Synthesis and microstructural characterization of low-molar-mass poly(vinylidene fluoride)

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The kinetic features of vinylidene fluoride (VDF) radical polymerization in solution, initiated by bis(4-t-butylcyclohexyl)peroxydicarbonate, have been investigated in three different solvents (acetone, ethyl acetate and methyl acetate) under homogeneous conditions. Many significant deviations of the dependence of the polymerization rate on the 'ideal' 1.0 and 0.5 exponent values of monomer and initiator concentrations, respectively, are indicative of anomalous kinetic behaviours linked to concurrent reactions, which are operative during such polymerization. The complexity of the kinetic behaviour prevents, *inter alia*, the correct evaluation of chain transfer constants to the solvents from kinetic data. ^{19}F nuclear magnetic resonance spectroscopy has been used in order to get full microstructural characterization of the low-molar-mass poly(vinylidene fluoride) (PVDF) synthesized under the above conditions. Both chain transfer constants to the solvent and extent of chain inversions in PVDF have been evaluated by this technique.

(Keywords: poly(vinylidene fluoride); synthesis; ^{19}F nuclear magnetic resonance; characterization; microstructure)

INTRODUCTION

In the last two decades, many studies on the industrial applications of high-molar-mass poly(vinylidene fluoride) (PVDF), mostly focused on its excellent piezo- and pyroelectric behaviours, have been the subject of hundreds of papers and patents. This increasing interest in PVDF has stimulated extensive studies on its morphology and physical properties, as well as on its microstructure. An excellent review on the whole subject[1] has been published in 1982.

In order to clarify the role of structural defects on various polymer properties, it is necessary to synthesize PVDF of well defined microstructure, under rigorously controlled conditions[2,3]. The synthesis of low-molar-mass PVDF is particularly suitable in this respect, since it can provide high-purity standards for identification of various types of enchainments and end-groups by ^{19}F n.m.r. However, the homopolymerization of vinylidene fluoride (VDF) to low-molar-mass products has received little attention so far, despite its further relevant importance not only as model studies in polymerization kinetics but also for potential applications of this material, e.g. as a processing aid. Very recently, low-molar-mass PVDF has been prepared by suspension polymerization of its monomer in aqueous medium[4].

The present study is part of a research programme devoted to the homo- and copolymerization of VDF to low-molar-mass products[5-7]. Since 1986, we have undertaken a systematic investigation of VDF solution polymerization in order to study the kinetic features of its polymerization under strictly homogeneous conditions. Here, ^{19}F n.m.r. spectroscopic techniques have been applied in order to evaluate both the extent of chain inversions and the experimental values of chain transfer constants to three solvents (i.e. acetone, methyl acetate and ethyl acetate) at 55°C.

EXPERIMENTAL

Acetone, ethyl acetate and methyl acetate were purified by distillation. VDF was supplied by Ausimont, Italy, and used without further purification. The initiator, bis(4-t-butylcyclohexyl)peroxydicarbonate (Percadox 16), was provided by Akzo Chemicals, The Netherlands, and recrystallized from acetone/water mixture.

Polymerizations were carried out in a stainless-steel reaction vessel with two inlets — one in the form of a small cylinder for injecting the initiator solution, and the other for introducing the gaseous monomer. On the head of the reaction vessel there were two outlets, one for

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sampling the solution mixture to be analysed by gas chromatography, and the other connected to a pressure gauge.

