Controlled Radical Polymerization of *n*-Butyl α-Fluoroacrylate. 1. Use of Atom Transfer Radical Polymerization as the Polymerization Method

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ABSTRACT: Atom transfer radical polymerization (ATRP) of *n*-butyl α-fluoroacrylate with CuCl and CuBr as the catalyst and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the ligand has been studied. Ethyl 2-bromoisobutyrate (2-EBiB) and 3-(trimethylsilyl)propyl 2-bromopropionate (2-SBP) were used as initiators. The latter was used as a probe for ^{1}H NMR analysis in order to determine the true molecular weight up to about 10 000. In these conditions at $T = 90$ °C, polymerization was controlled as indicated by a plot of $M_n = f(\alpha_M)$, and the effect of the halogen of the catalyst perfectly agrees with the current knowledge of ATRP. In addition, analysis of the CFBr end groups by ^{19}F NMR further confirmed that the polymerization follows the ATRP mechanism. By calibration of size exclusion chromatography with standards prepared with the 2-SBP initiator, it was shown that the experimental molecular weights were close to the theoretical values. The results were better than those where the molecular weights were determined with polystyrene or poly(methyl methacrylate) calibration. The characteristic values of the Mark−Houwink coefficients have been calculated for poly(*n*-butyl α-fluoroacrylate) in tetrahydrofuran at $T = 30$ °C.

Introduction

α-Fluoroacrylates are particularly interesting monomers, especially when they are bearing groups with a very high fluorine content such as $-CH_2-CF_3$, $-CH(CF_3)_2$, and $-C_6F_5$ in the α position. Indeed, these polymers present exceptional physical properties such as a very low absorption in the near-infrared,[1] a glass transition temperature generally 30 °C higher than their methacrylic homologues,[1,2] and a thermal stability which is also strongly improved in comparison with their methacrylic homologues. These properties open the door to the application of polymers of high added value in areas such as materials for optics (plastic optical fibers,[3] components for optics, etc....). The big issue which remains to be solved concerns the synthesis of the monomers.[4] Many synthetic pathways exist but they are tedious and time-consuming.

In polymerization, these monomers are interesting because they are very reactive. They have the same or even higher reactivity than acrylates.[4] Many studies were dedicated to the polymerization of these monomers by conventional radical polymerization, but nothing has yet been reported of their polymerization by the most recent techniques of controlled radical polymerization. This is of special interest since it is known that the substitution of a carbonyl at the α position strongly modifies the reactivity of acrylic derivatives. Therefore, it is worth studying the behavior of this particular monomer, namely *n*-butyl α-fluoroacrylate, by these new polymerization methods.

In this first report, we investigate the ATRP[5] method, which has an advantage over other methods (except reversible addition−fragmentation chain transfer, RAFT) in controlling the polymerization of acrylates and methacrylates. Fluorinated (meth)acrylates[6−10] such as 1,1-dihydroperfluorooctyl (meth)acrylate and fluorinated styrenics[11,12] such as 4-fluorostyrene were previously polymerized by ATRP. The case presented herein is different since the fluorine atom is directly located on the reactive double bond.

Results and Discussion

ATRP is a method which uses a very wide variety of reagents (metals, ligands, initiators) as shown perfectly in the recent review by Matyjaszewski et al.[13] Nevertheless, in this work, copper was chosen as the metal because it is the most studied metal up to now. Also, two ligands were chosen, namely 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) proposed by Matyjaszewski et al.[14] and *N*-(*n*-octyl)-2-pyridylmethanimine (*n*-Oct-L) proposed by Haddleton et al.,[15,16] both leading to a good solubility of the metallic derivative. The chosen monomer is *n*-butyl α-fluoroacrylate (FABu) which provides a sufficiently high boiling point to perform the polymerization at atmospheric pressure. The synthesis of this monomer was carried out using the method previously reported by Gassen et al.[17] (Scheme 1).

The polymerizations were performed in anisole (50 vol %) because this solvent provides a homogeneous medium at $T = 90$ °C. The first trials showed that HMTETA leads to a better control than *n*-Oct-L, in particular, where the polydispersity index I_p is concerned. Indeed, the polydispersity index is slightly higher with *n*-Oct-L ($I_p = 1.2-1.3$) than with HMTETA ($I_p = 1.1-1.2$). For this reason, HMTETA was used as the ligand for the subsequent studies.

The polymerization of FABu was performed with catalytic systems CuBr/HMTETA and CuCl/HMTETA in anisole (50 vol %) at 90 °C. CuBr has been tested in conjunction with a chlorinated initiator, namely *p*-toluenesulfonyl chloride, which is usually a good initiator with CuBr.[18] The polymerization did not proceed in the given conditions of temperature and solvent. The low efficiency of *p*-toluenesulfonyl chloride as an initiator could be ascribed to the strong electrophilicity of the

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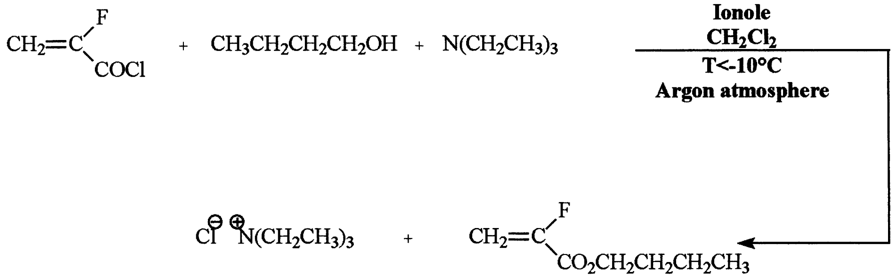
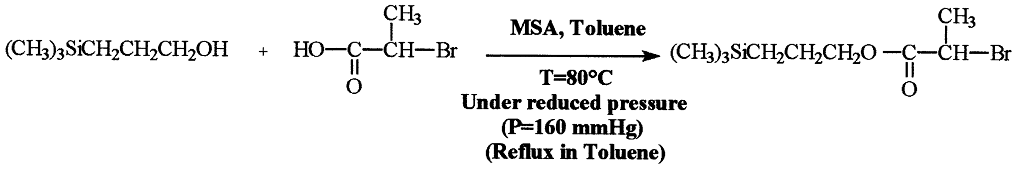
Scheme 1. Synthesis of *n*-Butyl α-Fluoroacrylate



