

INFRARED SPECTROSCOPY AND POLYMER STRUCTURE

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INTRODUCTION

The power of infrared spectroscopy as a tool in studying the structure of small molecules is well known. This insight into structure results largely from our ability to analyse the spectrum theoretically by means of a normal coordinate analysis. This technique consists of calculating the normal vibration frequencies of a molecule from information on its structure and internal force field. From such a calculation we obtain the values of the frequencies and the forms of the vibrations of the molecule which can be observed in infrared absorption and in Raman scattering. By comparing such calculated frequencies with the observed spectrum it is possible to evaluate our assumptions concerning the structure and force field of the molecule.

A review article published in 1960¹ stressed the importance of extending such theoretical methods of analysis to the study of the infrared spectra of high polymers. Only in this way could the full power of spectroscopy be brought to bear on answering questions related to the structure of, and interactions between, macromolecules. Prior to 1960 the few normal coordinate calculations which had been done (see 1 for references to such studies) were limited in their detailed predictive capability by the lack of a sufficiently complete force field for the molecule and by simplifying approximations made about the structure. The derivation of satisfactory force fields for polymers, which is still the most basic problem associated with a normal coordinate analysis, began in the early 1960s, with the use of extended Urey-Bradley force fields^{2, 3} and the development of a detailed valence force field for hydrocarbons^{4, 5}. Since then the technique of normal coordinate analysis has been applied to the interpretation of the infrared spectra of many regular polymer structures (see, for example, polyethylene^{4, 6-9}; polypropylene, both isotactic¹⁰⁻¹⁴ and syndiotactic^{15, 16}; isotactic polybutene-1¹⁷; syndiotactic 1,2-polybutadiene¹⁸; polyoxymethylene¹⁹; polyethylene oxide^{20, 21}; polytetrahydrofuran²²; poly(vinyl chloride)^{23, 24}; polyacrylonitrile^{25, 26}; poly-3,3-bis(chloromethyl) oxacyclobutane²⁷). In some of these cases the chain structure was already known from x-ray diffraction studies; in other cases vibrational analysis shed light on aspects of the structure which were not obtainable from x-ray studies.

In this paper the author wishes to illustrate some of the facets of polymer structure which can be illuminated by means of detailed vibrational analysis. These aspects include not only the structure of the individual regular chain in the crystalline phase, but also features of the arrangement of chains in

the crystal. In addition, it is possible to determine to a certain extent the nature of non-crystalline structures present in a polymer system. Examples will be chosen from work in the author's laboratory on poly(vinyl chloride) (PVC) and polyethylene.

STRUCTURE OF CRYSTALLINE POLY(VINYL CHLORIDE)

The ability to distinguish between different regular chain structures of a polymer by means of normal coordinate analyses is well illustrated by the case of poly(vinyl chloride).

Early x-ray diffraction studies²⁸ had suggested, as a result of the observation of an approximately 5·1Å fibre-axis identity period, that the structure in the crystalline regions of PVC was that of a head-to-tail planar zig-zag syndiotactic chain, as shown in *Figure 1*. A more recent investigation²⁹ supports this proposal, although variations in x-ray spacings seem to be

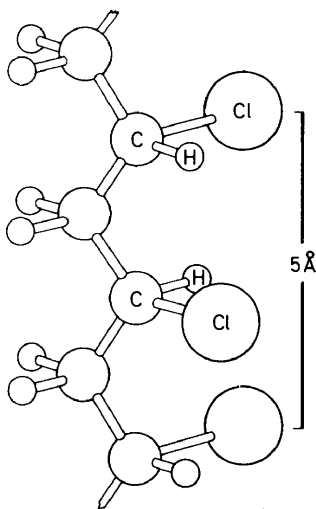


Figure 1. Planar zig-zag structure of syndiotactic PVC. The structure can be described as $-(-T)-_n$, where T denotes a *trans* arrangement across a carbon-carbon bond

found between polymers prepared by different methods³⁰. The x-ray diffraction pattern of PVC is in general quite poor, probably primarily as a result of poor order³¹ and small crystallite size³², and therefore a complete structure analysis has not been feasible. It is therefore particularly important to have supporting evidence on this structure from spectroscopic studies.

Previous normal coordinate analyses of PVC^{23, 24} were based on an assumed planar zig-zag syndiotactic structure. They depended, however, on simplified force fields which had not been checked extensively on small molecules. In addition, calculations were made only for the one structure, so it was not possible to tell if other structures would have given comparably good agreement with the observed frequencies. Thus, while fair agreement with the observed spectrum was obtained, the uncertainties in the force fields left a question concerning the significance of the results.

We have recently derived^{33, 34} a detailed force field for secondary chlorides which is an extension of the valence force field for hydrocarbons^{4, 5}. It gives very good agreement when tested out on small molecules: for example, the average deviation between observed and calculated frequencies in the region of 600 to 1400 cm^{-1} for the most stable conformers of DL- and *meso*-2,4-dichloropentanes is 0.6% and 0.8% respectively. This force field has been applied³³ to the calculation of the normal vibration frequencies of the planar zig-zag structure of syndiotactic PVC, *Figure 1*, and to the two other structures shown in *Figures 2* and 3. The structure of *Figure 2*, a two-fold helix

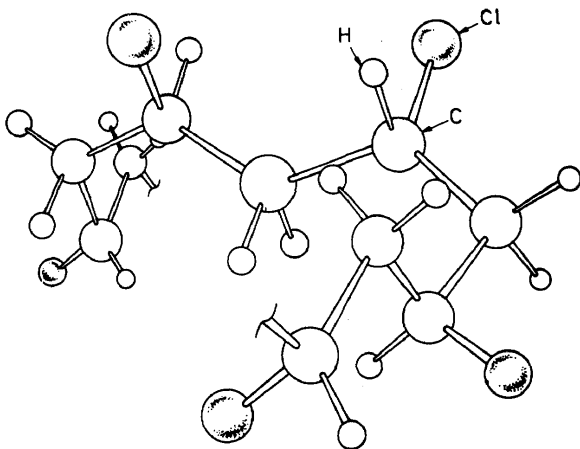


Figure 2. Helical (D_2) structure of syndiotactic PVC. The structure can be described as $-(TTGG)-_n$, where *G* denotes a *gauche* arrangement across a carbon-carbon bond.

with D_2 symmetry, is similar to that found in one form of syndiotactic polypropylene³⁵, and since the latter polymer also occurs in a planar zig-zag conformation³⁶ it was felt that the D_2 helical structure might similarly be a possible one for PVC. If PVC were isotactic, its conformation, by analogy with isotactic polypropylene³⁷, might be a three-fold helix, and therefore the spectrum corresponding to the C_3 helix in *Figure 3* was calculated.

