

# Molecular dynamics of a crystal-crystal phase transition in an alternating copolymer of ethylene and chlorotrifluoroethylene using the Raman active longitudinal acoustical mode (*LAM*)

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A low frequency Raman band assignable to the longitudinal acoustical mode (*LAM*) in an alternating copolymer of ethylene and chlorotrifluoroethylene (E/CTFE) has been observed. The anisotropic scattering properties of an oriented filament have been determined by polarized Raman measurements and the results confirm this assignment. The frequency-chain length variation characteristic of the *LAM* has also been observed and studied through carefully-controlled annealing experiments. The dynamics of the 150°C crystal-crystal phase transition was investigated using the bandwidth and frequency position of the *LAM* as a molecular probe. It was found that its shift to lower frequency upon crossing the phase boundary reflected a decrease in the *c*-axis Young's modulus consistent with a deviation of the backbone conformation away from a planar structure.

## INTRODUCTION

The observation of the Raman active longitudinal acoustical mode (*LAM*) in polymers has yielded useful information on morphological structure and crystallization kinetics<sup>1-10</sup>. Unfortunately these studies have been limited to homopolymers existing in either the planar zigzag or helical conformation<sup>11-16</sup>. A recent investigation of block copolymers<sup>17</sup> was a natural extension of studies on *LAM* and found that a low frequency Raman active mode, characteristic of the segment length of the crystallizable block, could be identified. Further studies indicate that although the band frequency varied inversely with chain length, its position was somewhat perturbed from its location in the crystalline homopolymer<sup>14</sup>. In an attempt further to understand the effects of copolymerization on both the position and intensity of the *LAM*, an investigation of an alternating copolymer of ethylene and chlorotrifluoroethylene (E/CTFE)<sup>18,19</sup> was undertaken.

Of particular interest in the E/CTFE copolymer is a crystalline relaxation<sup>20</sup> or phase transition which occurs at 150°C. Studies<sup>19</sup> which have appeared in the literature indicate that an abrupt increase in the coefficient of thermal expansion takes place at the transition temperature with a consequent reduction in shear modulus. This contributes to the onset of solid state extrudability according to a recent study by Aharoni and Sibilis<sup>21</sup> since above this transition temperature polymer chains can slide past one another with a minimum of resistance. Unfortunately, little is known about the molecular dynamics of this crystal-crystal phase transition and hence the use of the *LAM* as a probe of molecular structural changes occurring during the phase transition was investigated.

## EXPERIMENTAL

The E/CTFE used in this study was a commercial material (HALAR) obtained from the Allied Chemical Company. The highly oriented transparent filament was manufactured by the Newton Filaments Co. (Code: 11H-NRL) and had a diameter of 0.11 in. All filaments were annealed in an air oven at constant length with temperatures which varied by  $\pm 3^\circ\text{C}$ .

D.s.c. melting point measurements were determined by using a Du Pont Model 990 thermal analyser.

FT i.r. spectra of copolymer films were obtained on a Digilab FTS-15B Fourier transform interferometer at a resolution of  $4\text{ cm}^{-1}$ . Thin films suitable for transmission studies were prepared by submitting the melted copolymer to high pressures between the plates of a Carver press.

Raman spectra were recorded with a Jobin-Yvon Ramanor HG-2S double monochromator using the 5145 Å line of a Spectra Physics 165-04 argon-ion laser equipped with a temperature stabilized etalon. An optical cell containing  $\text{I}_2$  vapour maintained at 80°C was placed between the collection lens and the monochromator. The etalon allows selection of only 1 of the 60 or more resonant modes which normally appear under the 5145 Å Doppler gain curve. Adjustment of the etalon so as to choose a mode which corresponds exactly to the energy difference between two rotational energy levels of  $\text{I}_2$  can then be made. Thus passing of the collected scattered light from the sample through the  $\text{I}_2$  filter can cause attenuation of the elastically scattered Rayleigh component by as much as 6 orders of magnitude while the intensity of the Raman scattering will be decreased by 50% due to absorption in the cell<sup>22</sup>. This technique in conjunction with the superior stray light rejection afforded by the 4 slit

