

Supplementary Material

Cationic polymerization of isobutyl vinyl ether in aqueous media: physical chemistry tricks to fight against thermal runaway

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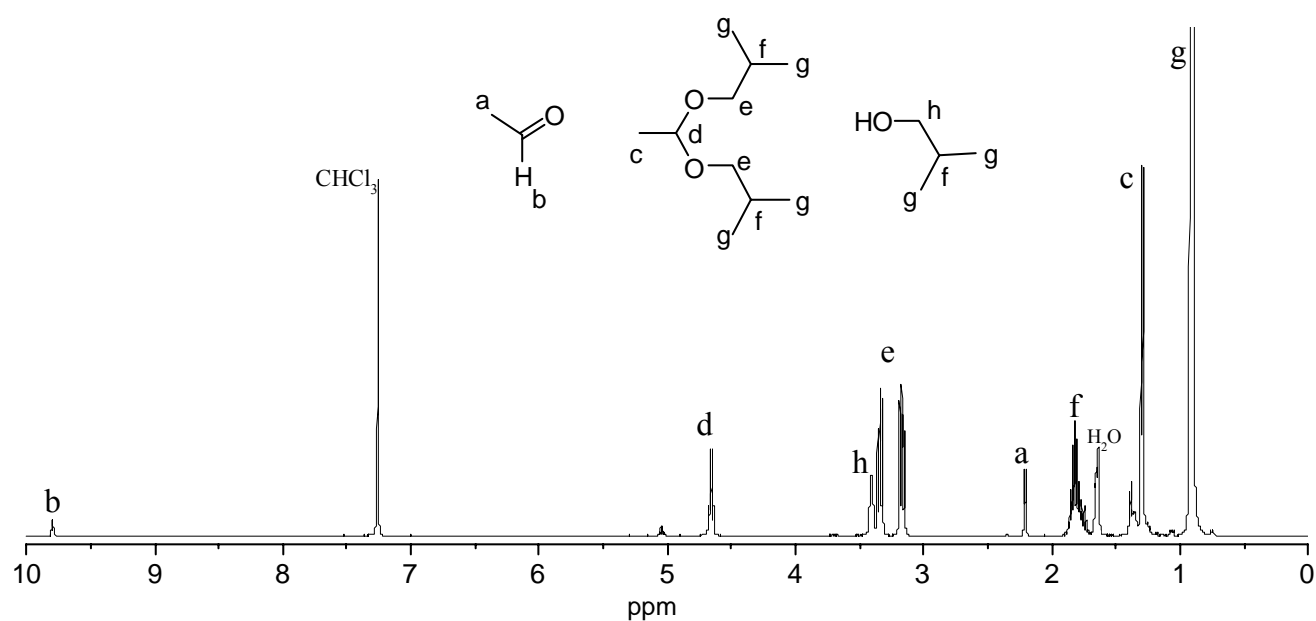


Figure S1. ¹H NMR spectrum of the reaction mixture (organic phase) after IBVE polymerization with DBSA at 20 °C (run 2, Table 1)

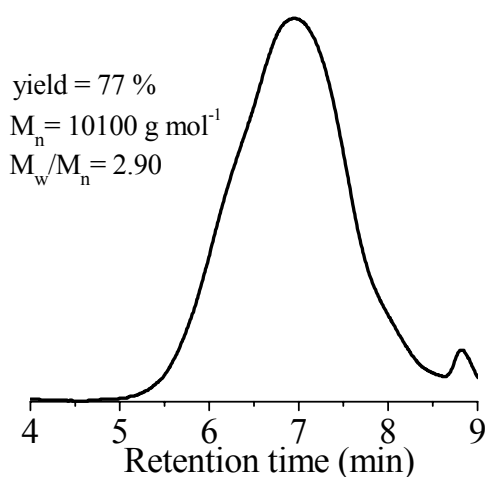


Figure S2. SEC trace of poly(isobutyl vinyl ether) synthesized in with BF_3OEt_2 as a catalyst *n*-hexane at 0 °C: IBVE: 1 mL; *n*-hexane: 1 mL; BF_3OEt_2 : 0.055 g; reaction time: 4 min. Terminal groups: acetal: 45.6%; aldehyde: 31.9%; alkenal: 4.9%; internal double bond (per chain): 0.56.