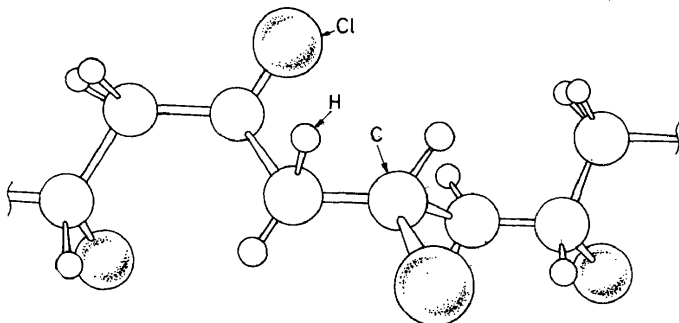


Figure 3. Helical (C_3) structure of isotactic PVC. The structure can be described as $-(TG)-_n$.

Differences between the calculated frequencies of the above three structures are evident throughout the spectrum, but for purposes of easiest comparison we will concentrate here on the region of the carbon-chlorine stretching vibrations. The calculated frequencies of these modes^{33, 38} are given in *Table 1*, together with the values of the two observed bands found

Table 1. Carbon-chlorine stretching frequencies of crystalline PVC

Observed (cm ⁻¹)	Calculated (cm ⁻¹)		
	Planar Zig-Zag Syndiotactic	Helical (D ₂) Syndiotactic	Helical (C ₃) Isotactic
601 σ^*	607 σ	622 π	
639 σ	634 σ	651 σ	646 π
		707 σ	700 σ
		[762]†	

* σ = perpendicular, π = parallel; † [] = infrared inactive.

in this region in the essentially completely crystalline polymer which can be prepared by polymerization of the monomer in a urea canal complex³⁹⁻⁴². The dichroic characteristics of the observed bands were obtained from polarized spectra of oriented films of less highly crystalline material⁴³.

On the basis of the results in *Table 1*, the assignment of a planar zig-zag syndiotactic structure to the chain in the crystalline regions of PVC is highly compelling. The remainder of the calculated spectrum exhibits comparably good agreement with the observed bands^{33, 38}, as is shown in *Table 2*. (In this table bands labelled σ^* show parallel dichroism in the early stages of drawing⁴⁴, thus serving to identify B_1 species modes in the spectrum and providing another constraint on possible assignments.) While this result is not particularly surprising in the present case, it does illustrate the potential which a normal coordinate analysis provides for discriminating between various postulated structures of a regular chain.

NON-CRYSTALLINE POLY(VINYL CHLORIDE) STRUCTURES

A highly stereoregular polymer will usually also be highly crystalline in the solid state, and this implies the presence of a single predominant conformation of the chain. This was the case for urea-complex PVC, and this is true of other stereoregular polymers. As we have noted, the normal vibration analysis of the linearly periodic structures associated with such conformations is relatively straightforward, permitting both a ready interpretation of the spectrum as well as a verification of the structure of the chain.

A polymer with poor steric regularity, however, cannot usually take up a regular chain conformation. For example, the presence in a predominantly syndiotactic PVC chain of two neighbouring chlorine atoms having an isotactic arrangement would tend to cause the chain to depart at that point from a planar zig-zag structure, primarily because of the steric repulsion which would exist between two such chlorine atoms if the chain were to

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remain planar zig-zag. Since the energy as a function of torsion angle about a carbon-carbon bond is locally a minimum near the staggered positions (120° apart), the chain in the above example would be expected to twist away from the planar zig-zag form by any appropriate $\sim 120^\circ$ rotation which would relieve the steric repulsion. The introduction of such new rotationally isomeric structures would in general be expected to alter the

Table 2. Calculated and observed frequencies for planar zig-zag syndiotactic poly(vinyl chloride)

Av. $|\nu_{\text{obs}} - \nu_{\text{calc}}|$ (in 600–1500 cm^{-1} region) = 1.3%

Calculated (cm^{-1})	Observed (cm^{-1})	Potential Energy Distribution (contributions $\geq 10\%$)
(125) A_2		CCCl bend (71) — CCC bend (24)
291 B_1	315 m σ	CCCl bend (45) — CCC(Cl) bend (22) + CC stretch (11)
300 B_2	345 w π	CCCl bend (84)
344 A_1	358 m σ	CCCl bend (63) — CCH(Cl) bend (23)
461 B_1	490 w π	CCC(Cl) bend (44) — CCH(Cl) bend (22) + CH_2 rock (14)
(562) A_2		CCC bend (54) + CCl bend (18)
607 B_1	601 vs σ^*	CCl stretch (75)
634 A_1	639 s σ	CCl stretch (74)
833 B_2	830 m π	CH_2 rock (78) + CCH(Cl) bend (14)
982 B_1	962 m σ^*	CH_2 rock (41) — CC stretch (37)
(1046) A_2		CC stretch (68) — CCH(Cl) bend (17) — CH_2 twist (11)
1083 A_1	1086 w σ	CC stretch (49) — CCC bend (18) — CCC(Cl) bend (18)
1099 B_1	1102 m σ^*	CC stretch (51) + HCl bend (19) + CH_2 rock (17)
1102 B_2	1118 vw π	CC stretch (48) + CH_2 wag (43)
(1158) A_2		CH_2 twist (66) + CC stretch (18) + CCH(Cl) bend (11)
1173 A_1	1190 w σ (?)	HCl bend (56) + CH_2 twist (26) — CCH(Cl) bend (15)
1185 B_2	1227 m π	CCH(Cl) bend (53) + CH_2 wag (26)
1253 B_1	1257 s σ^*	HCl bend (58) — CCH(Cl) bend (31)
1320 A_1	1336 m σ	CH_2 twist (58) — HCl bend (22) + CCH(Cl) bend (14)
(1322) A_2		CCH(Cl) bend (67) — CH_2 twist (18)
1353 B_1	1351 w σ^*	CH_2 wag (80) — CC stretch (15)
1424 B_2	1380 w π	CC stretch (36) — CH_2 wag (33) + CCH(Cl) bend (27)
(1449) A_2		CH_2 bend (77) — CCH bend (20)
1455 A_1	1426 vs σ	CH_2 bend (76) — CCH bend (22)

vibrational spectrum from that of the regular chain. Through the understanding of such differences we hope to learn something about the kinds of non-crystalline structures which are present⁴⁵.

