

A HIGH THROUGHPUT APPROACH TO CRYSTALLIZATION IN THIN FILMS OF ISOTACTIC POLYSTYRENE

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Introduction

In recent years there has been a paradigm shift in the pharmaceutical industry fueled by the use of combinatorial methods of drug discovery that has accelerated the pace of marketing new products while reducing research and development costs. The vast success of this methodology has prompted its application in a host of other fields including materials science and catalysis.¹ Perhaps the most adaptable element of this method is the high-throughput screening process, which has recently been successfully applied to the characterization of several physical properties of polymeric thin films including dewetting,² and surface pattern formation in block copolymer³ and phase separating films.⁴ Here we report the extension of this method to the characterization of crystallization in thin polymer films.

The ability to direct or suppress order in polymeric thin films has many practical implications for industrial applications. In particular, the degree of crystallinity in semi-crystalline polymer films can be dramatically affected by a host of processing conditions such as solvents, thermal history, additives, etc. Developing a high-throughput method of screening these effects has the potential to quickly optimize the processing of materials, as well as probe many of the outstanding theoretical issues regarding the nature of polymer crystallization. At first glance, the gradient film technology developed at NIST presented itself as a promising solution. Concerns regarding the continuity of the films, however, prompted a general 'proof of principle' test application. Hence, isotactic polystyrene, an extensively studied, slowly crystallizing polymer, was investigated. In one continuous film, the crystal growth rates were measured as a function of temperature and film thickness, yielding data from one experiment, which previously would have required the preparation of as many as 100 or more discrete films.

Experimental

Materials. A solution of 90 % isotactic polystyrene (*ipS*) in toluene (provided as 4.5 % solids) was obtained from Scientific Polymer Products⁵ ($M_w = 6 \times 10^5$, $M_w/M_n = 3.0$).⁶ A sample of the polymer was dried in a vacuum oven at 110 °C for 48 h and the melt temperature, T_m , determined to be 218 °C using a Perkin Elmer DSC 7⁵ at a scan rate of 5 °C/min for heating and cooling. The original solution was diluted with reagent grade toluene and filtered through a 0.2 μm PTFE syringe filter before use.

Library Preparation. Silicon wafers (Polishing Corporation of America⁵) were cleaved to the desired size and cleaned using either $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ or UV radiation to generate an oxide layer followed by buffered HF etch to leave an exposed, hydrophobic Si-H layer. Each wafer was immediately fixed to a robotic stage and a 3 cm knife-edge was lowered to 200 μm above the surface at a 5° angle. An aliquot of the *ipS* solution was deposited by syringe under the knife-edge and the stage was immediately accelerated under the knife-edge to spread the solution.³ The solvent evaporated quickly leaving a thin film with a thickness proportional to the velocity. This procedure is typically referred to as "flow-coating." The range of thickness achieved depends on the viscosity of the solution as well as the velocity of the stage. Thickness was measured using a 0.5 mm spot-interferometer mounted over two orthogonal robotic stages such that a two dimensional array of points spaced from 1 mm to 2 mm apart was obtained. Figure 1 shows a typical array of points obtained by these measurements. The films were dried overnight in a vacuum oven at 100 °C, heated above the melt temperature on a hot stage at 250 °C for 3 min to 4 min and quenched to room temperature. No change in the gradient of film thickness was observed upon repeating the interferometry measurements.

Crystallization Measurements. A Nikon Optiphot-2 microscope⁵ was mounted with two orthogonal robotic stages and a preheated linear-gradient temperature stage. The *ipS* film was placed with the thickness gradient

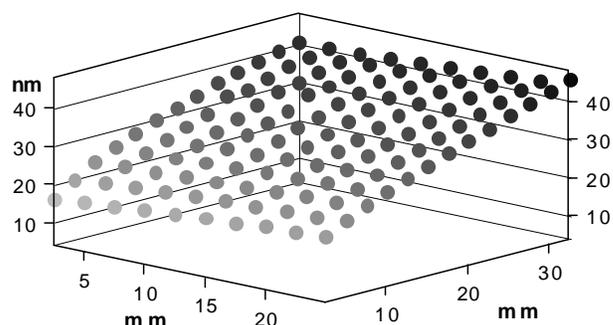


Figure 1. A two-dimensional array of film thickness (h) measured using interferometry on an *ipS* film prepared by flow-coating.

