


Cite this: *RSC Adv.*, 2020, 10, 10932

Received 2nd December 2019
Accepted 6th January 2020

DOI: 10.1039/c9ra10069e

rsc.li/rsc-advances

Reduction of liquid terminated-carboxyl fluoroelastomers using $\text{NaBH}_4/\text{SmCl}_3$

Yunfei Chang,  Mingyi Liao * and Xueyan Li 

Using a simple one-pot method, the reduction of liquid terminated-carboxyl fluoroelastomers (LTCFs) by sodium borohydride and samarium chloride ($\text{NaBH}_4/\text{SmCl}_3$) was successfully realized and liquid terminated-hydroxyl fluoroelastomers (LTHFs) were obtained. The structure and functional group content of LTCFs and LTHFs were analyzed by FTIR, ^1H -NMR, ^{19}F -NMR and chemical titration. The results showed that $-\text{C}=\text{C}-$ and carboxyl groups of LTCFs were reduced efficiently, the reduction rate reached 92% under optimum reaction conditions. Compared with other frequently-used metal chlorides, SmCl_3 with a high coordination number could increase the reduction activity of NaBH_4 more effectively and the reduction mechanism was explored.

1. Introduction

As an important polymer material, fluoroelastomers have been widely utilized in the field of chemical engineering, machinery and aerospace^{1–3} due to their inherent resistance to fuel, oil, high temperature and oxidation. The stabilized carbon–fluorine single bond ($\text{C}-\text{F}$ 485 kJ mol^{-1}) and the shielded effect of fluorine atoms on the main chain^{4,5} make the chemical properties of fluoroelastomers more stable than other rubbers. Curable liquid fluoroelastomers with lower molecular weight have attracted much attention using solvent-free sealant and adhesive formulators because of their liquidity and plasticity. Low molecular weight LTCFs with M_n ranging from 500 to 10 000 were prepared by oxidative degradation of fluoroelastomers.^{6,7} However, due to the properties of carboxyl groups, the LTCFs are difficult to react with cross-linking agents at low temperature and have low heat resistance stability,⁸ which will inevitably affect their comprehensive properties and limit their application fields. Therefore, it is particularly important to convert the carboxyl groups into hydroxyl groups to improve the thermal stability and reduce the curing temperature of liquid fluoroelastomers.

While significant advances had been made in reduction reactions including for carbonyl compounds, these processes often did not reduce carboxyl groups directly.^{9–12} Because in contrast to ketones,¹³ aldehydes¹⁴ and esters,¹⁵ which easily engage in reactions with reductive agents, carboxylic acids are generally unreactive.¹⁶ On the other hand, although lithium aluminium hydride was widely used as a strong reductant in carboxyl reduction,¹⁷ its poor chemical selectivity, flammability and explosive nature are unfavorable for large-scale production.

Kamochi and Kudo reported the reduction of aryl carboxylic acid derivatives and some aliphatic carboxylic acids using SmI_2 ,^{18,19} however this strategy was low yielding and limited in scope for aliphatic carboxylic acids. Szostak *et al.*²⁰ developed a method for efficient electron transfer reduction of carboxylic acids using $\text{SmI}_2\text{-H}_2\text{O-Et}_3\text{N}$ and achieved excellent yield, the protocol was not suitable for large-scale production because SmI_2 was costly and difficult to store.

NaBH_4 has attracted much attention due to its applications in reduction in organic chemistry. Compared with lithium aluminium hydride and SmI_2 , NaBH_4 , with moderate cost, mild reaction conditions and excellent chemical selectivity, is conducive to safe production. Nonetheless, NaBH_4 does not directly reduce the carboxylic acids by reason of its relatively weak reductive activity. To reduce carboxylic acid compounds effectively, many Lewis acids have been developed to improve the reduction activity of NaBH_4 including I_2 ,²¹ ZnCl_2 ,²² LiCl ,²³ AlCl_3 ,²⁴ CoCl_2 (ref. 25) and so on. Although the LTCFs were reduced by NaBH_4/I_2 , the addition of I_2 complicated the post-treatment process and the residual iodine would severely affect the stability of products.²⁶ Hence, further systematical studies on the reduction of LTCFs are academically and industrially significant. Rare earth ions with strong positive electricity, high coordination number and outer empty orbit have strong oxygen affinity.²⁷ Therefore, they can complex with ethers, carbonyl compounds, nitrogen compounds and so on.²⁸ The unique electronic and chemical properties of rare earth ions make them have many advantages, for instance, mild reaction conditions, satisfactory selectivity, less environmental pollution and high efficiency catalytic cycles.²⁹ Hence, our interest in a new strategy for reductive transformations by using NaBH_4 and rare earth ions led us to introduce $\text{NaBH}_4/\text{SmCl}_3$ as the first reagent to selectively reduce LTCFs. This mainly involves a simple one-pot process with mild reaction conditions

College of Transportation Engineering, Dalian Maritime University, No. 1 Linghai Road, Dalian, 116026, China. E-mail: liaomy2000@sohu.com



and the $\text{NaBH}_4/\text{SmCl}_3$ dosage, reaction temperature, reaction time and organic solvents were systematically studied. To the best of our knowledge, few facile methods have been reported to date for the reduction of carboxylic acids by $\text{NaBH}_4/\text{SmCl}_3$.

