Radical solution copolymerisation of vinylidene fluoride with hexafluoropropene

Bruno Ameduri, Marie Pierre Gelin

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Marie-Pierre Gelin, Bruno Ameduri[*]

Laboratoire de Chimie Macromoléculaire, UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier,
8, Rue Ecole Normale, 34296 Montpellier Cedex 05, France

Dedicated to our friend Dick Chambers in honour of his 70th birthday.

Abstract

The radical copolymerisation in solution of vinylidene fluoride (or 1,1-difluoroethylene (VDF)) with hexafluoropropylene (HFP) initiated by di-*tert*-butyl peroxide is presented. A series of eight copolymerisation reactions was investigated with initial $[VDF]_o/[HFP]_o$ molar ratios ranging from 5.0/95.0 to 85.2/14.8. Both co-monomers copolymerised in this range of copolymerisation. Moreover, only VDF homopolymerised in these conditions. The copolymer compositions of these random-type copolymers were calculated by means of ^{19}F NMR spectroscopy which allowed the respective amount of each monomeric unit in the copolymer to be quantified. The Tidwell and Mortimer method led to the assessment of the reactivity ratios, r_i, of both co-monomers showing a higher incorporation of VDF in the copolymer ($r_{HFP} = 0.12 \pm 0.05$ and $r_{VDF} = 2.9 \pm 0.6$ at 393 K). Alfrey–Price's Q and e values of HFP were calculated to be 0.002 (from $Q_{VDF} = 0.008$) or 0.009 (from $Q_{VDF} = 0.015$) and +1.44 (versus $e_{VDF} = 0.40$) or +1.54 (versus $e_{VDF} = 0.50$), respectively, indicating that HFP is an electron-accepting monomer. The thermal properties of these fluorinated copolymers were also determined. Except for those containing a high amount of VDF, they were amorphous. Each showed one glass transition temperature (T_g) only, and from known laws of T_g, that of the homopolymer of HFP was assessed. It was compared with that obtained from the literature after extrapolation and is discussed.

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1. Introduction

Radical copolymerisations of fluorinated monomers with hydrogenated or fluoroolefins have recently been reviewed [1]. In the case of the copolymerisation of vinylidene fluoride (1,1-difluoroethylene), VDF, numerous investigations have been performed with non-halogenated [2,3] or fluorinated co-monomers [1,4,5]. Among them, hexafluoropropylene (HFP) has already led to commercially available thermoplastics [6] (Table 1), elastomers [7] (Table 2) or thermoplastic elastomers [1,7,8], since the discovery of poly(VDF-co-HFP) copolymers in 1957 by Du Pont de Nemours company [9]. These copolymers are produced on an industrial scale by Du Pont, Solvay Solexis, 3M/Dyneon, Daikin and Atofina (now Arkema). They are endowed with good thermal properties and chemical inertness to acids and petroleum and have found numerous applications in various fields such as automobiles, space, aeronautics, electronics and engineering.

The kinetics of copolymerisation of VDF with HFP have been studied by Moggi et al. [10] and by Pianca et al. [11] under emulsion polymerisation. However, kinetics was not carried out in solution.

The objectives of this paper are to revisit the radical copolymerisation of VDF with HFP in solution and in batch.

Table 1
Main commercially available VDF-containing thermoplastics (HFA stands for hexafluoroacetone)

Monomers	Composition (mol%)	Trade name	Producer	Melting point (°C)
VDF/CTFE	90/10 or 95/5	FORAFLON®	Arkema	165–167
	id.	KF POLYMER®	Kureha	–
		SOLEF®	Solvay Solexis	150–165
VDF/TFE	80/20	KYNAR®SL, 7299	Arkema N.A.	120
VDF/HFA	88/12	–	Central Glass	121
VDF/HEP	95/5 or 85/15	KYNARFLEX®	Arkema N.A.	135–160
		SOLEF®	Solvay Solexis	130–160
VDF/TFE/HFP	72/18/10	KYNAR® ADS	Arkema N.A.	90
VDF/TFE/HEP	30/55/15	HOSTAFLON®	Dyneon	160–185
(VDF/CTFE)-g-VDF	(37.5/12.5)/50	CEFRALSOFT®	Central Glass	170

Table 2
Main commercial VDF-containing elastomers

	HFP	PMVE	CTFE	P	HPFP
VDF	Daiel 801® (Daikin)	–	Kel F® (Dyneon)	–	Tecnoflon SL® (Montecatini)
	Fluorel® (3M/Dyneon)		SKF-32® (Russia)		
	Tecnoflon® (Solvay Sol)		Voltalef® (Elf Atochem)		
	SKF-26® (Russia)				
	Viton A® (Du Pont)				
TFE	–	Kalrez® (Du Pont)	–	Aflas® (Asahi Glass)	–
				Extreme®	
				(Du Pont Dow Elastomers)	
VDF + TFE	Daiel 901® (Daikin)	Viton GLT® (Du Pont)	–	–	Tecnoflon T® (Montecatini)
	Fluorel® (Dyneon)				
	Tecnoflon® (Solvay Sol)				
	Viton B® (Du Pont) + ethylene:				
	Tecnoflon® (Solvay Sol) + X:				
	Viton GH® (Du Pont)				

