

Longitudinal acoustic modes of polytetrafluoroethylene copolymers and oligomers

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Raman active longitudinal acoustic modes (*LAM*) have been observed in the perfluoro *n*-alkanes and in a random copolymer of tetrafluoroethylene and hexafluoropropylene (TFE–HFP). Low frequency bands were found in both the melt and solid phases of the oligomers, and their comparison indicates that regular extended helical conformations exist in the melt phase of perfluoro *n*-alkanes below $n\text{-C}_{12}\text{F}_{26}$. Good agreement is found between the lamellar long spacings of the copolymer and that calculated from the *LAM* frequencies. Normal mode calculations, using available force fields, have been performed on the infinite homopolymer (PTFE) and $n\text{-C}_{16}\text{F}_{34}$. It was found that the helix reversal type of chain defect does not affect *LAM* frequencies and intensities.

INTRODUCTION

Currently, there is considerable interest in the use of longitudinal acoustic modes (*LAM*) of vibration, observed by Raman spectroscopy, to elucidate aspects of the structure and chemical bonding in chain molecules. These modes are characterized by frequencies which are inversely proportional to chain length and by atomic displacements confined essentially along the chain axis direction with a node (zero atomic displacements) at the chain centre.

Extensive theoretical and experimental investigations of *LAM* in solid *n*-alkanes and lamellar textured polyethylene have been carried out^{1–8}. Frequency–chain length relationships established from *n*-alkane data have been of considerable utility in characterizing the straight chain segment lengths in polyethylene lamellar crystals. The use of this Raman characterization technique in other polymeric materials has been limited in part by the unavailability of suitable oligomeric data. Initial attempts to observe *LAM* in other chain molecules were mostly unsuccessful, although recently *LAM* of several helical homopolymers [isotactic polypropylene^{9–10}, poly(ethylene oxide)¹¹, and polyoxymethylene¹⁰] have been observed. Attempts^{9–13} to interpret *LAM* frequencies in terms of lamellar fold periods and Young's moduli have raised questions concerning the frequency–chain length relationship in non-transplanar chain molecules.

Using the elastic rod model the relationship between the frequency and chain length becomes:

$$\nu = m/2L(E/\rho)^{1/2} \quad (1)$$

where E is the Young's modulus, ρ the density, L the length and m the number of displacement nodes. Recent studies¹⁰ have shown that large discrepancies exist between Young's moduli determined from *LAM* by spectroscopic techniques (Raman and coherent inelastic neutron scattering) and by X-ray methods¹⁴ in which changes in lattice parameters are measured on specimens under stress. The differences have been particularly striking (up to a factor of 6) for helical polymers, and have brought into question the uniform stress approximation used in the X-ray method and the comparison

of moduli determined by static and dynamic methods.

Various composite elastic rod models have been introduced^{12,13} to account for the variances in moduli. In the composite rod model crystalline and amorphous phases are represented by different moduli and lengths. The modulus for the crystalline phase of polyethylene may be determined from *LAM* data of the *n*-alkanes, in which only crystalline phase is present. There are no commercially available oligomers for the helical polymers in which *LAM* have recently been observed^{9–12} and hence no independent determination of the dynamic Young's modulus is possible.

In an attempt to better understand the relationship between longitudinal acoustic modes and chain length in helical polymers we have initiated studies of these motions in polytetrafluoroethylene, the perfluoro *n*-alkanes and a random copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP). The number of fluorocarbon oligomers available is modest in comparison to the *n*-alkanes, but adequate to establish the frequency–chain length relationship.

A necessary condition to establish the crystalline Young's modulus of the polymer from oligomeric data is that the polymer and its oligomers be isostructural. Structural studies¹⁵ of $n\text{-C}_{16}\text{F}_{34}$ have confirmed that its chain conformation is identical to the 15/7 helical form exhibited by polytetrafluoroethylene above 19°C. We have compared the Raman spectra of the fluorocarbon oligomers to that of the polymer to verify that the chain conformations are identical. The 15/7 helical form is nearly transplanar and represents an intermediate structure between that of polyethylene and those more helical forms represented by isotactic polypropylene and poly(ethylene oxide).

In order to observe *LAM* in PTFE by Raman spectroscopy it is estimated from coherent inelastic neutron scattering measurements^{16–18} that the lamellar thickness should not exceed approximately 25 nm. The usual fold periods exhibited by PTFE lie in the range of 100 nm, much too long to be observed by Raman spectroscopy using conventional techniques. The random copolymer TFE–HFP, on the other hand, forms lamellar structures in which the fold periods are in the range 17–35 nm. The *LAM* frequencies

of lamellae in this thickness range are accessible to measurement by Raman spectroscopy and we have examined a series of TFE–HFP copolymer monofilaments with long spacings in the range 18–23 nm and report herein the results of the spectroscopic studies. We have also verified from the Raman spectra in the range of 250–1500 cm^{-1} that the chain conformation of the copolymer is identical to that of PTFE.