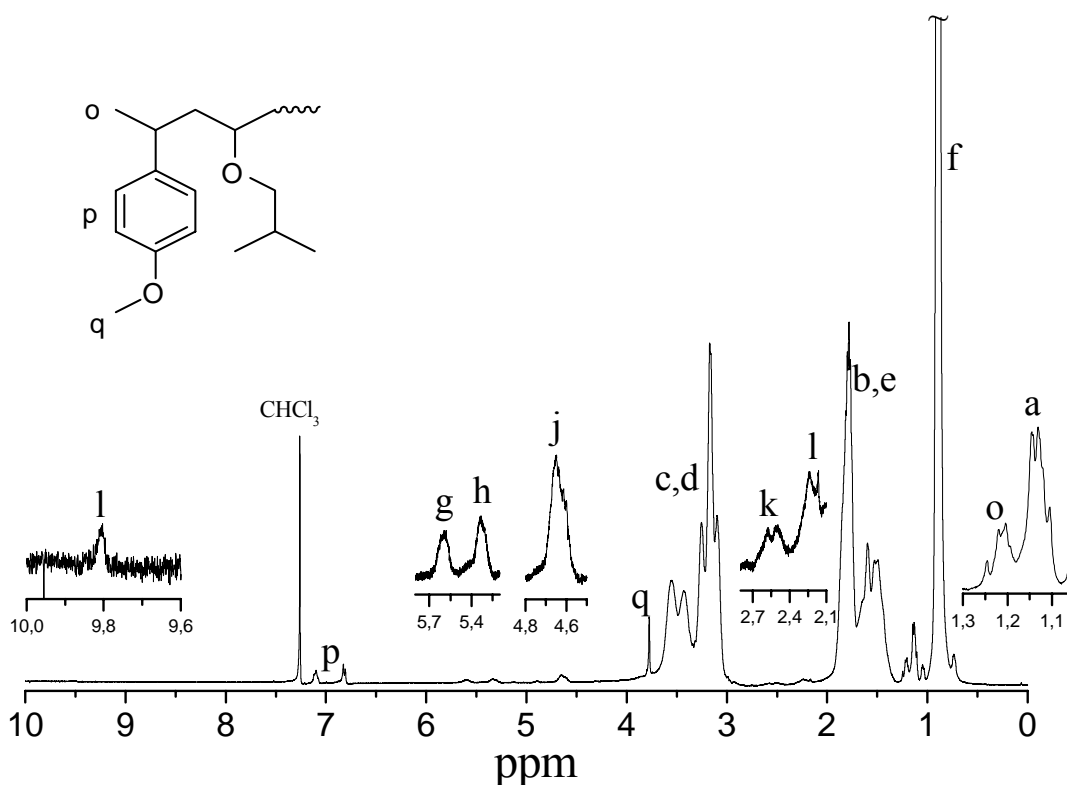


Figure S3. ^1H NMR spectrum of poly(isobutyl vinyl ether) synthesized with 1-(4-methoxyphenylethanol)/ BF_3OEt_2 initiating system in aqueous dispersion at 0 °C (run 14, Table 3).

