# Examples of Catalytic and Selective Routes for Fluorinated Building Blocks

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**ABSTRACT:** Examples are presented for the catalytic fluorination of chlorinated starting materials in order to produce building blocks or HFCs. The fluorination of  $CF_3CH_2Cl$ , of  $CCl_2=CCl_2$ , of trichloromethoxylbenzenes and trichloromethoxybenzene involving nucleophilic substitution are reported. In all cases, HF was the fluorinating agent. Depending on the chlorinated substrate and the degree of fluorination required, liquid- or gas-phase processes were involved. Usually, catalysts were  $SbCl_5$  in liquid phase and chromium oxide in gas phase. In the presence of  $SbCl_5$ , at 90 °C under an initial pressure of 10 bar, the fluorination of  $CCl_2=CCl_2$  leads mainly to the formation of  $CClF_2CHCl_2$ , and the active catalyst is an antimony mixed halide ( $SbCl_3F_2$ ). In the same way, the presence of  $SbCl_5$  favored the formation of 1-trifluoromethyl-3-trichloromethylbenzene from bis-1,3-trichloromethylbenzene at low temperature (50 °C) and in the presence of a low amount of HF. Moreover, trichloromethoxybenzene was totally transformed into trifluoromethoxybenzene. At 380 °C and at atmospheric pressure, the transformation of  $CF_3CH_2Cl$  into  $CF_3CH_2F$  was favored over chromium oxide-based catalyst modified by zinc (corresponding to a (Zn/Zn + Cr) molar ratio of 0.22).

### 1. INTRODUCTION

The manufacture of some hydrofluorocarbons and fluorinated aromatic rings involves fluorination processes entailing multistage gas-phase and/or liquid-phase reactions in the presence of chlorinated reactants, a catalyst, and anhydrous hydrofluoric acid (HF) as the fluorinating agent. The liquid phase reactions are usually performed at lower temperatures (<150 °C) rather than in the gas phase (up to 380 °C). Liquid-phase processes are often more economical in terms of energy consumption and investment and they can show better selectivities towards making specific HFCs. However, the degree of fluorination achieved in the liquid phase is usually lower. At the industrial level, the strategic choice of a route will depend on the access to raw materials, the complexity of the process (number of steps, difficulty of the operation), and especially the performance of the chemistry (conversion and selectivity, life of the catalyst, quality of the final product, and technological difficulty (corrosion, etc.)).

Depending on the applications, catalysts used for the substitution of fluorine for chlorine can be Lewis acids  $(SbCl_5)$ , metal oxides  $(Cr_2O_3)$ , or metal fluorides  $(MgF_2, BaF_2)$ . Our objective was to achieve highly selective catalytic reactions using hydrogen fluoride and varying the catalyst. As such conditions require extremes of pressure and temperature, the development of a good process is important for also safety, cost, and environmental reasons. This manuscript will describe our work, with various examples, in optimizing several fluorination reactions useful for commercial use and viable for large-scale manufacture by catalytic processes.

### 2. RESULTS AND DISCUSSION

**2.1. Fluorination of Chlorinated Hydrocarbons.** Different synthetic routes for  $CF_3CH_2F$ , a refrigeration agent, involve either the addition of HF, a chlorine–fluorine exchange, or

hydrogenolysis.<sup>1,2</sup> Two main industrial routes have been developed: one from perchloroethylene (three reaction steps) and the other one from trichloroethylene (two reaction steps). Both pathways involve multistage fluorination processes including gas and/or liquid phases in the presence of HF.

In order to optimize the different steps, the research focused on the identification of:

- the reactions, the mechanisms involved, and the catalytic sites in order to improve the activity of catalysts used or the development of new catalysts;
- (2) different sources of deactivation of the catalyst materials.

