

# Supporting Information

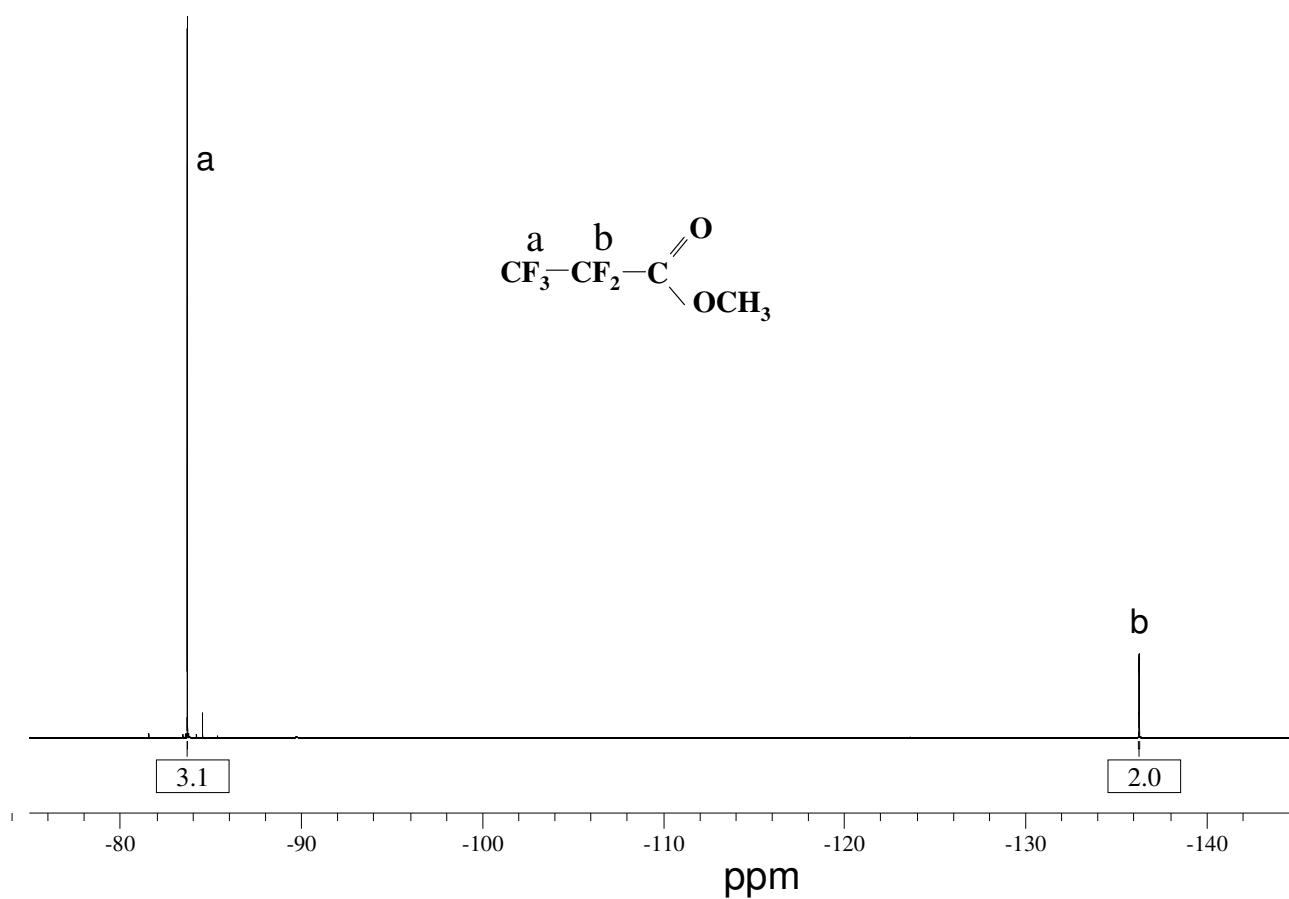
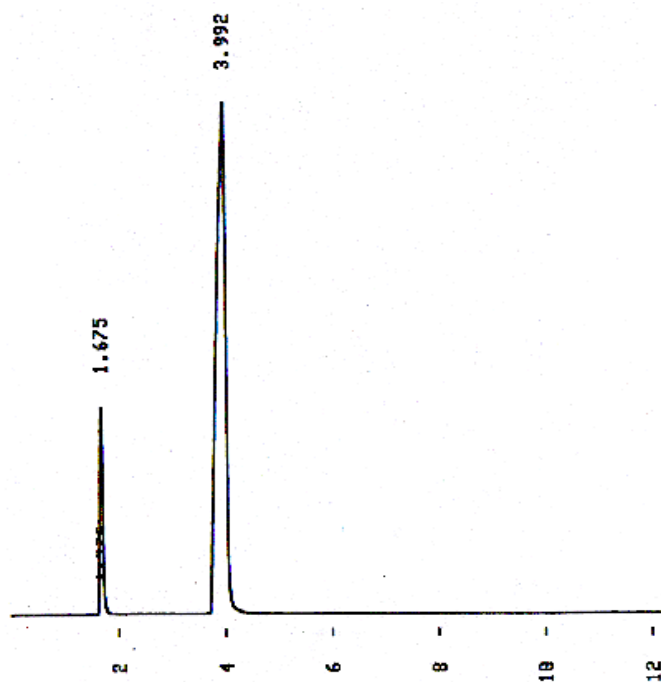
## Anionic Ring–Opening Polymerization of Hexafluoropropylene Oxide using Alkali Metal Fluorides as Catalysts: a Mechanistic Study

