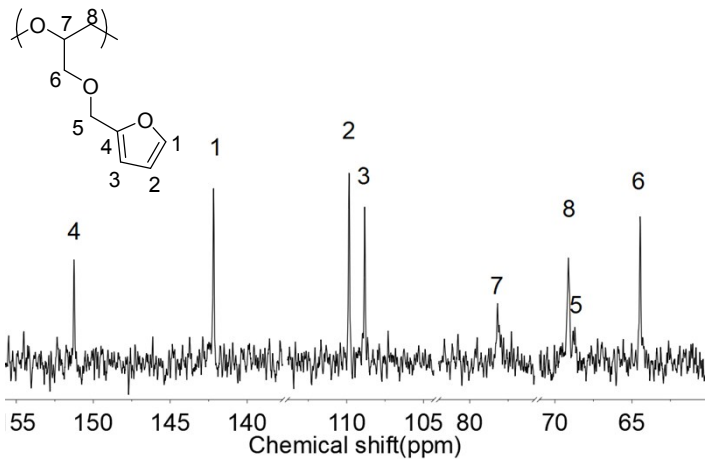

Fig. S2 ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$, r.t.) spectrum of homopoly(FGE) prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, run 9).

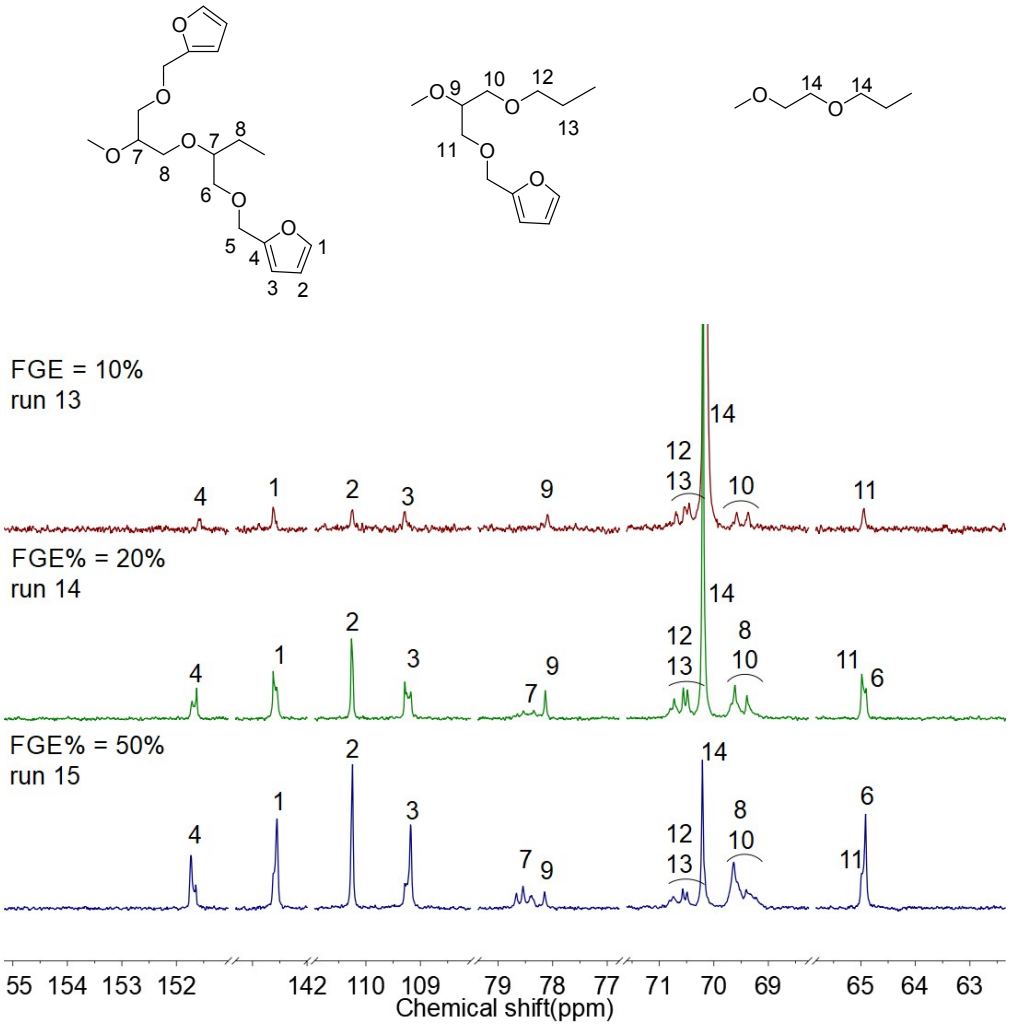

Fig. S3 ^{13}C-NMR spectra (100 MHz, $C_2D_2Cl_4$, r.t.) of FGE/EO copolymers with different FGE contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 13–15).

