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Synthesis and Properties of some Hexafluoropropene -1,1-Difluoroethene Copolymers

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SUMMARY

Hexafluoropropene (HFP) - 1,1-difluoroethene (VDF) copolymers have been synthesized in the 0-16 mole % HFP range and the results of a physico-chemical characterization by means of XRD (cristallinity index) and DSC techniques are related to the microstructure of the polymers, as determined by ^{19}F NMR. The addition of a small percentage of the HFP comonomer does not affect the polymorphism of poly(vinylidenefluoride).

INTRODUCTION

As important properties of vinylic copolymers are greatly dependent upon their composition and microstructure, we have modified the polymeric chain of highly crystalline poly(1,1-difluoroethene) (PVDF) by introducing variable amounts of hexafluoropropene (HFP). The composition of the copolymer and the mean length of the monomer sequencies, as determined by NMR spectroscopy, are correlated to crystallinity and thermoanalytical data. In view of the poor crystallinity of the products in the compositional range of high HFP values we have limited ourselves to the study of the 0-16 mole % HFP range. The residual crystallinity of the commercial fluororubbers, such as Tecnoflon, Viton, Fluorel (HFP > 17 mole %) may be investigated by means of other physico-chemical techniques, such as SAXS.

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EXPERIMENTAL

Synthesis

Aqueous emulsion copolymerizations were carried out in batch in a stainless steel autoclave (5 l) at 85°C under continuous stirring. The autoclave was charged with 850 ml of demineralized water and a mixture of the monomers, up to attaining a pressure of 14 atm at 85°C. After injection of an aqueous solution (150 ml) of 2 g $(NH_4)_2S_2O_8$, the reaction was blocked by interruption of stirring and cooling to room temperature, when a pressure drop of 2 atm was observed. As previously reported (ARNOLD et al.), surfactants are not required in this process. After venting the gases, the latexes were cooled to room temperature without stirring. The polymers were coagulated by pouring the emulsion in 500 ml 37% HCl under stirring, washed with demineralized water and dried at 45°C under vacuum for 7 h. The number average molecular weight of the copolymers was of the order of 10^5. It was calculated according to relations between intrinsic viscosity and molecular weight developed for a copolymer of VDF and HFP (FOGIEL) and for PVDF homopolymer (STALLINGS and HOWELL).

Table 1

^{19}F chemical shifts of poly-(VDF/HFP)

	δ	Structural unit
a	-71.4	$-CH_2CF_2CF(C\underline{F}_3)CF_2CH_2-$
b	-75.9	$-CF_2CF_2CF(C\underline{F}_3)CH_2CF_2-$
c	-91.9	$-CF_2CH_2C\underline{F}_2CH_2CF_2-$
d	-95.7	$-CH_2CH_2C\underline{F}_2CH_2CF_2-$
e	-103.7	$-CF_2CH_2C\underline{F}_2CF(CF_3)CF_2-$
f	-109.4	$-CF_2CH_2C\underline{F}_2CF_2CF(CF_3)-$
g	-110.7	$-CF(CF_3)CH_2C\underline{F}_2CF_2CF(CF_3)-$
h	-113.0	
i	-114.0	$-CF_2CH_2C\underline{F}_2CF_2CH-$
j	-116.3	$-CH_2CF_2C\underline{F}_2CH_2CH_2-$
k	-118.9	$-CH_2CF_2C\underline{F}_2CF(CF_3)CH_2-$

δ (in ppm from $CFCl_3$) refers to $\underline{F}$ atom(s)

Physico-chemical characterization

^{19}F NMR spectra, recorded at 56.4 MHz using a Varian EM 360 L spectrometer, were interpreted on the basis of the chemical shifts (Table 1) according to literature (FERGUSON; SCHMIEGEL; MOGGI et al.) data.

The experimental parameters derived from these spectra are reported in Table 2. Elementary chemical analysis was carried out to verify the copolymer composition. Glass transition temperatures (Tg) and endothermal effects were determined by means of DSC, using a Du Pont 900 Thermal Analyzer; their dependency upon the composition is given in Table 2.

Wide angle x-ray patterns of unoriented samples were recorded on a Philips powder diffractometer using Cu K α radiation. Relative crystallinities (Table 3) were determined with respect to reference specimens of PVDF homopolymers which exhibit the highest degree of observed crystallinity and of high HFP containing copolymers which approach most closely to the completely amorphous state.