Perfluoroethylene can be used as a starting material for fluorinated compounds for various applications (HCFs and building blocks).<sup>2,3</sup> The fluorination of  $CCl_2 = CCl_2$ , which is an unreactive molecule, involves the addition of HF and successive Cl/F exchanges (Scheme 1).<sup>4</sup> The main catalytic system used was composed of SbCl<sub>5</sub> as the Lewis acid and HF as the fluorinating agent. At 90  $^\circ C$  and under 10 bar as initial pressure, two main families of products were observed: fluorinated products (CHCl2-CCl2F corresponding to the addition of HF on the double bond and CHCl2-CClF2 corresponding to Cl/F exchange) and chlorinated products resulting in the addition of HCl or Cl<sub>2</sub> to the double bond. HCl was produced during Cl/F exchanges and Cl<sub>2</sub> during the reduction of Sb<sup>V</sup> into Sb<sup>III</sup>. To identify the active species for the fluorination of perfluoroethylene under our operating conditions, performances of various commercial antimony mixed halides SbFCl<sub>4</sub>, SbCl<sub>3</sub>F<sub>2</sub>, SbCl<sub>2</sub>F<sub>3</sub>, and SbClF<sub>4</sub> were measured for the transformation of the perfluoroethylene. The perform-

Special Issue: Fluorine Chemistry 14

Received: June 6, 2014

Scheme 1. Transformation of perchloroethylene in the presence of HF-SbCl<sub>5</sub> catalytic system ( $T = 90^{\circ}$ C,  $P_{N2} = 10$  bar)



ances of these antimony mixed halides was compared in Table 1 to the in situ SbCl<sub>5</sub> preprepared with HF and to SbCl<sub>5</sub>

Table 1. Transformation of  $CCl_2 = CCl_2$  in the presence of various mixed halides; comparison of the conversion and the selectivities and the formation of Sb<sup>III</sup> ( $T = 90^{\circ}C$ ,  $P_{N2} = 10$  bar)

catalyst	conversion (%)	$\begin{array}{c} CHCl_2-\\ CClF_2\\ (\%) \end{array}$	$\begin{array}{c} CHCl_2-\\ CCl_2F\\ (\%) \end{array}$	chlorinated products (%)	Sb <sup>III</sup> (%)
SbCl <sub>5</sub>	47	46	38	16	71
SbCl <sub>5</sub> prefluorinated	57	57	31	12	57
SbCl <sub>4</sub> F	58	54	33	13	72
SbCl <sub>3</sub> F <sub>2</sub>	52	53	37	10	64
SbCl <sub>2</sub> F <sub>3</sub>	68	70	22	8	69
SbClF <sub>4</sub>	70	66	26	8	40

without prefluorination. First, the prefluorination of SbCl<sub>5</sub> increases the total conversion and the selectivity towards CF<sub>2</sub>ClCHCl. Similar conversion and selectivities are obtained with prefluorinated SbCl<sub>5</sub>, SbCl<sub>3</sub>F<sub>2</sub>, and SbCl<sub>4</sub>F. The great conversion and selectivity towards fluorination can be observed with the antimony mixed halides which contain a high degree of fluorination, SbCl<sub>2</sub>F<sub>3</sub> and SbClF<sub>4</sub>. In every case, a significant reduction of Sb<sup>V</sup> into Sb<sup>III</sup> occurs. This reduction corresponds to a loss of catalyst activity since Sb<sup>III</sup> is inactive. It could result from a loss of chlorine from the antimony-active species. The addition of HF to CCl<sub>2</sub>=CCl<sub>2</sub>, which involves an electrophilic or a nucleophilic mechanism, does not seem to reduce Sb<sup>V</sup> (Scheme 2). The catalyst would be regenerated after the

# Scheme 2. Change of the catalyst during the reaction of addition of HF on $CCl_2 = CCl_2$

$$SbCl_5 + HF \longrightarrow SbCl_xF_{5-x} \longrightarrow SbCl_xF_{6-x}, HF \longrightarrow SbCl_xF_{6-x}$$

 $CCl_2=CCl_2+SbCl_xF_{6-x},H^+ \underbrace{CCl_2FCCl_2}_{CHCl_2CCl_2} CFCl_2CHCl_2+SbCl_xF_{5-x}$ 

addition of HF, without having suffered any reduction. We suggest that the reduction of  $Sb^V$  could occur during Cl/F exchanges as described in the cycle reported in Scheme 3. This catalytic cycle explains the formation of  $Cl_2$  from antimony mixed halides. The addition of  $Cl_2$  to  $CCl_2$ =CCl<sub>2</sub> favors the  $Sb^V$  reduction. It would be difficult to obtain a good fluorinating activity and a good selectivity towards fluorination without a reduction of  $Sb^V$ .

