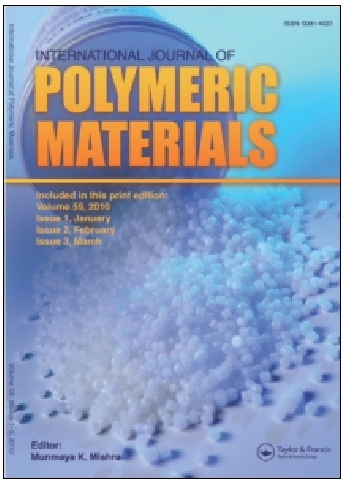

**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Micro-Raman Characterization of Anisotropic Dimethyl Terephthalate Crystallites

R. Rodrígueza[ab]; S. Jiménez[c]; S. Vargas[ab]; S. Pacheco[d]; V. M. Castaño[a]
[a] Física Aplicada y Tecnología Avanzada, IFUNAM, Querétaro, Qro., Mexico [b] Departamento de Física, UAM-lztapalapa, Mexico, D.F. [c] Laboratorio Investigación Materials, CINVESTAV, IPN, Querétaro, Qro., México [d] Subdirección Exploración Producción, IMP, México, D.F.

**To cite this Article** Rodrígueza, R. , Jiménez, S. , Vargas, S. , Pacheco, S. and Castaño, V. M.(2001) 'Micro-Raman Characterization of Anisotropic Dimethyl Terephthalate Crystallites', International Journal of Polymeric Materials, 49: 1, 1 — 13

**To link to this Article: DOI:** 10.1080/00914030108035863
**URL:** http://dx.doi.org/10.1080/00914030108035863

*Intern. J. Polymeric Mater.*, 2001, Vol. 49, pp. 1-13
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

# Micro-Raman Characterization of Anisotropic Dimethyl Terephthalate Crystallites

R. RODRÍGUEZ[a,b,*], S. JIMÉNEZ[c], S. VARGAS[a,b],
S. PACHECO[d] and V. M. CASTAÑO[a]

[a]*Física Aplicada y Tecnología Avanzada, IFUNAM,*
*Apdo. Postal 1-1010, Querétaro, Qro. 76001, México;*
[b]*Departamento de Física, UAM-Iztapalapa, Apdo. Postal 55-534,*
*México, D.F. 09340;*
[c]*Laboratorio Investigación Materiales, CINVESTAV, IPN,*
*Apdo. Postal 1-1010, Querétaro, Qro. 76001, México;*
[d]*Subdirección Exploración Producción, IMP, Eje Lázaro Cárdenas 152,*
*Apdo. Postal 14-805, México, D.F. 07730*

*(Received 5 December 1999; In final form 9 December 1999)*

Dimethyl terephthalate (DMT) is one of the most widely employed precursors for fabricating Poly(Ethylene Terephthalate) (PET). PET is in turn one of the most important commercial polymers due to its wide spectrum of applications, ranging from fibers and films, to molding materials, *etc*. The mechanical properties of PET depend strongly on its crystallinity which can be modified by the presence of different contaminants. This is the reason why the technical specifications for the monomers employed in commercial applications of polyester are highly restrictive. Therefore, industrially speaking, it is extremely important to use a simple and reliable way to characterize this anisotropic material.

In this work, an alternative way to characterize DMT molecules by using Micro-Raman Spectroscopy is proposed. Because DMT forms large crystals, their anisotropic characterization represents an interesting way to determine the degree of purity of the product. All samples were also characterized by Calorimetric Analysis.

*Keywords*: Dimethyl terephthalate; Polymer crystal; Micro-Raman Spectroscopy

---

[*] Corresponding author. e-mail: rogelior@servidor.unam.mx

# INTRODUCTION

Poly(ethylene terephthalate) (PET) is produced by using either dimethyl terephthalate (DMT), $C_6H_4$-1,4-$(COOCH_3)_2$ or terephthalic acid (TPA), $C_6H_4$-1,4-$(COOH)_2$ as precursors. These substances react with ethylene glycol under high vacuum and heat conditions producing, through a condensation/esterification reaction, either methanol or water, depending on the specific route. The resulting polymer has a melting point of 250°C.

