tion because the chemical shift of a protonated amide group should differ from that of an unprotonated amide group by several parts per million. No such chemical shift dependence has been reported.

The proposal of slow solvation as the cause of the separate peak by Scheraga *et al.*[9] has been shown by E. M. Bradbury *et al.*[28] to be inconsistent with the nmr data. He pointed out that for a slow solvation mechanism the relative area of the "solvated coil" peak should increase with addition of acid because all the random-coil residues will eventually contribute. In fact, the integrated areas of the two peaks remain constant.

Goodman *et al.*[13] in a recent study suggested that the separate peaks arise from the presence of oligomers in the polypeptide samples. However, extension of Goodman's explanation would require invocation of reversible change in oligomer content during transition.

One explanation which has gained some credence is that of Ullman,[12] E. M. Bradbury *et al.*, and Nagayama and Wada,[10] who indicate that the nmr results might arise from polydispersity. We have examined this hypothesis in detail in a recent paper[21] and determined that fractionation of the polypeptide samples does not significantly alter the nmr spectra. The mutliple peaks are present even for samples with very narrow molecular weight distributions. These results indicate that polydispersity cannot be used to explain the nmr data. However, similar experiments by Nagayama and Wada led to one broad peak near the transition midpoint. The origin of this discrepancy is unknown at present. One possible explanation is that both polydispersity and exchange broadening (*i.e.*, slow nucleation) contribute to the line shape in the transition region. To envision this particular possibility it is helpful to consider the exchange broadening and polydispersity effects separately. Neglecting polydispersity, one might conceive of the situation wherein the line width near the transition midpoint would be exchange broadened but not split into two peaks (*i.e.*, above coalescence). Then the effect of polydispersity on this broadened line could be the cause of peak doubling, depending on the nature of the molecular weight distribution. The precise form of the lineshape would be dependent on the distribution and could explain the differences between the results of ours and Wada's experiments. In this case the magnitude of τ determined in the previous section might be overestimated by as much as a factor of two.

The explanation in this paper requires a helix nucleation time τ long enough to lead to two separate nmr peaks. The alternative explanation based on polydispersity also gives satisfactory agreement with experiment for the same chain-length polypeptide. However, the polydispersity advocates have not explained the observed behavior for the longer chain lengths. An independent determination of τ is therefore of the greatest importance in distinguishing between these two alternate interpretations of the nmr double peak behavior.

---

(28) E. M. Bradbury, P. Cary, C. Crane-Robinson, L. Paolillo, T. Tancredi, and P. A. Temussi, *J. Amer. Chem. Soc.*, **93**, 5916 (1971).

Dynamics of Polymers as Structurally Disordered Systems. Vibrational Spectrum and Structure of Poly(tetrafluoroethylene)[1]

Giuseppe Zerbi* and Mario Sacchi

Istituto di Chimica delle Macromolecole del CNR, Milan 20133, Italy. *Received March 21, 1973*

ABSTRACT: The problem of the structure and vibrational spectrum (infrared, Raman, neutron scattering) of poly(tetrafluoroethylene) (PTFE) considered as a solid containing structurally ordered and disordered regions is treated in two works, one following the other. In paper I the theoretical aspects of the problem are considered and the calculation of the vibrational spectrum is carried out first using the classical lattice dynamical approach on a perfect system. In these calculations phonon dispersion curves $\omega(k)$, density of states $g(\omega)$ and $k = 0$ phonon frequencies are calculated for several models of PTFE chain which should be most stable ones on the basis of theoretical considerations. Lattice dynamical calculations are then performed on the polymer chain considered as a disordered system. Predictions are derived where to look in the vibrational spectrum for absorption in infrared or scattering in the Raman originating from geometrical defects. The results from calculations discussed in paper I, together with the experimental verification discussed in paper II, provide new information for a more comprehensive understanding of the experimental data from X-ray scattering, nmr broad line, dielectric and mechanical experiments. A detailed interpretation of the vibrational spectrum is suggested.

In a previous paper[2a,b] it has been shown that the analysis of the vibrational spectrum of a polymer as a geometrically disordered system based on a calculation of the density of states $g(\omega)$ by numerical methods seems to provide a more satisfactory interpretation of the observed spectral features. From this type of analysis structural information was derived.[2a]

In this paper (paper I) we study with the same technique and with standard methods the lattice dynamics of poly(tetrafluoroethylene) [$(\mathrm{CF}_2)_\infty$, PTFE], which, from the available literature, seems to contain disordered regions. The theoretical predictions derived in paper I are compared with the experimental findings in the following paper (paper II). The purpose of our work is twofold: (i) to further analyze the validity of the method we have proposed and complete the interpretation of the spectrum of PTFE; (ii) to derive information on the structure of PTFE as seen from the vibrational spectrum.

The conclusions seem to us quite gratifying. Conclusive evidence is collected for the existence of chain structures predicted theoretically but never experimentally verified. A mechanism for the phase transition at 19°C is proposed. Information is collected for a further reanalysis of recent nmr and dielectric experiments. An alternative explana-

---

(1) This work was partly presented at the IUPAC International Symposium on Macromolecules. Helsinki, July 1972.

(2) (a) G. Zerbi, L. Piseri, and F. Cabassi, *Mol. Phys.*, **22**, 241 (1971). (b) G. Zerbi, *Pure Appl. Chem.*, **26**, 499 (1971).

tion is suggested for the extra features observed in recent coherent inelastic neutron scattering experiments.

Structure and Dynamics of PTFE

The structural properties of PTFE have been the subject of many investigations; while the gross features of its structure are basically understood, various models have been proposed for the explanation of the details of its structure which, however, substantially affect the macroscopic properties of the material[3] and are clearly revealed in most of the physical measurement performed on it.