Table 2

Composition, mean length of VDF sequence and Tg

mole % HFP	$\bar{L}_n$ (VDF) exp.	$\bar{L}_n$ (VDF) calc.	Tg from DSC °C	Tg calculated according to FOX °C
0	-	-	-45.5	-
2.9	24.3	25.6	-42.5	-37
7.8	12.9	13.1	-42.0	-25
7.9	12.4	12.5	-37.5	-25
8.2	12.1	11.9	-43.5	-24
9.7	10.1	9.8	-35.0	-21
15.9	5.9	6.0	-31.0	-5
16.2	5.8	6.0	-28.6	-5

Table 3

Crystallinity index (C.I.)

mole % HFP	C.I. %	$2\theta_{am}$ (*)	Phase distribution
0	33	18.5	β + some α_r
2.9	29	18.5	β
7.8	21	18.4	β
7.9	20	18.4	β + some α_r
8.2	20	18.3	β + some α_r
9.7	12	18.0	β
15.9	5	17.0	β
16.2	-	17.0	-

(*) Position of maximum of the amorphous fraction (CuK α radiation)

RESULTS AND DISCUSSION

The polymers were synthesized in conditions in which as well known, homopolymerization of HFP is impossible. Therefore also the formation of HFP sequences in the copolymer is avoided (SCHMIEGEL).
Consequently, only VDF sequences were examined. The mean sequence lengths L_n (VDF) were derived from NMR data following previous works (FERGUSON; SCHMIEGEL; MOGGI et al.). The values of $\bar{L}_n$ were found to be in good accordance with those obtained theoretically according to RIOS and GUILLOT, by means of the relationship :

$$\bar{L}_n\,(A)-1 = r_{AB}\,\frac{[A]}{[B]}$$

where [A] and [B] are the concentrations of the comonomers during polymerization and r_{AB} is the reactivity ratio. A reactivity ratio rVDF/HFP = 3.0 ±0.5 was assumed, which was deduced from our experimental data according to the procedures of FINEMAN and ROSS.

As well known, polimerization with chemical initiation leads to β-PVDF (GAL'PERIN et al.), even though the planar zigzag (or TT) conformation of the chain in this

crystalline form is less stable than the 2/1 helical (or TGT$\overline{G}$) conformation (HASEGAWA et al.). Accordingly, our homopolymer sample assumes the ß form, as shown in Table 3. Addition of small percentages of HFP comonomer does not affect the polymorphism of PVDF. As a matter of fact, it is well known (DOLL and LANDO) that introduction of perfluorinated units in the PVDF chain favours crystallization in phase ß for steric and electronic reasons. This tendency is more pronounced in case of introduction of tetrafluoroethylene units in PVDF (DOLL and LANDO) and apparently also holds for hexafluoropropene units. It further appears that the PVDF orthorhombic cell is not appreciably deformed by the introduction of HFP units. Only small amounts of the random α form (α_r) (GAL'PERIN et al.) are present in most samples. By annealing at 145°C the crystallites take on the highly ordered α-form (α_h).
The crystallinity of the copolymers decreases with an increase of the HFP fraction, according to the linear relationship of Fig. 1.

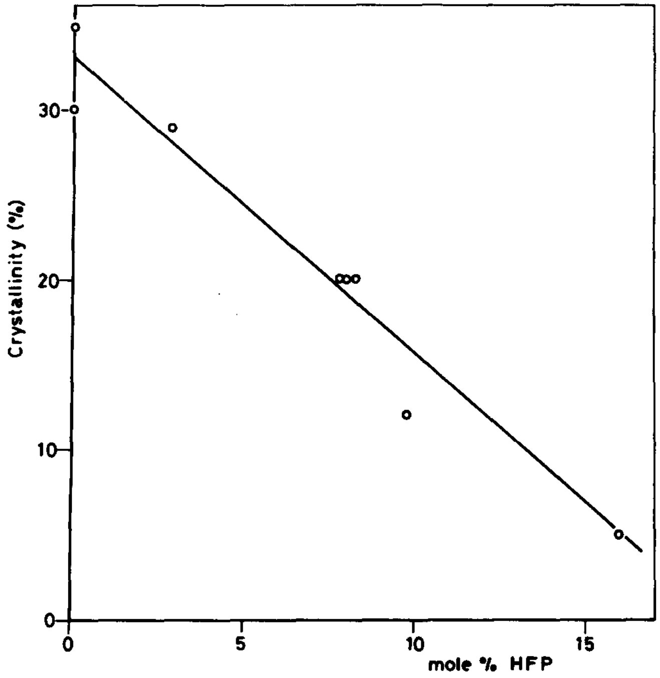

Figure 1. Crystallinity index of VDF-HFP copolymers

This is expected on the basis of the perturbation of the constitutional regularity due to the trifluoromethyl groups.

