

Supporting Information

RAFT Polymerization of Vinyl Sulfonate Esters for Controlled Synthesis of Poly(lithium vinyl sulfonate) and Sulfonated Block Copolymers

Hideharu Mori^{†}, Eisuke Kudo[†], Yousuke Saito[†], Atsuhiko Onuma,[‡] and Makoto
Morishima[‡]*

[†]Department of Polymer Science and Engineering, Graduate School of Science and
Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan

[‡]Hitachi Research Laboratory, Hitachi, Ltd, 7-1-1, Omika, Hitachi, 319-1292, Japan

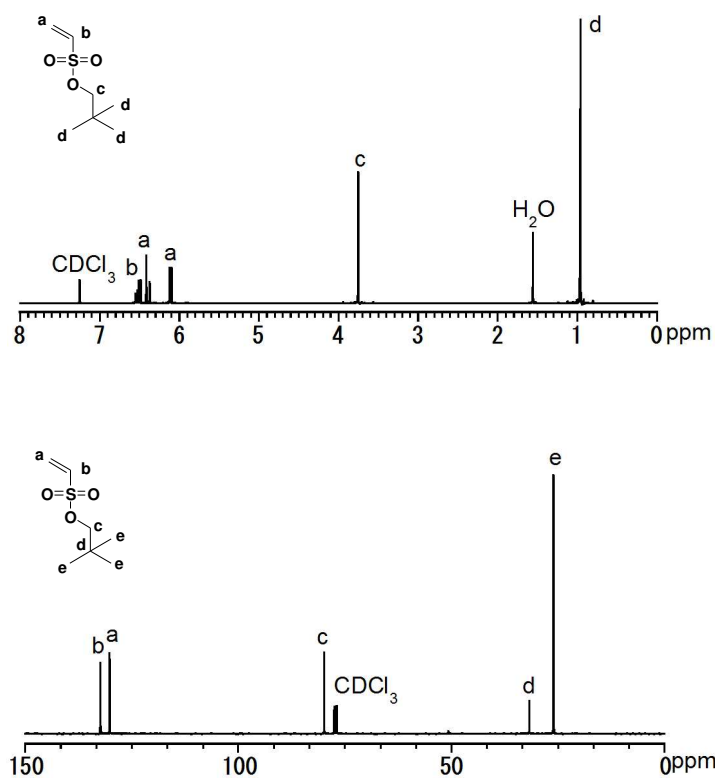


Figure S1. ¹H and ¹³C NMR spectra (CDCl₃) of neopentyl ethenesulfonate (NES).

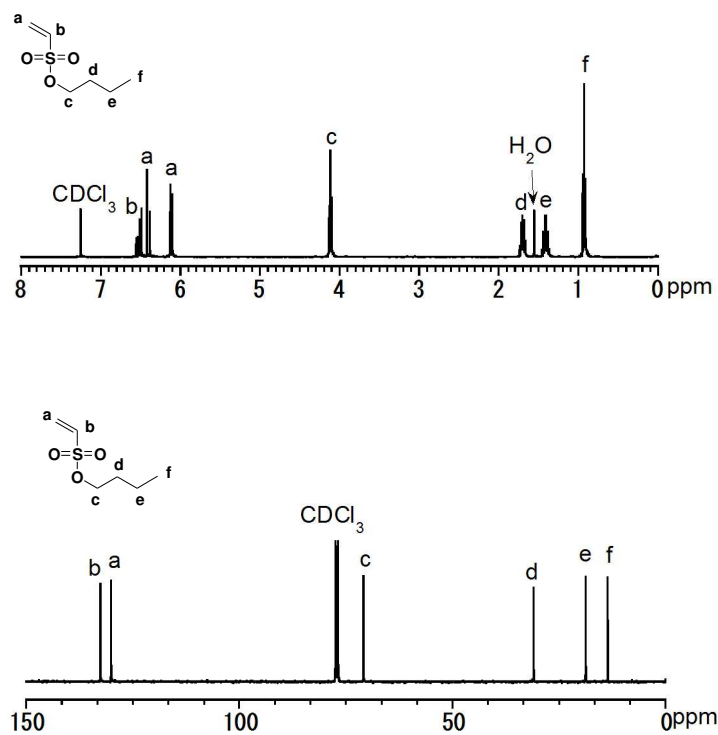


Figure S2. ¹H and ¹³C NMR spectra (CDCl₃) of 1-butyl ethenesulfonate (BES).