Ordinary commercial PVC has long been recognized to be a not very highly stereoregular polymer. Such material exhibits differences in its infrared spectrum when compared with highly syndiotactic PVC, particularly in the C-Cl stretching region. In *Figure 4*⁴² this region of the spectrum is shown for a PVC polymerized at 50°C ; for comparison the spectrum of a urea-complex polymer is also given. New bands appear in the spectrum of the former at 612, 622, 635, 685, and 693 cm^{-1} ; furthermore, their relative intensity is found to be a function of the physical state of the specimen. The latter observation was interpreted⁴⁶ as indicating a dependence of conformational structure on physical state, the new bands being considered to be associated with new conformations of the polymer chain. It is thus apparent that an understanding of the nature of the non-crystalline structures, and of their variation with the physical state of the polymer, depends upon a

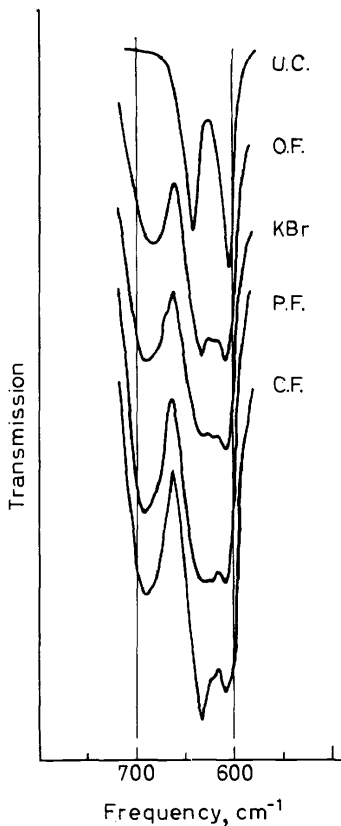


Figure 4. Infrared spectra of a PVC polymerized at 50°C, in various physical states. O.F. = oriented film, KBr = KBr pellet, P.F. = pressed film, C.F. = cast film. The spectrum of a urea-complex PVC (U.C.) is shown for comparison⁴²

satisfactory analysis of these new bands. Since their presence is associated with a non-stereoregular chain, it is also clear that the proper interpretation of these bands is basic to any infrared method of determining the tacticity of the polymer.

The analysis of this region of the spectrum of PVC has been the subject of some disagreement. We will therefore briefly review the previous assignments which have been suggested, based mainly on experimental studies of model compounds, and then indicate how our recent calculations help to resolve this question.

Empirical model compound studies

The basis for the experimental association of C-Cl stretching frequency with polymer chain conformation was the preliminary observation of a correlation in small secondary chloride molecules⁴⁷. This was refined by further studies on a large number of model compounds which revealed⁴⁸ that the C-Cl stretching frequency depends on the nature of the two substituents *trans* to the Cl atom across neighbouring C-C bonds as well as on

the local conformation of the carbon chain. The experimental data on model compounds of unique conformation are summarized in *Figure 5*, which incorporates the analysis of the spectrum of chlorocyclohexane in specifying the $S_{HH'}$ and S_{CC} frequencies³⁴.

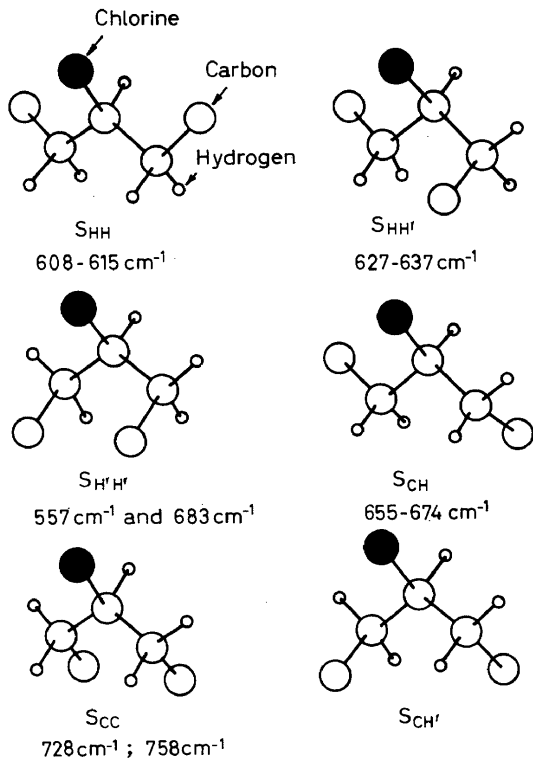


Figure 5. Conformations of secondary chlorides and empirically determined C-Cl stretching frequencies³⁴

These correlations were used to assign the stable conformers of DL- and *meso*-2,4-dichloropentane⁴⁹ and of syndiotactic, heterotactic, and isotactic 2,4,6-trichloroheptane^{50, 51}. For the former molecule, for example, the room temperature spectra were interpreted to indicate the presence of only one stable conformer of each isomer, viz., the *TT* form for the DL compound and the *TG'* form for the *meso* compound^{49, 50} (see *Figure 6*^{33, 52}). The *TT* form gives rise to two S_{HH} frequencies and the *TG'* form to one S_{HH} and one S_{CH} frequency. From a similar analysis of the spectra of the 2,4,6-trichloroheptanes it was concluded^{50, 51} that in the spectrum of PVC the absorption in the S_{HH} region was associated entirely with syndiotactic pairs of Cl atoms while absorption in the S_{CH} region was due to isotactic pairs. This assignment has been used^{50, 53-55} to obtain a measure of the tacticity in the polymer sample.

