

Selective Etching of Polyolefines. I. Isotactic Polypropylene

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Synopsis

The kinetics of isothermal etching of isotactic polypropylene samples having different thermal treatment was studied using a mixture of concentrated sulfuric or 85% *o*-phosphoric acid with various amount of potassium permanganate. The course of etching was confronted with morphological features of the etched surface. It was shown that on a macroscopical scale the etching proceeds in an indiscriminate way, whereas on a scale of the basic structural elements—lamellae—it proceeds through stages of selective etching. Selective etching of isotactic polypropylene using mentioned etchants was successfully applied for morphology investigation of various kinds of surfaces.

INTRODUCTION

For electron-microscopical examination of morphological features of bulk polymer samples following techniques may be used: examination of ultrathin sections, free, cut, fracture, or mold surfaces. Ultramicrotomy of polymers is not easy, and the transformation of the native morphology during sectioning cannot be fully excluded. Moreover, the ultrathin slices are of low contrast making further treatments for its enhancing necessary which might be another source of artefacts. The examination of free surfaces is simple and often used. Its disadvantage is that the morphology of the free surface may not be the same as it is in the interior of the sample. The surface is often modified by oxidation or by exuded low molecular material. Even at cryogenic temperatures, polymer fracture is not entirely brittle, and one can observe traces of microplastic deformation on fracture surfaces. Therefore, it is desirable to remove the fracture surface or deformed layer in case of cut or mould surfaces.

Several techniques based on different physical and chemical properties of ordered and disordered domains may be used to remove the surface layer and to improve the morphological contrast of crystalline polymers.¹⁻³ In principle, selective dissolving and selective etching may be considered. The former could be successful only if there is a big difference in solubility of ordered and disordered domains. In most crystalline polymers both kinds of domains are molecularly connected, and the selective dissolving usually is not successful. In practice, it could be applied only for dissolving the exuded low molecular material.

The methods of selective etching could be divided into etching by glow discharge or ion beam and chemical etching. The etching mechanism by

glow discharge or ion beam is not yet understood in greater detail and there are no conclusive indications about the selectivity of this process.⁴ Our own experiments in this field with polyolefines were unsuccessful. Chemical etching consists of selective oxidation. Many chemical etchants were tried, e.g., sulfuric acid,⁵ solutions of CrO_3 in aqueous H_2SO_4 ,⁶ fuming nitric acid,⁷ chromic acid, aqua regia,⁸ or ozone⁹ without showing selectivity on the resolution level of the transmission electron microscope. The only exception is the mixture of KMnO_4 with concentrated H_2SO_4 or $\text{H}_2\text{SO}_4 + o\text{-H}_3\text{PO}_4$, used by Olley et al.^{10,11} for selective etching of polyolefines. However, limited information on this procedure was presented, and therefore we decided to investigate the basic factors governing the course and selectivity of etching by this etchant. Preliminary experiments disclosed that selective etching could be achieved also with the solution of KMnO_4 in $o\text{-H}_3\text{PO}_4$, and we have also studied this system.

EXPERIMENTAL

Materials. The measurements were performed with commercial samples of isotactic polypropylene Mosten 58412 (Záluží, ČSSR) crystallized from the melt in shape of pressed sheets. Two kinds of samples were used: One was quenched from the melt (220°C) into ice water (PP-Q); the other was slowly cooled (5 h) from the melt to room temperature (PP-T). The densities of PP-Q and PP-T sample were 0.866 and 0.887 g/cm³, respectively.

The Etching Solution. For etching the solution of KMnO_4 in 96% H_2SO_4 or 85% $o\text{-H}_3\text{PO}_4$ was used. The weighted amount of fine powdered KMnO_4 was slowly added under agitation to the known volume of the acid. The solution of KMnO_4 in H_2SO_4 (Mn-S) was dark green and that in $o\text{-H}_3\text{PO}_4$ (Mn-P) was dark violet.