It has been shown both theoretically³ and experimentally^{3,19} for polyethylene that *LAM* frequencies are only weakly influenced by interchain interactions and therefore details of the lateral chain packing are unimportant. For helical polymers where torsional deformations are involved in the *LAM* it may not be possible to neglect lattice interactions as forces between chains may become comparable to the dominant intrachain force in longitudinal acoustic motion. The helical conformation of the PTFE chain, 15/7, is nearly transplanar which would minimize the contributions of torsional motions to longitudinal acoustic vibrations. Furthermore, the perfluoro *n*-alkanes have the same hexagonal rod-like packing as is observed in PTFE²⁰. The hexagonal lattice parameters of the TFE–HFP copolymer are dependent on the comonomer content, increasing with increased HFP content²¹. In this case some variation of *LAM* frequency might be expected, although in light of the similarity of chain conformation with polyethylene the frequency shift should be small.

The regular progression of narrow bands observed in the Raman spectra of the solid *n*-alkanes and assigned to *LAM* are replaced in the melt spectra of the longer *n*-alkanes^{2,22} by a series of broad overlapping bands with a dominant maximum whose frequency approaches a limiting value of approximately 200 cm^{-1} with increasing chain length. These experimental observations taken together with theoretical studies⁴ on the effects of disordered conformations on *LAM* intensities and frequencies demonstrated that *LAM* can be used as a measure of the regular segment length in partly disordered systems.

We have recorded the Raman spectra of a series of perfluoro *n*-alkanes in the melt in order to determine the maximum rigid rod length. Recent n.m.r. work on²³ the short perfluoro *n*-alkanes (up to $\text{n-C}_8\text{F}_{18}$) has demonstrated that these molecules persist as rigid rods in the liquid phase. The Raman results confirm this finding and led to the determination of the maximum length of the rigid rods in the melt. The latter result is compared to recent theoretical work²⁴ on the energetics of chain conformations in polytetrafluoroalkanes.

EXPERIMENTAL

The perfluoro *n*-alkanes, $\text{C}_{20}\text{F}_{42}$, $\text{C}_{16}\text{F}_{34}$, $\text{C}_{12}\text{F}_{26}$ and $\text{C}_{10}\text{F}_{22}$, were high purity (99.999%) research samples provided by the Du Pont Company*. A sample of C_9F_{20} was furnished by the Minnesota Mining and Manufacturing Company while C_7F_{16} was obtained from Peninsular Chemical Research, Inc. All samples were used as received without further purification or chemical treatment.

The highly oriented tetrafluoroethylene–hexafluoropropy-

lene (TFE–HFP) random copolymer monofilament was a commercial Du Pont product (FEP 100). Transparent samples with diameters of 20 and 50 mil (1 mil = 2.54×10^{-5} m) were supplied and will be referred to in the text by this designation. Infra-red intensity measurements²⁵ indicated that this copolymer contained 13–14 mol % of HFP. A Spex 1401 double monochromator equipped with Jobin–Yvon holographic gratings (1800 lines/mm) was used in conjunction with a Coherent Radiation CR-12 Ar^+ laser to record the Raman spectra. All spectra were recorded using a 90° scattering geometry.

Solid state spectra were recorded by compressing small amounts of material into a sealed capillary tube. The spectra of the melt were obtained by passing heated nitrogen gas over these capillaries in a Harney–Miller cell. At the first sign of sample melting, the temperature was stabilized and the remaining material allowed to melt. In this way, severe sample degradation was avoided.

Wide-angle and low-angle X-ray diffraction patterns were obtained on a flat plate camera using a Rigaku–Denki X-ray system. Long spacings were determined with a Joyce–Loebl microdensitometer.

RESULTS AND INTERPRETATION

Raman spectra of solid perfluoro n-alkanes

Solid phase spectra of PTFE and four perfluoro *n*-alkanes, $\text{n-C}_{10}\text{F}_{22}$, $\text{n-C}_{12}\text{F}_{26}$, $\text{n-C}_{16}\text{F}_{34}$, and $\text{n-C}_{20}\text{F}_{42}$ are compared in *Figure 1*. The longitudinal acoustic modes of the perfluoro *n*-alkanes lie below 200 cm^{-1} , modes of frequencies above 200 cm^{-1} involve localized vibrations of the $-\text{CF}_2-$, $-\text{CF}_3$ groups and optical skeletal vibrations. The terminal group vibrational bands are easily discernible by their decreasing intensity relative to band intensities of $-\text{CF}_2-$ vibrations as the chain length increases. A band at 1325 cm^{-1} in the perfluoro *n*-alkane spectra is identified in this manner as arising from the terminal groups. Band progressions which arise from chain length dependent vibrations are found in the frequency range near 750 cm^{-1} . These vibrational frequencies provide information on the shape of the phonon dispersion curves for intramolecular branches of the polymer and will be treated in a future publication. The remaining bands above 200 cm^{-1} are identifiable with Brillouin zone centre vibrations of the polymer and are indicative of the chain conformation.

