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Journal of Fluorine Chemistry 74 (1995) 233–240

JOURNAL OF FLUORINE CHEMISTRY

Synthesis and polymerization of novel fluorinated morpholino acrylates and methacrylates

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Received 30 December 1994; accepted 17 February 1995

Abstract

The synthesis of four fluorinated acrylates and methacrylates bearing a morpholino group in the lateral chain was achieved in four steps in very high yield: the radical addition of perfluoroalkyl iodides on to allyl acetate followed by an alkaline cyclization led to fluorinated epoxides. These compounds reacted with an excess of morpholine and yielded morpholinofluorinated alcohols that, condensed with acrylic or methacrylic anhydride, produced the expected fluorinated acrylic or methacrylic monomers, respectively. The behaviour in homopolymerization of such new olefins involved the study of the square of the propagation rate constant to the termination rate constant ratio (k_p^2/k_{te}) by two different methods. The poor reactivity of these monomers has been shown by a GC kinetic study and also by the calculation of the yield. The values of k_p^2/k_{te} show that they are two-hundred-times less reactive than usual fluorinated acrylic monomers. We finally propose a reactivity scale for such fluorinated monomers.

Keywords: Monoaddition; Acrylic derivatives; Kinetics; Morpholinofluorinated compounds; NMR spectroscopy; Mass spectrometry

1. Introduction

Fluorinated or perfluorinated acrylates exhibit very interesting properties such as hydrophobic and oleophobic behaviour that allow them to be used in numerous applications [1]: coatings for optical fibres [2], for paper, leather [3], metals and textiles [4]. Our interest has been focused on that last field.

Among textile coatings, Scotchgards (from 3M Company) or Foraperles (from Elf-Atochem Company) are prepared from both hydrophobic and oleophobic monomers and hydrophilic monomers able to react with the substrates. For example, these monomers are derived from acrylamide (e.g. hydroxymethyl acrylamide) or from hydroxyethyl acrylate.

Other methods are also possible to improve the compatibility of fluorinated acrylates. Copolymers from morpholinoethyl methacrylate (MEMA) [5,6] can be used. Such monomers lead to a better emulsification of fluorinated olefins, moreover they contribute to the swelling behaviour of textile fibres.

Two different kinds of investigations have been performed in our laboratory. The first concerns the synthesis of copolymers from fluorinated acrylates, α-functionalized or not, with MEMA including the determination of the reactivity ratio of these comonomers [7]. The second consists of the synthesis of monomers that bear both a perfluorinated chain and a morpholinated group. This latter method is described in this article, and the behaviour to homopolymerization of these (meth)acrylates is also detailed.

2. Results and discussion

For the synthesis of new fluorinated acrylic monomers that bear both a perfluorinated part and a morpholino group, two main possibilities of introduction on to the double bond can be planned. It is taken into account that one ethylenic carbon must remain unsubstituted so that the monomer is reactive in homopolymerization. The first consists of linking both groups on to the same ethylenic carbon, whereas the second method involves their introduction on to the ester group. The latter way has been preferred in order to obtain an optimal reactivity of the monomer.

Previous works showed that an acrylate is more reactive than a methacrylate in radical homopolymerization [8,9] and that α-functionalized acrylic monomers exhibit a similar behaviour to that of these methacrylates. Furthermore, El Bachiri et al. [10] synthesized α-(perfluorooctylmethyl) ethylacrylate and mentioned that this monomer homopolymerizes with difficulty. Thus, new morpholinofluorinated

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SSDI 0022-1139(95)03281-9

Table 1
Synthesis of fluorinated epoxides from $C_nF_{2n+1}CH_2CHXCH_2Y$ (n=4,6,8; X or Y = OAc or I)

R_F	$[KOH]_0/[R_F]_0$	Solvent	Temp. (°C)	Time (h)	Yield (%)
C_8F_{17}	2.5	pentane	25	16	30
C_8F_{17}	2.5	pentane	reflux	5	30
C_8F_{17}	3.0	hexane	25	16	60
C_8F_{17}	2.0	hexane	reflux	16	80
C_8F_{17}	2.0	hexane	reflux	5	80
C_6F_{13}	2.0	hexane	reflux	16	57
C_4F_9	2.4	hexane	reflux	16	55

acrylates and methacrylates have been prepared by introducing such heteroatomic groups on the side of the ester function.

2.1. Synthesis of fluorinated monomers

Fluorinated acrylic monomers are usually synthesized from the condensation of a fluorinated alcohol with an acid chloride or an unsaturated acid [11,12] or, more rarely, from transesterification [13,14].

Morpholinofluorinated alcohols were produced by reacting an excess of morpholine with fluorinated epoxides as described previously [15,16]. These authors supplied the spectral characteristics but they did not continue their investigations for the synthesis of acrylic monomers.

