Anionic Ring-Opening Polymerization of Hexafluoropropylene Oxide Using Alkali Metal Fluorides as Catalysts: A Mechanistic Study

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Received June 2, 2008; Revised Manuscript Received November 24, 2008

ABSTRACT: The anionic ring-opening polymerization of hexafluoropropylene oxide using the conventional alkali metal fluorides/tetraglyme catalytic system in the presence of different fluorinated solvents at various temperatures and under batch conditions is reported. Basically, the sodium fluoride (NaF)/tetraglyme system gave only monoadduct $CF_3CF_2CO_2CH_3$, while cesium fluoride (CsF)/tetraglyme produced oligomeric product with number-average degree of polymerization (DP_n) less than 5. The higher molar mass polymers were synthesized using the potassium fluoride (KF)/tetraglyme catalytic system and 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$) or 1,3-bis(trifluoromethyl)benzene as solvent at 0 °C. Under these conditions, polymers with number-average molar masses ranging between 2500 and 3500 g mol^{-1} were obtained in high contents (>90%) and almost without any low molar mass ($DP_n \leq 5$) contaminants (4−7%). Polymers which chain ends were derived into methyl esters were fully characterized by gas chromatography, ^{19}F and ^{1}H NMR, and MALDI-TOF-MS spectroscopy. A kinetic study allowed us to propose a tentative mechanism entailing (i) the livingness of the polymerization of the hexafluoropropylene oxide with KF/tetraglyme catalytic system and (ii) the importance on the control of molar masses of the biphasic gas/liquid environment in the batch autoclave.

Introduction

Perfluoropolyethers represent a special class of liquid fluoropolymers, which are characterized by high thermal stability, chemical inertness, low surface energy, low T_g, and low friction coefficient. These unique properties make such polymers useful in a wide range of applications, e.g., as lubricants for magnetic recording media,[1] in aerospace engines,[2] as fluids for vacuum pumps[3] and elastomers,[3−6] in electronic industry,[7] or as additives in creams and soaps for the cosmetic industry.[4,7] Four main families of perfluoropolyethers are commercially available: Fomblin (Solvay Solexis), Demnum (Daikin, Japan), Krytox (DuPont, USA), and Aflunox (Nippon Mektron, Japan).[2,3,8] Fomblin is prepared by copolymerization of tetrafluoroethylene and hexafluoropropylene in the presence of oxygen under UV,[4,7] while Demnum is synthesized by ring-opening polymerization of 2,2,3,3-tetrafluorooxetane followed by a fluorination step.[3,4,7] Both Krytox and Aflunox are obtained via anionic ring-opening polymerization of hexafluoropropylene oxide (HFPO).[9]

Early investigations on the anionic ring-opening polymerization of HFPO were reviewed by Eleuterio[10] and Hill and Erdman.[11] Among nucleophiles that are able to open the epoxide ring of HFPO molecule, the fluoride ion was preferentially selected since it preserves the perfluorinated nature of the products. Initially, a number of fluoride salts were investigated as catalysts for HFPO polymerization, and it was found that cesium fluoride (CsF) was the most effective source of F$^-$ due to its low lattice energy and highly ionic nature.[10] To facilitate the formation of active fluoride ion, it was necessary to use strongly coordinated solvents, such as dimethyl ether of tetramethylene glycol (tetraglyme, TG) or other glymes, which were found to be the best over a number of polar and nonpolar solvents tested.[11] The last requirement for a successful anionic polymerization of HFPO in the presence of CsF/tetraglyme complex was to select good solvents for polyHFPO to overcome the phase separation during polymerization.[10,11]

According to early studies, the polymerization of HFPO catalyzed by CsF/tetraglyme was carried out in the presence of hexafluoropropylene at −30 to −35 °C, as depicted in Scheme 1.[12,13] Basically, the naked fluoride ion is generated from the dissociation of CsF by the complexation of Cs$^+$ countercation by the tetraglyme. It reacts with one monomer molecule to form cesium alkoxide **1**. Then, further monomer additions to **1** lead to growing polymeric chain **2**, which by elimination of the fluoride anion generates back cesium fluoride solvated by tetraglyme and produces acyl fluoride **3**, respectively. The latter are dormant species which are reactivated by F$^-$; i.e., anionic polymerization of HFPO behaves like a living system, unless F$^-$ initiates a new polymer chain, the result of which corresponds to a "chain transfer reaction". Because the solubility of CsF in tetraglyme or polymerization solvent is very low,[11] only a few molecules of solvated cesium fluoride are formed at the beginning of the process and initiate the polymerization. Still, the chain transfer is the predominant reaction because the ratio of monomer to solvated CsF is considerably higher than the **3**/CsF ratio. As a result, only low molar mass oligomers were typically obtained during conventional solution HFPO polymerization with the CsF/tetraglyme system.

Synthesis of polyHFPO of larger number-average molar masses (M_n), in a range 2500−25 000 g mol^{-1}, was claimed by using soluble perfluoroalkoxide initiators derived by F$^-$ addition to corresponding perfluoroacyl fluorides (usually oligomers of HFPO) or perfluoalkyldiacyl fluorides in the case of difunctional initiators.[11,12] In addition, to avoid any chain transfer reactions, monomer and solvent were slowly and continuously added into the polymerization system, typically for 6−50 h.[11,12] Usually, hexafluoropropylene (HFP) was used as a solvent with the aim to keep the viscosity of the polymerization media low and to ensure efficient heat transfer provoked by the exothermic

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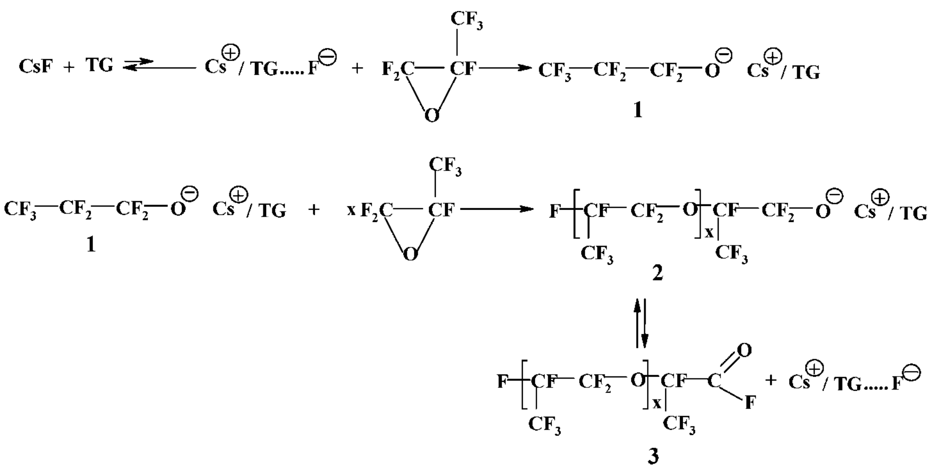
10.1021/ma8012338 CCC: $40.75

