ELSEVIER

Polymer Vol. 37 No. 1, pp. 183–185, 1996

0032-3861/96/$15.00 + 0.00

polymer communication

Surface morphology study of poly(ethylene oxide) crystals by scanning force microscopy

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(Received 29 May 1995; revised 28 June 1995)

Scanning force microscopy (SFM) images of the surfaces of poly(ethylene oxide) (PEO) crystals revealed oriented fibril-like growth with increasing annealing temperature. Some clear nucleation centres on the melt-crystallized surface and typical lamellar morphologies with a step height of 11.7 ± 0.5 nm were observed. Molecular folding structure (near four-fold symmetry structure with the nearest neighbour spacing of 7.4 Å) was also imaged on the PEO single crystal with SFM. The spacings and angles of the periodic array in the molecular image were consistent with the positions of the top of the molecular chain folds on the PEO single crystal surface.

(Keywords: scanning force microscopy; poly(ethylene oxide); molecular fold)

Introduction

In the research and development of polymer surfaces, it has been becoming important to understand or reveal surface phase-transition mechanisms in real space, such as phase-separation and single crystal growth. Relatively little is known about polymer surfaces at present since the conventional methods such as electron microscopy (EM), requiring a thin conductive coating layer, are incapable of detecting microstructures on surfaces. The atomic force microscopy (AFM)-based techniques[1–3] followed by the invention of scanning tunnelling microscopy (STM)[4] opened a new world for surface observation together with the local property measurement of non-conductive materials on a nanometre scale. In comparison with EM, they can be operated in air and require little pretreatment of the sample surfaces which is potentially a non-destructive method. It has a strong advantage for investigating polymer surfaces.

Single crystals of linear polymers generally show a structure where the chains arrange perpendicular to the large lamellar surfaces, necessitating chain folding in order to connect one crystal traverse (or stem) with another[5]. However, it is not yet clear how the polymer chains are folded, or how perfectly the molecular folds order on the crystal surface[6]. The study of the famous spiral growth from the screw dislocations terminating at the surface is crucial in order to understand the numerous processes in the phase transitions. Recently, a number of reports[7–10] have been reported with the use of scanning force microscopy (SFM) as a new probe for studying polymer single crystal surface structures. They proved that measurement of heights with SFM was much easier and more accurate than with EM. However, a few reports showed molecular-scale resolution of some polymer single crystals[11–14].

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In this work we present SFM results showing the change in the morphological features on PEO crystals, and a folded conformation of PEO single crystal surfaces grown from the molten phase.

Experimental

The PEO (repeat unit $-C_2H_4-O-$) used here was purchased from Aldrich Chemical Company Inc. and used without further purification. The characteristics of the PEO are summarized in *Table 1*. The property of the low glass transition temperature caused by the high flexibility (due to the ether linkage) is a good system to observe the morphological change. The PEO samples were prepared by dissolving in a good solvent of benzene and were then spin-coated on freshly cleaved mica substrates at 2000 rev min^{-1} to make uniform 200–300 nm thick films (2 wt% concentration). They were annealed at 23, 40, 55 and 65°C for 24 h, respectively, and cooled to room temperature under vacuum (0.5 torr).

The topography images were obtained by commercial AFM (SPA-300, Seiko Instruments Inc., Japan) using the deflection of a laser beam to measure the bending of the cantilever in a constant repulsive force of 1×10^{-9} N in ambient air. A V-shaped micro-fabricated cantilever (Olympus Opt. Inc., Japan) with a length of 100 μm, Si_3N_4 pyramidal tip, and a spring constant of 0.1 N m^{-1} was used. The piezoelectric translator could scan a tip over a maximum surface area of $20 \times 20\ \mu m^2$. Lateral force microscopy (LFM) for the observation of the molecular

Table 1 Characteristics of PEO

Weight-average molecular weight, M_w	100 000
Density, d	1.13
Glass transition temperature, T_g(°C)	−67
Melting temperature, T_m (°C)	66

folds of a PEO single crystal was performed with a quadrant photodiode system (monitored by detecting the torsion of the cantilever). Morphological features are enhanced in LFM images because the torsion signal contains the derivative information of corrugated surfaces.

Results and discussion

Figure 1a–d shows the AFM images of PEO annealed at 23, 40, 55, and 65°C, respectively. In *Figure 1a–c*, fibril-like structures with certain orientations reflecting the molecular order were observed with AFM below the melting temperature of PEO. These orientations are independent of the centrifugal direction caused by the spinning. It is reported that the ridge lamellae radiate from the centre of the spherulite, the shape of the growing spherulite is round, and the size is as large as a few hundred micrometres[15,16]. However, the maximum scan range of our AFM ($20 \times 20\ \mu m^2$) is not wide enough to find the centre of the spherulite. Nevertheless, we could estimate that the fibril directions correspond to those of the spherulite.

