

A REAL-TIME AFM STUDY ON CRYSTAL NUCLEATION AND GROWTH IN NANODROPLETS OF ISOTACTIC POLYPROPYLENE*

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Abstract Isotactic polypropylene (*i*PP) nanodroplets were prepared by using the classical droplet method in this study. The formation of nanodroplets allowed the controlled observation of polymer nucleation as well as access to crystal growth at exceptionally high supercooling in *i*PP. Three cases including the heterogeneous nucleation and fast crystallization in *i*PP droplets, the formation of multiple independent homogeneous nuclei within a single droplet and a single nucleus within a single droplet were detected by using atomic force microscopy (AFM) during gradually cooling after remelting the nanodroplets. Moreover, it is found that when the volume of droplet is larger than the value of *ca.* 130000 nm³, the first case was observed. Otherwise, the latter two cases appeared. The temperature at which the onset of nucleation was observed in individual droplets was found to be mainly dependent on height of the droplets when the size scale of the droplet is comparable to the size of the critical nucleus in at least one dimension, which indicates the nucleation behavior under confinement.

Keywords: Atomic force microscopy (AFM); Isotactic polypropylene (*i*PP); Nanodroplets; Homogeneous nucleation.

INTRODUCTION

Crystallization of polymers provides not only stable nano-scale structures, but also anisotropies of electrical conductivity, mechanical strength and optical dichroism *etc.* Therefore, understanding the crystallization behavior of polymers under nano-confinement is of essential importance in the fabrication of functional nanostructures involving crystalline polymers.

Crystallization behaviors of polymeric materials are characterized by primary nucleation and crystal growth rates. There are two types of primary nucleation: homogeneous and heterogeneous nucleation. Homogeneous nucleation can be defined by spontaneous aggregation of polymer molecules to form a three-dimensional nucleus, which must be above a certain critical size below the melting point. Above this size, the nucleation occurs sporadically. In heterogeneous nucleation, nucleation sites pre-exist in a sample and are activated instantaneously or sporadically with an induction time. These sites can be related to impurities in a bulk sample, a substrate surface, and some crystal fragments in the melt.

The difficulty in studying crystal nucleation is that it is not easily accessible in bulk measurements. That is, it is not easy to separate the process between nucleation and growth. However, the division of semi-crystalline polymeric material into small domains is an effective tool for studying crystal nucleation. If the number of domains is larger than the number of defects, then some of the domains must nucleate *via* a homogeneous

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nucleation event. Researchers have achieved such samples through a number of methods, including polymer droplets dispersed in immiscible matrices^[1, 2], droplets sprayed on slides^[3], phase-separated block copolymers^[4, 5], alumina nanopores^[6, 7] and dewetted polymer droplets^[8–13]. Massa *et al.*^[8] studied the nucleation mechanism within discrete droplets of poly(ethylene oxide) (PEO) that are formed by the dewetting of a thin film on an unfavourable substrate using optical microscopy. Both heterogeneous and homogeneous nucleations were observed in a single sample. In their later study^[11] it is proven that for the highly supercooled systems, the formation of a nucleus is influenced by its immediate surroundings and does not depend on the entire length of the constituent chains. Namely, nucleation was independent of chain length for PEO with two different molecular weights. Although researchers observed the homogeneous nucleation of PEO, the droplet volumes are in the range of 10^{-4} down to $10^2 \mu\text{m}^3$, and only the stacked lamellae were clearly shown within droplets. Later, the crystallization behavior in nanodroplets of *i*PP formed by “droplet method”^[8–13] was investigated using temperature-controlled atomic force microscopy (AFM). Homogeneous nucleation in nanodroplets of *i*PP could be found at supercooling of almost 125 °C, which signified crystal growth in the smectic form^[14]. In parallel to extensive experimental investigations, a series of dynamic Monte Carlo simulations on polymer crystallization confined in nanodroplets, consisting of homopolymers, was performed. It is observed that with the decrease of droplet size, both initiation and evolution of crystallization inside droplets become slower. A strong edge-on preference of crystal orientations occurs at interfaces. And the nucleation rate for pancake-like droplets depends on both the thickness and the volume of these droplets^[12].

Recently, Carvalho *et al.*^[14] investigated the role of the interface in inducing crystal nucleation by using isotactic polystyrene (*i*-PS) as a substrate for PEO droplets, rather than smooth amorphous atactic PS. It is shown that the nucleation probability changes from being volume, to surface, then to line dependent by tuning the property of substrate. Therefore, changing the substrate-droplet interface properties would result in nucleation occurring within the bulk, the surface, or the three-phase contact line of the droplet. Subsequently, in their later paper^[15], the process of crystal nucleation in a system of dewetted polyethylene (PE) droplets was detected. It is found that the nucleation is a surface-driven mechanism for droplets of PE on a PS substrate.

Above-mentioned studies demonstrated that the nucleation mechanism under confinement is not completely clear yet. Therefore, gaining new insights at the molecular level into the formation of the primary nucleus and its growth is imperative in order to understand fully the mechanisms that govern crystallization. For the previous studies of polymer nucleation using the “droplet method”, the smallest volume of droplets reaches 4800 nm^3 , and the smallest height approaches 0.5 nm under the experimental situation. Moreover, the phase transformation from the smectic to α -form in nanodroplets has been observed by AFM^[14]. However, the questions still remain as to when the size scale of droplets is comparable to the critical nucleus size in at least one dimension whether the nucleation mechanism in such small droplets would be changed from bulk to confinement. And as the size scale of the droplet approaches the critical nucleus size in one dimension, whether the crystallization within *i*PP droplets was completely suppressed just like the crystallization behavior of *i*PP under hard confinement of nanoporous aluminum oxide (AAO) with diameters of 20 nm and below^[7]. All the answers to these questions would be found in this article, in which the crystallization behavior of *i*PP nanodroplets with volume ranging from 1300 nm^3 to 710000 nm^3 is investigated in detail.

