

End groups in fluoropolymers

Maurizio Pianca^{*}, Emma Barchiesi, Giuseppe Esposto, Stefano Radice

Ausimont S.p.A., Via S Pietro 50/a, 20021 Bollate Milano, Italy

Abstract

IR and NMR spectroscopies are the most important techniques used to identify and quantify end groups in fluoropolymers. We review here some literature studies about the characterisation of end groups in some fluoropolymers based on tetrafluoroethylene, vinylidene fluoride and vinyl fluoride, adding the contribution of our investigation on the matter. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluoropolymers; End groups; IR spectroscopy; NMR spectroscopy

1. Introduction

It is normally accepted that end groups have no significant influence on macroscopic properties of polymers, because their weight is negligible as compared with the whole mass of the polymer and because energy values for bonds in end groups and in the constitutive units are practically equal.

This statement cannot be applied to perfluoro polymers where hydrogen containing end groups (produced for instance by a hydrogen containing peroxide initiator) do have a definite influence on their thermal stability, as can be expected by comparing the bond strength of C–H with C–F (about 410 and 460 kJ/mol, respectively).

It has been demonstrated that also hydrogen and fluorine containing polymers, for example poly(vinylidene) fluoride (PVDF), are influenced, as far as thermal stability and fire resistance are concerned, by the end groups generated in the presence of different initiators. Since in this case the relative strength of C–H and C–F bonds cannot be the determining factor, this unexpected behaviour was attributed to different degradation mechanisms induced by the nature of the end groups [1].

In PVDF other properties, such as fluidity and electrical conductivity, were demonstrated to be significantly influenced by end groups.

End groups can also determine the crystallisation kinetics from the melt of thermoplastic fluoropolymers, and hence the processing and end-use properties [2].

Being aware of the importance of end groups in determining the properties of fluoro polymers, we will review here the studies about their identification and quantitative determi-

nation in some commercial fluoropolymers adding, where possible, the original results of our work on this subject. All literature data reported herewith have been experimentally confirmed in our laboratories.

We will consider the following polymers:

- poly(tetrafluoroethylene) (PTFE) and TFE based thermoplastic fluoropolymers,
- poly(vinylidene fluoride) (PVDF) and VDF based fluoroelastomers, and
- poly(vinyl fluoride) (PVF).

2. PTFE and TFE based thermoplastic fluoropolymers

The end groups identified in thermoplastic fluoropolymers can be generated during the polymerisation process (initiator, transfer agent, solvent, contaminants, etc.), or by handling of the polymer (ageing, heating, extrusion, chemical reactions and so on).

IR spectroscopy is a particularly useful technique in the determination of end groups in TFE based polymers, since they are insoluble in common solvents. Moreover, many functional groups show absorptions in spectral regions that are free from the main absorption bands of the polymer. One of the major features of infrared Fourier transform spectroscopy is the high sensitivity due to the high energy available and the possibility to enhance the signal to noise ratio by increasing the number of scans. In fact it is possible to evaluate end groups concentration in the range 10^{-3} – 10^{-5} mol/kg.

In our laboratories IR spectra of polymers have been recorded with a Nicolet 20 SX or a Nicolet 850 FT–IR instrument. Collection parameters included 2 cm^{-1} resolution and 500 scans. Spectra have been elaborated on a PC

^{*}Corresponding author.

with Lab Calc software (Galactic Industries). The samples have been analysed as pellets obtained by cold pressing, while model compounds have been analysed in the best condition according to their physical nature. Since most of the results have been obtained through spectral subtraction, as a reference sample we used a polymer exposed for several hours to elemental fluorine at 100–150°C; such a treatment transforms almost all end groups to perfluoromethyl groups [3,8].

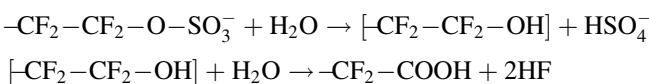
To assign the absorption bands to distinctive functional groups, we used both literature data [3,4,7–16] and model compounds. Sometimes, we performed simple chemical reactions to confirm assignments. Model compounds have been used for the determination of extinction coefficients. The data here reported have been obtained for PFA polymers (tetrafluoroethylene/perfluoropropylvinylether copolymers TFE/PFPVE). These results can be extended to other TFE based copolymers.

The following end groups have been identified:

- carboxylic acid ($-\text{CF}_2-\text{COOH}$),
- amide ($-\text{CF}_2-\text{CONH}_2$),
- perfluorovinyl ($-\text{CF}_2-\text{CF}=\text{CF}_2$),
- acyl fluoride ($-\text{CF}_2-\text{COF}$),
- difluoromethyl ($-\text{CF}_2-\text{CF}_2\text{H}$), and
- ethyl ($-\text{CF}_2-\text{CH}_2-\text{CH}_3$).

2.1. Carboxylic acid groups

These groups are generated in the polymer when a persulphate initiator is used, according to the following [4]:

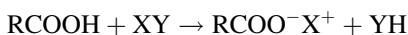


Carboxylic groups are identified by IR spectroscopy by the following group frequencies due to the O–H and the C=O stretching:

- 3557 cm^{-1} (sharp, O–H stretching, free),
- 3300–3000 cm^{-1} (broad, O–H stretching, bonded),
- 1813 cm^{-1} (sharp, C=O stretching, free), and
- 1775 cm^{-1} (C=O stretching, bonded).

The nature of the observed bands was verified by means of chemical reactions and model compounds.

The most simple reaction of a carboxylic group is its salification by a base.



This reaction from the spectroscopic point of view leads to the disappearance of both O–H and C=O stretching bands and to the appearance of new bands due to the in phase and out of phase $-\text{COO}^-$ stretching vibration.

A polymer powder containing $-\text{COOH}$ groups, exposed to the vapours evolved by an ammonia solution, showed the decreasing of the 1813 and 1775 cm^{-1} bands. The appear-

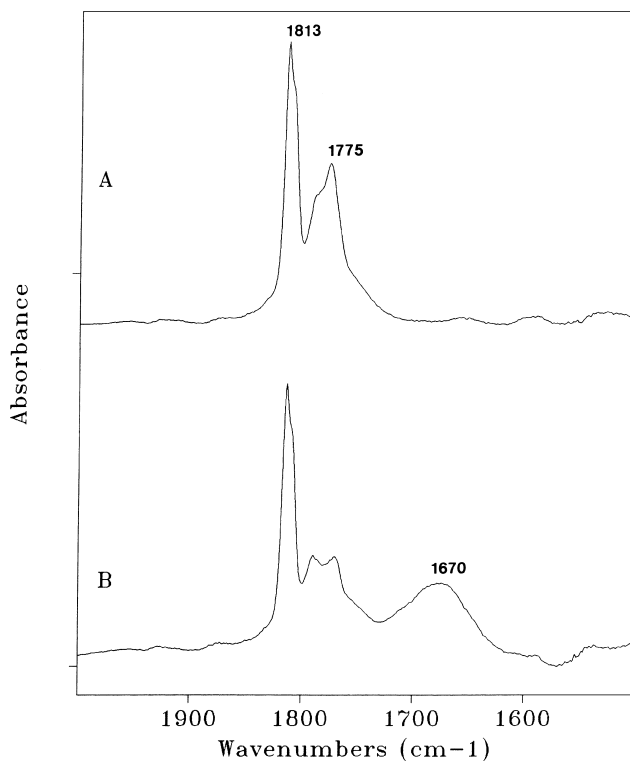


Fig. 1. (A) IR absorption bands (C=O stretching region) due to carboxylic end groups in a PFA polymer. (B) The same spectral regions observed after exposure to ammonia.

ance of a broad absorption at about 1675 cm^{-1} is due to the out of phase stretching of the $-\text{COO}^-$ group (Fig. 1).

Changes in the 3300–3000 cm^{-1} region are mainly attributed to the complex pattern due to $(\text{NH}_4)^+$ stretching.

The salification reaction is reversible. As a matter of fact, by exposing the powder to HCl vapours we observe the increasing of the bands at 3557, 1813 and 1775 cm^{-1} and the decreasing of the 1673 cm^{-1} absorption.

Carboxylic groups can decompose by thermal treatment following different mechanisms:

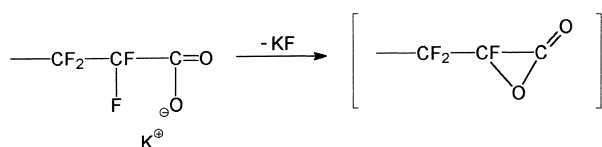
- $-\text{CF}_2-\text{CF}_2-\text{COOH} \rightarrow -\text{CF}=\text{CF}_2 + \text{CO}_2 + \text{HF}$
- $-\text{CF}_2-\text{CF}_2-\text{COOH} \rightarrow -\text{CF}_2-\text{COF} + \text{HF} + \text{CO}$
- $-\text{CF}_2-\text{CF}_2-\text{COOH} \rightarrow -\text{CF}_2-\text{CF}_2\text{H} + \text{CO}_2$

Mechanism (a) is observed for instance during press treatment at 380°C for some minutes. We noted the decreasing of the absorptions due to carboxylic groups and the formation of a band at 1784 cm^{-1} due to perfluorovinyl groups [3].

