Notes

Application of Molecular Simulation Techniques To Simulate Vibrational Spectroscopic Features Associated with Hydrogen Bonds in Crystalline Polymers

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Introduction

When bands are properly assigned, vibrational spectroscopy can be one of the most effective techniques for characterization of polymer chemical composition and structure. Spectroscopic analysis is usually accomplished by a theoretical normal vibrational analysis based on Wilson's GF matrices method and force constants transferred from small molecules.[1] More sophisticated analyses are based on fundamental considerations of the type and magnitude of interatomic energies.[2,3] In this study, we propose an approach utilizing the molecular simulation technique for assignment of low-frequency vibrations in polymers. Low-frequency vibrations, which are important as many vibrations in this region are delocalized, can be extremely sensitive to differences in chain conformation and packing. However, these low-frequency data often cannot be readily analyzed due to the high degree of coupling between intra- and intermolecular forces.

The molecular dynamics simulation technique has recently proven to be a suitable alternate approach for simulation of vibrational spectroscopy.[4-6] In this study, molecular dynamics were utilized in studies of low-frequency vibrations in highly ordered poly(*p*-phenylene terephthalamide). A key structural feature of this polymer is the presence of hydrogen bonds. There is little question that this strong localized secondary force is directly responsible for the structural formation and properties of this high-performance aromatic amide. Few studies, however, have been pursued to more fully understand the spectroscopic features observed.[7]

The advantages of utilizing molecular dynamics to simulate vibrational spectra include the following: (1) The broad frequency range can be simulated, generally in the 0–4000-cm^{-1} region. (2) Molecular dynamics simulation involves not only individual molecules but also the aggregation of molecular systems including weak and strong intermolecular or interchain interactions. (3) Parameters pertaining to vibrational spectroscopic features, such as band frequency, intensity, and shape, can all be simulated. (4) Vibrational spectra for polymers under stress or at various temperatures can be examined. The crystalline structure of poly(*p*-phenylene terephthalamide) has previously been simulated.[8] On the basis of that study, the vibrational spectra in the crystalline state have been calculated; our results are reported here.

Method

The correlation function can be envisioned by considering the relationship, of either positions or velocities, of individual atoms of a polymer in states evaluated at any two different times. The resulting quantity is a function of time. This trajectory or evolution of the state as a function of time is directly associated with the dynamics of the system and therefore contains all the molecular vibrations in the high-frequency region. A form of vibrational spectra can be obtained by transforming the correlation function from the time domain to the frequency domain. Strictly speaking, in this study this spectrum does not contain intensity information as neither changes in dipole moment or polarizability are considered. Trajectory of atomic motion or position can be obtained via a molecular dynamics calculation. The position and velocity of individual atoms can usually be obtained at a time interval of 0.02–0.001 ps apart.[9,10]

If $A(t)$ is a real dynamic property of the system, the time correlation function $C(t)$ is defined by the ensemble average

$$C(t) = \langle A(0)\, A(t) \rangle \tag{1}$$

$$C(t) = \lim_{T\to 0} \frac{1}{T} \int_0^T \mathrm{d}\tau\, A(\tau)\, A(t+\tau) \tag{2}$$

The actual expression used in our analysis involves discrete steps. The correlation function used is then

$$C(t) = \frac{1}{M} \sum_{m=1}^{M} A(t_m)\, A(t_{m+n}) \tag{3}$$

where M is the total number of time intervals and n is the varying time interval associated with the correlation function.

The finite time duration of the trajectory is the principal cause for the statistical imprecision of the entire process. In order to reduce errors in the time correlation function calculated in molecular dynamics simulation, a suitably long time interval needs be considered. To obtain a relative precision of approximately 1% in the correlation function,[11] a run of 100 000 steps is necessary. The average velocity of the system is usually chosen as the dynamic property to be correlated to vibrational spectroscopic features. Additional properties, such as the pressure of a crystalline cell, can also be used to obtain the spectra.[12]

To carry out the Fourier transform, the $C(t)$ obtained in a finite time is truncated. Truncation, however, causes perturbative effects which often result in rapidly varying side lobes around a peak and loss of resolution. Window functions are thus usually utilized to reduce effects of discontinuity at the truncation point (at the maximum time). The Blackman function[13] is used in this study:

$$W(t) = 0.42 - 0.5 \cos(\pi t/t_{\max}) + 0.08 \cos(2\pi t/t_{\max})$$

$C(t)$ multiplied by the window function is then transformed.

