New etching method for poly(ethylene oxide)*

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By choosing proper etching conditions, the internal structure of water-soluble poly(ethylene oxide) could be analysed by electron microscopy. Sodium ethoxide in ethanol was the etching medium used.

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INTRODUCTION

The common spherulitic superstructure of polymer crystals grown from the melt was analysed first using optical microscopy (OM)[1]. In order to explain the relationship between morphology and crystal growth rate a competition between molecular diffusion and crystal growth was assumed[1,2]. By transmission electron microscopy (TEM) it was found that a lamellar, chain-folded crystal structure is the basic texture of bulk crystallized polymers over a wide crystallization temperature range[2,3]. The lamellar structures were first reported by observation of free surfaces, and then, after the development of etching and decoration methods, also seen as internal textures of bulk materials. For polyethylene (PE), for example, the effect of nitric acid[4], ozone[4,5] and chlorosulphonic acid[6] are well known. Permanganic acid[7] has been used for several polymers to reveal the texture for TEM. Changing the etching conditions allows differentiation between different components of the morphology[8]. The study of lamellar polymer crystals is still an active field of research[9,10]. One of the aims of our laboratory is to find the connection between observations of crystal morphology, as found by OM and TEM, kinetics of crystallization, as studied by thermal analysis, and rejection of non-crystallizable species, as identified by fractional dissolution.

Our recent research on segregation in mixtures of poly(ethylene oxide) (PEO) of different molecular masses revealed that the crystalline texture changes at different levels of molecular segregation[11]. The OM observation of binary mixtures of PEO indicated changes down to a scale of 1 μm. There were, however, no techniques for etching PEO or, for that matter, any other water-soluble polymer to help in the recognition of the internal structure of melt-crystallized PEO down to a scale of 1 nm. All etching techniques mentioned above need water to wash away the etched debris. The analysis of the PEO morphology has thus in the past been restricted to solution-grown crystals and the study of free surfaces[2,12].

In this paper, we report results of a new etching method, making use of a solution of sodium ethoxide in absolute ethanol. Two species of segregated crystals of different molecular mass could be identified by this method[13]. The results obtained by using different etching times, concentration and washing times in absolute ethanol are reported.

EXPERIMENTAL

Materials and samples

The two low molecular mass PEO fractions used in this study had $M_w = 3500$ and 7000 with polydispersities of less than 1.1. A high molecular mass sample of PEO with $M_w = 100\,000$ was mixed with each of these fractions. All samples were purchased from Polyscience Inc. All were powders and had an approximate particle diameter of 20 μm.

The PEO mixtures that were studied were: PEO (2*M*-1) of which the volume fraction v_2 of the high molecular mass component ($M_w = 100\,000$) was 27.9% mixed with the low molecular mass of $M_w = 3500$; and PEO (2*M*-7) of $v_2 = 29.9\%$ mixed with the low molecular mass of $M_w = 7000$. The initially prepared mechanical mixtures were heated for 24 h in glass tubes under dry nitrogen atmosphere to a fixed temperature, about 30 K above the equilibrium melting temperature T_m° (342.2 K) to effect homogenization. After cooling to room temperature, the samples were subsequently cut to sizes of 10 × 10 × 1.5 mm. The pieces were then heated again to 373.2 K and held for 15 min to melt all the existing crystals. Then they were cooled to selected crystallization temperatures and held for fixed periods of time. After crystallization, the samples were quickly cooled to room temperature. Temperatures were controlled in a water bath to ±0.1 K and the samples were always kept under nitrogen atmosphere.

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Etching

The etching procedure consisted of placing the crystalline samples in NaC_2H_5O dissolved in absolute ethanol. The PEO samples were etched for certain periods of time at room temperature (298.2 K) with frequent agitation. After this treatment the samples were washed in absolute ethanol for fixed times. The etched samples were then allowed to dry. In order to clearly observe the internal crystalline texture, an attempt was made to search for the best etching conditions. The following were considered: the etching time of the samples in the solution of NaC_2H_5O in absolute ethanol, the concentration of the NaC_2H_5O solution, and the washing time of the samples in absolute ethanol after etching. The temperature of etching and washing was always kept at 298.2 K.

Electron microscopy

A standard, one-state replication process by shadowing the etched samples with heavy metal (Au/Pd, 0.4/0.6) and backing with carbon was used. The polymer was then washed off the replica with water. Then the replicas were transferred to acetone and picked up with TEM grids. The replicas were examined in the TEM mode of a Hitachi HS-7S electron microscope with 50 kV acceleration.

