

Supporting Information

Superior Thermostability and Hydrophobicity of poly(Vinylidene Fluoride-*co*-Fluoroalkyl 2-trifluoromethacrylate)

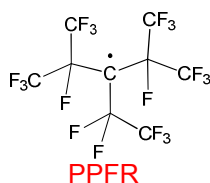
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List of Abbreviations:

CTA	Chain Transfer Agent
ITP	Iodine Transfer Polymerization
MAF	2-Trifluoromethacrylic acid
MAF- <i>t</i> Bu	Tertiary-butyl 2-Trifluoromethacrylate
MAF-C ₆ F ₁₃	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-(trifluoromethyl)acrylate
M _n	Number Average Molecular Weight
PPFR	Perfluorinated persistent radical
TAPPi	Tertiary amyl peroxyvalate
TBPPi	Tertiary butyl peroxyvalate
VDF	Vinylidene Fluoride

Structure of persistent branched fluorinated radical (PPFR)



Procedure for the radical copolymerization of VDF and MAF-C₆F₁₃

Synthesis of **P4** Copolymer. The preparation of copolymer (**P4**) was carried out in similar manner as **P1** using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) (1.031 g, 0.9 mol%) as the free radical initiator. Other details regarding the solvent mixture and

comonomer concentrations used were similar to that of run **P1**. The copolymerization was carried out at 65 °C, while stirring mechanically. The maximum pressure, P_{\max} reached was 16 bars. The reactor pressure was dropped to 10 bars at the end of the reaction (after 60 hours). The autoclave was weighed, chilled using ice for 30 minutes, and then unreacted VDF (8 g) was released. A white powder and a yellowish liquid were obtained on opening the autoclave. Purification of the obtained mass was carried out in identical fashion to that of **P1**. 8 g (35 wt %) of yellowish powder was obtained (run **P4**, Table 1).

Copolymers **P5-P9**

Other radical copolymerizations (runs **P5-P9**) were accomplished in the similar procedure as that of **P4**. The polymerization temperatures were 75 °C for **P5** (polymerization time: 24 hrs), and 90 °C for **P6**, **P7** and **P9**. An acetonitrile/ $C_4F_5H_5$ /water mixture was used as the medium for **P5** and **P6** runs, only $C_4F_5H_5$ was used for run **P7** whereas dimethyl carbonate was involved as the solvent in runs **P8** and **P9**. The initial pressure P_{ini} , maximum pressure P_{\max} and pressure attained at the end of polymerization, P_{\min} , for all copolymerizations are listed in Table S1.

Copolymers **P10** and **P11**.

After the insertion of MAF- C_6F_{13} (7.292 g, 15 mmol) and PPFR (1.031 g, 0.9 mol%) in acetonitrile/ $C_4H_5F_5$ /water solvent mixture, the autoclave was cooled to around -50 °C, where trifluoromethyl iodide (2.5 g, 12.7 mmol) and VDF (15 g, 234 mmol) were transferred. Then, the vessel was slowly heated to 90 °C, under mechanical stirring, for 18 hrs. At the end of the reaction, the autoclave was weighed, chilled in an ice bath and then 8 g of unreacted gases (VDF and CF_3I) were released. After opening the autoclave, the solvents were removed using vacuum and the white colored polymer was redissolved in minimum quantity of acetone. The total product mixture was precipitated from chilled pentane, filtered and then dried under

vacuum (10^{-2} bar) at 50 °C for 12 h which led to 14 g of white polymer powder (62 wt %, run **P11** in Table 1).

The reaction conditions for **P10** were similar to those of **P11** with [MAF-C₆F₁₃ ester]₀:[VDF]₀:[PPFR]₀:[CF₃I]₀ ratio was 88:12:0.3:1.

All CF₃-(polyVDF-*co*-MAF-C₆F₁₃)-CF₃ and CF₃-(polyVDF-*co*-MAF-C₂H₄C₆F₁₃)-CF₂I copolymers, obtained typically as white powders and were characterized by ¹H and ¹⁹F NMR spectroscopy (Figures S3-S22).

Various phases in the media

The polymerization reactions, carried out at different temperatures and pressures (Tables 1 and S1), were achieved in a metallic high pressure reactor that does not have any window to check the phase medium. It is assumed that VDF is located in both the liquid phase (that also contained the solvent, MAF-C₆F₁₃ monomer and short macroradicals) and in the gas phase, (i.e., the “sky” of the vessel also composed of other gases such as CF₃I for experiments **P10-P11** and the fluorinated solvent that is also volatile). Useful information on gaseous and liquid VDF in solvents has been published elsewhere.¹ In addition, the experimental conditions (various temperatures and pressures) can also make complex the medium with respect to the phase behavior of the polymerization mixture, and solubility of copolymeric chains (page 23 of the revised manuscript). The radical copolymerization should occur in the liquid phase and can be faster in case of higher pressure that induces a higher incorporation of VDF. The appropriate paragraph has been completed in page 14.

The different temperatures and initial, maximum and minimum pressures of the different experiments have been gathered in Table S1 in the supporting information.

As soon as certain molecular weights were reached, the copolymeric chains could also precipitate from the solution as evidenced by the presence of a white powder when the autoclave was opened (see experimental part in page 8). In addition, the solubility of the

copolymeric chains can also be strongly influenced by the comonomer composition (i.e., *elastomers* should be more soluble than *thermoplastic* crystalline copolymers). It can also be considered that at high temperature and at atmospheric pressure, the polymerization can be affected.

Table S1. Pressure changes in high pressure autoclaves during the radical copolymerization of vinylidene fluoride (VDF) and MAF-C₆F₁₃. P_{ini}, P_{max}, P_{min} are the initial pressure in the autoclave at room temperature after VDF was transferred and mechanical stirring was started, maximum pressure, after the desired polymerization temperature attained and minimum pressure reached at the end of polymerization. Solvent mixture for the copolymerization was C₄H₅F₅/acetonitrile/deionized water in 47.5:47.5:5.0 ratio, except for **P7**, C₄H₅F₅ (a) and for **P8** and **P9**, dimethyl carbonate (b) were used as solvents. Polymerization times for **P1-P3**, **P4** (as well as **P8**), **P5** were 20 hrs, 50 hrs, and 24 hrs respectively, whereas for **P6**, **P7** and **P9-P11**, the reaction time was 18 hrs.

Expt. No.	Temperature (°C)	P _{ini} (bar)	P _{max} (bar)	P _{min} (bar)
P1	65	10	20	8
P2	65	10	15	5
P3	55	8	15	10
P4	65	8	16	10
P5	75	12	25	12
P6	90	16	32	24
P7^{a)}	90	15	35	15
P8^{b)}	65	10	15	5
P9^{b)}	90	15	30	12
P10	90	10	20	15
P11	90	12	25	10

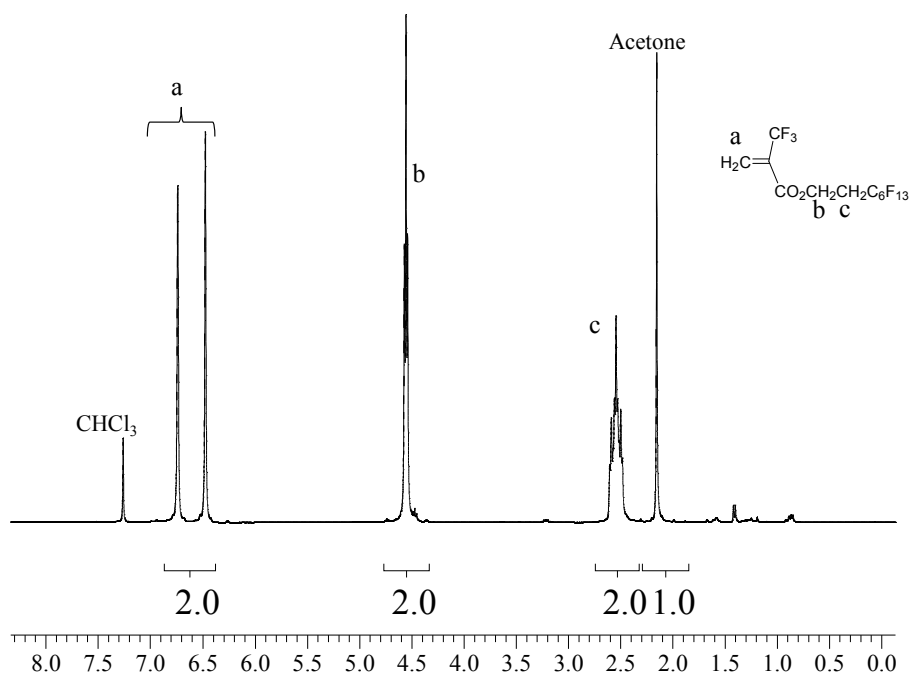


Figure S1. ^1H NMR spectrum of MAF- $\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}$ monomer recorded in CDCl_3 at room temperature.