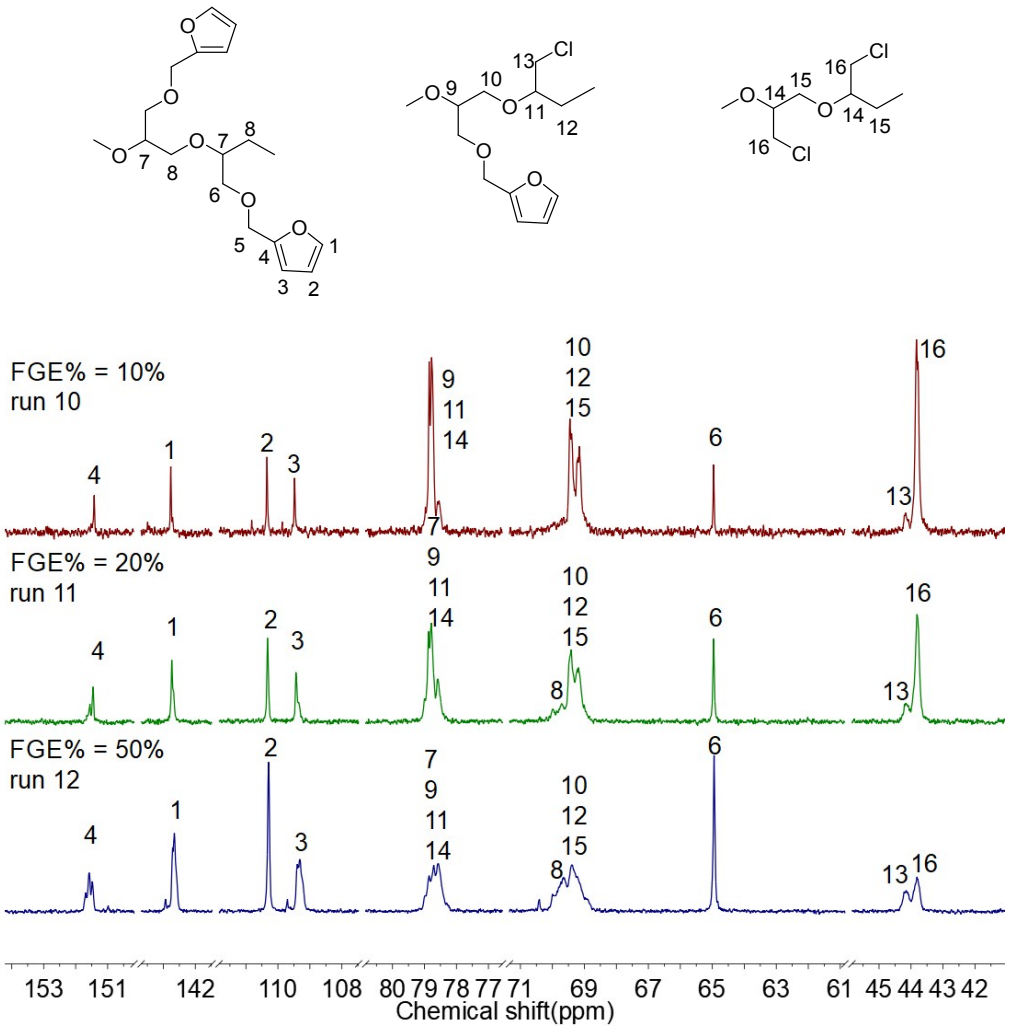

Fig. S4 ^{13}C-NMR spectra (100 MHz, $C_2D_2Cl_4$, r.t.) of FGE/ECH copolymers with different FGE contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 10–12).

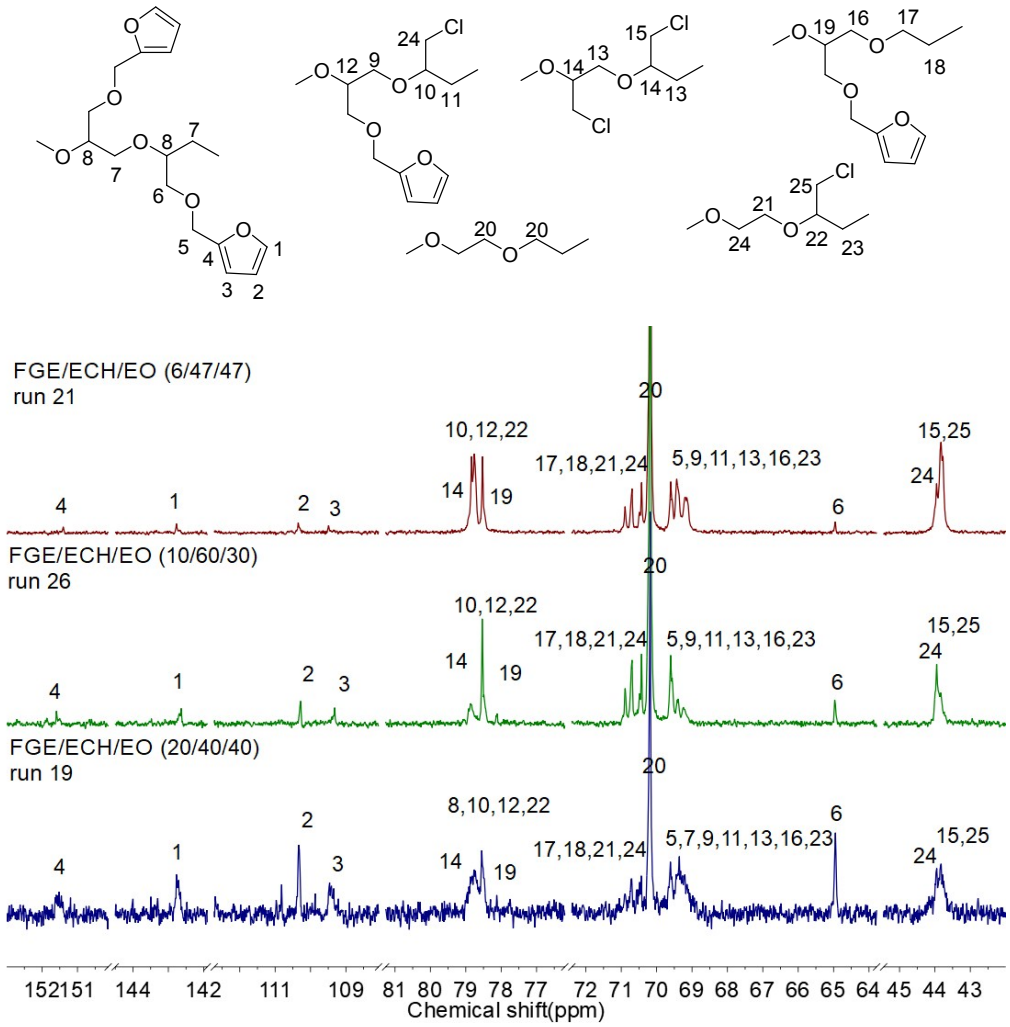

Fig. S5 ^{13}C-NMR spectra (100 MHz, $C_2D_2Cl_4$, r.t.) of FGE/ECH/EO terpolymers with different composites prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 19, 21, 26).

