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Molecular Vibrations in Nylon 6 Studied by Inelastic Neutron Scattering

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ABSTRACT: Incoherent inelastic neutron scattering experiments were performed on highly drawn fiber of nylon 6. The sample was about 47% crystalline in the thermodynamically most stable α form. The spectra were measured in the 35−125 meV range with a filter-analyzer spectrometer using a Be-graphite low-pass Bragg cutoff filter. By employing two scattering geometries, we were able to discriminate between vibrational modes with hydrogen displacements along polymer chains from modes perpendicular to chains. In the low-frequency range we have observed exclusively parallel modes at 45, 54, and 65 meV due to polymer skeleton deformations. CH_2 rocking and twisting vibrations and some of the amide modes are also observed, and their polarization is discussed. A preliminary vibrational analysis of a single polymer chain using force constants calculated by the semiempirical Hartree−Fock AM1 method has been performed, and the calculated and measured spectra are compared. Overall, a good agreement between the neutron scattering spectra, the AM1 calculation, and IR and Raman data is found.

I. Introduction

Nylons, or polyamides, are a class of polymers with broad industrial applications. The chemical structure of nylon 6 is $[-(CH_2)_5NHCO-]_n$, where the number added to the name of the polymer denotes the number of carbon atoms in the repeating unit. Nylon 6 crystallizes in two different forms, α and γ, which have been well characterized using X-ray diffraction.[1,2] In the thermodynamically most stable α form, the polymer chains are in the fully extended planar *trans* conformation and are arranged in sheets by means of hydrogen bonding between antiparallel chains. In the γ form, the polymer chains are in the twisted helical (i.e., nonplanar) conformation and the crystal consists of sheets of parallel chains joined by H-bonds, with chain directions opposite in alternating sheets. The γ form can be prepared by spinning fibers at high speed or by iodinating nylon 6 in an aqueous KI/I_2 solution, followed by the removal of iodine using aqueous sodium thiosulfate.[3]

Infrared and Raman spectroscopies have been employed extensively in the characterization of nylons. The vibrations of the planar and strongly polar secondary amide group −NHCO− determine many of the features in the IR spectra. Furthermore, the characteristic bands of the amide group are quite sensitive to the physical state of the sample. Numerous studies were reported in which the correlations between the structure of nylons, their crystallinity, polymorphous modifications, and IR spectra were investigated.[4]

Raman spectroscopy provides information on vibrational modes complementary to that obtained by IR. Hendra *et al.*[5] measured the Raman spectra of nylon 6 and, more recently, also performed a systematic study of single number nylons[6] using the Fourier transform technique.

Inelastic neutron scattering (INS) spectroscopy can contribute additional information about the vibrational properties of polymers. Whereas in IR and Raman spectra, one observes the vibrational modes at the center of the Brillouin zone (BZ), neutron scattering probes the whole BZ, and from the measured data, phonon dispersion curves (in the case of monocrystalline, coherently scattering samples) or phonon density of states (in the case of incoherent scatterers) can be extracted. A distinct advantage of the INS method over the optical spectroscopic techniques is that the neutron scattering intensity is completely independent of the symmetry of vibrational modes and, therefore, may permit the observation of modes which are IR or Raman inactive or involve only very small changes of dipole moments and polarizabilities.

Our primary aim in this paper is to present INS spectra of semicrystalline, highly drawn fiber of nylon 6. By using an oriented sample, we were able to discriminate between vibrational modes with hydrogen displacements perpendicular to polymer axes and modes parallel to polymer axes. Such measurements on oriented polyethylene (PE) have already been performed by Jobic,[7] allowing now the comparison of the phonon densities of states of these two polymers in the measured frequency range. The harmonic analysis of an infinite nylon 6 chain, based on force constants calculated by the semiempirical Hartree−Fock AM1 method, is also briefly described, and the results and assignment of modes are discussed.

II. Experimental Section

A round cross section nylon 6 fiber was used for these measurements. The fiber was hot-drawn (4.5×) at a roll temperature of 175 °C using a pin temperature of 75 °C. The fibers were not heat set and were wound without any relaxation. The final diameter of the drawn fiber was 28 μm as determined from optical micrographs. The density of the nylon fiber as measured using a density gradient column was 1.146 g cm^{-3}.

The crystallinity of the sample was measured by wide-angle X-ray diffraction. The fiber is 47% crystalline as determined from the ratio of the areas of the crystalline peaks between

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$2\theta = 5^\circ$ and 35° to the total integrated scattered intensity in the same angular range.[8] The fibers are in the α crystalline form, though the presence of a very small (<2%) fraction of the γ form cannot be ruled out. The crystallite sizes or the coherence lengths calculated from the width of the (200) and (002 + 202) reflections using the Scherrer equation are 104 and 51 Å, respectively. As a result of the drawing procedure, the fibers are highly oriented. The azimuthal width of the (200) reflection is 13.8°, and the Hermans orientation function is 0.969.[9]

About 400 mg of the nylon fiber was used in the neutron scattering experiments. The fiber was carefully wound about a thin aluminum frame such that the orientation was preserved and the chain axis (the crystallographic **b** axis) was parallel to one side of the frame. The packet was then hermetically sealed in a cylindrical Al container filled with He gas.

