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RELATIONSHIPS BETWEEN RADIAL ATOMIC DISTRIBUTION CURVES AND THE MECHANISM FOR THE PARACRYSTAL–CRYSTAL TRANSITION OF ISOTACTIC POLYPROPYLENE

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Abstract—Unoriented specimens of isotactic paracrystalline polypropylene were annealed at various temperatures until completely transformed into the monoclinic crystal form. Their X-ray diffraction patterns were examined by the technique of radial atomic distribution analysis. The results are correlated with an essentially intramolecular mechanism for transformation which seems to be very probable and to provide a basis for further consideration of the lateral packing of the chains during the transformation and afterwards.

INTRODUCTION

WE HAVE recently described(1) the theoretical and experimental parts of a study of the analysis of the radial atomic distribution of unoriented isotactic polypropylene (PP) during its transformation from the paracrystalline to monoclinic form.

A careful investigation of the results has permitted some conclusions on the probable mechanism of this previously discussed(2–5) complex transition in the solid state; such a mechanism, moreover, should be characteristic of many disorder-order phenomena observed in stereoregular polymers as a result of annealing and of temperature in general. On the basis of the X-ray diffraction fibre patterns of the quenched form of PP, Natta and Corradini(6,7) proposed a transformation mechanism in which the passage to the higher degree of order led to marked rearrangements among adjacent chains; in the paracrystalline form, these would already have a significant degree of order in the c crystallographic direction (c = fibre axis), while the lateral structural order would be considerably less marked. Therefore, annealing would produce a gradual improvement in the lateral packing of the chains, bringing them gradually towards the more stable monoclinic form.

The results of some further studies(8–12) on the conformation of isotactic PP in the molten state and in solution suggested that the paracrystalline form might have instead a frozen liquid type structure, and that the paracrystal–crystal transition would take place by means of a mechanism requiring mainly intramolecular rearrangements.

The hypothesis was also supported by difficulties encountered in the preparation of a completely paracrystalline form when the melted polymer was quenched, such as the necessity of working with very thin films and the need for rapid quenching.

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Otherwise, a very quick crystallization process starts and X-ray diffraction patterns clearly show that there is much monoclinic form present.

We have therefore considered a working hypothesis based on a starting structure for the quenched form characterized by frequent points of inversion in the spiralization of its sequences; it was absolutely impossible to employ traditional X-ray diffraction methods.

The techniques for analysis of the radial atomic distribution, although complicated and time consuming, have provided the means of explaining, in a rather conclusive manner, the real mechanism of transformation. In this work, we report the results of such a study.

EXPERIMENTAL TECHNIQUE AND RESULTS

The details of the experimental procedures and treatment of data have been amply reported in a previous work.(1) Nevertheless, we will summarize again the essential arguments: X-ray diffraction patterns were carefully registered with a diffractometer (proportional counter, CuK_α radiation, angular range 3°–150°, 2θ) and the diffracted intensities were evaluated at suitable 2θ intervals. The intensities were corrected for instrumental background, polarization, absorption (since the *infinite thickness* condition(13) was not satisfied) and angular variation in diffracting volume. The corrected intensities were finally converted to electron units allowing also for incoherent Compton scattering. The interference function $i(s)$ was evaluated from these data, and used in the calculation of the radial atomic distribution function:

$$4\pi\, r^2 \rho\,(r) = 4\pi\, r^2 \rho_0 + \frac{2r}{\pi}\int_0^\infty s\, i(s)\, \mathrm{e}^{-as^2} \sin rs\, \mathrm{d}s \qquad (1)$$

where:

r = interatomic distance as a function of which the distribution curve is calculated;

$\rho\,(r)$ = radial atomic distribution function;

ρ_0 = average atomic density of the specimen;

$s = 4\pi \sin\theta/\lambda$ (with θ = Bragg angle and λ = wavelength of the X-radiation);

e^{-as^2} = artificial temperature factor to reduce the termination errors of the series; determination of the constant a has been given in detail in a previous work;(1)

$$i(s) = \text{interference function} = \frac{I_{\mathrm{coh}} - Nf^2}{Nf^2}$$

(where I_{coh} is the coherently diffracted experimental intensity, N the number of carbon atoms contributing to the diffraction and f their atomic scattering factor).