configuration of the Ramanor (containing holographic gratings) allow spectra to be recorded within  $3\text{ cm}^{-1}$  of the exciting line. All data were collected and processed with a Nicolet 1180 data system. Sufficient signal-to-noise spectra were obtained at  $1\text{ cm}^{-1}$  band pass in the  $3\text{--}75\text{ cm}^{-1}$  region by the co-addition of 150–200 scans. Correction of the Raman intensities for  $\text{I}_2$  absorption, stray light, temperature and frequency were made according to Snyder and Scherer<sup>6</sup>.

High temperature Raman measurements were obtained using a vertical Harney–Miller cell containing a 50 W cartridge heater connected to a variable voltage supply. Helium gas was passed over the heater and used to raise the temperature of the sample. A digital thermocouple placed within 1–2 mm of the sample was used to record the temperature which was kept constant to within  $\pm 1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Evidence against $(-\text{CH}_2)_n$ block formation

In order to characterize the E/CTFE copolymer structurally a series of spectroscopic measurements was undertaken to determine the extent of  $(-\text{CH}_2)_n$  block formation. Earlier studies by Sibiliala *et al.*<sup>19</sup> have shown that polymerization defects (e.g. methyl branches) and  $(-\text{CH}_2)_n$  sequences with  $n > 2$  could be formed in E/CTFE copolymers containing 60–80 mol % ethylene.

N.m.r. measurements of the copolymer used in this study were obtained after dissolution in 2,5-dichlorobenzotrifluoride at  $120^\circ\text{C}$ . By comparison with those spectra obtained as a function of ethylene content and reported in an earlier study<sup>19</sup> it was concluded that the spectral results obtained in this investigation were consistent with that of an alternating copolymer containing 50 mol % ethylene.

Differential scanning calorimetry (d.s.c.) yielded a peak melting temperature for the copolymer monofilament of  $235^\circ\text{C}$ . Although the thermal and mechanical processing history of this material would slightly affect the crystalline melting point, the observed value is within the range  $233\text{--}241^\circ\text{C}$  reported<sup>18,19</sup> for 50–50 mol % alternating copolymer.

Infra-red results by Sibiliala *et al.*<sup>19</sup> on a series of E/CTFE copolymers indicated that a band at  $1470\text{ cm}^{-1}$ , attributable to a  $\text{CH}_2$  bending motion of the methylene group, decreased in intensity as the ethylene content decreased. Subsequently this band was assigned to a  $\text{CH}_2$  vibration in groups containing 3 or more methylene units. Fourier transform i.r. studies were conducted on a melt-crystallized film of the copolymer. Two strong bands are observed at  $1450$  and  $1397\text{ cm}^{-1}$  with a weak shoulder located at  $1470\text{ cm}^{-1}$ . The  $1450$  and  $1397\text{ cm}^{-1}$  bands were found by Sibiliala *et al.*<sup>19</sup> to increase in intensity with an increase in CTFE content and were thus assigned to the methylene bending and wagging modes, respectively, of an isolated  $-\text{CH}_2\text{CH}_2-$  unit. The observation of the weak shoulder at  $1470\text{ cm}^{-1}$  in the melt-crystallized film indicates the presence of a small amount of  $(-\text{CH}_2)_n$  sequence with  $n > 2$ .

Raman measurements of the unoriented copolymer were also made in the  $(-\text{CH}_2)_n$  bending region,  $1400\text{--}1500\text{ cm}^{-1}$ , where intensity patterns containing 3–4 bands are found in paraffins and are specifically characteristic of the triclinic or orthorhombic subcell packing<sup>16,23</sup> of  $(-\text{CH}_2)_n$  groups. A single intense band was observed at  $1437\text{ cm}^{-1}$

in the copolymer which precludes the presence of any paraffinic crystallites in the sample under investigation.

