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Phase transition in ethylene–tetrafluoroethylene (ETFE) alternating copolymer. A spectroscopic study

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The study of temperature dependent infrared (i.r.) and Raman spectra of alternating ethylene–tetrafluoroethylene (ETFE) copolymer suggests that the transition from orthorhombic to hexagonal phases may be driven by the generation and propagation of conformational solitons (gentle mobile chain twist). © 1997 Elsevier Science Ltd.

INTRODUCTION

In this work vibrational spectroscopy (i.r. and Raman) has been used to investigate the mechanism, at the molecular level, of the phase transition of the alternating ethylene–tetrafluoroethylene (ETFE) copolymer from the orthorhombic to the hexagonal structure. Such a phase transition has been previously studied mainly with X-ray diffraction experiments[1,2]. Tanigami *et al.*[1] observed that:

(a) The equatorial reflections indexed (1 2 0) and (2 0 0) in the orthorhombic structure approach one another with increasing temperature.
(b) When the temperature is approximately 100°C the two reflections cannot be distinguished, only one reflection is observed. Moreover, the halfwidths of the reflections decrease showing that the dimensions of the crystalline domains increase[1–3] thus indicating that long-range order increases with increasing temperature.
(c) The intense meridian reflection (0 0 4) decreases its intensity and shifts toward lower θ values with increasing temperature, showing that some kind of short-range disorder is produced.

I.r. and Raman spectroscopy have been used in this work with the aim to describe the phenomena involved in the disordering of the crystalline structure. We wish to proceed along the line followed in the study of conformational disordering of polymethylene chains. Vibrational spectroscopy of conformational defects has been the key for these kinds of studies (refs 4–6 and literature therein).

Generally, in the amorphous phase of polymeric systems or during order–disorder phase transitions of macromolecular systems the existence of various kinds of conformational defects has to be considered. These defects may be *topologically localized* and sometimes give rise to characteristic absorption frequencies which are used as 'defect markers'[4–6]. While localized defects of the type G, GG and GTG, introduce a large distortion of the chain from the all *trans* straight chain, GTG′ defects are to be considered as highly probable and energetically favourable kinks which do not change the direction of the CH_2 *trans* segment.

The second kind of defect is that which involves in a collective way a long section of a polymer chain in a regular lattice. It consists of a deviation from the regular tridimensional arrangement (chain shift, chain rotation–translation). These defects are the result of an interplay between intra- and intermolecular forces and cannot generally be described with a short sequence of *gauche–trans* conformations with well-defined torsional angle θ_i, but involve a large number of skeletal carbon atoms with values of torsional angles not too different from the generally observed G or T conformations.

One of the most interesting characteristics of these collective conformational defects is their dynamical behaviour. They can be treated as solitonic waves, i.e. they can move along the chain without changing their shape and speed. Their existence has been claimed to account for a series of phenomena such as molecular diffusion in polymeric systems[7] and collective excitations in biological systems[8].

EXPERIMENTAL

ETFE powder samples with equimolar composition prepared in our laboratories have been pressed at $T = 300°C$ in order to obtain films of suitable thickness for i.r. analysis (about 20 μm). I.r. spectra were recorded with a Nicolet *FT*-i.r. 20SX spectrometer with a resolution of 2 cm^{-1} and 10 scans for each sampled temperature. We used the SPECAC high temperature cell operating over the range between room temperature and 500°C.

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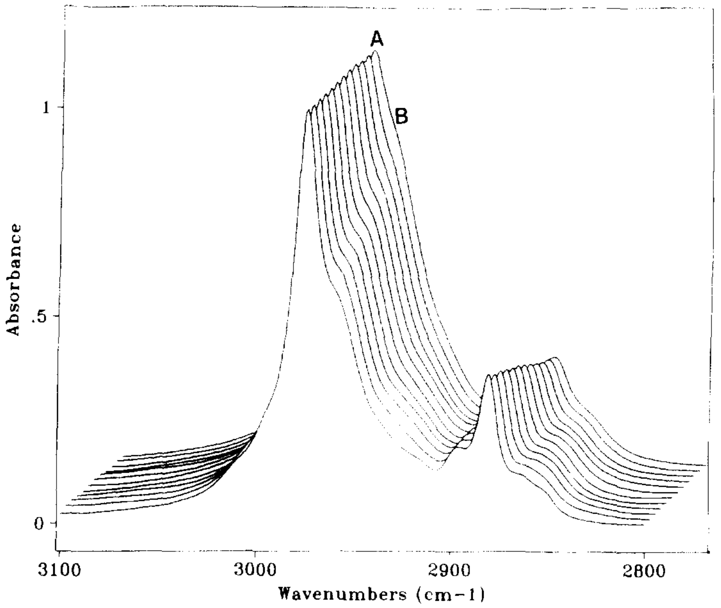


