

Evaluation of the Amount of Defects in the Comonomer Alternation Included in the Crystal Phase for Ethylene–Tetrafluoroethylene and Ethylene–Chlorotrifluoroethylene Alternating Copolymers

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SYNOPSIS

A method for the evaluation of the amount of defects in the comonomer alternation included in the crystalline phase of alternating ethylene–tetrafluoroethylene (ETFE) and ethylene–chlorotrifluoroethylene (ECTFE) copolymers, is proposed. The method is based on a comparison between X-ray fiber diffraction profiles and calculated Fourier transforms for isolated chain models. The proposed method is not affected by the regioirregularities and stereoirregularities possible for ECTFE. For the considered ECTFE sample, the chains in the crystalline phase present an amount of defects in the comonomer alternation much lower than those evaluated for all the considered ETFE samples. Substantial differences in the melting temperatures between ETFE samples are accounted for by the different amounts of defects in the comonomer alternation included in the crystalline phase. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Several X-ray diffraction studies on the alternating ethylene–tetrafluoroethylene (ETFE) copolymer have been reported in the literature.^{1–6} The ETFE copolymer shows at low temperatures ($T < 0^\circ\text{C}$) an orthorhombic form,^{1,2} which gradually and reversibly, in a large temperature range (0–100°C), is transformed into a hexagonal form.^{3,5} In some samples this transition is ill-defined, and it can be better described as a transition from a pseudohexagonal to a hexagonal form.³

As suggested by Tanigami et al.² the orthorhombic form contains chains in *trans*-planar conformation, packed in a unit cell with axes $a = 8.57 \text{ \AA}$, $b = 5.60 \text{ \AA}$, $c = 5.04 \text{ \AA}$.

In a recent work from our group⁶ the disorder in the relative positions of neighboring chains in the orthorhombic form has been studied through a com-

parison of the observed X-ray diffraction profiles on the layer lines with the calculated Fourier transform of models of isolated chains. It was shown that in the orthorhombic phase of ETFE large, nearly random, translational displacements of the chains are present,⁶ and correlations in relative positions of the chains do not go much beyond the first neighbors. Moreover, on the basis of this kind of analysis the inclusion in the orthorhombic phase of defects in comonomer alternation, also for nearly perfect 50/50 comonomer compositions, was proved. In particular, for models with perfectly alternated comonomer units, the calculated values of the intensities for the odd layer lines are too high with respect to the intensities for the even layer lines. This disagreement with the observed pattern can be easily adjusted by introducing in the chain models a few defects in the comonomer alternation. A rough evaluation of the amount of defects in the monomer alternation included in the crystalline phase for the considered sample was also attempted.

The ethylene–chlorotrifluoroethylene (ECTFE) alternating copolymer presents X-ray diffraction

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patterns (of unoriented and oriented samples) similar to those of ETFE.⁷⁻¹¹ Contrary to previous conclusions,⁸ the chain conformation in the crystal phases of the two polymer are possibly similar (*trans*-planar for ETFE and nearly *trans*-planar for ECTFE).¹⁰ The crystalline form of ECTFE (as the two crystalline forms of ETFE) is a disordered form, with a pseudohexagonal packing of the chain axes and a substantial translational disorder along the chain axes.¹⁰

Also for an ECTFE sample, to account for the relative diffraction intensities on odd and even layer lines, the presence of defects in the comonomer alternation, included in the crystalline phase, has been suggested.¹⁰ However, for ECTFE, the evaluation of these constitutional defects, possibly further complicated by the presence of stereoirregularities and regioirregularities in the enchainment of the C₂ClF₃ comonomer, was not attempted.

In this study the method for the evaluation of the amount of the defects in the comonomer alternation included in the crystal phase of ETFE, based on comparisons between the observed diffraction profiles and the calculated Fourier transforms of isolated chains, is presented and extended to ECTFE.

