Journal of Fluorine Chemistry, *43* (1989) 15–25

Received: June 6, 1988; accepted: October 25, 1988

RADICAL TELOMERIZATION OF VINYLIDENE FLUORIDE IN THE PRESENCE OF 1,2-DIBROMOTETRAFLUOROETHANE

SILVANA MODENA, MAURIZIO PIANCA, MARCO TATO', GIOVANNI MOGGI
Montefluos C.R.S., via S.Pietro 50, 20021 Bollate (Italy)

and SAVERIO RUSSO
Department of Chemistry, University of Sassari and CNR Center of Macromolecules, Genoa (Italy)

SUMMARY

Vinylidene fluoride (VDF) telomerization has been investigated using 1,2-dibromotetrafluoroethane (I) in the presence of different initiators as telogen. End groups determined by NMR spectroscopy show the different role of the initiator radicals in the telomerization process. The presence of short branch structures, formed by intramolecular transfer, has been demonstrated through ^{13}C, ^{19}F and ^{1}H NMR spectroscopy.

INTRODUCTION

In the course of a research programme devoted to study of vinylidene fluoride (VDF) polymerization to low molecular mass products, we have paid special attention [1,2] to the effective relevance of the telomerization reaction when 1,2-dibromotetrafluoroethane (I) is used as a potential telogen agent in the presence of various peroxide initiators. The use of (I) as telogen appears to be a convenient way to obtain almost exclusively CF_2Br-CF_2-CH_2- and CF_2Br-CH_2- terminal groups in the PVDF chain and has not been previously described.

Radical reactions of VDF in the presence of various halogenated telogens (R-X, where X is halogen) have often been reported in literature, either under thermal [3,4] or photochemical conditions [5] or in presence of free radical initiators [6]. Products of general formula $R\text{-}(CH_2\text{-}CF_2)_n\text{-}X$ are claimed to be obtained, with n usually ranging from 1 to 8. Attention has been mainly focused both on the effect of the specific telogen on structure and properties of the derived telomers, and on conditions necessary to obtain the equimolar adduct [6].

The aim of our study is to correlate the extent of the telomerization reaction in the presence of (I) with the type of radical initiator. In the present work some preliminary results are given. From the evaluation of the average degree of polymerization ($\overline{X}_n$) as well as from the microstructural analysis of the telomers we can throw some light on the relative role of initiation, transfer and termination reactions. A further characterization of the telomers, which includes determination of their melting and glass transition temperatures, allows us to compare their thermal properties with those of high molecular mass PVDF.

EXPERIMENTAL

The reactions have been carried out in a 500 ml stainless steel autoclave in batch under the following conditions:

- CF_2Br-CF_2Br / VDF : from 0.05/1 to 5/1 (molar ratio)
- Peroxide (initiator): from 0.5 to 4.0 mol% referred to VDF
- Temperature : from 60^o to 147^o C
- Reaction time : from 1 to 8 hours

The low molecular mass products have been characterized by ^{19}F and ^{1}H NMR spectroscopy. The spectra of hexa-deuteroacetone solutions (10 mg of telomer in 0.5 ml) were recorded on a Varian XL-200 spectrometer, operating at 188.22 MHz for ^{19}F and at 200.02 MHz for ^{1}H, using TMS as internal standard for ^{1}H and $CFCl_3$ for ^{19}F.

$\overline{X}_n$ values have been calculated both from NMR data and vapour pressure osmometry (VPO).

Glass transition temperatures have been measured by differential scanning calorimetry, using a Perkin Elmer DSC-2 calorimeter, with a heating rate of 10^o K min^{-1}. The intercept of the line of maximum slope with the baseline was assumed to be the Tg. The other thermal analyses were run in the same apparatus with heating and cooling rates of 10^o and $5^oC/min$ respectively.

In a typical run the autoclave was charged with 102 g (0.39 moles) of 1,2-dibromotetrafluoroethane (I) and 1.14 g of ditertbutylperoxide (DTBP). The autoclave was cooled to Dry Ice temperature and 25.1 g (0.39 moles) of vinylidene fluoride (VDF) was added. The autoclave was shaken for 5 hours at 147^oC. After cooling, the unreacted products, mainly (I), were removed by evaporation under vacuum and the telomer was recovered from the autoclave and consisted of a sticky wax. The average molecular mass calculated by NMR data was 800 and the glass transition temperature -90°C.