The commercial production of polyester fibers dates back to the late 40's and early 50's, and has reached a tremendous demand nowadays, with an industrial production even larger than nylon [1]. Polyester fibers currently represent the largest-volume synthetic fiber in the world. The commercial success of polyester fibers can be explained by the fact that it has been undoubtedly demonstrated that the presence of aromatic rings in a linear molecule of high enough molecular weight produces high melting temperatures, good chemical stability and strong and tough fibers.

These polyester fibers are extremely versatile because their drawing conditions can be used conveniently to modify the crystallization, thus producing a stronger fiber; this means that the toughness and elongation of the fiber can be controlled through the processing. They represent perhaps the most versatile fibers available in the market because of their strength, abrasion resistance, higher moduli than nylon and yet lower moisture absorption [2].

As mentioned above, the primary use of DMT is as fiber-forming polyester, films and molding materials (such as bottles), *etc.*, which obliges the polymer-grade DMT or TPA to be subjected to highly restrictive specifications. A number of different methods have been developed to determine the degree of purity of these monomers. The standard way to determine the absolute purity of DMT, with considerable accuracy, is by performing cryoscopic measurements of its freezing point. These measurements are normally made to at least a hundredth of a degree Celsius or better. In order to obtain a great accuracy, this test requires a sophisticated and expensive equipment [2].

Accordingly, in the present work an alternative way to characterize DMT molecules by using Micro-Raman Spectroscopy [3] is proposed, based on DMT tendency to produce large anisotropic crystals, as will be explained below.

## EXPERIMENTAL

Raw commercial samples from Petrocel, S.A., México, were used for this study as produced. Upon visual inspection, the samples showed some bright and opaque regions (or grains) of the order of few millimeters in size. Different regions of the sample were characterized by using Micro-Raman Spectroscopy (MRS) to elucidate the origin of this difference in aspect.

Additionally, a number of long and thick DMT crystals were selected and characterized by aligning the crystals parallel and perpendicular to the direction of the incident Raman laser light. The diameter of the polarized He – Ne laser probe was always smaller than the thickness of the DMT crystal. For all samples, MRS experiments were performed at room temperature in a DILOR apparatus model Labram equipped with a confocal optical microscope; the wavenumbers range of the scattered light range from 50 to 4000 $\mathrm{cm}^{-1}$; the objective selected was 50 x, which produces a 2 μm diameter laser spot on the sample.

The DSC experiments were performed in a Dupont 910, while TGA results were obtained from a thermobalance Dupont 2100. The TGA experiments were performed up to 300°C, while the DSC was carried out up to 180°C.

## RESULTS AND DISCUSSIONS

The sample was visually inhomogeneous from the beginning: some parts of the sample were brighter than others. Micro-Raman spectra of both visually different regions of the sample, were obtained. Figures 1 and 2 show Raman spectra of both parts of the sample, the bright and the opaque ones, respectively. Although these Raman spectra look similar to each other, there exist a number of important differences that will be discussed later on.

Large crystals of DMT were selected from the raw sample in order to obtain the Raman spectrum along and perpendicularly to the

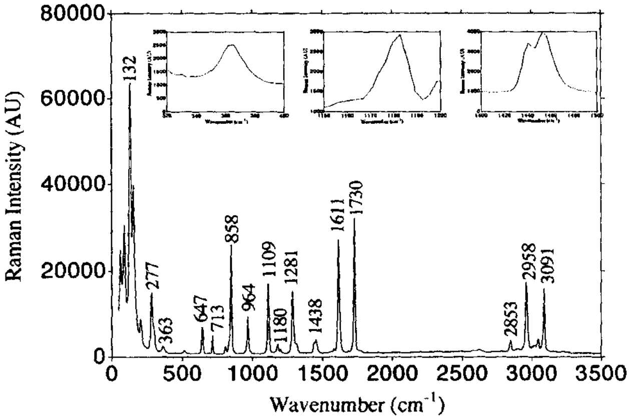

FIGURE 1 Micro-Raman spectrum of a bright part of DMT commercial sample. The three inserts in the upper part of the plot show magnifications of some specific bands: 363, 1180 and 1438 cm$^{-1}$.

