cently shown[30] that eigenvectors from calculations on a single chain can be used for that purpose (a listing of eigenvectors is available upon request).

Of particular importance for the study of the dynamics of disordered PVC, which will be discussed in paper II, is the fact that from the treatment of single infinite chains reported in this paper we know precisely where gaps and frequency bans occur in the whole vibrational spectrum. The search for characteristic gap or resonance modes is the main task of the work on disordered materials. This is discussed in paper II which follows.

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References and Notes

(1) Work partly presented at the Meeting of the Chemists of Croatia, Zagreb, Yugoslavia, 1973.

(2) On leave from the University of Zagreb, Faculty of Science, Zagreb, Yugoslavia.

(3) For a collection of references, see J. Dechant, "Ultrarotspektroskopische Untersuchungen an Polymeren," Akademie-Verlag, Berlin, 1972.

(4) V. Fawcett and D. A. Long, Vibrational Spectroscopy of Macromolecules, "Molecular Spectroscopy," Vol. 1 Burlington House, London, 1973.

(5) (a) T. Shimanouchi and M. Tasumi, *Bull. Chem. Soc. Jap.*, **34**, 359 (1961); (b) M. Tasumi and T. Shimanouchi, *Polym. J.*, **2**, 62 (1971).

(6) (a) Calculated frequencies obtained by C. G. Opaskar, Ph.D. Thesis, University of Michigan, 1966, are reported by J. L. Koenig and D. Druesedow, *J. Polym. Sci., Part A-2*, **17**, 1075 (1969); (b) J. E. Lynch and G. C. Summerfield, The Fourth IAEA Symposium on Neutron Inelastic Scattering, Vol. II, Copenhagen, Vienna, IAEA, 1968.

(7) C. G. Opaskar and S. Krimm, *J. Polym. Sci., Part A-2*, **7** 57 (1969).

(8) G. Zerbi, 10th Microsymposium on Conformational Structure of Polymers, Prague, 1972, *Pure Appl. Chem.*, **36**, 35 (1973).

(9) G. Zerbi, "Enrico Fermi Summer School" on Lattice Dynamics and Intermolecular Forces, 1972, Varenna, Nuovo Cimento, in press.

(10) G. Zerbi, L. Piseri, and F. Cabassi, *Mol. Phys.*, **22**, 241 (1971).

(11) G. Zerbi, 1971, *Pure Appl. Chem.*, **26**, 499 (1971).

(12) G. Zerbi, "Phonons," M. A. Nusimovici, Ed., International Conference, Rennes, Flammarion, Paris, 1972.

(13) G. Zerbi and M. Sacchi, *Macromolecules*, **6**, 692 (1973).

(14) G. Masetti, F. Cabassi, G. Morelli, and G. Zerbi, *Macromolecules*, **6**, 700 (1973).

(15) T. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).

(16) C. G. Opaskar and S. Krimm, *Spectrochim. Acta, Part A*, **23**, 2261 (1967).

(17) L. Piseri and G. Zerbi, *J. Mol. Spectrosc.*, **26**, 259 (1968).

(18) E. B. Wilson, Jr., C. J. Decius, and P. C. Cross, "Molecular Vibration," McGraw-Hill, New York, N. Y., 1955.

(19) L. Piseri, B. M. Powell, and G. Dolling, *J. Chem. Phys.*, **58**, 158 (1973).

(20) G. Gilat and L. J. Raubenheimer, *Phys. Rev.*, **144**, 390 (1966).

(21) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 17 (1963).

(22) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).

(23) R. G. Snyder and G. Zerbi, *Spectrochim. Acta, Part A*, **23**, 391 (1967).

(24) G. Zerbi, *Appl. Spectrosc. Rev.*, **2**, 1 (1969).

(25) L. Piseri and G. Zerbi, *J. Chem. Phys.*, **48**, 356 (1968).

(26) J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, **52**, 4826 (1970).

(27) H. R. Danner, G. J. Safford, H. Boutin, and M. Berger, *J. Chem. Phys.*, **40**, 1417 (1964).

(28) S. Trevino and H. Boutin, *J. Macromol. Sci., Chem.*, **1**, 723 (1967).

(29) A. V. R. Warrier and S. Krimm, *Macromolecules*, **3**, 709 (1970).

(30) J. F. Twisleton and J. W. White, *Polymer*, **13**, 40 (1972).

Dynamics of Poly(vinyl chloride). II. Model with Conformational and Configurational Disorder[1]

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ABSTRACT: In connection with the results presented in the preceding paper I, the problem of the understanding of the dynamics and the vibrational spectrum of poly(vinyl chloride) containing conformational and configurational disorder is treated on the basis of a theoretical and numerical method which has given in the past satisfactory results for other polymers. The dynamical matrices for chains containing different kinds of defects have been constructed and the density of states and a few eigenvectors corresponding to frequencies associated to particular defects have been calculated. The nature of the calculated gap and resonance modes and their dynamical coupling is discussed. A comparison with the results both from experiments and theory presented by previous authors restricted to the C–Cl stretching region (600–700 cm^{-1}) is attempted. It is felt that the theoretical approach adopted in this paper is the one which describes as close as possible the physical reality of such a polymeric material. The results of this work indicate that the complex chemical structure of PVC (conformation and stereospecificity) gives rise to a complicated and overlapping pattern in the C–Cl stretching region. Attempts for a vibrational assignment are made.

In paper I[3] the dynamics of a translationally symmetrical, *i.e.*, ordered, PVC has been treated in detail for a better interpretation of the vibrational spectrum. From several independent techniques, however, it is known that the structure of PVC is not regular since it contains geometrical (conformational) and stereochemical (configurational) (sterical structure, configuration, and tacticity are synonymous terms; analogously geometrical structure and conformation may be considered synonymous; these terms will be freely used throughout this paper) defects.[4-7] The concentration of defects may be so large that the actual structure of a sample of solid PVC approaches that of a disordered polymeric material.

The problem of the determination of the type and concentration of disorder in PVC has been tackled by many authors in the past few years using different physicochemical techniques. The configurational impurities have been quite successfully studied and their concentration determined by nmr measurements.[4-6] To our knowledge the dependency of nmr spectra of PVC on conformational disorder has not been normally considered because of the intrinsic limitation of nmr techniques for this particular structural feature. In principle, instead, the vibrational spectrum should provide information both on conformation and/or configuration (as well as chemical structure). A few groups of investigators (for a sample of previous works see

Table I
Experimental Frequencies (cm^{-1}) and Proposed Interpretation as Reported in the Literature for PVC in the C–Cl Stretching Region

Tasumi *et al.*[8,9]	Krimm, *et al.*[10]			Pohl, *et al.*[11]		Opaskar and Krimm[18] [c]	
603 (B_1)	601	TTTT	s[a] (B_1)	603 (B_1)	TTTT	606, 615, 618, 638	TTTGTT
615 synd part	612	TTTT	s	613	TT	616, 619, 692	$TTTG^+TT$
638 (A_1)	622	$(TG)(TT)(G^+T)$	i[b]	624	$TGTTG^+T$	617, 623, 687	TTG^+G^+TT
680 isotactic	635	$(TG)(TG^+)(TG)$	i	636		615, 638, 730	$TTTG^+G^+T$
690 part	639	TTTT	s (A_1)	647 (A_1)	TTTT		
	685	(TG)(TG)(TG)	i	677	TGGT		
	693	$(TTG^+G^+TTTG^+)$	s	696	TGTG		

[a] s = syndiotactic part. [b] i = isotactic part. [c] Calculated from short chain models.

ref 8 to 12, see also ref 7) have developed their own experimental or theoretical criteria and proposed several interpretations of the observed vibrational spectrum of PVC. These proposals do not always lead to mutually satisfactory conclusions and we feel that a unique solution of the problem has not yet been reached.