Scheme 1. Main Reactions in the Polymerization of Hexafluoropropylene Oxide in the Presence of CsF/Tetraglyme (TG) Catalytic System



polymerization. Moreover, there were some evidence that HFP could trap fluoride ions through an oligomerization reaction, thus suppressing the chain transfer reaction.[11] However, even under these conditions fair amounts of low molar mass by-product (typically with $DP_n \le 5$) were still present in the crude polymer.[12]

Surprisingly, from the time when both basic papers from Eleuterio[10] and Hill[11] reviewed the patent literature published during the 1970s, few articles have been published on HFPO polymerization, in addition with little interest in understanding the polymerization mechanism and improving molar masses on simple batch processes. Recent studies from Mobbs and co-workers[5,6,12] for instance reproduced faithfully the industrial recipes of DuPont. Other recent reports were mainly devoted to the functionalization of as-given polyHFPO[13] or its utilization as building blocks in the synthesis of their block copolymers with hydrocarbon monomers.[14]

In contrast to perfluorooctanoic acid, ammonium perfluorooctanoate, or perfluorooctyl bromide surfactants which are bioaccumulable and persistant,[15] oligoHFPO of sufficient molar masses (typically above 1500 g mol^{-1}) are known to be environmentally benign products and could thus be interesting substitutes in the context of REACH. To do so, highly toxic products such as cesium-based initiator, a heavy metal, or R-113 solvent, which has recently been banned alike others CFCs, would better be discarded from the synthesis procedure. This paper aims at giving simple experimental conditions to generate relatively high molar mass perfluoropolyethers ($M_n \sim 2000-3000$ g mol^{-1}) without low molar mass contaminants ($DP_n \le 5$) and using harmless reactants. An extensive investigation of the polymerization of hexafluoropropylene oxide using the alkali metal fluoride/tetraglyme system is proposed, looking specifically at the influence of the temperature, nature of alkali metal fluorides, and solvents on the polymerization mechanism.

Experimental Part

Materials and Methods. Hexafluoropropylene oxide (99%, 3F, Changzhu, China) and hexafluoropropylene (HFP, 99%, Solvay) were used as received. Tetraethylene glycol dimethyl ether or tetraglyme (99%, Aldrich) was stirred over CaH_2 under argon for 48 h and then vacuum-distilled (~89 °C/0.02 mmHg). 1,1,2-Trichlorotrifluoroethane ($C_2F_3Cl_3$, 99.9%, DuPont), 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$, Solvay), 1,3-bis(trifluoromethyl)benzene (HFX, 99%, Aldrich), perfluorooctane (C_8F_{18}, 98%, Aldrich), 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoro-methylhexane (HFE-7500, 99%, Solvay), and 2,2,3,3,4,4,5-heptafluoro-5-(1,1,2,2,3,3,4,4,4-nona-fluorobutyl)tetrahydrofuran (FC-75, >95%, Acros Organics) were dried over CaH_2 for several days and distilled under argon flow before use. CsF (99.9%, Lancaster), KF, and NaF (99%, Aldrich) were dried at 90 °C under vacuum (0.02−0.03 mmHg) at least 12 h. Methanol (99.9%, Aldrich) was used without any purification. Silver trifluoroacetate (98%, Aldrich) and 2,3,4,5,6-pentafluorocinnamic acid (97%, Aldrich) were used as received.

Gas chromatography (GC) analyses were performed on a Delsi apparatus (model 330) equipped with an OV 17 WHP 80-100 column (3 m; $^1/_8$ in. i.d.). The nitrogen pressure at the column entry was maintained at 0.6 bar, and the detector and injector temperatures were set at 255 °C. The temperature program started from 50 °C and reached 250 °C at a heating rate of 10 °C/min. The GC apparatus was connected to a Hewlett-Packard integrator (model 3390), which automatically calculated the area of each peak on the chromatogram. Number-average degree of polymerization (DP_n), number-average (M_n), and weight-average (M_w) molar masses as well as molar mass distribution (MMD, M_w/M_n) were calculated from data of GC analyses using conventional equations:

$$DP_n = \sum_i n_i i / \sum_i i \tag{1}$$

$$M_n = \sum_i n_i M_i / \sum_i n_i \tag{2}$$

$$M_w = \sum_i n_i M_i^2 / \sum_i n_i M_i \tag{3}$$

where n_i and M_i represent the percentage and molar mass of the i adduct, respectively. i was estimated from a calibration curve set by determining the exact retention times for $F[CF(CF_3)CF_2O]_xCF(CF_3)COOCH_3$, where $x = 0$, 1, and 2 (as given by ^1H NMR, vide infra), and taking into account that each molecule of oligoHFPO possesses one fluorine atom at the α-end and one methoxy group at the ω-end.

^1H and ^{19}F NMR (400 MHz) spectra of oligo(hexafluoropropylene oxide)s were recorded in bulk on a Bruker AC-400 instrument at 25 °C, using a capillary filled with acetone-d_6 as an external locking reference. The number-average molecular weight of synthesized oligomers was calculated from ^{19}F NMR spectra according to an equation given in Figure 4.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on an Ultraflex spectrometer (Bruker Daltonik, Bremen, Germany), equipped with a 337 nm, 50 Hz N_2 laser, a delayed extraction, and a reflector. The apparatus was operated at an accelerating potential of 20 kV in reflected mode. The matrix 2,3,4,5,6-pentafluorocinnamic acid was dissolved in hexafluoro-2-propanol with a 10 g/L concentration. 1 μL of the matrix solution, then 1 μL of product solution, and 1 μL of silver trifluoroacetate used as a cationizing agent were placed onto MALDI plots irradiated typically for 250 scans.