Because hydrogen is a strong incoherent scatterer with a cross section much greater than that of other nuclei, the inelastic scattering of H-rich materials is almost exclusively incoherent and sensitive only to hydrogen motions. It can then be shown that in the one-phonon approximation the incoherent inelastic scattering is directly related to the amplitude weighted vibrational density of states.[10] The scattering function $S_{\mathrm{inc}}(\mathbf{Q},\omega)$ also depends on the product $\mathbf{Q}\cdot\mathbf{e}_j^d(\mathbf{q})$, where $\mathbf{Q} = k_i - k_f$ is the wave-vector transfer and $\mathbf{e}_j^d(\mathbf{q})$ is the displacement vector of the dth hydrogen atom for the jth normal mode and phonon wave vector **q**. Thus, two scattering geometries may be designed such that **Q** is either mainly perpendicular or parallel to the chain axis (the **b** axis) of the oriented polymer, and the spectra measured in these two geometries reflect the contribution of vibrational modes with displacements normal or parallel to the chain axes (the precise expressions for the differential cross section for scattering from oriented samples were derived by Myers *et al.*[11]). A more detailed description of the experimental setup is given in our recent neutron scattering study of stretch-oriented poly(*p*-phenylenevinylene).[12]

The experiments were performed using the beryllium filter spectrometer BT-4 at the NIST research reactor facility. In this filter-analyzer spectrometry (FAS), monochromatic neutrons with initial energy E_i are inelastically scattered through ~90° by the sample and then pass through a Bragg cutoff filter before detection. Only neutrons with final energy $E_f < E_{\mathrm{cutoff}}$ are recorded. The filter consists of cooled polycrystalline Be and powdered graphite which gives a cutoff of ~1.1 meV. However, the resolution is also limited by the performance of the monochromator and worsens with increasing energy transfer E. We used a copper Cu(220) monochromator, and collimators with 40′ divergence were placed both in the pile and between the monochromator and the sample. The covered energy transfer (phonon frequency) range was from 35 to 125 meV (i.e., from 280 to 1000 cm^{-1}).

III. Results

The FAS spectra were recorded by scanning the neutron incident energy and detecting all scattered neutrons through the low-pass filter for a fixed monitor count of incident neutrons. The measurements were performed at 150 K. The scattering spectrum obtained in the **Q** ⊥ **b** geometry is shown in Figure 1(a). In this geometry the vibrational modes with displacements of H atoms perpendicular to polymer axis produce the strongest features. The FAS spectrum measured for the same monitor count in the **Q** || **b** geometry is shown in Figure 1(b). The background (i.e., the scattering from empty sample holder under the same conditions) has been subtracted from both spectra.

The measured spectra display several distinct features as well as obvious differences between the two polarizations. The strongest peak is observed in the parallel polarization at 118 meV. At the same value in the **Q** ⊥ **b** spectrum there is only a smaller peak, and thus the vibrational mode at this frequency is polarized mainly parallel to the chain axis. The next strongest feature occurs at 91 meV with about the same intensity in both polarizations. In fact, in the parallel spectrum this seems to be a double peak with maxima at 91 and 93 meV; however, in order to resolve better the structure of this peak, much longer counting times and shorter energy steps would be required. We note that a strong peak near 90 meV is also found in the scattering spectra of polyethylene, albeit with pronounced perpendicular polarization,[7] where it is attributed to a $\mathrm{CH_2}$ rocking mode. Hence, we may assume that a significant part of the feature at 91 meV in our sample is due to similar type of vibration of the methylene sequences in nylon.

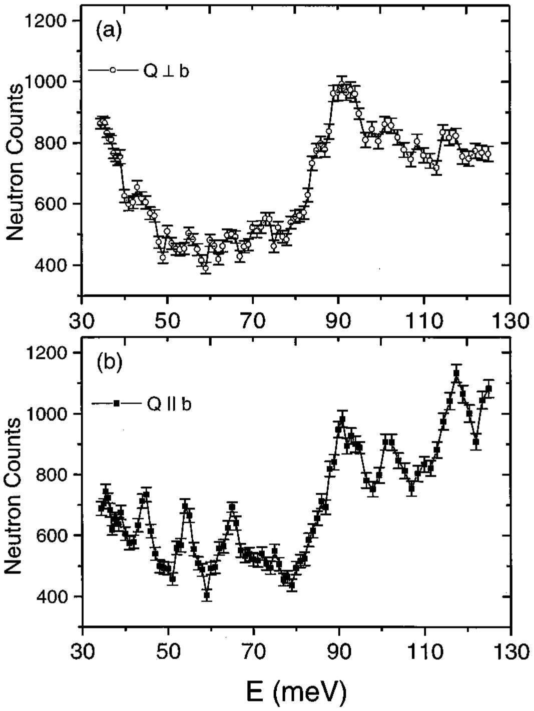

Figure 1. The FAS spectra of oriented nylon 6 measured at $T = 150$ K: (a) scattering measured in the **Q** ⊥ **b** geometry; (b) scattering measured in the **Q** || **b** geometry.