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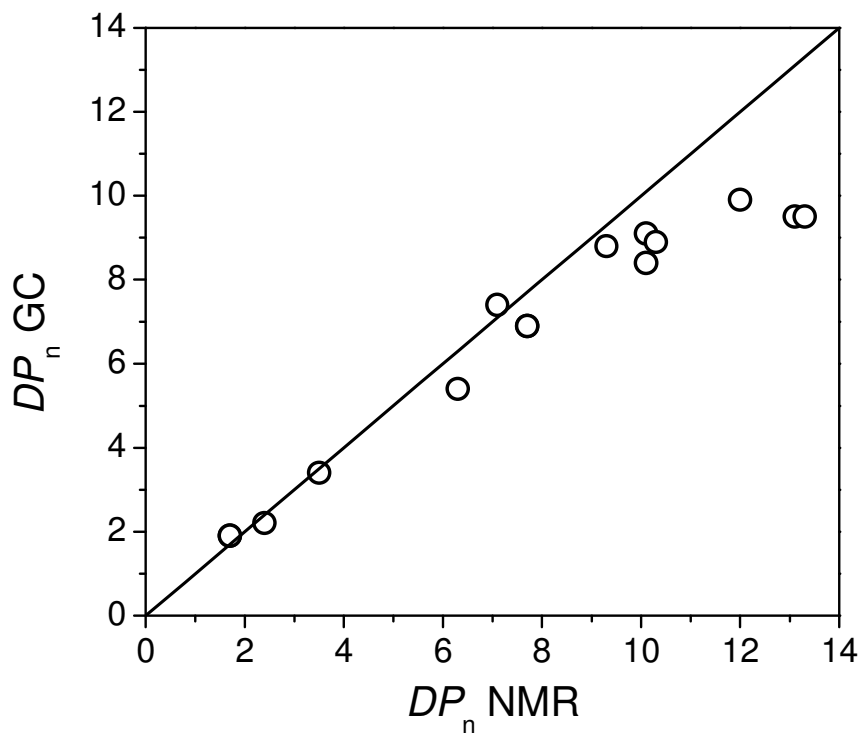
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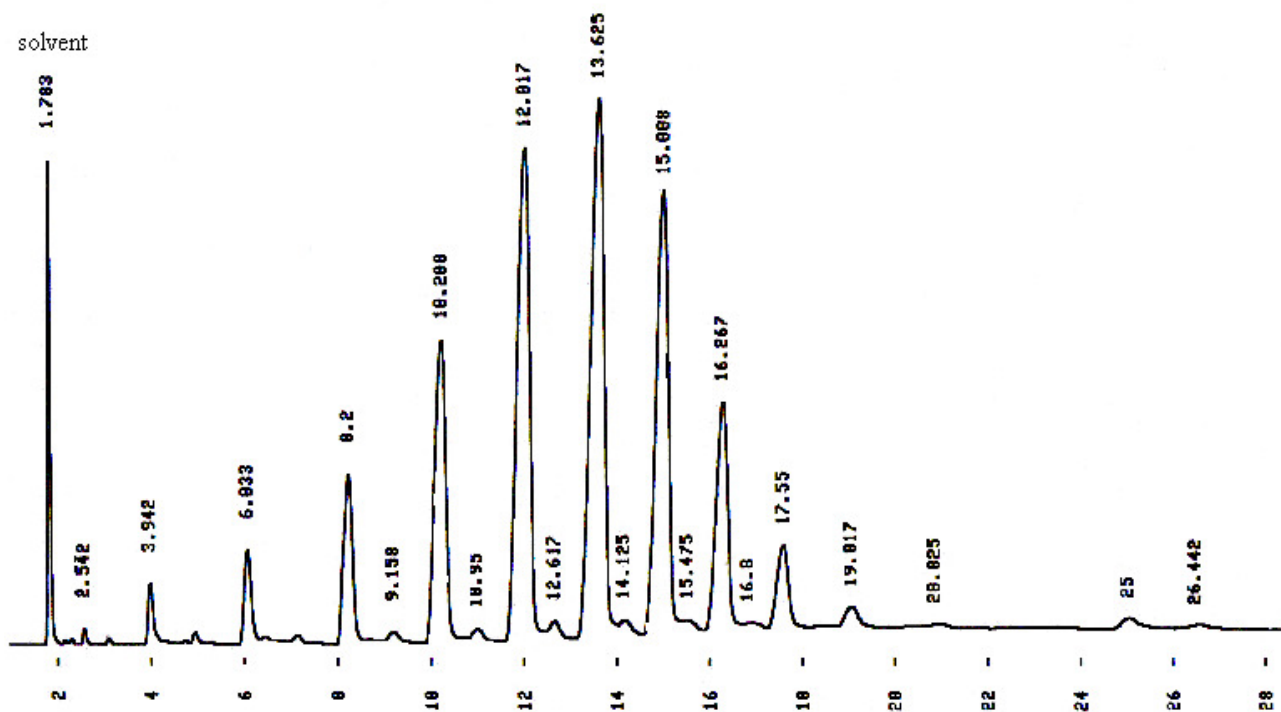
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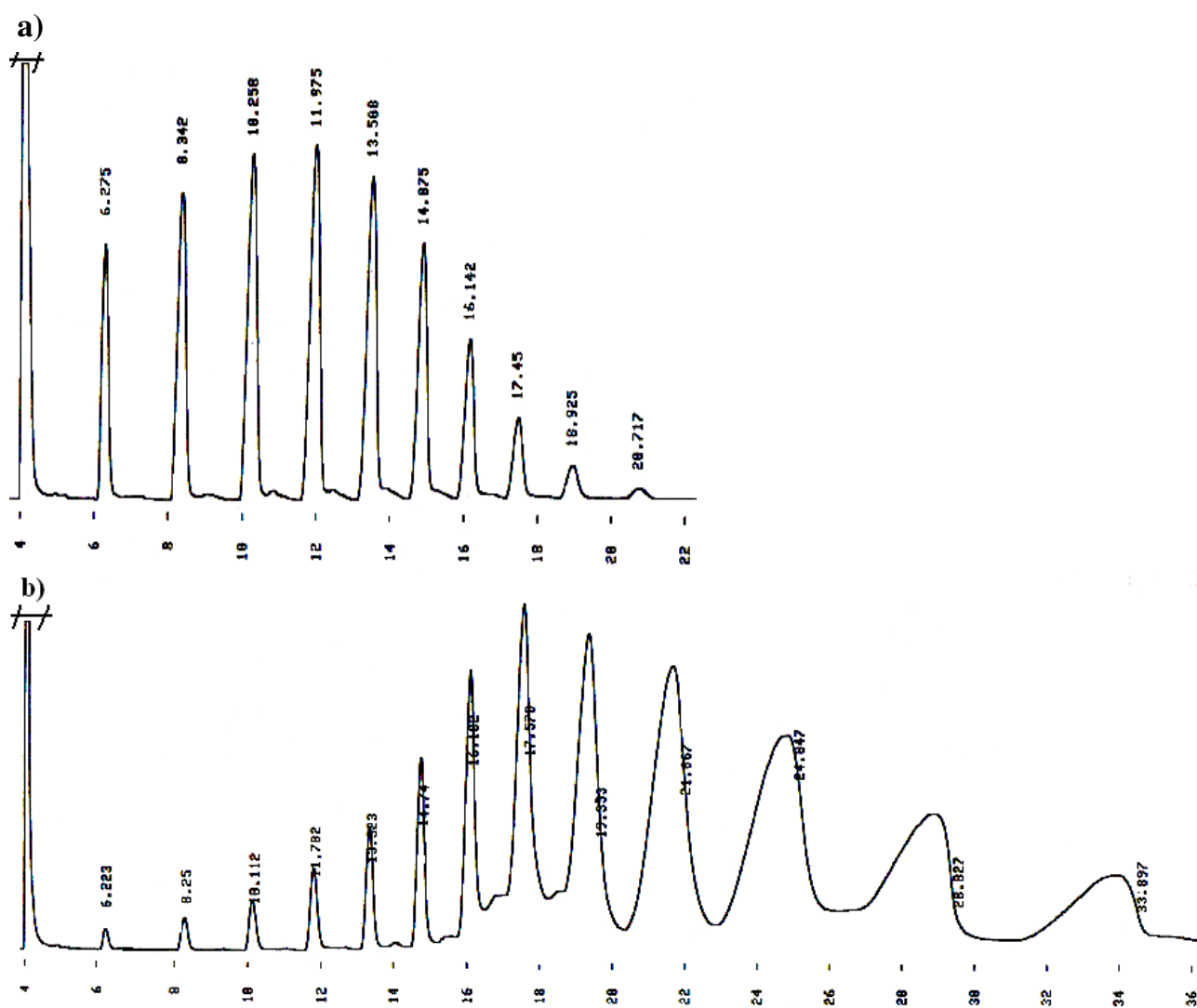