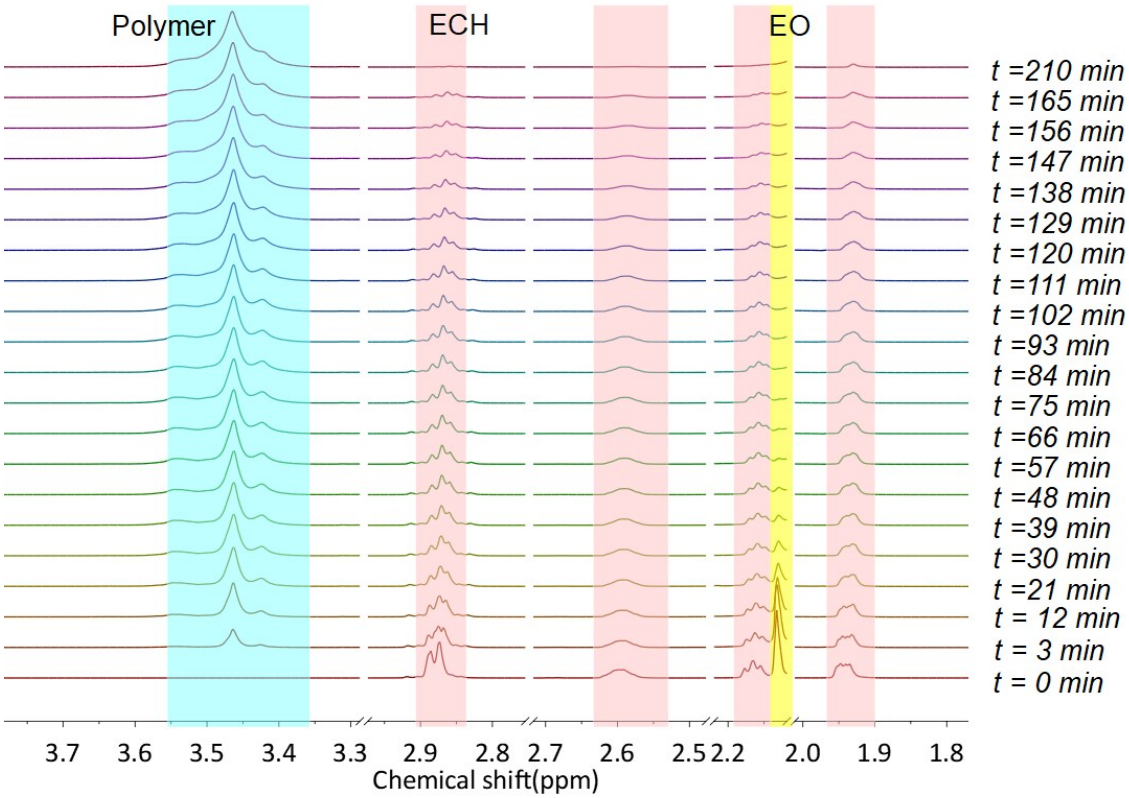

Fig. S6 ^{1}H-NMR spectra (500 MHz, toluene-d_8, 25°C) of the copolymerization ECH and EO. ECH resonances are shaded in pink, and EO resonances are shaded in yellow. Resonances associated with the copolymer are shaded in blue.

