Supporting Information

RAFT Polymerization of *S*-Vinyl Sulfide Derivatives and Synthesis of Block Copolymers Having Two Distinct Optoelectronic Functionalities

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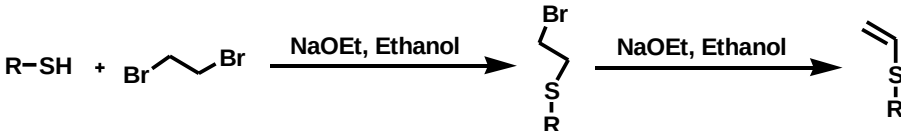


Scheme S1. Synthesis of *S*-vinyl sulfide derivatives.

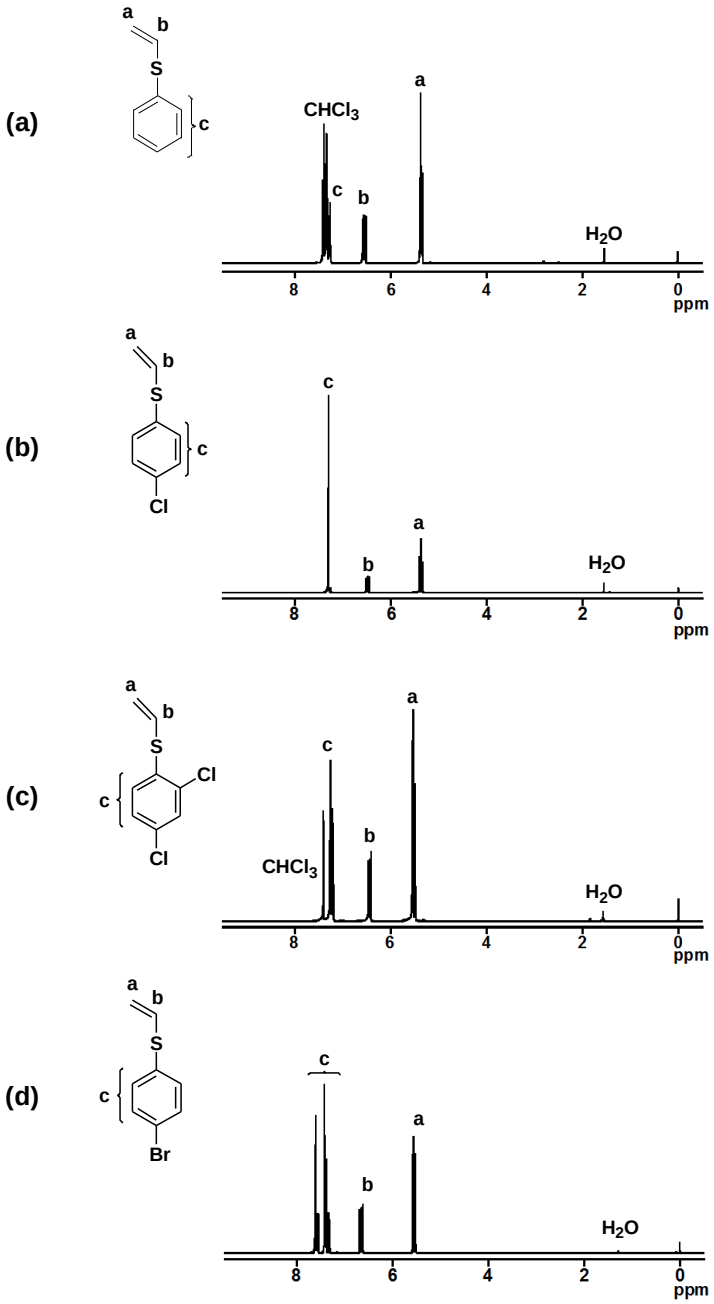


Figure S1. ^{1}H NMR spectra ($CDCl_3$) of *S*-vinyl sulfide derivatives, (a) PVS, (b) CPVS, (c) DCPVS, and (d) BPVS.