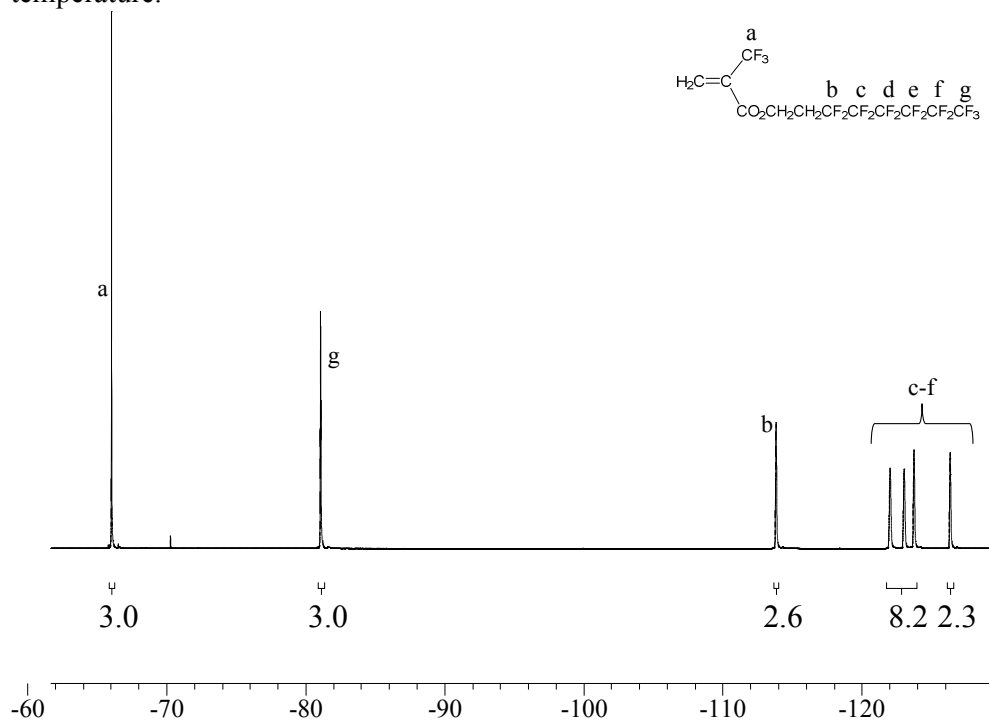


Figure S2. ^{19}F NMR spectrum of MAF- $\text{C}_2\text{H}_4\text{C}_6\text{F}_{13}$ monomer recorded in CDCl_3 at room temperature.

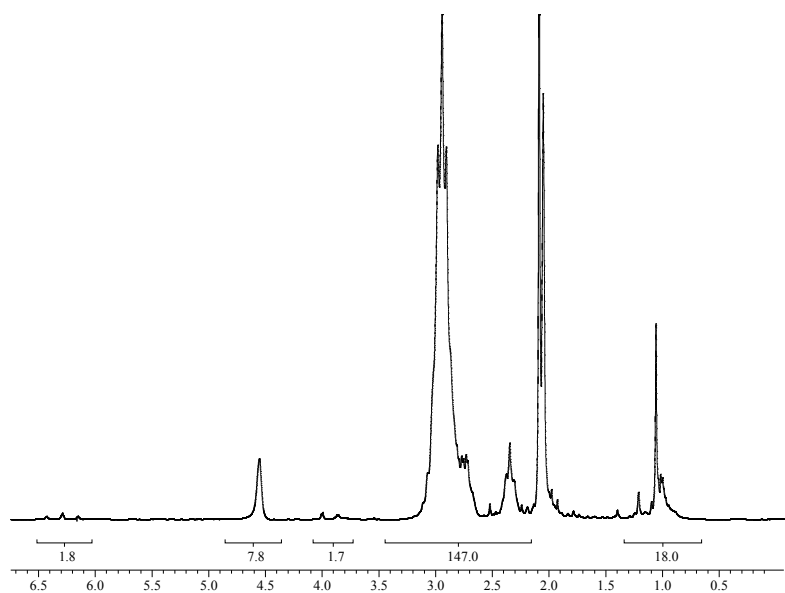


Figure S3. ^1H NMR spectrum of **P1** copolymer recorded in d_6 -acetone at room temperature.

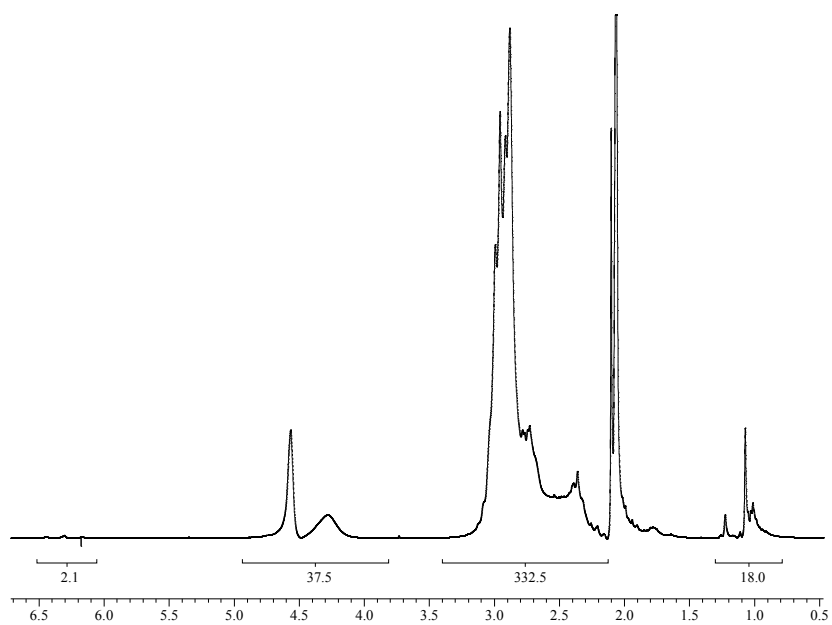


Figure S4. ^1H NMR spectrum of **P2** copolymer recorded in d_6 -acetone at room temperature.

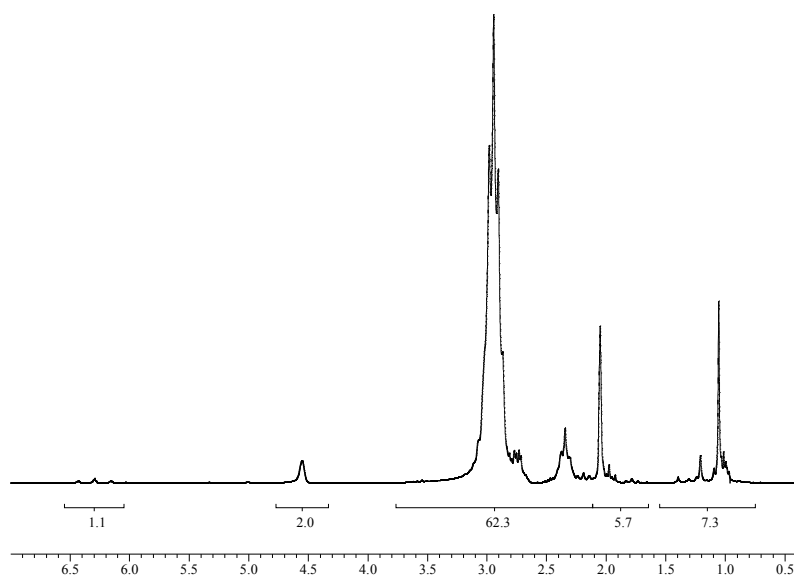


Figure S5. ^1H NMR spectrum of **P3** copolymer recorded in d_6 -acetone at room temperature.

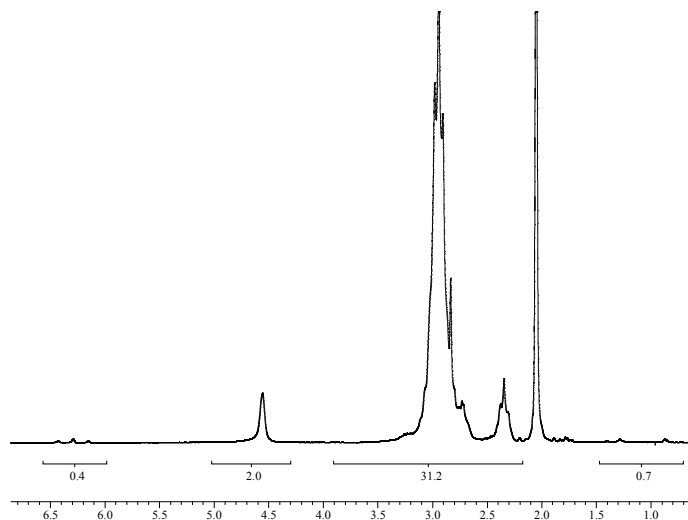


Figure S6. ^1H NMR spectrum of **P4** copolymer recorded in d_6 -acetone at room temperature.

