Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Organocatalytic Cationic Degenerate Chain Transfer Polymerization of Vinyl Ethers with Excellent Temporal Control

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General procedure for the synthesis of CTA

The synthesis was carried out by reaction between IBVE (5.0 mL, 50 mmol) and *n*-butanethiol (4.5 mL, 50 mmol) in the presence of trace amount of *p*-toluenesulfonic acid monohydrate (19 mg, 0.1 mmol) in dry CH_2Cl_2 (20 mL) at -78 to -40 °C for 2 h. After the reaction, the solution was diluted with Et_2O and washed with 5 wt % $NaHCO_3$ aqueous solution and water. The solvent was removed by evaporation. The remaining liquid was distilled under reduced pressure to give the desired product as colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (q, J = 6.5 Hz, 1H), 3.42 (t, J = 6.9 Hz, 1H), 3.18 (t, J = 6.8 Hz, 1H), 2.62 - 2.53 (m, 2H), 1.84 - 1.83 (m, 1H), 1.59 - 1.53 (m, 5H), 1.43 - 1.39 (m, 2H), 0.93 - 0.91 (m, 9H).

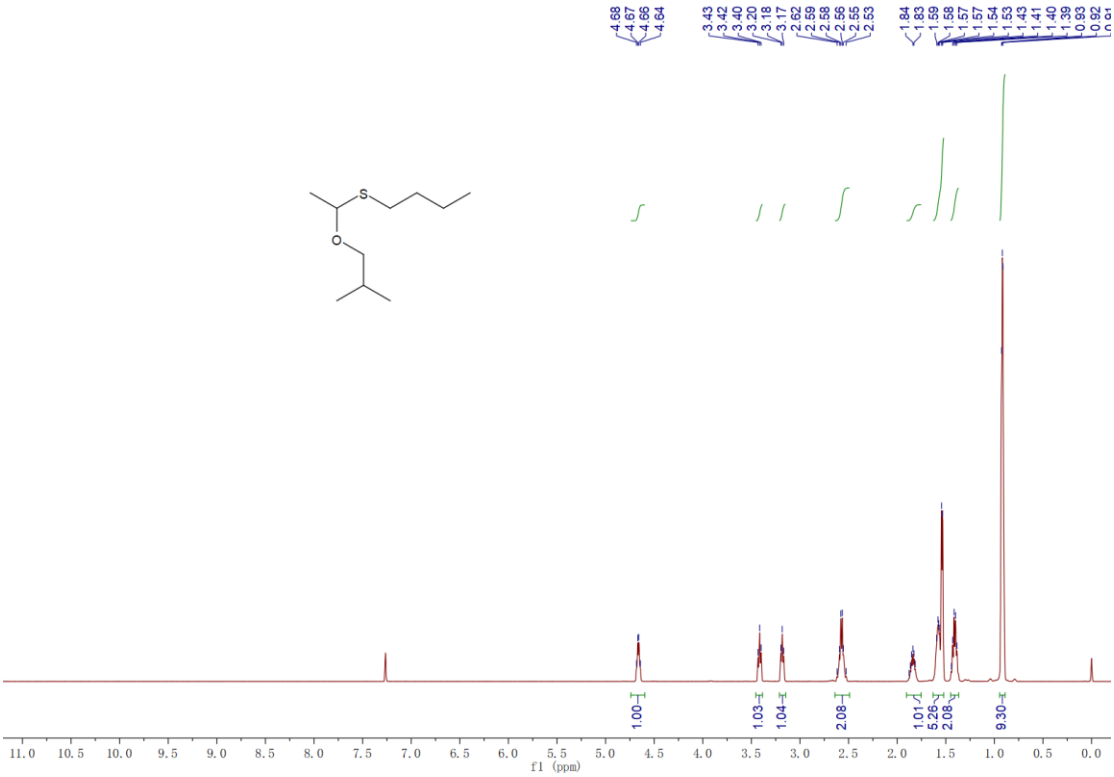

Figure S1. ^{1}H NMR of CTA

Light On/Off experiment:

Table S1. Light On/Off experiment of Figure 3a.

