

STUDIES ON THE PORE FORMATION MECHANISM OF β -CRYSTALLINE POLYPROPYLENE UNDER STRETCHING*

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Abstract The pore formation mechanism of β -crystalline polypropylene under stretching was investigated. The porosity of the samples increases rapidly with stretching, having a maximum at draw ratios around 2 and then decreases monotonically. An abrupt formation process of initial micropores at very low draw ratios was evidenced by *in situ* SAXS measurements. At the same time the phase transition from β -crystal to α -crystal proceeds slowly in the whole deformation process up to large draw ratios around 5. Comparative studies of α - and β -crystalline polypropylene samples before stretching indicate that in addition to difference in crystal forms the α - and β -crystalline polypropylene samples exhibit quite different morphological features. There are a lot of interfaces in β -crystalline polypropylene samples, which may have a lower density value and can be easily etched by argon ions and penetrated by small molecules. It was concluded from these experimental facts that the pore formation and crystal transition are two independent phenomena during the deformation of β -crystalline polypropylene samples, and phase transition from β -crystal to α -crystal could hardly be the origin of pore formation. A defect initiation mechanism was proposed to understand the pore formation behavior of β -crystalline polypropylenes.

Keywords Pore formation under stretching, β -crystalline polypropylene, Mechanism

INTRODUCTION

The polymorphism of isotactic polypropylene is well known. There are three main crystal modifications, i.e. the monoclinic α form, hexagonal β form and the triclinic γ form^[1]. It is accepted that the α form is the thermodynamically stable one, and the commercial polypropylene grades have crystallized mostly in the α form under the usual industrial thermal conditions. The γ form can be obtained in degraded low molecular weight polypropylene or in samples crystallized under high pressure. A small amount of β form is found to accompany the α form under conventional thermal conditions, especially at high supercooling^[2, 3]. High content of β form can be obtained under special crystallization conditions^[4, 5] or by using selective β -crystal nucleating agents^[6–9].

It has been found that the β -crystalline polypropylene may exhibit some unique mechanical properties as compared with the α -crystalline polypropylene. One of its notable features is the ease of stress whitening. It starts just beyond the yield point and may occur even at high temperatures up to 120 °C or more. While the α -crystalline polypropylene is not so easily stress whitened even at lower temperatures. These phenomena inspired us to investigate the preparation of microporous films by stretching polypropylene of high β -crystal content. A biaxial stretching technology for preparing polypropylene microporous films has been developed successfully on the bases of these studies^[10].

The stretching method is economic and technologically convenient as compared to the conventional solution method for preparing microporous films and membranes, because no solvents are required. This is especially

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important for polymers such as polypropylene, which do not dissolve in conventional solvents. The main advantage of the biaxial stretching technology is the good uniformity of its product films in structure and properties along different directions within the film plane. These films may have high porosity and almost circular pore shape, the sub-micrometer pore size and narrow size distribution and the combination of high permeability and good mechanical properties^[11].

Studies on the pore formation mechanism of β -crystalline polypropylene under stretching are of great importance not only for controlling the structure and properties of these novel microporous films, but also for developing new methods and technologies for preparing polymeric microporous films in general. A characteristic mechanism suggested by Shi and his coworkers for the formation of micropores in β -crystalline polypropylene under stretching is the so-called phase transition mechanism^[12]. It was supposed that micropores may originate from a volume contraction during $\beta \rightarrow \alpha$ or $\beta \rightarrow$ smectic crystal transformation in β -crystalline polypropylenes under stretching and enlarge with increasing draw ratio, since the density of β -crystals (0.920 g/cm^3) is lower than that of the α -crystals (0.936 g/cm^3). Similarly, Chu *et al.*^[13] proposed that the pore formation is caused by the volume contraction due to the $\beta \rightarrow \alpha$ crystal transition in the presence of stable β -crystals. The phase transformation mechanism is logically reasonable, because the unique pore formation phenomenon of β -crystalline polypropylene is ascribed to its special crystalline structure and structure changes under stretching. However, no direct evidence of the relation between pore formation and phase transition was given in these studies. In another paper Chu *et al.*^[14] has postulated a mosaic model of β -crystalline polypropylene for explaining the pore formation under stretching. On drawing the initial micropores are formed in the weak boundaries between lamellar blocks. The mosaic model seems quite common for crystalline polymers and does not reflect the specialty of the pore formation behavior of β -crystalline polypropylene under stretching. In this paper the pore formation mechanism of β -crystalline polypropylene is analyzed on the basis of systematic studies of the structure and properties of α - and β -crystalline polypropylenes and also their variations under stretching.