Scheme 3. Catalytic cycle of the reduction of Sb<sup>V</sup> into Sb<sup>III</sup> during the transformation of the perchloroethylene



The fluorination of CF<sub>3</sub>CH<sub>2</sub>Cl into CF<sub>3</sub>CH<sub>2</sub>F is also studied. This fluorination is particularly difficult due to the presence of the CF<sub>3</sub> group and requires more drastic conditions, (380 °C and atmospheric pressure), HF in excess, and chromium oxidebased catalyst supported over fluorinated alumina.<sup>5-7</sup> Under these operating conditions, the fluorination reaction is the main reaction (eq 1). However, a dehydrofluorination reaction also occurs which leads to the formation of  $CF_2$ =CHCl, the main byproduct from the  $CF_3CH_2Cl$  transformation (eq 2). The Deacon reaction is also observed (eq 3). Indeed, the presence of dioxygen which prevents the catalyst deactivation leads to Cl<sub>2</sub> formation by reaction with hydrogen chloride liberated during the fluorination of CF<sub>3</sub>CH<sub>2</sub>Cl into CF<sub>3</sub>CH<sub>2</sub>F.<sup>8,9</sup> The presence of oxygen is also necessary to refresh the surface of the catalyst in order to keep fluorine labile and avoid irreversible solid fluorination.<sup>5</sup> As reported in Figure 1, the presence of zinc



**Figure 1.** Activity of  $Zn-Cr/AlF_3$  catalytic systems for the transformation of  $CF_3CH_2Cl$ , Deacon and dehydrofluorination reactions versus the Zn/(Zn+Cr) ratio (T = 380 °C,  $HF/CF_3CH_2Cl = 4$ ).

in a small amount corresponding to a Zn/Zn+Cr ratio of 0.22 promoted the fluorination reaction and decreased the secondary reactions. In this case, the selectivity towards fluorination calculated as the ratio between the activity for the fluorination reaction and the global activity is multiplied by 2 (Table 2). This is due on one hand to the modification of the strength of Lewis acidity of the chromium atoms (the active

Table 2. Selectivity towards fluorination versus Zn/(Zn+Cr) ratio ( $T = 380^{\circ}C$ , HF/CF<sub>3</sub>CH<sub>2</sub>Cl = 4)

Zn/(Zn + Cr) atom	1	0.50	0.22	0
fluorination selectivity	-	0.20	0.59	0.26

site) and on the other hand to an increase of metal dispersion on the surface of the support.  $^{10,11}\,$ 

Main reaction:

$$CF_3CH_2C1 + HF \rightleftharpoons CF_3CH_2F + HC1$$
 Fluorination (1)

Secondary reactions:

$$CF_3CH_2C1 \rightleftharpoons CF_2 = CHC1 + HF$$
 Dehydrofluorination
(2)

$$O_2 + 4HC1 \rightleftharpoons 2Cl_2 + 2H_2O$$
 Deacon reaction (3)

**2.2. Fluorination of Chlorinated Aromatics.** Fluorination of a model compound, trichloroanisole, was studied in order to determine the general conditions suitable for the selective synthesis of aromatic compounds with an  $-OCF_3$  group (Scheme 4). The reaction is very fast: only 1 h is required to obtain a total conversion of the substrate. However, the presence of a Lewis acid with an oxidation state of V (SbCl<sub>5</sub>) is needed to activate the last Cl/F exchange corresponding to the formation of trifluoromethoxybenzene (Table 3). Indeed, after 1 h at 50 °C in the presence of the SbCl<sub>5</sub>-HF system with a stoichiometric HF amount, the trifluoromethoxybenzene was prepared with a selectivity of 100%.<sup>12</sup>

Furthermore, Cl/F exchanges can be controlled by the presence of a solvent. For example, dioxane in combination with HF leads to systems for the selective monofluorination of trichloroanisole. This system is comparable to that of the common fluorinating agent:<sup>13</sup> HF-pyridine system without the disadvantages of the latter, i.e. excessive corrosion of industrial equipment. Other base-HF associations are also known, and we have also shown that this could be extended to other substrates such as chlorinated trichloromethylbenzenes. In fact, it is possible to selectively prepare the products of mono-, di-, or trifluorination.<sup>14,15</sup>

Alternatively, the fluorination of bis-1,3-trichloromethylbenzene ( $PF_{00}$ ) is much more complex. The desired product is 1,3trichloro-trifluoromethylbenzene ( $PF_{30}$ ), a useful building block<sup>16</sup> (Scheme 5). It has the advantage of possessing the CF<sub>3</sub> moeity while retaining a highly reactive  $-CCl_3$  group.

