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# RADIATION-INDUCED MORPHOLOGICAL CHANGES IN POLYAMIDE FIBERS

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*Crystalline nylon 6–12 fibres were submitted to various dose of γ-radiation with a $^{60}Co$ source (50 up to 300 kGy). The morphological changes induced by γ-irradiation have been investigated by X-ray diffraction, small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). Significant changes on nylon 6–12 fiber surfaces are detected as the dose of irradiation increases. The mean crystallite size shows changes too, obeying a tendency to grow up as the irradiation dose is increased. These modifications are attributed to the chain scission during the process of irradiation provoking a crystal reorganization.*

*Keywords*: polyamides, nylon 6–12, gamma radiation

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## INTRODUCTION

It has been reported that high-energy irradiation induces alterations on the chemical bonds of organic materials. These changes are irreversible and they do not differ from those produced conventionally [1]. The high-energy irradiation has the advantage that it is possible to work in solid state; time and expenses are then saved.

Polymers are most sensitive to slight variations of the chemical bond, in this way initial features and properties may be varied and new materials may eventually be tailored [2, 3]. If the geometry of the bond structure is modified using $\gamma$-irradiation, the characteristics of the long chains of polymers vary [1], then some changes in polymer properties can be explained through induced chain strength, chain orientation and crystallinity. Therefore, lateral chain ordering may, indeed, avoid sites between them. On the other hand, depending on the dose crosslinking or chain scissions may be present in irradiated polymers. It has been claimed that chain scission occurs either in the amorphous region [4–6] or inside the crystals [7, 8]. It has been shown that mechanical and thermal properties are enhanced if nylon 6, 12 polymer was exposed to $\gamma$-irradiation [9–12]. Moreover, in a recent paper [13], chain scission was proposed to occur mainly when nylon 6, 12 was irradiated with $\gamma$-rays. In order to contribute to study the effect of $\gamma$-radiation on nylon 6, 12 this communication deals with the morphological and structural changes in crystalline nylon 6, 12 $\gamma$-irradiated.

## EXPERIMENTAL

### (a) Materials

Nylon 6–12 fibers were obtained from Dupont (Zytel) in the crystalline form with 0.2 mm of diameter. Six types of samples were studied, one of them was taken as reference (without radiation), and the others were exposed to $\gamma$-irradiation the required time until 15, 50, 100, 200 and 300 kGy final dose were obtained. The samples were identified as follows based on the final dose: NY means nylon 6, 12 fiber followed by VIR (reference) or 15, 50, 100, 200 or 300 which mean the irradiation dose; for example, NY50 indicates a nylon 6, 12 fibre 50 kGy $\gamma$-irradiated.

### (b) Sample Irradiation Procedure

Polyamide fibres were submitted to $\gamma$-irradiation doses of 15–300 kGy at room atmosphere. The dose rate was 3.64 kGy/h (*i.e.*, 0.364 Mrad/h) in a 55–6500 Atomic Energy of Canada Limited (AECL) $\gamma$-irradiator using a $^{60}Co$ source. The irradiation process was controlled with a red acrylic dosimeter L9-C1 (Nordion, 1994).

## (c) Characterization Techniques

### *X-ray Diffraction*

X-ray diffractograms were obtained with a Siemens D500 coupled to a copper anode X-ray tube. K-$\alpha$ radiation was selected with a diffracted beam monochromator. From the (100) and (010) [14] interplanar distances, whose values were 4.38 and 3.84 Å respectively, crystallite size distributions were estimated using the XTL-SIZE program [15, 16].

### *Small Angle X-ray Scattering*

Small Angle X-ray Scattering (SAXS) studies were performed on a Kratky camera coupled to a copper anode X-ray tube. The K-$\alpha$ radiation was selected with a nickel filter. Intensities were measured with a linear proportional counter. The data were interpreted as shown by Glatter [17, 18] and Martin *et al.* [19].

### *Scanning Electron Microscopy*

Scanning Electron Microscopy (SEM) was carried out in a JEOL 5200 microscope at 5 kV. The fibers were sticked with colloidal silver paint to the microscope holders and then, they were covered with a thin layer of coal to prevent electrostatic charge.

## RESULTS AND DISCUSSION

Crystallite size distributions of the non-treated sample in the two chosen crystallographic directions can be compared in Figures 1(a) and (b). In the [100] direction whose interplanar distance ($d_{100}$) is 4.38 Å the distribution is trimodal showing the presence of 13, 48 and 75 Å crystallites. However in the [010] direction ($d_{010} = 3.84$ Å) the distribution only presents a peak for a diameter of 11 Å and no crystallites larger than 46 Å are observed. Therefore, it seems that the shape of the crystallites may be similar to a sphere of 10–15 Å as well as elongated crystallites, which in one direction are 13 Å whereas in the other they may be either 48 Å or 75.

In Sample NY200, Figures 2(a) and (b), the trimodal distribution was again obtained in the [100] direction as in the previous sample, but in the [010] direction three peaks were also obtained at 10, 30 and 50 Å. This result differs from the curves of samples NY15 and NY50 which, in the [100] as well as in the [010] directions, reproduce the distributions obtained in the neat sample. The same was found for NY100 and NY300 samples. We present only the distributions of the NY300 sample, Figures 3(a) and (b).