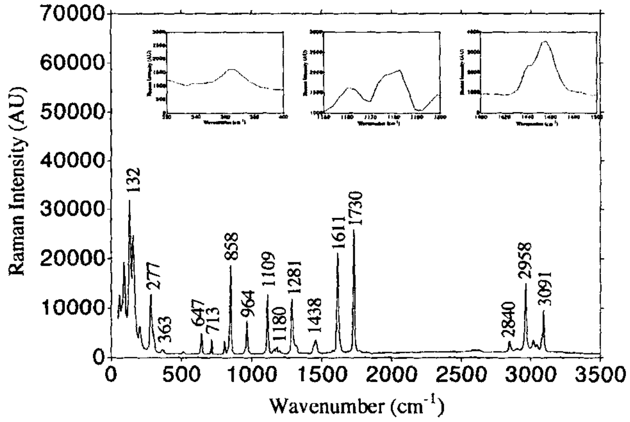

FIGURE 2 Micro-Raman spectrum of an opaque part of the same commercial DMT sample as in Figure 1, with the corresponding magnifications shown in the inserts.

crystal axis. Figure 3 corresponds to a typical Raman spectrum of a crystal taken with the laser direction of propagation parallel to the direction of the main symmetry axis of the crystal, *i.e.*, with the laser light hitting the end of the crystal. On the other hand, Figure 4 shows the Raman spectra of the same crystal, but taken perpendicularly to the crystal axis, *i.e.*, with the laser light hitting the middle of

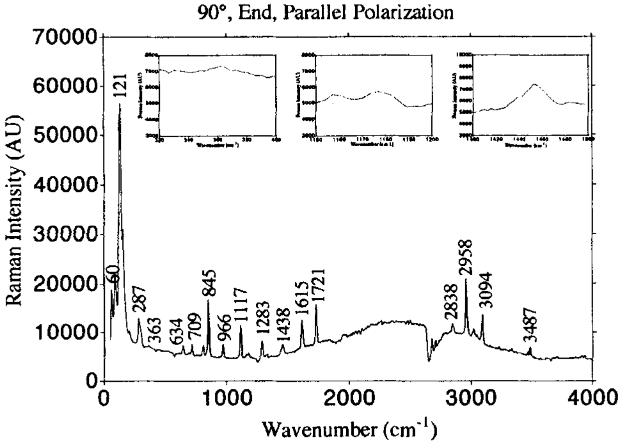

FIGURE 3 Micro-Raman spectrum of a single DMT crystal taken with the laser light parallel to the symmetry axis of the crystal. The three inserts shown in the upper part of the plot correspond to the bands at 363, 1180 and 1438 cm$^{-1}$.

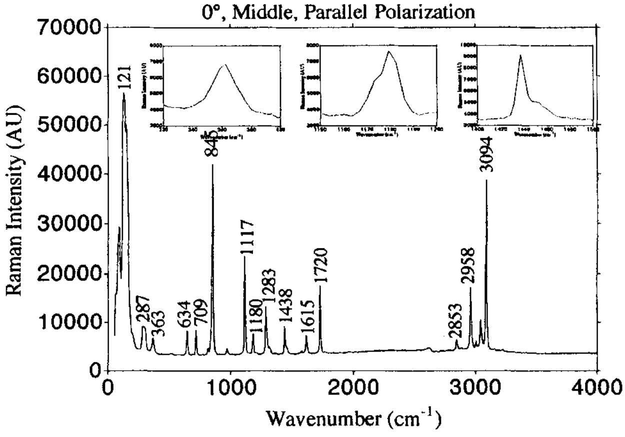

FIGURE 4 Micro-Raman spectrum of the same crystal as in Figure 3 but with the laser light perpendicular to the symmetry axis of the crystal. Here, as in Figure 3, the three corresponding inserts are included.