The synthesis of such morpholinofluorinated (meth)-acrylates was performed in four steps as follows:

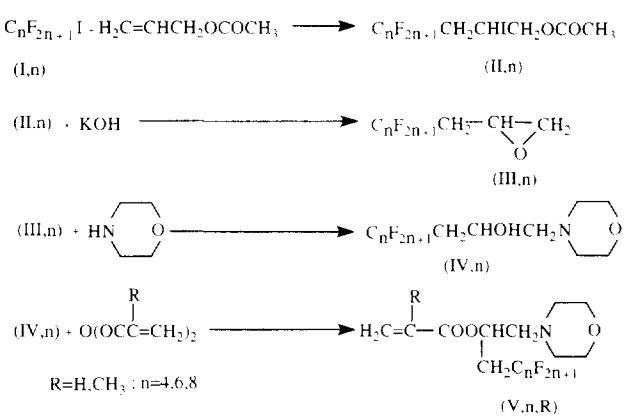

Table 2
Synthesis of morpholinofluorinated alcohols by condensation of morpholine on to fluorinated epoxides

R_F	[morpholine]$_0$/[epoxide]$_0$	Temp. (°C)	Time (h)	Yield (%)
C_4F_9	5.5	120	2	97
C_6F_{13}	5.0	140	2	90
C_8F_{17}	5.4	140	2	90

2.1.1. First step

This is the synthesis of perfluoroalkyl iodoacetates from the stoichiometric addition of perfluoroalkyl iodides (R_FI) on to allyl acetate. Previous work indicated that these additions when initiated by radicals led to the expected fluoro-iodo acetates with quantitative conversion of R_FI [17]. However, at temperatures higher than 150 °C, the 1:1 monoadduct underwent a thermal rearrangement [18,19,20] as follows:

$$\mathbf{II,}n \xrightarrow{\Delta} C_nF_{2n+1}CH_2CH(OCOCH_3)CH_2I$$

2.1.2. Second step

This is the formation of fluorinated glycidic epoxides from the fluoro-iodo acetates **II,*n*** [21,22]. Such syntheses were performed in different solvents in the presence of potassium hydroxide from the total product mixture of the preparation of **II,*n***. The results are collected in Table 1.

Best conditions were obtained when the reaction occurred at hexane reflux for at least 5 h. After distillation, epoxide **III,8** was produced in yields higher than 80%.

The compound was characterized by ^1H NMR spectroscopy. A multiplet was observed between 2.1 and 2.54 ppm corresponding to the protons in the α-position of the perfluorinated chain. The multiplet assigned to the proton linked to the asymmetric carbon was detected at 3.21 ppm and the coupling constants of the peaks corresponding to the ABX system are given in Experimental details. The carbon atoms of compound **III,8** were identified exactly by multiplicity sequence (J-modulated) ^{13}C NMR spectroscopy.

2.1.3. Third step

This consists of the addition of morpholine on to the fluorinated epoxides **III,*n***. Such reactions were performed at reflux in morpholine for 2 h. The corresponding alcohols were produced quantitatively (Table 2). Each alcohol was carefully characterized by ^1H and ^{13}C NMR spectroscopy (see Experimental details).

The ^1H NMR spectrum of **IV,8** alcohol shows the absence of an ABX system in the 2.5–4.8 ppm range of the epoxide but exhibits a quintet at 4.20 ppm characteristic of the proton of the asymmetric carbon. Furthermore, the signals centred at 3.67 and 2.40 ppm are assigned to the morpholino group.

In the mass spectrum are noted the fragments of the perfluorinated chain $m/z^+ = 69$, i.e. CF_3^+; $m/z = 119$, i.e. $C_2F_5^+$, $m/z^+ = 77$, i.e. $CF_2CH_2CH^+$ and the mass peak $m/z^+ = 564$.

2.1.4. Fourth step: synthesis of morpholinofluorinated acrylics

In order to find the most favourable way to prepare such fluorinated monomers, a model reaction was studied.

(a) Modelling from 2-propanol

Several ways of obtaining (meth)acrylic monomers from such a secondary alcohol were attempted: transesterification,

Table 3
Rate conversion and yield in the synthesis of isopropyl methacrylates by different methods

Method	Rate conversion by GC (%)	Yield (%)
methacrylic acid + DCCI	40	30
methacrylic anhydride	100	90
methacryloyl chloride	100	90

esterification with (meth)acrylic acid or with (meth)acrylic anhydride, or by condensation with (meth)acryloyl chloride.

Transesterification: As it is well known that secondary alcohols are less reactive than primary alcohols, the transesterification with methyl or ethyl methacrylate was not attempted.

Esterification: Esterification of these alcohols with methacrylic acid in the presence of a water scavenger [20] such as dicyclocarboxydiimide (DCCI) was performed. However the use of methacrylic anhydride or methacryloyl chloride as reactants required harsher experimental conditions (e.g. anhydrous medium).

In order to find the best synthesis, the preparation of the isopropyl methacrylate from 2-propanol was investigated as a model reaction. Each reaction was monitored by gas chromatography that allowed determination of the conversion rate of the alcohol into methacrylate. The results are shown in Table 3.

The best results were obtained from esterification of this alcohol with methacrylic anhydride or from the condensation of methacryloyl chloride. On the contrary, the direct esterification of morpholinofluorinated alcohol with methacrylic acid in the presence of DCCI in equimolar quantities led to medium yields (40%) confirmed by the obtained weight of the corresponding urea produced by the reaction between DCCI and the water formed.