But, if the mean crystallite size in the [100] direction is plotted against irradiation dose, Figures 4 and 5, the sample NY100 clearly differs from the

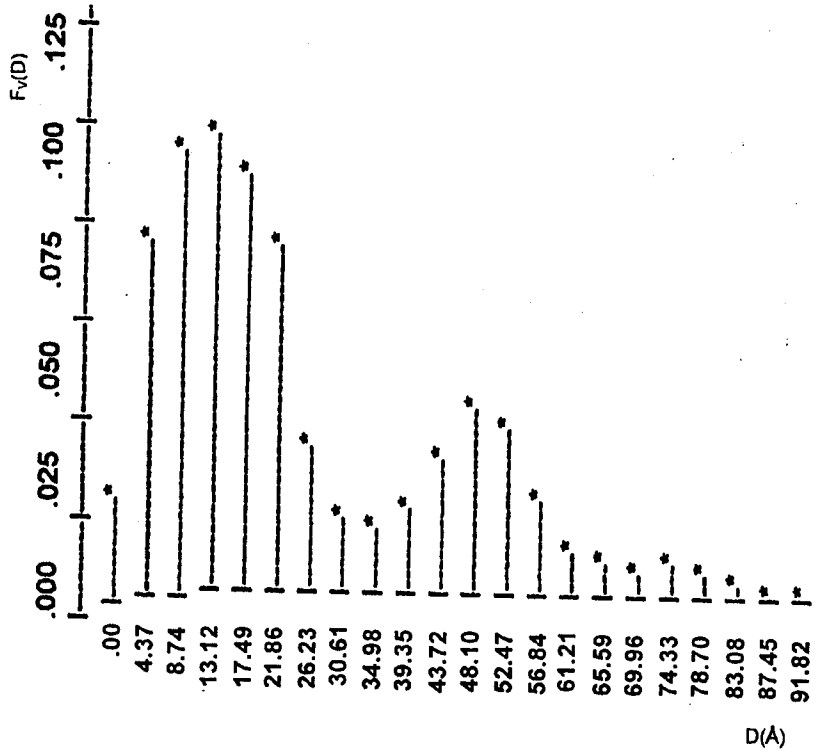


**FIGURE 1a** Crystallite size distribution of NYVIR in the [100] crystallographic direction.

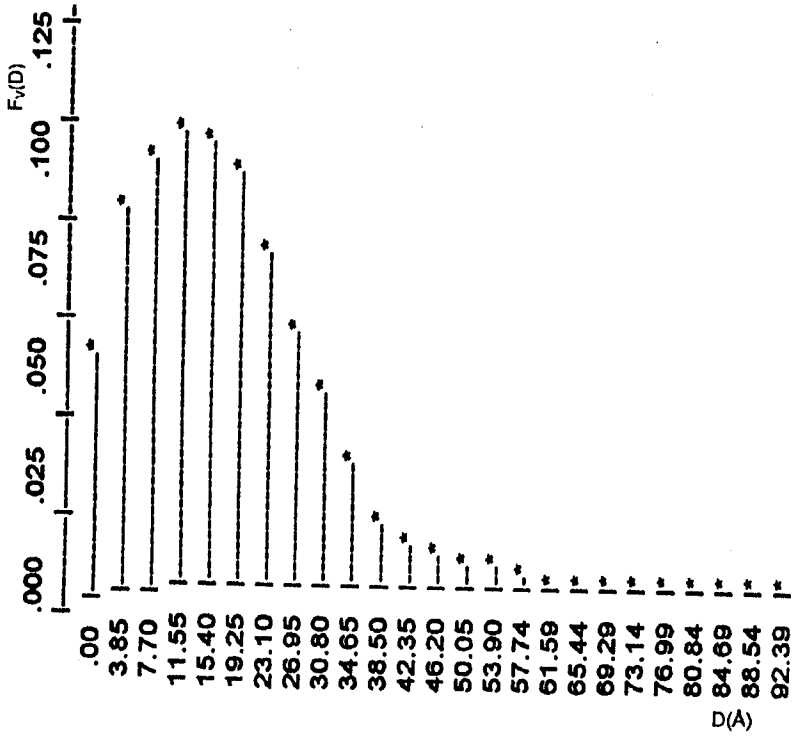


**FIGURE 1b** Crystallite size distribution of NYVIR in the [010] crystallographic direction.

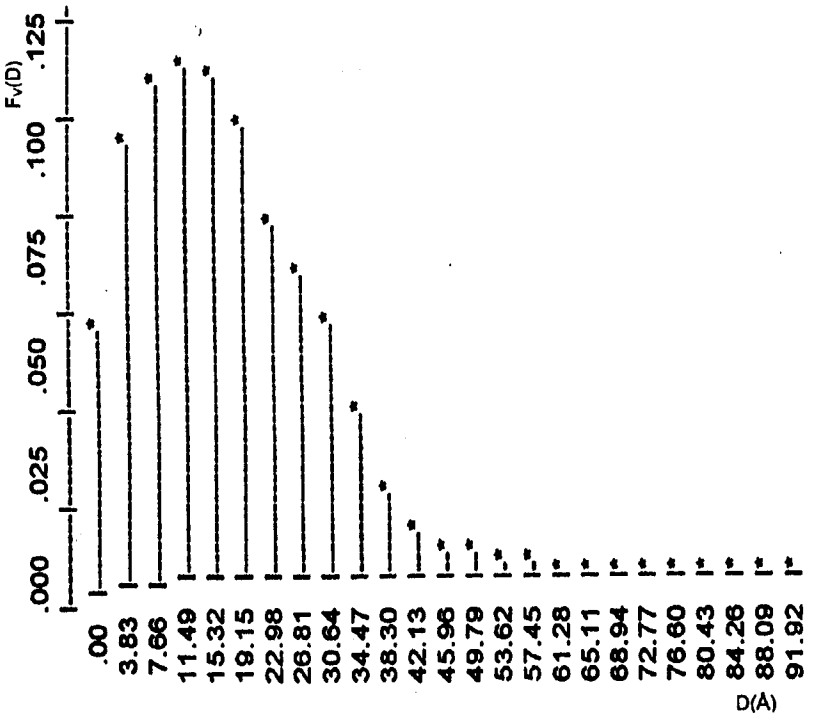


**FIGURE 2a** Crystallite size distribution of NY200 in the [100] crystallographic direction.

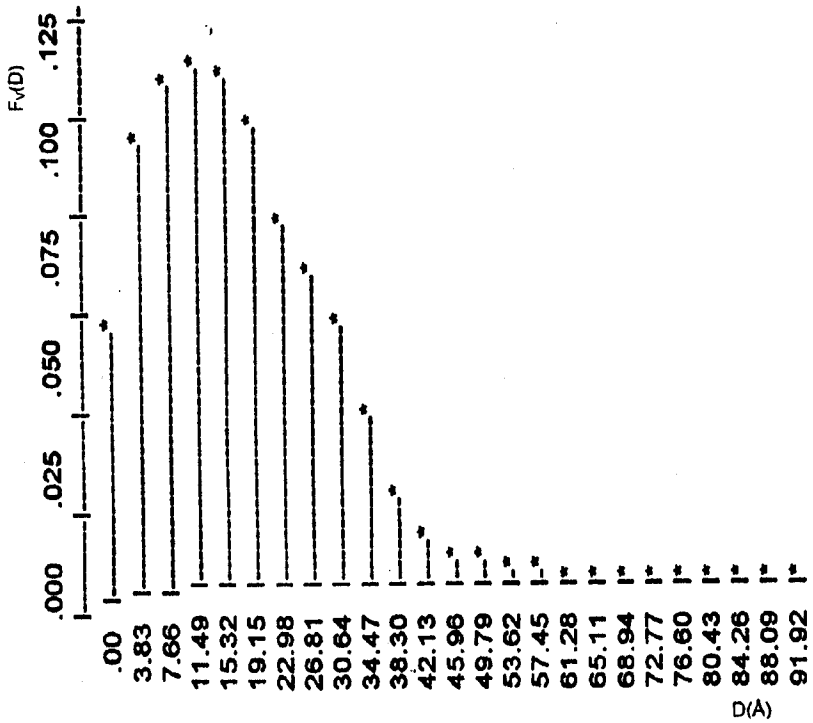


**FIGURE 2b** Crystallite size distribution of NY200 in the [010] crystallographic direction.

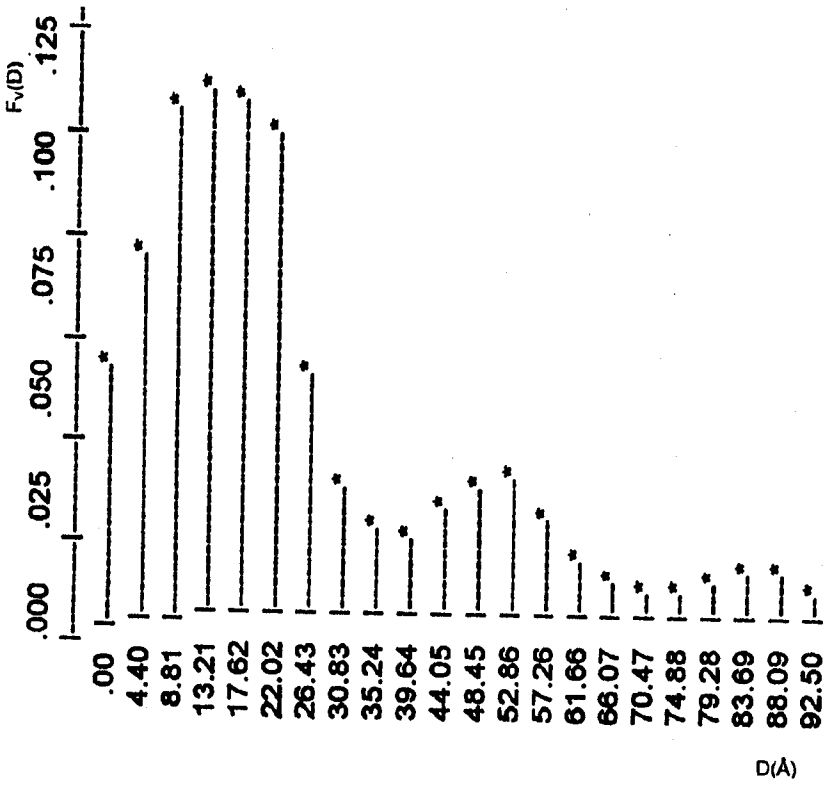


