

Isotactic Polybutene-1: Modification 3 and its Transformations

By F. DANUSSO, G. GIANOTTI, and G. POLIZZOTTI

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SUMMARY:

Modification 3 of isotactic polybutene-1, prepared by crystallization from a solution at room temperature, was studied by dilatometric and X-ray examinations at different temperatures. At high degrees of crystallinity, its specific volume is intermediate between that of modification 1 and 2. By rapid heating its melting can be observed at about 102°C., while by a sufficiently slow heating it can even be totally converted into modification 1 before melting, by a solid-solid transformation. Modification 1 obtained in this way melts surprisingly low, at 109°C., probably because of morphological memory. During the melting of modification 3, or modification 1 originated by modification 3, crystallization of available liquid phase usually takes place, giving modification 2, which happens to be the most highly melting polymorph under these particular conditions.

ZUSAMMENFASSUNG:

An der durch Kristallisation aus einer Lösung bei Zimmertemperatur erhaltenen Modifikation 3 von isotaktischem Polybuten-1 wurden bei verschiedenen Temperaturen dilatometrische und röntgenographische Untersuchungen durchgeführt. Bei hoher Kristallinität liegt der Wert des spezifischen Volumens zwischen den Werten der Modifikationen 1 und 2. Bei schnellem Aufheizen der Proben kann man bei etwa 102°C. ein Aufschmelzen beobachten, während bei genügend kleiner Aufheizgeschwindigkeit vor dem Schmelzen im festen Zustand eine Umwandlung in die Modifikation 1 stattfindet. Die so erhaltene Modifikation 1 schmilzt überraschend niedrig bei 109°C., wahrscheinlich wegen eines „morphologischen“ Erinnerungsvermögens. Bereits während des Schmelzens der Modifikation 3 — oder der aus der Modifikation 3 entstandenen Modifikation 1 — findet gewöhnlich eine Kristallisation der entstehenden flüssigen Phase statt. Man erhält so die Modifikation 2, welche die unter diesen besonderen Bedingungen am höchsten schmelzende polymorphe Form dieses Polymeren darstellt.

Introduction

In a previous paper¹⁾ we dealt with a thermodynamic study of the three known polymorphic modifications of the isotactic polybutene-1. In particular, the preparation and properties of modification 3 have been

described there. This polymorph was found some time ago in our laboratory and was mentioned later in a paper of other authors²⁾, in which a first X-ray diffraction diagram has been reported.

In the first paper¹⁾, we prepared modification 3 by crystallization from a supersaturated solution and gave an X-ray diagram; from a study of the melting in the presence of diluents, we calculated a melting temperature of 106.5°C ., a fusion enthalpy of 1550 ± 150 cal./unit and consequently a fusion entropy of 4.1 ± 0.3 cal./unit $^{\circ}\text{K}$. Quick dilatometric tests that, however, cannot be considered definitive on account of the difficulty in the preparation of the polymer sample in a suitable form gave an experimental melting temperature of *ca.* 103°C .

Recently, other authors³⁾ have pointed out by DTA and X-ray measurements that heating of modification 3 in a temperature interval between 94 and 96°C . would lead to the formation of modification 2 *via* a transformation which the same authors suggested to be of the solid-liquid-solid or solid-solid type.

In the present paper the nature of the transformations which modification 3 may undergo when heated is discussed on the basis of our own observations; actually, the matter appears to be more complex than considered in ref.³⁾.

Experimental

The measurements were carried out with the same polymer sample as in ref.¹⁾.

a) Preparation of modification 3

For the preparation of polymer specimens in modification 3, we proceeded in the following way which proved¹⁾ to supply a polymorph completely free from modification 1 and modification 2.

A 5% solution of polymer in decalin, obtained by heating at 100°C ., was filtered when hot and supersaturated by cooling at room temperature. After a few days the polymer, separated by crystallization, was carefully washed with toluene and then with methanol, and finally dried in vacuum. In the cases in which it was not advisable to work with powders (e.g., for dilatometric measurements) the polymer powder was cold pressed to laminae not totally coherent, but sufficiently consistent for easy handling. It was ascertained that pressing did not modify the polymorphic state of the specimen.

b) Measurements

Dilatometric measurements were carried out with capillary dilatometers, according to the technique already described⁴⁾. X-ray diffraction was measured with an X-ray spectrometer and a GEIGER counter of the North American PHILIPS Co. Inc. The spectra were obtained by Ni-filtered Cu-K α radiation, from very fine powder samples or polymer laminae prepared as described above.

For measurements at different temperatures we constructed a sample carrier, the constant temperature of which was secured by circulation of a thermostatic liquid.