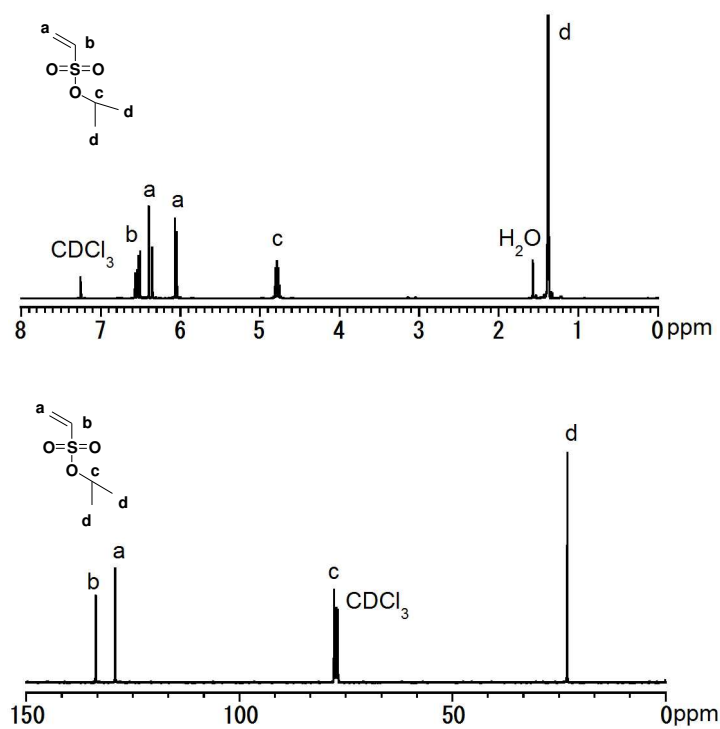


Figure S3. ^1H and ^{13}C NMR spectra (CDCl_3) of isopropyl ethenesulfonate (IPES).

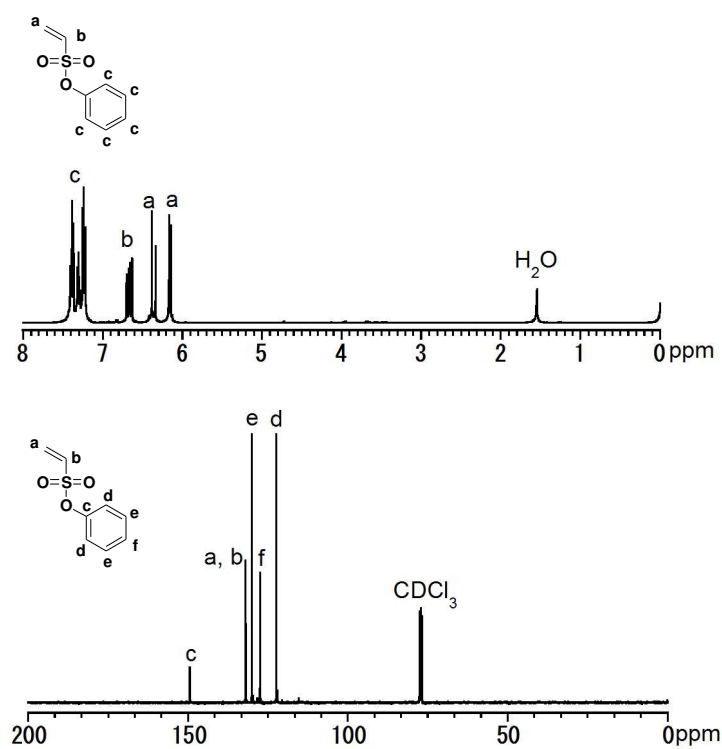


Figure S4. ^1H and ^{13}C NMR spectra (CDCl_3) of phenyl ethenesulfonate (PES)