The Etching Procedure. The usual etching procedure was as follows. The samples with dimensions of $27 \times 19 \times 0.5$ mm were etched with fresh etching solution. First, each sample was washed 15 min in acetone, dried, weighed, and submerged in 20 cm³ of the etchant for the determined time without stirring. No important differences were found between stirred and unstirred experiments. After etching, the samples were sucked off by filter paper, washed 30 min in streaming water, rinsed 15 min in H_2O_2 to remove MnO_2 , soaked in distilled water, washed 15 min in acetone, dried over P_2O_5 *in vacuo*, and weighed.

Each point of the etching curve represents at least two independent measurements. The thickness of the etched layer l was calculated from the weight loss under assumption of uniform surface etching. Taking into account the errors in measuring the sample surface and weight, the experimental scatter of l values should be approximately at $l = 1 \pm 0.1 \mu\text{m}$ and at $l = 10 \pm 0.01 \mu\text{m}$.

Electron Microscopy. Sample morphology was studied via replication. The examined sample surface was shadowed by Pt under 30° angle and backed with a thin C-film. The replica was stripped off by poly(acrylic acid). The examination of sample morphology was done with a transmission electron microscope (Tesla BS 613).

RESULTS AND DISCUSSION

Preliminary experiments of selective etching using mixtures Mn-S and Mn-P for three polyolefine samples have brought the following results:

1. Selective etching of linear polyethylene and isotactic polypropylene could be achieved in Mn-S with KMnO_4 concentration varying in a wide range (measured range 0.1–15%). Selective etching was not observed in branched polyethylene using this mixture.

2. Using Mn-P selective etching was observed with isotactic polypropylene and linear and branched polyethylene. The concentration of KMnO_4 in the mixture could be varied in a wide range (0.1–10%).

3. Selectivity of etching does not markedly depend on temperature (–30–80°C); however, with increasing temperature the tendency to overetching and formation of artefacts grows and the mixture loses the selectivity faster.

4. Selectivity of etching is not susceptible to small variations in water content ($\pm 5\%$ in Mn-S and 0–15% in Mn-P).

5. Success in selective etching depends on the character of the etched surface and decreases in the following row: free, mold, fracture, and cut surfaces, respectively. With the exception of the cut surface, the differences are small.

6. The easy achievement of selective etching strongly decreases with increasing degree of sample orientation.

7. With samples of higher crystallinity and of more perfect structure, selective etching is easier compared to those of low crystallinity.

8. With Mn-P the etching is more uniform without excessive forming of artefacts, in contradiction to Mn-S.

9. Using the ternary mixture $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + o\text{-H}_3\text{PO}_4$ essentially does not influence the course or selectivity of etching. The resulting etching curve represents approximately an average of individual curves obtained in pertinent binary mixtures.

10. In isotactic polypropylene the stable α -modification [Fig. 8(a)] is more susceptible to overetching than the metastable β -modification [Fig. 8(b)].

To extend these results, we have quantitatively investigated the course of isothermal etching at 25°C of polyolefine samples with twofold mold surface. In this paper there are shown only the results of etching isotactic polypropylene samples PP-Q and PP-T in mixtures Mn-P and Mn-S with various KMnO_4 content. The course of etching of these samples is illustrated in Figures 1 and 2, where the thickness of the etched surface layer l is plotted against the time of etching, t . The etching curves for Mn-P and Mn-S mixtures are different. In the case of Mn-P the situation is simple. In the first stage the etching proceeds faster than at longer etching times. This seemingly agrees with the conception of selective etching, according to which the etchant attacks amorphous and defective structures at the surface first and later on the same structures deeper under the surface. However, this simple idea is not fully acceptable, as is discussed below. With the exception of the first steep part of the etching curve, the etching proceeds linearly with $t^{0.5}$, which is a definite sign of a process controlled by diffusion. In Mn-P the amount of the etched material after a certain time grows