EXPERIMENTAL

The original un-stretched polypropylene films of thickness around 0.3 mm were prepared by the extrusion method. The melting index of the polypropylene used was in the range of 1.8–2.0 g/10 min (230°C). Films with high content of β -crystals are obtained by extruding polypropylene granule with nucleating agents.

An X-ray diffraction method was used to characterize the relative amount of the β -crystals, and a K parameter was defined by the formula^[1]:

$$K = H(\beta 300) / [H(\beta 300) + H(\alpha 110) + H(\alpha 040) + H(\alpha 130)] \quad (1)$$

where the H 's are the heights of four main peaks in the 2θ range of 10 – 20° . $\beta 300$ is the strongest peak for β -crystals, and the other three are for α modifications. A Rigaku rotating anode X-ray diffractometer D/max-DB was used for these measurements with the Ni-filtered $\text{CuK}\alpha$ radiation. X-ray diffraction method is not convenient for measurements of samples after stretching. The diffraction has azimuthal dependence due to the orientation of crystals. A DSC method was used to measure the K value of oriented samples in this work. It is supposed that

$$K \propto K' \equiv \Delta H_\beta / (\Delta H_\alpha + \Delta H_\beta) \quad (2)$$

where ΔH_α and ΔH_β are the melting enthalpy of α - and β -crystals of samples obtained in DSC measurements. The relationship between K and K' can be calibrated by measurements for unoriented samples of different β -crystal content.

A two-axis tester made by Toyoseiki Co. Ltd. was used to prepare biaxially stretched specimens of different draw ratios. The samples were stretched simultaneously in two axes with the same linear draw ratio. Uniaxially stretched specimens were obtained by using testers Instron 8501 or Instron 1122.

The porosity of the films was defined as their volume content of pores and was determined according to the following equation:

$$\text{Porosity} = V_p / V_f = (V_f - V_r) / V_f \quad (3)$$

where V_f is the gross volume of the film specimen, which consists of two parts, the volume occupied by the polymer resin V_r and the volume occupied by the pores V_p . Regular round film specimens were used for porosity determination. V_f was obtained from direct size measurement of the specimens. V_r was derived from the weight of the specimen and the average density of the polymer regions in the specimen, the latter can be determined according to the crystallinity of the specimen.

The permeation properties of the films were characterized by the permeation coefficient P for gases or liquids:

$$P = V_e d / p A t \quad (4)$$

where V_e is the volume of the effluent permeated through a film of area A and thickness d in a time period t under pressure difference p across the film. The measurement procedure has been described elsewhere^[15], and nitrogen was used as the working gas.

A Hitachi S450 scanning electron microscope and a Hitachi H800 transmission electron microscope were used for morphological studies. The evolution of pore structure and morphology of specimens under stretching was *in-situ* monitored by small angle X-ray scattering using the synchrotron radiation facilities at 4C2 beamline of the Pohang Accelerator Laboratory, Pohang, Korea. The sample was stretched in the direction perpendicular to the incident beam at a rate of 0.2 mm/min. Data were taken every 30 s by a one-dimensional detector. Data collection time was 5 s. The scattering intensity I was measured as function of scattering angle, and from which the scattering invariant Q was determined as follows:

$$Q = 4 \int_0^\infty I(q) q^2 dq \quad (5)$$

$$q = (4\pi \sin \theta) / \lambda \quad (6)$$

where q is the scattering vector, 2θ is the scattering angle and λ is the wavelength of the X-ray used. For a polymer/pore system the scattering invariant Q can be used to characterize the pore content in a first approximation.