Figure 1 3D plot of temperature dependence of the infrared spectrum of ETFE in the CH_2 stretching region

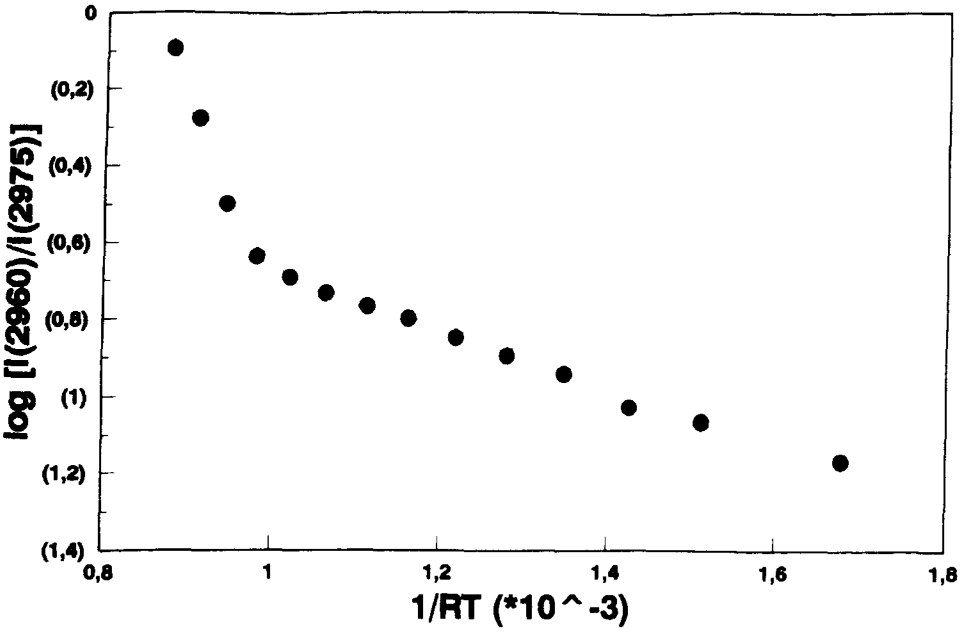


Figure 2 Van't Hoff plot of the relative concentrations vs $1/T$ of the infrared bands A and B of *Figure 1*

Raman spectra were recorded with an XY Dilor multichannel spectrometer equipped with an Olympus BH2 microscope stage and a Mettler temperature controller. As exciting line we used the 5145 Å line of a Spectra Physics Ar^+ laser.

The numerical treatment of the data has been carried out on a Nicolet 680 workstation and on a PC with Lab Calc Software (Galactic Industries Corporation, Salem, USA).

RESULTS

It is known that vibrational group frequencies of molecules in different conformations may differ[3]. Let N_A and N_B be the population of two conformers A and B which may give rise to two i.r. bands at frequencies ν_A and ν_B with intensity $I_A = \alpha_A N_A$ and $I_B = \alpha_B N_B$ where α_A and α_B are the absorption coefficients of the corresponding modes in the two conformers. The temperature dependent relative population of A and B is given by the Boltzmann relation $N_A/N_B = A\,e^{-\Delta E/RT}$ which can be re-written as $(I_A/I_B) = (\alpha_B/\alpha_A)\ A'\,e^{-\Delta E/RT} = A\,e^{-\Delta E/RT}$.

Independently from the values of the absorption coefficients the plot of the experimentally measured $\ln(I_A/I_B)$ as a function of $1/RT$ (see *Figure 2*) provides the experimental value of ΔE (since the value of absorption coefficients ratio is included in the pre-exponential factor). We consider as meaningful for our work the temperature range from room T to the phase transition near 100°C.