EXPERIMENTAL

In this study, two kinds of *i*PP samples with M_w of 12000 and 190000, respectively, from Sigma-Aldrich were used as received. It was dissolved at a concentration of 0.1 mg/mL in *p*-xylene at 110 °C, and 120 °C for M_w of 12000 and 190000, respectively. The hot solution was dropped onto a silicon wafer, spinning at the rate of 2500 r/min for a time period of 30 s. The thin film obtained was dried at ambient temperature for 12 h, followed by drying in vacuum at 60 °C for 24 h. Subsequently, the film was annealed for 10 min at 210 °C in a nitrogen atmosphere on a Linkam hot stage to allow dewetting into isolated droplets and then cooled to room temperature. The dewetted *i*PP droplets obtained on annealing were examined at various temperatures during cooling after remelting at 200 °C in a nitrogen atmosphere. The molten sample was quenched by transferring it to a hot stage

that was preheated to 60 °C and kept under the AFM scanner, and then was slowly cooled down from the melt while imaging with the AFM.

Tapping-mode AFM observations were performed by using a NanoScope III MultiMode AFM (Digital Instruments). Both height and phase images were recorded simultaneously during scanning. The height and phase images were flattened using AFM software to eliminate the height error from the sample. The resonant frequency and the force constant of the probe are about 280 kHz and 34 N·m⁻¹, respectively.

RESULTS AND DISCUSSION

Morphology of Nanodroplets of iPP at Different Conditions

In order to observe homogeneous nucleation and crystal growth in small confined volumes, the droplets were formed on the silicon wafer by a dewetting mechanism^[8–14]. Figure 1(a) shows the AFM height images of *i*PP nanodroplets formed on the surface of silicon after melting at 200 °C and then cooling to room temperature, the scan range is of 20 μm × 20 μm. And Fig. 1(b) gives a closer view of the *i*PP nanodroplets. It can be seen that a range of polymer droplets with different sizes is apparent. The diameter is from tens of nanometers to hundreds of nanometers, and the height is in range of few nanometers to more than ten nanometers. The broad distribution of droplet diameter and height facilitates the measurement of the dependence of the nucleation temperature on the length scale of the droplets.

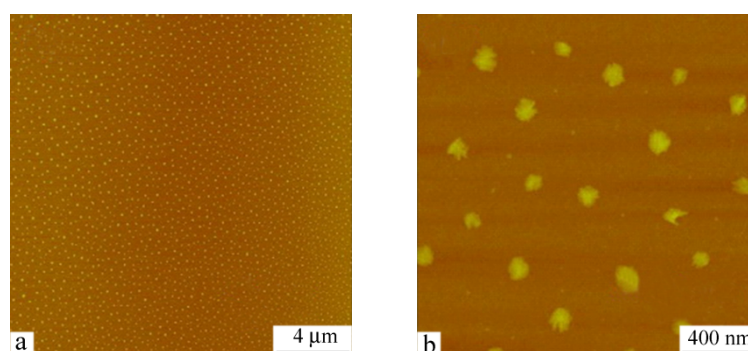


Fig. 1 AFM height images showing the dewetted *i*PP ($M_w = 190000$) film on silicon wafers: (a) the scan range, 10 μm × 10 μm and (b) a closer view of the isolated *i*PP droplets, scan range is 2 μm × 2 μm

Figure 2 gives the AFM height (left) and phase (right) images which show the crystal morphology of *i*PP droplets formed at two different conditions with one quenched into room temperature and the other into liquid nitrogen. In these phase images, the amorphous areas appear as dark and the crystallized ones as bright areas. For the first condition, as shown in Figs. 2(a) and 2(b), the morphology of lamellae and many granules were detected within droplets after remelting the *i*PP droplets at 200 °C and subsequently quenching into room temperature. For this case, the droplets have diameter of more than 200 nm and height of about 8 nm. Figures 2(c) and 2(d) present the second case and it shows that for the large *i*PP droplets with diameter of more than 200 nm and height of about 8 nm, and the small ones with diameter of 20–40 nm and height of 3–5 nm, both of them can crystallize after remelting at 200 °C and subsequently quenching into liquid nitrogen. It is easy to see that a lot of small granules were formed within the large droplets after quenching. Although not very clear, few lamellae can be still observed from the height image, as marked by white arrows. Moreover, in the corresponding phase image, from an enlarged droplet it can be found that the lamellae seemed to be made up of the small granules. However, the contrast between the amorphous and crystalline phase is not very striking. The reason is that probably the crystals formed in such a high supercooling have more defects and lower crystallinity. In addition, one can see that the crystal morphology formed by quenching into liquid nitrogen is very coarse compared to that of quenching at room temperature. Furthermore, it is interesting to note that the morphology of granules formed within the large droplets presented in Figs. 2(c) and 2(d) is similar to that of quenched mesomorphic *i*PP

film with tens of micrometer in thickness^[16]. Therefore, it can be concluded that the cooling medium can efficiently affect the crystal morphology of *i*PP nanodroplets.