Dielectric properties of the specimens were measured isothermally by using a TA Instruments type DEA-2970 dielectric analyzer in a frequency range of 10^{-2} – 10^5 Hz.

RESULTS AND DISCUSSION

The β -crystal content of the samples decreases with the draw ratio in stretching processes. Figure 1 shows the dependence of the K value on the draw ratio for samples under biaxial stretching at 115°C. The K value decreases slowly throughout the whole process, approaching zero at a draw ratio of about 5.0. Similar results were obtained for samples under uniaxial stretching (Fig. 2). The rate of decrease is slightly increased on raising the stretching temperature. It was found that annealing of original samples at 115°C for 10 min did not reduce the β -crystal content of the samples. So the observed results of crystal phase transition shown in Figs. 1 and 2 are deformation induced.

Figure 3 gives the porosity change of samples under biaxial stretching. The porosity increases quickly with drawing at the beginning, having a maximum of around 40% in the range of draw ratio $R = 1.8$ – 2.5 . After that the porosity decreases monotonically. In the case of uniaxial stretching the porosity was lower than that observed under biaxial stretching, and the maximum peak became broader. The permeability behavior is tightly related with the pore formation in the samples and can be used to characterize their porosity. The variation of permeation coefficient to nitrogen for samples under biaxial stretching is given in Fig. 4. The samples become quite permeable at the very beginning of the draw process. The permeation coefficient reaches a maximum at $R \sim 1.8$. The permeability results are consistent with those from porosity measurements. Both the porosity and permeability studies indicate that the behavior at very low draw ratios should be very important for understanding the pore formation.

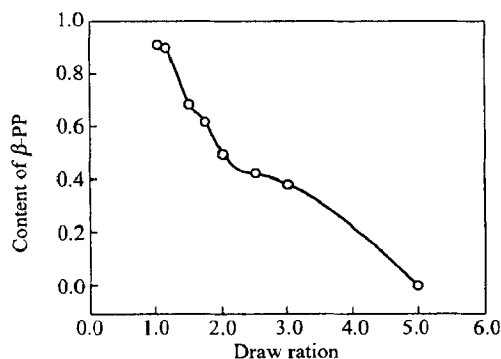


Fig. 1 Dependence of β -crystal content on draw ratio for samples under simultaneous biaxial stretching at 115°C

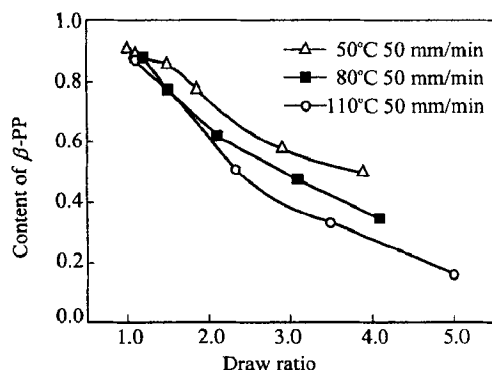


Fig. 2 Dependence of β -crystal content on draw ratio for samples under uniaxial stretching at different temperatures

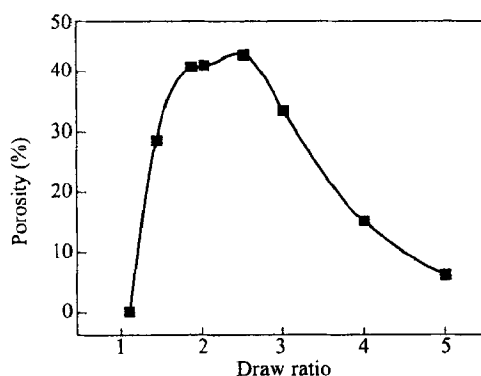


Fig. 3 Dependence of porosity on draw ratio for samples under simultaneous biaxial stretching at 115°C