A well resolved peak in the parallel spectrum can be seen at 101 meV, and it also appears with somewhat smaller intensity in **Q** ⊥ **b**. Interestingly, in polyethylene a peak approximately in this frequency range has been identified in the *transverse* polarization and is due to two-phonon scattering from a combination of the acoustic mode peaked at ~20 meV and the sharp 90 meV rocking mode. However, the feature that we observe is extremely well resolved and quite sharp, especially in **Q** || **b**, and our vibrational analysis (as discussed in the next section) also confirms a single phonon band at this frequency.

In the lower frequency range, we find three sharp and almost exclusively parallel peaks at 45, 54, and 65 meV. The latter is also observed in PE as the lowest longitudinal peak at 64 meV[7] and corresponds to the cutoff frequency of the longitudinal acoustic band. The 45 and 54 meV peaks in nylon 6 have no counterparts in the scattering spectra of polyethylene and thus have to be attributed to the amide groups—either as localized vibrations of these groups or as the consequence of the distortion of phonon bands, since the amides act as a periodic perturbation of the methylene sequence.

Finally, we point out several features in the spectra which are close to the detection limits of our experiments. At 74 meV a weak feature is found in both **Q** ⊥

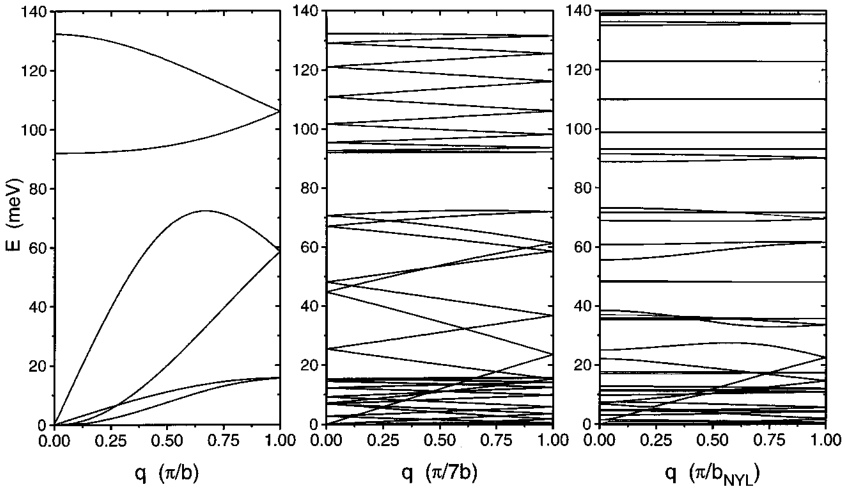

Figure 2. Phonon dispersion curves derived from the AM1 calculation. Left: polyethylene; middle: polyethylene, with periodicity increased to 7 times the original unit cell length; right: nylon 6. Only the phonon bands below 140 meV are shown.

b and **Q** || **b** geometries, which would suggest a vibrational mode at this frequency with mixed polarization. Next, a shoulder is situated at 86 meV and is resolved slightly better in the perpendicular polarization. Finally, a barely visible peak is located close to 110 meV. Because it is observed in *both* independent measurements for **Q** ⊥ **b** and **Q** || **b**, it is less probable than this feature is due to statistical noise, and we consider it as a real feature in the vibrational density of states of nylon 6.

IV. Calculations and Assignment of Modes

Our assignment of observed features in the INS spectra to particular vibrational modes is based on available IR and Raman data, on the polarization of peaks, and on the vibrational analysis of a single infinite polymer chain. Since the interchain interactions are completely neglected in our vibrational analysis, the calculations cannot reproduce the phonon bands with phonon wave vectors **q** transverse to polymer axes and in which interchain forces play an important role, e.g., whole-chain librations. However, these modes occur generally below 30 meV, and we may expect that in the frequency range that was experimentally measured the intrachain interactions will be the most important.

In order to make a comparison between the normal modes of nylon 6 and polyethylene, we carried out similar calculations for both polymers. Rather than adopt some experimentally fitted set of force constants, we calculated the intramolecular force field by the Hartree–Fock semiempirical Austin model 1 (AM1) method.[13] The obtained results may then serve as a test of performance of the AM1 parametrization in predicting the lower frequency modes, which is less often addressed due to the lack of available experimental data. These AM1 calculations are not expected to give the best fit to experimental data. Many times such results serve only as a first guess for further refinement of the force constants, using for example the scaled quantum mechanical oligomer force field method.[14] Since the phonon density of states will be measured for even lower frequency range, we did not attempt to perform such refinement at this time. Nevertheless, the AM1 results can be used as a solid basis for the assignment of modes.