Polymerization Procedures. Polymerizations were carried out in a Parr 100 mL Hastelloy (HC-276) autoclave equipped with a manometer, inlet and outlet valves, mechanical stirrer (stirring rate 800 rpm), and a rupture disk in a batch process. After heating the reactor under vacuum at 50−70 °C for 1 h and filling it with argon (typically, three vacuum/argon cycles were performed), it was charged with KF under an argon atmosphere. The reactor was further heated under vacuum for an additional 1 h, filled by argon, and charged with tetraglyme and $C_4F_5H_5$ through a transfer by suction of liquids by means of vacuum. After liquid reactants were introduced, the autoclave was cooled in an acetone/liquid nitrogen bath, and the required amount of hexafluoropropylene oxide was introduced by double weighing of the reactor. Then, the reactor was connected to the external bath and warmed up to +10 °C (before heating, the temperature inside the reactor was typically −20 °C). When the temperature inside the vessel reached +10 °C (the pressure was ca. 0.5 bar), the temperature was decreased to the targeted value in typically 2−3 min. Further, polymerization was stopped after 2 or 3 h by quickly adding 15−20 mL of methanol. Esterification of ω-chain ends proceeded for 1 h at 30 °C, after which the reaction mixture was poured typically into 10−15 g of water and separated, and the solvents were evaporated by a rotary evaporator. Monomer conversions were determined gravimetrically. To observe visually the polymerization process, several experiments were performed in 100 mL glass Schlenk tubes equipped with magnetic stirrer bar (stirring rate ~800 rpm).

As a typical example, the reactor was charged by 0.41 g (7.1 mmol) of KF, 2.9 mL (13.2 mmol) of tetraglyme, and 10 mL of $C_4F_5H_5$. Then, 45 g (0.27 mol) of hexafluoropropylene oxide was slowly transferred into the reactor. The polymerization started when the temperature reached 0 °C and was stopped after 2 h by adding 15 mL of methanol. After esterification, the polymer was washed three times by distilled water to remove tetraglyme, methanol, and catalyst. The resulting polymer was obtained by removing the solvent by rotary evaporator (10−20 mmHg/40−50 °C) typically for 5−10 min. The final results were as follows: conversion = 89%; M_n(NMR) = 2500 g mol^{-1}; M_n(MALDI) = 2370 g mol^{-1}.

Results

To simplify the procedure of production of oligoHFPO, all experiments throughout the paper were performed under batch conditions in contrast to most modern industrial processes, where slow and continuous additions of monomer have been carried out.[16,17] To our knowledge, batch conditions were exclusively used for the synthesis of oligomers of HFPO, particularly dimers to tetramers.[18,19]

Preliminary Tests. Hexafluoropropylene oxide was first polymerized using CsF/tetraglyme complex as the catalyst, in the presence of 1,1,2-trifluoro-1,1,2-trichloroethane ($C_2F_3Cl_3$, R-113) as the solvent, and applying the recipe from the literature[12] (Table 1). Changing the polymerization temperature (runs 3 and 4, Table 1), monomer or catalyst contents (runs 1−3), or solvents (runs 4 and 5) had insignificant effects on the number-average degree of polymerization (DP_n) (targeted between 1.8 and 3.5) and conversion (between 57% and 75%) of obtained oligomers. The observed low conversions (runs 2−5) could be connected with some loss of single addition product ($C_2F_5COOCH_3$, bp = 61 °C/739 mmHg) after solvent evaporation,[20] whereas the low conversion in run 1 arose from a slow polymerization rate (high $[HFPO]_0/[CsF]_0$ molar ratio). One important conclusion from these preliminary batch experiments is the possibility of using a "safer" solvent, 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$), in place of the expensive, toxic, and banned R-113 ($C_2F_3Cl_3$) without any deleterious effect on reaction (compare runs 4 and 5 in Table 1).

Table 1. Preliminary Results on the Anionic Polymerization of Hexafluoropropylene Oxide Initiated by CsF/Tetraglyme Catalytic System[a]

run	CsF (mmol)	temp (°C)	$[HFPO]_0/[CsF]_0$	conv[b] (%)	DP_n (GC)	DP_n[e] (NMR)
1	3.5	−20	83	35	2.2	
2	20.5	−20	7	57	2.2	2.4
3	6.0	−20	22	76	3.4	3.5
4	10.0	−35	22	69	2.2	
5[c]	9.0	−35	20	56	1.9	1.7
6[c,d]	12.5	−35	2.5 + 22	98	7.4	7.1

[a] Reaction conditions: $C_2F_3Cl_3$ 10 mL; $[CsF]_0/[tetraglyme]_0$ ca. 1:1.8; polymerization time 2 h. [b] Conversion can be lower than expected due to the loss of low molar mass products (DP_n = 1, bp = 61 °C/739 mmHg) after solvent evaporation. [c] Solvent $C_4F_5H_5$ instead of $C_2F_3Cl_3$. [d] Experiment under monomer-starved conditions. [e] DP_n(NMR) was calculated according to Figure 4.

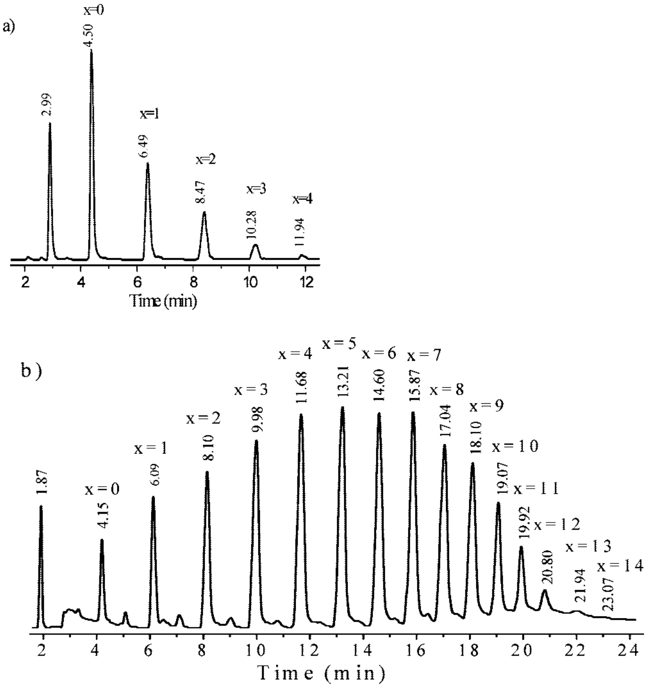


Figure 1. Gas chromatograms of $F[CF(CF_3)CF_2O]_xCF(CF_3)COOCH_3$ corresponding to run 4 (a) and run 6 (b) in Table 1.

Although the obtained oligomers showed quite low molar masses, more insight can be brought on the mechanism of polymerization through their characterization. A typical gas chromatogram of oligo(hexafluoropropylene oxide) synthesized with CsF/tetraglyme under batch conditions is presented in Figure 1a. Oligomers with DP_n values ranging between 1 (x = 0) and 5 (x = 4) (or average molar masses 180−800 g mol^{-1}) represent the main population in the GC chromatogram. DP_5 is present in the crude oil in very low amount, whereas oligomers with $DP_n > 5$ are absent. The targeted DP_n of 22, assuming that one CsF molecule effectively generates one polymer chain, was not reached at all in this case, thus leading to the conclusion that intensive chain transfer reaction occurred under these conditions (Scheme 1).

