

## Measurement of the Smectic Content in Undrawn Polypropylene Filaments\*

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### Synopsis

By the use of x-ray diffraction techniques a method is proposed for the measurement of the "smectic" content (interpreted here as material of intermediate order) of undrawn polypropylene filaments. The method involves two estimates of crystallinity by x-ray methods. One is considered to measure the amount of diffraction from the normal crystalline monoclinic lattice and the other the total amount of diffraction from crystalline, "smectic" and noncrystalline material. By separation of these various quantities the amount of "smectic" polypropylene can be deduced. It was found by this technique that the "smectic" content of quenched polypropylene samples decreased from 40°C. onward and approached zero at about 85°C.

### Introduction

Rapidly quenched polypropylene gives an x-ray diffraction pattern which when scanned by a microdensitometer gives a trace similar to that in Figure 1a. This has been claimed as a smectic configuration by Natta,<sup>1</sup> that is, right- and left-handed helices are considered to be randomly placed to one another to give a pseudohexagonal structure, whereas in the normal crystalline monoclinic unit cell are regularly placed to one another.<sup>2</sup> There is no change in the structure of a helix in itself. On the other hand, besides accepting the possibility that this could be a smectic form, Miller<sup>3</sup> has suggested that it might be described as paracrystalline, in the sense postulated by Hoseman.<sup>4</sup> In other words, the crystal lattice is considered to be deformed and the unit cell edges are replaced by statistically determined vectors in both length and direction.

Both these suggestions are reasonable, and there is also the third possibility that part of the diffraction pattern is produced by the broadening effect of small crystallites. There seems little doubt, however, that in general quenched polypropylene samples contain a reasonable proportion of material of intermediate order. It is, therefore, of interest to try and measure this quantity quantitatively as it may have a considerable influence on the final properties of the drawn fiber. To avoid confusion with other postu-

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lated states of intermediate order in polymer<sup>5</sup> this state of order in quenched polypropylenes will be referred to as "smectic," even though it may be a type of order other than this as already discussed in the above section.

### Experimental

The normal method of measuring the crystallinity of a sample has already been fully described.<sup>6</sup> In the case of a spun (undrawn) or drawn fiber, the filaments are made into a randomized sample by a pelleting technique. The sample is placed on the circumference of a focusing camera (evacuated to eliminate air scatter) and exposed to a strictly monochromatic beam of x-rays. The x-ray diffraction lines are recorded on film which, after processing and drying, is scanned by a microdensitometer. From the resultant trace the crystallinity is determined by measuring the integrated area of the crystalline reflections and the integrated area of the noncrystalline background and comparing the two.

The method to be described, involves in reality, an additional measurement of crystallinity. It is best illustrated with reference to Figure 1. Figure 1c is a trace of an unoriented, heat-crystallized sample of spun poly-

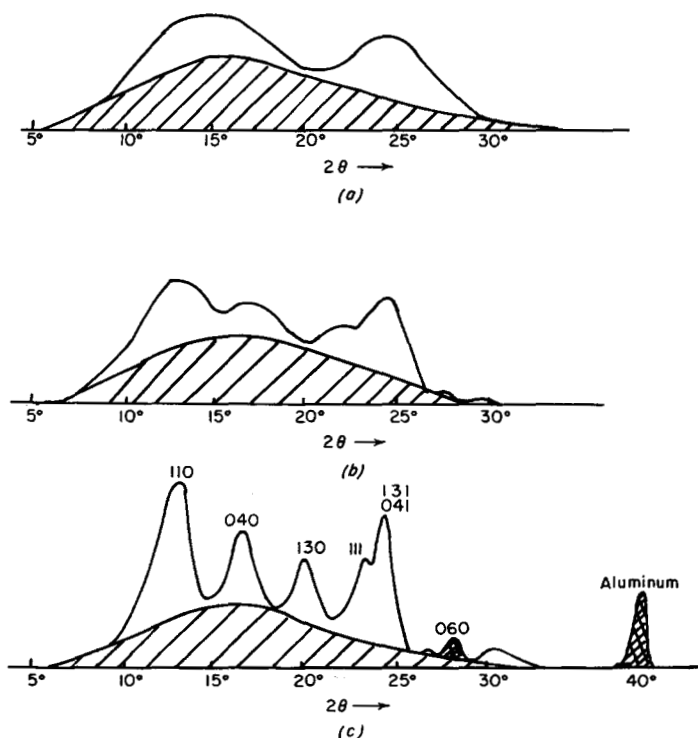


Fig. 1. Microdensitometer traces of x-ray diffraction patterns: (a) rapidly quenched polypropylene spun fiber; (b) rapidly quenched polypropylene spun fiber after heat treatment for  $\frac{1}{2}$  hr. at  $70^{\circ}\text{C}$ .; (c) rapidly quenched polypropylene spun fiber after heat treatment for  $\frac{1}{2}$  hr. at  $140^{\circ}\text{C}$ .

propylene. On it are listed the indices of the principal peaks together with that of a minor peak the 060. In Figure 1a, the trace of a wholly smectic sample of polypropylene, there is no longer any sign of the 060, and the other peaks have merged into the two broad peaks of the smectic configuration. On x-ray photographs showing the 060 reflection, the background beneath this peak is almost linear, and consequently no complications arise over the drawing in of the background to this peak. If, therefore, the appearance of this peak is associated with the appearance of normal type crystallinity in polypropylenes and if it can be equated to give a measure of the "true" crystallinity, it is then possible to obtain a measure of the smectic content from the difference between the normal method of measuring crystallinity where the reduced trace of a noncrystalline sample is used as a background as in Figure 1c and the use of the 060 peak.