In the calculation, the cluster method[15,16] with periodic boundary conditions was employed to mimic an infinite chain, and clusters of quite large size were considered in order to avoid spurious interactions. For nylon 6 the cluster size was 2 unit cells (i.e., 4 chemical repeats), and for polyethylene 14 unit cells. Molecular geometry was optimized by energy minimization in internal coordinates with full use of the symmetry of each polymer. The relaxed geometries were found to be in satisfactory agreement with experimental values; e.g., the repeat distance along the chain axis calculated for nylon 6 is $b = 17.355$ Å (17.24 Å from experiment[1]) and for polyethylene $b = 2.499$ Å (2.546 Å from experiment;[17] we denote this lattice parameter of PE as b in accordance with the labeling for nylon).

After relaxing the geometry, the tensor of second derivatives of potential energy with respect to nuclear coordinates has been evaluated by numerical differentiation of the analytical first derivatives. Then the phonon dispersion curves for polyethylene and nylon 6 have been calculated by standard methods. The results, plotted in the reduced zone scheme, are shown in Figure 2 (the phonon frequency is given as $\hbar\omega$ in millielectronvolts, and only the bands below 140 meV are shown). We find it quite illustrative to replot the phonon lines for PE once more in the reduced zone corresponding to a unit cell 7 times larger than the true period of PE, which is approximately the size of the unit cell of nylon 6. Now, as a consequence of such an artificially increased translational period, the typical folding of the phonon bands appears (Figure 2, middle). Since in nylon 6 some of the methylenes are periodically replaced by the heavier amide groups, the phonon branches become discontinuous, separated by gaps (Figure 2, right). This can be nicely seen in the acoustic bands of PE which are split into several optical bands in nylon. In the same manner, the lowest optical band in PE (between 92 and 133 meV) is also split into several almost flat lines in nylon 6. We also notice the anticrossing behavior of some of the nylon 6 phonon curves, since the lines for which the eigenvectors have the same symmetry (with respect to the reflection by a mirror plane containing the chain axis) cannot cross.

Another consequence of introducing the amide groups is the occurrence of localized vibrations of the amides. By analyzing the calculated eigenvectors in the 0–140 meV range, we could identify such vibrations at 35.8 and 71.5 meV, which are almost q-independent and correspond to vibrations of amides out-of-plane of the polymer skeleton, and near 90 and 136 meV, corresponding to in-plane amide vibrations. In fact, the calculated 136 meV mode is not a true amide mode but C−CO stretching, which is usually identified near 115 meV in IR and Raman spectra. We do not know the reason for such large deviations; however, since this mode does not produce a strong INS intensity, we did not study this problem in more detail. We should also stress that many of the other modes involve some deformation of the −NHCO− groups as well.

In order to make a connection with the INS spectra, it is necessary to calculate the amplitude-weighted phonon density of states. Our single chain analysis allows only the evaluation of the one-dimensional frequency distribution function; as discussed earlier, this may be a good first approximation to the true density of states except for the very low frequency range (e.g., in the 1-D case there is a van Hove singularity even at 0 meV because of the parabolic behavior of the acoustic lines). We have calculated the amplitude-weighted 1-D phonon densities multiplied by nuclear cross section/mass ratios to approximate the INS intensity for both **Q** ⊥ **b** and **Q** ∥ **b** polarizations. They are given by the expressions

$$G_{\perp}(\omega) = \frac{1}{N}\sum_{d}\frac{\sigma_d}{M_d}\sum_{\mathbf{q}j}\frac{1}{2}|\mathrm{e}^{d}_{\perp j}(\mathbf{q})|^2\delta(\omega-\omega_j(\mathbf{q})) \qquad (1)$$

$$G_{\parallel}(\omega) = \frac{1}{N}\sum_{d}\frac{\sigma_d}{M_d}\sum_{\mathbf{q}j}|\mathrm{e}^{d}_{\parallel j}(\mathbf{q})|^2\delta(\omega-\omega_j(\mathbf{q})) \qquad (2)$$

where $\mathbf{e}^{d}_{\parallel j} = (\mathbf{e}^{d}_{j}\cdot\mathbf{b}_0)\mathbf{b}_0$ and $\mathbf{e}^{d}_{\perp j} = \mathbf{e}^{d}_{j} - \mathbf{e}^{d}_{\parallel j}$ are the parallel the perpendicular components of the eigenvectors with respect to the chain axis, $\mathbf{b}_0$ is the unit vector along chain axis, σ_d and M_d are the cross section and the mass of the dth nucleus, and N is the appropriate normalization constant determined by normalizing the total unpolarized and unweighted frequency distribution to unity. The prefactor $^1/_2$ in eq 1 follows from the averaging over all relative orientations of $\mathbf{Q}_{\perp}$ (perpendicular component of **Q**) with respect to $\mathbf{b}_0$, assuming that the sample is completely isotropic in the plane perpendicular to chain axis (i.e., drawing direction).