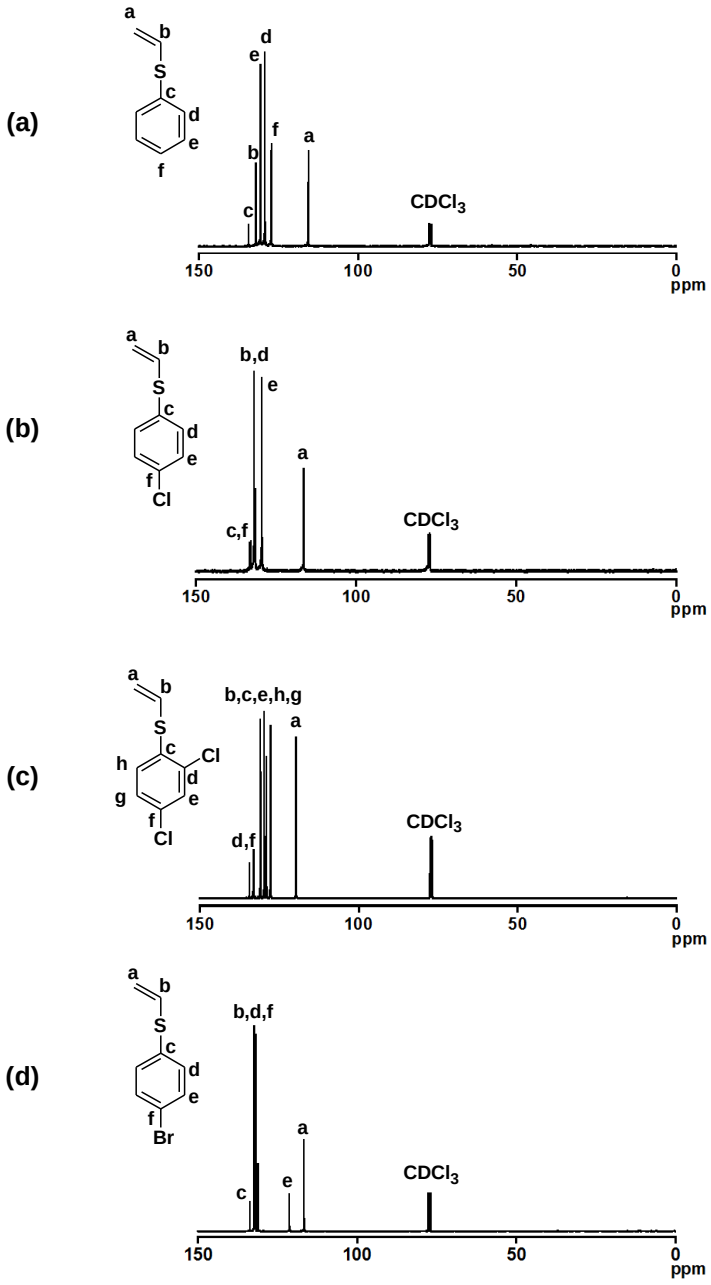


Figure S2. ^{13}C NMR spectra ($CDCl_3$) of *S*-vinyl sulfide derivatives, (a) PVS, (b) CPVS, (c) DCPVS, and (d) BPVS.