Mechanism (b) is quite interesting and deserves a more detailed discussion. It has been observed during industrial extrusions of perfluoropolymers manufactured by aqueous emulsion polymerisation with $\text{K}_2\text{S}_2\text{O}_8$ as initiator. In the IR spectra of the extruded items we observed a substantial decrease of the absorptions due to the carboxylic groups and the formation of a band at 1884 cm^{-1} attributable to the $-\text{CF}_2-\text{COF}$ end groups. The same mechanism was observed

by heating at 350°C a sample of γ irradiated PTFE, that showed a high content of $-\text{COOH}$ end groups; in the gas evolved by the sample were identified HF and CO. A similar carboxylate thermolysis with CO elimination has been described in [5].

Since the carboxylic groups could be present either as K^+ salts or in the protonated form, a unimolecular reaction pathway was proposed similar to that shown in the following scheme.



KF and/or HF, eliminated α to the carbonyl, results in a zwitterionic intermediate which can evolve into a cyclic form. Upon heating, loss of carbon monoxide from the cyclic intermediate results in the observed end groups. This mechanism is not unusual and closely resembles the thermal extrusion of difluorocarbene from hexafluoropropene oxide to give acetyl fluoride. Very recently a similar mechanism has been claimed to account for the vacuum thermolysis of sodium fluoropropionate derivatives to give a trifluoroacetate ester [6].

Mechanism (c) is followed when the carboxylate end group is in ionic form and the polymer is treated with water at 210–250°C [7,9–12].

As a model compound for the determination of molar extinction coefficients of the carboxylic group bands, we used perfluorooctanoic acid. IR spectra of this compound have been recorded as solutions at different concentration in a perfluorinated fluid (Galden[®] D100). As expected, the bands of bonded carboxylic groups decrease with dilution up to complete disappearance. Molar extinction coefficients relative to the 3557, 1813 and 1775 cm^{-1} bands have been determined and reported in Table 1.

In Table 1 we have also collected all the molar extinction coefficients determined experimentally as reported further in this paper. Literature data, as for example in [8,9] are consistent with our results.

2.2. Amide groups

Amide end groups can be generated during the polymerisation step when ammonium salts are used. Their presence is revealed by four bands at 3555, 3438, 1768 and 1587 cm^{-1} . We assign the two high frequencies to asymmetric and symmetric NH_2 stretching of R_fCONH_2 groups, the 1768 cm^{-1} band to C=O stretching and the 1587 cm^{-1} to the N–H deformation.

The assignment was confirmed by means of hydrolysis and pyrolysis reactions:

- acid hydrolysis: $-\text{CF}_2\text{CONH}_2 + \text{H}_2\text{O} + \text{HCl} \rightarrow -\text{CF}_2\text{COOH} + \text{NH}_4\text{Cl}$
- pyrolysis: $-\text{CF}_2\text{CONH}_2 \xrightarrow{\Delta} -\text{CF}_2-\text{C}\equiv\text{N} + \text{H}_2\text{O}$

Table 1
IR spectroscopy end groups assignments and extinction coefficients

| Frequency (cm^{-1}) | Group | Assignment | Extinction coefficient (l/mol cm) |
|--------------------------------|---------------------------------|-----------------------------|--|
| 3557 | COOH | OH str. | 165 |
| 3555 | CONH ₂ | NH ₂ asymm. str. | 220 |
| 3438 | CONH ₂ | NH ₂ symm. str. | 220 |
| 3300–3000 | COOH (H) | OH str. | Not available |
| 3005 | CF ₂ H | CH str. | 351 ^a |
| 3003 | CH ₂ CH ₃ | CH str. | 34 |
| 1884 | COF | CO str. | 215 |
| 1813 | COOH | CO str. | 230 |
| 1784 | CF=CF ₂ | CC str. | 455 |
| 1775 | COOH (H) | CO str. | 1700 |
| 1768 | CONH ₂ | CO str. | 940 |
| 1670 (broad) | COO ⁻ X ⁺ | COO ⁻ asymm.str. | Not available |
| 1587 | CONH ₂ | NH ₂ def. | 220 |

Asymm. str.=asymmetric stretching.

Symm.str.=symmetric stretching.

Def.=deformation motion.

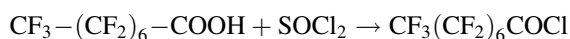
H=hydrogen bonded.

^a l/mol cm^2 , integrated absorbance data were used (see text).

Hydrolysis was carried out in a 20% hydrochloric acid boiling solution for 24 h. After the treatment the absorptions of the amide bands were decreased and the bands of the carboxylic group appeared (Figs. 2 and 3); NH_4Cl was also observed in the acid solution.

Pyrolysis experiments basically consisted in a thermal treatment at 360°C (2 h) in nitrogen atmosphere. IR spectra after this treatment show the decreasing of the amide absorptions and the appearance of a band at 2263 cm^{-1} due to $\text{C}\equiv\text{N}$ stretching.

As a model compound for the determination of the absorption coefficients we used perfluorooctanoic amide, prepared according to the following reactions:



The spectra of this compound have been recorded as solution in Galden[®] D100.

2.3. Perfluorovinyl groups

In the IR spectra of some PFA polymers we have observed a band at 1784 cm^{-1} (Fig. 4). The same absorption was observed during the thermal degradation of $-\text{COOH}$ end groups. This band is not affected by the ammonia vapours treatment; accordingly we attributed it to perfluorovinyl double bond stretching.

The attribution has been confirmed by examining the IR spectrum of perfluoro-1-heptene; this model compound was also used, as a Galden[®] D100 solution, to determine the extinction coefficient of the 1784 cm^{-1} band (Table 1).

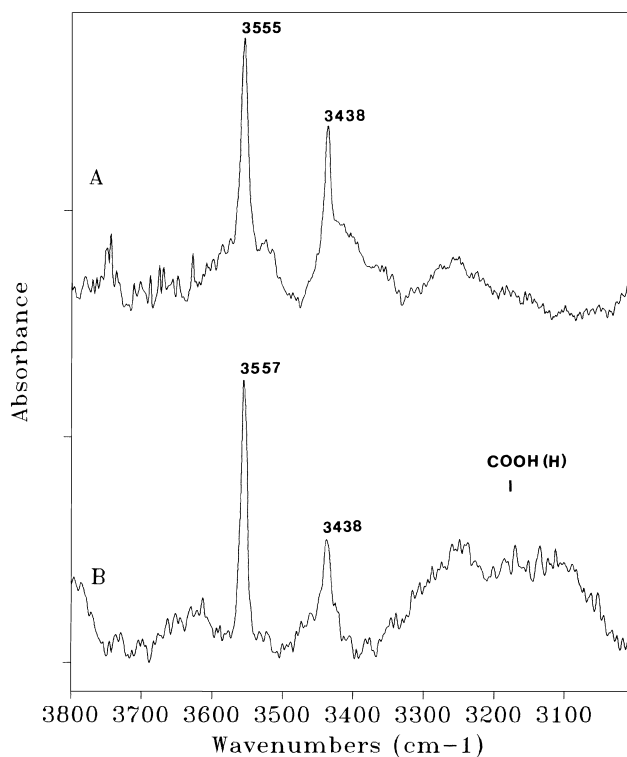
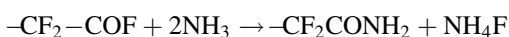


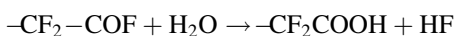
Fig. 2. (A) IR absorption bands (N–H stretching region) due to amidic end groups in a PFA polymer. (B) The same spectral regions observed after acid hydrolysis.

2.4. Acyl fluoride groups

In the IR spectra of some extruded TFE perfluorinated copolymers we noticed a band at 1884 cm^{-1} (Fig. 5(A)), which is assigned to C=O stretching in $R_f\text{COF}$ groups. By exposition to ammonia vapours we transformed the $R_f\text{COF}$ groups into amide groups (Fig. 5(B)) according to the following reaction:

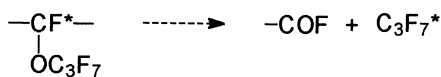


Exposition to water vapour leads to carboxylic groups:



We proceeded in the evaluation of the $-\text{COF}$ extinction coefficient indirectly, determining the content of the $-\text{COOH}$ groups after complete hydrolysis of the perfluoroacyl groups.

