

# Combinatorial Approach for Studying the Effects of 4-Biphenyl Carboxylic Acid on Polypropylene Films

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The crystallization behavior of thin polypropylene films with and without 4-biphenyl carboxylic acid as a nucleating agent was investigated using high-throughput methodology in conjunction with optical microscopy. The high-throughput approach involves the use of thin films cast with a gradient in thickness, placed on a hot stage possessing a temperature gradient orthogonal to the thickness gradient. This system is used to study the effect of the nucleating agent on the morphology at different temperature and film thickness combinations. The addition of the nucleating agent, upon annealing and undercooling, results in spherulite formation 10–15 °C higher than neat crystallization temperatures and spherulite sizes an order of magnitude smaller than those of neat polypropylene. 4-Biphenyl carboxylic acid can have a significant effect on the morphology of thin polypropylene films.

## Introduction

Polypropylene, a semicrystalline polymer with a wide range of current uses and large potential for new applications such as in thin films, blends, and composites, has been extensively studied for many years. Numerous techniques, including differential scanning calorimetry,<sup>1–11</sup> optical microscopy,<sup>1–5,12</sup> scanning electron microscopy,<sup>9,13–15</sup> transmission electron microscopy,<sup>16,17</sup> and X-ray diffraction/scattering<sup>1,18–19</sup> have been used to investigate the parameters relevant to crystallization in this polymer. Other techniques, such as Raman imaging<sup>20</sup> and atomic force microscopy (AFM),<sup>17–19,21–23</sup> have supplemented the understanding of the correlation between surface and bulk

morphology (including crystallinity effects) and material properties, which are ultimately important in determining new uses.

Nucleating agents are used to influence the dynamics of crystallization in polymers such as polypropylene. These agents can affect the speed, temperature, and extent of crystallization and have a direct effect on the size of crystalline domains.<sup>3–6,8</sup> To our knowledge, the effects of one agent, 4-biphenyl carboxylic acid (C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H), on the morphology in thin polypropylene films (approximately 100 nm thick) processed at various undercooling temperatures have not yet been well-studied. Understanding these fundamental interactions would lead to more efficient use of this agent in industrial processes involving thin polypropylene films.

The evaluation of the actions of nucleating agents in thin polymer films using conventional approaches would require numerous samples and significant time expenditure to cover the various anticipated film thickness (*h*) and temperature (*T*) combinations needed to comprehensively explore the crystallization behavior of polymers (i.e., polypropylene) under these conditions. Combinatorial and high-throughput methods, however, have been developed in other disciplines to explore large experimental multiparameter spaces and have been used successfully in drug discovery, in catalyst preparation, and more recently in problems in polymer science.<sup>24–26</sup> In this report, combinatorial methodology is used to examine the effects of 4-biphenyl carboxylic acid on polypropylene film morphology as a function of (*h*) and (*T*).

## Experimental Section

The procedure used to create film libraries is outlined more extensively elsewhere;<sup>24,25</sup> the procedures specific to creating “as-cast” polypropylene samples (flow-coating) are described below. The compound 4-biphenyl carboxylic acid (BCA) was chosen as the nucleating agent in these experiments because of its efficiency as determined by Fillon et al.<sup>3</sup> Commercial isotactic polypro-

