

# Tetrafluoroethylene telomerization using dibromohaloethanes as telogens

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## Abstract

Carrier mediated telomerization (CMT) between  $C_2F_4$  and bromochlorofluoroethanes has been evaluated in terms of product distributions arising from CMT and ‘normal’ telomerization. The effect of parameters like type of initiator and telogen, TFE pressure and temperature on the reaction has been studied. The peroxide initiated telomerization between dibromohaloethanes and  $C_2F_4$  offers an easy synthetic route to  $\alpha,\omega$ -dibromo perfluoroalkanes  $Br(CF_2)_nBr$  with  $n = 2, 4, 6$  and  $8$ . The selectivity of the CMT products versus those from ‘normal’ telomerization depends mainly on the choice of telogen and on its ability to act as ‘bromine donor’ in the radical telomerization. These perfluoroalkyl dibromides are useful intermediates for other derivatives, for example, perfluorinated mono- and diolefins,  $Br(CF_2)_nCH=CH_2$  and  $CH_2=CH(CF_2)_nCH=CH_2$ . © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

A generally accepted procedure for the synthesis of fluorinated diolefins  $CH_2=CH(CF_2)_nCH=CH_2$  (**1**), with  $n = 2, 4, 6$  and  $8$ , is the addition of perfluorinated diiodides  $I(CF_2)_nI$  (**2**) to ethylene followed by dehydrohalogenation [1,2]. For example, the fluorinated diolefin (**1**) with  $n = 6$  [3] is used in radical polymerization as a cross-linking agent for fluorinated elastomers [4,5].

The synthesis of (**1**) starting from 1,2-dibromo-1,2-difluoroethane, further telomerization with  $C_2F_4$  to give  $Br(CF_2)_nBr$  telomers (**3**) followed by the addition of  $CH_2=CH_2$  and further dehydrobromination has already been discussed in detail in the literature [6–8]. A reaction which does not involve iodinated precursors, but employs  $Br(CF_2)_nBr$  as the starting material for the synthesis of diolefins is in fact appealing since it avoids handling of highly toxic, corrosive and expensive starting materials such as iodine which in turn produces, during telomerization, toxic intermediates (diiodo derivatives and especially 1,2-diiodo-1,2-difluoroethane) [9].

One of the main drawbacks of the telomerization of 1,2-dibromo-1,1,2,2-tetrafluoroethane with  $C_2F_4$  is the difficulty of having a constant high concentration of the propagating radical  $Br(CF_2)_{n-1}CF_2\cdot$  in order to obtain the desired telomeric distribution [10]. This difficulty is encountered both with a thermally induced as well as with a peroxide initiated telomerization mainly because the significant bond strength of the carbon–bromine bond:  $-CF_2-Br$  has a bond dissociation energy,  $E_D = 293 \text{ kJ mol}^{-1}$ , while the  $-CF_2-I$  bond dissociation energy is much lower ( $E_D = 226 \text{ kJ mol}^{-1}$ ) [11].

In this work a new, unexpected and efficient synthetic route to  $\alpha,\omega$ -dibromo perfluoroalkanes  $Br(CF_2)_nBr$  via a ‘‘carrier mediated telomerization’’ (CMT) between bromochlorofluoroethanes and  $C_2F_4$  has been discovered, without the difficulties described in the literature [10,11]. CMT has already been described in the literature for other telogens such as vinyl chloride, ethyl methacrylate and styrene [12a] but, to the best of our knowledge, never for  $C_2F_4$ . In particular, we found that CMT between  $C_2F_4$  and  $CFCIBrCFCIBr$  leads to the efficient formation of  $\alpha,\omega$ -dibromo perfluoroalkanes  $Br(CF_2)_nBr$  with  $n = 4, 6$  and  $8$  [13]. The ratio between products derived from CMT and ‘normal’ telomerization depends mainly on the ability of the telogen to act as a bromine donor, i.e. on the susceptibility of the telogen to bromine abstraction by free

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radicals and disproportionation of the resulting radical into a bromine radical and an olefin.

## 2. Results and discussion

TFE telomerization with halogenated telogens is a radical process [8]. When employing dibromohaloethanes as telogens with a radical initiator there are always two reaction mechanisms competing. The first one is the classical, “normal”, mechanism observed in most telomerizations with TFE [7,14]:  $C_2F_4$  adds to the telogen  $BrC(Z)_2C(Z)_2Br$  yielding  $Br(CF_2CF_2)_x C(Z)_y C(Z)_2 (CF_2CF_2)_y Br$ , where  $x$  is not necessarily equal to  $y$  (indicating the presence of both symmetrical and asymmetrical structures) or both  $x$  and  $y$  are equal to 1 or 2;  $Z = Cl$  and  $F$ . The second competitive mechanism is carrier mediated telomerization [15]. In this type of telomerization, the brominated telogen acts as a source of  $Br^\bullet$ . As a consequence, the main products observed are  $\alpha,\omega$ -dibromo perfluoroalkanes  $Br(CF_2)_n Br$  with  $n = 2, 4, 6$  and  $8$ , formally the result of the bromine telomerization with  $C_2F_4$ . Scheme 1 shows the two competing reactions.

