The structure and morphology of vinylidene fluoride and trifluoroethylene copolymers studied by 'wide-line' nuclear magnetic resonance

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Both hydrogen and fluorine nuclear magnetic resonance measurements have been performed on copolymers of vinylidene fluoride (VF_2) and trifluoroethylene (TrFE) containing from 30 to 100 mol% VF_2. The temperature study of the 70/30 copolymer reveals that two crystalline and one amorphous phase must be considered to describe the ferroelectric transition. At low temperature, the structural change from α to β crystalline form with increasing TrFE content is clearly detected. At room temperature, the morphology of VF_2-rich copolymers is well analysed with two components having the same ^1H to ^{19}F ratio. On the other hand, below 70 mol% VF_2 the two components have different ^1H to ^{19}F ratio, which implies segregation between TrFE-rich and VF_2-rich sequences.

(Keywords: nuclear magnetic resonance; ferroelectrics; phase transition; crystallinity of polymers; vinylidene fluoride–trifluoroethylene copolymers; piezoelectric polymers)

INTRODUCTION

The piezoelectric behaviour of poly(vinylidene fluoride) (PVF_2) is known to be related to the ferroelectricity of the crystalline β structure[1] and the composite character of the semicrystalline structure, i.e. ferroelectric lamellae embedded in an amorphous fraction[1]. Copolymers of vinylidene fluoride and trifluoroethylene $P(VF_2$–TrFE), which present a clear Curie point below the crystalline melting point[2], are able to crystallize despite the chemical inhomogeneity of the polymer chain. We have used hydrogen and fluorine solid-state n.m.r. to gain information on:

(i) the crystalline fraction and crystalline morphology of the copolymers, and

(ii) the relative fraction of VF_2 and TrFE units in the rigid and mobile phases.

METHOD

A series of copolymers with VF_2 mole fractions between 30 and 100% have been provided by Atochem Co. (France). Films of copolymers have been cast at 180°C, quenched at room temperature and eventually annealed at 120°C by Thomson CSF Laboratories, where parallel d.s.c. and X-ray measurements are carried out. N.m.r. measurements have been carried out on a Bruker SXP spectrometer operating at 60 MHz (^1H) and 56.4 MHz (^{19}F). The resonance field is maintained with a field-frequency lock (Drusch, RMN gaussmeter and regulation unit TAO2) within 2 mG. The free induction decay (FID) signal following a $\pi/2$ pulse is digitized with a Bruker BC100q (8 bits, up to 10 MHz), averaged and treated on-line on a Nicolet BNC12 minicomputer. A polynomial procedure (POLFIT) has been used to extrapolate the signal at $t=0$ (the middle of the pulse) through the dead time of the receiver and to calculate the second and fourth moments of the n.m.r. absorption line according to ref. 3 (*Figure 1*). At temperatures above the glass transition temperature of the amorphous fraction and below the melting point of the crystalline fraction, the dipolar interaction in the amorphous phase is partly averaged out by the motion: a long tail appears in the FID which can be approximated by a Gauss-Lorentz function $A\exp[-(t/T_2)^n]$, with $n=1$, 1.5 or 2. Fittings are performed by non-linear least-squares adjustments, n being fixed. After subtraction from the FID, the resulting signal (which can still present a residual tail attributed to a less mobile amorphous fraction to which the same treatment can be applied giving parameters A', T_2' and n') corresponds to the rigid fraction. Its fitting by the POLFIT procedure gives the moments M_2 and M_4 of the rigid part. From the ordinate C at $t=0$ one gets an evaluation of the rigid fraction $X=C/(A+A'+C)$.

Strictly speaking the amorphous signal cannot be purely exponential ($n=1$) up to the origin $t=0$ but should present a downward curvature corresponding to a finite M_2. Therefore, X is in principle slightly underestimated.

RESULTS

Preliminary ^1H study of the 70/30 $P(VF_2$–TrFE) copolymer

The FID signal has been analysed on a sample that underwent many thermal cycles to avoid effects of annealing. The total second moment undergoes a large change above 60°C with a large hysteresis loop reflecting the first-order crystalline transition, in agreement with previous ^{19}F resonance results[4].