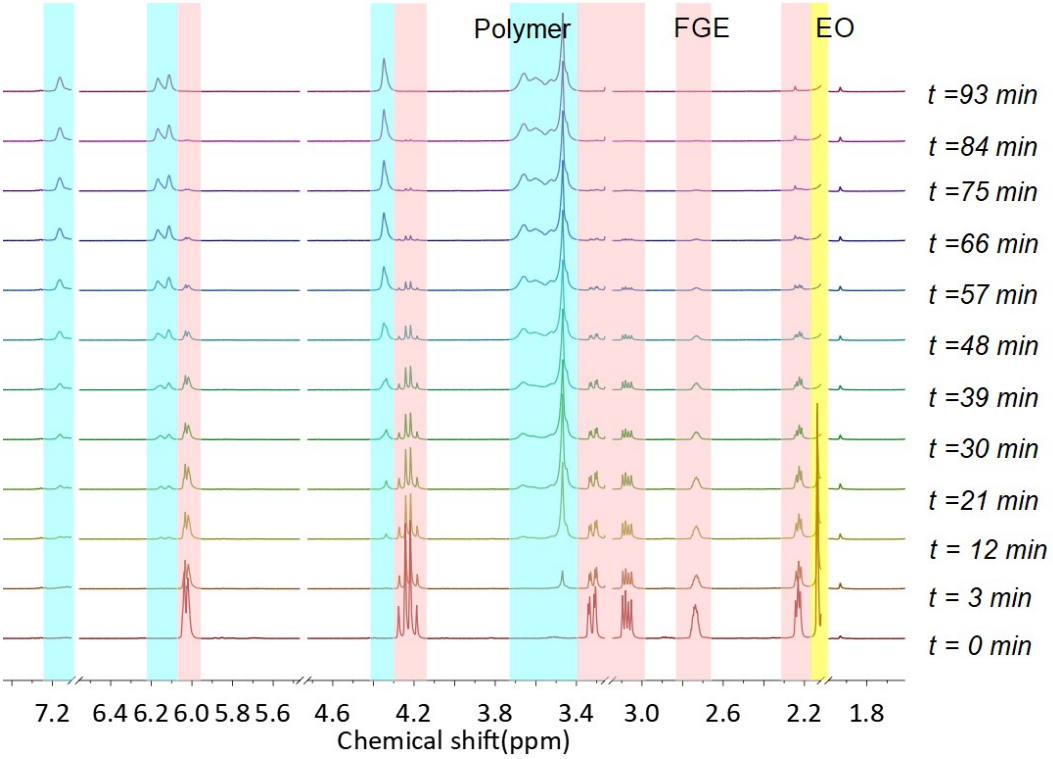

Fig. S7 ^{1}H-NMR spectra (500 MHz, toluene-d_8, 25°C) of the copolymerization EO and FGE. FGE resonances are shaded in pink, and EO resonances are shaded in yellow. Resonances associated with the copolymer are shaded in blue.

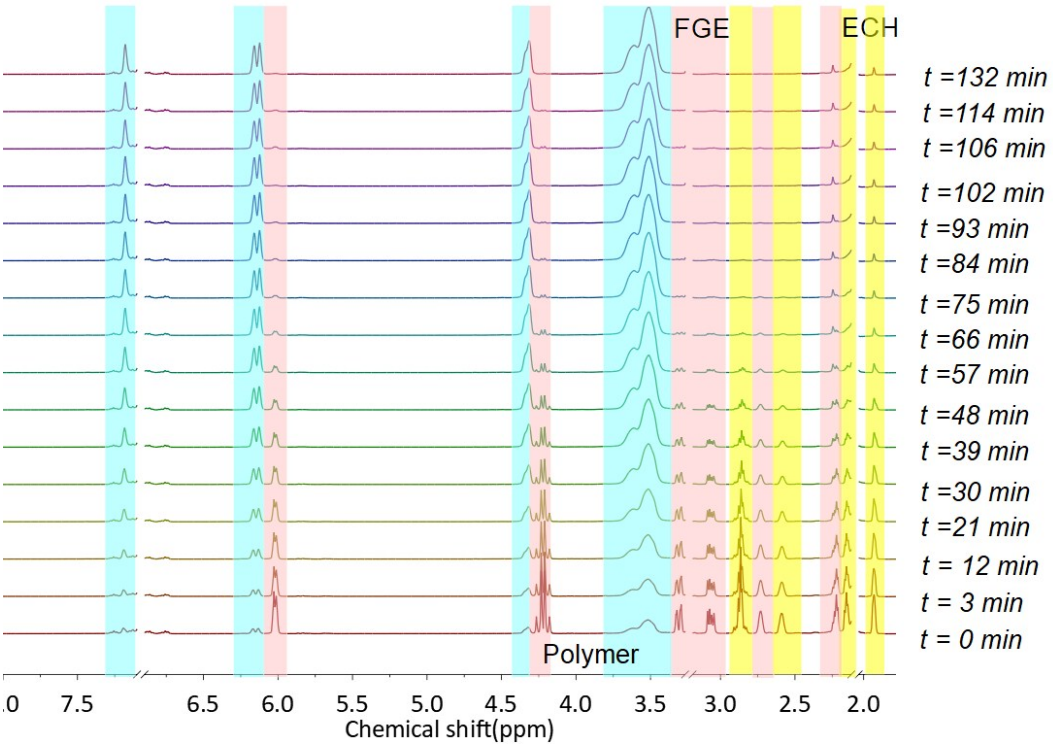

Fig. S8 ^{1}H-NMR spectra (500 MHz, toluene-d_8, 25°C) of the copolymerization ECH and FGE. FGE resonances are shaded in pink, and ECH resonances are shaded in yellow. Resonances associated with the copolymer are shaded in blue.

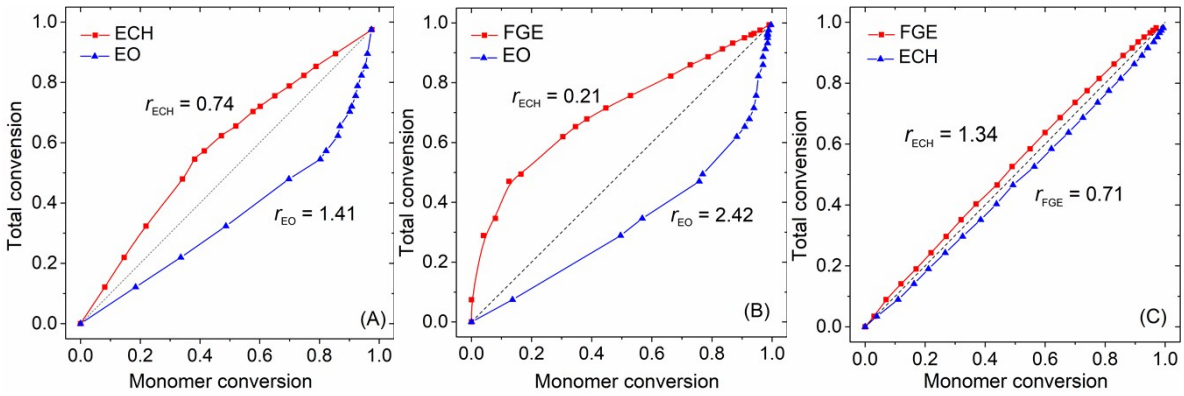

Fig. S9 Compositional drift data of (A) (■) ECH and (▲) E0; (B) (■) FGE and (▲) E0; (C) (■) ECH and (▲) FGE.