The CsF/tetraglyme catalytic system was also tested under monomer-starved conditions; i.e., the monomer was slowly and continuously added to the polymerization system (run 6, Table 1). In this case, the experiment was carried out in two steps: (i) a soluble initiator was obtained by a batch experiment in far excess of catalyst ($[HFPO]_0/[CsF]_0$ = 2.5); (ii) then, the monomer was added stepwise in small increments (ca. 2 g every 10 min).

The GC chromatogram presented in Figure 1b shows a broad distribution (ranging from DP_n = 1 (x = 0) to DP_n = 15 (x =

Table 2. Anionic Polymerization of Hexafluoropropylene Oxide with Different Alkali Metal Fluorides (MF)[a]

run	catalyst	MF content (mmol)	lattice energy[22] (kcal mol^{-1})	$[HFPO]_0$/ $[catalyst]_0$	conv (%)	DP_n (GC)	DP_n[b] (NMR)
7	CsF	9.0	176	20	56	1.9	1.7
8	KF	19.5	192	15	53	6.9	7.7
9	NaF	24.0	215	15	12	1.0	

[a] Reaction conditions: $C_4F_5H_5$ 10 mL; $[MF]_0$:$[tetraglyme]_0$ ca. 1:1.8 (M = Cs, K, Na); temperature −35 °C; polymerization time 2 h. [b] DP_n(NMR) was calculated according to Figure 4.

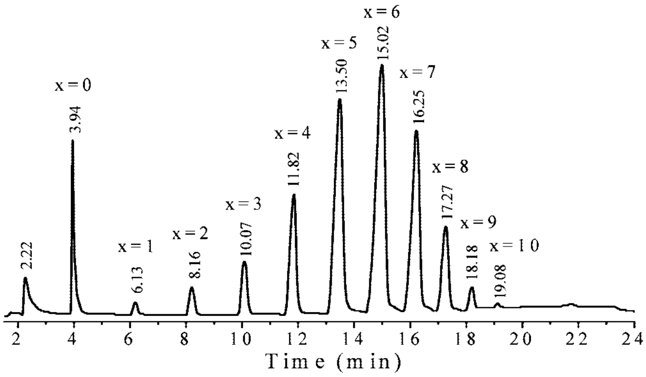


Figure 2. Gas chromatogram of $F[CF(CF_3)CF_2O]_xCF(CF_3)COOCH_3$ obtained in run 8 in Table 2.

14), M_n = 180−2660 g mol^{-1}) centered on an average DP_n of 7.4 (M_n = 1410 g mol^{-1}). The fact that the addition of monomer was performed through ∼2 g shots, rather than by slow continuous addition, explains that chain lengths not larger than DP_n = 16 were obtained in this experiment. It was also noticed that even if the rate of monomer feeding could be perfectly adjusted so as to increase the average DP_n, low molar mass byproduct would still be present in the polymer since, at this stage, transfer reaction to monomer was not fully suppressed.[6]

The structure and functionality of obtained oligomers were examined by ^{1}H and ^{19}F NMR spectroscopy (see spectra and full assignment in the following characterization part). From the ^{1}H NMR spectrum, it was confirmed that all polymer chains contain a $-COOCH_3$ group on their ω-extremity, which arises after esterification of growing chains by methanol. The average DP_ns were calculated by integrating the C*F* moieties of the main chain and that adjacent to the ester chain end and were in good agreement with those calculated from GC data (see calculation procedure in the Experimental Part), albeit for such low molar masses (vide infra).

Influence of Various Alkali Metal Fluorides. Since the polymerization of HFPO proceeds via an anionic process, the nature of the counterion should strongly influence both propagation and transfer reactions. As shown in Table 2, the monomer conversion systematically decreased (CsF > KF > NaF) while increasing the lattice energy of alkali metal fluorides.[21] On the other hand, the number-average DP_n increased up to 8 with KF as the catalyst, whereas the monoadduct was exclusively generated in the case of NaF as evidenced by its GC chromatogram and ^{19}F NMR spectrum (Figure S1 of the Supporting Information). Close inspection of the GC chromatogram of oligo(hexafluoropropylene oxide) obtained with the KF/tetraglyme system reveals a main population with a broad distribution centered at DP_n = 7, while a large content of DP_1 deviates from the main distribution (Figure 2). Interestingly, only a very low amount of products with DP_n ranging between 2 and 4 (near 5%) was detected by GC.

Effect of Temperature and Catalyst Content. Table 3 reports a summary of different experimental results where the influence of the polymerization temperature and $[HFPO]_0/[KF]_0$ ratio on the monomer conversion and average DP_n (M_n) of the obtained poly(hexafluoropropylene oxide)s were studied. An increase in the polymerization temperature from −35 to −15 °C led to a significant enhancement in the monomer conversion (from 50 to 90%) as well as an increase in the number-average degree of polymerization from 8 (M_n ∼ 1600 g mol^{-1}) to 10 (M_n ∼ 2000 g mol^{-1}) (see runs 10 and 11 in Table 3). Still, the amount of low molar mass byproduct in both experiments remained high (15−20%). It should be noted that, for oligo(hexafluoropropylene oxide)s of molar masses larger than 1500 g mol^{-1}, DP_n values calculated using GC data were systematically underestimated compared to those determined by NMR spectroscopy (see also Figure S2). Such a result arises from the limit of our GC technique; i.e., higher molar mass fractions do not appear in GC chromatograms. These discrepancies have not been found detrimental for concluding on this mainly qualitative mechanistic study (see Discussion part).

Table 3. Polymerization of Hexafluoropropylene Oxide with KF/Tetraglyme System at Different Temperatures and Different $[HFPO]_0/[KF]_0$ Ratios[a]

run	temp (°C)	$[HFPO]_0$/ $[KF]_0$	conv (%)	DP_n (GC)	DP_n[c] (NMR)	M_n[d] (NMR) (g mol^{-1})	M_w/M_n[e]	content of $DP_n \leq 5$ (GC) (%)
10	−35	15	53	6.9	7.7	1620	1.07	20.5
11	−15	15	88	9.1	10.1	2020	1.10	14.3
12	0	15	89	8.9	10.3	2050	1.08	10.5
13[b]	0	40	89	9.5	13.1	2500	1.10	6.9
14[b]	0	60	92	9.9	12.0	2330	1.08	4.0
15[b]	0	120	90	8.4	10.1	2020	1.09	7.5
16[b]	10	40	90	8.8	9.3	1890	1.06	4.3
17[b]	20	40	91	5.4	6.3	1390	1.11	37.3

[a] Reaction conditions: $C_4F_5H_5$ 10 mL; $[KF]_0$:$[tetraglyme]_0$ ca.1:1.8; polymerization time 2 h. [b] Polymerization time 3 h. [c] DP_n (NMR) was calculated according to Figure 4. [d] M_n(NMR) = DP_n(NMR) × 166 + 185 (headgroup) + 159 (tail group). [e] Calculated based on GC data, see Experimental Part for details.

