

Supplementary Information

Random copolymer of styrene and diene derivatives via anionic living polymerization followed by intramolecular Friedel-Crafts cyclization for high-performance thermoplastics

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Figure S1. Size-exclusion chromatograms of cyclized *r*-SIR obtained with CF₃SO₃H in cyclohexane for 1 h at 23 °C at various concentrations of *r*-SIR.

Scheme S1. Postulated reactions during cationic cyclization of styrene-diene copolymers.

Table S1. Copolymers (*r*-SIR) of styrene (St) and isoprene (Ip) prepared by anionic living polymerization^a

Code	<i>r</i> -SIR	F_{st} , mol% ^b	M_n^c	M_w/M_n^c	Microstructure in Ip, % ^b			T_g , °C ^d
					1,4	1,2	3,4	
1	<i>r</i> -SIR-1	48	119,400	1.03	68	1	31	16
2	<i>r</i> -SIR-2	48	112,400	1.04	67	1	32	20
3	<i>r</i> -SIR-3	37	119,200	1.10	77	1	22	-1
4	<i>r</i> -SIR-4	47	128,400	1.05	67	1	32	19

^aCopolymerization was initiated by adding solutions of premixed St/Ip mixture (St: 1.2 mol; Ip: 1.2 mol) at 3.3mL/min by syringe pump into a *sec*-butyl lithium solution containing cyclohexane (840 mL), tetrahydrofuran (6.0 mmol), and *sec*-butyl lithium (2.0 mmol) at 40 °C.

^bDetermined by ¹H NMR. ^cThe number-average molecular weight (M_n) and distribution (M_w/M_n) were determined by size-exclusion chromatography against PSt standards. ^dThe glass transition temperature (T_g) was determined by differential scanning calorimetry.

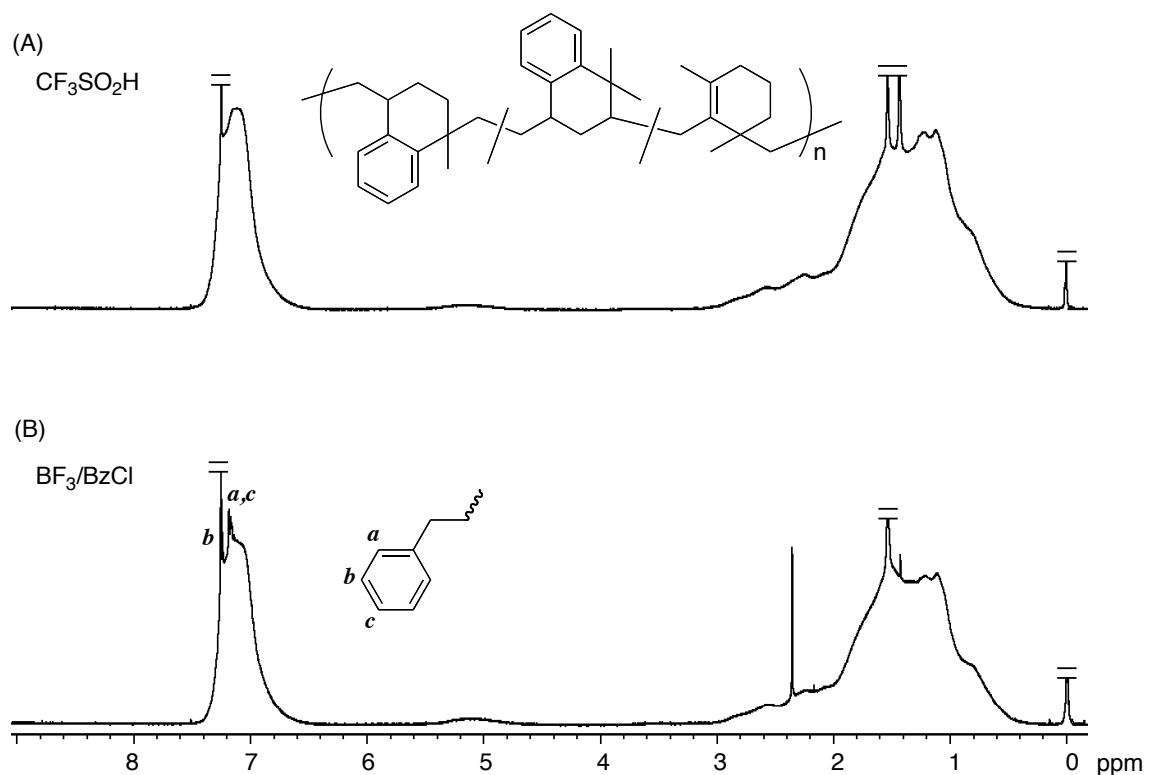
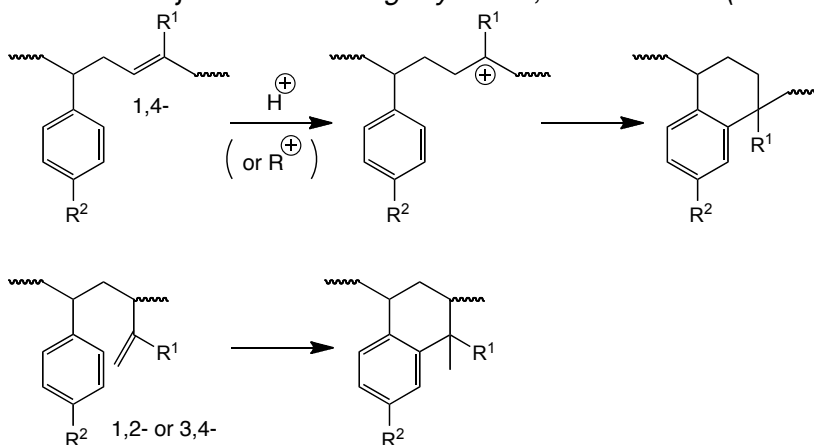