EXPERIMENTAL

We have analyzed three different fiber samples of ETFE, with a molar ratio C₂H₄/C₂F₄ nearly equal to 1, all containing small percentages of a third comonomer. Their compositions and melting temperatures are reported in Table I.

The molar compositions were determined by infrared spectroscopy.¹² The melting temperatures correspond to the melting endothermic peaks of differential scanning calorimetry (DSC) scans conducted at a heating rate of 10 K/min. The DSC scans were carried out in a Perkin-Elmer DSC7 calorimeter, in a flowing N₂ atmosphere.

Table I Compositions (Mol %) and Melting Temperatures (*T_m*) of the ETFE Samples

Sample	C ₂ H ₄ (%)	C ₂ F ₄ (%)	Termonomer (%)	<i>T_m</i> (°C)
A	49.5	49.8	0.7 ^a	268
B	47.0	51.9	1.07 ^a	259
C	46.8	52.4	0.8 ^b	259

^a Perfluorobutylethylene.

^b Perfluoropropylvinylether.

The composition of the ECTFE fiber is 49.2 mol % of ethylene and 50.8 mol % of chlorotrifluoroethylene, as determined by elemental analysis.

Sample A of ETFE and the ECTFE sample are the same as used in Refs. 6 and 10, respectively.

The X-ray diffraction patterns for the ETFE and ECTFE fibers were obtained by using a CAD4 Nonius automatic X-ray diffractometer with Ni-filtered CuKα radiation. The Lorentz polarization (LP) correction was applied [LP = (1 + cos²2θ)/sin 2θ] for all the layer lines according to the diffraction geometry.

The procedure for the calculation of the Fourier transforms is that already used for ETFE⁶ and ECTFE.¹⁰

Owing to the broadness of the diffracted intensities on the layer lines for the ETFE and ECTFE fibers, the calculations of Fourier transforms have been performed on models of isolated chains.⁶

The square of the modulus ($|F(\xi, \varphi, \zeta)|^2$) of the Fourier transform was calculated for each model as a function of the cylindrical reciprocal lattice coordinates ξ and ζ for a fixed value of the third coordinate. The mean value with respect to φ , $\langle |F(\xi, \zeta)|^2 \rangle$, was obtained by averaging the results for 90 different rotations of the models around the chain axis.

The calculated averages $\langle |F(\xi, \zeta)|^2 \rangle$ were multiplied by a thermal factor of the kind:

$$\exp(-\frac{1}{2} B_{\xi} \xi^2) \exp(-\frac{1}{2} B_{\zeta} \zeta^2)$$

As in Ref. 6, the thermal parameter B_{ζ} has been fixed by an approximate optimization of the ratio between the maximum intensities on the second and fourth layer lines. In fact, these intensities are substantially independent of the presence of defects in the comonomer alternation.⁶ In particular the parameter B_{ζ} has been fixed equal to zero and 2 Å² for ETFE and ECTFE, respectively. The present evaluation method is poorly dependent on the value assumed for B_{ζ} ; in the next section, results relative to $B_{\xi} = 0$ and $B_{\xi} = 8$ Å² are compared.

The broadness along ζ of the meridional diffraction on the fourth layer line ($\Delta\zeta = 0.018$ Å⁻¹, $\Delta(2\theta) \approx 2^\circ$, as shown for instance by Fig. 4 of Ref. 10) indicates an average coherent length along the chain axis of the order of 50 Å, for all samples. Calculations of Fourier transforms were then performed on models with a chain length of nearly 50 Å (chains with 20 monomer units in *trans*-planar conformation, that is, with 40 carbon atoms).

The results for disordered models are averaged

over 50 different calculations, that is, over 50 different models of chains, in which the same amount of defects is distributed along the chain in different statistical positions.

To allow a comparison of diffraction intensity maxima on the meridian (that is, at $\xi = 0$), at variance with previous studies,^{6,10} the integration of the intensities over the reciprocal cylindrical coordinate φ (obtained by multiplying the intensities by $2\pi\xi$) was avoided.