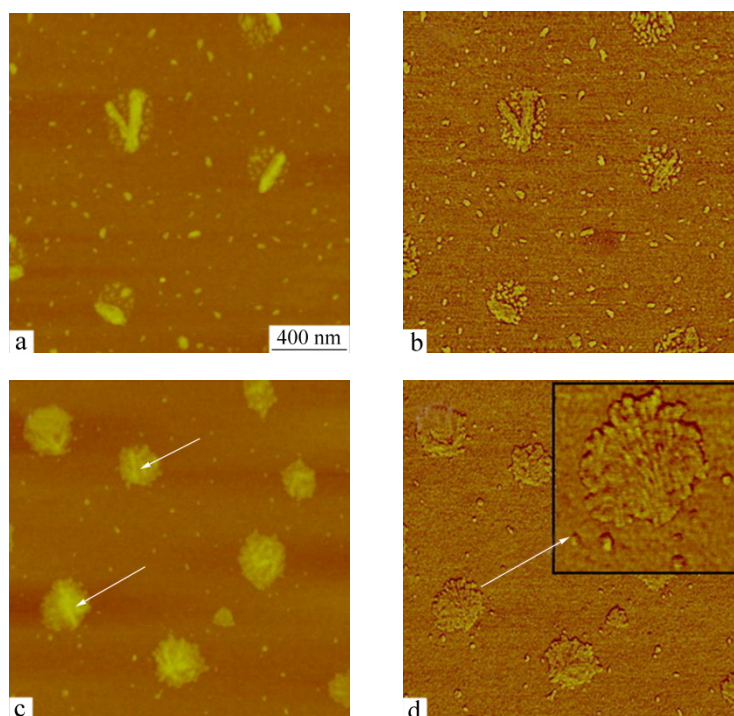


Fig. 2 AFM height (left) and phase (right) images showing the dewetted *i*PP ($M_w = 190000$) films on silicon wafers after remelting at 200 °C then quenched into (a) and (b) room temperature; (c) and (d) liquid nitrogen

Three Modes of the Crystal Nucleation and Growth in *i*PP Nanodroplets

To investigate the crystal nucleation and growth in *i*PP nanodroplets, atomic force microscopy (AFM) was used to observe the morphology in real time during gradually cooling after remelting the nanodroplets. In the cooling process, three modes of nucleation and growth behavior in *i*PP droplets were detected, that is, the fast crystallization within the droplets, and the formation of a single or multiple independent homogeneous nuclei within a single droplet, respectively. Figure 3 presents a series of AFM phase images which shows the first case of heterogeneous nucleation and fast crystallization in *i*PP droplets. For this case, the crystallization in these droplets is so fast that the mode of nucleation and growth has not been observed when the sample was cooled after remelting at 200 °C. It can be inferred that perhaps the nucleation sites have been seemingly not destroyed after remelting at 200 °C, which leads to the fast crystallization in the *i*PP droplets. In addition, for the first case presented in Fig. 3, it is found that the diameter and height of the droplets under investigation are about in the range from 100 nm to 300 nm and from 10 nm to 20 nm, respectively.

Figure 4 displays a series of AFM phase images which show the case that the multiple nuclei inside one *i*PP nanodroplet were formed during cooling after the sample was remelted at 200 °C. It is evident that in Fig. 4(a) all droplets appear as dark areas, indicating that they are still in the molten state at 55 °C. For the two droplets marked by white circles, the nuclei appeared at the edge of droplets when the temperature is cooled to 50 °C (Fig. 4b). Moreover, for the upper white circle, the nucleus presented at 50 °C has no obvious change in the subsequent cooling and other new nuclei in this droplet cannot be produced until temperature is decreased to 34 °C (Fig. 4h). But for the lower white circle, the nucleus formed at 50 °C quickly grew into a lamella when the temperature is decreased to 46 °C (Fig. 4c). Then it did not vary any more with temperature decreasing. For the droplet marked by the black circle, the nucleus cannot be seen until the temperature is cooled to 35 °C (Fig. 4g).

Once the first nucleus came forth, the other new nuclei appeared one after another and grew with temperature decreasing further, as shown in Figs. 4(g) to 4(l). It is reported that the lowest crystallization temperature for PP is about 40 °C, and this is generally considered the crystallization temperature for homogeneous nucleation^[17, 18]. Therefore, for the *i*PP droplets marked by white circles, both the heterogeneous and homogeneous nucleations were observed when the droplets were cooled from 200 °C to 26 °C. It is considered that nuclei occurred at 50 °C were ascribed to the heterogeneous nucleation, while the nuclei appeared at 35 °C or even lower were attributed to the homogeneous nucleation. In the same way, nucleation of droplets marked by black circle was attributed to the homogeneous nucleation. Nuclei will grow into a lamella at last with temperature decreasing, as marked by a white arrow in Fig. 4(l).