We thought to contribute to the clarification of the problem by applying a new method of analysis which has already provided seemingly satisfactory results for other polymers.[13-16] This method basically treats theoretically and numerically the dynamical problem of impure or disordered polymer chain and leads to the so called "island analysis" of the experimental spectrum. The "island analysis" presented here includes for the first time the stereochemical disorder.

In this paper we mainly discuss the C–Cl stretching region of the spectrum (700–600 cm^{-1}), which has received great attention in the past by many authors since the C–Cl stretching modes turned out to be sensitive to the local environment of the polymer chain;[17] the other regions of the spectrum will be discussed in subsequent papers.

It is shown in this paper that the "island analysis" completes the knowledge of the dynamics of PVC and the related structural implications. A comparison with the results reached by previous authors will be presented.

As the result of extensive work by several investigators, the present knowledge of the experimental spectrum of PVC and the consequent interpretation is the following: mostly syndiotactic and highly crystalline PVC is obtained with a polymerization in urea complex. As already discussed in paper I, the two C–Cl stretching $k = 0$ phonon frequencies of syndiotactic PVC occur approximately at 604 and 640 cm^{-1}. Physical treatments (such as temperature or pressure) modify the spectrum and give rise to a few new overlapping bands whose position is variously described by different authors mainly depending on the resolving power of the spectrometer or on the graphical method of resolution. This also happens if the same physical treatments are performed on PVC samples obtained from different polymerization conditions.

These different polymerization conditions yield a polymer which contains stereochemical defects clearly revealed by nmr measurements.[4-6] In such a case an additional absorption is observed in the infrared centered at ~690 cm^{-1}. Again, additional peaks are variously reported by different authors. The locations of the bands reported by a few authors are collected in Table I (the literature on PVC is very rich because the polymer has a wide application; in Table I we collect the data of a few most representative authors in this field) together with the proposed interpretation.

Theory

In paper I the translational invariance of the polymer chain allowed the calculation of dispersion curves and the related density of states by the calculation of the appropriate phonon coordinates and the diagoalization of the k dependent dynamical matrix. When the translational invariance is removed by the introduction of some sort of defect the standard methods of lattice dynamics fail and one has to turn to special analytical or numerical methods. The principles of such analytical[19,20] or numerical[21] methods have already been presented and their applicability to the case of impure or disordered polymers is at present a matter of active consideration in a few laboratories.[13-16,22-25] On the basis of our experience so far, we think that the numerical approach is much more applicable when one wishes: (i) to treat realistic models of polymeric materials, (ii) to handle a flexible method which enables one quickly and easily to construct and analyze models with any desired type, concentration, and mixture of physically conceivable defects.

The presently available analytical treatments, mathematically very elegant but algebraically very cumbersome, are only applicable to very simplified models and are inapplicable to realistic models of polymers such as those we wish to treat in our work, especially when highly disordered systems must be considered.

The basic concept of the numerical method is to account for all the degrees of freedom of a very large and finite section of the crystal (in one or three dimensions) by solving the dynamical matrix without considering each single eigenvalue but their distribution. This can be achieved by the application of the so called negative eigenvalue theorem (NET) which provides directly the density of states.[21,26] Algorithms are also available[25,27] for the calculation of approximate eigenvectors corresponding to approximate eigenvalues chosen in $g(\omega)$. (The authors of this work wish to thank Dr. M. Gussoni for letting them use her computing programs.) By suitable increase of the resolving power of our computer experiments using NET it is possible to obtain the single eigenvalue and the corresponding precise eigenvector.[25]

The main effort consists in setting up the dynamical matrix of the long finite chain in a convenient and practical way such as to allow a certain freedom in the choice of the models during the work. In this paper we present a more general modification of the algorithms previously reported by Tasumi and Zerbi[13] for mass defects and by Piseri and Zerbi[14,28] for conformational defects of a chain of CX_2 repeat units (X = H for polyethylene, X = F for poly(tetrafluoroethylene). We consider here the problem of a chain which may contain simultaneously conformational, configurational, and mass defects. The repeating monomer unit may have a more complicated chemical structure.

The dynamical matrix

$$\mathbf{D} = \mathbf{M}^{-1/2}\tilde{\mathbf{B}}\mathbf{F}_R\mathbf{B}\mathbf{M}^{-1/2} \tag{1}$$

which generates $g(\omega)$ by application of NET requires the construction of the **B** matrix (see paper I eq 2). Contrary to the treatment of paper I, we require in this approach the **B** matrix of the whole long finite polymer chain. The size of

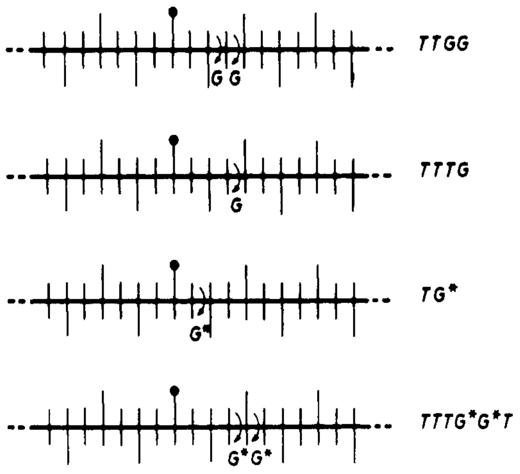

Figure 1. Conformational defects introduced in an otherwise all trans syndiotactic PVC chain. The dots refer to the starting point of the conformational sequence considered as defect.

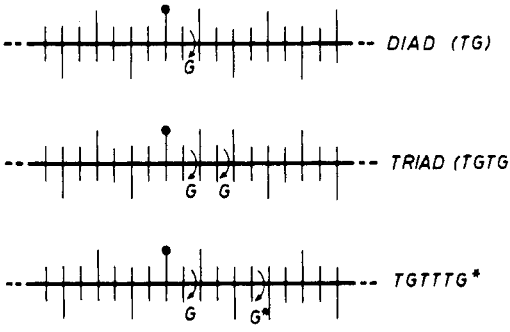

Figure 2. Configurational defects introduced in an otherwise syndiotactic PVC chain. The conformational changes required by the introduction of a configurational defect are also indicated.

B, as well as that of the derived dynamical matrix (of the order of ~10^3 to ~10^4), is very large. The construction of the **B** matrix requires the knowledge of the Cartesian coordinates of all atoms of the chain.

The Cartesian coordinates of all atoms can be generated by the following expression which we apply here directly to the case of PVC but which can be easily modified to account for other chemical structures. Let i label the chemical unit in the polymer chain. The "chemical unit" considered in this treatment is neither the chemical monomer unit nor the crystallographic repeat unit. For "chemical unit" we mean the smallest set of atoms which can generate the whole chain by proper computer manipulation as is shown in what follows. The index i labels also the corresponding carbon atom; α (equal to 2 and 3 for PVC) labels the atoms directly bonded to the carbons. Atoms 2 and 3 may be H or Cl in the case of PVC. In this work we arbitrarily take atoms 2 and 3 in the first unit to be hydrogens

$$X_i^1 = X_{i-1}^1 + dt_{i-1}$$

$$X_i^\alpha = \left\{ \prod_{n=1,\, i-1} \Gamma_n X_1^\alpha + X_i^1 \right\} f_i^\alpha \qquad \alpha = 2,3 \qquad (2)$$

$$t_i = \prod_{n=1,\, i-1} \Gamma_n t_1$$

where X_i^1 are the coordinates of the ith carbon atom, $X_1^1 = (0,0,0)$ are the coordinates of the first carbon atom which lies at the origin of the coordinate system (for the orientation of the coordinate system with respect to the chain see ref 14); d is the C–C bond length, t_i is the unit vector along the ith C–C bond, $t_1 = (1,0,0)$; X_1^α are the Cartesian coordinates of the atoms α in the first unit which must be known at the beginning of the calculation. Γ_n is the rotation matrix (see ref 14) and f_i^α is a factor which takes into account the fact that the αth atom in the ith unit is chlorine or hydrogen: $f_i^\alpha = 1$ if α refers to hydrogen; f_i^α = ratio of C–Cl to C–H bond lengths if α refers to chlorine.