RESULTS AND DISCUSSION

ETFE

The corrected diffraction intensities (I), for samples A, B, and C of ETFE, are reported in Figure 1(A), (B), and (C), respectively, for the equator and for the four layer lines, as a function of the reciprocal lattice coordinate ξ .

For the X-ray diffraction patterns of the three ETFE samples, significant differences can be

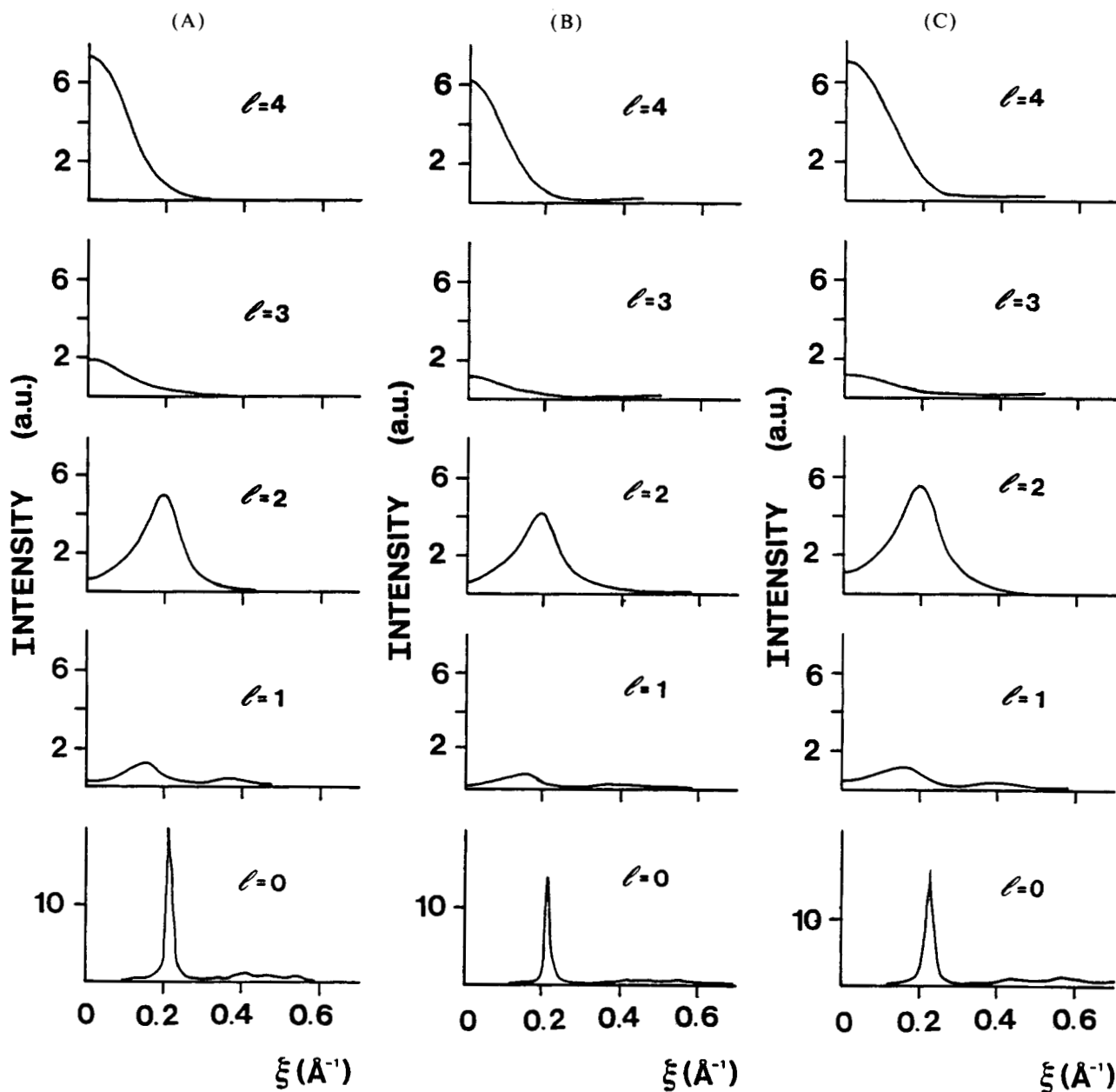


Figure 1 Experimental X-ray diffraction intensities (I), corrected by the Lorentz polarization factor, for the equator ($l = 0$) and four layer lines ($1 \leq l \leq 4$), as a function of the reciprocal coordinate ξ for (A) sample A, (B) sample B, and (C) sample C of ETFE.

pointed out by measurements of the ratios of the maximum diffraction intensities on the layer lines. In Table II are reported, for instance, for the spectra of Figure 1(A), (B), and (C), the ratios between the intensity peaks on the third layer line (I_3) and those on the second (I_2) and fourth (I_4) layer lines. It is apparent that for samples B and C of ETFE the ratios I_2/I_3 and I_4/I_3 are higher than those for sample A.

The Fourier transform on the nonequatorial layer lines, for a perfectly alternating ETFE isolated chain (for $B_\xi = 8 \text{ \AA}^2$), is shown in Figure 2. This calculated pattern reproduces the positions of the experimental intensity maxima on the layer lines, with the exception of the first layer line. In fact, on the first layer line the calculated pattern presents the intensity maximum at $\xi = 0$, while for the experimental patterns the intensity maxima are located at $\xi \approx 0.15 \text{ \AA}^{-1}$ (Fig. 1).