It is worth enough to say that in PFA copolymers $-\text{CF}_2\text{COF}$ end groups can also be generated during polymerisation through the following radical rearrangement:



2.5. Difluoromethyl groups ($-\text{CF}_2-\text{CF}_2\text{H}$)

When these end groups are present, they give rise to weak absorptions in the CH stretching region [7,9–12]. Actually,

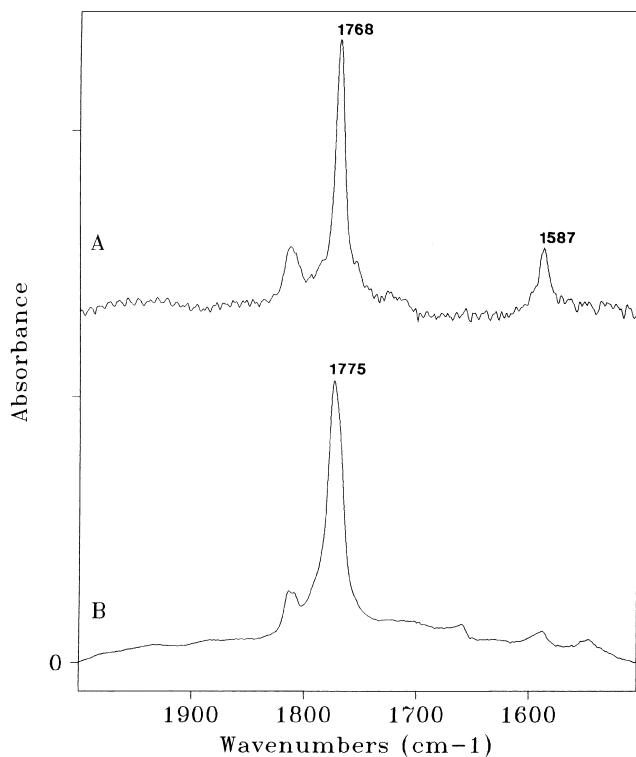


Fig. 3. (A) IR absorption bands (C=O stretching region) due to amidic end groups in a PFA polymer. (B) The same spectral regions observed after acid hydrolysis.

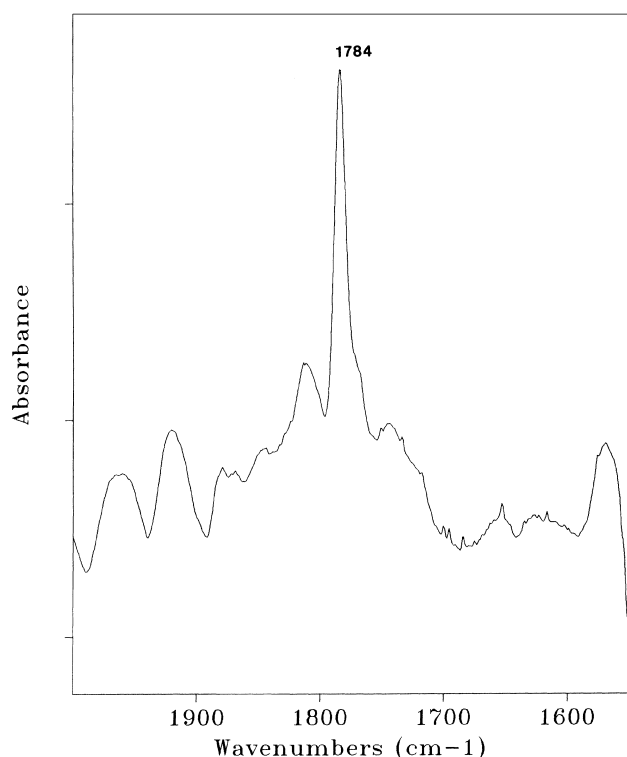


Fig. 4. IR spectrum (C=C stretching region) of a PFA polymer (perfluorovinyl end groups).

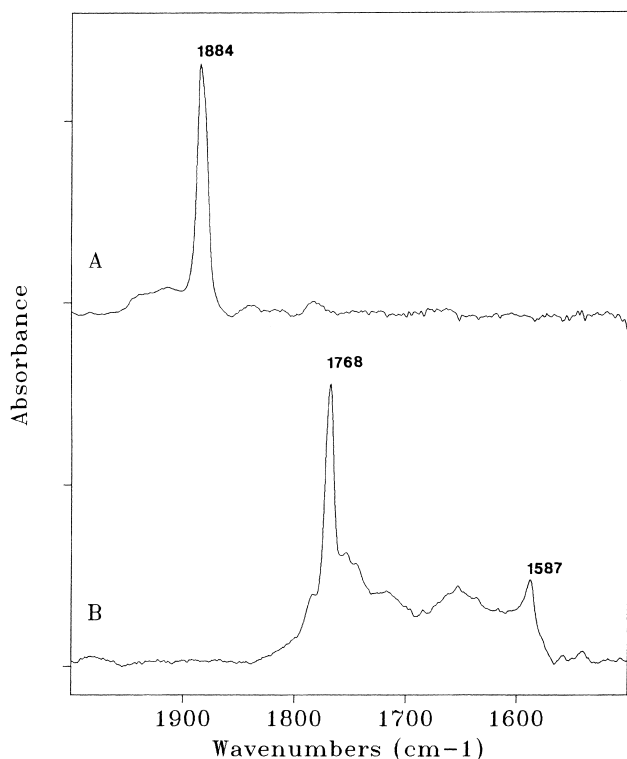


Fig. 5. (A) IR spectrum (C=O stretching region) of a PFA polymer (acylfluoride end groups). (B) The same spectral regions observed after exposure to ammonia and water vapours.

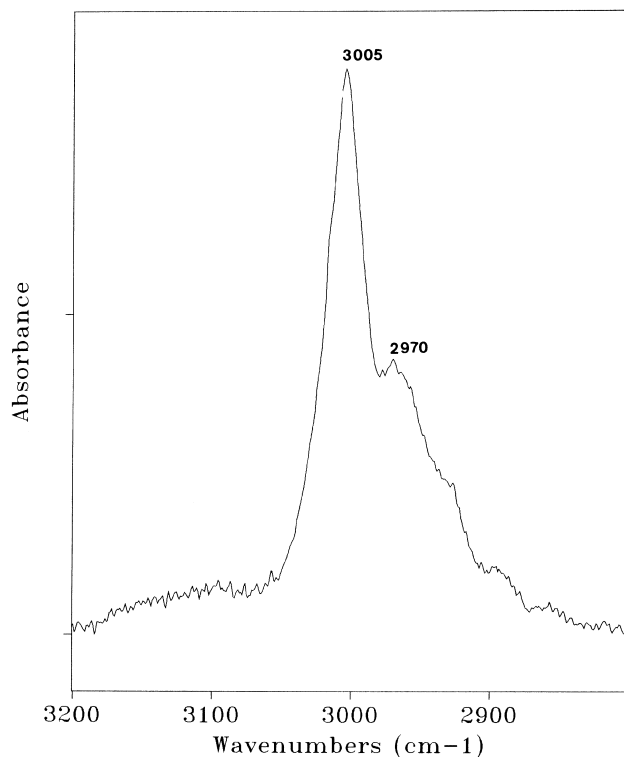


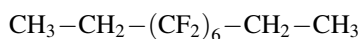
Fig. 6. IR spectrum (C–H stretching region) of a PFA sample (difluoromethyl end groups).

we observe two bands at 3005 and about 2970 cm^{-1} (Fig. 6). We used as a model compound $\text{CF}_2\text{Cl}-(\text{CF}_2)_6-\text{CF}_2\text{H}$. Its IR spectrum shows these two bands in the CH stretching region. The presence of two bands is justified by the existence of two different conformers. The hypothesis has been confirmed recording IR spectra at different temperatures (from room temperature to about 150°C). A Van't Hoff plot (Fig. 7) gave an energy difference for the two conformers of about 0.5 Kcal/mol.

In this case the integrated absorbance of the two bands (3005 and 2970 cm^{-1}) has been used to determine the extinction coefficient of $-\text{CF}_2\text{H}$ group. The result has been obtained using $\text{CF}_2\text{Cl}-(\text{CF}_2)_6-\text{CF}_2\text{H}$ in Galden[®] D100 solution and is reported in Table 1.

2.6. Ethyl groups ($-\text{CF}_2-\text{CH}_2-\text{CH}_3$)

By using ethane as a chain-transfer agent in the emulsion polymerisation of TFE based thermoplastic fluoropolymers, we expect to obtain $-\text{CF}_2-\text{CH}_2-\text{CH}_3$ end groups. As a matter of fact in the complex pattern observed in the CH stretching region of the IR spectra of these polymers we identify three bands at 3003, 2960 and 2900 cm^{-1} (Fig. 8). The assignment of the three bands to the ethyl groups is confirmed by the following model compound:



that has also been used to determine the extinction coefficient relative to the 3003 cm^{-1} band (Table 1).