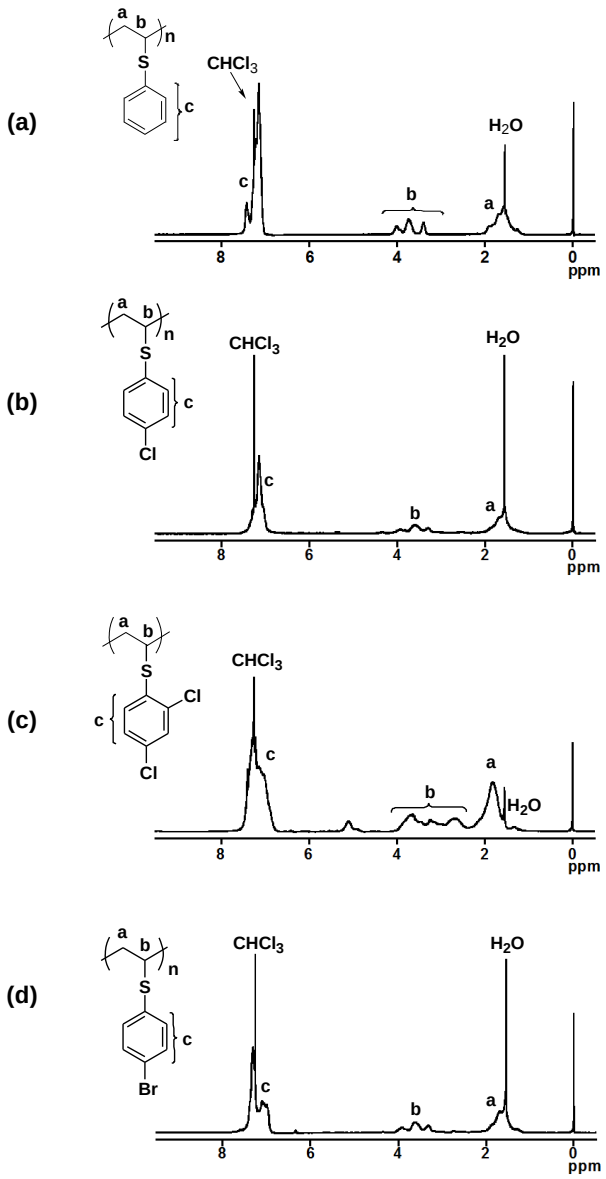


Figure S3. ^{1}H NMR spectra ($CDCl_3$) of poly(*S*-vinyl sulfide) derivatives, (a) poly(PVS), (b) poly(CPVS), (c) poly(DCPVS), and (d) poly(BPVS).