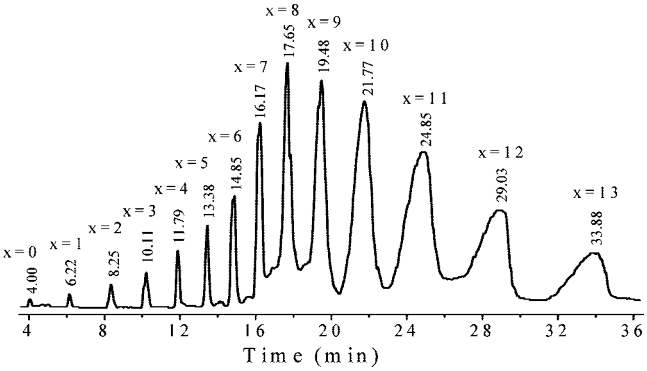


Figure 3. Gas chromatogram of oligo(hexafluoropropylene oxide)s obtained in run 13 in Table 3.

A further increase of the polymerization temperature up to 0 °C did not significantly affect the monomer conversion or the average DP_n but led to a decrease of low molar mass oligomers content (down to 10%, run 12, Table 3). This content was even further decreased by raising the $[HFPO]_0/[KF]_0$ ratio from 15 to 40 or 60, for which the number-average degree of polymerization reached 12−13 (M_n = 2300−2500 g mol^{-1}) and oligomeric byproduct settled down to ca. ∼ 4−7% (runs 13 and 14 in Table 3). An additional increase in the $[HFPO]_0/[KF]_0$ ratio almost did not influence either the DP_n or the content of low molar mass oligomers (runs 14 and 15, Table 3). Indeed, a comparison of GC chromatograms of polymers obtained at −35 °C (Figure 2) and 0 °C (Figure 3) reveals a large shift of the oligomer distribution toward the high molar mass region, where peaks are no more resolved (Figure 3). Importantly, only low quantities of low molar mass oligomers are present in the crude

Table 4. Polymerization of Hexafluoropropylene Oxide with the KF/Tetraglyme System in Bulk or in Different Solvents[a]

run	solvent	miscibility with tetraglyme	conv (%)	DP_n (GC)	DP_n[b] (NMR)	M_n[c] (NMR) (g mol^{-1})	M_w/M_n[d]
18		*e*	36	4.0	4.8	1140	1.09
19	HFP	*e*	24	3.4	4.1	1020	1.10
20	$C_4F_5H_5$[f]	yes	95	11.2	14.4	2730	1.10
21	HFX[f]	yes	88		19.2	3530	
22	C_8F_{18}	no	93	5.1	5.3	1220	1.05
23	HFE-7500	no	95	5.2	6.6	1440	1.08
24	$C_4F_5H_5$/HFE-7500[g]	yes	90	10.7	12.9	2480	1.08
25	$C_4F_5H_5$/FC-75[h]	yes	90	9.5	13.3	2550	1.12

[a] Reaction conditions: solvent: 10 mL; $[KF]_0$:$[tetraglyme]_0$ ca. 1:1.8; $[HFPO]_0/[KF]_0 = 40$; polymerization time 3 h; HFP = hexafluoropropylene, HFX = 1,3-bis(trifluoromethyl)benzene, C_8F_{18} = perfluorooctane, HFE-7500 = 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoromethylhexane; FC-75 = 2,2,3,3,4,4,5-heptafluoro-5-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)tetrahydrofuran. [b] DP_n (NMR) was calculated according to Figure 4. [c] M_n(NMR) = DP_n(NMR) × 166 + 185 (head group) +159 (tail group). [d] Calculated based on GC data, see Experimental Part for details. [e] Not determined. [f] 30 mL. [g] $C_4F_5H_5$/HFE-7500 10 mL/10 mL. [h] $C_4F_5H_5$/FC-75 10 mL/5 mL.

polymer. Finally, raising the polymerization temperature to 20 °C generated back low molar mass polymer (runs 16 and 17, Table 3), in which average DP_n and distribution profile are similar to the ones obtained at −35 °C (see GC chromatogram of oligoHFPO obtained at 20 °C in Figure S3). An interesting point is that all oligomers synthesized using the KF/tetraglyme catalytic system are characterized by very narrow molar mass distributions, typically, $M_w/M_n \leq 1.10$ (see Table 3), indicating that chain transfer or termination reactions were strongly suppressed under investigated conditions.

Effect of the Nature of the Solvent. Different fluorinated compounds were further tested to investigate the influence on the polymerization mechanism of solubility or miscibility of the various reactants, monomer, and polymer within these solvents (Table 4). Basically, when hexafluoropropylene (bp = −28 °C) was used as the solvent or when the polymerization proceeded without fluorinated solvent, the chain length of thus-produced oligoHFPO dramatically decreased (compare run 13 in Table 3 with runs 18 and 19 in Table 4). Hexafluoropropylene, which is a liquid and a good solvent for oligoHFPO when polymerization proceeds at −35 °C,[12,13] was found inefficient at higher temperature, i.e. 0 °C, probably due to its exclusive gaseous partitioning at this temperature. These data confirm the importance of the presence of solvent for oligoHFPO in the liquid phase. As is also obvious from Table 4, in order to reach targeted high molar masses, the fluorinated solvents must be miscible with tetraglyme. Indeed, when C_8F_{18} or HFE-7500 was used, low molar mass products with $DP_n \leq 5$ (M_n < 1500 g mol^{-1}) were obtained in high conversion (runs 22 and 23 in Table 4). The dilution of the polymerization media also allowed us to increase the molar mass of the synthesized polymers (compare run 13 in Table 3 and run 20 in Table 4). The highest average molar mass (M_n = 3530 g mol^{-1}) obtained in this study made use of 1,3-bis(trifluoromethyl)benzene as a solvent (run 21, Table 4). In addition, independent of the nature of the solvent, all polymers were characterized by very narrow molar mass distributions (Table 4); i.e., polymerization proceeded in a living fashion.