Time	on/off	Conv (%)	M_n	$Đ$
0	off	0	/	/
7	on	31	3.0	1.30
37	off	31	3.0	1.29
44	on	55	5.3	1.29
74	off	55	5.3	1.30
81	on	72	7.1	1.34
111	off	72	7.1	1.35

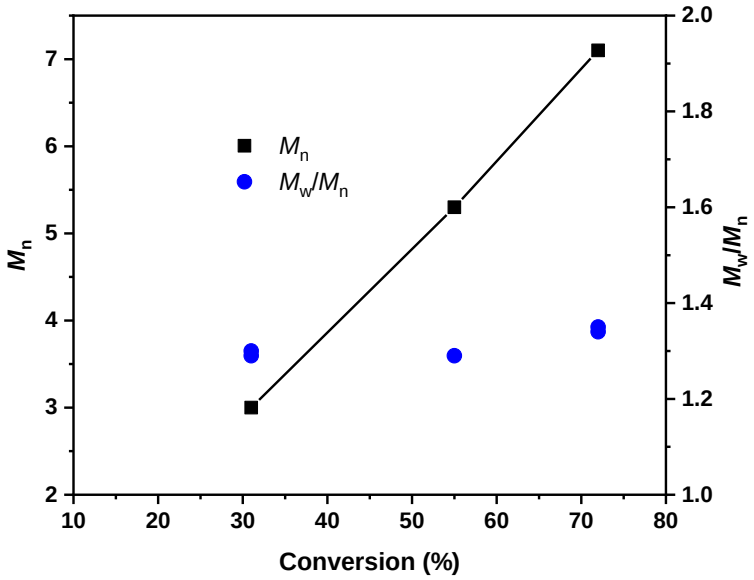

Figure S2. M_n and $Đ$ *vs* Conversion.

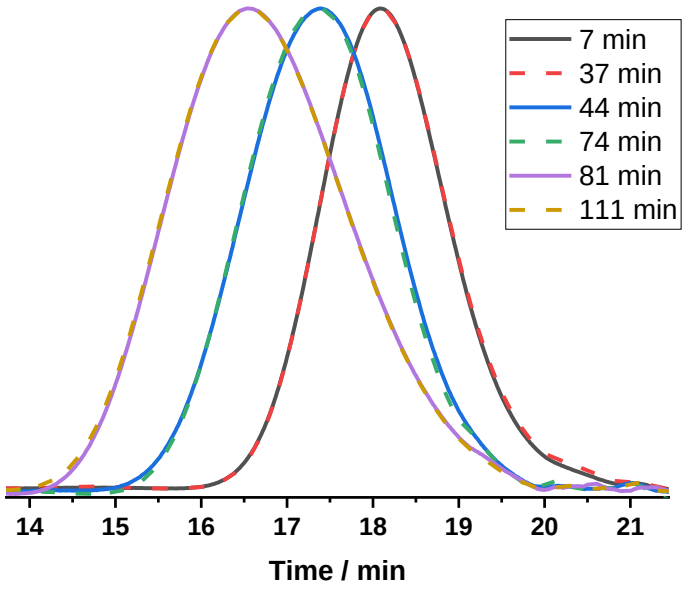

Figure S3. The GPC trace of Figure 3a.

Table S2. Light On/Off experiment of Figure 3b.

Time	on/off	Conv (%)	M_n	$Đ$
0	off	0	/	/
15	on	62	5.9	1.29
195	off	62	5.9	1.29
210	on	90	8.8	1.32

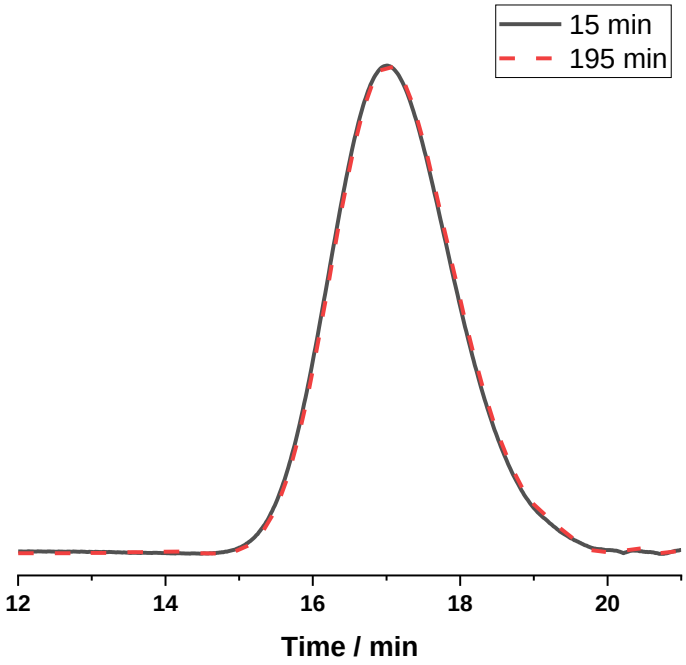

Figure S4. The GPC trace of Figure 3b.