The conversion to  $PF_{30}$  strongly depends on the operating conditions.<sup>17</sup> In the presence of HF alone, the fluorination is carried out systematically on both trichloromethyl groups, obtaining  $PF_{11}$ ,  $PF_{21}$ , and  $PF_{22}$  (Figure 2). A slight excess of HF (8 equiv) allows obtaining products of greater degrees of fluorination ( $PF_{32}$  and  $PF_{22}$ ). Adding SbCl<sub>5</sub> in small amounts (2 mol %) at 50 °C, fluorination of  $PF_{00}$  is very fast (within 1 h) and complete to form  $PF_{33}$ . The formation of the desired product  $PF_{30}$  with good selectivity is obtained with 2 equiv of HF at 150 °C (Figure 2) or in the presence of SbCl<sub>5</sub> (Figure 3) at 50 °C.

Table 3. Transformation of trichloromethoxybenzene ( $P_i = 10$  bar,  $T = 50^{\circ}$ C, time = 1 h, 0.125 mol, HF = 0.5 mol): Effect of the amount of SbCl<sub>5</sub>

SbCl <sub>5</sub> (mmol)	Conversion <sup>a</sup> (TCMB) (mol %)	$CDFMB^b$ (mol %)	$\begin{array}{c} \text{TFMB}^c\\ (\text{mol }\%) \end{array}$
0	100	98	2
0.196	100	49	51
0.393	100	7	93
0.589	100	9	91
0.786	100	0	100
2.5	100	0	100

<sup>*a*</sup>Conversion: Amount of trichloromethoxybenzene transformed. <sup>*b*</sup>CDFMB: (chlorodifluoromethoxy)benzene. <sup>*c*</sup>TFMB: trifluoromethoxybenzene.

All catalysts with an oxidation state of +V (SbCl<sub>5</sub>, SbF<sub>3</sub>Cl<sub>2</sub>, SbF<sub>5</sub>, TaCl<sub>5</sub>, and NbCl<sub>5</sub>) were able to effect Cl/F exchanges as well to achieve selectively to form PF<sub>30</sub>. However, the most efficient catalyst at lower temperature remains SbCl<sub>5</sub>. As mentioned above, this activity was linked to their strong Lewis acidity and their ability to form complexes to obtain good nucleophilic systems. At moderate temperatures, the preferential formation of PF10, PF11, PF21, and PF22 corresponds to the formation of the most stable intermediate carbocations. The kinetics therefore governs the formation of these fluorochemicals. In contrast, at higher temperature, a redistribution of fluorine or chlorine can take place, resulting in scrambling of the fluorine/chlorine distribution. Low energy values of enthalpies of formation calculated for PF<sub>ii</sub> confirm these results. This redistribution leads to the formation of  $PF_{20}$ ,  $PF_{30}$ , and PF<sub>31</sub>.

## 3. CONCLUSION

Whatever the chlorinated starting substrates, it can be possible to determine the best operating conditions and catalyst in order to prepare selectively the fluorinated product desired.

At 90 °C under an initial pressure of 10 bar, the fluorination of  $CCl_2 = CCl_2$  leads mainly to the formation of  $CClF_2CHCl_2$ , and the active catalyst was an antimony mixed halide  $(SbCl_3F_2)$ . The addition of HF on the double bond and Cl/F exchanges were involved. However, a reduction of Sb<sup>V</sup> into Sb<sup>III</sup> was observed during Cl/F exchanges which decreased the selectivity towards fluorination. Trifluoromethoxybenzene could be produced from trichloromethoxybenzene in the presence of HF in equimolar amount and SbCl<sub>5</sub> which activated the last Cl/ F exchange. In the same way, 1-trifluoromethyl-3-trichloromethylbenzene could be prepared from bis-1,3-trichloromethylbenzene at low temperature (50 °C) in the presence of a low amount of HF and SbCl<sub>5</sub>. The presence of a catalyst such as SbCl<sub>5</sub> reduced the temperature to obtain 1-trifluoromethyl-3trichloromethylbenzene and offers new opportunity for the fluorination of more complex and sensitive chlorinated substrates.