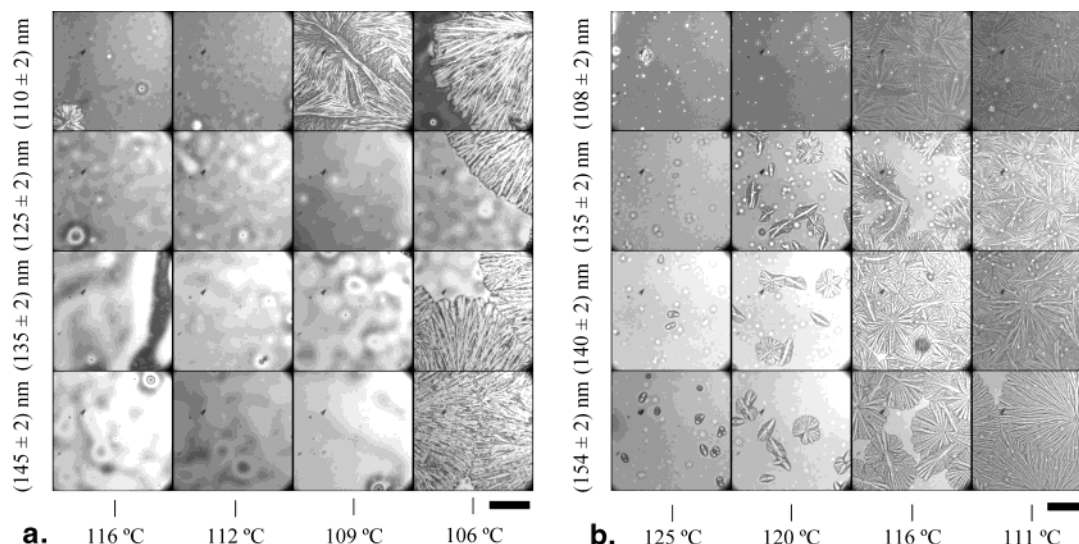
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**Figure 1.** (a) Subset of the high-throughput optical image data set of neat polypropylene undercooled at different temperatures for different thicknesses at approximately 14 min after the start of undercooling. Scale bar = 100  $\mu\text{m}$ . (b) Subset of the high-throughput optical image data set of polypropylene containing 4-biphenyl carboxylic acid undercooled at different temperatures for different thicknesses at approximately 14 min after the start of undercooling. Scale bar = 100  $\mu\text{m}$ .

polypropylene, having  $M_n = 50\,000$ ,  $M_w/M_n = 3.8$  (ref 27), and a listed melting temperature ( $T_m$ ) range between 160 and 165  $^\circ\text{C}$ , and BCA were purchased from Aldrich<sup>28</sup> and used as received. Differential scanning calorimetry confirmed the reported melting temperature for this polypropylene and determined the temperature of maximum crystallization rate (peak max) to be approximately 109  $^\circ\text{C}$ , using a heating and cooling rate of 10  $^\circ\text{C}/\text{min}$ . Solutions of 3% by mass of polypropylene in mixed xylenes were heated carefully to approximately 120  $^\circ\text{C}$  and constantly stirred to facilitate dissolution of the polymer. After establishing a modest solubility of BCA in heated mixed xylenes, solutions containing 2% by mass of BCA to polypropylene were also made as described above. Film libraries with thickness gradients ranging approximately from 50 to 150 nm were created by using a flow-coating apparatus consisting of a steel blade (roughly 30 mm wide) angled at 5 $^\circ$  and situated above a home-built constant temperature hot stage<sup>24</sup> mounted on a computer-controlled translation platform (Daedal).<sup>28</sup> Si substrates (routinely 20 mm  $\times$  30 mm in size, generated from wafers from Polishing Company of America<sup>28</sup> and piranha-etched) were individually placed onto the heating stage and brought to the casting temperature of 90  $^\circ\text{C}$ . A heated syringe was used to apply 50 mL aliquots of either hot solution rapidly to the edge of the steel blade located 300  $\mu\text{m}$  above the heated Si substrate. The substrate was immediately moved at a constant, predetermined acceleration underneath the blade edge, spreading the polymer solution to create a gradient in the desired thickness. Thickness measurements were made, after the cast films were quenched to room temperature and allowed to dry, using a Film Tek spectral reflectometer.<sup>28</sup> These measurements were made at intervals of 2 mm across the sample and agreed with AFM control measurements to within 5% (Digital, Dimension 3100).<sup>28</sup> The resulting morphology is the subject of a subsequent publication and will not be discussed here.