A more precise analysis implies a decomposition into three components: an exponential ($n=1$) or Gaussian

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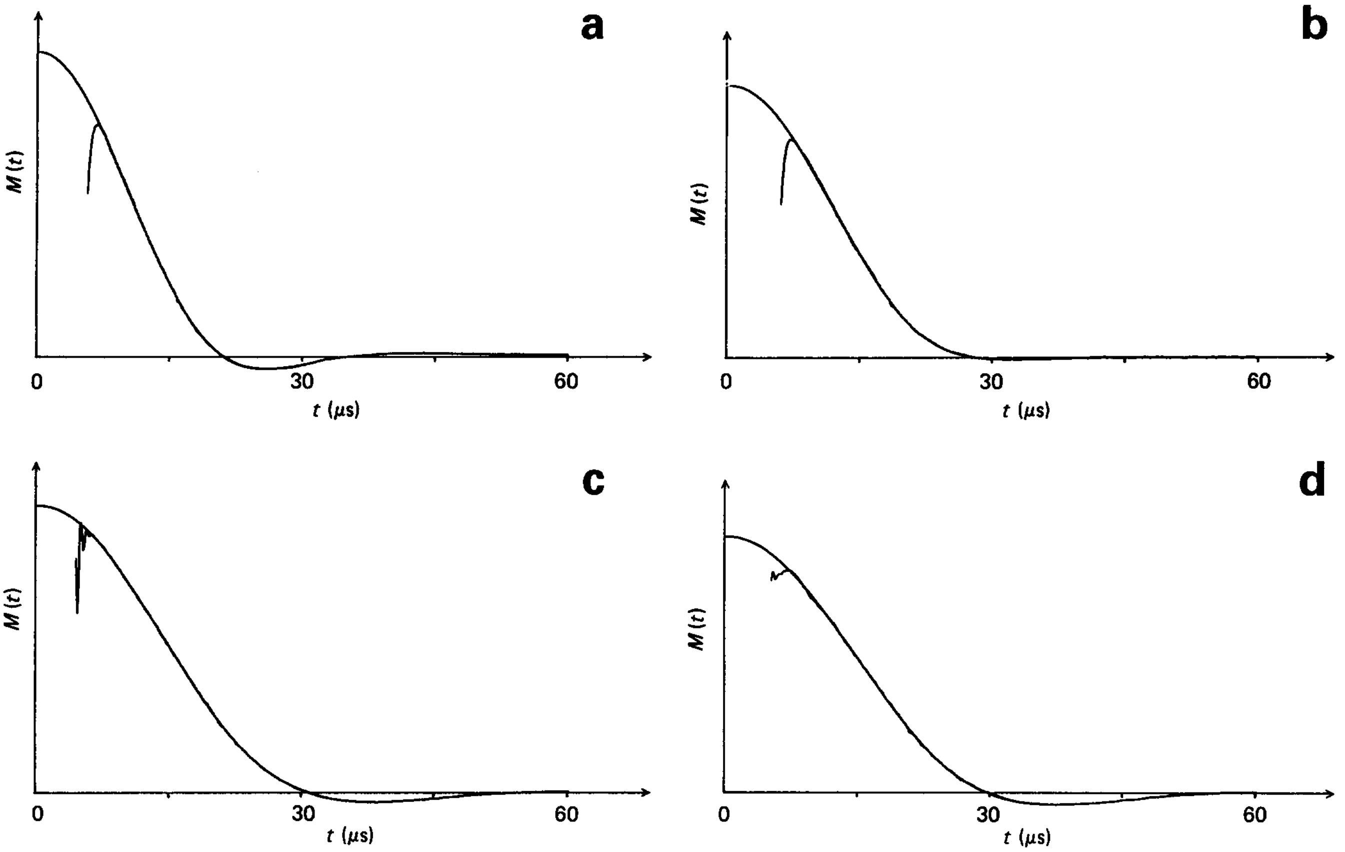

Figure 1 Best fit and extrapolation to zero time (POLFIT procedure) of the rigid lattice FIDs ($T=140$ K). (a) ^{1}H on PVF$_2$, $M_2=14.9$ G^2; (b) ^{1}H on a 50/50 P(VF$_2$–TrFE) copolymer, $M_2=11.4$ G^2; (c) ^{19}F on PVF$_2$, $M_2=9.2$ G^2; (d) ^{19}F on the copolymer of (b), $M_2=8.6$ G^2

exponential ($n=1.5$) long tail, a Gaussian ($n=2$) intermediate signal and a rigid signal (*Figure 2*). This latter one has the oscillating shape observed below T_g (-15°C). Between T_g and 60°C the exponential and Gaussian signals amounting in total to 10% are believed to originate from the free and constrained amorphous phases. Above 60°C, the rise of the Gaussian signal up to 80% corresponds to the transformation of the crystalline ferroelectric phase into the paraelectric phase. This is evidenced by its large hysteresis (*Figure 3*) and its nearly constant second moment (*Figure 4*). The slight decrease of M_2 can be accounted for by lattice thermal expansion. At the transition, the amorphous signal changes from exponential ($n=1$) to Gaussian exponential ($n=1.5$) with a change in amplitude but no discontinuity in the time constant T_2 (*Figure 5*).