Figure 1 shows the $4\pi r^2\, \rho\,(r)$ curves for the significant group of specimens examined in connection with the paracrystal–crystal transition. The group includes specimens of the untreated paracrystalline form and those annealed at temperatures between 80° and 160°.

For evaluation of the data obtainable from curves such as those in Fig. 1, it must be noted that the peak areas depend on the average number of atoms at a distance r_m from an origin atom. The averaging may be considered as taking each atom of the repeat unit in turn as origin and summing the number of atoms in the remainder of

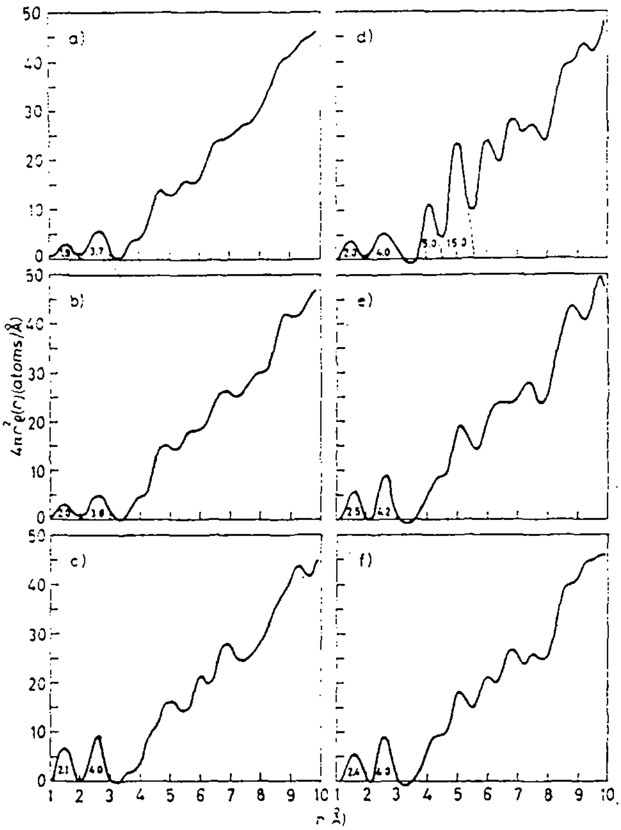

FIG. 1. Experimental radial atomic distribution curves $4\pi r^2\ \rho\ (r)$ for the six PP specimens examined during the temperature induced paracrystal–crystal transition: (a) untreated paracrystalline form, (b) the same annealed at 80°, (c) at 100°, (d) at 120°, (e) at 140°, (f) at 160° (totally monoclinic form).

the unit at each distance r_m and finally dividing the totals by the number of atoms in the repeat unit.

For example, in the case of the repeat unit of polypropylene

$$(\text{—CH}_2\text{—}\underset{\displaystyle \text{CH}_3}{\underset{|}{\text{CH}}}\text{—}),$$

the following coincidences at $r_m = 1 \cdot 54$ Å occur:

2 when the origin is on the CH_2 carbon atom;
3 when it is on the CH carbon atom;
1 when it is on the CH_3 carbon atom.

The total of six C—C distances is then divided by 3 (the number of carbon atoms in the repeat unit), thus obtaining the average value of 2 to which the experimental values of Fig. 1 are very close.

