Polymer Bulletin 17, 567-571 (1987)

Polymer Bulletin

A new etching method for the electron microscopy of semicrystalline poly(ethylene oxide)

H.S. Bu*, Stephen Z.D. Cheng, and Bernhard Wunderlich**

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Summary

Poly(ethylene oxide) (PEO) is one of the water-soluble polymers. We have developed a first etching method for water-soluble polymers using sodium ethoxide dissolved in ethanol.

Introduction

Etching by preferential oxidation of amorphous areas in semicrystalline macromolecules is a well-known method to reveal the crystal morphology [1]. For polyethylene, for example, nitric acid [2], ozone [2,3], and chlorosulfonic acid [4] are well known etchants. Permanganic acid [5] has been used for several polymers to reveal the texture for transmission electron microscopy (TEM). Even with etching techniques long established, the study of lamellar polymer crystals is still an active field [6,7]. Our recent interest in segregation of molecular masses on crystallization of poly(ethylene oxide) [8,9] (PEO) revealed that there are no well developed techniques of etching of water-soluble polymers. All techniques just mentioned need water to wash away the etched debris. The analysis of PEO morphology has thus in the past been restricted to solution grown crystals and the study of free surfaces [1,10]. Our main interest is the search for segregated crystals of different molecular mass, grown out of two-component solutions of PEO. In this paper we report on first results of a new etching method, making use of a solution of sodium ethoxide in absolute alcohol. The two different types of crystals could be identified by this method.

Experimental

Two component PEO mixtures were prepared out of one high molecular mass fraction (MW=1000,000) and one low molecular mass fraction (MW=3,500, 7,000 and 20,000). The samples of a size of 10x10x1.5 mm were molten at 373.2 K and held for 15 minutes to destroy all prior crystal nuclei. Then they were cooled down to selected crystallization temperatures and held for fixed time periods. After the crystallization the samples were quickly cooled to room temperature. The detailed crystallization procedure is described in Ref. 9. Temperatures were controlled in a water - bath to ± 0.1 K under

---

* Visiting professor from Fudan University, Shanghai, PRC

** To whom offprint requests should be sent nitrogen atmosphere. Two different specimen preparations were used for the sample. First, an attempt was made to observe the crystalline texture on the free surfaces. A standard, one-stage replication process by shadowing the samples with heavy metal and backing with carbon was used. The polymer was then washed-out with water. The second method was developed to observe the internal crystalline texture of PEO samples. The crystalline samples were placed in 25 ml of NaC_2H_5O dissolved to 0.21 weight fraction in absolute ethyl alcohol. The PEO samples were etched for 10 minutes at 298.2 K with frequent agitation. After this treatment the samples were washed in absolute ethyl alcohol for 5 minutes. the etched samples were then allowed to dry. They were examined in the TEM using the same replication process as described above. The resulting micrographs thus have the appearance of negative relief. The electron microscope used was a Hitachi HS-75 with 50kV-acceleration voltage.

Results and Discussion

Figure 1 shows the free surface of a PEO two-component sample crystallized at 273.2 K. The figure is practically

