Transformation of Isotactic Polypropylene Droplets from the Mesophase Into the $\alpha$-Phase

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ABSTRACT: The structural transformation of homogeneously nucleated metastable mesophase of polypropylene (PP) particles was investigated in this study. We demonstrated the formation of heterogeneity-free mesophase by slow cooling of the droplets unlike mesophase formation by quenching of the PP melt, which contained large number of bulk nuclei. Submicron size PP droplets were produced by thermal break up of PP and polystyrene layered film assembly. When cooled from melt, the PP droplets crystallized into mesophase at 44°C revealing granular morphology. Subsequent heating thermogram of the PP particles showed a broad exotherm, which was attributed to the transformation of mesophase into $\alpha$-phase. This transformation was investigated during heating by annealing the PP particles at different temperatures. Annealed PP particles were analyzed by means of thermal, morphological and structural properties measurements. Results revealed a two-step process for the transformation process. In the first step, the internal rearrangement of PP chains, as against melting and recrystallization of the mesophase, was observed. Since granular morphology was not affected significantly up to 120°C, it was suggested that translational and rotational motions of PP helices produced ordered $\alpha$-phase. In the second step, increment in grain size distribution was observed, when the droplets were annealed at 140°C. The results were attributed to enhanced chain mobility and merging of the grain boundaries. Annealing at 160°C revealed the formation of short lamellar structures. Crystal thickening, melting and recrystallization of $\alpha$-phase were suggested at high temperature annealing. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 49: 1672–1682, 2011

KEYWORDS: fractionated crystallization; mesophase formation; nucleation; polypropylene

INTRODUCTION Isotactic polypropylene (PP) exhibits various crystal modifications such as $\alpha$, $\beta$, $\gamma$, and mesophase as a function of crystallization conditions. 1–4 Slow cooling of a quiescent PP melt leads to the formation of thermodynamically favored monoclinic $\alpha$-phase in the absence of special nucleating agents. Various nucleating agents can also be added to selectively crystallize PP in the $\alpha$- or the $\beta$-phase, while the $\gamma$-phase is usually crystallized at high pressure. 5,6
In contrast to the ordered PP phases, an intermediate phase with ordering in between an amorphous and a crystalline phase, commonly recognized as mesophase, has been identified by characteristic broad X-ray halos. Metastable mesophase constitutes a collection of randomly arranged left and right-handed $\alpha$ helices of PP and is usually developed by rapid quenching into a granular morphology with domain sizes on the order of 10–25 nm.4,7–9 Current literature identifies fast cooling of the liquid melt as a prerequisite for mesophase formation. Cooling at rates on the order of $10^2$ to $10^3$ °C/s is known to suppress development of monoclinic $\alpha$-phase crystals and promoting mesophase formation.5 Such mesophase formed by fast quenching can be a kinetically frozen structure. The mesophase is discussed by Muthukumar as a preliminary step for the nucleation in polymers leading to the formation of folded chain crystals.10
Jin et al. describe use of a layer multiplying, forced assembly coextrusion process was used to produce high concentrations of PP droplets forming in the mesomorphic phase by slow cooling.11 It is inherent in the process of forced assembly coextrusion of multilayered films that the nanolayers may not be stable when heated into the melt state. Layer break-up has been successfully used to produce droplets of PP to investigate the fractionated crystallization. 12,13 Fractionated crystallization of the PP droplets in the submicron size range leads to the formation of the mesophase by homogeneous nucleation. In contrast to fast quenching of the quiescent melt into the mesophase, the slow cooling of the droplets has been identified as an alternate route to develop mesophase. It is important to note that the mesophase formed in the droplets did not contain any heterogeneities unlike the mesophase in quenched films that contained bulk heterogeneities.
The stability of the quenched PP mesophase has been investigated by temperature dependent reorganization of the mesophase PP into an ordered monoclinic structure. It is generally accepted that the mesomorphic to monoclinic transformation occurs over a broad temperature range. Morphotological investigation during heating suggested internal rearrangement of the PP helices into an ordered formation of monoclinic crystals by solid–solid phase transformation in the quenched PP. At higher temperature, however, the annealing studies of quenched mesophase have shown different morphologies. It is speculated that the presence of nuclei in quenched PP mesophase play a significant role during the transformation process upon heating. At higher transformation temperatures, increased chain mobility and activation of nuclei can direct the growth of PP lamellae. Because the PP droplets in the current work did not contain any bulk heterogeneities, the thermal transformation of the mesophase in the droplets may be different from the quenched PP mesophase wherein the bulk heterogeneities are eliminated from the transformation process.

The goal of the current study is to investigate transformation of the slowly formed heterogeneity-free mesomorphic phase into a monoclinic phase during heating. The transformation of mesophase into monoclinic α-phase was analyzed using standard techniques. The morphological changes of the transformation process were also tracked. Our study which shows direct visualization of the transition of the mesomorphic granular phase into α-phase in the absence of heterogeneous nucleation, provides useful insights in understanding the crystallization of polymers.