The modification of the strength of the Lewis acidity of the active sites by the presence of zinc with a (Zn/Zn+Cr) molar





Scheme 5. Transformation of bis-1,3-trichloromethylbenzene  $(PF_{00})$ 





**Figure 2.** Transformation of the bis-1,3-trichloromethylbenzene. Effect of the temperature on the formation of the various fluorinated intermediates  $PF_{ij}$  in the presence of HF alone. ( $T = 50-200 \text{ }^{\circ}\text{C}$ ,  $PF_{00} = 0.125 \text{ mol}$ , HF = 0.25 mol, HF/PF<sub>00</sub> = 2/1).



**Figure 3.** Transformation of bis-1,3-trichloromethylbenzene. Effect of the temperature on the formation of the various fluorinated intermediates  $PF_{ij}$  in the presence of SbCl<sub>5</sub>. (T = 50-200 °C,  $PF_{00} = 0.125$  mol, HF = 0.25,  $SbCl_5 = 1.25$  mmol,  $HF/SbCl_5/PF_{00} = 2/0.01/1$ ).

ratio of 0.22 favored the fluorination of  $CF_3CH_2Cl$  to produce  $CF_3CH_2F$ .

# 4. EXPERIMENTAL SECTION

All the experiments in liquid phase (transformation of the perchloroethylene, of the bis-1,3-trichloromethylbenzene, and

of the trichloromethylbenzene) were carried out in a 100 mL Teflon autoclave in liquid HF under an initial pressure of 10 bar.

The transformation of the perchloroethylene (PCE) was performed at 90 °C.4 The catalyst was prepared, prior to reacting PCE with HF. For this, SbCl<sub>5</sub> (0.027 mol) was reacted with HF. After 1 h, the autoclave was cooled down and vented with dry dinitrogen in order to eliminate the HCl and the HF in excess. Perchloroethylene (0.25 mol) and HF (1.3 mol) were then added. The reaction was carried out for 4 h at 90 °C under 10 bar of dinitrogen. The contents were quenched with 20 mL 6 M H<sub>2</sub>SO<sub>4</sub>. The organic phase was dried and analyzed by temperature-programmed GC with a BP1 column from 40 to 150 °C. The products were identified by GC-MS. Since the reaction was accompanied by a partial reduction of Sb<sup>V</sup> into Sb<sup>III</sup>, the amounts of these two species were determined by titration of the aqueous phase. Both Sb species were measured by atomic adsorption. The amount of Sb<sup>III</sup> was determined by oxidation with a KMnO<sub>4</sub> solution. In another series of experiments, the catalyst SbCl<sub>5</sub> or antimony mixed halides, HF (1.35 mol) and perchloroethylene (0.25 mol) were added sequentially, and the mixture was heated at 90 °C. The reaction was carried out as mentioned above. The different antimony mixed halides SbFCl<sub>4</sub>, SbCl<sub>3</sub>F<sub>2</sub>, SbCl<sub>2</sub>F<sub>3</sub>, and SbClF<sub>4</sub> were purchased at the Ozarvi-Mahoning, an Elf Atochem North America, Subsidiary, with a purity of 99.5%.

The transformation of the bis-1,3-trichloromethylbenzene was performed at the desired temperature (from 50 to 200 °C) and under autogene pressure.<sup>17</sup> At the end of the reaction, the autoclave was cooled down and vented with dry dinitrogen in order to eliminate the HCl and the unreacted HF. The contents were guenched with 30 mL of water/decane mixture (50/50), using a 316 L stainless steel tank. After extraction with decane, the organic phase was dried with MgSO<sub>4</sub> and analyzed by GC. The fluorinated products and the chlorinated reactant were quantified by gas chromatography using an internal standard quantification method with decane as the internal standard. The yield corresponds to the mol % of the bis-1,3trichloromethylbenzene transformed into various products (byproducts included). Yields of 100% were not attained, because of the uncertainty of the experiment. The conversion of the bis-1,3-trichloromethylbenzene represented the amount transformed into fluorinated products. The chromatograph was a Varian 3800 equipped with 30m VF-5 ms capillary column (Varian) with a temperature program from 50 to 300 °C. The

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various products were identified by coupling GC-MS and by comparison with commercial products.

