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Influence of constitutional defects on polymorphic behaviour and properties of alternating ethylene–tetrafluoroethylene copolymer

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The influence of constitutional defects (those resulting from variations of the comonomer molar ratio from 50/50 and those due to the introduction of termonomer units) and thermal history on the polymorphic behaviour of ethylene–tetrafluoroethylene (ETFE) copolymer is investigated. At low temperatures, while well developed orthorhombic structures are obtained for copolymers with a C_2F_4 content in the range 50–70 mol%, a content of the perfluoropropylperfluorovinylether termonomer of 1.8 mol% is already sufficient to favour formation of the so-called pseudo-hexagonal mesophase. At high temperatures, the degree of crystallinity as well as the correlation length of the hexagonal domains remain essentially unaltered by an increase of the C_2F_4 molar content from 50 to 80%, while both are strongly reduced by low concentrations (1–3 mol%) of the termonomer units (substantially excluded from the crystalline phase). This is expected to be a determinant factor for the improved ultimate properties typical of commercial terpolymers of ETFE.

(Keywords: ETFE copolymer; terpolymers; crystalline transitions)

INTRODUCTION

Several X-ray diffraction studies on the alternating ethylene–tetrafluoroethylene (ETFE) copolymer have been reported in the literature[1-8]. At low temperatures ($T<0°C$) the ETFE copolymer shows an orthorhombic form[1,2] which gradually and reversibly, in a large temperature range (0–100°C), is transformed into a hexagonal mesophase[3,6].

In the low-temperature orthorhombic mesomorphic form, besides the intramolecular order corresponding to a *trans*-planar conformation of the chains, a nearly perfect intermolecular order in the *ab* projection, similar to that of polyethylene, is present. However, a nearly complete absence of intermolecular order (corresponding to nearly random relative displacements of neighbouring chains) occurs along the *c* axis[2,7]. This is clearly suggested by the fibre spectra, which show sharp reflections on the equator and only diffuse intensity maxima on the other layer lines[2,7]. In the high-temperature hexagonal form of ETFE, besides a translational disorder, a rotational disorder of the chain is also present. A long-range order is possibly maintained only inside each chain (remaining *trans*-planar) and in the pseudo-hexagonal arrangement of the chain axes[3,6].

In the transition from the orthorhombic form towards the hexagonal mesophase, the two peaks observed in the X-ray powder diffraction spectra at low temperatures (indexed as 1 1 0 and 2 0 0 reflections according to the unit cell with $a=8.57$ Å, $b=5.60$ Å and $c=5.04$ Å, refs 2 and 6*) become a single peak at high temperatures (indexed as $1\,0\,0_h$, where h indicates hexagonal). Correspondingly, in this transition, a strong reduction of the half-width of the reflections is observed[3,6]. This of course indicates that the coherent size of the domains, in which an ordered disposition of the chain axes is maintained, is larger for the more disordered (hexagonal) mesophase. A possible explanation for this phenomenon is the topotactic transformation of hexagonal mesophase domains into smaller orthorhombic domains, related to the three possible different orientations of the orthorhombic cell with respect to the hexagonal frame[6].

Depending on the thermal history, some ETFE samples present in their X-ray powder spectra at room temperature only a single but broad and asymmetric peak, which, like the two reflections of the orthorhombic form, becomes sharper at higher temperatures, showing the usual transition region in the temperature range 0–100°C (refs 3 and 6). The mesomorphic domains contained in these samples have been described as 'pseudo-hexagonal' (their single asymmetric peak has been indexed as $1\,0\,0_{ph}$

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*The 1 1 0 peak has been more frequently cited[2,6] as 1 2 0 according to a problematic unit cell with a double *b* value[2] reflection[3]) and possibly present lateral dimensions much smaller than the orthorhombic domains[2,3].

In this paper, the influence of constitutional defects and thermal history on the polymorphic behaviour of ETFE is investigated. In particular, possible conditions for the achievement of the orthorhombic form and pseudo-hexagonal mesophase (that is, of the modifications observed at low temperatures) are studied. Two different kinds of constitutional defects are considered: those derived by variations of the comonomer molar ratio from 50/50 and those due to the introduction of termonomer units. The variations of the crystallinity and crystal size in the presence of these constitutional defects have been also investigated. The aim is to attempt to account for the large improvement of the ultimate mechanical properties, in high-temperature stress-strain tests, observed for the commercial ETFE terpolymers with respect to the pure copolymers.

EXPERIMENTAL

The ethylene-tetrafluoroethylene (ETFE) copolymer samples were supplied by Ausimont S.p.A. The percentages of C_2F_4 units are given in mol% throughout the paper.

