

Structural variations in random copolymers of tetrafluoroethylene with kind and content of comonomer units

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Random copolymers of tetrafluoroethylene with minor amounts of fluorinated comonomers (hexafluoropropene, perfluoromethylvinylether and perfluoropropylvinylether) of different compositions are characterized mainly by X-ray diffraction but also by differential scanning calorimetry and density measurements in an attempt to establish the possible inclusion of the respective side groups into the crystallites. Structural characterizations are conducted at room temperature (where all the considered copolymer samples are in the less ordered crystalline form I) as well as at -40°C (where all the considered copolymer samples are in the more ordered crystalline form II). Increases of the lateral dimension of the unit cell and decreases of the size and amount of crystalline domains, with comonomeric unit content, are observed which are similar for different comonomer units (of largely different bulkiness) as well as for the two crystalline forms. The reported experimental results suggest a substantial exclusion from the crystallites not only of the bulkier comonomeric units (from perfluoropropylvinylether), but also, at least for high comonomer compositions, of the smaller comonomeric units (from perfluoromethylvinylether and hexafluoropropene). © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Random copolymers of tetrafluoroethylene (TFE) with minor amounts of fluorinated comonomers are industrially relevant since they present useful mechanical and chemical properties (analogous to those of the homopolymer) while they can be processed by usual melt processing technologies¹. The most relevant copolymers are those with hexafluoropropene (FEP), with perfluoromethylvinylether (MFA) and with perfluoropropylvinylether (PFA)¹.

On the basis of X-ray diffraction studies, mainly the increase of the intermolecular distances with the hexafluoropropene content, the inclusion of the $-\text{CF}_3$ groups of FEP in the crystallites has been suggested^{2–6}. However, structural characterizations of copolymers of ethylene have indicated that the lattice expansion is not necessarily a reflection of inclusion of comonomer units in the crystallites^{7,8}. In fact, lattice expansions perpendicular to the chain axis could be caused by strain at the interface of thin crystallites related to the congregation of bulkier comonomer units in this region.

As far as the TFE copolymers with different perfluoroalkylvinylethers are concerned, the independence of the thermal behaviour on the size of the side group ($-\text{OCF}_3$ or $-\text{OCF}_2\text{CF}_3$ or $-\text{OCF}_2\text{CF}_2\text{CF}_3$) has suggested at least a partial exclusion of the side group from the crystalline phase⁹. The possible exclusion of the bulky side groups for

the TFE copolymers with perfluoroalkylvinylether has been also suggested by molecular mechanics calculations¹⁰.

In this paper, several FEP, MFA and PFA copolymer samples of different compositions have been characterized mainly by X-ray diffraction but also by differential scanning calorimetry and density measurements in an attempt to establish the possible inclusion of the respective side groups into the crystallites.

Of course, the study of the possible inclusion of the comonomer units into the crystalline phase can be further complicated by the polymorphic behaviour of polytetrafluoroethylene (PTFE). Let us recall that PTFE, at atmospheric pressure, presents two reversible first order transitions at 19°C and 30°C ^{11,12}. The low temperature form (form II) has an ordered structure with a triclinic unit cell¹³, and the intermediate temperature form (form IV) presents a partial intermolecular rotational disorder^{14,15}. The high temperature form (form I) is highly disordered, presenting a long range three-dimensional order only in the periodic pseudo-hexagonal placement of the chain axes^{14,15}. In fact, in form I there is conformational disorder corresponding to helix reversals^{16–18} associated with a nearly complete intermolecular rotational disorder.

For random copolymers of TFE, even for low comonomer concentrations, the two solid–solid transitions coalesce and only forms I and II are generally observed^{19,4}.