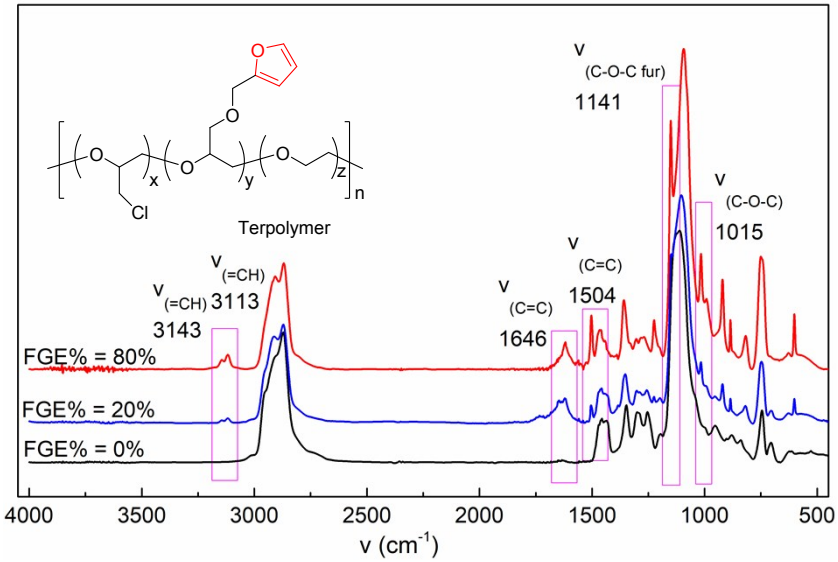

Fig. S10 FT-IR spectra of FGE/ECH/EO terpolymers with different FGE contents prepared by *i*-Bu_3Al/H_3PO_4/DBU.

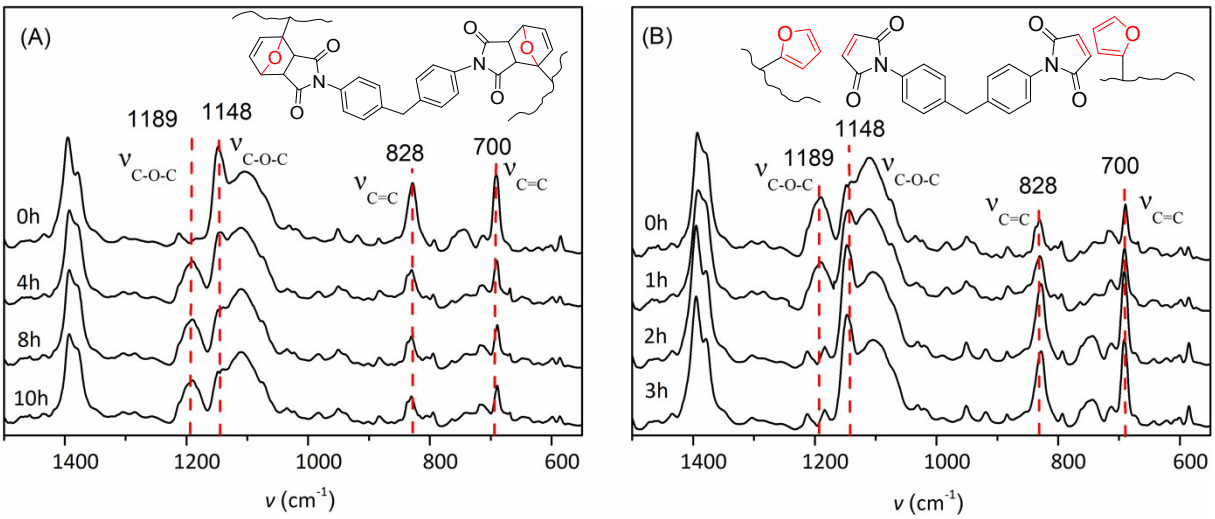

Fig. S11 FT-IR spectra of a ECO/FGE_{20}/BMI_{10} terpolymer in the procedure of DA cross-linking (A) at 70 °C and retrocross-linking (B) at 150 °C.

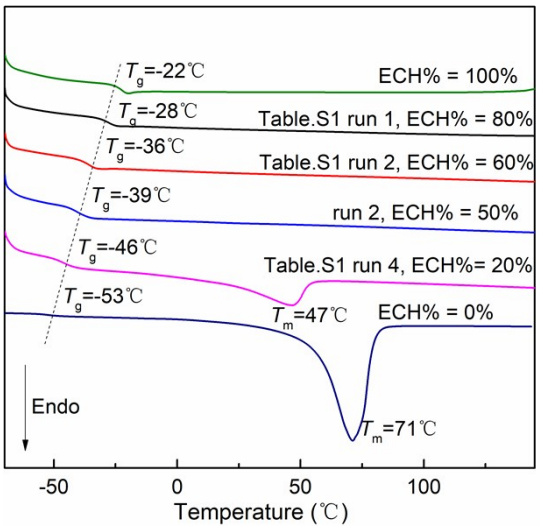

Fig. S12 DSC curves of ECH/EO copolymers with different ECH contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 2, Table.S1 run 1, 2, 4).

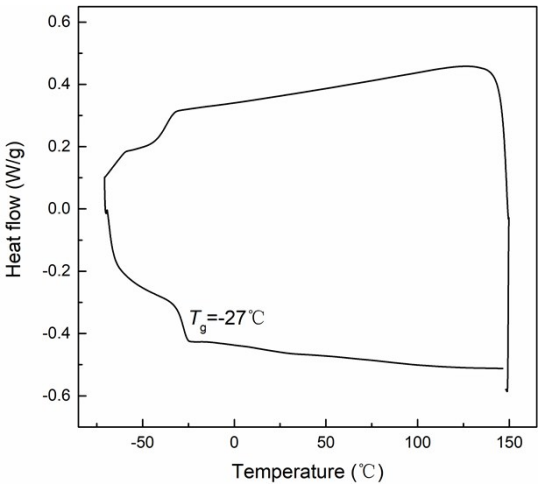

Fig. S13 DSC curve of a FGE homopolymer prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, run 9).