the crystal. The polarization of the incident laser light was selected to be on the plane where the crystal was rotated. As observed, both spectra show some differences. Before discussing these, it is important to note that the strongest band in Figures 3 and 4 are practically of the same intensity; this band is located at 121 cm$^{-1}$. A number of interesting considerations can be drawn from these spectra, as follows:

1. There is a well defined band at 363 cm$^{-1}$ in the perpendicular Raman spectrum (Fig. 4) which practically does not appear in the parallel Raman spectrum (Fig. 3). This band is characteristic of aromatic esters which show bands in the range 370 – 270 cm$^{-1}$ due to the in-plane deformation of the COO group which is of medium-to strong intensity [4]. Figures 3 and 4 contain an insert at the upper left part of the plots, where the peak at 363 cm$^{-1}$ is amplified. As observed, for the perpendicular spectrum there is a well defined band, whereas it practically does not appear for the parallel case. This band appears also in Figures 1 and 2, but in Figure 1, corresponding to the bright grain, is more intense than in Figure 2 (*i.e.*, the opaque grain). This means that for the bright grains there is a higher proportion of crystals perpendicularly oriented to the direction of observation, whereas for the opaque grains there are more crystallites parallelly oriented to the direction of observation. This local crystallographic texture could explain the visual inhomogeneity of the sample. One possible way to explain this behavior is that the aromatic ring has a preferential orientation with respect to the crystal symmetry axis because of topological restrictions: the normal direction of the ring's plane should be preferentially perpendicular to the symmetry axis of the crystal.
2. The band at 634 cm$^{-1}$ is also characteristic of aromatic esters due to the COO deformation vibration, and particularly, the 1,4 disubstituted aromatic esters have a band in the range 650 – 615 cm$^{-1}$ due to the in-plane ring deformation of the aromatic ring. For this band, the same effect is observed as in the case of the peak at 363 cm$^{-1}$: the band at 634 cm$^{-1}$ is stronger (almost 3-fold) for the perpendicular spectrum with respect to the parallel one. Since the intensity of the Raman's bands depends on the relative orientation of the polarization direction of the incident radiation with respect to the normal mode of vibration which is being excited, when all the scattered light produced by this coupling is collected by the detector (*i.e.*, when no analyzer is used in the output), it is possible to estimate the angle between the crystal axis relative, in this case, to the normal of the aromatic ring; in this case this angle should be around 72°. This is

schematically depicted in Figure 5. It is important to compare this result with the one obtained elsewhere for a similar compound [5], where an angle of around 62° was reported. This analysis can also be applied to the 363 $cm^{-1}$ band to obtain an angle between the crystal axis and the normal of the DMT molecule axis of 72°.

3. The band at 709 $cm^{-1}$ should be infra-red inactive for 1,4 disubstituted benzene provided the two substituents are identical,

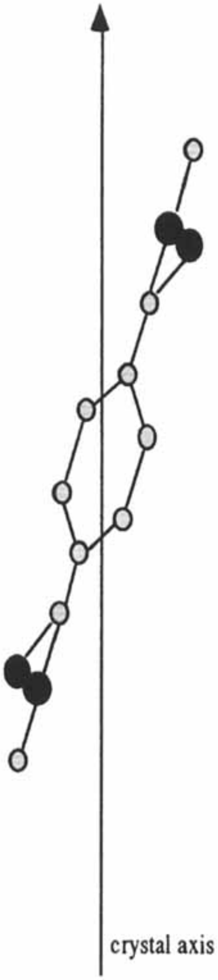

FIGURE 5 Schematic orientation of DMT molecules respect to the symmetry crystal axis.

because in this particular case symmetry results in this vibration making the center of the ring the center of symmetry. The appearance of this band in the Raman spectra indicates a symmetry breakdown, produced by the orientation of the disubstituted benzene with respect to the crystal axis. For this band, the ratio of the peaks intensities is 2.6, corresponding to an orientation angle of 69° between the normal of the aromatic ring and the symmetry axis of the crystal.