**FIGURE 3a** Crystallite size distribution of NY300 in the [100] crystallographic direction.

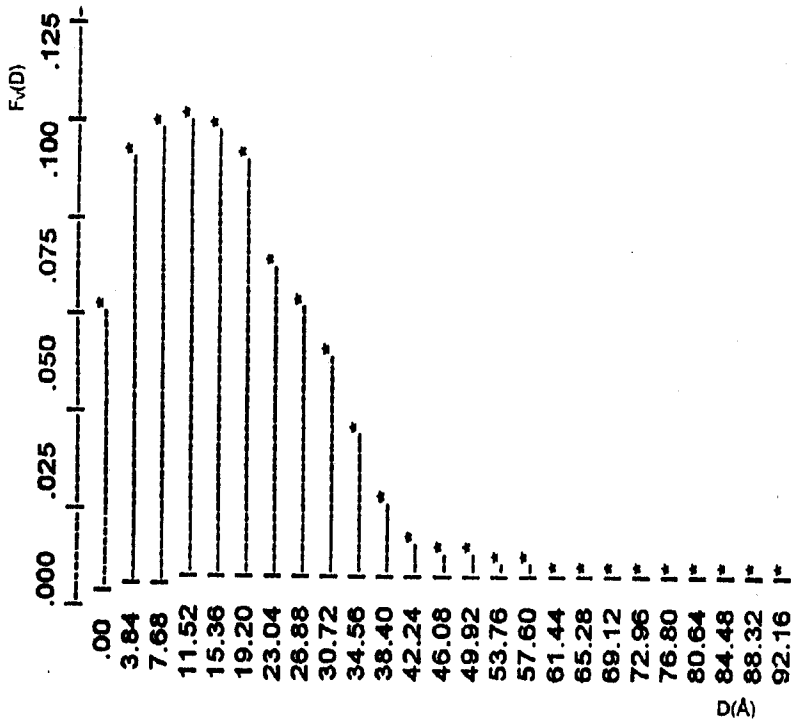


**FIGURE 3b** Crystallite size distribution of NY300 in the [010] crystallographic direction.

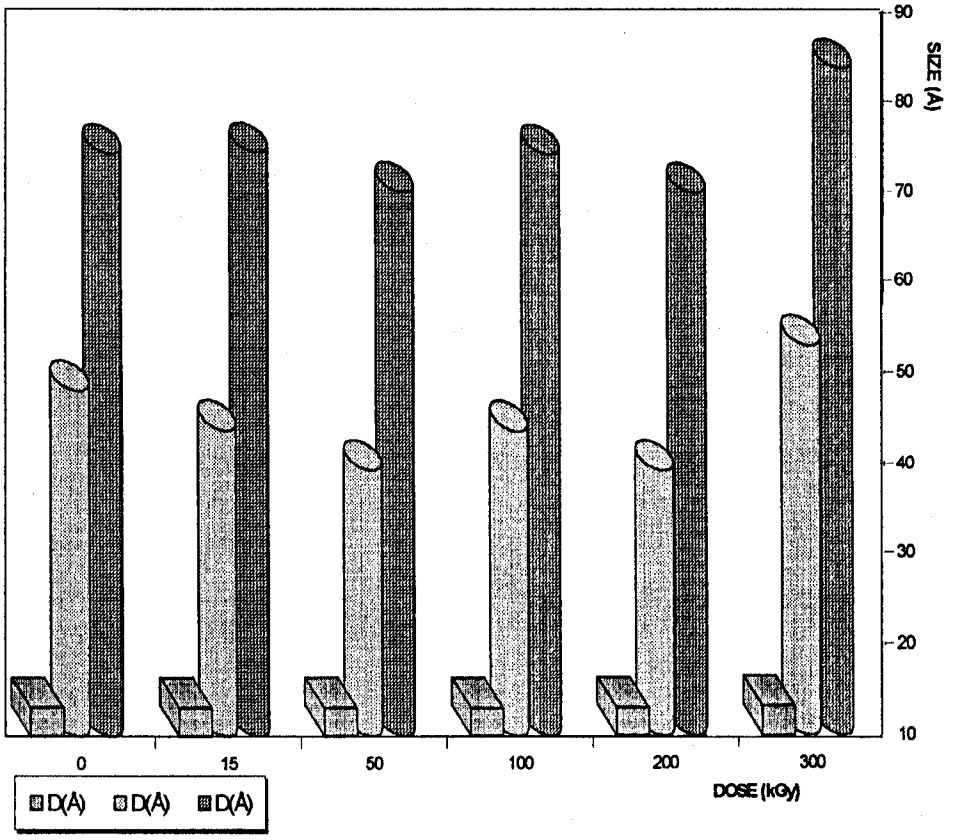


**FIGURE 4** Crystallite size of $\gamma$-irradiated nylon 6, 12 fibers in the [100] crystallographic direction.

others. The results of other analytical techniques reported in the bibliography (like DSC [13], Raman [20], PAL [21]), are in agreement. But in the (010) direction, Figure 5, once again, the NY200 sample shows evident differences.

The Guinier curves (log $I$ *vs.* $h^2$), obtained by the SAXS technique are not linear *i.e.*, the heterogeneity which cause the X-ray scattering at low angles are not monodisperse, Figures 6(a) and (b). This remark may be correlated with the heterogeneity distribution curves where four maxima are found at radii of 20, 60, 120 and 160 Å. The distributions of all samples are similar, Figures 7(a) and (b). Only the NY200 sample differs, in this case five maxima are present. Up to radii of 80 Å the shape of the other curves is reproduced, then, a small peak at 100 Å is found followed by a clear peak at 135 Å and a small one at a radius of 165 Å.

Therefore, in this material, the larger number of heterogeneities has a radius of 135 Å whereas in all the other solids the heterogeneities are mainly of 160 Å. The results obtained by SAXS confirm the X-ray Diffraction results in the sense that the NY200 sample is different from the others, it is different, indeed, in the crystallite as in the heterogeneity sizes.