Results

In Fig. 1, three dilatometric curves are given, obtained from three runs with a single specimen. The specimen of modification 3 was introduced in the dilatometer and with heating steps of $3^{\circ}\text{C.}/15\text{ min.}$ curve A was obtained. With its first branch this curve indicates a melting of modification 3 at *ca.* 102°C. ; with a second branch the formation of a certain quantity of a second polymorph (melting at $117\text{--}118^{\circ}\text{C.}$) can be seen which we shall show to be modification 2.

The melted polymer was then crystallized at 100°C. as modification 2, and this gave curve B by the same heating procedure. We re-crystallized the polymer at 100°C. and then kept it at room temperature for a few days in order to obtain its transformation to modification 1; we obtained curve C, again by the same heating procedure.

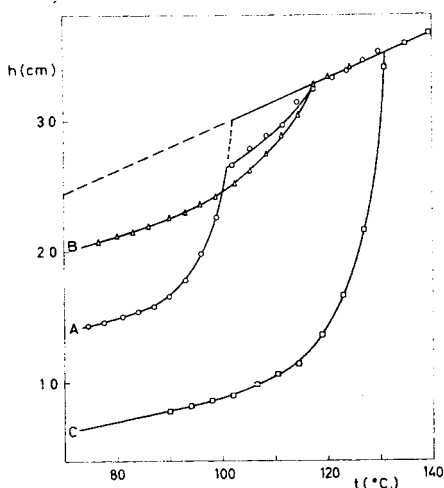


Fig. 1

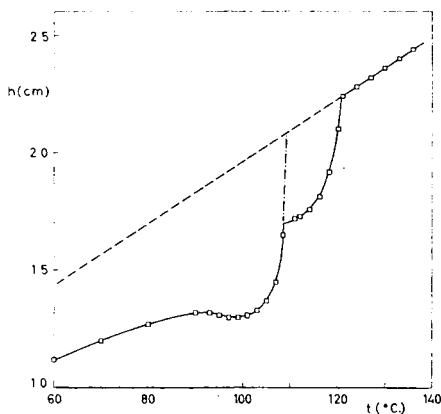


Fig. 2

Fig. 1. Comparison between the dilatometric behaviour of the 3 polymorphs of isotactic polybutene-1 (3 heating cycles of 1 sample, as described in the text; heating steps of $3^{\circ}\text{C.}/15\text{ min.}$). Curve A: modification 3; curve B: modification 2; curve C: modification 1

Fig. 2. Dilatometric curve of a sample, originally modification 3, heated slowly to 111°C. (1 reading/12 hrs.) and then rapidly to 140°C. ($2^{\circ}\text{C.}/15\text{ min.}$)

Although certain for modifications 1 and 2, the accuracy of these specific volume data is rather uncertain for modification 3. Actually, it is rather difficult to fill dilatometers with modification 3, in a more or less

subdivided state without creating empty spaces which are filled up by mercury at the first melting only; hence, on the ordinates of Fig. 1 we indicated the level of the mercury column in the capillary instead of the values of specific volume.

However, from the data of Fig. 1 we can deduce that, at high degrees of crystallinity, the specific volume of modification 3 is intermediate between that of modification 2 and 1 and, furthermore, that modification 3 melts at a temperature below that of modification 2¹⁾.

In Fig. 2 we show the results of a second dilatometric test, which was started with a specimen of modification 3 at a lower heating rate. Between 60 and 111°C. the Hg-levels in the dilatometer were read *ca.* every 12 hrs.; beyond 111°C. the readings were effected at each heating step of 2°C./15 min.

We notice that the slow heating allows modification 3 to undergo a transformation that leads to a lowering of the specific volume, apparently between 80 and 100°C. At about 108°C. there is a break, which might indicate the melting of a polymorph (probably at about 109°C.) and the persistence of a second polymorph, melting just above 120°C.

In order to clarify this complex phenomenology, X-ray counter diagrams were recorded at different temperatures of samples originally in modification 3, by applying a suitable heating schedule.

It turned out that, by a relatively fast heating as in the test of Fig. 1, modification 3 melted and a partial crystallization of modification 2 took place from the melt, whereas by a slow heating as in the test of Fig. 2,

Table 1. Positions and intensities of the main X-ray reflections of the polymorphous modifications of isotactic polybutene-1

Polymorphous modification	Diffraction angle 2θ (°)	Intensity
1	10.1	strong
	17.4	medium
	20.5	very strong
2	11.7	strong
	16.7	weak
	18.2	very strong
3	12.2	strong
	14.2	weak
	17.2	strong
	18.6	medium

modification 3 was transformed to modification 1 before melting and, as above, some crystallization of modification 2 took place from the liquid phase available.