The inclusion of constitutional defects (in the present case, comonomer units) could be in principle expected to be easier in disordered structures like form I than in

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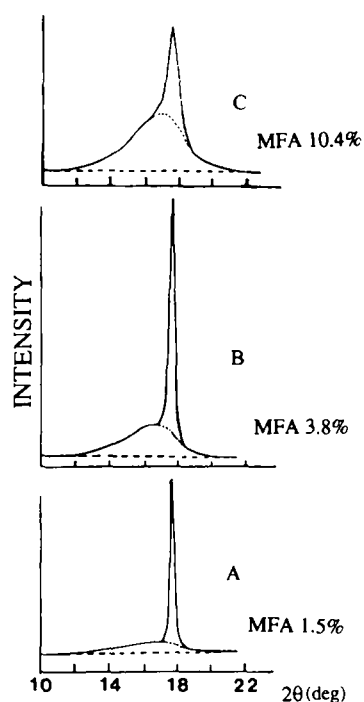


Figure 1 X-ray diffraction patterns of tetrafluoroethylene copolymers in the 2θ range 10° – 22° , for the case of copolymers with perfluoromethylvinylether at room temperature. The comonomer unit contents are: (A) 1.5%; (B) 3.8%; (C) 10.4%; dashed lines indicate the assumed amorphous halo

three-dimensionally ordered structures like form II. For this reason, our structural characterizations have been conducted at room temperature (where all the considered copolymers are in the less ordered form I) as well as at -40°C (where they are in the more ordered form II).

EXPERIMENTAL

The homopolymer and copolymer samples, supplied by Ausimont S.P.A., were obtained by aqueous dispersion polymerization. The comonomer concentrations, ranging from 0.5 to 10 mol%, were determined by mass balances during the polymerization; the results are roughly in agreement with the values obtained by the infrared analytical method²⁰.

Copolymer samples used for the X-ray diffraction measurements, obtained by compression molding, had a thickness in the range 1–2 mm. The compression molding samples were obtained by melting powder samples at 330°C under press and successive cooling to room temperature at a cooling rate of $10^\circ\text{C}/\text{min}$. 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 $\pm 1^\circ\text{C}$. The platelets were accurately placed into a same sample holder, in order to get similar surface positionings and, for each composition, three samples were measured. The spacings corresponding to the intense (100) reflections were determined with a standard deviation lower than 0.003 \AA .

Evaluation of the correlation length D of the crystalline domains in the directions perpendicular to the chain axes was effected using the Scherrer formula for the main equatorial reflection:

$$D = 0.9\gamma/\beta\cos\theta \quad (1)$$

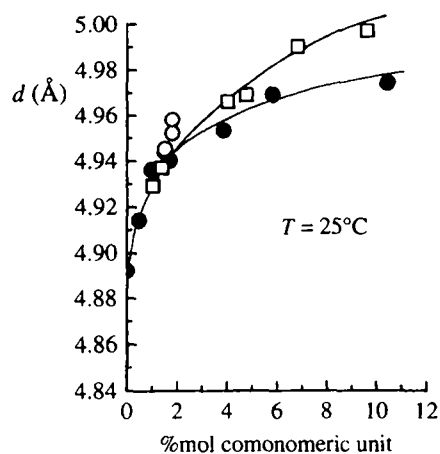


Figure 2 The spacing of the intense equatorial reflection (d_{100}) reported versus the copolymer molar composition for all the considered samples, at room temperature: (□) FEP; (●) MFA; (○) PFA

where β is the half-maximum line breadth. For $\beta < 1.0^\circ$ (in 2θ units) the procedure described in Ref.²¹ 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 10° and 22° , 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

$$x_c = \frac{I_c}{I_c + I_a} 100 \quad (2)$$

The shape of the amorphous halo was obtained by measurements on poorly crystalline copolymer samples containing 10.4 mol% of perfluoromethylvinylether units.

The densities of the samples were determined by flotation, at room temperature, in carbon tetrachloride/bromofrom mixtures. A crystallinity index x_d was evaluated according the usual relation:

$$x_d = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \quad (3)$$

where ρ is the measured density while ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. In our calculations we have assumed $\rho_c = 2.30 \text{ g/cm}^3$ and $\rho_a = 2.06 \text{ g/cm}^3$.²² Of course, the use of equation (3) implies the approximation of negligible variations of ρ_c and ρ_a , in the presence of comonomeric units, which possibly holds only for low concentrations.

