Polarized Raman Measurements of Uniaxially Oriented Poly(ϵ-caprolactam)

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ABSTRACT: The anisotropic scattering properties of a uniaxially oriented filament of nylon-6 have been investigated by polarized Raman scattering measurements. The high orientation of polymer chains which resulted during processing allowed the recording of unique polarized Raman spectra whose relative intensity pattern reflected the ordered chain conformation and the symmetry of the unit cell. To assign the observed bands to their respective symmetry species, the anisotropic scattering results for four different combinations of incident and scattered polarization were compared with those predicted by group theoretical analysis, existing IR data, and the results from normal coordinate calculations. In this way a complete assignment of the Raman bands of nylon-6 has been possible for the first time.

Introduction

The relationship between macroscopic properties and microscopic structure encompasses much of the goal of materials science. Tensile strength, modulus, and properties like expansion coefficient are all derived from organization and microstructure at the molecular level. Hence, it is critically important that molecular characterization methods be developed so that insight into structure−property relationships can be used to design the next generation of advanced materials.

Polyamides have received considerable interest for many years because they are extremely important as industrial commodity polymers and as model compounds for biological molecules. Poly(ϵ-caprolactam) (nylon-6) is a simple polyamide having a chemical repeat unit of the form $-(CH_2)_5C(O)N(H)-$. Early investigations of the crystal structure by X-ray scattering studies indicated that poly(ϵ-caprolactam) exists in two different crystalline forms.[1−3] In the more common α crystalline structure, the chain is fully extended and the amide group is in the same plane as the methylene groups. Holmes et al.[1] have shown that the structure of the α-form is composed of sheets of fully extended planar zigzag backbones joined by hydrogen bonds between the antiparallel chains. A second crystal structure of nylon-6, the γ-form, was obtained by the iodine treatment of the α-form and is composed of pleated sheets of parallel backbones with hydrogen bonding between adjacent chains.[2,3] Infrared studies have been reported on two crystalline forms of nylon-6 with band assignments being made from polarized measurements obtained from oriented films.[2,4−7] In many cases the agreement between the observed bands and those determined from normal coordinate calculations has been satisfactory, but a complete set of assignments has not been available due to the lack of availability of polarized Raman measurements.

In general, Raman studies on oriented films are much more complicated due to the relatively small thickness of films after orientation and due to the polarization scrambling of the incident and scattered light from domains in the film whose size is comparable to the wavelength of visible excitation. Another major problem that has prevented Raman studies of polyamides, in particular, is fluorescence. Commercial samples usually contain an additive that prevents UV degradation. This same UV stabilizer can give rise to fluorescence levels in the visible that overwhelm the Raman signal by orders of magnitude. With the recent advent of FT-Raman spectroscopy,[8,9] much of this problem was alleviated, and Raman spectra of polyamides were successfully obtained. The importance of polarized Raman studies arises because these measurements provide a mechanism to identify the symmetry assignment of the observed bands,[10,11] information that can then be used to refine existing force fields. Another important utility of polarized Raman measurements is to differentiate between proposed conformational structures since alternate structures dictate a different set of spectroscopic selection rules from which a comparison with experimental observations can be made.[12,13] In this work the anisotropic Raman scattering properties of a highly oriented transparent filament of nylon-6 have been used together with the factor group analysis of the chain molecule to make assignments of the observed Raman bands.

Experimental Section

The nylon-6 used in this study was provided by the Albany Monofilament Plant and contained no UV stabilizer. It was extruded and then highly drawn into an oriented transparent monofilament with a diameter of 0.007 in. All Raman spectra were taken on the filament sample as received. Polarized Raman spectra were recorded with a Jovin-Yvon HG-2S double monochromator equipped with holographic grating and a spatial filter to enhance stray light rejection. The source of excitation was provided by a Spectra Physics 2020 argon ion laser operating at 515 nm with 400 mW of power on the sample. The scattered light was recorded by a cooled RCA 31034A-02 photomultiplier tube using standard photon counting electronics. Digital data were collected and processed with a Nicolet 1180 data system. Spectra with sufficient signal-to-noise ratio were obtained at 4 cm^{-1} resolution by the coaddition of 20 scans. To collect the polarized Raman spectra, the incident laser beam was passed through a polarizer and then focused on the filament sample. The scattered Raman signal was collected with a *f*/1.8 lens and passed through an analyzer before entry into the double monochromator. Because of the anisotropic diffraction properties of holographic gratings, a polarization scrambler was placed between the analyzer and