2. Experimental section

2.1 Chemicals

Vinylidene fluoride-hexafluoropropylene copolymer (VDF-HFP) with VDF/HFP = 3/1 and $M_n = 78\,000$ was purchased from Chenguang Research Institute of Chemical Industry (China). Hydrogen peroxide (H_2O_2), potassium biphthalate ($\text{C}_8\text{H}_5\text{KO}_4$), phenolphthalein, bromothymol blue, potassium hydroxide (KOH), acetone and benzyltriethylammonium chloride (BTEAC) were purchased from Alfa Aesar (China). NaBH_4 , AlCl_3 , CoCl_2 , ZnCl_2 , CaCl_2 and SmCl_3 were purchased from Aladdin Industrial Corporation (Shanghai, China). Tetrahydrofuran (THF), 0.1 mol L^{-1} hydrochloric acid (HCl) and diglyme were purchased from Kermel Reagent (Tianjin, China).

2.2 Synthesis of LTCFs⁹

LTCFs were prepared through chemically degradation of high molecular weight solid VDF-HFP copolymer. High molecular weight VDF-HFP (100 g) and acetone (300 mL) were added into a 2000 mL flask. The mixture was stirred at room temperature for 24 h till the copolymer was completely dissolved. Under stirring at 0 °C, BTEAC (6.5 g), 30 wt% H_2O_2 aqueous solution (60 g), 45 wt% KOH aqueous solution (43 g) were added sequentially. The reaction mixture was then warmed up to 24 °C and stirred for 7 h. After the reaction, the organic and inorganic phases were separated by filtration. HCl was used to acidify the organic phases and then the mixture was washed by excess deionized water for 3 times. Finally, the deposition was dried under 60 °C for 48 h in a vacuum drying chamber to obtain LTCFs.

2.3 Synthesis of LTHFs

5.000 g LTCFs (2.66% carboxyl content) were dissolved in a mixture of THF (15 mL) and diglyme (15 mL) for 1 h, then 0.447 g NaBH_4 was dissolved into the solution under stirring for 1 h at 0 °C. Subsequently, 1.506 g SmCl_3 was added into the system and temperature rose to 90 °C. After 6 h, the inorganic impurities were dissolved by 30 mL 0.1 mol L^{-1} HCl and the mixture was washed by excess deionized water for 3 times. Finally, the deposition was dried under 60 °C for 48 h in a vacuum drying chamber to obtain LTHFs.

2.4 Characterization

ATR-FTIR measurement was performed using a PerkinElmer Instruments Spectrum One. FTIR spectra were obtained at the resolution 4 cm^{-1} in the range 650–4000 cm^{-1} . The NMR spectra were analyzed by Bruker AC 80 spectrometers (500 MHz for ^1H , 470 MHz for ^{19}F) at room temperature, using acetone- d_6 as the solvent and TMS as internal standard the references for ^1H (or ^{19}F) nuclei. Chemical shifts are reported in ppm.

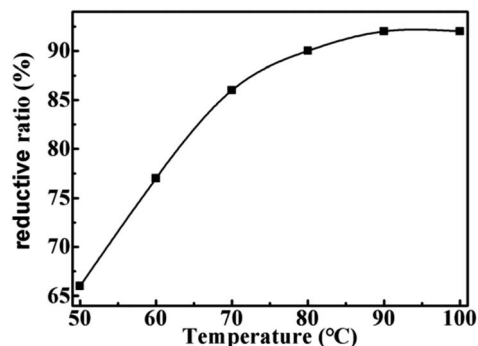


Fig. 1 The effect of temperature on the reductive rate of LTCFs.

2.5 Chemical titration

2.5.1 Preparation and calibration of KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution. 0.1 mol L^{-1} KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution was prepared in volumetric bottle according to the China National Standards GB/T 603-2002 and GB/T 601-2002. 0.2 g of potassium biphthalate and 40 μL phenolphthalein solution (10 g L^{-1}) was dissolved in water (50 mL). KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution was added dropwise into the potassium biphthalate and phenolphthalein aqueous solution and when the aqueous solution changed from colorless to pink, it was the end point of titration. Blank experiment as the comparison was done. The concentration of KOH/ $\text{C}_2\text{H}_5\text{OH}$ standard titration solution was calculated by formula (1):

$$C_{(\text{KOH}-\text{C}_2\text{H}_5\text{OH})} = \frac{m \times 1000}{(V_1 - V_2)M} \quad (1)$$

V_1 : volume of KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution consumed by the potassium biphthalate and phenolphthalein solution (mL), V_2 : volume of KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution consumed by blank sample (mL), m : weight of potassium biphthalate (g), M : 204.22 g mol^{-1} .

2.5.2 Determination of carboxyl content. 0.75 g of LTCFs and 40 μL bromothymol blue (10 g L^{-1}) was dissolved in acetone (40 mL). KOH/ $\text{C}_2\text{H}_5\text{OH}$ solution was used for titration and the LTCFs and bromothymol blue solution changed from light yellow to green, which was the end point of titration. Carboxyl content of LTCFs was calculated by formula (2):

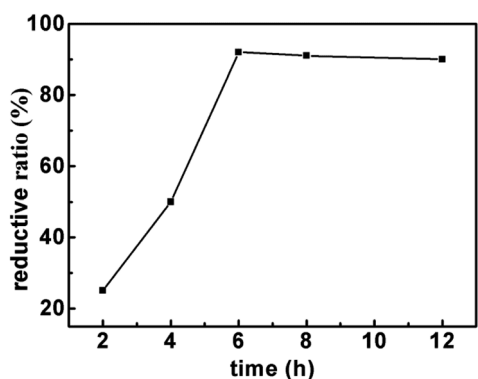


Fig. 2 The effect of time on the reductive rate of LTCFs.

