Supplementary Information

Terpenoid-derived conjugated dienes with *exo*-methylene and a 6-membered ring: high cationic reactivity, regioselective living cationic polymerization, and random and block copolymerization with vinyl ethers

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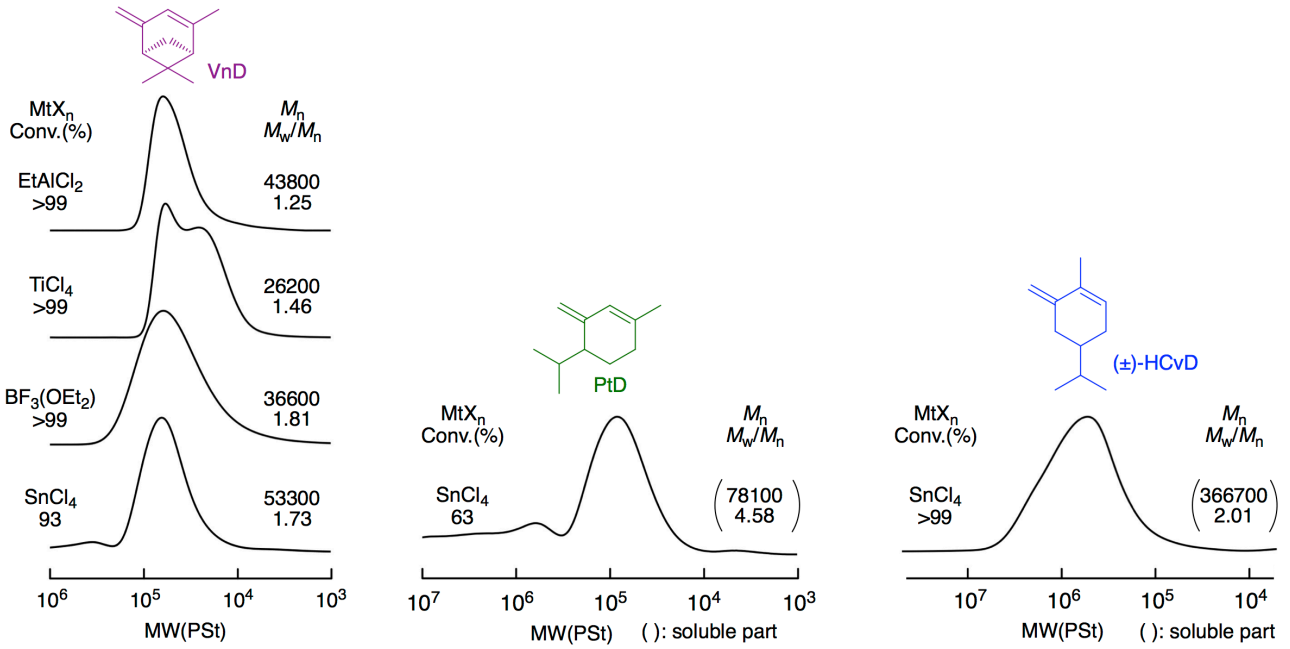

Fig. S1. SEC curves of the polymers obtained in conventional cationic polymerization of (–)-VnD, PtD, and (±)-HCvD: $[M]_0/[\text{Lewis acid}]_0$ = 100/5.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

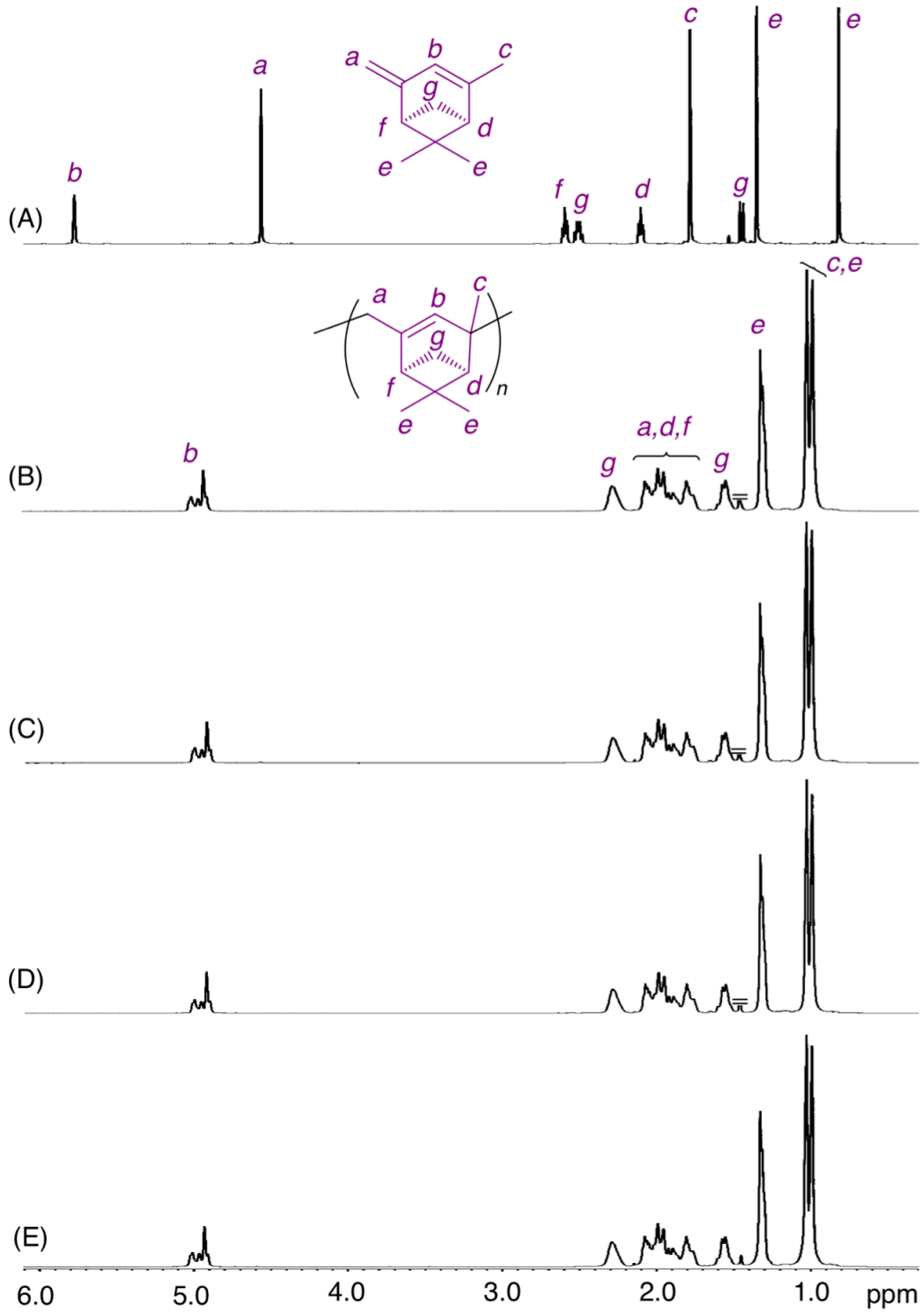

Fig. S2. ^{1}H NMR spectra (in $CDCl_3$ at 55 °C) of (–)-VnD (A) and poly((–)-VnD) obtained in conventional cationic polymerization using $EtAlCl_2$ (B), $TiCl_4$ (C), BF_3OEt_2 (D), and $SnCl_4$ (E): $[(–)\text{-VnD}]_0/[\text{Lewis acid}]_0$ = 100/5.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

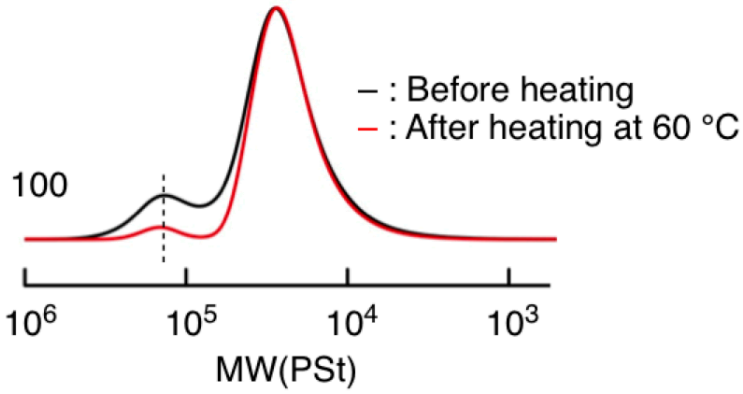

Fig. S3. SEC curves of poly(PtD) obtained in conventional cationic polymerization before heating (black) and after heating in THF at 60 °C (red): $[PtD]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