The **B, F,** and **M** matrices of eq 1 and the derived dynamical matrix are constructed in partitioned form since each block accounts for a particular chemical or structural feature of the chain. The dynamical matrix is written in block form

$$\mathbf{D} = \left| \begin{array}{lllllll} D_{i-1}^0 & D_{i-1}^1 & D_{i-1}^2 & D_{i-1}^3 & D_{i-1}^4 & & \\ & D_i^0 & D_i^1 & D_i^2 & D_i^3 & D_i^4 & \\ & & D_{i+1}^0 & D_{i+1}^1 & D_{i+1}^2 & D_{i+1}^3 & D_{i+1}^4 \\ & & & & & & \\ \text{symm} & & & & & & \end{array} \right| \qquad (3)$$

where

$$D_i^0 = M_i^{-1/2}\{\tilde{B}_{i-2}^2 F_{i-2}^0 B_{i-2}^2 + \tilde{B}_{i-1}^1 F_{i-1}^0 B_{i-1}^1 + \tilde{B}_i^0 F_i^0 B_i^0 + \tilde{B}_{i+1}^{-1} F_{i+1}^0 B_{i+1}^{-1} + \tilde{B}_{i-2}^2 F_{i-2} B_{i-1}^1 + \tilde{B}_{i-1}^1 \tilde{F}_{i-2} B_{i-2}^2 + \tilde{B}_{i-1}^1 F_{i-1} B_i^0 + \tilde{B}_i^0 \tilde{F}_{i-1} B_{i-1}^1 + \tilde{B}_i^0 F_i B_{i+1}^{-1} + \tilde{B}_{i+1}^{-1} \tilde{F}_i B_i^0\} M_i^{-1/2}$$

$$D_i^1 = M_i^{-1/2}\{\tilde{B}_{i-2}^2 F_{i-2} B_{i-1}^2 + \tilde{B}_{i-1}^1 F_{i-1}^0 B_{i-1}^2 + \tilde{B}_{i-1}^1 F_{i-1} B_i^1 + \tilde{B}_i^0 \tilde{F}_{i-1} B_{i-1}^2 + \tilde{B}_i^0 F_i^0 B_i^1 + \tilde{B}_i^0 F_i B_{i+1}^0 + \tilde{B}_{i+1}^{-1} \tilde{F}_i B_i^1 + \tilde{B}_{i+1}^{-1} F_{i+1}^0 B_{i+1}^0 + B_{i+1}^{-1} F_{i+1} B_{i+2}^{-1}\} M_{i+1}^{-1/2}$$

$$D_i^2 = M_i^{-1/2}\{\tilde{B}_{i-1}^1 F_{i-1} B_i^2 + \tilde{B}_i^0 F_i^0 B_i^2 + \tilde{B}_i^0 F_i B_{i+1}^1 + B_{i+1}^{-1} \tilde{F}_i B_i^2 + \tilde{B}_{i+1}^{-1} F_{i+1}^0 B_{i+1}^1 + \tilde{B}_{i+1}^{-1} F_{i+1} B_{i+2}^0\} M_{i+2}^{-1/2}$$

$$D_i^3 = M_i^{-1/2}\{\tilde{B}_i^0 F_i B_{i+1}^2 + \tilde{B}_{i+1}^{-1} F_{i+1}^0 \tilde{B}_{i+1}^2\} M_{i+3}^{-1/2}$$

$$D_i^4 = M_i^{-1/2}\{\tilde{B}_{i+1}^{-1} F_{i+1} B_{i+2}^2\} M_{i+4}^{-1/2} \qquad (4)$$

All the quantities in the expressions above which depend upon the index i are determined in advance by several series of codes which are given as input parameters. The flexibility of the calculation lies in the possibility of choosing the desired sets of codes which tell the machine the structure of the systems one wishes to study.

Models and Calculations

Since we take for granted, as discussed at the beginning, that an actual sample of PVC contains geometrical as well as configurational defects at nonnegligible concentrations, we decided to study the dynamics of pure PVC (*i.e.*, with small concentration or noninteractive defects) and disordered PVC (*i.e.*, with large concentration of supposedly interacting defects). In order to disentangle the various contributions of defects on the dynamical quantities (*i.e.*, frequencies and atomic displacements) we have considered the following models.

(i) Chains of PVC containing only conformational isolated or supposedly interacting defects. The following conformational defects were considered (Figure 1): GG, G^+G^+, TTTG, $TTTG^+$. These are the conformational sequences generally accepted in the literature.[18]

(ii) Chains of PVC containing isolated or supposedly interacting configurational defects. The introduction of con-

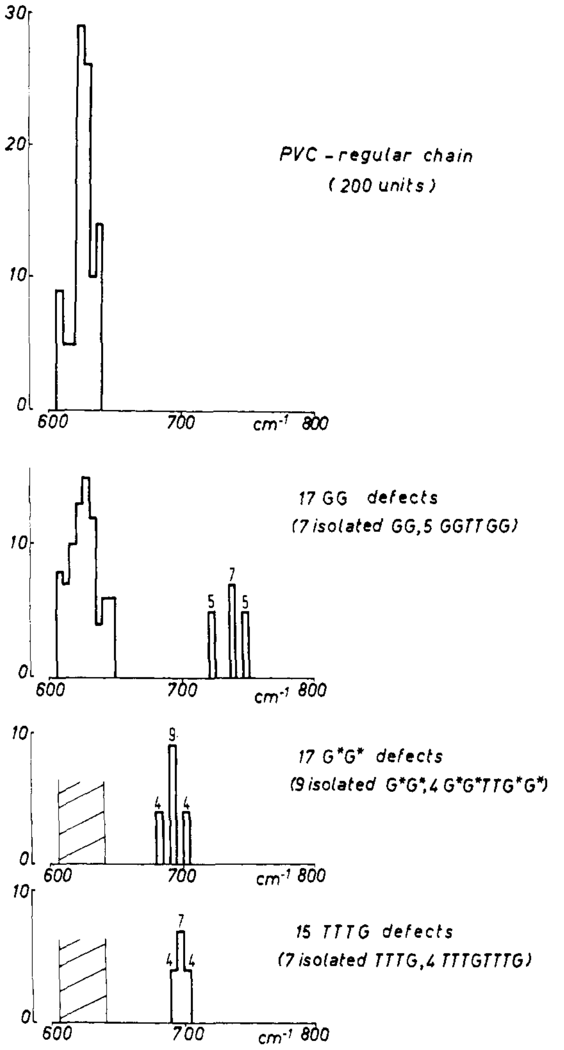

Figure 3. Comparison between the density of states in the C–Cl stretching region of a conformationally and configurationally regular syndiotactic PVC chain with that of conformationally impure chains. Notice the correspondence between the population of defects and the number of gap frequencies indicated in the histograms.

figurational defects implies a certain conformational change determined by steric factors. The local conformation at the defect (Figure 2) is either that of the iso- or syndiotactic ideal chain. As discussed in paper I, we have adopted the force field by Opaskar and Krimm[29] (hereafter referred to as OK) which contains all the necessary constants required by the geometry and configuration of the models considered. For the sake of completeness we have also carried out the calculations with the force field refined on PVC (see paper I). A comparison and discussion of the results will be given later in this paper.