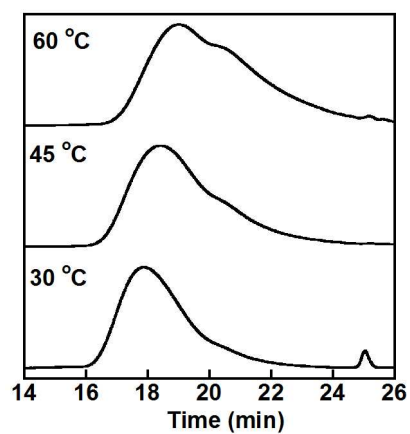


Figure S5. SEC traces (THF) of poly(NES)s obtained by free radical polymerization. See Table 1 for detailed polymerization conditions.

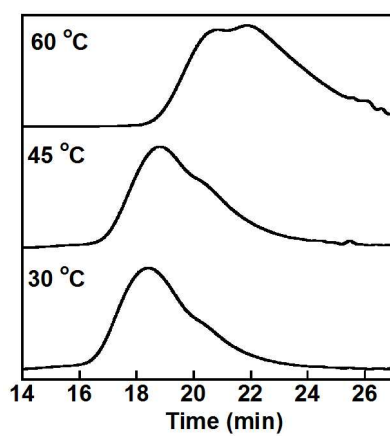


Figure S6. SEC traces (THF) of poly(BES)s obtained by free radical polymerization. See Table 1 for detailed polymerization conditions.

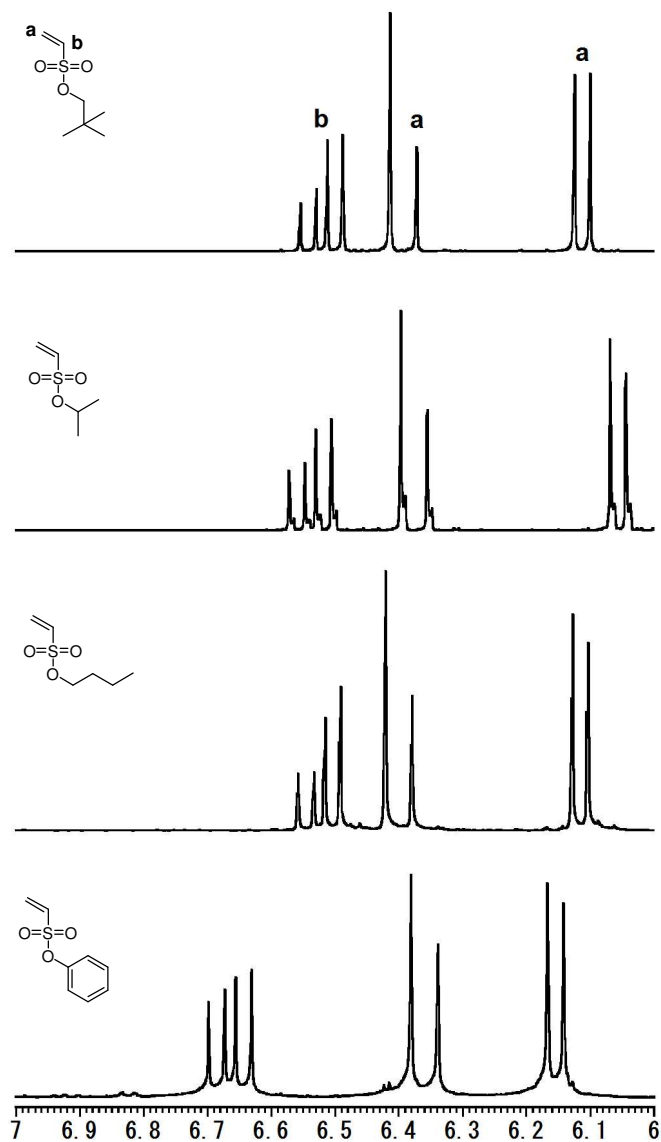


Figure S7 ^1H NMR spectra (CDCl_3) of vinyl sulfonate esters.

