Research Article

Interfacial Effects on the Spherulitic Morphology of Isotactic Polystyrene Thin Films on Liquid Substrates

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The influence of interfaces on the morphology of flat spherulites of isotactic polystyrene (iPS) grown in thin films on liquid substrates was investigated. Amorphous iPS thin films spin-cast from a solution were annealed for cold crystallization on glycerol and silicone oil (nonsolvents for iPS). The number density of grown spherulites was revealed to be higher on the glycerol substrate than on the silicone oil substrate. This implies that the primary nucleation rate of crystallization is greater at the iPS/glycerol interface than at the iPS/silicone oil interface. The results may be consistent with the previous findings that concern the molecular interaction between atactic polystyrene and nonsolvents at the interface. In some cases, holes were formed in the thin films during the cold crystallization due to dewetting, which also significantly affect the spherulite morphology via, for example, transcrystallization.

1. Introduction

Since anomalous dynamics of nanosized polymer materials was reported, growing interest is focused on polymer thin films of which the thickness is typically smaller than 100 nm [1–3]. The origin of the dynamical properties (such as glass transition) of nanosized polymers that are different from bulk ones is still unclear. However, there is considerable evidence that the surface (interface) of the materials plays an important role [3]. The interfacial effects are emphasized as the size of the material becomes small. This is also the case for polymer crystallization behaviors, where the nucleation event that controls the crystallization rate and resulting morphology is very susceptible to the material's interfacial feature [4]. It is most likely that crystallization in thin films mainly occurs via heterogeneous nucleation, and the interfacial effects on the crystallization behaviors are closely related to the nucleation process at the interface.

The effects of the interface on polymer crystallization may be interpreted in principle, in terms of surface energetics and rheological properties. However, it seems to still be a long road to complete elucidation of the mechanism of the interfacial influence based on detailed molecular interactions. This

issue is essentially important to develop nucleating reagents for polymer crystallization to achieve desired thermal and mechanical properties.

Crystallization in thin polymer films is considered to proceed in a quasi-two-dimensional manner; in particular, at high supercoolings, flat crystallites or spherulites frequently grow, reflecting the geometry of the substrate that supports the film. For example, crystallites composed of flat-on lamellae were found to grow in ultrathin films of poly(ε-caprolactone) [5]. A branching morphology of a flat-on lamellar crystal was observed for isotactic polystyrene (iPS) in an ultrathin film with a thickness of 11 nm [6]. On the other hand, depletion-induced banding has been reported for melt-grown iPS in thin films with a thickness of <100 nm [7]. Poly(ethylene oxide) (PEO) exhibits a finger-like crystalline morphology in dewetting holes where very thin polymer layers still remain even after the dewetting [8–10]. This characteristic finger-like morphology observed for ultrathin layers is considered to occur via a diffusion-controlled growth mechanism. An apparent surface effect on the rate of crystallization was reported for porous poly(L-lactic acid) (PLLA) prepared through freeze-drying [11, 12]. The overall crystallization rate is raised as the specific surface area of

the porous PLLA increases. The enhanced crystallization rate is at least partially relevant to the large surface area of the porous PLLA. It has also been reported recently that the crystallization is activated at air/PLLA interface [13].

Dewetting is frequently observed when a polymer ultrathin film undergoes crystallization on a substrate [4], which is governed by the mechanical properties of the polymer film as well as the polymer/substrate interfacial free energy. On a liquid substrate of a nonsolvent, dewetting tends to become remarkable: the polymer film on the liquid shrinks when heated above its glass transition temperature (T_g), which can provide a simple method to measure T_g of a polymer thin film [14–16]. When a crystallizable polymer thin film is annealed on a liquid substrate, both shrinkage and crystallization are expected to occur. In this case, the shrinkage can significantly affect the crystallization behaviors, which are expected to give rise to characteristic crystalline morphologies. For some cases, the shrinkage induces hole formation in thin films, which act as a nucleation promoter for crystallization.