Table 1 The effect of NaBH₄/SmCl₃ system on the reduction of LTCFs

No.	R ₀ COOH	NaBH ₄	SmCl ₃	THF/diglyme (mL)	Reductive rate (%)
1	1	0	3	1/1 (30 mL)	0
2	1	6	0	1/1 (30 mL)	12
3	1	1	0.5	1/1 (30 mL)	13
4	1	2	1	1/1 (30 mL)	48
5	1	3	1.5	1/1 (30 mL)	61
6	1	4	2	1/1 (30 mL)	92
7	1	5	2.5	1/1 (30 mL)	88
8	1	4	2	1/0 (30 mL)	80
9	1	4	2	2/1 (30 mL)	85
10	1	4	2	1/2 (30 mL)	86
11	1	4	2	1/1 (20 mL)	53
12	1	4	2	1/1 (40 mL)	59
13	1	4	2	1/1 (50 mL)	42

Table 2 Comparison of reduction activity between NaBH₄/MCl_x and NaBH₄/SmCl₃

Reduction system	Ratio (mol)	THF/diglyme (mL)	Reductive rate (%)
NaBH ₄ /SmCl ₃	4/2	1/1	92
NaBH ₄ /AlCl ₃	4/2	1/1	64
NaBH ₄ /ZnCl ₂	4/2	1/1	72
NaBH ₄ /CaCl ₂	4/2	1/1	44
NaBH ₄ /CoCl ₂	4/2	1/1	20

reductive rate reaches the maximum. It indicates that the optimum reaction temperature is 90 °C and optimum reaction time is 6 h.

3.2 Effect of reduction system proportion

Table 1 shows the effect of NaBH₄/SmCl₃ system and solvents on the reduction reaction under the optimum reaction temperature and time. We find that on the basis of the chemical titration, the NaBH₄/SmCl₃ system in THF/diglyme could reduce LTCFs efficiently. As shown in No. 1 and 2 of Table 1, the necessity of each component of the reduction system is investigated. No reductive reaction is observed without NaBH₄ and only 12% reduction rate is obtained at the absence of SmCl₃, which indicates that SmCl₃ has no reducibility to LTCFs and NaBH₄ only has little reducibility. However, the reducibility increases significantly when the reductive system is composed of the two above reagents. The reductive rate of LTCFs increases with increasing the NaBH₄/SmCl₃ dosage and the optimal molar ratio of R₀COOH/NaBH₄/SmCl₃ is 1/4/2 (No. 3–6). When molar ratio of R₀COOH/NaBH₄/SmCl₃ further increases to 1/5/2.5, the reduction rate is decreasing due to the coating of the NaBH₄ particles with the excess SmCl₃, which likely impedes the efficient solubility of NaBH₄ (No. 7). Furthermore, as shown in Fig. 3, the SmCl₃ addition amount is investigated. When the molar ratio of NaBH₄/SmCl₃ changes from 4/0 to 4/2, the reductive rate of LTCFs increases with increasing amount of SmCl₃. Nevertheless, when the molar ratio is 4/3, the excess SmCl₃ make the reductive rate decrease because the coating of the NaBH₄ particles with the excess SmCl₃.

$$\text{COOH}\% = \frac{V \times C \times 45.02}{m} \times 100\% \quad (2)$$

V : volume of KOH/C₂H₅OH solution consumed by the LTCFs and bromothymol blue solution (mL), C : the concentration of KOH/C₂H₅OH standard titration solution (mol L⁻¹), m : weight of LTCFs (g).

2.5.3 Determination of hydroxyl content. Reductive rate of hydroxyl was calculated by the LTCFs and LTHFs content of carboxyl (3).

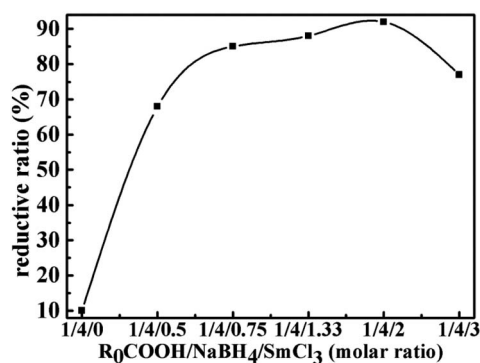
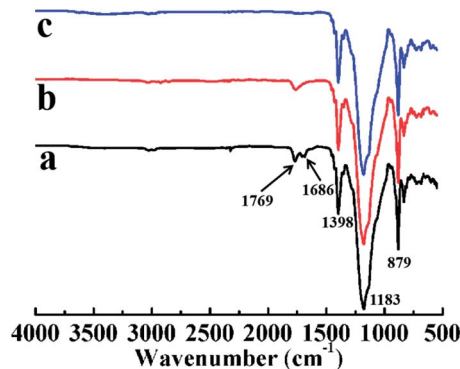
$$\alpha\% = \frac{\omega_0 - \omega_1}{\omega_0} \quad (3)$$

where ω_0 : LTCFs content of carboxyl, ω_1 : LTHFs content of carboxyl.