It has been shown^{26,27} that vibrational bands in the frequency range 570–625 cm^{-1} in PTFE are particularly sensitive to helical conformation. Comparisons between the oligomeric spectra and that of PTFE led to the conclusion that the chain conformations are identical to that of PTFE at room temperature, i.e., 15/7 helix. No Raman bands are observed in PTFE below 200 cm^{-1} †, a consequence of the exceeding long fold period and concomitantly the diminishing low frequency value for acoustic vibrations.

In the solid state Raman spectra of the perfluoro *n*-alkanes a series of bands are observed below 220 cm^{-1} ²⁸. One of these bands corresponds to the polymer band at 210 cm^{-1} , but the remaining two or three bands (see *Table I* for a compilation of frequencies) arise from the finite

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for this purpose.

† A Raman band at 14 cm^{-1} has been observed in both sintered and unsintered PTFE films (Willis, H. A., Cudby, M. E. A., Chalmers, J. M., Fleming, J. W., Chantry, G. W. and Nicol, E. A. *Chem. Phys. Lett.* 1975, 33, 381). We have been unable to confirm these observations on either PTFE or the perfluoro *n*-alkanes.

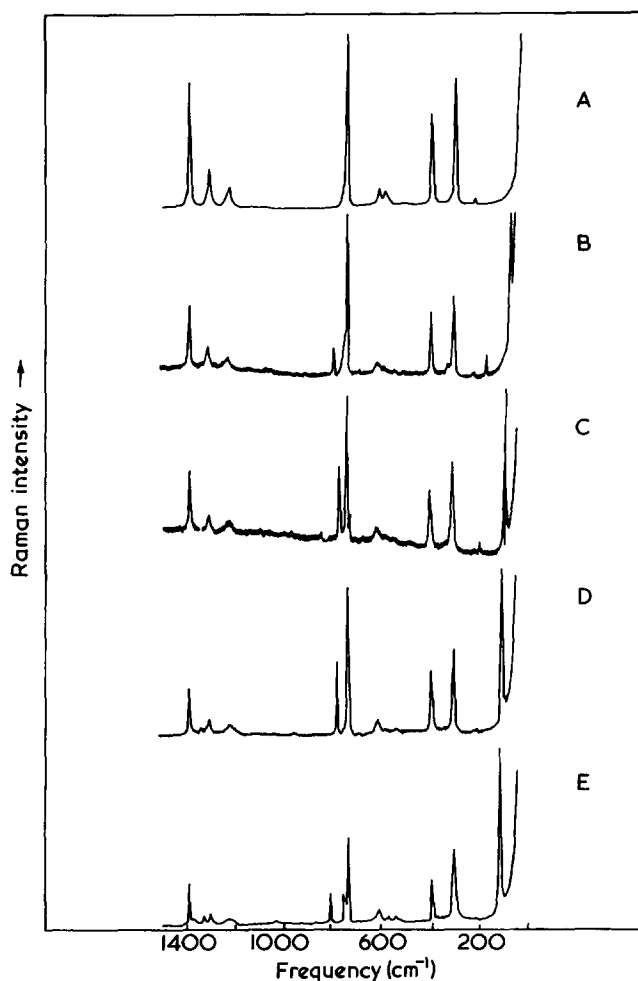


Figure 1 Raman spectra of solid perfluoro n-alkanes and polytetrafluoroethylene. A, PTFE; B, $n = 20$; C, $n = 16$; D, $n = 12$; E, $n = 10$

Table 1 Longitudinal acoustic mode frequencies for the solid perfluoro n-alkanes

n	Frequency (cm^{-1})		
	$m = 1$	$m = 3$	$m = 5$
20	60	154.3	206.6
16	74	184.1	204.5
12	96	205	—
10	112	202.4	—
9	125	—	—
7	146	—	—
6	—	—	—

chain nature of the oligomers. The lowest frequency band is particularly intense which is characteristic of the *LAM* in the n-alkanes with a single node at the chain centre. The intensity of the higher frequency band(s) is greatly diminished relative to the lowest frequency band which is typical of the intensity pattern found in the n-alkanes for *LAM* containing higher numbers of vibrational nodes.

