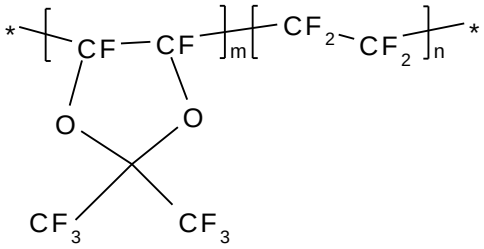
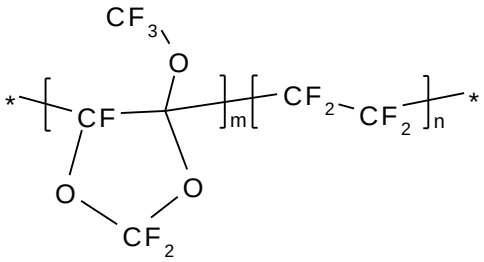
SCHEME CAPTIONS

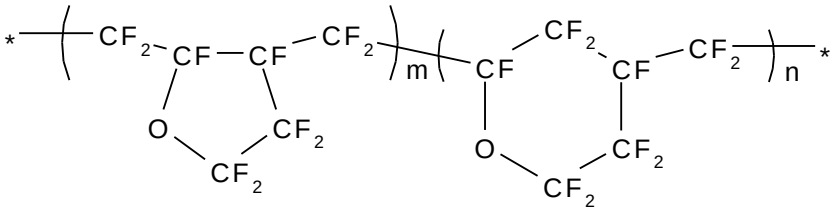
Scheme 1. The chemical structures of Teflon AF®, Cytop®, and Hyflon AD®.