The above experimental results collectively suggest that the E/CTFE material used in this study is a highly alternating 1:1 copolymer.

### Observation and interpretation of LAM

As seen in Figure 1, a highly polarized Raman band was observed at  $12.2\text{ cm}^{-1}$  in an oriented E/CTFE filament. Stems in the crystalline lamellae are highly oriented along the filament axis as shown by wide- and low-angle X-ray diffraction and as schematically illustrated in Figure 2. No apparent chain inclination to the lamella surface is observed. The Raman polarization measurements shown in the upper two panels of Figure 1 were conducted with the electric vector of the incident light parallel to the filament axis. The spectrum (ZZ) in the top panel resulted when the polarizer (analyser) was positioned so as to allow observation of only the scattered polarization component parallel to the filament axis, while the second panel contains the spectrum (ZX) obtained with the polarizer (analyser) perpendicular to the filament axis. In the absence of any polarization scrambling the ZZ

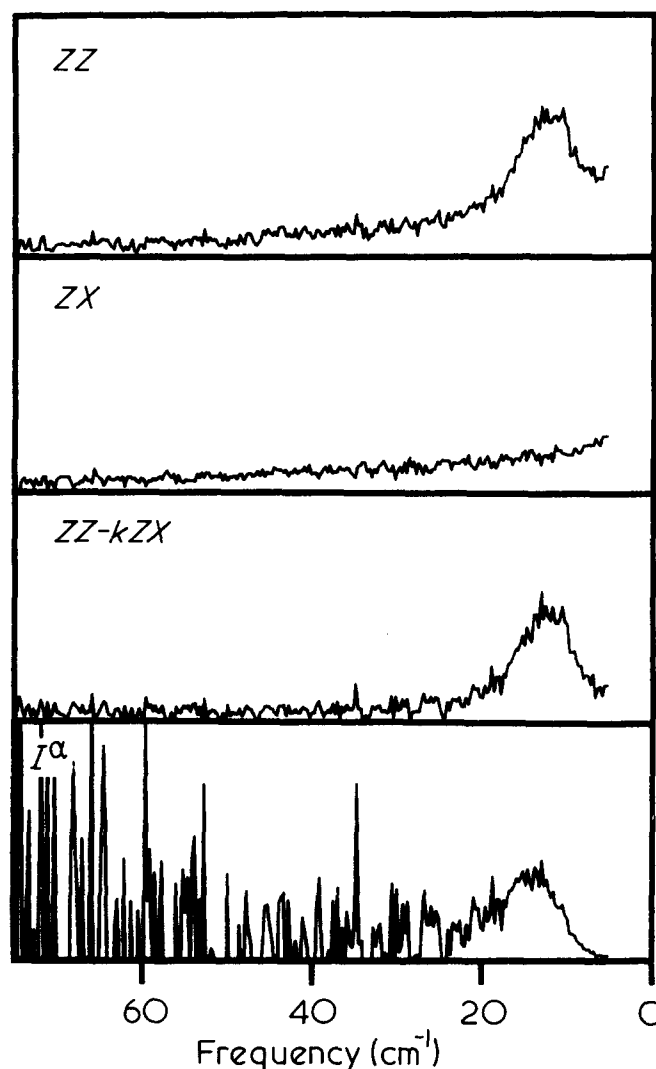


Figure 1 Polarized Raman spectra of oriented E/CTFE monofilament before (ZZ, ZX) and after (ZZ-kZX,  $I^\alpha$ ) corrections for stray light, frequency and temperature have been made (see text)