Other studies, however, had shown that the situation was not so simple. Model compound correlations⁴⁸ had suggested the presence of the $S_{HH'}$

'DL-Form' Conformation	<i>TT</i>	<i>TG</i> (<i>GT</i>)	<i>TG'</i> (<i>G'T</i>)	<i>GG</i>	<i>GG'</i> (<i>G'G</i>)	<i>G'G'</i>
Structure						
Isomeric structures	S_{HH}, S_{HH}	S_{HH}, S_{CH}	$S_{HH}, S_{HH'}$	S_{CH}, S_{CH}	$S_{HH'}, S_{CH}$	$S_{HH'}, S_{HH'}$
Calculated frequencies	624 605 —	675 615 —	632 (608) 572	715 627 —	699 619 531	694 619 595
'Meso Form' Conformation	<i>TT</i>	<i>TG</i> (<i>GT</i>)	<i>TG'</i> (<i>GT</i>)	<i>GG</i> (<i>G'G'</i>)	<i>GG'</i>	<i>G'G</i>
Structure						
Isomeric structures	S_{HH}, S_{HH}	$S_{HH}, S_{HH'}$	S_{HH}, S_{CH}	$S_{HH'}, S_{CH}$	S_{CH}, S_{CH}	$S_{HH'}, S_{HH'}$
Calculated frequencies	615 (614) —	643 618 564	675 614 —	699 617 537	714 627 —	692 (615) 595

Figure 6. Conformers of DL- and meso-2,4-dichloropentane and their calculated C-Cl stretching frequencies^{33,32}, () denotes expected weak intensity

conformer in 2-chlorobutane at room temperature; this has now been confirmed by normal coordinate analyses³⁴. The presence of this as well as other higher energy conformations was therefore believed to be possible in PVC^{39, 41, 42, 46}. In fact, it has now been shown⁵⁶ that isomeric structures other than S_{HH} can be introduced into the highly stereoregular urea-complex PVC by pressing. This is shown in Figure 7, where it can be seen that the development of absorption near 690 cm^{-1} suggests the introduction of S_{CH} structures while the increase in absorption near 635 cm^{-1} would be consistent with the presence of the $S_{HH'}$ structure. It appears, therefore, that the simplified interpretations suggested for the origins of the additional bands in ordinary PVC are in need of modification.

One part of the problem has been the absence of a detailed analysis, both experimental and theoretical, of the spectra of the model compounds. We discuss such an analysis for the 2,4-dichloropentanes in the next section, and show that even for this model system conformers other than the lowest energy one are present at room temperature. This should make it less difficult to acknowledge their possible existence in the polymer. The other part of the problem has been the reluctance to recognize that polymers in the solid state are not completely equivalent to small molecules in solution, in the liquid state, or in the relatively highly ordered structure of the crystal. Polymer chains in the solid state are subject to constraints imposed by the special conditions of their morphology, such as crystalline-non-crystalline

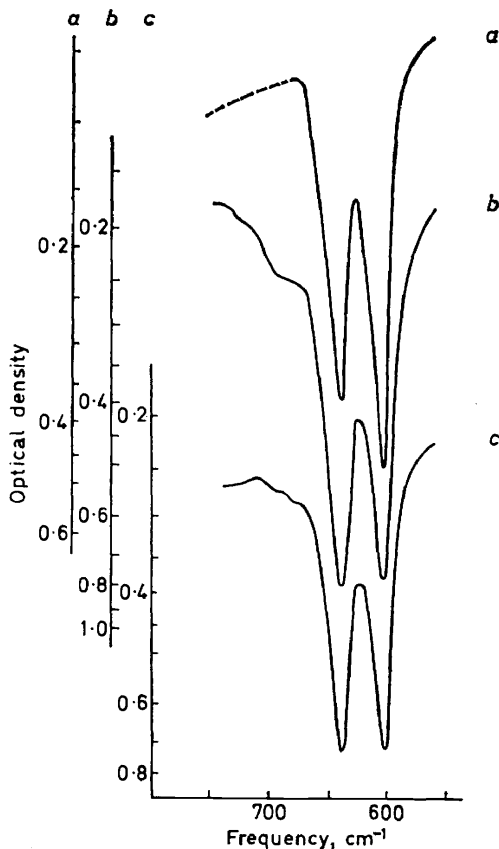


Figure 7. Infrared spectra of urea-complex PVC⁵⁶: (a) powder in nujol mull (dotted portion of curve represents nujol band); (b) film pressed from powder at about 200°C and cooled rapidly; (c) film pressed from powder at about 200°C and cooled slowly (by being left overnight in press)

ratio, single crystal and spherulitic texture, chain entanglements, and so forth. Under these circumstances it is not unlikely that chains will be forced to assume spatial arrangements which occasionally involve higher energy conformations than are normally found in comparable small molecules. The results on pressed urea-complex PVC⁵⁶ bear this out. It is therefore not completely valid to transfer the results of model compound studies to polymers without taking such factors into account.

Normal coordinate analysis of model compounds

The availability of a detailed force field for secondary chlorides which reproduces very well the observed spectra of the most stable conformers of both DL- and *meso*-2,4-dichloropentanes³⁴ has made it feasible to calculate the vibrational spectra of the other conformers of these molecules. This

calculation has been done^{33, 52}, and the predicted C-Cl stretching frequencies are given in *Figure 6*. The observed spectra in this region⁵², both at room temperature and at low temperatures, are shown in *Figures 8* and *9*.

The strong bands in the liquid at room temperature are clearly accounted for by one conformer, the *TT* in the case of the *DL* form and the *TG'* in the case of the *meso* form. It is evident from *Figures 8* and *9*, however, that there