Scheme 2. Synthesis of 3-(Trimethylsilyl)propyl 2-Bromopropionate



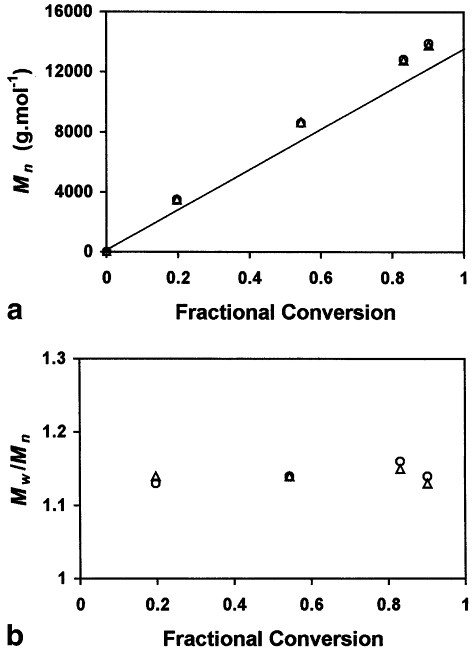


Figure 1. Atom transfer radical polymerization of *n*-butyl α-fluoroacrylate with the system CuBr/HMTETA/2-EBiB (1/1/10), 50 vol. % in anisole, T = 90 °C, R = 1000. Targeted molecular weight of 13700. (a) Evolution of M_n with conversion. (b) Evolution of M_w/M_n with conversion. Key: (○) experimental values determined by SEC analysis with PMMA calibration; (△) experimental values determined by SEC analysis with PS calibration; (—) theoretical values.

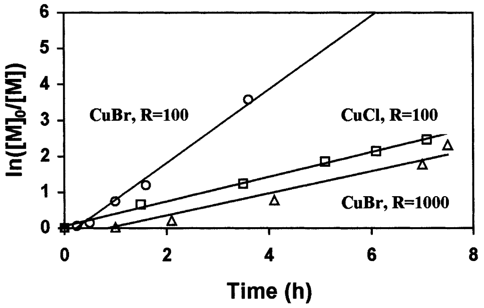


Figure 2. Atom transfer radical polymerization of *n*-butyl α-fluoroacrylate, 50 vol % in anisole, T = 90 °C. Key: (○) CuBr/HMTETA/2-EBiB (1/1/1), R = 100; (△) CuBr/HMTETA/2-EBiB (1/1/10), R = 1000; (□) CuCl/HMTETA/2-EBiB (1/1/1), R = 100. Lines are only for the eyes.

monomer and its slower reaction with the electrophilic sulfonyl radical. Consequently, alkyl bromides were tested as initiators. Two different brominated initiators were used. The first one is ethyl 2-bromoisobutyrate (2-EBiB). In this case, the molecular weights were determined by size exclusion chromatography (SEC) with PMMA and PS calibrations. They were not attainable by proton NMR because there are not enough protons available on this initiator for this purpose. The molecular weights by SEC are apparent ones and they only approximate the true molecular weights. The second brominated initiator, namely 3-(trimethylsilyl)propyl 2-bromopropionate (2-SBP), was synthesized as described in the Experimental Section (Scheme 2).

This 2-SBP initiator allows the determination of true molecular weights by ^{1}H NMR due to the resonance of the protons of the trimethylsilyl group located in a clear region of the spectrum (providing that the sample is free of any silicone grease). However, this is only possible for relatively low molecular weights (M_n < 13000) otherwise the signal of this trimethylsilyl group becomes negligible in comparison with the signals of the other protons in the polymer chain.

Polymerization of FABu with the System CuBr/HMTETA and Initiator 2-EBiB. A molecular weight of about 15000 was targeted, corresponding-to-a ratio [monomer]/[initiator] ≈ 100. The polymerization was performed for two different ratios R = [monomer]/[catalyst]: R = 100 and R = 1000. In both cases, there is a good control of the polymerization as indicated by the evolution of molecular weight and polydispersity index vs conversion (Figure 1 shows only the data for R = 1000 for clarity, similar results are obtained with R = 100) as well as by the linear trend of the plot of ln([M]$_0$/[M]) vs time (Figure 2). As expected, the reaction is slower when a smaller amount of catalyst is used, i.e., for R = 1000 (about 4 times slower than for R = 100). Moreover, an inhibition time of about 2 h was observed for R = 1000. Concerning the polydispersity index, it is about the same in both cases and remains constant, close to 1.1, throughout the polymerization.

