

Supplementary information

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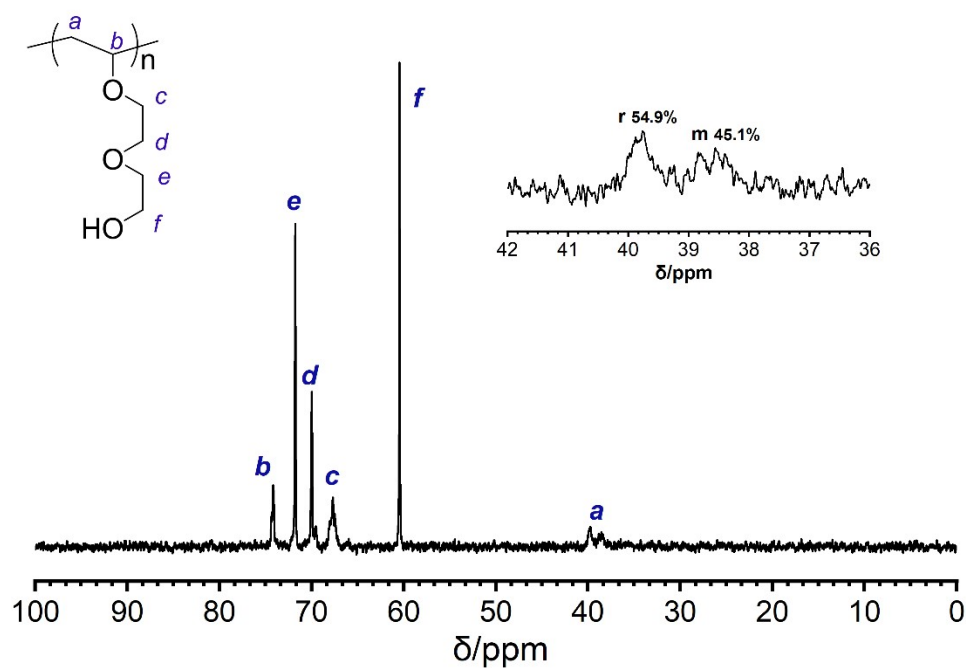


Figure S1. ^{13}C NMR spectrum of poly(DEGV) in D_2O . The inset shows the chemical structures of the poly(DEGV) with full peak assignments. The structures correspond to those estimated in Figure S1.

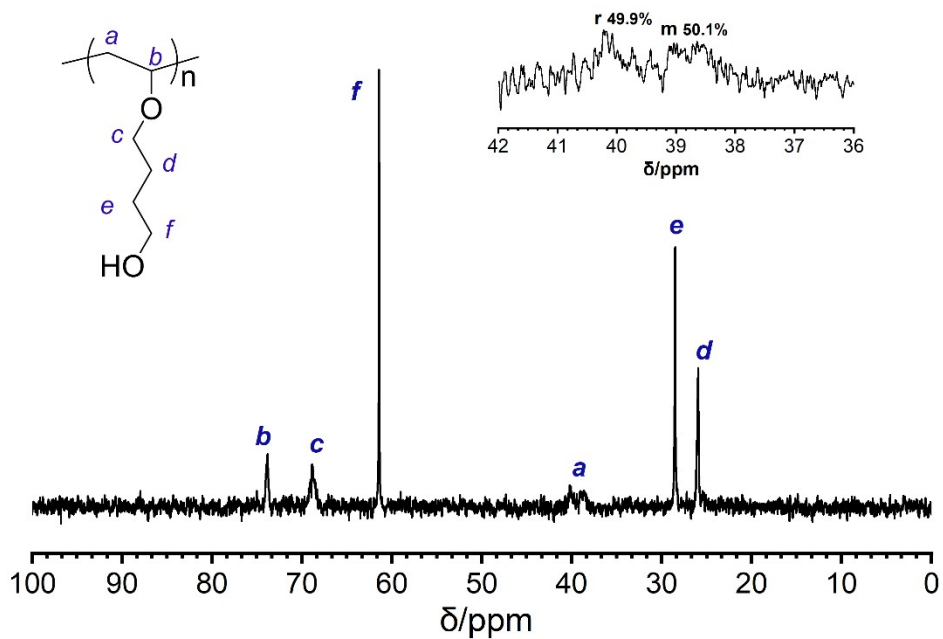


Figure S2. ^{13}C NMR spectrum of poly(HBVE) in D_2O . The inset shows the chemical structures of the poly(HBVE) with full peak assignments. The structures correspond to those estimated in Figure S2.