In this work we observe an interesting behaviour of the

CH_2 stretching as a function of temperature. In a previous study[9] we analysed and proposed new assignments of the CH_2 stretchings of the regular and disordered structures in ETFE. In *Figure 1* we report the temperature dependent i.r. spectra of an ETFE sample of equimolar composition in the temperature range 20–280°C. These spectra have been normalized to the optical density measured for the CH_2 symmetric stretching of the regular alternating structure at $2975\,cm^{-1}$. When the temperature increases we observe that the shoulder near $2960\,cm^{-1}$ increases its intensity with respect to the more intense band at $2975\,cm^{-1}$.

We used methods of spectral deconvolution to evaluate separately the intensity of the two components from which we derived the corresponding Van't Hoff diagram reported in *Figure 2*. The linear behaviour confirms that the components A and B are due to the same normal mode of identical groups of atoms embedded in an environment along the same chain where different conformations exist. The slope of the straight line allowed us to determine the energy difference ΔE between the minima of the conformational potential; ΔE turned out to be $\approx 750\,cal\,mol^{-1}$ ($3.2 \times 10^{-2}\,eV\,particle^{-1}$).

These experimental results are consistent with a phenomenon of thermally induced generation of 'distorted' conformations, which gradually reduces the content of *trans*-planar segments in the polymer chain.

Raman spectra

Useful information about thermally induced molecular motion can also be obtained from Raman spectroscopy,

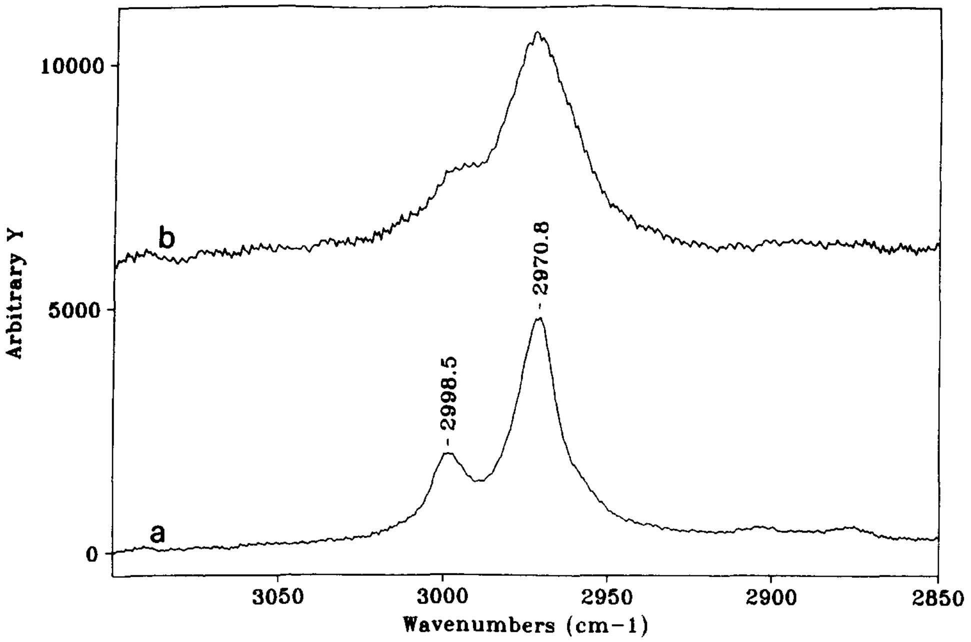


Figure 3 Temperature dependence of the Raman spectra in the CH_2 stretching region: (a) $T = 23°C$; (b) $T = 260°C$

