Reduction of liquid terminated-carboxyl fluoroelastomers using NaBH₄/SmCl₃

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 (NaBH₄/SmCl₃) 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, ¹⁹F-NMR and chemical titration. The results showed that –C═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, SmCl₃ with a high coordination number could increase the reduction activity of NaBH₄ 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 due to their inherent resistance to fuel, oil, high temperature and oxidation. The stabilized carbon–fluorine single bond (C–F 485 kJ mol⁻¹) and the shielded effect of fluorine atoms on the main chain 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 LTCFs. 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, 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. Because in contrast to ketones, aldehydes and esters, which easily engage in reactions with reductive agents, carboxylic acids are generally unreactive. On the other hand, although lithium aluminium hydride was widely used as a strong reductant in carboxyl reduction, its poor chemical selectivity, flammability and explosive nature are unfavorable for large-scale production.
and the NaBH₄/SmCl₃ 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 NaBH₄/SmCl₃.

2. Experimental section

2.1 Chemicals

Vinylidene fluoride-hexafluoropropylene copolymer (VDF-HFP) with VDF/HFP = 3/1 and Mn = 78 000 was purchased from Chenguang Research Institute of Chemical Industry (China). Hydrogen peroxide (H₂O₂), potassium biphasthalate (C₈H₅KO₄), phenolphthalein, bromothymol blue, potassium hydroxide (KOH), acetone and benzyltriethylammonium chloride (BTEAC) were purchased from Alfa Aesar (China). NaBH₄, AlCl₃, CoCl₂, ZnCl₂, CaCl₂ and SmCl₃ 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 LTCFs

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% H₂O₂ aqueous solution (60 g), 45 wt% KOH aqueous solution (43 g) were added subsequently. 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 NaBH₄ was dissolved into the solution under stirring for 1 h at 0 °C. Subsequently, 1.506 g SmCl₃ 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 ¹⁹F) at room temperature, using acetone-d₆ as the solvent and TMS as internal standard the references for ¹H (or ¹⁹F) nuclei. Chemical shifts are reported in ppm.
COOH% = \frac{V \times C \times 45.02}{m} \times 100\% \quad (2)

\[ V: \text{volume of KOH/C}_2\text{H}_5\text{OH solution consumed by the LTCFs and bromothymol blue solution (mL)}, \ C: \text{the concentration of KOH/C}_2\text{H}_5\text{OH standard titration solution (mol L}^{-1}) , \ m: \text{weight of LTCFs (g).} \]

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 \( \omega_0 \): LTCFs content of carboxyl, \( \omega_1 \): 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 reductive 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 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 NaBH\textsubscript{4}/SmCl\textsubscript{3} 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 NaBH\textsubscript{4}/SmCl\textsubscript{3} 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 NaBH\textsubscript{4} and only 12% reduction rate is obtained at the absence of SmCl\textsubscript{3}, which indicates that SmCl\textsubscript{3} has no reducibility to LTCFs and NaBH\textsubscript{4} 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 NaBH\textsubscript{4}/SmCl\textsubscript{3} dosage and the optimal molar ratio of R\textsubscript{0}COOH/NaBH\textsubscript{4}/SmCl\textsubscript{3} is 1/4/2 (No. 3–6). When molar ratio of R\textsubscript{0}COOH/NaBH\textsubscript{4}/SmCl\textsubscript{3} further increases to 1/5/2.5, the reduction rate is decreasing due to the coating of the NaBH\textsubscript{4} particles with the excess SmCl\textsubscript{3}, which likely impedes the efficient solubility of NaBH\textsubscript{4} (No. 7). Furthermore, as shown in Fig. 3, the SmCl\textsubscript{3} addition amount is investigated. When the molar ratio of NaBH\textsubscript{4}/SmCl\textsubscript{3} changes from 4/0 to 4/2, the reductive rate of LTCFs increases with increasing amount of SmCl\textsubscript{3}. Nevertheless, when the molar ratio is 4/3, the excess SmCl\textsubscript{3} make the reductive rate decrease because the coating of the NaBH\textsubscript{4} particles with the excess SmCl\textsubscript{3}.

| No. | R\textsubscript{0}COOH | NaBH\textsubscript{4} | SmCl\textsubscript{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 NaBH\textsubscript{4}/MCl\textsubscript{x} and NaBH\textsubscript{4}/SmCl\textsubscript{3}.

