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Published in:
Polymer Chemistry

DOI:
[10.1039/c7py00209b](https://doi.org/10.1039/c7py00209b)

Publication date:
2017

Document Version
Peer reviewed version

[Link to publication in Discovery Research Portal](#)

Citation for published version (APA):

Banerjee, S., Tawade, B., Ladmiraal, V., Dupuy, L. X., MacDonald, M., & Ameduri, B. (2017). Poly(fluoroacrylate)s with tunable surface hydrophobicity via radical copolymerization of 2,2,2-trifluoroethyl -fluoroacrylate and 2-(trifluoromethyl)acrylic acid. *Polymer Chemistry*, 2017(12), 1978-1988. <https://doi.org/10.1039/c7py00209b>

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Poly(fluoroacrylate)s with tunable surface hydrophobicity *via* radical copolymerization of 2,2,2-trifluoroethyl α -fluoroacrylate and 2-(trifluoromethyl)acrylic acid

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Abstract: The synthesis of poly(fluoroacrylate)s with tunable wettability and improved adhesion for potential application as functional coating was achieved *via* radical copolymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) with 2-(trifluoromethyl)acrylic acid (MAF), an adhesion-promoting monomer. These copolymerizations, initiated by *tert*-butyl peroxyvalate at varying the comonomer feed ($[FATRIFE]_0/[MAF]_0$) ratios led to a series of poly(FATRIFE-*co*-MAF) copolymers with different molar compositions in fair to good conversions (32-87%) depending on the MAF feed content. The microstructures of the synthesized poly(FATRIFE-*co*-

MAF) copolymers were determined by ^{19}F NMR spectroscopy. Even at MAF feed contents higher than 50%, MAF incorporations in the copolymers were lower than 50%, since MAF does not undergo any homopolymerization under radical initiation. The reactivity ratios of the (FATRIFE; MAF) monomer pair were also determined ($r_{\text{FATRIFE}} = 1.65 \pm 0.07$ and $r_{\text{MAF}} = 0$ at 56 °C) evidencing the formation of statistical copolymers. Initiation involving a highly branched perfluorinated radical that released a $\cdot\text{CF}_3$ radical enabled to demonstrate the regioselective attack of the latter radical onto the CH_2 of FATRIFE. The resulting poly(FATRIFE-co-MAF) copolymers exhibited various glass transition temperatures (T_g s) depending on their compositions. T_g values increased with increasing MAF contents in the copolymer. In addition, their thermal stability (the temperature for 10% weight loss under air, $T_{d10\%}$) increased with increasing FATRIFE content in the copolymer and reached 348 °C (for that containing 93 mol% of FATRIFE). Finally, high copolymer MAF content led to both a good adhesion onto metal substrates and to improved hydrophilicity, as revealed by the decrease of the water contact angle from 101° (for a reference poly(FATRIFE) copolymer) to 81° (for a copolymer containing 42 mol % of MAF).

Introduction

Fluorine, also called the “super halogen”, is the most electronegative and reactive of all the elements.¹ This feature, as well as its small van der Waals radius, generate exceptionally strong C-F bonds in fluoropolymers and unique properties such as exceptional thermal and chemical stabilities, inertness to acids and common solvents, low inflammability, low dielectric constant and dissipation factors, as well as interesting oil and water repellency.^{2, 3} Consequently, fluoropolymers play an important role in the development of new materials for advanced

applications in aeronautics and aerospace, building industries, petrochemicals, automotive industries, Li-ion batteries, high performance membranes, textile treatment, wires and cables, and microelectronics.³⁻⁷ Two main kinds of fluoropolymers are available: (a) those containing fluorine atoms in the backbone and which possess higher thermal stability and chemical resistance; (b) those bearing fluorinated groups as side chains generating remarkable surface properties (hydrophobicity and oleophobicity). In that latter family, poly[fluoro(meth)acrylate]s⁸⁻¹¹ are probably the most studied. In contrast to fluorinated poly[(meth)acrylate]s, poly(α -F-acrylate)s are much less explored.¹⁰ The fluorine atom on the α -carbon of the ester group in poly(α -F-acrylate)s generates a unique combination of good optical and mechanical properties with heat resistance and thermal properties.¹² 2-(Trifluoromethyl)acrylic acid (MAF) and alkyl 2-(trifluoromethyl)acrylates (MAF-esters) have emerged as another particularly attractive class of functional fluorinated monomers. Fluorinated copolymers containing MAF or MAF-esters exhibit potential adhesion property.¹³ Furthermore, MAF containing copolymers exhibit excellent aging resistance.¹⁴

Poly[fluoro(meth)acrylate]s are remarkable materials^{9, 10, 15} owing to the easy polymerization of (meth)acrylates under radical (co)polymerization conditions; their good reactivity with other monomers (they offer more cost-effective and convenient synthesis pathways than other fluoropolymers), and their low crystallinity and good solubility which improve their processability.¹¹ Compared to poly[(meth)acrylate]s, poly[fluoro(meth)acrylate]s copolymers possess unique characteristics^{11, 16, 17} such as low surface energies, reduced friction coefficients, strong incompatibility with conventional solvents,^{18, 19} and can arrange into smectic layers in the solid state.¹¹ In coating applications, the fluoroalkyl segments tend to segregate to the outer surface of the coating to minimize the surface free energy.^{14, 17} They thus find

applications as chemical resistant coatings, noncorrosive materials, antifouling coatings,^{20, 21} and interlayer dielectrics.^{9, 16, 22-24} Fluorinated poly[(meth)acrylate]s are usually prepared via radical copolymerization of fluorinated (meth)acrylates with a vinyl monomer containing a hydrocarbon group or a functional pendant group able to favor cross-linking reactions, and occasionally with ionic monomers with water solubilizing anions.⁹ Boutevin et al.²⁵ reported the synthesis of highly transparent organic materials based on fluoroacrylates. Okamoto's team²⁶ disclosed tacticity control in the radical polymerization of 2,2,2-trifluoroethyl methacrylate in the presence of fluoroalcohol. Perrier et al.^{26, 27} prepared fluorinated methacrylic copolymer by copper-mediated reversible deactivation radical polymerization. Li et al.²⁸ synthesized a novel perfluorocyclobutyl -containing random copolymer by copolymerization of p-(2-(p-(benzenesulfonyl)phenoxy)perfluorocyclobutoxy)phenyl methacrylate and methyl methacrylate (MMA). He et al.²⁹ reported the synthesis of a fluorinated polyacrylate copolymers by radical copolymerization of dodecafluoroheptyl methacrylate, n-butyl acrylate (nBA), and MMA. Singha *et al.* reported homo and copolymerization of fluorinated acrylates via reversible addition-fragmentation chain transfer (RAFT) polymerization.³⁰⁻³³ Cracowski *et al.* mentioned the conventional radical copolymerization of 2,2,2-trifluoroethyl α -fluoroacrylate with 2,2,2-trichloroethyl α -fluoroacrylate (FATRICE)³⁴ and 2,2,2-trifluoroethyl methacrylate with 2,2,2-trichloroethyl α -fluoroacrylate.³⁵ The same team³⁶ subsequently studied the conventional radical copolymerization of electron accepting *tert*-butyl α -trifluoromethacrylate (MAF-TBE) with electron donating 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane (FAV8) that led to alternated copolymers and determined their reactivity ratios ($r_{MAF-TBE} = 0.03 \pm 0.01$ and $r_{FAV8} = 0$, at 74 °C). Junyan *et al.*³⁷ prepared three core-shell fluoroacrylate copolymer latex bearing different fluorinated side chain by semi continuous seed emulsion polymerization, using