This indicates that our simplified models consisting of isolated chains are not suitable to account for the diffraction intensity on the first layer line, since also intermolecular effects should be considered. As a consequence, as parameters indicative of the amount of defects in the alternation of the comonomers, which are present in the crystalline phase of ETFE, we assume the ratios between the intensity maxima on the second and third layer lines (I_2/I_3) and on the fourth and third layer lines (I_4/I_3).

The Fourier transforms on the nonequatorial layer lines for isolated chains of ETFE with 3.3 and 6.7 defects (a pair of consecutive C_2F_4 units) per 100 monomer units are also shown in Figure 2 (again for $B_\xi = 8 \text{ \AA}^2$).

The calculated ratios I_2/I_3 and I_4/I_3 , as a function of the number of defects per 100 monomer units, are reported in Figures 3 and 4, respectively. Two different values of the B_ξ parameter have been cho-

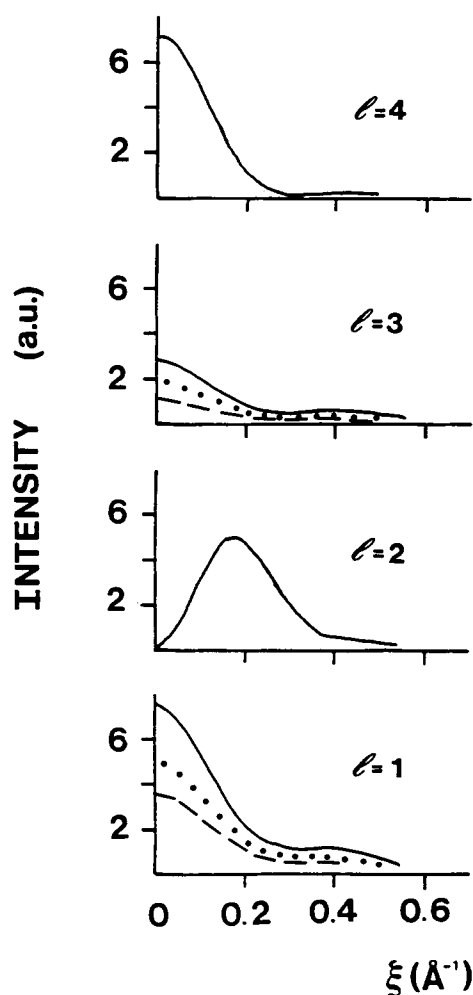


Figure 2 Results of the calculations of the Fourier transforms on the layer lines for zig-zag planar chains of ETFE: (—) regular alternation of comonomers, (····) 3.3 defects in the comonomer alternation per 100 monomer units, and (---) 6.7 defects per 100 monomer units.