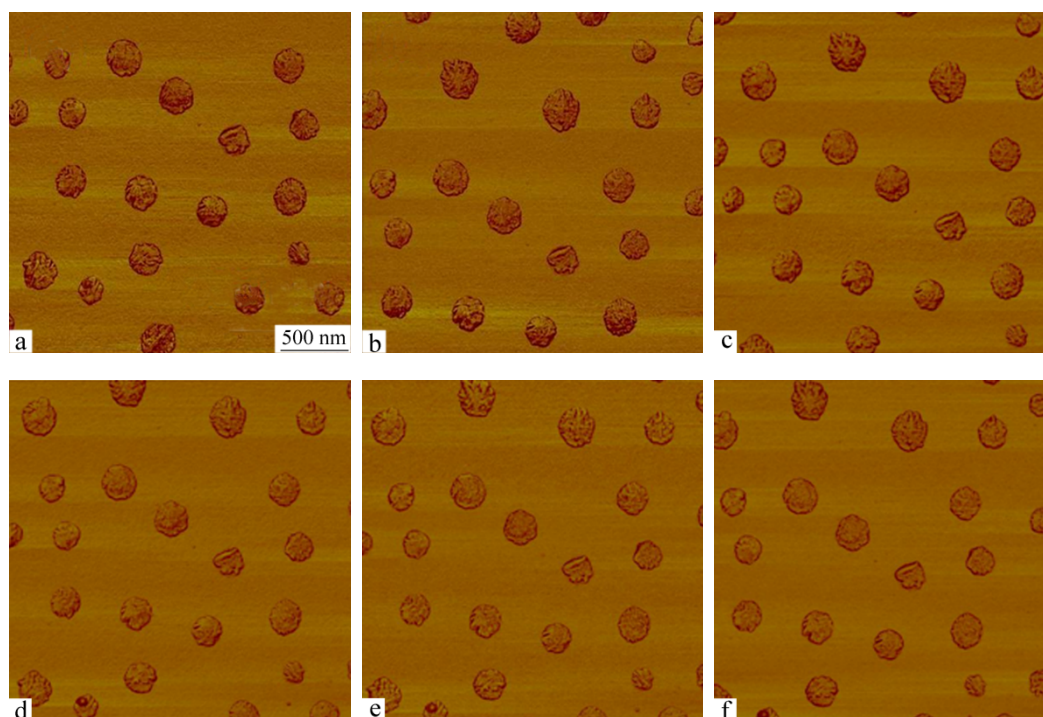


Fig. 3 A series of AFM phase images of *i*PP ($M_w = 190000$) droplets on silicon wafers showing the first case of heterogeneous nucleation and fast crystallization in *i*PP droplets after remelting at 200 °C for 5 min and cooling to different temperatures: (a) 55 °C, (b) 48 °C, (c) 42 °C, (d) 35 °C, (e) 32 °C and (f) 28 °C

In conclusion, from Fig. 4, it is clear that the droplets crystallized at 50 °C by heterogeneous nucleation have the diameter and height of more than 200 nm and about 8 nm, respectively. While for the droplets with the diameter and height of less than 200 nm and 8 nm, it crystallized at 35 °C or even lower by homogeneous nucleation. Furthermore, for some droplets the diameter is large but their nucleation temperature is lower than that of the small ones, it was because of the small height, which means the dependence of the nucleation temperature on the droplet volume. In addition, it is sure that impurities or other nucleation sites exist in the droplets in which nuclei may appear when the temperature is decreased to 50 °C.

It is worth noting that the coexistent morphology of granules and lamellae can be found at the end of cooling (Fig. 4l). Unfortunately, the formation process of lamellar structure cannot be followed in Fig. 4 due to the limited scan range and scan velocity. However, Fig. 5 captures the formation process of lamellar structure. In order to interpret the images distinctly, a white circle is used to indicate the droplets under investigation. The diameter and height of the droplet marked by the white circle in the upper part of the image in Fig. 5(a) are about 56 nm and 3.4 nm, respectively. It can be seen that crystal nuclei have appeared at 35 °C, as shown in Fig. 5(c).

Afterwards, the two independent crystal nuclei shown in the white circle conglutinated into one lamella with temperature decreasing, which can be observed from Figs. 5(c) to 5(f). However, the growth of the formed lamella within the droplet is limited after nucleation.