3. Poly(vinylidene fluoride) (PVDF)

In many papers dealing with the investigation of PVDF microstructure by means of ^{19}F NMR spectroscopy, the presence of peaks which cannot be related to any units in the linear polymer chain is reported and generally attributed to impurities, oligomers, end groups or branching sites. Namely, some of these peaks have been assigned in [17]: the weak resonances at -100.3 , -104.52 and 107.54 ppm have been associated to branched structures such as $-\text{CH}_2-\text{CF}_2-\text{CH}<$ or $-\text{CH}_2-\text{CF}_2-\text{CF}<$. However, the assignments are based only on the empirical rules for the calculation of chemical shifts developed by Murasheva et al. [18] and no proof of these assignments is given. Furthermore, in [19] the multiplet at -114.15 ppm, which is detectable in almost all PVDF ^{19}F NMR spectra, is attributed to an unidentified end group and in [20] the same signal is assigned to an impurity.

A paper [21] dealing with PVDF telomers (with number average molecular weights in the range 2000–3000) obtained using 1,2-dibromotetrafluoroethane as telogen in the presence of different initiators, gave the detailed ^{19}F and ^1H NMR information about end groups, originated by the

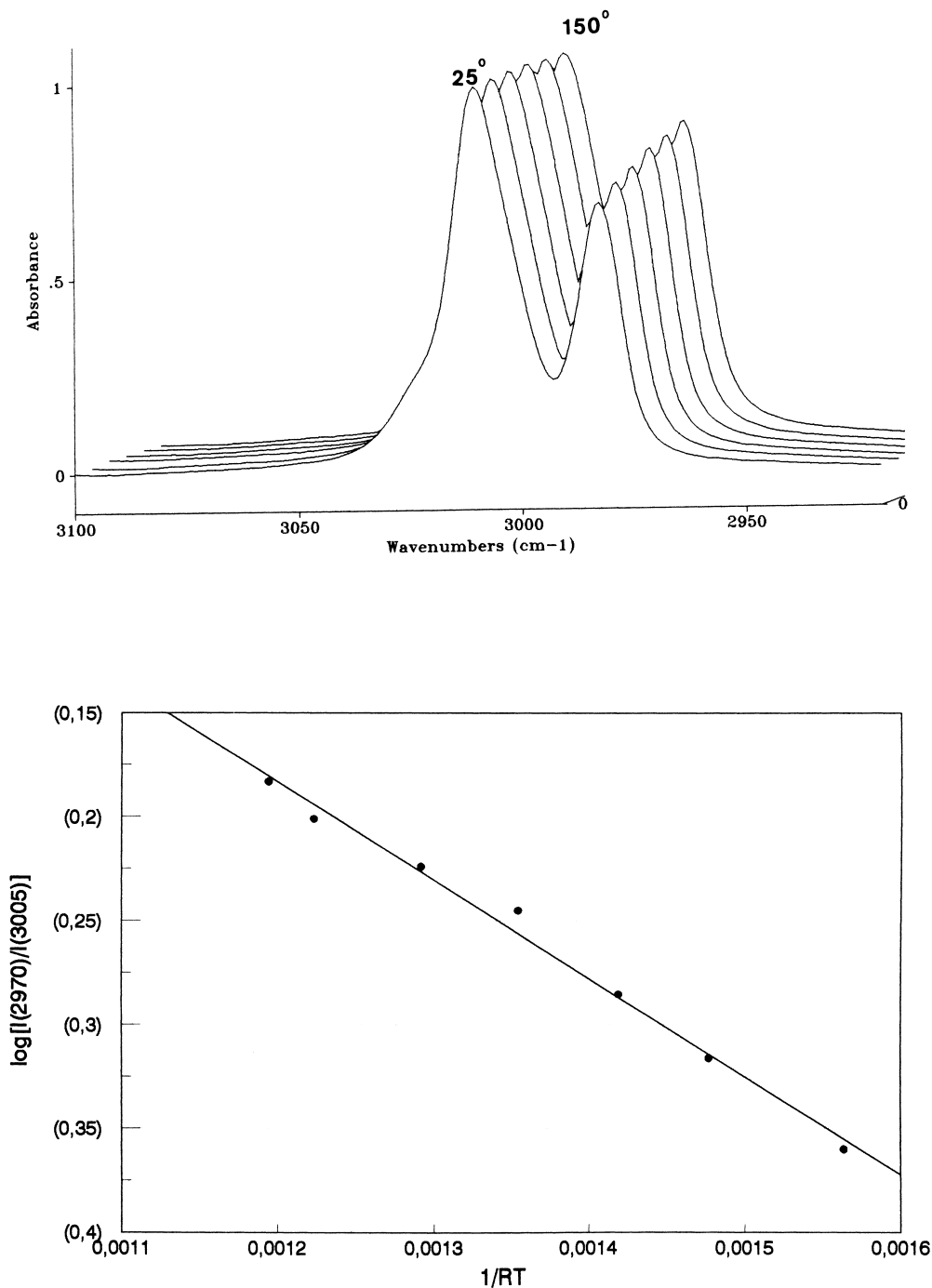


Fig. 7. Evolution of the IR spectrum (C–H stretching region) of $\text{CF}_2\text{Cl}-(\text{CF}_2)_6\text{CF}_2\text{H}$ as a function of temperature (20–150°C) and relative Vant'Hoff plot. $I(2970)$ and $I(3005)$ are the optical densities of the two bands.

initiator or by transfer reactions, reported at the beginning of Tables 2 and 3.

Assignments were performed by comparison of ^1H and ^{19}F NMR spectra and by the use of two-dimensional fluorine–fluorine chemical shift correlation spectroscopy (COSY).

Particular attention was paid to the signals attributed to $-\text{CF}_2-\text{CF}_2-\text{CH}_3$ and $-\text{CH}_2-\text{CF}_2\text{H}$ end groups, that are

present in the spectra of many authors, but had never been identified and often misinterpreted. 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 $-\text{CF}_2\text{H}$ and the $-\text{CH}_3$ groups could be a short chain-branching process involving an intramolecular 1–5

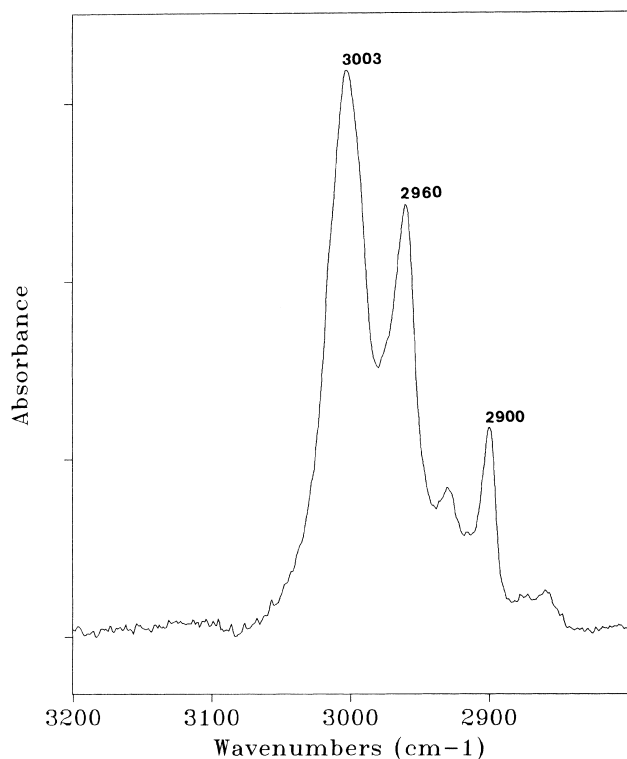
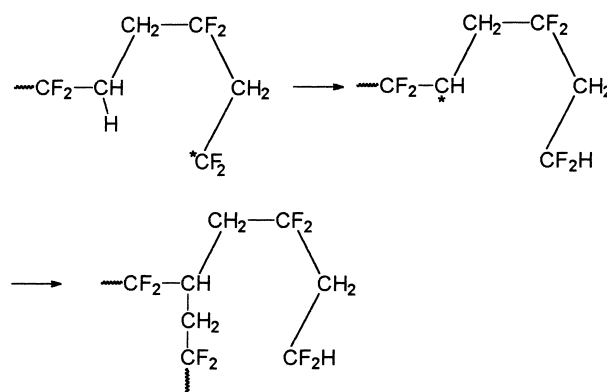


Fig. 8. IR spectrum (C–H stretching region) of a PFA sample (ethyl end groups).

hydrogen shift analogous to similar radical reactions reported in [22].