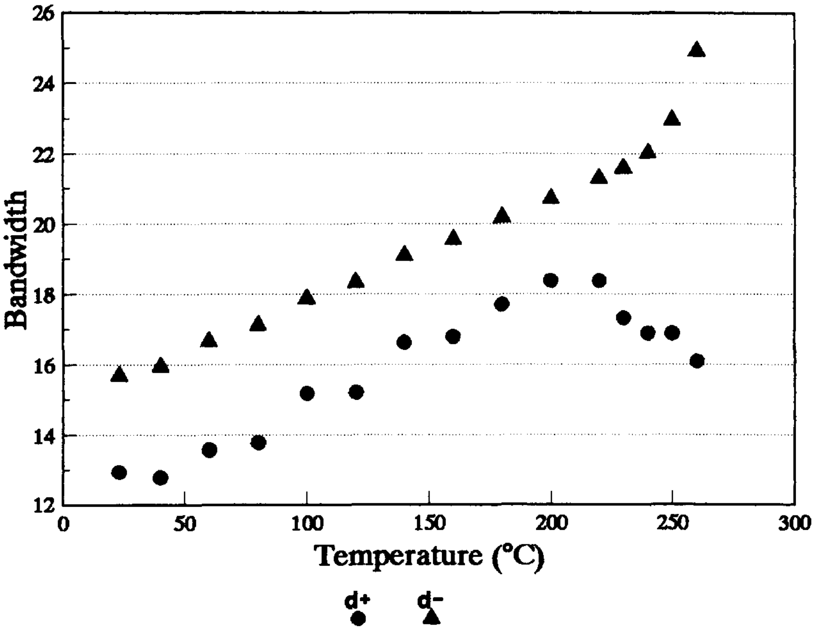


Figure 4 Temperature dependence of the full width at half height of the bands obtained by fitting of Raman spectra

namely from band frequency and band shape as a function of T. We report some of the criteria recently proposed[10] in order to rationalize the behaviour with T of frequency and shape of the antisymmetric CH_2 stretching (d^-) in *n*-alkanes:

(a) if chains perform large amplitude motions associated with low frequency rigid rotations, the bandwidth of d^- should be large compared to the mean value of the widths of other Raman bands. The lowering of the temperature should result in band narrowing because of an increase in strength of the intermolecular interactions;
(b) also, torsional motions give rise to band broadening;
(c) if chains, originally in *trans*-planar conformations, change significantly their conformation frequency shifts both in i.r. and Raman spectra should be observed;
(d) if torsions are large the i.r. absorption coefficient should decrease.

We measured Raman spectra as a function of temperature and applied the above concepts. In *Figure 3* we report the Raman spectra in the CH stretching region of ETFE at room temperature and 270°C and in *Figure 4* the full bandwidth at half height of d^- and d^+ as a function of T. Since the two bands overlap we used a curve-fitting procedure using Lorentzian functions. A physically more relevant observation is that the bandwidth of d^- increases with increasing T but does not change frequency. This means that the chains either perform rigid rotation and/or undergo torsional motion with relatively small amplitudes around the *trans* conformation.

The experimental data obtained suggest that the 'distorted' conformation thermally generated has the characteristic of a collective defect; this defect may involve several atoms of the polymer backbone with low values of the torsional angle between neighbouring CC bonds. The formation of the so-called 'twiston' defect, described by several authors as a collective defect involving many atoms in the polymer chain and with particular dynamical properties, may then be proposed as a way to justify the experimental observations.

Fermi resonances

The Raman spectrum of the alternating copolymer of ETFE shows an interesting case of CH_2 stretching motion (Raman active) free from the Fermi resonances usually encountered in other organic systems containing CH_2 groups. It is known[11] that for systems containing CH_2 groups in *trans*-planar conformation, the i.r. active CH_2 rocking vibration (ungerade (u), with frequency at about $720\,cm^{-1}$) has its first overtone ($u \times u = g$, Raman active, at about $1440\,cm^{-1}$) very close in frequency to the Raman active totally symmetric CH_2 deformation vibration, thus generating Fermi resonances.

Analogously, the CH_2 bending vibration (i.r. active, u) at about $1460\,cm^{-1}$ has its first overtone in a spectral region where the totally symmetric[12] CH_2 stretching vibration ($1460 \times 2 = 2920$) is observed. Fermi resonances in the CH_2 bending and CH_2 stretching regions are known and have been the subject of various studies[11-13]. For ETFE copolymers the vibrational levels of CH_2 symmetric stretching and of $2\nu(CH_2)\delta$ are too far apart to give rise to Fermi resonances and we observe the usual and traditional intensity ratios for d^- and d^+, approximately equal to 0.2[11,12].