Etching kinetics

In order to find the rate of etching for the different PEO fractions and mixtures, the fully crystallized samples of both fractions and mixtures were prepared at a fixed crystallization temperature. After being ground to powders in liquid N_2, their initial weights were measured. The etching was then performed for predetermined time periods, as described above. The samples were washed in absolute ethanol for 10 min and dried in a vacuum oven at room temperature for 12 h. Finally, their weights were again measured to find the amount of polymer etched and dissolved.

RESULTS AND DISCUSSION

The effect of changing etching time was determined for the mixed samples, as well as for the two pure fractions, all crystallized at 325.2 K. The etchant consisted of 25 ml of NaC_2H_5O dissolved to 0.21 weight fraction in absolute ethanol. After treatment for various lengths of time, weight losses of the samples with respect to time were measured. The results are shown in *Figure 1* for both mixtures and fractions. For the high molecular mass fraction ($M_w = 100000$), an initial quick drop in weight loss corresponds to etching of the amorphous PEO. This first, fast etching stops when about 20% of the sample weight was lost after about 10 min etching time. Note that the crystallinity of PEO of $M_w = 100000$ crystallized under such conditions is about 76%[11]. The weight loss becomes much slower after this initial drop. Another, even quicker decrease can, however, be observed after about 18 min of etching time.

For the low molecular mass PEO, on the other hand, a continuous weight loss is found for the initial etching period. There remains the second, quick drop, starting at about 20 min of etching time. For the mixture of PEO (2*M*-1), the initial drop is not as steep as that for the high molecular mass PEO (*Figure 1*). The drop is slowed at an etching time of 10 min and 15% weight loss, and then is followed by the second, steeper drop. The etching behaviour of the mixture is clearly in between that of the two fractions. Etching in the case of the mixture is expected to initially remove predominantly the amorphous portion of the high molecular mass PEO. The low molecular mass crystals that are crystallized as extended chain crystals are etched continuously, but at a slightly lower rate than the amorphous, high molecular mass sample. The second increase in etching rate can at present not be fully explained, but may be related to the decrease in crystal size which may ultimately lead to dissolution.

The next experiment dealt with the sample morphology. *Figures 2a–c* show the appearance of sample (2*M*-1) after etching times of 2, 10 and 20 min, respectively. *Figure 2d* shows the surface structure of the PEO sample under the same crystallization conditions but without etching. The latter figure is practically identical to one published in reference 2 (Figure III.60). It is seen that *Figure 2b* displays the most detailed internal crystalline texture. The texture of *Figure 2a* is not much different from the surface structure shown in *Figure 2d.* The etching time used (2 min) seems too short to expose the internal crystalline texture. On the other hand, the structure in *Figure 2c*, although still visible, is somewhat over-etched, i.e. it corresponds to an etching time after the second break in *Figure 1.* From *Figure 2d*, it can be seen that the poorly visible lamellar crystals form what are often called incipient spherulites[2]. Lamellae that grow normal to the melt surface extend considerably above the sample level, leading to the rough sample surface. The crystallization temperature of 273.2 K is within crystallization region III delineated in reference 11 as the temperature range in which both molecular masses cocrystallize. From *Figure 2b* one can see that the lamellae are, indeed, of uniform thickness and are stacked regularly. The same texture can be observed from the other photographs, but with less detail.

A set of PEO (2*M*-7) samples crystallized at 331.2 K are shown in *Figures 3a–c*. Their etching times are 5, 10 and 20 min, respectively. The internal, lamellar texture shown in *Figure 3c* seems again to be over-etched. *Figures 3a* and *b* are both acceptable. Crystallization at $T_c = 331.2$ K is at