General procedure for the synthesis of block polymers

In an argon filled glove box, a flame dried three times Schlenk tube was equipped with a stir bar and charged with isobutyl vinyl ether (1 mmol, 40 equiv), **BPS** (10 ppm), CTA (1 equiv) and 0.1 mL DCM were added. The Schlenk tube was sealed with a septum cap under an atmosphere of argon, and placed in the blue LEDs reactor (6 W, λ_{max} = 460 nm, 30 mW/cm^2) outside of the glove box. After reacted for 0.5 h, and aliquots for NMR and GPC analysis were taken in glove box. After that, another 40 equivalents of IBVE or NBVE were added, the Schlenk tube was sealed with a septum cap under an atmosphere of argon again, and then exposed to light again for 1 h.

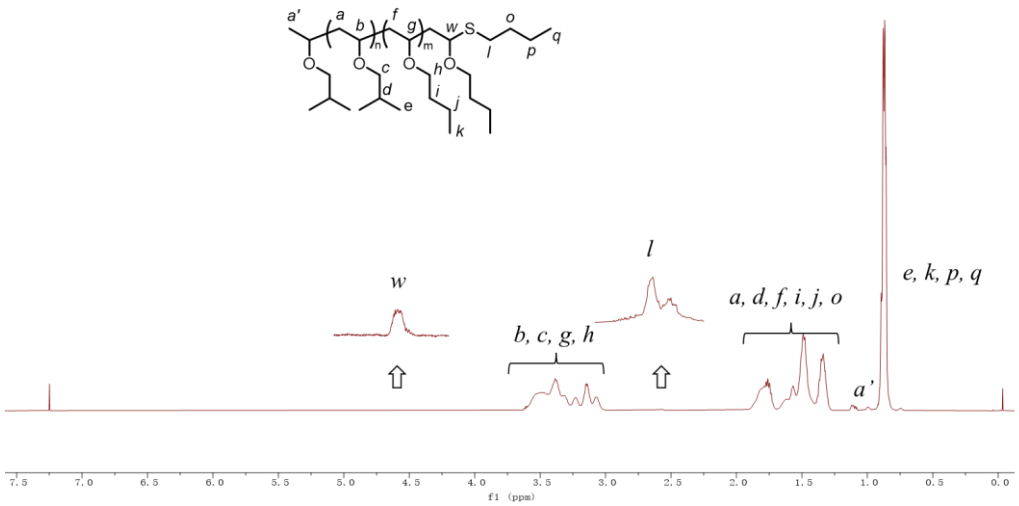

Figure S5. ^{1}H NMR of IBVE-*b*-NBVE ($M_{n,\,NMR}$ calculated based on $I_{bcgh}/I_{a'}$)

General procedure for the in situ chain-end functionalization of poly(IBVE):

In an argon filled glove box, a flame dried three times Schlenk tube was equipped with a stir bar and charged with isobutyl vinyl ether (3.0 mmol), BPs (0.003% mmol), CTA (0.03 mmol), and 0.5 mL DCM were added at room temperature with irradiation from a 6W Blue LEDs for 0.2 h. Immediately following the polymerization, alcohol (0.06 mmol, 3 equiv), 2,6-di-tert-butylpyridine (0.01 mmol, 1 equiv), and 0.2 mL of DCM were added, and then exposed to light again for 5 h. Later on, the reaction was quenched by the addition of MeOH/NEt_3 (9:1, 1 mL) and the reaction mixture stirred at room temperature for another 0.5 h. The solvent evaporated under reduced pressure to afford the crude poly(IBVE)s. The crude polymer was diluted with THF (1 mL) again and precipitated in MeOH (20 mL), afforded the desired poly(IBVE)s, and the polymer was analyzed by GPC and ^{1}H NMR.

