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Distribution of Infrared Intensity in the Spectra of Conformationally Disordered Chain Molecule Assemblies

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ABSTRACT: The distribution of intensity of the infrared spectrum of a simple model system of flexible chain molecules has been examined as a function of conformational disorder in order to establish a basis for the characterization of disorder by vibrational spectroscopy. A finding of practical importance is that the band intensity associated with a delocalized mode is nonlinearly related to the concentration of disorder measured in terms of the conformational state of the bonds and that the degree of the nonlinearity increases with the chain length. Therefore, to determine quantitatively the degree of conformational disorder for an assembly of flexible chain molecules, it is necessary to employ bands associated with modes that are highly localized. A second aspect of this study concerns the well-known observation that, for a given chain molecule system, the degree to which the intensity distribution is affected by a change in the average conformation of the system is dependent on the type of vibrational mode involved. There are two principal factors that determine the sensitivity of an infrared band to conformation. One is the relation, within the repeating unit of the chain, between the direction of the local dipole moment derivative associated with the mode and the direction of the skeletal bond whose internal rotational states determine the conformation of the chain. The second factor concerns how the normal coordinate of the mode is dependent on the conformation of the chain. These two factors are interrelated, and, in fact, depending on the direction of the dipole moment derivative, their effects may cancel. This leads to different modes having different sensitivites to conformational change.

I. Introduction

In this paper we call attention to some general relations between intensity and disorder that bear on the use of infrared and Raman spectroscopy for the determination of conformational disorder in assemblies comprised of chain molecules. These relations are peculiar to the spectra of chain molecules and do not appear to have been previously considered. We will show that the intensities of most infrared and Raman bands in the spectra of chain molecule systems are not linearly related to the degree of conformational disorder if, as is ordinarily the case, the disorder is measured in terms of the concentrations of the various possible conformational states of the skeletal bonds. The departure from linearity may be very large and may therefore lead to correspondingly large systematic errors in the quantitative evaluation of disorder. The nonlinearity is a consequence of the fact that the band intensities used for conformational analysis are associated with modes that are largely delocalized; that is, the normal coordinate of the mode tends to extend over the length of the chain, whereas the conformational statistic that is to be measured, namely, the average conformation of a bond, is a highly localized quantity. On the other hand, we note that a linear relation between intensity and disorder does occur in the less common situation where the band whose intensity is to be used as a measure of disorder is associated with a vibrational mode that is highly localized.

This problem of nonlinearity has been discussed for one particular case by Pink et al.,[1] who recognized that the Raman intensity of the 1130-cm^{-1} C–C stretching band of acyl chains, which is commonly used to estimate conformation disorder in the hydrocarbon component of lipid bilayer membranes, was not, as had been previously assumed, linearly related to chain disorder. These authors used statistical mechanical methods and the results of normal coordinate calculations that had been reported earlier for the C–C stretching modes of hydrocarbon chains[2] to achieve a more accurate calibration. After their results were reported,[1] the high nonlinearity in the relation between the intensity of the 1130-cm^{-1} band and the number of gauche bonds per chain was verified exper-

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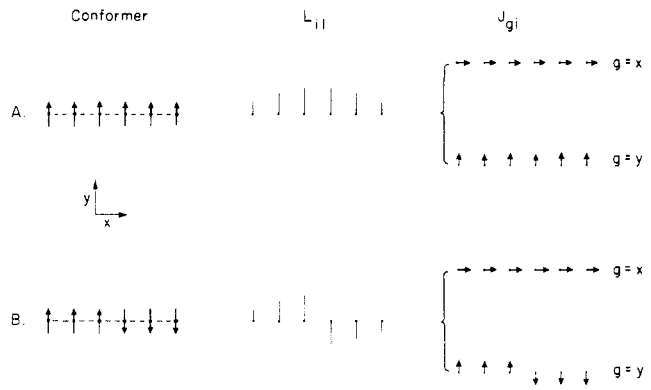

Figure 1. Conformations, normal coordinates of the $k = 1$ mode, and local dipole moment derivatives for the ordered ($\tau_i = 0°, 0°, 0°, 0°, 0°$) conformer (A) and a disordered ($\tau_i = 0°, 0°, 180°, 0°, 0°$) conformer (B) of a model chain of six oscillators.

imentally in a study on the disordered solid phase of crystalline n-$C_{21}H_{44}$.[3]

In the present paper, we will use a simple model chain system to explore how intensity and disorder are related. We will confine ourselves to a discussion of infrared spectra. To identify the principal factors that underlie the intensity–disorder relation, we have used a model system that has one great virtue, namely, that the vibrational frequencies of any given chain are independent of the conformation of the chain and the eigenvectors are related in a simple way to the conformation. This enables us to write explicit relations between intensity and conformational disorder.

