

Free Radical Copolymerization of 2,2,2-Trifluoroethyl a-Fluoroacrylate and tert-Butyl a-Trifluoromethylacrylate: Thermal and Optical Properties of the Copolymers

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▶ **To cite this version:**

Jean-Marc Cracowski, V. Montembault, Dominique Bosc, Bruno Ameduri, Isabelle Hardy, et al.. Free Radical Copolymerization of 2,2,2-Trifluoroethyl a-Fluoroacrylate and tert-Butyl a-Trifluoromethylacrylate: Thermal and Optical Properties of the Copolymers. Journal of Polymer Science Part A: Polymer Chemistry, 2008, 46, pp.4383-4391. 10.1002/pola.22761 . hal-00353669

HAL Id: hal-00353669
https://hal.science/hal-00353669

Submitted on 16 Jan 2009

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Free radical copolymerization of α-fluoroacrylates for optical materials: Synthesis and characterization.

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ABSTRACT: Copolymers based on 2,2,2-trifluoroethyl α-fluoroacrylate (FATRIFE) and 2,2,2-trichlororoethyl α-fluoroacrylate (FATRICE) were synthesized in good yields by radical process initiated by *tert*-butyl 2,2-dimethylperoxypropanoate. Molar composition of the obtained poly(FATRIFE-*co*-FATRICE) copolymers were assessed by means of ^{19}F nuclear magnetic resonance spectroscopy. The reactivity ratios, r_i, of both comonomers were determined from the Kelen-Tüdos method ($r_{FATRIFE}$ = 0.56 ± 0.01 and $r_{FATRICE}$ = 0.11 ± 0.01 at 74°C) showing that FATRIFE is the more reactive monomer. Thermal and optical properties of the resulting polymers were examined. Thermogravimetric analyses showed good thermal stability, thermal decomposition occurring from 300 °C to 310 °C for all copolymers. Moreover, the glass transition temperature of copolymers varied from 113 °C to 127 °C, increasing with the molar ratio of FATRICE in the copolymers. The refractive indices were measured at 633, 1320 and 1550 nm, ranging from 1.375 to 1.4812 at 1550 nm and were found to increase linearly with the chlorine content of the copolymer, allowing a precise control of the refractive index.

Keywords: radical copolymerization; reactivity ratios; thermal properties; optical properties; refractive index; 2,2,2-trifluoroethyl α-fluoroacrylate; 2,2,2-trichloroethyl α-fluoroacrylate.

Introduction

Fluorinated polymers are high value-added materials for various applications, due to their outstanding properties[1-6]. Such polymers exhibit high potential for optical communication applications due to their advantages over conventional glass materials, like low weight, flexibility, easiness to handle and high transparency at the transmission wavelengths (*i.e.* visible and near infrared)[7-12]. The use of amorphous copolymers for both core and cladding of polymeric optical waveguides (POW) is on particular interest to tune the refractive index linked to the numerical aperture (NA) of the waveguide and to avoid compatibility problem at core/cladding interface. The NA is a very important parameter of POW which defines the maximum angle of acceptance (θ_A) of the light:

$$NA = \sin\left(\frac{\theta_A}{2}\right) = \frac{1}{n_0}\sqrt{(n_1^2 - n_2^2)} \qquad (1)$$

where n_1, n_2, n_0 are the refractive indices of the core, the cladding, and the medium where the light is coming from, respectively[13]. Another main characteristic for an optical component is the optical loss at the transmission wavelengths. Polymer optical loss is mainly due to the intrinsic absorption of the C-H bond vibrations. The replacement of hydrogen atoms by heaviest elements, like deuterium, fluorine or chlorine, leads to the vibration shifts towards longer wavelengths, decreasing the intrinsic absorption to negligible values[14].

A lot of fluoropolymers have been developed for optical applications including perfluorocyclobutane aryl ether polymers[15], fluoroacrylate copolymers and terpolymers[16], deuterated polysiloxanes[17]… Among those candidates for POW materials, halogenoalkyl α-fluoroacrylates polymers are considered to be well suited, offering not only low attenuation losses but also good thermal properties and very good solubility[18, 19]. Since it is well known that the refractive index of a polymer can be tuned by copolymerization of two appropriate monomers, we have been interested in the preparation of new α-fluoroacrylate copolymers for adjusting the refractive index and the thermal properties according to the copolymer composition.