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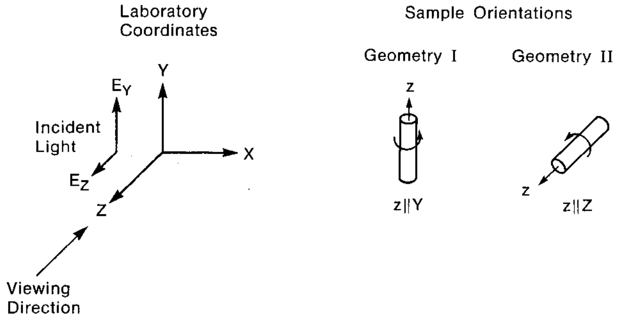

Figure 1. Schematic diagram of the two different scattering geometries used for polarized Raman measurements.

the entrance slit of the monochromator. All the polarized Raman experiments were carried out using the right angle scattering geometry.

The conventional right angle scattering geometry for recording Raman spectra is shown in the laboratory coordinate frame of reference in Figure 1. Satisfactory classification of all Raman bands of an oriented sample to their respective symmetry species often requires different sampling geometries as illustrated in Figure 1 since each position of the sample gives only four polarized spectra. In geometry I, the filament was clamped in a vertical position so that the *z*-axis of the sample is parallel to the laboratory fixed coordinate *Y*. With the incoming laser polarization being adjusted to lie either parallel or perpendicular to the laboratory *Y* axis, four independent polarized Raman measurements were recorded by changing the polarization of the analyzer to the two orthogonal positions (*Y* and *X*). To assist in making assignments of some bands to a specific symmetry species, a second scattering geometry was also used as shown in geometry II of Figure 1. In this case, a piece of nylon-6 filament that had been cut with a sharp razor blade and polished was placed inside the bore of a glass capillary. After the capillary was mounted so that it was aligned along the *Z*-axis of the laboratory coordinate, the scattered light could be collected at the end of the filament with the right angle viewing experimental setup.

Unpolarized Raman spectra were obtained with a Kaiser spectrograph through a polarizing fiber-optic probe head in the backscattering sample geometry. The working distance of the lens (*F*/1.8) was 2.5 in. to the sample, and a scrambler was placed between them. Although the laser light delivered by the probe is linearly polarized, after it passes through the scrambler and impinges on the sample, it is unpolarized. Likewise, the Raman scattered light is collected through the scrambler, ensuring that a totally isotropic Raman spectrum is obtained. The excitation source comes from a diode-pumped solid state laser at a wavelength of 532 nm (Coherent Lasers, Verdi). The power level at the sample was approximately 25 mW. A liquid nitrogen cooled CCD detector operated at −120 °C was integrated into this Raman system (Roper Scientific, LN/CCD-EB1-1340x1000). All measurements were carried out with an exposure time of 2 s, and 10 consecutive measurements were averaged to achieve a high signal-to-noise ratio. For verification of the polarization properties in the spectra obtained with the right angle geometry, the Kaiser Raman system was also used to collect polarized Raman spectra in the backscattering geometry.