3. Results and discussion

3.1 Effect of reaction conditions

Firstly, the effect of temperature on reductive rate is examined. As shown in Fig. 1, the reduction rate of LTCFs increases with the increasing temperature and reaches the maximum at 90 °C. Secondly, the effect of reaction time is also investigated and the results are shown in Fig. 2, the reductive rate of LTCFs increases with increasing reaction time. When reaction time is 6 h, the

**Fig. 3** The effect of amount of SmCl₃ on the reductive rate of LTCFs.**Fig. 4** FTIR spectra of (a) LTCFs, (b) reduction product of single NaBH₄ (No. 2) and (c) LTHFs (No. 6).

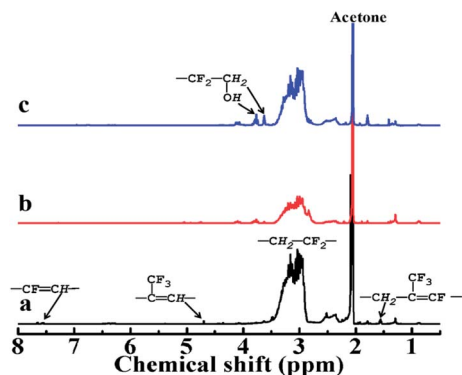


Fig. 5 ^1H -NMR spectra of (a) LTCFs, (b) reduction product of single NaBH_4 reductant (No. 2) and (c) LTHFs (No. 6).

3.3 Effect of solvent on reductive rate

As shown in Table 1 from No. 8, although the $\text{NaBH}_4/\text{SmCl}_3$ system in THF readily reduces LTCFs to their corresponding LTHFs, it has a lower reduction rate. The low reduction rate is possibly due to the weak solubility of NaBH_4 in THF. To improve the solubility of NaBH_4 in THF, varying amounts of diglyme, a known excellent solvent for NaBH_4 , are added. After some optimizations, the 1/1 volume ratio of THF/diglyme mixed solvent is adequate to solubilize NaBH_4 (No. 6, 8–10). In

addition, the effect of mixed solvent amount on reduction rate is also investigated (No. 6, 11, 12, 13). The results show that the maximum reduction rate is obtained as the amount of mixed solvent is 30 mL. The lower solvent amount will lead to the decrease solubility of NaBH_4 and the excessive use will affect the complexation of $\text{NaBH}_4/\text{SmCl}_3$ with carboxyl group. Consequently, 30 mL of THF/diglyme (1/1 volume ratio) mixed solvent is selected to investigate the reduction of LTCFs.

From above experimental results we can conclude that the optimal reaction conditions are as follows: the reaction temperature is 90°C , the reaction time is 6 h, the molar ratio of the $\text{R}_0\text{COOH}/\text{NaBH}_4/\text{SmCl}_3$ is 1/4/2 and the THF/diglyme volume ratio is 1/1. Under the optimal reaction conditions the LTCFs are converted to LTHFs in a reductive rate about 92%. For the scale-up, when we expand the experiment by 30 times, the reduction rate do not decrease significantly. Therefore, the method can be expected in industrial utility.

As comparison, several other metal chlorides (MCl_x) are also evaluated. Through the optimization studies, the optimal reaction conditions of $\text{NaBH}_4/\text{MCl}_x$ are consistent with $\text{NaBH}_4/\text{SmCl}_3$. As shown in Table 2, only $\text{NaBH}_4/\text{SmCl}_3$ gives excellent reductive rate of LTCFs (No. 1). It is concluded that the unique electronic structure and high coordination number of samarium ions provide a new method for efficient reduction of LTCFs and a potential scheme for the reduction of other carboxyl organic compounds.

3.4 Structure characterization

FTIR spectra of LTCFs is shown in Fig. 4(a). It can be seen from Fig. 4(a) that the absorption peaks at 1769, 1686, 1398, 1183, and 879 cm^{-1} ascribed to stretching vibration of $-\text{CF}_2\text{COOH}$, $-\text{C}=\text{C}-$, $-\text{FCH}_2-$, $-\text{CF}_2-$, and $-\text{CF}_3$, respectively.^{30,31} Fig. 4(b) shows the FTIR spectra of reduction product by single NaBH_4 . Comparing the Fig. 4(b) with Fig. 4(a), the absorption peak of $-\text{C}=\text{C}-$ at 1686 cm^{-1} is weakened and the absorption peak of $-\text{CF}_2\text{COOH}$ is still obvious (1769 cm^{-1}) indicating that the structure of $-\text{C}=\text{C}-$ is reduced significantly but only little $-\text{CF}_2\text{COOH}$ is reduced *via* single NaBH_4 without SmCl_3 . Fig. 4(c) shows the FTIR spectra of LTHFs reduced by $\text{NaBH}_4/\text{SmCl}_3$. From Fig. 4(c) can be seen that the absorption peaks of $-\text{C}=\text{C}-$ and $-\text{CF}_2\text{COOH}$ are weakened ascribed to effective reduction of $\text{NaBH}_4/\text{SmCl}_3$. LTHFs exhibits absorption peaks at 1398, 1183

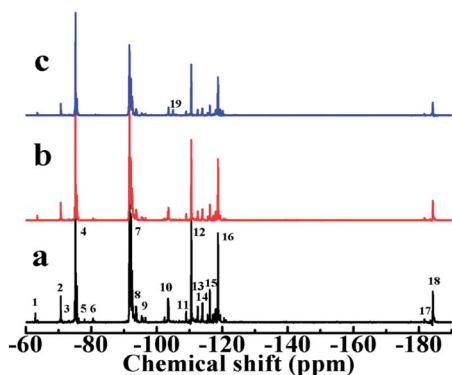


Fig. 6 ^{19}F -NMR spectra of (a) LTCFs, (b) reduction product of single NaBH_4 reductant (No. 2) and (c) LTHFs (No. 6).