Between T_g (-15°C) and 60°C the crystalline fraction and its second moment are essentially constant. Therefore a series of copolymers of different VF$_2$–TrFE contents have been analysed at low (-130°C) and room (27°C) temperature to gain information on the structure of their crystalline and amorphous phases.

Low-temperature study of the copolymers

The FID has an oscillating character (*Figure 1*). The variation of the second moment with the VF$_2$ content is shown in *Figure 6*. $M_2(^1\text{H})$ decreases with the introduction of TrFE while $M_2(^{19}\text{F})$ remains approximately constant. These values are in agreement with previous results on the 72/28 copolymer[5]. One notices, however, a significant discontinuity in the $M_2(^1\text{H})$ at a TrFE content of about 15%. The lineshape, as characterized by the ratio M_4/M_2^2 ($M_4/M_2^2=3$ for a Gaussian) remains constant and equal to 2.3 ± 0.1 for both ^{1}H and ^{19}F resonances.

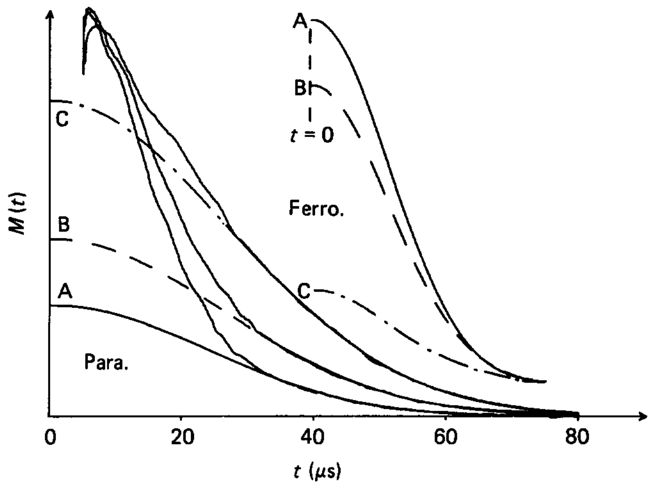

Figure 2 Analysis of the ^{1}H FID of the 70/30 P(VF$_2$–TrFE) copolymer as a function of temperature: paraelectric and ferroelectric components at (A) 357 K, (B) 365 K and (C) 380 K. The signal of the ferroelectric phase at the right is the best fit to the difference of the actual FID (after subtraction of the exponential long tail) and the Gaussian signal of the paraelectric phase

Room-temperature study of the copolymers

The separation of the amorphous and crystalline signals is easily performed for copolymers with a mole fraction of VF$_2$ higher than 60%, due to the differences in time constants of the components.

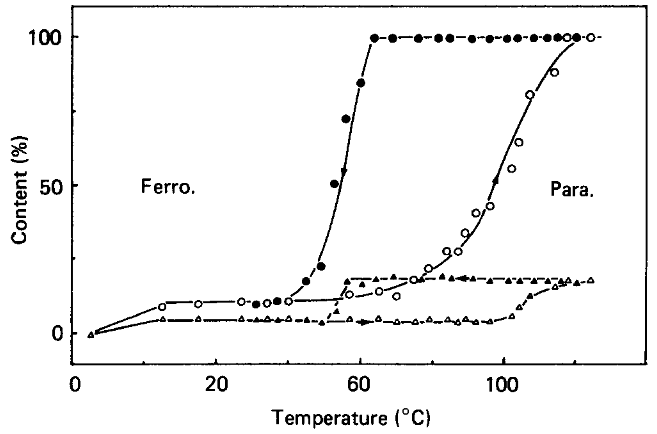

Figure 3 Percentage of amorphous (△,▲) and amorphous plus paraelectric (○,●) components of the 70/30 copolymers as a function of temperature. Open symbols, heating; filled symbols, cooling