Results and Discussion

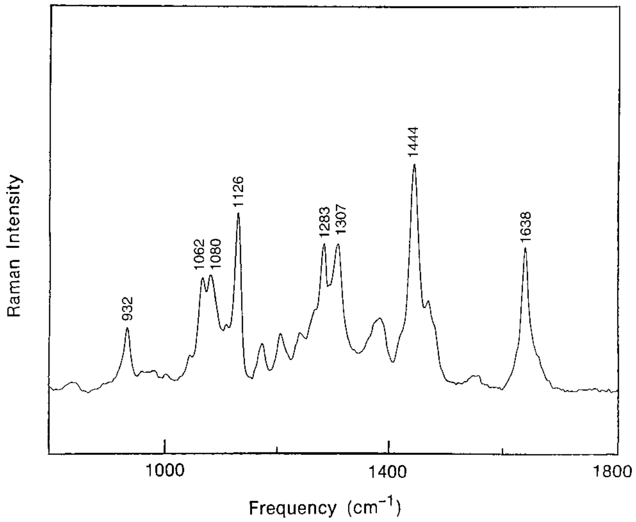

Figure 2. Unpolarized Raman spectra of nylon-6 filament.

Although Raman spectroscopic studies of nylon-6 were reported in the past,[14−17] the assignment of observed bands has not been complete due to the lack of both polarized IR and Raman data. Snyder[10] has derived expressions for Raman scattering activities in terms of principal axes of polarizability of a molecule for the case where the unique symmetry axis of the chain molecule is parallel to the orientation axis in a uniaxially oriented system. Since the 2-fold screw axis of the planar zigzag backbone of nylon-6 is parallel to the chain axis and thus parallel to the fiber orientation direction, the Raman scattering activities of nylon-6 were analyzed using Snyder's expressions. The conformation of nylon-6 samples was found to be planar zigzag, i.e., α-form, by observing the characteristic bands[17] at 1126 and 1283 cm^{-1} in the spectrum shown in Figure 2.

In the laboratory frame of reference shown in Figure 1, the incident laser beam propagates along the *X* direction while the scattered light is viewed along the *Z* axis. The incident light is polarized either along the *Y* or *Z* direction while the analyzer is placed parallel to either the *Y* or *X* axis (see Figure 1). The designation for each Raman spectrum describing the scattering geometry is due to Porto[18] and is used to label the Raman spectra obtained. The notation is of the form of A(BC)D, where A and D are the propagation directions of the incident and scattered radiation, while B and C refer to the direction of polarization of incident and analyzed radiation, respectively. All the polarized Raman experiments were carried out with the right angle scattering geometry since all the polarized spectra with the backscattering geometry could also be obtained with the right angle scattering experiment.

As seen in the polarized Raman spectra of Figure 3, the anisotropic scattering properties of the nylon-6 filament are evident. This set of polarized Raman experiments was carried out to select vibrational modes belonging to each of the symmetry species through knowledge of the factor group symmetry of the chain molecule and Raman scattering activities. For the planar zigzag structure of α-form nylon-6, the factor group of the line group is isomorphous to the C_{2v} point group in which four symmetry species of A_1, A_2, B_1, and B_2 exist. All four symmetry species contain Raman-active vibrational modes whereas all but the A_2 symmetry species are IR-active.

In Table 1 the results of Raman scattering activities for the experimental geometry I are summarized. By examination of this table, it is evident that the X(YY)Z experimental geometry provides Raman bands of A_1 symmetry species, and when it is taken in conjunction with the X(ZX)Z spectrum, it allows assignment of the A_2 bands since they are absent in the X(YY)Z spectrum (see Figure 3). Although the bands at 1466, 1444, and 1420 cm^{-1} exhibit stronger intensities in the X(ZX)Z spectrum compared to those in the X(YY)Z spectrum,

Table 1. Raman Scattering Activities for Nylon-6 in Sample Geometry I

experimental polarization	molecular polarizability	symmetry species			
		A_1	A_2	B_1	B_2
X(YY)Z	α^2_{zz}	α_{zz}	0	0	0
X(YX)Z	$^1/_2(\alpha^2_{zx} + \alpha^2_{yz})$	0	0	α_{zx}	α_{yz}
X(ZY)Z	$^1/_2(\alpha^2_{zx} + \alpha^2_{yz})$	0	0	α_{zx}	α_{yz}
X(ZX)Z	$^1/_8(\alpha_{xx} - \alpha_{yy})^2 + {}^1/_2\alpha^2_{xy}$	α_{xx}, α_{yy}	α_{xy}	0	0