Among α-fluoroacrylates, 2,2,2-trifluoroethyl α-fluoroacrylate (FATRIFE) and 2,2,2-trichloroethyl α-fluoroacrylate (FATRICE) are of particular interest. Indeed, poly(FATRIFE) produced from a classical radical homopolymerization[18, 20], shows a low refractive index (n = 1.385), a high glass transition temperature (Tg = 117-123 °C), and a low intrinsic propagation loss due to the low content of hydrogen atoms in the polymer.

FATRIFE has also been involved in copolymerization with numerous monomers, including *tert*-butyl trifluoromethacrylate[21], methyl methacrylate[22], methyl α-fluoroacrylate[23], 1,1,3,3-tetrafluoropropyl α-fluoroacrylate[24], methyl α-fluoroacrylate and (m)ethyl methacrylate[25-27], acrylates[28] and α-fluoroacrylates bearing nonlinear optical chromophore[29].

In recent patents, copolymers of FATRIFE and methyl α-fluoroacrylate have been widely used for cladding[28, 30-37]. In comparison with those copolymers, we have considered in high interest the radical copolymerization of FATRIFE and FATRICE (FATRICE homopolymer: n = 1.499, Tg = 124 °C[18, 38]) to increase the Tg and the refractive index while decreasing the optical loss. Furthermore, obtaining a wide range of refractive indices allows the use of these copolymers for cladding as well as for core. Only one copolymerization of FATRICE, with pentafluorophenyl α-fluoroacrylate, has been reported in the literature[38, 39].

To develop new copolymers for optical applications, this paper reports the radical copolymerization of FATRIFE with FATRICE, initiated by peroxides. The reactivity ratios of both comonomers have been determined using the Kelen-Tüdos method[40, 41] from ^{1}H NMR spectroscopy. In addition, main thermal and optical characteristics of the resulting copolymers as well as those of the homopolymers have been investigated.

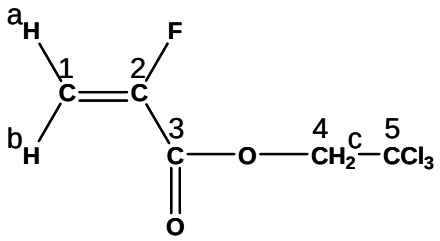
Experimental section

Materials α-fluoroacryloyl chloride (Scientific Industrial Application P&M Ltd, Russia), and *tert*-butyl 2,2-dimethylperoxypropanoate (or *tert*-butylperoxypivalate) (Akzo, France) were used as received. Acetonitrile 99% (Acros) was distilled over calcium hydride prior to use. 2,2,2-Trichloroethanol (98%) was purchased from Aldrich. All other reagents were purchased from Acros. 2,2,2-Trifluoroethyl α-fluoroacrylate was synthesized according to a procedure already reported in the literature[21].

Characterization. The NMR spectra were recorded on a Bruker AC 400 instrument using deuterated chloroform and deuterated acetone as the solvents and TMS (or $CFCl_3$) as a reference for ^{1}H and ^{13}C (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz and parts per million, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra are the following: flip angle 90° (30°), acquisition time 4.0 s (0.9 s), pulse delay 2 s (5 s), number of scans 16 (32), and pulse width 5 μs for ^{19}F NMR. Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 µm guard column) followed by two columns (Polymer