In order to use the 060 as a measure of the crystallinity it is necessary to measure the integrated intensity of this peak free of effects due to differences in exposure time to the x-ray beam, specimen size, absorption, etc. This was achieved by building into the focusing x-ray camera, just slightly above the sample under test, a standard reference sample in the form of a thin piece of aluminum foil, 0.0005 in. in thickness. An x-ray diffraction pattern is obtained from this sample, most of which conveniently falls outside the pattern from a polypropylene sample except for a line of reasonable intensity (dependent on the area and thickness of aluminum presented to the beam) which occurs at approximately  $2\theta = 40^\circ$  (Fig. 1c). This line is then used as a standard reference line, and the ratio between the integrated area of this and the 060 peak is obtained. The ratio was found to be constant, within experimental error, for a particular sample of polypropylene exposed to x-rays for different lengths of time. The masses of different sample of polypropylene were kept reasonably constant by making them up in a mold as cylindrical specimens of similar weight and using the same size x-ray beam in all cases.

Two films were placed in the x-ray camera, and exposure times were about  $2\frac{1}{2}$  hr. using Ilford G. film. The topmost film (most intense) was used for the measurement of the 060 and aluminum peaks and the second or weaker film for the normal type measurement of crystallinity. Films were developed and dried in a standard manner and were also set up on the microdensitometer using a standard technique. The peaks in question were scanned on any one film at least twice, and more than one exposure was taken of each specimen. The average of the results was then taken for each individual specimen.

### Results

The first stage in the measurement of smectic content was to obtain a correlation between the crystallinity measured by the normal method and the proposed one using the 060 peak. To do this it was necessary to select polypropylene samples which contained no smectic content. From previous work<sup>7</sup> and that of our own on measurements of crystallinity in

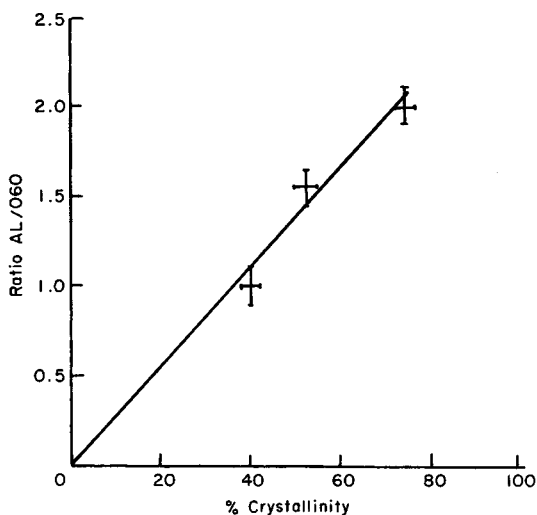


Fig. 2. Correlation of the two methods of crystallinity measurement in polypropylene.

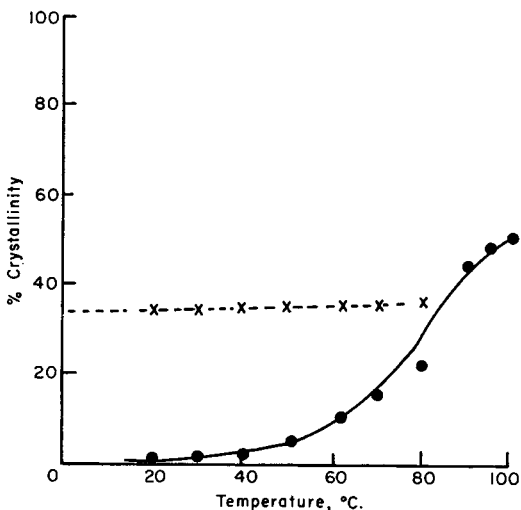


Fig. 3. Change of smectic configuration to normal type crystallinity in polypropylene with heat treatment.

heat-treated unoriented specimens, it seemed safe to presume that specimens which had been heat-treated for about  $\frac{1}{2}$  hr. above a temperature of  $90^{\circ}\text{C}$ . contained little or no smectic content. Three levels of crystallinity (approximately 40, 55, and 70%) were chosen and achieved in polypropylene specimens of either powder or spun fiber. These were then used for the correlation measurements between two methods.