RESULTS AND DISCUSSION

Three different initiators, all of which have a peroxy structure have been tested under comparable experimental conditions, i.e. using temperatures able to give similar dissociation rate constants at the same initiator concentration.

For di-benzoylperoxide (DBP) the reaction temperature was 92° C, whereas 60° and 147° C, respectively, were chosen for bis(4-tertbutylcyclohexyl)peroxy-dicarbonate (Pk 16) and di-tertbutylperoxide (DTBP).

The NMR analysis of the reaction products has shown the presence of the groups reported in Table 1. NMR assignments A-E, relating to the VDF units in the chain, are based on a work of Cais and Kometani [7] on the high molecular mass PVDF microstructure. In this paper [7] some signals are not assigned, but its authors suggest that they are due to branched structures. We have proposed for some of those signals the structures J-L' originated from a branching process, as reported below. Our assignments have been made on the basis of chemical shifts and literature data [8, 9, 10].

Comparison of ^{1}H and ^{19}F NMR spectra and the use of two dimensional fluorine-fluorine chemical shift correlation spectroscopy (COSY) [11], allowed us to identify the pairs of CF_2 groups which are spin-coupled and led to unambiguous assignments.

TABLE 1

VDF telomers; assignments of ^{19}F and ^{1}H NMR resonances.

Signal	Assignments	^{19}F (δ) ppm vs.$CFCl_3$	^{1}H (δ) ppm vs.TMS
A	$-CH_2-CF_2-\underline{CH}_2-\underline{CF}_2-\underline{CH}_2-CF_2-CH_2-$	-91.3	3.0
B	$-CF_2-\underline{CH}_2-\underline{CH}_2-\underline{CF}_2-CH_2-CF_2-CH_2-$	-95.0	2.4
C	$-CH_2-CF_2-CH_2-\underline{CF}_2-CF_2-\underline{CH}_2-\underline{CH}_2-$	-113.5	2.4
D	$-CF_2-CH_2-CF_2-\underline{CF}_2-\underline{CH}_2-\underline{CH}_2-CF_2-$	-115.9	2.4
E	$-CH_2-CF_2-CH_2-\underline{CF}_2-CF_2-CH_2-CF_2-CH_2-$	-113.7	
F	$-CH_2-CF_2-\underline{CH}_2-\underline{CF}_2Br$	-43.0	3.5
F'	$-\underline{CH}_2-\underline{CF}_2-CH_2-CF_2Br$	-93.5	ca 3.0
G	$-CF_2-\underline{CH}_2-\underline{CH}_2-\underline{CF}_2Br$	-45.0	ca 2.4
H	$-CF_2-\underline{CH}_2Br$		3.9
I	$-CH_2-CF_2-CH_2-CF_2-\underline{CF}_2Br$	-67.0	
I'	$-CH_2-CF_2-CH_2-\underline{CF}_2-CF_2Br$	-110.0	
J	$-CH_2-CF_2-CH_2-\underline{CF}_2\underline{H}$	-114.1	6.28
J'	$-CH_2-\underline{CF}_2-CH_2-CF_2H$	-91.8	
K	$-CF_2-CH_2-CH_2-\underline{CF}_2\underline{H}$	-117.0	6.24
L	$-CH_2-CF_2-\underline{CF}_2-\underline{CH}_3$	-107.0	1.77
L'	$-CH_2-\underline{CF}_2-CF_2-CH_3$	-114.0	
	Pk 16:		
M'	$-C(\underline{CH}_3)_3$		0.85
M"	$(CH_3)_3-(C_6\underline{H}_{10})-O-$		1.0-2.2
M"'	$>\underline{CH}-O-$		ca 3.0
M""	$-O-\underline{CH}_2-\underline{CF}_2-CH_2-CF_2-$	-102.1	4.48-4.50
	DBP:		
N'	$Ph-\underline{CH}_2-\underline{CF}_2-CH_2-CF_2-$	-88.0	ca 2.5
N"	$Ph-COO-\underline{CH}_2-\underline{CF}_2-CH_2-CF_2-$	-101.0	4.7

Signals A-L' are present in all the samples.