Optical images were taken with a Nikon Optiphot<sup>28</sup> microscope equipped with both a CCD camera (Kodak ES 1.0)<sup>28</sup> and a computer-controlled motorized translation sample stage on which a crystallization stage was mounted. The sample stage could move in two dimensions, allowing computer-synchronized data acquisition over a grid of  $h$  and  $T$  conditions. Film libraries were annealed on a constant temperature stage for 5 min at 190  $^\circ\text{C}$

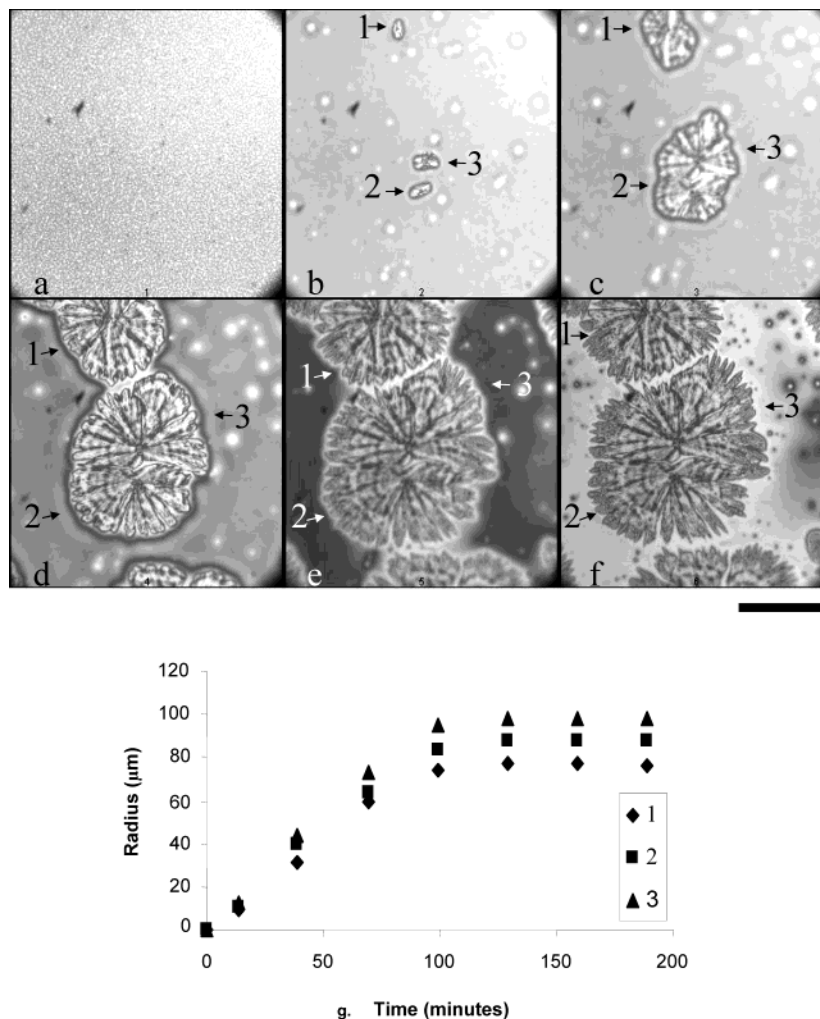
to ensure complete melting, including loss of initial structure, as observed optically under high magnification. Libraries then were placed directly onto the crystallization stage possessing a near-linear temperature gradient ranging from 100 to 150  $^\circ\text{C}$  and were oriented such that the temperature gradient was orthogonal to the thickness gradient. Images were acquired before annealing and at regular intervals after placement on the crystallization stage, allowing the evaluation of film behavior as a function of thickness and undercooling temperature with respect to time. Samples were undercooled for approximately 200 min and then quenched to room temperature. No changes in the film morphology formed during undercooling were observed upon the quench to room temperature.