Teflon AF

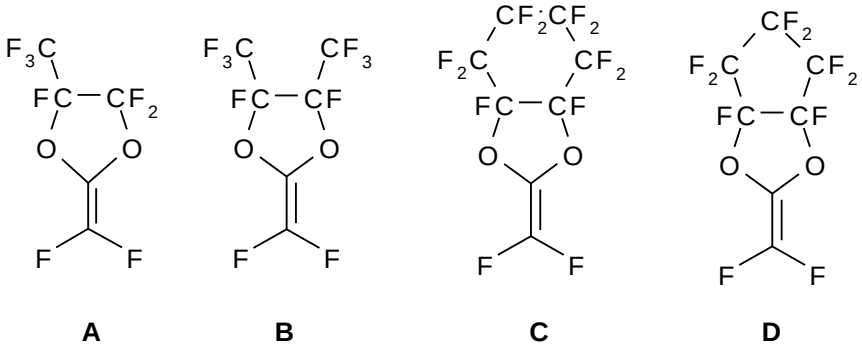


Hyflon AD

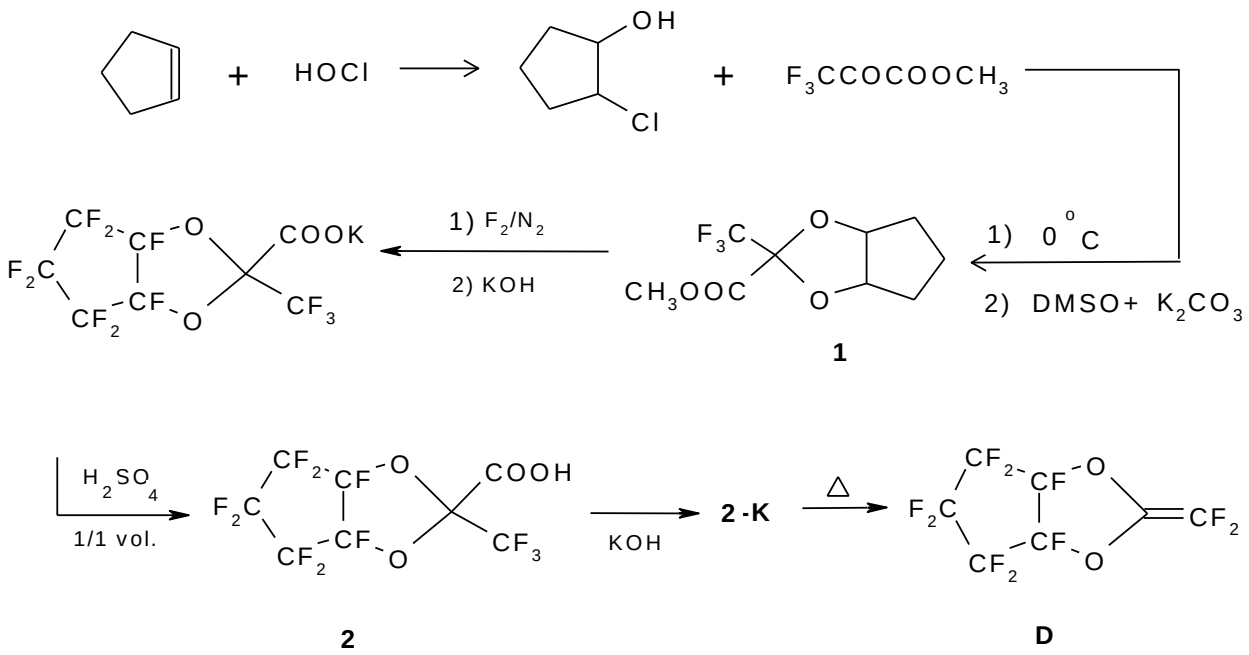


Cytop

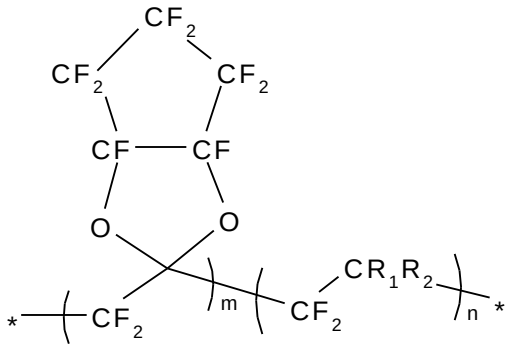
Scheme 2. Chemical structures of substituted perfluoro-2-methylene–1,3-dioxolane derivatives.



Scheme 3. Synthetic route for perfluoro-3-methylene-2,4-dioxabicyclo[3,3,0] octane (monomer D).



Scheme 4. Structure of copolymers based on perfluoro-3-methylene-2,4-dioxabicyclo[3,3,0] octane (monomer D) with fluorovinyl monomers.



R_1, R_2 = F, Cl, H, OCF_3 or OC_3F_7

FIGURE CAPTIONS

Figure 1. Polymerization rates of perfluorodioxolane monomers versus their methylene double bond polarity.

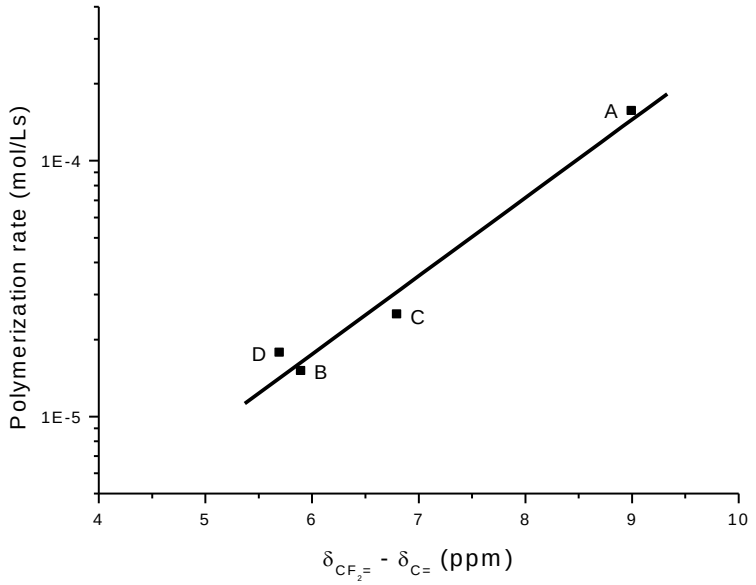


Figure 2. Monomer/polymer composition curve for the radical copolymerization of perfluoro-3-methylene-2,4-dioxabicyclo[3,3,0] octane (monomer D) with CTFE (curve 1 from Kelen-Tudos and curve 2 from Fineman-Ross law).