The ETFE terpolymers contain percentages of termonomer units [from perfluoropropylperfluorovinylether (FPVE)] in the range 0–2.7 mol%. The C_2F_4/C_2H_4 ratio in the terpolymer samples is close to 1.1.

Samples used for the X-ray diffraction measurements, obtained by compression moulding, had a thickness in the range 0.8–1.2 mm. X-ray diffraction patterns at different temperatures were obtained with an automatic Philips powder diffractometer (Ni-filtered Cu $K\alpha$ radiation), with a temperature control of ± 0.5°C.

Evaluation of the correlation length D of the mesomorphic domains (in which an ordered disposition of the chain axes is maintained) in the directions perpendicular to the chain axes, was effected using the Scherrer formula for the main equatorial reflection

$$D = 0.9\lambda / \beta \cos\theta$$

where β is the half-maximum line breadth. For $\beta < 1.0°$ (in 2θ units) the procedure described in ref. 9, for the correction of the half-width for experimental effects, was applied. In particular, we used a standard quartz specimen having a half-maximum line breadth, under similar geometrical conditions, of 0.18°.

A measure of crystallinity index (x_c) was obtained by resolving the X-ray diffraction patterns of unoriented samples, between 2θ values of 13 and 25°, into the diffraction area relative to the crystalline peaks (I_c) and the diffraction area relative to the amorphous halo (I_a), and using the equation

$$x_c = \frac{I_c}{I_c + I_a} 100$$

The shape of the amorphous halo was obtained by measurements on melt samples. The 2θ position of the halo in the X-ray diffraction patterns of crystalline samples was assumed by extrapolation, to the temperature of measurement, of the observed values for patterns collected in the temperature range 240–280°C on previously melted samples. To minimize the error in these extrapolations, evaluations of the crystallinity indices were performed on patterns taken at 180°C.

Mechanical tests were carried out as a function of temperature following ASTM D 3159 at a testing speed of $50\,\mathrm{mm\,min^{-1}}$; the corresponding strain rate was $3.55 \times 10^{-2}\,\mathrm{s^{-1}}$.

The long-term behaviour (1000 h) at high temperatures, which is indicative of the so-called thermal stress cracking phenomenon, was also determined at 150°C by means of tensile creep testing (ASTM D 2990); the range of the applied load was between 1.5 and 5 MPa.

RESULTS

Copolymers

The X-ray diffraction patterns of the copolymer with a C_2F_4 content of 55 mol%, measured at different temperatures on cooling stepwise from the melt, are shown in *Figure 1*. Below room temperature, the 1 1 0 and 2 0 0 peaks typical of the orthorhombic form are observed. However, as in all the X-ray diffraction patterns of unoriented orthorhombic ETFE samples reported in the literature[2,3,5,6], the two peaks are poorly resolved and the 2 0 0 peak is always much smaller than the 1 1 0 peak.

The resolution between the two peaks in the ETFE copolymer samples is largely improved when the crystallization occurs on rapid cooling from the melt state. Moreover, these quenched copolymer samples present a markedly increased intensity of the 2 0 0 peak with respect to the 1 0 0 peak. For instance, the X-ray diffraction patterns measured at −80°C of copolymer samples of different compositions, quenched from the melt state into water at 0°C, are shown in *Figure 2*. Patterns typical of the orthorhombic form, better resolved than previously reported, are obtained for samples with a C_2F_4 content in the range 50–70 mol%. For the sample with 80 mol% content of C_2F_4, which is constitutionally

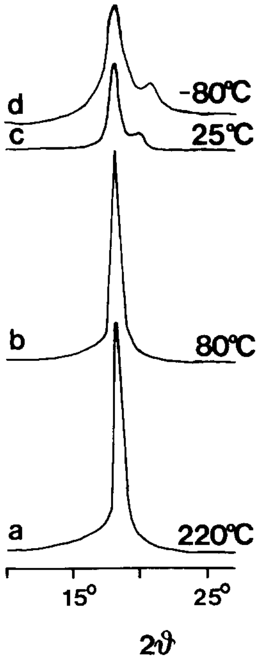

Figure 1 X-ray diffraction patterns of the ETFE copolymer with a C_2F_4 content of 55 mol%, measured at different temperatures on cooling from the melt

closer to polytetrafluoroethylene than to the alternating copolymer, only a single peak typical of a hexagonal form is observed.

The quenched samples of *Figure 2* were subjected to thermal cycles comprising heating from −80 to 180°C, followed by cooling to −80°C (always with steps of 10°C). Some of the X-ray diffraction patterns at different temperatures of samples having 55% and 70% of C_2F_4 units are reported in *Figures 3* and *4*, respectively. It is apparent that, by increasing the temperature, the usual transition of the orthorhombic form towards the hexagonal mesophase occurs. However, on cooling, 200 reflections less intense than those present at the same temperatures before the heating are obtained. For successive analogous thermal cycles, the transition becomes substantially reversible; in fact, diffraction patterns very similar to those of curves e–i of *Figures 3* and *4* are observed.