Table 3 Assignments of ^{19}F -NMR peaks in liquid fluoroelastomers

No	δ (ppm)	Assignment	No	δ (ppm)	Assignment
1	-63.46	$-\text{CF}_2\text{CF}_2\text{COOH}$	11	-108.96	$-\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2-$
2	-70.67	$-\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{CH}_2-$	12	-110.51	$-\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$
3	-73.71	$-\text{CF}_2\text{CH}=\text{C}(\text{CF}_3)\text{CF}_2-$	13	-112.53	$-\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2-$
4	-75.19	$-\text{CF}_2\text{CH}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2-$	14	-113.95	$-\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2-$
5	-80.66	$-\text{CH}=\text{CFCF}(\text{CF}_3)-$	15	-116.24	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$
6	-81.30	$-\text{CF}=\text{CHCF}(\text{CF}_3)\text{CF}_2-$	16	-118.72	$-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2-$
7	-91.62	$-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$	17	-181.74	$-\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2\text{CH}_2-$
8	-93.56	$-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}(\text{CF}_3)-$	18	-184.33	$-\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2-$
9	-95.64	$-\text{CH}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$	19	-104.90	$-\text{CF}_2\text{CH}_2\text{OH}$
10	-103.62	$-\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}(\text{CF}_3)\text{CF}_2-$			



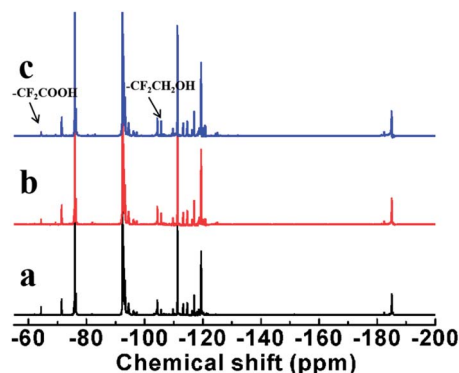


Fig. 7 ^{19}F -NMR spectra of LTHFs in different reaction times ((a) 1 h, (b) 3 h, (c) 5 h).

Table 4 Effect of charging sequence on the reduction of LTCFs^a

No.	Step 1a	Step 2b	Reductive rate (%)
1	NaBH_4 , SmCl_3 , LTCFs	—	33
2	SmCl_3 , LTCFs	NaBH_4	48
3	NaBH_4 , LTCFs	SmCl_3	92

^a First, chemical reagent of Step 1a were added into the reactor and reacted 1 h. Then, chemical reagent of Step 2b was added for reaction.

and 879 cm^{-1} ascribed to stretching vibration of $-\text{FCH}_2-$, $-\text{CF}_2-$, and $-\text{CF}_3$, respectively, which clearly shows that LTHFs have the same backbone structure as LTCFs.

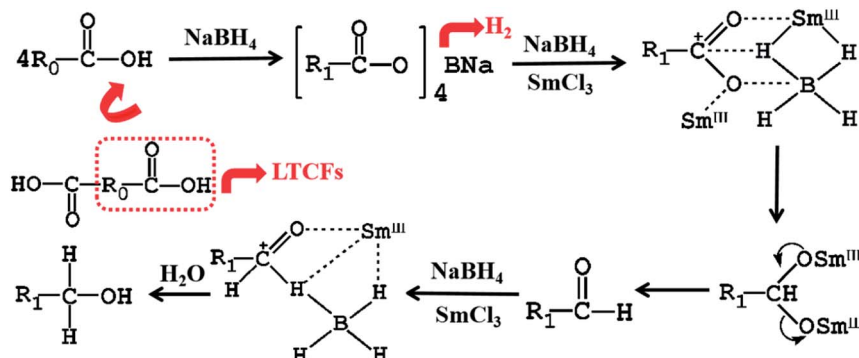
As seen from Fig. 5(a), in the ^1H -NMR spectra of LTCFs the multiple peaks at 3.51–2.86 ppm, the peaks at 1.55 ppm, 4.68 ppm and 7.50–7.70 ppm are assigned to the structures of $-\text{CH}_2\text{CF}_2-$, $-\text{CF}=\text{C}(\text{CF}_3)\text{CH}_2-$, $-(\text{CF}_3)\text{C}=\text{CH}-$ and $-\text{CH}=\text{CF}-$,^{32,33} respectively. Fig. 5(b) shows the disappearance of $-\text{C}=\text{C}-$ peaks at 1.55 ppm, 4.68 ppm and 7.5–7.70 ppm, respectively, indicating that $-\text{C}=\text{C}-$ converted to $-\text{C}-\text{C}-$. In general, single NaBH_4 does not reduce $-\text{C}=\text{C}-$ and it is commonly necessary to add Lewis acids to improve the reduction activity.^{34,35} However, $-\text{C}=\text{C}-$ of LTCFs can be directly reduced by single NaBH_4 ascribed to effect of F atom, which increases the activity of $-\text{C}=\text{C}-$

$\text{C}-$ through the electronic induction effect. Compared with the LTCFs, as seen from Fig. 5(c), LTHFs exhibit new peaks at 3.63 ppm and 3.75 ppm, which are assigned to the structure of $-\text{CH}_2\text{OH}$,³⁰ it clearly confirms the formation of hydroxyl groups.