The calorimetric measurements were carried out on a Mettler type differential scanning calorimeter (d.s.c. 30) in flowing N_2 . The melting temperatures (T_m) were evaluated on samples previously cooled from the melt at 10 K/min , as the peak temperatures of the melting endotherms, obtained from d.s.c. scans at 10 K/min .

RESULTS

Typical X-ray diffraction patterns of tetrafluoroethylene copolymers are shown in the 2θ range 10° – 22° in Figure 1, for the case of some copolymers with perfluoromethylvinylether at room temperature. For all the considered samples, the diffraction profiles show an intense (100)

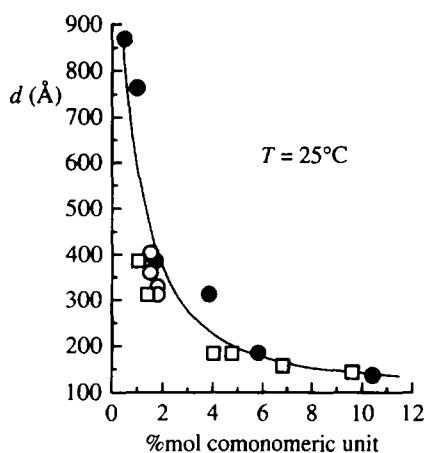


Figure 3 The correlation length D of the crystalline (mesomorphic) domains, in the directions perpendicular to the chain axes, reported versus the copolymer molar composition for all the considered samples, at room temperature: (□) FEP; (●) MFA; (○) PFA

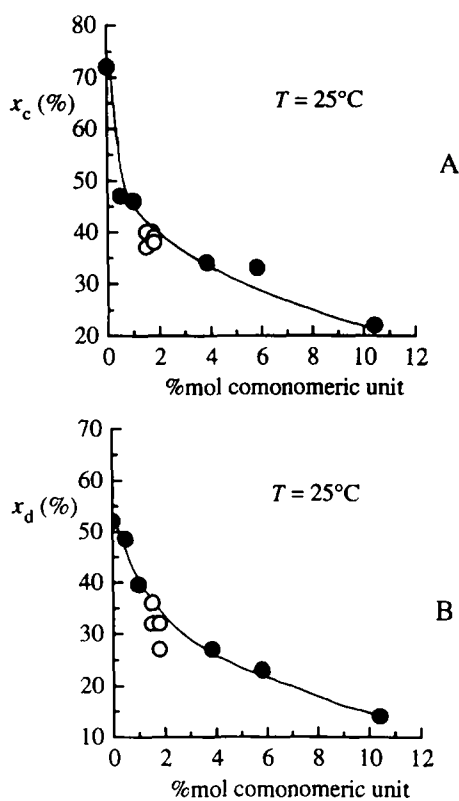


Figure 4 The crystallinity indexes versus the copolymer composition: (A) evaluated on the basis of X-ray diffraction profiles, x_c ; (B) evaluated on the basis of density measurements, x_d : (●) MFA; (○) PFA

reflection located at $2\theta \approx 18^\circ$ superimposed on an amorphous halo (dashed in the patterns of Figure 1).

The spacing of this intense equatorial reflection (d_{100}) is reported versus the copolymer molar composition for all the considered samples in Figure 2. It is apparent a significant increase of d_{100} of PTFE with comonomeric unit content, corresponding to increases of the a parameter of the hexagonal unit cell (distance between axes of adjacent helices) from nearly 5.65 Å up to nearly 5.76 Å. It is also worth noting that, although the encumbrance of the side groups of the comonomers are largely different ($-\text{CF}_3$, $-\text{OCF}_3$, $-\text{OC}_3\text{F}_7$), the lateral expansion of the unit cell is similar for all the considered copolymer samples.