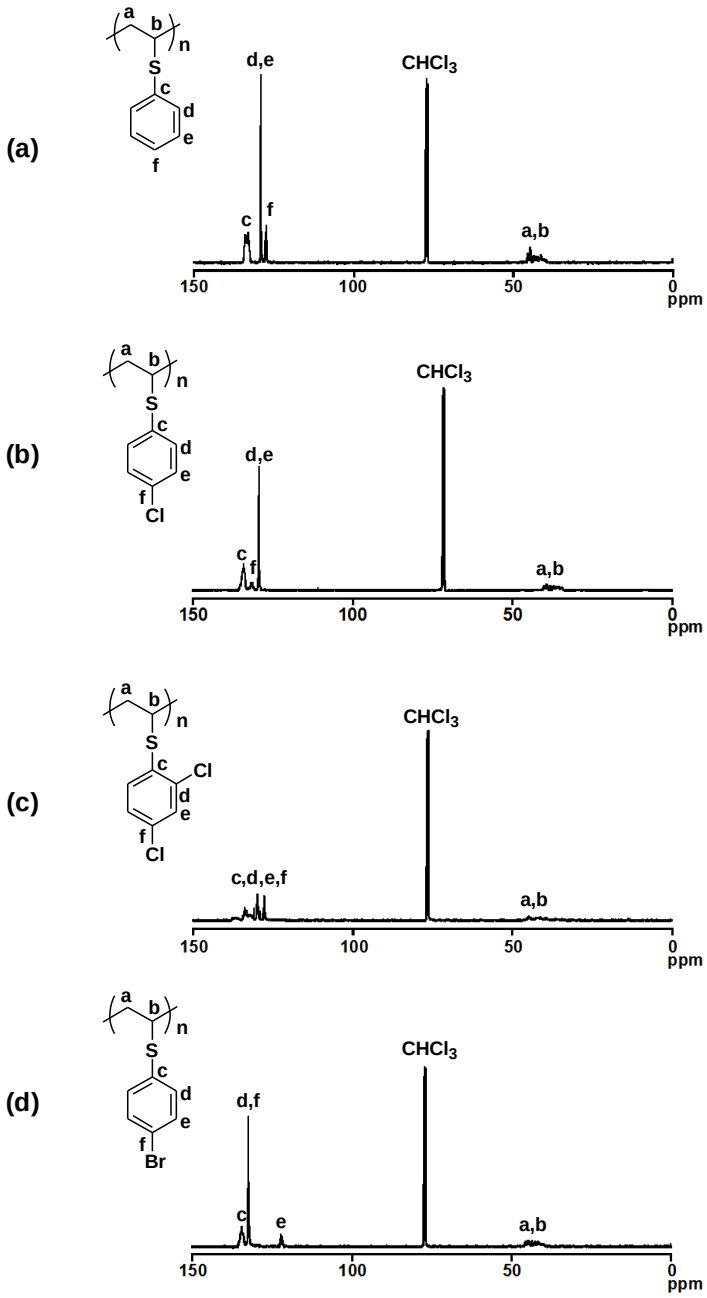


Figure S4. ^{13}C NMR spectra ($CDCl_3$) of poly(*S*-vinyl sulfide) derivatives, (a) poly(PVS), (b) poly(CPVS), (c) poly(DCPVS), and (d) poly(BPVS).

Table S1. Solubility of *S*-vinyl sulfide derivatives and resulting polymers [a)]

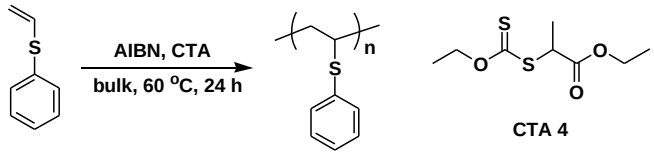
Solvent	PVS	PPVS	CPVS	PCPVS	DCPVS	PDCPVS	BPVS	PBPVS
Hexane	＋－	－	＋	－	＋	－	＋	－
Toluene	＋	＋	＋	＋	＋	＋	＋	＋
Diethyl ether	＋－	＋－	＋	＋－	＋	＋－	＋	＋－
Chloroform	＋	＋	＋	＋	＋	＋	＋	＋
Dichloromethane	＋	＋	＋	＋	＋	＋	＋	＋
Acetone	＋	＋	＋	＋	＋	＋－	＋	－
THF	＋	＋	＋	＋	＋	＋	＋	＋
AcOEt	＋	＋	＋	＋	＋	＋	＋	＋
MeOH	＋	－	＋	－	＋	－	＋	－
EtOH	＋	－	＋	－	＋	－	＋	－
2-Propanol	＋	－	＋	－	＋	－	＋	－
1,4-Dioxane	＋	＋	＋	＋	＋	＋	＋	＋
DMSO	＋	＋	＋	＋	＋	＋	＋	＋
DMF	＋	＋	＋	＋	＋	＋	＋	＋
H_2O	－	－	－	－	－	－	－	－

[a)] ＋: Soluble at room temperature, －: Insoluble at room temperature, ＋－: Partial soluble.

Table S2. Solubility of resulting polymers obtained by postmodifications [a)]

Solvent	Poly(BPVS-An)	Poly(BPVS-Flu)	Poly(BPVS-DPA)	Poly(BPVS-PTZ)
Hexane	−	−	−	−
Diethyl ether	−	−	−	−
Chloroform	+	+	+	+
Acetone	−	−	−	−
THF	+	+	+	+
AcOEt	−	−	−	−
MeOH	−	−	−	−
DMF	+	+	+	−
H_2O	−	−	−	−

[a)] +: Soluble at room temperature, −: Insoluble at room temperature, +−: Partial soluble.



Scheme S2. RAFT polymerization of PVS with CTA 4.