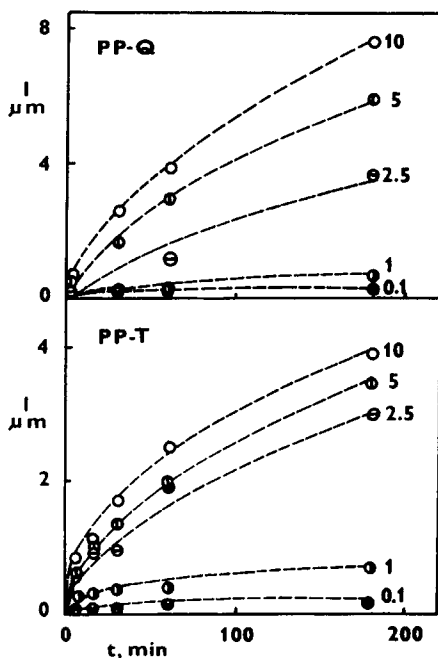


Fig. 1. Plots of the thickness of the surface layer 1 of samples PP-Q and PP-T etched off in the mixture Mn-P with various KMnO_4 content (shown in figure) at 25°C against etching time.

monotonously with increasing KMnO_4 concentration, as is clear from l_{180} values (the thickness of the layer etched within 180 min), shown in Figure 3. From the plots in Figures 1–3 it is also evident that the PP-T samples with higher crystallinity are etched more slowly than PP-Q samples.

The etching behavior of the Mn-S solution is complicated. Till to about 1% KMnO_4 the Mn-S behaves in analogy with Mn-P. At higher KMnO_4 concentration in Mn-S the shape of the etching curves is different. After a short initial period of fast etching, further etching essentially halts. In this concentration range the amount of etched material even decreases with increasing KMnO_4 content (Fig. 4). However, if we take into account the l values determined after a shorter time, e.g., 5 min, instead of l_{180} values, then the plot of l_5 values against KMnO_4 content approaches the shape determined in the Mn-P mixture (Fig. 4). It is evident that in the Mn-S solution some kind of saturation of the etching solution or passivation of the sample takes place which prohibits further etching.

Several reasons for the explanation of this effect may be considered:

1. Aging of the etchant showing itself by turning brown by precipitated MnO_2 .
2. Exhausting of active species in the concentrated etchant.
3. Formation of a mechanical barrier on the etched surface from precipitated MnO_2 or volatile etching products.
4. Formation of a surface layer of chemically transformed material resisting to additional etching.

Our measurements excluded all these assumptions. It was found that within 1 week the etching capacity of the Mn-S mixture did not change

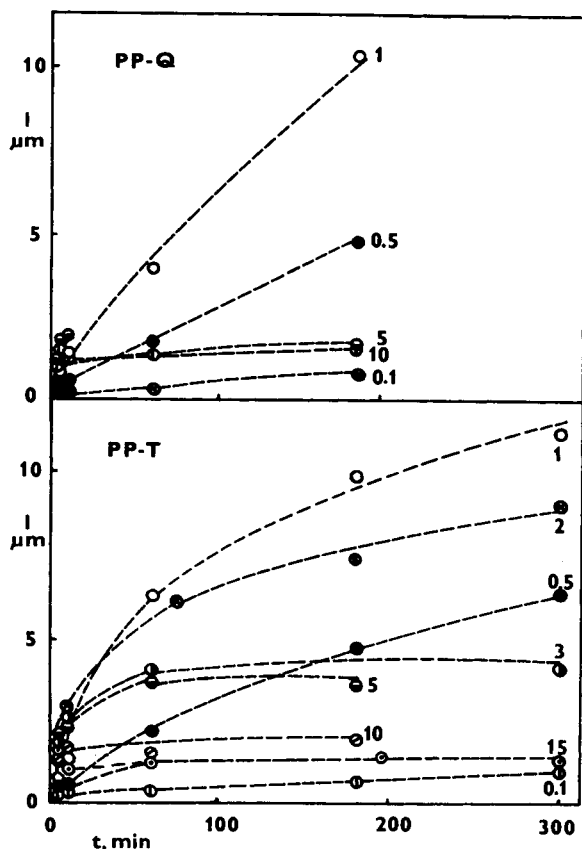


Fig. 2. Plots of the thickness of the surface layer 1 of samples PP-Q and PP-T etched off in the mixture Mn-S with various KMnO_4 content (shown in figure) at 25°C against etching time.

essentially and the active species were not exhausted by repeated etching in the same solution. Repeated etching of samples where the MnO_2 surface layer was not dissolved gave identical results as with usual procedure. MnO_2 precipitated on the sample surface in form of isolated grains instead of a coherent layer (Fig. 12). Experiments performed *in vacuo* and at atmospheric pressure did not differ. Figure 5 shows etching curves where the samples, already etched for different time in the 5% Mn-S mixture, were subjected to additional etching. The samples preliminary etched behaved during repeated etching in the same manner as the unetched samples did. Therefore, on the etched surface, there does not form any chemically different to the etching-resistant layer. This conclusion was confirmed by IR spectra. The most probable explanation for the passivation of the etched surface is to be searched in the mechanism of complicated chemical reactions taking place during etching and the way of releasing of active species in the concentrated Mn-S mixture.