Polymerization of FABu with the System CuCl/HMTETA and Initiator 2-EBiB. Similar experiments were carried out with CuCl/HMTETA/2-EBiB, i.e., polymerizations at R = 100 and R = 1000. In both cases, the polymerization was controlled. In comparison with the system CuBr/HMTETA, the system CuCl/HMTETA

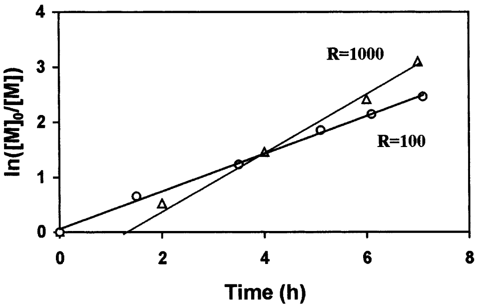


Figure 3. Atom transfer radical polymerization of *n*-butyl α-fluoroacrylate with the system CuCl/HMTETA/2-EBiB, 50 vol % in anisole, $T = 90$ °C. Key: (○) $R = 100$; (△) $R = 1000$. Lines represent best fit through data.

for $R = 100$ gives a slower polymerization (about two times slower) (Figure 2). The control of the molecular weight is better with CuCl than with CuBr: slightly lower polydispersity index values were obtained with CuCl. This confirms what is reported in the literature: a mixed system brominated initiator/CuCl usually gives better control than a system brominated initiator/CuBr.[19] Otherwise, for the system CuCl/HMTETA, going from $R = 100$ to $R = 1000$ does not lead to a significant decrease of the polymerization rate (on the contrary to the system CuBr/HMTETA). However, an inhibition period of about 1 h was observed for $R = 1000$, but then the polymerization proceeds at a higher rate than for $R = 100$ (Figure 3).

The different systems allow the control of the polymerization of FABu for targeted molecular weights of about 15000. It would be interesting to target different molecular weights, i.e., lower and higher targeted molecular weights, to see if the control of the polymerization remains good.

Furthermore, the use of an excess of Cu(II) should theoretically afford the possibility of estimating the equilibrium constant between dormant and active chains[20] to make a comparison with analogous butyl methacrylate and butyl acrylate. This will be reported in a subsequent paper.

Polymerization of FABu with the Initiator 2-SBP. Similar trials were carried out with the specially designed 2-SBP initiator and the polymer was precipitated at the end of the polymerization in order to eliminate all the potential impurities. The ^{1}H NMR spectra of the initiator and the polymer are given in Figures 4 and 5, respectively.

In the spectrum of the polymer after precipitation, one can clearly distinguish the signal (a) of the trimethylsilyl group of the initiator (9 protons, integral I_a) and the signal (d) of the methylene group of the monomer units (2 protons per monomer unit, integral I_d). Note that the latter also includes 2 protons of the initiator ($-OCH_2-$). The degree of polymerization DP_n is given by eq 1. The molecular weight of the polymer M_n is given

$$DP_n = 9(I_d - 2I_a/9)/2I_a \qquad (1)$$

by eq 2, where $M_{monomer}$ and $M_{initiator}$ stand for the molecular weight of monomer and initiator, respectively.

$$M_n = DP_n \times M_{monomer} + M_{initiator} \qquad (2)$$

For the sample shown in Figure 5, the molecular weight found by ^{1}H NMR is slightly lower than the one determined by SEC with PMMA or PS calibration. It means that an even better agreement between theoretical and experimental values should be obtained in Figure 1 providing that an appropriate calibration is used (i.e. with poly(FABu) standards).

Determination of the Mark−Houwink Coefficients for Poly(FABu). Universal Calibration. One possibility to determine the molecular weight of poly(FABu) samples with a better accuracy than by SEC with PMMA or PS calibration is to use SEC with universal calibration. One needs to determine first the Mark−Houwink coefficients for poly(FABu) under the conditions of solvent (THF) and temperature ($T = 30$ °C) used in the SEC analysis.

In SEC, the separation of molecules depends on the volume of the solvated polymer chain. Two polymer chains which have the same volume in a given solvent and at a given temperature will have the same retention time. This is expressed by the equation of Flory (eq 3),[21]

$$[\eta] = (\phi\langle R^2\rangle^{3/2})/M_v \qquad (3)$$

where ϕ = universal constant, $\langle R^2\rangle$ = mean-square end to end distance, $[\eta]$ = intrinsic viscosity, and M_v = molecular weight by viscosimetry.

Therefore, the product $[\eta]M_v$ is a measure of the volume of the solvated macromolecules. Benoit et al.[22,23] have shown that the plot $\ln([\eta]M_v) = f(\text{retention time})$ could be used as a universal calibration for linear or graft macromolecules. For two different macromolecules with the same volume in a given solvent and at a given temperature, this leads to eq 4, where the indexes 1 and 2 refer to macromolecules of type 1 and 2, respectively.

$$[\eta_1]M_1 = [\eta_2]M_2 \qquad (4)$$

By using the law proposed by Mark−Houwink−Sakurada (eq 5), eq 6. is derived. (Remark: the molecular weight by viscosimetry M_v is often used as the weight-average molecular weight M_w. The authors know that M_v is slightly lower than M_w.)

$$[\eta] = KM_v\alpha \qquad (5)$$

$$K_1M_1^{(\alpha_1+1)} = K_2M_2^{(\alpha_2+1)} \qquad (6)$$

If both the Mark−Houwink coefficients for poly(FABu) and those of the standard (PS or PMMA) are known, then it will be possible to determine the true molecular weight $M_{w,t}$ of the sample from the apparent molecular weight $M_{w,a}$ obtained by SEC with PS or PMMA standards. This is given by eq 7.

$$M_{w,t} = ((K_{standard}M_{w,a}^{(\alpha_{standard}+1)})/K_{PFABu})^{1/(\alpha_{PFABu}+1)} \qquad (7)$$