In the calculation of the density of states generally chains of 200 "chemical units" (as defined earlier) were adopted. Shorter chains were also studied. Eigenvectors were calculated on chains of 50 "chemical units" since the answers from the longer chain turn out to be the same as those obtained from a chain of 50 units. The resolution of the calculated $g(\omega)$ histograms is 5 cm^{-1}. For the calculation of eigenvectors the resolution of our computer experiments has been increased up to the order of 10^{-2} cm^{-1} when necessary.

Computer experiments were carried out with a UNIVAC 1106 computer; the time required for the construction of a dynamical matrix for a chain of 200 "chemical units" is of the order of 3 min. The density of states over 100 cm^{-1} with a mesh of 5 cm^{-1} and from a dynamical matrix with 30 codiagonals requires a time of the order of 10 min. The calculation time of a single eigenvector is of the order of 2.5 min. Most of the calculations reported here refer to the C–Cl stretching region from ~600 to ~700 cm^{-1}. Other portions of the spectrum have been and are being analyzed; more work is presently in progress.

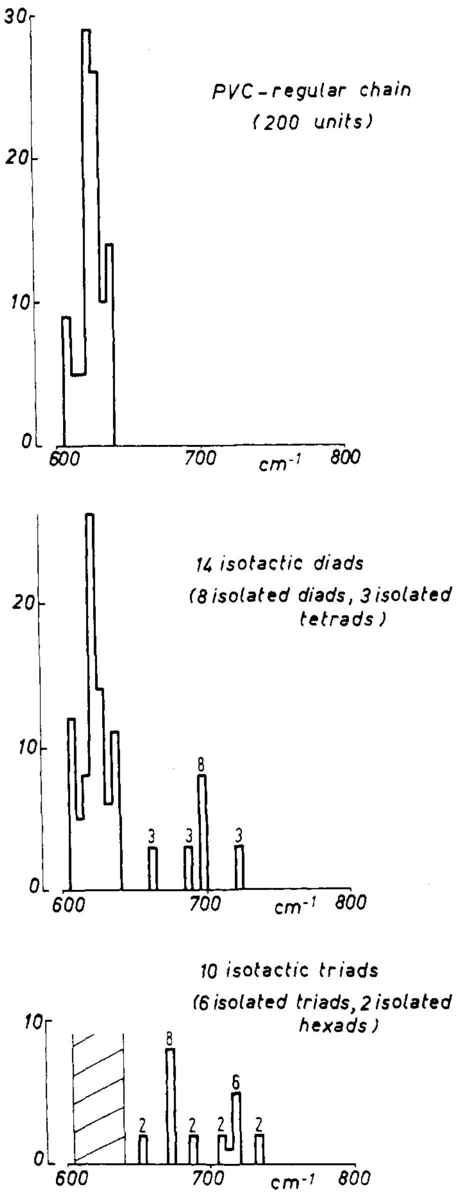

Figure 4. Comparison between the density of states in the C–Cl stretching region of a conformationally and configurationally regular syndiotactic PVC chain with that of configurationally impure chains. Notice the correspondence of the population of defects and the number of gap frequencies indicated in the histograms.

Results

From paper I the phonon dispersion curves for the various ideal translationally invariant and infinite PVC chains are known together with the derived histogram of the density of vibrational states. $k = 0$ phonon frequencies, atomic displacements, band cut-offs, and energy gaps are then established. The density of states from a chain of 200 "chemical units" with perfect conformational and configurational structure obtained from NET turns out to be identical with that calculated for the infinite model. The knowledge of $\omega(k)$ from the infinite model is essential for the assignment of the peaks of $g(\omega)$ for infinite as well as for finite models.

Table II
Gap Frequencies in the C–Cl Stretching Region for Various Isolated or Interacting Conformational and Configurational Defects in a Trans Syndiotactic Host Lattice

Type of defect	Position of gap frequencies (cm^{-1}) in histogram of density of states[a]
	Conformation
GG	735–740
TTTG	695–700
G^+G^-	690–695
$TTTG^+$	650–655
GGTTGG	720–725; 745–750
$G^+G^+TTG^+G^+$	680–685; 700–705
TTTGTTTG	690–695; 700–705
$TTTG^+TTTG^+$	660–665
	Isoconfiguration
Diad	695–700
Triad	670–675; 715–720
Tetrad	660–665; 685–690; 720–725
Hexad	650–655; 670–675; 685–690 705–710; 730–735

[a] The histogram is calculated with a 5-cm^{-1} mesh.

It is well known that the introduction of defects in an otherwise perfect host lattice may give rise to out-of-band, gap, and resonance modes.[30] For common polymeric materials we expect only gap or resonance modes. In our calculations we direct our attention, when possible, to gap and resonance modes generated by the geometrical or configurational defects discussed above. Furthermore from eigenvectors attempts are made to determine the corresponding shape of the normal modes.

When conformational (Figure 3) or configurational (Figure 4) defects are introduced in the chain in the C–Cl stretching region, clear gap frequencies are generated. Correspondingly, the shape of the density of states in the band is modified, thus showing that resonance modes are generated. When the mutual distance of the defects along the chain is shortened, a coupling between gap modes takes place giving rise to frequency splittings which are a function of the distance. Such a coupling takes place, however, only when defects are very close and sometimes adjacent. In the frequency range considered, gap frequencies from conformational defects occur quite often at values close to those obtained from configurational defects. A very complex spectral pattern is then obtained (see Table II).

The nature of gap and resonance modes has also been verified by calculation of the corresponding eigenvectors. The fact that each of the characteristic gap frequencies occurs in an energy region free from neighboring modes allows one to improve the resolution of the computer experiments to a very narrow value ($\sim 10^{-2}$ cm^{-1}) in order to have an accurate calculation of the corresponding atomic displacements from eigenvectors. Because of the difficulty of visualization of the atomic displacements in Cartesian coordinates in three dimensions for a kinked and coiled chain, we report in Figures 5–7 the vibrational amplitudes expressed as total displacements. The main purpose of these drawings is to derive some information concerning the localization in space of the gap modes. The modes corresponding to gap frequencies are clearly localized in space since the vibrational amplitudes decay very rapidly along the chain, the maximum amplitude being centered at the defect. The number of "chemical units" involved in these gap modes is, however, considerable; the vibrational modes extend throughout approximately 7 to 12 "chemical units." The fact that several "chemical units" move in a gap mode determines and justifies the dynamical coupling calculated when two defects approach each other along the chain. Such a coupling is clearly revealed in the calculation of eigenvalues as well as from eigenvectors. The preliminary results of the calculation in sections of the vibrational spectrum other than C–Cl stretching reveal additional features (Figure 8) which have not been observed in the 600–700-cm^{-1} region. Even though more work is being carried out by us for these regions of the spectrum, examination of the results already obtained indicates that gap and resonance frequencies may also be found for other normal modes of the systems considered. An additional feature is that resonance frequencies are grouped together and give rise to sharp peaks in density of states within the frequency band. Total displacement amplitudes for one CH_2 localized and one CH_2 resonant rocking modes are shown in Figures 9 and 10. The possible assignment of these $g(\omega)$ peaks will be the subject of a further investigation.

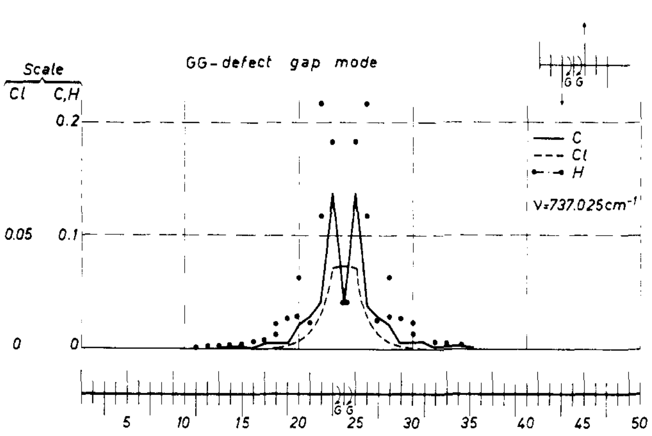

Figure 5. Gap mode (described in terms of total displacements of atoms) for a GG defect in a syndiotactic PVC chain.

Discussion

Our interpretation of the vibrational spectrum of impure or disordered PVC is first based on the understanding of its dynamics. Comparison with the actual experimental spectrum is a second step in the analysis. We feel that the method we have adopted is the one which should approach as closely as possible the physical and chemical reality of such a substance. Indeed, when the vibrations of a long chain are thus considered, local or cooperative motions as well as their mutual interactions, if any, should be properly accounted for.

All the responsibility of the results is taken by the force field which we have adopted in the calculations. For this reason we have carried out our studies with a parallel comparison of the results obtained with the use of the force field from OK and of the force field refined on PVC itself, as already discussed (see paper I). It turns out that gap frequencies shift and split by a different amount with the two force fields (Figure 11); however, the overall description of the phenomenon is qualitatively the same. We prefer to discuss particularly the results obtained from the OK force field because comparison can be made with the results already available in the literature. Furthermore, the few experimental data on which we can base our analysis seem to favor again the force field by OK.

Part of the results from our work can be compared only with those by Opaskar and Krimm[18] derived from short chain model compounds. These authors limited their calculations to isolated conformational defects. The results from the present work are in fair agreement with their calculated frequencies even if we find slightly higher values for gap frequencies (Figure 11). OK also report frequencies which in our analysis fall in the C–Cl stretching band frequencies.

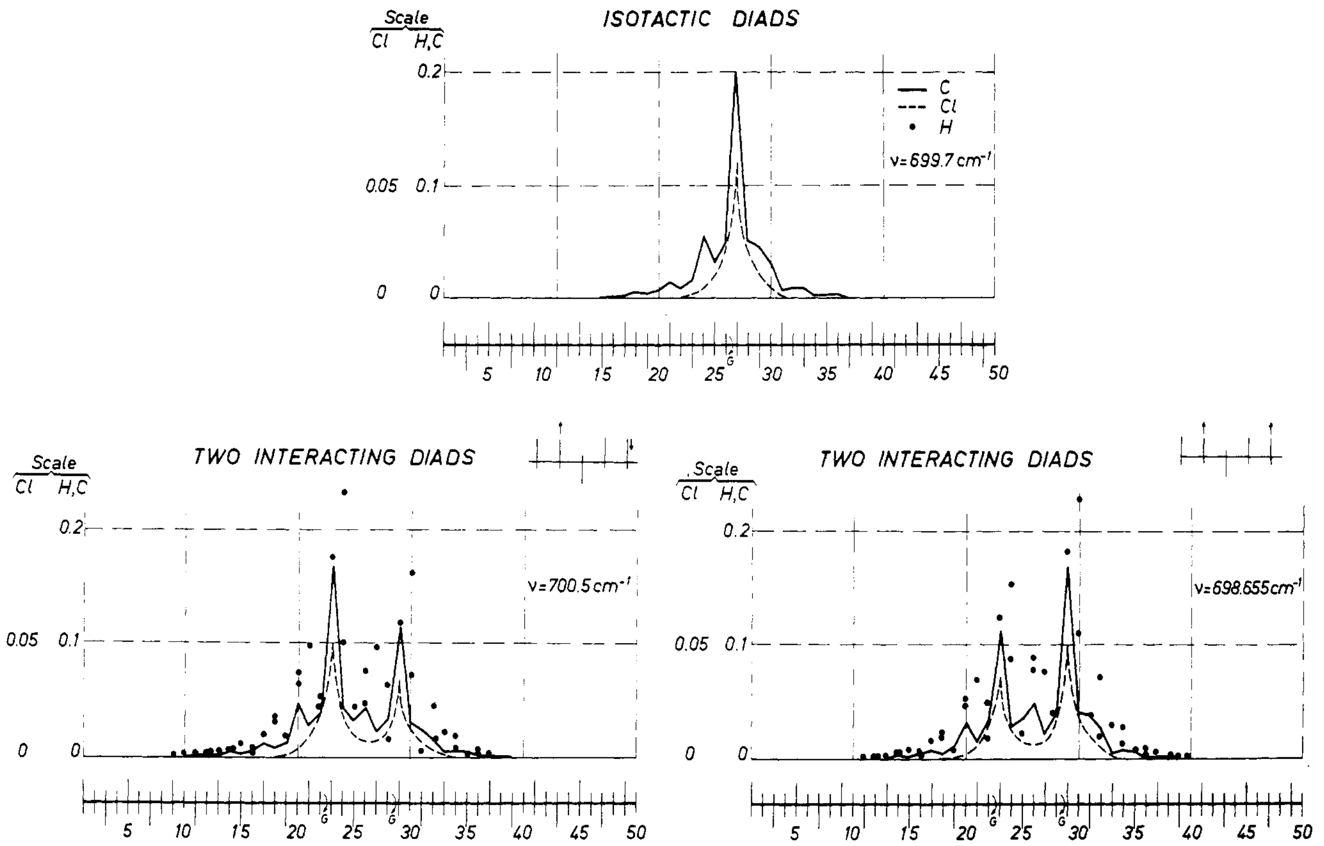

Figure 6. Gap modes (described in terms of total displacements of atoms) for isotactic isolated diads and two interacting diads in a syndiotactic PVC chain.

No definite statement can be made on the location of those frequencies which occur in-band since the modes are dynamically coupled with the phonons of the host lattice. Such a coupling cannot be revealed from model compounds. From our study on long chains, the density of states of impure or disordered PVC in the band region (~600–650 cm^{-1}) is modified but there is no clear indication of a grouping of frequencies which can be taken as an indication of existence of pseudolocalized modes.

Additional information is obtained in the present work as to the coupling between conformational defects which have not been treated by OK because of the shortness of the model compounds considered. The information on configurational defects and their vibrational interactions reported here to our knowledge have been never treated before.

The comparison of the theoretical results with the experimental spectrum can be carried out on the basis of only frequency fitting or taking into account the intensity associated with each normal mode by proper dipole or polarizability weighting of the calculated density of states. The problem of the calculation of transition moment weighted density of states is far from being solved and is hindered by the same difficulties which vibrational spectroscopists were faced with in dealing with the study of small molecules.[31,32] The lack of *a priori* knowledge of charge distributions and their fluctuations during vibrations has hindered the complete understanding of the vibrational spectrum of even small molecules.[33,34] Several attempts have been and are being made to improve our knowledge in this field.[25,35–37] Even more difficult is the calculation of the polarizability changes[31] associated with Raman active normal modes.