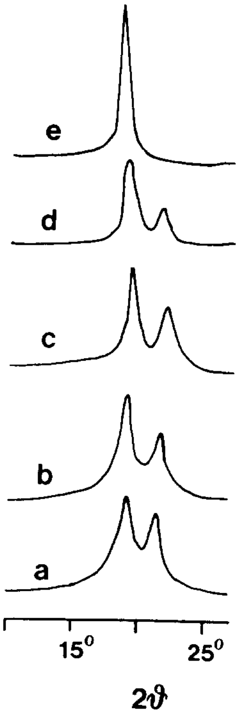

Figure 2 X-ray diffraction patterns measured at −80°C of copolymer samples of different compositions, quenched from the melt state into water at 0°C. C_2F_4 molar content: (a) 50%; (b) 55%; (c) 60%; (d) 70%; (e) 80%

The incomplete reversibility of the orthorhombic–hexagonal transition accounts for the observation that rapid cooling from the melt tends to favour the formation of a better developed orthorhombic form. In fact, slow cooling (as shown in *Figure 1*) first produces a hexagonal mesophase at high temperatures, which, on cooling (as shown by the patterns of *Figure 3*), is unable to generate a well formed orthorhombic form. The production of well formed orthorhombic domains, for fast cooling conditions, would be due to a direct crystallization in the orthorhombic form.

As in previous papers[3,6], these transitions can be also shown by plots of the half-width of the diffraction peaks *versus* temperature. For instance, the half-width of the main reflection for some of the compression moulded (and quenched) samples of *Figure 2*, for a thermal cycle including a heating, a cooling and a reheating, are shown in *Figure 5*. For the copolymer samples with a C_2F_4 content in the range 50–60%, the incomplete reversibility of the first heating cycle is well apparent.

It is also worth noting that, for the well formed orthorhombic samples, in the first heating the transition towards the hexagonal mesophase is sharper and located at higher temperatures for the copolymers with a C_2F_4 content in the range 50–60%. In particular, for the samples with a C_2F_4 content of 50, 55 and 60%, the sharper transitions of the first heating are centred around 110, 75 and 50°C, while the transitions for the successive thermal cycles are centred around 76, 65 and 40°C, respectively.

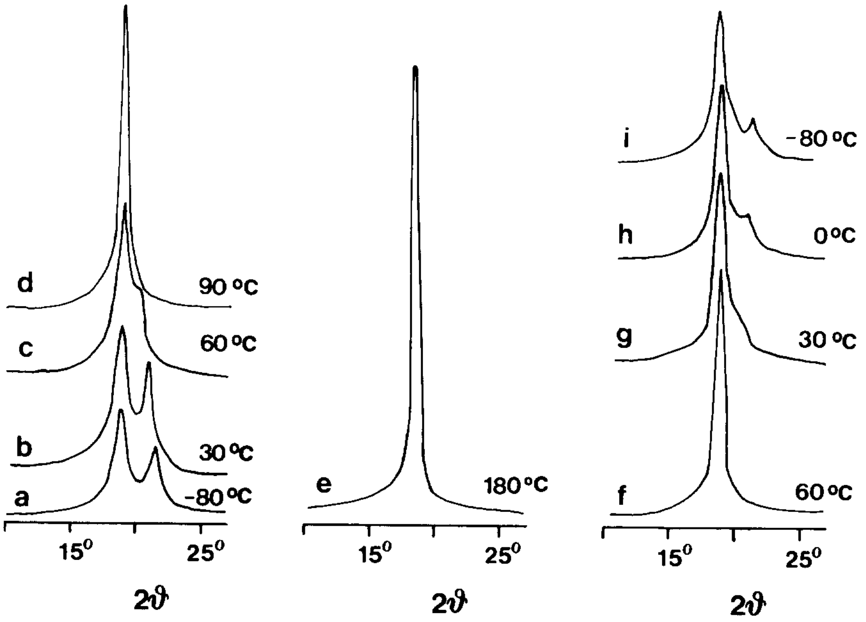

Figure 3 X-ray diffraction patterns at the indicated temperatures of a copolymer sample having 55% of C_2F_4 units. The thermal cycle comprises heating the quenched sample from −80 to 180°C, followed by cooling to −80°C