The trichloromethoxylbenzene<sup>18</sup> (0.125 mol) and the catalyst (2.5 mmol) were introduced into the autoclave.<sup>12</sup> The reaction then took place with continuous stirring, at the 50 °C during 1 h. At the end of the reaction, the autoclave was cooled down and vented with dry dinitrogen in order to eliminate the HCl and the unreacted HF. The content was quenched with 30 mL of water/decane mixture (50/50), using a stainless steel tank. After extraction with decane, the organic phase was dried with MgSO4 and analysed by GC. The fluorinated products and the chlorinated reactant were quantified by gas chromatography using an internal standard quantification method with decane as the internal standard. The yield corresponds to the mol % of trichloromethoxylbenzene transformed into chlorodifluoromethoxybenzene plus trifluoromethoxybenzene. The chromatograph was a Varian 3800 equipped with 25 m BP1 capillary column (SGE) with a temperature program from 50 to 240 °C.

The transformation of  $CF_3CH_2Cl$  into  $CF_3CH_2F^{19}$  was carried out under atmospheric pressure in a fixed bed reactor at 380 °C.<sup>10,11</sup>

The commercial alumina was fluorinated by HF at 400  $^{\circ}$ C in order to obtain a partial fluorinated support which was stabilized under fluorination conditions with a surface area of around 45 m<sup>2</sup>/g.<sup>10,11</sup>

Zinc-doped chromium oxide catalysts supported over partially fluorinated alumina (55% of AlF<sub>3</sub>) were prepared by wetness impregnation of the fluorinated alumina with an aqueous solution of chromic anhydride, zinc chloride, and methanol. The reduction of  $\rm Cr^{VI}$  into  $\rm Cr^{III}$  was carried out in the presence of methanol. The impregnation of AlF<sub>3</sub> was carried out at room temperature and atmospheric pressure. The quantities of chromium and zinc corresponded to a total amount of added components Zn+Cr) of around 10 wt % and atomic ratios of Zn/(Zn+Cr) varying from 0 to 1. Then the various catalysts were dried at 110 °C during one night under atmospheric pressure. The precursors were decomposed during the fluorination of the catalyst by HF at 380 °C during 2 h in a dynamic flow reactor to produce the corresponding fluorinated or oxyfluorinated materials. Chemical analyses of the elements (chromium, zinc) were carried out after the fluorination step. No significant variation of the specific surface could be noticed whatever the catalyst after the treatment by HF during 2 h, as reported in a previous paper.<sup>11</sup> All the reactants were diluted in helium. The flow rate of  $CF_3CH_2Cl$  was regulated at 50 °C (to avoid any condensation) by a Brooks mass flowmeter. The helium, O<sub>2</sub>, and HCl feeds were regulated at room temperature by a Brooks mass flowmeter. The catalyst (sieved to a diameter between 0.250 mm and 0.315 mm) was mixed with 6 cm<sup>3</sup> of Lonza graphite. When the reaction products emerged from the reactor they were washed successively in two flasks containing water and then in one containing potassium hydroxide (1 M) to neutralize the unreacted hydrogen fluoride and HCl produced by Cl/F exchanges. They were then dried on a 4 Å molecular sieve. The organic reaction products were analyzed online with a gas chromatograph (Varian GC 3400) equipped with a flame ionization detector and a DB5 capillary column (J and W Scientific). O<sub>2</sub>, HCl, and Cl<sub>2</sub> were analyzed online with a gas chromatograph equipped with a catharometer detector and a DB5 capillary column (J and W Scientific). HCl and dioxygen were injected into stoichiometric (HCl/O<sub>2</sub> = 4) ratio.

The various activity was calculated as defined:  $A \pmod{h/g} = F^*y$ /weight of catalyst with F: flow of the reactant (mmol/h), y: yield of each product (mol %). The activity in mmol/h/mmol metal was obtained by dividing the activity by the total amount of metal.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

My thanks to Arkema (Eric Lacroix) and Solvay (François Metz) companies for their financial support and many fruitful discussions.

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