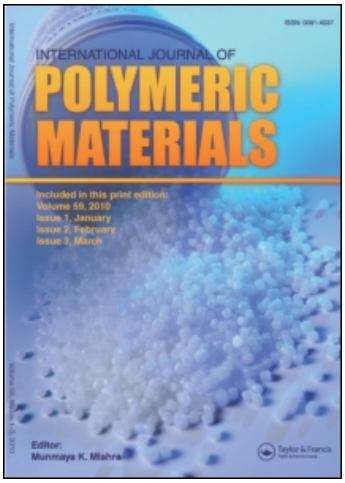

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

FT-Raman Studies of Semi-Crystalline Nylon 6, 12 Filaments

M. Olivares[ab]; M. A. Mondragón[a]; G. Vázquez-Polo[a]; E. Martínez[c]; V. M. Castaño[a]
[a] Instituto de Física, UNAM, Querétaro, México [b] Fac. de Ciencias Químicas e Ingeniería (UAEM), Av Universidad 1001, Cuernavaca, Mex. [c] Industrias Negromex, Altamira Tams., Mexico

To cite this Article Olivares, M. , Mondragón, M. A. , Vázquez-Polo, G. , Martínez, E. and Castaño, V. M.(1998) 'FT-Raman Studies of Semi-Crystalline Nylon 6, 12 Filaments', International Journal of Polymeric Materials, 40: 3, 213 — 218
To link to this Article: DOI: 10.1080/00914039808034839
URL: http://dx.doi.org/10.1080/00914039808034839

Intern. J. Polymeric Mater., 1998, Vol. 40, pp. 213–218
Reprints available directly from the publisher
Photocopying permitted by license only

FT-Raman Studies of Semi-Crystalline Nylon 6,12 Filaments

M. OLIVARES[a,b], M. A. MONDRAGÓN[a], G. VÁZQUEZ-POLO[a], E. MARTÍNEZ[c] and V. M. CASTAÑO[a,*]

[a]*Instituto de Física, UNAM, A.P. 1-1010, Querétaro, Qro-76001, México;*
[b]*Fac. de Ciencias Químicas e Ingeniería (UAEM), Av Universidad 1001, Cuernavaca, Mex. 62215;*
[c]*Industrias Negromex, Carr. Tampico-Mante km 28.5, Altamira Tams. 11700 México*

(Received 23 July 1997)

Semicrystalline nylon 6, 12 filaments were analyzed by Raman spectroscopy at two different orientations with respect to the exciting laser beam: either with the fiber axis parallel or perpendicular to the beam. The Raman spectra show differences between these two orientations, demonstrating the feasibility of this technique for studying molecular anisotropy. The relative intensities of the principal bands at each orientation are described. Also, X-ray diffraction data are presented to corroborate the anisotropy of the fibers.

Keywords: Nylons; Raman spectroscopy; X-ray diffraction

INTRODUCTION

Raman spectroscopy has been successfully applied to the study of polyamides synthesized either by self-condensation of an ω-aminoacid or from polymerization of their cyclic anhydro-derivatives. In particular, to the so called double number nylons, with general structure $-[NH-(CH_2)_x-NH-CO-(CH)_2)_y-CO]_m-$ which are of special relevance for their practical applications. Among this type of polymers, nylon 6, 6 and nylon 6, 10 have been previously studied by dispersive

*Corresponding author.

Raman spectroscopy [1]. The application of the relatively new FT-Raman technique to this type of materials has proved to be quite convenient in terms of the fast acquisition times, absence of fluorescence and good quality of the data obtained, as can be noticed from the reports of several double number nylons found in the literature [2]. In the case of nylon fibers or filaments, the extrusion process by which these are obtained is known to induce a preferential orientation of the polymer chain along the main axis of the fiber. It has been shown in the past, that it is possible to observe orientation effects by dispersive Raman of drawn polymers [3]. In the present work, the Raman spectra of nylon 6, 12 fibers, commercially known as Zytel, were analyzed at two different orientations with respect to the incident laser light by using FT-Raman spectroscopy.