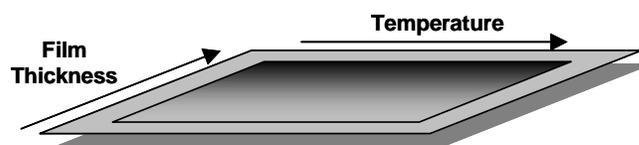


Figure 2. A schematic representation of the crystallization experiment, showing the orthogonal gradients of film thickness and temperature.

orthogonal to the temperature gradient such that the temperature of the film spanned 200 °C to 130 °C. A Kodak ES 1.0 CCD camera⁵ was used to obtain multiple arrays of optical images. The spherulite size was determined by averaging measurements of between 10 and 30 structures in each image and the standard deviation in each radius value was typically $\pm 3 \mu\text{m}$. Tapping mode atomic force microscopy (AFM; Digital Instruments Dimension 3100 Nanoscope III;⁵ 30 N/m cantilevers with silicon tips) was used to further investigate the crystal morphologies at late times, after the film had been quenched to room temperature.

Results and Discussion

Depending on the molecular weight of the polymer, the solution concentration and the velocity gradient used to flow coat, a range of thickness gradients can be obtained. A pair of two gradient films with ranges of thickness that overlapped between 12 nm and 130 nm were prepared from solutions having mass fractions of 1.0 % and 1.5 % *ipS*, respectively. Figure 2 illustrates the configuration of the experiment, with the thickness gradient placed orthogonal to the linear temperature gradient. By collecting a series of high magnification optical images (100x) at intervals of $\Delta T = 10 \text{ }^\circ\text{C}$ and Δh between 2 nm and 10 nm at time intervals, t , a library of images, each representing a point (T, h, t) was obtained. The shallow gradient in temperature ($\Delta T = 0.4 \text{ }^\circ\text{C}$) and height ($\Delta h = 0.3 \text{ nm}$) across each image was considered negligible. For all points at $h > 20 \text{ nm}$, spherulitic crystal growth was observed, in agreement with previous results.⁷ Typical optical micrographs are shown in Figure 3. The spherulite radii, r , are plotted as a function of time and representative data is shown in Figure 4.

Because *ipS* crystallizes comparatively slowly, it is possible to study the kinetics over a wide range of temperatures, from just below T_m to close to the glass transition temperature, $T_g = 100 \text{ }^\circ\text{C}$. In this case, a span of 70 °C was typically covered (from 130 °C to 200 °C), a range in which it has been shown that the rate increases as the undercooling ($T_m - T$) increases, passing through a maximum between 175 °C and 180 °C and then slowing again as the polymer approaches T_g .⁷⁻¹⁰ Good agreement was found in the high-throughput experiment on continuous films for these rates as a function of temperature. For example, at $T = 170 \text{ }^\circ\text{C}$, growth rates (G) of 0.205 $\mu\text{m}/\text{min}$ ⁷ and 0.21 $\mu\text{m}/\text{min}$ ⁹⁻¹¹ were reported previously, in discrete films fairly thick in comparison to the gradient films discussed here. Nevertheless, in our gradient films at $h = 121 \text{ nm}$ and $T = 170 \text{ }^\circ\text{C}$ we obtain, $G = 0.229 \mu\text{m}/\text{min}$ (see Table 1). Similar trends in the rate as a function of temperature were observed along uniform thickness contours, although G did not remain constant for a given T as h decreased.

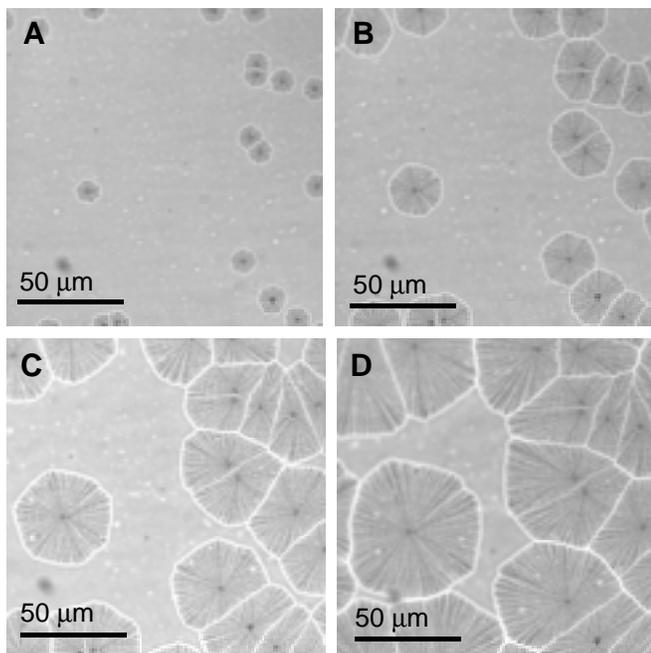


Figure 3. Optical images of ipS crystallizing at $T = 170^{\circ}\text{C}$. $h = 45$ nm, (A) $t = 21$ min, (B) $t = 51$ min, (C) $t = 96$ min and (D) $t = 146$ min.