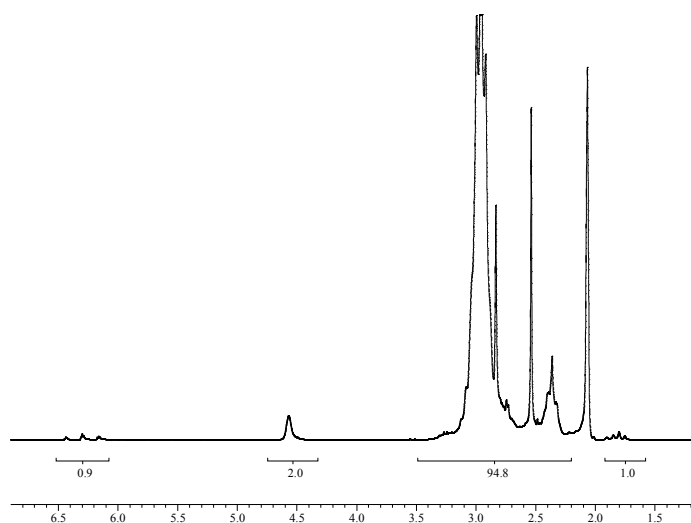


Figure S7. ^1H NMR spectrum of **P5** copolymer recorded in d_6 -acetone at room temperature.

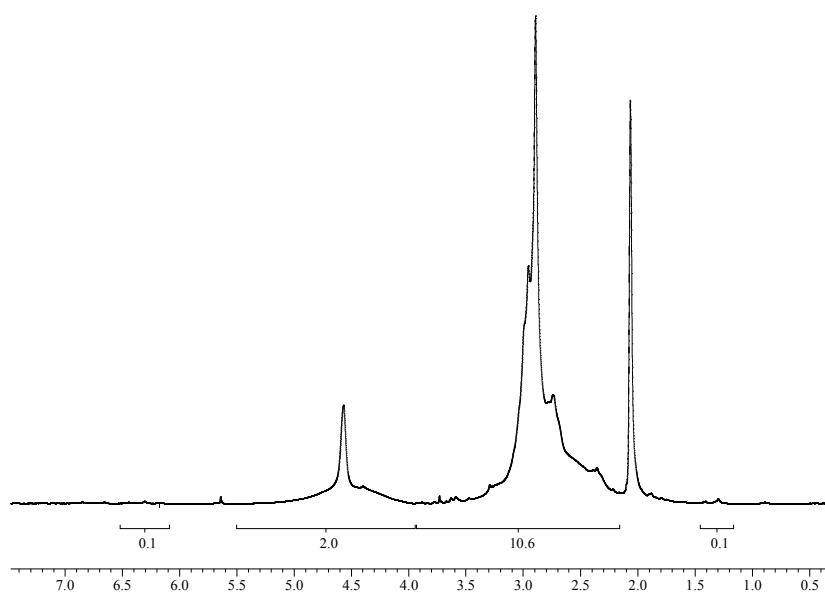


Figure S8. ^1H NMR spectrum of **P6** copolymer recorded in d_6 -acetone at room temperature.

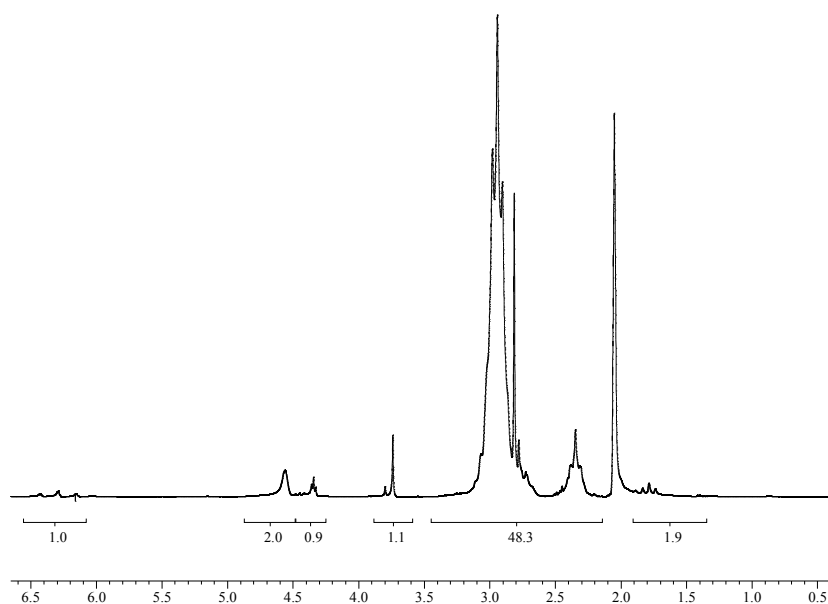


Figure S9. ^1H NMR spectrum of **P8** copolymer recorded in d_6 -acetone at room temperature.

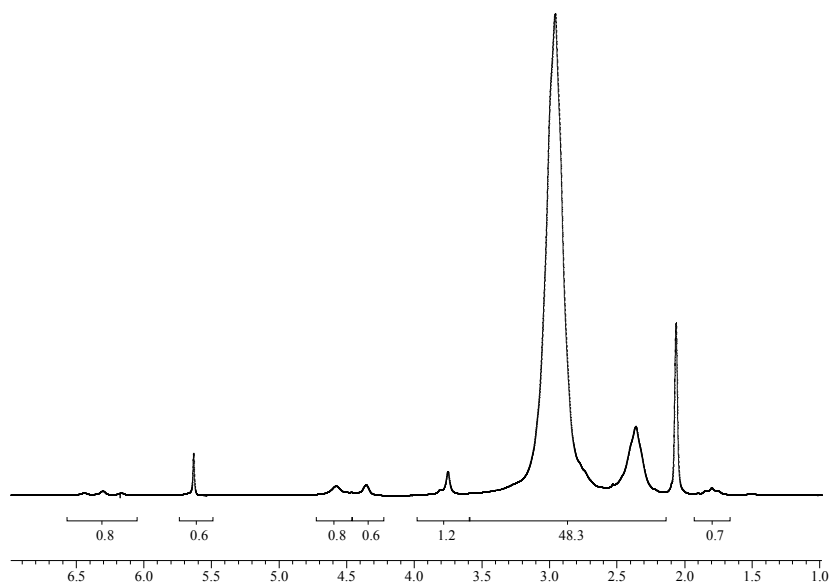


Figure S10. ^1H NMR spectrum of **P9** copolymer recorded in d_6 -acetone at room temperature.

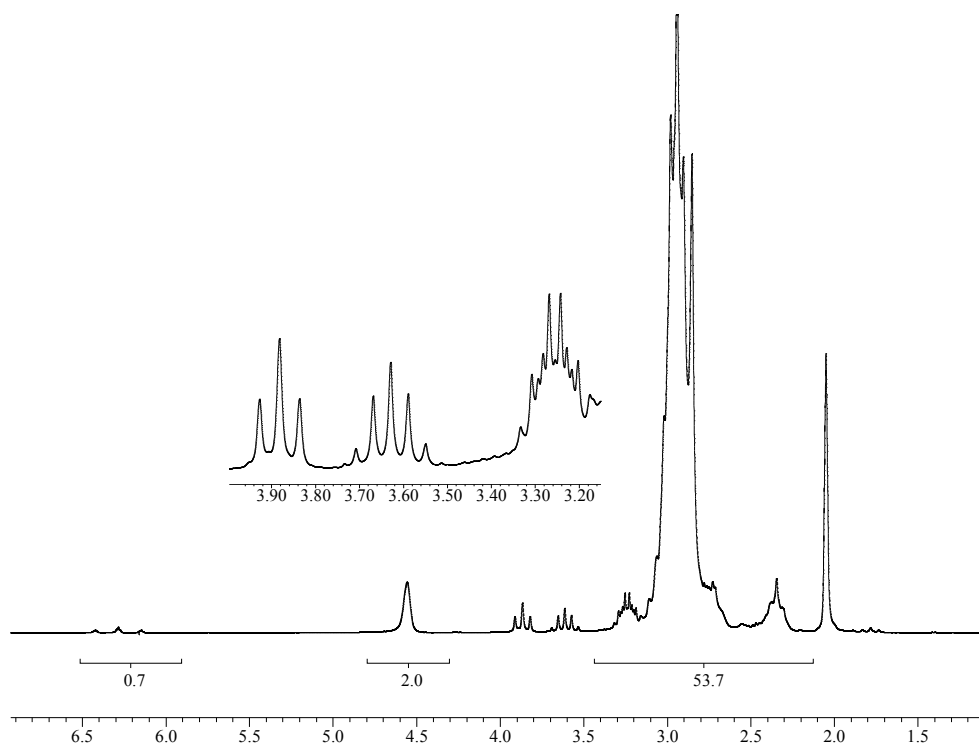


Figure S11. ^1H NMR spectrum of **P11** copolymer recorded in d_6 -acetone at room temperature.