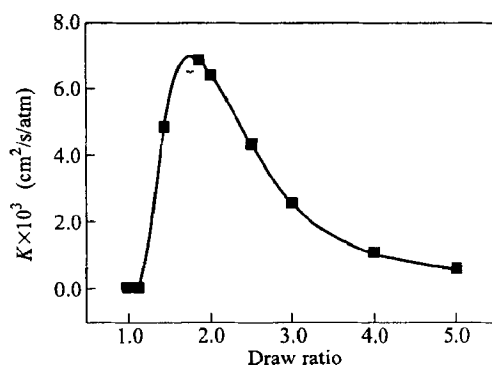


Fig. 4 The plot of permeation coefficient versus draw ratio for samples under simultaneous biaxial stretching at 115°C

In order to get information about the formation of the initial micropores in samples at small draw ratios *in situ* SAXS measurements were carried out for monitoring the structure changes of an uniaxially stretched sample by using the synchrotron radiation apparatus. In a first approximation our samples can be considered as a two-phase system composed of a polymer phase and a pore phase. For this model the scattering invariant can be expressed as:

$$Q \propto \varphi_1(1 - \varphi_1)\Delta\rho^2 \quad (7)$$

where φ_1 is the volume content of the pore phase, and $\Delta\rho$ is the difference of the two constituent phases in electron density. It implies that in the range of small φ_1 ($\varphi_1 < 0.5$) Q is a parameter increasing with the increase of the pore content of the sample. Figure 5 shows the dependence of the scattering invariant Q on the draw ratio for a sample under uniaxial stretching. The Q value keeps almost unchanged in the range of small draw ratios. It increases abruptly when $R \sim 1.05$. Then a steady increase of Q values follows. These phenomena may strongly suggest the existence of a clear formation process of initial micropores at small drawings and their enlargement in further deformation.

It is clear from comparison of the experimental results given above that the features of pore formation are not consistent with those of the phase transition during a stretching process. The porosity increases rapidly with draw ratio in the beginning and decreases after a maximum at a draw ratio around 2, while the phase transition proceeds slowly and monotonically. At a draw ratio of 1.05, at which the initial micropores are formed abruptly,

the crystal phase transition is almost not detectable. It seems that the crystal phase transition and the pore formation are two independent phenomena occurring in the stretching process of β -crystalline polypropylenes, and phase transition from β -crystal to α -crystal could hardly be the origin of pore formation.

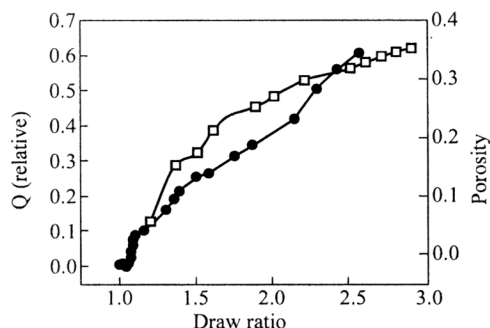


Fig. 5 Dependence of scattering invariant Q (—●—) on draw ratio determined by *in situ* SAXS measurements for a sample under uniaxial stretching at room temperature

It is reasonable to expect that the special pore formation behavior of β -crystalline polypropylenes should be related with their structural features before stretching, especially with those features that are unique for β -crystalline polypropylenes, but not observed for α -crystalline polypropylenes. A comprehensive comparative studies of α - and β -crystalline polypropylenes may give insight into the mechanism for pore formation in β -crystalline polypropylenes under stretching. Figure 6 shows the surface morphology of α - and β -crystalline polypropylenes. It was found that the surface of α -crystalline polypropylenes was plain and uniform, while that of the β -crystalline polypropylene was quite crude, and many holes can be observed. After slight etching by argon ion a very clear crystallite structure of submicron size was observed for β -crystalline polypropylene samples (Fig. 6b). At the same time even the effect of strong etching on α -crystalline polypropylenes was very weak (Fig. 6d). It means that the amorphous phase between crystallites and/or the crystalline/amorphous interface in β -crystalline polypropylenes are very weak and can be destroyed easily.