CTFE	Chlorotrifluoroethylene	$F_2C = CFCl$	
HFP	Hexafluoropropylene	$F_2C = CFCF_3$	
HPFP	1-Hydro-pentafluoropropylene	$FHC = CF–CF_3$	
P	Propylene	$H_2C = CHCH_3$	
PMVE	Perfluoromethyl vinyl ether	$F_2C = CFOCF_3$	
TFE	Tetrafluoroethylene	$F_2C = CF_2$	
VDF	Vinylidene fluoride (or 1,1-difluoroethylene)	$F_2C = CH_2$	
X	Cure site monomer	$XCY = CZ-R-G$ (G: function)	

A kinetic approach enabled us to assess the reactivity ratios of both co-monomers and to compare them with those in the literature; then, the thermal properties (especially glass transition temperatures) of these fluorocopolymers have been investigated.

2. Results and discussion

The radical copolymerisation of vinylidene fluoride (VDF) with hexafluoropropylene (HFP) was performed in batch and in solution (in acetonitrile), initiated by di-*tert*-butyl peroxide at 393 K for about 10 h, as follows:

$$CH_2=CF_2 \ + \ \underset{CF_3}{CF=CF_2} \ \xrightarrow{\text{Radical}} \ \underset{CF_3}{\left[(CH_2CF_2)_n-CF_2CF\right]_p}$$

At 393 K, half-life of the organic peroxide was ca. 6 h.

Acetonitrile was chosen as solvent because it solubilises both fluoroalkenes and does not generate much transfer [12]. Because both co-monomers are gaseous (b.p. of VDF and HFP are 191 and 245 K at atmospheric pressure, respectively), the copolymerisation reactions of VDF with HFP were carried out in an autoclave or in thick Carius tubes. Eight experiments were carried out under these conditions assuming that ca. 10–12% of VDF was converted; the results are listed in Table 3.

Table 3
Experimental results of the radical copolymerisation of VDF with HFP at 393 K (initiated by di-*tert*-butyl peroxide)

Experiment no.	Mol.% VDF (in feed)	C_0 (%)	Time (h)	Mol.% VDF in the copolymer
1	85.2	1.2×10^{-3}	11	93.7
2	75.0	1.1×10^{-3}	10	89.3
3	69.3	1.0×10^{-3}	10	88.4
4	49.5	1.1×10^{-3}	11	78.1
5	39.7	1.1×10^{-3}	10	71.0
6	29.5	1.1×10^{-3}	11	65.3
7	21.6	1.1×10^{-3}	10	53.4
8	5.0	1.3×10^{-3}	11	27.0

2.1. Characterisation of the microstructure of the copolymers

After reaction, poly(VDF-co-HFP) copolymers were precipitated from cold pentane, leading to viscous oils which were characterised by NMR spectroscopy. As extensively reported by Pianca et al. [11], all ^{19}F NMR spectra (Fig. 1) show the presence of signals in the range of −90 to −95, at −104, −110, −113, −116 ppm characteristic of CF$_2$ in VDF units (normal and reversed) [12–14] and at −70, −75, −119 and −182 ppm assigned to HFP units. As mentioned by Schmiegel [15], two consecutive HFP units were not observed, in contrast to the situation previously noted in R$_F$(HFP)$_2$I telomers produced by stepwise telomerisation of HFP with perfluoroalkyl iodides [16].

The mol.% of VDF in the copolymer was calculated as follows (Eq. (1)), taking into account I_{-i} which represents the integral of the signal centred at $-i$ ppm:

$$\text{mol.}\% \text{ VDF}$$
$$= \frac{I_{-91} + I_{-93} + I_{-104} + I_{-110} + I_{-113} + I_{-116}}{I_{-91} + I_{-93} + I_{-104} + I_{-110} + I_{-113} + I_{-116} + I_{-119}} \tag{1}$$

In addition, the defects of chaining are very low (these defects of chaining are the head-to-head VDF units or reversed VDF diad –CH$_2$CF$_2$–CF$_2$CH$_2$–), which was deduced from the calculation of $I_{-116}/(I_{-91} + I_{-93} + I_{-104} + I_{-110} + I_{-113} + I_{-116})$ [=3.4%] from Fig. 1 (the copolymer containing 78.0 mol.% VDF).