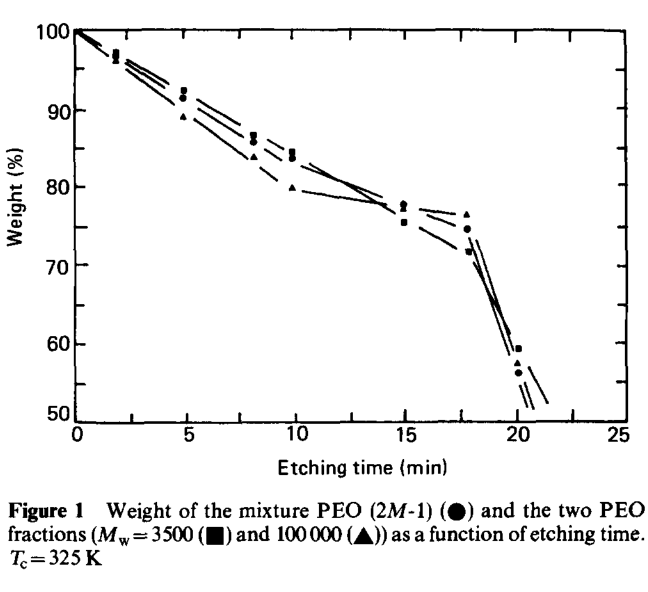


Figure 1 Weight of the mixture PEO (2*M*-1) (●) and the two PEO fractions ($M_w = 3500$ (■) and 