nBA and MMA as acrylate monomers and 2,2,2-trifluoroethyl methacrylate, hexafluorobutyl methacrylate, and dodecafluoroheptyl methacrylate (DFHM) as fluorine-containing methacrylate monomers. In addition, our team achieved the synthesis of novel copolymers composed of cyano co-monomer such as acrylonitrile, methacrylonitrile, methylvinylidene cyanide, and TFEM.³⁸⁻⁴⁰ Chen and Wu⁴¹ synthesized fluorinated terpolymers latex by copolymerizing fluorinated monomers such as hexafluorobutyl acrylate, DFHM, and perfluorononoxylene ethanyl acrylate with nBA, and MMA via aqueous emulsion polymerization.

Among α -fluoroacrylates,⁴² homopolymers of 2,2,2-trifluoroethyl α -fluoroacrylate (PFATRIFE), prepared by conventional radical homopolymerization,^{10, 43} possess a low refractive index ($n = 1.385$) due to the low content of hydrogen atoms in the polymer and a high glass transition temperature ($T_g = 117-123$ °C). FATRIFE was also used in copolymerization with numerous comonomers, including *tert*-butyl trifluoromethacrylate,⁴⁴ MMA,⁴⁵ methyl α -fluoroacrylate,⁴⁶ 1,1,3,3-tetrafluoropropyl α -fluoroacrylate,⁴⁷ methyl α -fluoroacrylate and ethyl methacrylate,⁴⁸⁻⁵⁰ acrylates⁵¹ and α -fluoroacrylates bearing a nonlinear optical chromophore.⁵² (Co)polymers based on alkyl-2-trifluoromethyl acrylate were reviewed in 2013.¹⁴ This review article underlines that only a few studies reported the copolymerization of alkyl-2-trifluoromethyl acrylate and α -F-acrylates. Our group studied the free radical copolymerization of FATRIFE with *tert*-butyl-2-trifluoromethylacrylate and obtained fluorinated polyacrylates with interesting optical properties.⁴⁴ However, due to their inferior adhesive properties, application of these materials as functional coatings, printing inks, or paints is challenging.⁵³ These drawbacks may be overcome by incorporating vinyl monomers containing polar functional groups which can act as adhesion promoters. The main objective of this study is the

development of such fluoropolymers with tunable wettability and improved adhesion for potential applications as functional coatings.

Experimental section

Materials

All reagents were used as received unless stated otherwise. 2-Trifluoromethyl acrylic acid (MAF) was kindly offered by Tosoh F-Tech Company (Shunan, Japan). *Tert*-butyl peroxyphthalate (TBPPi) was kindly supplied by Akzo Nobel (Compiègne, France). Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (PPFR), synthesized and characterized by a reported procedure kindly supplied by Dr. Ono (AIST, Nagoya, Japan).⁵⁴ 2,2,2-Trifluoroethyl α -fluoroacrylate (FATRIFE) was purchased from Scientific Industrial Application P and M, Russia. Analytical grade acetonitrile (AcN, Sigma-Aldrich Chimie, France) was distilled over calcium hydride prior to use. Laboratory reagent grade methanol and methyl ethyl ketone (MEK, $\geq 99\%$) were purchased from Sigma-Aldrich. Deuterated acetone (acetone- d_6) used for NMR spectroscopy was purchased from Euriso-top (Grenoble, France) (purity $>99.8\%$).

Characterization

Nuclear magnetic resonance (NMR) spectroscopy. The compositions of the copolymers were determined by ^1H and ^{19}F NMR spectroscopies. The spectra were recorded on a Bruker AC 400 Spectrometer (400 MHz for ^1H and 376 MHz for ^{19}F) using acetone- d_6 as the solvent. Coupling constants and chemical shifts are given in Hertz (Hz) and parts per million (ppm), respectively. The instrumental parameters for recording ^1H [or ^{19}F] NMR spectra were as follows: flip angle

90 ° [or 30 °, acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 μ s for ^{19}F NMR.

Fourier transform infrared (FTIR) spectroscopy. FTIR analyses of the copolymers were performed using a PerkinElmer Spectrum 1000 in ATR mode, with an accuracy of $\pm 2 \text{ cm}^{-1}$.

Thermogravimetric analysis (TGA). The thermogravimetric analysis of the purified and dried copolymer samples were performed under air using a TGA 51 apparatus from TA Instruments at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $580 \text{ }^\circ\text{C}$.

Differential scanning calorimetry (DSC). DSC analyses of the poly(FATRIFE-co-MAF) copolymers were carried out using a Netzsch DSC 200 F3 instrument under N_2 atmosphere. The DSC instrument was calibrated with noble metals and checked before analysis with an indium sample ($T_m = 156 \text{ }^\circ\text{C}$). The heating or cooling range was from $-40 \text{ }^\circ\text{C}$ to $170 \text{ }^\circ\text{C}$ at a scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$. After its insertion into the DSC apparatus, the sample was initially stabilized at $20 \text{ }^\circ\text{C}$ for 10 min. Then, the first scan was made at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ up to $170 \text{ }^\circ\text{C}$. It was then cooled to $-40 \text{ }^\circ\text{C}$. Finally, a second scan was performed at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ up to $170 \text{ }^\circ\text{C}$. T_g was evaluated from the second heating, taken at the half-height of the heat capacity jump of the glass transition. This ensured elimination of the thermal history of the polymers during the first heating.

Water contact angle (WCA). WCA measurements were carried on the copolymer cast thin films prepared from acetone solution (10 wt%) of the polymers on glass slides. The coated glass slides were then dried at room temperature (ca. $20 \text{ }^\circ\text{C}$) for 16 h. WCA measurements were carried out at ambient temperature on a Contact Angle System OCA-DataPhysics goniometer using the water sessile drop method. The probe liquid was water ($\theta_{\text{H}_2\text{O}}$) and the dispensed drop

volume was 5.0 μL . The average CA values were determined from five different drops per sample deposited on these same sample.