## Results

Parts a and b of Figure 1 are subsets of the optical data set generated using combinatorial methodologies for neat polypropylene and polypropylene with 4-biphenyl carboxylic acid, respectively. Upon annealing and placement on the crystallization stage, the time evolution of spherulite formation in the film samples was followed as a function of thickness and undercooling temperature,  $T$ . Both montages are composed of 16 individual images, each image representing a discrete and different ( $h, T$ ) point at virtually the same undercooling time, assembled together for ease of viewing. Images along a row correspond to a region of constant thickness in the sample, with the thickness value indicated to the left of that specific row. Images along a column correspond to an isotherm, with the center value indicated at the bottom of the column. The "width" of an isotherm (column) is approximately 0.4  $^\circ\text{C}$ . The temperature gradient for the sample containing BCA is steeper in order to better monitor the expected nucleation and crystallization at higher temperatures. Though each montage is only a subset of the experimental data for the corresponding film sample, several trends along isotherms or lines of constant thickness are consistent with the entire data set and are easily visualized. It is seen readily that extent of crystallization increases with higher undercooling (lower) temperatures in both data sets, and crystallization clearly begins at higher processing temperatures in the sample containing BCA as compared to the neat sample. An isolated spherulite can be seen, for example, at 116  $^\circ\text{C}$  and 110 nm in the neat film, as compared to more extensive crystallization present

(27) According to ISO 3108, the term "molecular weight" has been replaced by "relative molecular mass,"  $M_r$ . The conventional notation has been employed here.

(28) The use of brand names is for identification purposes only. Such identification does not imply endorsement by NIST, nor does it imply the materials are necessarily the best available for the intended purpose.



**Figure 2.** (a–f) Optical images (a) before annealing and at times (b) 14, (c) 39, (d) 69, (e) 99, and (f) 129 min after placement on the gradient temperature stage. Spherulites are numbered. Scale bar = 100  $\mu\text{m}$ . (g) Size of spherulites 1, 2, and 3 in (b–f) as a function of time, at 125  $^{\circ}\text{C}$  and an initial film thickness of approximately 140 nm.

in the nucleated sample at the same temperature. Examination of the complete data sets (data not shown) at long times reveals eventual spherulite formation at temperatures as high as 133  $^{\circ}\text{C}$  for films with BCA and 121  $^{\circ}\text{C}$  in neat films, though the spherulites are isolated and sparse in these higher temperature regions. More complete crystallization is evident in the films with BCA at higher processing temperatures, as compared to the neat films. It is seen that when spherulites are formed, spherulite size is larger in neat films than in nucleated ones by up to an order of magnitude. This corresponds to a proportional increase in the number of active nucleating sites in the film containing BCA, resulting in more numerous but smaller spherulites per unit area.

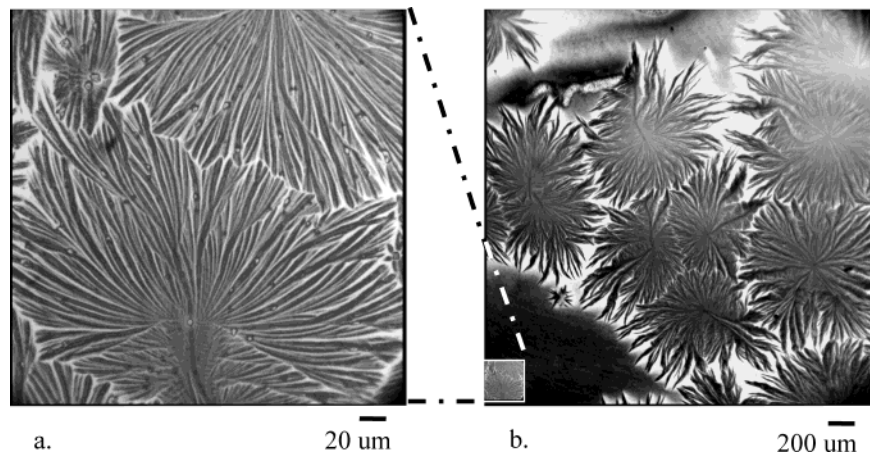
Time evolution of slices of the type shown in Figure 1 allows the investigation of the kinetics of any ( $h$ ,  $T$ ) combination within the library. For instance, images of the time evolution of the size of spherulites in the nucleated film located at  $h \approx 140$  nm and  $T \approx 125$   $^{\circ}\text{C}$  as depicted in Figure 1b are shown in Figure 2a–f. In evaluation of their growth, spherulites in the image are assumed to be approximately circular in shape and measured by drawing a “path” around the perimeter, using the software package ImageJ.<sup>28</sup> This path is equated to the circumference of a circle, from which an “effective” radius is calculated. Even when the growth fronts of spherulites impinge on each other (as is evident with spherulites 2 and 3 in Figure 2c),