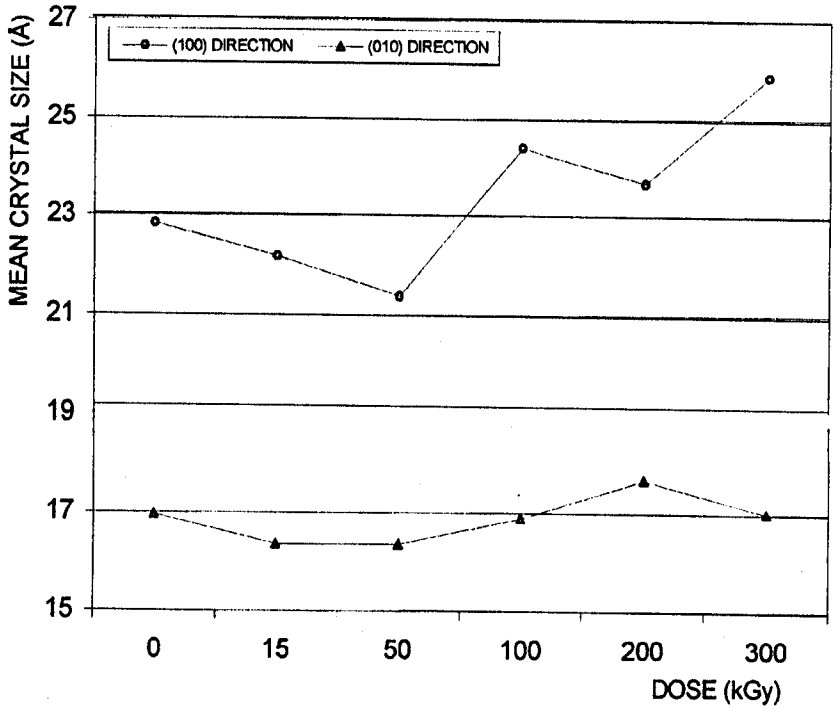


**FIGURE 5** Mean crystal size of $\gamma$-irradiated nylon 6, 12 fibers.

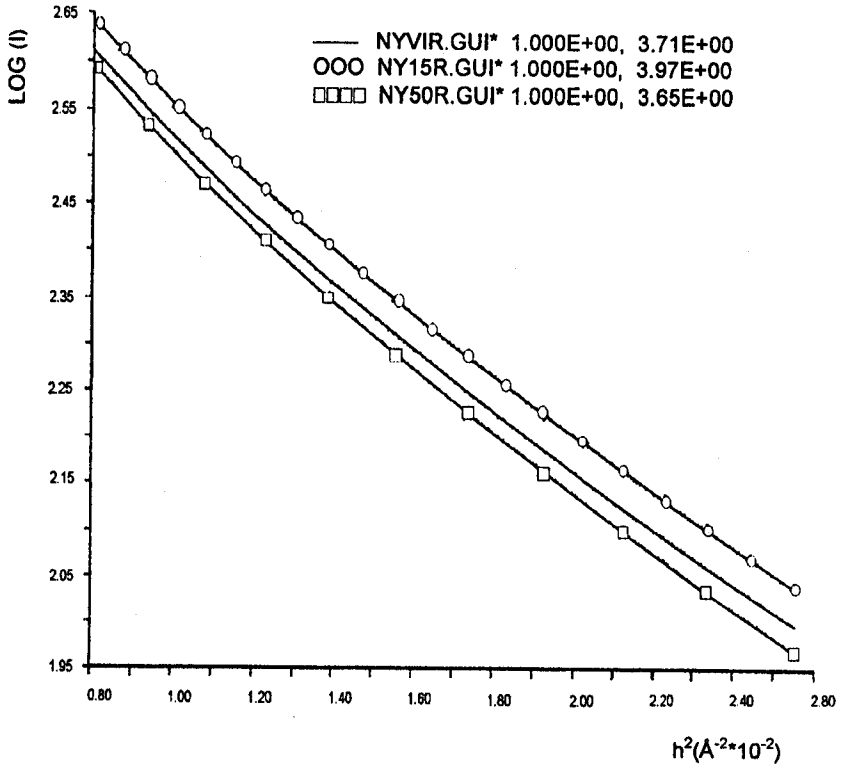


**FIGURE 6a** Guinier curves of $\gamma$-irradiated nylon 6, 12 fibers (NYVIR, NY15 *y* NY50).

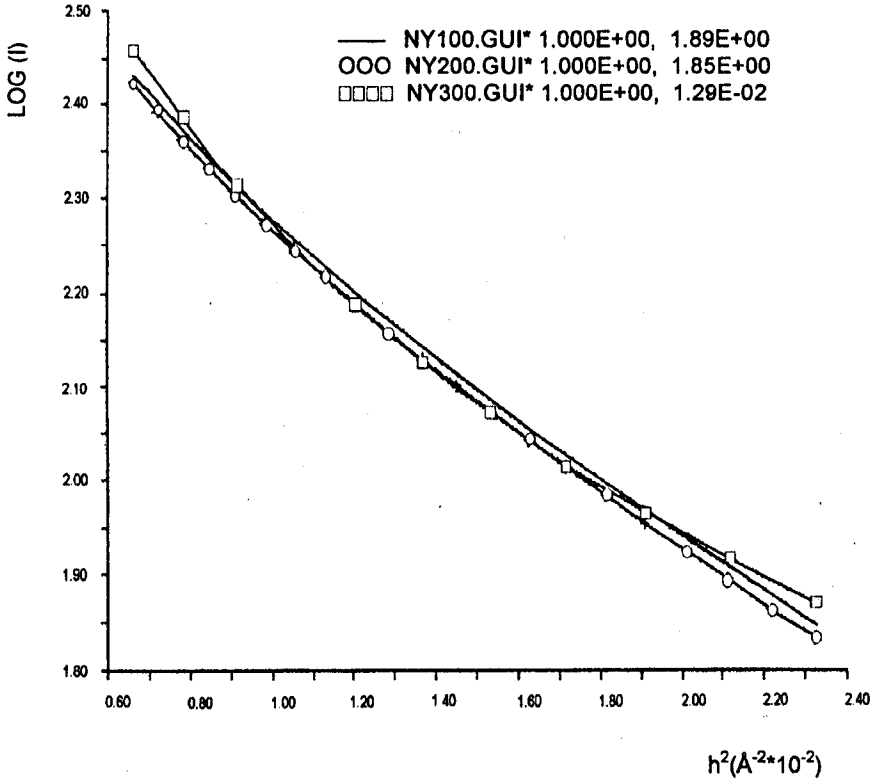


**FIGURE 6b** Guinier curves of $\gamma$-irradiated nylon 6, 12 fibers (NY100, NY200 *y* NY300).

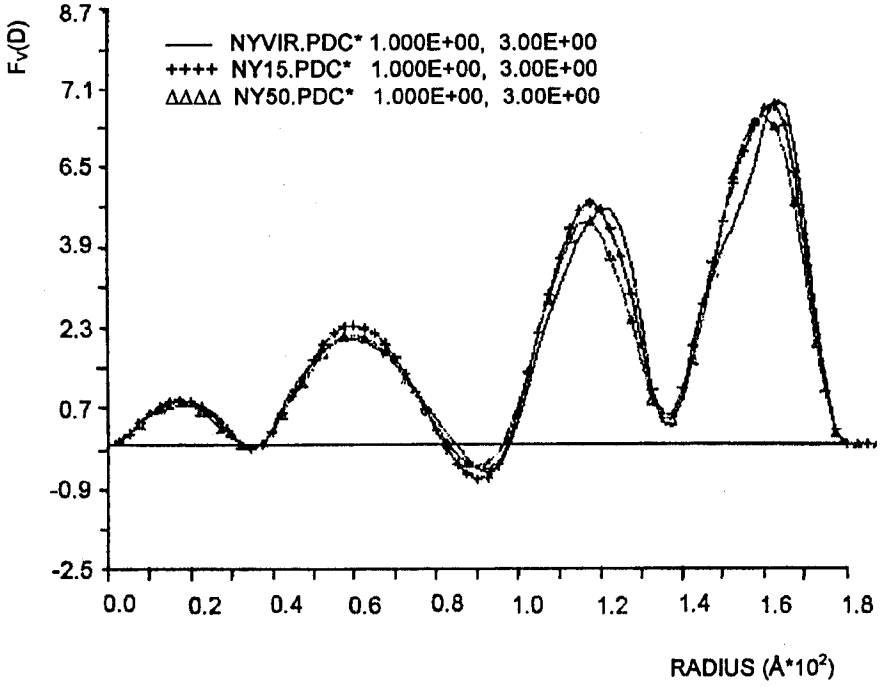


**FIGURE 7a** Heterogeneity distribution curves of $\gamma$-irradiated nylon 6, 12 fibers (NYVIR, NY15, NY50).

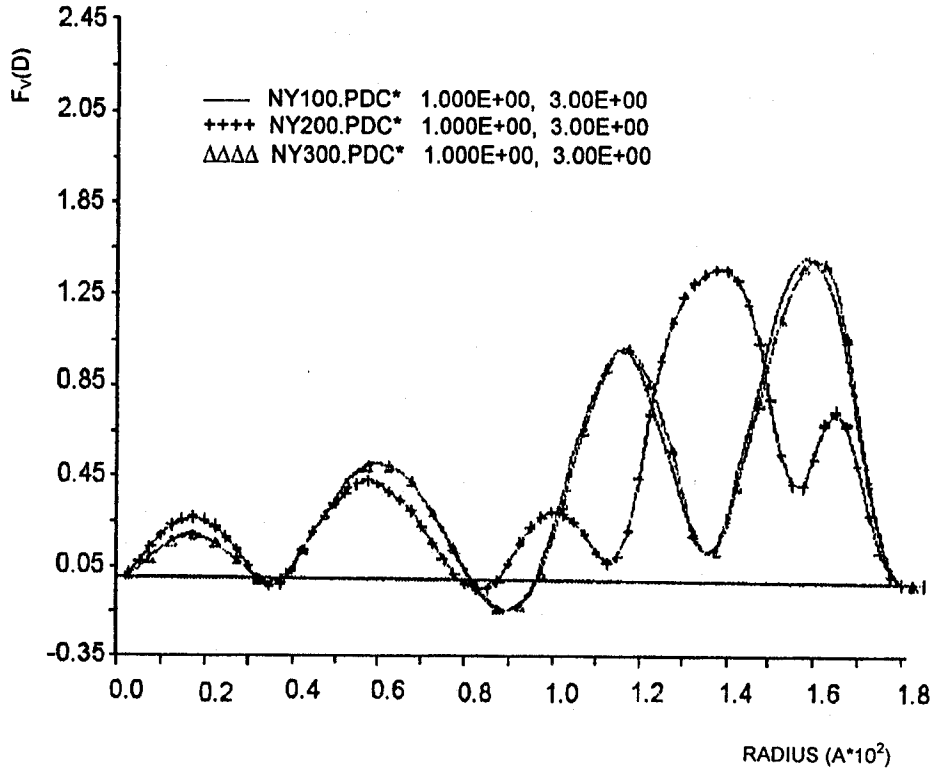