Radical copolymerization of FATRIFE with MAF

All copolymerizations were performed using Schlenk techniques under nitrogen atmosphere. A typical copolymerization (P2, Table 1) of FATRIFE with MAF was performed as follows (Scheme 1): TBPPi (46 mg of 75% solution, 0.2 mmol) and MAF (0.28 g, 2 mmol) were placed into a Schlenk flask which was then purged by three vacuum-nitrogen cycles. Then, degassed AcN (2.0 mL) and FATRIFE (3.1 g, 18 mmol) were added under a nitrogen flux and the reaction mixture was heated at 56 $^{\circ}\text{C}$ under stirring. Samples were withdrawn periodically from the reaction medium during the entire duration of the copolymerization to determine the monomer conversions by ^1H NMR spectroscopy using equation 1 (for FATRIFE conversion) and equation 2 (for MAF conversion):

% *FATRIFE conversion*

$$= 100 - \left[\frac{\left(\int_{5.60}^{5.70} \text{CH} + \int_{5.75}^{5.95} \text{CH} \right)_{t=0} - \left(\int_{5.60}^{5.70} \text{CH} + \int_{5.75}^{5.95} \text{CH} \right)_{t=t}}{\left(\int_{5.60}^{5.70} \text{CH} + \int_{5.75}^{5.95} \text{CH} \right)_{t=0}} \times 100 \right] \quad (1)$$

% *MAF conversion*

$$= 100 - \left[\frac{\left(\int_{6.55}^{6.65} \text{CH} + \int_{6.75}^{6.85} \text{CH} \right)_{t=0} - \left(\int_{6.55}^{6.65} \text{CH} + \int_{6.75}^{6.85} \text{CH} \right)_{t=t}}{\left(\int_{6.55}^{6.65} \text{CH} + \int_{6.75}^{6.85} \text{CH} \right)_{t=0}} \times 100 \right] \quad (2)$$

where $\int_i^j \text{CH}$ stands for the integral of the signal assigned to CH ranging from i ppm to j ppm.

At the end of the reaction, the crude product was precipitated twice from chilled methanol, filtered through a filter funnel, and then dried under vacuum (10^{-3} bar, 60 $^{\circ}\text{C}$) for 16 h. The purified copolymer, a white powder, was characterized by ^1H and ^{19}F NMR spectroscopy.

^1H NMR (400 MHz, CDCl_3 , δ ppm of P5, Table 1, Fig. 3): 0.9 to 1.5 (s, $\{-\text{C}(\underline{\text{CH}}_3)_3$ signal of the α -end group arising from TBPPi fragments}; 2.45 to 3.35 ($-\underline{\text{CH}}_2$ groups in FATRIFE and MAF); 4.65 (m, $-\text{O}\underline{\text{C}}\text{H}_2\text{CF}_3$ of FATRIFE).

^{19}F NMR (376 MHz, CDCl_3 , δ ppm of P5, Table 1, Fig. 4): -69 (s, $-\underline{\text{C}}\text{F}_3$ of MAF in the copolymer); -75 (s, $-\underline{\text{C}}\text{F}_3$ of FATRIFE in the copolymer); multiplets centered in the -162 to -178 ppm range (α -F atom of FATRIFE units in the copolymer).

The molar fractions of FATRIFE in the copolymer were determined by ^1H NMR spectroscopy using the integrals of the $-\text{O}\underline{\text{C}}\text{H}_2$ signals (signal a , Fig. 3) corresponding to FATRIFE and subtract its intensity from the peak labeled with (b, b') to get the signal intensity b' (corresponding to $-\underline{\text{C}}\text{H}_2$ signals MAF),⁵⁵ equation (3):

$$\text{FATRIFE mol\% in copolymers} = \frac{\int_{4.30}^{5.10} \text{OCH}_2(a)}{\int_{4.30}^{5.10} \text{OCH}_2(a) + (\int_{2.25}^{3.35} \text{CH}_2(b+b') - \int_{4.30}^{5.10} \text{OCH}_2(a))} \times 100 \quad (3)$$

The molar fraction of FATRIFE in the copolymer was determined by ^{19}F NMR spectroscopy using the integrals of the $-\text{CF}_3$ signals corresponding to FATRIFE and MAF,⁵⁵ equation (4):

$$\text{FATRIFE mol\% in copolymers} = \frac{\int_{-73}^{-77} \text{CF}_3}{\int_{-73}^{-77} \text{CF}_3 + \int_{-68}^{-70} \text{CF}_3} \times 100 \quad (4)$$

Determination of the reactivity ratios of FATRIFE and MAF.

The reactivity ratios were determined using nonlinear fitting of instantaneous copolymer composition curve from the Mayo-Lewis⁵⁶ copolymerization (equation 5).⁵⁷ First, the instantaneous copolymer compositions were obtained using ^1H NMR spectroscopy (equations 1 and 2) from copolymerization experiments carried out at various FATRIFE/MAF monomer feeds and stopped at low (< 10 %) monomer conversions (data points are supplied in Table S2).

These low conversion (< 10 %) composition data points were then used to draw the copolymer-monomer composition curve (Fig. 5). This curve was then fitted, using Origin®, to the Mayo-Lewis copolymerization equation (5) using the least squares method, depicted by the red line.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (5)$$

where F_1 , f_1 , f_2 , r_1 and r_2 stand for the molar percentages of MAF in the copolymer, of MAF and FATRIFE in the comonomer feed, and the reactivity ratios of MAF and FATRIFE, respectively.

Adhesion Properties. 1.00 g of the (co)polymer was dissolved in 5.0 mL MEK in a flask and stirred magnetically at room temperature for 30 min to obtain a homogeneous solution. This solution was deposited onto galvanized steel plates using a BarCoater (300 μm Braive Instruments). Coated steel plates were left at room temperature for 16 h to allow MEK to evaporate, leading to a colourless varnish (ca. 20-30 μm). Adhesion properties were characterized using the D3359 ASTM standard test method (Tape test).

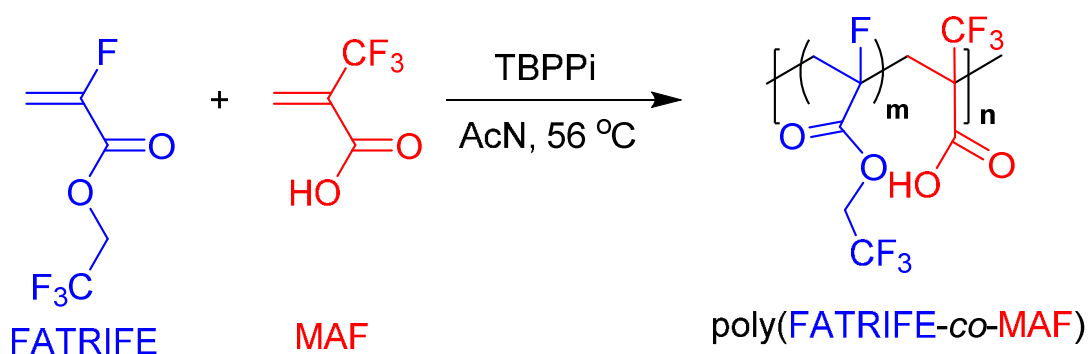
Results and discussion

Synthesis of poly(FATRIFE-co-MAF) copolymers

The radical copolymerizations of FATRIFE and MAF, and the homopolymerization of FATRIFE were initiated by *tert*-butyl peroxyvalate (TBPPi) as initiator at 56 °C in acetonitrile (AcN) (Scheme 1). This solvent is known to induce a few transfer reactions in the polymerization of FATRIFE.^{34, 35, 43} Detailed experimental conditions and characteristics of the obtained poly(FATRIFE) (P1) and poly(FATRIFE-co-MAF) copolymers (P2-P7) are listed in Table 1.