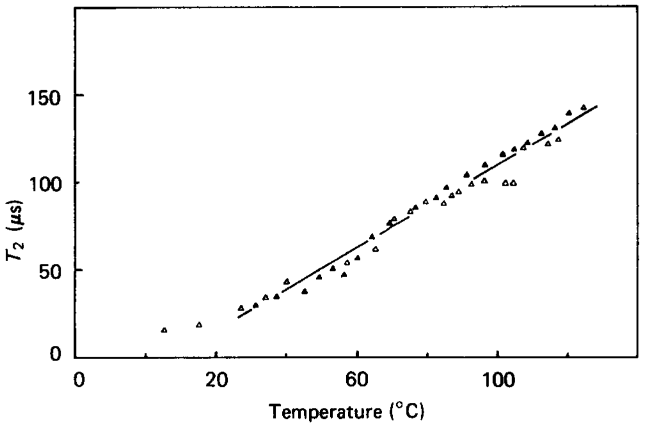

Figure 5 Time constant T_2 of the amorphous fraction of the 70/30 copolymers as a function of temperature. Open symbols, heating; filled symbols, cooling

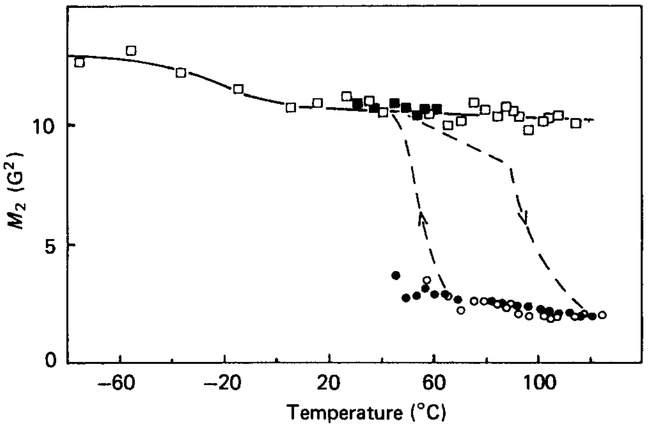

Figure 4 ^{1}H second moments of the rigid (□,■) and Gaussian (○,●) signals of the 70/30 copolymers as a function of temperature. The broken curve gives the total crystalline second moment in the transition range. Open symbols, heating; filled symbols, cooling

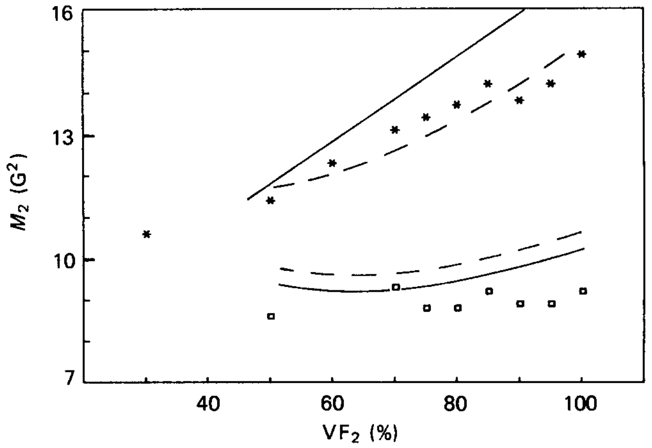

Figure 6 ^{1}H (★) and ^{19}F (□) rigid lattice second moments as a function of VF$_2$ content. The calculated values are shown as full (β form) and broken (α form) curves

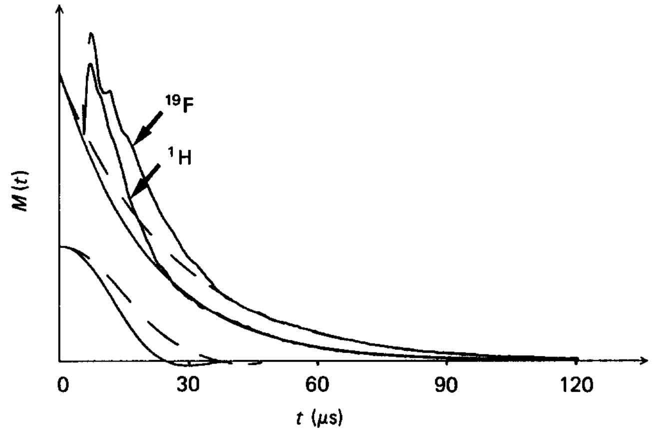

Figure 7 FIDs and their component analysis on a quenched sample of 90/10 P(VF$_2$–TrFE) at room temperature. The ^{1}H (full curves) and ^{19}F (broken curves) signals give equal mobile fractions ($T_2(^1\mathrm{H})=20\,\mu s$, $T_2(^{19}\mathrm{F})=26\,\mu s$) and oscillating rigid decays ($M_2(^1\mathrm{H})=10.8\,\mathrm{G}^2$, $M^2(^{19}\mathrm{F})=7.9\,\mathrm{G}^2$)

In the 70–100% VF$_2$ range. The crystalline fractions as measured by ^{1}H and ^{19}F are equal (*Figure 7*). Their values show that the efficiency of the annealing increases with decreasing VF$_2$ content (*Figure 8a*).