In this study, we examine the morphology of iPS spherulites grown via cold crystallization in ultrathin films. iPS is a typical polymer that has been reported to exhibit characteristic crystalline morphologies in thin films under various conditions [6, 7, 17, 18]. Here we employ for the first time liquid substrates, that is, silicone oil and glycerol; these are nonsolvent for iPS. The iPS thin films with a thickness of 35 nm were prepared through spin-casting, and they were annealed for cold crystallization on the liquid substrates to investigate the interfacial effects on the crystalline morphology in thin films.

2. Materials and Methods

iPS was purchased from Scientific Polymer Products Inc. (M_w = 400,000, triad tacticity 90%) and was used without further purification. Silicone oil (Sigma-Aldrich Inc. #175633) was used as received. Spin-casting was performed to prepare the iPS thin films: iPS was dissolved in cyclohexanone at 150°C for 30 min with stirring to obtain a solution of 0.63 wt% iPS content. After filtration of the solution, spin-cast films were prepared at 2,000 rpm for 10 s on a clean glass substrate (SiO$_2$). The thickness of the obtained films was estimated to be 35 nm from transmission electron microscopy (TEM) by using a Jeol JEM-2100 operated at 200 kV (the specimens were obliquely shadowed with Au). We confirmed that the above thickness was consistent with that from the ellipsometry measurement, which was performed by using an Otsuka Electronics FE-5000. For cold crystallization experiments on liquid substrates, the iPS thin film was peeled off the glass substrate by immersing the specimen into water. The peeled film floating on water was then moved carefully onto glycerol (liquid substrate) by using a handmade wire mesh. Then the film floating on glycerol was covered with a small amount (less than 1.0 mL) of another liquid (silicone oil or glycerol), or with no liquid (air). Schematics of the film on these liquid substrates are shown in Figure 1. As the sample has an iPS/SiO$_2$ interface, we used spin-cast films without pealing.
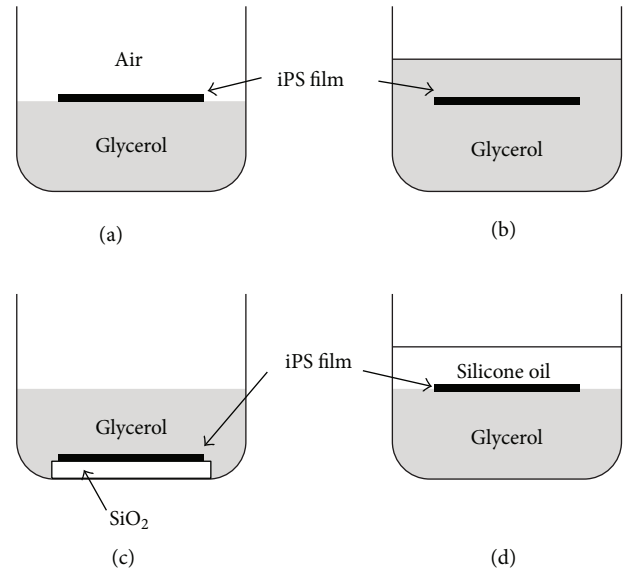

Figure 1: Schematics of the iPS film possessing polymer/liquid interfaces; (a) air/iPS/glycerol, (b) glycerol/iPS/glycerol, (c) glycerol/iPS/SiO$_2$, and (d) silicone oil/iPS/glycerol.
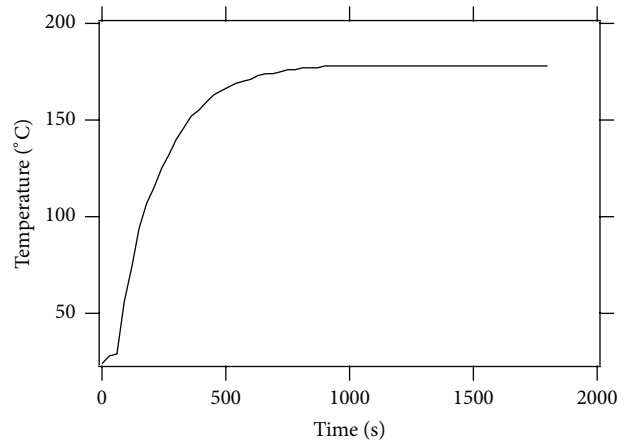

Figure 2: Typical profile of sample temperature versus time during the heating for cold crystallization. Here the final crystallization temperature $T_{c,f}$ was found to be 178°C.