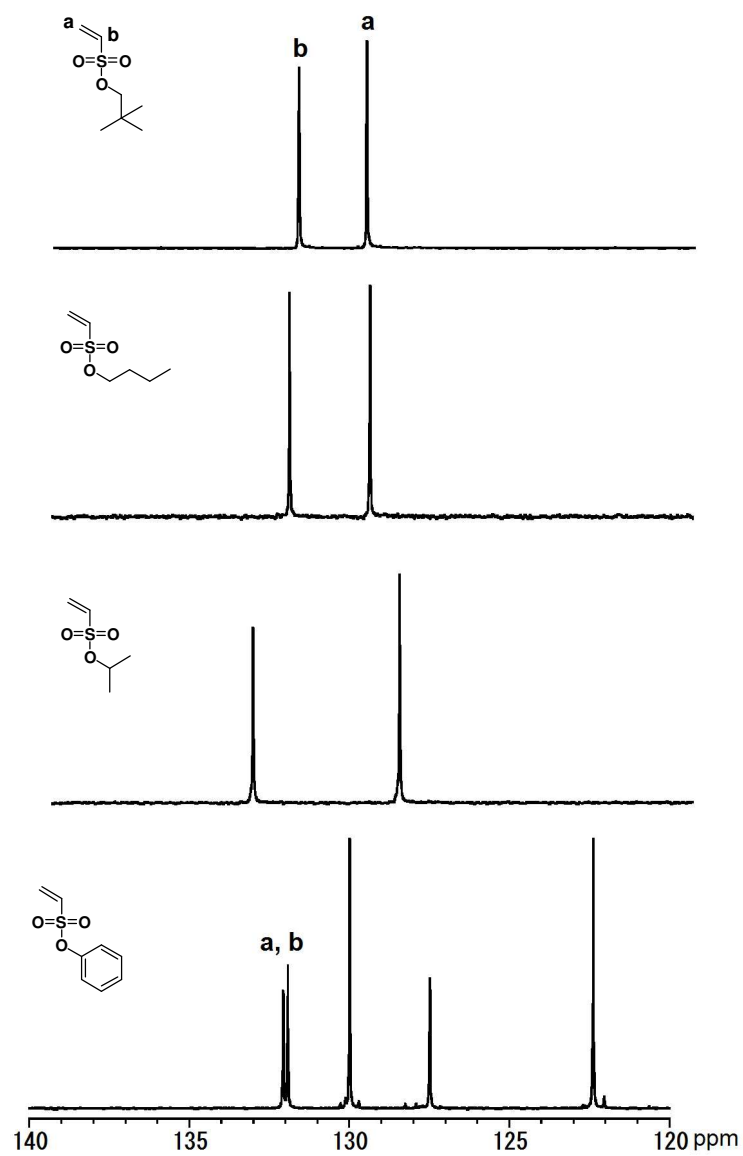


Figure S8. ^{13}C NMR spectra (CDCl_3) of vinyl sulfonate esters.

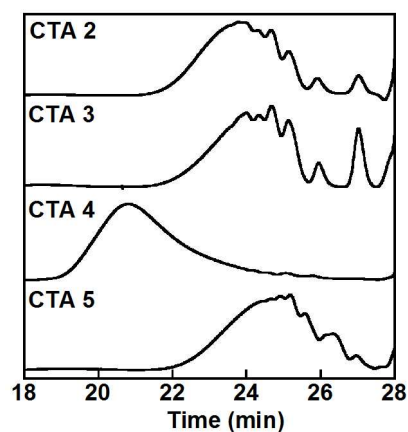


Figure S9. SEC traces (THF) of poly(NES)s obtained by RAFT polymerization of NES using different CTAs. See Table 2 for detailed polymerization conditions.