Starting from a VDF mol.% in the feed of ca. 49.5%, such a value (78.0 mol% VDF) is consistent with those of fluoroelastomers [10,11], taking into account the following reactivity ratios of VDF and HFP:

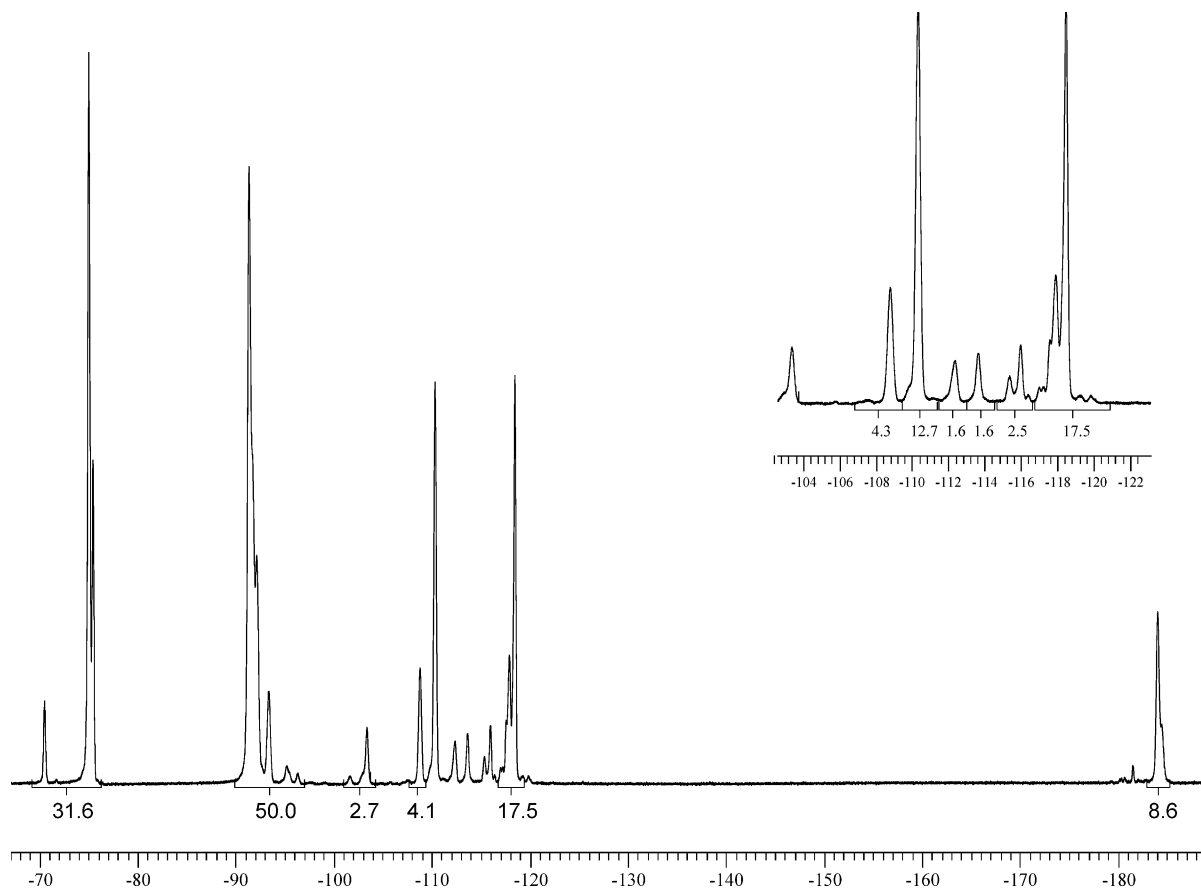$r_{VDF} = 6.70$, $r_{HFP} = 0$ [10], $r_{VDF} = 2.45$ and $r_{HFP} = 0$ [11]

Fig. 1. ^{19}F NMR spectrum of poly(VDF-co-HFP) copolymer obtained from the radical copolymerisation of VDF with HFP (molar feed 49.5/50.5) initiated by di-*tert*-butyl peroxide at 393 K for 10 h.

for which these copolymerisations were achieved in emulsion.

Table 3 shows the results of copolymerization and indicates that for the eight copolymerisation reactions, the molar amounts of VDF in the copolymers are always higher than those introduced in the feed, showing that the VDF incorporates the copolymer better than does HFP.

Regarding the ^{1}H NMR spectra of the copolymer, the absence of both the triplet of triplets and the doublet of multiplets centered at 6.2 and 7.0 ppm, assigned to CH_2CF_2H and $–CH_2–CF(CF_3)H$, respectively, indicates the absence of any hydrogen abstraction and hence of any transfer [12,13,16].