Signals M are present in the samples initiated with Pk 16.

Signals N are present in the samples initiated with DBP.

Relative signal intensities are depending on the ratio telogen/VDF as well as on initiator concentration.

Assignments F-I', related to bromine containing end groups, and assignments N-M related to end groups originated by the initiator, have been made analogously.

The above data have demonstrated the different role of the three initiators. Indeed in the case of DTBP a pure telomerization reaction can be suggested, as indicated by the chemical nature of the terminal groups. No residue from the initiator has ever been found in the telomer structure.

The scheme for this telomerization is as follows :

Initiation

$$\mathrm{I_n \longrightarrow 2\ I_n^{\bullet}} \qquad (1)$$

$$\mathrm{I_n^{\bullet} + CF_2Br\text{-}CF_2Br \longrightarrow CF_2Br\text{-}CF_2^{\bullet} + I_n\text{-}Br} \qquad (2)$$

$$\mathrm{CF_2Br\text{-}CF_2^{\bullet} + CH_2{=}CF_2 \longrightarrow CF_2Br\text{-}CF_2\text{-}CH_2\text{-}CF_2^{\bullet}} \qquad (2a)$$

Propagation

$$\mathrm{CF_2Br\text{-}CF_2\text{-}CH_2\text{-}CF_2^{\bullet} + n\ CH_2{=}CF_2 \longrightarrow CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_nCH_2\text{-}CF_2^{\bullet}} \qquad (3)$$

Inversion

$$\mathrm{CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CH_2\text{-}CF_2^{\bullet} + CF_2{=}CH_2 \longrightarrow CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_{n+1}\text{-}CF_2\text{-}CH_2^{\bullet}} \qquad (4)$$

Transfer

$$\mathrm{CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CH_2\text{-}CF_2^{\bullet} + CF_2Br\text{-}CF_2Br \longrightarrow CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CH_2\text{-}CF_2Br + CF_2Br\text{-}CF_2^{\bullet}} \qquad (5)$$

$$\mathrm{CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CF_2\text{-}CH_2^{\bullet} + CF_2Br\text{-}CF_2Br \longrightarrow CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CF_2\text{-}CH_2Br + CF_2Br\text{-}CF_2^{\bullet}} \qquad (5')$$

Termination

$$2\ CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CH_2\text{-}CF_2^\bullet \longrightarrow$$

$$CF_2Br\text{-}CF_2\text{-}(CH_2\text{-}CF_2)_n\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}(CF_2\text{-}CH_2)_n\text{-}CF_2\text{-}CF_2Br \quad (6)$$

There is no indication that any inversion occurs on addition of $CF_2Br\text{-}CF_2^\bullet$ to the first monomer unit.

For Pk 16 and DBP initiators, also some residues from the peroxy radicals are incorporated as end groups in the polymer chain, as shown in Table 1. These additional groups are:

$C_6H_5\text{-}CH_2\text{-}CF_2\text{-}$, $C_6H_5\text{-}COO\text{-}CH_2\text{-}CF_2\text{-}$ for DBP

$tC_4H_9\text{-}C_6H_{10}\text{-}O\text{-}CH_2\text{-}CF_2\text{-}$ for Pk 16

NMR data suggest that, in the presence of these initiators, a competition between monomer and telogen molecules towards primary radicals occurs and a pure telomerization is prevented, analogously to what has recently been found in ester and ketone type solvents [12]. Thus the kinetic scheme of the process can be most appropriately described in terms of a classical chain transfer mechanism.

Further involvement of Br-terminated oligomers in transfer or telomerization reactions does not seem to be relevant at all. Indeed the model compound $BrCF_2\text{-}CF_2\text{-}CH_2\text{-}CF_2Br$ (1:1 adduct) when added to VDF under conditions similar to those previously described for the oligomerization does not react with primary radicals or growing chains.