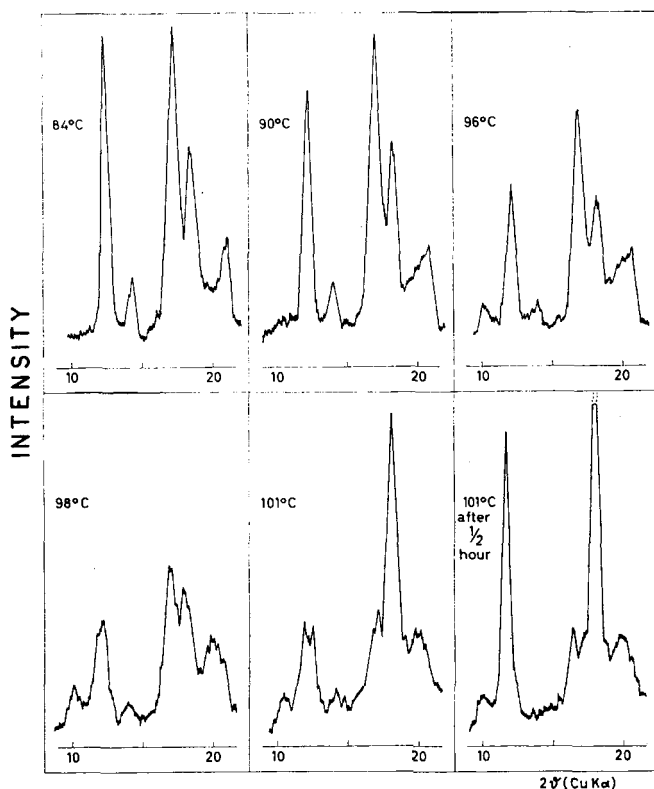


Fig. 3. X-ray diagrams recorded during a rapid heating of a sample of modification 3 (details in the text)

In order to facilitate the understanding of the X-ray diagrams, we have indicated in Table 1 the positions of the most significant peaks of the 3 pure modifications.

Some of the diagrams recorded during a rapid heating of a sample in modification 3 are reported in Fig. 3. The heating steps were $3^{\circ}\text{C.}/20\text{ min.}$, *i.e.*, similar to those of the dilatometric run in Fig. 1, curve A. It may be noted that the sample in modification 3 (brought to 84°C. from room temperature), melts during the subsequent heating; in the course of the first registration at 101°C. , the crystallization of modification 2 starts

from the nearly complete melt and becomes substantial in about 30 min. (second diagram at 101°C.).

On the other hand, in Fig. 4 we have reported some of the X-ray diagrams obtained during a slow heating to 102°C. of the polymer in modification 3, *i.e.*, by a heating procedure comparable with that of the curve of Fig. 2. For convenience, diagrams were recorded at room temperature after each heating step of *ca.* 2°C./12 hrs., cooling the sample only for the time strictly required for the recording. This time was sufficiently short to prevent noticeable transformation of modification 2, if present, to modification 1 (in other tests⁵) the minimum halftime for the transformation of the same polymer was found of the order of 20 hrs. at 25°C.).

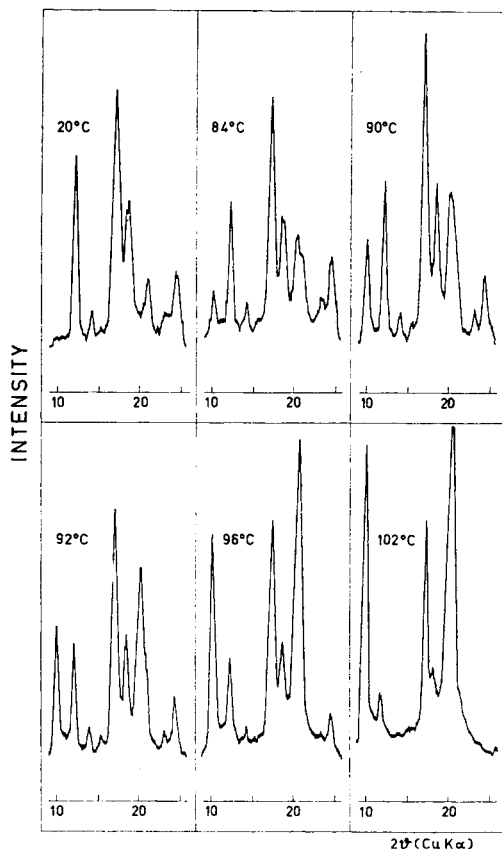


Fig. 4. X-ray diagrams showing the transformation of modification 3 to modification 1 by slow heating to 102°C. (for details see text)

From Fig. 4 it may be observed that the sample (in modification 3 at room temperature) already contains some modification 1 at the end of the first heating step at 84°C. (e.g., the peak at $2\theta = 10.1^\circ$). As the slow heating proceeds, the intensity of the peaks of modification 3 decreases slowly, while those of modification 1 become stronger. At the end of the last heating step, at 102°C., the diagram is practically that of pure modification 1. No peak of modification 2 was visible at any stage of the experiment.