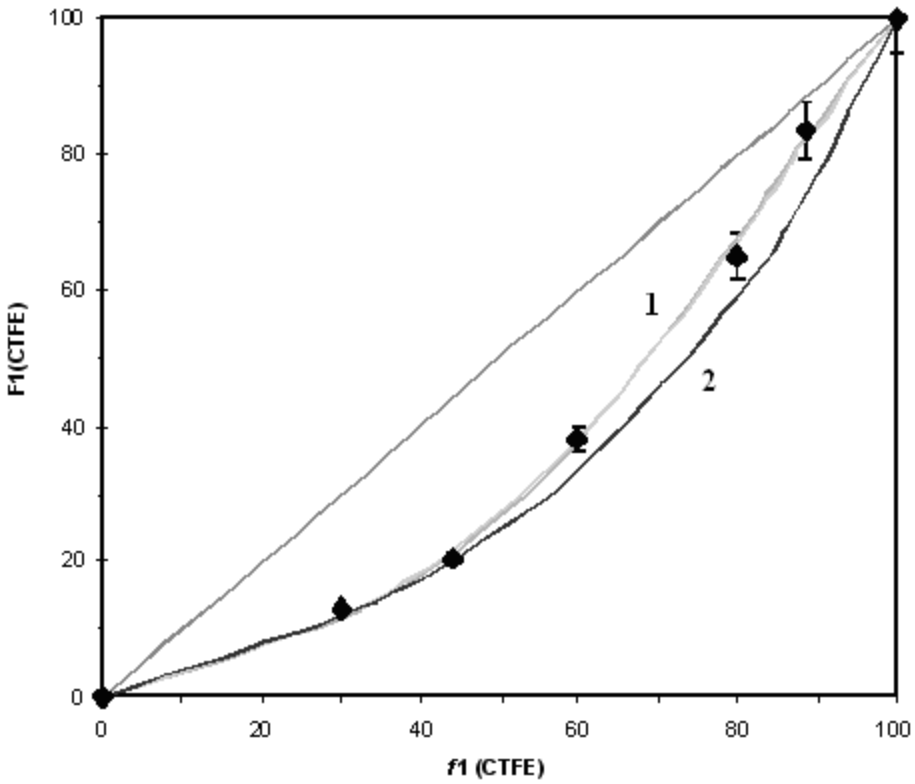


Figure 3. Composition dependence of perfluoro-3-methylene-2,4-dioxabicyclo[3,3,0] octane (monomer D) on T_g values of poly(CTFE-co-D) copolymer.