The correlation length D of the crystalline (mesomorphic)

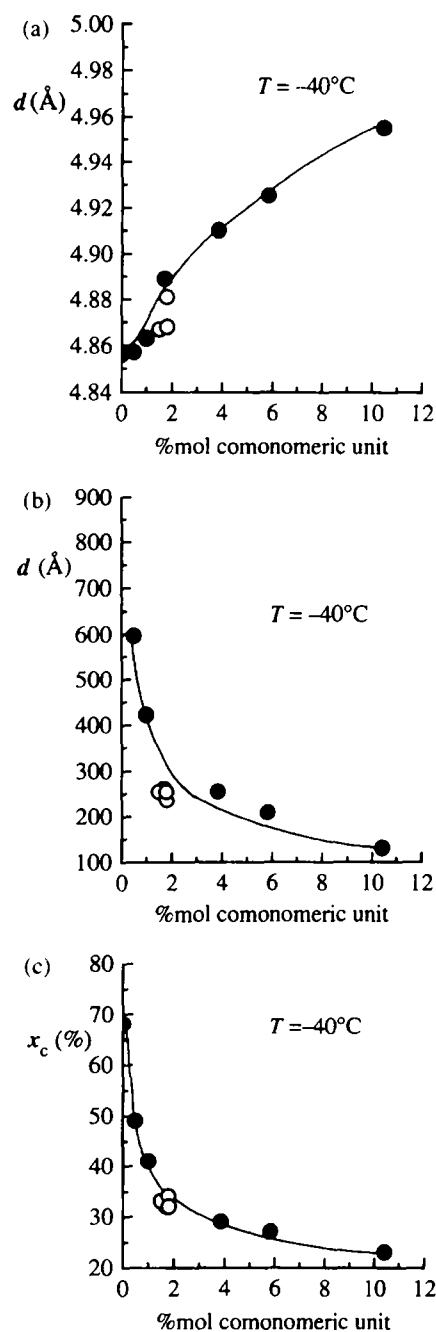


Figure 5 (a) Spacing d_{100} (b) correlation length D , and (c) crystallinity index x_c versus the copolymer composition, by X-ray diffraction measurements affected at -40°C : (●) MFA; (○) PFA

domains, in the directions perpendicular to the chain axes, is reported versus the copolymer molar composition for all the considered samples in Figure 3. The correlation length of the homopolymer sample is not reported, since the error in the evaluation method becomes too large (the observed narrowness of the peak is only $B \approx 0.2^\circ$). However, its value is large (>1000 Å) and a strong decrease of D with comonomer unit content is well apparent (values lower than 400 Å are generally observed already for copolymer compositions close to 1% by mol). Moreover, the observed behaviour is similar for all the considered copolymer samples.

The crystallinity indexes, evaluated on the basis of X-ray diffraction profiles (x_c) and of density measurements (x_d), are reported for MFA and PFA samples versus the copolymer composition in Figure 4a and b, respectively.

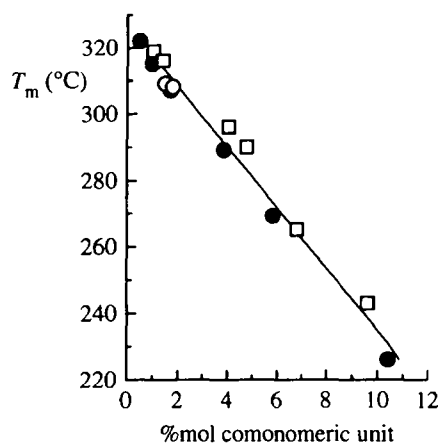


Figure 6 Melting temperatures T_m , measured for as polymerized samples, as a function of the copolymer molar composition: (□) FEP; (●) MFA; (○) PFA

These plots indicate that the crystallinity is strongly reduced with increasing the comonomeric unit content. Moreover, at least for copolymer composition lower than 2% by mol, the reduction of crystallinity is similar for the two copolymers.

Similar X-ray diffraction measurements have been affected at -40°C for MFA and PFA samples. The spacing d_{100} , the correlation length D , and the crystallinity index x_c are reported versus the copolymer composition in Figure 5a, b, and c, respectively.

It is apparent that, although at -40°C the three-dimensionally ordered triclinic structure of form II is present, the behaviours are analogous to those observed at room temperature (Figures 2–4a, respectively), where the conformationally and rotationally disordered hexagonal form I is present.

Hence, the increase of the lateral dimension of the unit cell and the decrease of the size and amount of crystalline domains, with comonomeric unit content, are substantially similar not only for different comonomer units (of largely different bulkiness) but also for the two crystalline forms.