Laboratories (PL), 2 PL gel 5 μm MIXED-D columns), with a SpectraSYSTEM RI-150 detector. THF was used as the eluent at a flow rate of 1 $mL.min^{-1}$ at 35 °C. Polystyrene standards (580 – 4.83 10^5 $g.mol^{-1}$) were used to calibrate the SEC. Differential Scanning Calorimetry (DSC) measurements were conducted using a TA instruments Q100 connected to a computer. A nitrogen flow rate was used. After its insertion into the DSC apparatus, the sample was initially stabilized at 20 °C for 10 min. Then the first scan was made at a heating rate of 20 $°C.min^{-1}$ up to 150 °C. It was then cooled to 20 °C. Finally, a second scan was performed at a heating rate of 10 $°C.min^{-1}$ up to 150 °C giving the values of Tg reported, taken at the half-height of the heat capacity jump of the glass transition. Thermogravimetric analyses were carried out with a TA instruments Q500 apparatus under nitrogen atmosphere at a heating rate of 10 $°C.min^{-1}$ from room temperature up to a maximum of 600 °C. A spin coating technique was used to prepare thin films from a solution of polymer in THF (at a concentration of 0.33 $g.mL^{-1}$) onto a glass substrate, using an acceleration of 1000 revolutions per $minute.seconde^{-1}$ and a rotation rate of 1000 revolutions per minute, for 10 seconds. FTIR spectra were recorded using a Nicolet Avatar 370 DTGS spectrometer in Transmittance mode. High resolution mass spectra were recorded on a Waters Micromass® GCT Premier™ (GC, CI+, methane) using a HP 6890 GC apparatus equipped with a chromatographic column of 25 m, diameter 250 μm, thickness 0.25 μm. The sample was warmed at a temperature of 40 °C for 5 min and then further heated at a heating rate of 10 $°C.min^{-1}$ up to 220 °C. Refractive indices were measured using a Metricon 2010 Prism Coupler at room temperature and at three wavelengths (633 nm, 1320 nm and 1550 nm).

Synthesis of 2,2,2-Trichloroethyl α-fluoroacrylate. In a solution of 15.089 g (101 mmol) of 2,2,2-trichloroethanol and 7.293 g (92.2 mmol) of pyridine in a round bottom flask equipped with a condenser and a magnetic stirrer, were added dropwise 10 g (92.2 mmol) of α-fluoroacryloyl chloride at room temperature. The solution was stirred for 1 hr and washed three times with acidic water (HCl, pH = 2). The organic layer was extracted three times with diethyl ether and dried over magnesium sulfate. 2,2,2-Trichloroethyl α-fluoroacrylate was then distilled (bp_{5mmHg} = 39 °C) to give a colorless liquid with a yield of 65%.



^{1}H NMR ($CDCl_3$) δ (ppm), J (Hz): 4.88 (s, 2H^{c}), 5.51 (dd, H^{a}, $^{3}J_{H\text{-}F}$ = 12.76, $^{2}J_{H\text{-}Hb}$ = 3.54), 5.86 (dd, H^{b}, $^{3}J_{H\text{-}F}$ = 42.69, $^{2}J_{H\text{-}Ha}$ = 3.54). ^{19}F NMR ($CDCl_3$) δ (ppm), J (Hz): -117.33 (dd, 1F, $^{3}J_{F\text{-}Ha}$ = 12.62, $^{3}J_{F\text{-}Hb}$ = 42.45). ^{13}C NMR ($CDCl_3$) δ (ppm), J (Hz): 74.58 (d, C^{4}, $^{4}J_{C\text{-}F}$ = 1.10), 94.22 (s, C^{5}), 104.8 (d, C^{1}, $^{2}J_{C\text{-}F}$ = 14.64), 152.07 (d, C^{2}, $^{1}J_{C\text{-}F}$ = 260.53), 158.69 (d, C^{3}, $^{2}J_{C\text{-}F}$ = 38.06). IR ν (cm^{-1}): 3062 (H-C=C), 2970 (C-H), 1759 (C=O), 1660 (C=C), 1421 (C-C), 1279 (C-O), 1153 (C-F), 780 and 665 (C-F). GC-MS: [M+H] = 220.9335 (Calc. 220.9339).

Copolymers synthesis. The radical copolymerization of FATRIFE with FATRIFE was performed in a 25 mL Schlenk tube equipped with a magnetic stirrer. *tert*-Butyl 2,2-dimethylperoxypropanoate (1.0 mol % relative to the monomer mixture), FATRIFE, FATRICE, and acetonitrile (1.0 g.mL^{-1}) were introduced under inert atmosphere. After three cycles of freeze-pump-thaw, the Schlenck tube was heated to 74 °C under stirring for 10 hrs. After reaction, the solution was precipitated from 50 mL of methanol and stirred for 12 hrs. The polymer formed was isolated by filtration and dried under vacuum at 60 °C for 12 hrs, yielding a white powder. The compositions of poly(FATRIFE-*co*-FATRICE) copolymers (i.e. the mol % of both comonomeric units in the copolymers) were determined by ^{19}F NMR.