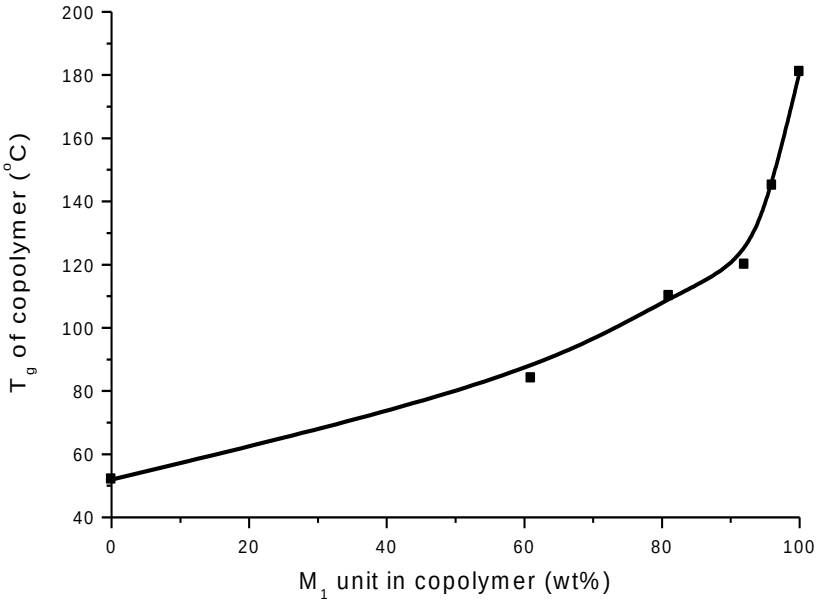


Figure 4. FTIR spectra of copolymers (run 2 and run 3 in Table 3).

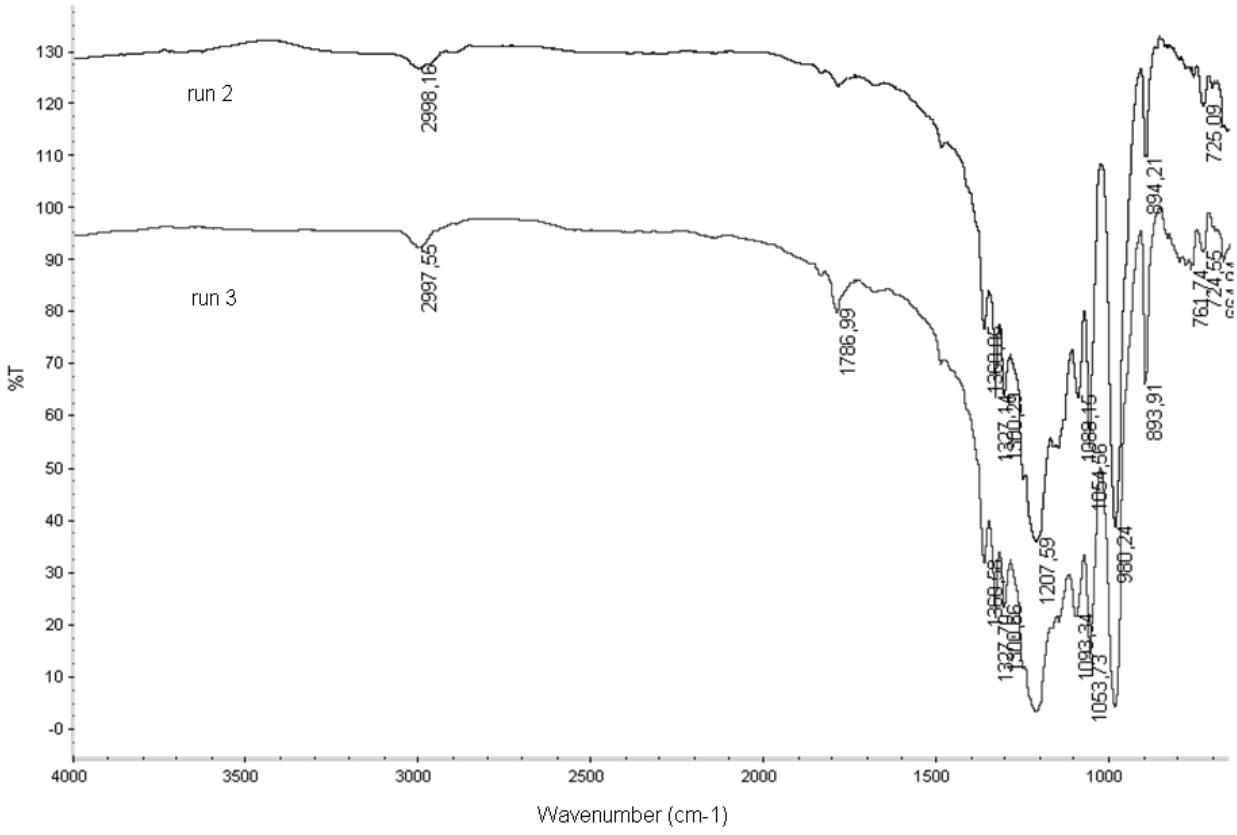


Figure 5. ^{19}F-NMR spectrum of copolymer Run 2 in Table 3.