^{19}F -NMR spectra were used further to characterize. ^{19}F -NMR spectra of (a) LTCFs, (b) reduction product of single NaBH_4 reductant (No. 2) and (c) LTHFs (No. 6) are shown in Fig. 6. The assignments of peaks are listed in Table 3. As seen from Fig. 6(a), a peak at 63.67 ppm is ascribed to $-\text{CF}_2\text{COOH}$. The peaks at -73.71 ppm, 80.66 ppm and 81.30 ppm are ascribed to the fluorine atoms on the structure of $-(\text{CF}_3)\text{C}=\text{CH}-$, $-\text{CH}=\text{CF}-$ and $-\text{CF}=\text{C}(\text{CF}_3)\text{CH}_2-$ for LTCFs^{36–38} respectively. Fig. 6(b) shows that $-\text{C}=\text{C}-$ peaks at -73.71 ppm, 80.66 ppm and 81.30 ppm disappear by reductive transformation using NaBH_4 , this result is similar to Fig. 5(b). Fig. 6(c) clearly shows new peak at -104.9 ppm, which is assigned to $-\text{CF}_2\text{CH}_2\text{OH}$.³⁰ Therefore, the above results of ^{19}F -NMR spectra, ^1H -NMR and FTIR spectra consistent with each other and LTHFs is prepared successfully. ^{19}F -NMR spectra of LTHFs in different reaction times is shown in Fig. 7. It can be seen from Fig. 7 that no byproducts are detected in all times.

3.5 Reduction mechanism

The reported literatures on reduction mechanism of NaBH_4 and Lewis acid has predominantly considered that borane (BH_3) was formed by the reaction of NaBH_4 with Lewis acid initially, and then BH_3 reduced the substrates.^{21,39} To investigate the applicability of this reduction mechanism in our experiment for LTCFs, the sequence of reagent addition is investigated first (Table 4). When NaBH_4 , SmCl_3 and LTCFs are added into the reactor simultaneously, the reduction rate of LTCFs is 33% (No. 1). When SmCl_3 and LTCFs are first added into the reactor under stirring for 1 h, then, NaBH_4 is added and the reduction rate is 48% (No. 2). The above two addition sequence experiments can ensure the reaction of NaBH_4 with SmCl_3 firstly and have low reduction rate indicating the mechanism is not suitable for LTCFs. Nevertheless, when NaBH_4 and LTCFs are first added into the reactor under stirring for 1 h, then SmCl_3 is added (No. 3), the reduction rate increase dramatically to 92%. Hence, according to our experimental results and



Scheme 1 Scheme of reduction mechanism of LTCFs (R_0 is composed of $-\text{CH}_2\text{CF}_2-$, $-\text{CF}_2\text{CF}(\text{CF}_3)-$, $-\text{CFCHCH}(\text{CF}_3)-$, $-\text{CF}_2\text{C}(\text{CF}_3)\text{CHCF}_2-$, and $-\text{CFCH}-$; R_1 is composed of $-\text{CH}_2\text{CF}_2-$ and $-\text{CF}_2\text{CF}(\text{CF}_3)-$).



literatures,^{20,40} the reduction mechanism of LTCFs is proposed, as shown in Scheme 1. Firstly, --C=C-- of LTCFs is directly reduced by NaBH_4 and R_0COOH react with NaBH_4 to form $(\text{R}_1\text{COO})_4\text{BNa}$ and release H_2 . Secondly, the complexation of Sm^{3+} with carbonyl oxygen of LTCFs makes the electrons of carbonyl group move to oxygen and increase the electrophilicity of carbonyl carbon. Electrophilicity of carbonyl carbon is facily attacked by the borohydride anion (BH_4^-) of NaBH_4 .⁴⁰ Thirdly, with the departure of Sm^{3+} and the other oxygen atom, aldehyde group is formed.²⁰ Aldehyde group is then reduced by $\text{NaBH}_4/\text{SmCl}_3$ and the LTCFs is successfully reduced to the final formation of LTHFs. In contrast to carboxyl group, aldehyde group is readily reactive. The generated aldehyde group in the reaction could be immediately reduced by the strong reduction system of $\text{NaBH}_4/\text{SmCl}_3$. Therefore, no byproduct of liquid terminated-aldehyde fluoropolymers is generated.

4. Conclusion

In summary, the combination of affordable and readily available $\text{NaBH}_4/\text{SmCl}_3$ provided a method for the selective reduction of LTCFs in THF/diglyme and the 1/4/2 molar ratio of $\text{R}_0\text{COOH}/\text{NaBH}_4/\text{SmCl}_3$ was suitable for LTCFs reduction at 90 °C. LTCFs were reduced to their corresponding LTHFs in excellent reduction rate (92%). FTIR spectra and NMR spectra analysis showed that --C=C-- and $\text{--CF}_2\text{COOH}$ of LTCFs were effectively reduced to --C-C-- and $\text{--CF}_2\text{CH}_2\text{OH}$. We have proposed the reduction mechanism that Sm^{3+} complex with the carbonyl group increase the electroaffinity of the carbon of carbonyl and make carbon of carbonyl more receptive to the hydride moiety transfer from the borohydride anion. Application of this method to reduction of other carboxylic acid derivatives will be presented in our future work.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

The authors gratefully acknowledge the financial support of National Natural Science Foundation of China (Grant No. 51873026).