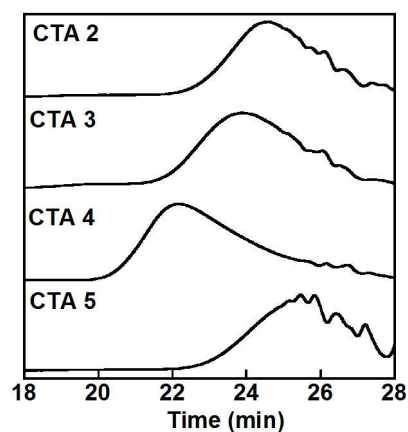


Figure S10. SEC traces (THF) of poly(BES)s obtained by RAFT polymerization of BES using different CTAs. See Table 2 for detailed polymerization conditions.

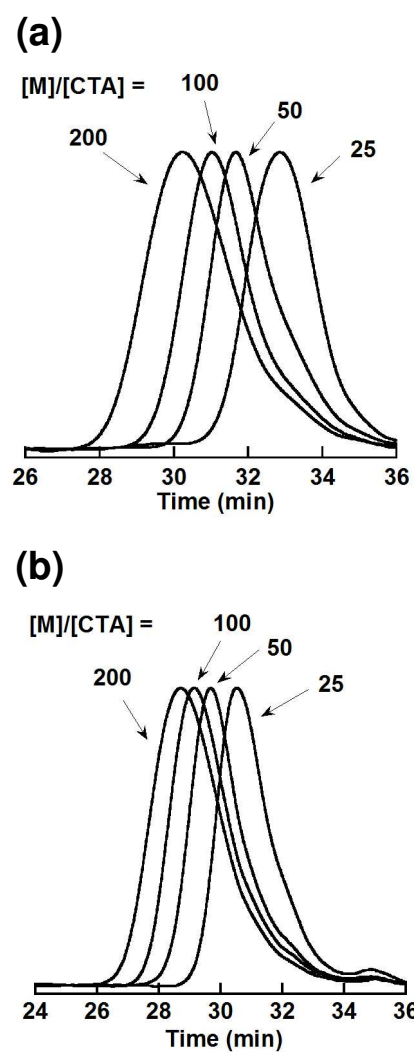
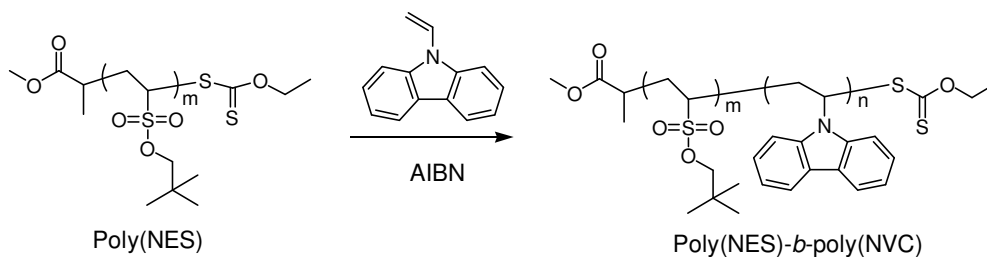


Figure S11. SEC traces (DMF) of (a) poly(NES)s and (b) poly(BES)s obtained at different $[M]_0:[CTA]_0$ ratios. See Table 4 for detailed polymerization conditions.



Scheme S1. Synthesis of block copolymer by polymerization of NVC using poly(NES) as macro-CTA.