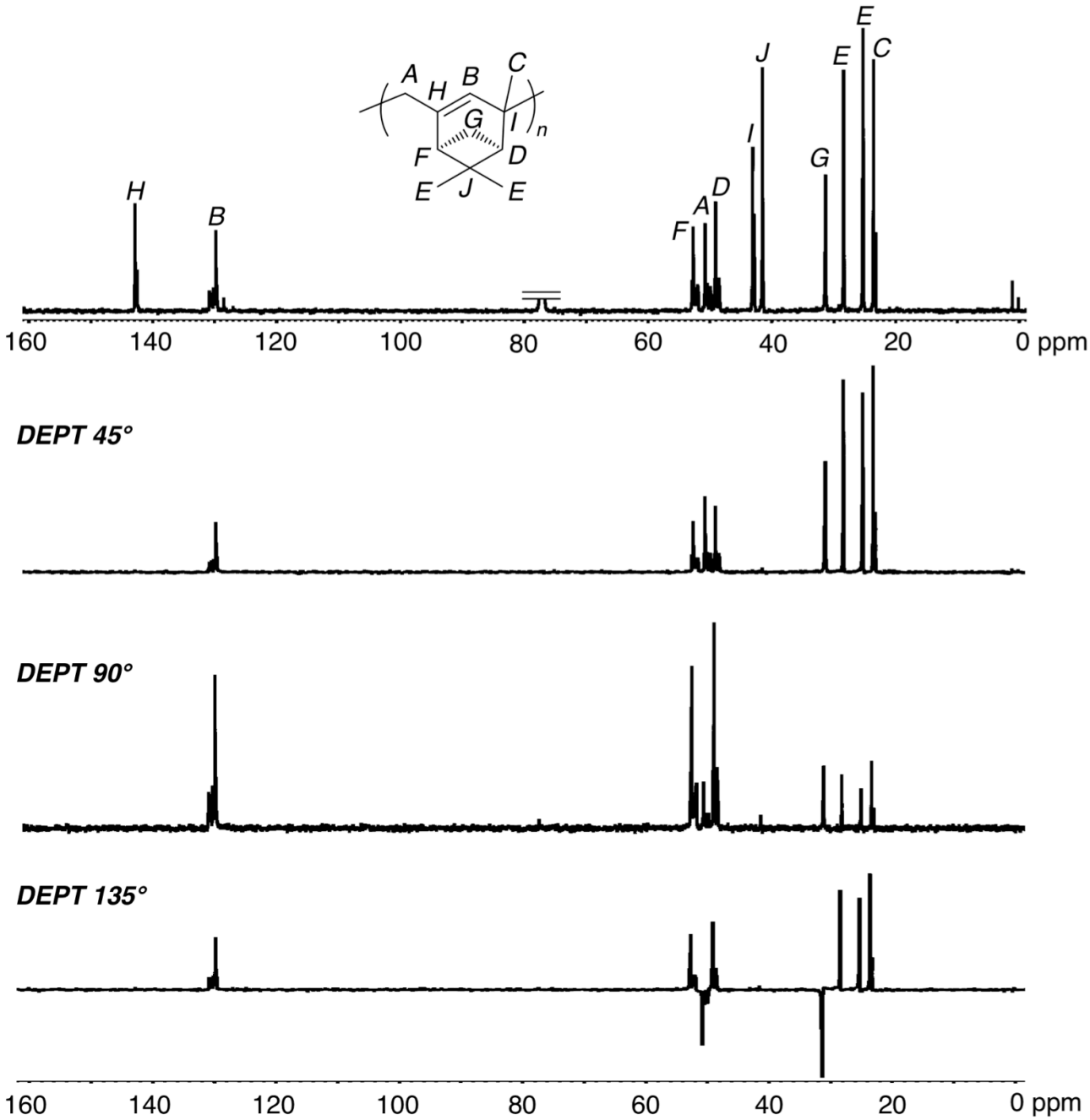

Fig. S4. ^{13}C NMR and DEPT spectra of poly((–)-VnD) in $CDCl_3$ at 55 °C: $[(–)\text{-VnD}]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

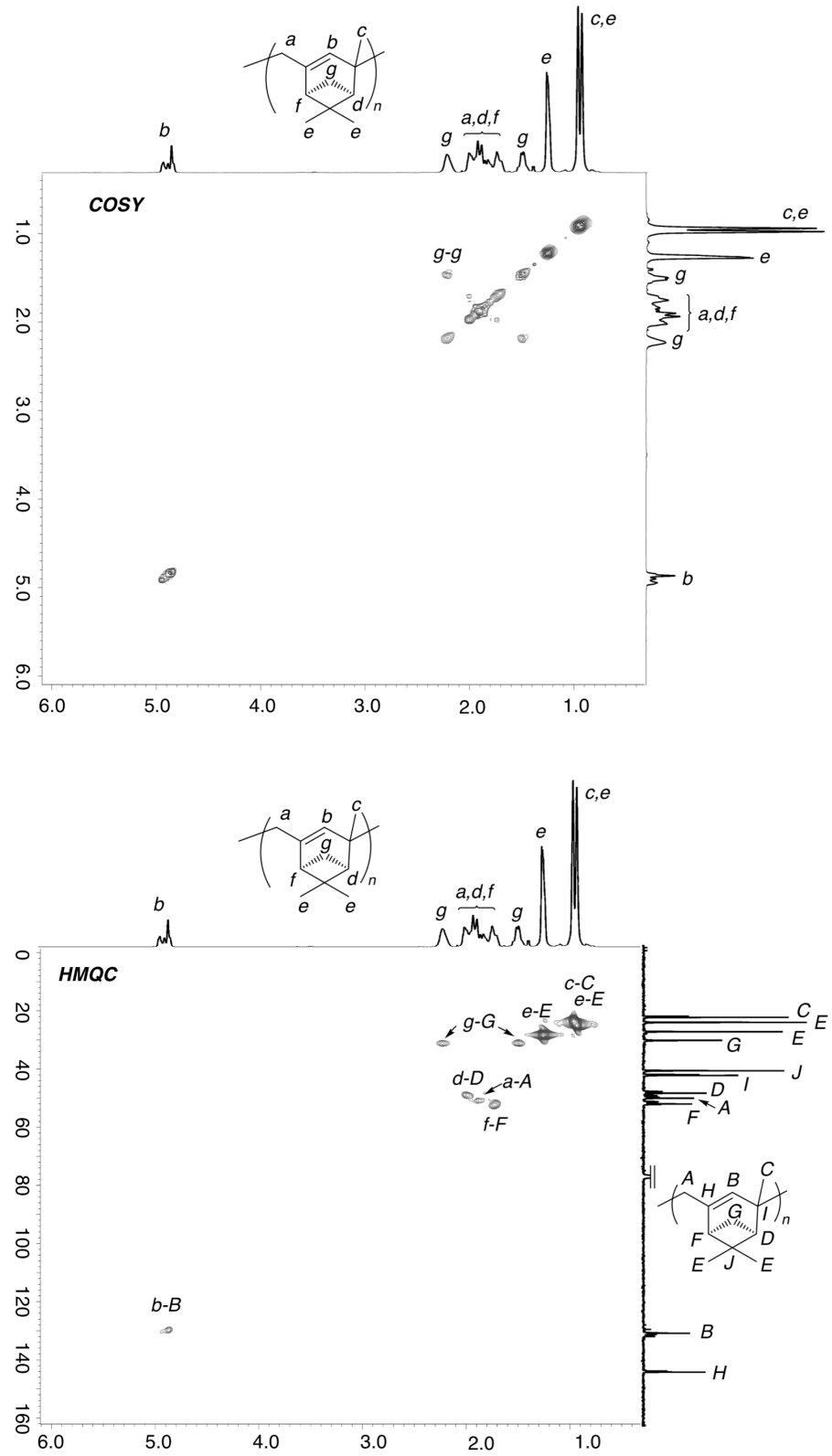

Fig. S5. ^{1}H-^{1}H COSY and HMQC spectra of poly((–)-CvD) in $CDCl_3$ at 55 °C: $[(–)\text{-VnD}]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/4.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol %) at –78 °C.