Table II Ratios Between the Maximum Intensities on the Second and Third Layer Lines (I_2/I_3) and on the Fourth and Third Layer Lines (I_4/I_3) Observed in the X-ray Fiber Diffraction Spectra of ETFE (Fig. 1) and ECTFE (Fig. 5) Samples

Sample	I_2/I_3	I_4/I_3
ETFE A	2.7	4.2
ETFE B	3.9	5.7
ETFE C	4.4	5.9
ECTFE	2.1	2.2

sen for the I_2/I_3 ratio (Fig. 3). The experimental values of these intensity ratios, observed for the three samples A, B, and C of ETFE (Table II), are shown by dashed lines in the same figures.

In the framework of our assumptions, Figures 3 and 4 indicate that the amount of defects in the comonomer alternation per 100 monomer units, included in the crystalline phase, is in the range of 2–4 for sample A and in the range of 5–7 for samples B and C.

It is worth noting that the results obtained from these calculations, that is, the lower amount of comonomer alternation defects present in the crystalline phases of sample A, can account for the higher melting temperature (Table I).

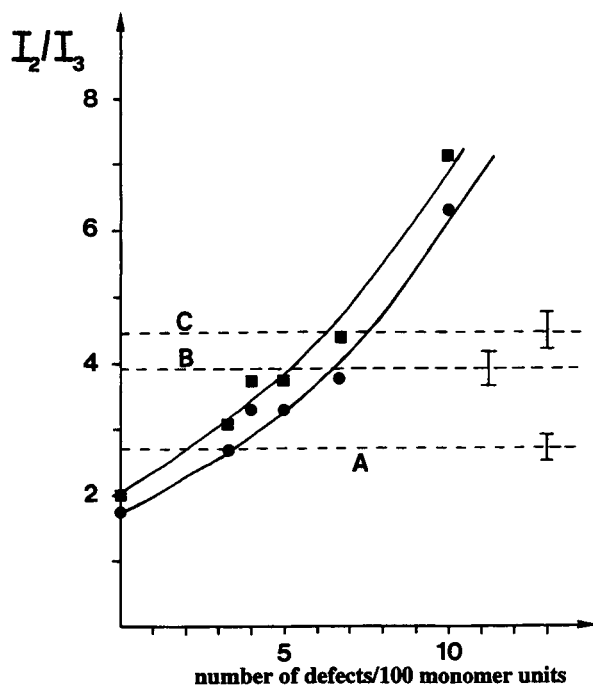


Figure 3 Calculated ratios between the maximum intensities on the second and third layer lines (I_2/I_3), as a function of the number of defects per 100 monomer units, for $B_k = 0$ (squares) and $B_k = 8 \text{ \AA}^2$ (circles). The experimental ratios I_2/I_3 , observed for the three samples A, B, and C of ETFE (taken from Fig. 1 and Table II) are shown as dashed lines.

In fact, it is well established that, besides comonomer defects excluded by the crystalline phase,¹³ constitutional defects included in the crystalline phase also generate a depression of the crystalline melting temperature, caused by a defective heat of fusion.¹⁴

It is also worth noting that both constitutional defects (termonomer units and defects in the comonomer alternation) are detrimental for the thermal properties of these materials. Let us recall that, according to the ASTM standard specification, the melting temperature should be always higher than 250°C .¹⁵ Instead the influence of the two kinds of constitutional defects on the mechanical properties is completely different. The termonomer units, which are substantially excluded from the crystal phase, produce a strong reduction of the crystal size and improve substantially the ultimate mechanical properties.¹⁶ On the contrary, stress-strain tests, at different temperatures on ETFE samples A, B, and C, indicate that the defects in the comonomer alternation, which are instead included in the crystal phase, do not produce any improvement of the me-

chanical properties. This is not surprising since neither exclusion from the crystalline phase nor improvement of the ultimate mechanical properties has been found also for the case of defects in the comonomer alternation resulting from large variations of the comonomer molar ratio from 50/50.¹⁶

ECTFE

The corrected diffraction intensities (I), for the ECTFE sample, is reported in Figure 5, for the equator and for the four layer lines, as a function of the reciprocal lattice coordinate ξ .