Results are plotted in Figure 2, and it can be seen that quite a good straight line is obtained between the ratio of the areas of the aluminum to

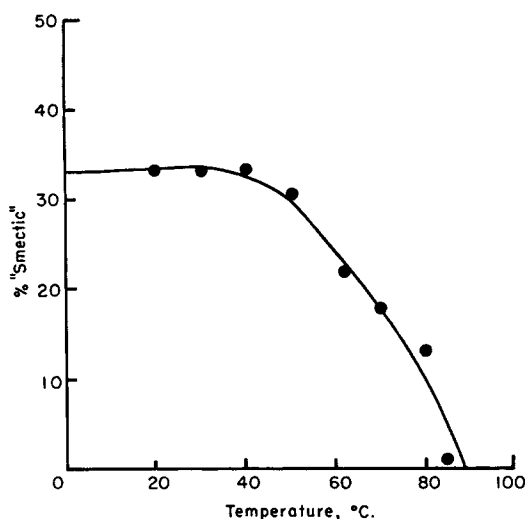


Fig. 4. Decrease of smectic content in quenched polypropylene sample with increasing temperature.

the 060 peak on the one hand and the normal measurement of crystallinity on the other. Each point on the graph is a mean of a number of measurements and the sort of error involved is indicated. Figure 2 was then used for the determination of smectic content in an unoriented spun fiber which showed the completely smectic pattern but was then heat-treated for  $1/2$ -hr. periods at increasing temperatures. This is further illustrated in Figure 3 which actually shows the increase in the "true" crystallinity with temperature; Figure 4 shows the decrease in smectic content with increasing temperature.

By way of illustration of how the method is applied, consider the following example. If the aluminum to 060 ratio is 0.5, then reference to Figure 2 gives us a value of 18% for the "true" crystallinity. Measurement of crystallinity by the normal method which involves fitting a noncrystalline background beneath the principal x-ray diffraction peaks would give a value of about 34%. Consequently the smectic content is  $34 - 18\% = 16\%$ , and the noncrystalline content would be 64%.

### Discussion

It can be seen from the results obtained so far, on unoriented specimens, that the smectic content begins to change about 40°C. and decreases quite rapidly from 50°C. onward with a corresponding increase in the normal type crystallinity. The smectic content reaches a minimum at about 85°C.

The method is unfortunately time-consuming, for to obtain a reasonable average of the intensity of the 060 peak three separate exposures were found to be necessary. On the other hand, preliminary results using a

finer grain x-ray film (Ilford B) indicates that only one exposure will be necessary, but this will be of the order of 10 hr. This is not too inconvenient as it could be done overnight. The finer grain on the film in addition facilitates drawing in of the contour of the 060 peak, particularly when it is of low intensity.

### Conclusions

These preliminary results indicate that the measurement of smectic content by this method appears feasible. It requires, however, further development and in particular needs to be applied to oriented specimens.

### References

1. Natta, G., *SPE J.*, **15**, 368 (1959).
2. Natta, G., P. Corradini, and M. Cesari, *Atti. Accad. Nazl. Lincei (Rend. Classe Sci. Fis. Mat. Nat.)*, **21**, 365 (1956).
3. Miller, R. L., *Polymer*, **1**, 135 (1960).
4. Hoseman, R., *Acta Cryst.*, **4**, 520 (1951).
5. Farrow, G., and I. M. Ward, *Polymer*, **1**, 330 (1960).
6. Farrow, G., *Polymer*, **2**, 409 (1961).
7. Turner-Jones, A., I.C.I. (Plastics Division), Welwyn Garden City, England, unpublished work.

### Résumé

Au moyen de techniques de diffraction des rayons-X, on propose une méthode de mesure du contenu "smectique" (interprété ici comme étant le matériel d'ordre intermédiaire) de filaments de polypropylène non filé. La méthode implique deux estimations de la cristallinité par des méthodes aux rayons-X. L'une mesure la quantité de diffraction provenant du réseau cristallin monoclinique normal, et l'autre la quantité totale de diffraction provenant du matériau cristallin, "smectique" et non-cristallin. En séparant ces différentes quantités, on peut déduire la proportion de polypropylène "smectique." On a trouvé par cette technique que la teneur "smectique" du polypropylène ponté diminue progressivement à partir de 40°C et approche de zéro vers 85°C.

### Zusammenfassung

Eine Methode unter Verwendung von Röntgenbeugungsverfahren wird zur Messung des "smektischen" Gehalts (hier als Material mit intermediärer Ordnung interpretiert) ungereckter Polypropylenfäden vorgeschlagen. Es werden zwei Kristallinitätsbestimmungen durch Röntgenmethoden vorgenommen. Die eine soll den Betrag der Beugung des normalen kristallinen monoklinen Gitters messen und die andere den Gesamtbetrag der Beugung des kristallinen, "smektischen" und nichtkristallinen Materials. Durch die Trennung dieser verschiedenen Größen kann die Menge an "smektischem" Polypropylen abgeleitet werden. Diese Methode lieferte das Ergebnis, dass der "smektische" Gehalt von abgeschreckten Polypropylenproben von 40°C an abnimmt und sich bei etwa 85°C null nähert.

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