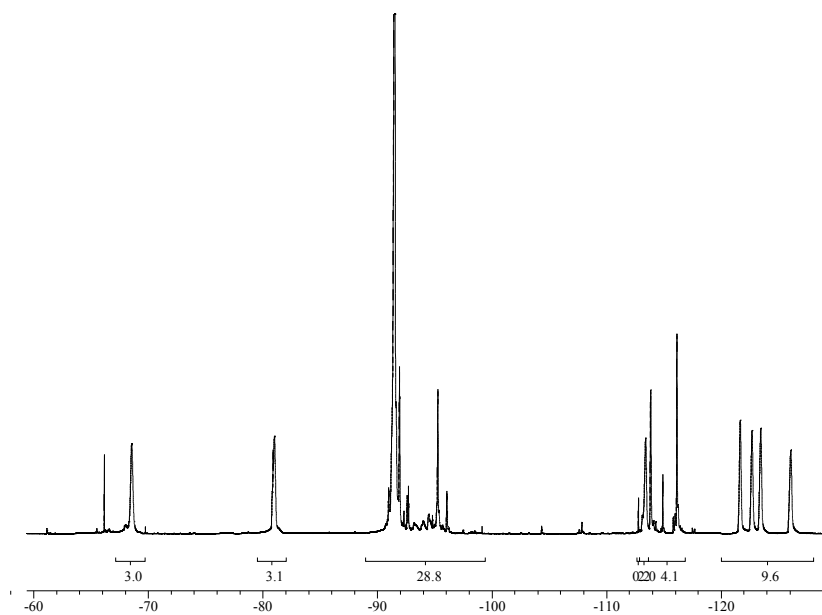


Figure S12. ^{19}F NMR spectrum of **P1** copolymer, recorded in d_6 -acetone at room temperature.

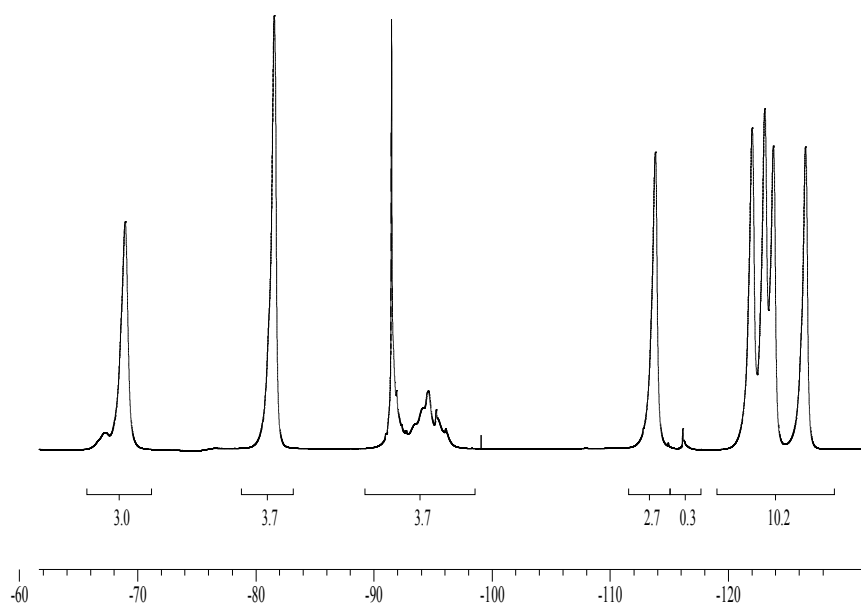


Figure S13. ^{19}F NMR spectrum of **P2** copolymer, recorded in d_6 -acetone at room temperature.

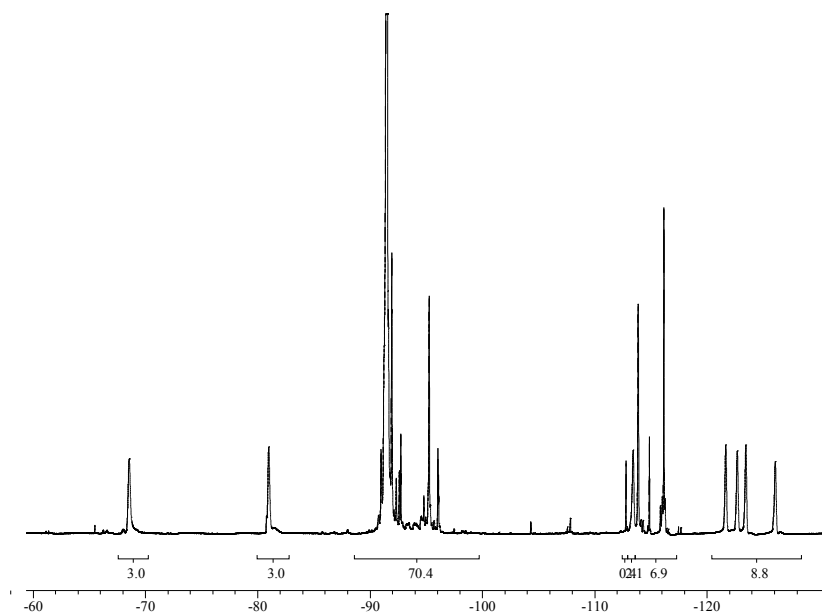


Figure S14. ^{19}F NMR spectrum of **P3** copolymer recorded in d_6 -acetone at room temperature.

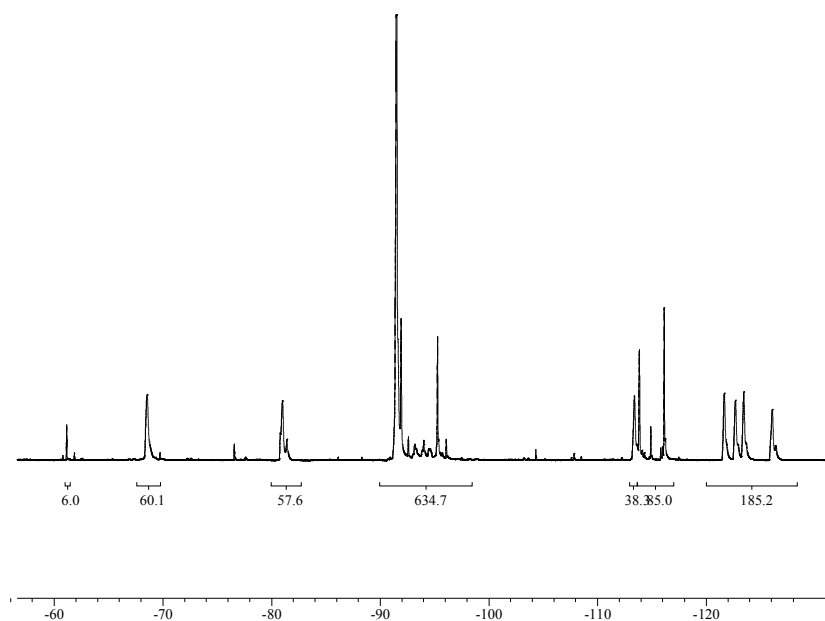


Figure S15. ^{19}F NMR spectrum of **P4** copolymer, recorded in d_6 -acetone at room temperature.

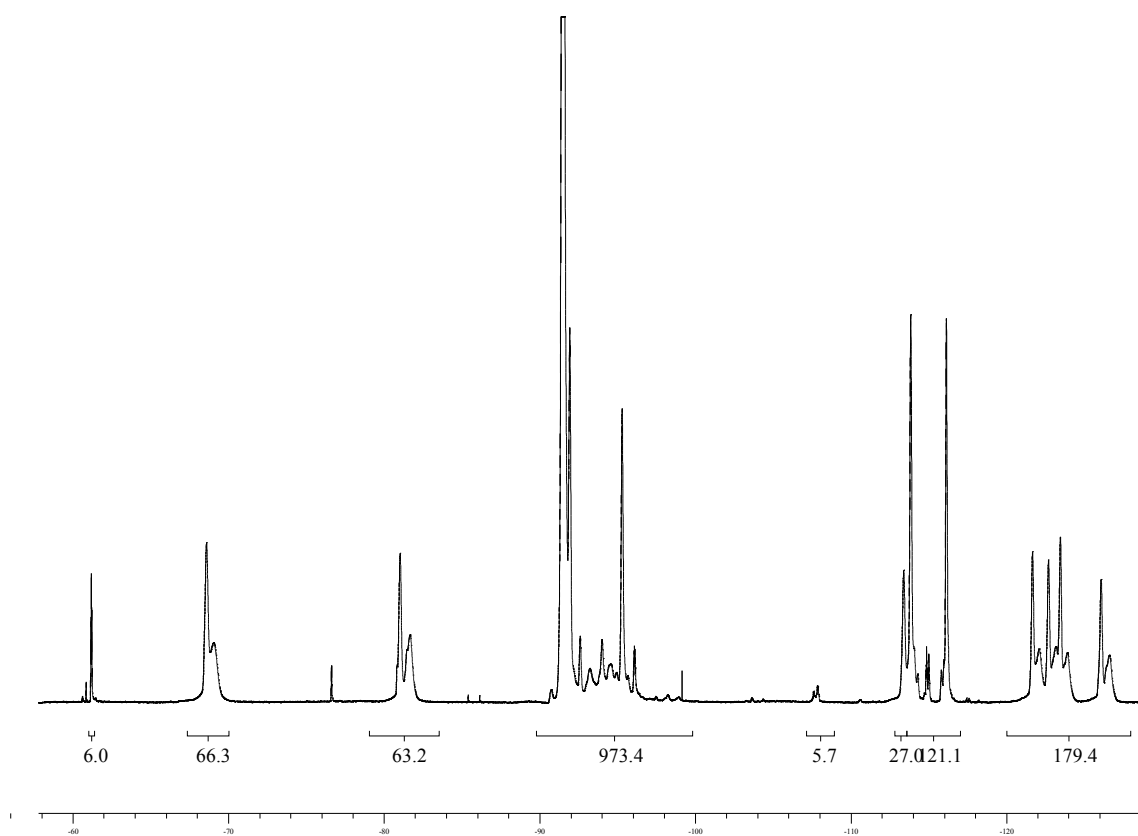


Figure S16. ^{19}F NMR spectrum of **P5** copolymer recorded in d_6 -acetone at room temperature.