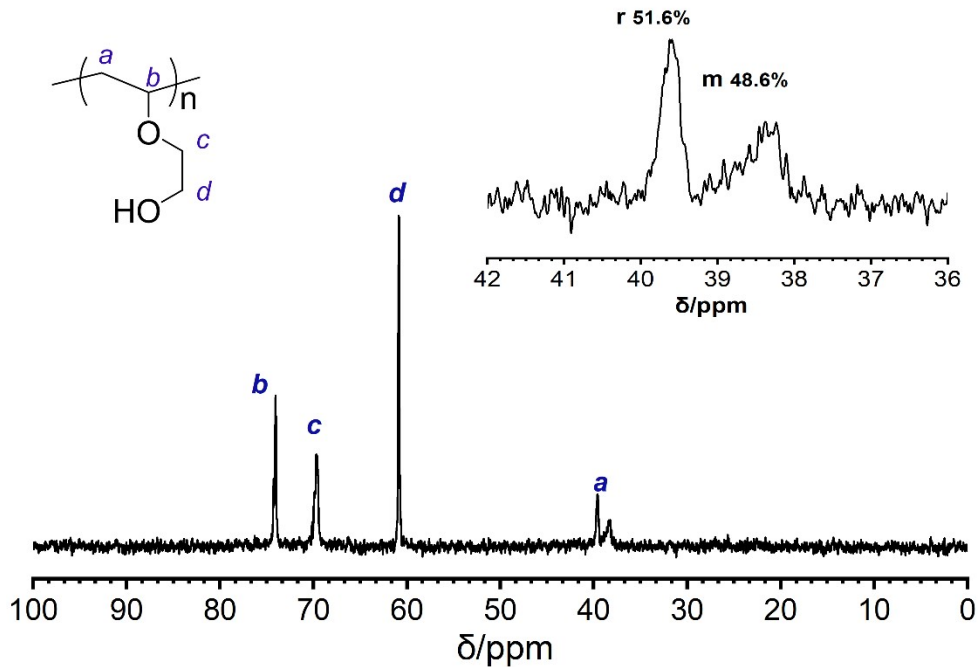


Figure S3. ^{13}C NMR spectrum of poly(HEVE) in D_2O . The inset shows the chemical structures of the poly(HEVE) with full peak assignments. The structures correspond to those estimated in Figure S3.