**Figure S1.** GC-chromatogram (top) and  $^{19}\text{F}$  NMR spectrum (bottom) of the product obtained by HFPO reaction with NaF/tetraglyme catalytic system:  $\text{C}_4\text{F}_5\text{H}_5$  10 mL; CsF:tetraglyme ~1:1.8; HFPO 59 g; [HFPO]:[CsF]=15; temperature  $-35^\circ\text{C}$ ; polymerization time 2 h.



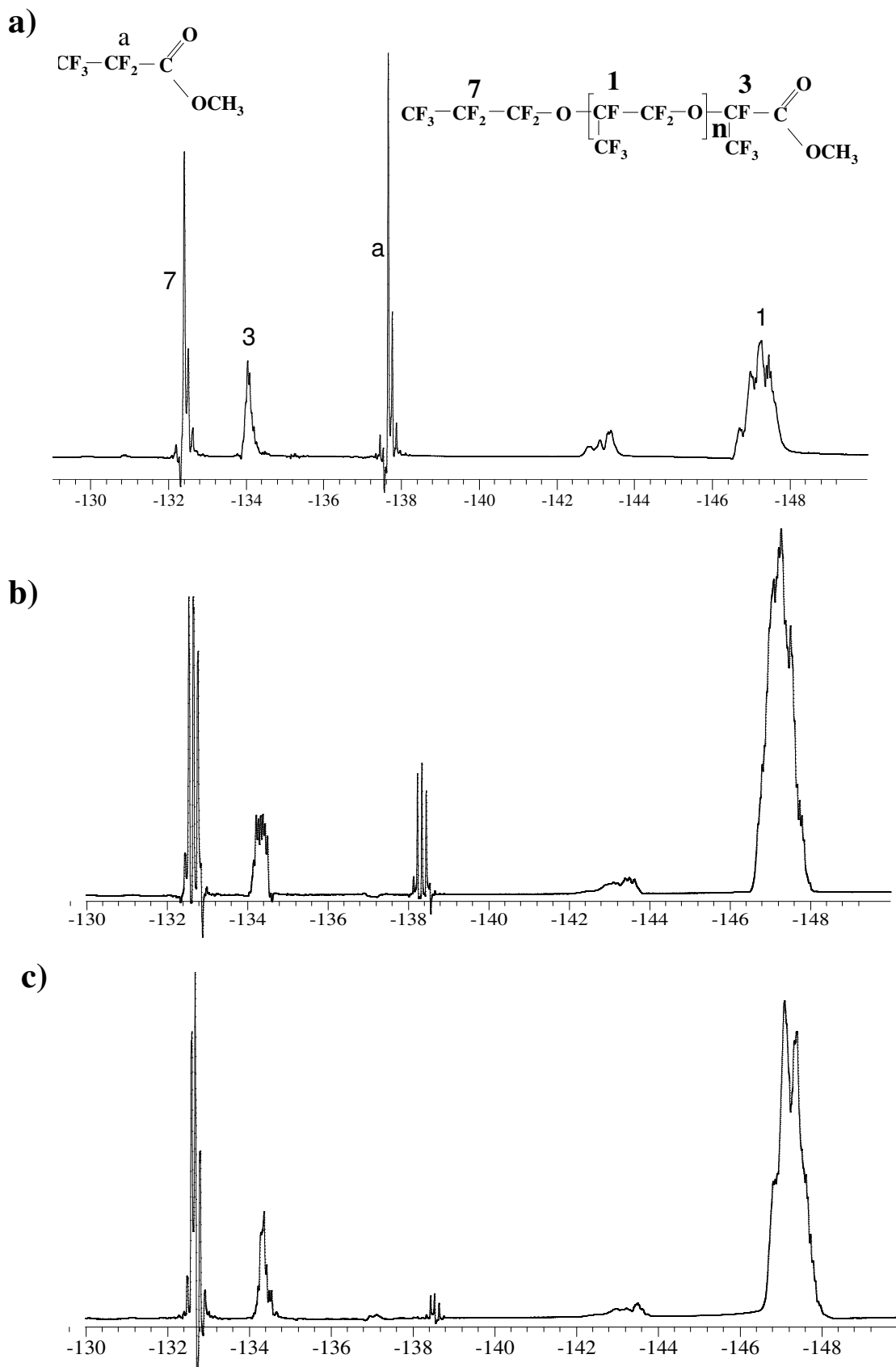
**Figure S2.** Correlation between average degree of polymerization  $DP_n$  as calculated from NMR and GC (for precise procedure of calculation, see main text).