Individual points of etching curves show a greater scatter than that corresponding only to experimental error, which is a sign of a certain heterogeneity of the etching process. Light microscopical examination confirmed

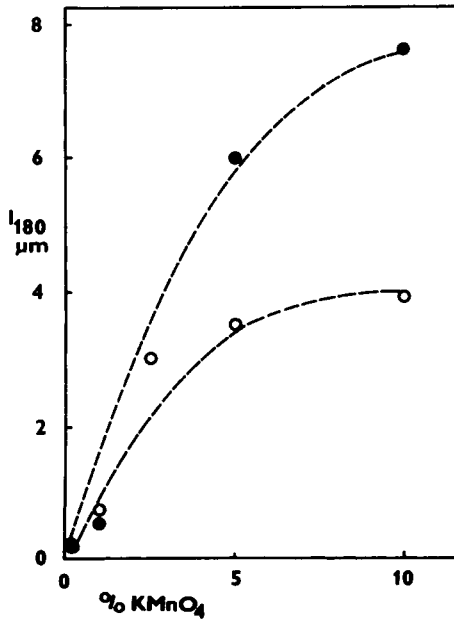


Fig. 3. The thickness of the surface layer removed after 180 min etching at 25°C in Mn-P of the PP-Q (●) and PP-T (○) samples as a function of KMnO₄ content.

the local heterogeneity of etching, especially using Mn-S (Fig. 6). Here small dimples on the surface may grow to craters and holes. With Mn-P the etching is much more uniform (Fig. 7).

Morphological study by electron microscopy confirmed the possibility of revealing the typical texture of the α or β crystalline modification (Fig. 8) of isotactic polypropylene in all kinds of surfaces by suitable etching with

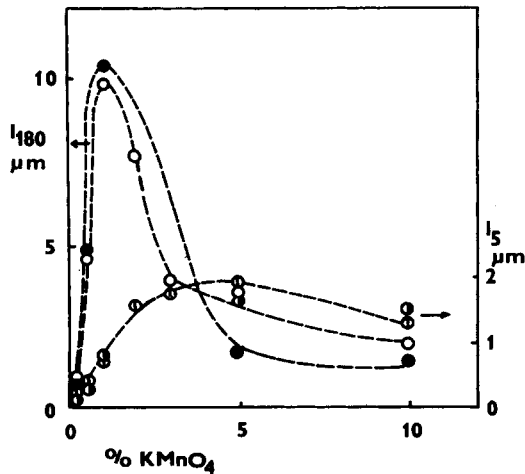


Fig. 4. The thickness of the surface layer removed after 180 min (○, ●) and after 5 min (●, ○) at 25°C in Mn-S as a function of the KMnO₄ content, for PP-Q (●, ○) and PP-T (○, ●) samples.

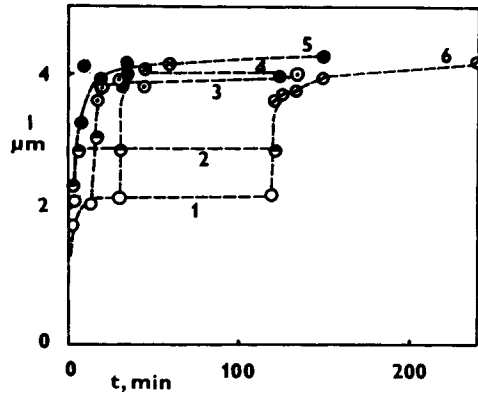


Fig. 5. Repeated etching of PP-T samples at 25°C in Mn-S containing 5% of KMnO_4 . Etching curves: (1) usual procedure; (2-6) samples were removed at corresponding times and after usual treatment resuspended in etchant.