For the ECTFE chains, besides defects in comonomer alternation, other kinds of disorder can be present. In fact, regioirregularities, that is, constitutional defects in the head to tail structure of the copolymer ($-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$ or $-\text{CFCl}-\text{CH}_2-\text{CH}_2-\text{CFCl}-$) and stereoirregularities, that is, configurational disorder due to the presence of the asymmetric carbon atom $-\text{CFCl}-$, can be present in the ECTFE chains.

The Fourier transform on the nonequatorial layer

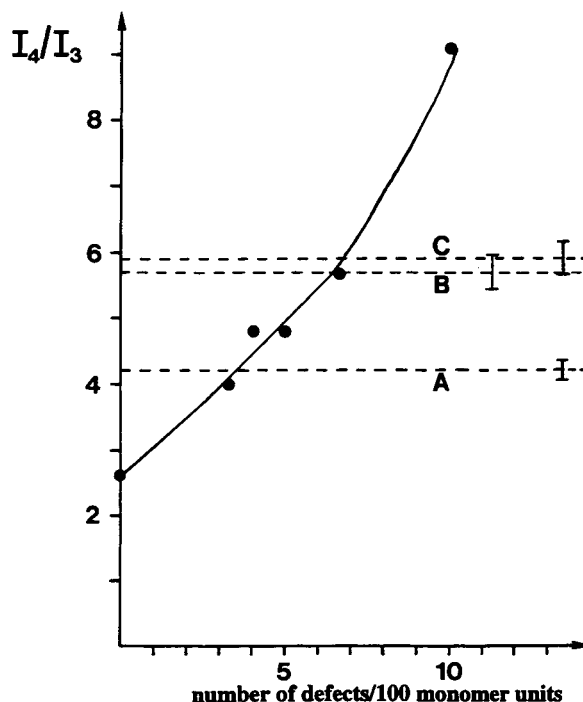


Figure 4 Calculated ratios between the maximum intensities on the fourth and third layer lines (I_4/I_3), as a function of the number of defects per 100 monomer units. The experimental ratios I_4/I_3 , observed for the three samples A, B, and C of ETFE (taken from Fig. 1 and Table II) are shown as dashed lines.