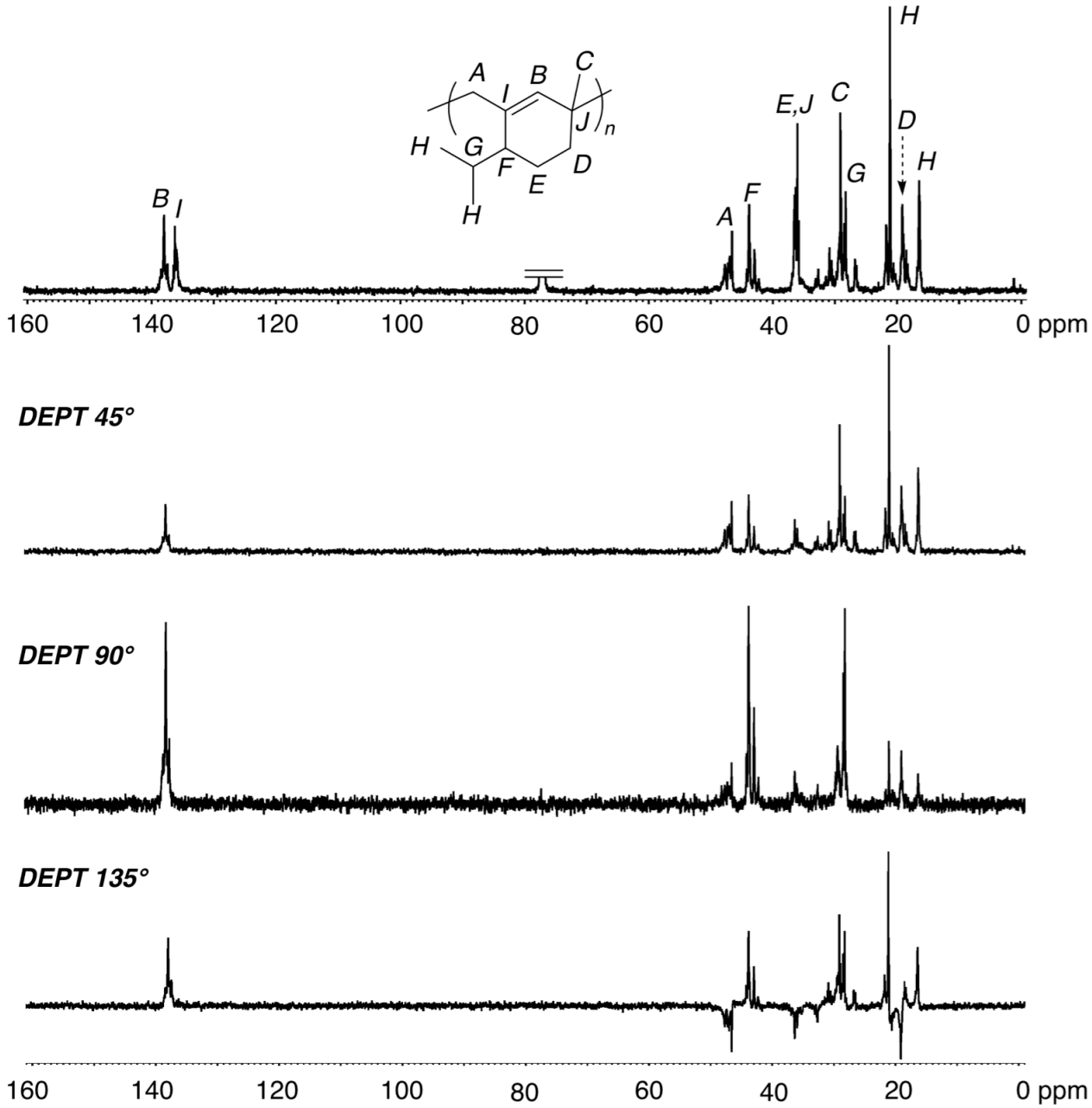

Fig. S6. ^{13}C NMR and DEPT spectra of poly(PtD) in $CDCl_3$ at 55 °C: $[PtD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

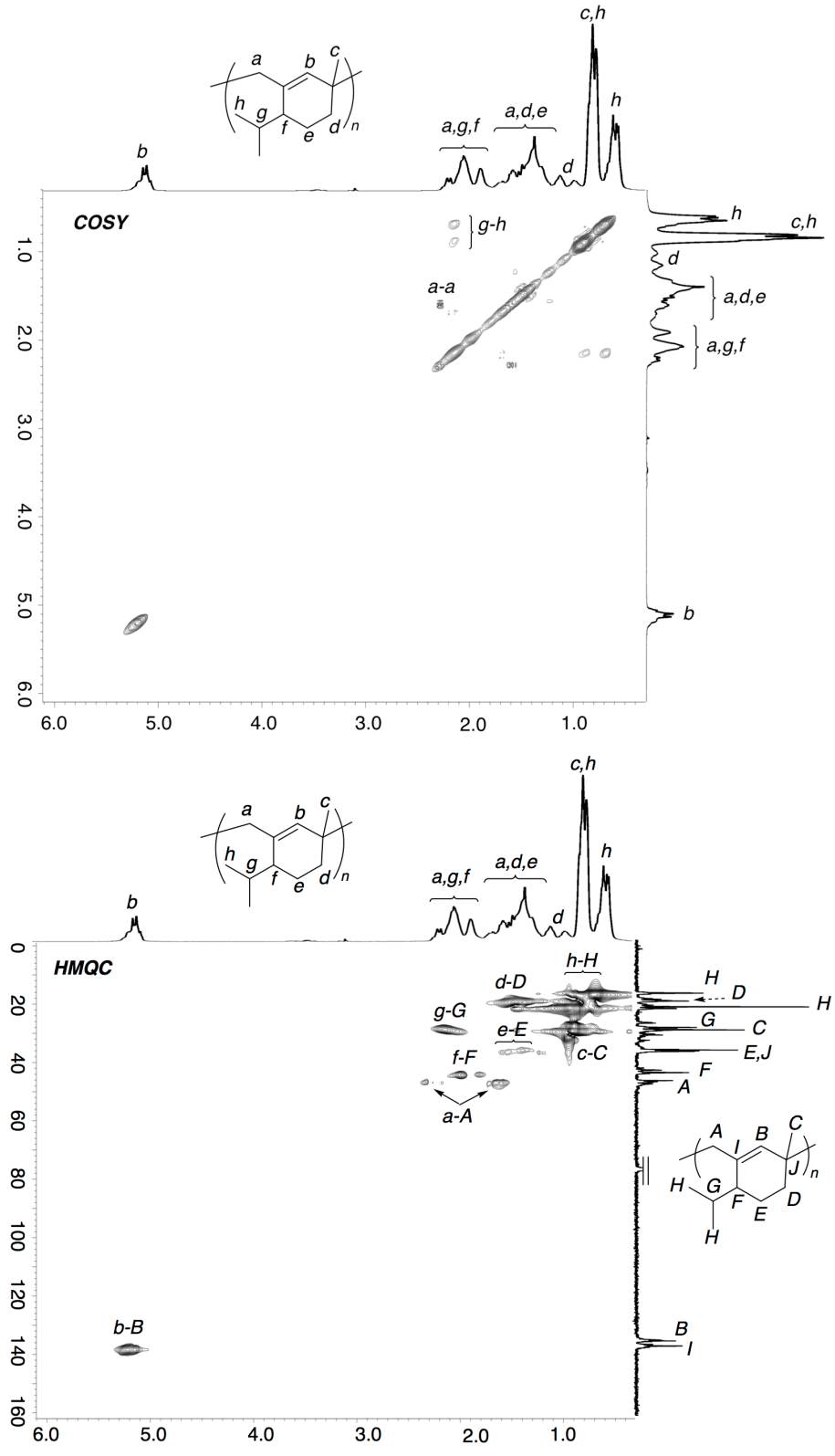

Fig. S7. ^{1}H-^{1}H COSY and HMQC spectra of poly(PtD) in $CDCl_3$ at 55 °C: $[PtD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol %) at –78 °C.

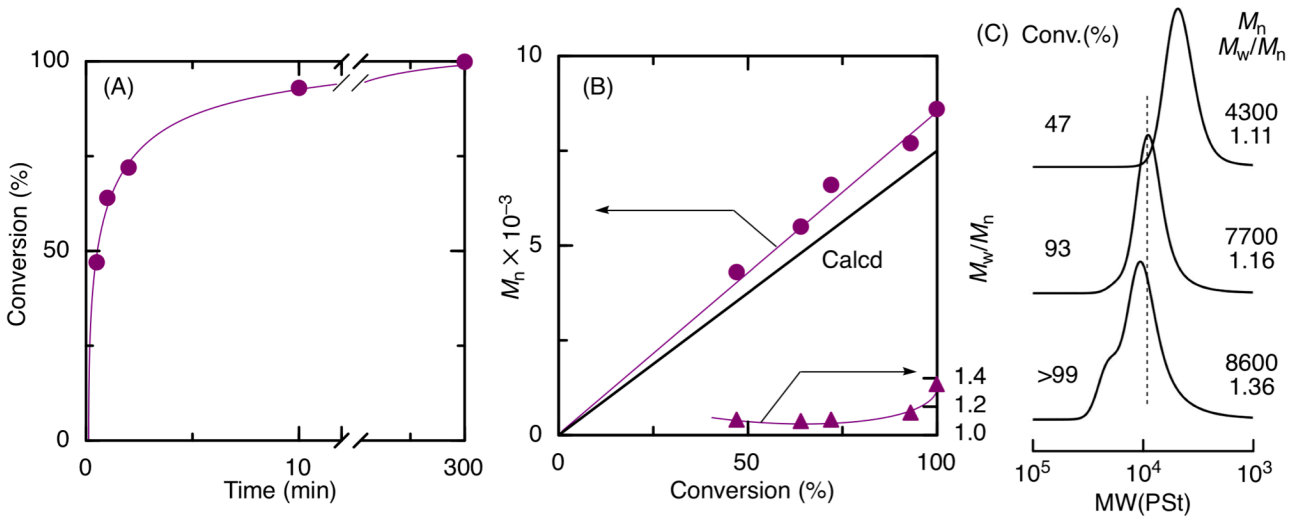

Fig. S8. Time-conversion (A), M_n and M_w/M_n (B), and SEC curves (C) of poly((–)-VnD) obtained in living cationic polymerization: $[(–)\text{-VnD}]_0/[\mathbf{2}]_0/[ZnCl_2]_0$ = 500/10/10 mM in toluene/Et_2O (19/1 vol%) at –78 °C.

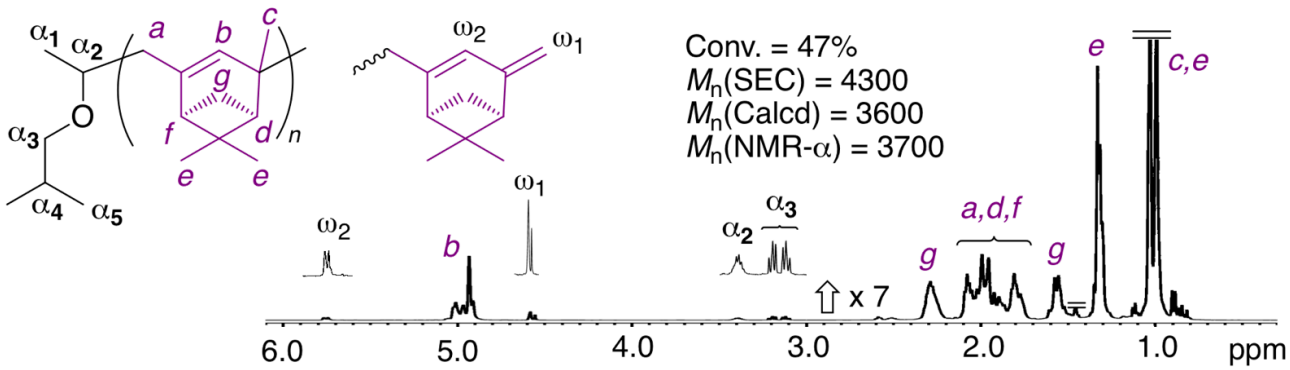

Fig. S9. ^{1}H NMR spectra (in $CDCl_3$ at 55 °C) of poly((–)-VnD) obtained in living cationic polymerization: $[(–)\text{-VnD}]_0/[\mathbf{2}]_0/[ZnCl_2]_0$ = 500/10/10 mM in toluene/Et_2O (19/1 vol%) at –78 °C.