A similar procedure is used for all other interatomic distances. In order to compare better the experimental data with the proposed mechanism, the electronic radial distribution curve has also been evaluated according to Finbak's method(14) which requires the use of a modified interference function:

$$i'(s) = I_{coh} - Nf^2 \tag{2}$$

and the distribution curve calculated by means of the expression:

$$\sigma(r) = \frac{2r}{\pi}\int_0^\infty s\, i'(s)\, e^{-as^2} \sin rs\, ds. \tag{3}$$

The functions $\sigma(r)$ calculated for the six above mentioned specimens are shown in Fig. 2.

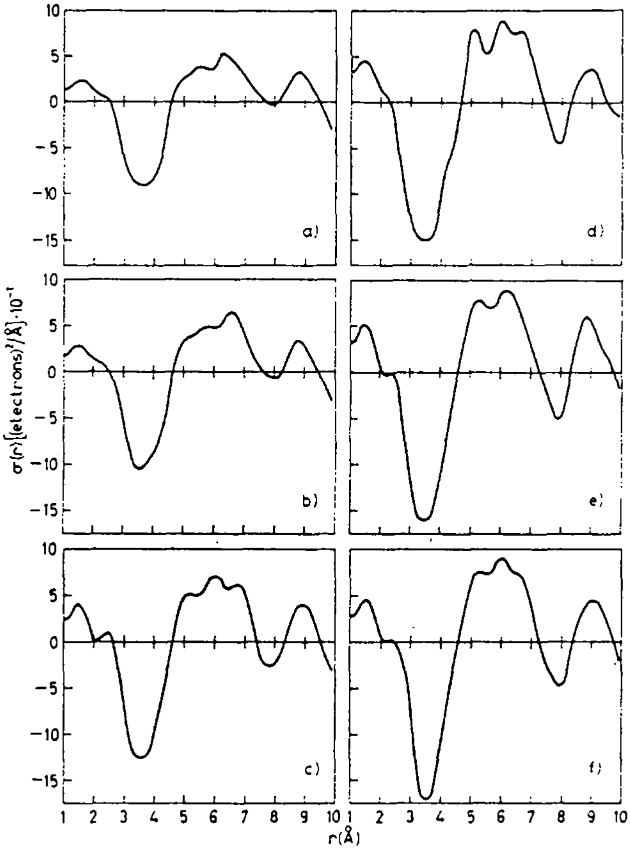

FIG. 2. Experimental radial electronic distribution curves $\sigma(r)$ for the same six specimens.

Finally, theoretical distribution curves were calculated by two different methods: the first, based on the paracrystal theory,(15,16) has already been described in detail(1) and makes use of the expression:

$$4\pi r^2 \rho_{th}(r) = \sum_i N_i \frac{e^{-(r_i - r)^2/a^2(r_i)}}{\sqrt{(\pi)}\cdot a(r_i)} \tag{4}$$

where N_i is the number of correlated atoms at a distance r_i, ρ_{th} is the theoretical distribution function and $a(r_i) = K\sqrt{r_i}$, with K the proportionality constant to be determined by means of the least squares method to give the best fit with the experimental distribution.

The second method[17,18] calculates the theoretical curve by means of the addition of partial curves due to the interactions between pairs of atoms:

$$\sigma_{\text{th}}(r) = \sum_{n=1}^{N} \sigma_n(r)\, \nu(R_n) \tag{5}$$

where:

$$\sigma_n(r) = \frac{2r}{\pi} \frac{1}{R_n} \sum_{s=s_{\min}}^{s_{\max}} f^2(s) \cos[(R_n - r)s](\Delta s); \tag{6}$$

$\nu(R_n)$ = frequency with which the various interatomic distances R_n repeat themselves in the particular structural model;

$\sigma_n(r)$ = distribution curve for a diatomic system.