The calculated weighted frequency distribution functions for polyethylene and nylon 6 are shown in Figure 3. Since the van Hove singularities are due to the flat regions in dispersion curves, their number for nylon 6 is much greater than for polyethylene. In general, the results for PE compare quite well with experiment[7] and with previous calculations based on optimized force constants.[18] The biggest difference between the experiment and our calculation is for the cutoff frequency of the longitudinal acoustic modes in PE, which is observed at 64 meV and calculated at 72 meV. Hence, it seems that the AM1 method slightly overestimates the stiffness of the C−C−C bond angle with regard to in-plane bending involved in these vibrational modes. As we can now see, due to the splitting of this longitudinal band into several optical bands in nylon 6, the three parallel features centered at ca. 48, 60, and 70 meV emerge. They all involve in-plane skeletal deformation and to some degree also in-plane deformation of the amides. We note that the skeletal vibrations are visible so well in the INS experiments because the hydrogens are displaced together with carbons to which they are connected.

In order to reproduce the INS spectra of nylon more realistically, the polarized weighted phonon densities were multiplied by the Debye−Waller factor (for simplicity calculated for H atoms only) and broadened in correspondence with the FAS instrumental resolution. Because the relation $Q^2 \sim E$ holds for the FAS measurements, as discussed elsewhere,[7,12] the results shown in Figure 4 can now be regarded as calculated scattering intensity in the one-phonon emission approximation for $T \rightarrow 0$. Of course, in the experiment additional broadening occurs because of multiphonon processes.

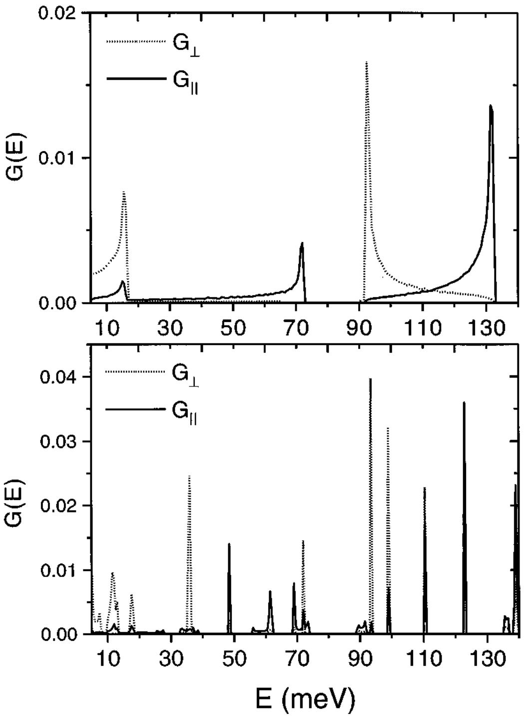

Figure 3. The AM1 calculated single chain neutron-weighted polarized phonon densities of states for polyethylene (upper figure) and nylon 6 (lower figure). Dotted line: perpendicular polarization; solid line: parallel polarization.

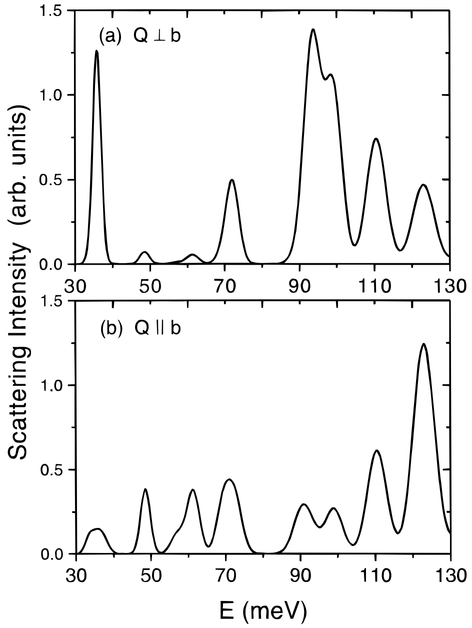

Figure 4. Polarized FAS spectra of nylon 6 based on the results of the AM1 calculation: (a) for **Q** ⊥ **b**; (b) for **Q** ∥ **b**.