These results explain the lowering of the specific volume of Fig. 2 in the corresponding interval of temperature: according to Fig. 1 modification 3 has a lower density than modification 1. The subsequent shape of the curve of Fig. 2 shows, however, the melting of a polymorph at *ca.* 109°C. From the results of Fig. 4, such a fusion must be attributed to modification 1 originated by modification 3, even if a terminal temperature of 109°C. seems to be too low.

In order to check this point and to clarify the meaning of the second branch of the curve of Fig. 2, we made a third series of X-ray diagrams, recorded at each aging temperature, and in a wider range of temperatures. The heating was effected with the following steps: 2°C./30 min. from 75 to 95°C.; 1°C./30 min. to 104°C.; final quick heating to 115°C.

It was thus noticed that, between 75 and 100°C., a gradual and partial transformation of modification 3 to modification 1 takes place; then, up to 104°C., a melting of the remaining modification 3 occurs; at the same time the characteristic peaks of modification 2 appear; at 115°C., finally, only modification 2 is present.

All this confirms that the first break in the dilatometric curve of Fig. 2 corresponds to the melting of modification 1, whereas the second break of the same curve corresponds to the melting of modification 2. Although this modification 2 has its normal melting temperature in this case, it does exist at temperatures higher than the melting temperature of modification 1 formed by transformation of modification 3.

It is to be noted that in Fig. 2 modification 2 melts a few degrees higher than in Fig. 1. This should depend upon a different crystallization temperature⁶⁾ in the two cases; actually, in Fig. 1 it is formed at about 100°C., whereas in Fig. 2 it is formed at a higher temperature, in the melting range of modification 1 instead of that of modification 3. This confirms that the formation of modification 2 takes place by crystallization, as soon as a sufficient quantity of amorphous polymer becomes available as product of the melting of the other two polymorphs.

Kinetic data of crystallization of modification 2 from the melt⁵⁾ confirm that, between 100 and 110°C., the times required for crystallization are shorter than those during which liquid phase was available during the melting of modification 3 or of modification 1. In particular at about 100°C. crystallization takes place in a few tens of minutes⁵⁾.

For the same reason, the absence of modification 2 in the diagrams of Fig. 4 proves that modification 1 is formed directly from modification 3, by a solid-solid transformation. In fact, the absence of modification 2 in the diagrams recorded at room temperature demonstrates the unavailability of liquid phase during the transformation. On the other hand, modification 1 cannot be thought as being formed from a melt; furthermore, it has been ascertained that modification 2 practically cannot be transformed into modification 1 at 95–110°C., this transformation being kinetically feasible only at much lower temperatures⁵⁾. All this enables us to exclude also that modification 2 might be formed as intermediate phase during the transformation of modification 3 to modification 1.

As for the relatively low stability of modification 1 stemming from modification 3, it is probable that, due to a memory effect of the morphological state of modification 3, crystallized at low temperature, a defective morphology causes a relatively low melting temperature of modification 1. Actually, transformation of modification 2, crystallized at relatively high temperatures (90–100°C.) yields samples typical of modification 1. In this case, too, a memory effect exists⁶⁾, and modification 1 can exhibit a high stability and melting temperatures as high as 134–136°C.^{1, 6)}.

Conclusions

We can draw the following conclusions:

a) Modification 3 of isotactic polybutene-1 known as thermodynamically less stable than modification 1¹⁾ can be transformed to modification 1 and such a transformation is of the solid-solid type.

b) Modification 3 has a specific volume intermediate between modification 1 and modification 2, and, when prepared by crystallization from solution at room temperature, and heated with a sufficient rapidity, it has a melting temperature of *ca.* 102°C.

c) Modification 3, when heated at a rate sufficiently low is completely transformed before melting to modification 1.

d) Modification 1 obtained by transformation of modification 3 (between 80 and 102°C.) melts at about 109°C. This melting temperature is remarkably below that of modification 1 (reported and prepared so far

by transformation of modification 2); surprisingly it is even below that normally observed for modification 2. This last stability inversion can probably be attributed to a morphological state of modification 1, originated by modification 3, particularly defective if compared with that of modification 1 prepared as usual from modification 2.

e) During the transformation of modification 3 to modification 1, no intermediate formation of modification 2 takes place.

f) Conversely, modification 2 may be formed (and it usually is formed) from the melt which becomes available during the fusion of modification 3 or modification 1 (the latter derived from modification 3); this depends, of course, on the kinetic possibilities for crystallization of modification 2.

¹⁾ F. DANUSSO and G. GIANOTTI, *Makromolekulare Chem.* **61** (1963) 139.

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⁶⁾ F. DANUSSO and G. GIANOTTI, *Makromolekulare Chem.* **80** (1964) 1.