Preparation of Poly(FABu) Standards. To determine K and α for poly(FABu), four samples of different molecular weights have been prepared. The initiator 3-(trimethylsilyl)propyl 2-bromopropionate allowed the determination of the true molecular weight of these samples by ^{1}H NMR. The trimethylsilyl group, which is at the end of the polymer chains, serves as a probe in ^{1}H NMR to calculate the true molecular weights. The calculation of the DP_n of the polymer obtained after precipitation is done from its ^{1}H NMR spectrum and one can then calculate the true molecular weights $M_{n,t}$ of the samples of poly(FABu). These samples were also characterized by SEC with PMMA or PS standards. A better fit was obtained with PS rather than with PMMA

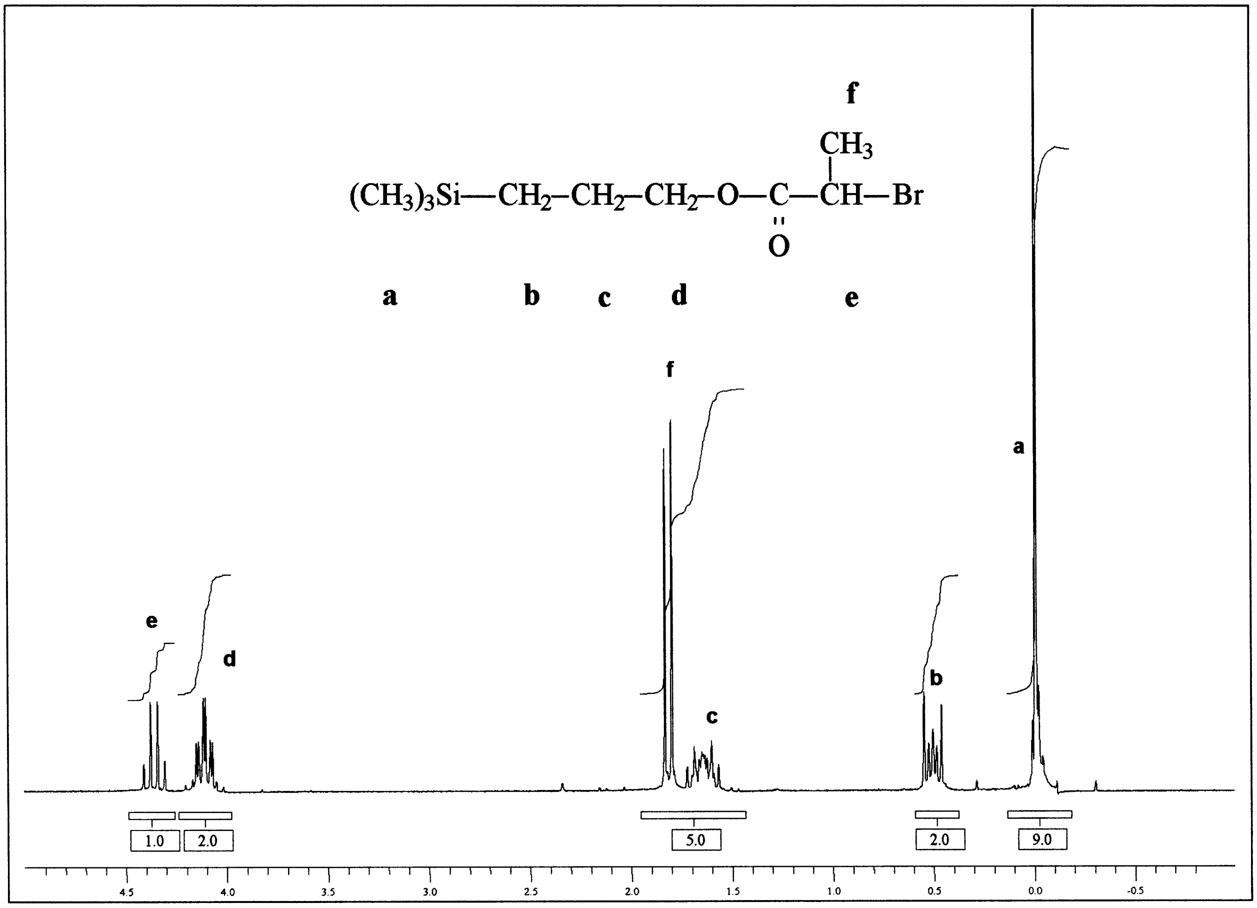


Figure 4. ^{1}H NMR spectrum of 3-(trimethylsilyl)propyl 2-bromopropionate (in $CDCl_3$).

standards, in agreement with a similar observation for poly(butyl acrylate) by Schmitt.[24] These SEC analyses gave the apparent molecular weight $M_{w,a}$ as well as the polydispersity index. The true $M_{w,t}$ was calculated by $M_{w,t} = M_{n,t}I_p$, where $M_{n,t}$ is given by ^{1}H NMR and the polydispersity index I_p comes from the SEC analysis. Then, $\ln(K_{\mathrm{standard}}M_{w,a}{}^{(\alpha_{\mathrm{standard}}+1)})$ was plotted vs $\ln(M_{w,t})$ for both standards. In both cases, a linear trend was obtained, and one can calculate K and α for poly(FABu) from a linear regression (Figures 6 and 7).