The frequencies tabulated in Table 1 for $m = 1$ are plotted against $1/n$, the reciprocal of the number of carbon atoms, in Figure 2. This plot yields a dispersion curve equivalent to that in which the wavevector is expressed in units of its maximum value, $\pi/1.31 \text{ \AA}^{-1}$. The number of vibrational nodes, m , assigned to a *LAM* frequency (Table 1) is limited by group theoretical arguments to odd integers (modes with even integer values are Raman inactive). The observed *LAM* frequencies for a particular n-alkane monotonically increase with m/n so that successively higher frequency bands are

assigned to successively larger odd integers¹. A necessary requirement is that the plotted frequencies fall on a smooth curve and this condition was also employed in making the assignments indicated in Table 1.

In the shorter perfluoro n-alkanes of Table 1, we do not observe *LAM* beyond the single node vibration. The lack of a value for the single node vibration in solid $n\text{-C}_6\text{F}_{14}$ is due to the inability to obtain this material in the solid state. It, however, was observed at 173 cm^{-1} in the melt of $n\text{-C}_6\text{F}_{14}$. A general observation¹ in the n-alkane spectra is that no Raman bands are observed on the high phase angle side of the frequency maximum. If this observation applies equally to perfluoro n-alkane spectra we would conclude that the lower oligomers would not exhibit higher node *LAM* vibrations which is consistent with our observations.

Raman spectra of perfluoro n-alkanes in the melt

Examples of representative low frequency Raman spectra of perfluoro n-alkanes in the melt are shown in Figure 3. The $n\text{-C}_{20}\text{F}_{42}$ melt spectrum is typical of perfluoro n-alkanes above $n\text{-C}_{12}\text{F}_{26}$ in that the $m = 1$ *LAM* band is both significantly broader and shifted to higher frequencies when compared to the solid phase spectrum. The melt spectra of perfluoro n-alkanes shorter than $n\text{-C}_{12}\text{F}_{26}$ exhibit *LAM* band frequencies and bandwidths which are nearly identical to those of the solid phase. An intermediate case is found for $n\text{-C}_{12}\text{F}_{26}$, shown in Figure 3, in which the peak frequency is the same in both the melt and solid phases, but the band in the melt is asymmetrically broadened to higher frequencies. The frequency values for the *LAM* are plotted against reciprocal number of carbon atoms in Figure 2. For comparison, Figure 2 also includes the solid phase curve which shows that the perfluoro n-alkane *LAM* frequencies are essentially the same for the melt and solid phases for lengths up to 12 carbons, but deviate appreciably for longer chain lengths.

The increased peak frequency and bandwidth upon melting is indicative of conformational disorder normally asso-

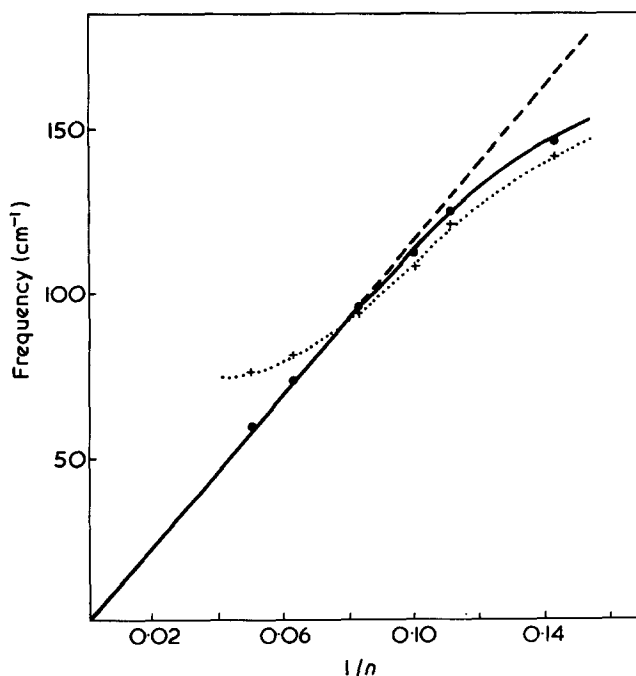


Figure 2 *LAM* frequencies vs. reciprocal degree of polymerization for perfluoro n-alkanes in the solid state (—) and melt (·····) — — —, is the frequency—chain length expression from equation (1)