Measured amounts of solvent (which acts also as a chain transfer agent) were introduced into the reaction vessel and, by freezing, pumping and thawing cycles, the dissolved oxygen was almost completely removed. Additional flushes of dry nitrogen were used in order to remove residual traces of oxygen. VDF was then introduced into the reaction vessel, kept at liquid nitrogen temperature. The amount of monomer introduced was calculated from the decrease in pressure of a glass reservoir of known volume. The reaction vessel was then kept in a water bath, maintained at 55°C. At the pressure developed in the vessel at that temperature, VDF is partly solubilized in the solvent; its concentration in the solution was calculated from the mass balance between the moles of monomer introduced and those in the gas phase (both in the empty space of the reactor and in the cylinder). The latter was evaluated, using the compressibility factor Z and its dependence on pressure, according to the equation[8]:

$$Z = 1.0003 - 6.3683 \times 10^{-3} p(\text{atm})$$

The concentration of monomer in solution was also directly measured by gas chromatography and values obtained by both methods agreed within ±5%. The polymerization started after injection of the initiator solution.

The weight of the polymer was determined by precipitation with a 10-fold volume of n-hexane, overnight stirring and Gooch filtration. No detectable traces of unprecipitated polymer were ever found.

The rate of polymerization was calculated from the expression:

$$R_p = \frac{10^3}{64.02} \frac{\text{grams of polymer}}{V_s t_p} (\text{mol dm}^{-3}\,\text{s}^{-1})$$

where 64.02 g mol^{-1} is the molar mass of the monomer, t_p is the polymerization time (s) and V_s is the volume of the solution (cm^3) at 55°C.

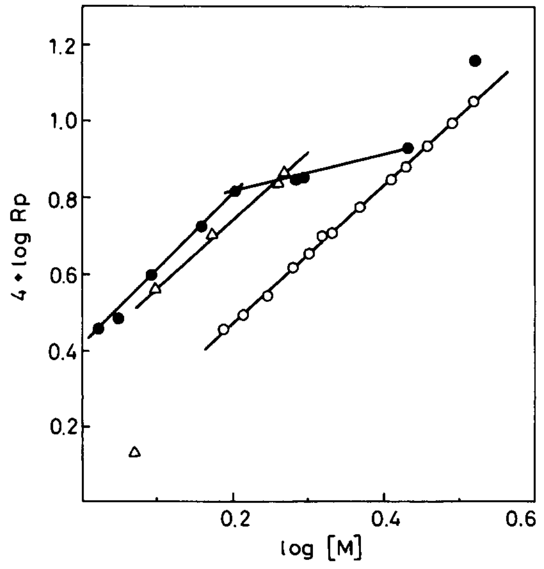

Figure 1 Double-logarithmic plot of the rate of polymerization R_p vs. the initial monomer concentration at 55°C. [Initiator] = 4.8×10^{-2} mol dm^{-3}. Solvent: acetone, open circles; methyl acetate, full circles; ethyl acetate, open triangles

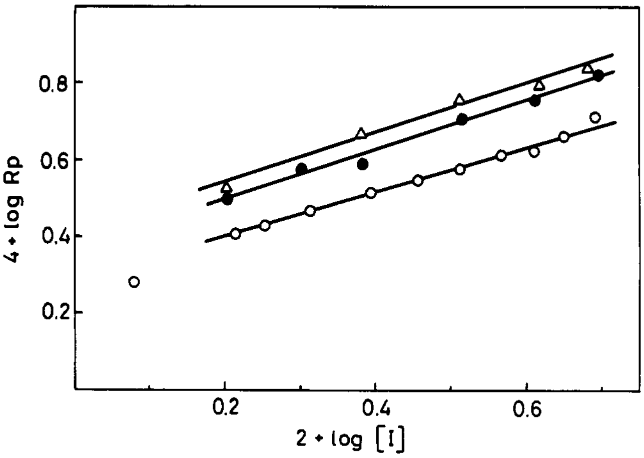

Figure 2 Double-logarithmic plot of the rate of polymerization R_p vs. the initial initiator concentration at 55°C. Acetone: open circles, [VDF] = 2.0 mol dm^{-3}. Methyl acetate: full circles, [VDF] = 1.5 mol dm^{-3}. Ethyl acetate: open triangles, [VDF] = 1.8 mol dm^{-3}

Preliminary experiments in pressurized glass vessels showed that all reacting systems remained homogeneous throughout the polymerization time chosen. During this period the conversion was linear with time. ^{19}F n.m.r. spectroscopic measurements were performed in hexadeuteroacetone solutions of the PVDF samples on a Varian XL 300 spectrometer operating at 300 MHz for ^{1}H and at 282.2 MHz for ^{19}F.