Fermi resonances cannot take place for the polymer studied in this work because of the strong inductive effect of the fluorines which change the electronic and dynamical properties of the CH oscillators[9]. This observation is relevant since it is the first case of a system containing CH_2 groups where Fermi Resonances are absent.

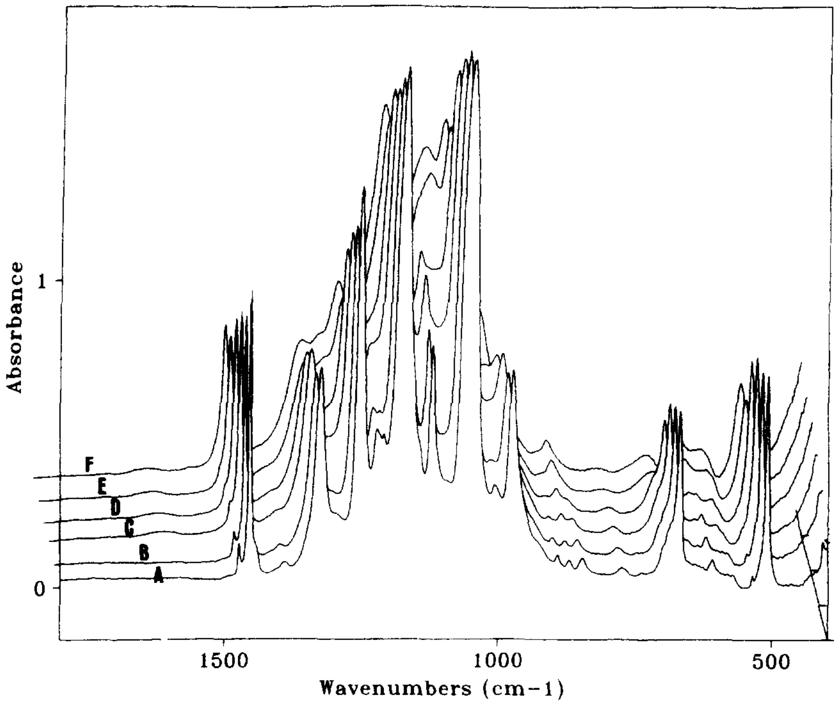
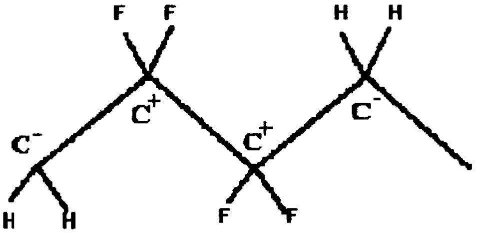


Figure 5 3D plot of temperature dependence of i.r. spectrum of ETFE in the frequency range of skeletal vibrations (A = 4°C, B = 100°C, C = 220°C, D = 260°C, E = 300°C, F = 360°C)

1500–400 cm^{-1} spectral region (i.r.)

Another experimental observation which supports the possible existence of a cooperative defect consisting of slight distortions from *trans*-planarity comes from the i.r. spectra as a function of temperature for a very thin film of ETFE. In *Figure 5* some i.r. spectra as function of temperature in the frequency range 1600–400 cm^{-1} are shown. In this range we observe the strong bands due to CF_2 stretching and other bands due to various deformation motions of CF_2, CC, and CH_2 groups whose intensities are strongly enhanced because of their dynamical coupling with extremely strong CF_2 stretchings.

This experiment shows that, besides a general broadening of the spectrum, no bands are observed which could be assigned to *gauche* CH_2–CH_2 defects until the melting temperature is reached (270°C). From 270°C to higher temperatures we observe very clearly a band at about 1090 cm^{-1} which increases its intensity with increasing *T*. This band is assigned to a C–C stretching of CH_2–CH_2 groups in *gauche* conformation. The same band was calculated[10] for a polymethylene chain and observed in the Raman spectrum. We observe this band in the i.r. spectra because of the different electronic configuration in our polymer[9], where the C–C bonds are strongly polar because of the electronegativity of the fluorine atoms. Indeed the electron distribution can be sketched in the following way:



The dipole transition moment (i.e. the i.r. intensity) associated to the C–C stretching of the CH_2–CF_2 groups then become very large.