In addition to the nonlinearity between intensity and disorder, we will also discuss why the intensities of different types of vibrational modes vary in their sensitivity to conformational change. It is well-known that these differences exist. Thus, it has been observed that in going from an ordered to a disordered chain system, some infrared or Raman bands are drastically affected while others remain virtually unchanged.

An understanding of relations of this kind is essential if vibrational spectra are to be used for the analysis of the conformation of disordered chain molecule assemblies. However, while studies on simple model chain systems enable us to isolate the more dominant factors that interrelate spectra and disorder, we must ultimately deal with real chains whose spectra are much more complex. To help bridge the gap between the spectra of the very simple chain system discussed here and those of real chain molecule systems, we will present in a subsequent paper[4] a more general and rigorous treatment in which we consider systems whose structure and conformation are nearer those of real chains. It turns out, however, that the relations between spectra and disorder for these more complex systems are much the same as those determined here for a simple model chain.

II. Infrared Spectrum of a Single Chain

A. Description of the Model. Figure 1 depicts our model chain. It consists of n identical harmonic oscillators, which are to be associated with the repeat units of a chain molecule. Each oscillator has just one degree of vibrational freedom and is coupled to its adjoining neighbor or neighbors.

As seen in Figure 1, the oscillators are aligned either parallel or antiparallel to the y axis. Adjacent oscillators are connected by "bonds", which are analogous to the bonds that represent the skeletal backbone of a real chain. Each bond of the model chain assumes one of two possible conformations. If the oscillators adjoining a bond are parallel to one another, the bond has a "cis" conformation, and if the oscillators are antiparallel, the bond has a "trans" conformation. The conformation of a chain thus may be altered by a 180° rotation about one of the bonds. We note that a change in the conformation of one particular bond results in a major change in the geometry of the chain, namely, a 180° rotation about the x axis of one part of the chain relative to the other.

The conformation of the "bond" between the pair of adjoining oscillators i and $i + 1$ is designated by the value of the dihedral angle τ_i. As indicated, this angle equals 0° for parallel alignment and 180° for antiparallel alignment.

Our intensity model is of the simplest kind. Each oscillator has associated with it a vector that represents a local dipole moment derivative. The magnitude of the vector is the same for each oscillator and the direction of the vector is that of the oscillator.

As we will discuss below, the value of τ_i determines the relative orientation of pairs of adjoining dipole moment derivatives (or induced dipole moment derivatives in the Raman case).[4] In addition, τ_i determines the vibrational coupling constant between the oscillators. The fact that τ_i determines *both* orientation and coupling is responsible for the relations between spectra and disorder that are peculiar to chain molecule systems. The probability that a pair of adjacent oscillators is parallel is p. We will assume that the conformation of each bond is independent of all others. Thus, while p applies to individual bonds, it is also a measure of the average conformational state of an ensemble of chains.

B. Calculated Infrared Spectra. The frequencies and normal coordinates of the model chain are associated with the eigenvalues and eigenvectors that result from diagonalizing a matrix **H** of the form[5]

$$\mathbf{H} = \begin{pmatrix} a & b_1 & & & 0 \\ b_1 & a & b_2 & & \\ & b_2 & a & b_3 & \\ & & b_3 & a & . \\ & 0 & & . & . & . \\ & & & & . & . \end{pmatrix} \tag{1}$$

in which the diagonal element, a, is proportional to ν_0^2, where ν_0 is the frequency of an isolated oscillator and where the b_i values represent the interaction between oscillators i and $i + 1$.

For real chain molecules that do not involve conjugated bonds, the coupling terms, b_i, between nearest-neighbor internal coordinates are to a good approximation determined by kinetic energy coupling rather than by potential energy (force constant) coupling.[6] In the Wilson formulation of the vibrational problem,[5] the kinetic energy coupling is represented by the off-diagonal G matrix element, $G_{i,i+1}$. For bending and torsional coordinates, the value of this element is proportional to cos τ_i so that

$$b_i = b \cos \tau_i \tag{2}$$

where b is a constant. For our model chain, $b_i = b$ or $-b$ depending on whether oscillators i and $i + 1$ are aligned parallel or antiparallel to one another.