RESULTS AND DISCUSSION

Kinetics of polymerization

The rate of polymerization is correlated to the concentrations of monomer and initiator by the general equation:

$$R_p = k[\text{M}]^a[\text{I}]^b \tag{1}$$

In order to determine the values of exponents a and b, polymerizations were performed by changing the concentration of one of the reacting species and keeping the other constant. The experimental results are given in *Figures 1* and *2*.

In acetone (open circles), the values of a and b were found to be 1.78 and 0.49, respectively. However, the experimental points in *Figure 2* define a sigmoidal curve rather than a straight line, linear only in the central portion of the plot.

With methyl acetate as a solvent (full circles), the value a of monomer exponent (*Figure 1*) changes continuously as a function of [M]. For the sake of simplicity, two regions have been identified with almost linear dependences, corresponding to values of a close to 2.0 and 0.55 at lower and higher monomer concentrations, respectively. By contrast, a single value of b, equal to 0.65, was calculated over the whole range of initiator concentrations (*Figure 2*).

In ethyl acetate (open triangles), the values of a and b were found to be equal to 1.74 and 0.62, respectively. However, it is evident from *Figure 1* that, at the lowest [M], the corresponding R_p value is completely off the straight line and much lower than expected.

For homogeneous solution polymerizations, the classical expression for the rate of polymerization with respect to monomer and initiator concentrations is given by:

$$R_p=(2fk_dk_p^2/k_t)^{0.5}[M][I]^{0.5}$$
$$R_p=k'[M][I]^{0.5} \qquad (2)$$

where

$$k'=(2fk_dk_p^2/k_t)^{0.5}$$

The initiator exponent 0.5 implies that termination occurs solely by second-order termination reaction between the propagating chains[9]. Any process interfering with this assumption causes deviations from half-order dependence. As a consequence, monomer exponents different from unity can often be found. It is well known that such deviations may be due to various factors, such as primary radical termination[10], degradative chain transfer[11], or degradative addition[12].

In order to explain the experimental results of such non-ideal behaviour, different kinetic treatments have been proposed by various authors[13–15]. More recently, Deb[16,17] has given a detailed kinetic analysis for determining the effects of degradative chain transfer and primary radical termination, when acting simultaneously or alone. Unfortunately, plots of our data following any of the expressions given in the above references or similar equations failed to show a well defined pattern, despite the many (often unjustified) oversimplifications that have been introduced. As a consequence, rather complex reaction pathways should be envisaged for our systems and limitations of the kinetic analysis for interpreting the experimental results emphasized. Namely, true values of chain transfer constants to the solvent cannot be easily deduced from our kinetic data. On the contrary, careful evaluation of PVDF microstructure contains very useful information on the way growth and termination of PVDF chains can occur and permits an easy determination of the above chain transfer constants.

^{19}F n.m.r. studies

A typical ^{19}F n.m.r. spectrum of a low-molar-mass PVDF synthesized in acetone ($\bar{M}_n \approx 2300$) is given in *Figure 3*, where the capital letters, corresponding to the various peaks from A to E, identify signals attributed to sequences of seven carbon atoms having $-CF_2-$ in the centre, as shown in *Table 1*. The reported assignments are based on the corresponding attributions given in the literature[18–20] for high-molar-mass PVDF. Beside these, for our low-molar-mass PVDF it is also possible to identify various other signals (from F to N″, *Table 2*), pertaining to $-CF_2-$ groups situated close to the chain ends. The attribution of many of these signals has been confirmed by proton n.m.r. spectroscopy, as shown in *Figure 4*, which refers to a low-molar-mass PVDF synthesized in acetone, and *Table 3*, which contains also signals assigned to end-groups derived from other solvents. The signals correlated to $-CH_2-CF_2H$ and $-CF_2-CF_2-CH_3$ end-groups are present in the spectra published by many authors, but they had never been identified. Furthermore, the signal M (*Table 2*), which falls very close to signal E (*Table 1*), is not generally identified as a separate resonance and its intensity is usually added to that of signal E.