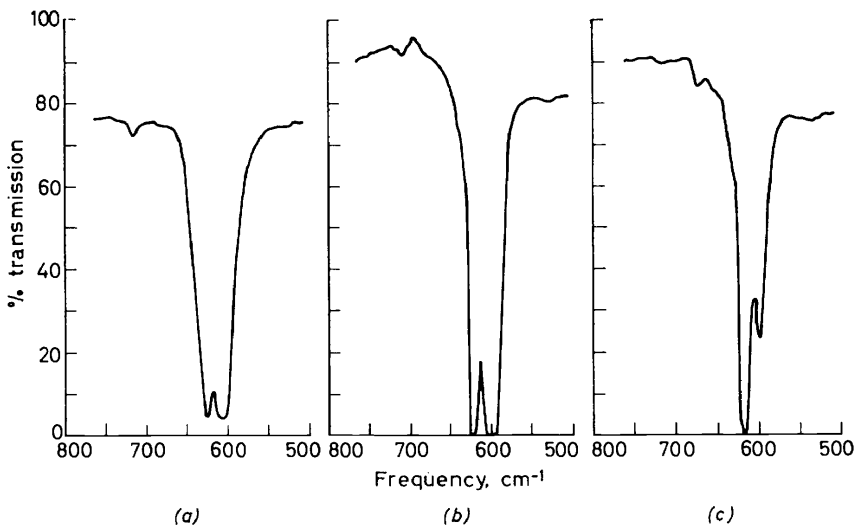


Figure 8. Infrared spectra of *DL*-2,4-dichloropentane: (a) at room temperature; (b) at -110°C ; (c) at -133°C (after previous sample had been warmed to room temperature)

are additional weak bands in the C-Cl stretching region. These do not appear to be assignable to impurities or to overtones or combinations⁵², but they can be explained satisfactorily as fundamental vibrations of other conformers. For example, in the spectrum of the *DL* form at room temperature, *Figure 8(a)*, the band at 715 cm^{-1} can be associated with the *GG* conformer and the band at 682 cm^{-1} can be correlated with the *TG* conformer (cf. *Figure 6*). Different conditions of cooling (which are not yet fully understood) can result in the retention of different amounts of these two structures, as seen in *Figures 8(b)* and *8(c)*. The other C-Cl stretching frequencies of these conformers, viz., near 627 cm^{-1} for the *GG* form and near 615 cm^{-1} for the *TG* form, undoubtedly are overlapped by the two strong bands of the *TT* conformer which are observed at 627 and 606 cm^{-1} . The changes in the relative intensities of these bands at low temperatures are consistent with the above assignment⁵². In the spectrum of the *meso* form at room temperature, *Figure 9(a)*, the band at 642 cm^{-1} is well correlated with the frequency predicted for the *TG* conformer (cf. *Figure 6*). Its counterpart, predicted at 618 cm^{-1} , would be expected to be overlapped by the strong component associated with the main *TG'* conformer, which is predicted at 614 cm^{-1} and observed at about 615 cm^{-1} . The weakening at low temperature of the 615 cm^{-1} band relative to that at 680 cm^{-1} , which is paralleled by the disappearance of the 642 cm^{-1} band [cf. *Figure 9(b)*], is consistent

with this assignment. Additional support for this correlation comes from the presence of a band at 552 cm^{-1} in the spectrum of the liquid which disappears at low temperature along with the band at 642 cm^{-1} (cf. Figure 9). This band is predicted at 564 cm^{-1} (see Figure 6), in a region in which no other modes are expected except for C-Cl stretching vibrations of three of the six conformers⁵². This region is therefore highly diagnostic for such structures. It is gratifying to note, for example, that the spectrum of the DL

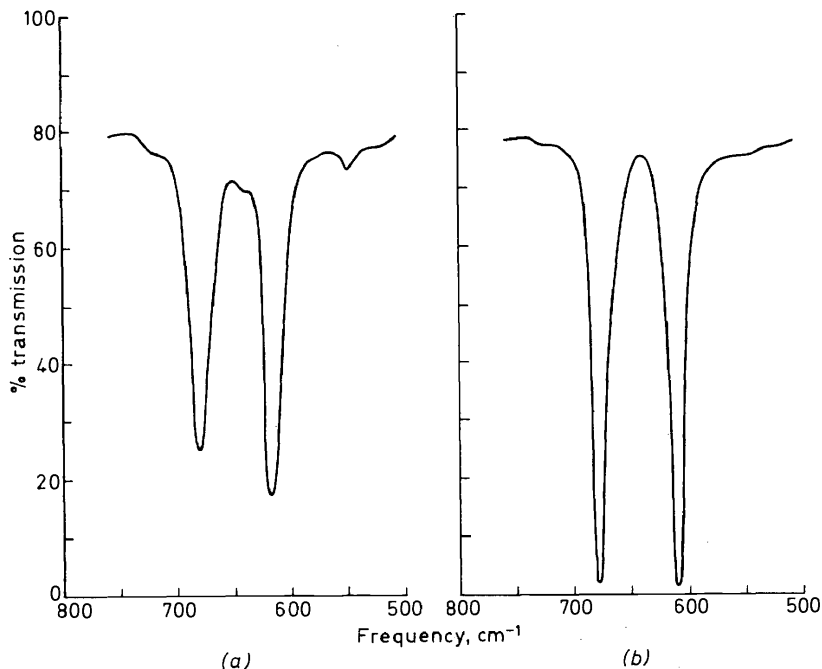


Figure 9. Infrared spectra of *meso*-2,4-dichloropentane: (a) at room temperature; (b) at -105°C

form shows no absorption in this region, as is predicted for the conformers found to be present from the analysis of the absorption bands above 600 cm^{-1} . Thus, the observation in the spectrum of the *meso* form of another band at 523 cm^{-1} which disappears on cooling strongly suggests that the *GG* conformer is also present (cf. Figure 6, and the predicted frequency of 537 cm^{-1}). In this case the other C-Cl frequencies, viz. 699 and 617 cm^{-1} , could well be overlapped by the strong bands of the main *TG'* conformer.

It can be seen, therefore, that the spectra of the 2,4-dichloropentanes at room temperature indicate the presence of conformers other than the single most stable ones. The changes in spectra with temperature can therefore be understood in terms of changes in the proportions of different conformers, and need not be attributed entirely to environmental effects^{57, 50}. If the additional conformers suggested by the above analysis are present, then we see that associated with the syndiotactic (DL) structure are S_{CH} modes (from the *TG* and *GG* conformers) as well as S_{HH} modes (from the dominant *TT*

conformer), while the isotactic (*meso*) structure can give rise to $S_{HH'}$ modes (from the *TG* and *GG* conformers) as well as S_{CH} modes (from the dominant *TG'* conformer). It should therefore not be surprising to find weak bands in the spectrum of ordinary PVC which can be associated with such structures. The assignments of such additional bands to conformations other than the most stable ones⁴² therefore is validated by the above analysis of the spectra of the 2,4-dichloropentanes.