As we can see, the agreement between the experiment (Figure 1) and the AM1 calculation (Figure 4) is by no means perfect. The calculated positions of the three parallel peaks are systematically shifted upward by ~3−6 meV; as mentioned earlier, this is due to the

Table 1. Summary of Vibrational Frequencies of Nylon 6 Observed by Inelastic Neutron Scattering, AM1 Results, Results of Jakeš and Krimm, Infrared and Raman Frequencies, and Assignment of Modes[a]

INS (meV)	AM1 calc (meV)	Jakeš−Krimm calc [meV (cm^{-1})] sym	IR/Raman [meV (cm^{-1})]	assignment
45	48	45.6 (368) A_1	45.9 (370, IR)[b]	in-plane skeletal bend
54	61	55.2 (445) A_1	55.4 (447, IR)[b]	in-plane skeletal bend
65	69	64.3 (519) B_1	64.8 (523, IR)[b]	in-plane skeletal bend
74	71.5	72.0 (581) B_2	71.9 (580, IR)[b]	amide VI
86	90	86.3 (696) B_2	85.9 (693, IR)[b]	amide V
91	93.5	90.1 (727) B_2	91.0 (734, IR)[c] 92.1 (743, R)[d]	CH$_2$ rock
101	99	95.1 (767) B_2		CH$_2$ rock
110	110	104.4 (842) B_2	103.9 (838, IR)[c]	CH$_2$ rock + twist
118	122.5	118.4 (955) B_2	118.4 (955, IR)[c]	CH$_2$ twist + rock

[a] Some data were transferred into millielectronvolts; 1 meV = 8.066 cm^{-1}. [b] Reference 19. [c] Reference 20. [d] Reference 6.

overestimating of the carbon skeleton stiffness by the AM1 method. Better agreement is obtained for the weaker 74 meV feature which is calculated near 72 meV. However, in the experiment it appears unpolarized, whereas the analysis predicts a perpendicular mode [the peak in Figure 4(a) is due to the flat amide line at 71.5 meV and should not be confused with the calculated longitudinal cutoff near 70 meV in Figure 4(b)].

The frequencies of the strong peaks observed at 91 and 101 meV are computed quite acceptably at 93.5 and 99 meV. The eigenvectors suggest CH$_2$ rocking vibrations, and the calculated peaks are therefore polarized mainly in the perpendicular direction. Interestingly, in the INS spectra we observe these peaks very strongly in both polarizations. The careful reader will also notice that the peak calculated for $\mathbf{Q} \parallel \mathbf{b}$ [Figure 4(b)] appears at ~90 meV and not 93.5 meV. The reason is that this peak is due to the weakly dispersed in-plane amide band centered near 90 meV (cf. Figure 2, right). Indeed, in the measured spectra, we have resolved a shoulder at 86 meV, curiously again with mixed or even perpendicular polarization. These discrepancies in the polarization of some of the modes will be discussed in more detail later. The unpolarized band calculated at 110 meV agrees well with the barely resolved feature in the scattering spectra near the same frequency. Finally, the strongest parallel peak observed near 118 meV is calculated with slightly larger difference at 122.5 meV. This band involves CH$_2$ rocking as well as considerable CH$_2$ twisting vibrations and thus contributes mainly in the parallel polarization.

The assignment of modes observed in the FAS spectra is summarized in Table 1. In the table we have also included the frequencies calculated by Jakeš and Krimm[21] (using a valence force field fitted for nylons and *N*-methylacetamides) as well as infrared and Raman data. The results of Jakeš and Krimm are given only for those symmetry species at $q = 0$ which lie on the phonon bands giving the strongest INS intensity.

There is overall a very good agreement between the INS frequencies and the IR/Raman values. This holds even for the lowest skeleton bending mode at 45 meV which appears in IR spectra as a barely resolvable shoulder at 45.9 meV (370 cm^{-1}).[19] The other two longitudinal modes produce stronger IR peaks positioned at 55.4 meV (447 cm^{-1}) and 64.8 meV (523 cm^{-1}), and it was already noticed by Hummel that their intensity seems to depend on the degree of crystallinity of the sample (cf. ref 4, spectra 101 and 102). This is understandable since the weakly dispersed phonon bands at these frequencies are characteristic only for the fully extended polymer conformation.

It is remarkable that the modes due to the secondary amides (amide V and amide VI at 85.9 and 71.9 meV, respectively) in nylon 6 are also identifiable in the neutron scattering spectra. With regard to these, the AM1 calculation performed quite well in reproducing the frequency as well as the character of the amide VI mode, which is mainly out-of-plane displacements of N and C(O) in opposite directions. On the other hand, the calculated amide band near 90 meV involves considerable C=O in-plane bending and thus resembles more the mode denoted as amide IV than amide V. One explanation of the absence of amide V in the AM1 results could be the lack of broader dispersion of the ~72 meV phonon band. For instance, such broadening could be caused by interchain interactions, and especially the hydrogen bonding between the amides. With respect to amide IV, it was already pointed out by Jakeš and Krimm[21] that this mode should lie above 700 cm^{-1} in nylons (733 cm^{-1} for nylon 6). Therefore, in the INS spectra it is probably buried in the strong 91 meV peak. One way to improve the signal from the amides would be to deuterate all the methylenes, which would effectively "turn off" the deuterated sites to incoherent scattering spectra. The individual amide bands should then be easily identifiable.