The following Mark–Houwink coefficients were used for the PMMA and PS standards at $T = 30$ °C in THF:

$$\text{PMMA:}^{25} \quad K = 9.44 \times 10^{-5}\ \text{dL/g} \quad \alpha = 0.719$$
$$\text{PS}^{26}: \quad K = 11.4 \times 10^{-5}\ \text{dL/g} \quad \alpha = 0.716$$

Mark–Houwink coefficients are calculated for poly(FABu) at $T = 30$ °C in THF for molecular weights in the range: $5000 < M_n < 12000$. Very similar results were obtained by using PMMA standards and PS standards.

with PMMA standards:

$$K_{\text{poly(FABu)}} = 11.13 \times 10^{-5}\ \text{dL/g} \quad \alpha_{\text{poly(FABu)}} = 0.717$$

with PS standards:

$$K_{\text{poly(FABu)}} = 13.86 \times 10^{-5}\ \text{dL/g} \quad \alpha_{\text{poly(FABu)}} = 0.697$$

As an illustration, universal calibration was then used to reconsider the previous results shown in Figure 1. The molecular weights determined by SEC with universal calibration now fit the theoretical line very well (Figure 8).

Validation of the Values of K and α Determined for Poly(FABu). To check the results obtained for K and α, two poly(FABu) samples of higher molecular weight in comparison to the previous standards used for ^{1}H NMR analyses were prepared (~40 000 and ~70 000). Consequently, these samples can be analyzed by viscosimetry in order to determine their intrinsic viscosity. From the universal calibration using the Mark–Houwink coefficients of poly(FABu) determined previously, the SEC analysis with PMMA or PS standards also gives the intrinsic viscosity of the samples. Thus, by performing the analysis of viscosimetry in the same conditions of temperature and solvent as the SEC analysis, one can directly compare the values of viscosity given by the two methods. The results are shown in Table 2 and indicate a very good agreement between the two methods (viscosimetry and SEC with universal calibration).

Validation of the Polymerization Mechanism by ^{19}F NMR. A poly(FABu) sample was prepared by polymerization with the system 3-(trimethylsilyl)propyl 2-bromo-2-methylpropionate/CuBr/HMTETA, and analyzed by ^{19}F NMR. The spectrum shows signals in the region between −161 and −173 ppm (integral I_1) which is typical of poly(α-fluoroacrylates)[4] (Figure 9). The different peaks arise from the strong sensitivity of fluorine atoms to the stereochemistry. According to the ATRP mechanism, the other signals in the region between −116 and −122 ppm (integral I_2) can be assigned to the CFBr end groups. This was confirmed by reacting the polymer with excess phenylmagnesium bromide (in anhydrous tetrahydrofuran at $T = 50$ °C for 15 h) to remove the bromide end group, resulting in

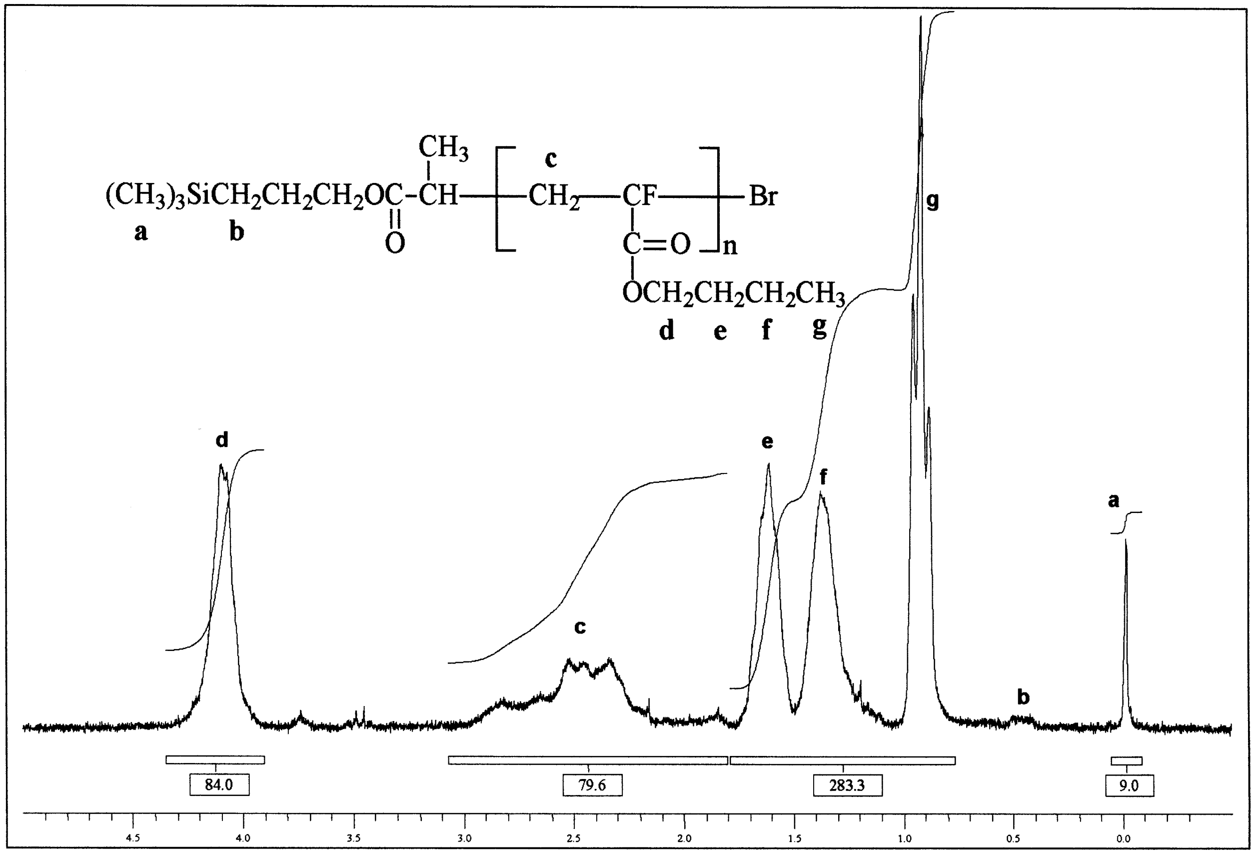


Figure 5. ^{1}H NMR spectrum of poly(FABu) sample ($DP_n \approx 41$) prepared using 2-SBP (in $CDCl_3$).