Moreover, the copolymerisation of both co-monomers occurred over the entire range of composition used, assuming that no homopolymerisation of VDF occurred under these conditions. On the basis of solubility, it was found that except for the polymer obtained from the radical homopolymerisation of VDF (soluble in dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and in dimethyl acetamide (DMAc)), all the poly(VDF-co-HFP) copolymers were soluble in acetone, DMF, DMAc, or in DMSO. This also evidences that no PVDF was produced in the copolymerisation.

2.2. Kinetics of copolymerisation

Fig. 2 represents the monomer–polymer copolymerisation curve of mol.% VDF in copolymer versus mol.% VDF in feed. All points are located above the bisector showing a higher reactivity of VDF than HFP. By nonlinear curve fitting, using the Tidwell and Mortimer method [17], the reactivity ratios of both co-monomers were assessed. We have found:

$$r_{VDF} = 2.9 \pm 0.6 \quad \text{and} \quad r_{HFP} = 0.12 \pm 0.05 \text{ at } 393 \text{ K}$$

The maximum intervals of confidence calculated according to Carcano et al. [18] seem to be overestimated. The reactivity ratio of HFP was almost nil confirming that this
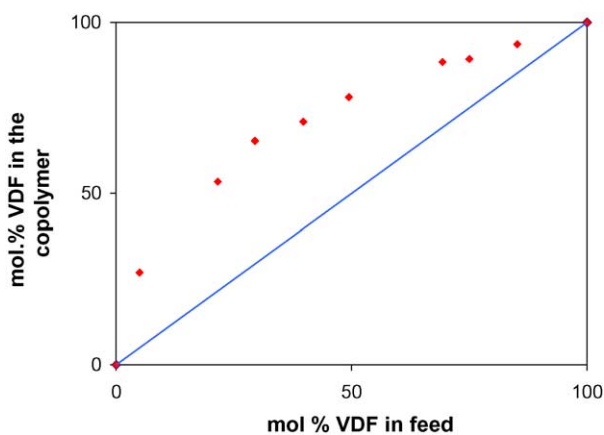

Fig. 2. Polymer/monomer composition curve for the radical copolymerisation of VDF with HFP (initiated by di-*tert*-butyl peroxide at 393 K).

fluoroalkene does not homopolymerise. The product $r_{VDF} \times r_{HFP} = 0.348$, higher than 0, shows that random copolymers have been formed. Because $r_A > 1$ and $r_B < 1$ (where A and B represent VDF and HFP, respectively), one can consider that the rate constants k can be compared as follows: $k_{AA} > k_{AB}$; $k_{BB} < k_{BA}$ showing that both radicals $\sim\sim CH_2CF_2^\bullet$ and $\sim\sim CF_2CF^\bullet(CF_3)$ have a high tendency to react with HFP. In addition, the large difference between both reactivity ratios shows that VDF radicals are more reactive than HFP radicals towards the monomer pair.

Table 4 enables the comparison of the reactivity ratios of these couples of monomers to those of other pairs involving VDF [19–39]. The co-monomers were classified according to the number of fluorine atoms or fluorinated groups born by their ethylenic carbon atoms. However, it is rather difficult to compare the behaviour in copolymerisation of all these couples of monomers since their kinetics of copolymerisation were not carried out in the same conditions of initiating systems, temperature, time, and monomer conversions. Furthermore, the interval of confidence is not given for the reactivity ratios of all the co-monomers.

A general tendency appears to be that the higher the number of fluorine atoms linked to the ethylenic carbons of the co-monomers, the lower the reactivity of this co-monomer, especially when bulky groups are born by the double bond (e.g., perfluoromethyl vinyl ether (PMVE), perfluoropropyl vinyl ether (PPVE), methyl trifluoroacrylate (MTFA), pentafluoropropene (PFP), pentafluoropropene-2-acid fluoride, and HFP).

The traditional method for the determination of relative reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the values $1/r_A = k_{AB}/k_{AA}$ as the ratio of rate constants of cross-propagation to that of propagation (k_{AA}). Thus, the higher the $1/r$ value, the more able the radical is to react with the second monomer. Table 4 allows us to suggest the following series of relative reactivities of monomers to $\sim\sim CH_2CF_2^\bullet$ radicals: HFO < PFP < HFP < PMVE < PPVE < VDF< C4Br < TrFE < CTFE (recent value) $\approx$ BrTFE < MDP< MTFA < TFE < FSAc < FAc < VF $\approx$ CTFE (old value) < E.

Q and e values (linked to the resonance and to the inductive effects of the monomer, respectively) of HFP can be determined from those of VDF taking into account Alfrey and Price's theory [40], as follows:

$$e_2 = e_1 \pm [-\ln(r_1 \times r_2)]^{1/2} \tag{2}$$

$$Q_2 = \frac{Q_1}{r_1}\exp[-e_1(e_1 - e_2)] \tag{3}$$

where Q_i and e_i represent these parameters and r_i the reactivity ratio of monomer i.