a distinct boundary between the spherulites is visible under high magnification that is suitable for path determination. Initial growth occurs within the first 14 min of placement on the undercooling stage, with relatively rapid growth (measured by the increase in the radius) subsequent for roughly 100 min. The growth of the spherulites levels off around 130 min upon undercooling. As can be seen in Figure 2g, the growth rate after nucleation appears to be linear (approximately  $(1 \pm 0.1)$   $\mu\text{m}/\text{min}$ ) up to about 100 min, after which time growth dramatically slows. This is possibly due to the active growth fronts of the spherulites impinging on each other, one of the conclusions reached by Hobbs and co-workers examining polyethylene crystallization in situ and in real time with AFM.<sup>29</sup> There are also apparent disruptions of the film (thinning and ultimately dewetting) in the region surrounding the spherulites at longer times, which could hinder further lateral growth.

Figure 3a,b depicts the optical micrographs acquired at 190 min of polypropylene spherulites with and without BCA for similar initial film thicknesses of 90 nm and higher crystallization temperatures of around 118  $^{\circ}\text{C}$ . The spherulites found in the neat polypropylene films ranged in sizes from 400  $\mu\text{m}$  to over 1.2 mm in diameter, somewhat

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**Figure 3.** Comparison of spherulite sizes for the nucleated (a) and neat (b) polypropylene films after undercooling for 190 min at roughly 118 °C; (a) is scaled as an inset in (b). The film thickness is approximately 90 nm.

similar to the findings in ref 23. Though some spherulites in the film samples containing BCA were as large as 300  $\mu\text{m}$  in diameter, typically they were less than 100  $\mu\text{m}$  in diameter, or about an order of magnitude smaller in size when compared to the neat samples (demonstrated by Figure 3a scaled as an inset in Figure 3b). Additionally, the spherulites in the nucleated films were found to be more uniform in size and shape.

In a comparison of the two samples throughout their respective parameter spaces, there was clearly a vast difference in morphologies at almost all ( $h$ ,  $T$ ) points. These findings are in general agreement with those for several different nucleating agents of polypropylene determined in the traditional one-sample, one-experiment approach: an increase in crystallization temperature by roughly 10–15 °C, a definitive decrease in spherulite size by at least a factor of 2 and as much as an order of magnitude, and a narrower distribution of spherulite sizes at higher undercooling temperatures.<sup>4,5,8</sup>

### Conclusions

The combinatorial approach is an excellent method of characterizing the effectiveness of 4-biphenyl carboxylic acid as a nucleating agent for polypropylene thin films. The evolution of the morphological changes induced by the presence of the nucleating agent within the film was followed as a function of film thickness and undercooling temperature. Further results from this combinatorial study, including the onset of dewetting at long times, will be discussed more extensively in following publications. This methodology, having an inherent flexibility of experimental design for probing requisite parameter space, should be applicable to the study of nucleating agents in other polymer films as well.

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