When results are obtained by the first method, they obviously must be compared with the data derived from functions like those of Eqn. (1), and in the second case, with the distribution curves calculated by means of Eqn. (3). In Fig. 3, the theoretical distribution curve is reported as calculated from (4) for the structure of crystalline isotactic

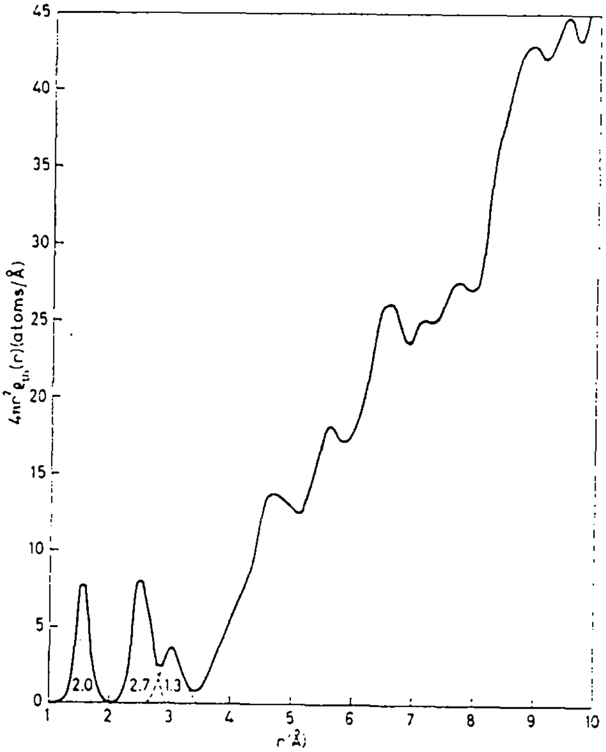

FIG. 3. Theoretical radial atomic distribution curve evaluated according to Hosemann–Voigtlaender–Tetzner method on the model of PP monoclinic form (space group Cc).

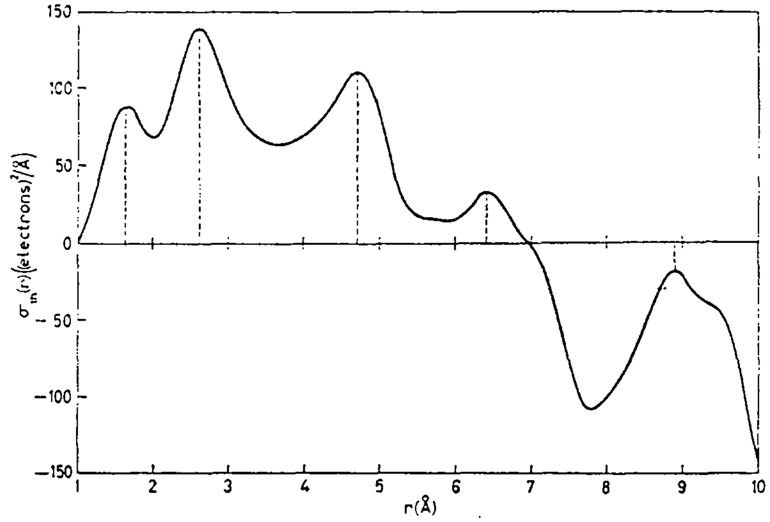

FIG. 4. Theoretical radial electronic distribution curve evaluated according to Bjørnhaug-Ellefsen-Tønnesen method on the model of a single 3_1 unperturbed PP helix.

PP (space group Cc) described by Natta.(19) Figure 4 shows the theoretical distribution curve evaluated from (5) for the model of a single ternary helix having the same interatomic distances and bond angles.

DISCUSSION

It is well known that many isotactic polymers, among them PP, crystallize with a helical conformation in which alternate chain bond sequences assume *trans* (internal rotation angle $\phi = 180°$) and *gauche* ($\phi = 60°, 300°$) positions. For the gauche positions, the rotation is always in that direction which relieves steric hindrance by setting R and H groups in a juxtaposition, thus generating either a left-hand (G_l) or a right-hand (G_r) helix.

Thus, in the crystal, long regular sequences occur of the type:

.... (TG) (TG) (TG) (TG) (TG) (TG) ....

or the equivalent:

.... (GT) (GT) (GT) (GT) (GT) (GT) ....