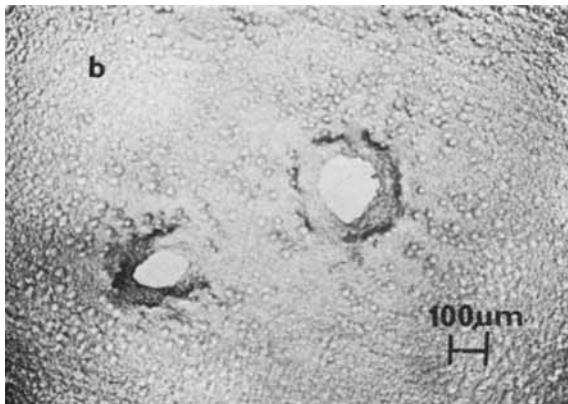
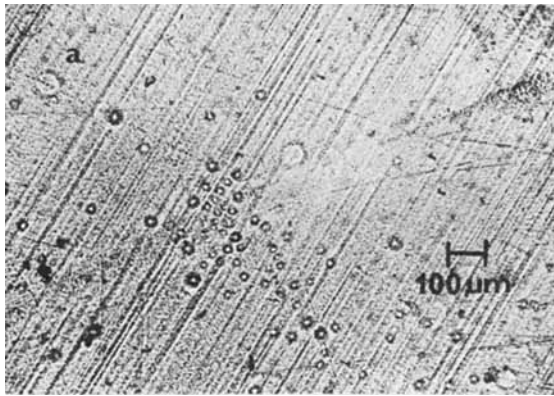


Fig. 6. Optical micrographs of PP-T samples etched at 25°C in 1% Mn-S mixture for 1 min (a) and 180 min (b), respectively.

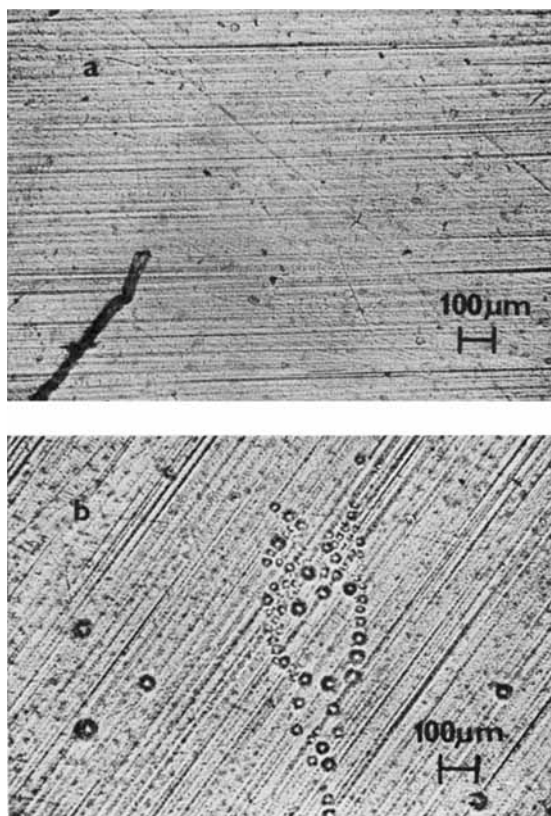


Fig. 7. Optical micrographs of PP-T samples etched at 25°C in 1% Mn-P mixture for 1 min (a) and 180 min (b), respectively.

Mn-P or Mn-S. Investigating the influence of etching time, we did not find essential differences in morphology. In accordance with the heterogeneous character of the etching process, we observed regions etched selectively, unetched, and overetched on the same sample. With increasing time and temperature and KMnO_4 concentration, the amount of overetched regions and artefacts increased, especially with Mn-S. It was not possible to see marked differences in morphology of samples etched for a very short time and of samples etched to the stage where the etching actually stopped. Electron micrographs in Figures 9 and 10 illustrate main features of morphological changes observed during etching in Mn-P containing various amount of KMnO_4 . In the initial stage, mainly at low KMnO_4 content, one can first see a relatively flat surface relief with lamellae oriented by their longer dimension approximately perpendicular to the sample surface. After a longer etching time, there begin to appear also the basal planes of lath-shaped lamellae in greater extent. Overetching manifests itself by destruction of lamellae. The surface relief becomes deeper and rougher, the number of thinner and shorter lamellae decreases, and an increasing number of thicker and longer lamellae appear. The material between lamellae is eaten