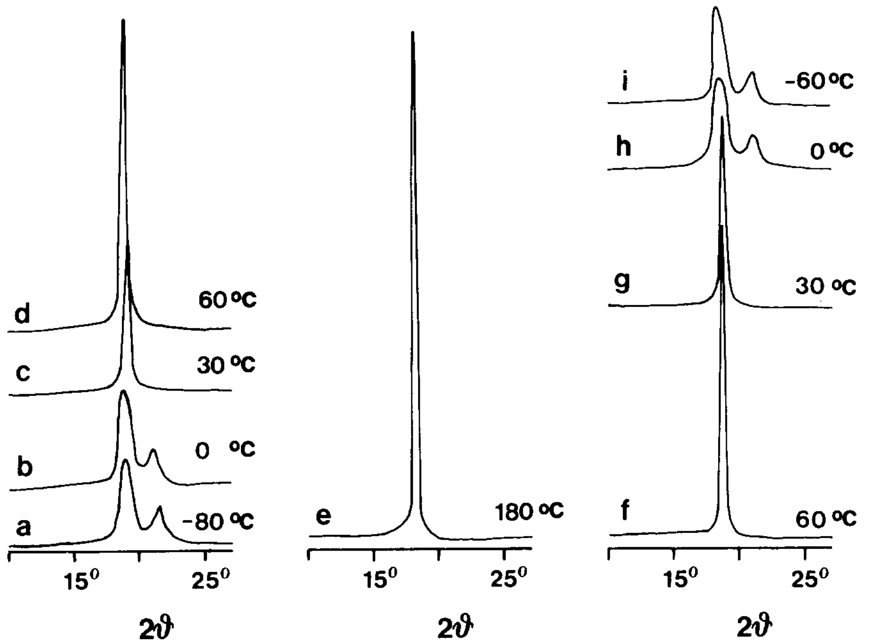

Figure 4 As for *Figure 3*, but for copolymer sample having 70% of C_2F_4 units

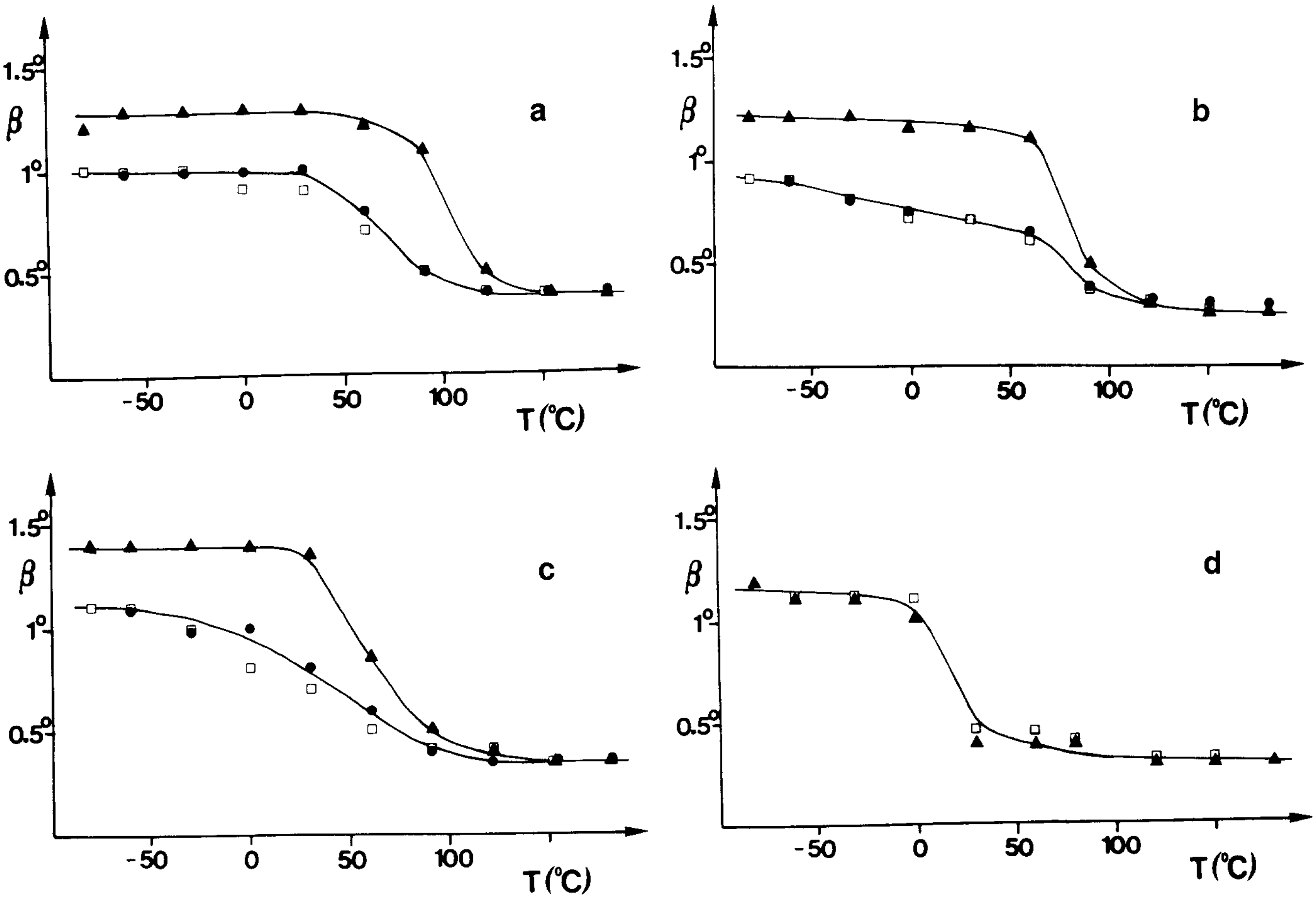

Figure 5 Half-widths (β) of the main peak of the X-ray diffraction patterns, for compression moulded and quenched samples of ETFE copolymers subjected to thermal cycles including a heating (▲), a cooling (□) and a reheating (●). C_2F_4 molar content: (a) 50%; (b) 55%; (c) 60%; (d) 70%

Terpolymers

The X-ray diffraction patterns collected at −80°C of compression moulded and quenched samples of ETFE terpolymers (with a nearly 50/50 ratio between ethylene and tetrafluoroethylene monomers), having FPVE contents in the range 0–2.7 mol%, are shown in *Figure 6*. For low FPVE concentrations, it is apparent that the 200 reflection typical of the orthorhombic form is already substantially decreased with respect to the 1 1 0 reflection. For higher FPVE concentrations only a broad peak with a shoulder, typical of the pseudo-hexagonal form, is present.

It is worth noting that patterns with intense 2 0 0 peaks, like those of *Figure 2*, are not present in the literature possibly because commercial ETFE samples (which are in fact terpolymers) have generally been studied.

X-ray diffraction patterns obtained at different temperatures (using a procedure analogous to that described for the patterns of *Figure 3*) for the terpolymers with 0.9 and 1.8 mol% of FPVE are shown in *Figures 7* and *8*, respectively. A transition towards the high temperature hexagonal mesophase is clearly observed for both samples, which at low temperatures present an orthorhombic form or a pseudo-hexagonal mesophase (*Figures 7* and *8*, respectively). As for the copolymers, the transition from the orthorhombic to the hexagonal phase (*Figure 7*) becomes substantially reversible only after the first heating procedure.