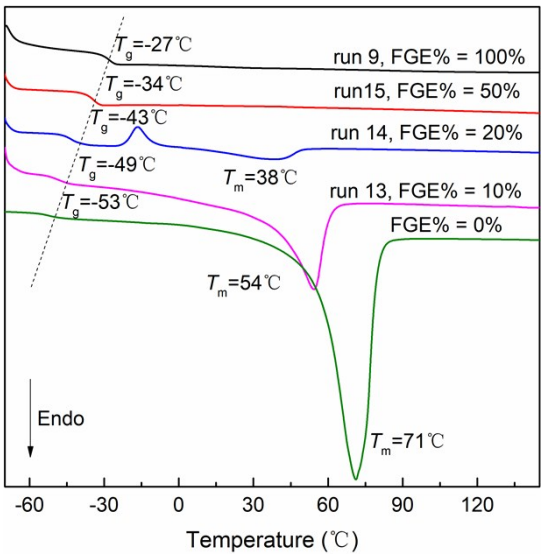

Fig. S14 DSC curves of FGE/EO copolymers with different FGE contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 9, 13–15).

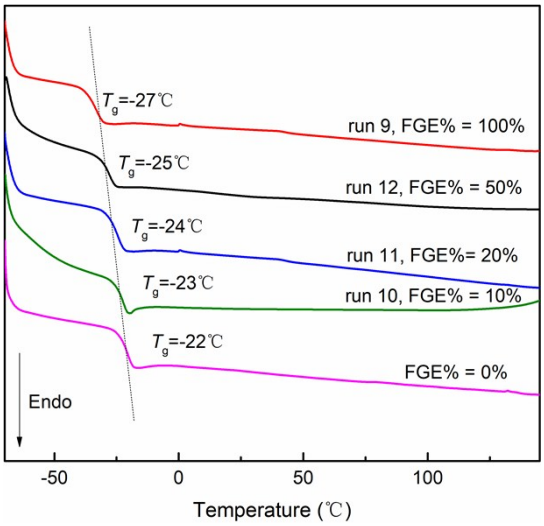

Fig. S15 DSC curves of FGE/ECH copolymers with different FGE contents prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 9–12).

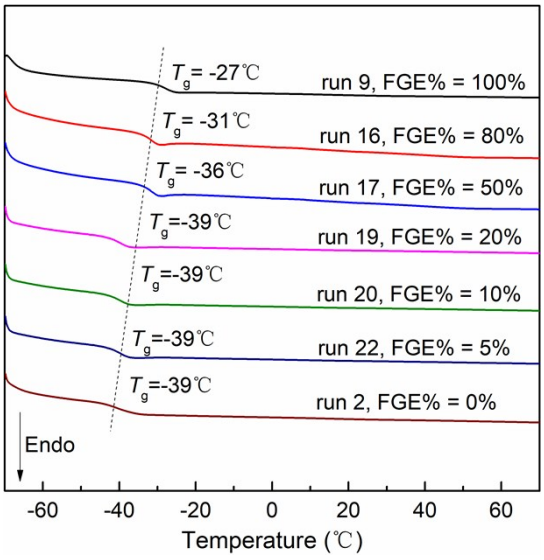

Fig. S16 DSC curves of FGE/ECH/EO terpolymers with different FGE contents (mole ratio of ECH/EO is 1/1) prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 2, 9, 16, 17, 19, 20, 22).

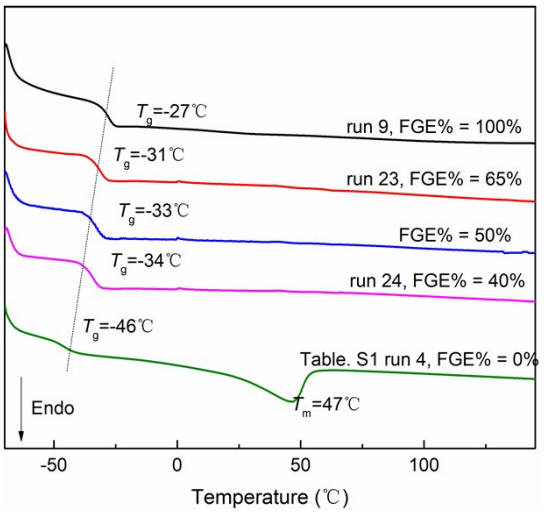

Fig. S17 DSC curves of FGE/ECH/EO terpolymers with different FGE contents (mole ratio of ECH/EO is 1/4) prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 9, 23, 24, Table. S1, run 4).

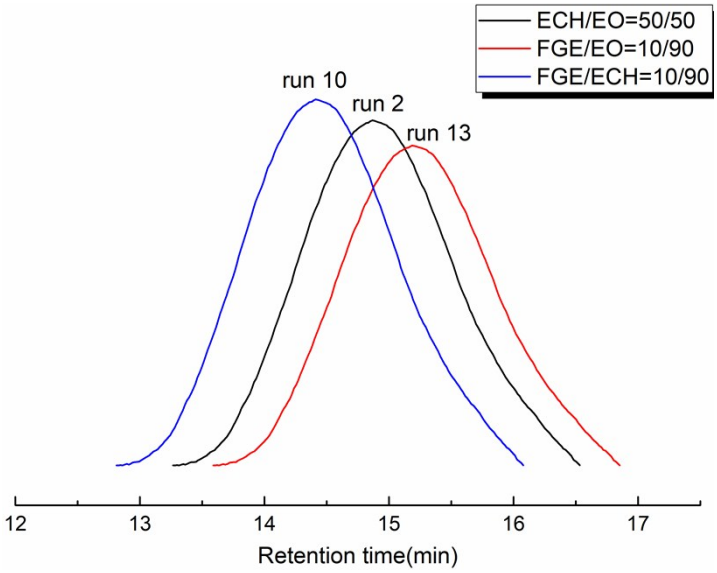

Fig. S18 GPC curves of a FGE/ECH copolymer, a FGE/EO copolymer and a ECH/EO copolymer prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 2, 10, 13).