This reaction cannot occur in a normal chain, since the growing $-\text{CF}_2^*$ radical is always in a 1,4 or 1,6 relationship to $-\text{CH}_2-$ groups. Therefore, the 1,5 shift will come from ‘head to head’ sites, which are present at a concentration of about 3–5%, according to the following reaction:



This type of reaction then leads to some tertiary hydrogen sites in the polymer. In fact, the signal of a CH tertiary group (triplet, 77 ppm) has been observed by ^{13}C NMR spectroscopy. The $-\text{CH}_3$ end group can come from species formed in the same way by a growing radical ending with an inverted monomer unit, according to the following

Table 2
 ^{19}F NMR end groups assignments

| Initiator/transfer agent | Assignment | ^{19}F δ (ppm) vs. CFCl_3 |
|-------------------------------------|--|--|
| $\text{BrCF}_2\text{CF}_2\text{Br}$ | $-\text{CH}_2-\overset{\text{B}}{\text{CF}_2}-\text{CH}_2-\overset{\text{A}}{\text{CF}_2}-\text{Br}$ | -43.0 (A); -93.5 (B) |
| | $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\overset{\text{C}}{\text{CF}_2}-\text{Br}$ | -45.0 |
| | $-\text{CH}_2-\overset{\text{H}}{\text{CF}_2}-\text{CH}_2-\overset{\text{G}}{\text{CF}_2}-\overset{\text{E}}{\text{CF}_2}-\text{Br}$ | -67 (E); -110.2 (F) |
| | $-\text{CH}_2-\overset{\text{H}}{\text{CF}_2}-\text{CH}_2-\overset{\text{G}}{\text{CF}_2}-\text{H}$ | -114.8 (G); -92.4 (H) |
| | $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\overset{\text{I}}{\text{CF}_2}-\text{H}$ | -117.3 |
| | $-\text{CH}_2-\overset{\text{M}}{\text{CF}_2}-\overset{\text{L}}{\text{CF}_2}-\text{CH}_3$ | -107.8 (L); -114.3 (M) |
| PK 16 ^a | $-\text{O}-\text{CH}_2-\overset{\text{Q}}{\text{CF}_2}-\text{CH}_2-\text{CF}_2-$ | -102.1 |
| Di-benzoilperoxide | $\text{Ph}-\text{CH}_2-\overset{\text{R}}{\text{CF}_2}-\text{CH}_2-\text{CF}_2-$ | -88.1 |
| | $\text{Ph}-\text{COO}-\text{CH}_2-\overset{\text{R}' }{\text{CF}_2}-\text{CH}_2-\text{CF}_2-$ | -101.1 |
| Ammonium persulphate | $-\overset{\text{T}}{\text{CF}_2}-\text{CH}_2-\text{OH}$ | -104.5 |
| | $-\overset{\text{T}' }{\text{CF}_2}-\text{CH}_2-\text{OAc}$ | -102.3 |
| Ethyl acetate | $\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_2-\overset{\text{U}}{\text{CF}_2}-\text{CH}_2-$ | -93.1 |
| | $\text{CH}_3-\text{COO}-\text{CH}(\text{CH}_3)-\overset{\text{V}}{\text{CF}_2}-\text{CH}_2-$ | -93.1 |
| Acetone | $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_2-\overset{\text{K}}{\text{CF}_2}-\text{CH}_2-\text{CF}_2-$ | -94.3 |
| Methyl acetate | $\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_2-\overset{\text{Z}}{\text{CF}_2}-\text{CH}_2-\text{CF}_2-$ | -93.1 |
| CCl_4 | $\text{CH}_2-\text{CF}_2-\text{CH}_2-\overset{\text{W}^* }{\text{CF}_2}-\overset{\text{W}}{\text{CF}_2}-\text{Cl}$ | -47.6 (W); -93.1 (W*) |
| | $\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CH}_2-\overset{\text{X}}{\text{CF}_2}-\text{Cl}$ | -50.7 |
| | $\text{CCl}_3-\text{CH}_2-\overset{\text{Y}}{\text{CF}_2}-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$ | -93.7 |

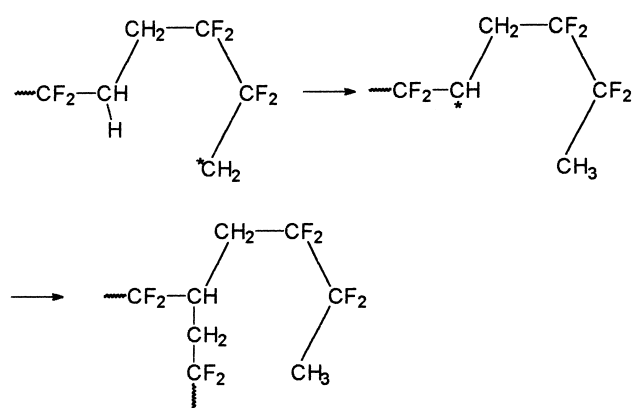
^a PK 16: bis(4-tertbutylcyclohexy)peroxy-dicarbonat.

Table 3
¹HNMR end groups assignments

| Initiator/transfer agent | Assignment | ¹ Hδ (ppm) vs. TMS |
|--------------------------------------|---|-------------------------------|
| BrCF ₂ CF ₂ Br | -CH ₂ -CF ₂ - ^A CH ₂ -CF ₂ Br | 3.5 |
| | -CF ₂ - ^C CH ₂ - ^C CH ₂ -CF ₂ Br | 2.6 |
| | -CF ₂ - ^D CH ₂ -Br | 3.95 |
| | -CH ₂ -CF ₂ -CH ₂ -CF ₂ - ^G H | 6.28 |
| | -CF ₂ -CH ₂ -CH ₂ -CF ₂ - ^I H | 6.28 |
| | -CH ₂ -CF ₂ -CF ₂ - ^L CH ₃ | 1.78 |
| PK 16 ^a | -C(^N CH ₃) ₃ | 0.85 |
| | (CH ₃) ₃ C-(^O C ₆ H ₁₀)-O- | 1.0–2.2 |
| | >CH- ^P O- | 3.0 |
| | -O- ^Q CH ₂ -CF ₂ -CH ₂ -CF ₂ - | 4.5 |
| Di-benzoilperoxide | Ph- ^R CH ₂ -CF ₂ -CH ₂ -CF ₂ - | 2.5 |
| | Ph-COO- ^{R'} CH ₂ -CF ₂ -CH ₂ -CF ₂ - | 4.7 |
| Di-tertbutylperoxide | ^S CH ₃ -CH ₂ -CF ₂ - | 1.0 |
| Ammonium persulphate | -CF ₂ - ^T CH ₂ -OH | 3.9 |
| | -CF ₂ -CH ₂ -OAc | 4.3 |
| Ethyl acetate | ^{U*} CH ₃ -COO- ^{U**} CH ₂ -CH ₂ -CF ₂ -CH ₂ - | 2.0 (U*); 4.2 (U**) |
| | ^{V*} CH ₃ -COO- ^{V**} CH(^{V***} CH ₃)CH ₂ -CF ₂ -CH ₂ - | 2 (V*); 5.2 (V**); 1.3 (V***) |
| Acetone | ^K CH ₃ -CO-CH ₂ -CH ₂ -CF ₂ - | 2.1 |
| Methyl acetate | ^Z CH ₃ -COO-CH ₂ -CH ₂ -CF ₂ - | 2.1 |
| CCl ₄ | CH ₂ -CF ₂ -CH ₂ -CF ₂ - ^{W**} CH ₂ -CF ₂ Cl | 3.4 |
| | CCl ₃ - ^Y CH ₂ -CF ₂ -CH ₂ -CF ₂ -CH ₂ -CF ₂ | 3.8 |

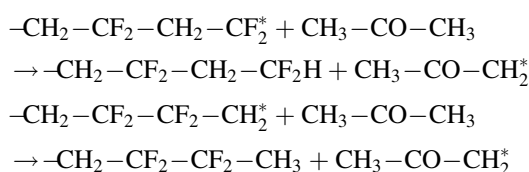
^a PK 16: bis(4-tertbutylcyclohexyl)peroxy-dicarbonate.

reaction:



-CH₂-CF₂H and -CF₂-CH₃ end groups have been observed also in [23], where is described the synthesis of low-molar-mass PVDF in three different solvents (acetone, ethyl acetate and methyl acetate). Here the solvent acts also as a chain transfer agent, by reacting with the growing macro-radical with a concurrent radical activity transferred to the solvent molecule by hydrogen abstraction.

With acetone we have the following reactions:



Reinitiation will give rise to the CH₃-CO-CH₂-CH₂-CF₂-CH₂-CF₂- end group. Tables 2 and 3 report ¹⁹F and ¹HNMR data related to such reinitiation end groups for the three solvents used.