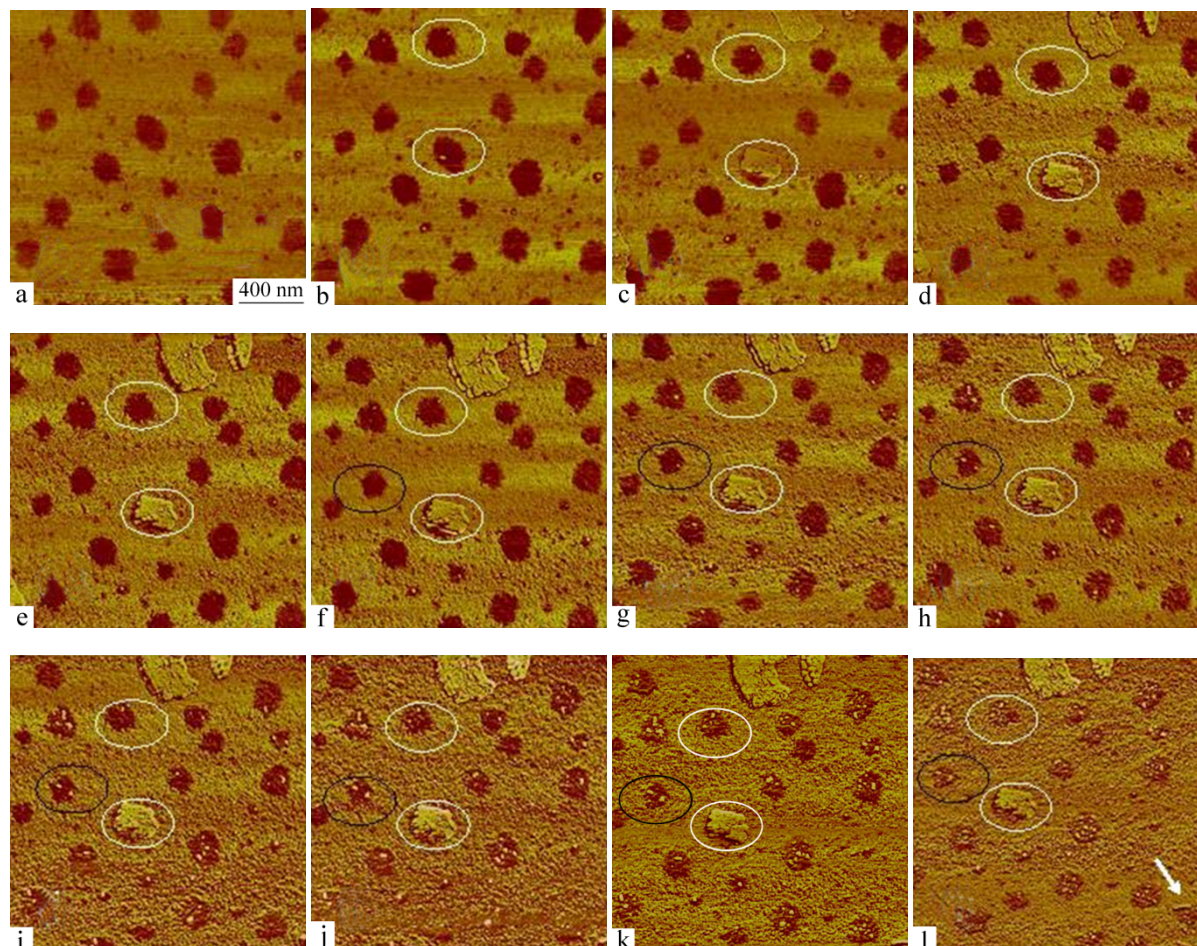


Fig. 4 A series of AFM phase images showing the formation of multiple independent homogeneous nuclei within a single *i*PP ($M_w = 190000$) droplet on silicon wafers during cooling after remelting at 200 °C for 5 min to different temperatures: (a) 55 °C, (b) 50 °C, (c) 46 °C, (d) 42 °C, (e) 38 °C, (f) 36 °C, (g) 35 °C, (h) 34 °C, (i) 33 °C, (j) 32 °C, (k) 30 °C and (l) 26 °C

Figure 6 depicts the nucleation and growth in *i*PP nanodroplets during cooling from 200 °C. It is the case that one *i*PP nanodroplet contained only one nucleus. For this case, the *i*PP nanodroplet has a diameter of about 43 nm and height of 3 nm. It is found that once the nucleus is formed, its growth is limited due to the small volume of the nanodroplet, similar to Fig. 5. A closer view of the *i*PP nanodroplet containing only one nucleus after cooling from melt down to 26 °C is shown in Fig. 6(i). It is obvious that the nucleus evolved into a lamella at last with limited growth during cooling.

In short, when the diameter and height of droplets are in the range of 100–300 nm and 10–20 nm, respectively, the heterogeneous nucleation may appear in these droplets, and the crystallization in the droplets was so fast that it had been finished when we began to scan at 55 °C. Therefore, nucleation and growth could not be followed by AFM. While, when the diameter and height of droplets are less than 300 nm and 10 nm, respectively, both heterogeneous and homogeneous nucleation can be observed. The former occurred at 50 °C and the latter appeared at about 35 °C or even lower.

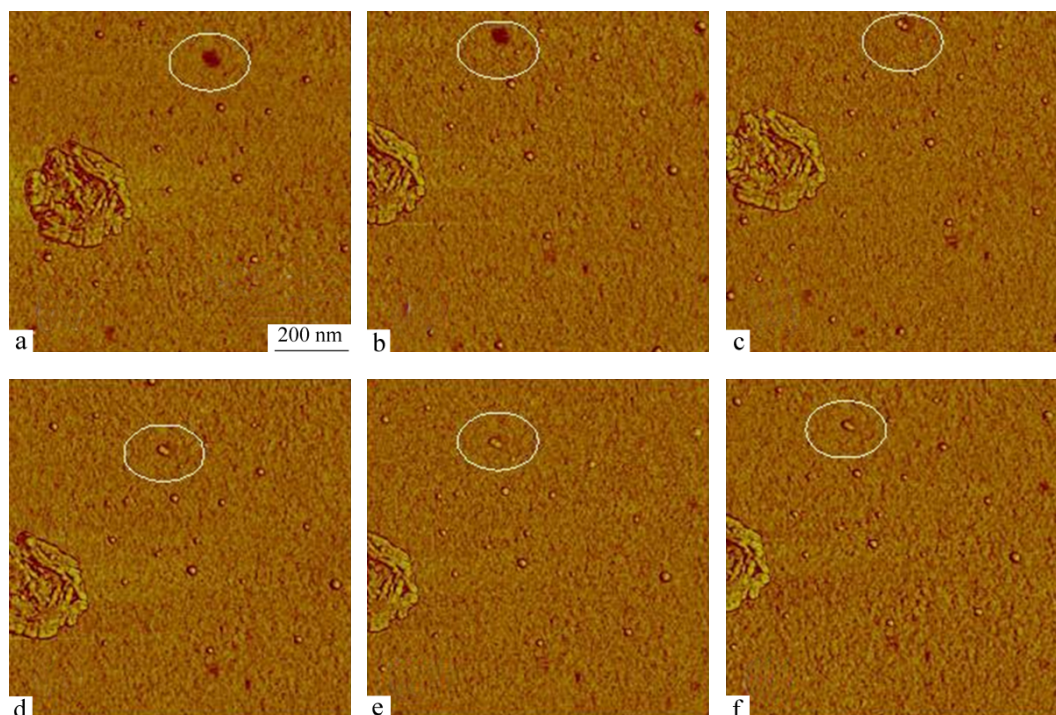


Fig. 5 A series of AFM phase images showing the formation of a lamellae within *iPP* ($M_w = 190000$) droplets on silicon wafers during cooling to different temperatures after remelting at 200 °C for 5 min: (a) 48 °C, (b) 38 °C, (c) 35 °C, (d) 32 °C, (e) 30 °C and (f) 28 °C