Polymer Characterization. All polymers were systematically characterized by GC and ^1H and ^{19}F NMR spectroscopy. The corresponding spectra of oligomers obtained from a typical batch experiment (run 3, Table 1) are shown in Figure 4a. The ^{19}F NMR spectrum[22] shows signals centered at −147.5 ppm (1) and −81.3/−81.8 ppm (2, 4) ascribed to the $-CF-$, $-CF_2O-$, and $-CF_3$ groups of main-chain fluorine atoms, respectively. The resonances at ∼−84.5 ppm (6, 8), −85.5 ppm (5), −132.4 ppm (7), and −134.2 ppm (3) are assigned to the fluorine atoms borne by the chain ends[3,5,23] (see Figure 4 for details). The ratio of integrals of signals 7 to 3 is 2, which confirms that F^- initiates the polymerization (see detailed mechanism below). The average DP_n, calculated as the ratio of (1 + 3) to 3 integrals, is estimated at 3.5, a value close to that obtained from GC data (see Table 1). The ^{19}F NMR spectrum of oligo(hexafluoropropylene oxide) of larger molecular weight (run 13, Table 3, Figure 4b) shows similar signals as its low molar mass counterpart (Figure 4a). The difference here lies in the larger intensity of the signals assigned to the main-chain fluorine atoms (1, 2, 4), in comparison to signals arising from functional groups at both chain ends (3, 5, 6, 7, 8). All oligo(hexafluoropropylene oxide) chains bear a $-COOCH_3$ group on their ω-extremity, which arises from termination of the growing chains with methanol, thus showing that termination reactions (particularly with water, which would generate −COOH chain ends) are virtually absent.[24]

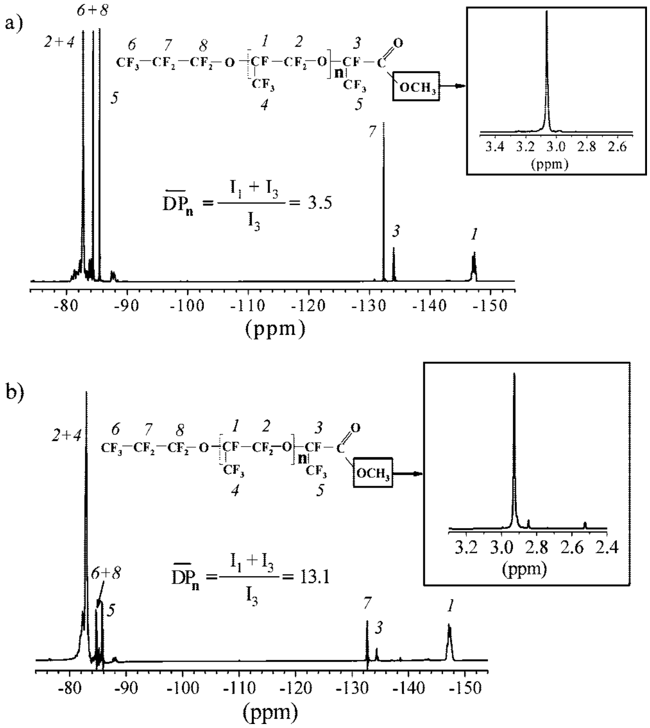


Figure 4. ^{19}F NMR and ^1H NMR (inset) spectra of oligo(hexafluoropropylene oxide) (a) obtained with the CsF/tetraglyme/$C_4F_5H_5$ catalytic system (run 3, Table 1) and (b) obtained with the KF/tetraglyme/$C_4F_5H_5$ catalytic system (run 13, Table 3).

The functionality of polymers was also confirmed by means of MALDI-TOF-MS spectroscopy.[25,26] The MALDI-TOF-MS spectrum of poly(hexafluoropropylene oxide) shown in Figure 5 gives, as expected, a narrow distribution with difference of mass between peaks of 166 g mol^{-1}, corresponding to one hexafluoropropylene oxide unit. The end groups also correspond to the expected ones: F^- at the α-end arising from initiation by KF and a methyl ester group at the ω-end created after reaction of oligoHFPO acyl fluoride chain ends with methanol. No other

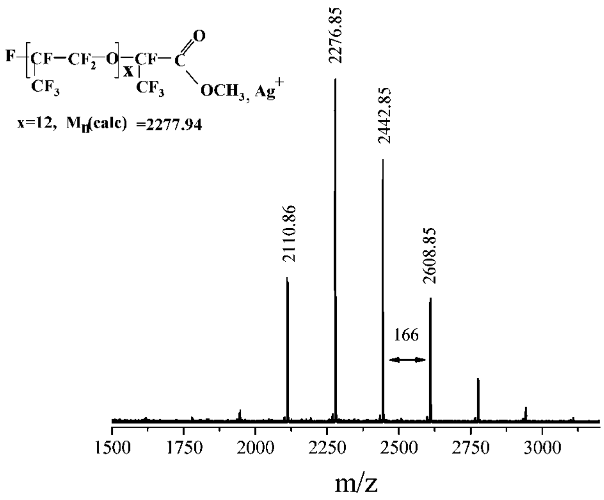


Figure 5. MALDI-TOF-MS spectrum of oligo(hexafluoropropylene oxide) obtained with KF/tetraglyme system at 0 °C (run 13, Table 3): $C_4F_5H_5$ 10 mL; HFPO 45 g; $[KF]_0$:$[tetraglyme]_0$ ca. 1:1.8; $[HFPO]_0/[KF]_0 = 40$.

signals have been noted in the spectrum indicating that side reactions, which would have led to the loss of functionality, are absent. As in the GC chromatograms (see also Tables 3 and 4), the MALDI-TOF-MS spectrum shows a very narrow distribution ($M_w/M_n = 1.07$ vs 1.10 for GC data): all signals range in a narrow 2000−3000 g mol^{-1} window with a number-average molar mass of 2370 g mol^{-1} (see ref 27 for the details of the calculation of M_n and MMD), in fair agreement with the molar mass obtained by ^{19}F NMR spectroscopy ($M_n = 2500$ g mol^{-1}).

Kinetics Investigations. For this study, we have chosen optimized batch conditions used to prepare HFPO homopolymers in the presence of the KF/tetraglyme catalytic system with an average molar mass up to 2500 g mol^{-1}, at high conversion (ca. 90%) and almost without any low molar mass contaminants (4−7%) (run 13 in Table 3). GC chromatograms obtained at different polymerization times give interesting insight into the mechanism of reaction (Figure S4). Basically, the accumulation of product with $DP_n = 1$ with retention time near 4 min took place at the early stage of the polymerization ($DP_1 = 28.5\%$ at a total conversion of 22.5%). The increase in monomer conversion led to a drastic decrease of the amount of $DP_n = 1$ ($DP_1 = 5.7\%$ and 1% at 72.0% and 90% conversions, respectively). It should also be noted that ^{19}F NMR spectra of polymers obtained at different conversions showed a similar accumulation of monoadduct at low conversion and its vanishing at high conversion (see Figure S5).