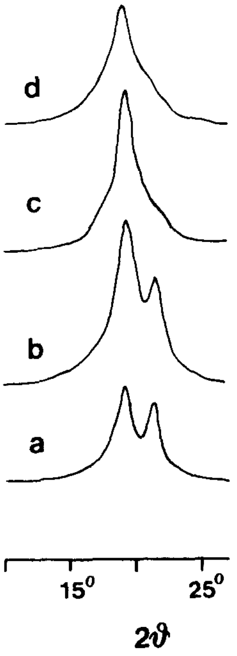

Figure 6 X-ray diffraction patterns collected at −80°C of compression moulded and quenched samples of ETFE terpolymers (with a nearly 50/50 ratio between ethylene and tetrafluoroethylene comonomers). Molar content of FPVE: (a) 0%; (b) 0.9%; (c) 1.8%; (d) 2.7%

The half-widths (β) of the main peak of the X-ray diffraction patterns, for all the terpolymer samples of *Figure 6*, are plotted against temperature in *Figure 9*. For the sake of clarity, only data corresponding to the cooling from 180 to −80°C (substantially coincident with those corresponding to the successive heating from −80 to 180°C) are plotted. The plot of *Figure 9* clearly indicates that increasing the termonomer concentration increases the broadness of the main peak, both of the low-temperature (orthorhombic or pseudo-hexagonal) and the high-temperature (hexagonal) forms. This corresponds, of course, to smaller correlation lengths (D) for the crystalline domains.

The X-ray diffraction patterns at 180°C for two terpolymer samples, with different termonomer compositions, are shown in *Figure 10*. The amorphous haloes and the baselines used for evaluation of the crystallinity indices are also drawn in this figure. Evaluation of the correlation lengths (D) and the crystallinity indices (x_c) for patterns collected at 180°C is particularly convenient, since all the samples are in the hexagonal form and the error in the extrapolation of the position of the maximum of the amorphous halo is minimized. Moreover, it is relevant to study possible structural differences in this temperature region, for which large differences in the ultimate mechanical properties are observed (see below).

