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PRELIMINARY NOTE

A Vinylidene Fluoride Block Copolymer containing Perfluoropolyether groups

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SUMMARY

Peroxide initiated vinylidene fluoride (VDF) telomerization was investigated in the presence of bromine terminated perfluoropolyethers $CF_3(OCF_2CF_2)_m(OCF_2)_pBr$, ($R_f$-Br). R_f-Br act as telogen agents producing the above reaction compounds of general formula R_f-$(VDF)_nBr$.
Data on telomer microstructure by fluorine NMR, glass transition temperature and crystallinity of $(VDF)_n$ moiety are also reported and discussed.
The products show properties of di-block copolymers.

In free radical polymerization the use of a chain transfer or a telogen agent is effective for molecular mass regulation. Over a wide range of molecular masses the use of a chain transfer agent has minimal influence on polymer bulk properties, such as glass transition temperature (Tg), melting point (Tm), degree of crystallinity, solvent compatibility, provided that the mass of end groups is small relative to that of polymeric chains.
However, when the telogen agent itself contains a long chain sequence, its introduction into the polymer chain gives rise to a di-block structure which can strongly affect properties of

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the polymer. This is exemplified in the present study where polyvinylidene fluoride (PVDF) chains are terminated by polyperfluoropolyether sequences.

Chemical structure

Peroxide-initiated VDF polymerization was investigated in the presence of a bromine terminated perfluoropolyether (PFPE) of general formula R_f-Br (I), where $R_f = CF_3(OCF_2CF_2)_m(OCF_2)_pOCF_2$-, m and p units are randomly sequenced in the chain. These compounds are prepared according to ref [1] and act as telogen agents forming in the above reaction compounds of general formula R_f-$(VDF)_n$Br (II)

TABLE 1

PFPE-VDF block telomers : ^{19}F-NMR assignments

Signal	Chemical Shift (ppm vs. $CFCl_3$)	Assignment
PFPE BLOCK:		
A	-52.0	$-OCF_2CF_2OC\underline{F}_2OCF_2CF_2O-$
B	-53.6	$-OCF_2CF_2OC\underline{F}_2OCF_2O-$
C	-55.3	$-OCF_2OC\underline{F}_2OCF_2O-$
D	-88.9	$-OCF_2CF_2OC\underline{F}_2CF_2O-$
E	-90.6	$-OCF_2OC\underline{F}_2CF_2O-$
F	-56.3	$-OCF_2CF_2OC\underline{F}_3$
G	-58.0	$-OC\underline{F}_2OCF_3$
PFPE/VDF LINKS:		
H	-78.0	$-OCF_2CF_2OC\underline{F}_2CH_2CF_2-$
I	-80.1	$-OCF_2OC\underline{F}_2CH_2CF_2-$
VDF BLOCK:		
L	-91.3	$-CH_2CF_2CH_2C\underline{F}_2CH_2CF_2CH_2-$
M	-95.0	$-CF_2CH_2CH_2C\underline{F}_2CH_2CF_2CH_2-$
N	-113.5	$-CH_2CF_2CH_2C\underline{F}_2CF_2CH_2CH_2-$
O	-113.7	$-CH_2CF_2CH_2C\underline{F}_2\underline{CF}_2CH_2CF_2CH_2-$
P	-115.9	$-CF_2CH_2CF_2C\underline{F}_2CH_2CH_2CF_2-$
Q	-43.0	$-CH_2CF_2CH_2C\underline{F}_2Br$
R	(^{1}H NMR: 3.9 ppm)	$-CF_2C\underline{H}_2Br$

Table 1 reports the more relevant assignments of ^{19}F resonances that enable us to understand the structure of compounds (II). Assignments have been made according to the literature [2, 3]. Average molecular mass was determined by NMR analysis. The structure of the products is fully in accord with the following reaction :

$$R_f\text{-Br} + nCH_2\text{=}CF_2 \longrightarrow R_f\text{-}(CH_2CF_2)_nBr \qquad \text{(II)}$$

The above scheme is similar to that recently reported for the VDF telomerization with $CF_2Br\text{-}CF_2Br$ as telogen [2].

Properties

$CF_3(OCF_2CF_2)_m(OCF_2)_pO\text{-}CF_2\text{-}(CH_2CF_2)_nBr$ compounds, abbreviated to $R_f\text{-}(VDF)_nBr$, exhibit two glass transition temperatures (Tg). The lower is due to the $\text{-}(OCF_2\text{-}CF_2)_m\text{-}(OCF_2)_p\text{-}$ sequences and depends on m/p ratio and on their molecular mass ($\overline{Mn}_1$); when m/p is 0.65 with molecular mass = 1,200 and 2,400, the lower Tgs were 130 K and 135 K respectively. These values are in good agreement with those calculated from the general equation for pure perfluoropolyethers recently reported [4]:

$$Tg = Tg^{\infty} - K_1/\overline{Mn}_1 \qquad (1)$$

where Tg^{∞} is the extrapolated Tg of infinite molecular mass perfluoropolyether (141.2 K) and K_1 is 14,900.

The upper Tg of di-block telomers is due to the $(VDF)_n$ sequences and depends only on n value.
Table 2 lists data on the preparation and properties of the products (II). In runs 1-4 Rf- had a value of $\overline{Mn}$ close to 1,200 and m/p ratio = 0.65; in runs 5-8 m/p was again 0.65 but $\overline{Mn}$ was about 2,400.