As an example of COSY application, Fig. 9 shows the 282 MHz ¹⁹F two-dimensional correlated spectrum of a low molar mass PVDF synthesized in acetone. The sample has been dissolved in acetone-d₆ at 30°C and the spectra have been collected by an INOVA 300 spectrometer. A total of 64 transients has been accumulated for each of 512 spectra with 2048 points covering 10 000 Hz in both dimensions. The off diagonal or cross peaks observed indicate a connection between fluorine pairs which have scalar couplings, either through three or four bonds. The cross peaks marked by letters in the figure, concern only end groups and are

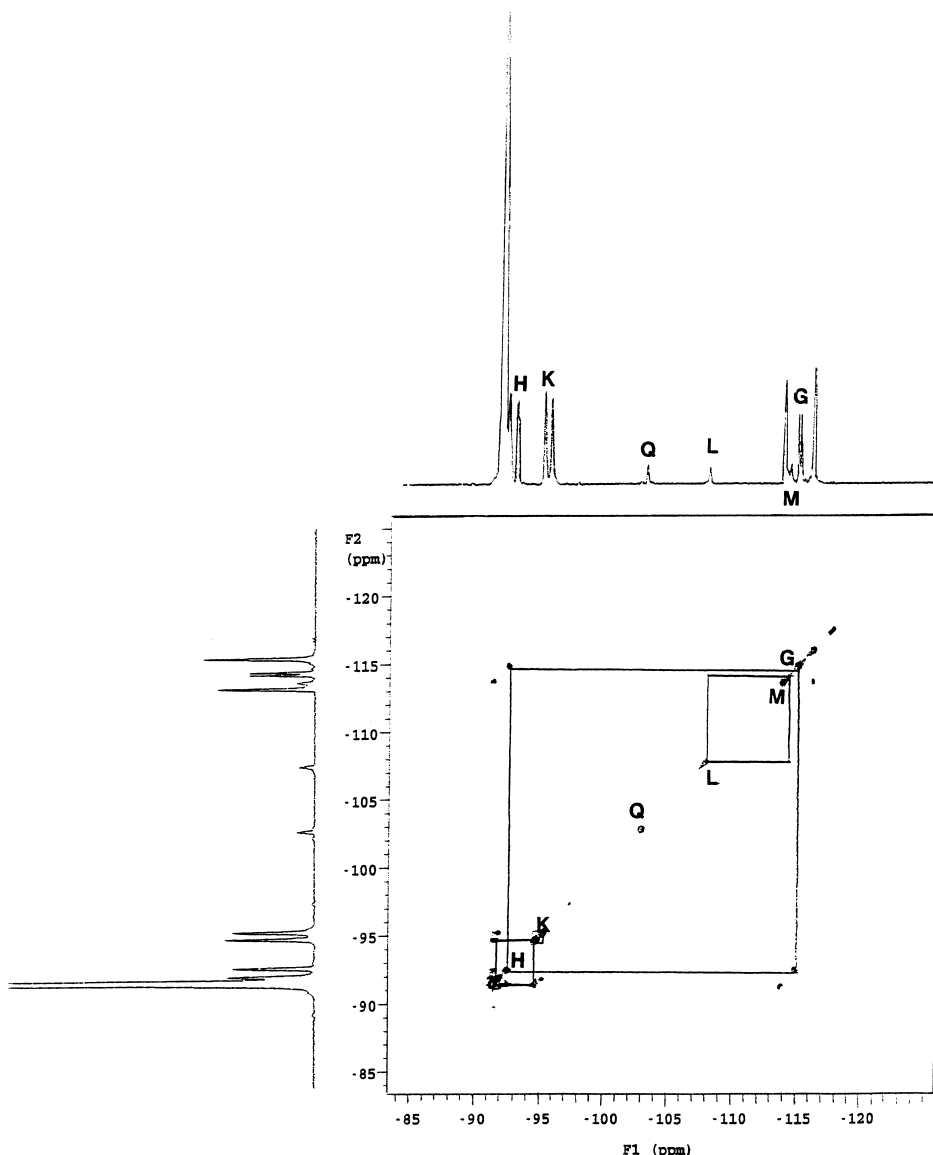


Fig. 9. 282 MHz ^{19}F 2D correlated NMR spectrum of a low molar mass PVDF synthesized in acetone. Attributions of the signals are reported in Table 2.

explained on the basis of the attributions reported in Table 2.

New end groups in VDF oligomers have been reported in [24], where it is demonstrated that the larger chain end groups ($-\text{Cl}$ and $-\text{CCl}_3$ as compared with $-\text{CH}_3$) tend to produce the conformational disorder in the molecules yielding the γ phase when the oligomers are crystallised from the melt. The new end groups were originated by CCl_4 present in the polymerisation system and were characterised by ^{19}F and ^{13}C NMR spectroscopy. In Fig. 10(A) and (B) are evidenced all the end groups observed on the ^{19}F and ^1H NMR spectra of a VDF oligomer obtained in conditions similar to those described in [24]. All assignments are reported in Tables 2 and 3.

End groups in VDF polymers at higher molecular weight (M_w about 90.000) have been studied by Madorskaya et al. [1]. They consider two types of PVDF, synthesised in an

aqueous medium either in the presence of potassium persulphate or of β -hydroxyethyl-*tert*-butyl-peroxide. The main difference between the two PVDF samples is in the structure of their end groups.

In persulphate polymerisation the end groups formed during initiation may be as follows:



End group (IV) gives HF and is almost instantaneously transformed into a carbonyl group ($-\text{CH}_2-\text{COF}$).

Hydrolysis of the ester group II takes place readily and leads ultimately to the formation of a terminal carbonyl ($-\text{CH}_2-\text{COF}$).

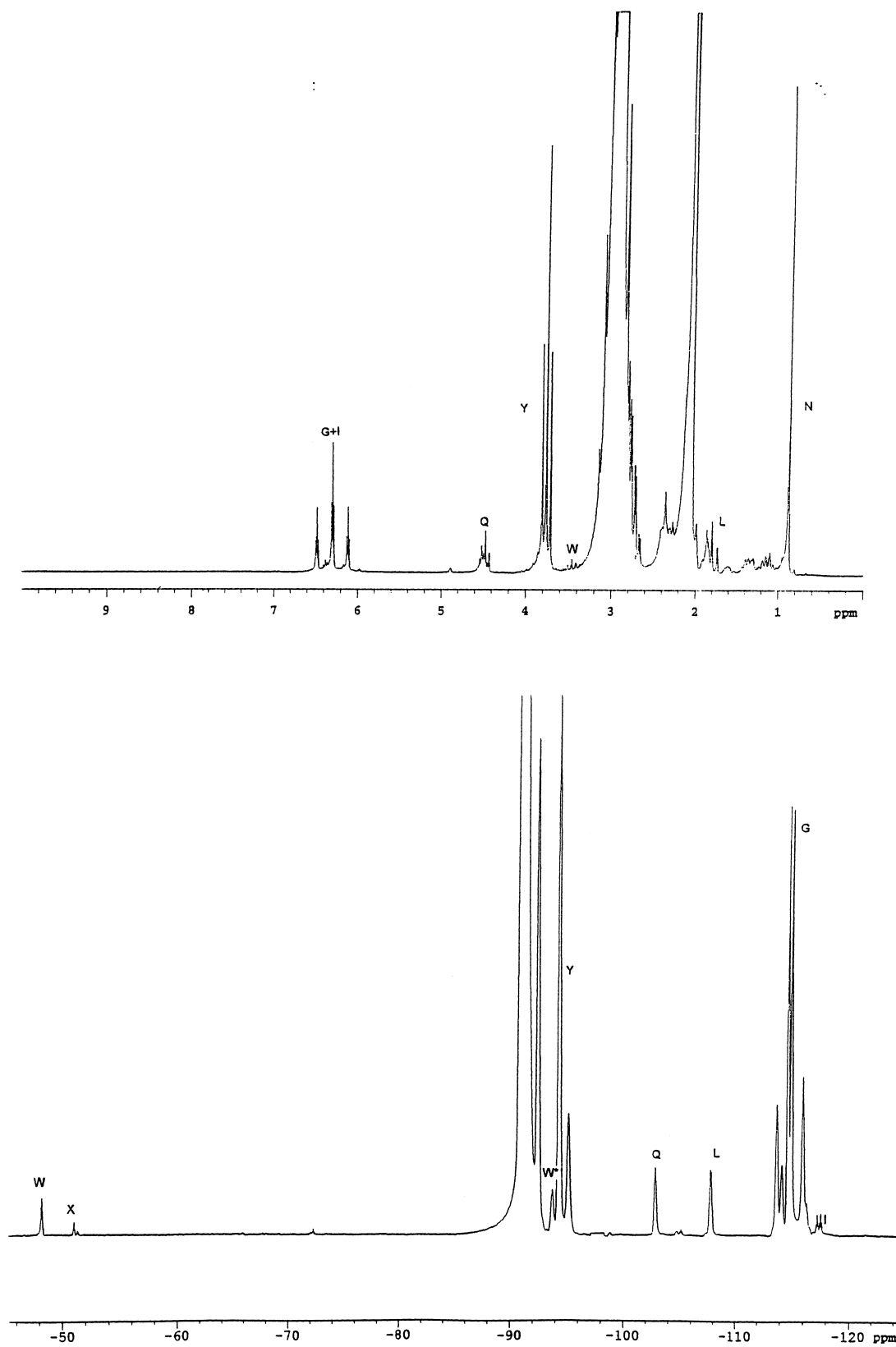


Fig. 10. (A) ^1H NMR spectrum of a low molar mass PVDF synthesized in CCl_4 . (B) ^{19}F NMR spectrum of the same sample. Attributions of the signals are reported in Tables 2 and 3.