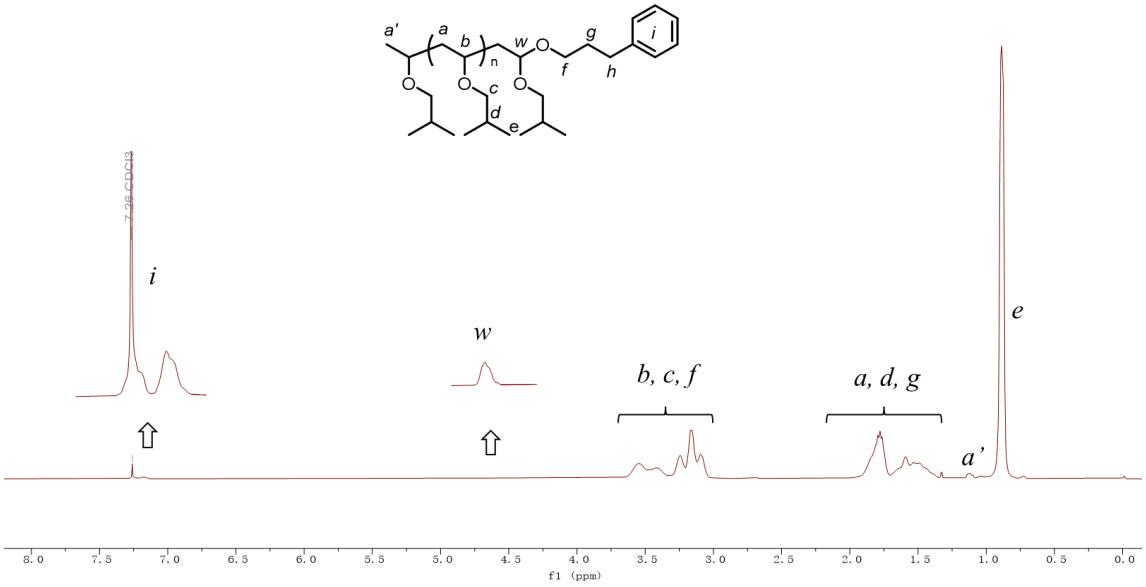

Figure S6. ^{1}H NMR of poly(isobutyl vinyl ether) functionalized with 3-phenyl-1-propanol ($M_{n,\,NMR}$ = 7.4 kg/mol based on I_{bc}/I_w, $M_{n,\,NMR}$ = 7.7 kg/mol based on I_{bc}/I_i, $M_{n,\,NMR}$ = 7.1 kg/mol based on $I_{bc}/I_{a'}$)

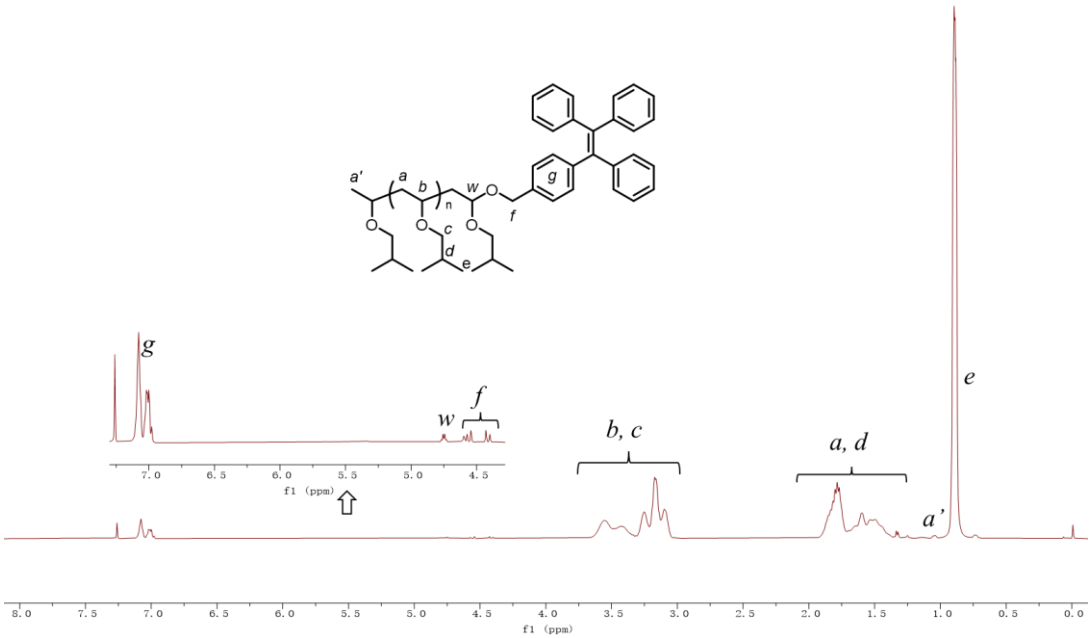

Figure S7. ^{1}H NMR of poly(isobutyl vinyl ether) functionalized with (4-(1,2,2-Triphenylvinyl)phenyl)methanol ($M_{n,\,NMR}$ = 7.2 kg/mol based on I_{bc}/I_{w}, $M_{n,\,NMR}$ = 7.1 kg/mol based on I_{bc}/I_{g}, $M_{n,\,NMR}$ = 6.9 kg/mol based on $I_{bc}/I_{a'}$)