For fluoromonomers, it is known that e value is always positive since these are electron-withdrawing monomers [1].

However, a low Q value indicates that the system is few stabilised by resonance. According to classic tables [1,41],

Table 4

Monomer reactivity ratios for the copolymerisation of VDF (A) with other fluoroalkenes (B) (and ethylene (E) and vinyl acetate (VAc))

Monomer B	r_A	r_B	$r_A r_B$	$1/r_A$	Ref.
$H_2C = CH_2$ (E)	0.05	8.5	0.42	20.00	[19]
$H_2C = CHOCOCH_3$ (VAc)	−0.40	1.67	−0.67	−2.5	[20]
	0.50	2.0	1.00	2.0	[21]
$H_2C = C(CF_3)CO_2H$ (TFMAA)	0.33	0	0	3.03	[22]
$FCH = CH_2$ (VF)	0.17	4.2–5.5	0.71–0.94	5.88	[23]
	0.20–0.43	3.8–4.9	0.76–2.11	2.33–5.00	[24]
$H_2C = CFCF_2OR_F$ (MDP)	0.38	2.41	0.92	2.63	[25]
$F_2C = CFH$ (TrFE)	0.70	0.50	0.35	1.43	[26]
$F_2C = CHCF_3$ (PFP)	9.0	0.06	0.54	0.11	[27]
$F_2C = CHC_6F_{13}$ (HFO)	12.0	0.90	10.80	0.08	[28]
$CFCl = CF_2$ (CTFE)	0.73	0.75	0.55	1.37	[29]
	0.17	0.52	0.09	5.88	[30]
$CFBr = CF_2$ (BrTFE)	0.43	1.46	0.63	2.33	[29]
$CF_2 = CF_2$ (TFE)	0.23	3.73	0.86	4.35	[11,29]
	0.32	0.28	0.09	3.13	[31]
$CF_3\text{-}CF = CF_2$ (HFP)	6.70	0	0	0.15	[10]
	2.45	0	0	0.40	[11]
	2.90	0.12	0.35	0.34	This work
$F_2C = CFOCF_3$ (PMVE)	3.40	0	0	0.29	[32]
$F_2C = CFOC_3F_7$ (PPVE)	1.15	0	0	0.86	[32]
$F_2C = CFO(HFP)OC_2F_4SO_2F$ (PSEPVE)	0.57	0.07	0.04	1.75	[1]
$CF_2 = CFCH_2OH$ (FA1)	0.83	0.11	0.09	1.02	[33]
$CF_2 = CF(CH_2)_2Br$ (C4Br)	0.96	0.09	0.09	1.00	[34]
$CF_2 = CF(CH_2)_3OAc$ (FAc)	0.17	3.26	0.59	5.56	[35]
$F_2C = CF(CH_2)_3SAc$ (FSAc)	0.60	0.41	0.25	4.07	[36]
$CF_2 = CFCO_2CH_3$ (MTFA)	0.30	0	0	3.33	[37]
$F_2C = C(CF_3)COF$	7.60	0.02	0.15	0.13	[38]
$F_2C = C(CF_3)OCOC_6H_5$	0.77	0.11	0.08	1.30	[39]

the value of HFP is among the lowest, confirming that this monomer is poorly reactive; this may explain why it does not homopolymerise ($r_{HFP} \approx 0$).

Taking into account that $e_{VDF} = 0.40$ [31] or 0.50 [41] and $Q_{VDF} = 0.008$ [31] or 0.015 [41], two e and Q values have been assessed for HFP. We have found that

$$e_{HFP} = 1.44 \text{ or } 1.54 \quad \text{and} \quad Q_{HFP} = 0.002 \text{ or } 0.009$$

The e_B (HFP) value is positive, $e_B = 1.44$ (from $e_A = 0.40$) or $e_B = 1.54$ (from $e_A = 0.50$) while those of VDF are lower than that of trifluoroethylene (TrFE) ($e_{TrFE} = 1.15$) [1,41], due to the lower electron-withdrawing effect because of both hydrogen atoms substituent versus the fluorine atom in TrFE. The e-values for VF given in the literature are rather different, and even negative [23] ($e_{VF} = −0.50$ [23] or −0.80 [24]). Thus, in the latter case, the hydrogen atom seems to act as an *electron-donating substituent*. But for HFP as for other co-monomers, the e-value is always positive due to the electron-withdrawing effect of fluorine atoms. Thus, mainly random copolymerisation between VDF and HFP is expected.

The Q-value of HFP is very small (0.002–0.009) which is good evidence for the poor ability of a fluorine atom for resonance stabilization of the radical on the adjacent carbon atom. Hence, the HFP radical has to be highly unstable.