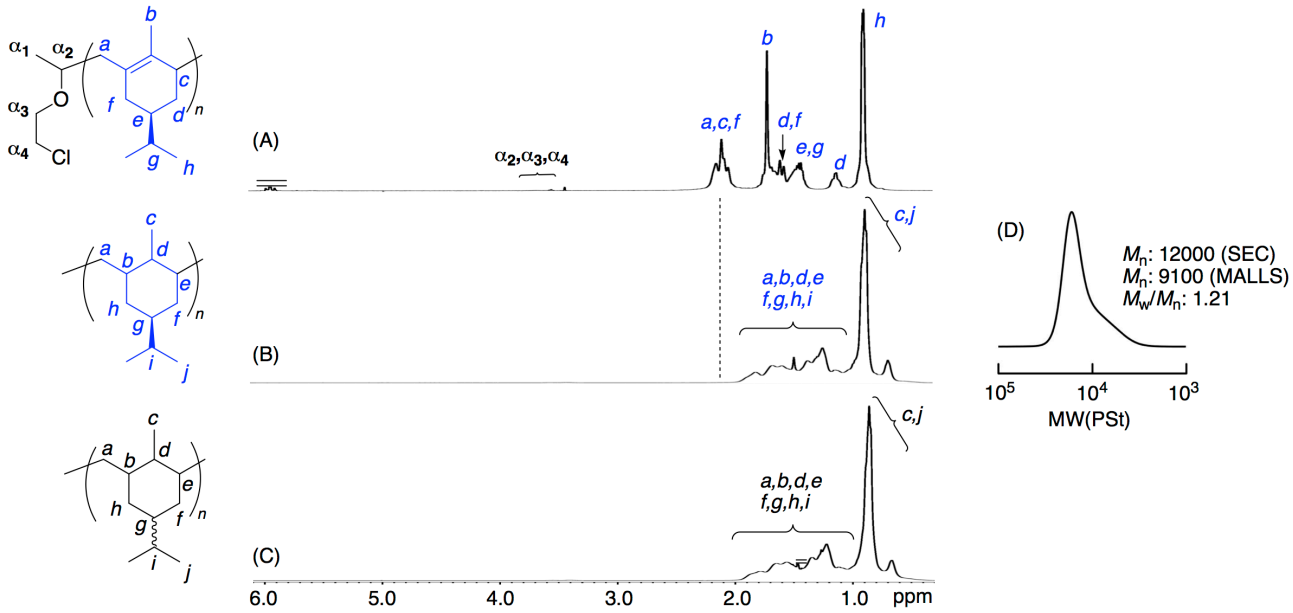

Fig. S10. ^{1}H NMR spectra (A: in $C_2D_2Cl_4$ at 100 °C; B and C: in $CDCl_3$ at 55 °C) of poly((–)-HCvD) (A), hydrogenated poly((–)-HCvD) (B), and hydrogenated poly((±)-HCvD) (C), and SEC curve of hydrogenated poly((–)-HCvD) (D) obtained in living cationic polymerization: $[HCvD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

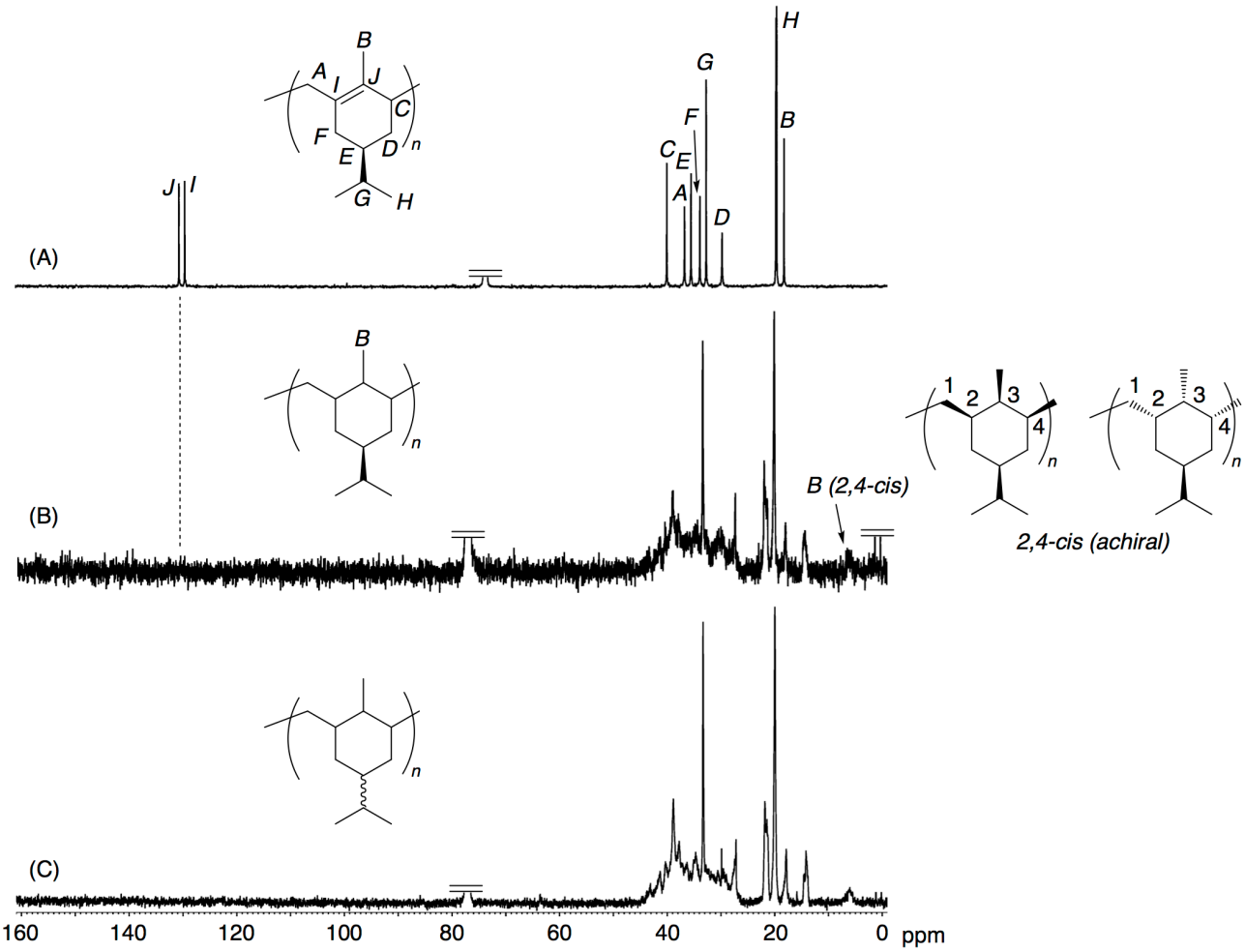

Fig. S11. ^{13}C NMR spectra (A: in $C_2D_2Cl_4$ at 100 °C; B and C: in $CDCl_3$ at 55 °C) of poly((–)-HCvD) (A), hydrogenated poly((–)-HCvD) (B), and hydrogenated poly((±)-HCvD) (C) obtained in living cationic polymerization: $[HCvD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at −78 °C.

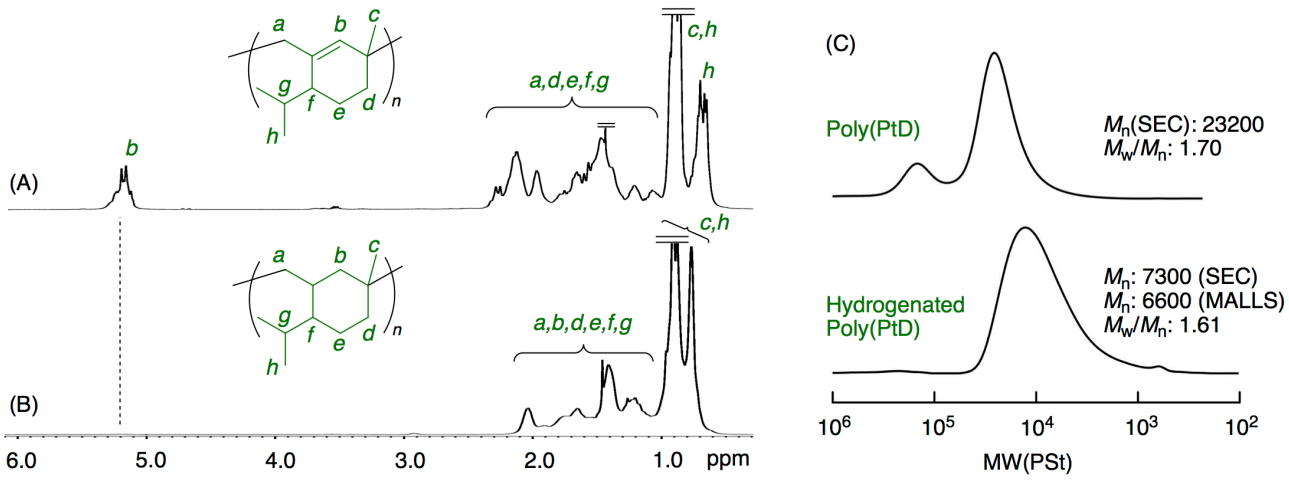

Fig. S12. ^{1}H NMR spectra (in $CDCl_3$ at 55 °C) of poly(PtD) (A) and hydrogenated poly(PtD) (B), and SEC curve of poly(PtD) and hydrogenated poly(PtD) (C) obtained in living cationic polymerization: $[PtD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