Determination of the reactivity ratios. The radical copolymerization of FATRIFE with FATRICE was performed in a 25 mL Schlenk tube equipped with a magnetic stirrer. *tert*-Butyl 2,2-dimethylperoxypropanoate (1.0 mol % relative to the monomer mixture), FATRIFE, FATRICE, acetonitrile (1.0 g.mL^{-1}), and anisole used as internal reference (0.1 equivalent relative to the monomer mixture), were introduced under inert atmosphere. After three cycles of freeze-pump-thaw, the Schlenk tube was heated to 74 °C under stirring and at a given time a sample was taken from the reaction media, cooled into liquid nitrogen and analyzed. The conversion was calculated on the basis of the amount of unreacted monomers determined by ^{1}H NMR.

Results and Discussion

Syntheses of 2,2,2-Trifluoroethyl α-fluoroacrylate and 2,2,2-trichloroethyl α-fluoroacrylate

FATRIFE and FATRICE have been synthesized using α-fluoroacryloyl chloride according to a classical esterification procedure[21] in 88% and 65% yields for FATRIFE and FATRICE, respectively (Scheme 1).

Copolymerization

The radical copolymerization of FATRIFE and FATRICE was carried out in acetonitrile at 74 °C in the presence of *tert*-butyl 2,2-dimethylperoxypropanoate as the initiator yielding random copolymer (Scheme 2), as shown in Table 1. Acetonitrile induces very low transfer reactions[42-44] and solubilize both monomers and copolymers.

The obtained copolymers had very high molecular weights by SEC. Some of the signals were out of the range of the calibration curve, leading to the use of $M_{p,}$ the molar weight at peak maximum, instead of $\overline{M_n}$ and $\overline{M_w}$. Although very high molecular weights were obtained, copolymers were soluble in common organic solvents (acetone, diethylether, THF…).
The monomers composition in feed and copolymer compositions were assessed by ^{1}H and ^{19}F NMR spectroscopy, respectively. Indeed, for the determination of copolymer compositions, ^{1}H NMR spectroscopy was not suitable because of the broad multiplets obtained from 2.4 to 3.3 ppm (assigned to the hydrogen atoms of the copolymer chain) and from 4.3 to 5.2 ppm (assigned to the hydrogen atoms of the trifluoroethyl and trichloroethyl ester). The ^{19}F NMR spectrum (Figure 1) of the poly(FATRIFE-*co*-FATRICE) copolymer shows the characteristic signal centered in the -73 to -75 ppm range, assigned to the fluorine atoms of the trifluoroethyl group of FATRIFE, which was likely decreasing with higher FATRICE content.

Multiplets centered in the -160 to -174 ppm range are assigned to the fluorine atom in alpha position of FATRIFE and FATRICE in the different diads and other sequences of the chain as shown by Majumdar *et al.*[45, 46]. Thus, the molar composition of the copolymers was assessed according to the integrals of the characteristic signals of FATRIFE and FATRICE. The results are gathered in Table 1 using the equations bellow:

$$F_{FATRIFE} = 1 - \left[\left(I_B - I_A / 3 \right) / I_B \right] \quad (2)$$

$$F_{FATRICE} = \left(I_B - I_A / 3 \right) / I_B \quad (3)$$

The absence of signal centered in the -185 to -220 ppm range, attributed to –$CH_2C\mathbf{FH}COOR$[47] end group, evidences the very low amount or absence of transfer to the

solvent, initiator, monomer or to the copolymer. In addition, the absence of signal centered at about 5.5 to 7 ppm in ^{1}H NMR spectrum confirmed this absence of transfer. The ^{1}H NMR spectra also exhibit various signals in the 0.6-1.2 ppm range arising from the initiator. Indeed, it has been shown that, when heated, *tert*-butyl 2,2-dimethylperoxypropanoate undergoes a homolytic scission of the oxygen-oxygen bond leading to two radicals. The *tert*-butyloxyl radical is able to rearrange into a methyl radical and acetone, while the *tert*-butylcarboxyl radical undergoes a decarboxylation to produce *tert*-butyl radical[44, 48] (Scheme 3). Hence, these four radicals may react either onto FATRIFE and FATRICE comonomers leading to various chain-ends evidenced by the small multiplets centered at about 1 ppm.