Nucleation Behavior in Nanodroplets of iPP

It is well known that AFM not only allows *in situ* observation of the nucleation and growth of the crystal, but also provides an opportunity to obtain the data from AFM images to analyze the relationship between the crystallization temperature and volume as well as the height of nanodroplets, which can give a clue to understand the nucleation behavior further. It is necessary for us to explain that on analyzing the data, we considered the nanodroplet as a spherical segment. The volume of all droplets was estimated according to the formula of the volume of spherical segment. That is,

$$V = \pi h \left(\frac{h^2 + 3r^2}{6} \right) \quad (1)$$

where, h , r , and V are the height, the radius, and the volume of the nanodroplet, respectively. In our experiment, h and r can be obtained from the section profiles of AFM height images using AFM software. The results show that the height is ranging from 1.3 nm to 20 nm. The volumes of nanodroplets calculated according to Eq. (1) are in the range from 1300 nm³ to 710000 nm³. Combining these data with corresponding AFM images it is found that nucleation and growth behavior of the crystal in *iPP* droplets are related to the volumes of the nanodroplets. With the value of the volume of *ca.* 130000 nm³ as a boundary, a single nucleus or multiple nuclei would be observed in the *iPP* nanodroplets during cooling from 200 °C when the volume is lower than the critical value. Otherwise, heterogeneous nucleation and fast crystallization may occur in the *iPP* droplets.

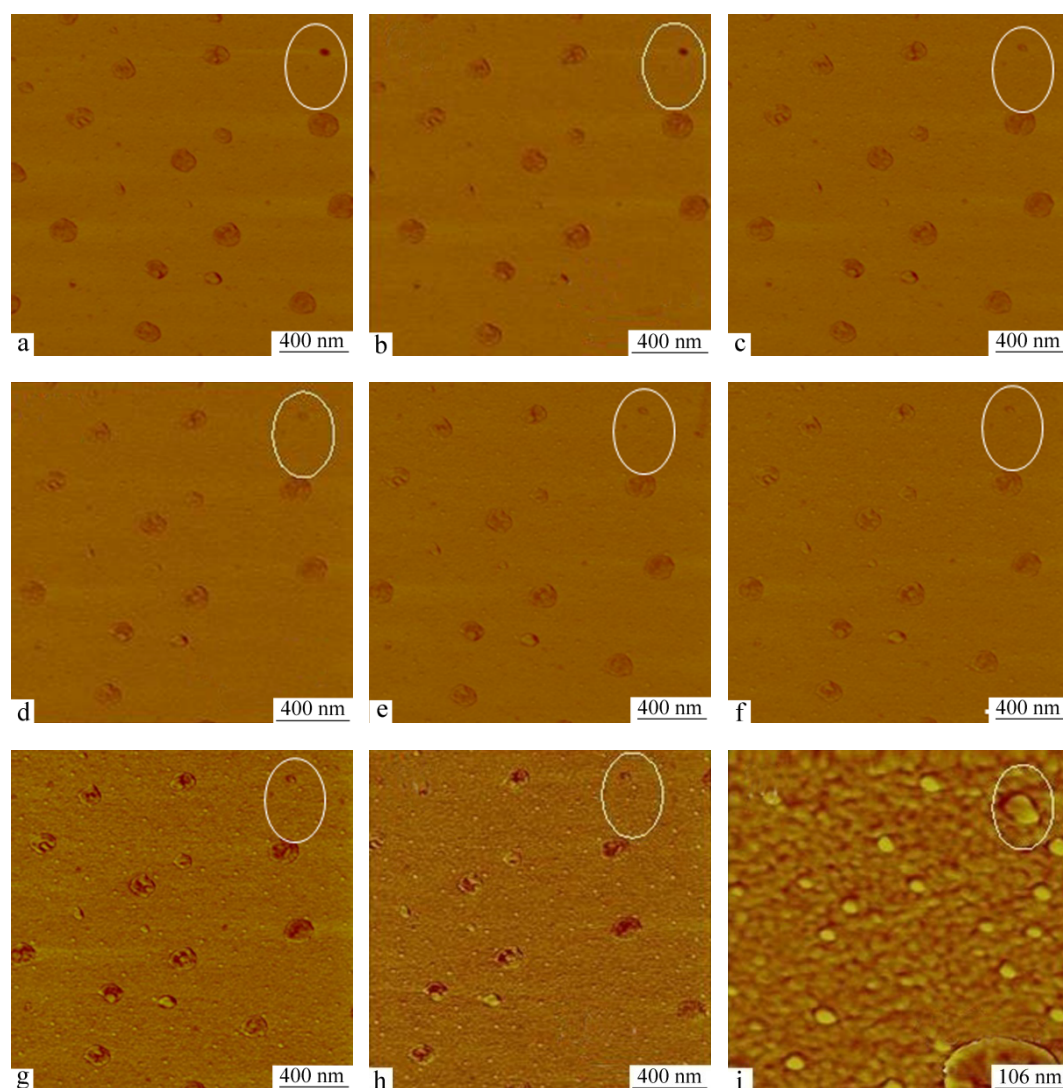


Fig. 6 A series of AFM phase images showing the formation of one nucleus within a single *i*PP($M_w = 190000$) droplet on silicon wafers during cooling to different temperatures after remelting at 200 °C for 5 min: (a) 46 °C, (b) 44 °C, (c) 42 °C, (d) 40 °C, (e) 38 °C, (f) 34 °C, (g) 32 °C, (h) 26 °C and (i) 26 °C