The effect is accompanied by a gradual shift in position of the maximum of the amorphous fraction (from 18.5° to 17.0°, 2θ Cu Kα), which is readily interpreted on the basis of the substituent effect of the HFP units. This trend sets through also for higher HFP percentages (max. at 16.3° for a 41 mole % C_3F_6 content). As shown in Table 2, the glass transition temperature varies regularly with the mean sequence length of VDF units. In terms of the composition of the copolymers, Tg increases linearly with the HFP content (Table 2, Fig. 2). This trend fits in with a report about a linear growth of Tg with the increasing C_3F_5H fraction in VDF-1,2,3,3,3-pentafluoropropene copolymers (MIGLIERINA and CECCATO) and is also in line with the fact that Tg increases if the hydrogen atoms of the main chain are substituted by groups of atoms, especially if these substituents have a polar character (JANACEK). Nevertheless, the observed trend does not agree with the reported non-linear relationships between Tg and composition, such as the FOX equation :

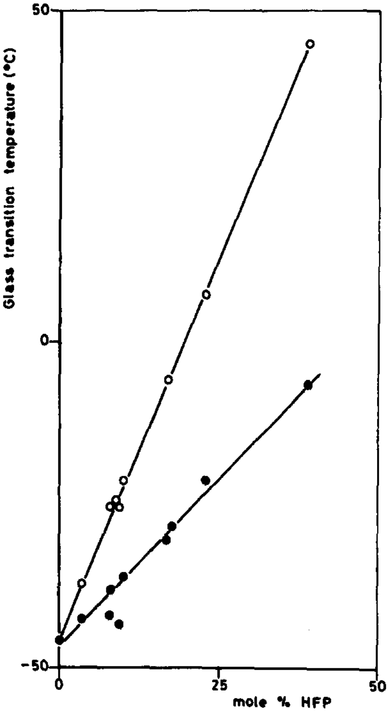

Figure 2. Glass transition temperatures of VDF-HFP copolymers : experimental Tg (●) and those according to the Fox equation (o)

$$(1/Tg) = (W_1/Tg_1) + (W_2/Tg_2)$$

where :

W_1, W_2 = weight fractions of monomers in the copolymer

Tg_1, Tg_2 = glass transition temperatures (°K) of the homopolymers

Tg = glass transition temperature (°K) of the copolymer.

Table 2 and Fig. 2 compare the results of calculations according to the FOX equation with experimental values of Tg.

As shown in Fig. 2 the linear growth of Tg with the increasing C_3F_6 fraction fits well also with the Tg values of two high HFP containing copolymers we have prepared as reference compounds (HFP = 22 mole %, Tg = -22°C; HFP = 38 mole %, Tg = -6°C).

However, extrapolation to PHFP leads to a Tg value of 59°C, which is in complete disagreement with the reported experimental values of 152°C (BROWN and WALL) and 167°C (ARNOLD et al.; ELEUTERIO and MOORE).

Various endothermal transitions have been observed in PVDF and VDF-HFP copolymers. The homopolymer (PVDF) exhibits a m.p. at 167°C, which is lowered by introduction of a very small fraction of the HFP comonomer into the polymeric chain. Namely, in a low HFP content polymer (2.9 mole %) two transitions are observed at 143 and 153°C, where the latter value can be considered as the melting temperature. Various other endothermal effects have been observed, but could not be interpreted. We intend to gain better understanding of these features by studying the behaviour of other VDF copolymers.

REFERENCES

ARNOLD, R.G., BARNEY, A.L. and THOMPSON, D.C. : Rubber Chem. Technol., 46,619 (1973)

BROWN, D.W. and WALL, L.A. : J. Polym. Sci., Part A-2, 7,601 (1969)

DOLL, W.W. and LANDO, J.B. : Amer. Chem. Soc., Div.Polymer Chem., Preprints 7 (2), 1146-51 (1966)

ELEUTERIO, H.S. and MOORE, E.P. : Preprints 2nd International Symposium on Fluorine Chemistry, Estes Park, Col., p. 3 (1962)

FERGUSON, R.C. : J. Am. Chem. Soc., 82, 2416 (1960)

FERGUSON, R.C. : Kautsch. Gummi Kunststt., 18, 723 (1965)

FINEMAN, M. and ROSS, S.D. : J. Polym. Sci., 5, 259 (1950)

FOGIEL, A.W. : J. Polym. Sci., Polym. Symp., 53, 333 (1975)

FOX, T.G. : Bull. Am. Phys. Soc., 1, 123 (1956)

GAL'PERIN, L. KOSMYNIN, B.P. and SMIRNOV, V.K. : Polym. Sci. USSR (Engl. Transl.), A 12, 2133 (1970)

HASEGAWA, R., KOBAYASHI, M. and TADOKORO, H. : Polymer J., 3, 591 (1972)

JANACEK, J. : Polymer Lett., 13, 409 (1975)

MIGLIERINA, A. and CECCATO, G. : Int. Syn. Rubber Symp., Lect., 4th, No. 2,65 (1969); Chem. Abstr., 74, 4403 j (1971)

MOGGI, G., GERI S., FLABBI, L. and AJROLDI, G. : Proc. Int. Rubber Conf. 1979, 1015; Chem. Abstr., 92, 199556 p (1980)

RIOS, L. and GUILLOT, J. : Makromol. Chem., 181, 941 (1980)

SCHMIEGEL, W.W. : Kautsch. Gummi Kunststt., 31, 177 (1978)

STALLINGS, J.P. and HOWELL, S.G. : Polym. Eng. Sci., 11, 507 (1971)

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