From both methods showing the best results, that involving the use of the anhydride was preferred since it required easier conditions of synthesis. Contrary to the condensation with the methacryloyl chloride that required an anhydrous medium and use of an inert atmosphere, such an esterification produced methacrylic acid in similar amounts to the expected monomer. However, such an acid can be easily isolated by simple filtration over alumina, leading to pure monomer.

(*b*) *Application to morpholinofluorinated alcohols*

Because of the efficient reactivity of secondary alcohols, such a method was applied to the morpholinofluorinated alcohols described above. From methacrylic anhydride, novel morpholinofluorinated methacrylates (**V,*n*** with $n = 4, 6, 8$) were obtained in yields higher than 90%. Their ^{1}H NMR spectra exhibit the presence of characteristic signals of the ethylenic protons in the 5.5–6.0 ppm range and the low field shift of the multiplet assigned to the proton adjacent to the ester group from 4.10 ppm for the alcohols **IV,*n*** to 5.4 ppm for methacrylates **V,*n***. The chemical shifts in the ^{1}H and ^{13}C NMR spectra of morpholinofluorinated methacrylates are under Experimental details.

Furthermore, the synthesis of morpholinofluorinated acrylates was attempted in a similar manner as the previous one, starting from the condensation of acrylic anhydride on to the morpholinofluorinated alcohols. The yields were about 90% and the products have been characterized by ^{1}H and ^{13}C NMR spectroscopy (see Experimental details).

It is interesting to note that in the presence of an acid catalyst (methanesulfonic acid), the reaction between morpholinofluorinated alcohols and (meth)acrylic anhydride gave lower yields, even if the conversion was total. This can be explained by the formation of a quaternary ammonium salt corresponding to the monomer.

2.2. Homopolymerization of morpholinofluorinated acrylics

The behaviour of fluorinated acrylic monomers in homopolymerization reactions was described in a previous paper. The determination of the k_p^2/k_{te} ratio showed that the fluorinated monomers are less reactive than the hydrogenated monomers. The determination of the k_p^2/k_{te} values was considered in order to compare the homopolymerization of the new morpholinofluorinated monomers to the other monomers described previously [8].

The kinetics of the polymerization was measured under the same conditions as those for commercial fluorinated monomers (GC with acetonitrile or tetrahydrofuran as the solvents, monochlorobenzene as the internal standard and AIBN as the initiator). The monomers MMF8 and AMF8 were taken as models. Various experiments were attempted from these monomers, but the plots of the monomer concentration versus time showed too small a slope to determine easily the k_p^2/k_{te} value, even if the reaction was performed over 8 h. We consider these monomers as less reactive in homopolymerization than fluorinated acrylic monomers.

Another way to determine the rate value concerns the conversion rate α:

$$\alpha = \frac{[M]_0 - [M]}{[M]_0}$$

where M denotes the monomer, and Meyerhoff's results [23] obtained from Tobolsky's relationship [24]:

$$\ln\left(\frac{[M]_0}{[M]}\right) = -\ln(1-\alpha) = 2\sqrt{\frac{k_p^2 f}{k_{te} k_d}} \cdot \sqrt{[I_2]_0} \cdot \left[1 - \exp\left(\frac{-k_d t}{2}\right)\right]$$

where k_p, k_{te}, k_d, f, $[I_2]_0$ and t represent the propagation rate constant, the termination rate constant, the initiator dissociation constant, the initiator efficiency, the initial initiator concentration and the time, respectively.

At 80 °C, we are in the case of a dead-end polymerization. This means that the $[I_2]/[I_2]_0$ ratio reaches a zero value,

Table 4
Determination of k_p^2/k_{te} values for different monomers by two different methods

Monomers	$[M]_0$ (mol l^{-1})	$10^4\,[I_2]_0$ (mol l^{-1})	Yield (%)	$10^3\,k_p^2/k_{te}$ (l $mol^{-1}\,s^{-1}$) by GC [8]	$10^3\,k_p^2/k_{te}$ (l $mol^{-1}\,s^{-1}$)
MAC8	0.2	5.813	70	8.88	12.98
MAC8	0.2	1.220	38	8.88	9.76
αAC8	0.2	4.040	52	9.09	6.94
αAC8	0.2	1.012	26	9.09	4.66
MMF8	0.2	7.290	30	–	0.91
AMF8	0.2	20.580	32	–	0.38

whereas the monomer is not totally consumed. Then, for infinite time, it can be written:

$$-\ln(1-\alpha_M) = 2\sqrt{\frac{k_p^2 f}{k_{te}k_d}}\cdot\sqrt{[I_2]_0}$$

where α_M represents the maximum conversion rate.

Then k_p^2/k_{te} could be determined using the homopolymerization yield and the initial initiator concentration:

$$\frac{k_p^2}{k_{te}} = \frac{[-\ln(1-\alpha_M)]^2\cdot k_d}{4f[I_2]_0}$$

Such a method was applied to 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (MAC8) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl-α-acetoxyacrylate (αAC8) [8] and led to realistic results. Then it was tested with MMF8 and AMF8. The results are given in Table 4. Values found for k_p^2/k_{te} are low and confirm that these monomers are poorly reactive in homopolymerization. This shows that the first method was difficult to use.