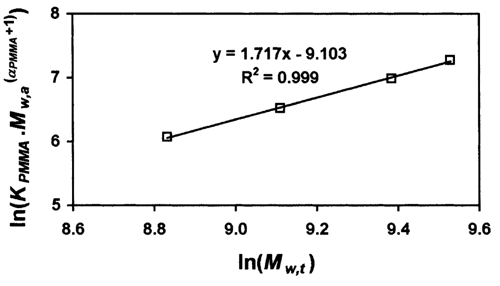


Figure 6. Determination of poly(FABu) Mark–Houwink parameters using SEC with PMMA calibration and ^{1}H NMR analysis of poly(FABu) samples of different molecular weights.

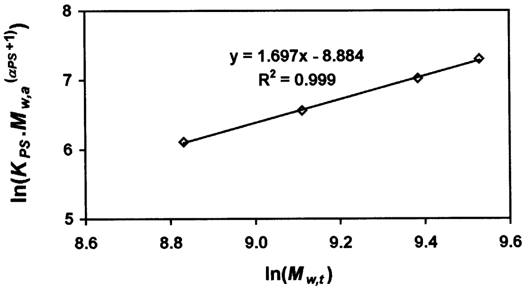


Figure 7. Determination of poly(FABu) Mark–Houwink parameters using SEC with PS calibration and ^{1}H NMR analysis of poly(FABu) samples of different molecular weights.

the disappearance of the signals between −116 and −122 ppm. Furthermore, the values for the number average molecular weights M_n determined by ^{19}F NMR (based on CFBr end groups, see eq 8), by ^{1}H NMR (based on the trimethylsilyl probe from the initiator), and by SEC using universal calibration with either PMMA or PS standards were in good agreement ($M_{n,F\,NMR} = 3150$, $M_{n,H\,NMR} = 3050$, $M_{n,SEC,PMMA} = 3140$, $M_{n,SEC,PS} = 2960$, $I_p = 1.14$).

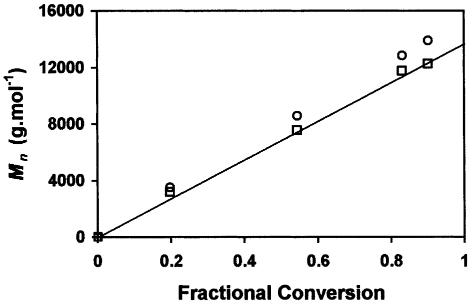


Figure 8. Atom transfer radical polymerization of *n*-butyl α-fluoroacrylate with the system CuBr/HMTETA/2-EBiB (1/1/10), 50 vol. % in anisole, $T = 90$ °C, $R = 1000$. Targeted molecular weight of 13700. Key: (○) experimental values determined by SEC analysis with PMMA calibration; (□) experimental values determined by SEC analysis with universal calibration (the coefficients determined with PMMA calibration were used: $K = 11.13 \times 10^{-5}$ dL·g^{-1}, $\alpha = 0.717$); (—) theoretical values.

$$M_n = [(I_1 + I_2)/I_2] \times M_{\text{monomer}} + M_{\text{initiator}} \qquad (8)$$

Conclusions

Atom transfer radical polymerization (ATRP) of *n*-butyl α-fluoroacrylate initiated by ethyl 2-bromoisobutyrate (2-EBiB) with CuCl or CuBr as the catalyst and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the ligand has been successfully performed in anisole at 90 °C, as demonstrated by the linear increase of M_n vs conversion and low polydispersity index values. This is the first successful ATRP of

Table 1. Values of Molecular Weight and Polydispersity Index Determined by SEC with PMMA and PS Calibration and by ^{1}H NMR Analysis of Poly(FABu) Samples[a]

			SEC			
			$M_{n,a}$		$M_{w,a}$	
sample	$M_{n,t}$ ^{1}H NMR	I_p	PMMA standards	PS standards	PMMA standards	PS standards
1	11750	1.17	12900	12000	15100	14000
2	10250	1.16	11000	10250	12800	11900
3	7800	1.16	8400	7850	9750	9100
4	5850	1.17	6400	6000	7500	7000

[a] $M_{n,t}$: true number average molecular weight determined by ^{1}H NMR. $M_{n,a}$: apparent number average molecular weight determined by SEC. $M_{w,a}$: apparent weight average molecular weight determined by SEC. I_p: polydispersity index determined by SEC.

Table 2. Comparison of Intrinsic Viscosity Given by Viscosimetry Analysis and by SEC Analysis of Poly(FABu) Samples

	[η]				
	SEC[a]			M_n (I_p)[a] SEC	
sample	PMMA standards	PS standards	viscosimetry	PMMA standards	PS standards
5	0.458	0.448	0.466 ± 0.002	73 550 (1.58)	72 800 (1.58)
6	0.252	0.251	0.261 ± 0.006	41 550 (1.18)	41 100 (1.18)

[a] Values calculated with universal calibration using the Mark–Houwink coefficients determined in this work. When PMMA standards were used, the coefficients determined with PMMA calibration were utilized ($K = 11.13 \times 10^{-5}$ dL·g^{-1}, $\alpha = 0.717$). When PS standards were used, the coefficients determined with PS calibration were utilized (K=13.86 × 10^{-5}dL·g^{-1}, $\alpha = 0.697$).