100 000 (▲)) as a function of etching time. $T_c = 325$ K

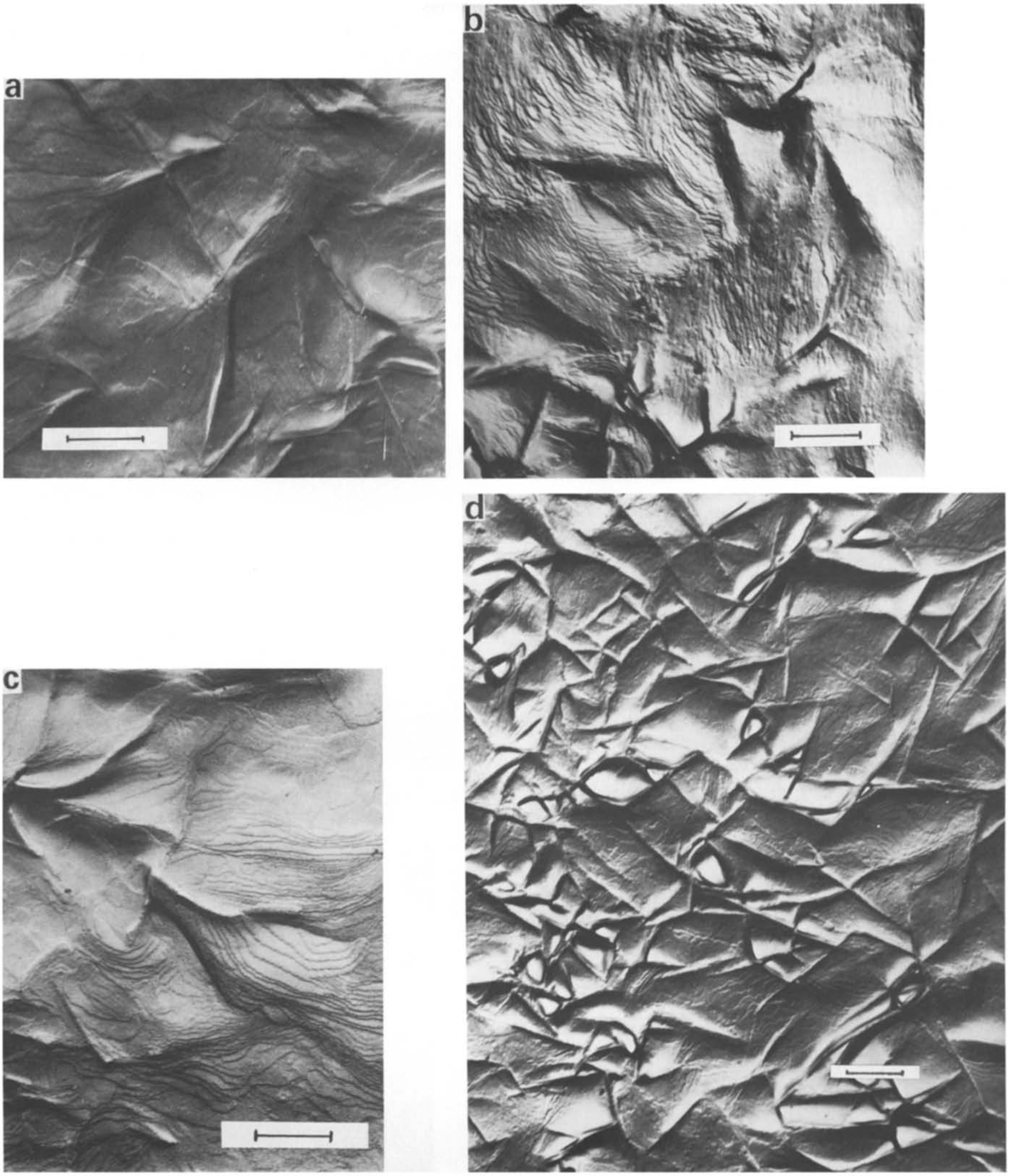
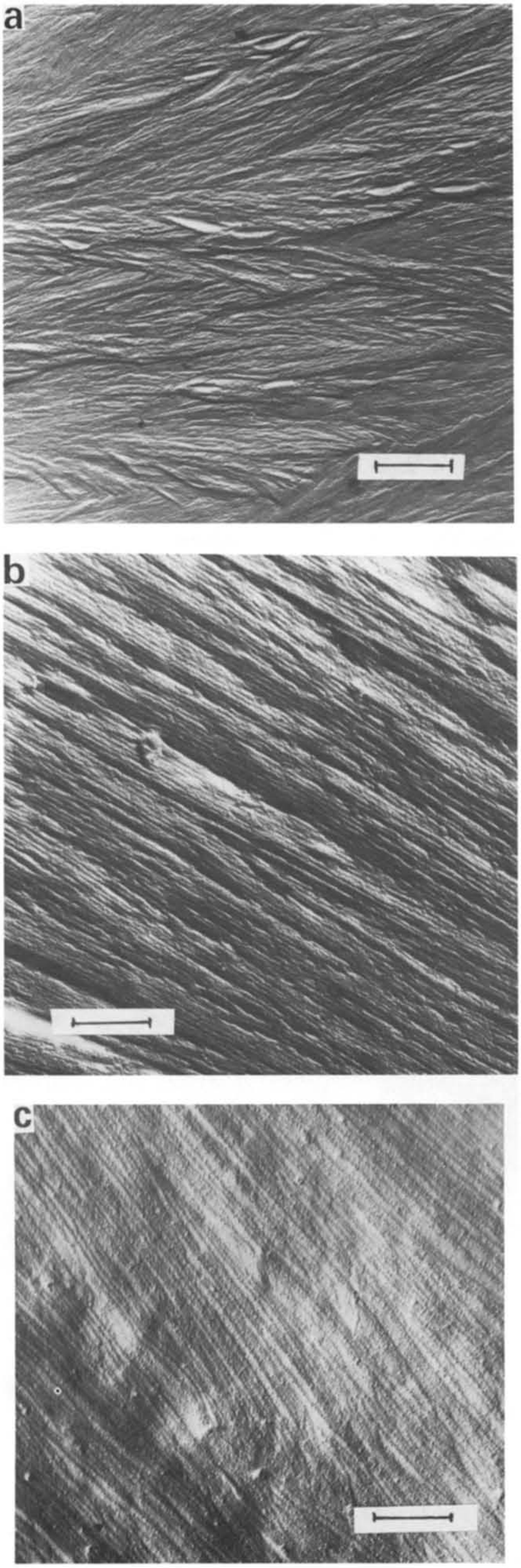