Assessment of the reactivity ratios

The reactivity ratios of FATRIFE and FATRICE have been determined using the Kelen-Tüdos method, under conditions for which the monomers conversions are lower than 10%. The reaction conditions were the same as those of the copolymerization, and anisole was used as an internal standard ($[anisole]_0/([FATRIFE]_0+[FATRICE]_0)$ = 10 mol%) as this product is known to induce very low transfer reaction and is widely used as reference for controlled radical polymerization[49].

After two minutes of reaction, the total product mixture was characterized by ^{1}H NMR spectroscopy. The spectra of total product mixture (Figure 2) show both characteristic doublet of doublets of FATRIFE and FATRICE. The signals of hydrogen atom in *trans* position (in respect to fluorine atom) of the double bond of FATRIFE monomer was centered at 5.81 (1H) with respective I_1 and I_2 integrals. Both doublets assigned to the hydrogen atom in *trans* position of the double bond of FATRICE monomer was centered at 5.86 (1H) with respective I_3 and I_4 integrals. Hence the monomer conversion can be assessed according to equations (4) and (5):

$$FATRIFE_conversion_(mol\%) = \left(1 - \frac{\left[\left(I_1 + I_2\right)_0 - \left(I_1 + I_2\right)_t\right]}{\left(I_1 + I_2\right)_0}\right).100 \qquad (4)$$

$$FATRICE_conversion_(mol\%) = \left(1 - \frac{\left[\left(I_3 + I_4\right)_0 - \left(I_3 + I_4\right)_t\right]}{\left(I_3 + I_4\right)_0}\right).100 \qquad (5)$$

The signal of both hydrogens of trifluoroethyl of FATRIFE centered at 4.62 ppm and those of both hydrogens of trichloroethyl group of FATRICE at 4.88 ppm cannot be used to determine the monomer conversion. Indeed, copolymer formed exhibit a broad multiplet in the 4.3 to 5.2

ppm region. Seven runs were realized, from an initial $[FATRIFE]_0/[FATRICE]_0$ molar ratio ranging from 0.939/0.061 to 0.166/0.834 as listed in Table 2.

Monomer reactivity ratios were found to be $r_{FATRIFE} = 0.56 \pm 0.01$and $r_{FATRICE} = 0.11 \pm 0.01$ at 74°C. Both reactivity ratios indicate that random copolymers are mainly obtained, nevertheless, those reactivity ratios lower than 1 indicated a low tendency to the alternation of the monomeric units in the copolymer. Moreover, those results confirmed the higher reactivity of FATRIFE toward FATRICE. In the system investigated in this work, the Kelen-Tüdos method (Figure 3) was almost linear, indicating that the terminal model adequately describes the radical copolymerization of FATRIFE and FATRICE under these conditions.

The experimental curve (*i.e.* the molar ratio of FATRIFE units in the copolymer *versus* the molar ratio of FATRIFE units in the feed) and the calculated instantaneous composition (plotted using the determined reactivity ratios) are shown in Figure 4. The instantaneous composition was calculated using equation 6:

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + r_B f_B^2 + 2 f_A f_B} \qquad (6)$$

where *Fi* and *fi* represent the instantaneous molar ratio of monomer *i* in the copolymer and the initial molar ratio of monomer (*i.e.* in the feed), respectively. The experimental and calculated curves were in very good agreement and equation 6 allows the determination of an azeotropic composition for $f_{FATRIFE} = 0{,}618$.

Thermal properties

Variation of the compositions of the poly(FATRIFE-*co*-FATRICE) copolymers led to a classical variation of Tg (Table 1). Tg increased from 113 to 127 °C as the mole % of FATRICE increased from 0 to 100%. The chlorine atoms borne by FATRICE induce a Tg increase effect as expected for α-chloroacrylates compared to α-fluoroacrylates[19]. Considering degradation temperature, every copolymer, whatever the composition of monomeric units, show a very good thermal stability. 5 % weight loss copolymers degradation occurred from 305 °C.

Refractive indices

Refractive indices of poly(FATRIFE-*co*-FATRICE) copolymers were measured at three different wavelengths, 633, 1320 and 1550 nm. Those wavelengths correspond respectively to the most efficient transmission wavelength for polymer optical fiber, the O band of data transmission and the C band of data transmission. Refractive indices of poly(FATRIFE-*co*-FATRICE) copolymers *versus* molar ratios of both monomeric units in copolymer are gathered in Table 3. Their values shift from 1.3838 to 1.4914 at 633 nm, representing a particularly wide variation.