The frequency ν_k of the kth vibrational mode of a chain of n oscillators is given by

$$\lambda_k = a + 2b \cos \phi_k \tag{3}$$

where λ_k is proportional to ν_k^2 and where

$$\phi_k = \frac{k\pi}{n + 1} \tag{3a}$$

From eq 3, we see that the vibrational frequencies are independent of the conformation of the chain. This follows because the polynomial equation for the eigvenvalues of the matrix defined by eq 1 involves terms containing b_i^2 but not b_i. Therefore, the eigenvalues are independent of the sign of b_i.[4,7]

The kth normal coordinate of the ordered chain ($\tau_i = 0°$) is given by the row vector

$$\mathbf{L}^*_k = \left(\frac{2}{n+1}\right)^{1/2}(\sin\phi_k, \sin 2\phi_k, \sin 3\phi_k, ..., \sin n\phi_k) \tag{4}$$

where ϕ_k is given by eq 3a. (Unless otherwise indicated, the vectors we use are column vectors. An asterisk indicates a transposition to a row vector.)

The normal coordinates, unlike the frequencies, are dependent on the conformation of the chain. However, the dependence is of a simple kind: The magnitudes of the elements of the normal coordinates are independent of conformation, but their signs are not. The situation is illustrated in Figure 1 for two chains that are closely related in conformation. Conformer A is ordered; that is, all its oscillators are parallel ($\tau_i = 0°$). Conformer B is like A except that adjoining oscillators 3 and 4 are antiparallel ($\tau_3 = 180°$). Figure 1 also depicts the normal coordinate associated with the $k = 1$ mode. The magnitude of the ith element of $\mathbf{L}_1$ is $(2/(n+1))^{1/2}\sin i\phi_1$ for both conformers, but, due to the antiparallel alignment of oscillators 3 and 4 in conformer B, all the L_{i1} elements from $i = 4$ through $i = 6$ have their signs reversed.

A simple expression for the infrared intensity of the kth mode can be derived. For this purpose, we will use the Cartesian axis system shown in Figure 1. In this system, the x axis is collinear with the chain direction.

The intensity equation we use contains only linear terms[5]

$$I^{(k)} = K\sum_g(\partial\vec{\mu}_g/\partial Q_k)^2 \tag{5}$$

in which $\vec{\mu}_g$ is the g component ($g = x, y, z$) of the dipole moment of the chain and K is a proportionality constant. The intensity $I^{(k)}$ is to be expressed in terms of contributions from the individual oscillators. The direction of the local dipole moment derivative associated with an oscillator is assumed to be either parallel or antiparallel to the x, y, or z axis. Generality is maintained since an arbitrary dipole moment derivative vector can be expressed in terms of these components.

Considering the intensity components separately and expanding eq 5 in terms of the oscillator coordinates, S_i, we have

$$I_g^{(k)} = K\left(\sum_{i=1}^{n}\frac{\partial\mu_g}{\partial S_i}\frac{\partial S_i}{\partial Q_k}\right)^2 \tag{6}$$

It is convenient to write this equation in the form

$$I_g^{(k)} = K(\mu'_g)^2(\mathbf{J}^*_g\mathbf{L}_k)^2 \tag{7}$$

where μ'_g represents the magnitude of the $\partial\mu_g/\partial S_i$ term in eq 6, which is the same for each oscillator. The elements of $\mathbf{J}_g$ are +1 or −1, depending on the sign of $\partial\mu_g/\partial S_i$. The ith element of the normal-coordinate vector $\mathbf{L}_k$ in eq 7 is equal to $\partial S_i/\partial Q_k$ in eq 6. In the example that follows, the elements in eq 7 will be written out.

C. Effects of Conformation. The effect of a conformational change on the intensity of the $k = 1$ mode will now be considered. This mode is of special importance because, for an ordered chain, the intensity of the band representing the $k = 1$ mode is by far greater than that of any other mode, and therefore this band is the one typically used to monitor chain disorder. In Figure 2 this band is marked on the top spectrum, which is that of an ordered chain of 20 oscillators. This mode corresponds to the zone center mode of the infinite chain and is, in fact, the only mode that appears in the spectrum of the infinite chain. The 1130-cm^{-1} band discussed in the Introduction is an example of a $k = 1$ mode.

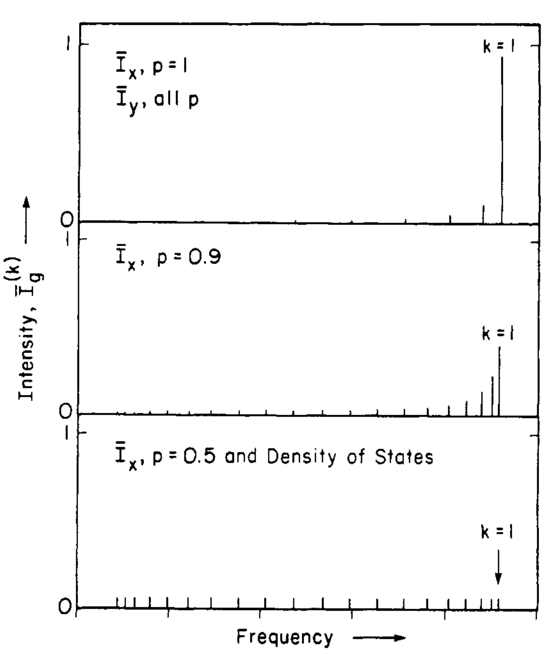

Figure 2. Calculated x- and y-component infrared spectra of an ensemble of chains comprised of 20 oscillators. The values of p (the probability for a pair of adjoining oscillators to be parallel) are equal to 1.0, 0.9, and 0.5.