Table S3. Effect of $[CTA\ 4]_0/[AIBN]_0$ molar ratio on RAFT polymerization of PVS in bulk at 60 °C for 24 h [a)]

Entry	$[CTA\ 4]_0/[AIBN]_0$	Conv. [b)] (%)	Yield [c)] (%)	M_n [d)] (theory)	M_n [b)] (^{1}H NMR)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)
1	2	71	64	9,900	10,400	4,900	1.44
2	3	67	63	9,400	9,700	5,000	1.51
3	5	52	45	7,300	8,900	4,300	1.58
4	10	40	37	5,800	7,100	3,700	1.63

[a)] $[PVS]_0/[CTA]_0$ = 100. [b)] Calculated by ^{1}H NMR in $CDCl_3$. [c)] Methanol-insoluble part. [d)] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of PVS) × $[PVS]_0/[CTA]_0$ × conv. + (MW of CTA). [e)] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr).

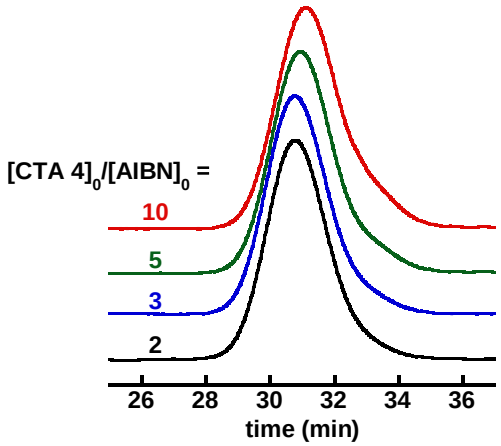


Figure S5. SEC traces of poly(PVS)s prepared at different [M]/[CTA 4] molar ratios.

Table S4. Effect of $[M]_0/[CTA\ 4]_0$ molar ratio on RAFT polymerization of PVS in bulk at 60 °C for 24

Entry	$[PVS]_0/[CTA\ 4]_0$ [a]	Conv. [b] (%)	Yield [c] (%)	M_n [d] (theory)	M_n [b] (^{1}H NMR)	M_n [e] (SEC)	M_w/M_n [e] (SEC)
1	100	71	64	9,900	10,400	4,900	1.44
2	200	54	50	15,200	15,300	6,800	1.65
3	400	43	34	23,700	25,900	5,500	1.76
4	600	37	33	30,800	40,000	7,500	2.05

[a] $[CTA\ 4]_0/[AIBN]_0 = 2$. [b] Calculated by ^{1}H NMR in $CDCl_3$. [c] Methanol-insoluble part. [d] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of PVS) × $[PVS]_0/[CTA]_0$ × conv. + (MW of CTA). [e] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr).

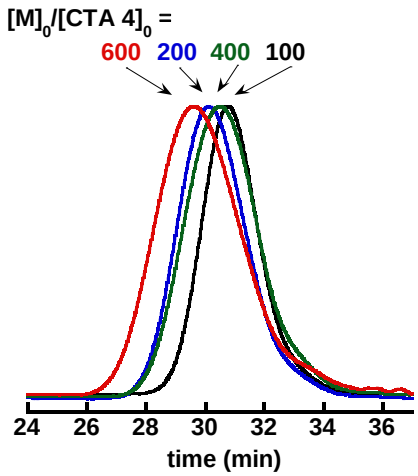
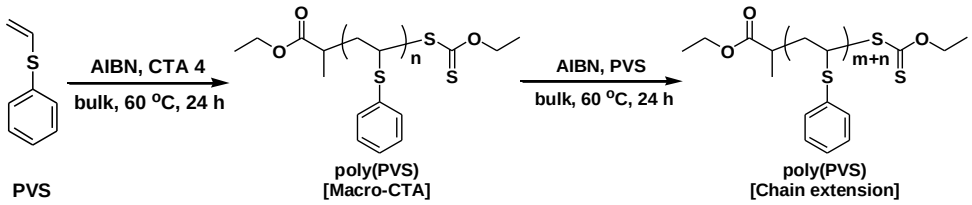


Figure S6. SEC traces of poly(PVS)s prepared at different $[CTA\ 4]_0/[AIBN]_0$ molar ratios.



Scheme S3. Post polymerization of PVS from the xanthate-terminated poly(PVS).