These low ratios can be explained by the steric hindrance brought about by the side-chain that reduces the reactivity.

However, it is observed that the ratio assigned to the acrylate is unexpectably lower than that of the analogous methacrylate. But it is necessary to consider that such a method leads to values less accurate than those obtained from a kinetic study. Finally we can complete the reactivity scale of fluorinated monomers proposed in a previous work [8] (AC8 means 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate) as follows: AC8 > MAC8#αAC8 > MMF8#AMF8.

Differential scanning calorimetry of these homopolymers resulted in a glass transition temperature (T_g) of +50 °C and +27 °C for MMF8 and AMF8 polymers, respectively. The tendency of these values for polymethacrylate relative to polyacrylate is in good agreement with that observed in a previous work [25]. Actually polyacrylate with a $C_2H_4C_6F_{13}$ group adjacent to the ester function exhibits a T_g of 9 °C whereas the corresponding polymethacrylate has a T_g of 49 °C [26].

3. Experimental details

Perfluoroalkyl iodides, (meth)acrylic anhydrides, F113 (Cl_2FCCF_2Cl) and MAC8 were kindly supplied by Elf-Atochem, whereas allyl acetate and dibenzoyl peroxide were purchased from Aldrich and did not require purification prior to use.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an OV 17 column, 1 m × 1/8 in. The nitrogen pressure at the entrance to the column was maintained at 0.6 bar, and the detector and injector temperatures were 270 °C and 250 °C, respectively. The temperature program started from 50 °C and reached 250 °C at a heating rate of 15 °C min^{-1}. The GC apparatus was connected to a Shimadzu CR 6A integrator which automatically calculated the area of each peak on the chromatogram.

The mass spectra were scanned on a GLC–mass spectrometer tandem JEOL DX-303 (JMA 5000, single focus, 70 eV, helium, GLC inlet via a capillary column of 1000 mm coated with silicon elastomer).

The products were analyzed at the CNRS Microanalysis Laboratory of ENSCM and characterized by ^1H and ^{13}C NMR spectroscopy, all undertaken at room temperature, recorded in $CDCl_3$ on a Bruker AC-200 or -250 apparatus with tetramethylsilane as the internal reference. The letters s, d, t, q and m designate singlet, doublet, triplet, quadruplet and multiplet, respectively. Chemical shifts are given in 10^{-6} (ppm).

Glass transition temperatures (T_g) were determined with a Perkin-Elmer DSC4 instrument calibrated with n-heptane during the second scan, under a helium atmosphere, from −100 °C to +100 °C at a heating rate of 20 °C min^{-1}.

3.1. Synthesis of perfluoroalkyliodo acetates (II,n)

3.1.1. Preparation of 2-iodo-4,4,5,5,6,6,7,7,7-nonafluoroheptyl acetate (II,4)

The experiment was similar to that described previously [18–20,22] using perfluorobutyl iodide (25.0 g, 72 mmol) and allyl acetate (7.22 g, 72.2 mmol). Dibenzoyl peroxide (0.3 g, 1.24 mmol) was added when the temperature was 95 °C. The exotherm reached 153 °C, leading to a decolouring of the mixture and then an amber colour. Monoadduct **II,4**

was not distilled. The yield determined by gas chromatography was estimated as 93%. ^{1}H and ^{19}F NMR characterizations were similar to those of previous work [18].

*3.1.2. Synthesis of 2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl acetate (**II,6**)*

A similar experiment as previously was performed using perfluorohexyl iodide (66.9 g, 150 mmol), allyl acetate (15.0 g, 150 mmol) and dibenzoyl peroxide (0.5 g, 2.1 mmol). The exotherm reached 172 °C with the same changes of colours as above. The reaction was completed within 15–30 min after addition of initiator. The yield based on gas chromatography was higher than 95% and NMR analyses were identical to those described previously [18].

*3.1.3. Preparation of 2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluorooctyl acetate (**II,8**)*

As previously, perfluorooctyl iodide (202.0 g, 370 mmol), allyl acetate (37.0 g, 370 mmol) were stirred at 95 °C. The exotherm reached 180 °C. The monoadduct was almost quantitatively obtained with the same NMR data as given recently [18].

*3.2. Synthesis of fluorinated epoxides (**III,n**)*

*3.2.1. Preparation of 1,1,2,2,3,3,4,4,4-nonafluorobutyl oxirane (**III,4**)*

In a 500 ml two-necked round-bottomed flask equipped with a condenser and a mechanical stirrer were introduced iodoacetate **II,4** (223.0 g, 0.5 mol) and powdered potassium hydroxide (67.3 g, 1.2 mol) dissolved in 1500 ml of hexane. The reaction mixture was refluxed for 16 h and then cooled. The salt observed in the product mixture was filtered off and washed with diethyl ether. Distillation led to 75.9 g (0.201 mol, 55%) of fluorinated epoxide **III,4**. Elemental analysis: Found: C, 28.89; H, 2.06; F, 60.42%. $C_9H_5OF_9$ requires: C, 30.45; H, 1.83; F, 61.93; M, 376.12. B.p. 117–120 °C/760 mm Hg. ^{1}H NMR ($CDCl_3$) δ: 2.19 (2H, m, $C_4F_9CH_2$); 2.45 (1H, q, $J_{AX}=2.47$ Hz, CH_aH_b–O); 2.73 (1H, t, $J_{AB}=4.88$ Hz, $J_{BX}=4.60$ Hz, CH_aH_b–O); 3.08 (1H, m, CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 34.74 (t, $J=6.23$ Hz, $CH_2C_4F_9$); 44.11 (s, CH); 44.22 (s, CH_2O); 104–123 (4C, m, C_4F_9) ppm. MS *m/e* (%): 57 (7); 77 (20); 107 (25); 119 (14); 136 (97); 137 (80); 154 (100); 169 (5).