The effect on the $k = 1$ mode of a conformational change is illustrated in Figure 1. The forms of the $\mathbf{J}_g$ and $\mathbf{L}_1$ vectors are indicated both for the "ordered" conformer (A) and for the "disordered" conformer (B). As noted earlier, the normal coordinates of the $k = 1$ mode are exactly the same for the two conformers except for the phase change between oscillators 3 and 4. The $k = 1$ normal coordinate for conformer A is given by eq 4 and is

$$\mathbf{L}^*_1(\mathrm{A}) = \left(\frac{2}{n+1}\right)^{1/2} \times (\sin\phi_1, \sin 2\phi_1, \sin 3\phi_1, \sin 4\phi_1, \sin 5\phi_1, \sin 6\phi_1) \tag{8}$$

while for conformer B it is

$$\mathbf{L}^*_1(\mathrm{B}) = \left(\frac{2}{n+1}\right)^{1/2} \times (\sin\phi_1, \sin 2\phi_1, \sin 3\phi_1, -\sin 4\phi_1, -\sin 5\phi_1, -\sin 6\phi_1) \tag{9}$$

These normal coordinates are depicted in Figure 1.

Analogous sign changes may or may not occur for $\mathbf{J}_g$ in going from conformer A to conformer B. This depends on g. Thus, the elements of $\mathbf{J}_x$ do not change sign due to the fact that the x component of the dipole moment derivative is not affected by rotation about the x axis. Therefore, we have for both conformers

$$\mathbf{J}^*_x(\mathrm{A}) = \mathbf{J}^*_x(\mathrm{B}) = (1\ \ 1\ \ 1\ \ 1\ \ 1\ \ 1) \tag{10}$$

For the y and z components, the situation is different. For conformer A

$$\mathbf{J}^*_y(\mathrm{A}) = (1\ \ 1\ \ 1\ \ 1\ \ 1\ \ 1) \tag{11}$$

but for B

$$\mathbf{J}^*_y(\mathrm{B}) = (1\ \ 1\ \ 1\ \ {-1}\ \ {-1}\ \ {-1}) \tag{12}$$

The z component behaves the same way as the y component.

For conformer A, the x- and y-component intensities of the $k = 1$ mode, which are given by eq 7, are

$$I_x^{(1)}(\mathrm{A}) = K(\mu'_x)^2\Big(\sum_i L_{i1}\Big)^2 \tag{13}$$

and

$$I_y^{(1)}(\mathrm{A}) = K(\mu'_y)^2\Big(\sum_i L_{i1}\Big)^2 \tag{14}$$

For conformer B, the y-component intensity is equal to that for the y component of conformer A:

$$I_y^{(1)}(\mathrm{B}) = I_y^{(1)}(\mathrm{A}) \tag{15}$$

However, the x-component intensity for conformer B is zero:

$$I_x^{(1)}(\mathrm{B}) = 0 \tag{16}$$

because $\mathbf{J}_y(\mathrm{B})$ introduces sign changes that cause the terms in the JL product to cancel.

As this example illustrates, the degree to which the intensity of a band is affected by a change in conformation depends critically on how the local dipole moment derivative is oriented relative to the bonds that define local conformation. The two types of modes we have considered, those whose local dipole moment derivatives are oriented along x and those oriented along y or z, represent extremes. The sensitivity of intensity to conformation is at a maximum for orientation in the x direction and at a minimum for the y or z directions.

The relative sensivities of the x- and y-intensity components may at first sight appear puzzling: It is the y-component intensity that is insensitive to conformation in spite of the fact that it is the y component, not the x component, of the local dipole moment derivative that is dependent on conformation. This is easily understood, however, when the normal coordinates are brought in. For the y component, both the normal coordinates *and* the dipole moment derivatives are dependent on conformation. However, these conformational dependencies cancel in the intensity expression in eq 7. In the case of the x component, the normal coordinates are dependent on conformation, but the dipole moment derivatives are not. Therefore, the cancellation cannot occur, and as a result, there is a dependence on conformation.

