Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 9015–9021
polymer
www.elsevier.com/locate/polymer

In situ AFM study of the growth of banded hedritic structures in thin films of isotactic polystyrene

Yongxin Duan[a], Ying Zhang[a], Shouke Yan[a,*], Jerold M. Schultz[b,*]

[a]State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[b]Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

Received 6 April 2005; received in revised form 1 July 2005; accepted 7 July 2005
Available online 11 August 2005

Abstract

The growth of banded hedrites of isotactic polystyrene (iPS) is followed in situ, using atomic force microscopy (AFM). The melt layer surrounding the growing hedritic front is much thinner than both the hedrite front and the far-field melt. Growth occurs simultaneously in three dimensions: radially, circumferentially and height. The height of the hedrite growth front being so much higher than the adjacent molten pool, the observed propagation of the front requires that it be covered by a thin film of molten material, likely drawn up the face of the front by capillarity. As the hedritic front grows in height, it demands material at a higher rate than can be delivered from the far-field melt and the stacked lamellae stop growing, layer by layer, from the top downward, until only the basal lamella continues to grow (at a constant velocity). The kinetics of the position of the lowest point ahead of the growth front slows with time during this process. Supplying only the basal layer, the adjacent molten pool is replenished and now begins to feed new layers of growing lamellae as the process repeats itself. The creation of the new lamellar layers appears to be coupled to morphological instability of the basal layer, in the form of growth front serrations, likely causal of the giant screw dislocations.

Keywords: Crystallization; Thin film; Isotactic polystyrene

1. Introduction

We recently reported on banded hedrites in thin films of isotactic polystyrene (iPS) [1]. The hedrites exhibit no change in orientation across the bands; the chain axis is uniformly normal to the plane of the film. The bands manifest a periodic variation in film thickness. There is a similarity between these structures and the non-banded spherulites reported a half century ago by Schuur [2], Schramm [3], and Keith [4]. It was demonstrated in the previous work that the banding derives from a competition of the growth velocity and the rate at which new molten polymer can be transported to the growth front. A conceptual model for this behavior was suggested. In the model, as the hedrite grows laterally, the growth velocity outstrips the rate at which melt from the far field can replenish the depleted melt at the growth front, the depletion arising from the specific volume difference between crystal and melt. Further, it was observed that the decrease in film thickness from peak to valley is steep, while the increase in thickness from the valley to the next peak is more gradual. It was suggested that this more gradual increase in thickness relates to the rather slow rate of formation of the giant screw dislocations necessary to creating new layers of crystal lamellae. The intention was to close our investigation of this phenomenon, but some further study has shed additional light on the banded hedrites, qualitatively validating features of the model and also revealing surprising new information on crystallization in thin films.

2. Experimental

iPS powder with $M_w = 400{,}000$ and isotacticity of 90% was purchased from Scientific Polymer Products, Inc. M_w/M_n is approximately 2.8. iPS has a fairly slow

* Corresponding authors. Tel.: +1 302 831 8145; fax: +1 302 831 1048.
E-mail addresses: skyan@iccas.ac.cn (S. Yan), schultz@che.udel.edu (J.M. Schultz).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.024