EXPERIMENTAL

Filaments of commercial semicrystalline nylon 6, 12, 0.20 mm in diameter (Dupont, ZYTEL 158), were employed. To perform the Raman study the fibers were cut to 10 cm length and join together in a tight bundle. A tight bundle of fibers of about 0.5 or 3 cm in diameter was placed in the sample compartment for the perpendicular and parallel measurements, respectively. The FT-Raman measurements were carried out on a 910 Nicolet FT Raman bench, equipped with a Nd:YVO_4 laser emitting at 1064 nm. A 180° refractive optical configuration was used, in which the detection takes place along the direction of the incident light.

Two orientations of the fibers were analyzed: a parallel one, in which the laser light was parallel to the axis of the fibers and a perpendicular one, with the laser light perpendicular to the same axis. Raman spectra were taken with a resolution of 4 cm^{-1} and a laser power of 400 mW.

Typically, 200 scans were taken in an 8 min. routine for each spectrum. The Raman data were subjected to a correction procedure which takes into account the variation with frequency of the interferometer throughput, the transmission characteristics of the filters and the detector sensitivity. The X-ray diffraction experiments were performed on a Siemens D-5000 diffractometer in the 2° to 70° range at a scanning

rate of 4°/min. in two orientations: parallel and perpendicular to the fiber axes.

RESULTS

The Raman spectra of nylon 6,12 filaments obtained for both orientations, parallel and perpendicular, as described above, are shown in Figure 1.

Table I summarizes the relative intensities of the main bands for both spectra along with a tentative assignment. All intensities are

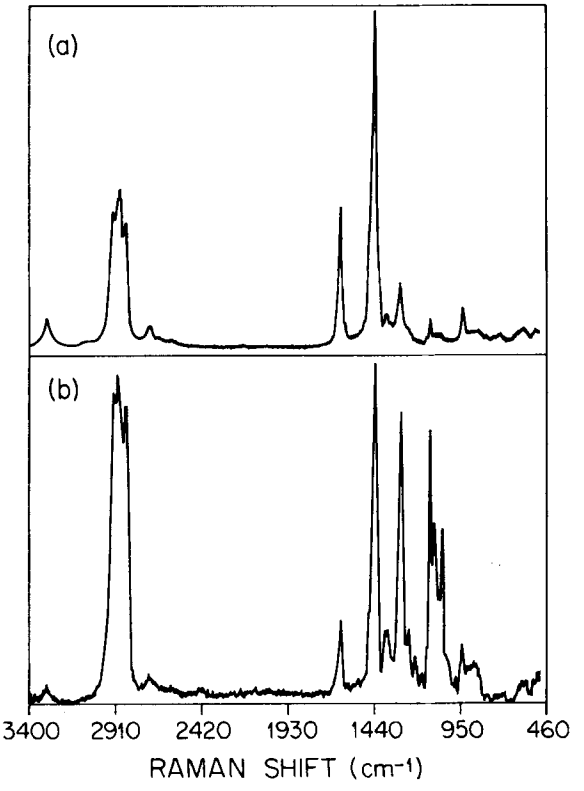

FIGURE 1 Raman spectrum of nylon 6,12 fibers oriented (a) with the fiber axis parallel to the incident laser light. (b) with the same axis perpendicular to the incident light.

TABLE I Relative intensities and assignments (2,4) of the Raman bands of nylon 6,12 fibers with their axis parallel and perpendicular to the incident laser light

Parallel			*Perpendicular*	
(cm^{-1}) ν	*Assignment*	I/I_0	(cm^{-1}) ν	I/I_0
3304	N—H stretching	11.3	3304	12.8
2884	CH_2 stretching	2.1	2902	1.0
1634	C═O amide I	2.4	1636	4.5
1439	CH_2 bending	1	1439	1
1298	$\nu_{C\ H} + \nu_{N-H}$ amide III	4.9	1294	1.2
1128	C—C stretching	7.8	1129	1.2

normalized to that of the 1439 cm^{-1} band, which is the most intense for both spectra. From these data it can be observed that in the perpendicular spectrum all modes, with the exception of the ν(C═O), appear more intense than in the parallel spectrum. Also, several small bands are discernible which are not observed in the parallel spectrum, namely the 1106 and 1064 cm^{-1} bands which have been previously observed in ref. [4] for nylon 12. Another point can be remarked from the experimental data: the two peaks observed in the CH_2 bending region, the strong one at 1439 cm^{-1} and the weak shoulder at 1475 cm^{-1} reliably indicate that this material crystallizes in the triclinic structure with one chain per unit cell, since similar peaks are have been observed for the $C_{26}H_{54}$ which crystallizes in this way [5].