It is well known that if the nucleation is truly random in space (*i.e.* independent of interfaces), the rate (*i.e.* number of nuclei per unit volume per unit time) would vary very strongly with volume and little with thickness^[9, 11]. Alternatively, a strong variation with thickness implies either a surface effect or some other confinement effect^[14]. Figure 7(a) shows the graph of the nucleation temperature versus the volume of the droplets while Fig. 7(b) gives the plot of the temperature against the height of the droplets. The temperature plotted is the one at which the onset of nucleation is detected. From Fig. 7(a) one can see that there is a remarkable influence of volume on the nucleation temperature for droplets with large volumes. For relatively small volumes, the curve is essentially vertical, indicating that the nucleation temperature is independent of the volume in this range. From Fig. 7(b), it is seen that the nucleation temperature versus height curve is linear for the entire data set, although very scattered. So it can be concluded that when the volume is large, both the volume and the height of the droplet influence the nucleation temperature. While when the volume is small, the effect of volume on the nucleation temperature becomes insignificant even vanished, as can be seen from the left

part of the broken line in Fig. 7(a) and its enlarged view of Fig. 7(c). And Fig. 7(d) presents the corresponding plot of temperature against height of droplets in this region. It is obvious that compared with large volumes, the droplets of small ones have little dependency on volume as well as height. The reason is not clear yet. Perhaps, it is because the data we obtained is limited to the extremely narrow range of temperature.

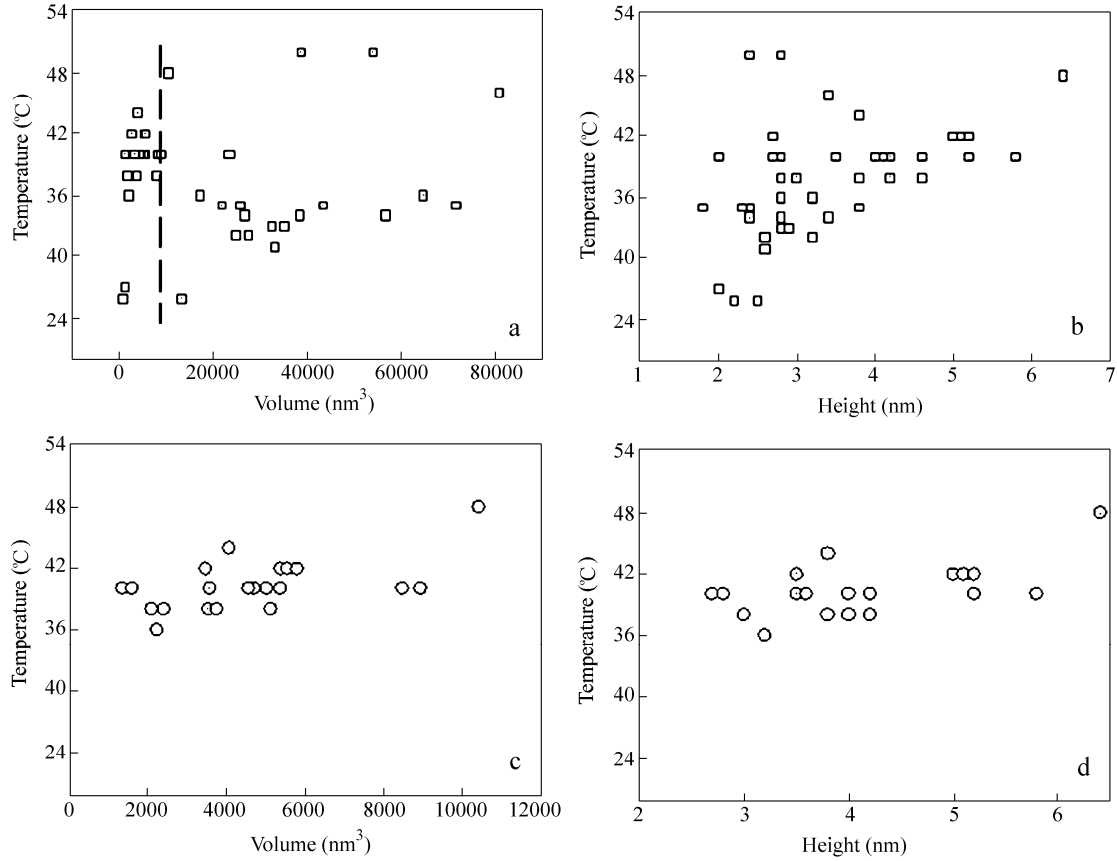


Fig. 7 Plot of the crystallization temperature versus (a) the volume, and (b) the height of the *iPP* ($M_w = 190000$) droplet. The enlarged view of the left part of broken line in (a) is shown in (c) and (d) gives the corresponding plot of the crystallization temperature vs the height of the droplets in this region.