The thin iPS films on various substrates thus prepared were subject to heating up to a final crystallization temperature $T_{c,f}$ of 160–178°C in an oil heating bath. The time-evolution of the sample temperature during the heating for crystallization ($T_{c,f}$ = 178°C) is shown in Figure 2; there was a rather long period for temperature raising; that is, the annealing was not isothermal. Similar profiles were observed for $T_{c,f}$ = 160–178°C. The gradual temperature rising was unavoidable because of a large heat capacity of the oil bath. The typical size of the liquid substrate was 10 g. The crystallized thin film was moved onto a microgrid covered with an elastic carbon layer for TEM observation. Here, we also prepared specimens with the film being upside down for the samples possessing two different interfaces, that is, air/iPS/glycerol,
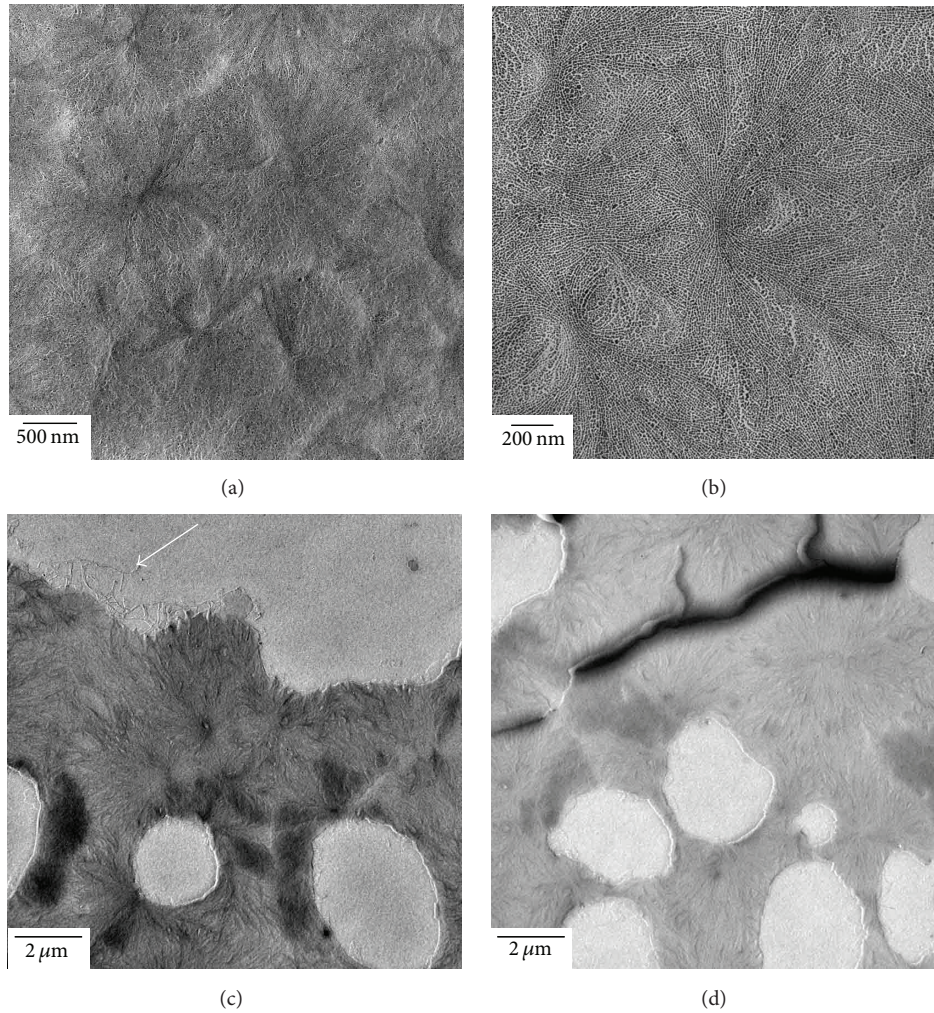
(a)