TABLE 2

Telomerizations

$R_f\text{-Br} + \text{VDF} \longrightarrow R_f\text{-(VDF)}_n\text{-Br}$

RUN	$\overline{Mn}_1$	VDF/Rf-Br	$\overline{Mn}_2$ (*) of the $(VDF)_n$ segments	Upper Tg (K)	Lower Tg (K)
1	1,200	122	4544	221	130
2	1,200	57	1613	215	130
3	1,200	27	992	201	130
4	1,200	18	806	191	130
5	2,400	95	3846	221	135
6	2,400	44	1350	206	135
7	2,400	24	915	199	135
8	2,400	13	672	188	135

(*) Determined by NMR.

Reaction conditions :
Autoclave 200 ml; T = 130°C; t = 50 min; 0.008 m of R_f-Br.
Solvent : 1,1,2 Trichlorotrifluoroethane (CFC 113) 100 g.
Initiator : di-t-butylperoxide (DTBP) 2 mol % based on VDF.

A good linear correlation exists in both the series between the upper Tg and $1/\overline{Mn}_2$ where $\overline{Mn}_2$ is the molecular mass of the $(VDF)_n$ moiety, according to the equation :

$$Tg = Tg^{\infty} - K_2/\overline{Mn}_2 \qquad (2)$$

where Tg^{∞} is the Tg of high molecular mass PVDF.
For the runs 1-4 and 5-8 we obtain, respectively :

$$Tg = 229.9 - 29{,}600/\overline{Mn}_2 \qquad R^2 = 0.979 \qquad (3a)$$

$$Tg = 227.1 - 26{,}400/\overline{Mn}_2 \qquad R^2 = 0.997 \qquad (3b)$$

The intercept values are very close to 227.3 the Tg reported [2, 5] for the high molecular mass PVDF. The Tg of $(VDF)_n$ is not dependent on the R_f- group. All the Tg data from runs 1-8 can be expressed by the equation :

$$Tg = 228.4-27{,}800/\overline{Mn}_2 \qquad R^2 = 0.987 \qquad (3c)$$

This result strongly suggests a complete immiscibility of the two blocks, without any thermodynamic interaction between the perfluorinated ether groups and the partially fluorinated VDF chains.

From FT-IR data it is evident that also the chain structure and regularity of PVDF sequences (presence of form α and/or β) are not affected by the R_f- group. This is noticeable from the comparison of the FT-IR spectra of a PVDF sample synthesized under our experimental conditions but in absence of R_f-Br and that of a typical R_f-$(VDF)_n$Br block copolymer. The spectra are superimposable over the region that better responds to differences in the conformational forms of VDF sequences [6] as illustrated in Figure 1.

According to Pezzin <u>et al.</u> [7] and with the assumptions therein the slope K of the equations <u>1</u> and <u>2</u> can be related to the polymer chain flexibility by the general equation

$$K = b/a\ MoTg \qquad (4)$$

where b/a is a quantity which decreases with increasing flexibility of the chain, while Mo is the molecular mass of a the monomeric unit.

In this study the lack of interaction between PFPE and $(VDF)_n$ segments in the A-B polymer allows the estimation of segment flexibility by eq. <u>4</u>. Accordingly using eq. <u>4</u> (Mo = 64; K_2 = 27,900 from eq. <u>3c</u> the flexibility of a PVDF chain is roughly 1.9 and that of a PFPE chain (average Mo = 78.6; K_1 = 14,900 from ref. 4) is 1.3. Pezzin <u>et al.</u> [7] reported a value for PVC of 3.6 and of 2.2 for polypropylene oxide (PPO). Then taking together the data the chain flexibility reasonably increases in the series PVC < PPO < PVDF < PFPE.

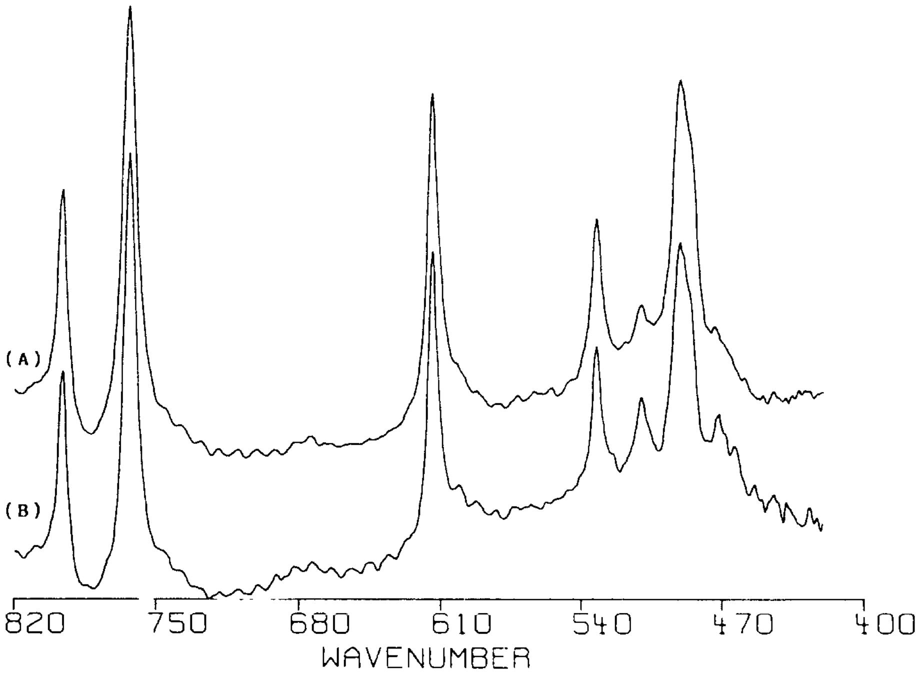

FIG. 1. FT-IR spectra of PVDF (A) and R_f-(VDF)n Br block copolymers (B).

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