Inspection of *Figure 10* reveals a large reduction of crystallinity index and an increase of the broadness of the reflection with increasing termonomer concentration. The correlation lengths and the crystallinity indices, evaluated from the X-ray diffraction patterns collected at 180°C, are plotted *versus* termonomer composition in *Figures 11a* and *b*, respectively. A reduction of crystallinity and crystal size with termonomer concentration was also observed for the analogous alternated ethylene–chlorotrifluoroethylene copolymers[10,11].

For the sake of comparison, the correlation lengths and crystallinity indices, evaluated at 180°C, for the

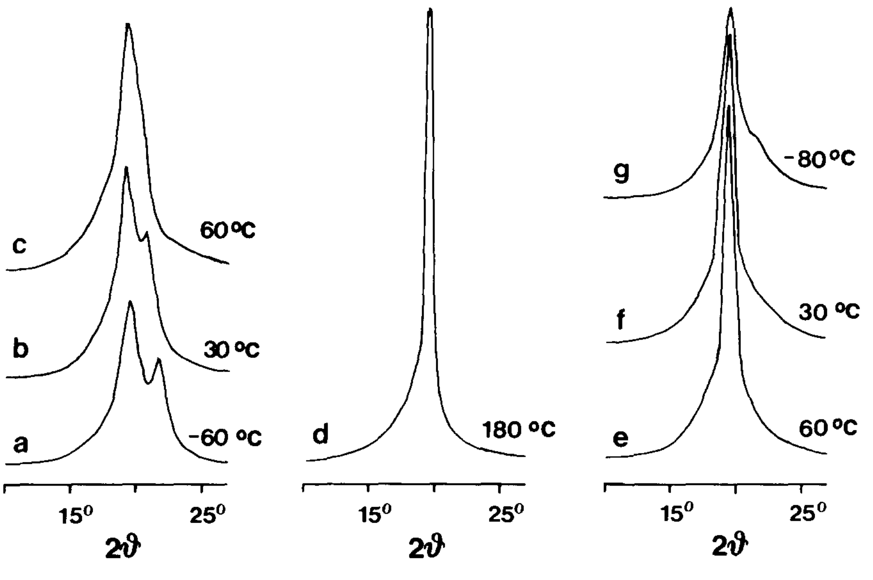

Figure 7 X-ray diffraction patterns at the indicated temperatures of a sample having 0.9% of FPVE termonomer units. The thermal cycle comprises heating the quenched sample from −80 to 180°C, followed by cooling to −80°C

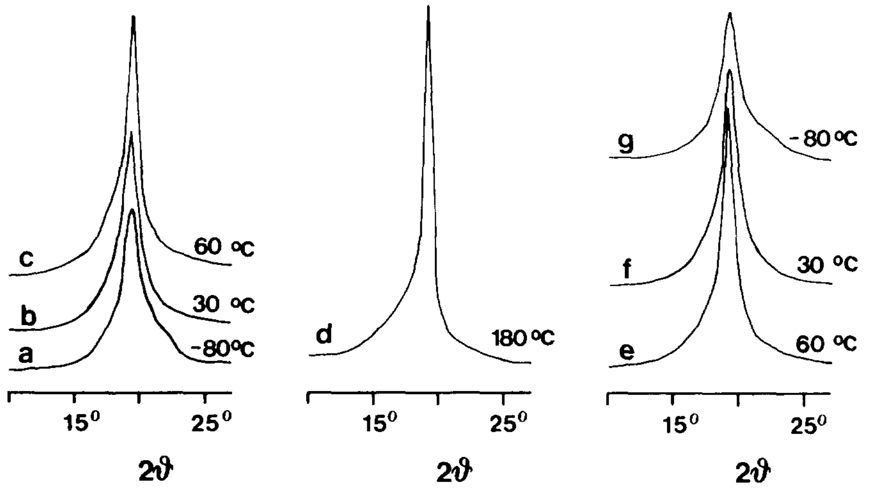

Figure 8 As for *Figure 7*, but for sample having 1.8% of FPVE termonomer units

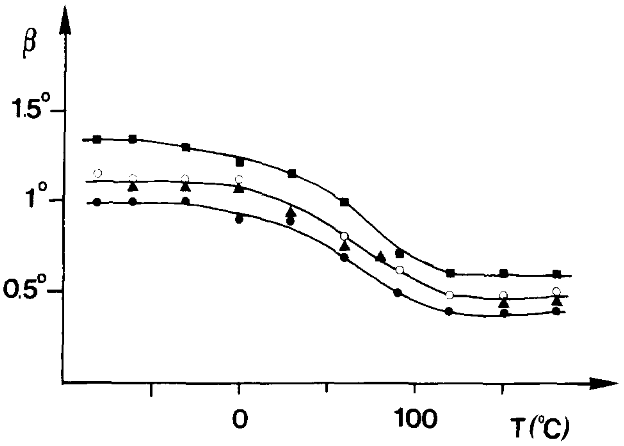

Figure 9 Half-widths (β) of the main peak of the X-ray diffraction patterns, for compression moulded and quenched samples of ETFE terpolymers with different molar contents of FPVE: (●) 0%; (▲) 0.9%; (○) 1.8%; (■) 2.7%. For the sake of clarity, only data corresponding to the cooling from 180 to −80°C (substantially coincident with those corresponding to the successive heating from −80 to 180°C) are plotted