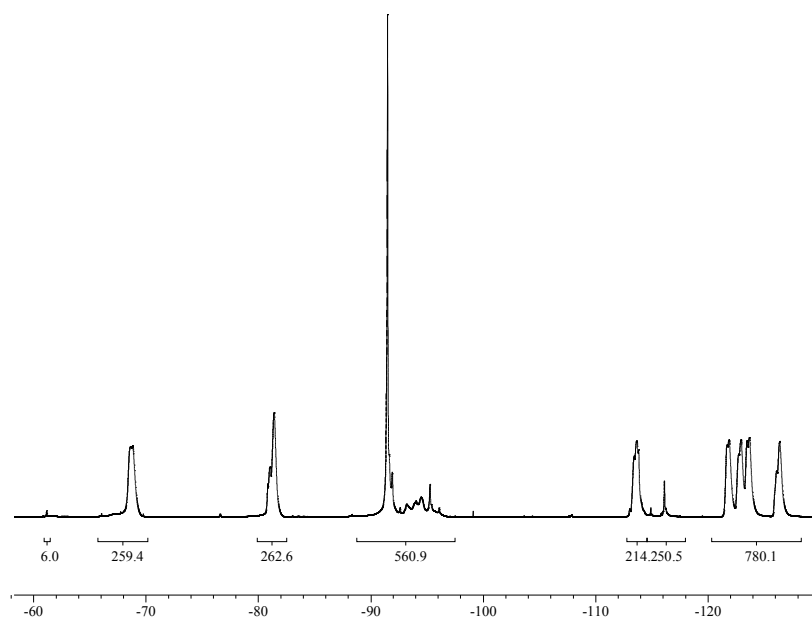


Figure S17. ^{19}F NMR spectrum of **P6** copolymer recorded in d_6 -acetone at room temperature.

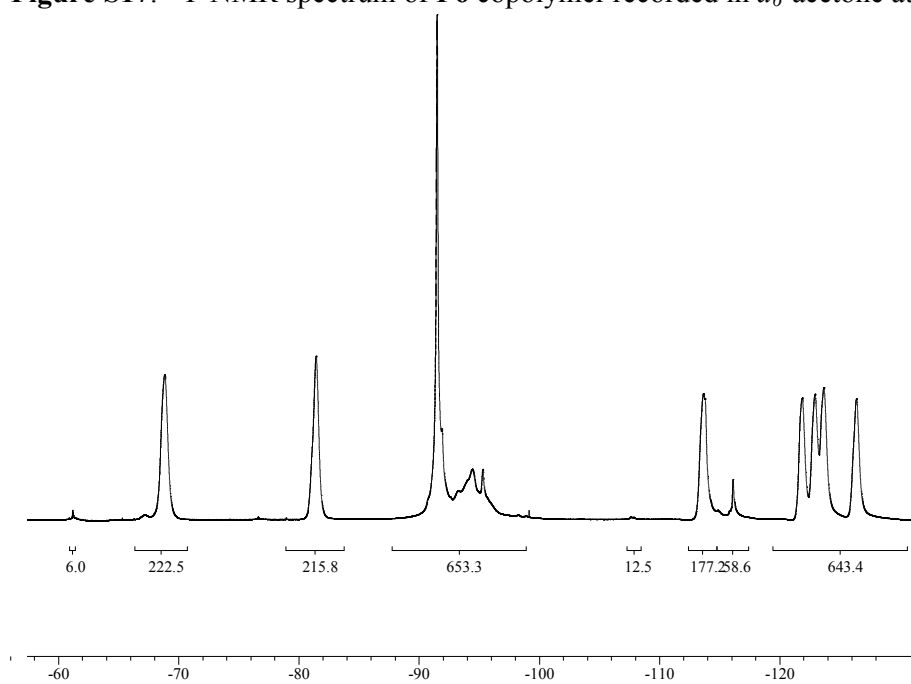


Figure S18. ^{19}F NMR spectrum of **P7** copolymer recorded in d_6 -acetone at room temperature.

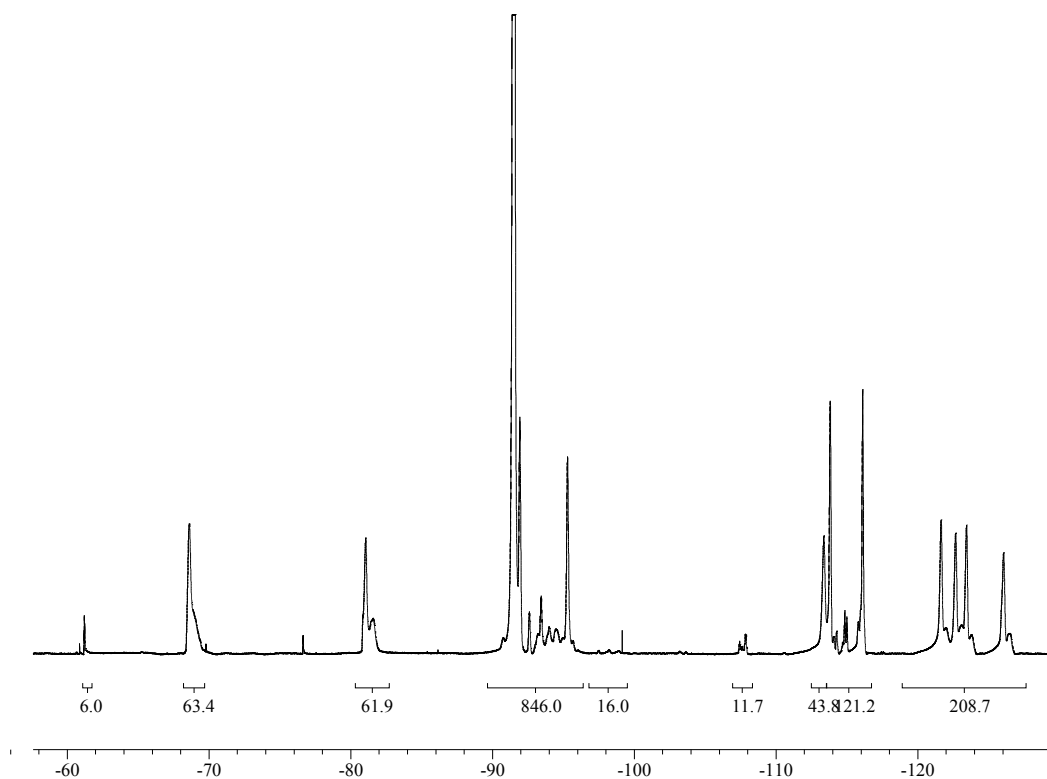


Figure S19. ^{19}F NMR spectrum of **P8** copolymer recorded in d_6 -acetone at room temperature.

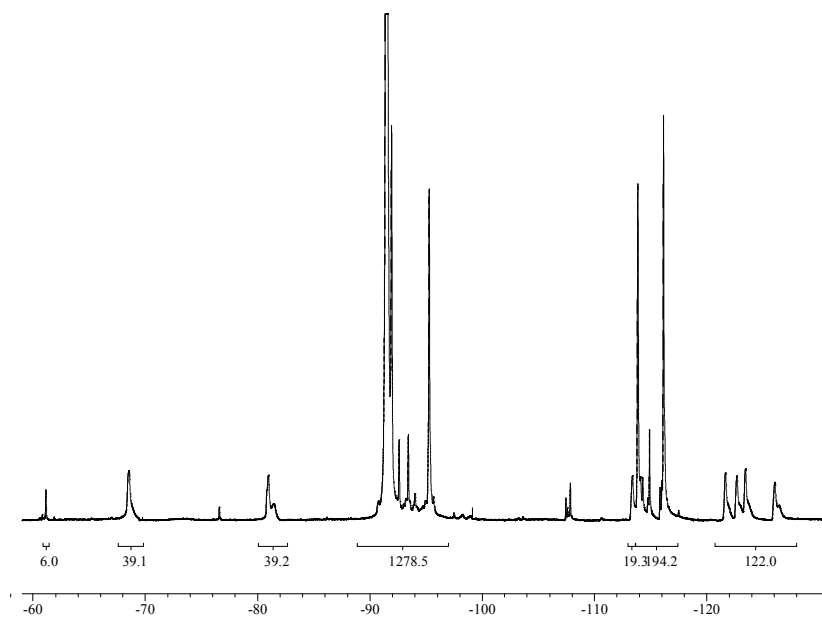


Figure S20. ^{19}F NMR spectrum of **P9** copolymer recorded in d_6 -acetone at room temperature.

