Polymer 54 (2013) 6628–6635

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Coupling between crystallization and evaporation dynamics: Periodically nonlinear growth into concentric ringed spherulites

Yiguo Li [a,b], Haiying Huang [a], Tianbai He [a,*], Zongbao Wang [c,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, China
[c] Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form
11 September 2013
Accepted 14 September 2013
Available online 8 October 2013

Keywords:
Poly(ε-caprolactone)
Ringed or banded spherulites
Rhythmic crystal growth

ABSTRACT

Despite the extensive study of periodic precipitation and rhythmic crystal growth into ringed patterns, the detail of the evolution process remains unclear, and thus the explanation is rather elusive. Herein, we focus on monitoring the detailed growth process and dynamic, elucidating the underlying mechanism, and exploring key factors for the generation of poly(ε-caprolactone) (PCL) concentric ringed spherulites in evaporating droplets. *In situ* observation exhibits that accompanying the rhythmic evolution of the crystal, the region ahead the growth face changes periodically and the radial growth within each period is non-linear. It shows that having an evaporation-driven convection that carries liquid to the growth face drives the periodic dimple generation and rupture that leads to the rhythmic growth into discrete ringed spherulites. The non-linear growth is attributed to the coupling of evaporation and crystallization. We find that there are two key factors in the drying process that ensure the occurrence of the evaporation-driven flow and then the periodic crystal pattern. The structure formation reveals a complex interplay among solvent extraction, solution flow, solute diffusion, and crystal growth.

1. Introduction

Droplet evaporation, as a fundamental process relevant to a wide range of biological and technological applications, has attracted much interest. Bonn et al., in a recent review, described the area of evaporating drops as being a hot topic for further investigation [1]. Although easily observable, the drying process of a solution drop on a solid surface leads to surprisingly rich patterns, depending on the evaporation geometry, solute size and chemistry, and substrate–solvent interaction [2–5]. Well known are the detailed studies of the coffee stain effect that analyze the deposition and resulting structures left behind by an evaporating drop of suspensions [6]. Exploring the mechanism behind diverse patterns, controlling or suppressing the coffee-ring, and using the drying droplet as a small scale fabrication procedure or diagnostic tool are a few topics of recent developments in this area [7–10]. However, much less work has been done on the evaporation of solutions with crystallizable solutes and thus the conditions for crystallization have remained unclear [11]. Herein, we focus on exploring the generation of an unusual crystal pattern in an evaporating polymer solution droplet.

For evaporating drops with crystallizable species, crystal growth under this non-equilibrium condition can give rise to complex morphologies [12–16]. The faster the solvent extraction rate is employed, the time scale allowed for the molecular motion and crystal growth is shorter, and thus the resulting crystal pattern is expected to be different. Paranjpe reported a sequence of morphological transitions during the dehydration of aqueous ascorbic acid solutions. With the increase of the humidity from 40 to 80, crystal patterns exhibited compact circular, compact radial, density modulated circular (periodic rings), density modulated dendritic, and dense branching features, whereas the underlying mechanism for the formation of these different morphologies was not well understood [15]. Pernstich et al. observed hierarchical ringed patterns via slow evaporation of the solution of an amorphous polymer solution blended with crystallizable Krogmann's slat, and ascribed the structure occurrence to a viscosity-gradient-induced rhythmic crystallization [16]. The viscosity gradient resulted in a position-dependent diffusion coefficient and concentration gradient. Moreover, periodic ringed spherulites were also observed in poly-L-alanine upon slow solvent extraction, likewise it was suggested that the rhythmic growth is responsible

---

* Corresponding authors.
E-mail addresses: tbhe@ciac.jl.cn (T. He), wangzongbao@nbu.edu.cn (Z. Wang).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.09.023

for the pattern generation [17]. These ringed spherulites are distinct from the classical banded spherulites, in which the banded feature is an optical phenomenon of twisted lamellae [18]. In particular, similar ringed patterns were also obtained in isotactic polystyrene (iPS) and poly(bisphenol A hexane ether) (BA-C6) from melt-crystallized thin films [19,20], but the case in evaporating droplets is quite different, so that the evolution process and thus the underlying formation mechanism must be different and more complex.

Recently, we obtained poly(ε-caprolactone) (PCL) ringed spherulites with discrete feature in solution-casting thin films upon slow solvent withdrawing [21]. Despite systemically investigated the microstructure, the exact nature and evolution process of the pattern formation remain inadequate. So far, all investigators agreed that discrete ringed spherulites can be attributed to a rhythmic growth mechanism which arises from the inability of the transport process to keep up with the radial growth. However, as yet no one has elucidated the interior molecular motion, growth dynamic, essential origin, and key factors for the rhythmic growth into ringed spherulites in such drying drops to gain a better understanding of how the evaporative process and fluid mechanics impinge on the crystal growth course.