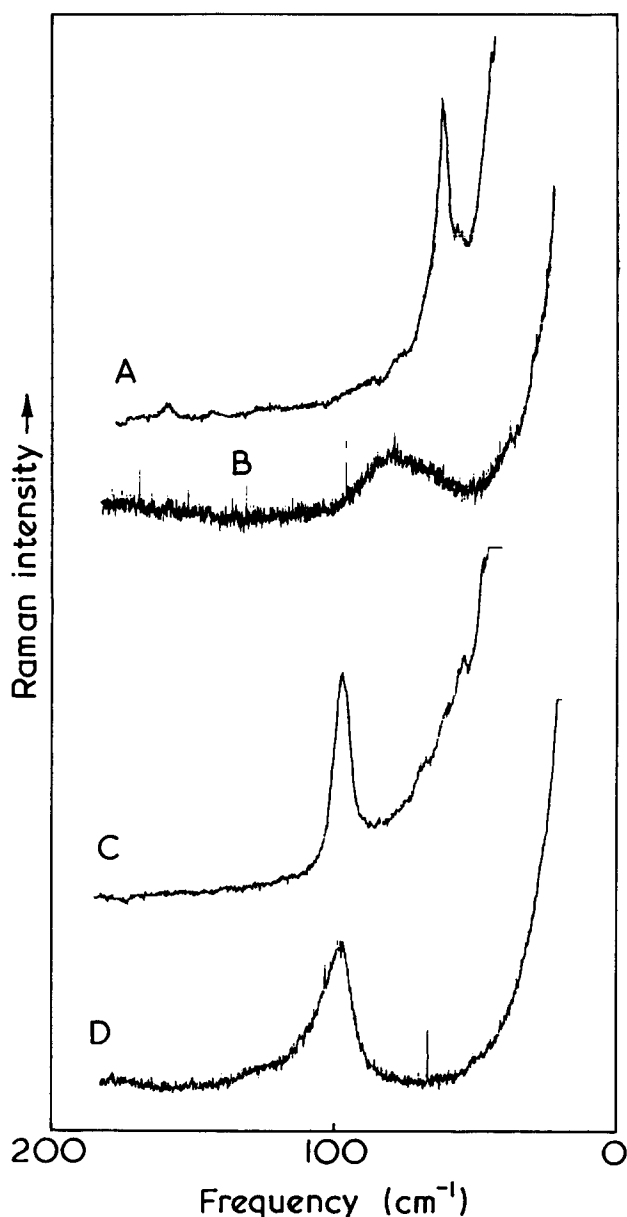


Figure 3 Representative Raman spectra of perfluoro n-alkanes in the melt. A, $n = 20$, solid; B, $n = 20$, melt; C, $n = 12$, solid; D, $n = 12$, melt

ciated with chain molecules in melt phase. Through equation (1) we can associate the frequency and also bandwidth with an effective chain length distribution, and hence serve as a measure of conformational disorder in the melt. Differentiation of equation (1) yields the variation of bandwidth with chain length:

$$\Delta\nu = \frac{-(m/2)(E/\rho)^{1/2} \Delta L}{L^2} \quad (2)$$

$$= (-\nu/n) \Delta n$$

The variation in chain length, ΔL , for a given bandwidth, $\Delta\nu$, depends on the square of the chain length.

The bandwidth (full width at half peak height) data, converted to Δn through equation (2) and shown in Figure 4, indicate similar behaviour with regards to the oligomeric length as that shown for LAM frequencies in Figure 2. The bandwidths for oligomers shorter than $C_{10}F_{22}$ are similar

and the bandwidths increase dramatically with increasing oligomeric length above $C_{11}F_{24}$.

A similar comparison of melt and solid phase spectra has been carried out for the n-alkanes²². The behaviour is nearly identical with the exception that the frequencies deviate at shorter chain lengths. A comparison of Δn values obtained from the melt spectra of the n-alkanes and perfluoro n-alkanes is given in Table 2. In the melt spectra of the shorter n-alkanes, a multiplet of bands is observed in the region of the single node LAM in the solid state spectrum. These are ascribed to longitudinal vibrations of molecules in different rotational isomeric states. As the n-alkane chain becomes longer, the number of possible states greatly increases and the multiplet band structure is replaced by a single broad width band whose peak frequency is used in the frequency-reciprocal chain length plot.

As the spectra in Figure 3 indicate the perfluoro n-alkanes do not yield multiplet structure in the LAM frequency region and hence it is concluded that distinct rotational isomers are not prevalent in the melt of chains shorter than $n-C_{12}F_{24}$. This conclusion is consistent with n.m.r. results²³ on oligomers shorter than $n-C_8F_{18}$. The rapidly increasing bandwidth for oligomeric lengths above $C_{11}F_{24}$ implies a growing number of rotational isomers. The limiting