Refractive index of poly(FATRIFE-*co*-FATRICE) copolymers *vs*. weight content of fluorine (Figure 5) and chlorine (Figure 6) shows an almost linear relation of particular interest. Indeed, a specific refractive index should be obtained by adjusting the exact amount of chlorine and fluorine content (*i.e.* the exact molar ratio of FATRIFE and FATRICE) in the copolymer.

Thanks to the equations of the curves reported in figure 5 and 6, relations between copolymers composition and refractive index can be obtained at 633 (equation 7), 1320 (equation 8) and 1550 (equation 9) nm:

$$F_{FATRIFE} = \frac{221.442.n_{(633nm)} - 341.184}{49.365.n_{(633nm)} - 91.886} \qquad (7)$$

$$F_{FATRIFE} = \frac{221.442.n_{(1320nm)} - 338.596}{49.365.n_{(1320nm)} - 90.887} \qquad (8)$$

$$F_{FATRIFE} = \frac{221.442.n_{(1550nm)} - 327.387}{49.365.n_{(1550nm)} - 91.229} \qquad (9)$$

where $F_{FATRIFE}$ and n are the molar ratio of FATRIFE in the copolymer and the desired copolymer refractive index, respectively.

Conclusion

Poly(FATRIFE-*co*-FATRICE) copolymers were synthesized by radical polymerization, using *tert*-butyl 2,2-dimethylperoxypropanoate as the initiator, with good yields, high molecular weights (reaching 10^5 g.mol^{-1}), high Tg (113 °C <Tg <127 °C) and good thermal stability (up to 300 °C). Reactivity ratios of both monomers were determined by the Kelen-Tüdos method using the compositions measured by ^{1}H NMR spectroscopy and

were found to be $r_{FATRIFE}$ = 0.56 and $r_{FATRICE}$ = 0.11 at 74 °C, showing that FATRIFE is the more reactive monomer. Those reactivity ratios indicated a low tendency to alternation, which constitutes an advantage for the decrease of light scattering of POW, even if mainly random copolymers are obtained. The refractive indices of the resulting films are in the wide range of 1.375 to 1.4812 at 1550 nm and can easily be correlated with the chlorine and fluorine content of the copolymer.

Those materials are of particular interest for optical waveguide application, for core and cladding, because of their properties and low content of hydrogen (*i.e.* low intrinsic optical absorption). Other monomers, containing higher contents of fluorine or chlorine, are under investigation to reach even larger range of refractive index values.

Acknowledgments

The authors thank Région Pays de la Loire for financial support (POSO project) and AkzoNobel for a free sample of *tert*-butyl 2,2-dimethylperoxypropanoate.

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Table 1. Feed and copolymer compositions for the radical copolymerization of FATRIFE and FATRICE[a)], yield of copolymerization, M_p and Tg of poly(FATRIFE-*co*-FATRICE) copolymers.

monomer in feed[b)] (mol %)		monomer in copolymer[c)] (mol %)				
FATRIFE	FATRICE	FATRIFE	FATRICE	Yield (weight %)	$M_{p,SEC}$[d)] ($\times 10^5$ g.mol^{-1})	Tg[e)] (°C)
100	0	100	0	88	1.17	113
80	20	82	18	88	1.42	114
65	35	64	36	88	1.26	115
50	50	49	51	84	1.52	118
35	65	35	65	87	1.25	119
20	80	21	79	84	1.42	121
0	100	91	9	82	2.05	127

[a)] Copolymerization conditions: $[t\text{Bu-OO-CO-}t\text{Bu}]_0/([\text{FATRIFE}]_0+[\text{FATRICE}]_0)$ = 1 mol %, acetonitrile, 74 °C, 10 hrs.[b)] Determined by ^{1}H NMR. [c)] Determined by ^{19}F NMR.[d)] Determined by SEC in THF, calibrated with polystyrene standards.[e)] Determined by DSC.

Table 2. Compositions of poly(FATRIFE-*co*-FATRICE) copolymers determined by ^{1}H NMR spectroscopy[a)].