ETFE copolymers of different compositions are also plotted in *Figures 11a* and *b*, respectively. The comparison indicates that when the constitutional order typical of the perfectly alternated copolymer is disturbed by a bulky termonomer, a drastic reduction of the crystal size and crystallinity is observed. On the contrary, if the constitutional order is disturbed by an increase of the C_2F_4/C_2H_4 ratio (constitutional defects included in the crystalline phase), no significant variations of the crystallinity and crystal sizes are observed.

In summary, the modification of the ETFE alternated copolymer with small amounts of the FPVE termonomer tends to favour the formation, at low temperatures, of the pseudo-hexagonal mesophase with respect to the orthorhombic form. For high temperatures, the presence of the termonomer units strongly reduces the crystal size and crystallinity of the hexagonal mesophase.

The trends of the elongation at break (ε_b) as a function of temperature for an alternating copolymer with about 53% of C_2F_4 monomer units and for a terpolymer with 1.8% of FPVE are compared in *Figure 12*. The terpolymer

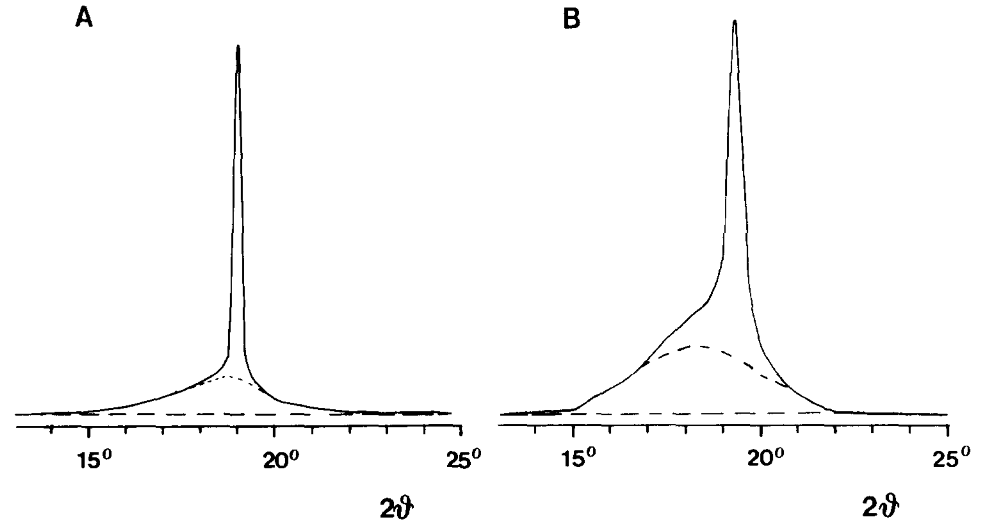

Figure 10 X-ray diffraction patterns at 180°C for two ETFE samples: (A) a 50/50 copolymer and (B) a 50/50 copolymer with 2.7% of termonomer units. The amorphous haloes and the baselines used for the evaluation of the crystallinity indices and half-widths are also drawn (broken lines)