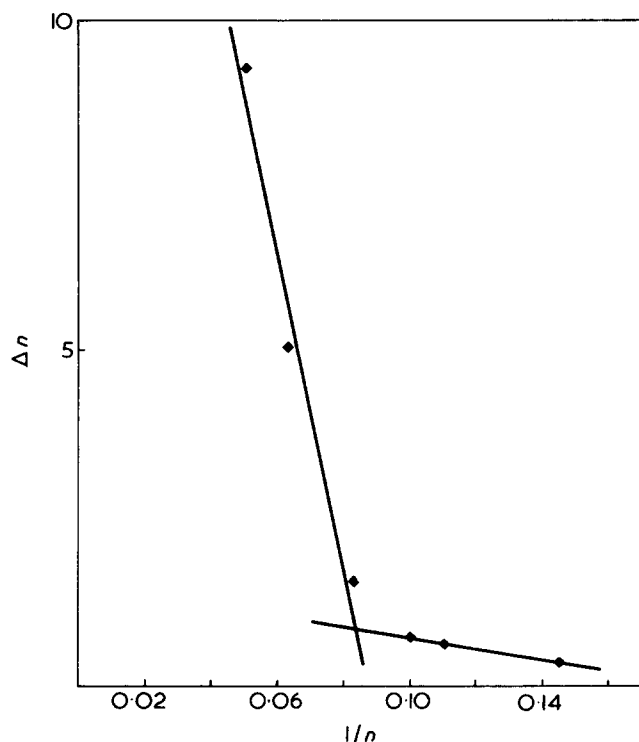


Figure 4 Plot of LAM bandwidths converted to Δn through equation (2) vs. reciprocal degree of polymerization for perfluoro n-alkanes in the melt

Table 2 Values of the distribution of effective chain lengths, Δn , for the melt spectrum LAM band of selected n-alkanes and perfluoro n-alkanes

n	Perfluoro n-alkanes Δn	n-Alkanes* Δn
20	9.25	17.64
16	5.07	10.06
12	1.62	4.85
10	0.73	3.13
9	0.58	2.08

* Data of Schaufele²²

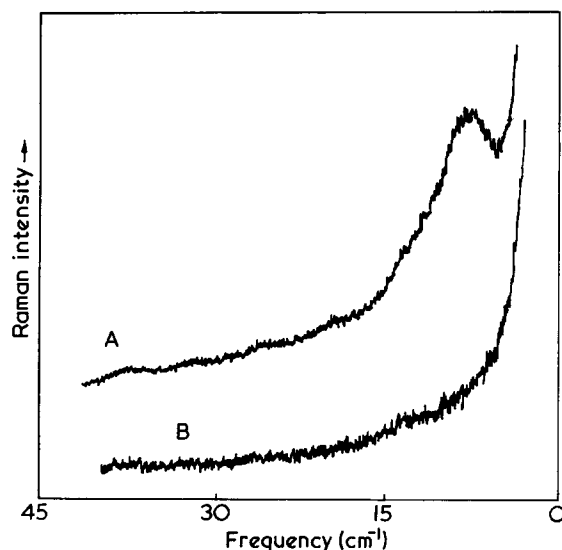


Figure 5 Low frequency Raman spectra of TFE-HFP copolymer monofilament. A, $X(z, z)Y$; B, $X(z, x)Y, 3X$

frequency value is consistent with a chain length of approximately 16 CF_2 units in the regular helical structure. We do not propose that this represents an average regular structure chain length in the melt, but rather the limiting effective vibrational frequency of a somewhat random structure in which shorter segments of regular structure are embedded. We shall return to this point in the discussion of our normal coordinate calculations.

Raman spectra of TFE-HFP copolymer

Typical low frequency Raman spectra from a commercial sample of a TFE-HFP monofilament are shown in Figure 5. The chain axes in these specimens are highly oriented along the filament axis as indicated by small and wide-angle X-ray diffraction and polarized Raman measurements. A four point diffraction pattern is obtained from low-angle X-ray measurements indicating that the lamellae are inclined at an angle of 31.7° with respect to the filament axis. The Raman polarization results shown in Figure 5 were conducted with the electric vector of the incident light parallel to the filament axis. The upper trace results when the polarizer is in a position which allows only the polarization component parallel to the filament axis to be observed. In this particular polarization experiment only A_1 modes should be observed. In the lower trace scattered radiation with a polarization component perpendicular to the filament axis is observed. Only E_1 modes should be seen in this polarization. Rotation of the incident polarization by 90° which should allow only E_2 modes to be observed gave a trace identical to the $X(z, x)Y$ case. Hence, the Raman polarization results are consistent with the symmetry expected for longitudinal acoustic modes. Furthermore, the low frequency Raman band was observed to shift to lower frequencies with increasing lamellar thicknesses which is indicative of LAM. The variation in lamellar thicknesses with monofilament diameter most likely results from the different thermal history during processing.