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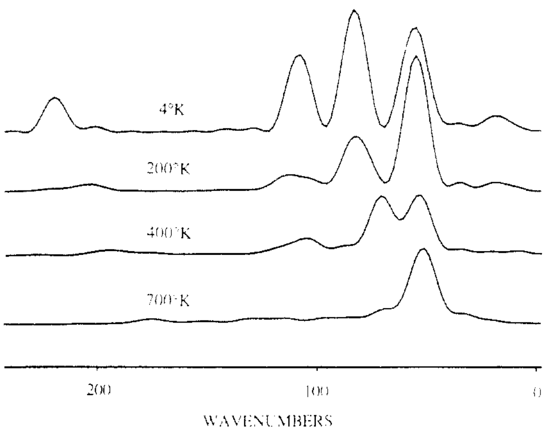

Figure 1. Simulated spectra of vibrational density resulting from fluctuation of the cell pressure during the molecular dynamics process at various temperatures.

Results and Discussion

The main emphasis of this study is assignment of the interchain hydrogen bond stretching vibration, generally thought to be in the 100-cm^{-1} region.[14] Changes of this vibration as a function of temperature and stress are of interest. The crystalline structure of poly(*p*-phenylene terephthalamide) has previously been successfully simulated.[8] Using the periodic boundary condition, the poly(*p*-phenylene terephthalamide) crystalline unit cell is described as an infinite 3-dimensional system. The calculated crystalline unit cell parameters agree well with experimental values.[15] The dynamics of this system are then evaluated at various temperatures ranging from 4 to 700 K. The calculated time interval is 33 ps.

We have used the correlation function of the pressure of the system for analysis. The correlation function weighted by the window function is then tranformed into the frequency domain. The calculated spectra as a function of temperature are presented in Figure 1. The spectra below 250 cm^{-1} may contain external modes arising from intermolecular interactions. Internal modes, such as skeletal bending or torsional vibrations, may also exist in this region. These low-frequency bands are usually analyzed by carrying out a normal-coordinate analysis. In our molecular dynamics calculation, bands can also be assigned either by choosing suitable dynamic variables or by switching specific energy terms in the system on or off as demonstrated below.

Among the various bands observed, the vibration at ~90 cm^{-1} in the simulated spectrum has been assigned to hydrogen bond stretching. This assignment is based on two criteria. It is important to establish that this vibration is associated with hydrogen bonds and is a stretching mode in character. Additionally, it is possible to follow the hydrogen bond energy term as a function of time. If this energy term is selected as the dynamic variable, the spectrum in the frequency space calculated from the correlation function obtained should be indicative of the band most closely associated with hydrogen bonds. Spectra of this type obtained in the present study on poly(*p*-phenylene terephthalamide) are shown in Figure 2. Clearly, only the mode at 90 cm^{-1} is present. With the simulation technique, it is possible to turn specific energy terms of intermolecular interaction on or off. The 90-cm^{-1} vibration is absent when secondary interactions due to hydrogen bonding are turned off.

The normal mode is a combination of various internal coordinates. The hydrogen bond stretching vibration is usually strongly coupled to bond stretching of the groups at each end of the hydrogen bond. Following the O···H distance only is insufficient since this intermolecular vibration may also contain contributions from skeletal bending or torsional motions of each chain.[16] It is possible, however, to locate hydrogen bond stretching from the band coupled to the C═O stretching, when C═O bond length is used as the dynamic variable. The spectrum obtained, which presents expected features in the high-frequency region, also shows an extremely small peak (~1/1500 in height) located at 90 cm^{-1} (Figure 2). This observation is also an indication that the band at 90 cm^{-1} is the hydrogen bond stretching mode. It should be emphasized that our assignment is based only on classical mechanics. Earlier studies have suggested that intensity should be considered in terms of bond delocalization theories.[17]