Figure 2 Incipient spherulites of a PEO sample (PEO(2*M*-1), 3500/100 000) crystallized at 273.2 K after etching in 21 wt% NaC_2H_5O in absolute ethanol, and washing for 10 min in absolute ethyl alcohol. (a) 2, (b) 10 and (c) 20 min etching time. (d) Without etching. The scale bar is 1 μm

the upper temperature limit of region II of reference 11 where macroscopic segregation between the two components (low and high molecular masses) should be observed. *Figure 3a* shows, in fact, mainly the lamellar crystals formed by the low molecular mass of 7000 during cooling after isothermal crystallization with a lamellar thickness of about 12 nm. In contrast, the lamellae which can be observed in *Figure 3b* are mainly of high molecular mass ($M_w = 100 000$). The lamellar thickness can be measured to be about 30 nm.

Considering the second aspect of the etching procedure, namely the washing time of the samples in absolute ethanol, we note that some artifacts may be observed with too short a washing time. *Figure 4a* shows a PEO (2*M*-1) sample crystallized at 310.2 K. The etching time was 5 min in 21 wt% NaC_2H_5O solution of ethyl



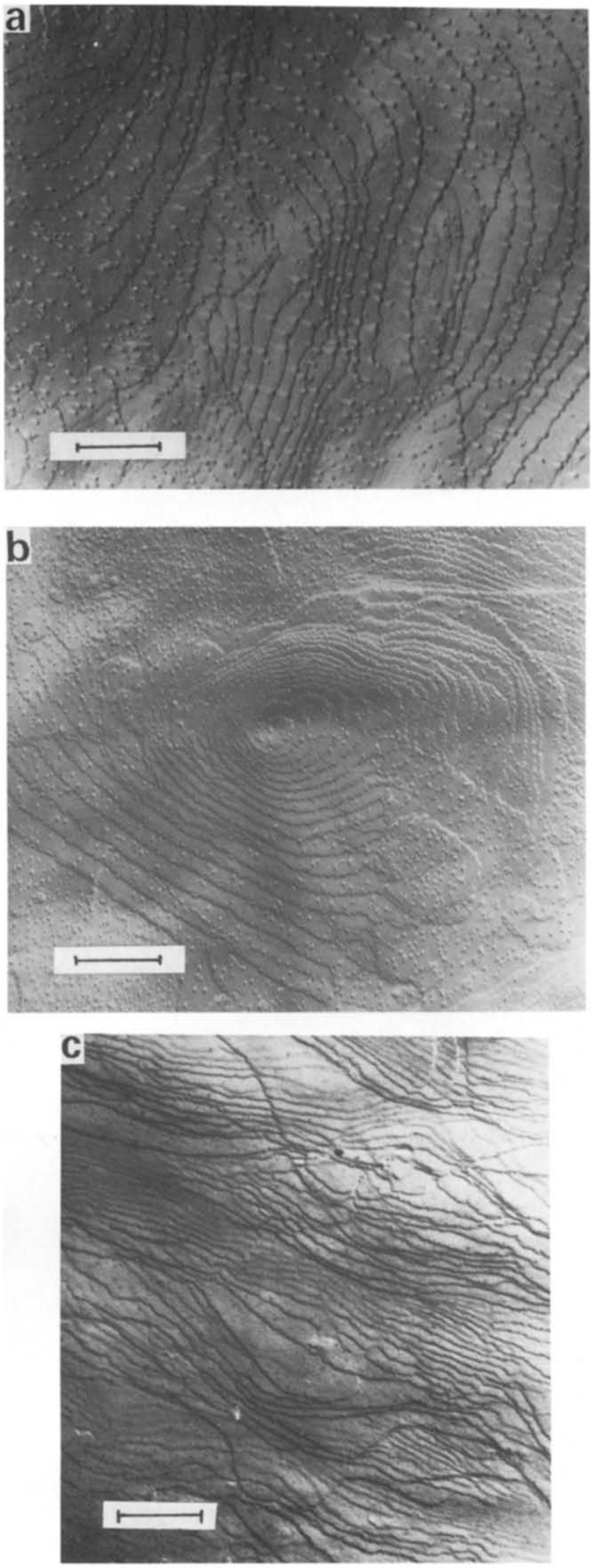


Figure 4 Internal lamellar texture of a PEO sample (PEO (2*M*-1) 3500/100 000) crystallized at 310.2 K after etching for (a) and (c) 5 and (b) 20 min. (a) 2, (b) 2 and (c) 7 min washing time. The scale bar is 1 μm

Figure 3 Internal lamellar texture of a PEO sample (PEO (2*M*-7) 7000/100 000) crystallized at 331.2 K after etching in 21 wt% NaC_2H_5O in absolute ethanol, and washing for 10 min in absolute ethanol. (a) 5, (b) 10 and (c) 20 min etching time. The scale bar is 1 μm