The plot of frequencies versus reciprocal fold periods, taken parallel to the chain axis and calculated from the four point small-angle X-ray patterns, fall on a straight line passing through the origin. Using the frequency-reciprocal degree of polymerization relationship from the perfluoro n-alkane data, Figure 2, a frequency of 7.2 cm^{-1} for the

copolymer would yield a predicted chain length of $21.7 \pm 0.6 \text{ nm}$ (repeat distance equals 1.31 \AA) compared to an X-ray determined value of $24.9 \pm 1 \text{ nm}$. The agreement is comparable to that found between polyethylene and n-alkane data. This result may appear remarkable at first glance when one considers the dissimilarity in the comonomer unit masses and the diversity in crystalline densities. However, if the hexafluoropropylene units are preferentially located in the regions between lamellae the effects on crystalline properties, such as LAM frequencies, would be minimized.

Normal coordinate calculations

We have calculated the normal modes of vibration for $n\text{-C}_{16}\text{F}_{34}$ and PTFE, both in the isolated chain conformation. The molecular geometry assumed for PTFE was identical to that used by Hannon *et al.*²⁹ for the 15/7 helical form. This geometry was one of several used for $n\text{-C}_{16}\text{F}_{34}$. Two different valence force fields, taken from the literature^{30,31}, were used in the PTFE calculation. The force field of Boerio and Koenig³⁰ (BK) gave imaginary frequencies near the E_1 mode phase value (168°) as previously reported in the literature^{31,32}. The other force field is due to Piseri, Powell, and Dolling (PPD)³¹ who modified the BK force field to remove the imaginary frequencies and also to improve the agreement with neutron inelastic coherent scattering results. The PPD force field was exclusively used for the oligomer $n\text{-C}_{16}\text{F}_{34}$ whereas calculations were performed with both force fields on PTFE. The longitudinal acoustical branches calculated from the two force fields are plotted in Figure 6 and compared to the experimental frequencies derived from the perfluoro n-alkanes. The agreement near the frequency maximum is slightly better with the BK force field than the PPD force field, otherwise the agreement between either set of calculated frequencies and the observed values is excellent. Thus, the derived longitudinal moduli are in excellent agreement with experimental results.

Calculations were carried out for $n\text{-C}_{16}\text{F}_{34}$ in several conformational modifications to assess the effect on the LAM of structural defects. Similar studies have been

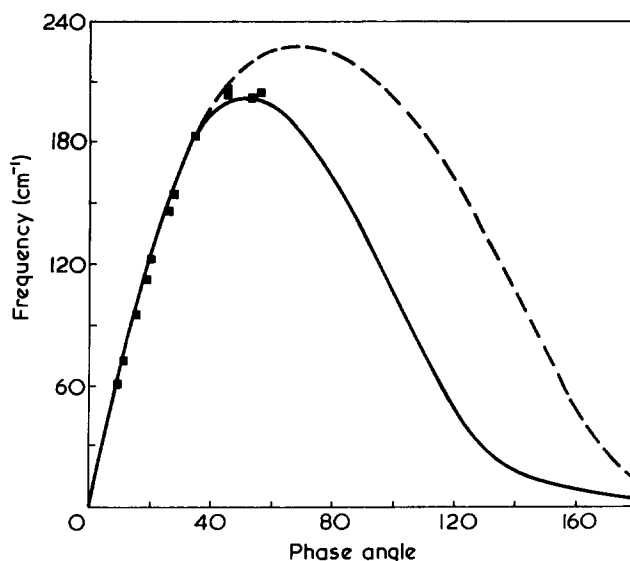


Figure 6 Longitudinal acoustic dispersion curve of PTFE in the isolated chain approximation. —, BK (Boerio, F. J. and Koenig, J. L. *J. Chem. Phys.* 1970, **52**, 4826) force field; - - -, PPD (Piseri, L., Powell, B. M. and Dolling, G. J. *J. Chem. Phys.* 1973, **58**, 158) force field; ■, observed values from perfluoro n-alkanes

Table 3 Calculated *LAM* frequencies for $n\text{-C}_{16}\text{F}_{34}$, isolated chain approximation, with helix reversal defects

Calculations on $\text{C}_{16}\text{F}_{34}$	$m = 1$	$m = 3$
Left handed helix	70.6	171.9
Helix reversal at centre	70.7	171.5
Helix reversal at end	70.5	171.7

reported⁴ for *n*-alkanes in which it was found that localized defects involving a series of bond rotations were sufficient to disrupt longitudinal acoustic modes of vibration. We investigated the influence of conformational disorder on *LAM* in $n\text{-C}_{16}\text{F}_{34}$ by incorporating structural modifications at various positions along the chain. The calculated eigen values and eigen vectors were compared to those of the chain in regular conformation.

Two different types of structural modifications were introduced, the simplest of which was a helix reversal point involving a transformation from a left to a right handed helix. With this type of structural modification, modes identifiable with *LAM* were found independent of the position of the helix reversal point, see *Table 3*. Helix reversals have been postulated as a type of structural defect in PTFE and our observations are not inconsistent with this view.