The early X-ray diffraction studies on the crystal structure indicate that PTFE exists in three main polymorphic forms with transition points at ≈19 and 30°C. Crystal disordering transitions were first observed by discontinuous change in density[4] and by specific heat maxima.[5] Early studies by Whitney *et al.*[6] suggested a triclinic structure below 19°C with a high degree of three-dimensional crystalline order. According to the same authors at ~19°C at the lattice transforms to hexagonal symmetry accompanied by a partial disorder probably associated with the onset of hindered rotations of the chain segments which brings two more CF_2 units in the chain identity period and accounts for the sharp anomaly in the specific heat *vs.* temperature. The second transition at 30°C is probably associated with the destruction of the crystalline order along the chain. The studies of Bunn and Howells[7] are in partial agreement with those of Whitney *et al.* While the first-order transition temperatures are confirmed, these authors determine the chain structure as a helix whose identity period of 16.8 Å contains 13 CF_2 groups in six turns. Bunn and Howells do not find any evidence of an increase of chain period at 19°C as reported previously but suggest that the increase of structural disorder at 19°C is due either to a rotation around the chain axis or to a longitudinal displacement in precise steps equal to the zigzag span. The second transition at 30°C is due to longitudinal displacements which are not in precise steps. The same problem was reanalyzed by Clark *et al.* in a series of papers.[8-11] These authors first supported the idea that the diffuseness in the X-ray pattern at 19°C is consistent with small angular displacement of one molecular segment with respect to its neighbor in the crystal. This is accompanied by a small change in the molecular conformation. On the basis of nmr data[10,11] Clark and Muus later suggested that the small angular displacements force a slight untwisting of the helical conformation of the chain. These concepts were later expanded. In a final paper Clark[12] on the basis also of more recent results of calculations of conformational potential energies[13] speculated that the transition may involve the creation of a helix reversal point from left- to right-handed helices through a trans conformation. In the opinion of these authors the introduction of these structural defects generates other structural changes within the helix.

The existence of crystalline and amorphous phases and their change with temperature in a sample of PTFE have been unquestionably detected in nuclear magnetic resonance linewidth studies. After Wilson and Pake[14] several authors have studied the temperature variation of nmr line widths. Three main temperature-dependent lines were observed namely the broad line, BL (from the crystalline phase), the narrow line, NL (from the amorphous phase), and the intermediate line, IL (of uncertain origin). Hyndman and Origlio[15] were mainly concerned with the BL component whose width undergoes a reduction from 10 to 6 G at 20°C. Such a reduction is ascribed to the onset of dynamic disorder in the crystal. Iwayanagy and Sakuray[16] supported the results of Hyndman and Origlio and collected more data on NL and IL. The NL component must come from the randomly kinked molecules that keep on their micro-Brownian motion.[16] At −60°C, the IL component separated from the BL component and had a different temperature behavior with clear narrowing at 20°C as in the case of the BL. The IL is ascribed to a third phase of aggregation different from the crystalline and amorphous phases. This third phase is assumed to consist of sheaves of straight rodlike chains with random intermolecular distances.

Substantial support to the previous nmr studies comes from anelastic and dielectric studies of various specimens of PTFE of different crystallinity. We refer to the excellent review by McCrum, Read, and Williams[17] for a collection of references and a critical analysis of the data.

A considerable contribution toward the understanding of the structure of PTFE has been derived by the calculation of conformational potential energy based on semiempirical nonbonded two-body potentials. On the basis of a modified Buckingham-type potential (first proposed by Mason and Kreewoy[18]) and of an electrostatic dipole–dipole interaction, Iwasaki[19] has calculated the minima in the conformational potential energy in the neighborhood of the trans conformation and found a minimum at ±19° in good agreement with the experimental value of 16°28′ (+ and − signs refer to two enantiomorphous helices, generally called left- and right-handed helices). In a more thorough investigation De Santis *et al.*[13] have performed a calculation of the conformational energy of a PTFE chain on the basis of other semiempirical nonbonded two-body interaction potentials. The interactions extended to the fifth neighbor. The potential energy calculated (Figure 1) shows three minima at τ = 60, 90, and 165° and the symmetric ones with respect to 180° corresponding to the enantiomorphous conformations. The deepest minimum lies at τ = 165°. Of particular interest is the fact that a very small barrier (at τ = 180°) separates to two minima at τ = 165 and 195°. The authors tentatively suggest that above 20°C the chains might consist of a mixture of segments of left- and right-handed helices. In order to avoid too short contacts between the fluorine atoms, helices should join through bonds in trans conformation. The

---

(3) For a comprehensive view of the physical and chemical properties of PTFE up to 1960, see C. A. Sperati and H. W. Starkweather, *Forthschr. Hochpolym. Forsch.*, **2**, 465 (1961).

(4) H. A. Rigby and C. W. Bunn, *Nature (London)* **164**, 583 (1949).

(5) G. T. Furukawa, R. E. McCoskey, and G. J. King, *J. Res. Nat. Bur. Stand.*, **49**, 273 (1952).

(6) J. W. Whitney, R. H. H. Pierce, Jr., and W. M. D. Bryant, 124th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1953.

(7) C. W. Bunn and E. R. Howells, *Nature (London)* **174**, 549 (1954).

(8) E. S. Clark and L. T. Muus, *Z. Kristallogr.*, **117**, 119 (1962).

(9) R. H. H. Pierce, Jr., E. S. Clark, J. F. Whitney, and W. M. D. Bryant, 130th National Meeting of the American Chemical Society, Dallas, Texas, Sept 1956.

(10) L. T. Muus and E. S. Clark, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **5**(1), 17 (1964).

(11) E. S. Clark and L. T. Muus, *Int. Union Crystallogr., 6th Int. Congr. Rome, 1963*, Abstr. A96.

(12) E. S. Clark, *J. Macromol. Sci., Phys.*, **1**(4), 795 (1967).

(13) P. De Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polym. Sci., Part A*, **1**, 1383 (1963).

(14) C. W. Wilson, III, and G. E. Pake, *J. Polym. Sci., Part A-2*, **27**, 115 (1957).

(15) H. Hyndman and G. F. Origlio, *J. Appl. Phys.*, **31**, 1849 (1960).

(16) S. Iwayanagi and J. Sakurai, *J. Polym. Sci., Part C*, **14**, 29 (1966).

(17) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley, New York, N. Y., 1967.

(18) E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.*, **77**, 5808 (1955).

(19) M. Iwasaki, *J. Polym. Sci., Part A*, **1**, 1099 (1963).