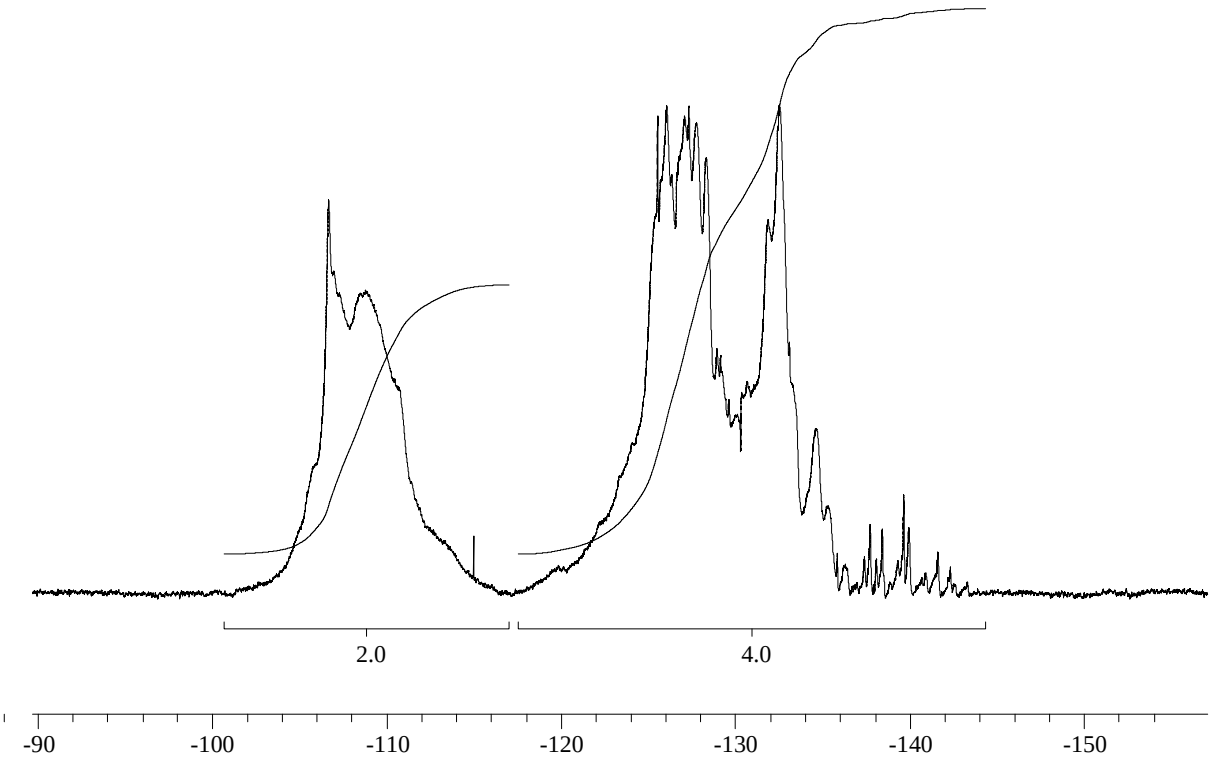
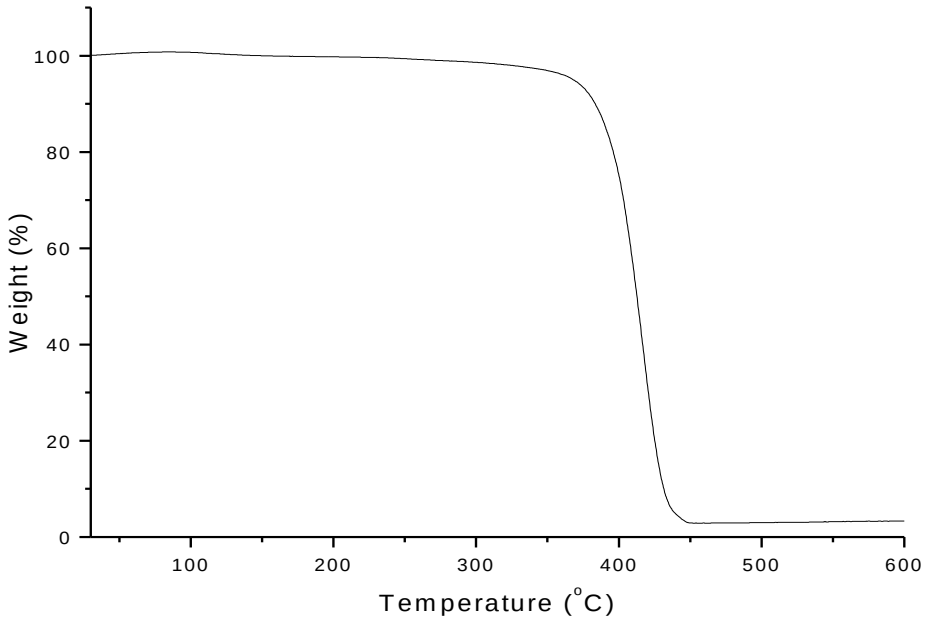
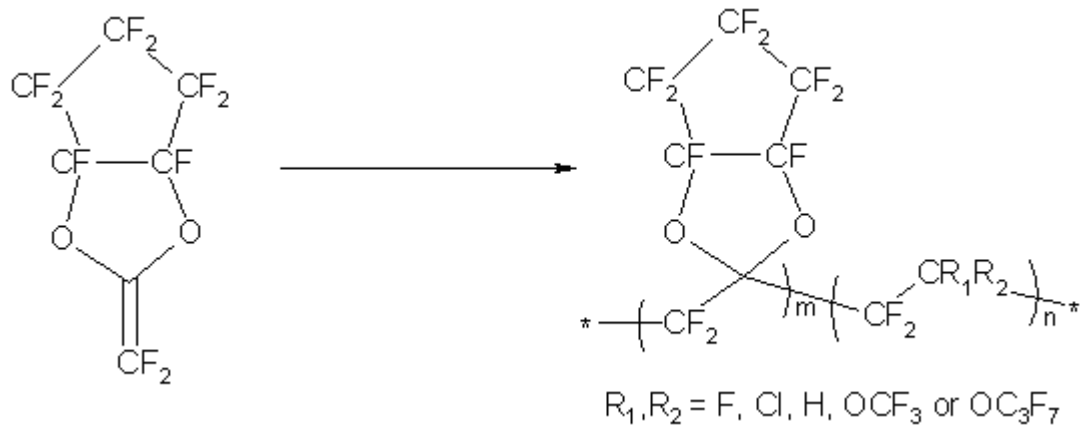


Figure 6. TGA thermogram of D/CTFE copolymer (Runs 3 in Table 3).



Graphical Abstract:



Perfluoro-3-methylene-2, 4-dioxabicyclo[3,3,0] octane was synthesized via direct fluorination of the corresponding hydrocarbon precursor by F_2/N_2. The homopolymer obtained was thermally stable with glass transition temperature (T_g) 180~190 ^oC. The film made from the homopolymer was transparent with refractive index 1.3290 at 633 nm. The copolymers of the monomer were prepared with chlorotrifluoroethylene, perfluoropropyl vinyl ether, perfluoromethyl vinyl ether and vinylidene fluoride. The copolymers obtained were soluble in hexafluorobenzene and perfluoro-2-butyltetrahydrofuran with T_g 84~145 ^oC. The films of the copolymers were flexible and transparent with a low refractive index (1.3350~1.3770 at 533 nm).