The above argument can be expressed in a more general way.[4] The intensities of the x and y components of a chain in any given conformation can be expressed in terms of the normal coordinates of the *ordered* chain through a simple transformation. The transformation matrix $\mathbf{D}$ that is needed is obtained from the relation

$$\mathbf{H} = \mathbf{D}\mathcal{H}\mathbf{D} \tag{17}$$

where $\mathbf{H}$ and $\mathcal{H}$, which are defined in eq 1, refer respectively to the given conformer and the ordered conformer. For the ordered chain, $\tau_i = 0$, so that $b_i = b$ from eq 2. For an arbitrary chain, $\tau_i = 0$ or 180°, so $\mathbf{D}$ is a diagonal matrix whose elements are 1 or −1. (For conformer B in the example discussed above, the diagonal elements of $\mathbf{D}$ are 1, 1, 1, −1, −1, −1.) We note that $\mathbf{D}^{-1} = \mathbf{D}$, so that $\mathbf{DD} = \mathbf{I}$, the unit matrix.

The normal coordinates, $\mathbf{L}_k$, of the disordered chain are then given by

$$\mathbf{L}_k = \mathbf{D}\mathcal{L}_k \tag{18}$$

where $\mathcal{L}_k$ is the corresponding normal coordinate given by eq 4 for the ordered chain. The $\mathbf{J}_g$ are then

$$\mathbf{J}_x = \mathbf{E}_n \tag{19}$$

$$\mathbf{J}_y = \mathbf{E}^*_n\mathbf{D} \tag{20}$$

where $\mathbf{E}_n$ is a column matrix of n elements, all equal to unity.

The infrared intensity of mode k given by eq 7 is

$$I_x^{(k)} = K(\mu'_x)^2 = (\mathbf{E}^*_n\mathbf{D}\mathcal{L}_k)^2 \tag{21}$$

$$I_y^{(k)} = K(\mu'_y)^2 = (\mathbf{E}^*_n\mathcal{L}_k)^2 \tag{22}$$

We note that the conformationally dependent term, $\mathbf{D}$, appears in the expression for $I_x^{(k)}$ but not for $I_y^{(k)}$. Thus, only the x-component intensity is dependent on conformation, in keeping with the results found in the example above.

III. Infrared Spectrum of an Ensemble of Disordered Chains

We now consider an ensemble of disordered model chains. The ensemble is characterized by just one parameter, p, the probability that a pair of adjacent oscillators are aligned parallel, that is, the probability for the occurrence of $\tau_i = 0°$. The expression for the x-component intensity distribution, which is derived in ref 4, is

$$\bar{I}_x^{(k)} = \frac{2K(\mu'_x)^2}{n+1}\sum_{i,j}^{n}(2p-1)^{|i-j|}\sin i\phi_k \sin j\phi_k \tag{23}$$

For the y component

$$\bar{I}_y^{(k)} = \frac{2K(\mu'_y)^2}{n+1}\cot^2\frac{\phi_k}{2} \tag{24}$$

an expression analogous to that given by Zbinden[8] for the ordered chain. The z-component intensity is, of course, given by an expression analogous to that for y.

We will discuss only the spectrum of the x component, since, as we have noted, the y- and z-component spectra are not dependent on p. In fact, the y and z spectra are identical with the spectrum of the ordered chain.

Of interest is the dependence of the x-component intensity of the $k = 1$ mode on the probability p. This dependence is indicated in Figure 2 for three ensembles that consist of chains of 20 oscillators. The spectra shown are for ensembles in which the chains are completely ordered ($p = 1.0$), mildly disordered ($p = 0.9$), and maximally disordered ($p = 0.5$). The intensity of the $k = 1$ band, which is identified on the figure, diminishes with increasing disorder. The $k = 1$ intensity is not, however, linearly related to p. For example, the intensity of the $k = 1$ band is reduced to less than 1/2 its value in going from $p = 1$ to $p = 0.9$. The intensity loss is distributed among the other modes, so that, at maximum disorder ($p = 0.5$), all modes have the same intensity. In this latter case the spectrum and the density of states are the same.

The intensities of the $k = 1$ and $k = 2$ modes are shown in Figure 3 as a function of p. In this figure, the intensities are scaled by the intensity of the $k = 1$ mode of the ordered chain to give a relative intensity, $R_g^{(k)}$, which is defined as

$$R_g^{(k)} = \bar{I}_g^{(k)}/I_g^{(1)}(p{=}1) \tag{25}$$

where $g = x$, y, or z. The relative intensity of the y component of the $k = 1$ mode is included in Figure 3, where it is seen to be independent of p. The nonlinearity between

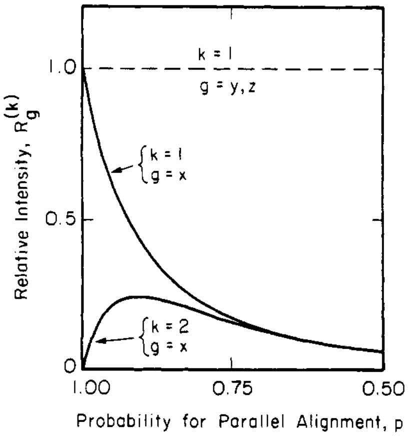

Figure 3. Relative infrared intensity of the $k = 1$ mode (x, y, and z components) and the $k = 2$ mode (x component) as a function of p for an ensemble of 20-oscillator chains. The intensities are scaled by the intensity of the $k = 1$ mode in the spectrum of the ordered $n = 20$ chain. (See eq 25.)