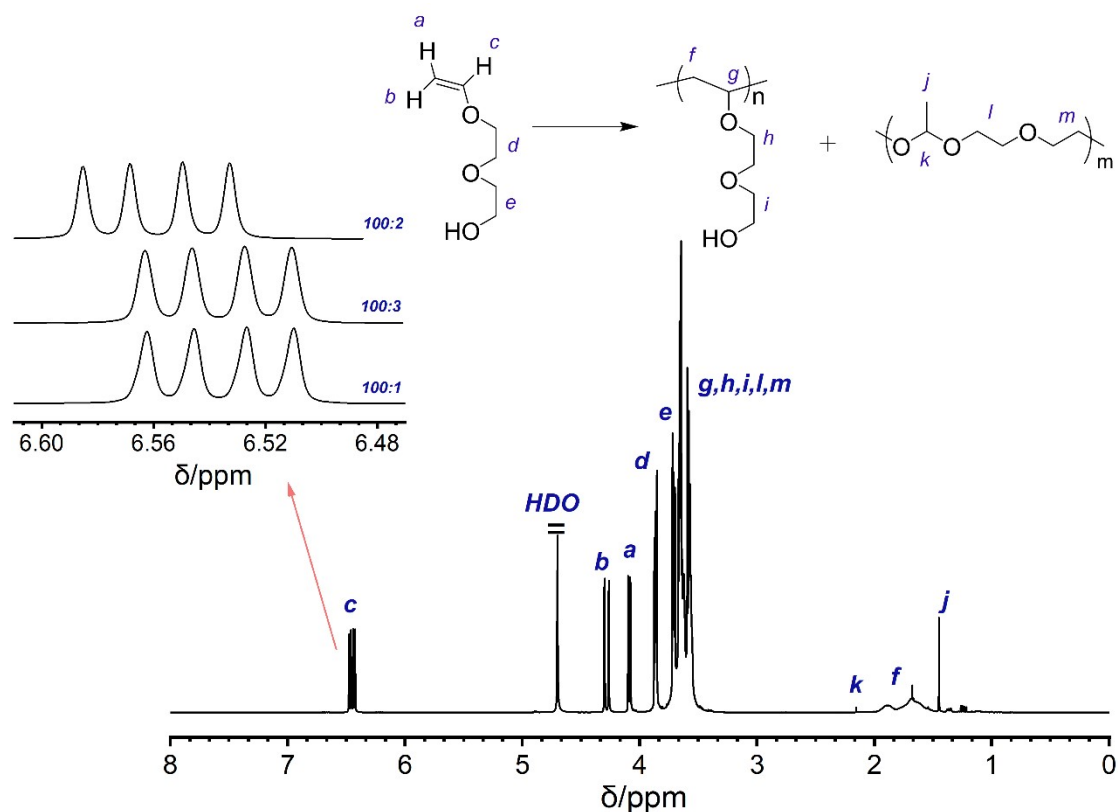


Figure S4. ^1H NMR spectrum (in D_2O at 20°C) of polymerization mixture of DEGV. The acetal contents (%) were calculated by the peak intensity ratio of the methyl proton of (poly)acetals at 1.1–1.2 ppm and the methylene proton of the main chain derived from poly (hydroxyl-functional vinyl ether) at 1.3–1.9 ppm.

Table S1. ^1H Chemical Shifts of Vinyl Group Adjacent to Ether Oxygen in Vinyl Ethers

Monomer	δ^a (ppm)		
	tran (H^a)	cis (H^b)	gem (H^c)
DEGV	4.16	4.36	6.52
HBVE	4.15	4.37	6.51
HEVE	4.17	4.38	6.55
IBVE	3.95	4.17	6.44

Chemical structure of a vinyl ether monomer with protons labeled a , b , and c .

^a Measured on a ^1H NMR (400 MHz) spectrometer at 20°C using a coaxial system (reference: CDCl_3 with 0.1% TMS). All the signals are averaged shift values of identical signals. Protons H^a , H^b , and H^c are shown on the right side of Table S1.