*3.2.2. Synthesis of 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl oxirane (**III,6**)*

As previously, iodoacetate **II,6** (30 g, 55 mmol) and potassium hydroxide (6.2 g, 110 mmol) dissolved in 20 ml of hexane were refluxed for 16 h. After similar work-up and distillation, 11.8 g of **III,6** were recovered (57%). Elemental analysis: Found: C, 28.96; H, 1.45; F, 66.43%. $C_9H_5OF_{13}$ requires: C, 28.74; H, 1.34; F, 65.67%; M, 376.12. B.p. 65–67 °C/18 mmHg. ^{1}H NMR ($CDCl_3$) δ: 2.32 (2H, m, $C_6F_{13}CH$); 2.60 (1H, q, $J_{AX}=2.48$ Hz, CH_aH_b–O); 2.79 (1H, t, $J_{AB}=4.76$ Hz, $J_{BX}=4.47$ Hz, CH_aH_b–O); 3.22 (1H, m, CH) ppm. ^{13}C NMR δ: (t, $J=6.20$ Hz, $CH_2C_6F_{13}$); 44.11 (s, CH); 44.22 (s, CH_2O); 104–123 (4C, m, C_6F_{13}) ppm. MS *m/e* (%): 57 (9); 77 (17); 107 (20); 136 (77); 154 (100).

*3.2.3. Synthesis of 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl oxirane (**III,8**)*

Using the same method as above, iodoacetate **II,8** (100.1. g, 155 mmol) and potassium hydroxide (20.0 g, 330 mmol) dissolved in 70 ml of hexane were stirred with reflux for 5 h. After work-up, 60.0 g of fluorinated epoxide **III,8**, were distilled (81%). Elemental analysis: Found: C, 27.55; H, 0.98; F, 65.78%. $C_{11}H_5OF_{17}$ requires: C, 27.75; H, 1.06; F, 67.83%; M, 476.13. B.p. 103–105 °C/18 mmHg. ^{1}H NMR ($CDCl_3$) δ: 2.32 (2H, m, $C_8F_{17}CH_2$); 2.59 (1H, q, $J_{AX}=2.50$ Hz, CH_aH_b–O); 2.88 (1H, t, $J_{AB}=4.80$ Hz, $J_{BX}=4.42$ Hz, CH_aH_b–O); 3.21 (1H, m, CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 34.8 (t, $CH_2C_8F_{17}$); 44.19 (s, CH); 45.04 (s, CH_2–O); 105–115 (8C, m, C_8F_{17}) ppm. MS *m/e* (%): 57 (7); 77 (20); 107 (26); 119 (6); 136 (100); 137 (80); 154 (100); 169 (5).

3.3. Synthesis of morpholinofluorinated alcohols

*3.3.1. Synthesis of 1-morpholino-4,4,5,5,6,6,7,7,7-nonafluoro-2 heptanol (**IV-4**)*

Into a 250 ml two-necked round-bottomed flask equipped with a condenser and a magnetic stirrer were introduced epoxide **III,4** (37.3 g, 135 mmol) and morpholine (65.9 g, 760 mmol). The mixture was refluxed for 2 h and after cooling and evaporation of the excess morpholine, the alcohol **IV,4** was distilled (47.6 g, 131 mmol, 97%). Elemental analysis: Found: C, 36.96; H, 3.95; N, 4.29; F, 47.26%. $C_{11}H_{14}O_2F_9N$ requires: C, 36.37; H, 3.88; N, 3.86; F, 47.07%; M, 363.22. B.p. 88–89 °C/18 mmHg. ^{1}H NMR ($CDCl_3$) δ: 2.00–2.55 (2H, m, $C_4F_9CH_2$); 2.44 (4H, t, $J=8.83$ Hz, N–CH_2–CH_2–O); 2.63 (2H, m, –CH_2N–C_2H_4O); 3.70 (4H, t, $J=5.89$ Hz, N–CH_2–CH_2–O); 4.13 (1H, sext, $J=4.41$ Hz, CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 35.6 (tdt, $J=20.87$ Hz, CH_2–C_4F_9); 53.3 (2C, s, –N–CH_2–CH_2–O); 60.07 (s, –CH–); 64.04 (s, CH_2N–C_2H_4O); 66.6 (2C, s, CH_2–O); 105–125 (4C, m, C_4F_9) ppm. MS *m/e* (%): 86 (95); 98 (98); 100 (100); 126 (16); 306 (50); 346 (80); 363 (100).