NMR of PVEs

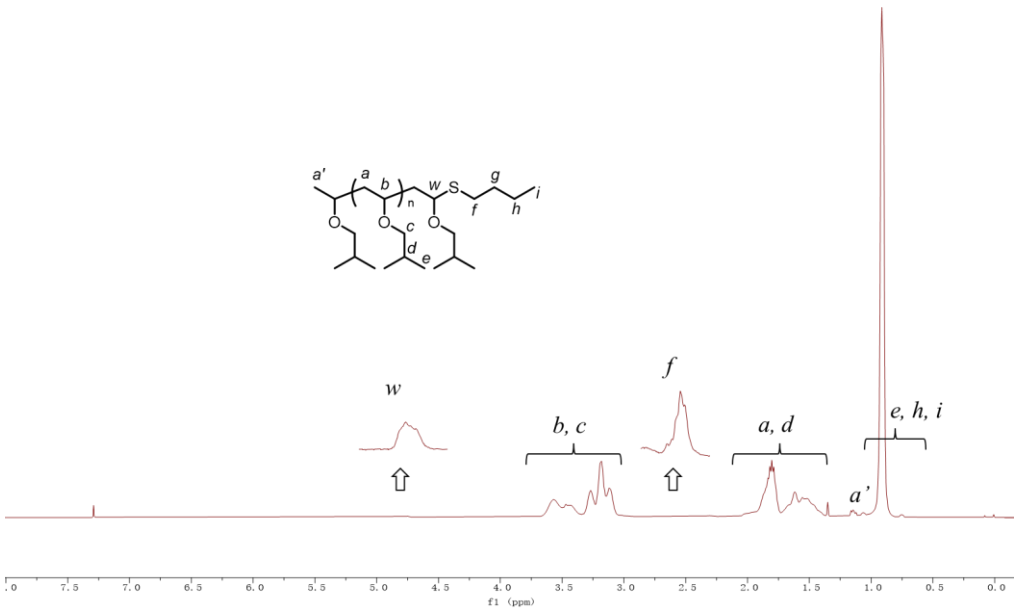

Figure S8. ^{1}H NMR of poly(IBVE) ($M_{n,\,NMR}$ calculated based on $I_{bc}/I_{a'}$)

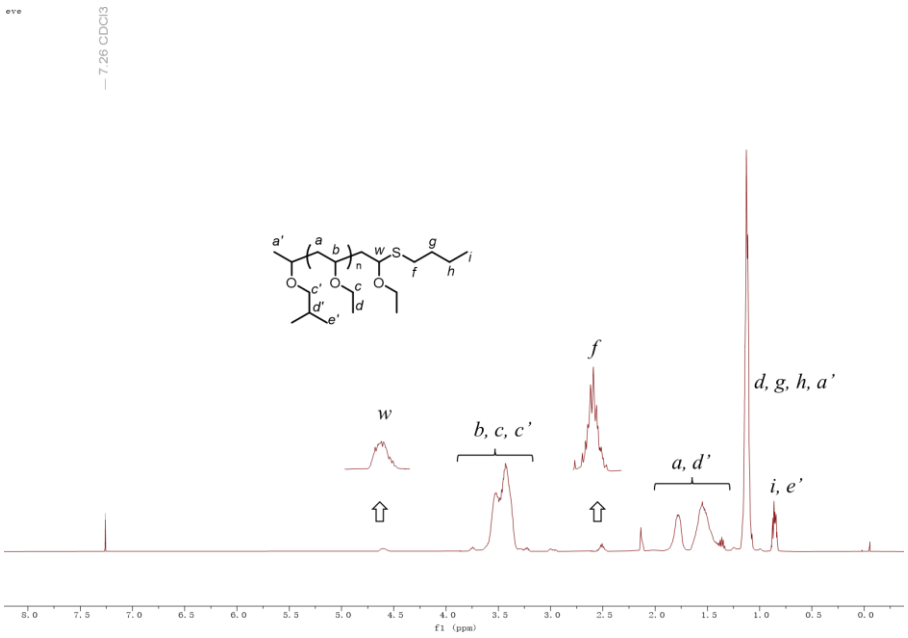

Figure S9. ^{1}H NMR of poly(EVE) ($M_{n,\ NMR}$ calculated based on $I_{bcc'}/I_{w}$)