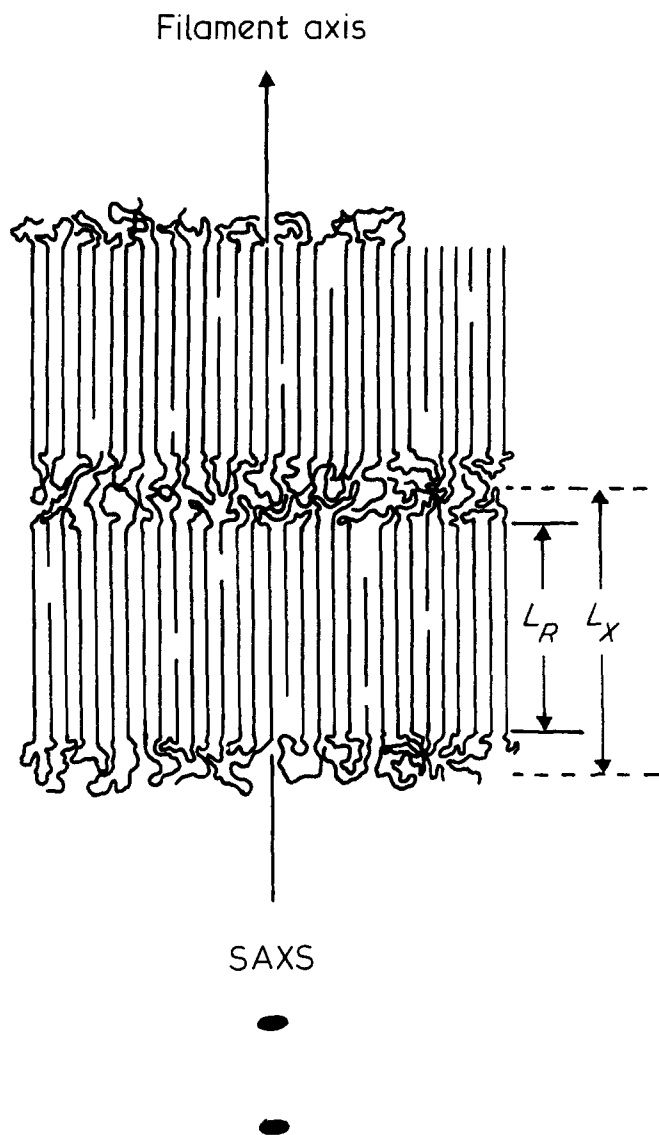


Figure 2 Schematic illustration of morphology of an oriented E/CTFE monofilament suggested by wide-angle (WAXS) and small-angle (SAXS) X-ray diffraction experiments.  $L_X$  = X-ray long period;  $L_R$  = Raman stem length; SAXS = observed small-angle X-ray diffraction pattern

spectrum would be expected to contain only bands assignable to the totally symmetric symmetry species. The character of the LAM is such that symmetric molecular motion occurs parallel to the chain axis about a node at the centre of the chain and hence the Raman polarization results are consistent with the symmetry expected for longitudinal acoustical modes<sup>24</sup>.

Furthermore, the peak position of the low frequency Raman band is observed to shift to lower frequency as the lamellar thickness increases upon annealing the filament at constant length. Thermal histories, long spacings and observed Raman frequencies for three of the samples are listed in Table 1. In addition, the bandwidth (full width at half maximum, *FWHM*) is also observed to narrow considerably upon annealing, reflecting a decrease in stem length distribution within lamellae and/or an increase in uniformity of the crystal thicknesses of different lamellae resulting from the annealing process<sup>6</sup>. These observations support assignment of this low frequency Raman active mode to the single nodal LAM-1 of the alternating E/CTFE copolymer.

Recent studies<sup>6,7,9</sup> on the interpretation of LAM in polymers have shown that since the position, *FWHM* and shape of the LAM reflect chain lengths, their distribution, and to some degree the effect of perturbations, care must be taken to relate the observed Raman intensity to molecular parameters. In the intensity expression:

$$I_v^{\text{obs}} \propto \frac{(v_0 - v)^4}{v(1 - e^{-hv/kT})} I^2 \quad (1)$$

where  $I_v^{\text{obs}}$  is the observed Raman intensity;  $v_0$  is the excitation frequency;  $v$  is the frequency of the Raman band (in this case LAM-1);  $\exp(-hv/kT)$  is the Boltzman factor and  $I^2 = (\partial\alpha/\partial Q)^2$  is the change in polarizability resulting from a particular normal mode, the only parameter directly relatable to molecular structure is  $I^2$ . Hence, division by the frequency and temperature factors and a recasting of the spectrum in terms of  $I^2$  is desirable and has been shown by Snyder and Scherer<sup>6</sup> to influence the peak position of LAM-1 to varying degrees, depending on the value of the *FWHM*.