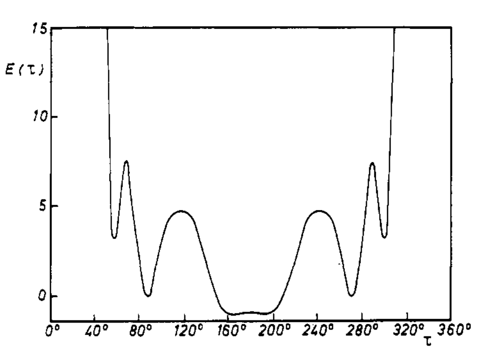

Figure 1. Conformational potential energy of helical poly(tetrafluoroethylene) chain from semiempirical nonbonded pairwise interaction potentials (from ref 13).

same authors, in disagreement with the many other authors previously quoted, suggest that the 20°C transition might be ascribed to a disorder within the molecular chains rather than to a rotation of the helices around their axes. As already mentioned this suggestion has been taken up by Clark who supports the view that both X-ray diffraction and nmr data can be accounted for on this basis.[12]

Vibrational Spectrum of PTFE

We are mainly concerned in the present work with the degree of understanding of the vibrational spectrum of PTFE (infrared, Raman and neutron scattering) in terms of its structure and with the wide use which has been made of the infrared spectrum in the characterization of PTFE samples.

The first full analysis of the infrared spectrum of PTFE has been carried out by Liang and Krimm[20] who also reported the spectra from 4000 to 70 cm^{-1}. Dichroic measurements on oriented samples were also reported in the region from 4000 to 350 cm^{-1}. The vibrational assignment of the ir active $k = 0$ modes was carried out by these authors on the basis of a one-dimensional space group (line group). A few two-phonon absorptions were assigned on the basis only of factor group analysis. Normal frequencies and normal modes were also calculated on a planar zigzag model. The same analysis has been latter rediscussed by Krimm.[21]

Of fundamental practical importance is the work by Moynihan[22] who reanalyzed the infrared spectrum of PTFE. His main interest lay in the location of a few absorption bands whose intensities vary with crystallinity. He located the spectral region at 850–700 and 384 cm^{-1} as being most sensitive to crystallinity. These bands are called "amorphous bands." Among those, the "amorphous" peak at 778 cm^{-1} was adopted for the measure of the amorphous content of a sample. The ratio between the intensity of the band at 778 cm^{-1} and that at 2367 cm^{-1} (assumed to be constant) is found to be linearly related with the percentage of X-ray crystallinity as well as with density data. This finding has developed into an analytical method for the determination of the "crystallinity" of PTFE samples and has received a very large application in all laboratories. The same author pointed out that the 19°C phase transition is accompanied by a spectral change near 650 cm^{-1}. These spectral variations are the subject of a subsequent work by Brown[23] who studied the temperature and pressure dependence of the vibrational spectrum of PTFE. It was pointed out that the infrared spectrum of PTFE at 100°K shows only one band at 640 cm^{-1}. By increasing the temperature, a second component at 625 cm^{-1} appears whose intensity increases suddenly near 20°C. The band at 640 cm^{-1} however does not disappear but still persists at 400°K. Brown suggested that the appearance of the band at 625 cm^{-1} accompanying the phase transition at 20°C is related to the reversal of the helical conformation of the polymer through a thermal structural defect.

The idea of the existence of thermal defects affecting the vibrational spectrum of PTFE has been qualitatively taken up by Koenig and Boerio (KB). In a series of papers on the Raman spectrum of this substance[24-28] these authors first carried out a vibrational assignment of the Raman spectrum on the basis of line-group selection rules on $k = 0$ modes and on the basis of normal coordinate analysis. Both the vibrational assignment and force field calculations were later modified.[26] In a subsequent work on the temperature dependence of the Raman spectrum, KB suggested on qualitative grounds that some temperature-dependent lines arise from gauche and transplanar conformations which are introduced in the regular helix.[27] The same authors have later reported on further temperature dependence of a few Raman lines which show splittings going toward lower temperatures. The splittings were interpreted as evidence of a factor group splitting due to the formation of a unit cell containing more than one chain.[28] These authors suggested the possible existence of a monoclinic phase at low temperature. To our knowledge no X-ray work has yet given an indication on the existence of such a lattice. Doubts on the interpretation of the Raman spectrum of PTFE by KB have been recently cast by Peacock *et al.* (P)[29] who on the basis of a qualitative reasoning modified the choice of a few fundamentals and the description of a few normal modes.

Models and Calculations

From the above discussion of the literature it is apparent that there is still a great uncertainty regarding the actual molecular model of PTFE which may resonably account for the observed vibrational spectrum. Our approach to the study of molecular dynamics of PTFE as a partially disordered system follows the following two lines: (1) study of the lattice dynamics of single infinite and perfect chains with various geometries predicted by calculation of conformational potential energies; standard lattice dynamical calculations are adopted;[30] (2) studies of molecular dynamics of conformationally disordered chains.[2a,b]

Lattice Dynamics of Perfect Chains

The normal modes of vibration propagating along the chain axis of an isolated chain were first considered; that means we are going to account for the observed spectral features in terms solely of intramolecular modes. For the more likely $14\pi/15$ chain we believe there is yet no unquestionable spectral evidence for intermolecular couplings which produce factor group splitting. Such a splitting is not expected for $k = 0$ modes for a triclinic lattice

---

(20) C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).
(21) S. Krimm, *Forthsch. Hochpolym. Forsch.*, **2**, 51 (1960).
(22) R. E. Moynihan, *J. Amer. Chem. Soc.*, 81, 1045 (1959).
(23) R. G. Brown, *J. Chem. Phys.*, **40**, 2900 (1964).
(24) J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, **50**, 2823 (1969).
(25) M. J. Hannon, F. J. Boerio, and J. L. Koenig, *J. Chem. Phys.*, **50**, 2829 (1969).
(26) J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, **52**, 4170 (1970).
(27) F. J. Boerio and J. L. Koenig, *J. Chem. Phys.*, **52**, 4826 (1970).
(28) F. J. Boerio and J. L. Koenig, *J. Chem. Phys.*, **54**, 3667 (1971).
(29) C. J. Peacock, P. J. Hendra, H. A. Willis, and M. E. A. Cudby, *J. Chem. Soc. A.*, 2943 (1970).
(30) L. Piseri and G. Zerbi, *J. Mol. Spectrosc.*, **26**, 254 (1968).