Using the customary nomenclature, introduced by Corradini in his conformational studies of stereoregular polymers and recently summarized,(7) we can so schematize the types of inversion in the chain:(12)

$$\ldots (TG_r)_m (TT) (G_l T)_n (G_l' G_r') (TG_r)_p (TT) (G_l T)_q \ldots \quad \text{(A)}$$

This model requires that to *n* (TT) repetitions, followed by an inversion in the sense of the helix spiralization, necessarily correspond *n*-1 (GG) repetitions; therefore, the helix axis is frequently distorted and the chain backbone appears rather undulating. In model (A), we have indicated with dashes the repetition (GG) for emphasizing that in such a chain defect are included not only the conformations with $\phi = 60°$, 300°, but also the distorted *skew* S_r ($\phi = 120°$) and S_l ($\phi = 240°$)[12] and other similar ones that can play a very important role during the intermediate transition phase and that are characterized by interatomic C—C distances which are very near to the values observed for the (TT) sequences.

The presence of (TT) and (GG) repetitions or others similar necessarily causes a distortion in the helix axis, thus the quenched form, if it reflects in some way the structure of molten PP where such inversions are very frequent,[20] must therefore be considered as arranged in a typical strongly perturbed paracrystalline lattice.

The structural information derivable from radial atomic distribution curves and from related considerations can be summarized as follows:

(1) The paracrystalline quenched form is on the average arranged in a 3_1 helix which remains unchanged during the whole transition to the monoclinic product obtained by annealing. This result has already been noted in examinations using infrared spectroscopy[5] which also assigned a ternary helix conformation to the paracrystalline form. In this regard, it must be observed that the first two peak areas, which are indicative of the average number of neighbouring atoms at a well defined distance, confirm such a result since they are only in agreement with a ternary helix conformation. In fact, from Fig. 3 it is seen that a complete quantitative agreement with the experimental data is reached only if the helix is 3_1. The poor resolution of the method prevents the separation of the peaks at about $r_m = 2{\cdot}5$ and $3{\cdot}0$ Å, but the experimentally determined area fits very well with the sum of the calculated areas.

(2) In the course of the paracrystal–crystal transition, the greatest differences are observed in specimens annealed at 100° and especially at 120°, i.e. at the half way point of the transition. The peaks corresponding to distances of 4·2 and 5·1 Å are here greatly increased, but this phenomenon gradually weakens as the transition proceeds to completion. Once a model with frequent inversions has been proposed, it is also necessary to postulate a transition mechanism based on the helices rewinding, both those of right and left conformation; it is now important to verify if, at the corresponding interatomic distances, an increase of the frequencies in the model takes place, since this would confirm the mechanism. Effectively, a scale model as indicated in Fig. 5, clearly shows that when the segments unwind starting from the single defect, there has to be a noticeable increase in the number of (TT) sequences, or of

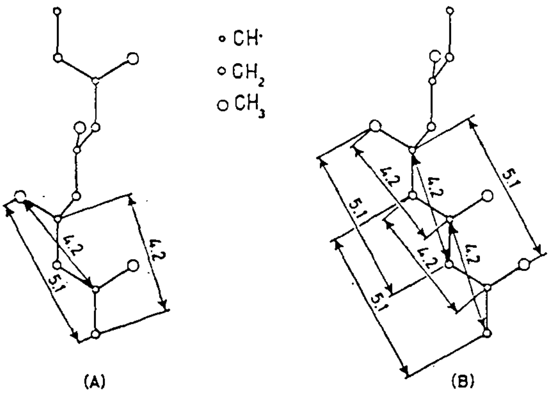

FIG. 5. Segments of a PP helix: (a) perfect; (b) perturbed by a (TT) defect: note in (b) the increase in frequency of the two intramolecular distances at 4·2 and 5·1 Å.

similar conformations. In a perfect 3_1 helix (without steric defects), where a (TT) sequence never occurs, the distance at 4·2 Å appears three times for every two pitches of the helix and distances of 5·1 Å are not found in the backbone, but only if the lateral methyl groups are also considered. The presence of distorted (TT) and (GG) sequences, or those very near to these conformations, that rewind themselves in the prevalent sense during the transition, justifies the marked increase in such frequencies.