*3.3.2. Preparation of 1-morpholino-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-nonanol (**IV,6**)*

The same experimental device as above was used containing the epoxide **III,6** (3.76 g, 10 mmol) and morpholine (4.36 g, 50 mmol). As previously, the morpholinofluorinated alcohol was distilled (4.16 g, 9 mmol, 90%). Elemental analysis: Found: C, 33.50; H, 2.89; N, 2.93; F, 52.86%. $C_{13}H_{14}O_2F_{13}N$ requires: C, 33.71; H, 3.05; N, 3.02; F, 53.32%; M, 463.20. B.p. 88–91 °C/18 mmHg. ^{1}H NMR ($CDCl_3$) δ: 2.00–2.55 (2H, m, $C_6F_{13}CH_2$); 2.48 (4H, t, N–CH_2–CH_2–O); 2.67 (2H, m, –CH_2N–C_2H_4O); 3.73 (4H, t, $J=4.11$ Hz, CH_2–O); 4.15 (1H, tdt, CH) ppm. ^{13}C NMR

($CDCl_3$) δ: 35.76 (tdt, J = 21.57 Hz, CH_2–C_6F_{13}); 53.3 (2C, s, N–CH_2–CH_2–O); 60.05 (s, –CH–); 64.06 (s, CH_2N); 66.6 (2C, s, O–CH_2); 105–125 (6C, m, C_6F_{13}) ppm. MS *m/e* (%): 86 (8); 98 (9); 100 (57); 126 (7); 379 (43); 446 (100); 464 (65).

*3.3.3. Synthesis of 1-morpholino-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-undecanol (**III,8**)*

As above, fluorinated epoxide **III,8** (20.8 g, 43.7 mmol) and morpholine (19.0 g, 218 mmol) were stirred magnetically at reflux in morpholine for 2 h. After work-up, morpholinofluorinated alcohol **IV,8** was distilled (22.4 g, 40 mmol, 91%). It can be purified by precipitation from water. Elemental analysis: Found: C, 32.17; H, 2.25; N, 2.56; F, 57.43%. $C_{15}H_{14}O_2F_{17}N$ requires: C, 31.99; H, 2.51; N, 2.49; F, 57.34%; M, 563.25. B.p. 122–126 °C/0.01 mmHg. ^{1}H NMR ($CDCl_3$) δ: 2.00–2.55 (2H, m, $C_8F_{17}CH_2$); 2.48 (4H, t, N–CH_2–CH_2–O); 2.67 (2H, m, –CH_2N–C_2H_4O); 3.73 (4H, m, O–CH_2); 4.20 (1H, tdt, CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 35.82 (tdt, J = 21.28 Hz, CH_2–C_8F_{17}); 53.3 (2C, s, N–CH_2–CH_2–O); 60.0 (s, –CH–); 64.07 (s, –CH_2N–C_2H_4O); 66.7 (2C, s, O–CH_2); 105–125 (8C, m, C_8F_{17}) ppm. MS *m/e* (%): 69 (22); 86 (13); 98 (22); 100 (83); 126 (5); 546 (30); 564 (100).

3.4. Synthesis of (meth)acrylic derivatives

3.4.1. Modelling: preparation of isopropyl methacrylate

(a) Esterification of methacrylic acid with 2-propanol

In a two-necked round-bottomed flask equipped with a condenser were placed 40 ml of methylene dichloride, 2-propanol (3.0 g, 50 mmol), methacrylic acid (4.3 g, 50 mmol) and dicyclocarboxydiimide (DCCI) (10.3 g, 50 mmol). The reaction was stirred at 40 °C and was monitored by gas chromatography.

The alcohol conversion increased with time and reached a maximum value of 40% after 5 h. Purification of methacrylate was performed by filtration of the urea produced (4.0 g, 67 mmol). The overall yield was 36%.

(b) Esterification of methacrylic anhydride with 2-propanol

In a two-necked round-bottomed flask equipped with a condenser and a dropping funnel were placed 2-propanol (5.0 g, 0.1 mmol) in 30 ml of methylene chloride and methacrylic anhydride (15.4 g, 0.1 mol) was added dropwise. The reaction mixture was heated at 40 °C and was monitored by gas chromatography. After 5 h, all the alcohol was converted leading to the expected methacrylate.

The solvent was evaporated and the methacrylate purified by column chromatography (eluent: pentane/diethyl ether, 95:5) producing 11.5 g (90 mmol, 90%) of pure monomer.

(c) Addition of methacryloyl chloride on to 2-propanol

Under an inert argon atmosphere, the following were placed in a 10 ml two-necked round-bottom flask equipped with a condenser: 2-propanol (5.0 g, 0.1 mmol), 50 ml of anhydrous diethyl ether and pyridine (7.9 g, 0.1 mmol). Under stirring, methacryloyl chloride (10.5 g, 0.1 mmol) was added dropwise at 40 °C. The mixture was left to stir and the formation of methacrylate was monitored by gas chromatography. After 5 h, the conversion of alcohol was quantitative. The crude product was filtered in order to get rid of the pyridinium salt. The solvent was evaporated and by purification on an alumina column (eluent: pentane/diethyl ether, 95:5) 11.5 g (0.09 mol, 90%) of monomer were recovered. ^{1}H NMR ($CDCl_3$) δ:1.25 (6H, d, J = 6.25 Hz, CH_3–CH–CH_3); 1.89 (3H, s, CH_3); 5.02 (1H, m, J = 6.26 Hz, CH); 5.48 (1H, d, *H*–CH=C); 6.04 (1H, d, H–C*H*=C) ppm. ^{13}C NMR ($CDCl_3$) δ: 17.76 (s, CH_3); 21.3 (2C, s, *C*H_3–CH–*C*H_3); 67.39 (s, –CH–); 126.07 (s, CH_2=C); 136.54 (s, CH_2=C); 166.34 (s, COO) ppm.