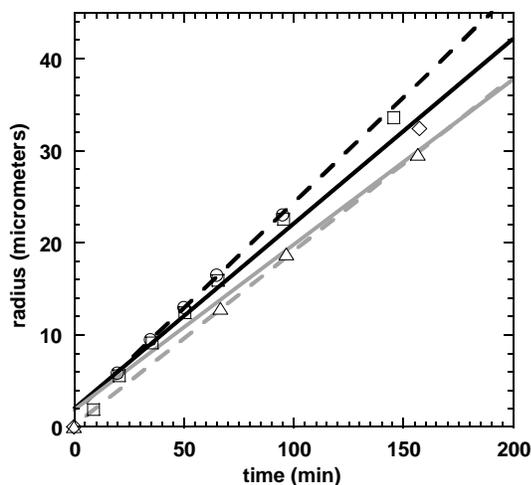


Figure 4. Spherulite size plotted as a function of time. $T = 170^{\circ}\text{C}$, $h = 121$ nm (O; black dashed line), 45 nm (□; black solid line), 31 nm (△; grey dashed line) and 22 nm (◇; grey solid line).

Sawamura, *et al.*¹² studied the effects of film thickness on the rate of crystallization in ipS thin films and reported a decrease in G when h fell below 50 nm. We observed a similar trend in the continuous films (Table 1). The rates were difficult to measure in regions of the film < 20 nm due to weak contrast in the optical images. While our data are comparable to previous studies along one axis in each dimension of the film, this method allows us to map the dependence of G as a function of each variable over an extended parameter space, as well as greatly reducing the time and material required for the experiment.

A dramatic change in crystal morphology was found as the films became sufficiently thin. AFM images collected from specimen quenched to room temperature, revealed the type of structures formed as well as the extent of crystallization at times in excess of 6 hours at T . Hexagonal, quasi-two dimensional dendrites were observed at all temperatures along height contours ≤ 15 nm. A representative example is shown in Figure 5. The nature of the transition to these structures is currently under investigation.

Table 1. Growth rate, G , measured as a function of film thickness, h .

$T (^{\circ}\text{C})$	h (nm)	G ($\mu\text{m}/\text{min}$)*
170	121	0.229 ± 0.007
170	45	0.201 ± 0.006
170	34	0.196 ± 0.009
170	22	0.179 ± 0.026

* The number following the \pm symbol is the standard deviation.

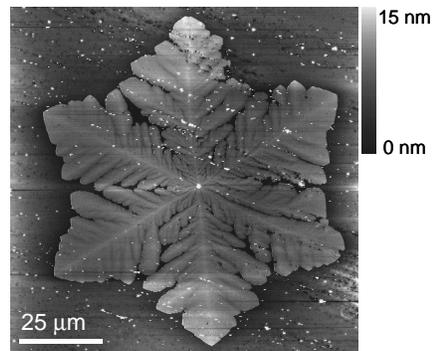


Figure 5. AFM image of the hexagonal dendrites of ipS formed in regions of the film with $h \leq 15$ nm. This particular image was obtained in a region with $T = 190^{\circ}\text{C}$ and $h = 15$ nm.

Conclusions

Crystal growth rates of isotactic polystyrene were measured as a function of temperature and film thickness on continuous gradient films. The measured rates as a function of temperature agree with those obtained previously. A decrease in G was also observed in progressively thinner regions of the film below $h = 50$ nm. These results validate the high throughput / combinatorial approach to investigating polymer crystallization in thin films, accelerating the pace of experimentation by increasing both the material and processing parameter space available for sampling. Furthermore, the dependence of G on h and T was explored in two dimensions to a degree previously considered unfeasible. Future work includes the investigation of temperature and film thickness effects on crystal morphology.

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- According to ISO 31-8 the term "molecular weight" has been replaced by "relative molecular mass", M_r . The number average molecular mass is given by M_n .
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