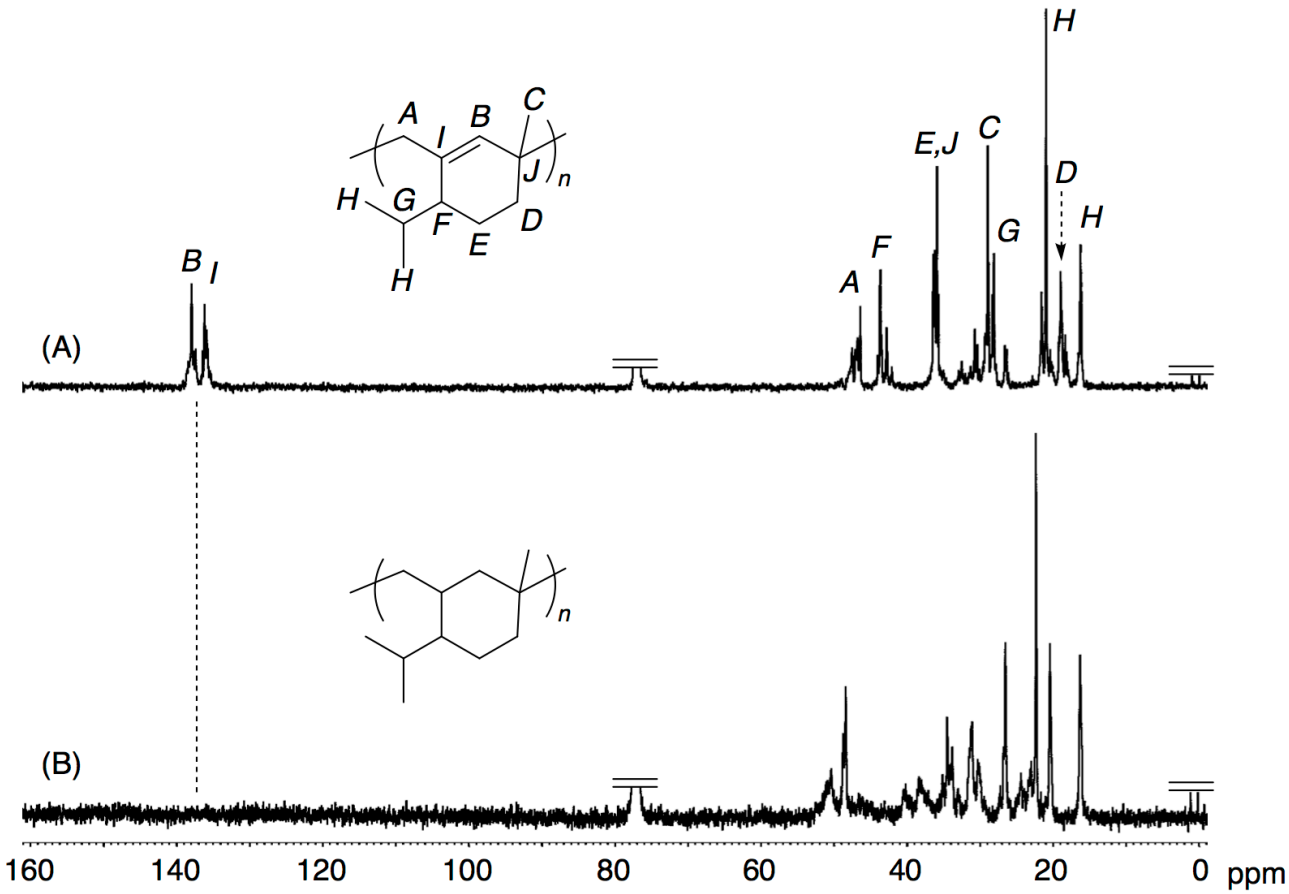

Fig. S13. ^{13}C NMR spectra (in $CDCl_3$ at 55 °C) of poly(PtD) (A) and hydrogenated poly(PtD) (B) obtained in living cationic polymerization: $[PtD]_0/[\mathbf{1}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

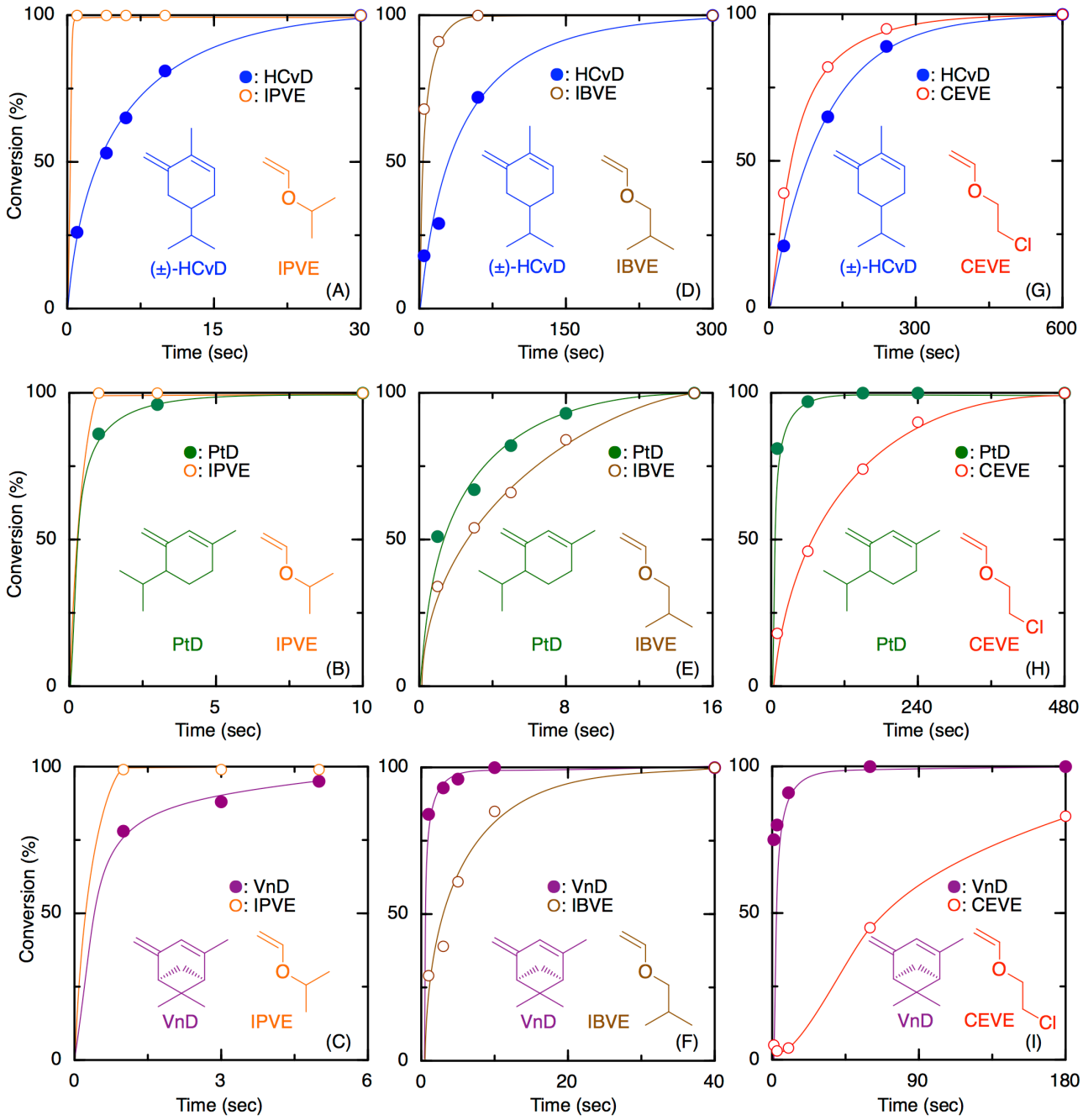

Fig. S14. Time-Conversion curves obtained in cationic copolymerization of *exo*-methylene conjugated dienes and vinyl ethers: $[\text{diene}]_0/[\text{VE}]_0/[\mathbf{2}]_0/[\text{SnCl}_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at −78 °C.