The ^{1}H and ^{19}F crystalline second moments are smaller than the overall low-temperature M_2 but are independent of the composition (*Figure 8b*).

The amorphous T_2 are independent of the change of crystallinity upon annealing and increase with decreasing VF$_2$ content (*Figure 8c*).

In the 60–30% VF$_2$ range. Owing to the decrease in second moment and amorphous T_2 observed in the 60% VF$_2$ copolymer as compared to the 70% VF$_2$ copolymer, the direct separation of the amorphous and crystalline signals in copolymers with a VF$_2$ content below 60% becomes very difficult.

Hydrogen spin–lattice relaxation (T_1) and hydrogen and fluorine spin–lattice relaxation in the rotating frame ($T_{1\rho}$) performed on the series of quenched copolymers reveal, however, a heterogeneous character: the relaxation is biexponential with the long component associated with the crystalline fraction (*Figures 9* and *10*). In hydrogen resonance, it is therefore possible to saturate the crystalline signal by a sequence of three $\pi/2$ pulses with a spacing of 10 μs to record the partially saturated signal and then easily adjust an exponential to its long tail (*Figure 11*). We checked then that the intensities of the fast and slow relaxing $T_{1\rho}$ components are in good agreement with the amorphous and crystalline fractions, an indication of inefficient spin diffusion^6.

In fluorine resonance, the crystalline fractions are directly deduced from intensities of $T_{1\rho}$ components. An exponential curve can be adjusted to the long tail of the FID signal to obtain the same crystalline fractions. The remaining crystalline signals are Gaussian, both in ^{1}H

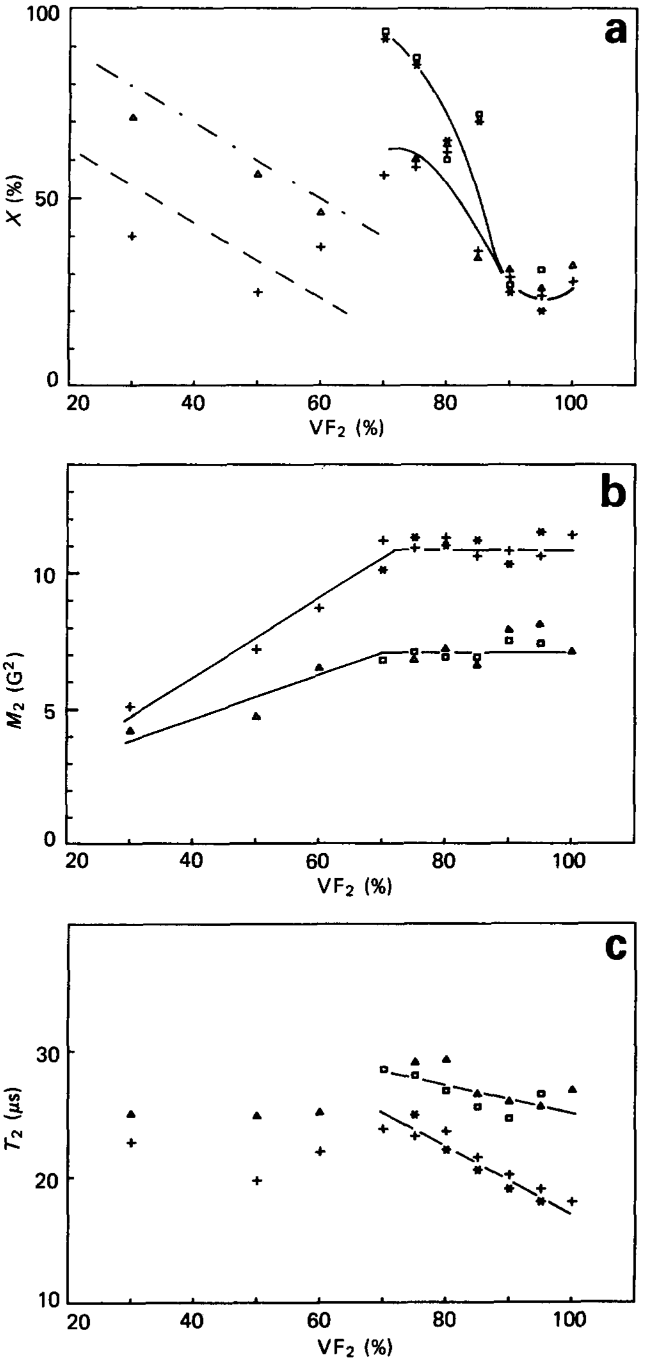

Figure 8 (a) Hydrogen and fluorine crystalline fractions, (b) rigid second moments and (c) mobile transverse relaxation times as functions of VF$_2$ content of copolymers at 300K: ^{1}H (+) and ^{19}F (△) on quenched samples; ^{1}H (★) and ^{19}F (□) on annealed samples. Broken lines are calculated fractions according to segregated units