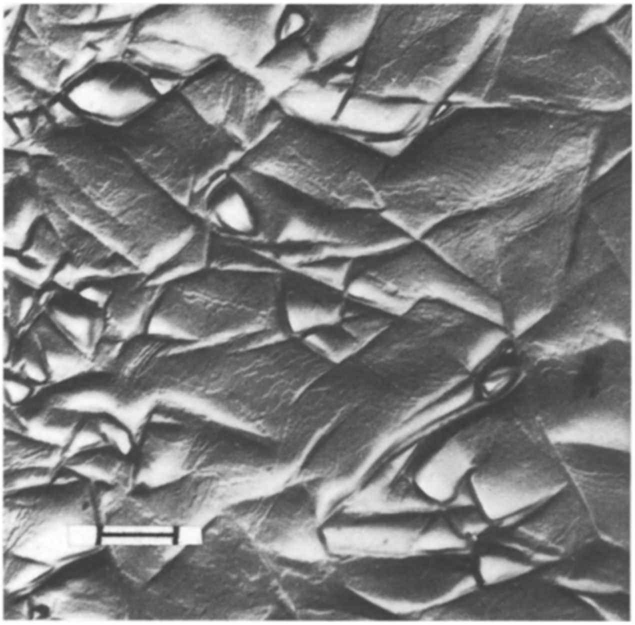

Figure 1. Immature spherulites on the free surfaces of a PEO sample (mixture 3500/100,000 mass ratio 0.72/0.28) crystallized at 273.2 K. The scale bar is 1 μm.

identical to one published in Ref. 1 (Fig. III.60) for pure PEO. Poorly visible lamellar crystals are organized into incipient spherulites. Lamellae growing normal to the melt surface grow condiserably out of the surface leading to a rough sample surface. The crystallization temperature of 273.2 K is within crystallization region III in which both molecular masses should cocrystallize [8,9]. More detail is seen in Fig. 2 which represents the same sample after etching with C_2H_5ONa. The lamellae are, indeed, of uniform thickness and stacked regularly.

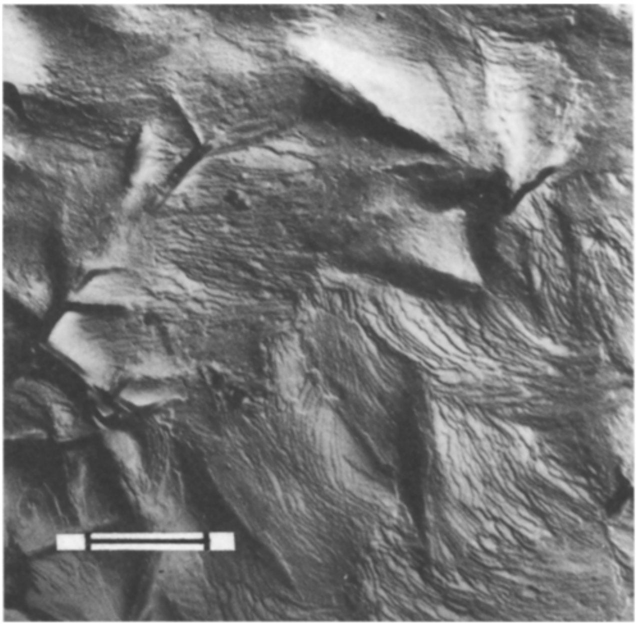

Figure 2. PEO crystals. Sample as in Fig. 1, after etching. The scale bar is 1 µm.

With increasing crystalliztion temperature the lamellar thickness increases [1], but also two-component melts get into crystallization region II where partial segregation of the molecular masses occurs, i.e. one expects two types of crystals. Figure 3 shows the free surface of a PEO two-component sample crystallized at 331.2 K. The lamellar structure is now much more regular with thicker lamellae. Growth spirals are visible in the areas that show lamellar surfaces. The lamellar thickness can be estimated to be about 30 nm. It is, however, difficult to identify two different types of crystals. A completely different picture results after etching (Fig. 4). Between the lamellae material has been etched away and on the lamellar surfaces irregular debris is visible. From the kinetics it is deduced that the high molecular mass component crystallizes first [9]. From Fig. 4 one can see that