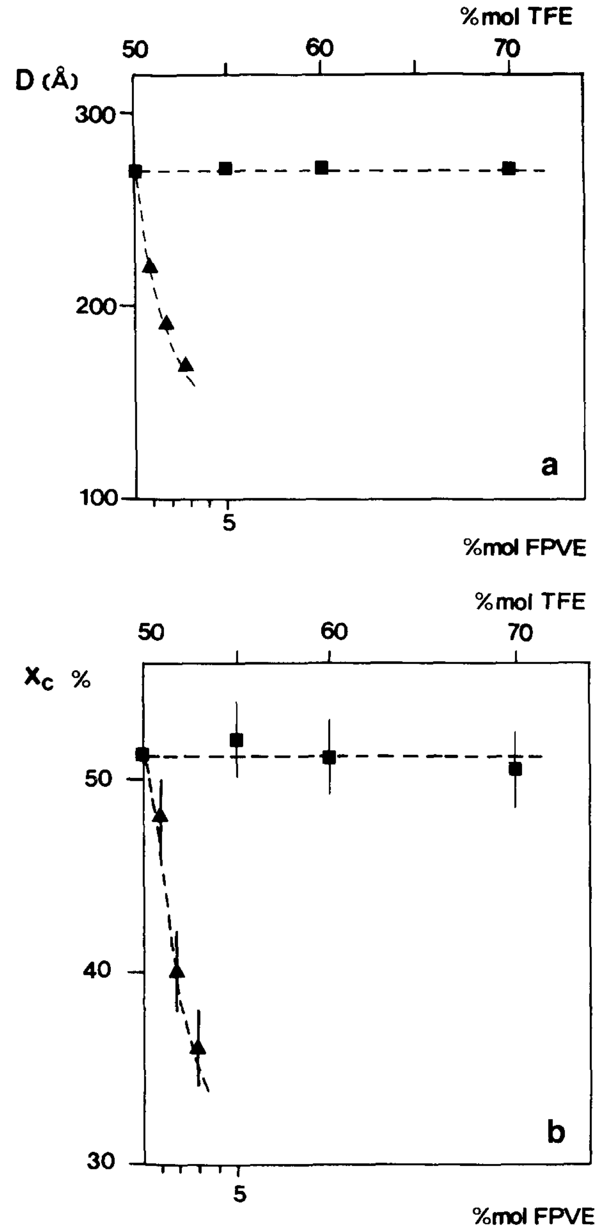

Figure 11 Correlation lengths of the mesomorphic domains (in the directions perpendicular to the chain axes) (a) and crystallinity indices (b), evaluated from the X-ray diffraction patterns collected at 180°C for ETFE terpolymers, plotted *versus* termonomer composition (bottom scale, ▲). For the sake of comparison, correlation lengths (a) and crystallinity indices (b), evaluated at 180°C for ETFE copolymers, are plotted *versus* comonomer composition (top scale, ■)

does not exhibit the sharp drop in elongation observed for the copolymer at temperatures above the maximum in elongation. Brittle failures in creep testing were also found for the copolymer at times less than 100 h for applied stresses higher than 3.5 MPa, while the terpolymer did not fail up to the end of the testing time.

It is reasonable to assume that this behaviour is related to the strong reductions of the crystal size and crystallinity observed for the terpolymers, but not for the copolymers with an altered C_2F_4/C_2H_4 ratio.

CONCLUSIONS

Orthorhombic phases more ordered than those previously reported in the literature are obtained for alternated ETFE copolymers, in the absence of termonomeric units, by quenching from the melt state. On the contrary, for slow cooling rates, first the high temperature hexagonal phase is obtained, which on cooling below the solid–solid transition temperature tends to produce an orthorhombic form of poorer quality.

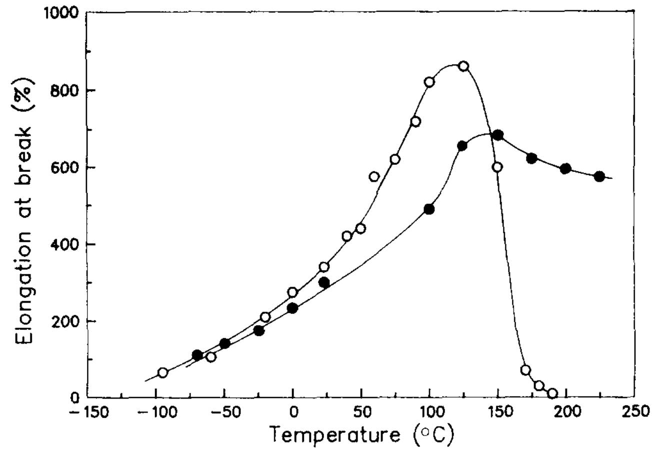

Figure 12 Elongation at break (ε_b) as a function of temperature for an alternate copolymer (○) with 53% of C_2F_4 monomeric units and a terpolymer (●) with 1.8 mol% of FPVE

Well developed orthorhombic forms are obtained for copolymers with a C_2F_4 content in the range 50–70 mol%, while only the hexagonal form is obtained for copolymers with a C_2F_4 content equal to or higher than 80%. A content of the FPVE termonomer of 1.8 mol% is, instead, already sufficient to favour the formation of the so-called pseudo-hexagonal mesophase.

The increase of the C_2F_4 molar content from 50 to 80% leaves essentially unaltered the crystallinity and the crystal size of the copolymer samples in the hexagonal form. In fact, for these samples, the constitutional defects with respect to the perfectly alternated 50/50 copolymer are included in the crystalline phase. On the other hand, small increases of the FPVE termonomer content, in the range 0–2.7 mol%, strongly reduce the degree of crystallinity as well as the crystal size. Hence, for the terpolymer samples the termonomer units are substantially excluded from the crystalline phase. This is expected to be a determinant factor for the improved ultimate properties (at high temperatures) typical of commercial terpolymers of ETFE.

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