3.5. Synthesis of morpholinofluorinated methacrylate (MMFn)

3.5.1. 1-Morpholinomethyl-3,3,4,4,5,5,6,6,6-nonafluorohexylmethacrylate (MMF4)

In a 100 ml two-necked round-bottomed flask equipped with a condenser were introduced morpholinofluorinated alcohol **IV,4** (8.62 g, 23.7 mmol) in 50 ml of methylene chloride. Then methacrylic anhydride (3.65 g, 23.7 mmol) was added dropwise. The mixture was refluxed with stirring for 5 h. The solvent was evaporated and MMF4 purified on an alumina column (eluent: pentane/diethyl ether, 95:5) when 9.1 g (21.1 mmol, 90%) were recovered. Elemental analysis: Found: C, 41.57; H, 4.34; N, 3.49; F, 40.27%. $C_{15}H_{14}O_2F_{17}N$ requires: C, 41.77; H, 4.21; N, 3.25; F, 39.64%; M, 431.30. ^{1}H NMR ($CDCl_3$) δ: 1.90 (3H, s, CH_3); 2.35–2.78 (8H, m, CH_2–N–CH_2–CH_2–O, CH_2–C_4F_9); 3.64 (4H, m, CH_2–O); 5.43 (1H, sext, CH); 5.5 (1H, d, *H*CH=C); 6.05 (1H, d, HC*H*=C) ppm. ^{13}C NMR ($CDCl_3$) δ: 17.77 (s, CH_3); 32.89 (t, J = 21.08 Hz, $CH_2C_4F_9$); 53.80 (2C, s, NCH_2–CH_2); 60.89 (s, CH); 64.52 (s, CH_2–N); 66.66 (2C, s, CH_2–O); 105–125 (4C, m, C_4F_9); 125.61 (s, CH_2=C); 135.75 (s, CH_2=*C*); 165.85 (s, COO) ppm.

3.5.2. 1-Morpholinomethyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylmethacrylate (MMF6)

As previously, methacrylic anhydride (2.7 g, 17.3 mmol) was added dropwise with stirring to alcohol **IV,6** (8.0 g, 17.3 mmol) dissolved in 50 ml of methylene chloride. After similar work-up, methacrylate MMF6 (8.1 g, 15.3 mmol, 88%) was recovered. Elemental analysis: Found: C, 38.67; H, 3.31; N, 2.80; F, 46.87%. $C_{17}H_{18}O_3F_{13}$ requires: C, 38.43; H, 3.41; N, 2.64; F, 46.48%; M, 531.31. ^{1}H NMR ($CDCl_3$) δ: 1.91 (3H, s, CH_3); 2.4–2.7 (8H, m, CH_2–N–CH_2–CH_2O, CH_2–C_6F_{13}); 3.65 (4H, t, J = 4.59 Hz, O–CH_2); 5.43 (1H, sext, CH); 5.5 (1H, d, *H*CH=C); 6.06 (1H, d, HC*H*=C) ppm. ^{13}C NMR ($CDCl_3$) δ: 17.95 (s, CH_3); 33.0 (t, J = 21.12 Hz, $CH_2C_6F_{13}$); 54.0 (2C, s, NCH_2–CH_2O); 61.0 (s, CH); 64.6 (s, CH_2–N); 66.7 (2C, s, CH_2–O); 105–125 (6C, m, C_6F_{13}); 125.80 (s, CH_2=C); 135.8 (s, CH_2=*C*); 166.05 (s, COO) ppm.

3.5.3. 1-Morpholinomethyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (MMF8)

As above, methacrylic anhydride (2.9 g, 18.8 mmol) was added dropwise to morpholinofluorinated alcohol **IV,8** (10.0 g, 18.6 mmol) in 50 ml of methylene chloride. The worked-up crude product after purification over column chromatography (same eluent as previously) led to methacrylate MMF8 (10.8 g, 17.1 mmol, 92%). Elemental analysis: Found: C, 36.90; H, 3.11; N, 2.31; F, 51.23%. $C_{19}H_{18}O_3NF_{17}$ requires: C, 36.15; H, 2.87; N, 2.22; F, 51.16%; M, 631.33. ^{1}H NMR ($CDCl_3$) δ: 1.93 (3H, s, CH_3); 2.4–2.65 (8H, m, CH_2–N–CH_2–CH_2–O, CH_2–C_8F_{17}); 3.67 (4H, m, O–CH_2); 5.44 (1H, sext, CH); 5.59 (1H, d, HCH=C); 6.09 (1H, d, HCH=C) ppm. ^{13}C NMR ($CDCl_3$) δ: 18.09 (s, CH_3); 33.25 (t, J = 21.6 Hz, $CH_2C_8F_{17}$); 54.00 (2C, s, NCH_2–CH_2O); 61.12 (s, CH); 64.80 (s, CH_2–NC_2H_4O); 66.92 (2C, s, O–CH_2); 105–125 (8C, s, C_8F_{17}); 125.97 (s, CH_2=C); 135.92 (s, CH_2=C); 166.14 (s, COO) ppm. MS *m/e* (%): 69 (42); 86 (9); 98 (33); 100 (100); 126 (23); 544 (37); 546 (100); 632 (13).