2.3. Assessment of the glass transition temperature (T_g) of poly(VDF-co-HFP) copolymers

It was first observed that all copolymers analysed by differential scanning calorimetry (DSC) showed a sharp transition from the glassy to viscoelastic zone, as noted by the presence of only one sharp T_g. Although DSC was also carried out on all these samples from 343 to 448 K, the presence of crystallisation or melting temperatures was observed for copolymers containing a high VDF percentage.

The T_g values range between 232.9 and 261.4 K (Table 5) indicates that the copolymers exhibit amorphous and elastomeric behaviours, as expected. Interestingly, it is observed that the higher the VDF content, the lower the T_g, since, as expected, the branched –CF$_3$ side group (arising

Table 5

Glass transition temperatures of poly(VDF-co-HFP) copolymers

Experiment no.	% VDF in the copolymer	T_g (K)
1	27.0	261.4
2	53.4	245.9
3	71.0	239.6
4	78.1	237.4
5	88.4	235.4
6	89.3	232.9

from HFP) about the polymeric backbone induces an increase of the T_g values.

Hence, it was worth determining the T_g of the homopolymer of HFP. To our knowledge, the only homopolymerisation of HFP was achieved by Eleuterio and Pensak [42], initiated by severe conditions of ultra-high pressure.

Usually, several relationships for the T_g of blends are used in the literature [43–47]. We have chosen Fox's [44] and Johnston's [45] relationships:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{4}$$

where T_g, T_{g_1} and T_{g_2} represent the glass transition temperatures (in Kelvin) of the copolymer, of PVDF and of poly(HFP) while w_1 and w_2 stand for the initial massic percentages of VDF and HFP, respectively.

This relationship is usually successful for high molecular weights and although we could not assess those of these copolymers (lack of standards), it was found that no transfer was observed in the course of the copolymerisations. This was checked by the absence of both the triplet of triplets centred at 6.3 ppm and of doublet of multiplets at -114.8 ppm in the ^1H and ^{19}F NMR spectra, respectively.

This law can be written as follows:

$$w_2 = T_{g_2} \left(\frac{1}{T_g} - \frac{w_1}{T_{g_1}} \right) \tag{5}$$

Thus, plotting w_2 versus $\left(\frac{1}{T_g} - \frac{w_1}{T_{g_1}} \right)$ leads to a straight line, the slope of which represents the glass transition temperature of poly(HFP) (Fig. 3).

Hence, poly(HFP) has a T_g of 264.47 K which is much lower than that determined by Bonardelli et al. [48] (Table 6).

On the other hand, the T_g value of this homopolymer is not surprising when compared to that of poly($H_2C=CFCF_3$) ($T_g = 315$ K) [47].

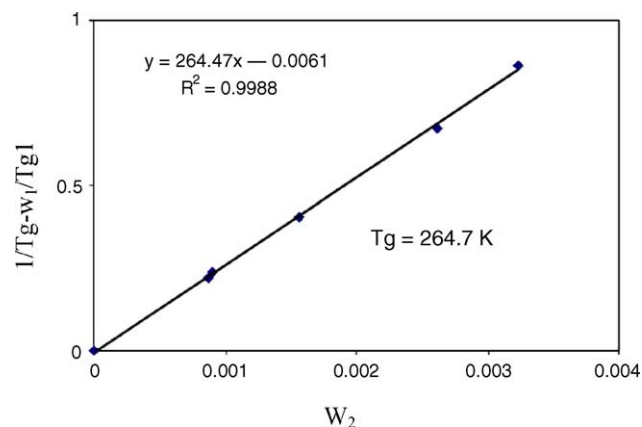But, another relationship has also been used as Johnston's equation [45] which seems more rigorous than the one above

Table 6
Results of different glass transition temperatures of poly(HFP) compared to those of the literature

T_g of poly(HFP) (°C)	Reference
284	[50]
425	[47]
433	[48]
265	Our work (from Fox' relationship)
270	Our work (from Johnson's relationship)
287	Our work (from Johnson's relationship)

because it takes into account the affinity of monomers, considering the probabilities of additions, as follows:

$$\frac{1}{T_g} = \frac{w_A P_{AA}}{(T_g)_{AA}} + \frac{w_B P_{BB}}{(T_g)_{BB}} + \frac{w_A P_{AB} + w_B P_{BA}}{(T_g)_{AB}} \tag{6}$$

where P_{AA}, P_{BB}, P_{AB} and P_{BA} represent the conditional probabilities of addition.

$$P_{AB} = \frac{1}{1 + r_A X}, \qquad P_{AA} = 1 - P_{AB},$$

$$P_{BA} = \frac{1}{1 + r_B / X}, \qquad P_{BB} = 1 - P_{BA}$$

where r_A and r_B represent the respective reactivity ratios.