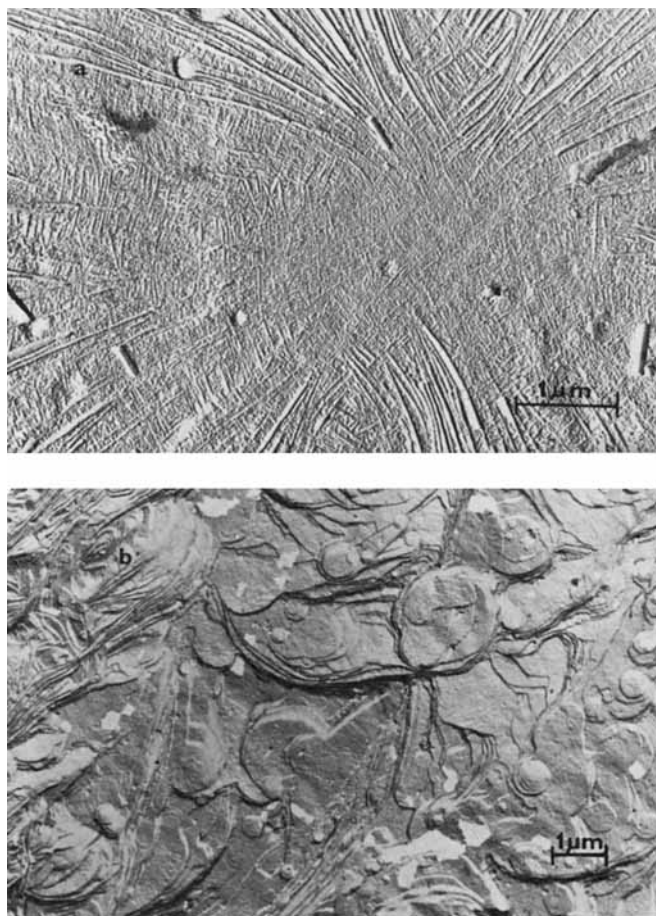


Fig. 8. Electron micrograph of the typical texture of the α -form (a) and β -form (b) of isotactic polypropylene. Etching 5 min in 5% Mn-S mixture at 25°C.

off faster, and one can see some separated and fractured lamellar parts. The overetching results in breaking off lamellae into small blocks or grains and in rounding off lamellar edges. On some micrographs one can see that etching is preceded by amorphization of lamellae (arrowed in Fig. 9 and 10). Figure 11 illustrates that β -lamellae resist to overetching better than α -lamellae do. On etched samples two kinds of artefacts could be observed: large star-shaped artefacts (marked by S in Fig. 12), described by Olley et al.,^{10,11} and small lens-shaped dimples (marked by L in Fig. 11). If the MnO_2 layer is not fully dissolved, one may observe grainy artefacts shown in Figure 12.

From the foregoing it follows that it is not yet possible to explain the detailed mechanism of etching with Mn-P or Mn-S. Evidently, during etching together with amorphous and defective structures also the crystalline regions are removed on a macroscopical scale, because the thickness of the removed layer (order of magnitude μm) largely surpasses the accepted di-