Table 1 ^{19}F n.m.r. peak assignments

Assignment	^{19}F δ (ppm) vs. CFCl$_3$
$-CH_2-CF_2-CH_2-\overset{A}{CF_2}-CH_2-CF_2-CH_2-$	−91.6
$-CH_2-CF_2-CH_2-\overset{A'}{CF_2}-CH_2-CF_2-CF_2-$	−92.1
$-CF_2-CH_2-CH_2-\overset{B}{CF_2}-CH_2-CF_2-CH_2-$	−94.8
$-CF_2-CH_2-CH_2-\overset{B'}{CF_2}-CH_2-CF_2-CF_2-$	−95.7
$-CH_2-CF_2-CH_2-\overset{C}{CF_2}-CF_2-CH_2-CH_2-$	−113.6
$-CH_2-CF_2-CH_2-\overset{E}{CF_2}-CF_2-CH_2-CF_2-$	−113.9
$-CF_2-CH_2-CH_2-\overset{D'}{CF_2}-CF_2-CH_2-CH_2-$	−115.6
$-CF_2-CH_2-CH_2-\overset{D}{CF_2}-CF_2-CH_2-CF_2-$	−116.0

Table 2 ^{19}F n.m.r. peak assignments

Assignment	^{19}F δ (ppm) vs. CFCl$_3$
$In-CH_2-\overset{F}{CF_2}-CH_2-CF_2-$	−102.4
$-CH_2-\overset{J}{CF_2}-CH_2-\overset{G}{CF_2H}$	−92.1(J) −115.1(G)
$-CF_2-CH_2-CH_2-\overset{K}{CF_2H}$	−117.3
$-CH_2-\overset{M}{CF_2}-\overset{L}{CF_2}-CH_3$	−107.3(L) −114.3(M)
$CH_3COCH_2-CH_2-\overset{N}{CF_2}-CH_2-CF_2-$	−94.3
$CH_3COOCH_2-CH_2-\overset{N'}{CF_2}-CH_2-CF_2-$	−93.1
$CH_3COOCH(CH_3)-CH_2-\overset{N''}{CF_2}-CH_2-CF_2-$	−92.9

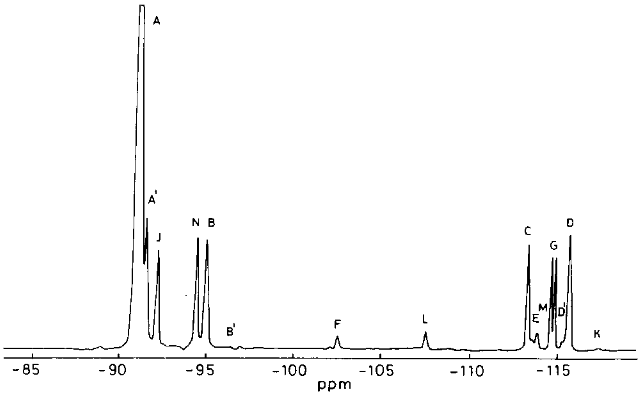

Figure 3 ^{19}F n.m.r. spectrum of a low-molar-mass PVDF synthesized in acetone

Using the information arising from n.m.r. analysis, it is possible to correlate the microstructure of PVDF to the different reaction pathways occurring during the polymerization. Namely, the signal F in the spectrum arises from the reaction of the first monomer molecule with the initiator:

$$In-CH_2-\overset{F}{CF_2}-CH_2-CF_2-CH_2-CF_2-$$

where In denotes the radical fragment from the initiator, after decomposition (primary radical). No detectable signal pertaining to primary addition to the monomer in inverted position has been found.