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

Fig. 3 The effect of amount of SmCl\textsubscript{3} on the reductive rate of LTHFs.

Fig. 4 FTIR spectra of (a) LTCFs, (b) reduction product of single NaBH\textsubscript{4} (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 NaBH₄/SmCl₃ 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 of solubility of NaBH₄ in THF. To improve the solubility of NaBH₄ in THF, varying amounts of diglyme, a known excellent solvent for NaBH₄, are added. After some optimizations, the 1/1 volume ratio of THF/diglyme mixed solvent is adequate to solubilize NaBH₄ (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 NaBH₄ and the excessive use will affect the complexation of NaBH₄/SmCl₃ with carbonyl 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 RₓCOOH/NaBH₄/SmCl₃ 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 (MCl₃) are also evaluated. Through the optimization studies, the optimal reaction conditions of NaBH₄/MCl₃ are consistent with NaBH₄/SmCl₃. As shown in Table 2, only NaBH₄/SmCl₃ 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 −CF₂COOH, −C==C−, −FCH₂−, −CF₂−, and −CF₃, respectively. Fig. 4(b) shows the FTIR spectra of reduction product by single NaBH₄. Comparing the Fig. 4(b) with Fig. 4(a), the absorption peak of −C==C− at 1686 cm⁻¹ is weakened and the absorption peak of −CF₂COOH is reduced significantly but only little −CF₃COOH is reduced via single NaBH₄ without SmCl₃. Fig. 4(c) shows the FTIR spectra of LTHFs reduced by NaBH₄/SmCl₃. From Fig. 4(c) can be seen that the absorption peaks of −C==C− and −CF₂COOH are weakened ascribed to effective reduction of NaBH₄/SmCl₃. LTHFs exhibits absorption peaks at 1398, 1183

![Fig. 6 19F-NMR spectra of (a) LTCFs, (b) reduction product of single NaBH₄ reductant (No. 2) and (c) LTHFs (No. 6).](image_url)

![Table 3 Assignments of 19F-NMR peaks in liquid fluoroelastomers](table_data)

| No | δ (ppm) | Assignment                      | No | δ (ppm) | Assignment                      |
|----|--------|---------------------------------|----|--------|---------------------------------|
| 1  | -63.46 | -CF₂CF₂COOH                     | 11 | -108.96| -CF₂(CF₃)CH₂CF₂CF₂(CF₃)CF₂−   |
| 2  | -70.67 | -CH₂CF₂CF(CF₃)CF₂CH₂−           | 12 | -110.51| -CF₂CH₂CF₂CF₂(CF₃)CF₂−        |
| 3  | -73.71 | -CF₂CH==C(CF₃)CF₂−              | 13 | -112.33| -CF₂(CF₃)CH₂CF₂(CF₃)CH₂−      |
| 4  | -75.19 | -CF₂CH₂CF(CF₃)CF₂CF₂−           | 14 | -113.95| -CF₂CH₂CF₂CF₂CH₂−             |
| 5  | -80.66 | -CH==CFCF(CF₃)−                 | 15 | -116.24| -CH₂CH₂CF₂CF₂CF₂(CF₃)−        |
| 6  | -81.30 | -CF==CF(CF₃)CF₂−                | 16 | -118.72| -CH₂CF₂CF₂CF₂(CF₃)CH₂−        |
| 7  | -91.62 | -CF₂CH₂CF₂CF₂CF₂CF₂−            | 17 | -181.74| -CF₂CF₂CF(CF₃)CF₂CH₂−         |
| 8  | -93.56 | -CF₂CH₂CF₂CF(CF₃)CF₂−           | 18 | -184.33| -CF₂CF₂CF(CF₃)CF₂CF₂−         |
| 9  | -95.64 | -CH₂CH₂CF₂CF₂CF₂−               | 19 | -104.90| -CF₂CH₂OH                      |
| 10 | -103.62| -CF₂CH₂CF₂CF(CF₃)CF₂−           |   |        |                                 |
NaBH₄ and Lewis acid has predominantly considered that borane (BH₃) was formed by the reaction of NaBH₄ with Lewis acid initially, and then BH₃ reduced the substrates.²⁸,²⁹ To investigate the applicability of this reduction mechanism in our experiment for LTCFs, the sequence of reagent addition is investigated (Table 4). When NaBH₄, SmCl₃ and LTCFs are added into the reactor simultaneously, the reduction rate of LTCFs is 33% (No. 1). When SmCl₃ and LTCFs are first added into the reactor under stirring for 1 h, then NaBH₄ is added and the reduction rate is 48% (No. 2). The above two addition sequence experiments can ensure the reaction of NaBH₄ with SmCl₃ first and have low reduction rate indicating the mechanism is not suitable for LTCFs. Nevertheless, when NaBH₄ and LTCFs are first added into the reactor under stirring for 1 h, then SmCl₃ is added (No. 3), the reduction rate increase dramatically to 92%. Hence, according to our experimental results and 