Table I
Models of Infinite One-Dimensional Lattices of Poly(tetrafluoroethylene) (PTFE) and Structure of the Irreducible Representations for Spectroscopically Active Phonons at $k = 0$

Model	θ^a (deg)	τ^b (deg)	No. of CF_2 in Identity Period	No. of Turns	Point Group	Distribution of $k = 0$ Optical Modes		
						$\varphi = 0$	$\varphi = \theta$	$\varphi = 2\theta$
1	180	180	2	1	D_{2h}	3 Ag (R) 2 B_{3g} (R) 1 A_u (inactive) 1 B_{3u} (ir $\parallel$)	2 B_{1g} (R) 1 B_{2g} (R) 2 B_{1u} (ir, $\perp$) 2 B_{2u} (ir, $\perp$)	
2	168	165.66	15	7	$D_{14\pi/15}$	4 A_1 (R) 3 A_2 (ir $\parallel$)	8 E_1 (ir $\perp$, R)	9 E_2 (R)
3	108	90.89	10	3	$D_{6\pi/10}$	4 A_1 (R) 3 A_2 (ir $\parallel$)	8 E_1 (ir $\perp$, R)	9 E_2 (R)
4	90	64.87	4	1	D_4	4 A_1 (R) 3 A_2 (ir $\parallel$)	8 E (ir $\perp$, R)	5 B_1 (R) 4B_2 (R)

[a] Rototranslational angle. [b] Torsional angle.

with one chain per unit cell. Splittings for phonons at certain zone boundaries were calculated to be very small for a three-dimensional model and remained unobserved in recent coherent neutron scattering experiments.[31] As previously mentioned the recent suggestions by KB on factor group splitting from a monoclinic lattice with more than one chain per unit cell wait for some other experimental support. We shall later suggest in papers I and II an alternative explanation for such splittings. Because of the lack of any indication of strong intermolecular interactions it is assumed that the conformational potential energy calculated by De Santis *et al.*[13] is a reasonable first-order approximation to the structure of the chain. It is expected that the positions of the energy minima and the relative energy content would not be strongly modified if interchain interactions are taken into account. The models considered in the present work, together with the necessary geometrical and vibrational characteristics are described in Table I.

The choice of the one-phonon transitions for the energetically most stable polymer chain (model 2, Table I) which determine the force field adopted in this work is based on the infrared experiments by Liang and Krimm[20] on oriented samples and on the Raman spectra by BK[24,27,28] and P.[29] The latest vibrational assignment of the spectroscopically active $k = 0$ phonon by KB and by P were carefully considered in this work for the consequent choice of the force field. The comparison showed that: (i) both groups of authors agree on the choice of the A_1 transitions (Raman active); (ii) both groups agree on the choice of the A_2 transitions (ir active) with $\parallel$ dichroism. A switching of assignment is found in the spectral region of C–F stretchings: BK 1217 cm^{-1} A_2, 1240 cm^{-1} E_1; P 1217 cm^{-1} E_1, 1240 cm^{-1} A_2. The assignment of C–F stretchings by BK is in agreement with Moynihan; (iii) both groups agree in the choice of those E_1 transitions (ir and Raman active) which occur as strong bands in the ir region with $\perp$ dichroism and find coincidence with a line in the Raman. For the remaining E_1 transitions and the always elusive E_2 transitions each author follows different criteria. Several choices more or less arbitrary were then proposed. We concluded that since there is a substantial agreement between the two groups on the choice of most of the fundamentals of A_1, A_2, and E_1 species for the perfect $14\pi/15$ chain we consider as working hypothesis that the KB assignment can be adopted with the exclusion of all E_2 modes whose choice is practically arbitrary and their appearance in the spectrum rather doubtful.

We believe however that the interpretation of the spectra should be supported as much as possible by calculations rather than by empirical and qualitative correlations. For this reason the two force fields presently available were considered: (a) a 19-parameter VFF by BK derived from (i) model molecules, (ii) chemically similar polymers, (iii) $k = 0$ modes whose choice seems unquestionable on experimental grounds, and (iv) the phonon dispersion curve of ω_8 acoustical branch;[32] (b) a 15-parameter VFF by Piseri *et al.*[31] derived from a few optical data and from phonon frequencies from ω_8 dispersion branch redetermined in recent coherent neutron scattering experiments.[31]

While the statistical dispersion of the BK force field is often quite large and sometimes unacceptable, those by Piseri *et al.* are more reasonable and lie within the limits generally accepted in force constant calculations.[33] Moreover BK force field gives imaginary values for the frequencies of the lowest acoustical branch for a phase shift between neighboring chemical units near 180°. We have calculated $\omega(k)$ for $k = 0$ and $g(\omega)$ for both force fields and compared the results. It was concluded that BK force field gives a better agreement with the optical spectrum (infrared and Raman) in comparison with that of Piseri *et al.* In the present work we have adopted BK force field[27] being however well aware of the fact that the force field is not unique and that the choice of the fundamentals is somewhat force field dependent.[33b] For models 3 and 4 we felt necessary to introduce an additional cross term of the type $\Phi_{\phi\phi}(C–\hat{C}–C/C–\hat{C}–C)$ whose value ($\Phi_{\phi\phi} = 0.2$ mdyn/Å) had been estimated by comparison with other molecules; its effect on the eigenfrequencies has been tested for several numerical values.

Having settled on the force field, we have carried out the calculations of dispersion curves $\omega(k)$ and density of states $g(\omega)$ for the energetically most stable models predicted by theoretical calculations.[13] In particular phonon frequencies were calculated for the following models of ideal infinite and isolated polymer chains: model 1, θ =

---

(31) L. Piseri, B. M. Powell, and G. Dolling, *Bull. Amer. Phys. Soc.*, 16, 311 (1971); see also *Phys. Can.*, 27, 32 (1971).

(32) V. La Gard, H. Prask, and S. Trevino, *Discuss. Faraday Soc.*, 48, 15 (1969).