4. For the band at 845 $\text{cm}^{-1}$ something similar to the former case is observed, corresponding to an angle of 73°. This band corresponds to the C—H out-of-plane deformation vibration for paradisubstituted benzene.
5. For the C—H in-plane bending, the 1,4-disubstituted benzene has a band at 1117 $\text{cm}^{-1}$; this band appears in Figures 3 and 4 and the ratio of the intensities is 2.9 corresponding to an angle of 71°. All these results are in good agreement within the experimental error.
6. There is a well defined band at 1180 $\text{cm}^{-1}$ in the perpendicular Raman spectrum (Fig. 4) which is significantly reduced in the parallel Raman spectrum (Fig. 3). Figures 3 and 4 show inserts above the central part of the plot where this band is amplified. This band has a contribution of the C—H in-plane bending for *p*-disubstituted benzene, and the additional contribution of the C—O—C symmetric stretching vibration. For this reason, the intensity ratio between the peaks at 1180 $\text{cm}^{-1}$ in both figures, is larger than in the former cases. Here, this ratio corresponds to an angle of 77°. This band appears in the Raman spectrum for the bright grain whereas for the opaque grain, two small bands at 1161 and 1183 $\text{cm}^{-1}$ appear. Thus, the strong band at 1180 $\text{cm}^{-1}$ in Figure 1 indicates, as before, that the bright part of the sample is predominantly formed by crystals oriented perpendicular to the direction of observation.
7. Esters of aromatic acids have two strong absorption bands due to the C—O—C stretching vibration; one occurs at the region 1310 – 1250 $\text{cm}^{-1}$ corresponding the asymmetric stretching vibration, while the other, as mentioned above, appears at 1180 $\text{cm}^{-1}$ and corresponds to the symmetric stretching vibration. In this case the band at 1283 $\text{cm}^{-1}$ corresponds to this mode of vibration

and the intensity ratio of the bands in the parallel and perpendicular cases produces an angle of 71°.

8. The band at 1438 cm$^{-1}$ has a contribution of the symmetric stretching vibration of the COO group of medium intensity and a deformation vibration of the $CH_3$ group. The ratio between the intensities of the peaks in Figures 3 and 4 implies an angle of 70°. As mentioned in the Introduction section of this article, the terephthalic acid is a precursor for DMT; in the case where the esterification reaction can not be carried out completely, the COOH group produces a band in the region 1440 – 1395 cm$^{-1}$, which is due to the combination of the C—O stretching and O—H deformation vibrations. Consequently, this can explain the presence of the doublet as observed (1438 and 1453 cm$^{-1}$) in this band. As before, Figures 3 and 4 contain inserts at the upper right hand side of the plot where this band is amplified. In Figure 4 the band is well defined and centered at 1438 cm$^{-1}$ with a small peak at higher wavenumbers, while in Figure 3 this band is slighted shifted towards 1453 cm$^{-1}$ with a small shoulder at lower wavenumbers, and substantially weaker. In Figure 1 a doublet with frequencies at 1438 and 1453 cm$^{-1}$, with approximately the same intensity is observed, indicating that the vibrational normal modes of the molecule corresponding to these bands, are present in the bright grain. Similarly, for the opaque grain, the doublet also appears but the intensity of the 1453 cm$^{-1}$ band is almost twice as intense as the 1438 cm$^{-1}$ band.
9. The band at 1615 cm$^{-1}$ corresponds to the ring C—C stretching vibration for *p*-disubstituted benzenes, while the band at 1721 cm$^{-1}$ is due to the C=O stretching vibration of aromatic esters; in this case the angle is 60°, meaning that the oxygen of the carbonyl group is slightly far from the symmetry axis of the crystal (see Fig. 5).
10. The band at 2958 cm$^{-1}$ is characteristic of methyl esters and corresponds to the $CH_3$ asymmetric stretching and deformation vibration. As can be noticed there, these peaks have intensities similar to each other.
11. Finally, the band at 3094 cm$^{-1}$ is characteristic of the =C—H stretching vibration of aromatic rings. In this case the ratio between the intensities of these peaks corresponds to an angle of 80°.