From NMR spectra no other anomalous groups have been found, except for a relatively small contribution of $\text{-}CF_2H$ and $\text{-}CH_3$ groups. These groups, whose concentration is strongly dependent on the type and concentration of initiator, may be due to hydrogen abstraction from either or both initiator molecules or PVDF chain. In this latter case a possible mechanism to justify the presence of the $-CF_2H$ and $-CH_3$ groups (signals J, K and L in Table 1) could be a short chain-branching process involving an intramolecular 1-5 transfer of the hydrogen atom, analogous to similar radical reactions reported in the literature [13]. This reaction cannot occur in a normal chain, since the growing $-CF_2^{\bullet}$ radical is always in a 1,4- or 1,6- relationship to $-CH_2-$ groups. Therefore the 1,5-shift will come from 'head to head' sites, which are present to a level of ca. 5%, according to the following reaction:

$$-CF_2-CH_2-CH_2-CF_2-CH_2-CF_2^{\bullet} \longrightarrow -CF_2-CH^{\bullet}-CH_2-CF_2-CH_2-CF_2H \longrightarrow$$
$$-CF_2-CH(CH_2-CF_2^{\bullet})-CH_2-CF_2-CH_2-CF_2H$$

This type of reaction then leads to some tertiary sites in the polymer. In fact, the signal of a >CH- tertiary group (triplet, 77 ppm) has been observed by ^{13}C NMR spectroscopy in a sample of relatively high molecular mass ($\bar{M}_n$ = 3,000). The very weak signals L and L' in Table 1, attributed to $-CH_3$ end groups, can come from species formed in the same way by a growing radical ending with an inverted monomer unit, according to the following reaction:

$$-CF_2-CH_2-CH_2-CF_2-CF_2-CH_2^{\bullet} \longrightarrow -CF_2-CH^{\bullet}-CH_2-CF_2-CF_2-CH_3 \longrightarrow$$
$$-CF_2-CH(CH_2-CF_2^{\bullet})-CH_2-CF_2-CF_2-CH_3$$

On the basis of the afore mentioned results, we have focussed our attention on the pure telomerizing system DTBP-VDF-(I) at 147°C. The evaluation of $\bar{X}_n$ as a function of (I)/VDF ratio is given in Fig. 1. The data, obtained both by NMR and VPO, show very close agreement. It is evident from figure 1 that (I) strongly affects the PVDF chain length, acting as a rather efficient telogen agent. Quantitative treatment of the above data in terms of the Mayo equation and evaluation of the chain transfer constant are prevented by the

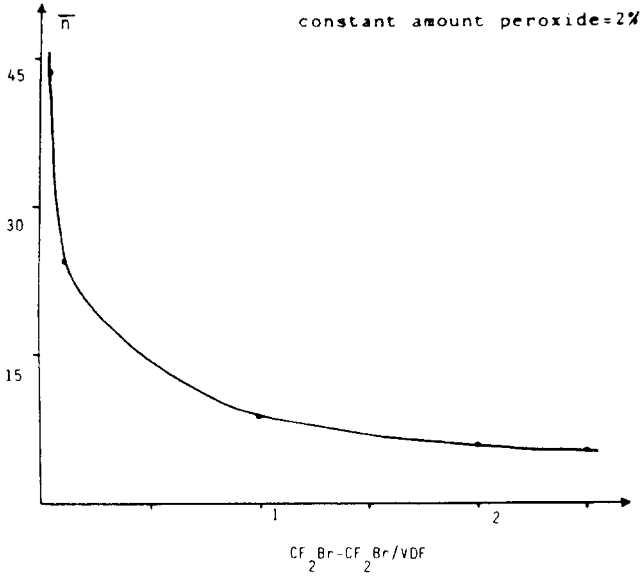

Fig. 1. Influence of the ratio CF_2Br-CF_2Br/VDF on the degree of polymerization.