**FIGURE 7b** Heterogeneity distribution curves of $\gamma$-irradiated nylon 6, 12 fibers (NY100, NY200, NY300).

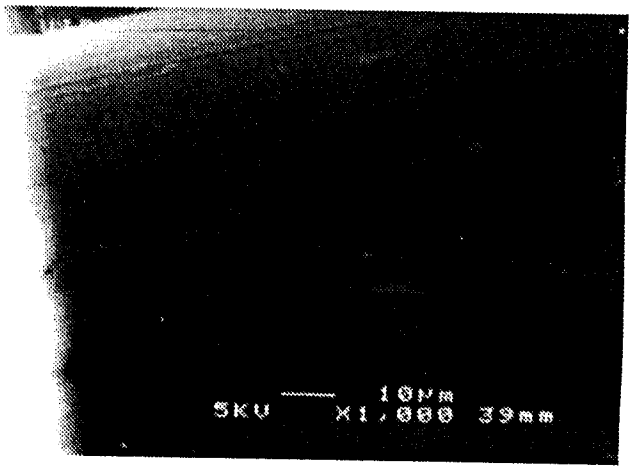


**FIGURE 8a** Morphological aspects of NYVIR (1000X).

SEM results show that nylon 6–12 fibers have been modified with $\gamma$-irradiation. Figures 8a, b, c, d, e and f shows the morphological variations at the fiber surface of fibers subjected to 0, 15, 50, 100, 200 y 300 kGy, respectively. As the irradiation dose is increased scratches at the surface increase, oriented preferentially in fiber direction. A crystal change having