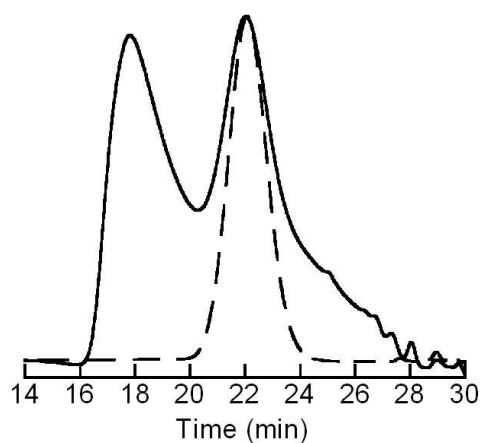
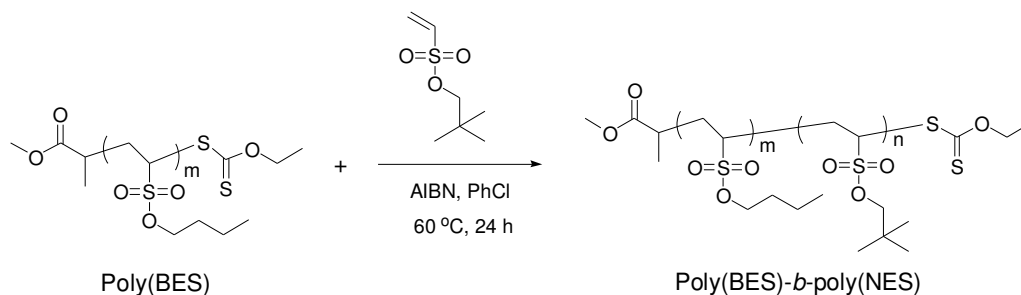


Figure S12. SEC traces (THF) of poly(NES) macro-CTA (dotted line, $M_n = 5700$, $M_w/M_n = 1.09$) obtained after dialysis, and the product (solid line, $M_n = 5500$, $M_w/M_n = 6.75$) obtained by the polymerization of NVC with the macro-CTA.



Scheme S2. Synthesis of block copolymer by polymerization of NES using poly(BES) as macro-CTA.

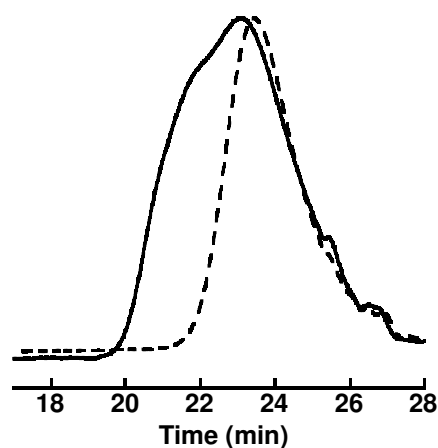


Figure S13. SEC traces (THF) of poly(BES) macro-CTA (dotted line, $M_n = 2400$, $M_w/M_n = 1.21$) obtained after decantation, and the product (solid line, $M_n = 3900$, $M_w/M_n = 1.46$) obtained by the polymerization of NES with the macro-CTA.