To further explore the dependence of nucleation temperature on the volume and height of droplets when the value of volume lies within the range that shown in Fig. 7(c), the *in situ* observation was performed to detect the crystallization behavior in droplets of *iPP* with M_w of 12000. On the whole, the size of droplets formed by *iPP* with M_w of 12000 is smaller than that of *iPP* with M_w of 190000, and also the value of volume is just in the range that we want to study. Figures 8(a) and 8(b) show the plots of nucleation temperature versus volume and nucleation temperature against height, respectively. It is necessary for us to explain the concept of the critical nucleus first. We can calculate the dimension of critical nucleus according to the above crystallization experiments. It was assumed that the critical nucleus was considered as a cuboid with equal length and width value of α , and the longitudinal dimension of critical nucleus is l . Both of them are expressed by the following equations^[19].

$$\alpha = 4\sigma T_m^0 / (\Delta h_f \Delta T \rho_c) \quad (2)$$

$$l = 4\sigma_e T_m^0 / (\Delta h_f \Delta T \rho_c) \quad (3)$$

where, σ_e is the surface free energy of the fold chains at the basal planes; σ is the surface free energy of the fold chains at the lateral surfaces; T_m^0 is the equilibrium melting temperature; Δh_f is the bulk specific heat of fusion; ΔT is the supercooling and ρ_c is the density of the fully crystallized polymer. In detail, we used the following values for the calculation: For *i*PP, $\sigma_e = 7 \times 10^{-6}$ J/cm²; $\sigma = 1.15 \times 10^{-6}$ J/cm²; $T_m^0 = 460.7$ K; $\Delta h_f = 207$ J/g; $\rho_c = 0.946$ g/cm³[20]. In our experiment, the highest crystallization temperature is considered to be 48 °C, and the lowest is 26 °C. So, the $\Delta T_{\max}$ and $\Delta T_{\min}$ equal to 161.55 K and 139.55 K, respectively. Subsequently, according to Eq. (3) the longitudinal dimension of the critical nucleus l of *i*PP can be calculated and the value is in a range from 4.1 nm to 4.7 nm. From Fig. 8, it can be concluded that when the size scale of nanodroplets is smaller than the critical nucleus size in at least one dimension, the dependence of the nucleation temperature on the volume is not evident, but on the height is significant.

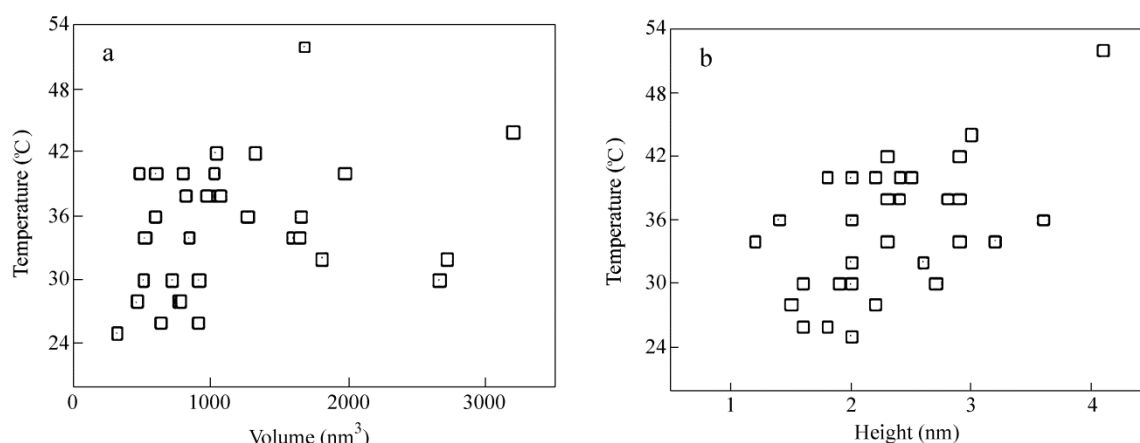


Fig. 8 (a) Plot of the crystallization temperature versus the volume and (b) plot of the crystallization temperature versus the height of the *i*PP ($M_w = 12000$) droplets

In short, Figs. 7 and 8 presented the relationship between crystallization temperature and volume as well as height of nanodroplets. It is clear that the nucleation involved in both bulk and confinement is observed in nanodroplets of *i*PP. Strikingly, we show that the crystallization of *i*PP droplets is not completely suppressed when the size scale of droplets is comparable to the critical nucleus size in one dimension, which is different from the crystallization behavior of *i*PP under the hard confinement of nanoporous aluminum oxide with diameters of 20 nm and below^[7].

CONCLUSIONS

In summary, three modes of crystal nucleation and growth in *i*PP nanodroplets have been observed by *in situ* AFM during gradually cooling after remelting the nanodroplets. That is, the heterogeneous nucleation and fast crystallization in *i*PP droplets, the formation of one nucleus or multiple independent homogeneous nuclei within a single droplet, respectively. Moreover, it is found that when the volume of droplet is larger than the value of *ca.* 130000 nm³, the first case was observed. Otherwise, the latter two cases appeared. By analyzing the relationship between the nucleation temperature and the volume, as well as the height of nanodroplets, respectively, it is clear that when the size scale of the droplet approaches or becomes smaller than the critical nucleus size in at least one dimension, the nucleation temperature is hardly dependent on the volume but strongly on the height of the droplets, which showed the nucleation behavior under confinement.

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