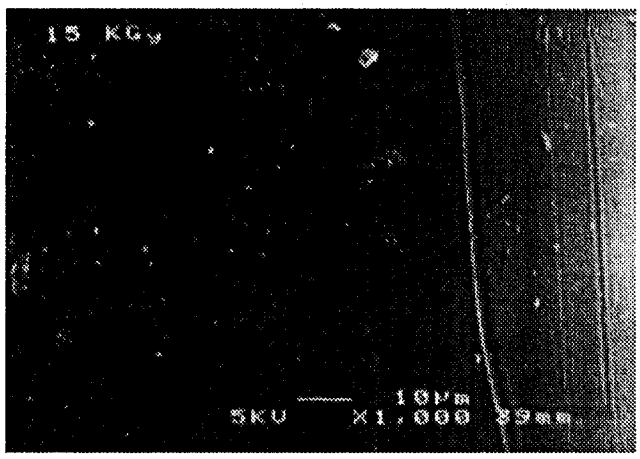


**FIGURE 8b** Morphological aspects of NY15 (1000X).

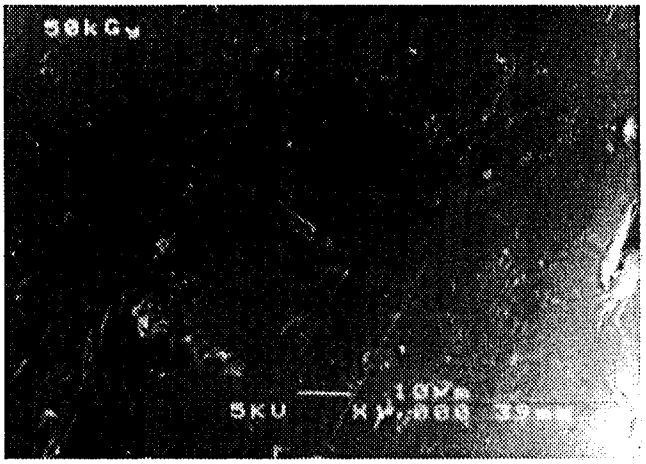


**FIGURE 8c** Morphological aspects of NY50 (1000X).

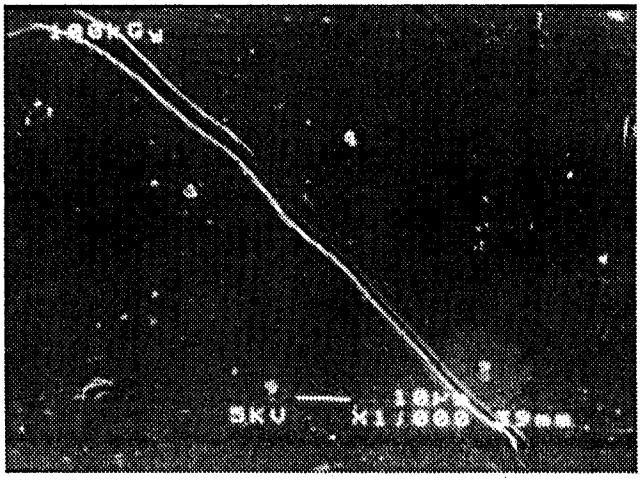


**FIGURE 8d** Morphological aspects of NY100 (1000X).

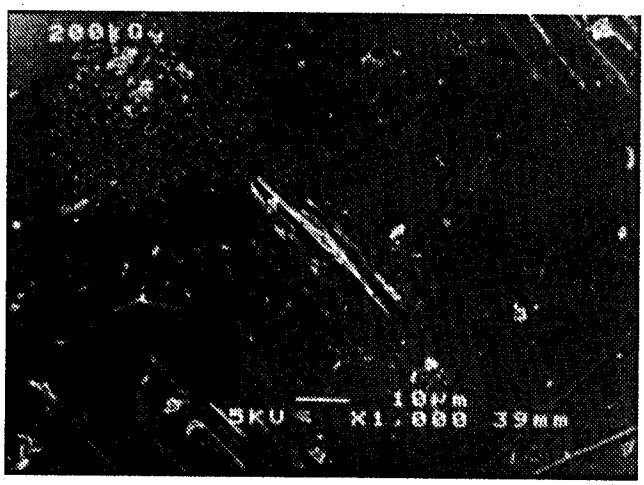


**FIGURE 8e** Morphological aspects of NY200 (1000X).

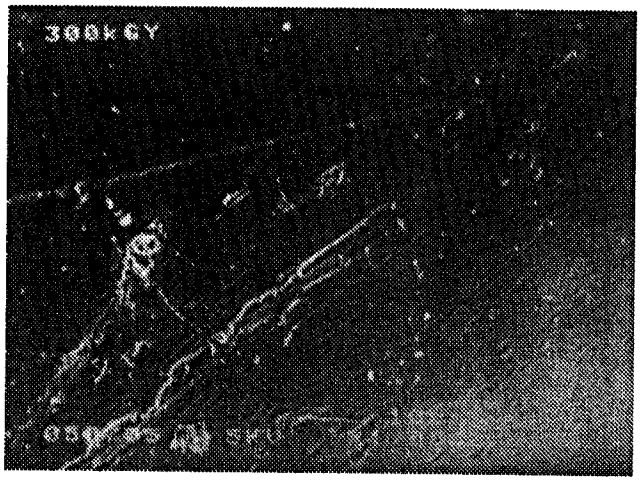


**FIGURE 8f** Morphological aspects of NY300 (1000X).

intrinsic direction is explained by the chain scission occurring into the amorphous zone of the fiber. This is due to the formation of Nylon 6–12 crystalline oligomers and to the crystallinity as the crystal size vary as a function of the $\gamma$-irradiation dose.

## CONCLUSION

Crystalline nylon 6, 12 fibers have been modified by the applied $\gamma$-radiation, not only in their spatial distribution (crystallinity) but also in the external morphology. The modification is more important as the dose of radiation is increased. A standard behavior must be established using other characterization techniques and higher irradiation dose than those used in the present work.

## REFERENCES


[1] Mohler, H., *Reacciones químicas bajo irradiación*, (Ediciones Urmo, 1970) Enciclopedia de la tecnología química, tomo II.

[2] Charlesby, A. (1952). *Pro. Real Soc.*, **A215**, 187.

[3] Dole, M. (1950). Chemistry and physics of radiation dosimetry, *Report of Symposium IX*, Army Chemical Center, Maryland.

[4] Patel, G. N. and Keller, A. (1975). *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 303.

[5] Jenkins, H. and Keller, A. (1975). *J. Macromol. Sci. Phys.*, **B11**, 31.