The analysis of the perpendicular and parallel spectra allows to determine the relative orientation of the DMT molecule with respect to the crystal axis. The differences between both spectra can be used to characterize the final product, allowing to detect the presence of

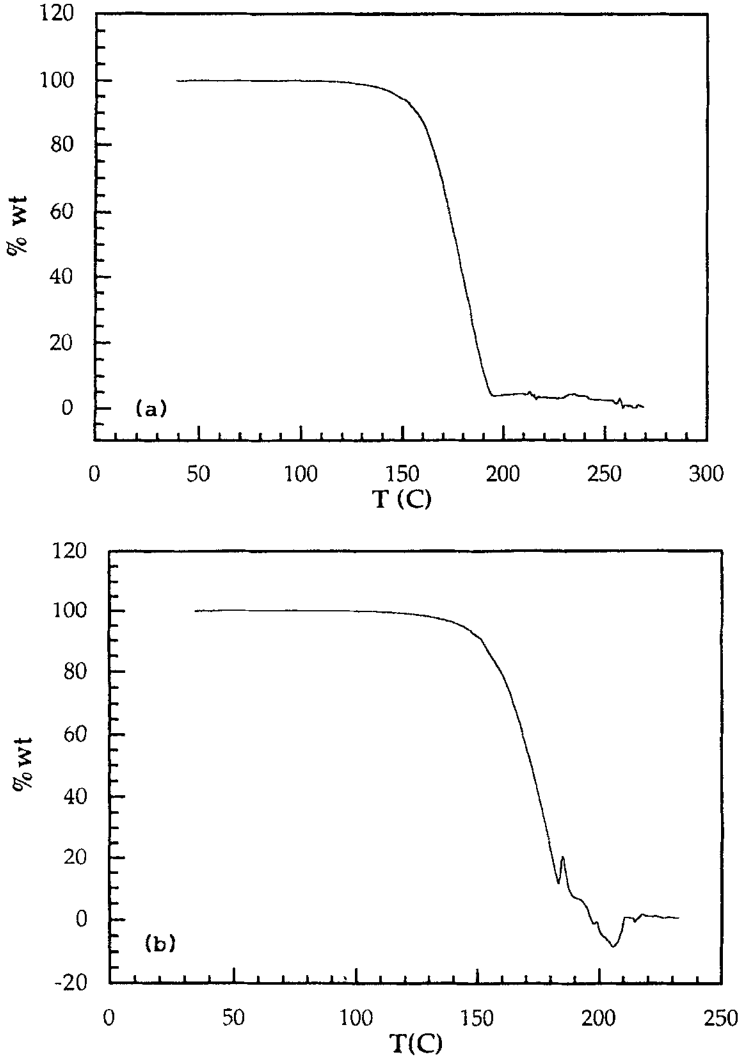

FIGURE 6 TGA thermogram of the (a) bright and (b) opaque parts of a DMT commercial sample.