The melting temperatures T_m , measured for as polymerized samples, as a function of the copolymer molar composition for all the considered samples are reported in Figure 6. The plots show that also the decrease of melting temperature with comonomeric unit content is substantially independent of the kind of comonomer. The substantial independence of the melting temperature on the bulkiness of the comonomer was already shown by Pucciariello for melt crystallized copolymer samples with equal molar contents of three different perfluoroalkylvinylethers⁹.

DISCUSSION

A plot of the hypothetical density of the crystalline phase at room temperature, evaluated on the basis of the experimental dimensions of the unit cells (Figure 2) by assuming a total inclusion of the comonomer units in the crystalline domains (ρ_{inc}), is reported in Figure 7 versus the copolymer composition.

The plot shows, for FEP and MFA copolymers, a decrease of the hypothetical density for copolymer compositions lower than 1–2% by mol, followed by increases to values definitely larger than the density of the crystalline

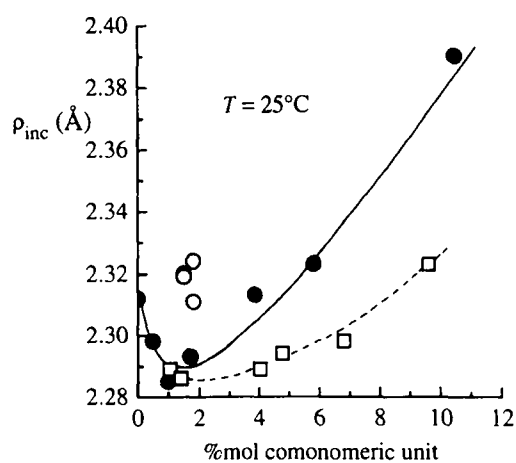


Figure 7 Hypothetical density of the crystalline phase, at room temperature, evaluated by assuming the experimental dimensions of the unit cells and a total inclusion of the comonomer units in the crystalline domains (ρ_{inc}) versus the copolymer composition: (□) FEP; (●) MFA; (○) PFA

form I of PTFE, when the copolymer composition exceeds 4% and 6% by mol, respectively. For all the considered PFA samples (presenting the copolymer composition in the range 1.5–1.8% by mol) ρ_{inc} is already larger than the crystalline density of PTFE.

Since the inclusion of constitutional defect can reduce but certainly not increase the density of the crystalline phase, it is reasonable to conclude that the exclusion is prevailing for PFA copolymers already for low comonomeric unit contents, as well as for MFA and FEP samples for compositions higher than 4% and 6%, respectively.

On the other hand, the poor dependence on the bulkiness of the side group of the comonomer ($-\text{CF}_3$, $-\text{O}-\text{CF}_3$, $-\text{O}-\text{C}_3\text{F}_7$), for a same comonomer unit content, of the melting temperature, of the unit cell lateral dimension, of the crystalline domain size and of the degree of crystallinity can be easily rationalized in the hypothesis of substantial exclusion of the three considered comonomer units.

This hypothesis helps also to rationalize the similar dependences on the comonomer unit content, which have been observed for the spacing d_{100} , the correlation length D , and the crystallinity index x_c for the low temperature three-dimensionally ordered form II and for the high temperature disordered form I. In fact, in the hypothesis of inclusion of comonomer units a more severe disturbance would be expected for the three-dimensionally ordered low temperature form II.

Moreover, the abrupt decrease of the correlation length in the crystalline domains and of the crystallinity indexes, with the comonomer unit content, suggests a prevailing exclusion of comonomer units from the crystallites. In fact, when a cocrystallization of different comonomeric units occurs, size and amount of crystallites tend to decrease more smoothly or even to remain nearly constant. Let us recall, for instance, that for alternated ethylene tetrafluoroethylene copolymers, D and x_c remain nearly constant as TFE content changes from 50% to 70%, while they strongly decrease already in the presence of 1–3% by mol of ter-monomer units from perfluoropropylvinylether (which are excluded from the crystallites)²³.

The exclusion of $-\text{CF}_3$ and especially of $-\text{OCF}_3$ groups by the crystal phase is also suggested by a related conformational and packing energy study²⁴.

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