For each composition, X, which stands for the molar ratio (A/B) has to be calculated.

By plotting $w_B P_{BB}$ versus $[1/T_g - (w_A P_{AB} + w_B P_{BA})/T_{gAB} - w_A P_{AA}/T_{gAA}]$, the slope supplies the glass transition temperature of poly(HFP). T_{gAB} represents the glass transition temperature of the alternating poly(VDF-alt-HFP) copolymer. According to the literature, such a value worths 273 K [48] but from the results mentioned above it is considered as 246 K. Such a latter value differs from the former because the copolymers were synthesised under different experimental conditions. Hence, the resulting copolymers were endowed with various molar masses, since from emulsion copolymerisation, high molar mass-polymers are usually produced in contrast to those obtained from solution copolymerisation.

Figs. 4 and 5 represent the straight lines obtained from the equation above in the case where the T_g of poly(VDF-alt-

Fig. 3. $1/T_g-w_1/T_g$ vs. w_2 for the assessment of the T_g of poly(HFP) according to Fox's relationship [44].
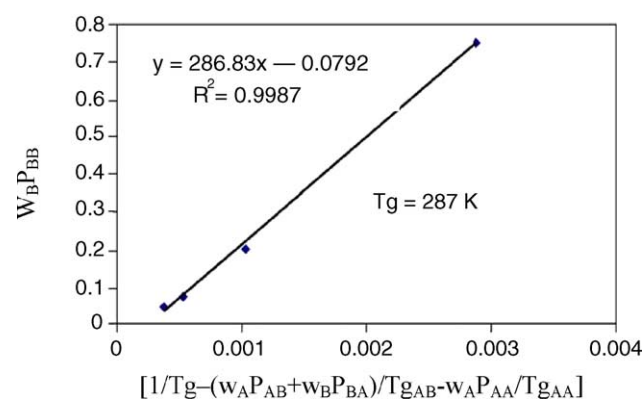

Fig. 4. Assessment of the T_g of poly(HFP) according to Johnston's equation [45] and $(T_g)_{AB} = 273$ K, by plotting $w_B P_{BB}$ vs. $[1/T_g - (w_A P_{AB} + w_B P_{BA})/T_{gAB} - w_A P_{AA}/T_{gAA}]$.
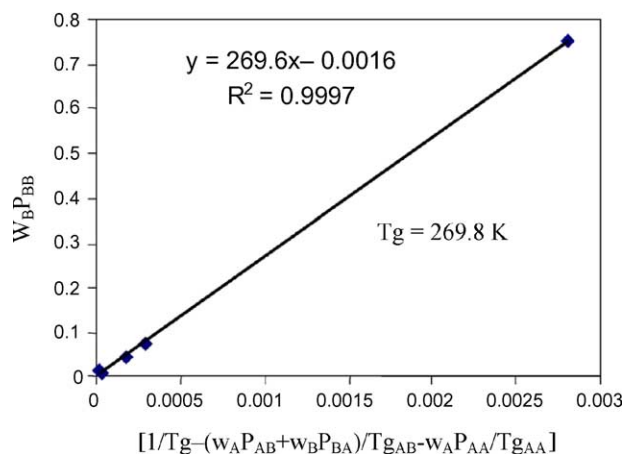
Fig. 5. Determination of the T_g of poly(HFP) according to Johnston's relationship [45] using $(T_g)_{AB} = 246$ K, by plotting $w_B P_{BB}$ vs. [$1/T_g - (w_A P_{AB} + w_B P_{BA})/T_{gAB} - w_A P_{AA}/T_{gAA}$].

HFP) copolymer worths 273 and 246 K, respectively. It is normal to find a value for poly(HFP) (ranging from 270 to 287 K, respectively) much lower than that assessed by Brown and Wall [49] and Bonardelli et al. [48] who carried out emulsion copolymerisation. However, T_g value of poly(HFP) calculated from Johnston's relationship (287 K) is close to that assessed by Rodriguez [50] (284 K, Table 6). This difference can be explained by the introduction of both the probabilities of addition and the reactivity ratios in that equation. Indeed, drifts in the determination of the reactivity ratios can also be observed.

In fact, the poly(VDF-co-HFP) copolymers obtained by solution polymerisation show lower molar masses than those achieved from emulsion copolymerisation.