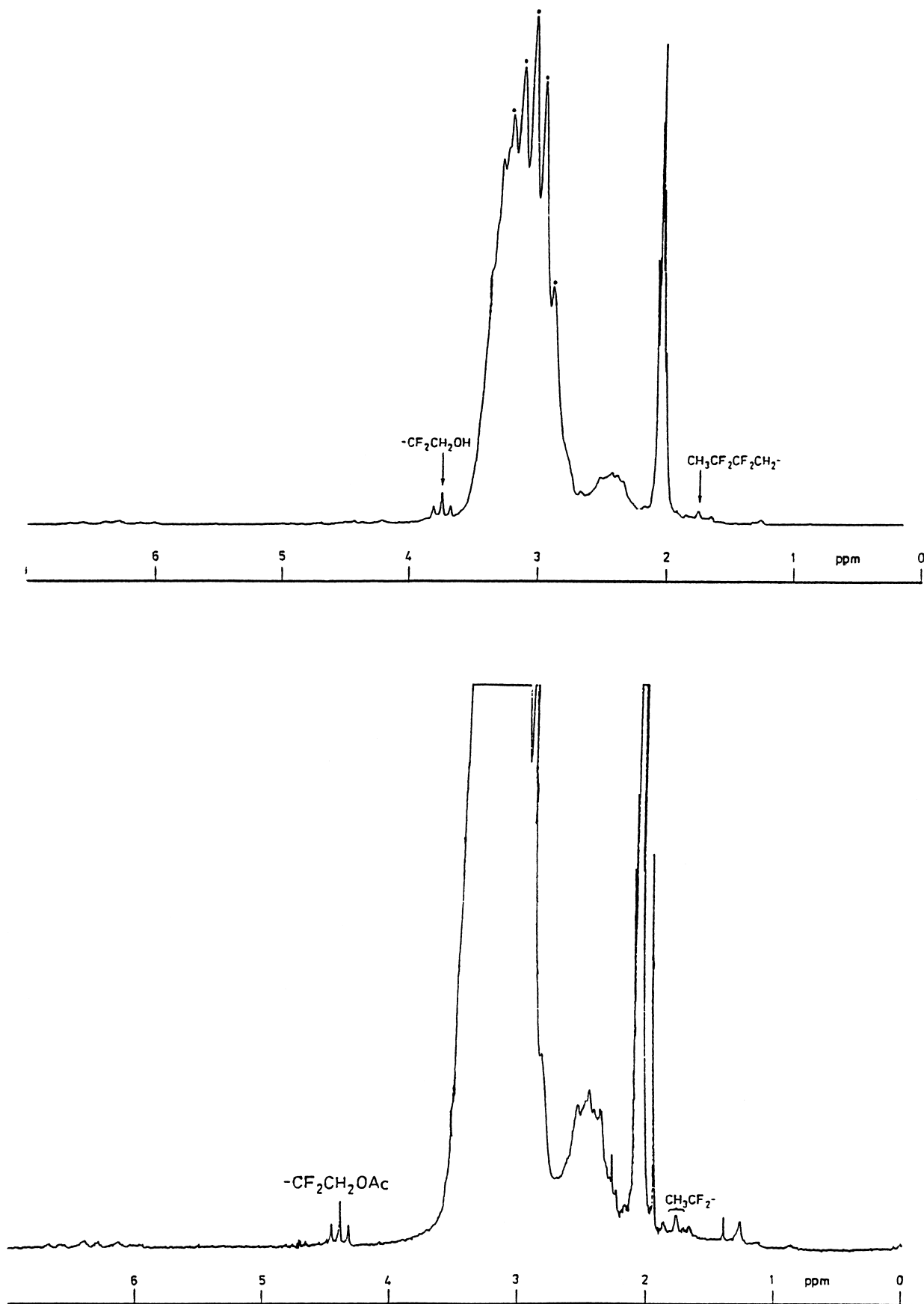


Fig. 11. $^1\text{H NMR}$ spectra of a high molar mass VDF-HFP copolymer before and after acetylation with acetic anhydride.

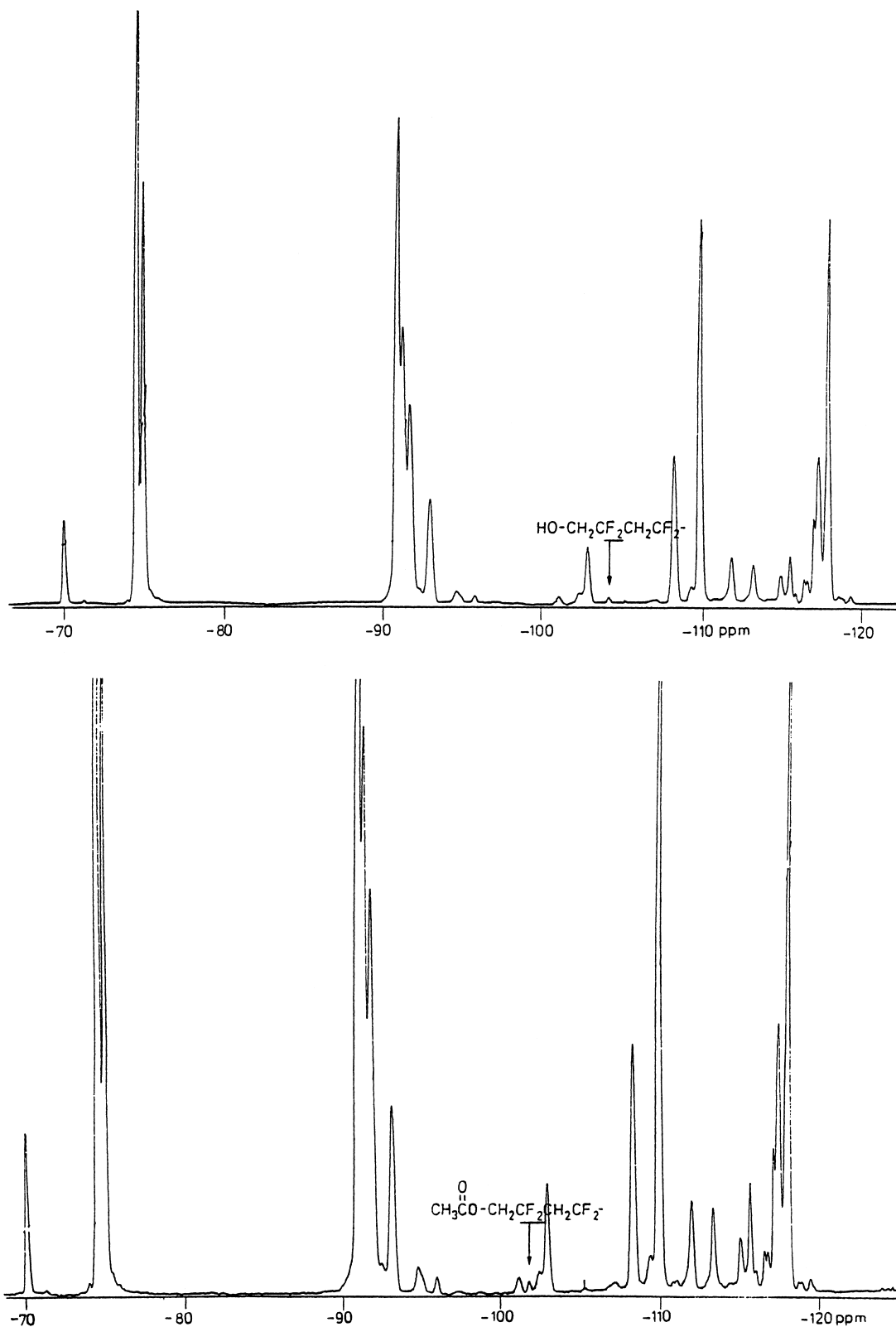


Fig. 12. ^{19}F NMR spectra of a high molar mass VDF-HFP copolymer before and after acetylation with acetic anhydride.

The ester bond in end group I is more stable than that in group II, but it is likewise subjected to hydrolysis giving a HO-CH₂-CF₂- terminal, as was evident from the appearance of an infrared band at 3550 cm⁻¹, related to an associated -OH group.