To examine the effect of the monomer feed ratios on the FATRIFE/MAF radical copolymerization, several copolymerizations were carried out starting from monomer feeds that

contain different MAF amounts ($f_{MAF} = 0.1$ to 0.9) and were monitored by ^1H and ^{19}F NMR spectroscopies (equations 1-4). Remarkably, for all feed ratios examined, the copolymerizations resulted in FATRIFE enriched copolymers (Fig. 1 and Fig. S1-S5, P2-P7, Table 1) in fair to satisfactory yields (32-87%). Since MAF cannot homopolymerize under radical conditions,^{58 59} the copolymerizations carried out with high MAF feed content ($f_{MAF} = 0.7$ and 0.8) stopped after complete consumption of FATRIFE.



Scheme 1. Conventional radical copolymerization of 2,2,2-trifluoroethyl α -fluoroacrylate (FATRIFE) and 2-trifluoromethyl acrylic acid (MAF) initiated by *tert*-butyl peroxyvalate (TBPPi).

The semilogarithmic kinetic plot of this copolymerization (Fig. 2, Fig. S6-S10) shows a linear tendency up to about 55 % total conversion (in 45 min-reaction time) indicating that the copolymerization followed a first order kinetics up to that point. The loss of linearity of this plot is probably due to the dramatic increase of the viscosity of the reaction medium and to the low concentration of FATRIFE left in this medium at that stage.

Table 1 Experimental conditions and results of the free radical copolymerization of FATRIFE and MAF.^a

Entry	Initiator	FATRIFE (mol%)			Temp. (°C)	Time (h)	Yield (%)	$T_{d10\%}^d$ (°C)	T_g^e (°C)	WCA^f (°)
		feed	copolymer ^b	copolymer ^c						
P1	TBPPi	100	100	100	56	2.0	100	350	37, 112	107
P2	TBPPi	90	89	93	56	2.0	94	348	48, 116	101
P3	TBPPi	80	86	88	56	4.0	75	335	47, 125	95
P4	TBPPi	70	80	82	56	4.0	66	308	44, 126	93
P5	TBPPi	50	76	73	56	4.0	65	232	42, 105, 136	88
P6	TBPPi	30	61	65	56	8.0	46	199	44, 145	84
P7	TBPPi	20	56	58	56	24.0	32	193	41, 146	81
P8	PPFR	70	87	84	80	16.0	71	304	52, 122	95

Acronyms: FATRIFE: 2,2,2-trifluoroethyl α -fluoroacrylate; MAF: 2-(trifluoromethyl)acrylic acid; TBPPi: *tert*-butyl peroxyvalate; PPFR: perfluoro-3-ethyl-2,4-dimethyl-3-pentyl. Solvent, AcN: acetonitrile. ^aConditions: Solvent used = 2.0 mL; $[TBPPi]_0/([FATRIFE]_0+[MAF]_0) = 1$ mol%. %. ^bCopolymer compositions were calculated by ¹H NMR spectroscopy using equation (3). ^cCopolymer compositions were assessed by ¹⁹F NMR spectroscopy using equation (4). ^ddetermined by thermogravimetric analysis (TGA), under air; 10 °C/min. ^eAssessed by differential scanning calorimetry (DSC). ^fWater contact angle (WCA) determined using a goniometer.

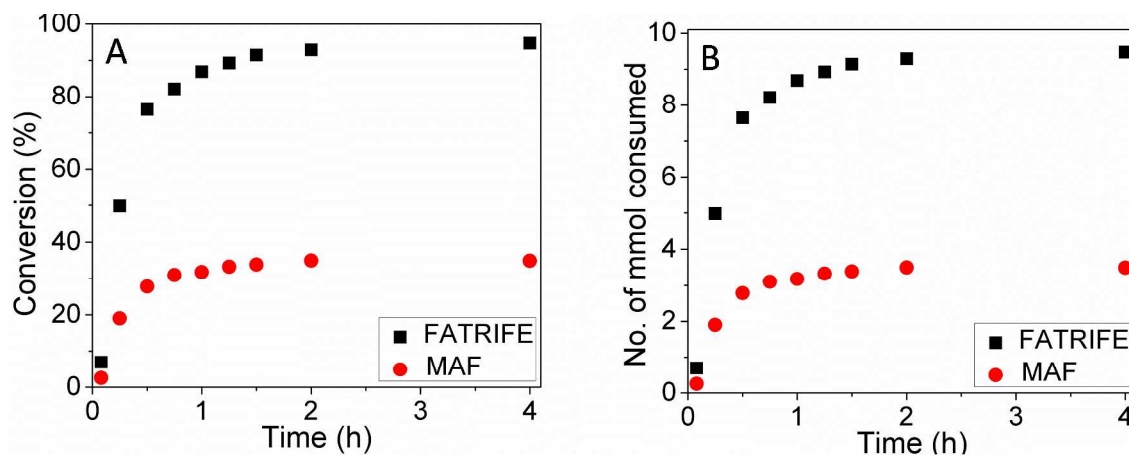


Fig. 1 Conversions of FATRIFE and MAF vs. time plots for a free radical copolymerization of FATRIFE and MAF ($f_{MAF} = 0.5$) initiated by TBPPi at 56 °C in AcN (P5, Table 1): (A) conversions expressed in %, and (B) conversions expressed in number of mmol consumed.

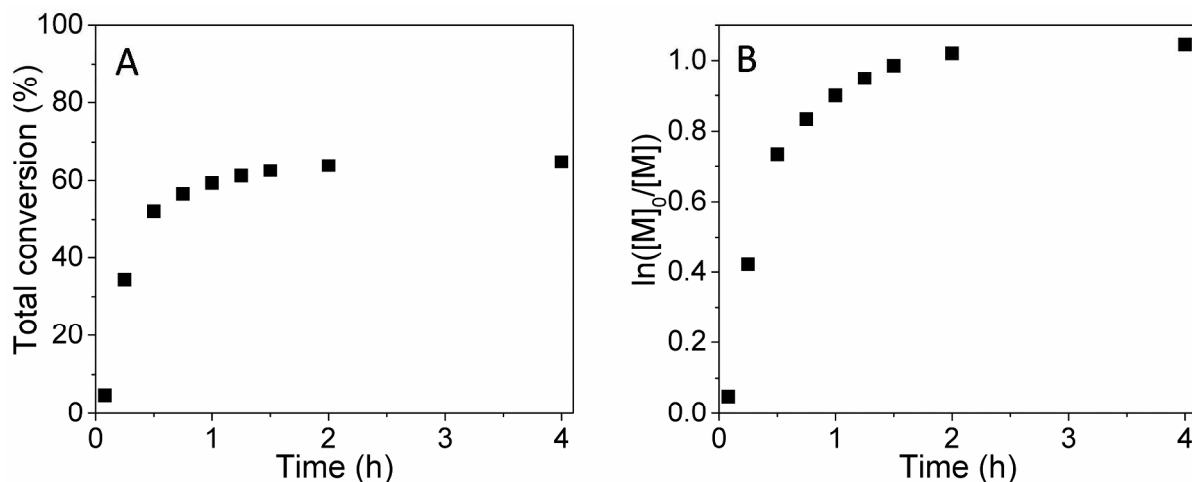


Fig. 2 (A) Total monomer conversion vs. time, and (B) $\ln([M]_0/[M])$ vs. time plots for a conventional radical copolymerization of FATRIFE and MAF ($f_{MAF} = 0.5$) initiated by TBPPi at 56 °C in AcN (P5, Table 1).