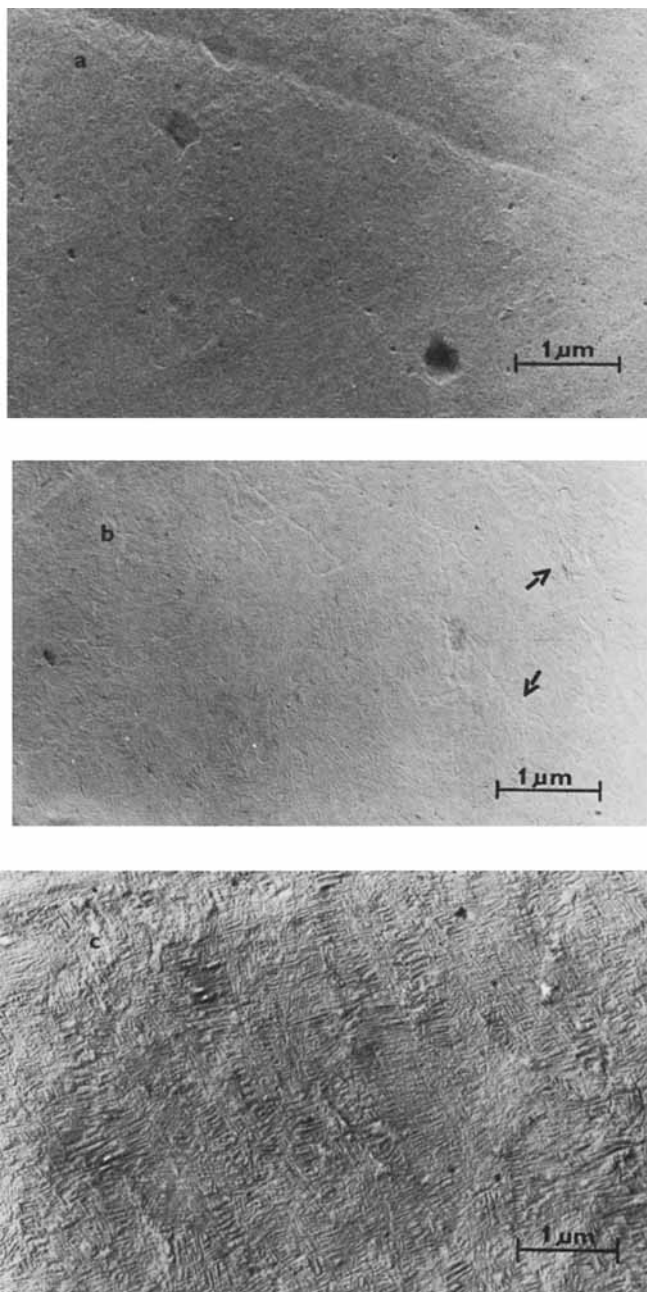


Fig. 9. Morphology of PP-Q samples etched at 25°C in Mn-P with 0.1% of KMnO_4 for different time: (a) original mold surface; (b) 1 min; (c) 30 min. The arrow marks fibrillar formations.