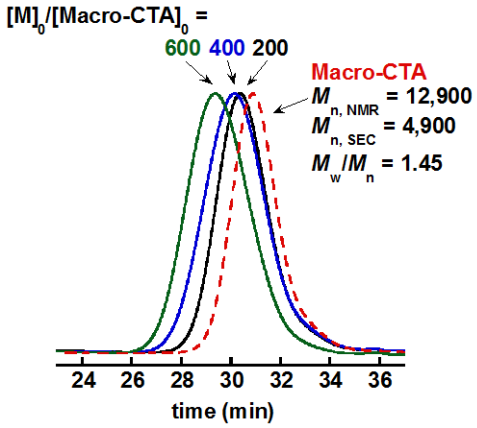


Figure S7. SEC traces of chain extended poly(PVS)s obtained by RAFT polymerization of PVS using the xanthate-terminated poly(PVS) prepared with CTA 4.

Table S5. Post Polymerization of PVS at 60 °C for 24 h in bulk [a].

Entry	$[M]_0$ /$[Macro\text{-}CTA]_0$ [a]	Yield [b] (%)	M_n [c] (theory)	M_n [d] (^{1}H NMR)	M_n [e] (SEC)	M_w/M_n [e] (SEC)
1	200	51	26,800	27,400	6,100	1.56
2	400	43	36,300	36,600	6,900	1.74
3	600	29	36,600	45,600	10,600	1.63

[a] $[Macro\text{-}CTA]_0/[AIBN]_0 = 2$, Macro-CTA = poly(PVS) : $M_{n,\,NMR} = 12900$, $M_{n,\,SEC} = 4900$, $M_W/M_n = 1.45$. [b] Methanol-insoluble part. [c] The theoretical molecular weight ($M_{n,\,theory}$) = (MW of PVS) × $[PVS]_0/[CTA]_0$ × yield + (MW of Macro-CTA). [d] Calculated by ^{1}H-NMR in $CDCl_3$. [e] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr).

Scheme S4. Synthesis of block copolymers, poly(PVS-*b*-NVC)s, by RAFT polymerization of PVS using poly(NVC) macro-CTAs.

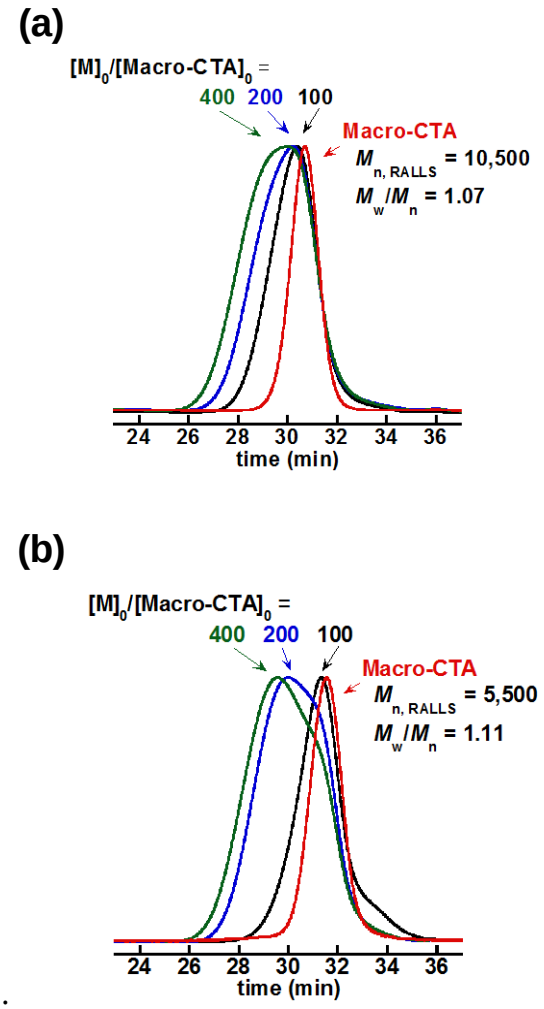


Figure S8. SEC traces of poly(NVC-*b*-PVS)s and poly(NVC) macro-CTAs.