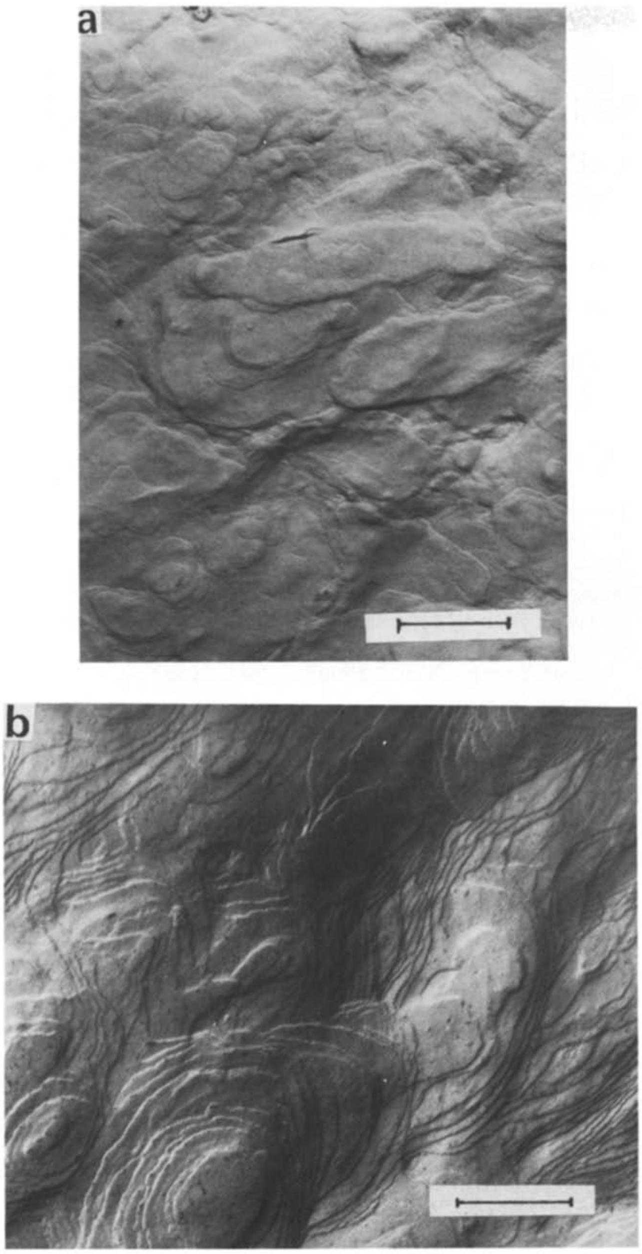


Figure 5 Lamellar texture of a PEO sample (PEO (2*M*-1), 3500/100000) crystallized at 310.2 K after etching for 10 min. (a) In 5 wt% NaC_2H_5O in absolute ethanol. (b) In 21 wt% NaC_2H_5O in absolute ethanol. Washing in both cases for 10 min. The scale bar is 1 μm

alcohol with a washing time of only 2 min. There are many small spots on top of the etched crystal surface. *Figure 4b* shows the sample with the same short washing time, but with a larger etching time (20 min, shadowed at different angles). A similar pattern can be seen. The internal crystalline texture of *Figure 4c*, on the other hand, is free of spots on the crystalline surface. The PEO sample used in *Figure 4c* is the same as in *Figure 4a*, but the washing time was extended to 7 min. Comparing the various photographs suggests that the spots are caused by insufficient washing in absolute ethanol.

Finally, the effect of NaC_2H_5O concentration during etching can be compared in *Figures 5a* and *b*. Both samples are PEO (2*M*-1), crystallized at $T_c = 310.2$ K. The samples were etched in 5 and 21 wt% NaC_2H_5O solution in absolute ethanol, respectively. The etching times were 10 min. After etching, the samples were washed in absolute ethanol for 10 min. It is obvious that *Figure 5b* shows a clear internal lamellar texture. On the other hand, *Figure 5a* shows only some texture near the surface. The features perpendicular to the figure plane are absent.

A successful etching method must thus meet three requirements. First, the internal crystalline texture must be clearly exposed. A chosen etchant must have different etching speeds for each crystal type and the amorphous regions. For best results the method must thus be tested for each sample for a set etching time. Second, the chosen conditions must not introduce artifacts on the observed crystal surface, as shown here by too short a washing period. Third, in order to avoid changing the crystalline morphology, the samples must not dissolve in the solvent used for etching. The method we developed can be made to fit all these requirements.

The chemical reaction that permits the etching is expected to involve an attack by the organic base on C–H, leading to the formation of $-CH{=}CH_2$, and ultimately chain scission.

CONCLUSIONS

We have developed a first etching method for PEO, one of the water-soluble polymers. The optimal condition for the etching seems to be in 21 wt% NaC_2H_5O in ethanol for 10 min at 298.2 K with frequent agitation. After this treatment the samples must be washed in absolute ethanol for 10 min. The internal lamellar texture of PEO crystals can then be clearly observed.

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