NMR characterization of poly(FATRIFE-*co*-MAF) copolymers

P1-P7 copolymers were characterized by ^1H and ^{19}F NMR spectroscopies. The ^1H NMR spectra of the poly(FATRIFE-*co*-MAF) copolymers (Fig 3 shows a typical spectrum) mainly exhibit three characteristic signals: (i) multiple signals between 0.9 to 1.5 ppm attributed to the $-\text{C}(\text{CH}_3)_3$ of the TBPPi fragment α -end group, generated due to the decomposition of TBPPi into *tert*-butoxyl and *tert*-butylcarboxyl radicals (Scheme S1); (ii) a broad peak ranging between 2.45 and 3.35 ppm corresponding to the overlapped signals of the methylene groups of FATRIFE ($-\text{CH}_2\text{CF}(\text{CO}_2\text{CH}_2\text{CF}_3)$) and MAF ($-\text{CH}_2\text{C}(\text{CF}_3)(\text{CO}_2\text{H})$), and (iii) a broad signal centered at 4.65 ppm assigned to the $-\text{OCH}_2\text{CF}_3$ of FATRIFE units. In contrast and as expected, ^1H NMR spectrum of PFATRIFE homopolymer (Fig. S11) exhibits the only characteristic signals for FATRIFE unit: (i) the $-\text{C}(\text{CH}_3)_3$ signal of the TBPPi fragment at ca. 1.35 ppm; (ii) methylene

groups in FATRIFE (in the 2.45 - 3.25 ppm range, and (iii) $-\text{OCH}_2\text{CF}_3$ of FATRIFE units at 4.65 ppm.

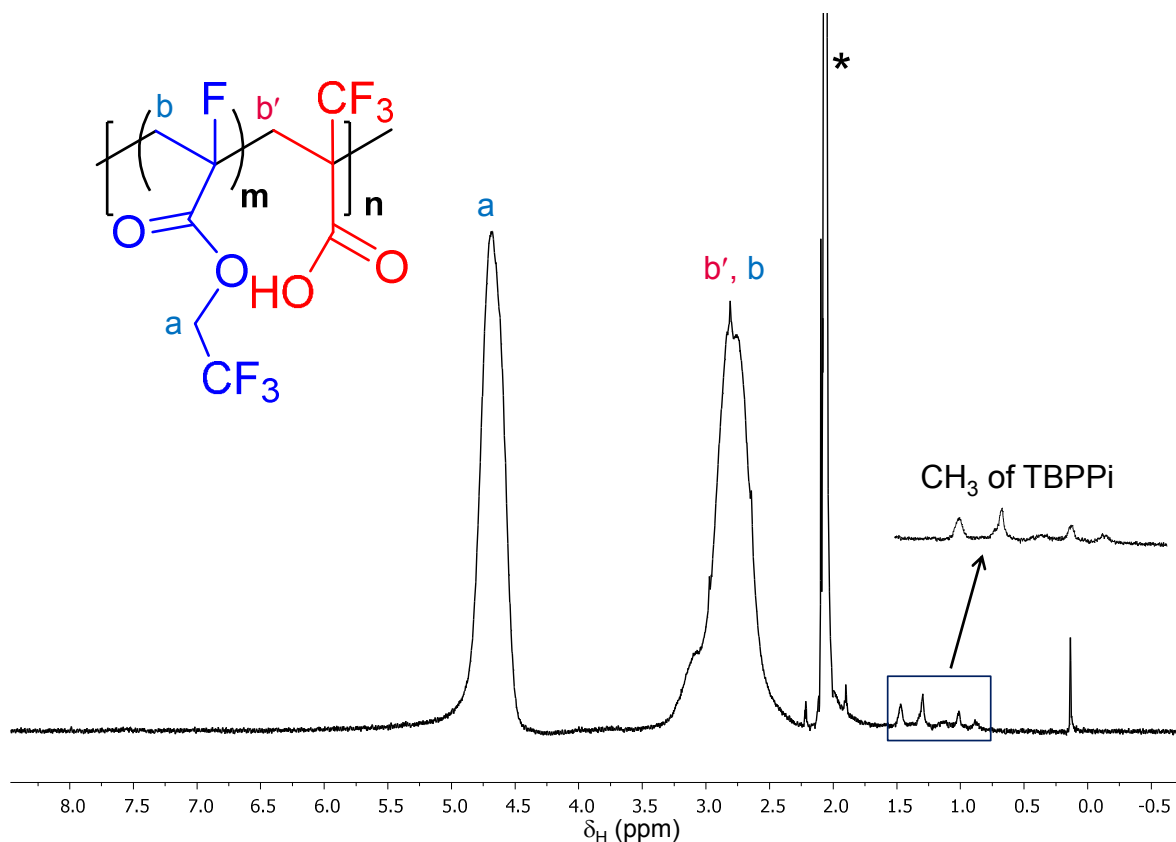


Fig. 3 Representative ^1H NMR spectrum of poly(FATRIFE-*co*-MAF) copolymer prepared by free radical copolymerization of FATRIFE and MAF using TBPPi in AcN at 56 °C (P5, Table 1), recorded in acetone- d_6 at 20 °C. (*) Solvent (acetone) peak.

The ^{19}F NMR spectrum of PFATRIFE (Fig. S12) exhibits two characteristic signals: (i) a signal corresponding to the fluorine atoms of the trifluoromethyl moiety $-\text{CF}(\text{CO}_2\text{CH}_2\text{CF}_3)$ of FATRIFE pendent group at -75.5 ppm and (ii) a complex multiplet ranging from -163 to -177 ppm assigned to the α -F atom in $-\text{CF}(\text{CO}_2\text{CH}_2\text{CF}_3)$ of FATRIFE.^{44, 60, 61} In contrast, the ^{19}F NMR spectrum of the poly(FATRIFE-*co*-MAF) copolymers (Fig. 4) mainly shows: (i) a broad

signal at -69 ppm attributed to the trifluoromethyl group of MAF in the copolymer; (ii) another signal at -75 ppm assigned to the trifluoromethyl moiety of FATRIFE in the copolymer; (iii) a broad and complex signal ranging between -162 ppm and -178 ppm corresponding to the α -F atom. These broad signals are caused by the different environment of the fluorinated atoms (different dyads and other monomer sequences, and tacticity of the copolymers which contain one stereocenter in every monomer unit).^{44, 60, 61} The absence of signal between -185 and -220 ppm previously assigned to the α -F atom in $-\text{CH}_2\text{CFH}(\text{CO}_2\text{CH}_2\text{CF}_3)$,⁴³ evidenced the absence of any transfer to the solvent, initiator, monomer, or copolymer. This is also confirmed by the absence of any $-\text{CFH}$ signal in the 5.5 - 7 ppm region in the ^1H NMR spectrum (Fig. 3).