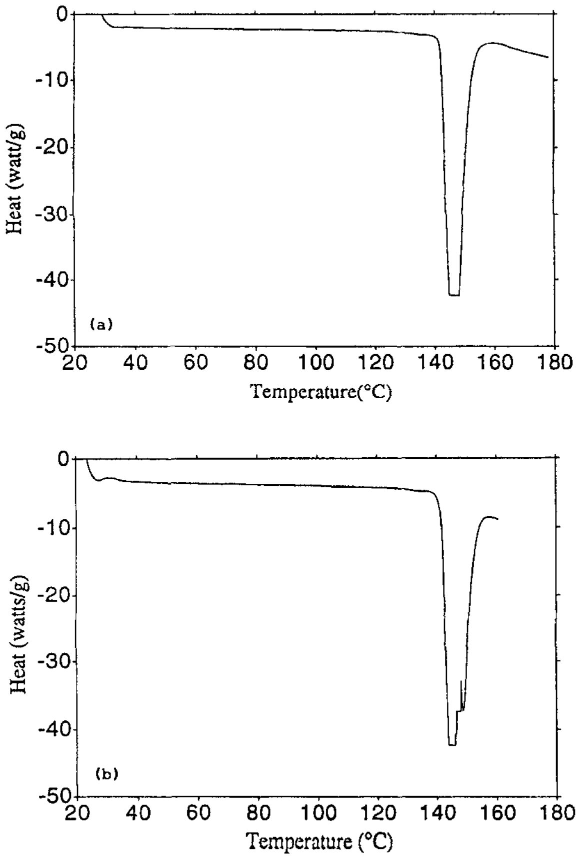

FIGURE 7 DSC thermogram of the same samples as in Figure 5.

contaminants, since impurities are known to modify substantially the crystallization of DMT. The intensity of the Raman bands may contain contributions from different normal modes, producing different values when the perpendicular and parallel spectra are compared; however, in practically all bands analyzed here, they produce results close to each other. It is possible to say that the normal direction of the DMT molecule makes an average angle of (73 ± 4)° with respect to the crystal symmetry axis.

DSC and TGA thermograms for all samples are shown in Figures 6 and 7. Figure 6 shows the TGA thermograms of the bright and opaque grains of the sample; these are essentially identical, indicating that the visual aspect is only a matter of relative orientation of crystals with respect to the observer, because they do not modify the calorimetric properties of the sample. On the other hand, Figure 7 shows the DSC spectra of the same samples, where an endothermic peak appears between 140 and 150°C, corresponding to the melting temperature of these crystals.

## CONCLUSIONS

A novel approach to characterize the anisotropy of the DMT crystals has been described. From this characterization it is possible to understand the way the DMT molecules are oriented with respect to the crystal symmetry axis. Raman results predict that the normal direction of the DMT molecule is oriented at an angle of around $(73 \pm 4)^\circ$ with respect to the crystal symmetry axis; this is in agreement with results obtained for similar molecules using X-rays diffraction. This fact controls to a large extent the mechanical and optical properties of the material. The presence of impurities modify the orientation of the DMT molecules with respect to the crystal, which results in a change in the Raman spectrum; this is, as mentioned, a key parameter for the performance of the monomer in the polymerization process. Thus, Micro-Raman Spectroscopy represents a simple, high resolution, reliable and fast test for this purpose.

### Acknowledgment

The authors thank Francisco Rodríguez Melgarejo for the Raman spectra obtained from the samples.

### References

[1] Mark, H. F., Mcketta, J. and Othmer, D. F. (1978). "*Encyclopedia of Chemical Technology*", 2nd edn., Vol. 10, Interscience Publishers, John Wiley and Sons, Inc., New York.

[2] Mark, H. F., Mcketta, J. and Othmer, D. F. (1989). "*Encyclopedia of Chemical Technology*", 2nd edn., Vol. 15, Interscience Publishers, John Wiley and Sons, Inc., New York.

[3] Loudon, R. (1964). *Adv. Phys.*, **13**, 423.

[4] Socrates, G. (1994). "*Infrared Characteristic Groups of Frequencies*", 2nd edn., John Wiley and Sons Ltd., England.

[5] Alvarez-Castillo, A. and Castaño, V. M. (1997). "Studies on the Characterization of Polyethylene Terephtalate Oligomers", *J. Mat. Sci. Lett.*, **14**, 139–141.