The fact that higly localized defects (such as *gauche* conformations) are observed only after the melting temperature supports again the idea that during the phase transition between orthorhombic to hexagonal phase ETFE chains are conformationally perturbed mostly by a collective defect (which we may label as a twiston), consisting of a large portion of the chain in a slightly distorted conformation, with torsional angles not too different from the original one at lower *T*.

Twiston defect

The theoretical description of the twiston has been carried out by Mansfield[7] and Skynner[14]. It has to be pointed out that the phenomenon of propagation of twistons in refs 7 and 14 is the result of an interplay between intra- and intermolecular forces. The distorted region in an infinite polymer chain can be considered an object separating two degenerate energy states. A gentle long conformational twist propagates along the polymer chain as a soliton wave.

Other phenomena related to the existence of cooperative defects as twistons have been proposed for fluorinated polymers as polyvinylidenefluoride (PVDF) and polytetrafluoroethylene (PTFE). In the former, the poling process has been studied[15,16], and a 'conformational soliton' has been proposed as responsible for the mechanism of chain reorentation in the crystalline region when a high electric field is applied to a film sample. Also in PTFE a soliton defect has been proposed[17] for describing the phenomenon of helix reversal[18–21]. In both cases the existence of a cooperative defect is required and is described by a sequence of torsional angles which can propagate along the chain.

Dynamical calculations[15,16] in the case of the process of poling of PVDF have estimated the time needed for these solitons to propagate along a chain of 100 Å length, namely 50×10^{-11} s. This implies a velocity of about 10^4 cm s^{-1}. Under these conditions, according to ref. 22 the upper limiting speed of propagation of the twiston in order to be observed spectroscopically is approximately 10^4 cm s^{-1}, close to what has been estimated in refs 7, 15 and 16 for other kinds of chain. We expect we would be able to observe i.r. or Raman bands characteristic of soliton defects if their concentration is sufficiently large to give reasonable intensity to the vibrational transitions. This implies that the activation energy of the twiston is very small. Theoretical estimates of such energy in fluorinated polymers are not yet available.

Zerbi and Longhi[22] have studied the conformational solitons in *n*-nonadecane (taken as model system) involved both theoretical calculations and experimental observations of the vibrational spectra of C_{19} as: (a) the all *trans* orthorhombic phase; (b) α-phase; and (c) a structure containing a conformational soliton as described in ref. 7. Significant coincidences between some calculated 'soliton bands' and features observed in the i.r. spectrum at 31°C have been found. If frequency fitting can be accepted as working hypothesis, to be further supported by other physical evidence, one may think that the concentration of solitons is sizeable also at room temperature, i.e. their formation energy is low, and much lower than that calculated in ref. 7 based on semiempirical non-bonded atom–atom potentials.

For a comprehensive discussion of the theoretical and experimental aspects of twistons on polymethylenic chains see ref. 10.

CONCLUSION

Our spectroscopic experiments, in conjunction with previous X-ray data, provide a description at the molecular level of the phase transition process in an ETFE copolymer.

During the phase transition of ETFE from the orthorhombic to the hexagonal structure we observe:

(a) Temperature dependent i.r. bands in the CH_2 stretching region which can be assigned to a slightly 'distorted' phase. The bands gradually increase their intensity with increasing temperature. The energy difference (evaluated with a Van't Hoff plot) between the equilibrium and the perturbed conformation is quite low (< 1 kcal mol^{-1}, 4.3×10^{-2} eV particle^{-1}).

(b) Evidence for a topologically localized conformational defect of the type *gauche* C–C appears only near the melting temperature (approximately 260°C).

(c) Raman band shapes and their temperature behaviour in the CH_2 stretching region support the idea that a collective defect is generated during the phase transition.

This experimental evidence confirms the hypothesis that in the case of ETFE during the phase transition from orthorhombic to hexagonal phases, conformational collective defects such as twistons are generated and propagate like solitonic waves. Though no 'direct' experimental evidence on the existence of twistons can be collected, in this work we have presented evidence that a collective defect of this kind could indirectly explain the spectroscopic behaviour observed during the phase transition of the ETFE alternating copolymers.

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