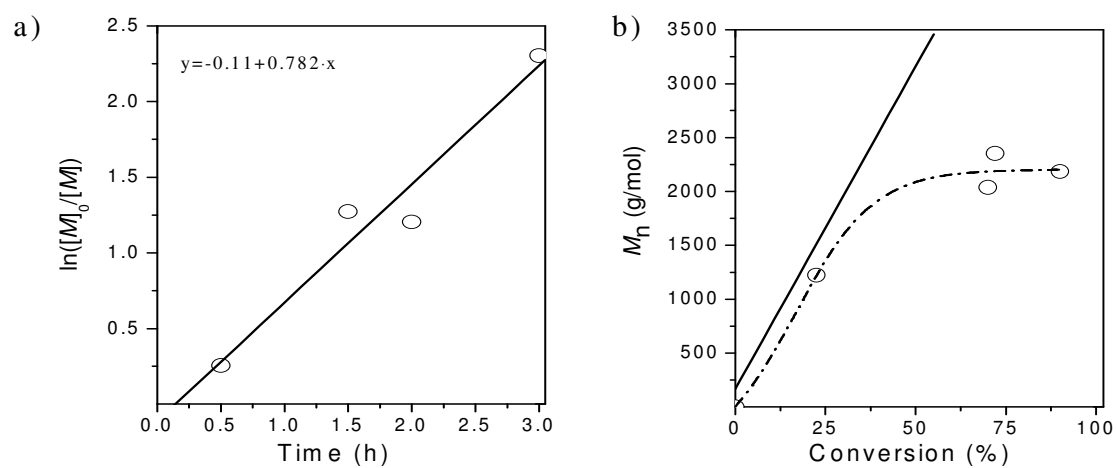
**Figure S3.** Gas chromatogram of the product obtained with KF/tetraglyme catalytic system at 20°C:  $C_4F_5H_5$  10mL; HFPO 46g;  $[KF]_0:[tetraglyme]_0 \sim 1:1.8$ ;  $[HFPO]_0/[catalyst]_0=39$ ; reaction time 3h.



**Figure S4.** Gas chromatograms of oligo(hexafluoropropylene oxide)s obtained with KF/tetraglyme system at 0°C and at different HFPO conversions: (a) Conv. 22.5%;  $DP_1=28.5\%$ ; (b) Conv. 72.0%;  $DP_1=5.7\%$ .



**Figure S5.** Fragments of  $^{19}\text{F}$  NMR spectra of the products obtained by HFPO polymerization with KF/tetraglyme catalytic system at  $0^\circ\text{C}$  and different conversions: (a) Conv. 22.5%;  $\text{DP}_1=28.5\%$ ; polymerization time 0.5h; (b) Conv. 72%;  $\text{DP}_1=5.7\%$ ; polymerization time 1.5h; (c) Conv. 90%;  $\text{DP}_1=1\%$ ; polymerization time 3h.



**Figure S6.** (a)  $\ln([M]_0/[M])$  vs. time plot and (b)  $M_n$  vs. conversion plot for the polymerization of hexafluoropropylene oxide in the presence of KF/tetraglyme system at  $0^\circ\text{C}$ :  $\text{C}_4\text{F}_5\text{H}_5$  10mL; HFPO 45 g;  $[\text{KF}]_0:[\text{tetraglyme}]_0 \sim 1:1.8$  (mol/mol);  $[\text{HFPO}]_0/[\text{KF}]_0=40$ .