We have indeed always observed HO-CH₂-CF₂- end groups in samples of PVDF or of vinylidene fluoride/hexafluoropropene (VDF/HFP) copolymers synthesised in emulsion using ammonium persulphate as initiator. The related -CH₂- and -CF₂- NMR signals appear on their ¹H and ¹⁹F spectra, and the -OH group is observed as a band at 3636 cm⁻¹ in the IR spectrum. We have confirmed the assignments of Tables 2 and 3 by means of an acetylation reaction: the polymer is dissolved in acetic anhydride and is analysed after evaporation of the reaction mixture. ¹H and ¹⁹F NMR spectra show the expected shift of the signals due to the transformation of the alcohol to the acetic ester (Figs. 11 and 12), while the IR -OH band disappears and a new band appears at 1760 cm⁻¹ as expected from a CH₃-CO-O-CH₂-CF₂- group. In these polymers we could observe, by IR spectroscopy, a band at 1722 cm⁻¹ that is shifted to 1572 cm⁻¹ by exposition of the sample to ammonia vapours. Analogously to what observed in thermoplastic fluoropolymers, this behaviour is explained by the transformation of a -CF₂-CH₂-COOH carboxylic group into its ammonium salt.

The intensities of the 1722 cm⁻¹ (-C=O) and 3636 cm⁻¹ (-O-H) bands are of the same order of magnitude; considering the different absorption coefficients of the two groups, this means that hydroxyl end groups are about 10 times more abundant than carboxyls.

To investigate the structure of end groups in a VDF copolymer containing 5–7 mol% of TFE, Madorskaya [25] applied a radiotagging method. Using as initiator different samples of β-hydroxyethyl-*tert*-butyl peroxide labelled with ¹⁴C or ³H in various positions, it was possible to identify and quantify the following end groups:

- -CH₃ (63% of the total number of end groups);
- -CH₂-CF₂H (34%);
- (CH₃)₃C-O- (2%);
- HO-CH₂-CH₂-O- (1%).

By comparing the average number molecular mass of the VDF-TFE copolymer (equal to about 55 000 as determined by GPC analysis) with the total number of end groups, it was also proved the presence of branches, about 1.5 per 100 monomer units.

Comparing the proton NMR spectra of PVDFs obtained by persulphate or di-*tert*-butyl peroxide initiated polymerisation, we have observed that CH₃-CH₂-CF₂- is the only end group related to the di-*tert*-butyl peroxide initiator, due to the reaction of a methyl radical with a VDF molecule. It is easily observed in the proton NMR spectrum as a triplet at 1.05 ppm (Table 3).

-CH₂-CF₂H and -CF₂-CH₃ end groups are present in every commercial PVDF. Their NMR identification has

been described above and their formation can be attributed to chain transfer reactions induced by any hydrogen source in the polymerisation environment. The molar ratio -CH₂-CF₂H/-CF₂-CH₃ can vary between 1.2 and 4; the total content of the two end groups is strongly dependent on the polymerisation temperature and we have observed values ranging from 0.05 to 1 mole per 100 monomer units. Considering that in commercial PVDF the degree of polymerisation is in the range 800–1600, the high concentration of these end groups demonstrates the presence of branches.

4. Poly(vinyl fluoride) (PVF)

¹⁹F NMR spectra of PVF are considerably more complicated than those of PVDF because two types of configurational disorder are possible: stereo-irregularity and regio-irregularity.

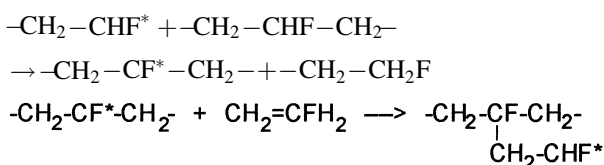
NMR and IR studies [26,27] have clearly established that PVF is largely stereo-irregular, irrespective of the polymerisation conditions used to prepare it, and detailed stereo-sequences assignments show that the polymer is predominantly atactic, with only a modest dominance of syndiotactic sequences.

The two main groups of peaks at about -180 and -190~-200 ppm in the ¹⁹F NMR spectra of PVF are due respectively to head to tail and head to head monomer sequences and their intensity ratio indicates that about 12–15% of the monomer units are reversed in commercial polymers.

In spite of their complexity, ¹⁹F NMR spectra of PVF give good information about end groups. As for PVDF, the more easily observable end groups are not originated by initiation or termination steps, but by an intra- or inter-molecular transfer of a hydrogen atom, leading to chain branching.

Weak peaks at -220 and -147 ppm, observed in the ¹⁹F NMR spectra run at 376.5 MHz of PVF samples swollen in Me₂SOD₆, have been attributed by Ovenal et al. [26] to -CH₂-CH₂F end groups and to tertiary fluorine atoms -CF< at branch points.

The -CH₂-CH₂F groups should arise from hydrogen abstraction by growing polymer radicals ending in -CHF*, according to the following mechanism, which results in the formation of tertiary fluorine atoms



The 400 MHz proton NMR spectrum of the same sample swollen in Me₂SOD₆ was too broad to directly identify weak peaks from branched structures, but by means of differential selective irradiation of the fluorine NMR spectrum at -220 ppm (corresponding to the weak -CH₂F resonances) a positive response from the -CH₂F protons was seen at

4.5 ppm and also a weaker response from the $-\underline{\text{CH}_2}-\text{CH}_2\text{F}$ protons was observed at 2.0 ppm.

The correct interpretation of the weak signals in PVF ^{19}F NMR spectra allowed Aronson et al. [27] to associate the observed changes in the melting point of the polymer primarily with differences in the number of chain branch points, and not the regio-regularity.

References

- [1] L.Ya. Madorskaya, N.N. Loginova, Yu.A. Panshin, A.M. Lobanov, *Polym. Sci. USSR* 25 (1983) 2490.
- [2] J. Scheirs (Ed.), *Modern Fluoropolymers, High Performance Polymers for Diverse Applications*, Wiley, New York, 1997.
- [3] R.A. Morgan, W.H. Sloan, US Patent 4 626 587 (1986).
- [4] M.I. Bro, C.A. Sperati, *J. Polym. Sci.* 28 (1959) 289.
- [5] M.J. Pellerite, *J. Fluorine Chem.* 49 (1990) 43.
- [6] R.D. Lousenberg, M.S. Shoichet, *J. Org. Chem.* 62 (1997) 7844.
- [7] H.C. Gibbard, US Patent 5 180 803 (1993).
- [8] J.F. Imbalzano, D.L. Kerbow, US Patent 4 743 658 (1988).
- [9] M.D. Buckmaster, US Patent 5 093 409 (1992).
- [10] R.C. Schreyer, US Patent 3 085 083 (1963).
- [11] P. Colaianna, J.A. Abusleme, N. Del Fanti, US Patent 5 608 020 (1997).
- [12] P. Colaianna, J.A. Abusleme, N. Del Fanti, US Patent 5 618 897 (1997).
- [13] D.P. Carlson, European Patent Application 0 178 935 A1 (1985).
- [14] W.K. Fisher, J.C. Corelli, *J. Polym. Sci. Polym. Chem. Ed.* 19 (1981) 2465.
- [15] H. Vanni, J.F. Rabolt, *J. Polym. Sci. Polym. Phys. Ed.* 18 (1980) 587.
- [16] D. Fisher, U. Lappan, I. Hopfe, K.J. Eichhorn, K. Lunkwits, *Polymer* 39 (1998) 573.
- [17] H. Yu, J. Mi, H. Ni, *Chin. J. Microwave Radiofrequency Spectrosc.* 1 (1984) 372.
- [18] Ye.M. Murascheva, A.S. Shashkov, A.A. Dontsov, *Polym. Sci. USSR* 23 (1981) 711.
- [19] R.E. Cais, N.J.A. Sloane, *Polymer* 24 (1983) 179.
- [20] G. Luttringer, B. Meurer, G. Weill, *Polymer* 32 (1991) 884.
- [21] S. Modena, M. Pianca, M. Tatò, G. Moggi, S. Russo, *J. Fluorine Chem.* 43 (1989) 15.
- [22] W.C. Mattiew, F.C. Stehling, *Macromolecules* 14 (1981) 1479.
- [23] S. Russo, K. Behari, S. Chengji, M. Pianca, E. Barchiesi, G. Moggi, *Polymer* 34 (1993) 4777.
- [24] Herman, T. Uno, A. Kubono, S. Umamoto, T. Kikutani, N. Okui, *Polymer* 38 (1997) 1677.
- [25] L.Ya. Madorskaya, V.M. Samoilov, G.A. Otradina, A.P. Agapitov, V.P. Budtov, T.G. Makeyenko, Ye.Yu. Kharcheva, N.N. Loginova, *Polym. Sci. USSR* 26 (1984) 2891.
- [26] D.W. Ovenal, R.E. Uschold, *Macromolecules* 24 (1991) 3235.
- [27] M.T. Aronson, L.L. Berger, U.S. Honsberg, *Polymer* 34 (1993) 2546.