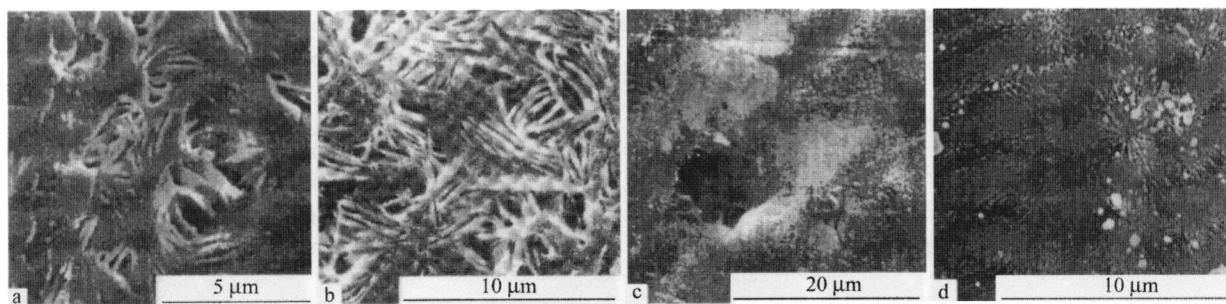


Fig. 6 SEM studies of surfaces of α - and β -crystalline polypropylenes, a) β -crystalline polypropylene, b) β -crystalline polypropylene etched by argon ion for 20 min (0.7 w), c) α -crystalline polypropylene and d) α -crystalline polypropylene etched by argon ion for 12 h (1.2 w)

To acquire more information about these structure defects the samples were also studied by density analysis. The measured density values of α - and β -crystalline polypropylenes are compared with those calculated according to the crystalline/amorphous two-phase model (Table 1). The density values of amorphous and α - and β -crystalline phases used for calculation are 0.850 g/cm³, 0.936 g/cm³ and 0.920 g/cm³^[16], respectively. The crystallinity of the samples was determined by DSC measurements. The results indicate that the density of the α -crystalline polypropylene can be explained by the two-phase model within experimental error. However, the

measured density of the β -crystalline polypropylene is much lower than the calculated one; the difference exceeds the range of experimental error in density measurements, which is usually less than 1.0%. These results imply the existence of many loose amorphous domains and/or interfacial regions in β -crystalline polypropylenes.

The α - and β -crystalline polypropylenes were also immersed in aqueous solutions of sodium ethoxide (NaOC_2H_5) for adsorption tests. After immersion the solutions on the surface of the samples were wiped away before dielectric measurements. It is supposed that the sodium ethoxide molecules may penetrate into the loose amorphous domains and interfacial regions of the β -crystalline polypropylenes, and the dielectric method will be a very sensitive technique for detecting the penetration of sodium ethoxide molecules due to their high polarity. Figure 7 gives the results for α -crystalline polypropylenes at room temperature. Both the dielectric permittivity and loss factor remain unchanged after immersion in the solution of sodium ethoxide. It means that the α -crystalline polypropylene samples are not penetrable for sodium ethoxide molecules under the experimental conditions. The results for β -crystalline polypropylenes are given in Fig. 8. After immersion in sodium ethoxide solutions the dielectric permittivity increases significantly from about 1.61 to 1.86. It clearly indicates the penetration of sodium ethoxide molecules into the β -crystalline polypropylene samples. However, at the same time no detectable change in dielectric loss factor is observed. These results may imply that there are many interfaces along which the sodium ethoxide molecules can easily penetrate into the β -crystalline polypropylenes.