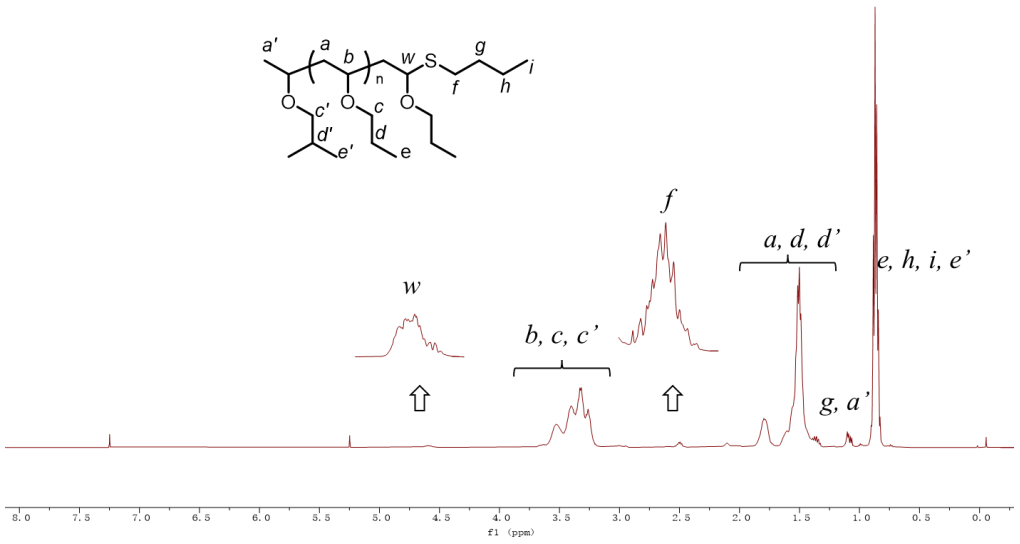

Figure S10. ^{1}H NMR of poly(NPVE) ($M_{n,\ NMR}$ calculated based on $I_{bcc'}/I_{a'}$)

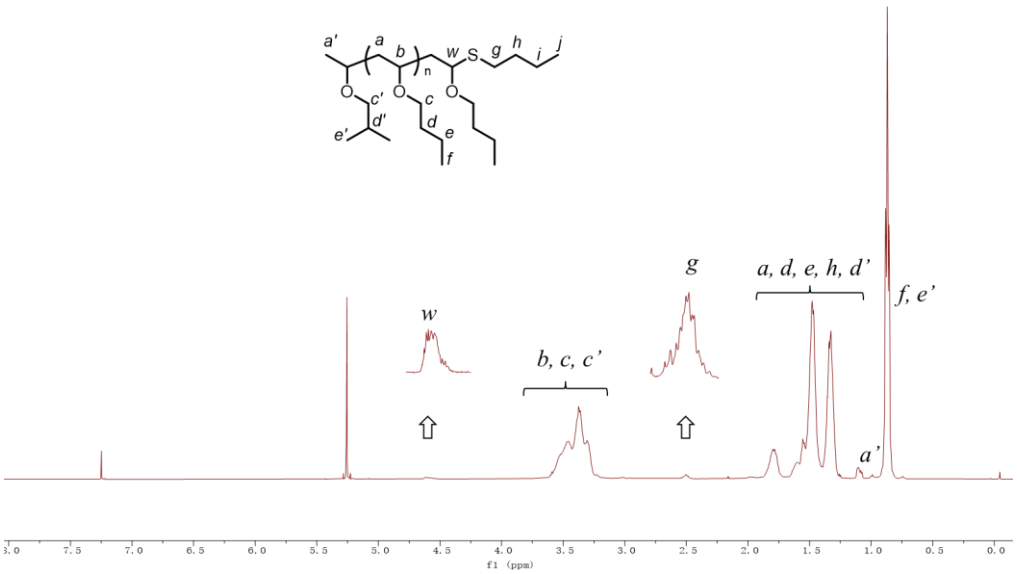

Figure S11. ^{1}H NMR of poly(NBVE) ($M_{n,\,NMR}$ calculated based on $I_{bcc'}/I_{a'}$)