(b)

(c)

(d)

FIGURE 3: TEM images of iPS thin films crystallized via a temperature profile with $T_{c,f}$ = 160˚C (a and b) and 178˚C (c and d) on glycerol substrates (air/iPS/glycerol). A fibril-like texture is seen outside the edge of the film, as indicated by the arrow in (c).

glycerol/iPS/SiO$_2$, and silicone oil/iPS/glycerol. The specimen was dried under vacuum for several hours at room temperature. Finally, the upper surface of the specimen was shadowed with Au for the TEM observation.

3. Results and Discussion

We confirmed from the TEM observation that spin-cast iPS film without annealing is homogeneously flat and it does not exhibit any signs of crystallization nor holes due to dewetting. Therefore, the morphologies of annealed films described below were formed via cold crystallization on annealing. Figure 3 shows TEM images of iPS thin films crystallized on glycerol substrate (air/iPS/glycerol). We found that the films crystallized via a temperature profile of $T_{c,f}$ = 160˚C are wholly packed with flat spherulites (Figures 3(a) and 3(b)), which have grown in an almost two-dimensional manner. In the case of $T_{c,f}$ = 178˚C, on the other hand, we observed holes of several μm in size in the film, which resulted from

dewetting (Figures 3(c) and 3(d)). In some of the holes, fibril-like morphology was observed as indicated by an arrow in Figure 3(c). This texture was considered to be formed on glycerol surface on annealing: after the formation of the hole, a very thin layer of iPS still remains on the dewetted surface of glycerol (pseudo-dewetting), which underwent crystallization to form thin crystallites. A similar behavior has been reported for PEO thin layers on silicone substrates, where finger-like branched structures are formed [8, 9]. The present thin texture that formed in the hole is composed of thin curved wires rather than a finger-like structure. Similar morphology of curved array that consists of lamellae has been reported to occur from the edge of a crystalline sheaf for melt-grown iPS crystallites [17].

Figure 4 shows TEM images of iPS thin films of which both sides contacted with glycerol on crystallization (glycerol/iPS/glycerol). The film exhibited a greater number density of spherulites than that of air/iPS/glycerol as shown in Table 1. This suggests that the primary nucleation is promoted at the iPS/glycerol interface compared with the
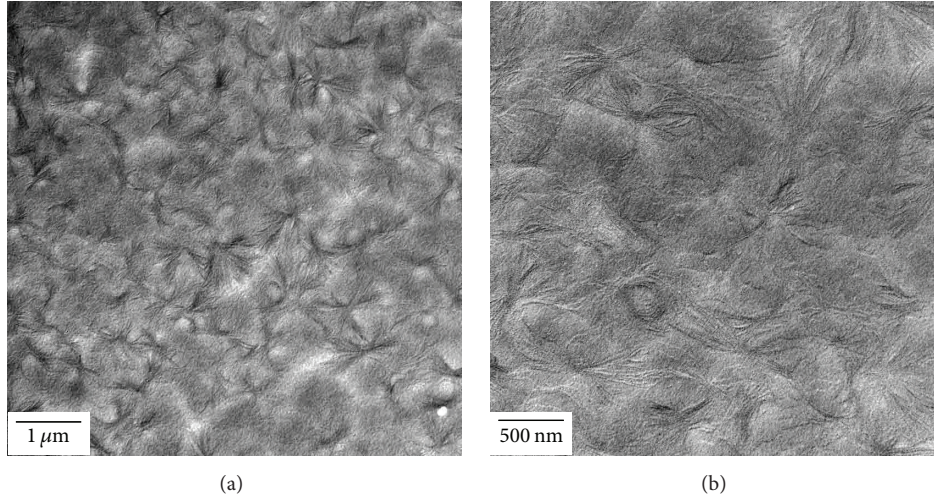
(a)

(b)

FIGURE 4: TEM images of an iPS thin film crystallized with both sides contacted with glycerol (glycerol/iPS/glycerol). The final crystallization temperature $T_{c,f}$ was 178°C.