Table 1. Density comparison

Sample	D_C (g/cm ³)	D_M (g/cm ³)	$(D_C - D_M)/D_C$
α PP	0.8810	0.8789	0.238%
β PP	0.8887	0.8534	3.97%

D_C : Density calculated according to crystallinity

D_M : Density measured

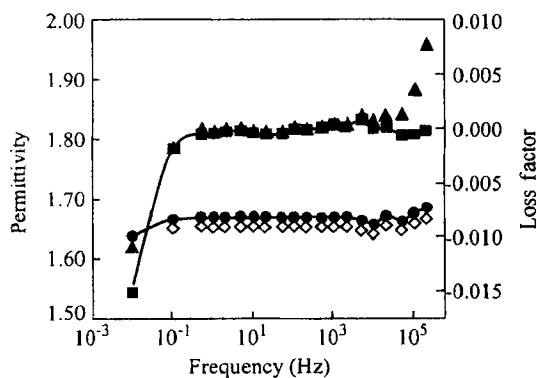


Fig. 7 Dielectric data of α -crystalline polypropylenes before and after immersing in aqueous solutions of sodium ethoxide

▲ Loss factor α -pp after immersion; ■ Loss factor α -pp before immersion; ◇ Permittivity α -pp after immersion; ● Permittivity α -pp before immersion

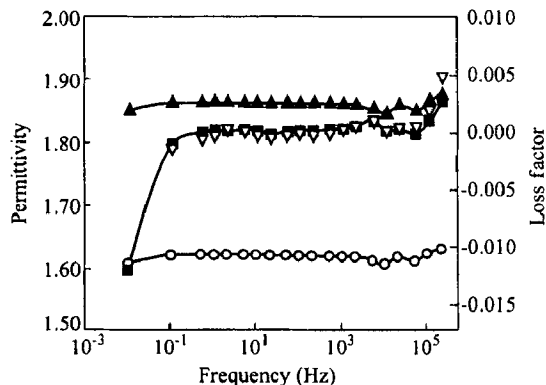


Fig. 8 Dielectric data of β -crystalline polypropylenes before and after immersing in aqueous solutions of sodium ethoxide

▲ Permittivity β -pp after immersion; ■ Loss factor β -pp after immersion; ◇ Permittivity β -pp before immersion; ● Loss factor β -pp before immersion

It is clear now that in addition to the difference in crystalline forms the α - and β -crystalline polypropylenes exhibit quite different morphological features. There are a lot of weak areas or interfaces in β -crystalline polypropylenes, which may have a lower density and can be easily etched by argon ions and penetrated by small molecules. These are special structure defects in polypropylenes formed in the crystallization process of β -crystals. According to these ideas concerning the special structure features of the β -crystalline polypropylenes a defect initiation mechanism for the pore formation under stretching can be proposed. The initial micropores are formed or created at the defect points under stress, because they are much weaker than their surroundings.

A formation process of micropores in β -crystalline polypropylenes under stretching can be described on the basis of the defect initiation mechanism. The initial micropores are formed in the very beginning of the stretching process until a specific low stress value is reached which is necessary for “breaking” the defects. The abrupt jumping of scattering invariant at a very low draw ratio, shown in Fig. 5, must be evidence of this initial stage of pore formation in β -crystalline polypropylenes. Figure 9 gives TEM photographs for carbon replica of a sample uniaxially stretched to a draw ratio of 1.1. Micropores with size of tens nanometers are observed. It seems that these micropores are initiated between crystallites. The initial micropores enlarge with further deformation and connect with each other, which may result in the formation of a microporous network within the film. A further increase of porosity and gas permeability can be observed at this stage. The surface morphology of β -crystalline polypropylene samples biaxially stretched to different draw ratios is shown in Fig. 10. The first two pictures given in Fig. 10 show the enlargement and combining stage of the micropores. Parallel to the pore formation process the polymeric matrix phase undergoes a deformation process similar to that for a conventional crystalline polymer. A structure rearrangement results in the appearance of the fibrillar structure. These microfibrils tend to take on a tight and parallel arrangement with each other. This process may press the pores and reduce their size, finally leading to the healing or closing of the micropores (Fig. 10c and 10d). In this stage the porosity and gas permeability decrease and level off at high draw ratios.