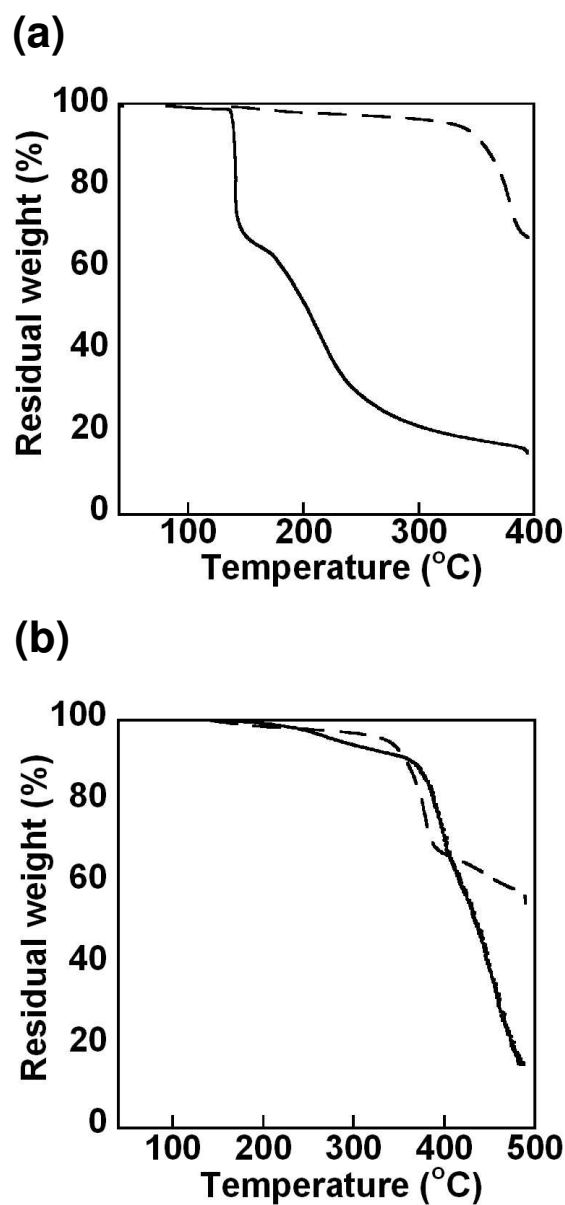


Figure S14. TGA thermograms of (a) poly(NES) (solid line) and poly(lithium vinyl sulfonate) (dotted line) obtained by RAFT polymerization, followed by the deprotection, and (b) poly(NVC)-*b*-poly(lithium vinyl sulfonate) (solid line) and poly(lithium vinyl sulfonate) (dotted line).

Table S1. Solubility of products ^{a)}

product	H ₂ O	MeOH	DMF	chloroform	acetone	diethyl ether	THF	hexane
NES	-	+	+	+	+	+	+	+
Poly(NES)	-	+	+	+	+	+	+	+
BES	-	+	+	+	+	+	+	-
Poly(BES)	-	+	+	+	+	+	+	-
IPES	-	+	+	+	+	+	+	-
Poly(IPES)	-	+	+	+	+	+	+	-
PES	-	+	+	+	+	+	+	-
Poly(PES)	-	-	+	+	+	-	+	-

+ = soluble at r.t., - = insoluble at r.t..

Table S2. Effects of temperature and initiator on polymerization of neopentyl ethenesulfonate (NES) and 1-butyl ethenesulfonate (BES) with CTA 4 at $[M]_0/[CTA\ 4]_0/[I]_0 = 250/5/1$

entry	M	initiator	temp °C	time h	conv. ^{b)} %	$M_n^{c)}$ (theory)	$M_n^{d)}$ (SEC)	$M_w/M_n^{d)}$ (SEC)
1		AIBN	60	48	86	7900	3400	1.36
2	NES	AIBN	45	48	16	1600	1500	1.14
3		V-70	30	48	53	4900	3700	1.18
5		AIBN	45	48	54	4600	3500	1.23
6	BES	V-70	30	48	44	3800	2500	1.23

^{a)} $[AIBN]_0/[CTA\ 4]_0/[M]_0 = 1/5/250$, AIBN = 2,2'-azobis(isobutyronitrile), V-70 = 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate. ^{b)} Calculated by ¹H NMR in CDCl₃. ^{c)} The theoretical molecular weight ($M_{n,theory}$) = (MW of M) \times $[M]_0/[CTA\ 4]_0 \times$ conv. + (MW of CTA 4). ^{d)} Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF.

Table S3. RAFT Polymerization of Neopentyl Ethenesulfonate (NES) with 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) and CTA 4 at different [M]/[CTA] ratios in bulk at 30 °C for 72 h ^{a)}

entry	[M] ₀ /[CTA 4] ₀	conv. ^{b)} (%)	M_n ^{c)} (theory)	M_n ^{d)} (SEC)	M_w/M_n ^{d)} (SEC)
1	25	48	2300	1900	1.15
2	50	66	5900	4000	1.19
3	100	70	12300	6700	1.30
4	200	70	23100	8900	1.41

^{a)} [CTA 4]₀/[AIBN]₀ = 2, CTA 4 = *O*-ethyl-*S*-(1-methoxycarbonyl) ethyldithiocarbonate. ^{b)} Calculated by ¹H NMR in CDCl₃. ^{c)} The theoretical molecular weight ($M_{n, \text{theory}}$) = (MW of M) × [M]₀/[CTA]₀ × conv. + (MW of CTA). ^{d)} Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF.