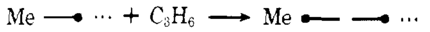

These findings are also in agreement with the fact that syndiotactic propylene homopolymers prepared in the presence of homogeneous vanadium catalysts consist of long syndiotactic blocks and shorter stereoirregular blocks.[11]

It might appear that a number of hypotheses could explain the observed experimental results and that our own conclusions are not rigorously based. This cannot be entirely denied. Nevertheless, one can easily convince oneself simply by drawing chain structures involving syndiotactic propagation occurring by primary insertion that it is not particularly easy to rationalize the observed experimental facts, *i.e.*, the proportion of $(CH_2)_2$ sequences in the copolymers,[3] the effect of ethylene on stereoregulation, and the stereoblock character of the syndiotactic homopolymers. A more detailed discussion of these hypotheses has been given in a previous review.[11]

Experimental Section

The ethylene–propylene copolymers and propylene homopolymer were prepared in liquid monomer at −78° using the VCl_4 (0.001 mol)–$Al(C_2H_5)Cl$ (0.01 mol) catalyst system described in a previous paper.[12] The polymer composition was evaluated by radiochemical analysis using ^{14}C-labeled ethylene. The $(CH_2)_2$ sequences were measured by infrared (13.30 μ band).[3] ^{13}C nmr analysis was carried out following the assignments of a previous paper[6] and under similar experimental conditions.[7]

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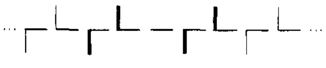

will also be generated. This does not affect our argument so long as one assumes a syndiotactic arrangement of propylene units on both sides of the ethylene unit.
(10) A referee has suggested that the effect of the central ethylene unit on the outer methyls of the pentad sequences shown may be less than an ϵ effect (nomenclature of D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964)) since in both homopolymer and copolymer they "see" the same number of carbon atoms within five bonds. If this were so, our conclusions would in fact be reinforced. The quantity plotted in Figure 1 would be $(rrrr) + 3E_{(CH_2)_3}$. It is not clear, however, that the argument from the Grant and Paul rules is conclusive. As an example of the incompleteness of these rules, it may be noted that they take no account of stereochemical configuration, the effects of which may be as large as 1.8–2.0 ppm.
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Dynamics of Poly(vinyl chloride). I. Infinite Perfect Model[1]

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ABSTRACT: A reanalysis of the dynamics and vibrational spectrum of poly(vinyl chloride) is presented in two papers one following the other. In paper I the dynamics of a translationally invariant infinite and isolated polymer chain is studied. Three most probable models of the polymer chain are considered. Dispersion curves and one-phonon density of states are calculated. $k = 0$ phonon frequencies are discussed in relation to the experimental spectrum. The problem of the force field and its influence on the results of the calculations is analyzed. The dynamical quantities calculated form the basis for a further analysis of the of the structure of PVC considered as conformationally and configurationally disordered material. This part of the problem is presented in paper II.

In the present paper (hereafter referred to as I) and in the following (hereafter referred to as II) the molecular dynamics of a single chain of poly(vinyl chloride) are considered. The dynamical properties of this material have already been the subject of several extensive investigations both from the experimental[3,4] and theoretical[5,6] viewpoints. In spite of the large amount of work, the dynamical properties as revealed from its vibrational spectrum and the corresponding structural features do not yet seem to be fully understood.

Practically all the previous authors have treated the normal modes of a translationally symmetrical, *i.e.*, structurally ordered, chain of PVC. The problem of the possible existence of different structures as revealed from the vibrational spectrum has been hinted and partially treated by several authors.[3-7] In the work we are reporting here we tackle the problem by treating the dynamics of a PVC chain containing configurational (tacticity) and conformational defects. When the concentration of such structural defects becomes large we deal with the dynamics of a disordered system.[8,9] It has already been shown that such an approach to polymer dynamics and polymer spectroscopy (infrared, Raman, and neutron scattering) provides the way to improve the interpretation of a few yet uninterpreted features of the experimental vibrational spectrum. Information on the structural properties of these materials can then be derived.[10-14]

In this paper (I) we briefly reanalyze the problem of a perfect PVC chain in order to determine some theoretical quantities which will be used in the analysis of the defect-containing or in the disordered chain. As already pointed out,[8] the vibrational analysis of a disordered material can be more easily performed if the vibrational spectrum of the ordered material is well known and is used as a reference point in the comparison. We have then calculated the phonon dispersion curves $\omega(k)$, the vibrational density of states $g(\omega)$, the $k = 0$ phonon frequencies, and the corresponding shape of the normal modes (from eigenvectors) for PVC in its three configurationally and conformationally most probable translationally symmetrical structures.[15]

A thorough collection of references on the experimental work in the infrared on PVC can be found in ref 3 and 4. As to the theoretical work on this substance most of the authors have limited their interest to the $k = 0$ normal modes. A Urey-Bradley force field was first adopted by Tasumi and Shimanouchi for the calculation of the $k = 0$ frequencies.[5a] Calculations were recently improved[5b] by the same authors including all possible deuterated derivatives of PVC and taking into account all vibrational degrees of freedom for a planar zig-zag syndiotactic chain. Opaskar[6a] has determined the $k = 0$ modes on the basis of a valence force field based on the work of Schachtschneider and Snyder and on the vibrational analysis of the secondary chlorides by Opaskar and Krimm (hereafter referred to as OK).[16] The only phonon dispersion curves and density of states so far available in the literature are those reported by Lynch and Summerfield for syndiotactic PVC[6b] who again used the force field of ref 16 to which they added the torsional force constant neglected in ref 16. A small section of $g(\omega)$ in the 600-640-cm^{-1} region has also been reported by OK.[7]

Theory and Calculation

The calculations presented here are based on a single chain model of the polymeric chain, *i.e.*, no interchain forces are considered. The whole problem is then reduced to the dynamical analysis of a one-dimensional crystal to which all degrees of freedom in three directions are allowed. For this model phonons are propagating only along the chain axis. The dynamical matrix in Cartesian space can be written[17] in the form

$$\mathbf{D}(k) = \mathbf{M}^{-1/2}\tilde{\mathbf{B}}(k)\mathbf{F}_R(k)\mathbf{B}(k)\mathbf{M}^{-1/2} \qquad (1)$$

where $\mathbf{M}$ is the matrix of masses, $\mathbf{B}$ is the transformation matrix from Cartesian to internal coordinate space defined by

$$\mathbf{R} = \mathbf{BX} \qquad (2)$$

F_R represents the matrix of the force constants derived from a valence force field expressed in terms of internal coordinates. For the definition of the basic internal coordinates the reader is referred to the well-known book by Wilson, Decius, and Cross.[18]

In general when the polymer chain can be generated by a rototranslation of a starting chemical repeating unit the $\mathbf{B}$ matrix is given by the relation[19]

$$\mathbf{B}(k) = \sum_{l=-n}^{n} \mathbf{B}_l e^{ik\cdot t(l)}\Gamma(l, \phi) \qquad (3)$$

where the index l labels the units generated by rototranslation, k is the wave vector, and $\Gamma(l, \phi)$ is the rotation matrix. ϕ defines the angle of rotation about the chain axis between two neighboring units, $t(l)$ is the translational vector. The matrix $\mathbf{F}_R$ is given by

$$\mathbf{F}_R(k) = \sum_{l=-n}^{n} \mathbf{F}_l e^{ik\cdot t(l)} \qquad (4)$$

where $\mathbf{F}_0$ is the force field matrix for the central chemical unit and $\mathbf{F}_l$ is the interaction matrix between the central unit and the one l units apart.

Dispersion curves $\omega(k)$ are obtained by direct diagonalization of the dynamical matrix of eq 1 at equidistant k values throughout the one-dimensional Brillouin zone. The frequency distribution $g(\omega)$ is calculated by a linear extrapolation method.[20] Essentially in this method the whole Brillouin zone is divided into equal intervals Δk of k which define the desired mesh. Eigenvalues and eigenvectors are calculated by diagonalization of eq 1 at k values at the center k_c of each mesh. In order to improve the details of $g(\omega)$, frequencies within the mesh are determined by calculation of the gradient at each k_c. The sections of the dispersion curves within each mesh are approximated by a straight line. By perturbation theory the gradient at k_c for the jth branch is given by

$$\text{grad}\,(\omega_j(k_c)) = \frac{1}{8\pi^2\omega_j(k_c)}\frac{\mathrm{d}_{jj}(k)}{\mathrm{d}k} \qquad (5)$$

where $\omega_j(k_c)$ is the frequency at k_c, $\mathrm{d}_{jj}(k)$ is the difference of the dynamical matrices at k_c and $k_c + \mathrm{d}k$. $\mathrm{d}k$ is chosen to be very small. The frequencies at equidistant points separated by δk along the straight line within the mesh are given by

$$\omega_j(k_c \pm n\delta k) = \omega_j(k_c) \pm (\text{grad}\,\omega_j(k_c))(n\delta k) \qquad (6)$$

where δk is a small and arbitrary wave vector interval (usually greater than $\mathrm{d}k$) into which the mesh Δk is subdivided; n is an integer running from 1 to $\Delta k/2\delta k$. Consideration of the Δk and δk gives the desired accuracy of $g(\omega)$.

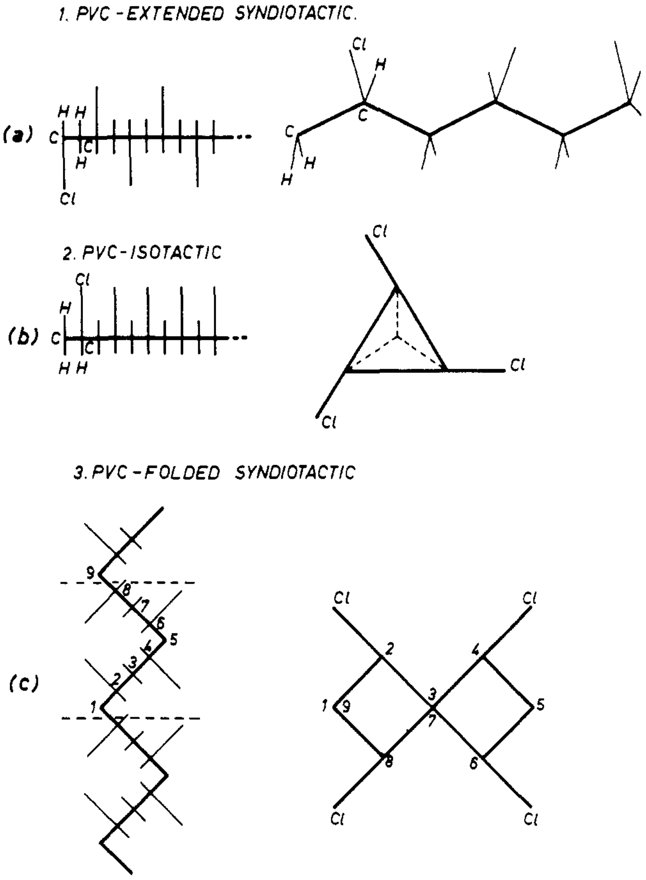

Figure 1. Structure of three translationally regular models of poly(vinyl chloride).

Calculations have been carried out for the three most likely structures of PVC: namely, (i) extended zig-zag syndiotactic structure (TTTT) (Figure 1a), its line group is isomorphous with the C_{2v} point group; (ii) isotactic threefold helical structure (TGTGTG) (Figure 1b) (helix 3/1, C_3 point group); (iii) folded syndiotactic structure (TTGGTTGG) Figure 1c (D_2 point group). The structure of the irreducible representations at $k = 0$ and the corresponding selection rules for the spectroscopically active $k = 0$ phonons are the following: model (i) = 9A$_1$ (ir,R) + 7A$_2$ (R) + 9B$_1$ (ir,R) + 7B$_2$ (ir,R); model (ii) = 16A (ir,R) + 17E

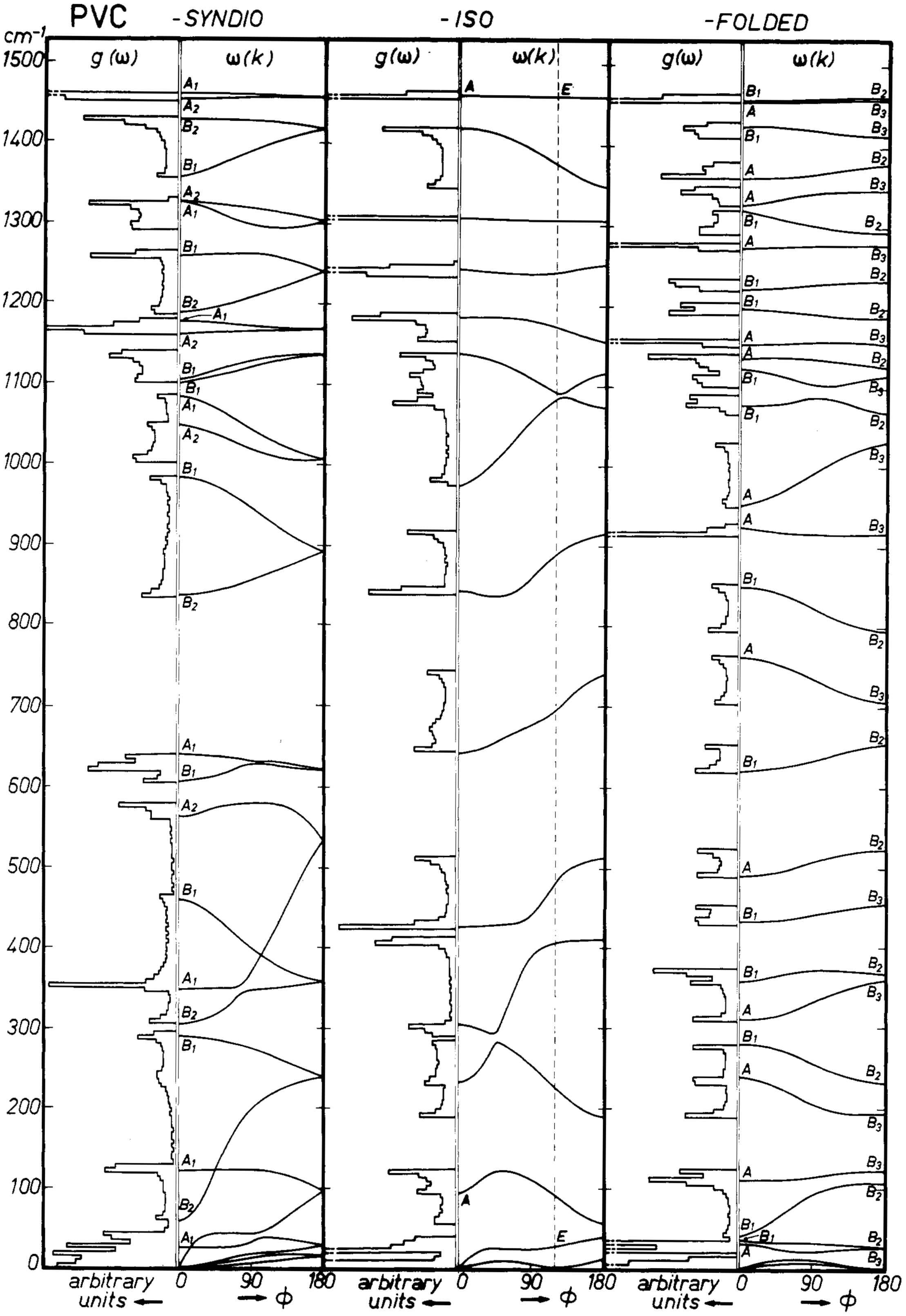

Figure 2. Dispersion curves $\omega(k)$ and density of states $g(\omega)$ from 0 to 1500 cm^{-1} of three possible models of the PVC single chain.

(ir,R); model (iii) = 17A (R) + 17B_1 (ir,R) + 17B_2 (ir,R) + 17B_3 (ir,R). The geometrical parameters adopted are the following: C–Cl = 1.795 Å (this value is that used in ref 16 and is taken from 2-chloropropane), C–C = 1.54 Å, and C–H = 1.09 Å; all bond angles are tetrahedral. For the sequences of torsional angles see above, where T = 180° and G = 120°.

For the reasons indicated at the beginning of this paper the problem of the force field was carefully analyzed. The most elaborated valence force field so far available is that by OK.[16] This force field is derived from a combination of the work by Schachtschneider and Snyder on paraffins[21] and on the secondary chlorides by OK. For sake of completeness we have verified the validity of this force field by calculating the normal frequencies of several deuterio derivatives of PVC. The comparison with experiment was based on the experimental frequencies reported by Tasumi and Shimanouchi.[5b] The fitting is not very satisfactory and

Table I: k = 0 Phonon Frequencies and Symmetry Species for Three Models of Poly(vinyl chloride)

Species	No.	Exptl freq in cm^{-1} (ref 4)	Calcd freq (cm^{-1}) for $k = 0$, OK force field	Description of modes from potential energy distribution
		I. Extended Syndiotactic PVC		
A_1	1	2970	2985	CH stretch
	2	2910	2856	CH_2 symm stretch
	3	1428	1460	CH_2 scissor
	4	1338	1324	CH_2 twist
	5		1177	CH bend
	6	1105	1084	Skeletal
	7	640	638	CCl stretch
	8	364	350	CCl bend
	9		26	Torsion
A_2	10		2855	CH_2 symm stretch
	11		1454	CH_2 scissor
	12		1326	CH bend
	13		1161	CH twist
	14		1047	CC stretch
	15		563	CCl bend
	16		125	CCl wag
B_1	17	2970	2985	CH stretch
	18	2930	2928	CH_2 asymm stretch
	19	1355	1356	CH_2 wag
	20	1258	1257	CH bend
	21	1030	1101	CC stretch, CH bend
	22	960	984	CH_2 rock, CC stretch
	23	604	606	CCl stretch
	24	490	462	CCC bend
	25	312	291	CCl bend
B_2	26		2928	CH_2 asymm stretch
	27	1387	1427	CH bend
	28	1230	1188	CH_2 wag
	29	1090	1105	CC stretch
	30	835	837	CH_2 rock
	31	340	306	CCl wag
	32		59	Torsion

Species	No.	Calcd freq (cm^{-1}), OK force field, $k = 0$	Species	No.	Calcd freq (cm^{-1}), OK force field, $k = 0$
		II. Isotactic PVC			
A ($\phi = 0°$)	1	2985	E ($\phi = 2\pi/3$)	17	2985
	2	2929		18	2928
	3	2856		19	2857
	4	1460		20	1457
	5	1419		21	1376
	6	1308		22	1305
	7	1244		23	1241
	8	1185		24	1173
	9	1139		25	1093
	10	980		26	1083
	11	848		27	894
	12	646		28	700
	13	426		29	480
	14	306		30	400
	15	233		31	226
	16	95		32	92
				33	28

Calcd frequencies (cm^{-1}), $k = 0$, for species A and B ($\varphi = 0°$) and B_2 and B_3 ($\varphi = \pi$)							
No.	A	No.	B_1	No.	B_2	No.	B_3
			III. Folded PVC				
1	2986	18	2985	35	2985	52	2985
2	2929	19	2928	36	2928	53	2928
3	2856	20	2857	37	2856	54	2857
4	1457	21	1458	38	1461	55	1457
5	1361	22	1426	39	1376	56	1413
6	1327	23	1319	40	1293	57	1346
7	1274	24	1224	41	1233	58	1278
8	1154	25	1199	42	1187	59	1156
9	1137	26	1123	43	1126	60	1114
10	954	27	1077	44	1069	61	1029
11	926	28	852	45	796	62	917
12	763	29	622	46	655	63	707
13	491	30	434	47	524	64	454
14	311	31	358	48	368	65	359
15	239	32	280	49	232	66	195
16	111	33	40	50	107	67	123
17	30	34	35	51	26	68	25

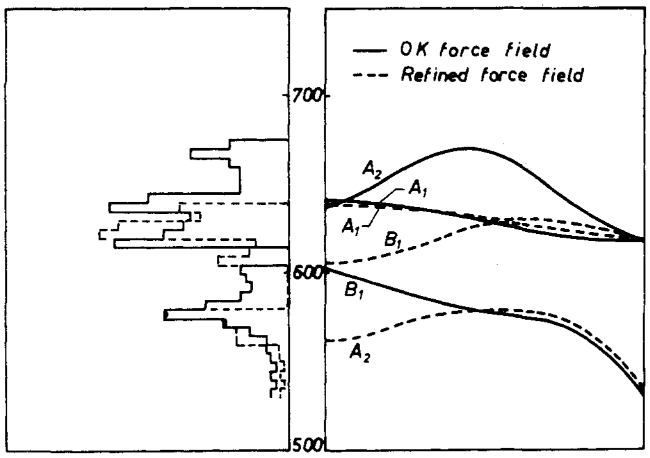

Figure 3. Dispersion curves and density of states of syndiotactic PVC in the energy region where C–Cl stretching occurs obtained with two sets of valence force constants.

seems to suggest that some important interaction constants are missing. It is common knowledge, even if this fact has not yet been fully understood or rationalized, that a force field derived from an overlay calculation on hydrogenated derivatives provides a set of valence force field parameters which does not give satisfactory fitting of deuterated derivatives of the molecules entering into the overlay calculation. This is also the case with the widely used valence force field of Schachtschneider and Snyder for linear[21] or branched[22] paraffins, as well as the less common valence force field for ethers from Snyder and Zerbi.[23] On the other hand, the valence force fields of refs 21–23 have been shown to be very useful in understanding spectra as well as in predicting structures. A certain self consistency and reliability can then be attached to the force fields derived from overlay calculations on hydrogenated derivatives only. The lack of knowledge of the anharmonicity of the vibrations has been generally suggested as one of the possible reasons, but this fact has not yet been proven. Again, for the sake of completeness, we have attempted a least-squares refinement of the force field from OK on PVC and on its deuterated derivatives. The number of experimental data allowed a least-squares calculation. Generally[24] the refinement on the polymer itself cannot find a reasonable justification since there is no good chemical reason to think that the chemical bonds in PVC are different from those of the short chain model compounds. Failure to reproduce the observed frequencies must be ascribed to the limitations of the force field and not to a peculiar chemical situation of the polymer. The results of an attempt to refine PVC and the deuterated derivatives give results analogous to those reported by Tasumi and Shimonouchi.[5b]

We decided, however, that for the purpose of our work on disordered PVC the force field by OK was applicable. The diagonal torsional force constant was added to the OK force field. After several attempts the "magic" value from paraffins[21] was adopted. It should be pointed out that the force field of OK is applicable as it is to the three structures considered in this work. The necessary force constants required by the geometry of the models adopted are available. The dependence on the force field of the calculated dynamical quantities will be presented and discussed in papers I and II.

Results and Discussion

Dispersion curves $\omega(k)$ for the three possible structures are reported in Figure 2, together with the corresponding density of states $g(\omega)$. Table I reports the phonon frequencies at $k = 0$ for the three models. Unlike some other polymers,[13,25,26] dispersion curves of PVC show a sizable k dependence for most of the branches from 0 to 1500 cm^{-1} thus showing that a nonnegligible intramolecular coupling takes place. A very large dispersion is observed for the lower energy branches. The number of branches in the lower energy region is not too large thus making PVC a good material to be studied by neutron scattering experiments. While crossing and repulsions of frequency branches clearly occur for syndiotactic PVC, this is not the case for other models. It follows that for syndiotactic PVC the location of the $k = 0$ modes may not occur at the boundaries of the frequency bands but inside the bands. This fact is important when peaks of $g(\omega)$ must be assigned to $k = 0$ modes as will be discussed in paper II.

As already mentioned attempts were made to test the dependency on the force field of $k = 0$ modes and of the dispersion curves. A least-square refinement, restricted each time to a very few force constants, was carried out only on PVC in order to evaluate whether an improvement of the fitting between observed and calculated $k = 0$ frequencies could affect the shape of the dispersion curves and the derived eigenvectors. Since in paper number II we mainly focus our attention on 600–700 cm^{-1} where C–Cl stretchings are known to occur we represent in Figure 3 the dependence of the calculated phonons in this energy range on a change of the force field. It should be pointed out that the force field refined on PVC is entirely reasonable as well as acceptable within the limits of acceptability commonly adopted in force constant calculations.[24]

The change in shape of the dispersion curves reported in Figure 3 corresponds to a change of the extent of mixing of C–Cl stretchings and C–Cl wagging motions. While the dispersion branch from the OK force field is mainly C–Cl stretching throughout the whole Brillouin zone, with the refined force field a very large contribution of C–Cl wagging comes in. A drastic change in the density of states $g(\omega)$ then follows. The extensive calculations on disordered PVC discussed in paper II made us prefer the OK force field (see paper II).

The experimental verification of the calculated quantities is at present only possible for the $k = 0$ phonons which become spectroscopically active for a syndiotactic chain, which is certainly the most probable structure obtained for PVC polymerized in urea complexes. All the phonon frequencies wait for an experimental verification either from the optical spectrum or from neutron scattering data. This has already occurred for polyethylene[27] and poly(tetrafluoroethylene).[19,28] Moreover, an ordered form of isotactic or folded PVC has not yet been obtained. To our knowledge very little has been done in this field for PVC. The determination of the phonon frequencies from neutron scattering data should be of an invaluable help in the determination of the intramolecular force field, thus helping in the clarification of the problem of the force constants previously mentioned. Moreover, it would add more information for the verification of the suggestion proposed in the literature[29] of the existence of an interchain bonding in the crystal.

Since there is still some controversy on the structure (stereoregularity and conformation) of a commercial sample of PVC, if the polymer were to contain isotactic or folded structure of a certain length the $k = 0$ calculated phonon frequencies should appear in the optical spectrum.

From our calculation the eigenvectors are known and allow one to follow the nature of the phonons propagating along the chain axis with changing k values. Eigenvectors are particularly useful for the determination of the scattering cross section in neutron experiments. It has been recently 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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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