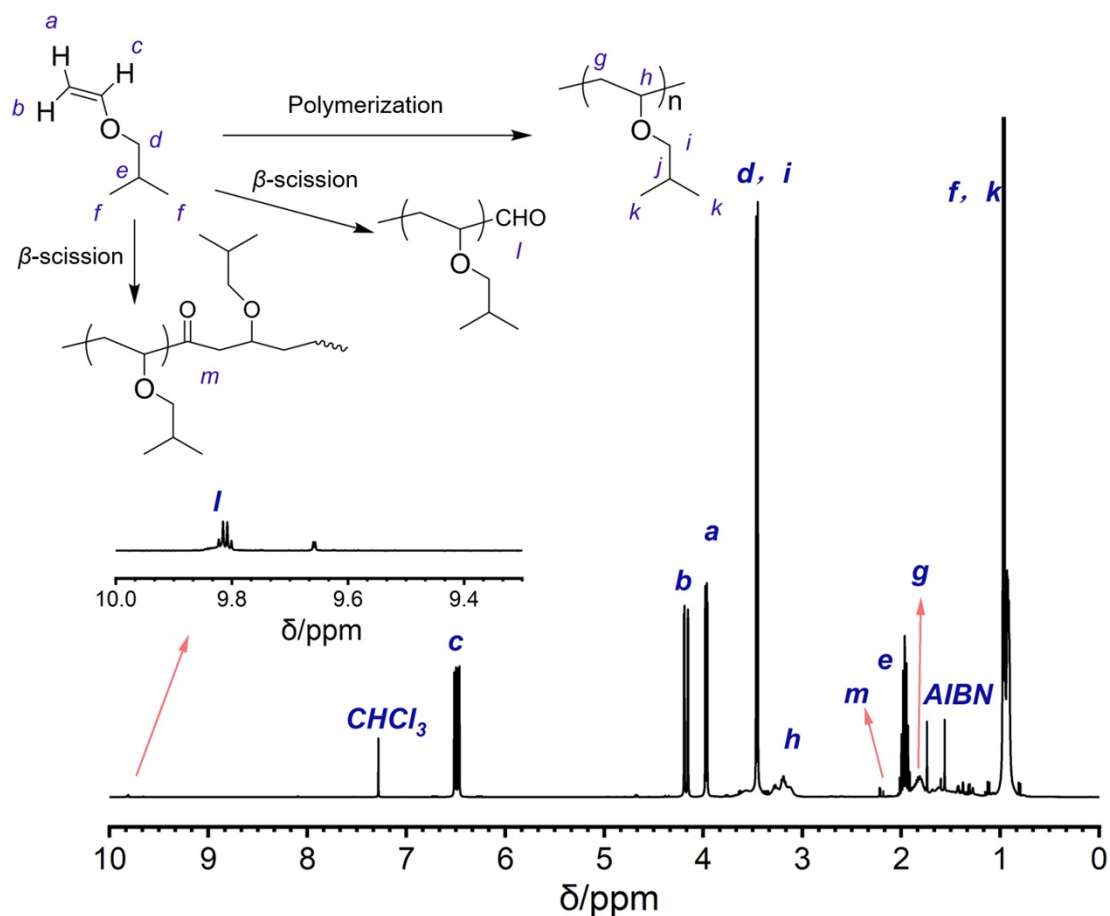


Figure S5. ^1H NMR spectrum (in CDCl_3 at $20\text{ }^\circ\text{C}$) of polymerization mixture of IBVE.

The selectivity (%) is obtained by integration values of $100 \times (g/2) / [c + (g/2) + (l/3)]$. The conversion (%) can be calculated by integration values of $100 \times (f/2) / [c + (g/2)]$ in the case of 100 % selectivity.

The structural identification of aldehyde as the terminal end-group of poly(IBVE) is not always performed from its mass spectrum, especially when other oligomers with the same molecular weight may be formed. Notably, an intensive peak assignable to $-\text{CH}_2\text{C}=\text{OCH}_2-$ protons was observed unexpectedly at 2.3-2.8 ppm although the peak assignable to the terminal $-\text{CHO}$ end-group generated via β -scission of growing polymer radical as a presumed chain-end forming reaction appeared only weakly at 9.8 ppm.

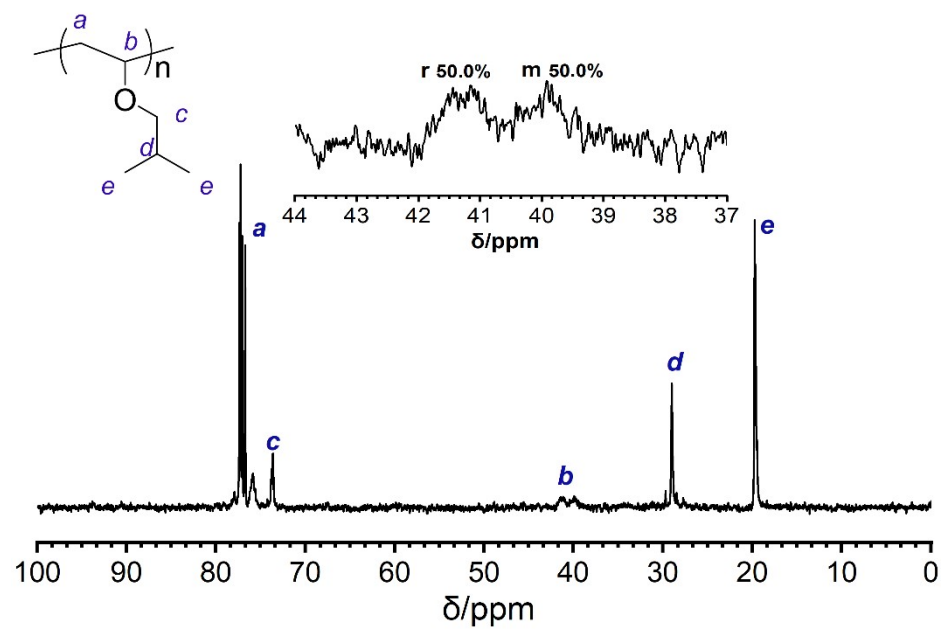


Figure S6. ^1H NMR spectrum (in CDCl_3 at 20°C) of poly(IBVE).