We conclude the discussion of amide bands with briefly mentioning the AM1 calculated perpendicular peak at 36 meV. This mode, involving out-of-plane torsions of the −NHCO− groups, could be assigned to amide VII mode. The calculation is somewhat consistent with the measured data, since in the FAS spectra we did observe higher scattering intensity near 35 meV in $\mathbf{Q} \perp \mathbf{b}$ than in $\mathbf{Q} \parallel \mathbf{b}$. Nevertheless, a neutron scattering experiment covering the 0−40 meV range (e.g., with the time-of-flight technique) is necessary to validate the presence of this mode.

The progression of the CH$_2$ rocking modes has been observed above 90 meV and reproduced quite well by the AM1 calculation. Whereas the lowest of these modes at 91 meV involves only the typical rocking motion of the hydrogens, the other modes also incorporate CH$_2$ twisting motions in increasing order, as depicted in Figure 5. This twisting is supported by the out-of-plane distortions of the planar carbon skeleton, and therefore, the higher frequency modes are characteristic for extended nylon chains. Also, because of the twisting, the polarization of these modes changes from perpendicular at 91 meV to predominantly parallel near 120 meV, as seen in Figure 4.

This interesting behavior provides important clues for explaining the observed polarization of peaks in the FAS spectra. The fact that near 91 meV we have measured equally strong scattering in both polarizations means

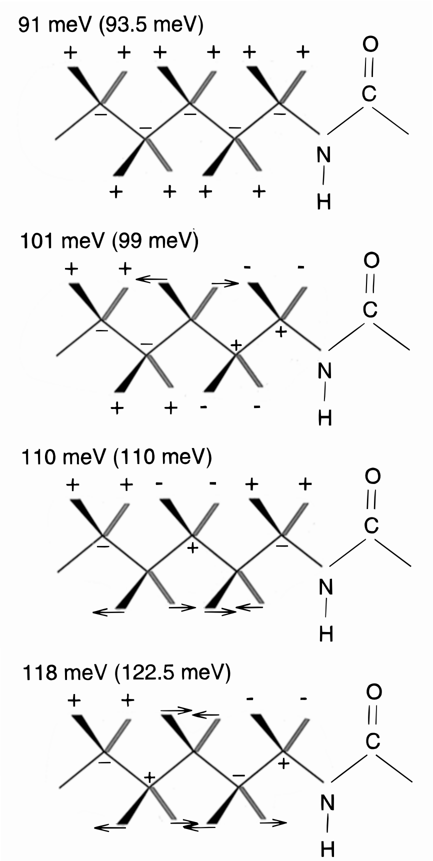

Figure 5. Schematic representation of the vibrational modes of nylon 6 (for $q = 0$) for the phonon bands above 90 meV and their frequencies (numbers in parentheses denote the AM1 calculated values).

that a large fraction of methylene units run in directions significantly different from the drawing direction. This cannot be explained by the ~14° mosaicity in the crystalline phase alone, and thus the scattering near 91 meV in $\mathbf{Q} \parallel \mathbf{b}$ must come from the chains in the amorphous region. Optical spectroscopic data support such a claim, as it is well-known that this frequency does not change much in different phases (e.g., in PE this rocking mode appears as a broader band at 720 cm^{-1} in liquid, and as a doublet at 731 and 725 cm^{-1} in the crystalline phase[22]). Furthermore, these chains in the amorphous region have to be in unextended conformation; otherwise, we would observe the characteristic parallel peaks (45, 54, 65, and 118 meV, which all require extended methylene sequence) in $\mathbf{Q} \perp \mathbf{b}$ as well. The presence of unoriented chains also explains the appearance of amide peaks in the FAS spectra for both geometries. Thus, our INS data provide an independent dynamical evidence that even after the drawing procedure there exists a rather large fraction of nylon chains in the amorphous region which are not extended or oriented in any way. This conclusion is also supported by the analysis of the position, width, and shape of the amorphous halo in the X-ray diffraction patterns of oriented nylon fibers.[23] The X-ray study reveals that the fraction of oriented amorphous phase is about 49%, and about half of the chain segments is unoriented, which conforms perfectly with the observed polarization in the neutron spectra. Our solid state NMR measurements[24] show that the mobility of solvents such as water, which selectively diffuse into the amorphous domains, is significantly affected by the type of orientation suggested by the INS polarization analysis. These results are particularly important, since the structure of the amorphous region directly influences many properties of the fiber such as strength, modulus, and shrinkage.[9]

V. Conclusion

We have demonstrated the power of the FAS neutron scattering technique to obtain information about frequency and polarization of vibrational modes in oriented nylon 6 samples. In general, the observed modes are in perfect agreement with infrared and Raman data, though we have also observed a peak which has not been identified by the optical methods (101 meV), and a peak for which the deviation from IR assignment is rather large (110 meV).