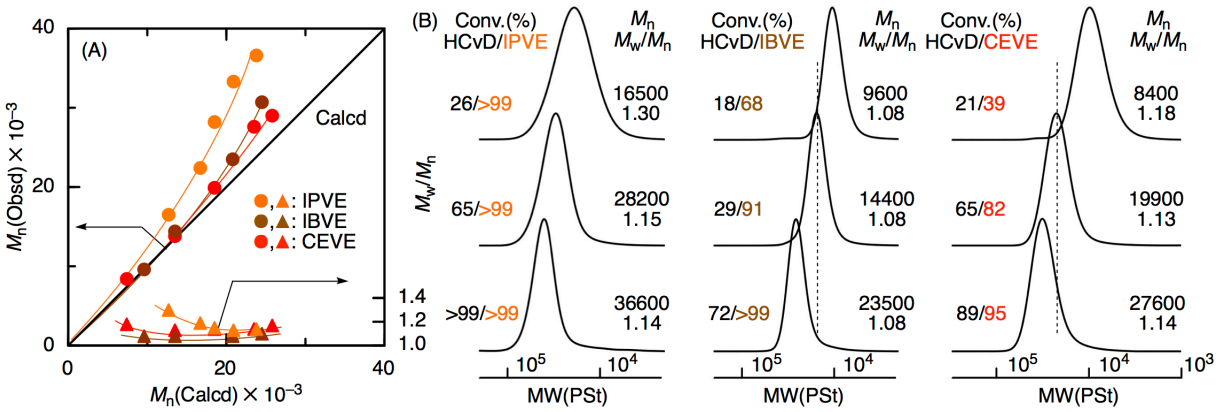

Fig. S15. M_n and M_w/M_n (A) and SEC curves (B) of copolymers obtained in living cationic copolymerization of (±)-HCvD and various VEs: $[(\pm)\text{-HCvD}]_0/[\text{VE}]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

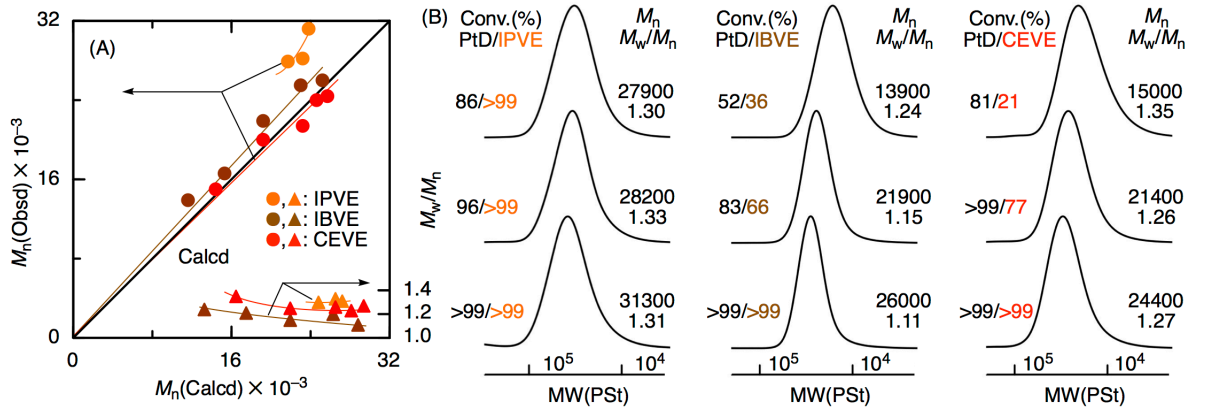

Fig. S16. M_n and M_w/M_n (A) and SEC curves (B) of copolymers obtained in living cationic copolymerization PtD and various VEs: $[\text{PtD}]_0/[\text{VE}]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

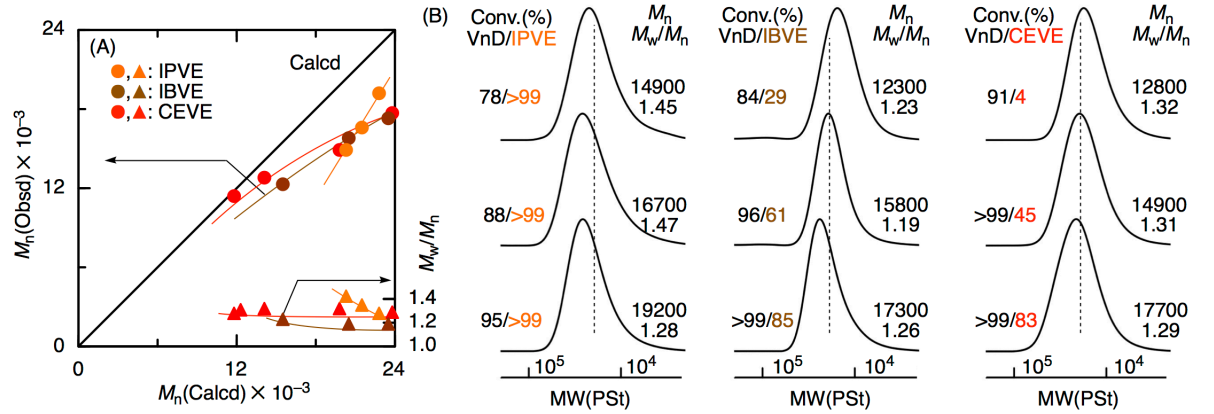

Fig. S17. M_n and M_w/M_n (A) and SEC curves (B) of copolymers obtained in living cationic copolymerization of (–)-VnD and various VEs obtained: $[(-)\text{-VnD}]_0/[\text{VE}]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

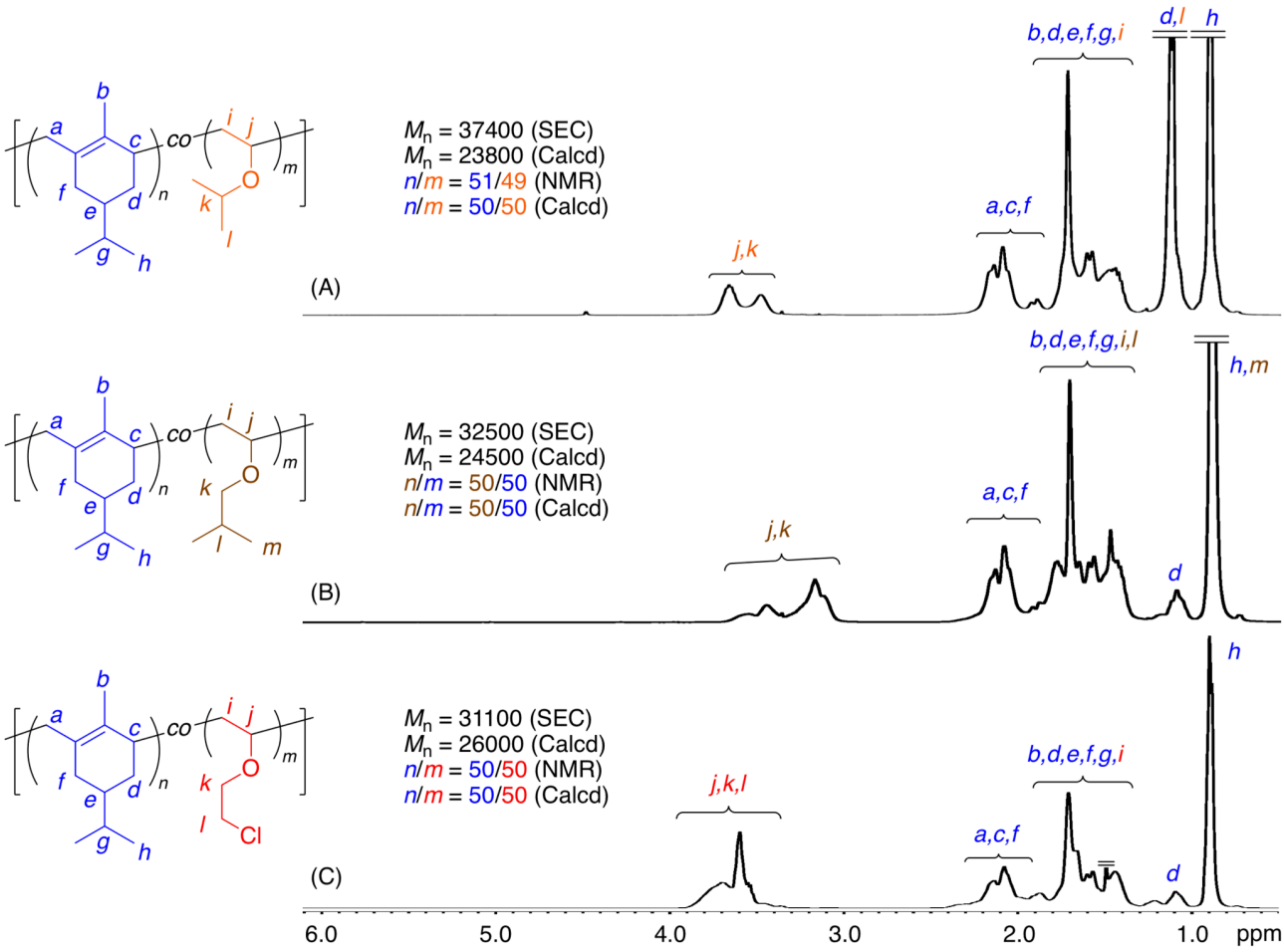

Fig. S18. ^{1}H NMR spectra of poly((±)-HCvD-*co*-IPVE) (A), poly((±)-HCvD-*co*-IBVE) (B), and poly((±)-HCvD-*co*-CEVE) (C) in $CDCl_3$ at 55 °C: $[(\pm)\text{-HCvD}]_0/[\text{VE}]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n\text{Bu}_4\text{NCl}]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