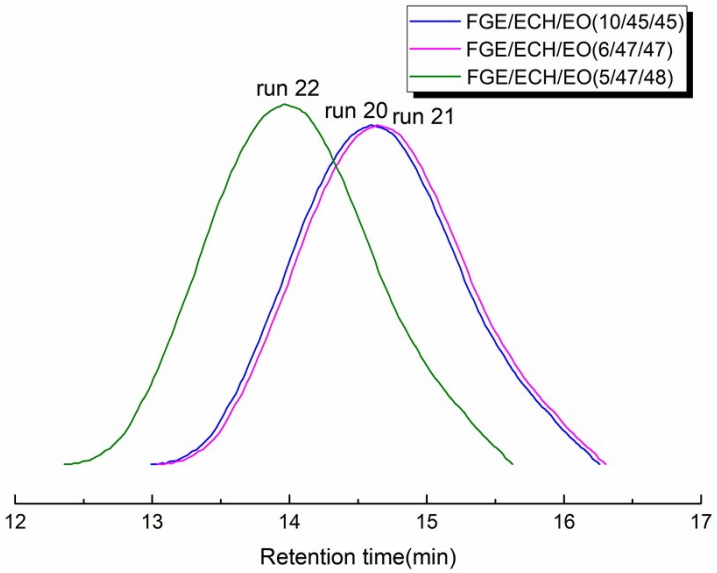

Fig. S19 GPC curves of FGE/ECH/EO terpolymers prepared by *i*-Bu_3Al/H_3PO_4/DBU (Table 1, runs 20–22).

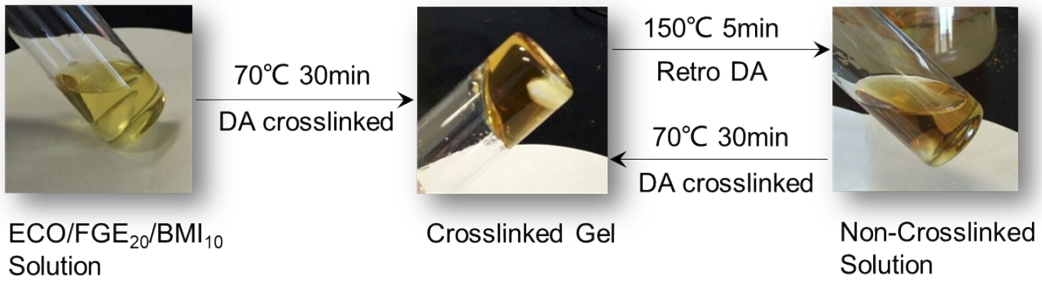

Fig. S20 Solubility evolution of ECO/FGE_{20} after DA and retro-DA process in $CHCl_2CHCl_2$ (20 mg polymer/mL).

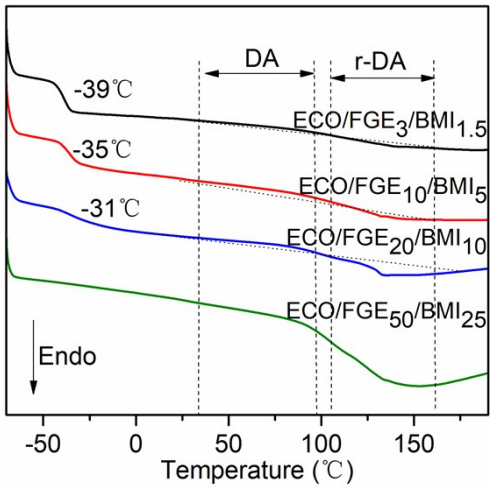

Fig. S21 Thermal changes of DA cross-linked polyepichlorohydrin elastomers in DA and retro-DA process.

Table. S2 Swelling Tests Data of DA Cross-Linked Polyepichlorohydrin Elastomers.

FGE content	Swelling ratio	Gel fraction	$[XLD]_S$ [a]	$[XLD]_S$ [b]
mol%	%	%	(10^{-4} mol /g)	(10^{-4} mol /g)
1	339.1	93.8	1.3	1.4
2	312.2	94.9	1.5	2.8
3	280.6	95.1	3.2	4.2
5	143.6	96.6	4.5	6.9
8	113.0	96.5	6.2	9.0
10	91.7	97.4	8.1	13.0
20	49.1	91.6	15.3	23.5
50	17.8	79.4	34.3	45.5

[a] Experimental value. [b] Theoretic value.

Table. S3 Thermal Properties of DA Cross-Linked Polyepichlorohydrin Elastomers.

Sample	$[XLD]_S$	T_g(°C)	$T_{d5\%}$	$T_{d10\%}$	T_{dmax}

	(10^{-4} mol /g)		(°C)	(°C)	(°C)
Raw material	0	-39	281	316	333
DA_ECO/FGE_5/$BMI_{2.5}$	4.5	-37	305	328	343
DA_ECO/FGE_{10}/BMI_5	8.1	-37	308	322	338
DA_ECO/FGE_{20}/BMI_{10}	15.3	15	308	317	338
DA_ECO/FGE_{50}/BMI_{25}	34.3	–	not determined	not determined	not determined
Vulcanized/Carbon[b]	3.7	-39	320	331	350

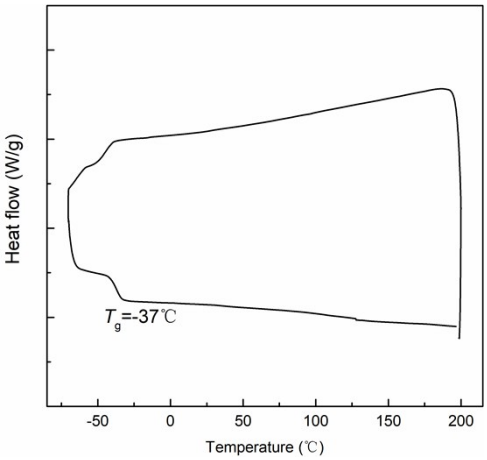

Fig. S22 DSC cruve of DA cross-linked polyepichlorohydrin elastomers (DA_ECO/FGE_5/$BMI_{2.5}$).