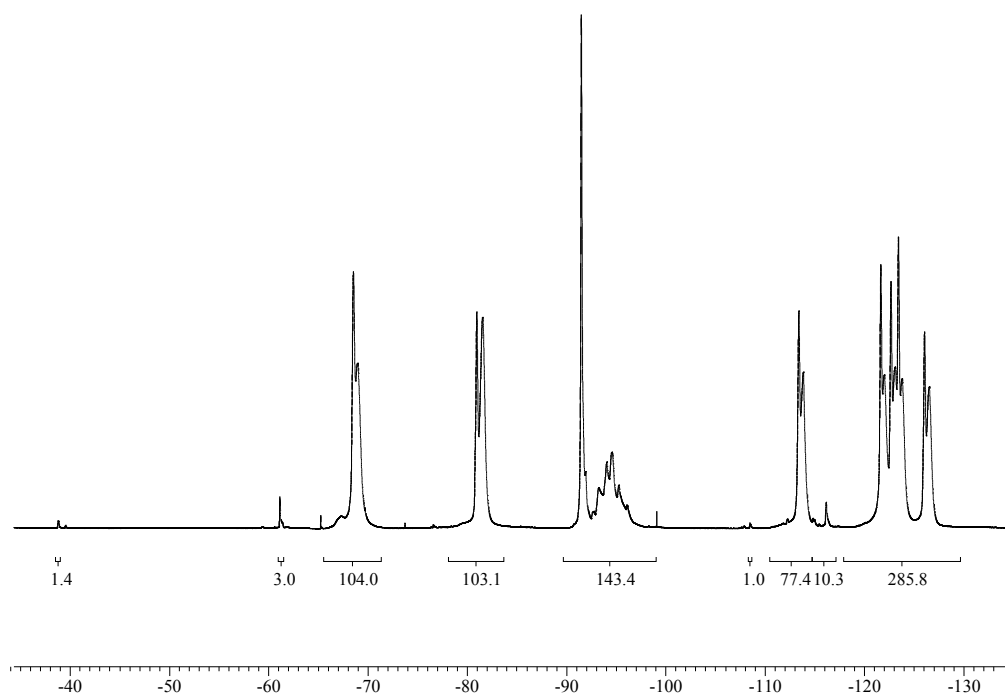


Figure S21. ^{19}F NMR spectrum of **P10** copolymer recorded in d_6 -acetone at room temperature.

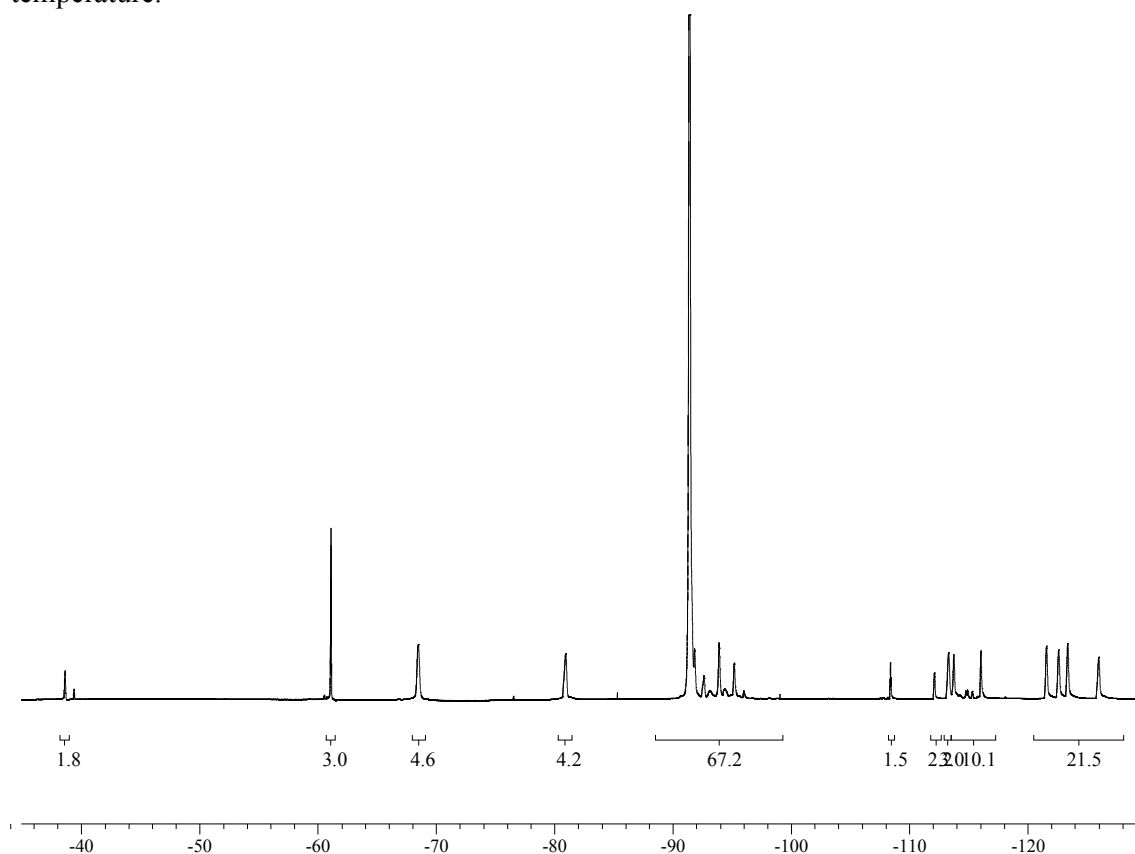


Figure S22. ^{19}F NMR spectrum of **P11** recorded in d_6 -acetone at room temperature.

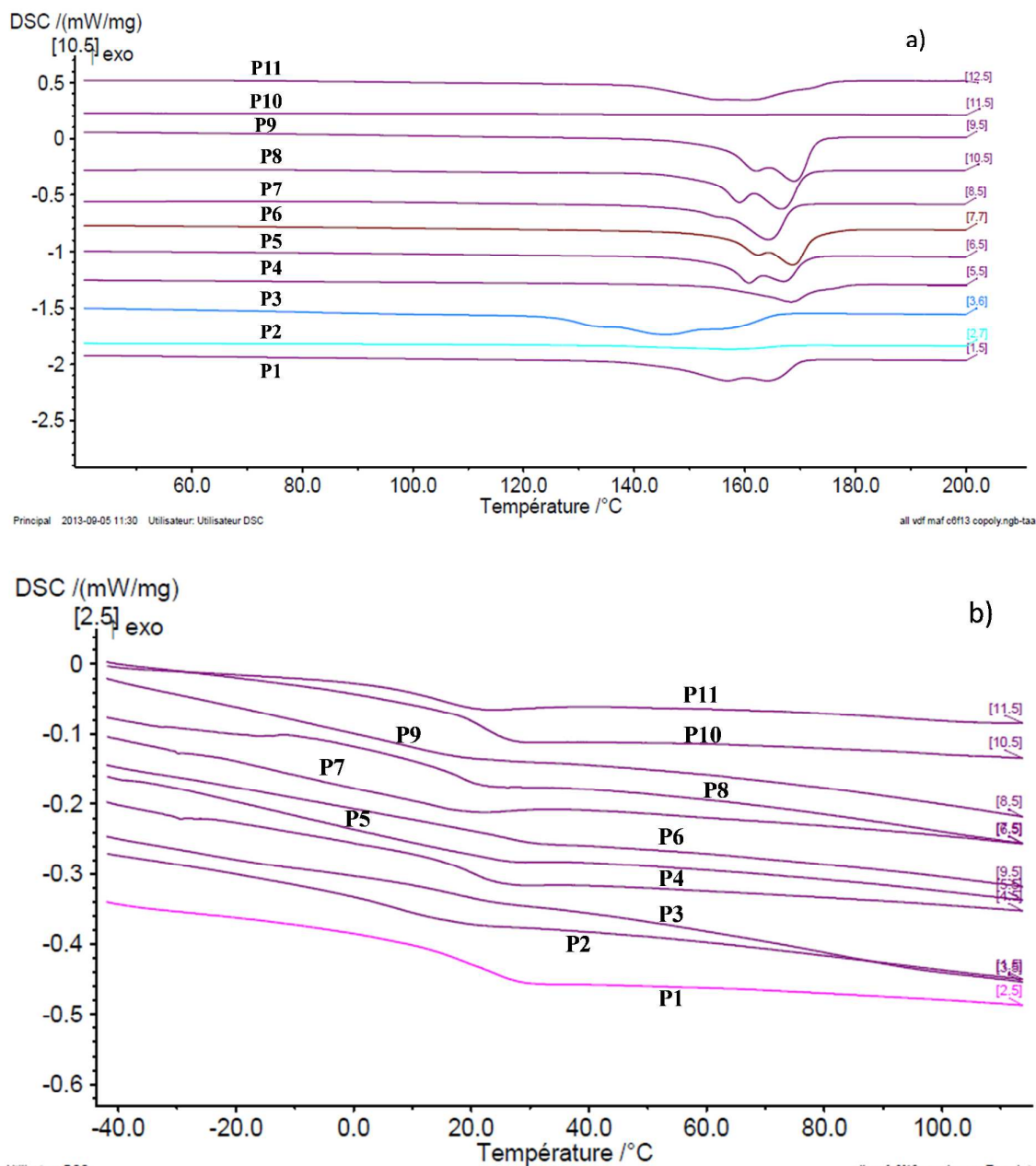


Figure S23. DSC thermograms, a) Melting signals obtained in the second heating scans and b) Glass transition signals in the second heating scans for **P1-P11** copolymer at the heating rates of 10 and 20°C min⁻¹ respectively, under nitrogen atmosphere.