Figure 2 shows X-ray diffractograms of the nylon 6–12 fibers taken in a parallel and in a perpendicular orientation with respect to the fiber axes. As observed there, in the perpendicular setup, two reflections are clearly defined, at 20° and 24°, corresponding to the (100) and (010) crystalline planes respectively, whereas the parallel case only shows the reflection corresponding to the (002) plane. These reflections have been previously observed for nylon 10,10 [6].

CONCLUSIONS

It was possible to observe the molecular anisotropy of commercial nylon 6,12 fibers by means of Raman spectroscopy and x-ray diffraction. The Raman data obtained provides an interesting indication of the crystalline structure of this material.

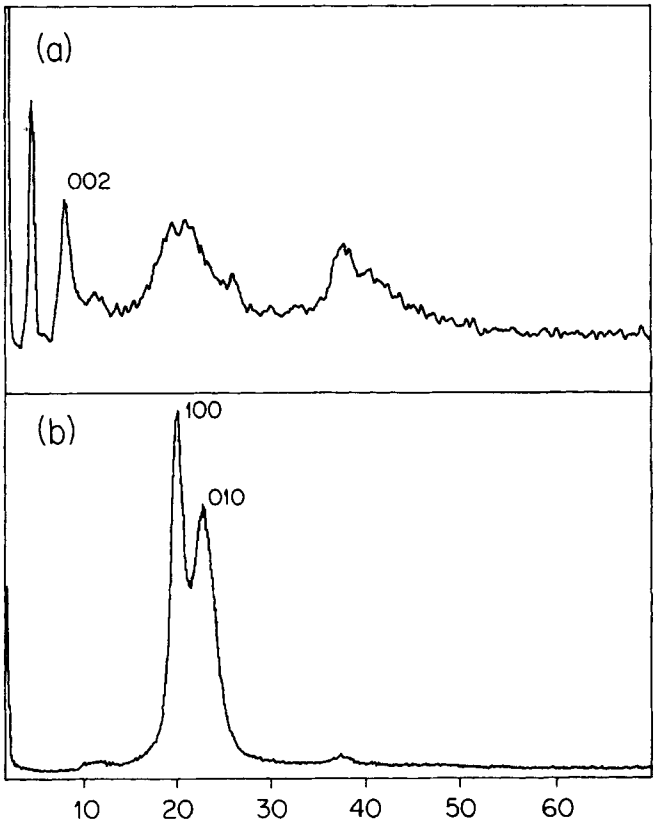

FIGURE 2 X-ray diffraction patterns of the semicrystalline nylon 6, 12 fibers taken (a) parallel to the axes of the fiber (b) perpendicular to the same axes.

Acknowledgement

The authors wish to acknowledge the technical assistance of Mr. Marco Antonio Leyva Ramirez in obtaining the X-ray diffraction data.

References

[1] Schaufele, R. F. (1967). *J. Opt. Soc. Amer.*, **57**, 105.
[2] Maddams, W. F. and Royaud, I. A. M. (1991). *Spectroch. Acta*, **47A**, 1327.
[3] Hendra, P. J. and Willis, H. A. (1968). *Chem. Commun.*, 225.

[4] Hendra, P. J., Maddams, W. F., Royaud, I. A. M., Willis, H. A. and Zichy, V. (1990). *Spectroch. Acta*, **46A**, 747.
[5] Fraser, G. V., Hendra, P. J., Chalmers, J. M., Cudby, M. E. A. and Willis, H. A. (1973). *Makromolek. Chem.*, **173**, 205.
[6] Zhang, L., Zhang, H., Yu, L., Zhang, W., Mo, Z. and Chen, D. (1994). *Polym. Intern.*, **35**, 355.