Table S6. Synthesis of poly(NVC-*b*-PVS) by RAFT polymerization of PVS using poly(NVC) macro-CTA in bulk at 60 °C for 24 h[a)]

Entry	$[M]_0$/ $[\text{Macro-CTA}]_0$	Yield [b)] (%)	M_n [c)] (Theory)	M_n [d)] (EA)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)	Composition [d)] PVS : NVC
1	100 [f)]	69	19,900	18,600	10,200	1.34	48 : 52
2	200 [f)]	65	28,200	27,200	12,240	1.43	31 : 69
3	400 [f)]	51	38,300	36,400	13,900	1.54	22 : 78
4	100 [g)]	58	13,400	12,200	4,900	1.51	64 : 36
5	200 [g)]	55	20,500	21,100	9,500	1.61	80 : 20
6	400 [g)]	33	23,500	30,700	10,800	1.72	87 : 13

[a)] $[\text{Macro-CTA}]_0/[\text{AIBN}]_0 = 2$. [b)] Methanol-insoluble part. [c)] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of Monomer) × $[\text{Monomer}]_0/[\text{Macro-CTA}]_0$ × yield + (MW of Macro-CTA). [d)] Calculated by elemental analysis. [e)] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). [f)] Macro-CTA = poly(NVC) : $M_{n,\ RALLS}$ = 10,500, M_w/M_n = 1.07. [g)] Macro-CTA = poly(NVC) : $M_{n,\ RALLS}$ = 5,500, M_w/M_n = 1.11.

Table S7. Synthesis of poly(NVC-*b*-BPVS) by RAFT polymerization of BPVS using poly(NVC) macro-CTA in bulk at 60 °C for 24 h [a)]

Entry	$[M]_0$/ $[Macro\text{-}CTA]_0$	Yield [b)] (%)	M_n [c)] (Theory)	M_n [d)] (EA)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)	Composition [d)] BPVS : NVC
1	100	57	18,900	17,800	5,400	1.66	40 : 60

[a)] $[Macro\text{-}CTA]_0/[AIBN]_0$ = 2, Macro-CTA = poly(NVC) : $M_{n,\,RALLS}$ = 6,600, $M_{n,\,SEC}$ = 3,000, M_w/M_n = 1.30. [b)] Hexane-insoluble part. [c)] The theoretical molecular weight ($M_{n,\,theory}$) = (MW of Monomer) × $[Monomer]_0/[Macro\text{-}CTA]_0$ × yield + (MW of Macro-CTA). [d)] Calculated by elemental analysis. [e)] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr).

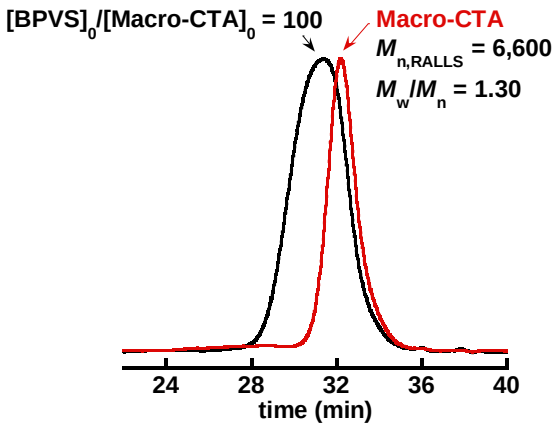
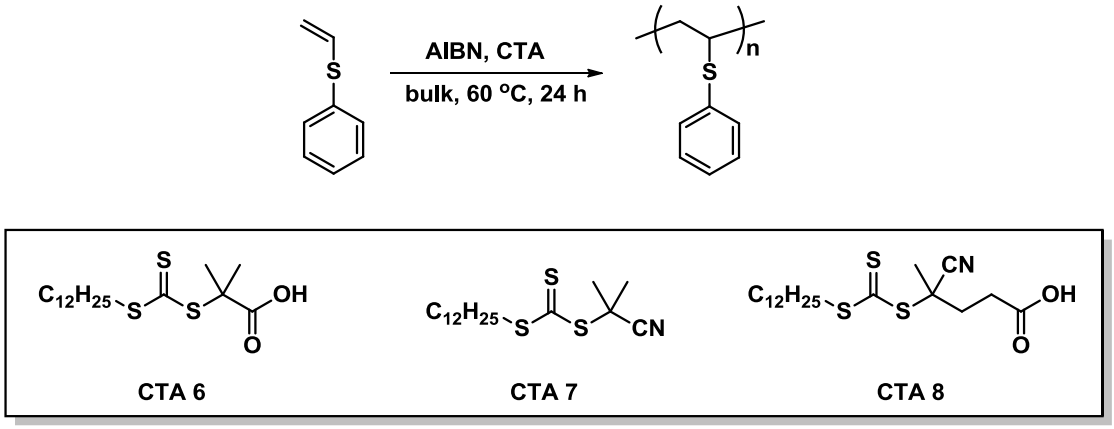