3.5.4. 1-Morpholinomethyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (AMF8)

As previously, acrylic anhydride (4.55 g, 36.1 mmol) was added dropwise with stirring to alcohol **IV,8** (20.2 g, 35.8 mmol) dissolved in 90 ml of methylene chloride. The worked-up crude product led to monomer AMF8 (19.0 g, 30.70 mmol, 90%) after purification over column chromatography (same eluent as previously). Elemental analysis: Found: C, 34.86; H, 2.83; N, 2.35; F, 52.08%. $C_{18}H_{16}O_3NF_{17}$ requires: C, 35.00; H, 2.61; N, 2.26; F, 52.34%; M, 617.31. ^{1}H NMR ($CDCl_3$) δ: 2.2–2.7 (8H, m, $CH_2N(CH_2)_2$, $CH_2C_8F_{17}$); 3.63 (4H, t, –CH_2–O–CH_2–); 5.44 (1H, m, CH); 5.7–6.2 (2H, m, CH_2=C); 6.4 (1H, m, =CH–) ppm. ^{13}C NMR ($CDCl_3$) δ: 33.21 (t, J = 21.0 Hz, $CH_2C_8F_{17}$); 53.97 (2C, s, N–CH_2–CH_2); 61.13 (s, CH); 64.42 (s, CH_2–N); 66.84 (2C, s, CH_2–O–CH_2); 127.96 (s, CH_2=); 131.13 (s, =CH–); 164.74 (s, COO) ppm. MS *m/e* (%): 69 (60); 84 (18); 86 (12); 100 (105); 119 (10); 544 (110); 617 (12).

3.6. Homopolymerization

In a 50 ml two-necked round-bottomed flask equipped with a condenser and under an inert argon atmosphere was introduced 25 ml of an acetonitrile solution containing monomer MMF8 (3.155 g, 0.005 mol, 0.200 mol l^{-1}) and AIBN (2.99×10^{-2} g, 1.822×10^{-4} mol, 7.29×10^{-3} mol l^{-1}). The mixture was refluxed for 12 h. The homopolymer was precipitated from methanol and dried under vacuum to constant weight (0.95 g, 30% yield). ^{1}H NMR (F-113 + $Cl_2DCCDCl_2$) δ: 1.0–2.0 (CH_3, proton of carbonated chain); 2.0–3.0 (8H, –CH_2–N–CH_2–CH_2–O; CH_2–C_8F_{17}); 3.5–3.8 (4H, CH_2–O–CH_2); 5.3 (1H, CH) ppm.

3.6.1. Homopolymerization of AMF8

In similar conditions as previously, a solution of 25 ml of acetonitrile containing AMF8 (3.085 g, 0.005 mol, 0.200 mol l^{-1}) and AIBN (0.0844 g, 5.145×10^{-4} mol, 2.05×10^{-2} mol l^{-1}) was refluxed for 12 h. After precipitation from methanol, the polymer was dried under vacuum to constant weight (1.0 g, 32%). ^{1}H NMR (F-113 + $Cl_2DCCDCl_2$) δ: 1.0–1.5 (H, protons of carbonated backbone); 2.2–2.7 (8H, –CH_2–N–CH_2–CH_2–O, CH_2–C_8F_{17}); 3.3–3.6 (4H, CH_2–O–CH_2); 5.4 (1H, CH) ppm.

4. Conclusions

The synthesis of new morpholinofluorinated monomers can be performed in four steps from perfluoroalkyl iodides to synthesize firstly the corresponding iodoacetate, and then the fluorinated epoxide. The addition step of morpholine gave the secondary morpholinofluorinated alcohol. Reaction with (meth)acrylic anhydride led to the desired monomers. The overall yield of such olefins was about 68%. Behaviour in homopolymerization of these monomers led to low values of k_p^2/k_{te}, probably resulting from the steric hindrance of the chain. These new acrylics seem to be two-hundred-times less reactive than usual fluorinated acrylics such as AC8, and the reactivity scale was determined as: AC8 > MAC8 # αAC8 > MMF8 # AMF8.

The T_g values were determined and even if the value for AMF8 (+27 °C) was lower than that for MMF8 (+50 °C), they were close. Such new monomers bearing a hydrophobic and hydrophilic chain should be very interesting in textile applications.

Acknowledgements

We thank the French Institute of Textiles for financial support, Elf Atochem and Vladimir Cirkva from Prague Institute of Chemical Technology for scientific contributions.

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