(a)

(b)

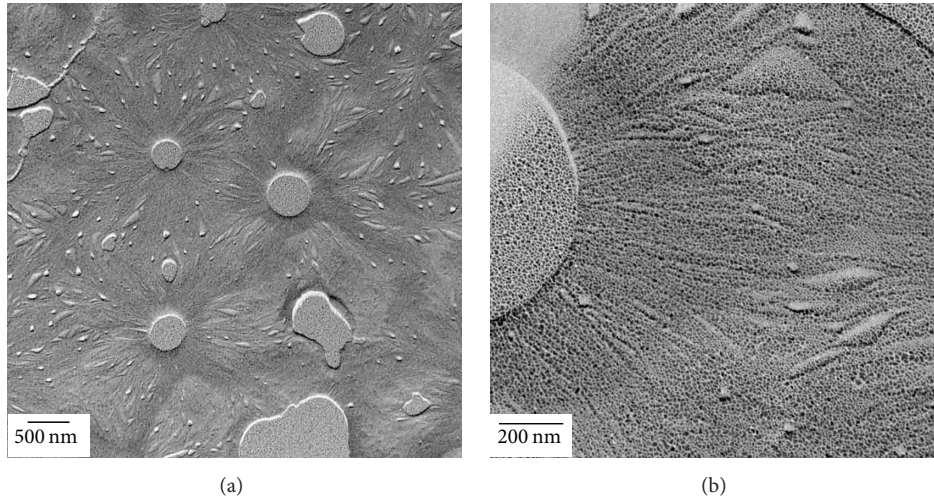FIGURE 5: TEM images of an iPS thin film crystallized between glycerol and SiO$_2$ substrates (glycerol/iPS/SiO$_2$). The final crystallization temperature $T_{c,f}$ was 178°C.

TABLE 1: Number density of spherulites n for $T_{c,f} = 178$°C.

Interfaces	$n/\mu m^{-2}$
Air/iPS/glycerol	0.15
Glycerol/iPS/glycerol	1.8
Glycerol/iPS/SiO$_2$	0.38
Silicone oil/iPS/glycerol	0.024

air/iPS interface; that is, glycerol tends to promote the primary nucleation of iPS crystal. It is also noted that no hole formation occurred in this glycerol/iPS/glycerol thin film on crystallization; this suggests that shrinkage as a whole occurs rapidly in viscous glycerol rather than forming small holes that could act as nuclei of hole formation. Furthermore, it may be considered that, for the glycerol/iPS/glycerol system, the primary nucleation is activated on both sides of the iPS film by glycerol, leading to an enhanced crystallization rate. As a result, the film becomes rigid before the hole formation starts to occur via dewetting.