In the ZZ and ZX spectra of sample no. 2 shown in Figure 1 contributions from the absorption of scattered light by  $I_2$  vapour contained in the pre-monochromator filter have been subtracted out. Further data reduction was accomplished by observing that the ZX spectrum is a good estimation of the stray light characteristics of the double monochromator. Therefore, subtracting the stray light contribution (also present in the ZZ spectrum) from the measured ZZ spectrum results in that shown in panel 3 of Figure 1. Subsequent frequency and temperature correction referred to earlier<sup>6</sup> yields the spectrum shown in panel 4. The net result has been a shift in peak frequency of this band by approximately  $1.0 \text{ cm}^{-1}$  towards higher frequencies. The peak positions of all bands listed in Table 1 have been determined after intensity corrections.

Interpretation of the results obtained for the E/CTFE alternating copolymer in terms of the continuous elastic rod model<sup>25,26</sup> is enlightening in spite of the scarcity of structural data available. Initial characterization studies<sup>19</sup> of a 50 mol % ethylene copolymer suggested a conformation of the backbone slightly removed from a planar zigzag structure. A hexagonal unit cell with a theoretical density of  $1.7 \text{ g cm}^{-3}$  was postulated based on X-ray data obtained from an oriented film. It is interesting to note that a determination of the crystalline elastic modulus using the uniform elastic rod model:

$$v = \frac{1}{2Lc} \left( \frac{E}{\rho} \right)^{1/2} \quad (2)$$

Table 1 Thermal pretreatment and experimental results for E/CTFE samples

Sample	Thermal treatment*	Lamella thickness (Å)	Frequency ( $\text{cm}^{-1}$ )†
1	As received	$173 \pm 10$	$17.5 \pm 0.3$
2	$T_A = 186 \pm 1^\circ \text{C}$ ; $t = 2 \text{ h}$	$214 \pm 10$	$13.1 \pm 0.3$
3	$T_A = 194 \pm 1^\circ \text{C}$ ; $t = 3.5 \text{ h}$	$206 \pm 10$	$12.9 \pm 0.3$

\* All samples annealed at constant length

† Determined after a correction for stray light, frequency and temperature was applied