We then decided to compare the dipole unweighted density of states with the experimental infrared spectrum. As already discussed, this is the same principle on which the vibrational analysis of small molecules or polymers has been so far carried out.[24] We mainly look at frequency fitting, keeping in mind the logically most probable structure of the polymer chain dictated by some sort of statistics which may also be indicated by some independent physicochemical measurements (*e.g.*, nmr spectra). For the systems we are considering with our approach we expect to find, possibly, in the infrared spectrum absorptions resulting from: (i) spectroscopically active $k = 0$ modes arising from infinite or long sections of a translationally invariant chain; (ii) gap modes from isolated or interacting configurational and conformational defects; (iii) activation of the density of states of band modes of the perfect host lattice due to the breakdown of selection rules because of the lack of translational symmetry; (iv) activation of characteristic in-band pseudolocalized motions. The infrared activity of gap modes or the mapping of the density of states may be strongly dependent on local symmetry on the site where the defect is located. For PVC the highest local symmetry can be reached with a GG conformational defect, which gives rise to a local C_2 symmetry. For such a point group all modes are, however, infrared active. It is then expected that practically all modes are activated in the infrared even if to a different extent. When the concentration of defects becomes large in the vibrational spectrum of the corresponding disordered material all the previous phenomena may become very complicated and the spectrum obtained will be the result of very complicated dynamics. This situation is represented in Figure 12, in which the density of states of configurationally very disordered PVC is calculated and compared with the experimental spectrum in the C–Cl stretching region. The calculated spectral behavior of gap frequencies from conformational and configurational defects is also given at the top of Figure 12 for the sake of comparison.

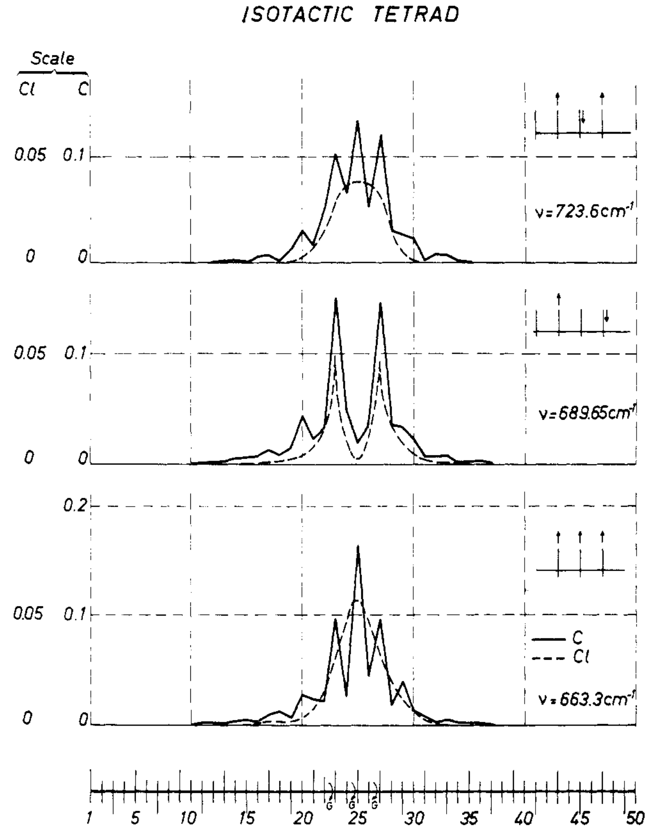

Figure 7. Gap mode (described in terms of total displacements of atoms) for isotactic tetrad in a syndiotactic PVC chain.

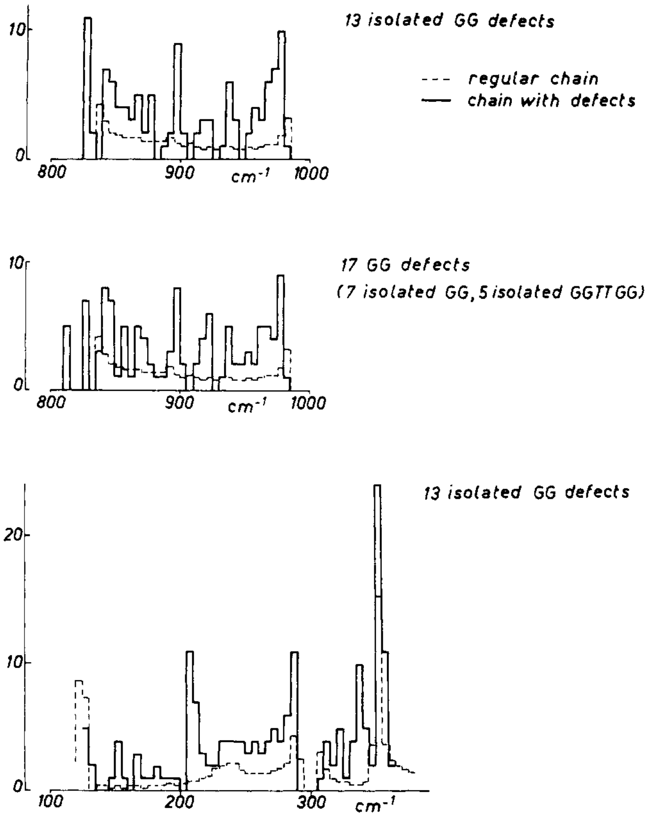

Figure 8. Examples of the density of states of the conformationally impure syndiotactic PVC chain in two regions of the vibrational spectrum other than the C–Cl stretching. The density of states of the perfect chain (shown with dotted lines) is obtained from the translationally invariant case by the extrapolation method (paper I) and is not normalized to $g(\omega)$ from NET.

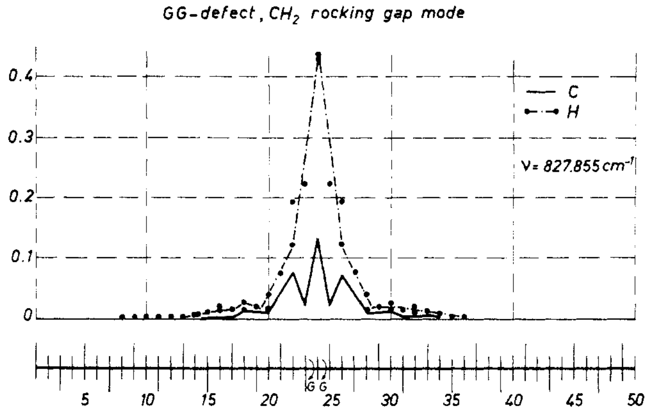

Figure 9. Example of a CH_2 rocking gap mode for GG defect in a syndiotactic PVC chain (total displacements of atoms are given).

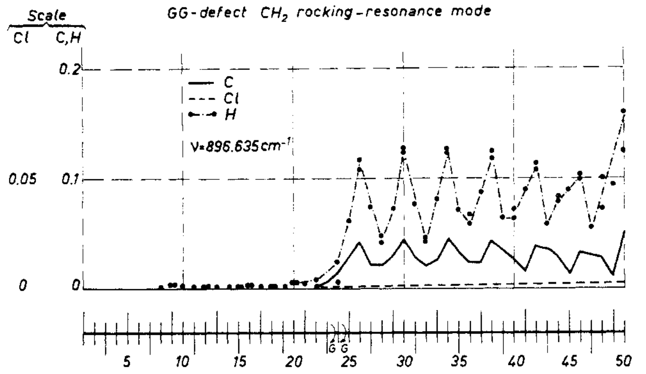

Figure 10. Example of CH_2 rocking resonance mode for GG defect in a syndiotactic PVC chain (total displacements of atoms are given).