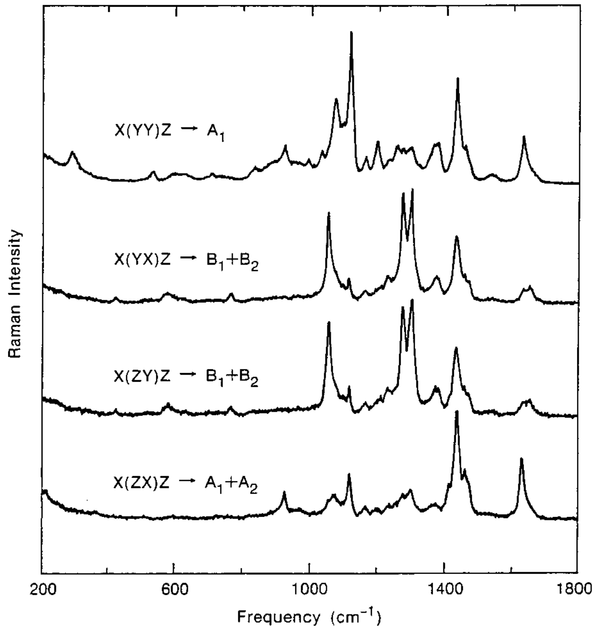

Figure 3. Polarized Raman spectra of nylon-6 filament obtained from four combinations of polarizer and analyzer positions.

Table 2. Symmetry Assignment of the Observed Raman Bands

symmetry species	frequency, cm^{-1}			assignment[b]
	Raman	infrared[a]	cacld[b]	
A_1	2925			$\nu_a(CH_2)$
	1638		1644	amide I
	1549	1545	1556	amide II
	1444		1443	$\delta(CH_2)$
	1380	1373	1382	$w(CH_2)$
	1264	1271	1270	$w(CH_2) + t(CH_2)$
	1204	1202	1203	$w(CH_2) + t(CH_2)$
	1126	1121	1128	$\nu(CC)$
	1080	1076	1081	$\nu(CC)$
	1040	1041	1048	$\nu(CC)$
	1001		1010	$\nu(CC)$
	932	928	933	$\nu(C-CO)$
	715		738	amide IV
	539	539	544	skeletal bend
	298	295	299	skeletal bend
B_1	3300	3290		$\nu(NH)$
	2870	2865		$\nu_s(CH_2)$
		1642	1645	amide I
	1441		1444	$\delta(CH_2)$
	1238	1244[b]	1247	$w(CH_2) + t(CH_2)$
	1216	1214	1216	$w(CH_2) + t(CH_2)$
	1062	1074	1067	$\nu(CC)$
	429	429	431	skeletal bend
B_2	2905	2930		$\nu_a(CH_2)$
	1307	1305[b]	1305	$t(CH_2)$
	1283	1282[b]	1281	amide III
	1170	1173[b]	1175	$t(CH_2)$
	773		767	$r(CH_2)$
	582	580	581	amide VI

[a] From ref 2. [b] From ref 4. ν, stretch; δ, bend; w, wag; t, twist; r, rock.

only bands at 1466 and 1420 cm^{-1} can be assigned to the A_2 symmetry species since the CH_2 bending peak at 1444 cm^{-1} is shown as one of the stronger peaks in all polarized spectra. Except for this CH_2 bending peak, all the other bands exhibit significant polarization behavior showing a dramatic change of relative intensity according to the different polarization measurements. In fact, however, the same CH_2 bending mode is found at a few wavenumbers shifted position (1441 cm^{-1}) in the X(YX)Z spectrum which has only nonzero values for the tensor components α_{zx} and α_{yz}. This indicates that the CH_2 bending peak observed in the X(YY)Z or X(ZX)Z spectrum is most likely different from that found at 1441 cm^{-1} in the X(YX)Z spectrum. Such an observation of the CH_2 bending mode with two different symmetry properties of A and B species is consistent with the result of the normal coordinate analysis[4] of nylon-6 where two frequencies at 1443 and 1444 cm^{-1} were calculated for the CH_2 bending mode with the A_1 and B_1 symmetry species, respectively.