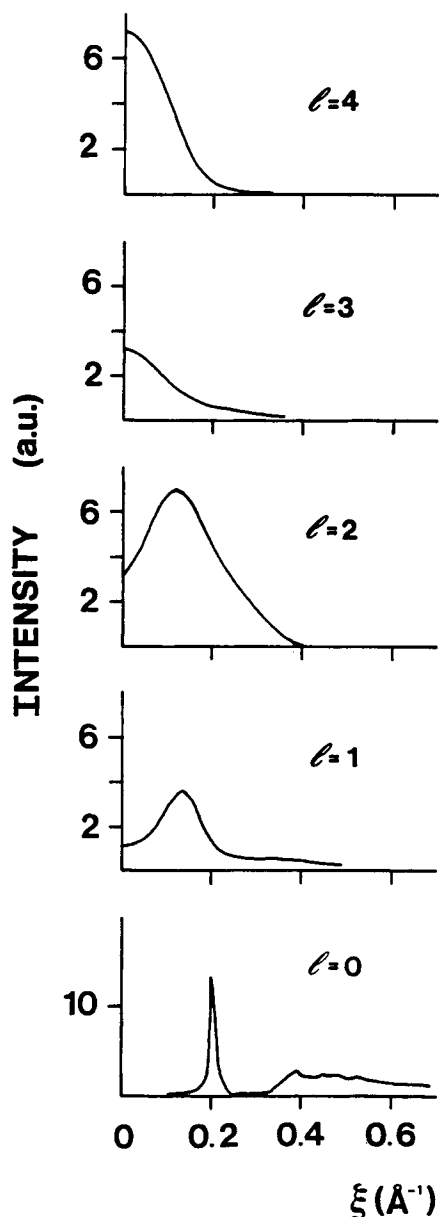


Figure 5 Experimental X-ray diffraction intensities (I), for the equator ($l = 0$) and four layer lines ($1 \leq l \leq 4$) of the ECTFE sample. The intensities are corrected by the Lorentz polarization factor and plotted as a function of the reciprocal coordinate ξ .

lines of an isolated, perfectly alternating, chain of ECTFE, in *trans*-planar conformation, without defects in the head to tail structure and perfectly stereoregular (isotactic), is shown in Fig. 6 (continuous lines), for $B_{\xi} = 8 \text{ \AA}^2$.

The Fourier transform of an isolated, perfectly alternating, chain of ECTFE, but with statistical disorder in the head to tail, tail to tail structure,

and/or with disorder in the configuration of the asymmetric carbon atoms (atactic chain) is substantially identical to that of Figure 6. Hence these kinds of disorder are essentially irrelevant for the Fourier transform. For the sake of simplicity, the successive calculations, for chains with defects in the comonomer alternation, have been performed, considering stereoregular (isotactic) and regioregular enchainments.

From a comparison between the experimental and the calculated patterns, it is apparent that, also for ECTFE, there is good agreement relative to the positions of the intensity maxima on the layer lines with $l = 2, 3$, and 4, while the intensity maximum

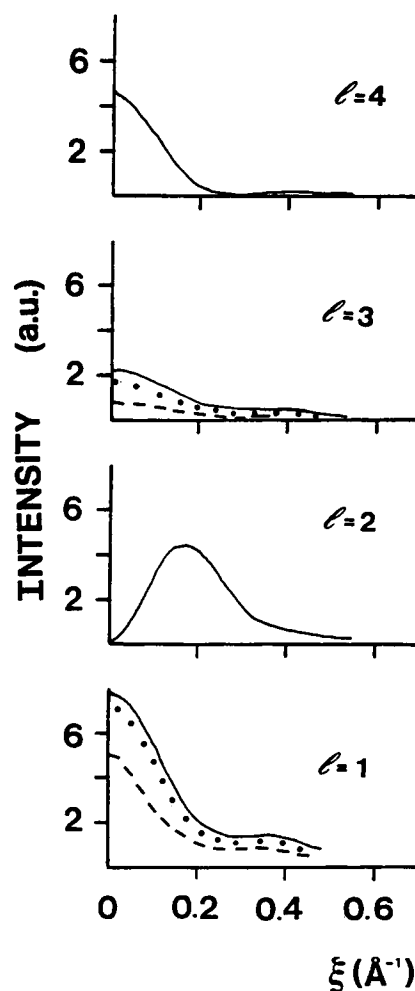


Figure 6 Results of the calculations of the Fourier transforms on the layer lines for zig-zag planar chains of ECTFE: (—) regular alternation of comonomers, (·····) 1 defect in the comonomer alternation per 100 monomer units, and (---) 3.3 defects per 100 monomer units.

of the first layer line is meridional for the calculated pattern (Fig. 6) and at $\xi \approx 0.135 \text{ \AA}^{-1}$, for the experimental pattern (Fig. 5). As a consequence, as for ETFE, for the definition of parameters indicative of the amount of defects in the alternation of the comonomers, which are present in the crystalline phase of ECTFE, we consider only diffraction intensity maxima on the second, third, and fourth layer lines.

The Fourier transform on the nonequatorial layer lines for isolated chain of ECTFE with 1 and 3.3

defects every 100 monomer units are also reported in Figure 6, again for $B_\xi = 8 \text{ \AA}^2$.