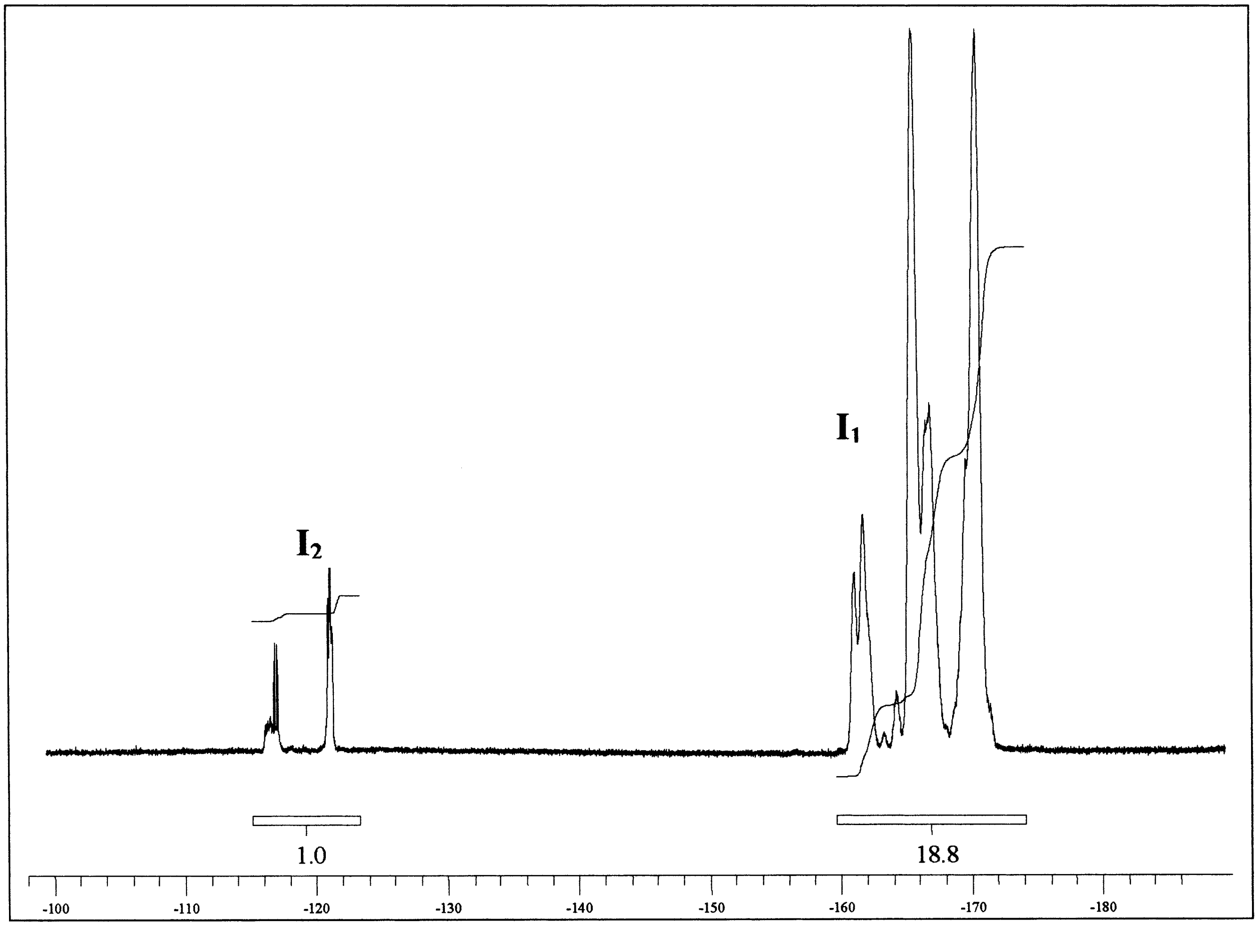


Figure 9. ^{19}F NMR spectrum of poly(FABu) sample prepared using 3-(trimethylsilyl)propyl 2-bromo-2-methylpropionate (in CDCl$_3$). M_n = 3150 calculated from the –CFBr end groups.

alkyl α-fluoroacrylate reported so far. Moreover, 3-(trimethylsilyl)propyl 2-bromopropionate (2-SBP) was also used as the initiator, serving as a probe for ^{1}H NMR analysis in order to determine the true molecular weight up to about 10 000. In addition, the –CFBr end groups were distinguished by ^{19}F NMR, confirming that the polymerization follows the ATRP mechanism. By calibration of size exclusion chromatography with standards prepared with the 2-SBP initiator, it was shown that the experimental molecular weights were close to the theoretical values. The results were better than when the molecular weights were determined with polystyrene or poly(methyl methacrylate) calibration. The characteristic values of the Mark–Houwink coefficients have been calculated for poly(n-butyl α-fluoroacrylate) in tetrahydrofuran at T = 30 °C.

Experimental Section

Materials. α-fluoroacryloyl chloride was supplied by the Russian company Scientific Industrial Association P & M (Moscow). The monomer contains an inhibitor of radical polymerization. CuBr (99% Aldrich) and CuCl (98% Aldrich) were purified by the method reported by Keller and Wycoff.[27] HMTETA, 2-EBiB, 3-(trimethylsilyl)-1-propanol, and 2-bromopropionic acid were purchased from Aldrich and were used as received. *n*-Oct-L was synthesized by the procedure reported by Haddleton et al.[15] from *n*-octylamine (99% Avocado) and 2-pyridinecarboxaldehyde (99% Aldrich). Anisole (99% Avocado) was dried and distilled prior to use.