As predicted in Table 1, the X(YX)Z and X(ZY)Z spectra in Figure 3 are identical. This polarized spectrum should be different from X(YY)Z and X(ZX)Z spectra since it has only bands belonging to the B_1 or B_2 symmetry species. By comparing the X(YY)Z and X(YX)Z spectra, therefore, all observed bands could be easily assigned to A_1, B_1, or B_2 symmetry species. If a band shows stronger intensity in the X(YY)Z spectrum compared to its intensity in the X(YX)Z spectrum, it belongs to A_1 symmetry species, and vice versa. The bands at 1638, 1549, 1380, 1126, and 1080 cm^{-1} can be assigned to the totally symmetric symmetry species (A_1), while those at 1307, 1283, and 1062 cm^{-1} exhibit B symmetry. The separation of the B symmetry bands into B_1 or B_2 symmetry species was aided by polarized infrared spectroscopic data on oriented films[2] and the result of the normal coordinate analysis, which have been reported in the literature.[4] The assignments of the polarized Raman bands are summarized in Table 2, where they are compared with IR measurements and normal coordinate calculations. The frequencies of the observed bands are in excellent agreement with those of the calculated result within 10 cm^{-1}, while most of them are within 5 cm^{-1}.

The strongest IR band observed at 1642 cm^{-1} is the amide I band (C=O stretching mode).[2] It shows perpendicular dichroism in the polarized IR spectrum and was assigned to the B_1 symmetry species.[2,4] However, the corresponding amide I band found at 1638 cm^{-1} in the Raman spectrum should be assigned to the A_1 symmetry species as seen in the spectra shown in Figure 3. By comparing the spectra obtained with different sample geometries as shown in Figure 4, the symmetry species of this Raman band could be clearly identified to be A_1. In Table 3 are listed the polarizability contributions to the band intensities for A_1 and A_2 symmetry species for two experiments with different sample geometry. Although the intensity of the band of A_2 symmetry should remain constant in both measurements, the intensity of those belonging to the A_1 species

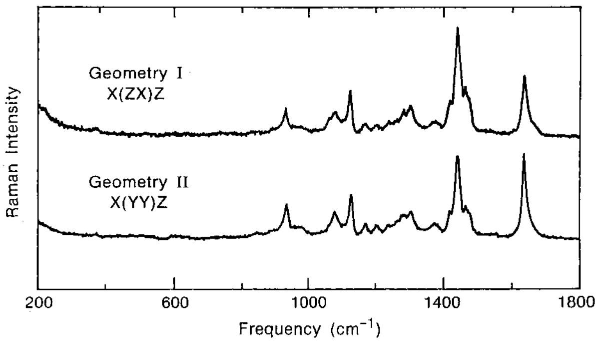

Figure 4. Polarized Raman spectra of nylon-6 filament obtained from two scattering geometries.

Table 3. Contributions of the Raman Scattering Activities to Symmetry Species for Nylon-6

sample geometry	experimental polarization	symmetry species	
		A_1	A_2
I	X(ZX)Z	$\frac{1}{8}(\alpha_{xx} - \alpha_{yy})^2$	$\frac{1}{2}\alpha^2_{xy}$
II	X(YY)Z	$\frac{1}{4}(\alpha_{xx} + \alpha_{yy})^2 + \frac{1}{8}(\alpha_{xx} - \alpha_{yy})^2$	$\frac{1}{2}\alpha^2_{xy}$