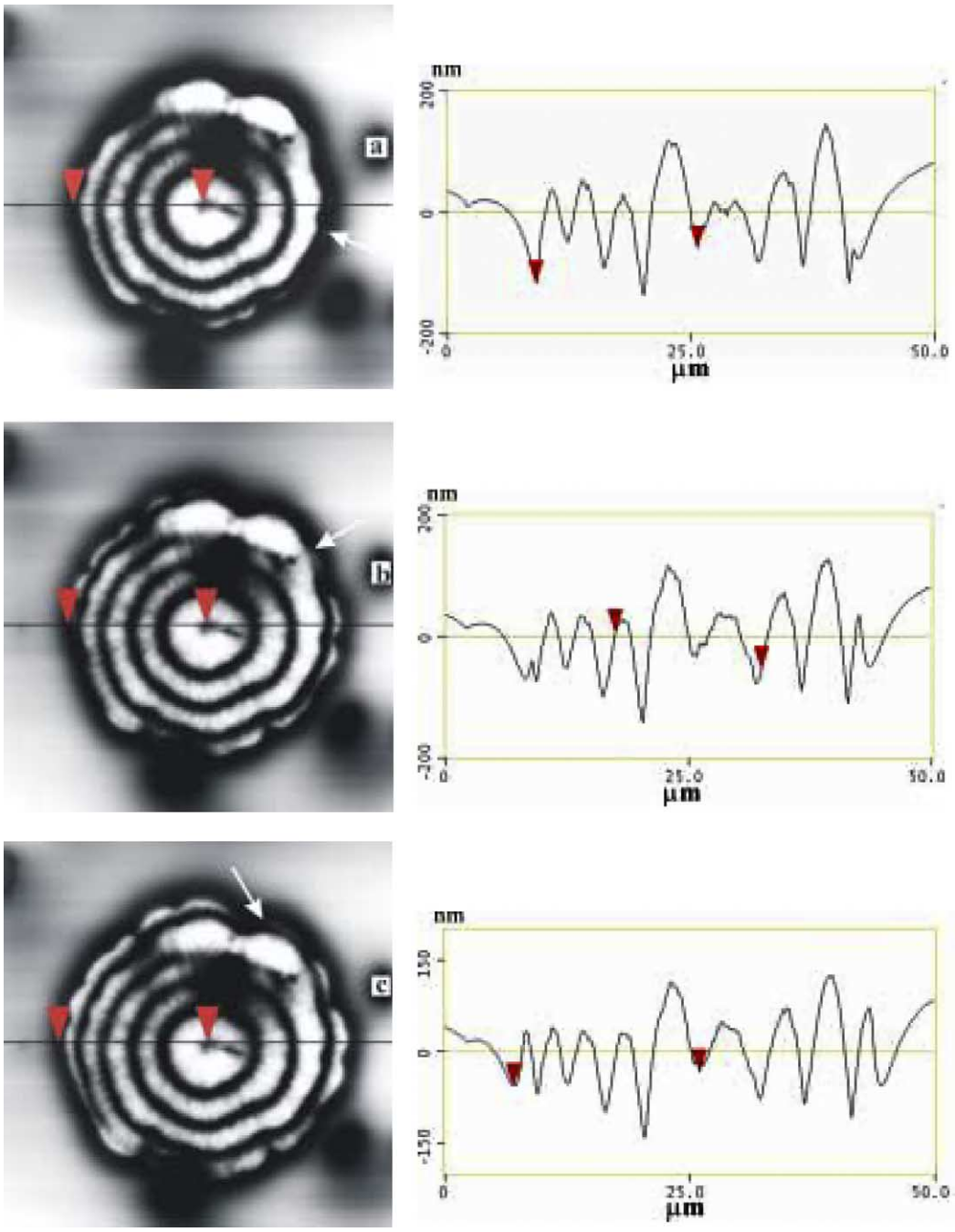

Fig. 1. A set of AFM height images of a banded iPS hedrite taken at different stages during crystallization at 160 °C, along with radial traces of height.

crystallization rate, which makes it easy to observe crystal growth in situ and to fix the structure by quenching.

Thin iPS films about 150–200 nm used for this banding morphology study were prepared by spin-coating 1.0 wt% iPS-xylene solution onto clean glass slides, (for TEM observation, onto carbon-coated mica). After complete evaporation of the solvent, the films were heat-treated at 250 °C for few minutes and then transferred directly to another hot stage preset at 160 °C for isothermal melt crystallization. The crystallization process at 160 °C was observed directly under tapping-mode AFM. A typical value for the set-point amplitude ratio (rsp) (defined as the ratio of the cantilever's oscillating amplitude to its freely oscillating amplitude) was 0.7–0.9. The amplitude of the free-oscillating cantilever was approximately 40 nm. TESP tips with a resonance frequency of approximately 300 KHz and a spring constant of about 30 N/m were used. For TEM observation, the thin iPS films experienced the same thermal treatments. The films, together with the carbon coated layers, were floated onto the surface of distilled water and mounted on 200-mesh copper grids. Electron microscopic observations were