In this study, we have therefore addressed these issues in an attempt to discover the underlying mechanism governing the rhythmic growth into ringed spherulites in such evaporating droplets. We *in situ* followed the whole evolution process, and found that accompanied by rhythmic crystal growth; the front of the growing face was also varied periodically. It is the first time to our knowledge that a non-linear growth within one period of periodic pattern was directly detected. We then discussed the ring formation mechanism and finally analyzed key factors for the generation of evaporation-driven flow that drives the periodic dimple rupture and then the rhythmic growth into discrete ringed spherulites.

2. Experimental section

2.1. Materials

PCL with a weight and number average molecular weight of 1.4×10^4 and 1.0×10^4 g mol^{-1} was purchased from Aldrich Chemicals and used as received. PCL was dissolved in toluene at ambient condition to prepare solution with various concentrations.

2.2. Evaporation and crystallization procedure

The detailed drying procedure was described previously [21]. Herein, convenient for *in situ* observation, a portion of 10 μL solution was injected onto a cleaned silicon wafer placed on a stage lodged inside a weighing bottle with the radius and height of 2.0 cm and 2.5 cm at ambient conditions and extra 200 μL solvent was added in the system. The bottle was then covered with a piece of glass immediately. Under this condition, the total time for complete solvent removal and solute crystallization was about 27 h. The average evaporation rate R_e, for the solvent in solution was calculated to be ca. 3.7×10^{-4} mL h^{-1}. Many concentric ringed spherulites were produced in the resulting thin film. The whole evolution process was *in situ* followed by optical microscope (OM). Note that in this paper, unless otherwise stated, radius, radial distance and other relevant terms indicate the corresponding parameters of spherulites rather than droplet. In addition, all experiments were performed at room conditions (temperature, 18–22 °C and relative humidity, RH, 20–40%).

2.3. Equipments

OM experiments were carried out using a Carl Zeiss A2m microscope equipped with a CCD camera, and a light source in Reflectance Mode was used to collect OM images. A continuous shooting mode with a time interval of 5 or 10 s was performed to *in situ* track the whole evolution process of evaporating droplets. Atomic force microscope (AFM; PICOSCAN SPM, Molecular Imaging Inc., now Agilent 5500AFM/SPM System (Agilent Technologies)) was employed to examine the surface microstructure. Tapping mode images were obtained using silicon cantilevers (PPP-NCL, Nanosensors) with cantilever length of 225 ± 10 μm, resonance frequency of 146–236 kHz, and force constant of 21–98 N m^{-1}. Typical value for the set-point was 3–5 and scanning rate range from 0.2 to 1 Hz. Topography, phase and amplitude images were captured simultaneously. All measurements were taken under room conditions with the resolution of 512 × 512 pixels/line.

3. Result and discussion

3.1. Microstructure of ringed spherulites

Although the condition alters (Experimental section), PCL concentric ringed spherulites are again observed, and their occurrence arising from a periodic variation of thicknesses is also apparent (Fig. S1). Previously, the microstructure was mainly analyzed by TEM [21]. Here the detailed morphology is further investigated via AFM (Fig. 1 and S2). In valley there is only very few lamellae, while lamellar crystals continuously increase with the ridge growth. The lamellae propagation via screw dislocation is evident from Fig. 1c. These spherulites are in fact discrete concentric rings, and the structural discontinuity is inevitably a common feature to all ringed spherulites (Fig. S3). In other words, the structural discontinuity is the essential characteristic of these

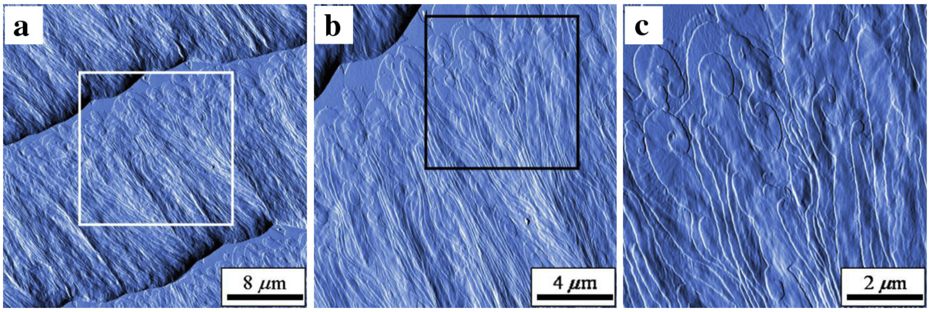

Fig. 1. AFM amplitude images showing the discrete nature and microstructure of PCL ringed spherulites formed from the evaporation of a drop of 10 mg mL^{-1} solution at a slow R_e of ca. 3.7×10^{-4} mL h^{-1} upon a silicon substrate. The corresponding height and phase pictures are given in Fig. S2, which further illustrate the construction of PCL discrete ringed spherulites.