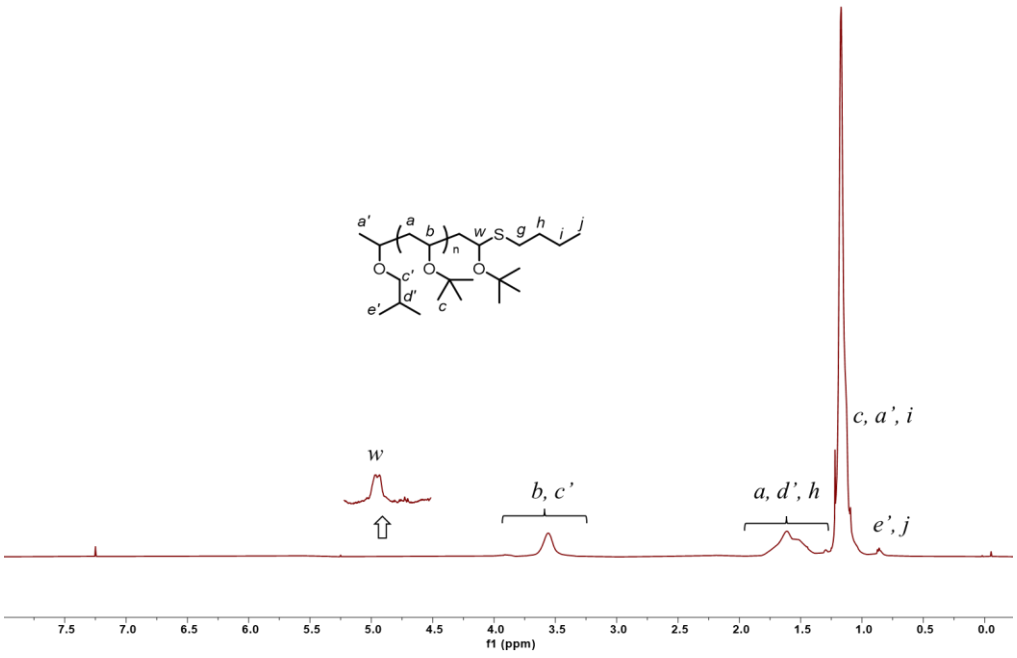

Figure S12. ^{1}H NMR of poly(TBVE) ($M_{n,\,NMR}$ calculated based on $I_{bc'}/I_{w}$)

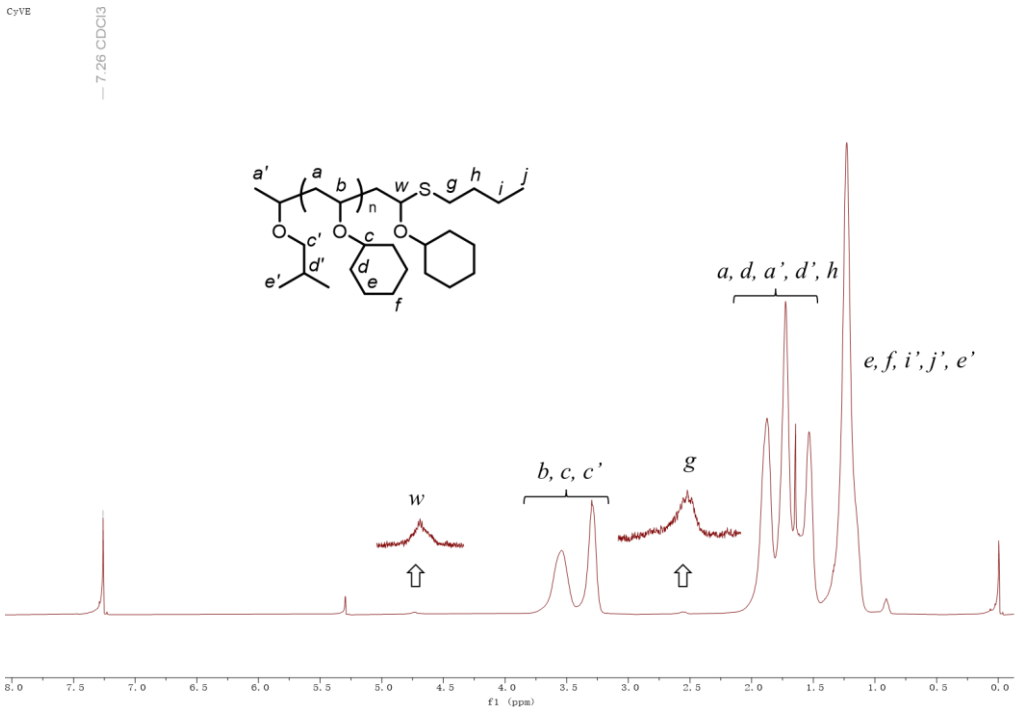

Figure S13. ^{1}H NMR of poly(CyVE) ($M_{n,\,NMR}$ calculated based on $I_{bcc'}/I_{w}$)