and ^{19}F resonance. Their second moments and the crystalline fractions are reported in *Figure 8*. In annealed samples the method fails: while T_1(^{1}H) and $T_{1\rho}$ remain biexponential, the shape of the FID is independent of the spin-lock duration.

INTERPRETATION OF THE RESULTS

Study of the ferroelectric transition in the 70/30 copolymers

The coexistence of the ferroelectric and paraelectric phases through the transition is in good agreement with X-ray studies[7,8]. Moreover, n.m.r. appears capable of easily quantifying the relative amounts of the two phases. The fact that the transition is smoother in the heating cycle also fits well with d.s.c. results[9].

The drop in second moment observed for the paraelectric crystalline phase ($M_{2\,\mathrm{para}}$(^{1}H) between 2 and 2.5 G^2) cannot result only from a change in molecular structure (introduction of *gauche* bonds) and crystal packing: the crystalline M_2(^{1}H) of a hypothetical rigid paraelectric phase calculated from X-ray results[7] is 11.6 G^2. This therefore implies some dynamic disorder in the crystalline phase, which may also be related to the increased amorphous fraction at the transition. For example, complete rod-like rotation of the crystalline chains about their main chain axes gives an M_2(^{1}H) of 3.5 G^2. More detailed studies on the dynamics of the two phases are required. Measurements of T_1 as a function of frequency and $T_{1\rho}$ are under way and will be presented subsequently.

Low-temperature second moments and the crystalline structure

The discontinuity noticed in M_2(^{1}H) at about 15% TrFE is reminiscent of the change from the α (*TGTḠ* conformation of the chain) to the β (*TT* conformation of the chain) form detected by X-ray diffraction[8,10] and i.r. spectroscopy[10]. Infra-red spectra at room temperature (*Figure 12*) clearly show the α form of 100–90% VF$_2$ copolymers. This discontinuity does not seem to come from the change in crystallinity (*Figure 8a*) since no

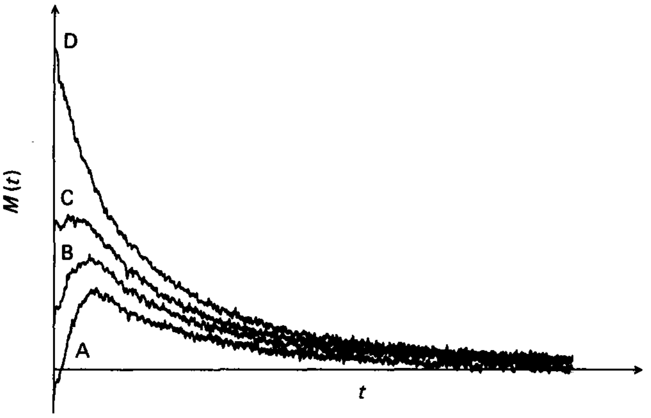

Figure 9 FIDs corresponding to different values of recovery after inversion of ^{1}H magnetization on quenched 70/30 P(VF$_2$–TrFE) with $T_{1c}=303$ ms and $T_{1a}=43$ ms: curve A, $\tau=90$ ms; B, $\tau=110$ ms; C, $\tau=140$ ms; D, $\tau=210$ ms

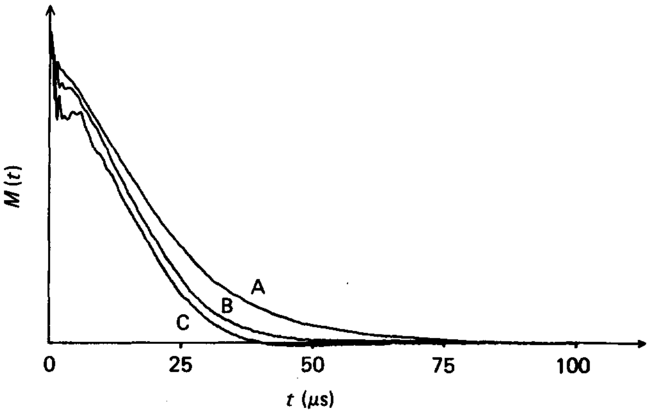

Figure 10 FIDs following ^{19}F spin locking on quenched 50/50 P(VF$_2$–TrFE) with $T_{1\rho c}=6.6$ ms and $T_{1\rho a}=1.7$ ms. Spin-lock duration: A, $\tau=0.1$ ms; B, $\tau=4$ ms; C, $\tau=10$ ms