[6] Ungar, G. and Keller, A. (1980). *Polymer*, **21**, 1273.

[7] Hoseman, R., Loboda-Cackovic, J. and Cackovic, H. (1972). *J. Mater. Sci.*, **7**, 963.

[8] Loboda-Cackovic, J., Cackovic, H. and Hoseman, R. (1974). *Kolloid and Polymer Sci.*, **252**, 738.

[9] Olivares, M., López-Valdivia, H., Vázquez-Polo, G., Carrasco, H., Álvarez-Castillo, A., Oliva, E. and Castaño, V. M. (1996). *Polymer Bull.*, **36**, 629–636.

[10] Melchiors, M., Keul, H. and Höcker, H. (1996). *Macromolecules*, **29**, 6442–6451.

[11] Olivares, M., López-Valdivia, H., Vázquez-Polo, G., Mondragón, M. A., Lima, R., Martínez, E. and Castaño, V. M. (1996). *Polymer Bulletin*, **37**, 221–228.

[12] Olivares, M., Mondragón, M. A., Vázquez-Polo, G., Martínez, E. and Castaño, V. M. (1998). *International Journal of Polymeric Materials*, **40**, 213–218.

[13] Menchaca, C., Rejón, L., Vázquez, F., Castaño, V. M. and Álvarez-Castillo, A. (2000). submitted to *Polym. Bull.*

[14] Biangardi, H. J. (1990). *J. Macromol. Sci.-Phys.*, **B29**(2 y 3), 139–153.

[15] Alvarez, A. G., Bonetto, R. D. and Guérin, D. M. (1987). *Powder Diffraction*, **2**, 220–224.

[16] Bonetto, R. D., Viturro, H. R. and Alvarez, A. G. (1990). *J. Appl. Cryst.*, **23**, 136–137.

[17] Glatter, O. (1980). *Acta Physica Austriaca*, **52**, 243–256.

[18] Glatter, O. (1981). *J. Appl. Cryst.*, **14**, 101–108.

[19] Martin, J. E., Wilcoxon, J. and Adorlf, D. (1987). *Physical Review A*, **36**, 1803–1810.

[20] Menchaca, C., Álvarez-Castillo, A. and Castaño, V. M. (1999). submitted to *Polymer.*

[21] Menchaca, C., Vázquez, F., Álvarez-Castillo, A. and Castaño, V. M. (2000). submitted to *Int. J. Polymer. Mater.*