3. Conclusion

The radical copolymerisation of vinylidene fluoride (VDF) with hexafluoropropene (HFP) was studied in a wide range of initial monomer compositions. ^{19}F NMR spectroscopy enabled the copolymer compositions to be determined. The reactivity ratios r_i of co-monomers were calculated by the Tidwell and Mortimer method, showing that, as expected, HFP was less reactive than VDF ($r_{VDF} = 2.9$ and $r_{HFP} = 0.12$ at 393 K). These values demonstrate that a random copolymerisation occurred. For HFP mol. contents higher than 15%, the resulting copolymers exhibit amorphous behaviour even with rather low T_g, confirming potential applications of these materials at low temperatures. Extrapolation of these results, taking into account the classical relationship of T_g, could enable the T_g of poly(HFP) to be assessed, although the relationship of determination of the glass transition temperatures have led to various values from Fox's or Johnston's equations. However, the second law led to a value close to that observed by Rodriguez [50].

Nevertheless, lowering the T_g of poly(VDF-co-HFP) fluoroelastomers below 241 K is still a challenge and such a research could be quite attractive for industrial and academic researchers.

4. Experimental

Vinylidene fluoride (VDF) and HFP were kindly donated by Solvay S.A., whereas di-*tert*-butyl peroxide and acetonitrile (freshly distilled over calcium hydride) were supplied by Aldrich and SDS, respectively.

Radical copolymerisations of VDF and HFP were performed in thick borosilicate Carius tubes in a batch process (length: 130 mm, internal diameter: 10 mm, thickness: 2.5 mm, for a total volume of 8 cm³). After having placed the initiator (ca. 1 mol.% to the monomer mixture), and acetonitrile in the tube, it was connected to a vacuum line and purged several times by evacuating and flushing with helium. After a minimum of six thaw–freeze cycles performed to remove oxygen, VDF was trapped under vacuum in the tube frozen in liquid nitrogen, after a release in an intermediate metallic container calibrated in pressure. The required amount of VDF (0.147–1.324 ± 0.008 g) introduced into the tube was assessed by the relative drop of pressure in this release container, initially fed from a cylinder of 300 g of VDF (Table 3). A beforehand calibration curve 'weight of trapped VDF (in g) versus drop of pressure (in bar)' was consulted (for 1.324 g of VDF, a difference of pressure of 0.90 bar was required). The same procedure was achieved for introducing HFP (from a cylinder containing 150 g of that monomer) in the frozen tube (after purging and flushing the tubings and connections). As above, the accurate introduction of HFP was achieved by taking into account a beforehand calibration curve 'weight of trapped HFP (in g) versus drop of pressure (in bar)' (in fact, for 1.000 g of HFP introduced, a difference of pressure of 0.25 bar was necessary). The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed into a shaking oven at 393 K for 10 h. In such a reaction time, it was considered that the VDF conversion was ca. 10–12% that was suitable for satisfactory conditions of kinetics of copolymerisation although VDF conversion was not assessed because of the lack of accuracy in weighing the opened frozen tube. Nevertheless, it was assumed that this conversion rate must be higher than that of HFP, taking into account both known reactivity ratios.

The reactant weights used in these eight copolymerisation reactions are listed in Table 3.

After copolymerisation, the tube was frozen in liquid nitrogen and then opened, and the total product mixture added dropwise into 50 ml of vigorously stirred cold pentane. This enabled the copolymer to be separately phased as a sticky oil (copolymer containing HFP contents higher than 15 mol%), wax or powder (for copolymers with high

VDF contents) deposited along the walls of the container. After removing the pentane solution, the remaining copolymer was dried at 80 °C under 10^{-2} Torr until constant weight was achieved.

The compositions of the copolymers (i.e., the content of VDF and HFP in copolymers) were determined by NMR spectroscopy at room temperature. The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC-200 or Bruker AC-250 instruments using deuterated acetone, and tetra-methyl silane (TMS) or $CFCl_3$, as the solvent and internal reference, respectively. The experimental conditions for recording ^{1}H (or ^{19}F) NMR spectra were the following: flip angle $90°$ $(30°)$; acquisition time 4.5 s (0.7 s); pulse delay 2 s (5 s); 64 (128) scans and pulse width of 5 µs for ^{19}F NMR. The letters s, t and m represent singlet, triplet and multiplet, respectively.

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer; the apparatus was calibrated with indium and with n-decane. After its insertion into the DSC apparatus, the sample was initially cooled to 168 K for 15 min. The first scan was made at a heating rate of 40 °C min^{-1}, up to 353 K, where it remained for 2 min. It was then cooled to 168 K at a rate of 320 °C min^{-1}. It was again left for 10 min at that temperature before a second scan was started at a heating rate of 20 °C min^{-1}. Finally, another cycle was performed and a third scan at a heating rate of 20 °C min^{-1} was initiated, giving the values of T_g reported herein, taken at the half-height of the heat capacity jump of the glass transition. A second series of scanning was also attempted from 343 to 448 K and the thermograms of all the samples containing a high VDF amount show crystallisation or melting peaks.

Acknowledgments

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