Figure 5 shows TEM images of the film crystallized between the glycerol and SiO$_2$ substrate (glycerol/iPS/SiO$_2$). Here again, holes due to dewetting are observed. In this system, the iPS film is attached to the solid substrate which prevents shrinking as a whole; as a result, small holes are sporadically formed. The size of the holes was less than $1\,\mu m$, which is smaller than those for the air/iPS/glycerol system. This may be due to a stronger adhesion to the iPS/SiO$_2$ interface, which limits the growth of the hole. In addition, it has been reported that the relaxation of polystyrene chains at an SiO$_2$ interface is rather hindered [19]. We should also note
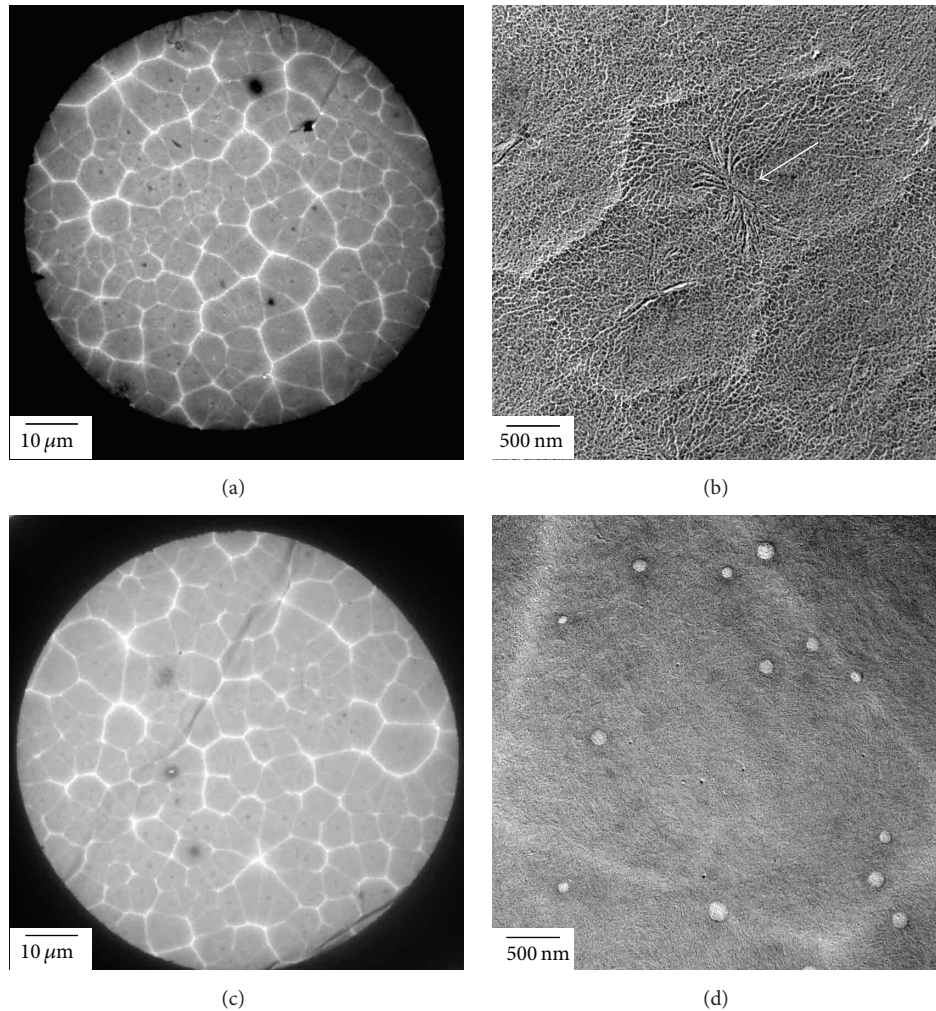
(a)

(b)

(c)

(d)

FIGURE 6: TEM images of iPS thin films crystallized between silicone oil and glycerol (silicone oil/iPS/glycerol); Au was deposited on the side that contacted with glycerol (a and b) and with silicone oil (c and d). The final crystallization temperature $T_{c,f}$ was 178°C. The arrow in panel (b) indicates a texture of dominant lamellae.

the lamellae that have grown in the direction perpendicular to the contour of the hole (transcrystallization). This suggests that the primary nucleation preferentially occurs at the edge of the hole. This indicates that the formation of the holes due to dewetting occurs first, and then the crystallization starts. The number density of the spherulites for glycerol/iPS/SiO$_2$ is smaller than that for glycerol/iPS/glycerol, while it is greater than that for air/iPS/glycerol (Table 1). The former result probably indicates that SiO$_2$ has a weaker tendency to activate the nucleation than glycerol. The latter may be due to the holes that provide nucleation sites for transcrystallization, which leads to a greater number of spherulites. The air/iPS/glycerol system also exhibits holes, but no morphological signs of transcrystallization were observed at the hole edge.