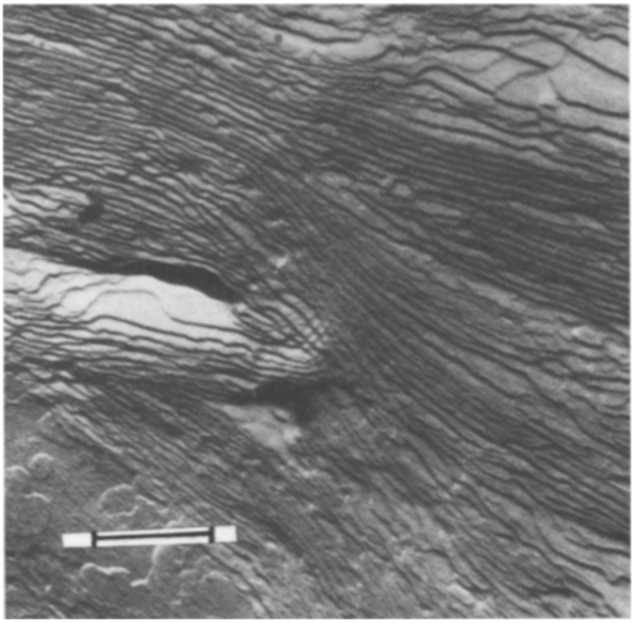

Figure 3. The lamellar microstructure on the free surface of a PEO sample (mixture 7000/100,000, mass ratio 0.75/0.25) crystallized at 331.2 K. Scale: 1 μm.

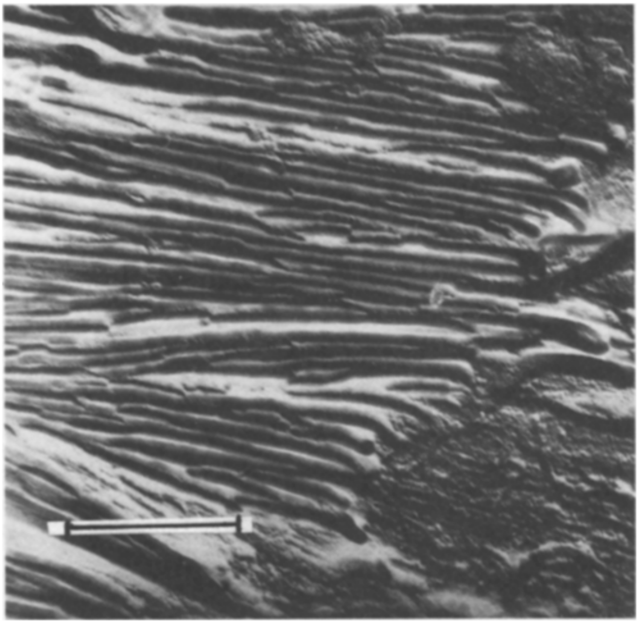

Figure 4. PEO crystals as in Fig. 3, after etching. The different crystals are clearly seen. Scale: 1 μm.

the rejectes species accumulate between the lamellae and is etched differently.

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

Acknowledgment

This work was supported by the National Science Fountadion, Polymers Program, Grant No. 83-17097.

References

1. WUNDERLICH, B.: Macromolecular Physics, Crystal Structure, Morphology, Defects, Chapter 4.1.4, Academic Press, New York, 1973
2. PALMER, R. P. and COBBOLD, A.: Makromol. Chem. **74**, 174 (1964)
3. PRIEST, D. J.: J. Polymer Sci., Part A-2, **9**, 1777 (1971)
4. KANIG, G.: Kolloid Z. **251**, 782 (1973)
5. OLLEY, R. H., HODGE, A. M. and BASSETT, D. C.: Polymer **23**, 1707 (1982)
6. KEITH, H. D. and PADDEN, F. J., Jr.: Polymer **27**, 1463 (1986)
7. BASSETT, D. C. and VAUGHN, A. S.: Polymer **27**, 1472 (1986)
8. CHENG, S. Z. D. and WUNDERLICH, B.: J. Polymer Sci., Polymer Phys. Ed. **24**, 577, 595 (1986)
9. CHENG, S.. Z. D., BU, H. S. and WUNDERLICH, B.: J. Polymer Sci., Polymer Phys. Ed. to be published 1987
10. ALLEN, R. C. and MANDELKERN, L.: J. Polymer Sci., Polymer Phys. Ed. **20**, 1465 (1982).

Accepted April 5, 1987 C