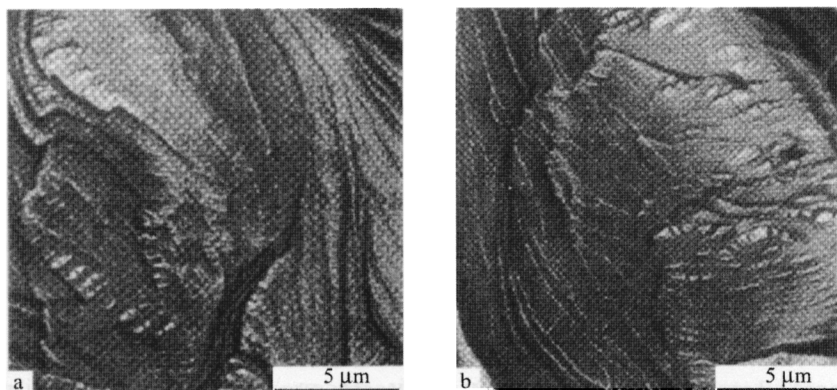


Fig. 9 TEM photographs for carbon replica of a sample uniaxially stretched to a draw ratio of 1.1

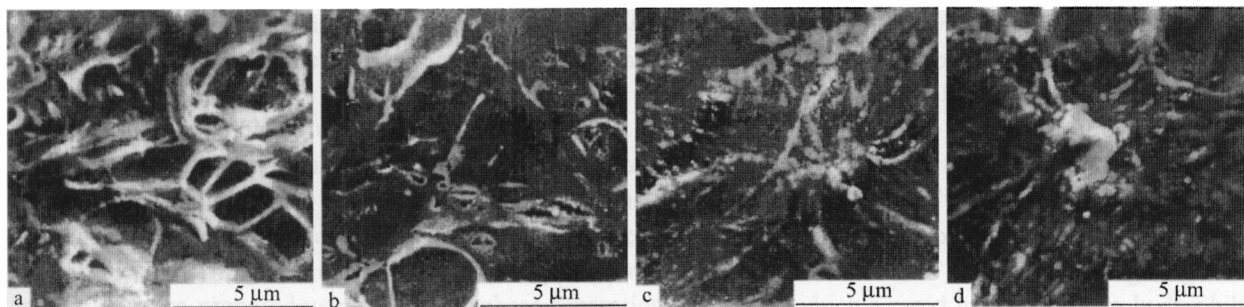


Fig. 10 Surface morphology of β -crystalline polypropylene samples biaxially stretched to different draw ratios a) 1.36, b) 1.85, c) 4.0 and d) 5.0

In conclusion there are several points which should be mentioned. The experimental results have indicated that the pore formation in β -crystalline polypropylenes under stretching could hardly be related with the conversion of different crystalline phases, but may suggest a defect initiation mechanism of pore formation. In this sense the pore formation phenomenon of β -crystalline polypropylenes under stretching is nothing new, having a common mechanism with the pore formation in Celgard films and other mechanical phenomena of

polymers, such as the stress whitening and initiation of fractures, because they all are defect induced. The special feature of the pore formation phenomenon in β -crystalline polypropylenes is that it shows a new way of creating and controlling a useful structure with rather uniformly distributed defects in polymer samples. It was well known that defects may appear in polymer composites with fillers, in polymer blends or after crystallization in a special stretching process. Now we know that this kind of structure may simply result from crystallization of a specific crystal modification.

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