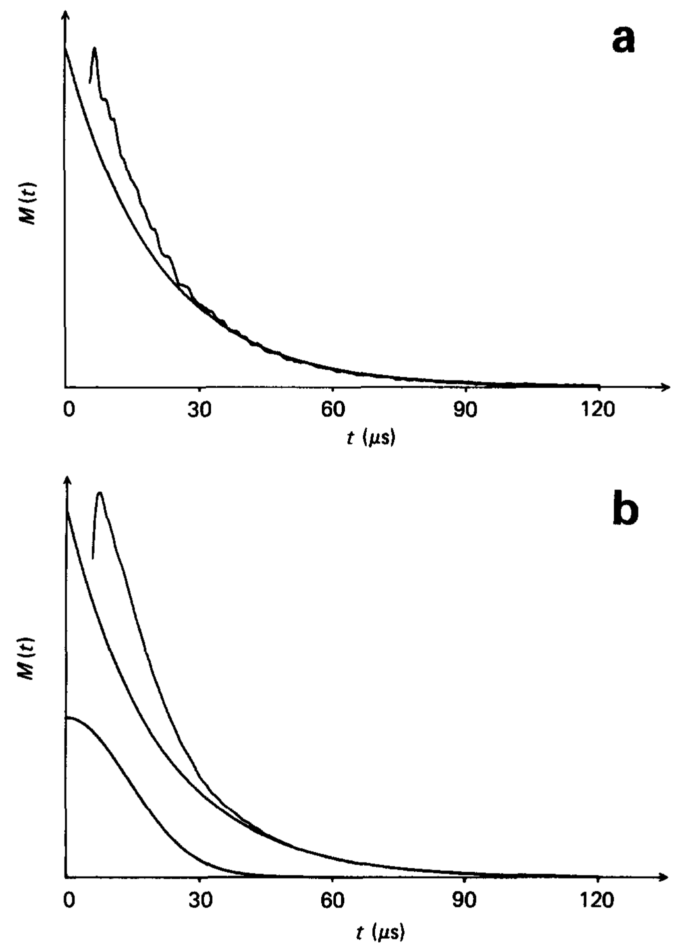

Figure 11 (a) Saturation and (b) component analysis of the ^{1}H FIDs on quenched 50/50 P(VF$_2$–TrFE). Rigid fraction 30%, $M_2 = 7.2\,G^2$. Mobile fraction: exponential of $T_{2a} = 20\,\mu s$

significant difference in the rigid second moment has been detected between quenched and annealed samples.

A calculation of the influence of the TrFE content on the second moment of hypothetical crystalline α and β forms has been performed under the following conditions: (a) The chain conformations are those given for PVF$_2$ by Hasegawa *et al.*[11] (b) The TrFE distribution is statistical and the sequence is taken as regularly head-to-tail. (We checked numerically that head-to-head linkages have little influence on the second moment, particularly in hydrogen resonance). (c) The lattice parameters are extrapolated from the values of Lovinger *et al.*[8].

The results of the calculation are reported in *Figure 6*. While the absolute values do not agree (particularly in the 85–70% VF$_2$ range—part of the difference can certainly be assigned to valence angle distortions), the trends concerning the hydrogen and fluorine resonance are respected. The ^{19}F resonance does not distinguish between the α and β forms and the variation of M_2 is very small. The ^{1}H resonance is more sensitive to the TrFE content with a shift of the data towards the calculated β form values at 85% VF$_2$ content. This substantiates the significance of the discontinuity observed at 15% TrFE as representative of the transition from the α to the β form.