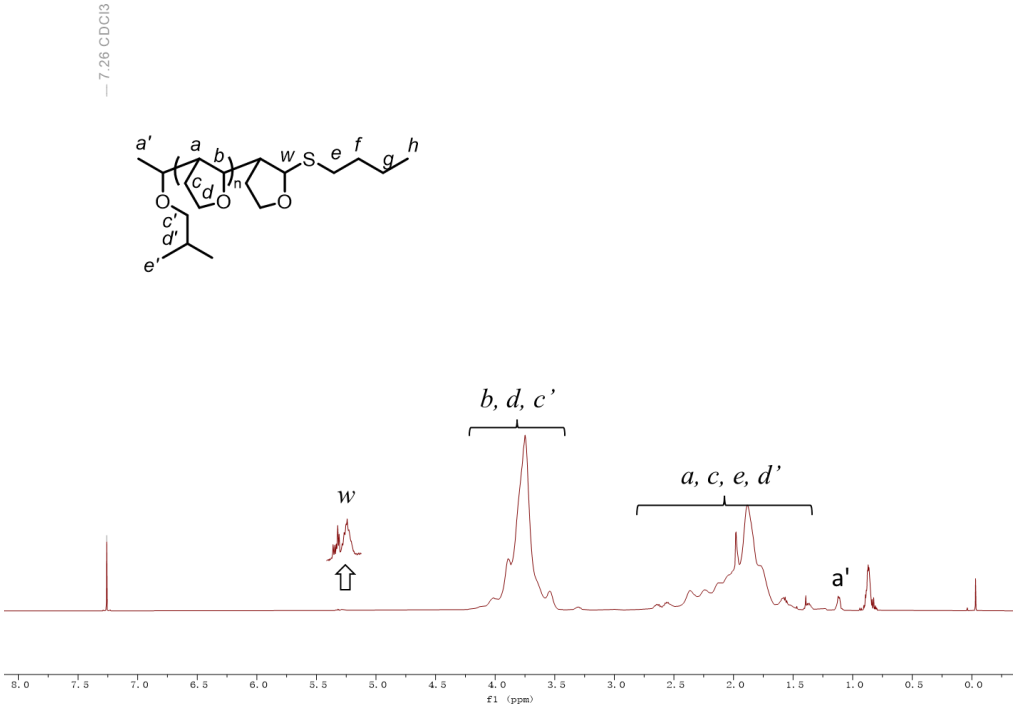

Figure S14. ^{1}H NMR of poly(DHF) ($M_{n,\,NMR}$ calculated based on $I_{bdc'}/I_{a'}$)

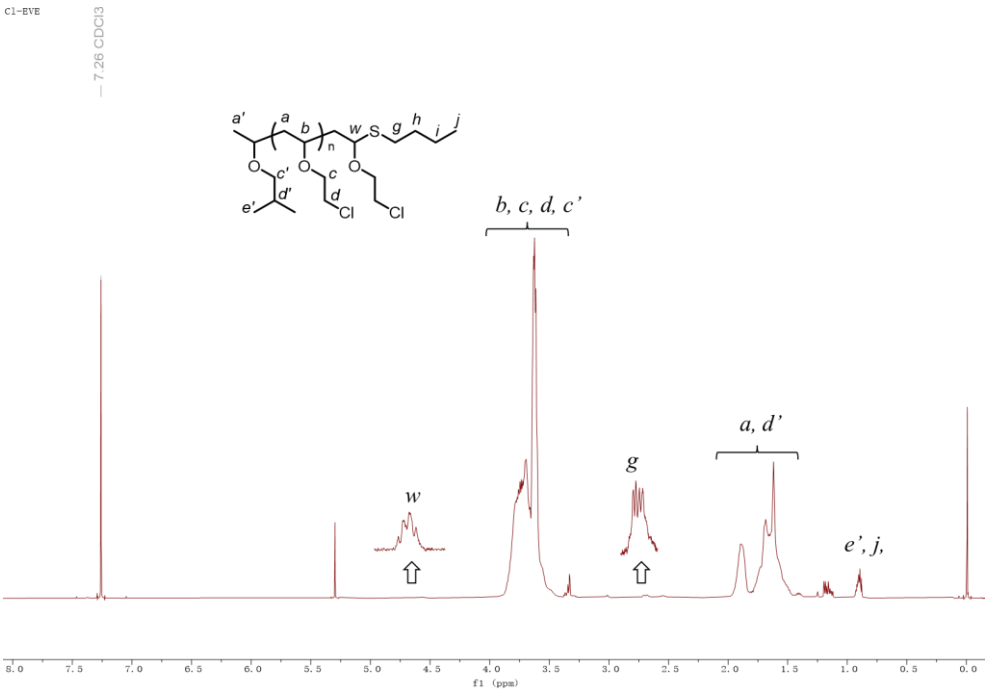

Figure S15. ^{1}H NMR of poly(Cl-EVE) ($M_{n,\,NMR}$ calculated based on $I_{bcdc'}/I_{w}$)