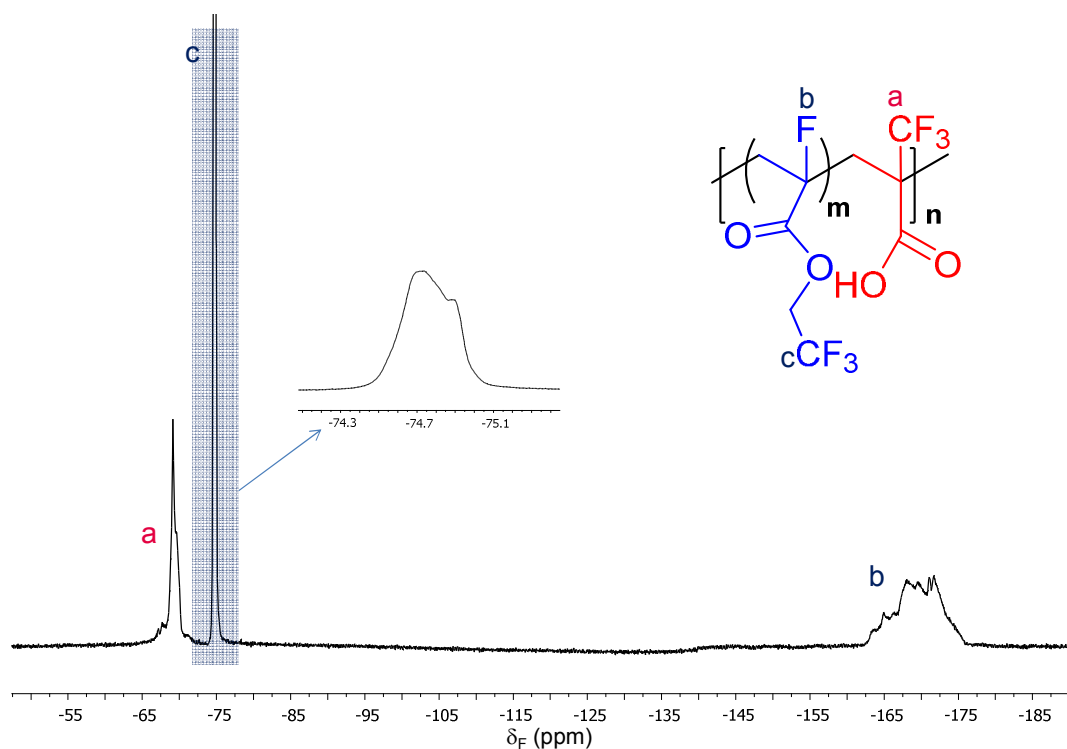


Fig. 4. Representative ^{19}F NMR spectrum of poly(FATRIFE-*co*-MAF) copolymer prepared by free radical copolymerization of FATRIFE and MAF using TBPPi in AcN at 56 °C (P5, Table 1), recorded in acetone- d_6 at 20 °C.

The molar composition of the copolymers was assessed using the integrals of the trifluoromethyl signals of FATRIFE and MAF (equation 4) in the ^{19}F NMR spectra. Molar compositions determined using the ^{19}F NMR were in agreement with those determined using the ^1H NMR spectra. As expected, the amount of FATRIFE in the copolymers decreased with decreasing FATRIFE amount in the feed (Table 1).

ATR-FTIR analyses (Fig. S13) confirmed the formation of poly(FATRIFE-*co*-MAF) copolymers with different MAF contents, as revealed by the increasing intensities of the C=O stretching band at ca. 1600 cm^{-1} and of the stretching vibration of the O-H bond of the carboxylic acid at 3500 cm^{-1} (from P2 to P7). The band corresponding to the carbonyl of the ester group in FATRIFE can be noted in all the IR spectra at 1720 cm^{-1} , while C-F stretching vibration is also identified at ca. 1100 cm^{-1} .⁴⁴

Compared to the copolymer initiated by TBPPi (Fig. S15), the ^{19}F NMR spectrum of the copolymer prepared using perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (PPFR, that releases $\cdot\text{CF}_3$ radicals upon heating⁵⁴) (P8, Table 1, Fig. S15) exhibits a characteristic signal of the $-\text{CF}_3$ initiating group (a quartet of doublets, $^3J_{\text{HF}} = ^4J_{\text{FF}} = 10\text{ Hz}$) at -67 ppm .⁶² This preliminary result suggests that the $\cdot\text{CF}_3$ radical generated by thermal decomposition of PPFR reacted mainly with FATRIFE. Indeed, addition of this radical onto MAF cannot be entirely ruled out, but the initiation on FATRIFE seems prevalent. Furthermore, this radical addition on FATRIFE seems to be almost completely regioselective and to occur only onto the less electrophilic and less hindered carbon (CH_2) site of FATRIFE (as evidenced by the ^{19}F NMR spectroscopy, Fig. S15). This addition is probably governed by the highly electrophilic trifluoromethyl radical and the polar, electronic, and steric effects of $\cdot\text{CF}_3$, CH_2 , $\text{CF}(\text{CO}_2\text{CH}_2\text{CF}_3)$ and $\text{C}(\text{CF}_3)(\text{CO}_2\text{H})$ sites.⁶³⁻⁶⁶

Determination of reactivity ratios

The reactivity ratios of (FATRIFE;MAF) comonomer couple were determined using nonlinear fitting of the Mayo-Lewis (ML) equation⁵⁶ of copolymerization (details are provided in the Experimental Section). The instantaneous compositions were determined using equation (4) and the ^{19}F NMR spectra provided in Fig. S16.

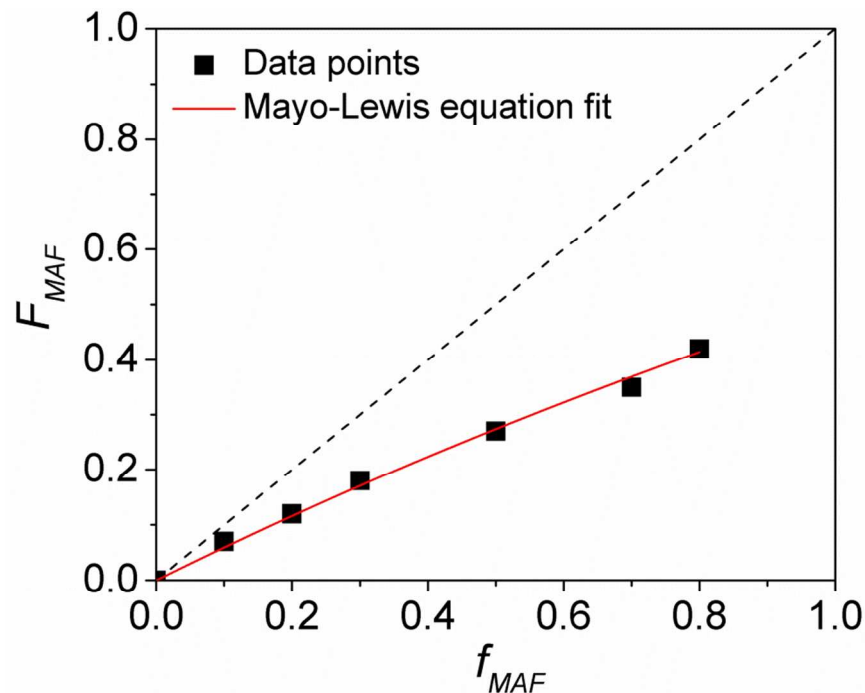


Fig. 5 Copolymer-comonomer instantaneous composition curve (F_{MAF} and f_{MAF} stand for the molar contents of MAF in the copolymer and in the comonomer feed, respectively) for the free radical copolymerization of FATRIFE with MAF initiated by TBPPi in AcN at 56 °C.