Characterization. ^{1}H NMR and ^{19}F NMR were performed at ambient temperature on a Brüker AC200 using $CDCl_3$ as the solvent (chemical shifts refer to tetramethylsilane and $CFCl_3$, respectively). SEC analyses were performed with a Spectra-Physics apparatus equipped with two columns PLgel 5 μm MIXED-C from Polymer Laboratories and a Spectra Physics SP8430 RI detector. The eluent is THF ($T = 30$ °C, flow rate 0.8 mL/min). PMMA and PS standards were purchased from Polymer Laboratories. Viscosity analyses were performed on an automatic viscosimeter equipped with Ubbelhode capillaries. Gas-phase chromatography (GPC) was performed with a Delsi Instruments 330 apparatus equipped with a Shimadzu C-R6A integrator and a 2 m long Carbowax 20M (poly(ethylene glycol)) column. Nitrogen is used as the gas vector at a pressure of 1.5 bar. The analysis is performed by rising the temperature of the oven from 60 up to 180 °C at a rate of 15 °C/min. GPC is used to determine the monomer conversion throughout the polymerization. Anisole is used as the internal standard.

Synthesis of *n*-Butyl α-Fluoroacrylate (FABu). Into a double-necked round-bottom flask (1 L) equipped with a mechanical stirrer were introduced 14.8 g (0.2 mol) of *n*-butanol, 20.9 g (0.205 mol) of triethylamine, a few milligrams of an inhibitor of radical polymerization (2,4-di-*tert*-butyl-6-methylphenol), and 500 mL of dichloromethane. Then, 22.5 g (0.207 mol) of α-fluoroacryloyl chloride was gradually added at low temperature ($T = -10$ °C). After 15 h of reaction while stirring at room temperature, the reaction medium was filtered to eliminate the insoluble quaternary ammonium salt. The filtrate was washed with an aqueous solution of hydrochloric acid (0.1 N) and then with water until neutrality of the aqueous phase was achieved. The organic phase was dried over anhydrous Na_2SO_4, concentrated by evaporating the solvent and then distilled under reduced pressure to recover the pure FABu monomer in high yield (yield = 90%). Bp = 50 °C at 40 mm Hg; $n_D^{22\,°C} = 1.407$. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.85 (t, 3H, $^2J_{H-H} = 7$ Hz, CH_3), 1.4 (sextet, 2H, $^2J_{H-H} = 7$ Hz, $\mathbf{CH_2}$-CH_3), 1.8 (quintet, 2H, $^2J_{H-H} = 7$ Hz, $\mathbf{CH_2}CH_2CH_3$), 4.2 (t, 2H, $^2J_{H-H} = 7$ Hz, OCH_2), 5.3 (dd, 1H, $^2J_{H-H} = 3$ Hz, $^3J_{H-F\,cis} = 14$ Hz, $H_{cis}C{=}CF$), 5.7 (dd, 1H, $^2J_{H-H} = 3$ Hz, $^3J_{H-F\,trans} = 43$ Hz, $H_{trans}C{=}CF$). ^{19}F NMR ($CDCl_3$), δ (ppm): −117.6 (dd, 1F, $^3J_{F-H\,cis} = 14$ Hz, $^3J_{F-H\,trans} = 43$ Hz, $H_2C{=}CF$).

Note: the acryloyl chloride is UV and moisture sensitive. It must be carefully handled accordingly.

Synthesis of 3-(Trimethylsilyl)propyl 2-Bromopropionate and 3-(Trimethylsilyl)propyl 2-Bromo-2-methylpropionate. Into a single-necked round-bottom flask equipped with a Dean Stark apparatus were introduced 3 g (2.27×10^{-2} mol) of 3-(trimethylsilyl)-1-propanol, 3.47 g (2.27×10^{-2} mol) of 2-bromopropionic acid, 109 mg (1.13×10^{-3} mol) of methanesulfonic acid, and 30 mL of toluene. The reaction mixture was heated at 80 °C and placed under vacuum until reflux of toluene proceeded. The water formed during esterification was eliminated by the Dean Stark apparatus, allowing total conversion to be reached. When there was no longer any formation of water, the reaction was stopped. The reaction mixture was then distilled under vacuum to remove toluene. The product was solubilized in chloroform, washed with an aqueous solution of potassium hydroxide (0.1 N) and then washed with water until neutrality of the aqueous phase was attained. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed by evaporation to obtain the pure 3-(trimethylsilyl)propyl 2-bromopropionate (yield 90%). 3-(Trimethylsilyl)propyl 2-bromo-2-methylpropionate was synthesized in high yield following a similar procedure.

Typical Polymerization of FABu. [FABu]:[CuBr]:[HMTETA]:[2-EBiB] = 100:1:1:1. Into a 50 mL Schlenk flask were introduced 5 g (3.42×10^{-2} mol) of FABu, 49.1 mg (3.42×10^{-4} mol) of CuBr, 78.9 mg (3.42×10^{-4} mol) of HMTETA, 66.8 mg (3.42×10^{-4} mol) of 2-EBiB, and 5 g of anisole. The oxygen was removed by several freeze−thaw pump cycles. The Schlenk flask was then placed in an oil bath previously heated at 90 °C. A 0.5 mL sample was withdrawn at $t = 0$ and then at different times throughout the polymerization. Each sample was diluted in 1 mL of THF and analyzed by GPC to determine the conversion by comparison with the reference sample. Then, the samples were filtered on alumina and on a 0.2 μm filter and finally analyzed by SEC to determine the molecular weights and polydispersity index. At the end of the reaction, the reaction mixture was diluted in ether and filtered on alumina to remove the catalyst. The polymer was precipitated in pentane, filtered, and dried under vacuum.

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