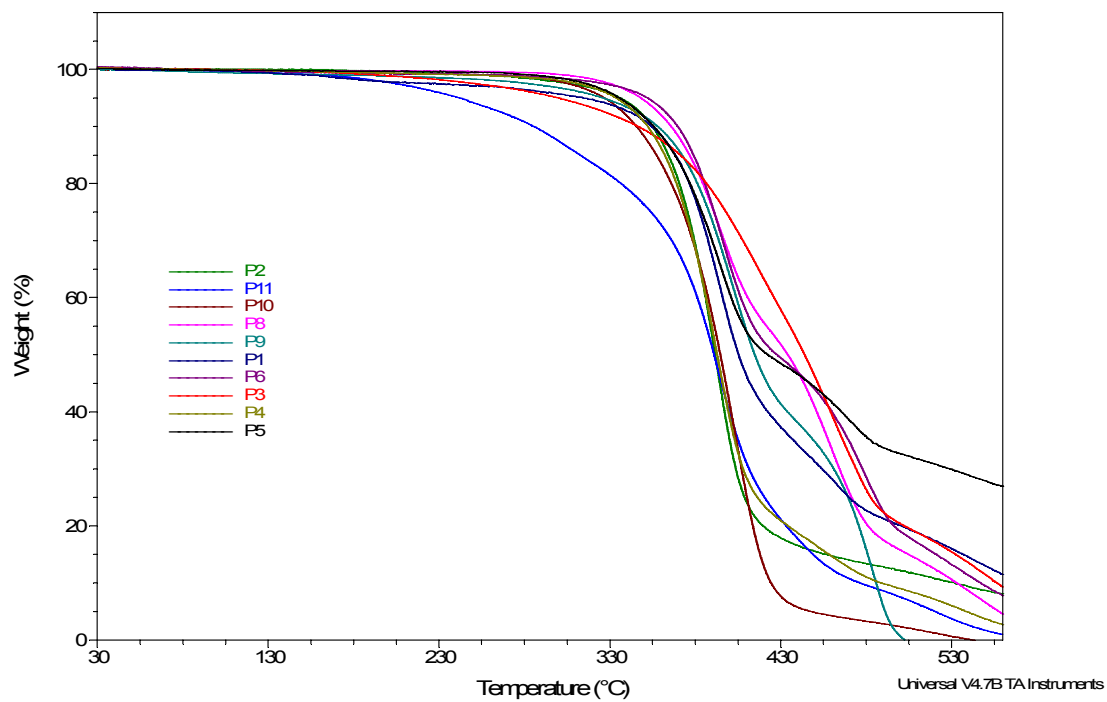


Figure S24. TGA thermograms for all copolymers. The experiments were carried out in air at $20\text{ }^{\circ}\text{C min}^{-1}$.

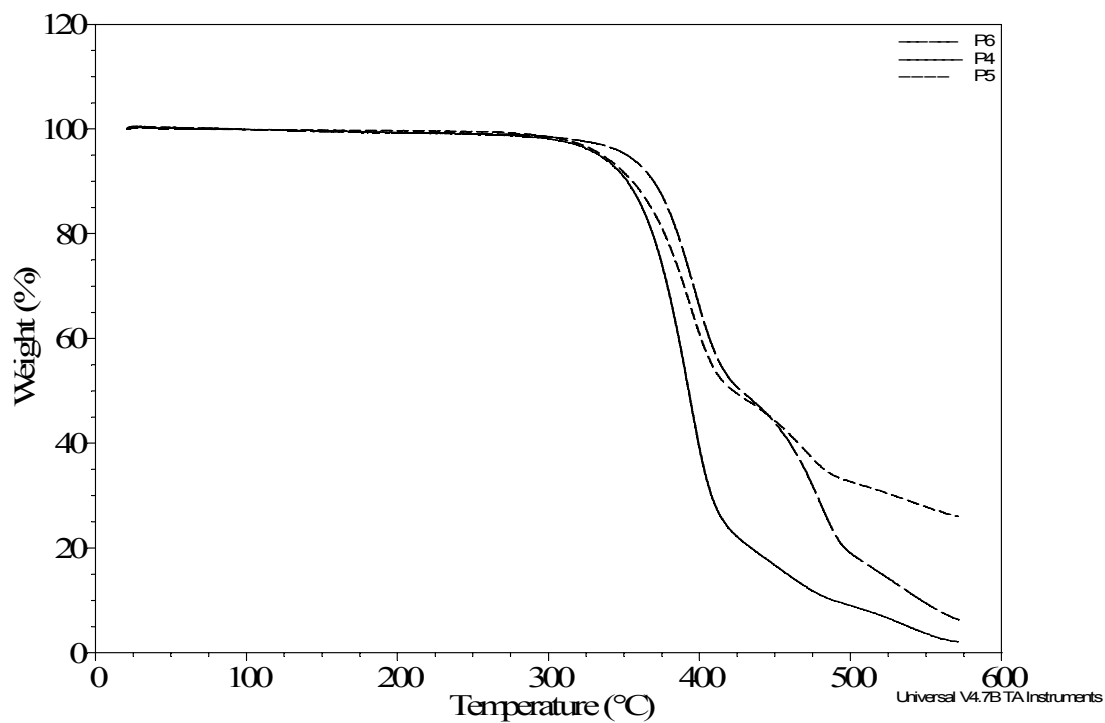


Figure S25. TGA thermograms of **P4-P6** copolymers. The experiments were carried out in air at $20\text{ }^{\circ}\text{C min}^{-1}$.

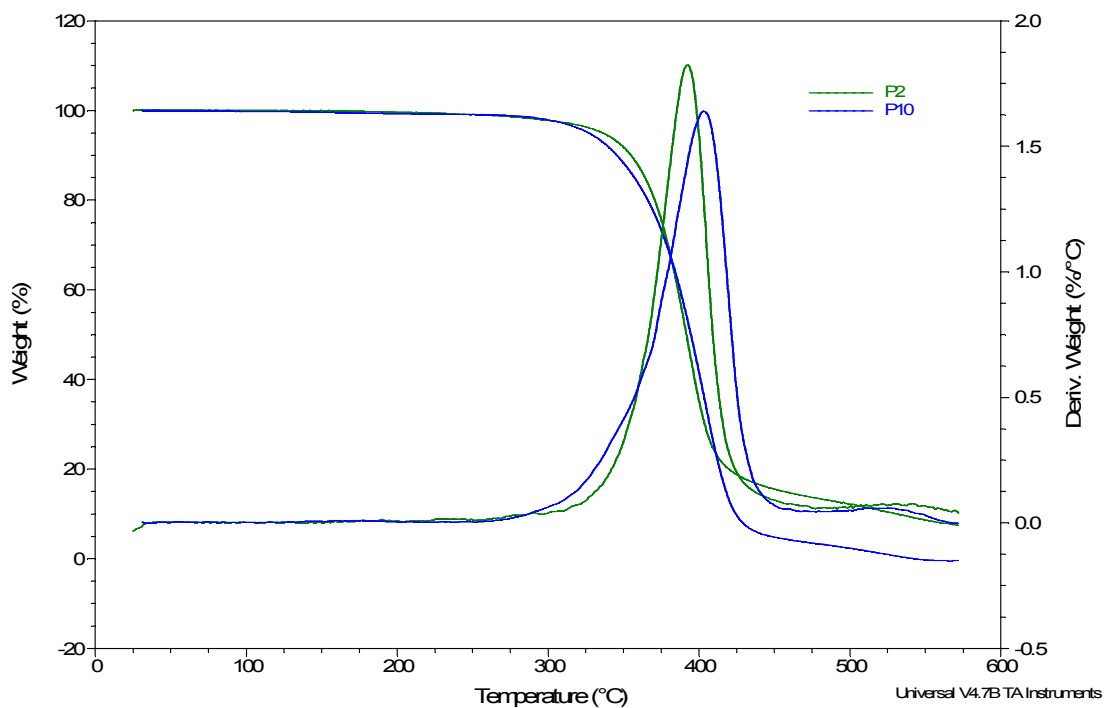


Figure S26. Plots of TGA thermograms and the first derivative of wt% with respect to temperature of **P2** and **P10** copolymers. The experiments were carried out in air at 20 °C min⁻¹.