The copolymer-comonomer instantaneous composition curve (Fig. 5) shows an almost monotonous increase of the instantaneous MAF content in the copolymer chains with increasing MAF content in the feed. The instantaneous composition data points were fitted with the Mayo-Lewis copolymerization equation (5) to obtain the following reactivity ratios: $r_{FATRIFE} = 1.65 \pm$

0.07 and $r_{MAF} = 0$ at 56 °C. MAF and MAF derivatives (esters) do not homopolymerize under radical conditions.^{14, 58, 59} Such a $r_{FATRIFE}$ value higher than 1 indicates the tendency of FATRIFE to homopropagate rather than crosspropagate with MAF. The reactivity ratios of the FATRIFE/MAF monomer pair was also determined using the well-established linear Finemann–Ross (FR)⁶⁷ and Kelen–Tüdös (KT)⁶⁸ laws (a detailed procedure is depicted in pages S5-S6, the parameters are provided in Table S3, and the corresponding plots are shown as Fig. S17). The reactivity ratios determined by the non-linear ML method are in close agreement with those obtained by linear (FR and KT) methods (Table S4). A comparison of such reactivity ratios with those reported in previous studies dedicated to the radical copolymerizations of MAF or MAF-esters with other monomers is provided in Table S5. The very high reactivity ratio of FATRIFE compared to that of MAF led to FATRIFE-enriched copolymer.

Thermal properties of poly(FATRIFE-*co*-MAF) copolymers

The thermal stabilities of P1-P7 copolymers, assessed by thermogravimetric analysis (TGA) under air (Fig. 6) revealed the dependence of thermal stability (decomposition started from 150 °C to 320 °C) on the MAF content in the copolymer. As expected, the thermal stability of the poly(FATRIFE-*co*-MAF) copolymers decreases with increasing the MAF content (the evolution of $T_{d,10\%}$, 10% weight loss temperature is listed in Table 1). FATRIFE-based copolymers containing higher MAF amounts (P6-P7, Table 1) exhibited a significant weight loss (~18%) when the sample was heated just above 200 °C. This could be attributed to either intramolecular anhydride formation through a loss of water and/or alcohol (trifluoroethanol in this case from FATRIFE) or decarboxylation reaction from CO₂H functions in MAF (Scheme S2).^{44, 69, 70} The thermal stability of the copolymer prepared using PPFR as the initiator (Fig. S18) was similar to that using TBPPi (compare P4 and P8, Table 1) showing that the decomposition really occurs

from such a decarboxylation rather than from an unzipping starting from the degradation of the end-groups.

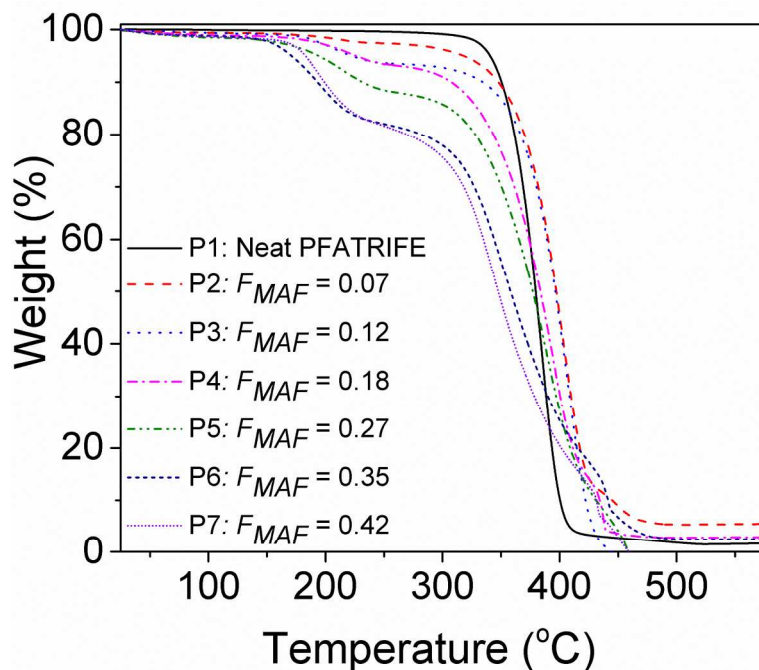


Fig. 6 TGA thermograms (under air) of PFATRIFE and poly(FATRIFE-*co*-MAF) copolymers prepared by free radical copolymerization of FATRIFE and MAF using TBPPi in AcN at 56 °C (P1-P7, Table 1) heated at 10 °C min⁻¹ under air.

Surprisingly, PFATRIFE and all the copolymers exhibited two glass transition temperatures (T_g), as revealed by differential scanning calorimetry (DSC) (Fig. S19-S26). This is in contrast with the earlier reports dealing with (co)polymers prepared from halogenoalkyl or aryl α -chloroacrylates, α -fluoroacrylates, and methacrylates, which were reported to exhibit a single T_g in the range of 120 to 160 °C.²⁵ These results revealed that the second T_g increased from 116 to 146 with a decrease of FATRIFE molar percentage in the copolymer from P2 (93 mol%) to P7 (58 mol%). Furthermore, the copolymers with 73 mol% FATRIFE exhibited a small T_g (ca. 105

°C), along with the other T_g s. The segmental mobilities of a polymer chain are controlled by local composition variations within a “cooperative volume” containing the segment. Thus, appearance of multiple T_g might arise from both chain connectivity and composition fluctuations.⁷¹ This could also be due to the presence of PFATRIFE homopolymer segments in the synthesized poly(FATRIFE-*co*-MAF) copolymers. The copolymer prepared using PPR as the initiator exhibited two T_g at 52 °C and 122 °C (Fig. S26).

Surface properties of poly(FATRIFE-*co*-MAF) copolymers

*Adhesion Studies of poly(FATRIFE-*co*-MAF) copolymers on Steel.* MAF has been shown previously to be an adhesion promoting monomer onto metals.¹³ This property was thus also evaluated here for poly(FATRIFE-*co*-MAF) copolymers. This can be useful for applications of these copolymers as protective (anti-corrosion) functional coatings.