The tendency of preferential nucleation at the iPS/glycerol interface was further confirmed by the morphology of the crystallized film between silicone oil and glycerol (silicone oil/iPS/glycerol). Figure 6 shows TEM images of the thin films of silicone oil/iPS/glycerol. The film was wholly packed with impinged spherulites, and no holes due to dewetting were observed. Au shadowing was executed on the side contacted with glycerol (Figures 6(a) and 6(b)) and on the opposite (silicone oil) side (Figures 6(c) and 6(d)). The average size of the spherulites was almost the same for the images observed on both sides, which implies that the spherulites are flat and penetrate from one side to the other. However, we found a detailed difference between the textures on the two sides: on the glycerol side, a fine texture of initial dominant lamellae is seen in the center part of the spherulite, which formed at an early stage of crystallization, as indicated by an arrow in Figure 6(b), whereas no such texture is observed on the silicone oil side (Figure 6(d)). This again indicates that the primary nucleation preferentially occurs at the glycerol interface, suggesting that glycerol has a strong tendency to activate the primary nucleation compared with silicone oil.

Dewetting behavior is mainly governed by the balance of interfacial force. Zisman's critical surface tension γ_c serves as a criterion of wettability of liquid to a substrate [20, 21]. When
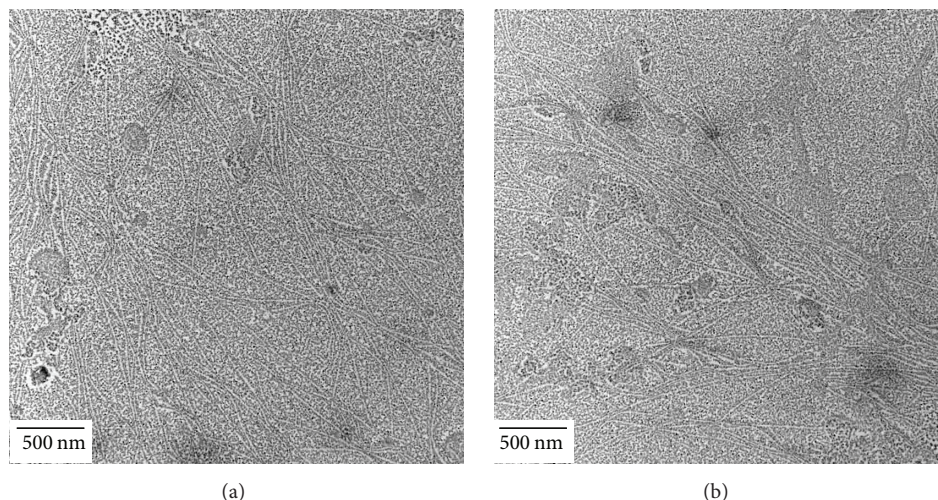
(a)   (b)

FIGURE 7: TEM images of an iPS thin film crystallized on SiO$_2$ substrate (air/iPS/SiO$_2$). The final crystallization temperature $T_{c,f}$ was 178°C.

a surface tension γ of a liquid is greater than γ_c, dewetting is expected to occur. The critical surface tension of wetting for polystyrene was estimated to be 33 mN m^{-1} [21], while γ (glycerol) = 63.3 mN m^{-1} and γ (silicone oil) = 14.6 mN m^{-1} at 25°C. Thus, glycerol is considered to promote the dewetting of iPS film, while silicone oil wets polystyrene. We estimated the interfacial free energy at 25°C for glycerol/iPS and silicone oil/iPS interfaces to be 35.4 and 14.7 mN m^{-1}, respectively, while the surface tension of polystyrene is 40.7 mN m^{-1} at 25°C (this is not equal to γ_c). Hole formations due to dewetting were observed for the systems of air/iPS/glycerol and glycerol/iPS/SiO$_2$; in these systems, glycerol plays a role in promoting the hole formation. In contrast, no holes formed for the system of silicone oil/iPS/glycerol; in this case, dewetting itself may be suppressed by silicone oil.