Incidentally, it is of interest to note that in the conformers which might have been thought unlikely to occur because of steric repulsions, viz., the *TG* form of the *DL*-isomer and the *TG* and *GG* forms of the *meso*-isomer, a Cl atom is adjacent to a CH_3 group. While it is possible to relieve this close contact by small rotations about C—C bonds, it may be that these structures are stabilized to some extent by an attractive interaction between CH_3 and Cl, what might be called a C—H · · · Cl hydrogen bond. Although such a bond may seem unusual, it should be noted that evidence is accumulating for the participation of C—H groups in such weak types of hydrogen bonding, both in small molecules^{58, 59} as well as in macromolecules⁶⁰.

Normal coordinate analyses of 2,4,6-trichloroheptane^{33, 61} indicate similarly that conformers are present at room temperature other than the single ones proposed earlier for each isomer⁵⁰. This is consistent with conclusions reached from NMR studies⁵¹. As a result we can expect isotactic sequences in a PVC chain to give rise to S_{HH} modes (from the *GTTG'* conformer) as well as to the S_{CH} and $S_{HH'}$ modes which we have seen are possible from the analysis of the 2,4-dichloropentanes. This is consistent with our earlier suggestion⁴², and points to the danger in determining tacticity on the basis of an oversimplified analysis of the infrared spectrum^{50, 53-55}.

Normal coordinate analyses of PVC fragments

In order to extend the normal coordinate analyses to the interpretation of the spectra of non-crystalline PVC structures, the C—Cl stretching frequencies of a fragment of a PVC chain were calculated^{33, 38}. It was hoped in this way to overcome any possible errors associated with a comparison using frequencies calculated for a small model molecule. The fragment chosen was $C-(CH_2CHCl)_3-CH_2-C$, and calculations were done for a structure with two syndiotactic pairs of Cl atoms and for one with one isotactic pair and one syndiotactic pair. The C—Cl stretching frequencies of some conformations of these fragments are given in *Table 3*. While these results contain many implications³⁸, we will concentrate here only on the interpretations they suggest of the spectra of the pressed urea-complex PVCs, which are shown in *Figure 7*.

We have seen that the pressing of urea-complex PVC results in the introduction of new absorption bands near 690 cm^{-1} and near 635 cm^{-1} . The former can be associated with the S_{CH} structure of the *TTTG'TT* conformation, which is analogous to the *TG* conformation of *DL*-2,4-dichloropentane. (The S_{CH} structure of the *TTG'G'TT* conformation could also qualify on the basis of frequency agreement, but it is a less likely possibility on the basis of steric and electrostatic repulsions between adjacent Cl atoms³⁸.) The

increased absorption near 635 cm^{-1} had been assigned to the S_{HH} structure⁵⁶, and this is still consistent with the results in *Table 3*. The calculations show, however, that another assignment is possible, namely to one component of the $S_{CH} S_{CH}$ structure of the $T'TTG'G'T$ conformation (which is analogous to the GG conformation of DL-2,4-dichloropentane). We expect in this

Table 3. Carbon-chlorine stretching frequencies of $C-(CH_2CHCl)_3-CH_2-C$

	<i>Conformation</i>	<i>Isomeric Structures</i>	<i>C-Cl Frequencies</i>
Syndiotactic fragment (two s pairs)	$T'TTGTT$	$S_{HH} S_{HH}' S_{HH}$	606 615 618 638
	$T'TTG'TT$	$S_{HH} S_{CH} S_{HH}$	616 619 692
	$T'TG'G'TT$	$S_{HH} S_{CH}' S_{HH}$	617 623 687
	$T'TTG'G'T$	$S_{HH} S_{CH} S_{CH}$	615 637 730
Isotactic fragment (one i, one s pair)	$T'TGTTT$	$S_{HH} S_{HH}' S_{HH}$	604 611 623 648
	$T'TG'TTT$	$S_{HH} S_{CH} S_{HH}$	614 619 693

case to find another component near 730 cm^{-1} ; in fact, the spectrum of the annealed pressed film [*Figure 7(c)*] shows weak absorption near 750 cm^{-1} . Since this mode might be expected to be weaker than that at 637 cm^{-1} (cf. the results for the GG conformer of DL-2,4-dichloropentane⁵²), such an assignment cannot be excluded. It is interesting to note that if this assignment for the 635 cm^{-1} band is correct, it implies that annealing has resulted in the enhancement of the (presumably) more stable GG conformation while fast cooling has frozen in the more accessible but (presumably) higher energy TG conformation. Since the physical properties of the polymer must depend on such conformational structural characteristics, it is obvious that a detailed understanding of the structure in non-crystalline portions of a polymer chain is fundamental to our ability to correlate physical properties with polymer structure.

A cautionary comment is pertinent at this point, and illustrates the subtleties often underlying the observed spectrum. The dispersion curve in the C-Cl stretching region of planar zig-zag syndiotactic PVC is shown in *Figure 10*^{33, 62}. While for the infinite chain only those modes with a phase

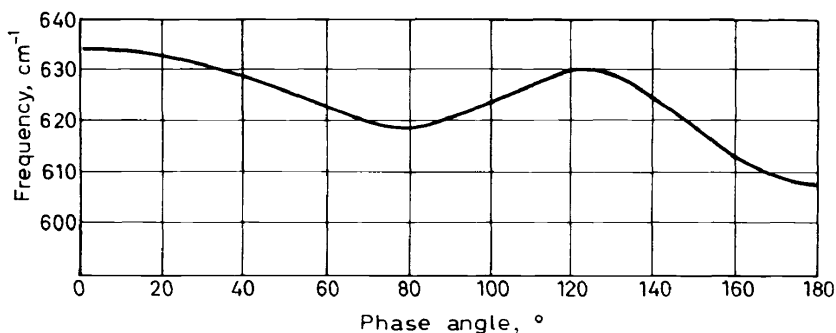


Figure 10. Calculated dispersion curve for C-Cl stretching vibrations in planar zig-zag syndiotactic PVC^{33,62}. The phase angle is between adjacent CH_2CHCl groups

angle of 0° or 180° can be infrared active, when defects are introduced into the chain it becomes possible for modes with other phase angles to gain activity^{63, 62}. If these were distributed uniformly with respect to phase angle, then it can be seen from *Figure 10* that absorption near the high frequency cut-off would be enhanced with respect to that near the low frequency cut-off. Such defects could be the $S_{HH'}$, S_{CH} , and $S_{CH} S_{CH}$ structures which we have discussed above. This mechanism for intensity enhancement complicates the picture, and makes it more difficult at present to be certain of the origin of the increased absorption near 635 cm^{-1} .