References

- P. Ferrandez, Fluoroelastomers, FKM and FEPM, in *Handbook of Specialty Elastomers*, ed. C. K. Robert, Taylor & Francis Group, New York, 2008, pp. 133–154.
- B. Ameduri, Controlled radical (co)polymerization of fluoromonomers, *Macromolecules*, 2010, **43**, 10163–10184.
- B. Ameduri, From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: recent developments and future trends, *Chem. Rev.*, 2009, **109**, 6632–6686.
- B. Ameduri and B. Boutevin, *Well-architected fluoropolymers: synthesis, properties and applications*, Elsevier, Amsterdam, 2004, pp. 187–230.
- B. Ameduri, B. Boutevin and G. Kostov, Fluoroelastomers: synthesis, properties and applications, *Prog. Polym. Sci.*, 2001, **26**, 105–187.
- D. H. Li and M. Y. Liao, Dehydrofluorination mechanism, structure and thermal stability of pure fluoroelastomer (poly(VDF-ter-HFP-ter-TFE) terpolymer) in alkaline environment, *J. Fluorine Chem.*, 2017, **201**, 55–67.
- D. H. Li and M. Y. Liao, Study on the dehydrofluorination of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) copolymer, *Polym. Degrad. Stab.*, 2018, **152**, 116–125.
- J. Li, Y. Lu, Y. Liu, Y. Li, X. Zhang and S. Qi, Synthesis, characterization, curing and properties of carboxyl-terminated liquid fluoropolymers, *Polym.-Plast. Technol. Eng.*, 2014, **53**, 46–53.
- N. Findlay, S. R. Park, F. Schoenebeck, E. Cahard, S. Zhou, L. E. A. Berlouis, M. D. Spicer, T. Tuttle and J. A. Murphy, Reductions of challenging organic substrates by a nickel complex of a noninnocent crown carbene ligand, *J. Am. Chem. Soc.*, 2010, **132**, 15462–15464.
- G. Pelletier, W. S. Bechara and A. B. Charette, Controlled and chemoselective reduction of secondary amides, *J. Am. Chem. Soc.*, 2010, **132**, 12817–12819.
- S. Das, D. Addis, S. Zhou, K. Junge and M. Beller, Zinc-catalyzed reduction of amides: unprecedented selectivity and functional group tolerance, *J. Am. Chem. Soc.*, 2010, **132**, 1770–1771.
- S. Das, K. Möller, K. Junge and M. Beller, Zinc-Catalyzed Chemoselective Reduction of Esters to Alcohols, *Chem.–Eur. J.*, 2011, **17**, 7414–7417.
- J. Collins, U. Rinner, M. Moser, T. Hudlicky, I. Ghiviriga, A. E. Romero, A. Kornienko, D. Ma, C. Griffin and S. Pandey, Chemoenzymatic Synthesis of Amaryllidaceae Constituents and Biological Evaluation of their C-1 Analogues. The Next Generation Synthesis of 7-Deoxypancratistatin and trans-Dihydrolycoricidine, *J. Org. Chem.*, 2010, **75**, 3069–3084.
- S. Chandrasekhar and A. Shrinidhi, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, *Synth. Commun.*, 2014, **44**, 2051–2056.
- C. P. Prasanth, E. Joseph, A. Abhijith, D. S. Nair, I. Ibnusaud, J. Raskatov and B. Singaram, Stabilization of NaBH_4 in Methanol Using a Catalytic Amount of NaOMe. Reduction of Esters and Lactones at Room Temperature without Solvent-Induced Loss of Hydride, *J. Org. Chem.*, 2018, **83**, 1431–1440.
- B. S. Bodnar and P. F. Vogt, An Improved Bouveault-Blanc Ester Reduction with Stabilized Alkali Metals, *J. Org. Chem.*, 2009, **74**, 2598–2600.
- M. S. Ganewatta, W. Ding, M. A. Rahman, L. Yuan, Z. Wang, N. Hamidi, M. L. Robertson and C. Tang, Biobased plastics and elastomers from renewable rosin via “living” ring-opening metathesis polymerization, *Macromolecules*, 2016, **49**, 7155–7164.