EXPERIMENTAL

Materials
Dow ZN5D98 isotactic PP was used in this study. This polymer has a bulk density of 0.900 g cm$^{-3}$ (ASTM D792) and melt flow index of 3.4 g/10 min (ASTM D 1238). An atactic polystyrene (PS), Dow STYRON 685D, with a bulk density of 1.040 g cm$^{-3}$ (ASTM D792) and melt flow index of 1.5 g/10 min (ASTM D1238), was coextruded against PP. The layer multiplying coextrusion process described previously was used to fabricate films with alternating PP and PS layers. Rheological compatibility of the polymers for coextrusion was assessed by measuring the viscosity using a Kayeness Galaxy rheometer at a low shear rate of 10 s$^{-1}$. Additional annealing experiments were carried out by heating the PP droplets to 140 and 160 °C for 2 hrs.

X-Ray Diffraction
Wide angle X-ray scattering (WAXS) of the PP particles dispersed in the PS matrix and PS control was carried out at ambient temperature, in the transmission mode, in a Rigaku diffractometer with a sealed-tube source of CuKα radiation, operated at 40 kV and 40 mA. Small-angle X-ray scattering (SAXS) was obtained with a rotating anode X-ray generator, Rigaku RU-200, 12 kW as a X-ray source and laterally graded multilayered optics to obtain a highly focused parallel beam of CuKα radiation (λ = 0.154 nm). The X-ray beam generated at 40 kV and 90 mA was collimated using 3 pinholes and the final diameter of the X-ray beam was 700 μm. The sample-to-detector distance was 1.5 m, and the scattering vector, q, was calibrated using a silver behenate (AgBe) standard, with a (001) peak position at q = 1.076 nm$^{-1}$. A beam stopper with the ability to measure intensity of the direct beam was placed in front of the area detector. Based on the intensity of the direct beam, all SAXS images were corrected for background scattering, dark current and sample absorption.

Atomic Force Microscopy
The multilayered films were embedded in epoxy and microtomed at −60 °C in a cryo-ultramicrotome (MT6000-XL from RMC), perpendicular to the plane of the film. Film integrity and layer thickness were viewed using a Nanoscope V atomic force microscope (AFM) from Veeco Instruments under the tapping mode at ambient conditions. Morphology of the PP droplets was also investigated using AFM. PP particles were isolated by selectively dissolving the PS matrix in toluene for 24 hrs, followed by casting a thin film of suspended PP particles on a glass slide. The film was dried at room temperature to remove the solvent before imaging. High resolution images of the PP particles’ morphology were scanned under tapping mode AFM at ambient conditions. The AFM tip diameter was 10 nm.

RESULTS AND DISCUSSIONS
Mesophase of PP
It is well known that the crystallization of polymers in the bulk usually initiates at heterogeneous nuclei, such as catalyst residues, high molecular weight gel particles, or dust
particles. The heterogeneous bulk nucleation usually covers the entire crystallization process of the sample. When a polymer is subdivided and dispersed in the form of droplets which well exceed the number of heterogeneous nuclei, two or more crystallization exotherms, also known as fractionated crystallization, are observed in the thermogram. In the crystallization thermogram, the lowest temperature exotherm is due to homogeneous nucleation in heterogeneity-free droplets, while the higher temperature exotherms are due to heterogeneity-containing droplets. In contrast to heterogeneous nucleation, the homogeneous nucleation process is very difficult to observe as heterogeneous nuclei always exist in the bulk material and are activated well before homogeneous nucleation occurs. The process of fractionated crystallization of PP droplets from the multilayered films resulted exclusively homogeneous nucleation.

A sample PP/PS multilayer film, with nominal PP layer thickness of 12 nm as shown in Figure 1, was used to produce PP droplets dispersed in an amorphous PS matrix. Thermal break-up the multilayered film resulted in the formation of large number of PP droplets. A representative AFM image of the PP particles cast in a thin film of PS in Figure 2(a) showed a large number of submicron size particles. Most of the particles produced were in 100–1000 nm size range, Figure 2(b). The structural changes that occur during the crystallization of the PP particles from the melt will be discussed in another publication. The fractionated crystallization of PP particles produced from thicker PP/PS multilayered films resulted in multiple crystallization exotherms.

Thermal properties of the submicron size PP particles produced from 12 nm layers are shown in Figure 3. When the PP droplets were cooled from the melt, the DSC thermogram showed a crystallization exotherm at 44 °C with a crystallization enthalpy of −35.8 J g⁻¹. This peak was assigned to the homogeneous nucleation of PP particles into the mesophase. Subsequent heating thermogram of the particles showed a broad exotherm ranging from 50 °C to up to the melting of α-phase PP. The exotherm represented the transformation of mesophase into a more stable α-phase, followed by an endotherm at 163 °C, which was the melting of the α-form. The mesomorphic phase trapped in a metastable state transformed irreversibly into monoclinic α-phase on heating, which was followed by melting of the transformed α-phase.