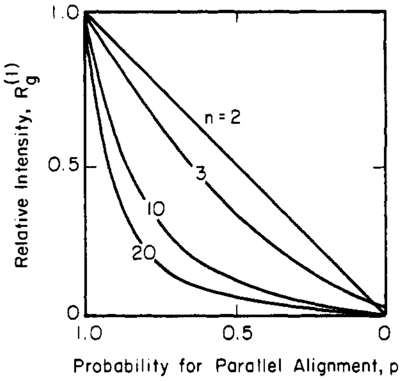

Figure 4. Infrared intensity of the x component of the $k = 1$ mode plotted as a function of p for chains having 2, 3, 10, and 20 oscillators. (For even-numbered chains, the $k = 1$ mode intensity vanishes at $p = 0$ for n even, but for odd-numbered chains ($n = 3$ here), the $k = 1$ mode retains some intensity at $p = 0$.)

the x-component intensity of the $k = 1$ mode and the degree of conformational disorder is strikingly apparent in Figure 3. The rate of intensity decrease with increasing disorder is largest nearest $p = 1$. This means that the sensitivity of intensity of the $k = 1$ mode to conformational change is greater for a more ordered ensemble.

For all modes other than $k = 1$, the x-component intensities of an initially ordered chain increase as the system begins to become disordered. An example is the $k = 2$ band, which is shown in Figure 3. Initially, for the system in a highly ordered state, the intensity of the $k = 2$ mode grows at the expense of the $k = 1$ mode. However, at a sufficiently high degree of disorder, the intensity of the $k = 2$ band reaches a maximum and then diminishes monotonically.

There is a chain-length effect on the relation between the intensity of the $k = 1$ band and the degree of chain disorder. This is demonstrated in Figure 4 where the x-component intensity of the $k = 1$ mode is plotted against p for ensembles of chains of different chain lengths: n = 2, 3, 10, or 20. The degree of linearity between intensity and disorder increases as chains become shorter. In the limiting case of $n = 2$, that is, for a chain with one "bond" and two conformations, the intensity–disorder relation is linear. This represents a case in which the vibrational mode is highly localized.

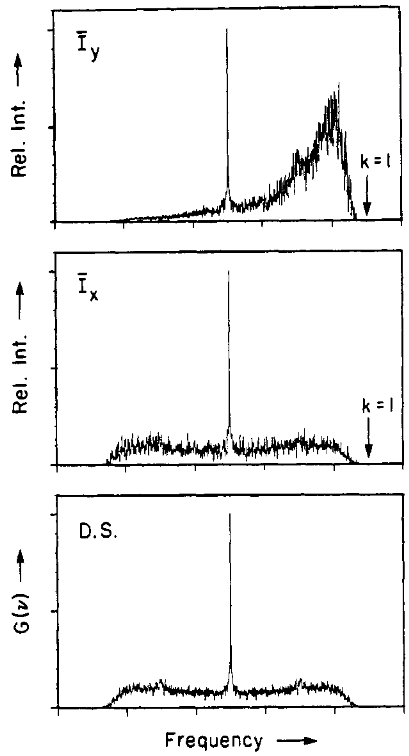

Figure 5. Calculated infrared spectra (x and y components) and density of states (D.S.) for an ensemble of 1000 chains that have bonds about which free rotation occurs; that is, the values of the dihedral angles, τ_i, are random. (To compare the intensities $\bar{I}_x$ and $\bar{I}_y$, the values of $\bar{I}_x$ in the figure must be multiplied by 1.56. The frequency scale is the same as that in Figure 2. The central spike originates in the density of states and is not relevant to the present discussion: see the text.)