FOLD PLANE STRUCTURE IN POLYETHYLENE CRYSTALS

The preceding discussion has been concerned with the vibrations of a single polymer chain, either in its regular conformation within a crystal or the conformations it assumes in non-crystalline regions. In some cases the interactions between chains manifest themselves in the vibrational spectrum, and it then becomes possible to study certain aspects of the crystal structure itself by analysis of the infrared spectrum. Our recent studies on the polyethylene system illustrate the kinds of questions which can be posed and answered as a result of the extension of normal coordinate analyses to the entire crystal structure of the polymer.

The early observation⁶³ that the CH_2 rocking mode in polyethylene is a doublet, with components near 720 and 731 cm^{-1} , led to the surmise^{64, 65} that such splitting was due to intermolecular interactions between the two chains in the orthorhombic unit cell⁶⁶ (see *Figure 11*). Subsequent experimental work^{67, 68} supported this interpretation, as did theoretical

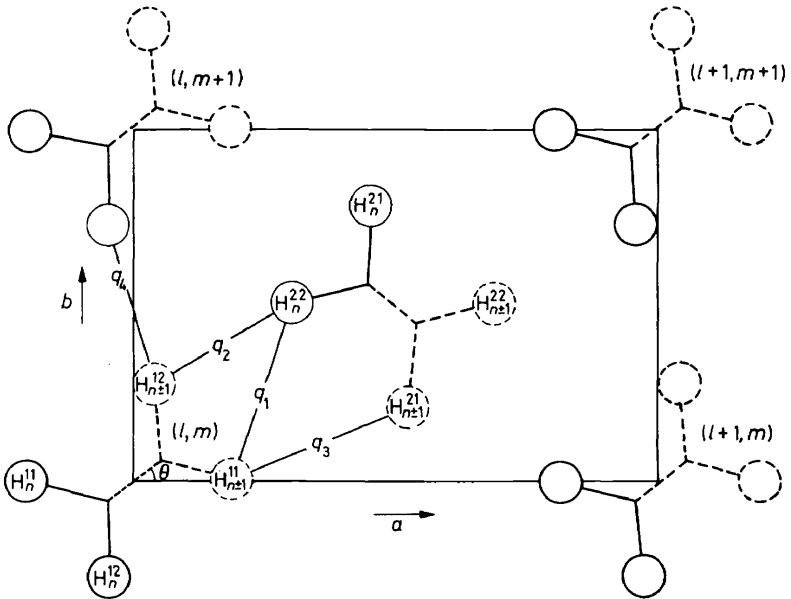


Figure 11. Cross-section of the unit cell of crystalline polyethylene. The q s indicate the dominant hydrogen-hydrogen interactions

studies^{69, 70}. Recent normal coordinate analyses^{71, 72} provide a detailed accounting not only of such splittings in the high frequency region of the spectrum, but also of the frequency of the observed^{73, 74} lattice translational mode near 71 cm^{-1} and its variation with temperature^{73, 72}. As a result of these studies we now have a reasonably good understanding of the intermolecular force field in crystalline polyethylene.

Polyethylene is widely known to form single crystals consisting of folded chains⁷⁵. Crystals grown from solution generally show a well-developed morphology which indicates that the chains are folded in the (110) planes, although under certain conditions crystal shapes are obtained which indicate that folding can also take place parallel to the (100) planes⁷⁵. The situation in melt-crystallized polyethylene is less clear. Some insight comes from studies of crystals grown from solution under conditions⁷⁶⁻⁷⁹ such that they display morphologies analogous to the spherulitic structures which occur in the melt crystallized polymer. In these circumstances the crystals are often found to be elongated, with the crystallographic *b*-axis parallel to the long direction of the crystal. No direct evidence, however, is available on the fold plane in such crystals or in the melt crystallized polymer, although it presumably is parallel to the (100) planes. X-ray diffraction is incapable of giving information on this point since it 'sees' only the interior of the crystal, whose structure⁶⁶ is essentially independent of the geometry of the folding.

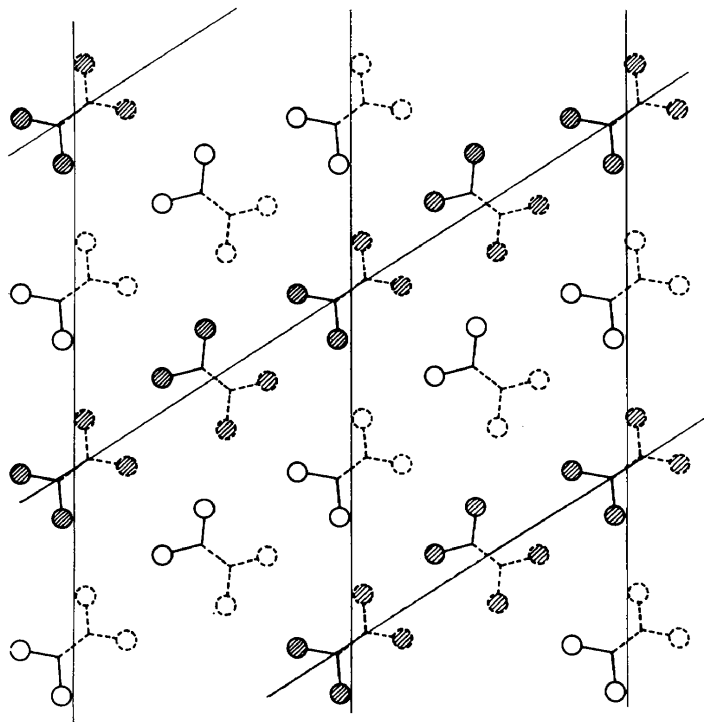


Figure 12. Cross-section of a uniform 1:1 folded chain co-crystal of normal (open circles) and fully deuterated (shaded circles) polyethylene in which the chains fold in the (110) planes. The folds on the top and bottom surfaces of the crystal are not shown

A vibrational analysis as a function of these features of crystallization, however, has been recently shown⁸⁰ to be capable of providing a method for studying such aspects of crystalline morphology.