(33) (a) G. Zerbi, *Appl. Spectrosc. Rev.*, 2, 193 (1969). (b) Another set of statistically well defined parameters has been more recently proposed by Piseri *et al.* (ref 34). Since it is based mainly on the vibrational assignment of BK, we did not think necessary to take that into account in the present calculation.

(34) L. Piseri, B. M. Powell, and G. Dolling, *J. Chem. Phys.*, 57, 158 (1973).

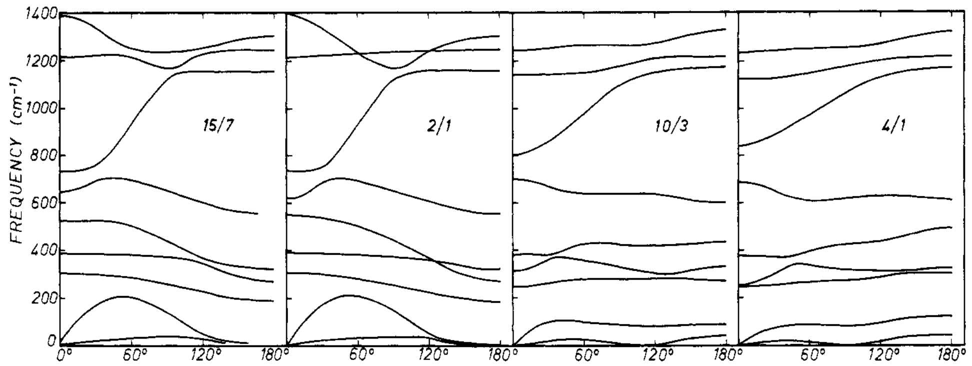

Figure 2. Dispersion curves for single-chain poly(tetrafluoroethylene): (a) 2/1 helix; (b) 15/7 helix; (c) 10/3 helix; (d) 4/1 helix.

Table II
Spectroscopically Active k = 0 Phonon Frequencies (cm^{-1}) for Various Models of One Dimensional PTFE Polymer Chains

	Model 1 $\theta = 180°$		Model 2 $\theta = 168°$		Model 3 $\theta = 108°$		Model 4 $\theta = 90°$	
$\varphi = 0$	A_g (R)	1388	A_1 (R)	1381	A_1 (R)	1142	A_1 (R)	1123
		731		731		701		687
		387		386		379		376
	B_{3g} (R)	1214		304		248		251
		542						
	A_u (inactive)	305	A_2 (ir, ∥)	1213	A_2 (ir, ∥)	1245	A_2 (ir, ∥)	1236
				640		802		841
	B_{3u} (ir ∥)	619		519		313		246
$\varphi = \theta$	B_{1g} (R)	1300	E_1 (ir ⊥, R)	1298	E_1 (ir ⊥, R)	1267	E (ir ⊥, R)	1257
		316		1241		1198		1175
	B_{2g} (R)	265		1150		1134		1065
	B_{1u} (ir ⊥)	1243		552		635		617
		182		322		417		421
	B_{2u} (ir ⊥)	1149		271		311		316
		548		187		277		272
				6.2		82		81
$\phi = 2\varphi$			E_2 (R)	1348	E_2 (R)	1304	B_1 (R)	1324
				1216		1217		1216
				741		1163		493
				677		615		301
				522		421		41
				385		308		
				300		278	B_2 (R)	1169
				145		84		612
				14		21		325
								123

180°; model 2, θ = 168°; model 3, θ = 108°; model 4, θ = 90° (see Table I). The structure of the irreducible representations and their spectroscopic activities for k = 0 phonons are given in Table I. Dispersion curves and densities of states are reported in Figures 2 and 3, respectively.

The main purpose of these calculations is to predict from theory the spectral variations from model 1 to 4. If the polymer sample under study does consist of a mixture of several energetically favored structures or if the solid undergoes a phase transition from one structure to another at a given temperature, we should find some correspondence between theoretical predictions and experimental observations for some of these models if they actually occur. The calculated k = 0 phonon frequencies, their symmetry species, and their spectral activity are given in table II. It is apparent from Figure 4 that while changes in the geometry of the polymer chain leave some normal modes practically unchanged, they do produce dramatic changes in a few fundamentals. As it will be discussed in paper II such changes are revealed in the vibrational spectrum.

In these calculations it has been tacitly assumed that most of the spectral changes which may actually occur should be ascribed to variations in the geometry of the polymer chain. As a consequence the force field remained the same for all the four models with the exception of the force constant $\Phi_{\Phi\Phi}$ which had to be introduced and reasonably guessed. The preceeding assumption is justified by the observation that the vibrational spectrum is not dramatically affected by slight changes of the force constants. This fact does not occur in the case of hydrogenic polymers where the dynamics is strongly affected by both the force field and the geometry.[2a]

The analysis of the calculations yields the following conclusions which can be better understood by a close look at Figure 4.

1. Phonon Dispersion Curves. The dispersion of the phonons propagating along the polymer chain axis shows regions of remarkable coupling between phonons of different branches and of the same symmetry species resulting in strong repulsions between optical branches. Of particular interest for the interpretation of recent coherent neutron scattering experiments[34] is the shape of the ω_7 and ω_8 dispersion branches which show flat regions starting from a phase shift $\varphi \approx 40°$ for models 3 and 4. Examination of eigenvectors and the derived potential energy distribu-