Rigid content and VF$_2$–TrFE partition in rigid and mobile fractions

In the 70–100% VF$_2$ range the rigid ('crystalline') fractions measured from ^{1}H to ^{19}F resonance are equal

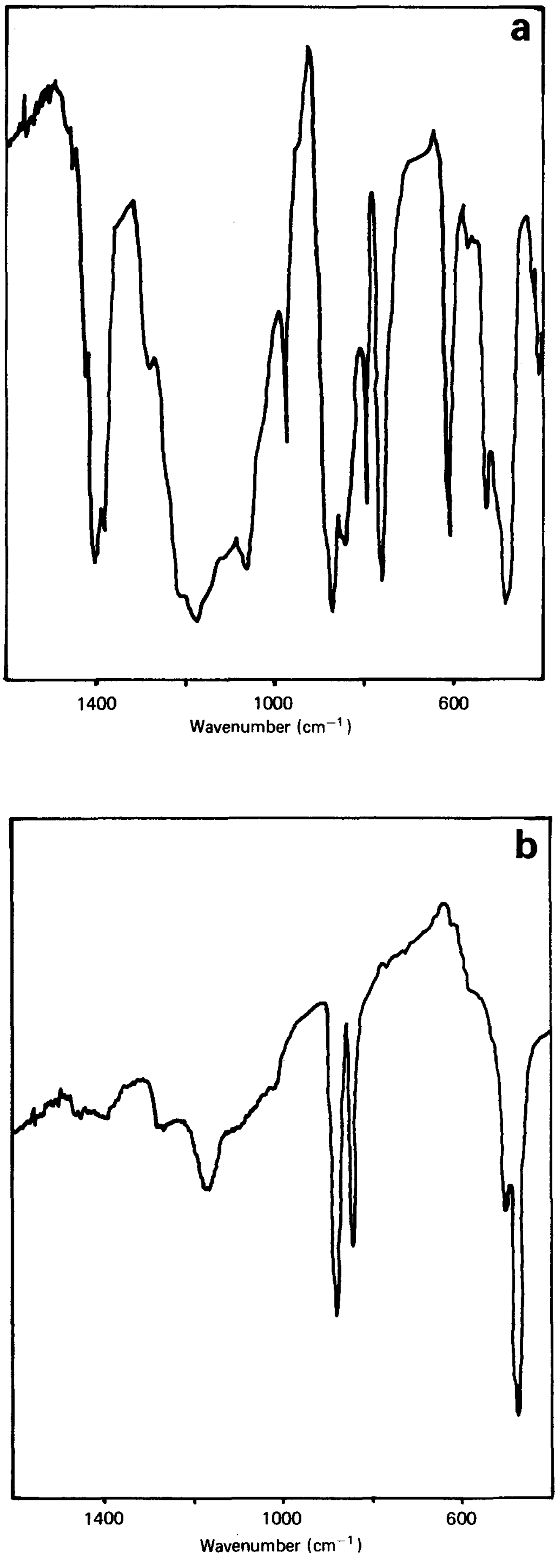

Figure 12 Infra-red spectra of P(VF$_2$–TrFE) copolymers recorded on a Perkin–Elmer 683 infra-red spectrophotometer: (a) 90/10 and (b) 85/15 molar ratios

(*Figures 7* and *8a*). This implies an equal partition of the comonomers in the crystalline and amorphous phases. Below 70% VF_2 the large difference in 'crystalline' fraction measured from ^1H and ^{19}F resonance on quenched samples implies a difference in composition of the rigid and mobile phases. This fits with previous proposals for a segregation of VF_2- and TrFE-rich phases as deduced from X-rays[12] (i.e. coexistence of two crystalline structures) or mechanical loss[10,13] measurements (i.e. coexistence of two glassy phases) in samples that have had different heat treatments. Since it is known that the T_g of PTrFE is close to 40°C[10], n.m.r. at room temperature is not able to distinguish between the amorphous or crystalline character of the TrFE-rich phase. It clearly shows, however, the liquid-like character of the VF_2-rich phase.

The variation with composition of the room-temperature M_2 of the crystalline part (*Figure 8b*) when compared to the low-temperature rigid lattice value (*Figure 6*) indicates some motional averaging, which precludes any quantitative interpretation.

The variation with composition of T_2, which reflects the mobility of the amorphous phase, is small but significant. The rise of T_2 at low TrFE content is surprising. One would expect both the incorporation of TrFE and the increase in crystallinity to lower mobility, i.e. decrease T_2.

CONCLUSIONS

The solid-state ^1H and ^{19}F n.m.r. study of a series of $P(VF_2–TrFE)$ copolymers clearly reveals the difference between the copolymers with low and high contents of TrFE: low contents favour the transformation from the α to β form; higher contents lead to a segregation of the two comonomers between two phases, the rigid one at room temperature being associated with TrFE-rich sequences, the mobile one with VF_2-rich sequences. A clearer understanding will require a characterization of the microstructure by high-resolution n.m.r.

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