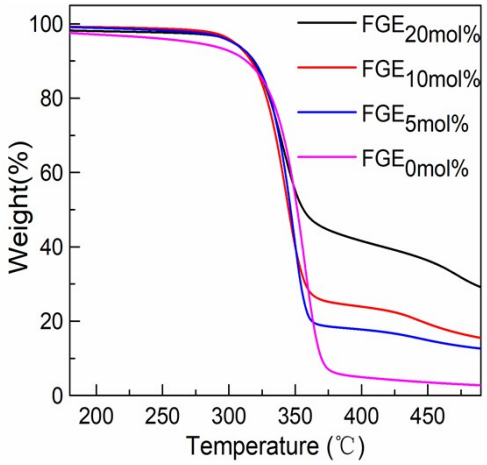

Fig. S23 TGA curves of DA cross-linked polyepichlorohydrin elastomers with different FGE contents.

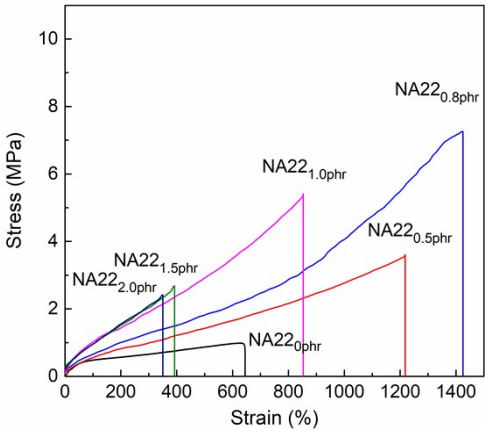

Fig. S24 Stress-strain curves of Vulcanized_ECO/NA22$_n$ materials verify different crosslinked agents NA22.

Table. S4 Mechanical Properties of DA Cross-Linked and Vulcanized Polyepichlorohydrin Elastomers.

Run	Sample	M_n (×10^{4}g/mol)	[XLD]$_s$ (×10^{-4}mol/g)	$\sigma^{[c]}$ (MPa)	$\varepsilon^{[d]}$ (%)	$E^{[e]}$ (MPa)	HS$^{[f]}$
1	ECO/NA22$_0$	9.3	0	1.0±0.3	644±80	0.1	35
2	ECO/FGE$_3$	10.6	0	1.1±0.3	620±75	0.1	36
3	DA_ECO/FGE$_1$/BMI$_{0.5}$	9.7	1.2	7.3±0.5	1221±86	0.7	44
4	DA_ECO/FGE$_2$/BMI$_1$	10.0	1.5	8.2±0.6	725±77	1.2	47
5	DA_ECO/FGE$_3$/BMI$_{1.5}$	10.6	3.2	15.0±0.5	504±73	2.1	70
6	DA_ECO/FGE$_4$/BMI$_2$	11.1	3.8	12.6±0.8	350±82	3.2	73
7	DA_ECO/FGE$_5$/BMI$_{2.5}$	10.5	4.5	11.5±1.2	244±56	3.7	74
8	DA_ECO/FGE$_8$/BMI$_4$	10.8	6.3	12.5±1.5	112±33	18.5	79
9	DA_ECO/FGE$_{10}$/BMI$_5$	12.5	8.1	11.1±1.5	58±20	25	83
10	DA_ECO/FGE$_{20}$/BMI$_{10}$[a]	12.7	15.3	–	–	–	95
11	Vulcanized_ECO/NA22$_{0.5}$	9.3	0.6	3.6±0.2	1220±82	0.4	40
12	Vulcanized_ECO/NA22$_{0.8}$	9.3	1.2	7.3±0.3	1423±86	0.6	46
13	Vulcanized_ECO/NA22$_{1.0}$	9.3	1.5	5.4±0.4	853±76	1.1	49
14	Vulcanized_ECO/NA22$_{1.5}$	9.3	2.6	2.7±0.4	390±69	1.3	52
15	Vulcanized_ECO/NA22$_{2.0}$	9.3	3.9	2.4±0.3	352±46	1.3	53
16	Vulcanized /Carbon[b]	9.3	3.7	12.9±0.5	621±53	2.0	74

[a] Samples were too brittle to give a measurable value. [b] Samples were vulcanized by 0.8 phr NA22 and reinforced by 40 phr carbon black. [c] σ represented ultimate stress. [d] ε represented elongations. [e] E represented Young's module. [f] HS represented Hardness (shore A).

Table. S5 Mechanical Properties of reprocessed DA Cross-Linked Polyepichlorohydrin Elastomers.

Run	Sample	$\sigma^{[c]}$ (MPa)	$\varepsilon^{[d]}$ (%)	$E^{[e]}$ (MPa)	HS$^{[f]}$
1	Original	15.0±0.5	504±73	2.1	70
2	1st Reprocessed	13.5±0.7	455.8±69	2.0	70
3	2nd Reprocessed	14.6±0.5	520.7±63	2.1	70
4	3rd Reprocessed	13.1±0.8	493.7±78	2.0	70