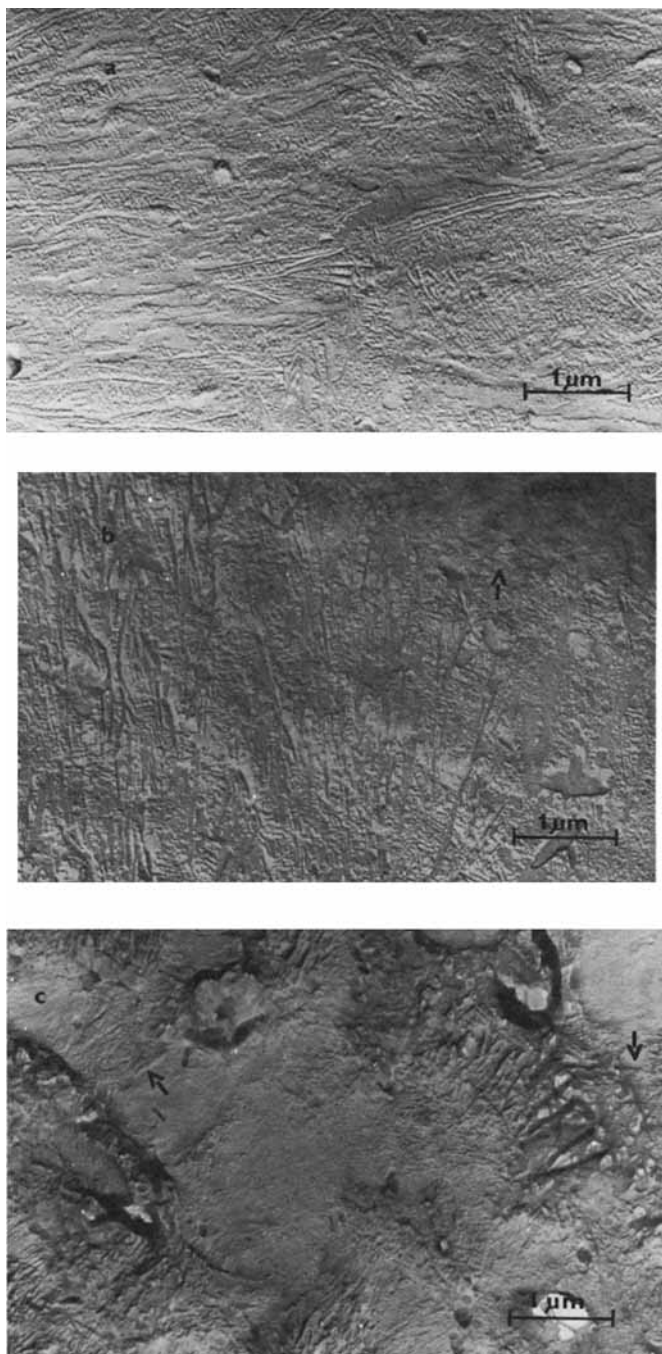


Fig. 10. Morphology of PP-T samples etched at 25°C in 5% Mn-P mixture for different times: (a) 5 min; (b) 30 min; (c) 180 min. Arrows mark fibrillar formations.

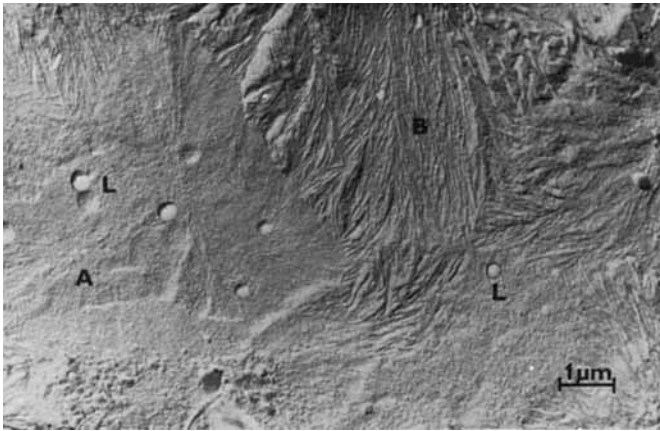


Fig. 11. Electron micrograph of the PP-Q sample etched 180 min at 25°C in 1% Mn-S showing higher tendency of the α -form (marked A) compared to β -form (marked B) to over-etching. L marks small lens-shaped artefacts.

mensions of amorphous and defective domains (order of magnitude nm). This macroscopical etching runs through a series of selective etchings on an nm scale. The initial etching is very fast, the sample submerged in 1% Mn-P for less than 1 s showed similar morphology as shown in Figure 9(c). During etching amorphous phase disappears faster, and, consequently, the surface of the denuded crystalline phase increases. With a larger crystalline surface, etching continues in spite of a lower etching rate in crystalline regions. All this repeats itself many times, and, therefore, one may observe various etching stages. Selective etching increases somewhat the crystallinity of the surface, which was confirmed with fine-powdered samples by X-ray and density measurements. The higher crystallinity of the surface does not markedly affect the overall etching rate, as was shown by repeated etching of etched samples (Fig. 5). The tendency to local differences in the depth of etching is not understood; however, it is not related to distinct



Fig. 12. Morphology of the PP-Q sample etched 5 min at 25°C in 5% Mn-S mixture. MnO_2 precipitated on the surface was not dissolved and forms a grainy structure. S marks a large star-shaped artefact.

features of the spherulitic texture (e.g., spherulite boundaries, centers, voids, etc.).

In conclusion one may see that etching of isotactic polypropylene in Mn-P and Mn-S proceeds by a different mechanism, where the active species differ in color and saturation effect. In spite of this, it is possible to find suitable etching conditions for visualization of the lamellar-spherulitic morphology in all surface types. It is also possible to remove a definite thickness of the sample surface. The advantage of this method is in that it is simple, fast, cheap, and suitable for examination of all surface types.

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