The most important observation here is that the molar mass distribution (MMD) curves normalized by their conversion gradually shift to higher molar mass region with increasing conversion, at least, up to 70% (see Figure 6). Moreover, number-average molar masses increase with monomer conversion, while MMDs of obtained polymers become narrower (Figure 6). Then, at 90% of conversion, some broadening of distribution is observed, as seen by the emergence of a tail in the low molar mass region (Figure 6), due to the formation of new chains by chain transfer reaction. In addition, the first-order plot is linear (see Figure S6), indicating that the concentration of the growing chain is constant, though it can be anticipated a slow initiation for the KF/tetraglyme system under the investigated conditions.[10,11] These results show that the polymerization of hexafluoropropylene oxide with KF/tetraglyme system under batch conditions proceeds in a living fashion.

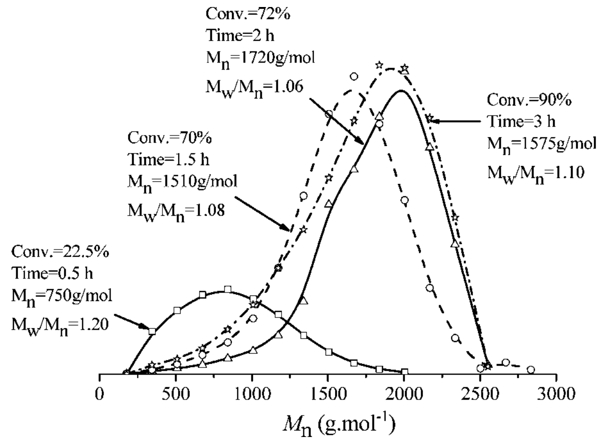
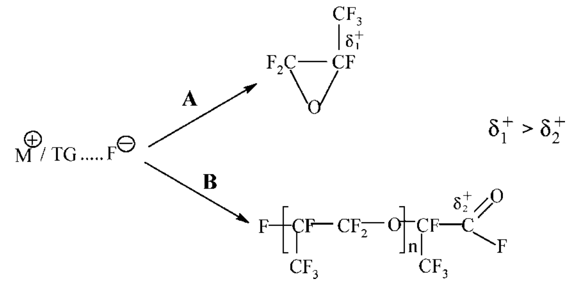


Figure 6. Molar mass distribution profiles for oligo(hexafluoropropylene oxide)s obtained with the KF/tetraglyme system at 0 °C and $[HFPO]_0/[KF]_0 = 40$ at different HFPO conversions. Symbols are integral values of GC peaks, whereas lines are only guides for the eyes.

Scheme 2. Competitive Reactions of MF (M = Na, K, Cs) with Monomer and "Dormant" Growing Chain[a]



[a] δ_i^+ represents the acidity of the carbon atom which reacts with F^-.

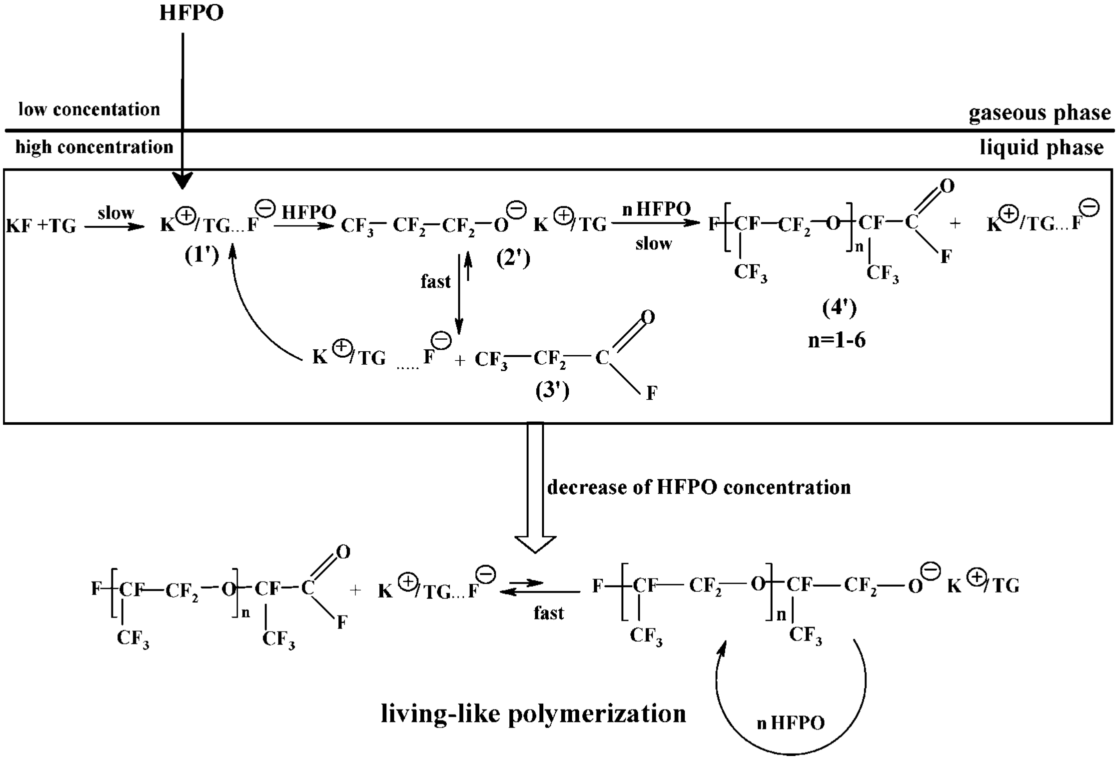
Discussion

The various experimental results gathered in this study allowed us to point out different features of the system. First, the accumulation of product with $DP_n = 1$ shows that the equilibrium between active and dormant species (species **2** and **3** in Scheme 1) shifts strongly to the dormant ones. Indeed, after initiation, i.e., the first step addition of fluoride anion to the monomer, immediate (or at least fast) chain deactivation by formation of an ω-acyl fluoride end group takes place.