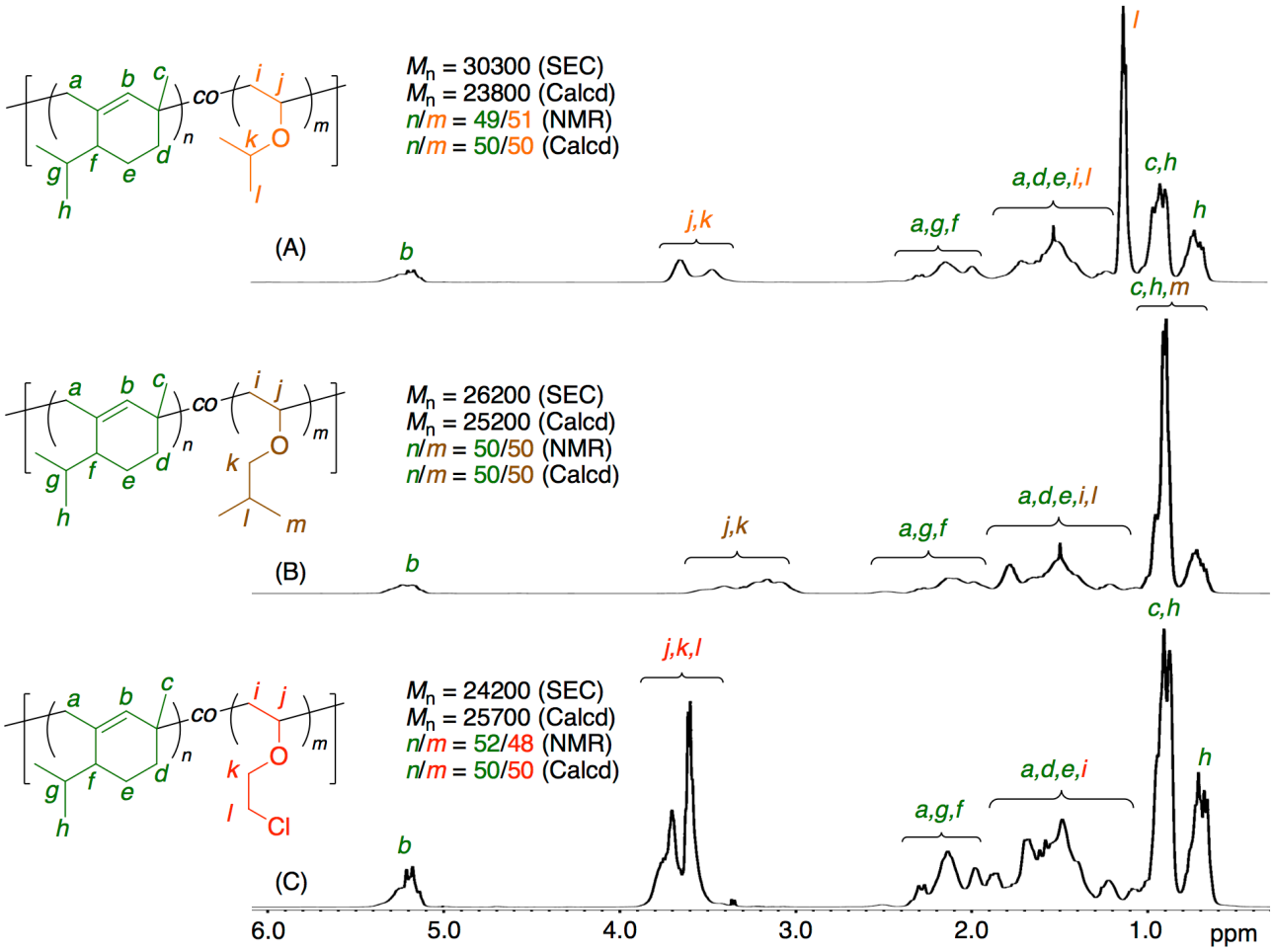

Fig. S19. ^{1}H NMR spectra of poly(PtD-*co*-IPVE) (A), poly(PtD-*co*-IBVE) (B), and poly(PtD-*co*-CEVE) (C) in $CDCl_3$ at 55 °C: $[PtD]_0/[VE]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n Bu_4NCl]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

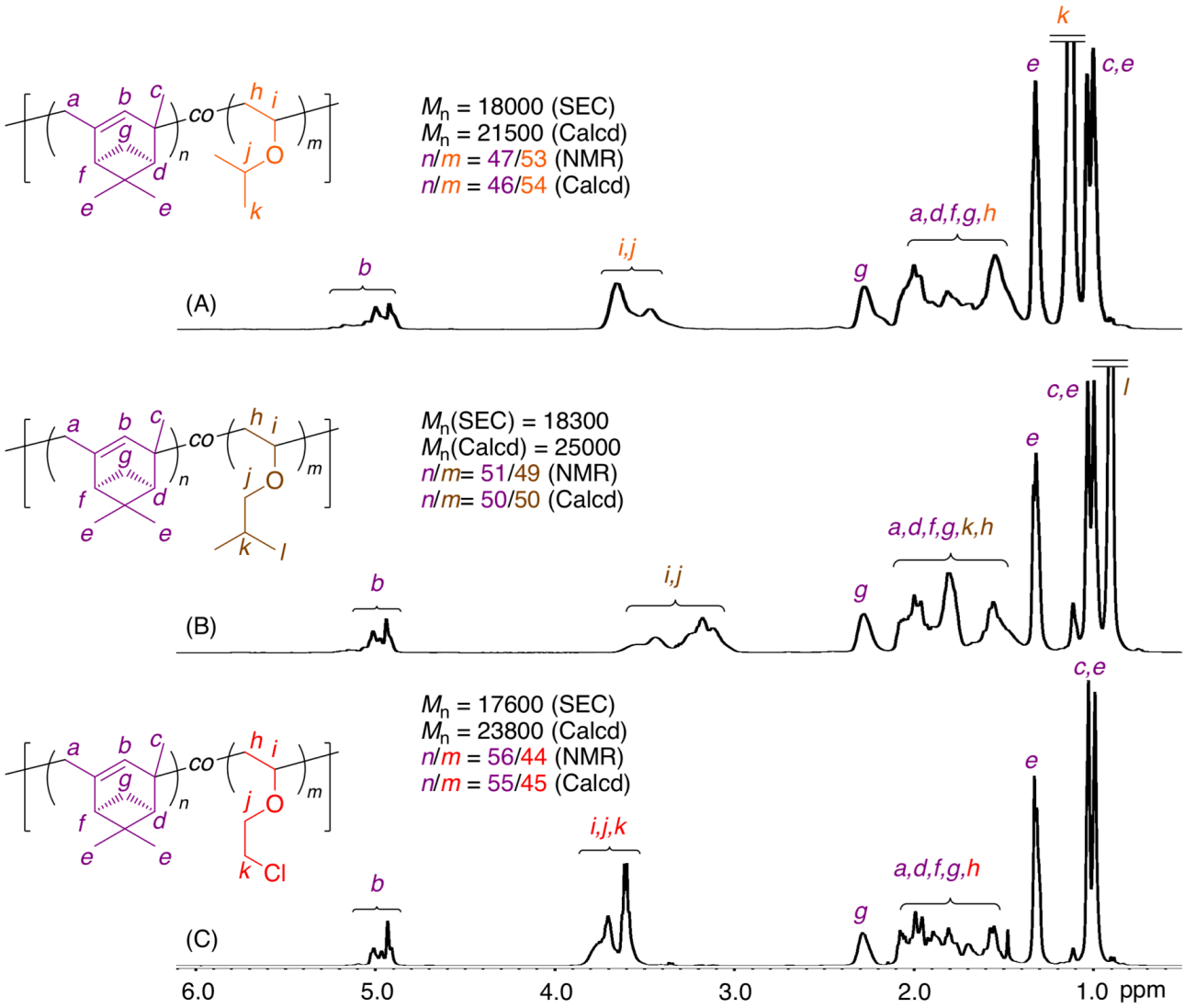

Fig. S20. ^{1}H NMR spectra of poly((–)-VnD-*co*-IPVE) (A), poly((–)-VnD-*co*-IBVE) (B), and poly((–)-VnD-*co*-CEVE) (C) in $CDCl_3$ at 55 °C: $[(–)\text{-VnD}]_0/[VE]_0/[\mathbf{2}]_0/[SnCl_4]_0/[n\text{Bu}_4NCl]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 °C.