Krimm, *et al.*, have experimentally shown[10,38] that the introduction of conformational disorder in PVC gives rise to two bands at 693 and 635 cm^{-1}. The 693-cm^{-1} peak, according to our calculation, can certainly be associated with gap modes arising from TTTG and/or G^+G^+ defects. The choice of these two defects or whether they are isolated or interacting cannot be decided from the examination of only this portion of the spectrum. The 635-cm^{-1} band cannot be associated with certainty with such defects since no pseudolocalized in-band modes have been found but instead a modification of the whole distribution of band modes has been calculated. (The possibility of selective enhancement of intensity of a few modes by suitable dipole weighting can neither be refused nor, on the other hand, calculated.)

Several groups of authors have shown[7] that the introduction of configurational defects in syndiotactic PVC is accompanied by a broad absorption in infrared and scattering in the Raman centered at ~690 cm^{-1}. Additional shoulders have been reported differently by a few authors. From our calculations the peak at 690 cm^{-1} can be associated with isolated isotactic diads.

The fact that diads do occur in large concentration in a stereochemically disordered chain of normal PVC is confirmed by nmr measurements which indicate that they amount to almost ~50% of the stereochemical impurities.[4-6] On the other hand, a large amount of infrared work in the past 10 years has justified the observed vibrational spectrum in terms of a large amount of stereochemical irregularities.[7]

Our calculations show that G^+G^+ and TTTG conformational irregularities as well as diads of stereochemical irregularities absorb in the infrared in the same frequency range. It is practically impossible to disentangle the contri-

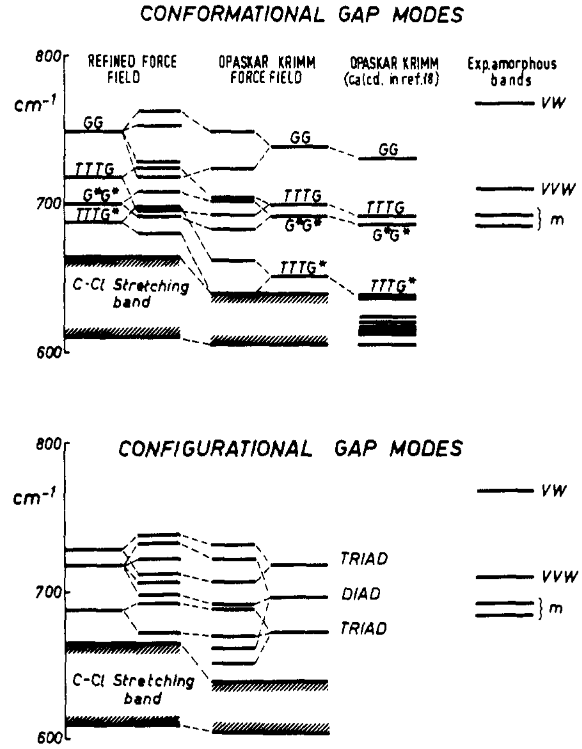

Figure 11. Graphical summary of the C–Cl stretching gap frequencies from disordered PVC obtained from two force fields and comparison with calculations from short chain models. The so called experimental amorphous bands are included.

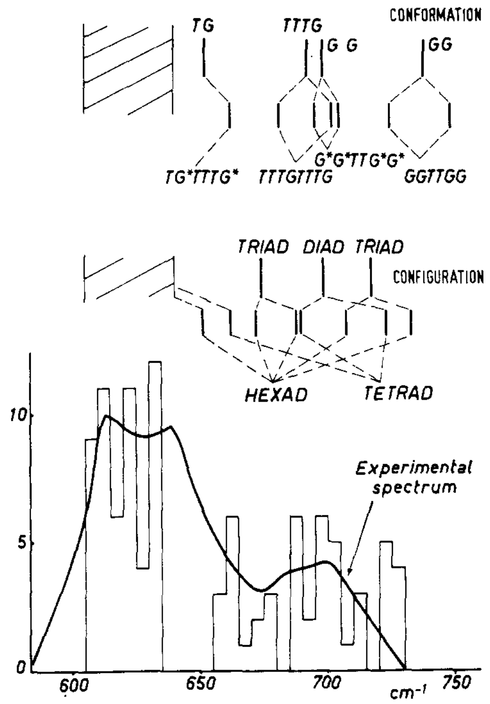

Figure 12. Density of vibrational states for a realistic model of configurationally disordered PVC (Bernoullian parameter P_m = 0.47 as in ref 5). Comparison with the experimental spectrum. At the top of the figure a schematic representation of calculated gap frequencies is given.

butions of the two types of irregularities and their relative concentration by only looking in the frequency range discussed in this paper. We feel, however, that it is more likely and logical to assume that the stereochemical irregularities mainly contribute to the spectrum in this frequency range. Such a viewpoint has also been taken by Stokr, *et al.*,[12] who report quantitative data in agreement with nmr. On the basis of such an assumption it can also be proposed that the broad shoulder centered at ~685 cm^{-1} may arise from two interacting diads (*i.e.*, tetrads) which are likely to occur in such a disordered material.

The assignment must be accepted with caution since our calculations, like those of all other authors, have been performed on geometries classically considered in a structural analysis of unstrained molecules. In a real polymeric solid material geometries may be slightly changed because of internal strain due to the structural irregularities of the substance. The calculated frequencies may depend to a different extent upon geometry changes. Such a dependence may result in a broadening of each absorption band centered around the frequency of the most stable geometry predicted by classical conformational analysis. The observed infrared spectrum is broad and may thus be the envelope of the absorptions from configurational and conformational irregularities whose contributions also depend on their population and distribution throughout the polymer chain.

Conclusions

From this work it is shown that the study of the dynamics of conformationally and configurationally disordered PVC is practically feasible by the numerical method which leads to the "island analysis," which consists in associating density of states peaks with particular segments or islands of defects in an otherwise regular host lattice. It has been shown that clear gap frequencies and gap modes characteristic of a given structural defect occur in the C–Cl stretching region. In other regions of the spectrum, which wait for a more complete treatment, analogous phenomena are predicted. Vibrational interactions between defects are clearly predicted by calculations. All computations have been based on the most reliable force field presently available.

The experimental spectrum does not give any indication contrary to the theoretical predictions in the frequency range from 700 to 600 cm^{-1} and allows a fitting between calculated and observed peaks in terms of conformational or configurational defects. The assignment proposed is not in disagreement with those suggested by previous authors on the basis of short chain models. However, we feel that our method presents a more complete view of the dynamics of such a structurally disordered polymer. Just for this reason our work shows that the geometrical complexity of PVC is reflected by a complex and overlapping pattern in the calculated and experimental spectrum. The assignment of the observed peaks can then be taken only as a suggestion dictated by some effort or rationalization. We feel that a deeper insight into the problem of the microstructure of PVC derived from the vibrational spectrum could eventually be obtained if a parallel analysis is extended to other regions of the spectrum in addition to that of the C–Cl stretchings.

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References and Notes

(1) Work partly presented at the 11th Congress on Molecular Spectroscopy, Tallinn, USSR, 1973.
(2) On leave from the University of Zagreb, Faculty of Science, Zagreb, Yugoslavia.
(3) A. Rubčić and G. Zerbi, *Macromolecules*, 7, 000 (1974).
(4) (a) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Phys. Chem.*, 71, 312 (1967); (b) L. Cavalli, G. C. Borsini, G. Carraro, and G. Confalonieri, *J. Polym. Sci., Part A-1*, 8, 801 (1970).

(5) (a) C. J. Corman, A. R. Tarpley, and G. H. Goldstein, *Macromolecules*, **4**, 445 (1971); (b) Y. Inoue, I. Ando, and A. Nishioka, *Polym. J.*, **3**, 246 (1972).