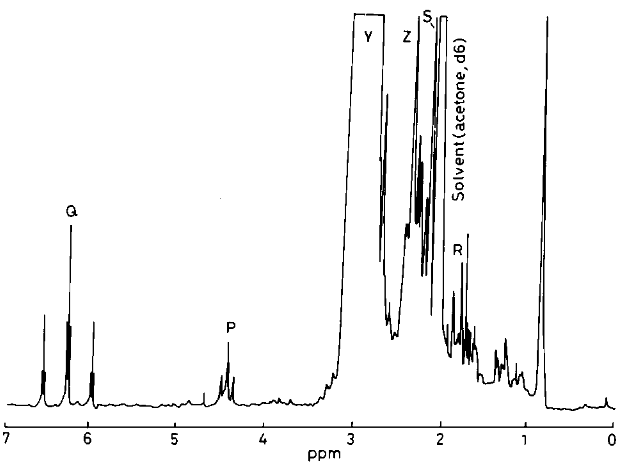

Figure 4 ^{1}H n.m.r. spectrum of a low-molar-mass PVDF synthesized in acetone (signals at 0.9 to 1.4 ppm are due to Percadox-16 initiator)

Table 3 ^{1}H n.m.r. peak assignments

Assignment	^{1}H δ (ppm) vs. TMS
$\text{In–}\overset{\text{P}}{\text{CH}_2}\text{–CF}_2\text{–CH}_2\text{–CF}_2\text{–}$	4.48–4.50
$\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\overset{\text{Q}}{\text{CF}_2\text{H}}$	6.28
$\text{–CH}_2\text{–CF}_2\text{–CF}_2\text{–}\overset{\text{R}}{\text{CH}_3}$	1.77
$\overset{\text{S}}{\text{CH}_3}\text{–CO–CH}_2\text{–CH}_2\text{–CF}_2\text{–}$	2.13
$\overset{\text{T}}{\text{CH}_3}\text{–COO–CH}_2\text{–}\overset{\text{U}}{\text{CH}_2}\text{–CF}_2\text{–}$	2.00(T) 4.30(U)
$\overset{\text{V}}{\text{CH}_3}\text{–COO–}\overset{\text{W}}{\text{CH}}(\overset{\text{X}}{\text{CH}_3})\text{–CH}_2\text{–CF}_2\text{–}$	1.26(X) 2.00(V) 5.22(W)
$\text{–CF}_2\text{–}\overset{\text{Y}}{\text{CH}_2}\text{–CF}_2\text{–}$	2.91
$\text{–CH}_2\text{–}\overset{\text{Z}}{\text{CH}_2}\text{–CF}_2\text{–}$	2.34

The signals G and J can be attributed to the reaction of the macroradical with the chain transfer reagent (in *Figure 3*, the solvent acetone), with the radical activity transferred to the solvent molecule by hydrogen abstraction:

$$\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2 + \text{CH}_3\text{COCH}_3 \rightarrow$$

$$\text{–CH}_2\text{–}\overset{\text{J}}{\text{CF}_2}\text{–CH}_2\text{–}\overset{\text{G}}{\text{CF}_2\text{H}} + \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$$

whereas the signal K is due to a chain transfer reaction of a radical containing a penultimate inverted unit to the solvent (e.g. acetone):

$$\text{–CF}_2\text{–CH}_2\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2 + \text{CH}_3\text{COCH}_3 \rightarrow$$

$$\text{–CF}_2\text{–CH}_2\text{–CH}_2\text{–}\overset{\text{K}}{\text{CF}_2\text{H}} + \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$$