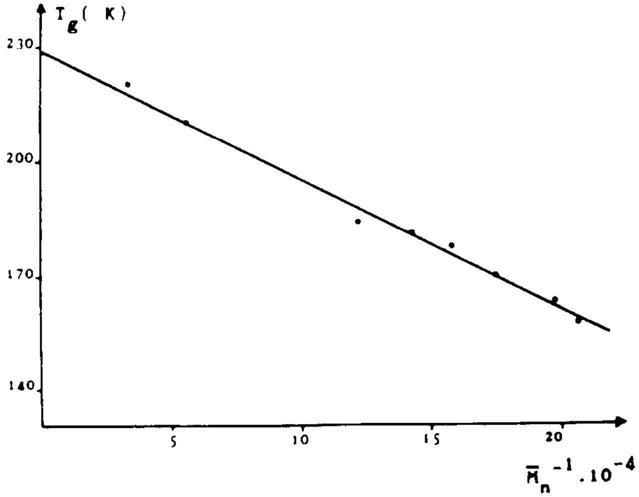

Fig. 2. Dependence of glass transition temperature (T_g) on the Molecular Mass.

non-homogeneity of the reaction system in the whole range of mixture composition.

The resultant telomers can be solid, waxy or liquid depending on their average molecular mass: they are liquid for $\overline{M}_n < 600$, waxy between 600 and 900 and solid at higher molecular masses.

The melting point and the heat of fusion (from DSC data on annealed samples) are 139°C and 8 cal/g, respectively, for a telomer having molecular mass close to 1,800, compared with usual values of about 165-175°C and 15-20 cal/g for commercial PVDF having high molecular mass.

Tg values of the telomers are given in Fig. 2. A good linear correlation exists between Tg and $1/\overline{M}_n$. Extrapolation to $1/\overline{M}_n = 0$ gives a Tg value almost coincident with that recently reported [14] for high molecular mass PVDF. These data suggest that a single equation [15] can be applied over the whole range of molecular masses with intercept 227.3 (Tg of high molecular mass PVDF) and slope 33,723.

CONCLUSIONS

PVDF telomers with well-defined microstructure can be prepared in a wide range of molecular masses. The bromine end groups can allow their utilization in several chemical reactions including chain extension, grafting etc.

ACKNOWLEDGEMENT

We wish to thank Prof. R.D. Chambers for helpful discussion and stimulating remarks.

REFERENCES

1 A.Fontana, S.Modena, M.Tatò and G.Moggi, 11th International Symposium on Fluorine Chemistry, Berlin, 5-9 August 1985, Abstract P 46.

2 M.Pianca, S.Modena, M.Tatò, G.Moggi and S.Russo, IUPAC International Symposium on Free Radical Polymerisation, S.Margherita Lig.(Italy) 17-22 May 1987. Preprints, pg 149.

3 M.Hauptschein, M.Braid and F.Lawlor, J.Am.Chem.Soc., 80 (1958) 846.

4 R.D.Chambers, J.Hutchinson, R.H.Mobbs and W.K.R.Musgrave, Tetrahedron, 20 (1964) 497.

5 D.S.Ashton, A.F.Mackay, J.M.Tedder, D.C.Tipney and J.C. Walton, J.Chem.Soc., Chem.Commun., (1973) 496.

6 P.Tarrant, M.R.Lilyquist, J.Am.Chem.Soc., 77 (1955) 3640.

7 R.E.Cais, J.M.Kometani, Macromolecules, 17 (1984) 1887.

8 H.Stahl-Lariviere, Org.Magn.Res., 6 (3) (1974) 170.

9 A.Battais, G.Bauduin, B.Boutevin and Y.Pietrasanta, J. Fluorine Chem., 31 (1986) 197.

10 M.Tatò, M.Pianca, G.Moggi and S.Russo, 8th International Meeting on NMR Spectroscopy, Canterbury, 6-10 July 1987, Communication 407.

11 A.Bax, R.Freeman and G.A.Morris, J.Magn.Reson., 42 (1981) 169.

12 G.Moggi, M.Pianca, M.Tatò, S.Russo, M.G.Cavaliere and G. Garbarino, IUPAC International Symposium on Free Radical Polymerization, S.Margherita Ligure (Italy), 17-22 May 1987, Preprints, pg 153.

13 W.C.Mattiew, F.C.Stehling, Macromolecules 14 (1981) 1479.

14 P.Bonardelli, G.Moggi, A.Turturro, Polymer, 27 (1986) 115.

15 R.J.Roe, in Encyclop.Polym.Sc.Eng., Wiley, New York, vol.7, (1987), pg 536.