- 18 Y. Kamochi and T. Kudo, Novel reduction of carboxylic acids, esters, amides and nitriles using samarium diiodide in the presence of water, *Chem. Lett.*, 1993, **22**, 1495–1498.
- 19 Y. Kamochi and T. Kudo, Lanthanoids in Organic Synthesis. I. The Novel Reduction of Carboxylic Acids with Samarium Diiodide-Base System, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3049–3054.
- 20 M. Szostak, M. Spain and D. Procter, Electron Transfer Reduction of Carboxylic Acids Using $\text{SmI}_2\text{-H}_2\text{O-Et}_3\text{N}$, *J. Org. Lett.*, 2012, **14**, 840–843.
- 21 P. A. S. Bhanu, J. V. Bhaskar and M. Periasamy, Convenient Methods for the Reduction of Amides, Nitriles, Carboxylic Esters, Acids and Hydroboration of Alkenes Using NaBH_4/I_2 System, *Tetrahedron*, 1992, **48**, 4623–4628.
- 22 S. Narasimhan, S. Madhavan and K. G. Prasad, Facile reduction of carboxylic acids to alcohols by zinc borohydride, *J. Org. Chem.*, 1995, **60**, 5314–5315.
- 23 H. J. Zhu and C. U. Pittman Jr, Reductions of Carboxylic Acids and Esters with NaBH_4 in Diglyme at 162 °C, *Synth. Commun.*, 2003, **33**, 1733–1750.
- 24 T. Hida, S. Mitsumori, T. Honma, Y. Hiramatsu, H. Hashizume, T. Okada, M. Kakinuma, K. Kawata, K. Oda, A. Hasegawa, T. Masui and H. Nogusa, Practical Diastereoselective Synthesis and Scale-up Study of (+)-2-((1R, 2R, 3R, 5S)-2-Amino-6, 6-dimethylbicyclo [3. 1. 1] hept-3-yl) ethanol: A Key Intermediate of the Novel Prostaglandin D2 Receptor Antagonist S-5751, *Org. Process Res. Dev.*, 2009, **13**, 1413–1418.
- 25 M. Ashot, T. Rafael, G. Sahak, A. Marina, P. Henry, M. Vahan and S. Raymond, Synthesis of 6-imino-5-tetrahydro-1H-2-pyrrolylidenhexahydro-2, 4-pyrimidinediones as intermediates for the synthesis of C-azanucleosides, *Tetrahedron Lett.*, 2010, **51**, 231–233.
- 26 S. C. Qi, J. Li, Y. F. Lu, X. A. Zhang, J. D. Wang, Y. P. Li, Y. Li, S. L. Jiang and R. P. Yuan, CN103193919B, 2013.
- 27 E. Murad and D. I. Hildenbrand, Dissociation energies of GdO , HoO , ErO , TmO , and LuO ; correlation of results for the lanthanide monoxide series, *J. Chem. Phys.*, 1980, **73**, 4005–4011.
- 28 W. A. Herrmann, R. Anwender and W. Seherer, Lanthanoiden-Komplexe, V [1]. Strukturchemie ein- und zweikerniger Seltenerdalkoxide, *Chem. Ber.*, 1993, **126**, 1533–1539.
- 29 S. Kobayashi, M. Moriwaki and I. Hachiya, The catalytic Fries rearrangement of acyloxy naphthalenes using scandium trifluoromethanesulfonate as a catalyst, *Chem. Commun.*, 1995, **15**, 1527–1528.
- 30 M. Pianca, E. Barchiesi, G. Esposto and S. Radice, End groups in fluoropolymers, *J. Fluorine Chem.*, 1999, **95**, 71–84.
- 31 L. R. Saint, A. Manseri, B. Ameduri, B. Lebreton and P. Vignane, Synthesis and properties of novel fluorotelechelic macrodiols containing vinylidene fluoride, hexafluoropropene and chlorotrifluoroethylene, *Macromol.*, 2002, **35**, 1524–1536.
- 32 G. J. Ross, J. F. Watts, M. P. Hill and P. Morrissey, Surface modification of poly (vinylidene fluoride) by alkaline treatment. The degradation mechanism, *Polym.*, 2000, **41**, 1685–1696.
- 33 S. R. Gondi, A. P. Vogt and B. S. Sumerlin, Versatile pathway to functional telechelics via RAFT polymerization and click chemistry, *Macromol.*, 2007, **40**, 474–481.
- 34 B. C. Ranu and S. Samanta, Remarkably Selective Reduction of the α , β -Carbon-Carbon Double Bond in Highly Activated α , β , γ , δ -Unsaturated Alkenes by the $\text{InCl}_3\text{-NaBH}_4$ Reagent System, *J. Org. Chem.*, 2003, **68**, 7130–7132.
- 35 J. M. Khurana and P. B. Sharma, Chemoselective reduction of α , β -unsaturated aldehydes, ketones, carboxylic acids, and esters with nickel boride in methanol-water, *Chem. Soc. Jpn.*, 2004, **77**, 549–552.
- 36 P. Wormald, B. Ameduri, R. K. Harris and P. Hazendonk, High-resolution ^{19}F and ^1H NMR of a vinylidenefluoride telomer, *Polymer*, 2008, **49**, 3629–3638.
- 37 R. Souzy, B. Ameduri, S. V. Ahsen, H. Willner and G. A. Argu ello, Use of bis (trifluoromethyl) peroxy dicarbonate as initiator in the radical homopolymerisation of vinylidene fluoride (VDF) and copolymerisation of VDF with hexafluoropropylene, *J. Fluorine Chem.*, 2003, **123**, 85–93.
- 38 E. M. James, *Polymer Data Handbook*, New York, Oxford University Press, 1999.
- 39 J. Z. Saavedra, A. Resendez, A. Rovira, S. Eagon, D. Haddenham and B. Singaram, Reaction of InCl_3 with various reducing agents: $\text{InCl}_3\text{-NaBH}_4$ -mediated reduction of aromatic and aliphatic nitriles to primary amines, *J. Org. Chem.*, 2012, **77**, 221–228.
- 40 H. C. Brown, S. Narasimhan and Y. M. Choi, Selective Reductions. 30. Effect of Cation and Solvent on the Reactivity of Saline Borohydrides for Reduction of Carboxylic Esters. Improved Procedures for the Conversion of Esters to Alcohols by Metal Borohydrides, *J. Org. Chem.*, 1982, **47**, 4702–4708.