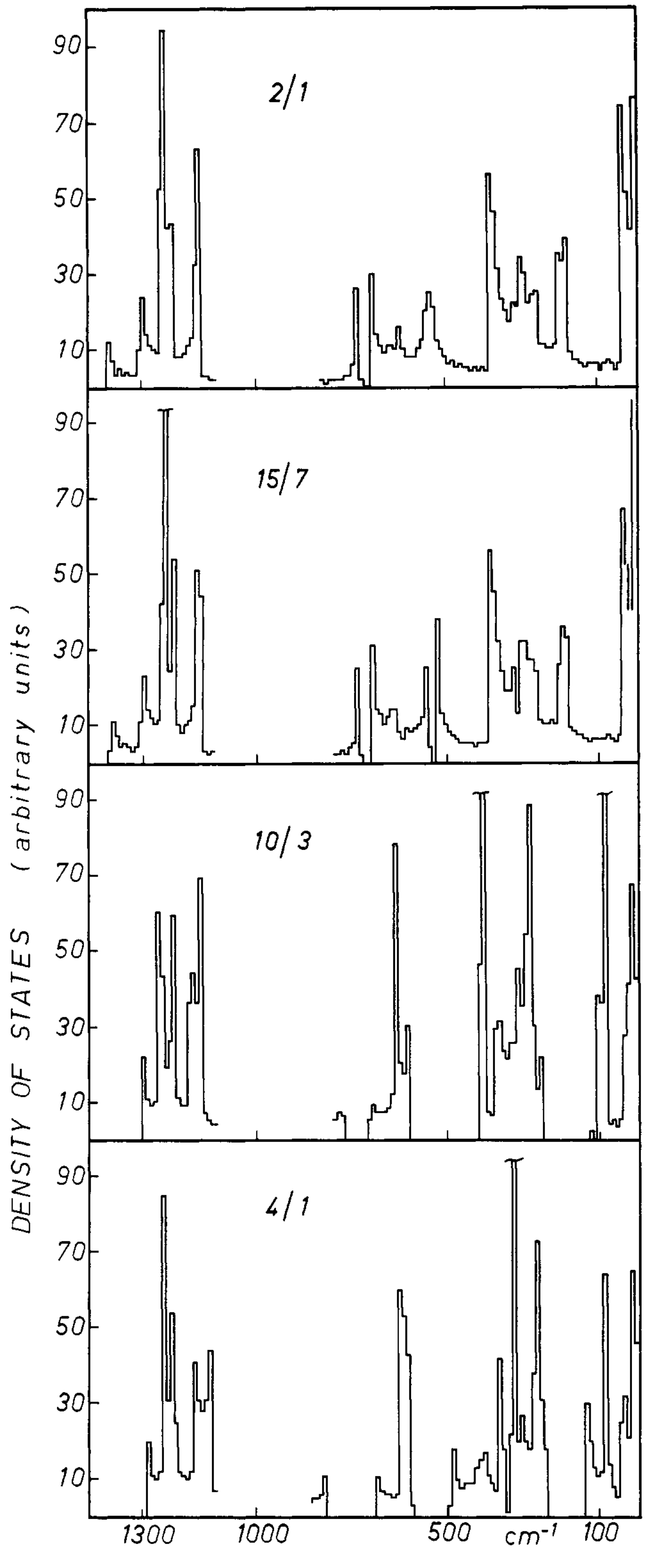

Figure 3. Density of vibrational states $g(\omega)$ for single-chain poly(tetrafluoroethylene): (a) 2/1 helix; (b) 15/7 helix; (c) 10/3 helix; (d) 4/1 helix.

tion[35] show a large mixing of the internal coordinates at various k values such that a precise labeling of the branches in terms of a description of the normal modes becomes impractical. The experimental verification of the dispersion of phonons has been carried out very reliably only for ω_8 branch on a stretch oriented sample of PTFE (model 2) first by La Gard *et al.*[32] and very recently in careful experiments by Piseri *et al.*[31,34] A few phonons have been observed for branches ω_7 and ω_6 but their origin and precise values are somewhat affected by experimental problems which seem mainly to be ascribed to the nature and structure of the sample examined.

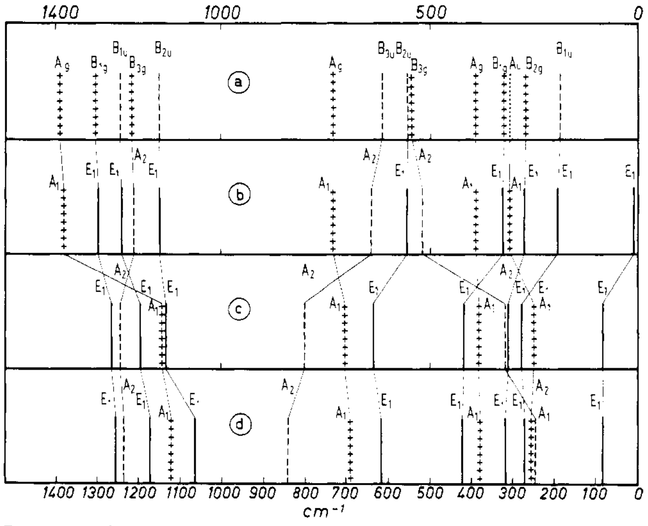

Figure 4. Correlation between $k = 0$ phonon frequencies of various models of poly(tetrafluoroethylene). For each spectrum the symmetry species, Raman, and infrared activities are indicated: (a) 2/1 helix; (b) 15/7 helix; (c) 10/3 helix; (d) 4/1 helix; (———) infrared and Raman active; (+++++) Raman active; (- - - - - -) ir active; (· · · · · ·) inactive.

2. Density of States. Let us first compare $g(\omega)$ for models 1 and 2 (Figure 1). As also indicated from the dispersion curves (Figure 2) such a small change in the geometry does not cause great changes in the position of the calculated singularities with the exception of the distribution of phonons in the energy range 500–600 cm^{-1}. For model 2 the singularity at 520 cm^{-1} ($k = 0$, A_2 phonon at the center of the EBZ) and the singularity at ~552 cm^{-1} (corresponding to a flat section of branch ω_5 containing the E_1 phonon toward the EBZ boundary) coalesce into a single peak at ~545 cm^{-1} for model 1 where branches ω_5 and ω_4 become almost accidentally degenerate. As later discussed this behavior finds a nice verification in the experimental infrared spectrum. Extending the comparison also to models 3 and 4 it can be noticed that strong singularities corresponding to flat branches for $k \neq 0$ phonons occur throughout the whole energy range from 1400 to 0 cm^{-1}. Some of these singularities can be taken as characteristic of the models. A possible coincidence between calculated $g(\omega)$ and experimental $g(\omega)$ from inelastic neutron scattering experiments may provide an indication of the actual existence of such models in a real polymer sample. Once the reliability of the force field is accepted as working hypothesis, the following singularities can be suggested as characteristic: model 1, ~545 cm^{-1}; model 3, ~630, ~405, ~285, and ~80 cm^{-1}; model 4, ~365, ~325, and 260 cm^{-1}. Time of flight neutron spectra of PTFE at various temperatures have been reported by Safford and Naumann.[36] While some rough correspondence between INS peaks and $g(\omega)$ calculated for 15/7 model can be approximately suggested for the higher energy region (~1200 to ~200 cm^{-1}) the reported fine structure at lower energies cannot be accounted for by our models. Before attempting any detailed interpretation of these unexplained features it is felt that additional experiments need to be performed.