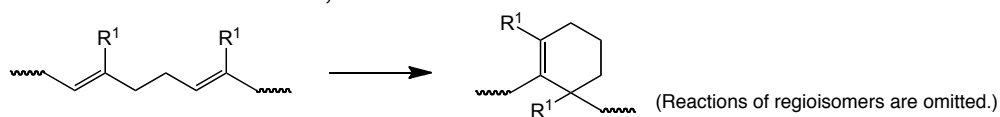
Figure S1. ^1H NMR spectra for the cyclization of *r*-SIR ($F_{\text{st}} = 48\%$, $M_n = 128,400$, $M_w/M_n = 1.05$) with (A) $\text{CF}_3\text{SO}_3\text{H}$ ($M_n = 76,500$, $M_w/M_n = 1.55$; see also Table 3 entry 1 in the manuscript) and (B) $\text{BF}_3 \cdot 2\text{AcOH}/\text{BzCl}$ ($M_n = 86,900$, $M_w/M_n = 1.14$; see also Table 2 entry 13 in the manuscript).

1. Intramolecular Cyclization Reactions

1-1. Between Adjacent Alternating Styrene-1,3-Diene Units (Friedel-Crafts Cyclization)

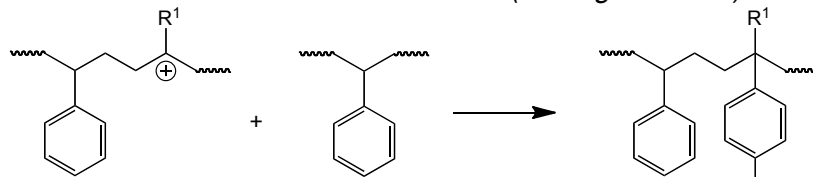


1-2. Between Consecutive 1,3-Diene Units

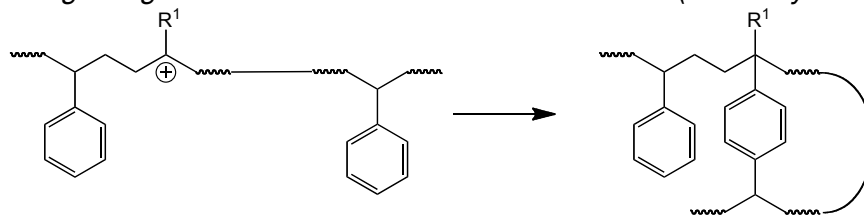


2. Side Reactions

2-1. Intermolecular Friedel-Crafts Reaction (Linking Reaction)



2-2. Long-Range Intramolecular Friedel-Crafts Reaction (Macro-cyclization)



2-3. Main Chain Scission (β -Cleavage)

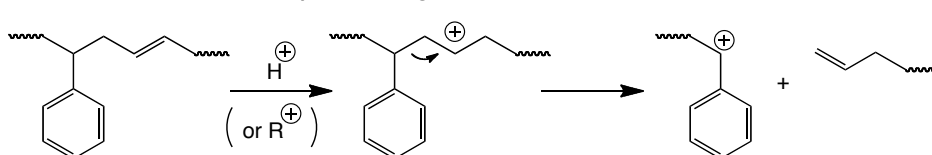


Figure S2. Postulated reactions during cationic cyclization of styrene-diene copolymers.