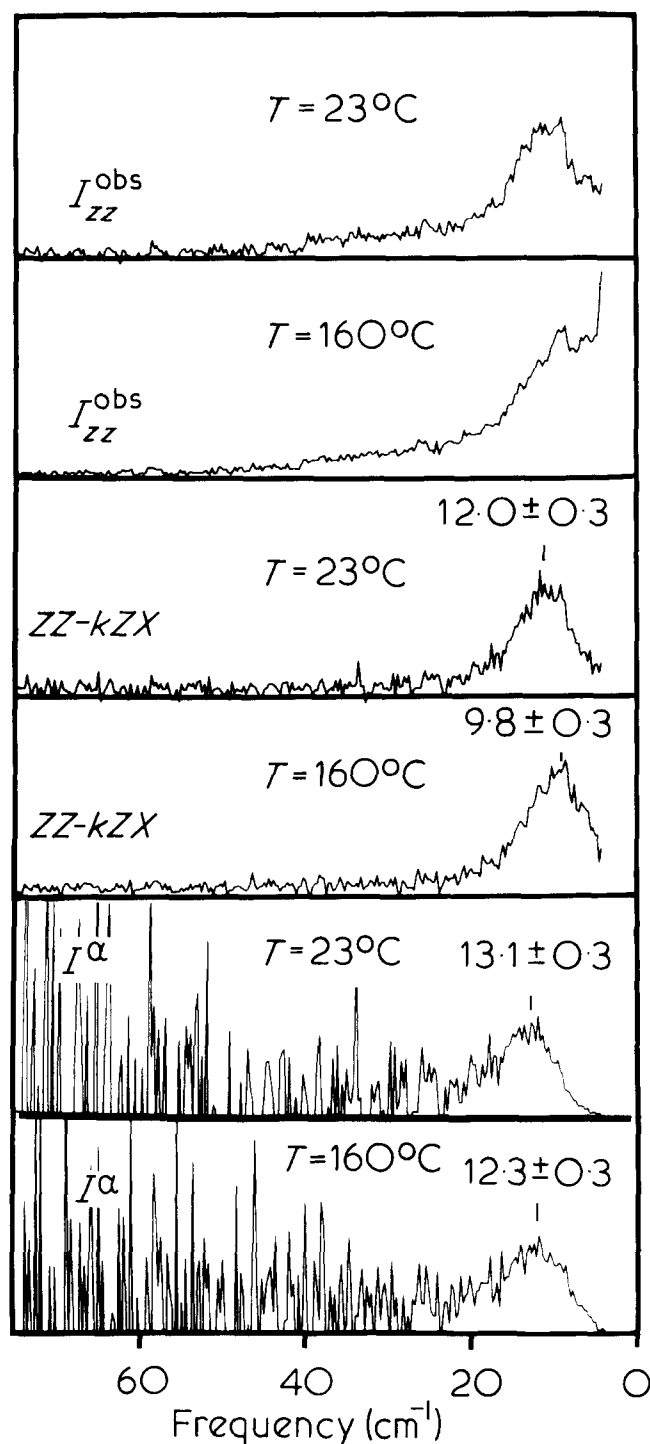


Figure 3 Raman spectra below and above the 150°C crystal-crystal phase transition in E/CTFE.  $I^\alpha$  has been corrected for stray light, frequency and temperature

(where  $\nu$  is the frequency of oscillation in  $\text{cm}^{-1}$ ;  $L$  is the length of rod;  $c$  is the speed of light;  $E$  is the  $c$ -axis Young's modulus;  $\rho$  is the crystalline density) together with the SAXS long period (without Lorentz correction) as an approximation of the 'rod' length yields a value of  $E$  which is 40–45% larger than that obtained by Schaufele and Shimanouchi<sup>26</sup> for polyethylene. This may result from a strengthening of the CCC bending angle force constant due to H...F and H...Cl non-bonded intramolecular interactions which effectively stiffen the backbone, but would be surprising since this would be offset by the non-zero torsional contribution to the modulus resulting from a non-planar conformation.

A more reasonable consideration involving the discrepancy between long spacing,  $L_x$ , and Raman length,  $L_R$ , is shown in Figure 2. Since SAXS measures differences in electron density it will include an amorphous layer in addition to the length of stem within the polymer crystal (see Figure 2). However, it has been demonstrated<sup>24,27</sup> that the LAM is a molecular vibration of the chain stem and hence  $L_R$  would be expected to be somewhat lower than  $L_x$ . It is interesting to note that a reduction in  $L_x$  of 20% yields identical  $c$ -axis Young's moduli for both PE<sup>25,26</sup> and E/CTFE.

A large amount of theoretical and experimental work<sup>16,28–34</sup> has recently been reported in an attempt to assess thoroughly the perturbative effects of forces and masses on the frequency and intensity of LAM. To some degree these effects contribute to the perturbation of the observed LAM frequencies in E/CTFE but a significant lack of structural data in the alternating copolymer precludes any quantitative estimate although in studies on other systems where sufficient data is available the contribution has been found to be small.