Owing to the fact that the 4·2 Å distance is the lower limit of the intermolecular distances (CH_3—CH_3 in adjacent chains) in the final crystalline monoclinic product, the increase of the peak at half transition and its subsequent decrease as the transition gradually proceeds towards the monoclinic form are not easily understood in terms of an exclusively intermolecular mechanism: this peak should be most prominent in the final monoclinic form; an appreciable frequency of such a minimum intermolecular distance in the course of the transition, when undoubtedly the packing is still less compact, is quite unexpected.

In addition, there are some publications(9,20) indicating that the crystal structure of most of the polymers is essentially determined by intramolecular interactions. In our case, where a marked crystallization process occurs during the transformation, such an intramolecular mechanism must play a very important role.

(3) Thermodynamic considerations of the transition(21) also demonstrate that an exclusively intermolecular mechanism is not in agreement with the establishing of well defined structural order that is exclusively a function of the annealing temperature; an intramolecular mechanism based on a rewinding of segments of different length can, on the contrary, explain the observed phenomena since the characteristic degree of order at every annealing temperature is a saturation value that does not change with time once the saturation itself is reached. In fact, the intramolecular mechanism is essentially discontinuous since the energies for rewinding of segments differ according to their length and structure (this explains the strict dependence on the temperature), while the intermolecular mechanism should be continuous because it consists of a progressive rotation of the helices so producing an improvement in the lateral packing (therefore, it should be a function of the amount of heat supplied, i.e. of the annealing time).

(4) Considerations of the packing of the helices have been made on the basis of the method of Bjørnhaug and co-workers;(18) this allows evaluation of an average cross section occupied by a polymeric chain perpendicular to the helix axis, by means of the expression:

$$f = \frac{m}{d\,l\,N} \tag{7}$$

where d is the polymer density, l the monomeric unit length projected on the chain axis, m the molecular weight of the same and N Avogadro's number.

These have yielded for PP the values:

$f = 34{\cdot}6$ Å^2 in the monoclinic form, and
$f = 36{\cdot}6$ Å^2 in the untreated paracrystalline form.

To evaluate the distance between the helix axes, it is necessary to form a hypothesis on the geometrical shape of the above mentioned cross section. This distance, in the case of the regular figures, is twice the radius of the inscribed circle. In Fig. 6, the

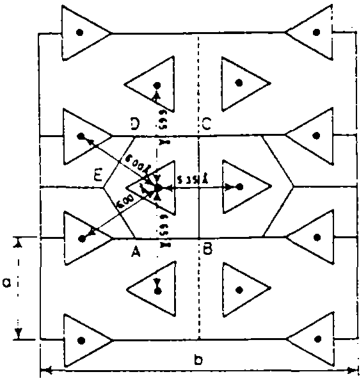

FIG. 6. Plane ab of the Natta structure of isotactic PP. There are represented three unit cells, helix axis projections, their mutual distances and the primitive bidimensional Wigner–Seitz cell of every helix (ABCDE pentagon).

plane ab of the PP unit cell described by Natta(19) is reported; the black dots indicate the projection on this plane of the helix axes. The five-sided ABCDE polygon represents the primitive Wigner–Seitz cell, i.e. the minimum space parallel to the plane ab available for every helix and therefore in a direction approximately normal to its axis; each helix is thus asymmetrically surrounded by five others, one at 5·35 Å, two at 6·00 Å and two at 6·65 Å. The average distance between the axes is thus 6·13 Å. The area of ABCDE is 34·8 Å^2, which is in good agreement with the value determined from (7).