The basis for a spectroscopic study of the geometry of the fold-plane in polyethylene arises from the fact that, as can be seen from *Figure 11*, a chain at the corner of the unit cell interacts with one at the centre of the cell as well as with neighbouring chains along the *b*-axis direction. Therefore, if we co-crystallize normal polyethylene with fully deuterated polyethylene we would anticipate a different pattern of interactions if the chain continuity is along the (110) plane than if it is parallel to the (100) plane. This is illustrated in *Figures 12* and *13* for a uniform 1:1 co-crystal of the two polymers. In the structure of *Figure 12* the interactions between similar

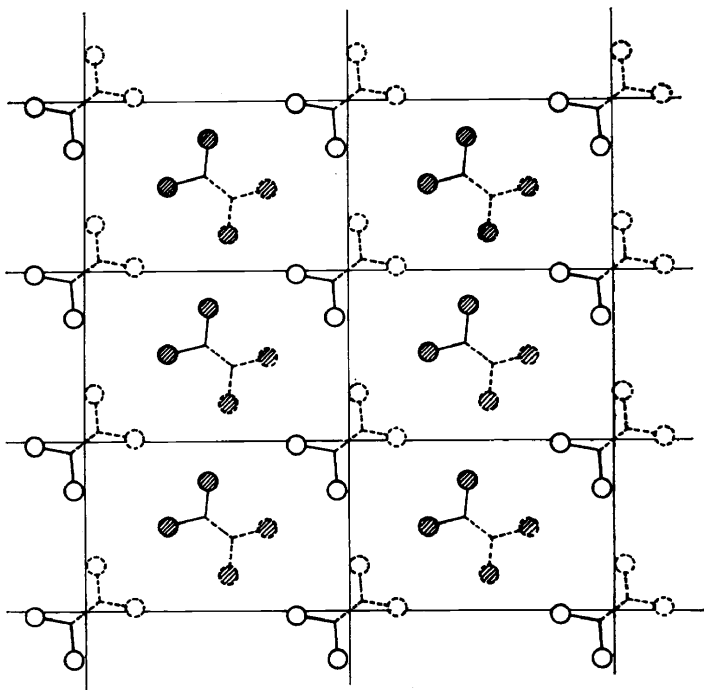


Figure 13. Cross-section of a uniform 1:1 folded chain co-crystal of normal (open circles) and fully deuterated (shaded circles) polyethylene in which the chains fold parallel to the (100) planes

oscillators are preserved between chains along the (110) plane but eliminated in the *b*-axis direction. The new enlarged unit cell still contains two chains of a given kind, however, so we expect splittings in the fundamentals, but of different magnitude than in the pure crystal. In the structure of *Figure 13* the unit cell contains only one chain of a given kind and such splittings should disappear. This is borne out by the calculations⁸⁰. For example, the CD_2 bending mode is predicted to be a doublet whose components are split by 8.1 cm^{-1} in pure $(CD_2)_n$ and by 4.1 cm^{-1} in the 1:1 structure of *Figure 12*, whereas it is predicted to be a singlet in the structure of *Figure 13*. Thus, it is

possible to use the predictions concerning the splittings in such a mixed crystal system to determine characteristics of the fold structure in polyethylene.

Experiments to test these ideas have been carried out^{81, 82}. Preliminary results are reported here. In *Figure 14(a)* is shown the CD_2 bending region of the spectrum of a film of fully deuterated polyethylene cast from *p*-xylene.

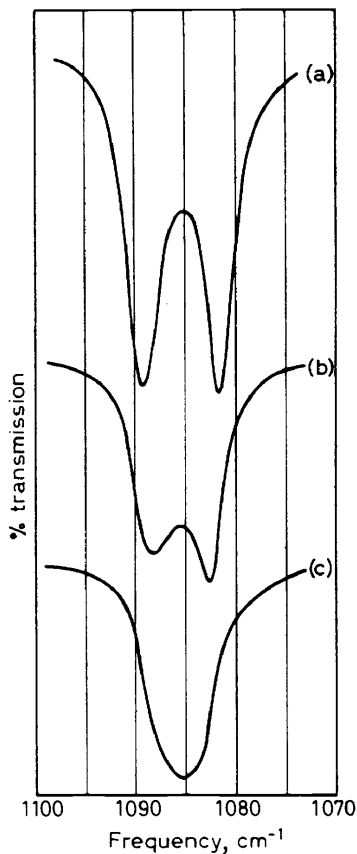


Figure 14. Infrared spectra of CD_2 bending mode: (a) in a cast film of fully deuterated polyethylene; (b) in a cast film of $1(CD_2)_n:2(CH_2)_n$ composition; (c) in a film obtained by melt-crystallizing sample (b)

(The same results are obtained from cast films as from single crystals grown from dilute solution.) The observed splitting of 7.5 cm^{-1} compares well with the predicted value of 8.1 cm^{-1} . Such a film, when melt-crystallized at 190°C and cooled to room temperature, shows the same 7.5 cm^{-1} splitting in the CD_2 bending doublet. The comparable spectrum of a cast film whose composition was $1(CD_2)_n$ to $2(CH_2)_n$ is shown in *Figure 14(b)*. The splitting of the CD_2 bending mode varies somewhat with the conditions under which the film is prepared (probably due to aggregation of the higher melting deuterated polyethylene); the smallest splitting that we have

observed is the $\sim 5.7 \text{ cm}^{-1}$ shown in *Figure 14(b)*. The predicted splitting for the CD_2 bending mode of the structure of *Figure 12*, in which the $(CD_2)_n$ chain is similarly surrounded by $(CH_2)_n$ chains as in our 1:2 sample, is, as we have noted, 4.1 cm^{-1} . The agreement seems good enough to permit us to conclude that in the cast film the chains are indeed folded along (110) planes. When this 1:2 cast film is melt-crystallized at 155°C , the spectrum of *Figure 14(c)* is obtained. The doublet is now replaced by a singlet, indicating that a fold structure similar to that of *Figure 13*, viz., with folds parallel to the (100) planes, has developed. It is important to note that re-casting of a film from this melt-crystallized sample brings about a return of the spectrum to that of *Figure 14(b)*, indicating that there has been no artifact accompanying the melting and that the fold geometry is indeed a property of the preparative technique. Other aspects of the fold geometry can be studied by analogous methods⁸⁰, thus demonstrating that inter-chain interactions in polymers can provide an important spectroscopic probe of crystalline morphology.

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