#### Dynamics of the crystal-crystal phase transition

A crystal-crystal phase transition in E/CTFE copolymer occurring at 150°C was first identified by Sibilia *et al.*<sup>20</sup> using i.r. absorption and X-ray diffraction techniques and by mechanical relaxation measurements. The X-ray results indicated that the lateral dimensions in the hexagonally-packed structure did not change as a result of transformation into the high temperature phase although narrowing of the  $2\theta = 17.4^\circ$  reflection did suggest increased or improved ordering of the system.

However, polarized infra-red studies indicated that a change in orientation of methylene groups occurred at the transition temperature. In particular, changes in the dichroism of the CH stretching mode at  $2975\text{ cm}^{-1}$  suggested that the plane made by the HCH group tended to become perpendicular to the chain axis above the phase transition, supporting a mechanism involving 'unkinking' of the backbone.

Since the Raman active LAM can be highly sensitive to structural changes which may occur at a phase boundary, a series of Raman measurements were made on an E/CTFE filament preannealed at 186°C for 2 h. This was done to ensure that no subsequent crystal thickening would occur when making measurements in the 160°–170°C range. As shown in Figure 3, the LAM band observed at ambient temperature shifts to lower frequencies upon heating to 160°C (approximately 10°C above the phase transition) without any appreciable change in bandwidth (bottom 2 panels). This shift is shown in Figure 4 where the peak positions (corrected for frequency and temperature effects) are plotted as a function of temperature. These band positions are readily reproducible after several cycles above and below the transition temperature. In contrast, the LAM in preannealed (129°C) polyethylene<sup>2,35</sup>, which exhibits no high temperature phase transition, exhibits no frequency shift upon heating to 121°C. Hence, the reversible changes in band position observed in E/CTFE can be attributed to a dynamical change in conformational or crystal structure which occurs at the 150°C phase transition.

It is interesting to note that a curve similar to that shown in Figure 4 was observed for the temperature dependence of the width of the equatorial X-ray reflection

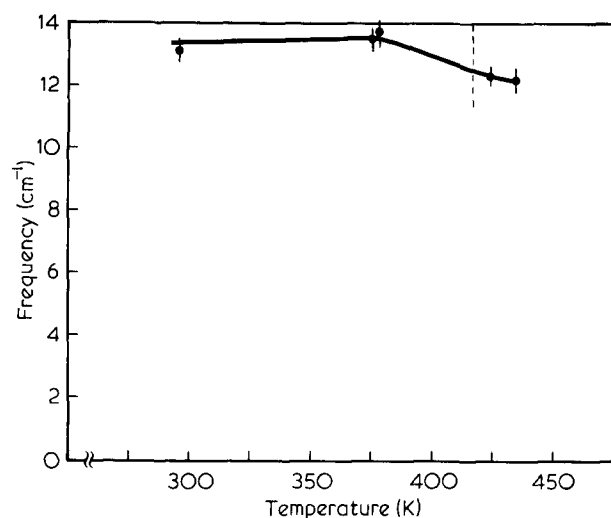


Figure 4 Observed LAM-1 frequencies as a function of temperature. The intensities and therefore the positions have been corrected for frequency and temperature. — — —, Phase transition temperature

at  $2\theta = 17.4^\circ$  reported by Sibilio *et al.*<sup>20</sup> and suggests that the phase transition occurs over a range of temperatures rather than at a discrete point. This is further confirmed by d.s.c. measurements made in this laboratory which show a broad (width =  $60^\circ$ – $70^\circ$ C) transition centred at approximately  $145^\circ$ C. In contrast, the  $19^\circ$ C crystal-crystal phase transition in PTFE has a breadth of  $\sim 15^\circ$ C.