The olefin  $C(Z)_2=C(Z)_2$  with  $Z$  defined as above, arising from the CMT mechanism (bromine carrier), can be separated from the crude reaction mixture, for example, by distillation. It can be converted easily to the starting telogen (bromine donor) by bromination and recycled in another telomerization.

### 2.1. Influence of the telogen

Different bromochlorofluoroethanes have been tried as telogens in the TFE telomerization:

- 1,2-dibromo-1,2-dichloro-1,2-difluoroethane ( $BrCFClCFCIBr$ );
- 1-chloro-1,2-dibromo-1,2,2-trifluoroethane ( $BrCF_2CFCIBr$ );
- 1,2-dibromo-1,1,2,2-tetrafluoroethane or Fluobrene<sup>®</sup> ( $BrCF_2CF_2Br$ );
- 1,2-dibromo-1,1,2-trichloroethane ( $BrCl_2CCHClBr$ );
- 1,2-dibromo-1,1,2,2-tetrachloroethane ( $BrCl_2CCCl_2Br$ ).

All telogens a–e give products resulting from a ‘normal’ and CMT telomerization. However,  $BrCFClCFCIBr$  is the telogen that generates most product and transfers bromine radicals most effectively during the reaction.

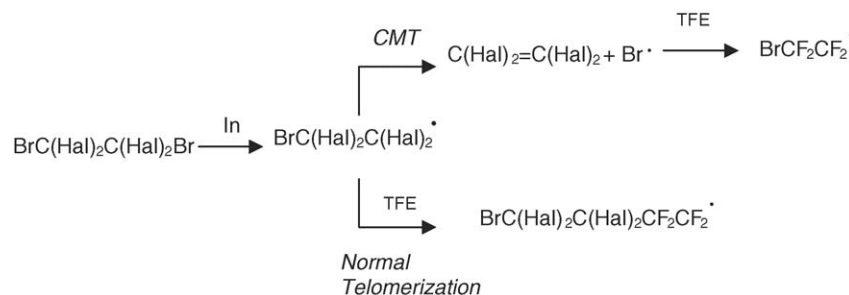
Table 1

Yield of  $Br(CF_2)_n Br$  telomers with  $n = 4, 6$  and  $8$  and of “normal” telomers  $Br(CF_2CF_2)_x CFCICFCI(CF_2CF_2)_y Br$  (**4**) (deriving from the insertion of  $C_2F_4$  between each respective  $Br-C$  bond) expressed in mol% with respect to the moles of the telogen employed

Telogen	$Br(CF_2)_n Br$ (mol%)	( <b>4</b> ) (mol%)
$BrCFClCFCIBr$	20.3	5.9
$BrCF_2CFCIBr$	14.6	6.5
$BrCF_2CF_2Br$	13.3	7.0
$BrCHClCCl_2Br$	5.5	8.9
$BrCCl_2CCl_2Br$	7.2	10.3

Each yield is calculated at complete telogen conversion as a function of the telogen. Telomerization conditions: 0.1 mol% of di-*tert*-butyl peroxide (DTBP) with respect to the starting moles of telogen,  $T = 134^\circ C$ ,  $P_{C_2F_4} = 18$  absolute atm (constant), telogen/ $C_2F_4$  molar ratio = 3.0.

A possible (but up to this point still speculative) explanation for the high efficiency towards CMT of telogen (a) with respect to the other telogens (b)–(e) regards both the ease of  $Br^\bullet$  formation and the concentration of the resulting olefin either in the gas or liquid phases. The formation of  $Br^\bullet$  from a  $-CF_2-Br$  bond requires greater energy due to the greater bond strength of  $-CF_2-Br$  (telogens ‘b’ and ‘c’) with respect to  $-CFCIBr$  (telogen a). Instead, telogens (d) and (e) have a bromine atom bonded to  $-CCl_2-$  which has a lower bond dissociation energy and therefore should easily afford a  $Br^\bullet$  [11]. A driving force of CMT, as shown in Scheme 1, is the formation of the olefin:  $CICF=CFCl$  (bp =  $21^\circ C$  at atmospheric pressure) from telogen (a),  $Cl_2C=CHCl$  (bp  $86^\circ C$  at atmospheric pressure) from telogen (d) and  $Cl_2C=CCl_2$  (bp =  $121^\circ C$  at atmospheric pressure) from telogen (e). In the telomerization conditions adopted in Table 1 ( $134^\circ C$  and 18 atm (absolute) of  $C_2F_4$ ) the olefin resulting from debromination of telogen (a) is still in the gas phase while the olefins which result from debromination of telogens (d) and (e) are in the liquid phase. Therefore, olefins from telogens (d) and (e) can sum  $Br^\bullet$  more quickly than the olefin generated from telogen (a). Comparing therefore telogens (e) and (a) in the same reaction conditions and at any point in time, there will be, respectively, a greater concentration of  $BrCCl_2Cl_2C^\bullet + Br^\bullet$  (and starting telogen e) than  $BrCFClCFCI^\bullet + Br^\bullet$  (and starting telogen a). This can at least in part explain the CMT and “normal” telomer trends observed for telomers (a)–(e) shown in Table 1.



Scheme 1. “Normal” vs. carrier mediated telomerization.

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