---

(35) For a definition of this quantity, see P. Torkington (*J. Chem. Phys.*, 17, 347 (1949)) and Y. Morino and K. Kuchitsu (*J. Chem. Phys.*, 20, 1809 (1952)).

(36) G. J. Safford and A. W. Naumann, *Advan. Polym. Sci.*, 5, 1 (1967).

3. *k* = 0 **Phonons and Interpretation of the Infrared and Raman Spectra of PTFE.** Figure 4 and Table I are taken as reference in the discussion which follows. We start with the consideration of the vibrational spectrum of 15/7 PTFE helix as being the energetically more stable structure. We focus our attention on all the infrared active phonons (A_2, ∥ and E_1, ⊥) and on part of the Raman active ones (A_1 and E_1). We do not take into consideration any E_2 phonons whose spectral occurrence is very doubtful even for simpler polymers. The choice of E_2 modes becomes really arbitrary and does not have yet any experimental support. If one of the observed phase transitions transforms model 2 into model 1 (transplanar chain), the predictions of the present work based on optical selection rules and on frequency calculations are graphically indicated in Figure 4. We predict that on going from model 2 to model 1 the E_1 mode at 1298 cm^{-1} and the A_2 mode at 1213 cm^{-1} should disappear in the infrared spectrum. The A_2 mode at 640 cm^{-1} shifts to 625 cm^{-1}. The E_1-A_2 552-519-cm^{-1} doublet narrows into a very close doublet at 548 B_{2u}-542B_{3g} of which one component is infrared inactive. The two E_1 modes calculated at 322 and 271 cm^{-1} should disappear.[37] It will be shown in paper II that most of these predictions are experimentally verified for the transition at 19°C. It will be shown that the sample at temperatures around 19°C does consist of a mixture of 15/7 and 2/1 helices. The concentration of 2/1 helices undergoes a sudden increase at the transition temperature.

For the existence of models 3 and 4 we look in the calculated spectrum for those phonons which should occur in an energy region free from overlapping with phonons from models 2 and 1. This decision stems from the fact that the energy required for the formation of chains with a structure similar to those of model 3 and 4 is calculated to be much larger than that for models 1 and 2, hence their concentration in a real polymer sample should be generally smaller. We must focus our attention to the generally strongest absorptions in the infrared or scattering in the Raman which will occur in this case as weaker signals. Neglecting the C-F stretches, the A_2 modes generally strong in infrared calculated at ~800 and ~850 cm^{-1} are taken to be the most characteristic for models 3 and 4, respectively. In the highly populated energy region at ~300 cm^{-1} a characteristic A_2 mode strongly geometry dependent is likely to occur for both models 3 and 4.

The experiments discussed in paper II will show that some experimental indication is found for the existence of more coiled helices (approaching models 3 and 4). Of particular interest is the fact that the so called "amorphous band" at 780 cm^{-1} whose intensity increases with increasing temperature (with ∥ dichroism) can be assigned to the A_2 mode of model 3 as discussed above. It has to be remembered that this band has been widely adopted in analytical determinations of the amorphous content in a PTFE sample.

4. $k \neq 0$ **Phonons and Experimental Phonon Dispersion Curves.** Very recent coherent neutron inelastic scattering studies on stretch-oriented PTFE have attempted to measure the frequencies of the normal modes belonging to the five lowest branches of the dispersion relation.[34] While narrow and well-defined peaks were measured for phonons belonging to the first half of the ω_8 branch, generally broad and poorly resolved peaks were detected in the second half of the EBZ. The experimental findings were not easily accounted for either on the basis of a single-chain model nor by a complete lattice dynamical treatment which takes into account intermolecular (chain-chain) interactions in a three-dimensional lattice. Piseri *et al.*[34] were also concerned with the interpretations of a series of neutron groups at different wave vectors which could suggest the existence of an additional almost flat branch above ω_8 and across ω_6 and ω_7 lying in the energy range 250-300 cm^{-1}.

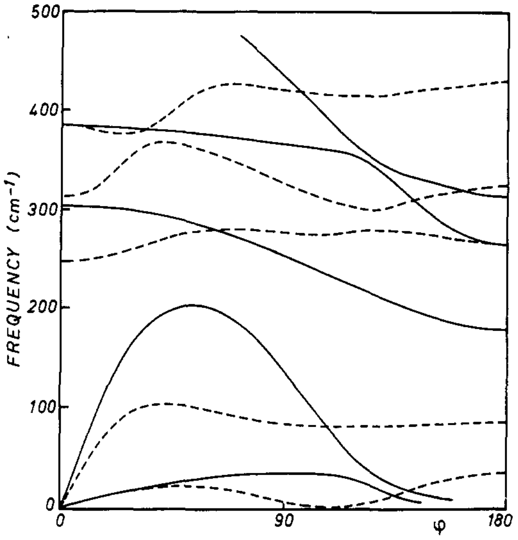

Figure 5. Comparison of the five lowest dispersion curves of poly(tetrafluoroethylene) calculated for two helical models: (——) 15/7 helix; (- - - -) 10/3 helix.