The calculated ratios I_2/I_3 and I_4/I_3 , as a function of the number of defects per 100 monomer units, are reported in Figure 7, for $B_\xi = 8 \text{ \AA}^2$. The experimental values of these intensity ratios, observed for the ECTFE sample (Table II), are shown by the dashed line in the same figure. It is apparent that the amount of defects in the chains of ECTFE included in the crystalline phase is lower than 2 per 100 monomer units.

In conclusion, the present analysis indicates that in our samples the chains of ECTFE included in the crystalline phase are characterized by a lower amount of defects in the comonomer alternation than the chains of ETFE.

CONCLUSION

Since for polycrystalline uniaxially oriented samples it is, in general, not completely sound to compare quantitatively the measured intensities of meridional and nonmeridional reflections (due to the difficulty to account for the real portion of matter contributing to the diffraction with varying ξ , for ξ values close to zero), we believe that the ratio between the intensity maxima of the meridional reflections on the fourth and third layer lines (I_4/I_3) is the most suitable for the comparison with the calculated Fourier transforms.

The measured of this intensity ratio, for ETFE and ECTFE samples, and the use of the calculated curves of Figures 4 and 7(B), respectively, allows an easy evaluation of the amount of comonomer alternation defects, included in the crystalline phase.

This kind of evaluation is relevant since the defects in the comonomer alternation have a remarkable influence on the melting temperatures of these nearly alternating copolymers.

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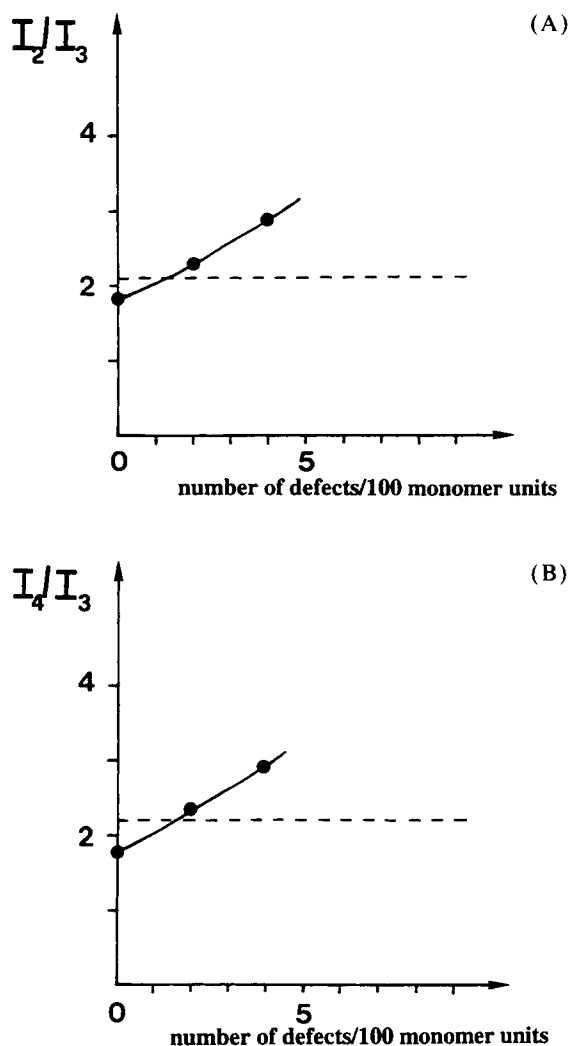


Figure 7 Calculated ratios between the maximum intensities on (A) the second and third layer lines (I_2/I_3) and (B) between the maximum intensities on the fourth and third layer lines (I_4/I_3), in the Fourier transforms of ECTFE, as a function of the number of defects per 100 monomer units, for $B_\xi = 8 \text{ \AA}^2$. The experimental ratios I_2/I_3 and I_4/I_3 , observed for the ECTFE sample (taken from Fig. 5 and Table II) are shown as dashed lines.

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