It is instructive to explore several factors which might influence the position of LAM using as a basis the continuous elastid rod model<sup>25,26</sup> (equation 2). A considerable insight into the effects of several structural parameters on LAM can be obtained simply by differentiating equation (1) with respect to the three quantities:  $\rho$ ,  $L$  and  $E$ . The following equations result:

$$\frac{\Delta v}{v} = -0.5 \frac{\Delta \rho}{\rho} \quad (3)$$

$$\frac{\Delta v}{v} = -\frac{\Delta L}{L} \quad (4)$$

$$\frac{\Delta v}{v} = +0.5 \frac{\Delta E}{E} \quad (5)$$

Although any quantitative interpretation would at best be speculative, it is useful qualitatively to examine the relative dependence of LAM frequency on these parameters. There are several interesting conclusions which can be drawn by reference to these expressions. First of all the relative change in frequency of the LAM may be positive or negative, i.e. a 10% increase in  $\rho$  or  $L$  would cause a shift of the peak position to lower frequency while the same 10% increase in modulus would shift the LAM peak to a higher frequency. Another consideration is the relative contributions of the independent variables in these equations to the overall frequency shift. It could be argued that changes in density due to phase transitions are relatively modest, perhaps 1–2%. Likewise, the relative change in length resulting from a conformational change accompanying a crystal-crystal phase transition would be expected to be relatively small (1–5%). However, the relative change in moduli which result from a conformational change can be large and is exemplified

by an almost 30–35% decrease in  $c$ -axis Young's modulus which occurs by introducing into the 2/1 planar backbone (e.g. PE) a small amount of torsional freedom as in the 2.14/1 (15/7) helical structure of PTFE. This has been illustrated both experimentally<sup>15,27</sup> and theoretically<sup>36</sup> in the case of PTFE and it has been shown in general that the  $c$ -axis moduli of chains arranged in an extended zigzag conformation are an order of magnitude higher than that of chains existing in a helical conformation, because helical chains can extend by rotation about bonds<sup>37</sup>. Further deviations from a planar zigzag conformation towards a more helical structure would cause substantially larger changes in modulus. In addition, since substantial changes in lamellar surface structure would not be anticipated in reversible crystal-crystal phase transitions, the perturbative effects of forces and masses would not be expected to change abruptly. Therefore, little or no effect of these perturbing influences on either the position or bandwidth of the LAM would be expected at the phase boundary. It can then be concluded that the greatest range of parametric variability and hence the greatest effect on LAM frequencies will result from conformational changes which accompany structural phase transitions.

In this light it is feasible to examine the dynamics of the  $150^\circ$ C phase transition in the E/CTFE copolymer. As previously mentioned, X-ray measurements<sup>19</sup> do not support any change in packing density occurring in the high temperature phase. Likewise, although SAXS long spacings as a function of temperature do not appear in the literature, significant changes (10%) would not be expected as a result of conformational change. Therefore the reversible  $0.8$ – $1.0 \text{ cm}^{-1}$  shift of LAM observed at the crystal-crystal phase transition can most reasonably be attributed to a change in conformational structure to one which exhibits a further deviation from planarity than the room temperature structure. As seen from equation (5) the resulting decrease in modulus resulting from the inclusion of a weak torsional contribution to the chain stiffness would be responsible for the substantial shift of the Raman-active LAM to lower frequencies. This interpretation would therefore support a further 'kinking' of the chain above the  $150^\circ$ C molecular transition and is at variance with earlier studies<sup>19</sup>. A similar kinking of the backbone is known to occur at the high temperature crystalline transition in *trans* 1,4-polybutadiene<sup>38</sup> and is in accordance with a general conformational disordering which occurs at elevated temperatures.

## CONCLUSIONS

The observation of the LAM has been extended to alternating copolymers with backbone conformations other than planar zigzag or helical. Support for this assignment was provided by polarized Raman measurements, SAXS studies and high temperature annealing experiments.

An investigation of the  $150^\circ$ C solid-state phase transition using the bandwidth and frequency position of the LAM as a probe of molecular order indicated that a change in conformation occurs at the phase boundary. Furthermore, this change in structure was characterized as a 'kinking' of the backbone resulting in increased torsional contribution to the stiffness of the chain with a subsequent decrease in the  $c$ -axis Young's modulus.

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