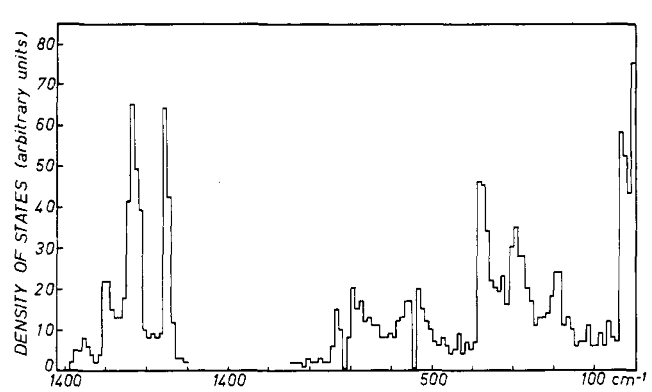

Figure 6. Density of vibrational states of conformationally disordered chain of poly(tetrafluoroethylene) consisting of 200 CF_2 units in a randomly kinked chain with a population of conformations given by a Boltzman distribution. The energy content of each conformation is assumed to be that given in ref 13; % distribution: 32%, τ = 165.66°; 32%, τ = −165.66°; 22%, τ = 180°; 6%, τ = 90°; 6%, τ = −90°; 1%, τ = 60°; 1%, τ = −60°.

As a contribution toward the understanding of these experimental findings from our work we could suggest an alternative explanation. The optical spectrum does give evidence of the existence of helical segments whose structure approaches the 10/3 helix and it seems that these segments become oriented in a stretched oriented sample. It can then be suggested that the diffuseness of the observed phonon groups and the appearance of the seemingly additional dispersion branch could be accounted for as arising from ω_9 and ω_8 branches respectively of the 10/3 helix. See Figure 5 for a more detailed comparison.

5. **Lattice Dynamics of Conformationally Disordered Chains.** Computational techniques previously developed in our laboratory[2a,38] allow to calculate the density of vi-

---

(37) For a discussion of the limitations of these predictions with regards to the actual observed spectrum, see paper II.

(38) M. Tasumi and G. Zerbi, *J. Chem. Phys.*, 48, 3813 (1968).

brational states $g(\omega)$ for polymer chains containing the desired geometrical disorder with a preassigned randomness along the chain. We focus our attention mainly to the possible spectral modifications introduced by geometrical defects and revealed as peaks in the calculated $g(\omega)$. We consider that a force field which reasonably justifies most of the vibrational spectrum of PTFE will also be capable to provide indications on the spectral regions which are going to be modified by the defects. The same force field adopted for perfects chains was used in the work on defects of PTFE.

According to our general criteria in this type of studies[2b] the dynamical matrices of the following models of conformationally disordered PTFE chains were constructed: (1) chains of the type $-(165.66°)_m-X-(165.66°)_n-$ with $m = n$ (regular distribution). The defect X corresponds to internal rotational angles of $\tau = 60$, 90, 180° variously and differently taken as singlets, doublets, or triplets (*e.g.*, $X = 60°-60°-90°$ etc.); (2) chains of the type $-(165.66°)_m-X-(165.66°)_n-$ with $m \neq n$ at random (random distribution); (3) a randomly coiled chain containing a statistical distribution of torsional angles whose population is given by a Boltzmann distribution at room temperature. The energy of each conformation is assumed to be that calculated by De Santis *et al.*[13] Segments of 200 CF_2 units were adopted in our calculations. The sequences of internal rotational angles were extracted as "well-balanced" sections from a series of 9900 random numbers suitably obtained from a computer.

The density of vibrational states for these defect containing polymer chains were calculated from the dynamical matrices by application of the negative eigenvalue theorem[39,40] and plotted as histograms with the desired resolution. The mathematical problems and computational devices have been discussed previously.[2a,b] The computational time required for the calculation of the eigenvalues of dynamical matrices with dimensions 1800 × 1800 with 60 codiagonals was of the order of 30 sec/step in the histogram.

The purpose of our calculations on structurally disordered polymer chains is to derive from the calculated $g(\omega)$ indications for the interpretation of the optical and neutron scattering spectra.

Since our models of disordered chains consist of sequences of ordered linear host lattice interrupted by geometrical defects the vibrational spectrum should display:[2a,b] $k = 0$ phonons of the host lattice; the activation of inactive $k = 0$ phonons of the perfect lattice and the activation of $k \neq 0$ phonons thus mapping the density of states dipole weighted (these two facts arise from the lack of translational symmetry); out-of-band, gap, or band modes; extra features due to coupling between defects or with phonons of the host lattices.

Of the many models analyzed[41] we report here the extreme case of a randomly coiled chain of PTFE containing a statistical distribution of torsional angles (Figure 6).

The analysis of the obtained results leads to the following conclusions. (i) Unlike the case of polyethylene,[2a] the vibrational spectrum of PTFE is not greatly changed by the introduction of conformational deformations. This fact may be understood in terms of the different dynamical behavior of the two polymers because of the different masses of the atoms attached to the carbon (H and F). This conclusion is derived only from the study of $g(\omega)$ dipole unweighted. To the present time a reliable prediction of the intensities of infrared absorption or scattering in the Raman is not yet possible. Further work is in progress in our laboratory for the elucidation of this important point. (ii) Unlike polyethylene,[2a] no clear indication of gap or resonance modes characteristic of a given defect were located with reasonable certainty. (iii) The main spectral modifications are predicted to occur because of the presence of geometrical defects in the following spectral regions: ~1250, ~650, ~540, and ~300 cm^{-1}. (iv) The evidence of short segments of the host lattice should arise from the activation in the infrared of $k = 0$ phonons only Raman active for the perfect case or *vice versa.*

Because of the well-known fact that the Raman spectrum always exhibits a number of lines much smaller than those expected even for the perfect case, we turn to the infrared spectrum for the search for activation. Namely we look for the activation in the infrared of the 4 A_1 modes which occur as very strong lines observed in the Raman spectrum at 1379, 729, 383, and 291 cm^{-1} for PTFE 15/7 helix.

As it will be discussed in paper II the clearest evidence of the activation is the occurrence in the infrared of a band at 384 cm^{-1} whose intensity increases with the content of "amorphous" substance.

Acknowledgments. We thank Dr. M. Gussoni for many helpful discussions and for her help. We thank Dr. P. Bosi for helping in some calculations.

---

(39) P. Dean, *Proc. Roy. Soc., Ser. A*, 260, 263 (1961).

(40) P. Dean and M. D. Bacon, *Proc. Roy. Soc., Ser. A*, 283, 64 (1965).

(41) M. Sacchi, Thesis, Istituto di Chimica delle Macromolecole, CNR, Milan, Italy, 1971.