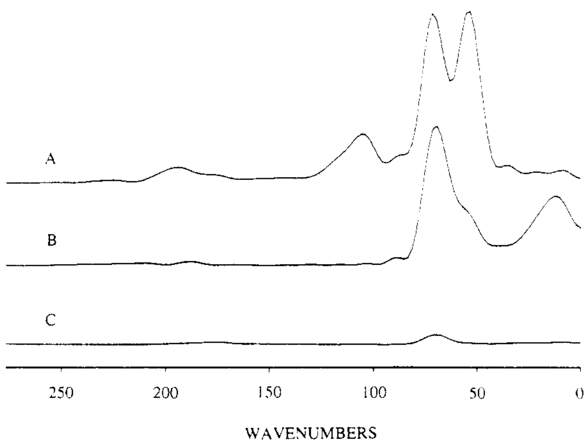

Figure 2. Simulated spectra of vibrational density resulting from various dynamical variables at 400 K: (A) the cell pressure; (B) the energy of hydrogen bond; (C) the length of C═O group.

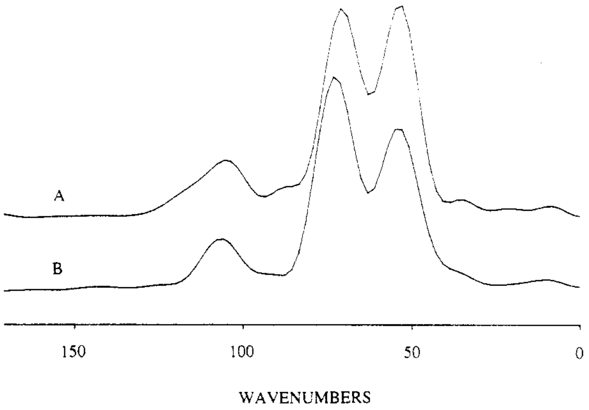

Figure 3. Simulated spectra resulting from fluctuation of the cell pressure during the molecular dynamics process at 400 K under stress: (A) 0 GPa; (B) 0.1 GPa.

With a rise in temperature, more kinetic energy is absorbed by polymer chains in the cell. This temperature increase significantly weakens the strength of the hydrogen bonds as the bond length is lengthened or the bond angle of O···HN contains more values in the higher energy states. Simulated vibrational spectra at 4, 200, 400, and 700 K are shown in Figure 1. The vibrational frequency clearly shifts downward when temperature is raised. Features sensitive to changes in the magnitude and specificity of hydrogen bonds are quickly *washed* away at higher temperature. Spectroscopic features known to be directly associated with hydrogen bonds are usually difficult to observe and can be clearly seen only at subambient temperatures.[18]

The relationship between macroscopic mechanical properties and molecular mechanisms responsible for deformation is often difficult to establish. Spectroscopic features are often perturbed for polymers under extenal stress.[19] Band frequency is often lower under stress, and band shape may become asymmetrical for most of the intramolecular modes along the backbone.[20,21] For the intermolecular mode in the low-frequency region, upward shifts were observed for poly(oxymethylene) in the crystalline phase.[21] These shifts were thought to be caused by lateral shrinkage which thus increases the intermolecular interaction.[21] Previous study has shown the applicability of simulation techniques in understanding stress-induced spectroscopic changes.[22] In this case, upon applying an extensional stress along the chain or *c* axis of the poly(*p*-phenylene terephthalamide) crystal, interchain interactions would presumably be perturbed as observed in our early study.[23] Molecular dynamics runs were performed at 400 K for poly(*p*-phenylene terephthalamide) under 0.1 GPa stress. The calculated low-frequency vibrations are shown in Figure 3. In comparison with the sample free from stress, the ~90-cm^{-1} band shifts upward with increasing stress suggest that lateral contraction has indeed occurred for the stressed sample.

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