It is possible to employ a similar polarization discrimination "strategy" also in neutron time-of-flight spectroscopy with which the energy transfer range 0−40 meV can be readily examined. This opens an exciting opportunity for investigating the interchain interactions in nylons. As we have seen in a recent study of pristine and Na-doped stretch-oriented polyacetylene, well-defined features (corresponding to whole-chain librations and translations in the crystalline phase) can be found in the polarized phonon density of states.[25] We may expect that the comparison of neutron spectra of nylon and polyethylene will provide important information about the strength of the interchain interactions and in particular the hydrogen bonds in nylon. Work in this direction is currently in progress.

The vibrational analysis of nylon 6 chain using the force constants calculated with the AM1 Hamiltonian proved to be a convenient method for obtaining a first insight into the vibrational properties. By comparing the results, we noticed that mainly the *parallel* modes seem to have the calculated frequencies shifted upward by 3−6 meV, whereas for the perpendicular vibrations the agreement between the calculation and experiment is better. Admittedly, the interchain interactions (which were completely neglected) may also affect the phonon bands in the investigated frequency range and cause the correlation and crystal field splitting, though such effects are usually of the order 1−2 meV. More complete lattice calculations are certainly necessary, especially if the density of states below 30 meV is to be calculated.

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References and Notes

(1) Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J. Polym. Sci.* **1955**, *17*, 159.
(2) Arimoto, H.; Ishibashi, M.; Hirai, M.; Chatani, Y. *J. Polym. Sci. A* **1965**, *3*, 317.
(3) Kinoshita, Y. *Makromol. Chem.* **1959**, *33*, 1.
(4) Hummel, D. O. *Infrared spectra of polymers in the medium and long wavelength regions*; Wiley: New York, 1966, and references therein.
(5) Hendra, P. J.; Watson, D. S.; Cudby, M. E. A.; Willis, H. A.; Holliday, P. *Chem. Commun.* **1970**, 1048.
(6) Hendra, P. J.; Maddams, W. F.; Royand, I. A. M.; Willis, H. A.; Zichy, V. *Spectrochim. Acta* **1990**, *46A*, 747.
(7) Jobic, H. *J. Chem. Phys.* **1982**, *76*, 2693.
(8) Murthy, N. S.; Minor, H. *Polymer* **1990**, *31*, 996.
(9) Murthy, N. S.; Correale, S. T.; Moore, R. A. F. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1991**, *47*, 185.
(10) Lovesey, S. W. *Theory of Neutron Scattering from Condensed Matter*; Clarendon: Oxford, 1984; Vol. 1, p 120.

(11) Myers, W.; Summerfield, G. C.; King, J. S. *J. Chem. Phys.* **1966**, *44*, 184.
(12) Papanek, P.; Fischer, J. E.; Sauvajol, J. L.; Dianoux, A. J.; Mao, G.; Winokur, M. J.; Karasz, F. E. *Phys. Rev. B* **1994**, *50*, 15668.
(13) Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(14) Cui, C. X.; Kertesz, M. J. *J. Chem. Phys.* **1990**, *93*, 5257.
(15) Dewar, M. J. S.; Yamaguchi, Y.; Suck, S. H. *Chem. Phys. Lett.* **1977**, *50*, 259.
(16) Stewart, J. J. P. *New Polym. Mater.* **1987**, *1*, 53.
(17) Wunderlich, B. *Macromolecular Physics*; Academic: London, 1973; Vol. 1.
(18) Lynch, J. E.; Summerfield, G. C.; Feldkamp, L. A.; King, J. S. *J. Chem. Phys.* **1968**, *48*, 912.
(19) Tadokoro, H.; Kobayashi, M.; Yoshidome, H.; Tai, K.; Makino, D. *J. Chem. Phys.* **1968**, *49*, 3359.
(20) Jakeš, J.; Schmidt, P.; Schneider, B. *Collect. Czech. Chem. Commun.* **1965**, *30*, 996.
(21) Jakeš, J.; Krimm, S. *Spectrochim. Acta* **1971**, *27A*, 19.
(22) Bower, D. I.; Maddams, W. F. *The vibrational spectroscopy of polymers*; University Press: Cambridge, 1989; p 166.
(23) Murthy, N. S.; Minor, H.; Bednarczyk, C.; Krimm, S. *Macromolecules* **1993**, *26*, 1712.
(24) Hutchison *et al.*, unpublished.
(25) Papanek, P.; Fischer, J. E.; Sauvajol, J. L.; Dianoux, A. J.; McNeillis, P. M.; Mathis, C.; Francois, B. In *Neutron Scattering in Materials Science*; Neumann, D. A., Russel, T. P., Wuensch, B. J., Eds.; Materials Research Society Symposium Proceedings 376; Materials Research Society: Pittsburgh, PA, 1995.

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