We will now consider a somewhat different type of ensemble in order to underscore the generality of the difference in the behavior of the x- and y-component spectra with respect to conformational disorder. The ensemble we consider consists of chains that are conformationally disordered through free rotation about the bonds connecting the oscillators. The conformation of each chain is defined by a set of dihedral angles, τ_i, each of which is allowed, independently of the others, to assume a random value between 0 and 360°. For this "random-τ" case, the values of the interaction constants, b_i, which are given by eq 2, are of course also random. In Figure 5 in histogram form are displayed the numerically calculated density of states and infrared spectra of an ensemble of 1000 such chains, each consisting of 20 oscillators. The frequency of the $k = 1$ mode of the $n = 20$ ordered chain is marked for reference. (We note as an aside that there is a very sharp spike at the center of the density of states plot, and as a result there are corresponding spikes in the calculated infrared spectra. This spike, whose area is negligible, is not relevant to the present discussion. Its origin is associated with the spike that appears in the density of states for odd-numbered chains. For each odd-numbered chain, regardless of conformation, there is one eigenvalue for which $\lambda = a$. Hence, the density of states of a random-τ ensemble of odd-numbered chains has an infinitely narrow spike at its center. In the even-numbered case, there is a corresponding, but less sharp, spike that is centered around $\lambda = a$. A second aside concerns whether 1000 chains is a sufficient number to determine in effect the density of states and the infrared spectra. We believe that it is sufficient since there are no unique or special conformations that would be expected to produce special features in the plots. Our calculations indicate the effect of increasing the number of chains is mainly to decrease the noise. The absolute value of the latter is, of course, a function of the relative width of the histogram interval.)

The general appearance of the spectra calculated for the random-τ ensemble (Figure 5) is quite different from that of the spectral calculated for the τ = 0, 180° ensemble (Figure 2). The random-τ spectra are characterized by a quasi-continuous distribution of intensity that reflects the fact that the vibrational frequencies of the conformers are dependent on the conformation of individual chains, unlike the situation for the τ = 0, 180° ensemble.

However, what is significant is that the intensity distributions in the spectra of the random-τ ensemble are similar to those in the spectra of the τ = 0, 180° ensemble for the latter in its most highly disordered state, that is, for $p = 0.5$. (The spectra shown in Figures 2 and 5 have the same frequency scale and therefore can be compared directly.) For both ensembles, the intensity distribution in the $\bar{I}_y$ spectrum is highly asymmetric, with intensity being concentrated at the $k = 1$ end. In addition, the $\bar{I}_x$ spectra of the two ensembles are alike in that they display a nearly uniform distribution of intensity.

Finally, we note that the $\bar{I}_x$ and $\bar{I}_y$ spectra of more complex chain molecule ensembles are found to exhibit these same intensity distribution characteristics and, in addition, that the distribution of intensity in the Raman spectrum can be characterized in a way analogous to the infrared case, that is, according to the component of the derivative of the local polarizability tensor.[4]

IV. Discussion and Summary

The present work shows that for an ensemble consisting of simple chains of three or more repeating units the intensities of bands in the calculated infrared spectrum are nonlinearly related to the degree of conformational disorder if the disorder is measured, as it normally is, in terms of the conformation of individual bonds. The degree of nonlinearity increases with chain length.

It is important to note that this nonlinearity is primarily a result of changes in intensities and is not a result of a scrambling of band positions. For chain systems more complex than the model chain studied here, the density of vibrational states will, of course, depend to some extent on conformation. However, our analysis here and elsewhere[4,9] indicates that the conformational dependence of vibrational spectra is generally less the result of changes in the density of states than a result of a redistribution of intensity due to phase changes in the elements of the normal coordinates. This is contrary to a commonly held view that disorder affects spectra primarily through changes in the frequency distribution of the vibrational modes, such as would occur, to use an extreme example, if adjoining oscillators became completely uncoupled from one another as a result of conformational change.

In practical terms, these results point to the necessity of using localized modes for the quantitative determination of conformational disorder in chain molecule assemblies. If bands associated with delocalized modes are used and linearity is assumed, the degree of disorder relative to the completely ordered system can be greatly overestimated if the system to be determined is fairly ordered.

Unfortunately, the number of bands associated with localized modes is relatively small for chain molecules. Except for a few vibrations associated with end groups, all the modes of ordered chains are essentially delocalized. The situation for disordered chains is not much better since in this case also most modes are more or less delocalized.[9] A few localized modes useful for the conformational analysis of chain molecules are known for the disordered polymethylene chain,[2] for example. Sometimes it is possible to induce mode localization by deuterium substitution. This approach has one great advantage in that it enables us to monitor conformation at specific positions along the chain. Conformational studies of this sort have utilized deuterium-isolated hydrogen stretching modes[10] and rocking modes of isolated CD_2 groups in polymethylene chains.[11]