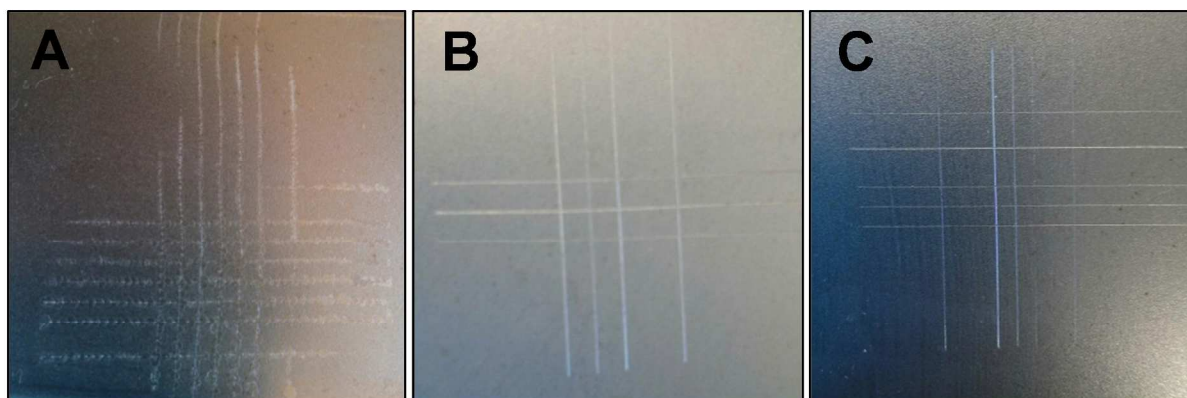


Fig. 7 Photographs of transparent films on steel plate: A) Reference PFATRIFE (P1, Table 1), B) poly(FATRIFE-*co*-MAF) copolymers with 88 mol% FATRIFE content (P2, Table 1), and C) poly(FATRIFE-*co*-MAF) copolymers with 58 mol% FATRIFE content (P7, Table 1).

Adhesion properties were assessed using the D3359 ASTM standard test method [tape test, Fig. 7, (from 0 to 5, 5 indicating the film endowed with the best adhesion properties)]. Films

achieved from the poly(FATRIFE-*co*-MAF) copolymers containing 12 and 42 mol% of MAF (P2 and P7, Table 1, respectively) were compared to a PFATRIFE reference (P1, Table 1) polymer film, prepared under similar experimental conditions. Whereas the reference copolymer was partially removed from the metal substrate, classified as 3 on the ASTM method, the copolymer films displayed very good adhesion properties, classified as 5. These enhanced adhesion properties can be ascribed to the chelation of the metal surface atoms by the carboxylic acid groups.

Water contact angle (WCA) of the poly(FATRIFE-*co*-MAF) copolymers. The surface properties of the PFATRIFE and the poly(FATRIFE-*co*-MAF) copolymers (P1-P7, Table 1) films were examined by means of water contact angle (WCA) measurements (Fig. 8).

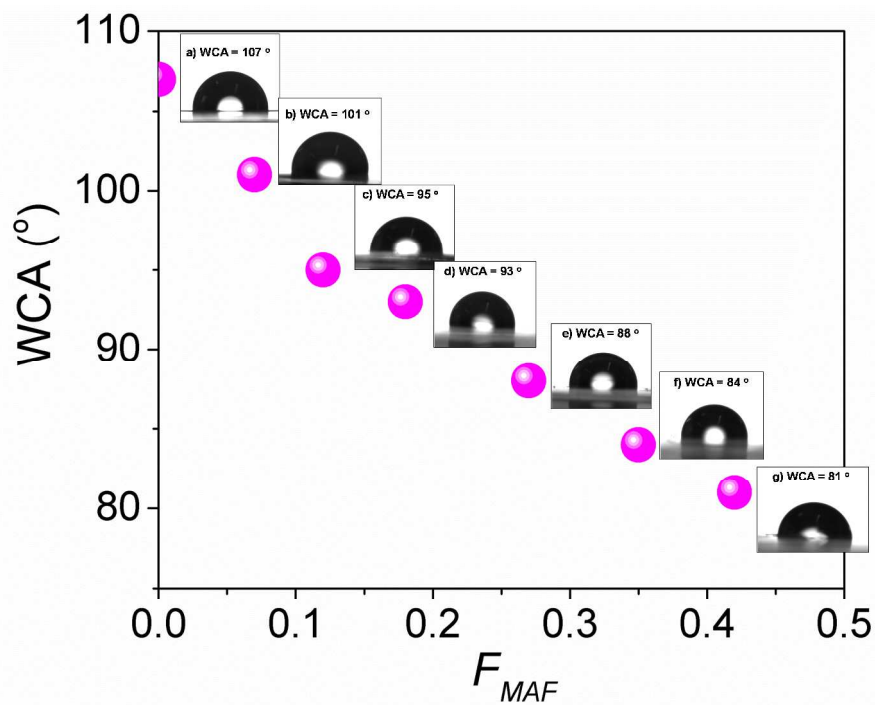


Fig. 8 Variation of water contact angles (WCAs) *versus* MAF content for poly(FATRIFE-*co*-MAF) copolymers films (P1-P7, Table 1) and images of water droplets deposited on the surfaces of such films.

Thin polymer films were prepared by spin-coating onto glass slides on which several drops of water were deposited by a water sessile syringe. Results revealed that, as expected, the PFATRIFE film was hydrophobic (exhibiting a high WCA value of 107°) due to the presence of $-\text{CF}_3$ pendant groups. It is well known that the presence of fluorinated moieties at the surface of the film increases WCA.^{72, 73} Incremental incorporation of MAF (bearing polar $-\text{COOH}$ groups) into the poly(FATRIFE-*co*-MAF) copolymer films resulted in monotonous decrease of the hydrophobicity of the film. Remarkably, the copolymer films containing high amounts of MAF (35 and 42 mol %, P6-P7 respectively, in Table 1) were even slightly hydrophilic (WCA = 84° and 81° for P6 and P7 films, respectively). The copolymer prepared using PFR radical (MAF Mol% = 16) exhibited a WCA value of 95° (Fig. S27) in satisfactory agreement with that obtained from TBPPi in same MAF content (P4 copolymer).

Conclusion

Carboxylic acid-functionalized poly(fluoroacrylate)s exhibiting tunable wettability were synthesized by batch conventional radical copolymerization of FATRIFE and MAF. Poly(FATRIFE-*co*-MAF) copolymers with various MAF contents were prepared by varying the MAF amount in the monomer feed. The reactivity ratios of the (FATRIFE;MAF) couple were determined using nonlinear fitting of the Mayo-Lewis copolymerization equation ($r_{\text{FATRIFE}} = 1.65 \pm 0.07$ and $r_{\text{MAF}} = 0$ at 56°C). These results show that: (i) FATRIFE tends to homopolymerize rather than to crosspropagate with MAF, and (ii) MAF does not homopolymerize under radical polymerization conditions, similar to other MAF-esters.^{14, 58, 59} The copolymerization of these monomers thus yielded statistical copolymers. Increasing MAF content in the copolymers

decreased their thermal stabilities because such units are prone to decarboxylation. Incorporation of higher MAF quantities into poly(FATRIFE-*co*-MAF) copolymers backbone led to polymer films with improved adhesion property onto metal plates and with increased wettability (increased hydrophobicity). Controlling the MAF amount in these poly(fluoroacrylate)s copolymers is thus an efficient way to produce valuable coatings with enhanced adhesion and adjusted wettability. These -COOH containing poly(fluoroacrylate) coatings could have increased adhesion⁷⁴ onto various substrates, especially onto metallic substrates which could be useful for applications requiring corrosion resistant coatings, binders or membranes.⁷⁵

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Acknowledgements

The authors thank Tosoh F-Tech Company (Shunan, Japan) and Akzo Nobel for providing MAF and TBPPi, respectively. This work was also supported by a consolidator fellowship from the European Research Council (ERC SENSOILS-647857).

Electronic Supplementary Information (ESI) available: Additional analyses including kinetics data, NMR and IR spectra, and DSC thermograms of the synthesized (co)polymers.

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