Table 4  Effect of charging sequence on the reduction of LTCFs

| No. | Step 1a | Step 2b | Reductive rate (%) |
|-----|---------|---------|-------------------|
| 1   | NaBH₄, SmCl₃, LTCFs | —       | 33                |
| 2   | SmCl₃, LTCFs       | NaBH₄   | 48                |
| 3   | NaBH₄, LTCFs       | SmCl₃   | 92                |

*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 –FCH₂–, –CF₂–, and –CF₃, 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 –CH₂–CF₂–, –CF=CF(CF₃)CH₂–, –(CF₃)C=CH– and –CF=CF(CF₃)CH₂– for LTCFs, respectively. Fig. 5(b) shows the disappearance of –C=–C– peaks at 1.55 ppm, 4.68 ppm and 7.5–7.70 ppm, respectively, indicating that –C=–C– converted to –C=C–. In general, single NaBH₄ does not reduce –C=–C– and it is commonly necessary to add Lewis acids to improve the reduction activity.²⁴,²⁵ However, –C=C– of LTCFs can be directly reduced by single NaBH₄ ascribed to effect of F atom, which increases the activity of –C=–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 –CH₂OH,³⁰ it clearly confirms the formation of hydroxyl groups.

¹⁹F-NMR spectra were used further to characterize. ¹⁹F-NMR spectra of (a) LTCFs, (b) reduction product of single NaBH₄ 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 –CF=C(CF₃)CH₂–. The peaks at –73.71 ppm, 80.66 ppm and 81.30 ppm are ascribed to the fluorine atoms on the structure of –(CF₃)C=CH–, –CH=CF– and –CF=C(CF₃)CH₂– for LTCFs, respectively. Fig. 6(b) shows that –C=–C– peaks at –73.71 ppm, 80.66 ppm and 81.30 ppm disappear by reductive transformation using NaBH₄, this result is similar to Fig. 5(b). Fig. 6(c) clearly shows new peak at –104.9 ppm, which is assigned to –CF₂CH₂OH.³⁰ Therefore, the above results of ¹⁹F-NMR spectra, ¹H-NMR and FTIR spectra consistent with each other and LTHFs is prepared successfully. ¹⁹F-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 NaBH₄ and Lewis acid has predominantly considered that borane (BH₃) was formed by the reaction of NaBH₄ with Lewis acid initially, and then BH₃ reduced the substrates.²¹,²⁹ To investigate the applicability of this reduction mechanism in our experiment for LTCFs, the sequence of reagent addition is investigated first (Table 4). When NaBH₄, SmCl₃ and LTCFs are added into the reactor simultaneously, the reduction rate of LTCFs is 33% (No. 1). When SmCl₃ and LTCFs are first added into the reactor under stirring for 1 h, then NaBH₄ is added and the reduction rate is 48% (No. 2). The above two addition sequence experiments can ensure the reaction of NaBH₄ with SmCl₃ first and have low reduction rate indicating the mechanism is not suitable for LTCFs. Nevertheless, when NaBH₄ and LTCFs are first added into the reactor under stirring for 1 h, then SmCl₃ 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 (R₁ is composed of –CH₂–CF₂–, –CF₂CF(CF₃)–, –CFCH=CH(CF₃)–, –CF₂C(CF₃)CHCF₂–, and –CFCH; R₂ is composed of –CH₂–CF₂– and –CF₂CF(CF₃)–).
4. Conclusion

In summary, the combination of affordable and readily available NaBH₄/SmCl₃ provided a method for the selective reduction of LTCFs in THF/diglyme and the 1/4/2 molar ratio of R₄COOH/NaBH₄/SmCl₃ 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 –CF₂COOH of LTCFs were effectively reduced to –C–C– and –CF₂CH₂OH. We have proposed the reduction mechanism that Sm³⁺ 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.

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