Similarly, the signals L and M arise from the inverted terminal unit of a PVDF chain after transfer to the solvent:

$$\text{–CH}_2\text{–CF}_2\text{–CF}_2\text{–}\dot{\text{C}}\text{H}_2 + \text{CH}_3\text{COCH}_3 \rightarrow$$

$$\text{–CH}_2\text{–}\overset{\text{M}}{\text{CF}_2}\text{–}\overset{\text{L}}{\text{CF}_2}\text{–CH}_3\text{H} + \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$$

Reinitiation will give rise to the signal N:

$$\text{CH}_3\text{COCH}_2\text{–CH}_2\text{–}\overset{\text{N}}{\text{CF}_2}\text{–CH}_2\text{–CF}_2\text{–}$$

The signals A, A′, B, B′, C, E, D and D′ are linked to the possible addition reactions in the propagation step. Among them, the signal E is the only one originated by a sequence of two regular VDF units followed by two consecutive inverted units; the probability of finding such a sequence in PVDF chains due to consecutive addition reactions is very low, as demonstrated and observed by Cais and Sloane[19]. In our low-molar-mass PVDF the measured intensity of E is much higher than its calculated probability to occur as a consecutive addition; therefore, we attribute it almost entirely to chain termination by coupling:

$$\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2 + \dot{\text{C}}\text{F}_2\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–} \rightarrow$$

$$\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\overset{\text{E}}{\text{CF}_2}\text{–}\overset{\text{E}}{\text{CF}_2}\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}$$

The same signal E would also arise from the coupling reaction between two growing chain ends, one with a regular head-to-tail enchainment and the other with an inverted terminal unit:

$$\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–CF}_2\text{–CF}_2\text{–}\dot{\text{C}}\text{H}_2 + \dot{\text{C}}\text{F}_2\text{–CH}_2\text{–CF}_2\text{–}$$

$$\text{CH}_2\text{–} \rightarrow \text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\overset{\text{E}}{\text{CF}_2}\text{–}\overset{\text{E}}{\text{CF}_2}\text{–CH}_2\text{–CF}_2\text{–}$$

$$\text{CH}_2\text{–CF}_2\text{–CH}_2\text{–}$$

The absence of a signal assigned to the terminal group $\text{–CH}_2\text{–CF}_2\text{–CH}_2\text{=CF}_2$ excludes the possibility of termination by disproportionation.

From the aforementioned n.m.r. signals, attributed to the various structural moieties in PVDF, it is possible to calculate the values of chain transfer constant to the solvent (C_s), by assuming that the ratio of the rate of chain transfer to the rate of propagation is equal to the ratio of the integrated signals pertaining to the structures generated by such reactions. Namely, the following reactions, when acetone is employed as the solvent for VDF polymerization, occur to the growing radical $\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2$:

$$\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2 + \text{CH}_3\text{COCH}_3 \xrightarrow{k'_{\text{tr,s}}} \text{–CH}_2\text{–CF}_2\text{H} + \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$$

$$\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2 + \text{CH}_2\text{=CH}_2 \xrightarrow{k'_{\text{p}}} \text{–CH}_2\text{–CF}_2\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2$$

Thus C'_s will be defined as follows:

$$C'_s = \frac{k'_{\text{tr,s}}}{k'_{\text{p}}} = \frac{R'_{\text{tr,s}}}{R'_{\text{p}}} \frac{[\text{M}]}{[\text{S}]} = \frac{\text{G}+\text{K}}{\text{A}+\text{A}'+\text{B}+\text{B}'+\text{F}+\text{J}+\text{N}} \frac{[\text{M}]}{[\text{S}]} \tag{3}$$

while the reactions originated by the inverted growing radical:

$$\text{–CF}_2\text{–}\dot{\text{C}}\text{H}_2 + \text{CH}_3\text{COCH}_3 \xrightarrow{k''_{\text{tr,s}}} \text{–CF}_2\text{–CH}_3 + \text{CH}_3\text{CO}\dot{\text{C}}\text{H}_2$$