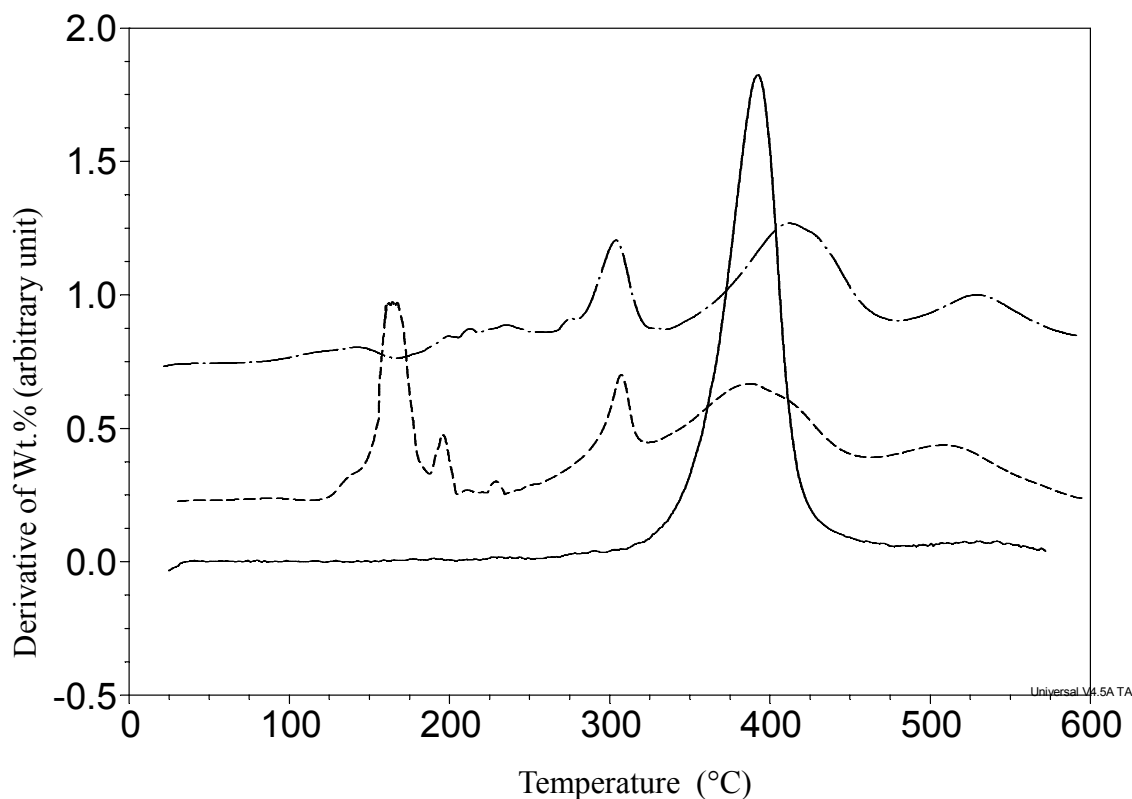


Figure S27. First wt%. derivative of TGA thermograms at various poly(VDF-*co*-MAF derivative) copolymers. sample **P2**, (Table 1), ($M_n = 17400 \text{ g mol}^{-1}$, VDF in copolymer = 67 mol%, $T_{d(10\%)} = 355 \text{ }^\circ\text{C}$, full line). Poly(VDF-*co*-MAF), ($M_n = 21000 \text{ g mol}^{-1}$, VDF in copolymer = 54 mol%, $T_{d(10\%)} = 233 \text{ }^\circ\text{C}$, semi-dotted line). c) Poly(VDF-*co*-MAF-*t*Bu), ($M_n = 49900 \text{ g mol}^{-1}$, VDF in copolymer = 49 mol%, $T_{d(10\%)} = 176 \text{ }^\circ\text{C}$, dashed line). Heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under air flow, where MAF, MAF-*t*Bu and MAF-C₆F₁₃ stand for 2-trifluoromethacrylic acid, *tert*-butyl 2-trifluoromethacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-(trifluoromethyl)acrylate.

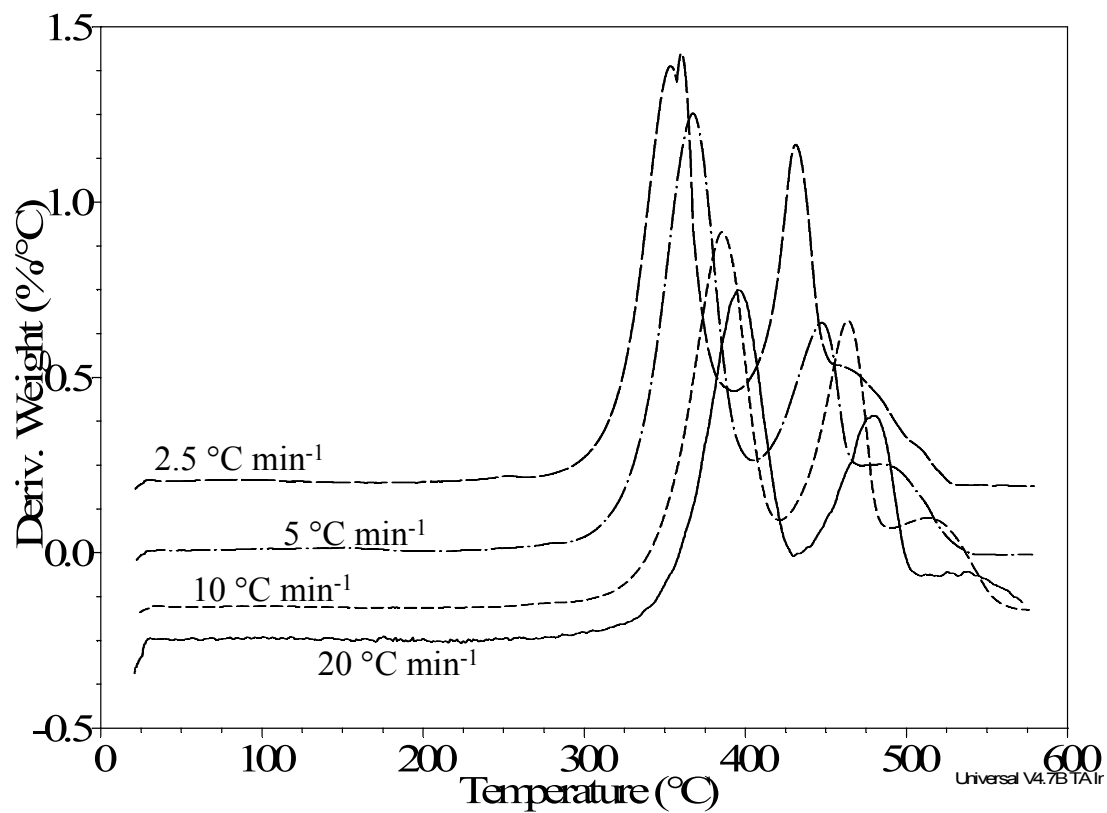


Figure S28. Plot of the first derivative of weight loss with respect to temperature of TGA thermograms under air flow of **P6** (Table 1) at various heating rates a) 2.5, b) 5, c) 10, and d) 20 °C min⁻¹.

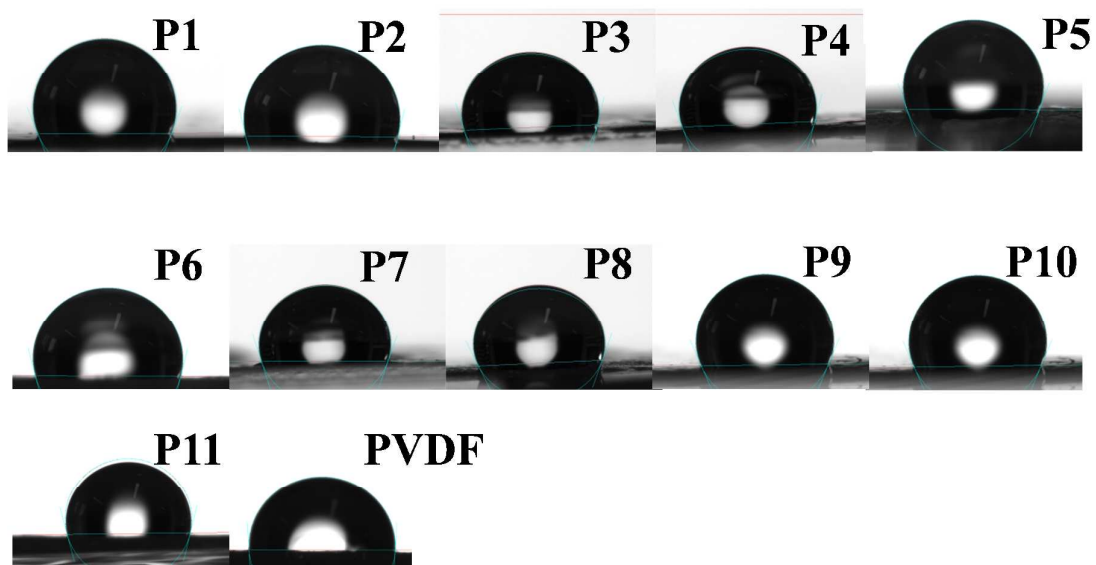


Figure S29. Static Water contact angle (WCA) measurement pictures of all synthesized copolymers at 20 °C.

Table S2. Static water contact angles for synthesized copolymers.

Expt. No.	WCA (°)
PVDF	94
P1	104
P2	106
P3	108
P4	110
P5	105
P6	108
P7 ^{a)}	113
P8 ^{b)}	114
P9 ^{b)}	112
P10	114
P11	104

References

The Matheson Company (Ed.), Matheson Gas Data Book, La Porte, USA, 4th Edition, pp 185-187.