Second, with an increase in lattice energy of alkali metal fluorides, the tightness of the corresponding ion pair increases and, in turn, the selectivity of F^- toward the monomer (step A, Scheme 2) in comparison with acyl fluoride (step B, Scheme 2) rises. Indeed, with NaF as the catalyst, no addition of F^- to the less acidic carbon atom in the acyl fluoride was observed, thus generating solely the monoadduct. On the contrary, with CsF, which forms a loose ion pair, there was no selectivity between A and B pathways (Scheme 2). In this case, the polymerization of HFPO under batch conditions proceeded in a very fast manner, and as a result, only low molar mass products were obtained. With KF, the polymerization was slower than with CsF, and after the accumulation of sufficient amount of CF_3-CF_2-COF at the beginning of the polymerization, the addition of F^- to acyl fluoride formed back a perfluoroalkoxide able to react with monomer and to generate higher molar mass oligomers (see Scheme 1 for details).

Third, since HFPO exhibits a boiling point of −27 °C, it can be assumed that increasing the polymerization temperature in a reactor would lead to a partitioning of the gaseous monomer between the liquid phase and the free volume of the reactor.

Scheme 3. Proposed Mechanism for the Polymerization of Hexafluoropropylene Oxide with the KF/Tetraglyme Catalytic System in Batch Conditions



Such equilibrium results in a decrease of [HFPO]/[KF] ratio in the reaction locus and, in turn, prevents or at least slows down chain transfer reactions. Moreover, rising the polymerization temperature decreases the solubility of hexafluoropropylene oxide in tetraglyme and HFPO oligomers, whereas the solubility of growing alkoxides increases.[28] Equilibrium between propagating and dormant species (Scheme 1) is thus shifted toward the growing alkoxides (species **2** in Scheme 1) with a rise in temperature. Some authors[10] noted that an increase of the polymerization temperature could also reduce the viscosity of the polymerization medium, thus facilitating the chains growth and suppressing the chain transfer reaction. Finally, at higher temperature (20 °C) the chain transfer reaction becomes predominant, which is typical for ionic polymerizations.[29]

Fourth, the nature of the solvents plays a major role in HFPO polymerization. One requirement concerns their miscibility with both tetraglyme and growing oligoHFPO to reach desired high molar mass polymers. When the solvent was immiscible with tetraglyme (see Table 4) or phase separation occurred during the polymerization process, the chain transfer reaction was dominant. Visually, the polymerization of HFPO using the KF/tetraglyme system at 0 °C started to occur in a homogeneous medium during which a gradual increase of M_ns and a narrowing of MMDs were observed (for example, see Figure 6). Then, when a sufficient amount of oligoHFPO was produced, the solution, as observed immediately after stopping the agitation, quickly separated into two phases, i.e., tetraglyme on the top layer and a fluorinated solvent solution of oligoHFPO below. Finally, at the end of the polymerization, the bottom layer became very viscous and small droplets of tetraglyme penetrated into oligoHFPO phase under vigorous agitation, leading to new chain transfer events.

A mechanism of the polymerization of hexafluoropropylene oxide using the KF/tetraglyme system under batch conditions at 0 °C is proposed in Scheme 3. Because of the poor solubility of KF in tetraglyme, only a low amount of active species (**1′**, in Scheme 3) are formed at the beginning of the polymerization. These species react with one molecule of HFPO to produce species **2′**, which forms immediately an acyl fluoride **3′** and the soluble K^+(glyme)/F^- complex. This latter complex creates a new chain, since the monomer is in high excess compared to **3′** species, rather than coming back to the active center **2′**, thus provoking a chain transfer reaction which limits the propagation of dormant chains.

In these intensive chain transfer conditions, slow solubilization of KF in the reaction medium and some accumulation of product with $DP_n = 1$ takes place at the beginning of the polymerization. During this period (up to 0.5 h), only a few molecules of acyl fluoride **3′** are reactivated to form **2′** that grows via propagation to form oligomers with $DP_n = 2-6$ (**4′**, in Scheme 3). The pressure inside the autoclave then gradually decreases from ~0.5 to ~0.2 bar, inducing a decrease of the concentration of monomer in the liquid phase and thus a slower chain transfer reaction to monomer. Therefore, after accumulation of a sufficient amount of $DP_n = 1$ and of low molar mass oligomers, the propagation becomes dominant and produces higher molar mass polymers. At this stage of the reaction, the polymerization proceeds in a living fashion: number-average molar mass increases, and molar mass distribution becomes narrower with increasing conversion. At the end of the reaction, phase separation occurs, and in these conditions, the chain transfer reaction becomes predominant again, as observed from some lowering of the molar masses and some broadening of MMDs of the obtained polymers.

Conclusion

In this study, various alkali metal fluorides (NaF, KF, CsF) in combination with tetraglyme as the catalytic systems were tested in the anionic ring-opening polymerization of hexafluoropropylene oxide in the presence of different fluorinated solvents ($C_2F_3Cl_3$, $C_4F_5H_5$, HFP, HFX, HFE-7500), at various temperatures (from −35 to 20 °C) and under batch conditions. Different parameters were varied to understand how propagation and chain-transfer reactions compete and to find the way to favor the former reaction. Careful characterization of the products, including gas chromatography, different nuclei NMRs, and MALDI-TOF, confirmed that all chains were perfectly functionalized and that no side reactions apart from chain-transfer reactions occurred. From these results, the simplest procedure to synthesize high molar mass hexafluoropropylene oxide polymers with a minimum amount of low molar mass oligomeric byproduct under batch conditions was established. Polymers with number-average molar mass ranging between 2500 and 3500 g mol^{-1}, at high conversion (>90%), and with low contents of short oligomeric contaminants (<7%) were prepared using the KF/tetraglyme catalytic system and $C_4F_5H_5$ or 1,3-bis(trifluoromethyl)benzene as the solvent at 0 °C.

Acknowledgment. The authors thank the Clariant Co. for providing a postgraduate grant and purchasing hexafluoropropylene oxide and Solvay for their gifts of $C_4H_5F_5$ and hexafluoropropylene. Dr. Gilles Vallete (MALDI-TOF-MS analysis) and Claire Negrell-Guirao (NMR analysis) are kindly acknowledged. S.K. is also grateful to Alexei Radchenko and Alexander Frolov for their help in the manuscript preparation.

Supporting Information Available: GC chromatogram and ^{19}F NMR spectrum of monoadduct $CF_3CF_2CO_2CH_3$; GC chromatograms, ^{19}F and ^{1}H NMR spectra of polymers obtained using the KF/tetraglyme catalytic system; DP$_n$ correspondence between GC and ^{1}H NMR evaluations; ln([M]$_0$/[M]) vs time and M_n vs conversion plots for model kinetics reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8012338