should be larger in the X(YY)Z spectrum of the geometry II. As observed in Figure 4, the previously assigned A_1 bands at 1638, 1126, 1080, and 932 cm^{-1} increase in intensity in going from the X(ZX)Z spectrum of the geometry I to the X(YY)Z spectrum of the geometry II. It is thus apparent that the amide I band at 1638 cm^{-1} belongs to the A_1 symmetry species. This assignment is further supported by the result of normal coordinate analysis[4] where two calculated frequencies, 1645 cm^{-1} with B_1 symmetry and 1644 cm^{-1} with A_1 symmetry, were found for the amide I band of nylon-6. In addition to the amide I band, one more band is found at 1660 cm^{-1} in the X(YX)Z spectrum of Figure 3. This band is also observed as a shoulder in the X(YY)Z spectrum of Figure 3 and can be assigned to the coupling of C=O stretching modes caused by hydrogen bonding between adjacent chains in the unit cell. The absence of this band in the IR spectrum indicates that it is the out-of-phase coupling between hydrogen-bonded C=O stretching modes and thus will only be Raman-active.

The amide II band due to NH in-plane bending and CN stretching motions is observed as a weak peak at 1549 cm^{-1} in the X(YY)Z spectrum of Figure 3. This band is weakly observable in the other polarized spectra in Figure 3 and thus was assigned to the A_1 symmetry species. This assignment agrees well with the results of the normal coordinate analysis[4] (1556 cm^{-1}) and of polarized IR measurements[2] (1545 cm^{-1}). Katagiri et al.[16] showed dramatic increases of the Raman band intensity for amide-related vibrational modes as the laser excitation wavelength becomes shorter. They identified the band at 1283 cm^{-1} as the amide III mode based on such selective enhancement due to a preresonance effect which occurs when the laser wavelength used for the Raman experiment approaches an electronic absorption of the material under investigation. This band is the strongest peak in the X(YX)Z spectrum of Figure 3 and classified as a B_2 symmetry species. Other amide bands are listed in Table 2 and exhibit good agreement with the calculated results.

It is interesting to note that the Raman-active amide I band, observed at 1638 cm^{-1} and unequivocally assigned to A_1 symmetry species by this polarized Raman study, corresponds to that calculated[4] at 1644 cm^{-1} for a single chain normal coordinate analysis that did not incorporate interchain hydrogen-bonding interactions. Likewise, the frequency of the Raman-active amide II vibration, observed at 1549 cm^{-1} and identified as belonging to the A_1 symmetry species in our study, was not significantly different from that calculated at 1556 cm^{-1}. This collectively suggests that, although intermolecular hydrogen bonding is thought to play an important role in stabilizing the α crystalline form of nylon-6, the strength of this interaction and the expected perturbation on the frequencies of the amide group vibrations is not realized. Snyder et al.[19] have shown, from matrix isolation studies on methyl *N*-alkyl and *C*-alkyl amides, that as the strength of the intermolecular hydrogen bond increases, the amide I vibration shifts to lower frequency while the amide II band shifts to higher frequency. Comparing the amide I and II vibrations in the α form of nylon-6 with those of β-sheet polypeptides[20] where strong hydrogen bonds are known to be present, it becomes clear that the observed amide I frequency is higher than that found in the polypeptide while the amide II frequency is lower than that observed in β-sheet polypeptides. Thus, this strongly supports the conclusion that the intermolecular hydrogen bond in nylon-6 is significantly weaker than that found in β-sheet polypeptides. This also provides compelling support for the observation of a relatively simple conversion[2] mechanism of the antiparallel extended sheet structure of the α form into the parallel chain pleated sheet γ-form of nylon-6 as found previously[2] in X-ray diffraction studies.

Conclusions

Polarized Raman scattering measurements on uniaxially oriented nylon-6 have been carried out to assign the observed bands to their respective symmetry species. The anisotropic Raman scattering profiles on an oriented filament have been analyzed by comparing the scattering results for four different combinations of incident and scattered polarization with those predicted by group theoretical analysis in two different scattering geometries. Our Raman data were compared to the existing results of IR and normal coordinate analysis in order to ensure that all vibrational bands exhibit consistent polarization properties. Results indicate that frequencies and symmetry assignments of the observed bands are in excellent agreement with those of the previous calculated results.

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