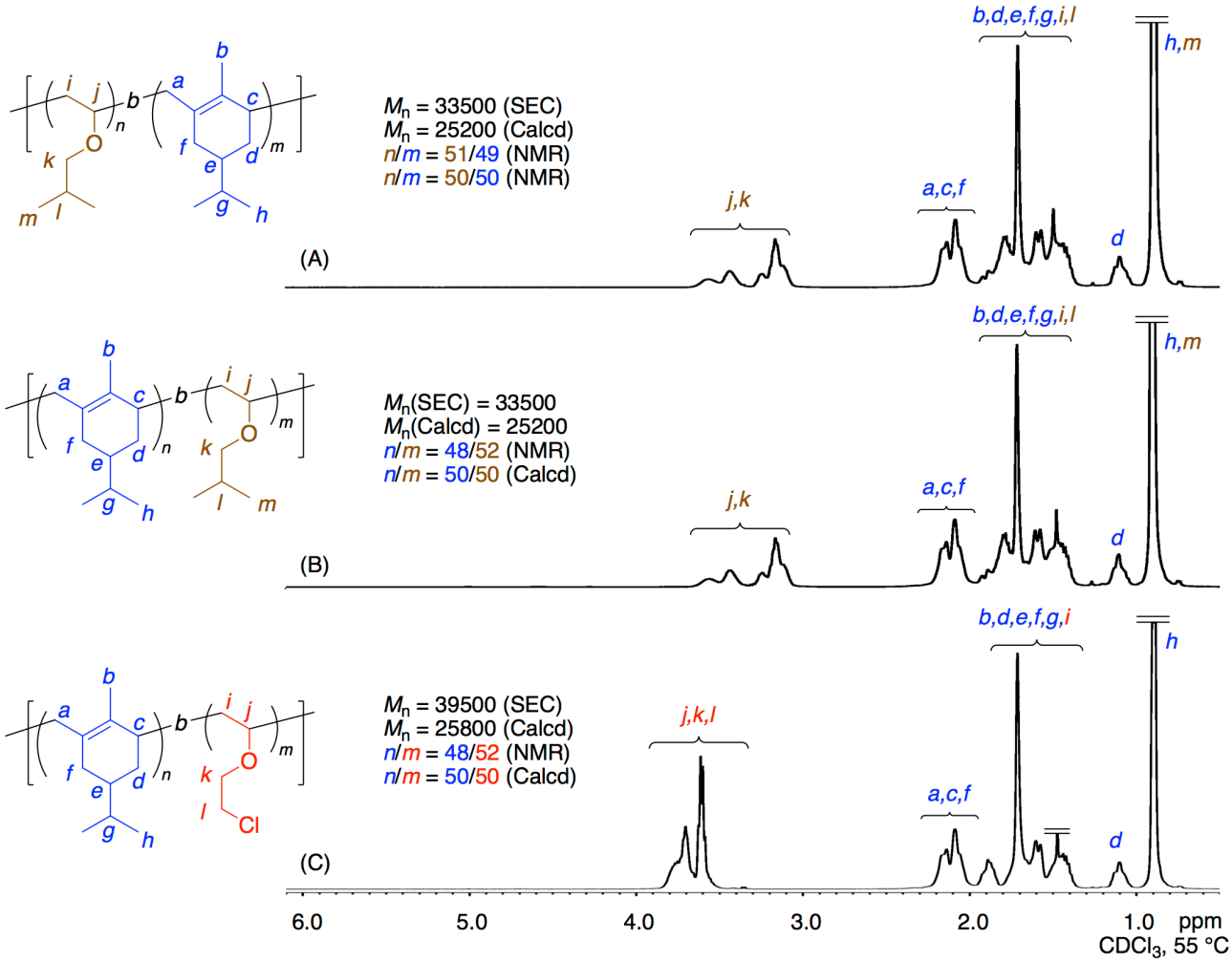

Fig. S21. ^{1}H NMR spectra of poly(IBVE-*b*-HCvD) (A), poly(HCvD-*b*-IBVE) (B), and poly(HCvD-*b*-CEVE) (C) in $CDCl_3$ at 55 °C: $[M_1]_0/[M_2]_{add}/[initiator]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 100/100/1.0/5.0/4.0 mM in toluene/CH_2Cl_2 (50/50 vol%) at –78 ºC: M_1/M_2/initiator = IBVE/HCvD/**2** (A), IBVE/HCvD/**2** (B), HCvD/CEVE/**1** (C).

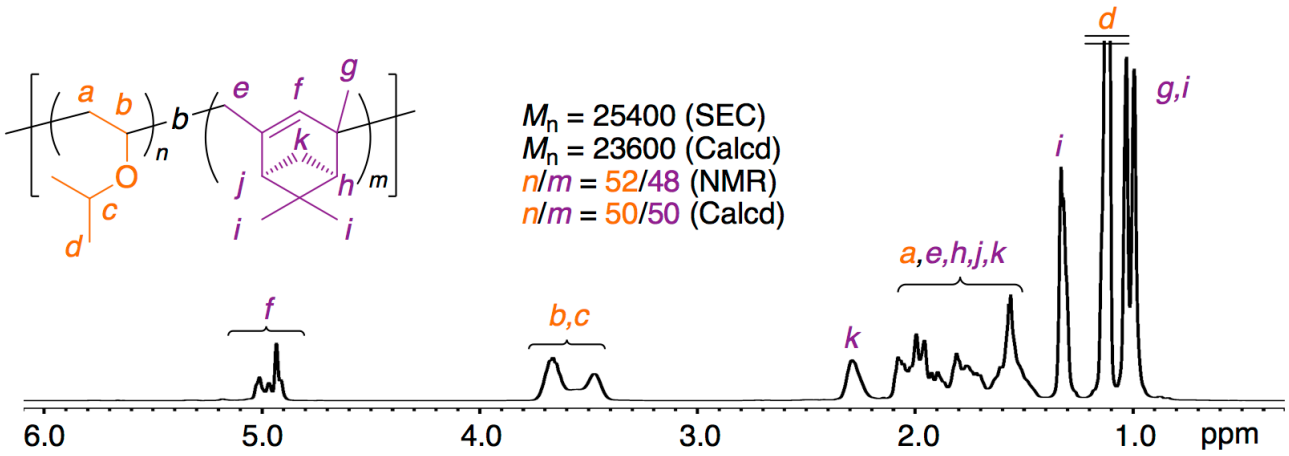

Fig. S22. ^{1}H NMR spectra of poly(VnD-*b*-IPVE) in $CDCl_3$ at 55 °C: $[IPVE]_0/[\mathbf{3}]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 100/1.0/5.0/7.0 mM, $[(–)\text{-VnD}]_{add}/[SnCl_4]_{add}$ = 100/8.75 mM.

Table S1. Living cationic polymerization of (–)-VnD, PtD, and (±)-HCvD[a]

Entry	Monomer	Initiating System (molar ratio)	Time	Conv. (%)[b]	M_n (SEC)[c]	M_n (Calcd)[d]	M_w/M_n[c]
1	(–)-VnD	**1**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/4)	1 sec	90	16800	13500	1.19
2		**2**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/4)	1 sec	89	14000	13300	1.12
3		**2**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/7)	2 h	84	10900	12600	1.74
4		**1**/$SnCl_4$/EtOAc[f] (1/5/3)	7 min	82	11500	12300	2.63
5		**1**/$SnCl_4$/EtOAc[f] (1/5/7)	48 h	74	10600	11000	4.73
6		**2**/$ZnCl_2$[g] (1/1)	10 min	93	7700	7000	1.16
7		**2**/$ZnCl_2$[h] (1/1)	90 min	79	6000	6000	1.25
8		**2**/$ZnCl_2$[i] (1/1)	10 min	85	6500	6400	1.16
9	PtD	**1**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/4)	1 sec	94	19600	14300	1.50
10		**2**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/4)	10 sec	>99	19200	15200	1.37
11		**1**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/7)	2 h	70	12000	10700	4.79
12		**1**/$SnCl_4$/EtOAc[f] (1/5/3)	10 sec	89	15200	13500	1.57
13		**2**/$ZnCl_2$[g] (1/1)	15 h	54	4300	4200	1.49
14	(±)-HCvD	**1**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/4)	2 sec	56	15500	8600	1.15
15		**1**/$SnCl_4$/*n*Bu_4NCl[e] (1/5/7)	40 h	59	12000	9000	1.20
16		**1**/$SnCl_4$/EtOAc[f] (1/5/3)	6 min	91	27900	13800	2.15
17		**2**/$ZnCl_2$[g] (1/1)	24 h	15	530	1300	1.20

[a]Polymerization temperature: –78 °C. [b]Determined by ^{1}H NMR. [c]Determined by SEC. [d]M_n (Calcd) = MW(monomer) × ($[M]_0/[initiator]_0$) × conv + MW(initiator). [e]$[M]_0/[initiator]_0$ = 100/1.0 mM in toluene/CH_2Cl_2 (1/1). [f]$[M]_0/[initiator]_0$ = 100/1.0 mM in toluene. [g]$[M]_0/[\mathbf{2}]_0$ = 500/10 mM in toluene/Et_2O (19/1). [h]$[M]_0/[\mathbf{2}]_0$ = 500/10 mM in toluene/Et_2O (9/1). [i]$[M]_0/[\mathbf{2}]_0$ = 500/10 mM in toluene/CH_2Cl_2/Et_2O (7/2/1).

Table S2. Optical rotation of monomers and polymers[a]

Entry	Sample	$[\alpha]_D$
1	(–)-VnD	–44°
2	Poly((–)-VnD)	+110°
3	PtD	+16°
4	Poly(PtD)	–11°
5	H-Poly(PtD)	+0.3°
6	(–)-HCvD	–143°
7	Poly((–)-HCvD)	n.d.[b]
8	H-Poly((–)-HCvD)	–14°
9	(±)-HCvD	–1.9°
10	Poly((±)-HCvD)	+0.7°
11	H-Poly((±)-HCvD)	–0.2°

[a] Measured in THF at 25 °C. [b] Insoluble in THF.

Table S3. Hydrogenation of polymers[a]

Entry	Polymer	Polymer (mg)	Catalyst	Catalyst (g)	H_2 pressure (MPa) at r.t.	Temp. (°C)	Time (h)	Conv. (%)	M_n(SEC)	Collecting solvent
1	Poly((–)-HCvD)		–						n.d.	
2		300	Pd/Al_2O_3	0.15	5	120	3	99	10600	$CDCl_3$
3	Poly(PtD)		–						23200	
4		100	Pd/Al_2O_3	0.01	5	120	3	98	7300	Hexane
5		100	Pd/C	0.01	5	100	3	74	3000	Hexane
6		100	Pd/SiO_2	0.05	5	100	3	60	14500	Hexane
7		100	Pd/CeO_2	0.05	5	100	3	56	17800	Hexane
8		100	Pt/Al_2O_3	0.05	5	100	3	29	18900	Hexane
9		100	Pt/CeO_2	0.05	5	100	3	18	22700	Hexane
10	Poly((–)-VnD)		–						17400	
11		100	Pd/C	0.01	5	30	3	<1	8600	Hexane
12		100	Pd/C	0.01	5	60	3	32	1200	Hexane
13		100	Pd/C	0.01	5	90	3	>99	460	Hexane
14		100	Pd/C	0.01	1[b]	90	3	3	17500	Hexane
15		100	none	–	5	90	3	0	17100	Hexane
16		100	Pd/Al_2O_3	0.01	5	120	3	>99	620	Hexane
17		100	Pd/SiO_2	0.05	5	60	3	23	3000	Hexane
18		100	Pt/Al_2O_3	0.01	5	100	3	78	1200	Hexane

[a] Reaction conditions: polymer 100 or 300 mg, catalyst 0.01–0.15 g, hexane 2 g, H_2 5 MPa or Ar 1 MPa (at r.t.), 30–120 °C. [b] Ar was used in place of H_2.