The step heights of each terrace part shown in *Figure 1a–c* are 2.4 ± 0.3, 2.4 ± 0.2, and 3.5 ± 0.3 nm, respectively. These results show that the crystal growth behaviour is influenced by annealing and the thickness increases with the annealing temperature. The widths of each terrace at 23 and 40°C were distributed from 20 to 30 nm, and the widths at 55°C from 25 to 35 nm, suggesting a kind of crystal growth process between 40 and 55°C. In contrast, the length of each terrace did not show a significant difference, distributing from 50 to 700 nm for all terraces.

The surface changed to the molecular fold structure of the PEO single crystal by annealing at 65°C as shown in *Figure 1d*. It is characterized as the appearance of typical spiral terraces with many clear nucleation centres and turns. This PEO single crystal was grown from the molten phase. *Figure 2* shows a cross-sectional profile along a line connected between points A and B indicated in *Figure 1d*. From the average over the various positions of several micrographs, the step height of 11.7 ± 0.5 nm was obtained. This value is in good agreement with that of PEO crystal grown in a toluene solution[9].

Molecular-scale images were obtained by scanning a terrace part in *Figure 1d*. *Figure 3* is a raw LFM image showing a periodic pattern with near four-fold symmetry (the inset is a 2D Fourier spectrum of this image) and the nearest peak-to-peak distance of *ca.* 7.4 Å. Since the SFM is sensitive to the small height difference, we conclude that the periodic feature is ascribed to the positions of the top of the molecular chain folds on the PEO single crystal. The lattice constant roughly agrees with the value of the distance between tops of the folds; *ca.* 6.5 Å ($a^* = 6.56$ Å or $b/2 = 6.52$ Å, reference 13) obtained by X-ray diffraction[17]. The molecular resolution area would correspond to the tight loop area since we occasionally

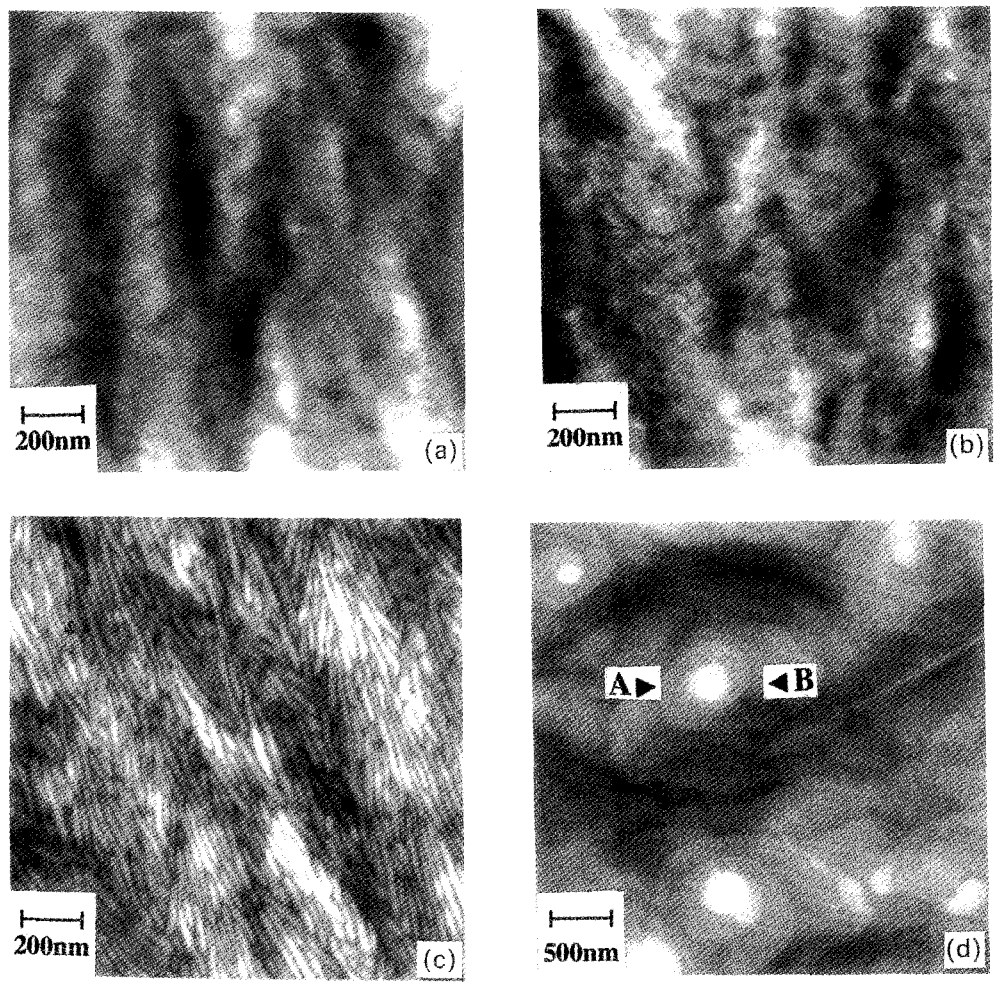

Figure 1 AFM images of PEO crystal surface treated at various temperatures for 24 h under vacuum (0.5 torr) at: (a) 23°C, (b) 40°C, (c) 55°C and (d) 65°C. The images of fibril-like structures in (a) and (b) are not so clear due to their small step height and large surface roughness