Another type of defect examined consisted of fully extended sequences. It was found that if three *trans* bonds were placed near the centre of the chain a deviation from the helix axis of 1.5 Å was observed at the chain end. In this case a mode, separated by 0.3 cm^{-1} and falling on the high frequency side of the *LAM* calculated for the regular helical polymer of the same length, was identified as containing sufficient *LAM* character to give appreciable Raman scattering intensity. One would therefore expect little band broadening to occur if all *trans* segmental defects are introduced into the fluorocarbon backbone. As noted previously, this is observed in the melt phase of perfluoro *n*-alkanes below $n\text{-C}_{12}\text{F}_{26}$, therefore, indicating the existence of regular helical segments with or without helix reversal points and all *trans* segments.

It would appear that the results obtained upon introduction of structural defects into perfluoro *n*-alkanes are markedly divergent from those found with *n*-alkanes. It should be noted, however, that the type of defect structures used in the *n*-alkane calculations are very different from those considered here, and, in fact, would have extremely high energies in fluoroalkanes due to the large van der Waals radii of fluorine.

CONCLUSIONS

The longitudinal acoustic dispersion curve, calculated from either the BK or PPD force field, is in excellent agreement with the Raman measurements in the linear region from which the modulus can be determined. Furthermore, the derived Young's modulus, 20.6×10^{10} Pa, agrees well with the value of 22.2×10^{10} Pa obtained from coherent inelastic neutron scattering measurements¹⁶. By contrast, the value found by X-ray scattering¹⁴ is 15.6×10^{10} Pa. Thus, we concluded, as previously reported,¹⁰ that the X-ray determined values are too low which is due at least in part to the uniform stress approximation.

We have demonstrated that longitudinal acoustic modes can be observed in copolymers (HFP-*T*FE) as well as in

homopolymers. Good agreement is found between the chain stem length, calculated from the X-ray long spacing and the chain inclination, and that found from the *LAM* frequencies although a slight difference outside the range of experimental error is evident. In comparing long spacings (stem lengths) directly we have not explicitly considered possible differences in density and modulus between the perfluoro *n*-alkanes and the copolymer. The difference in long spacings, with the X-ray value the larger of the two, may reflect the presence of amorphous material on the crystal surface. This material which may contain a larger percentage of hexafluoropropylene groups is detectable in the X-ray measurement but not necessarily by Raman spectroscopy.

In a recent paper³³, Chantry *et al.* reported the far infrared spectrum of $n\text{-C}_{14}\text{F}_{30}$ at room temperature and liquid nitrogen temperature. A series of bands observed at low temperature, was assigned to low frequency dispersion curves of PTFE, including the longitudinal acoustic branch. No assignments were made to lattice modes since it was concluded from the absence of layer lines in the room temperature X-ray diffraction studies that the material is disordered. It is known that perfluoro *n*-alkanes undergo a low temperature transition similar to the 19°C 15/7→13/6 transition in PTFE¹⁵. In the 13/6 helical form, PTFE exhibits five low frequency infrared bands which have been assigned^{34,35} to lattice modes. The lack of order in the low temperature phase with the resulting absence of bands due to lattice modes cannot be concluded from room temperature X-ray measurements.

Although the assignment by Chantry *et al.* of some bands in $n\text{-C}_{14}\text{F}_{30}$ may be suspect, the majority of observed bands can be properly assigned to Brillouin zone interior modes of PTFE. The resultant dispersion branch for *LAM* from Chantry *et al.* is in excellent agreement with our dispersion curve.

The fact that fluorocarbon chains containing up to eleven carbon atoms exist as rigid rods in the melt is reflected in the extremely low entropy of fusion of polytetrafluoroethylene. Recently, Tonelli²⁴ has estimated the constant volume contribution $[(\Delta S_f)_v]$ to the entropy of fusion of PTFE by calculating the gain in intramolecular conformational entropy (ΔS_{conf}) experienced by each polymer chain upon melting. These calculations were based on a model consisting of four isomeric states and assumed that each polymer chain in the crystal was restricted to a single conformation. The results show that half of the conformational entropy gain expected upon melting was not realized. As Tonelli points out²⁴ this discrepancy may be traced to either partial order in the melt or conformational disordering of the PTFE chains. In the latter case, the calculated ΔS_{conf} would be expected to be larger than $(\Delta S_f)_v$ since conformational regularity of the chain was assumed. Our results indicating order in the melt in conjunction with the high probability of structural disorder in PTFE chains predicted from X-ray studies³⁶ can, therefore, account for the discrepancy between $(\Delta S_f)_v$ and ΔS_{conf} .

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