$$\text{–CF}_2\text{–}\dot{\text{C}}\text{H}_2 + \text{CH}_2\text{=CF}_2 \xrightarrow{k''_{\text{p}}} \text{–CF}_2\text{–CH}_2\text{–CH}_2\text{–}\dot{\text{C}}\text{F}_2$$

will be defined by a different chain transfer constant C''_s:

$$C''_s = \frac{k''_{\text{tr,s}}}{k''_{\text{p}}} = \frac{R''_{\text{tr,s}}}{R''_{\text{p}}} \frac{[\text{M}]}{[\text{S}]} = \frac{\text{L}}{\text{B}+\text{B}'+\text{D}'/2} \frac{[\text{M}]}{[\text{S}]} \tag{4}$$

The signals G, K and L, although relatively weak, are well separated from all other resonances. Therefore, their intensities can be evaluated with great accuracy. This favourable circumstance, together with the availability of a large number of PVDF samples prepared at different initiator and monomer concentrations (see *Figures 1* and *2*), allowed a rather precise evaluation of chain transfer constants.

Mean values, obtained from the n.m.r. analysis of several PVDF samples, prepared in acetone at different concentrations of initiator and monomer, are:

$$C'_s = 3.91 \times 10^{-3} \quad C''_s = 2.63 \times 10^{-2} \quad C_s(\mathrm{av}) = 4.5 \times 10^{-3}$$

The ratio of C''_s/C'_s is ca. 6.70, which underlines that the inverted radical $-\mathrm{CF_2\dot{C}H_2}$ has a higher reactivity than the regular radical $-\mathrm{CH_2{-}\dot{C}F_2}$, in terms of the relative ratios between the corresponding chain transfer and propagation reactions.

Similarly, the average value of the chain transfer constant for ethyl acetate has been calculated as:

$$C_s(\mathrm{av}) = 4.46 \times 10^{-3}$$

and for methyl acetate:

$$C_s(\mathrm{av}) = 1.63 \times 10^{-3}$$

The (three times) lower C_s(av) value for methyl acetate compared to that of the other two solvents can be attributed to the lower tendency of hydrogen to be abstracted from this solvent.

For the last two systems, only average C_s values are reported here, owing to the smaller number of available samples that led to greater approximations in the evaluation of C'_s and C''_s.

The ^{19}F n.m.r. analysis allows the total inversions per chain to be evaluated from the following expression:

$$\text{inversions } (\%) = [\tfrac{1}{2}(\mathrm{C} + \mathrm{D} + \mathrm{D'}) + \mathrm{E} + \mathrm{L}]/(100 \times \text{total}) \tag{5}$$

where

$$\text{total} = \mathrm{A} + \mathrm{A'} + \mathrm{B} + \mathrm{B'} + \mathrm{C} + \mathrm{D} + \mathrm{D'} + \mathrm{E} + \mathrm{F} + \mathrm{G} + \mathrm{J} + \mathrm{K} + \mathrm{L} + \mathrm{M} + \mathrm{N}$$

The values of total inversions per chain in the three solvents have been calculated as 3.6% (acetone), 4.1% (ethyl acetate) and 4.5% (methyl acetate). The average value at 55°C is ca. 4.1%. Possible explanations for these fluctuations, which are higher than experimental errors, are linked to the unclear relevance of chain-end contributions in low-molar-mass PVDF samples.

CONCLUSIONS

The values of chain transfer constants to the solvents employed could not be easily obtained from any kinetic treatment of our polymerization data, owing to the non-ideal behaviour of all these systems, which also prevented the application of the Mayo equation.

More complex kinetic schemes, suggested in the literature, do not fit with the experimental results and in any case do not allow isolation of the C_s term from the various equations, without unjustified oversimplifications.

For these systems the problem of C_s evaluation can be overcome by accurate microstructural analysis of the resultant low-molar-mass polymer by ^{19}F n.m.r. spectroscopy.

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