A second area touched on in our analysis concerns the well-known observation that different kinds of bands exhibit different degrees of sensitivity to conformational change. The most important single factor determining conformational sensitivity is found to be the relation between the direction of the local dipole moment derivative and the direction of the bonds whose rotational states determine conformation. The repeat unit of a real chain molecule, unlike the one in our simple model, has associated with it more than a single degree of vibrational freedom. This leads to *sets* of bands, each set being associated with a specific kind of local coordinate, either internal or group. The intensity distributions associated with the various sets of bands will behave differently with respect to conformational change, depending on the direction of the local dipole moment, that is, according to the nature of the localized motion of the group. Differences in the conformational sensitivity of Raman bands can be similarly explained, except now the key relation is between the orientation of the derivative of the polarizability tensor and the orientation of the skeletal bonds.[4]

Finally, we note that those bands *most* sensitive to conformational change are those associated with vibrational modes whose local dipole moment derivatives are *least* affected in direction by conformational change. This relation, which seems rather contrary, can be understood by taking into account the fact that conformational change affects the elements of the normal coordinates as well as those of the local dipole moment derivatives and that the conformationally induced changes in the normal coordinates and those in the local derivatives are more or less correlated. A high correlation causes the two kinds of effects to cancel each other so that the effect on the intensity distribution is much diminished. However, the degree of correlation depends on the local direction of the dipole moment derivatives. For the special case where the dipole moment derivatives are parallel to the skeletal bonds, that is, parallel to the x axis, the derivatives are independent of conformation so that there can be no correlation between the changes in the normal coordinates and the dipole moment derivatives, and therefore there is no cancellation. In this case, the intensity distribution is maximally sensitive to conformational change.

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Monte Carlo Simulations of Polymer Degradations. 1. Degradations without Volatilization

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ABSTRACT: Polymer degradations, involving chain scissions without evolution of volatile products, have been simulated by Monte Carlo procedures in order to establish which parameters are useful to follow the degradation processes. Changes of the dispersity index (X_w/X_n), the ratio of weight- to number-average degrees of polymerization, give important information about randomness of the chain scissions, provided degradation is performed on polymer samples of different initial average degrees of polymerization or of different initial dispersity index. When scissions are completely random the dispersity index approaches the value of 2, independently of the fact that fragments formed in chain scissions might couple with each other. Changes of the value of X_n as the degradation proceeds and the formation of molecules larger than those present in the undegraded sample are also important features of the process.

Introduction

In our previous papers[1–4] we reported that a deeper insight into the mechanisms of thermal degradation of some polymeric materials could be achieved by simulating the degradation processes with Monte Carlo procedures. It has been possible to obtain some interesting information about depolymerization length of the two different chain radicals formed in random chain scissions, as well as about the reliability of the random chain scissions themselves, which occur either as homolytic bond scissions or as a consequence of intermolecular radical transfer.

In the present paper the simulation methods are applied to several hypothetical degradation processes of polymeric substances that take place without significant evolution of volatile products, in order to show their capabilities and limits in giving evidence to important features of polymer degradation. At the same time, these methods can be of value in providing useful suggestions about the choice of experiments to be conducted and of parameters to be measured. The simulation of degradation processes involving extensive volatilization will be a subject of our subsequent publication.

The Monte Carlo program (BASIC language, executable on a MS-DOS compatible PC) used in this study is practically the same as the one already described,[1,2] with minor changes to improve the flexibility in selecting degradation mechanisms and to allow treatment of macromolecules with a degree of polymerization (DP) up to 30 000. The simulation of a degradation process involving more than 10 scissions per original macromolecule or conversions to volatile products higher than 90% requires a few minutes.

The Monte Carlo procedure bears some resemblance with the one described several years ago by Malác[5] but is more exact, in the sense that macromolecules differing in one monomeric unit are separately treated, instead of treating macromolecules differing by less than 50 structural units together. This allows chemical changes (scissions, depolymerizations, coupling of radicals, intermolecular transfers, etc.) to be performed on individual chemical species and any averaging operation to be postponed until the right moment. Furthermore, the present procedure is not limited to closed systems but makes possible the investigation of the changes of parameters related with DP as a function of conversion to volatile products.

Polymer Degradation without Volatilization

In the simulations of polymer degradations it is assumed that fragments from different macromolecules interact with each other or with unbroken macromolecules. A possibility that branched molecules or cross-linked networks are formed is not taken into account. Therefore, when the formation of volatile products does not take place, the degradation is essentially a chain scission process. In the Monte Carlo calculations, however, it has been assumed that molecules with DP up to 5 have sufficient volatility and escape from the degrading sample. This implies a weight loss of less than 0.05% when each original macromolecule with DP higher than 1000 has been subjected, on the average, to ten scissions.

In a polymer degradation process involving almost exclusively chain scissions, the scissions can be either random or nonrandom. In the first case, each bond of a polymer chain has the same probability of cleavage, independent of the length of the chain: for instance, hydrolysis of ester groups in a polyester chain. There is a situation where

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