	Monomer in feed (mol %)		Copolymer composition (mol %)		
run	FATRIFE	FATRICE	FATRIFE	FATRICE	Total monomers conversion (mol%)
1	16.6	83.4	32.0	68.0	4.4
2	20.6	79.4	36.4	63.6	3.5
3	34.6	65.4	49.6	50.4	3.7
4	50.4	49.6	58.8	41.2	4.9
5	65.7	34.3	65.2	34.8	5.0
6	80.6	19.4	74.9	25.1	3.8
7	93.9	6.1	90.6	9.4	5.1

[a)] Copolymerization conditions: $[t\text{Bu-OO-CO-}t\text{Bu}]_0/([\text{FATRIFE}]_0+[\text{FATRICE}]_0) = 1$ mol %, 74 °C, 2 min.

Table 3. Refractive index (n) (20 °C) of poly(FATRIFE-*co*-FATRICE) copolymer *versus* molar ratios of FATRIFE and FATRICE in the copolymers, measured at 633, 1320 and 1550 nm.

copolymer molar ratio				
FATRIFE	FATRICE	n (633 nm)	n (1320 nm)	n (1550 nm)
1	0	1.3838	1.3767	1.3750
0.82	0.18	1.4081	1.4002	1.3979
0.64	0.36	1.4245	1.4171	1.4107
0.49	0.51	1.4420	1.4345	1.4332
0.35	0.65	1.4570	1.4447	1.4463
0.21	0.79	1.4723	1.4623	1.4615
0	1	1.4914	1.4826	1.4812

Scheme 1. Synthesis of 2,2,2-trifluoroethyl and 2,2,2-trichloroethyl α-fluoroacrylates.

Scheme 2. Radical copolymerization of FATRIFE with FATRICE.

Table 1. Feed and copolymer compositions for the radical copolymerization of FATRIFE and FATRICE[a)], yield of copolymerization, M_p and Tg of poly(FATRIFE-*co*-FATRICE) copolymers.

[a)] Copolymerization conditions: [*t*Bu-OO-CO-*t*Bu]$_0$/([FATRIFE]$_0$+[FATRICE]$_0$) = 1 mol %, acetonitrile, 74 °C, 10 hrs.[b)] Determined by ^{1}H NMR. [c)] Determined by ^{19}F NMR.[d)] Determined by SEC in THF, calibrated with polystyrene standards.[e)] Determined by DSC.

Figure 1. ^{19}F NMR spectrum of the poly(FATRIFE-*co*-FATRICE) copolymer 64/36 mol % (solvent: acetone-d_6, reference: $CFCl_3$).

Scheme 3. Thermal decomposition of *tert*-butyl 2,2-dimethylperoxypropanoate and rearrangment of resulting radicals[44, 48].

Figure 2. ^{1}H NMR spectrum of FATRIFE/FATRICE feed ratio of 16.6/83.4 mol % (solvent: $CDCl_3$, reference: TMS).

Table 2. Compositions of poly(FATRIFE-*co*-FATRICE) copolymers determined by ^{1}H NMR spectroscopy[a)].

[)] Copolymerization conditions: [*t*Bu-OO-CO-*t*Bu]$_0$/([FATRIFE]$_0$+[FATRICE]$_0$) = 1 mol %, 74 °C, 2 min.

Figure 3. Kelen–Tüdos graphic method ($\eta = f(\xi)$) for the determination of FATRIFE and FATRICE reactivity ratios.

Figure 4. Monomer-polymer composition curve for the FATRIFE/FATRICE system, calculated from ^{1}H NMR spectroscopy (the solid line represents the calculated curve using eq. 6).

Table 3. Refractive index (n) (20 °C) of poly(FATRIFE-*co*-FATRICE) copolymer *versus* molar ratios of FATRIFE and FATRICE in the copolymers, measured at 633, 1320 and 1550 nm.

Figure 5. Refractive index (20 °C) *versus* weight content of fluorine in poly(FATRIFE-*co*-FATRICE) copolymers, measured at 633 (solid line), 1320 (dashed line) and 1550 (dotted line) nm.

Figure 6. Refractive index (20 °C) *versus* weight content of chlorine in poly(FATRIFE-*co*-FATRICE) copolymers, measured at 633 (solid line), 1320 (dashed line) and 1550 (dotted line) nm.