Figure S9. SEC traces of poly(NVC-*b*-BPVS) and poly(NVC) macro-CTA.



Scheme S5. RAFT polymerization of PVS using different trithiocarbonate-type CTAs.

Table S8. RAFT polymerization of PVS using different CTAs in bulk at 60 °C for 24 h [a)]

Entry	CTA	Conv. [b)] (%)	Yield [c)] (%)	M_n [d)] (theory)	M_n [b)] (^{1}H NMR)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)
1	CTA 6	92	73	12,900	16,500	4,600	1.38
2	CTA 7	73	63	10,300	14,700	4,200	1.33
3	CTA 8	53	45	7,600	8,000	2,600	1.42

[a)] $[PVS]_0/[CTA]_0/[AIBN]_0$ = 200/2/1. [b)] Calculated by ^{1}H NMR in $CDCl_3$. [c)] Methanol-insoluble part. [d)] The theoretical molecular weight ($M_{n,\ theory}$) = (MW of PVS) × $[PVS]_0/[CTA]_0$ × yield + (MW of CTA). [e)] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr).

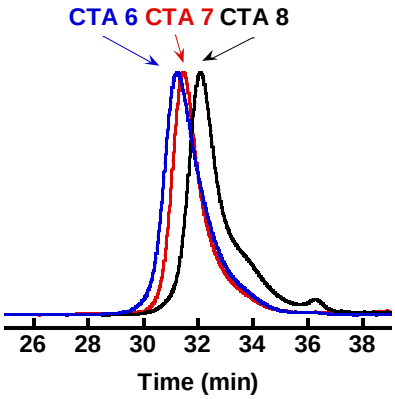


Figure S10. SEC traces of poly(PVS)s.

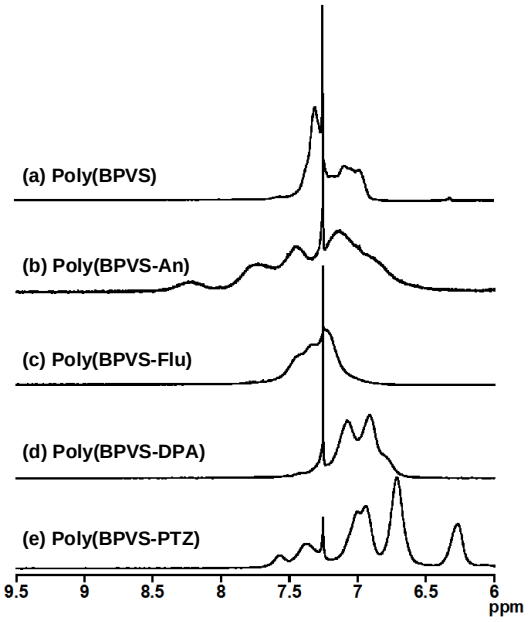


Figure S11. ^{1}H NMR spectra of resulting polymers obtained after the postmodifications. Magnification in the range of 6.0-9.5 ppm