(6) V. D. Mochel, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C8(2)**, 289 (1972).

(7) For a collection of references regarding the results from vibrational spectroscopy, see J. Dechant, "Ultrarotspektroskopische Untersuchungen an Polymeren," Akademie-Verlag, Berlin, 1972.

(8) M. Tasumi and T. Shimanouchi, *Spectrochim. Acta*, **17**, 731 (1961).

(9) T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965).

(10) S. Krimm, U. L. Folt, J. J. Shipman, and A. R. Berens, *Polym. Lett.*, **2**, 1009 (1964).

(11) H. U. Pohl and D. O. Hummel, *Makromol. Chem.*, **113**, 203 (1968).

(12) J. Stokr, B. Schneider, M. Kolinsky, M. Ryska, and D. Jin, *J. Polym. Sci., Part A-1*, **5**, 2013 (1967).

(13) M. Tasumi and G. Zerbi, *J. Chem. Phys.*, **18**, 3813 (1968).

(14) G. Zerbi, L. Piseri, and F. Cabassi, *Mol. Phys.*, **22**, 241 (1971).

(15) G. Zerbi and M. Sacchi, *Macromolecules*, **6**, 692 (1973).

(16) G. Masetti, F. Cabassi, G. Morelli, and G. Zerbi, *Macromolecules*, **6**, 700 (1973).

(17) S. Krimm, *J. Polym. Sci., Part C*, **7**, 3 (1964).

(18) C. G. Opaskar and S. Krimm, *J. Polym. Sci., Part A-2*, **7**, 57 (1969).

(19) K. Hölzl and C. Schmid, *J. Polym. Sci.*, **10**, 1853 (1972).

(20) C. Schmid and K. Hölzl, *J. Polym. Sci.*, **10**, 1881 (1972).

(21) P. Dean, *Rev. Mod. Phys.*, **44**, 127 (1972).

(22) C. Schmid and K. Hölzl, *J. Phys. C, Solid State Phys.*, **5**, L 185 (1972).

(23) K. Hölzl and C. Schmid, *J. Chem. Phys.*, **58**, 5173 (1973).

(24) G. Zerbi, 1972, 10th Microsymposium on Conformational Structure of Polymers, Prague, *Pure Appl. Chem.*, **36**, 35 (1973).

(25) G. Zerbi, "Enrico Fermi Summer School" on Lattice Dynamics and Intermolecular Forces, 1972, Varenna, Nuovo Cimento, in press.

(26) H. Jeffreys and B. S. Jeffreys, "Method of Mathematical Physics," Cambridge University Press, Cambridge, England, 1950, p 140.

(27) J. H. Wilkinson, "The Algebraic Eigenvalues Problem," Clarendon Press, Oxford, 1965.

(28) L. Piseri and G. Zerbi, *Chem. Phys. Lett.*, **2**, 127 (1968).

(29) C. G. Opaskar and S. Krimm, *Spectrochim. Acta, Part A*, **23**, 2261 (1967).

(30) L. Genzel, "Optical Properties of Solids," S. Nudelman and S. S. Mitra, Ed., Plenum Press, New York, N. Y., 1962.

(31) M. V. Vohlkenstein, L. A. Gribov, M. A. Eliashewich, and B. J. Stepanov, "Kolebaniya Molecul. Isdatelstwo Nauka," Moscow, 1972.

(32) G. A. Segal and M. C. Klein, *J. Chem. Phys.*, **47**, 4236 (1967).

(33) R. Bruns and W. B. Person, *J. Chem. Phys.*, **55**, 5401 (1971).

(34) L. M. Sverdlov and N. I. Prokofeva, *Opt. Spectrosc. (USSR)*, **15**, 227 (1963).

(35) M. Gussoni and G. Zerbi, to be submitted for publication.

(36) P. Palamidese, M. Gussoni, and G. Zerbi, Istituto di Chimica delle Macromolecole, Milan, Report, 1973.

(37) D. Tagliani, M. Gussoni, and G. Zerbi, Istituto di Chimica delle Macromolecole, Milan, Report, 1973.

(38) S. Krimm, J. J. Shipman, V. L. Folt, and A. R. Berens, *Polym. Lett.*, **3**, 275 (1965).

Carbon-13 Nuclear Magnetic Resonance Study of the Separation of Styrene from Ethylbenzene by Dense Polymer Films

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We have discovered a simple correlation between the ability of a dense polymer film to separate styrene from ethylbenzene and the observed ^{13}C nmr line widths of the absorbed species. The correlation for the seven polymers listed in Table I is shown in Figure 1. The greater the observed ^{13}C nmr line widths for both styrene and ethylbenzene the larger the separation factor for the film.

The separation factor, β, for two components absorbed in a dense polymer film is defined as

$$\beta = (C_1{}^0/C_2{}^0)(C_2{}^e/C_1{}^e)$$

where $C_i{}^0$ is the concentration of the ith (of two) species in the initial feed, and $C_i{}^e$ is the concentration of the ith species in the effluent. In Table I, ethylbenzene is component 1 and styrene component 2. The separation factors were measured on intact polymer films about 5 mils in thickness by classical pervaporation experiments,[1] in which the relative effluent concentrations of styrene and ethylbenzene were determined chromatographically. The relation of the relative solubilities of the permeants in a given film to the separation factor for that film was determined by a desorption procedure, in which the steady state concentrations[1] of styrene and ethylbenzene in the film at the conclusion of a pervaporation experiment were also determined chromatographically. The latter experiment leads to a quantity defined as

$$\beta_c = (C_1{}^0/C_2{}^0)(C_2{}^f/C_1{}^f)$$

where $C_i{}^f$ is the steady state concentration of the ith species within the film. As shown in Table I, β_c is not simply proportional to the separation factor. For example, the separation factors for polyethylene, poly(p-xylene), and nylon-11 increase in that order, even though the corresponding values for β_c do not.

Samples were prepared for the ^{13}C nmr experiments by cutting 15-mm strips of each film and wrapping these around a central Teflon spoon. The outside diameter of the entire assembly was made sufficiently less than the inside diameter of the 13-mm nmr tube to allow for swelling when the styrene and ethylbenzene were added. Both styrene and ethylbenzene were added at levels well below their solubilities in the films. The initial ratio of concentrations was chosen as the steady state ratio established in the separation experiments. Upon addition of the permeants, the nmr tube was sealed and the spectrum obtained after equilibrium was reached. The time to reach equilibrium at room temperature varied from a few days for polyethylene to a few months for the acrylonitrile copolymer.

Fourier transform ^{13}C nmr spectra were obtained using a Bruker spectrometer operating at 22.6 MHz with single-phase detection and with field stabilization provided by an external time-shared ^{19}F field-frequency lock.[2] A typical spectrum is shown in Figure 2. Since the α carbons of both the styrene and the ethylbenzene used in the nmr experiments were specifically enriched at the 90% level, these are the only lines observed in the spectrum. (The enriched styrene, with 50–100 ppm 4-*tert*-butylpyrocatechol added to inhibit polymerization, and enriched ethylbenzene were obtained from Merck Sharp and Dohme, Canada, Ltd., as custom syntheses.) The low-field olefinic methine-carbon line of styrene is asymmetric and about 50% broader than the high-field methylene-carbon line of ethylbenzene. These results are typical of those obtained for films showing separation factors larger than 1.5.

The separation factor for a dense polymer film depends upon *both* the relative solubilities of the pair of permeants in the film and the relative diffusional mobilities of the permeants within the film. In general, nmr line widths can be associated with characterizations of molecular mobility. However, the ^{13}C nmr line widths observed in these experi-