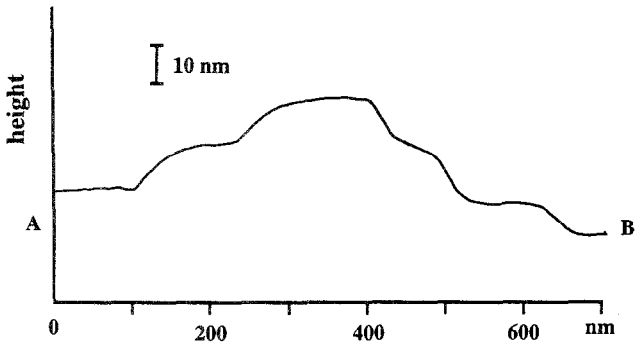

Figure 2 Cross-sectional view of PEO crystal connected between the points A and B (indicated in *Figure 1d*) (vertical axis is enhanced compared to the distance between A and B)

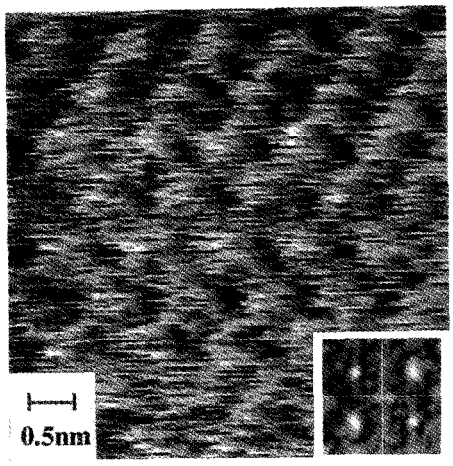

Figure 3 High resolution (5 nm × 5 nm) LFM image of the PEO single crystal surface in *Figure 1d*. A 2D Fourier spectrum is given in the inset

obtained no periodic molecular images on the PEO single crystal surface, which was probably due to the loop looseness, the softness of PEO, or the deformation by the AFM tip.

Conclusion

SFM has been successfully used to investigate surface microstructures down to a molecular-scale resolution. The images reported in this work shed light on speculations about PEO crystal growth on surfaces. The step height and the width of the terrace of the PEO crystal increased with annealing temperature, while the terrace length distribution did not change until the melting temperature of PEO. We imaged microstructures in the processes of lateral and vertical growth on surfaces, and spiral growth, which is the appearance of the single crystal. In the latter case, a step height of 11.7 ± 0.5 nm on the melt-crystallized PEO single crystal was measured. Moreover, on the single crystal surface, the molecular scale LFM image with near four-fold symmetry (nearest distance 7.4 Å) was also obtained.

Acknowledgement

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

References

1 Binnig, G., Quate, C. F. and Gerber, C. *Phys. Rev. Lett.* 1986, **56,** 930
2 Mate, C. M., McClelland, G. M., Erlandsson, R. and Chiang, S. *Phys. Rev. Lett.* 1987, **59,** 1942
3 Maivald, P., Butt, H. J., Gould, S. A. C., Prater, C. B., Drake, B., Gurley, J. A., Elings, V. B. and Hansma, P. K. *Nanotechnology* 1991, **2,** 103
4 Binnig, G., Rohrer, H., Gerber, C. and Weibel, E. *Phys. Rev. Lett.* 1983, **50,** 120
5 Keller, A. *J. Polym. Sci.* 1955. **17,** 291
6 Frank, F. C. *Disc. Farad. Soc.* 1949, **5,** 48
7 Patil, R., Kim, S.-J., Smith, E., Reneker, D. H. and Weisenhorn, A. L. *Polym. Commun.* 1990, **31,** 455
8 Nakagawa, Y., Hayashi, H., Takayanagi, T., Soeda, F., Ishitani, A., Toda, A. and Miyaji, H. *Jpn J. Appl. Phys.* 1994, **33,** 3771
9 Snétivy, D. and Vancso, G. *Polymer* 1992, **33,** 432
10 Nisman, R., Smith, P. and Vancso, G. J. *Langmuir* 1994, **10,** 1667
11 Grim, P. C. M., Brouwer, H. J., Seyger, R. M., Oostergetel, G. T., Bergsma-Schutter, W. G., Arnberg, A. C., Güthner, P., Dransfeld, K. and Hadziioannou, G. *Makromol. Chem. Macromol. Symp.* 1992, **62,** 141
12 Lin, F. and Meier, D. J. *Langmuir* 1994, **10,** 1660
13 Nie, H.-Y., Motomatsu, M., Mizutani, W. and Tokumoto, H. *J. Vac. Sci. Technol.* 1995, **B13,** 1163
14 Patil, P. and Reneker, D. H. *Polymer* 1994, **35,** 1909
15 Short, J. M. and Crystal, R. G. *Appl. Polym. Symp.* 1971, **16,** 137
16 Lovinger, A. J. and Gryte, C. C. *Macromolecules* 1976, **9,** 247
17 Takahashi, Y. and Tadokoro, H. *Macromolecules* 1973, **6,** 672