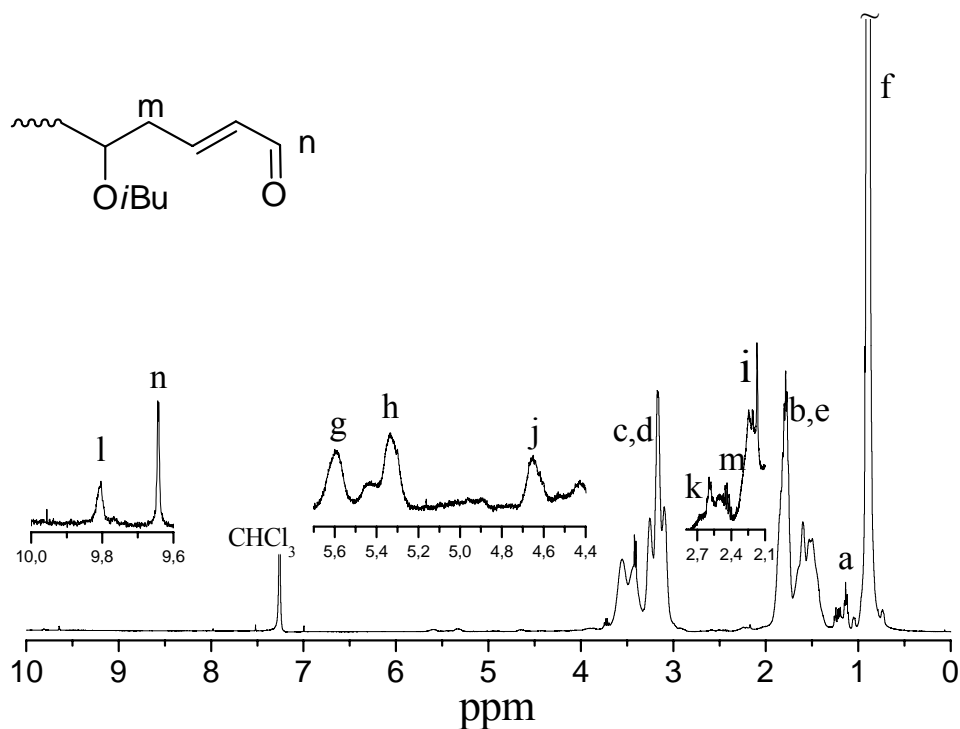


Figure S4. ¹H NMR spectrum of poly(isobutyl vinyl ether) synthesized with BF₃OEt₂ as co-initiator in aqueous dispersion at 0 °C: V(H₂O)=1ml, V(IBVE)=1ml, V(Hex)=1ml, m(BF₃OEt₂)=0.028g. M_n(SEC)=7530 g mol⁻¹, M_w/M_n=3.36, Yield=96%.

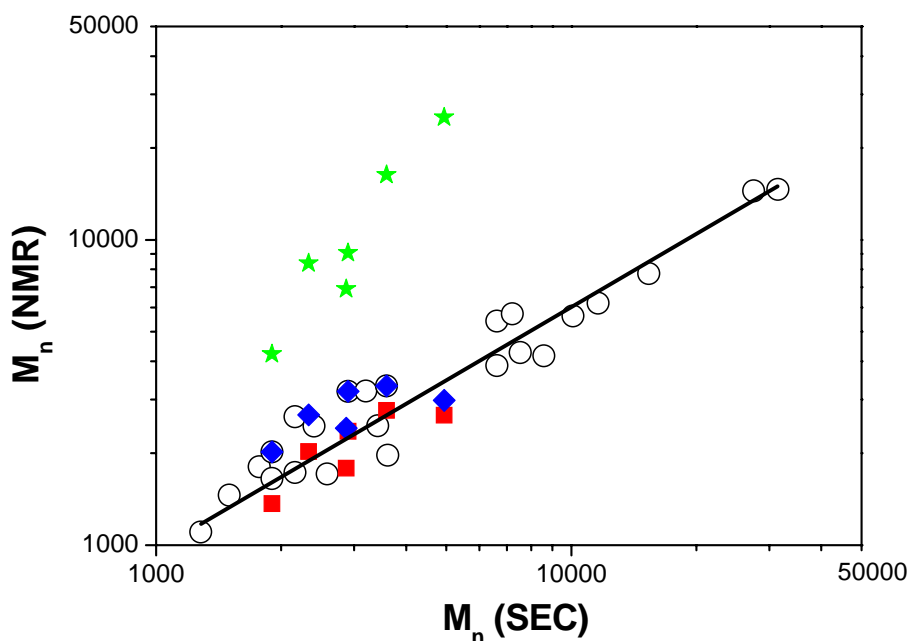


Figure S5. Correspondence between average molar masses of poly(isobutyl vinyl ether)s as determined by SEC and ¹H NMR spectrum from α -chain ends for experiments done in absence (○) or in presence (◆, ★, ■) of pMOS-OH, assuming α -chain ends arising uniquely from water, uniquely from pMOS-OH, or from both, respectively.

Table S1. Test of Stability of Non-Polymerizing IBVE Direct Emulsions (Without n-Hexane)

Entry	DBSA-Na (%)	Brij 35 (%)	Brij 78 (%)	Rewopol HV2 (%)	Visual stability (min)
1	2	2			0
2	2	4			1
3	2	11			15
4	2		6		5
5	2		14		10
6	2			6	10
7	2	8	4		35
8		8		6	> 120