Covering the plane with the only three possible regular figures (equilateral triangle, square and hexagon), from the above reported values of *f*, we get the following results for the two cases of crystal and paracrystal:

	triangle	square	hexagon
crystal	5·2 Å	5·9 Å	6·3 Å
paracrystal	5·3 Å	6·0 Å	6·5 Å

In the crystal, the best agreement therefore occurs at an intermediate value between square and hexagon, as was predicted by Fig. 6. The average distance between the helix axes of the paracrystalline form must necessarily be larger than that in the monoclinic form, especially because of the irregularity of the helix.

The only valid value is given by the hexagon and therefore the hexagonal packing, proposed by Natta(6) for the paracrystalline form, is quantitatively justified. Nevertheless, the essentially intramolecular transformation mechanism also requires, as the above reported considerations demonstrate, a rearrangement in the lateral packing of the chains (average distance between the axes from 6·50 to 6·13 Å); this would account for the slight variation in density during the transition.

(5) In connection with the information furnished by the theoretical radial distribution curves, the first curve shown in Fig. 3 was evaluated on a model consisting of many ideal helices packed in the crystalline structure described by Natta; it shows a fair agreement with the experimental curve of the final monoclinic form. However, the slight differences in the positions and profiles of the peaks indicate that, in the unoriented polymer, the organization is less perfect than in the model having the space group Cc, as determined by the fibre pattern.

The second theoretical curve (Fig. 4) has been calculated for a single isolated perfect helix and it shows that the above mentioned two maxima at 4·2 and 5·1 Å are not detectable; hence it can be concluded that these distances do not occur frequently in the unperturbed helix; their presence in the chain, which we clearly observed, is only explicable during the "dynamic" phase of the transition when the rewinding processes occur and higher order organizations are reached in the strongly perturbed zones.

We conclude by underlining the fact that the data provided by radial atomic distribution curves in the polymer diffractometric studies can be very interesting. In the past, this technique gave few and obscure results, but it must be noted that most of the difficulties were due to insufficient precision in the diffracted intensity measurements and to the lack of knowledge in the field of conformation of macromolecules. By improving the experimental precision up to the limits that can at present be attained, one observes that the data become more meaningful; our belief, supported by very recent works, is that the technique will expand in the near future, especially in the study of amorphous or partially crystalline materials.

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Résumé—Grâce à des analyses de la distribution atomique radiale, appliquées à des diagrammes de diffraction des rayons X, on a étudié des échantillons non orientés de polypropylène isotactique paracristallin différemment recuits jusqu'à leur transformation complète dans la forme cristalline monoclinique. Les résultats on été reliés avec un mécanisme de transformation essentiellement intramoléculaire qui semble très probable. Ils ont ensuite été utilisés pour obtenir des informations sur l'arrangement latéral des chaînes pendant la transformation et à la fin de celle-ci.

Sommario—Con le tecniche di analisi della distribuzione atomica radiale applicate a spettri di diffrazione dei raggi X sono stati studiati campioni non orientati di polipropilene isotattico paracristallino differentemente ricotti fino alla loro completa trasformazione nella forma cristallina monoclina. I risultati sono stati correlati con un meccanismo di trasformazione essenzialmente intramolecolare, che appare molto probabile, e sono serviti poi come base per successive considerazioni sull'impacchettamento laterale delle catene durante la trasformazione ed al termine della stessa.

Zusammenfassung—Proben von isotaktischem, nicht orientiertem, parakristallinem Polypropylen wurden untersucht mit Hilfe der radialen Atomverteilung an den Spektren der Röntgenstreuung. An den Proben sind bis zu ihrer vollständigen Umwandlung in die monokline Form mehrere Temperungen vorgenommen worden. Die Resultate wurden einem im wesentlichen intramolekularen Umwandlungsmechanismus zugeordnet, der sehr wahrscheinlich scheint und dienten ferner als Basis für weitere Betrachtungen bezüglich der seitlichen Anordnung der Ketten während der Umwandlung und am Ende derselben.