As for the system of air/iPS/SiO$_2$, only branched lamellar textures formed on annealing at 178°C, but no mature spherulites were observed as shown in Figure 7. We found no hole formation. In this system, the iPS layer seems to be strongly attached to the glass substrate as reported in [19] so that dewetting is inhibited. As a result the polymer layer is forced to retain the original geometry of a thin film. In such a confined system, lamellar growth in the direction normal to the film surface is rather limited, which results in the incomplete formation of spherulite.

We now discuss the origin of the observed interfacial effects on the primary nucleation described above. We speculate that the primary nucleation preferentially occurs at the interface of the iPS film; that is, the substrate acts as a nucleating reagent. The size of critical nucleus depends on the surface free energy [22]. This is smaller for a nucleation at an interface (phase boundary) than that in a bulk polymer phase because the increment of interfacial area due to nucleation is smaller for the former. It has been evidenced that the contacting phase material (solid, nonsolvent liquid, or air) significantly influences the conformational local structure of

atactic polystyrene at the interface [23–28]. The orientation of the phenyl groups of polystyrene has been reported to be dependent on the hydrophobicity and surface free energy of the substrate. In particular, a tilted orientation of the phenyl group has been revealed for hydrophobic liquids and air, whereas a flat orientation has been observed for hydrogen bonding liquids such as water and glycerol due to a phenyl π-hydrogen bond interaction [27]. The flat arrangement of the phenyls might lead to efficient chain packing such as 3/1 helix of iPS crystal [29], which promotes the primary nucleation.

In contrast, the present result shows that silicone oil is less active in promoting the nucleation than glycerol (Figure 6). The number density of spherulites for the silicone oil/iPS/glycerol system was found to be very small compared with the glycerol/iPS/glycerol system (Table 1). This suggests that the silicone oil/iPS interface is extremely unfavorable for the primary nucleation. It has been revealed that hydrophobic liquids, such as hexane, form a diffuse boundary on the polystyrene surface (surface swelling) [28]. In the present study, hydrophobic silicone oil may behave similarly as a surface plasticizer. The nanoscaled surface swelling may lower the equilibrium melting temperature, which leads to a reduction of the degree of supercooling ΔT. According to a standard nucleation theory [22], the rate of nucleation depends strongly on ΔT; that is, the nucleation rate is proportional to $\exp\left[-A/(\Delta T)^2\right]$, where A is a constant. This means that even a small decrease in ΔT induces a noticeable reduction in the nucleation rate. Thus it is likely that even the nanoscaled surface swelling can suppress the nucleation behavior as far as the nucleation occurs at the interface. Furthermore, we obtained consistent results of a greater crystallization rate at the iPS/glycerol interface than at the iPS/silicone oil interface from chip nanocalorimetry measurements (the method has been developed for the thermal analysis of nanosized materials [30, 31]). The details of this study will be reported in a separate paper.

4. Conclusions

In this paper, we demonstrated pronounced effects of interface on the morphology of the spherulites grown in iPS ultrathin films possessing interfaces with liquids. A strong tendency of promoting the primary nucleation of iPS crystallization at the glycerol/iPS interface was found, whereas the nucleation was shown to be unfavorable at the silicone oil/iPS interface. This may be attributed to a specific interaction between the hydroxyl groups of glycerol and the phenyl groups of iPS, as proposed in [27]. Hole formation due to dewetting was observed for the thin films of air/iPS/glycerol and glycerol/iPS/SiO$_2$, while no holes were found for those of glycerol/iPS/glycerol and silicone oil/iPS/glycerol. In the former case, the holes significantly affect the crystalline morphology: a fibril-like texture in the hole was seen for air/iPS/glycerol, and a transcrystallization morphology near the edge of the hole was observed for glycerol/iPS/SiO$_2$. To elucidate further the effect of molecular interactions at the interface on polymer crystallization process, experiments are to be carried out for variety of polymers and liquid substrates that possess specific functional groups.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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