Current work is particularly interesting since most of the prior work involved quenching of PP at high cooling rates to produce mesophase with a nodular morphology. The structural transformation of mesophase during heating showed a broad exotherm involving internal rearrangement.
of PP $3_1$ helices into an ordered crystal structure. It has been suggested that the starting structure of mesophase contained bundles of PP chains consisting of either the "random" or the "correct" handed assemblies of helical chains, which would be thermodynamically more feasible to reorganize into an ordered monoclinic structure. Our work provides insights into the understanding of the structural evolution that occurs during the transformation process in a slowly cooled mesophase. Also, the mesophase formed in the droplets did not contain any heterogeneities unlike the mesophase in quenched films that contained bulk heterogeneities. An alternate route for the transformation process is possible in the absence of any bulk nuclei.

Transformation of Mesophase During Annealing

Thermal Properties

Heating thermograms of the annealed PP droplets are shown in Figure 4. It was observed that annealing affected the exothermic peak of mesophase to $\alpha$-phase transformation. Droplets annealed at 60 °C showed a decreased intensity of the transformation exotherm suggesting conversion of a small fraction of mesophase into $\alpha$-phase. PP droplets showed initial mesophase crystallinity of 26%. When annealed at 60 °C for 30 min, the mesophase crystallinity decreased to 17% and the total crystallinity of the droplets increased to 27%. The enthalpy was reduced to $-8.1 \text{ J/g}$ and further decreased to $-7.1 \text{ J/g}$ at 80 °C. When the droplets were annealed at 120 and 140 °C, the mesophase fraction was entirely transformed into $\alpha$-phase and the total crystallinity increased to 32 and 37%, respectively, approaching the bulk PP crystallinity of 43%, Table 1. Melting thermograms also showed small endotherms at 15–20 °C higher than the annealing temperatures, which represented small or

![FIGURE 3](image3.png)

**FIGURE 3** The cooling and subsequent heating thermogram of the PP droplets produced from 12 nm PP layers from PP/PS film.

![FIGURE 4](image4.png)

**FIGURE 4** The melting thermograms of PP particles annealed at various temperatures for 30 minutes.

### TABLE 1: Melting Enthalpies of Annealed Smectic Polypropylene Particles

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Annealing Time (mins)</th>
<th>$\Delta H_{m \rightarrow a}$ at 100 °C (J/g)</th>
<th>$\Delta H_{m \rightarrow a}$ at 162 °C (J/g)</th>
<th>$X_s$ (%)</th>
<th>$X_{Total}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>-12.1</td>
<td>53.2</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>-8.0</td>
<td>57.4</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td>80</td>
<td>30</td>
<td>-7.1</td>
<td>63.5</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>0</td>
<td>68.5</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>120</td>
<td>30</td>
<td>0</td>
<td>66.3</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>140</td>
<td>30</td>
<td>0</td>
<td>77.7</td>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td>140c</td>
<td>120</td>
<td>0</td>
<td>80.1</td>
<td>0</td>
<td>38</td>
</tr>
<tr>
<td>160c</td>
<td>120</td>
<td>0</td>
<td>72.5</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>Bulk PP</td>
<td>0</td>
<td>0</td>
<td>90.0</td>
<td>0</td>
<td>43</td>
</tr>
</tbody>
</table>

*a* Calculated from $\Delta H_{m \rightarrow a}$ with $\Delta H_{f, a} = -46 \text{ J/g}$.

*b* Calculated from $\Delta H_{f}$ with $\Delta H_{f} = 210 \text{ J/g}$.

*c* The samples were cooled at 10 °C/min.
imperfect \( \alpha \)-crystals formed during the annealing experiments. It must be noted that the calculated enthalpy of the mesophase may be higher than the calculated enthalpy as there was overlapping of the small endotherms by the mesophase to \( \alpha \)-phase exotherm.

**Structural Transformation**

Internal chain packing and details of the global chain arrangement of the mesophase was obtained using WAXS and SAXS, Figures 5 and 6. WAXS profile of the mesophase obtained after subtracting the PS contribution showed two broad peaks at 2\( \theta \) = \( \approx \) 15° and \( \approx \) 21° without any crystalline reflection, which is typical of mesophase PP chains. In the profile, the first reflection maximum is related to the average \( d \)-spacing of the PP chains in the phase. The second maximum signifies the presence of chains with 3\( \beta \) helices. Annealed samples, where the transformation of mesophase to monoclinic transformation was observed, were also investigated using X-ray. Raw data for the annealed PP particles dispersed in the PS matrix is shown in Figure 5(a). PS contribution was subtracted to obtain the PP crystal reflections. The broad reflections at 15 and 21° were not affected significantly in the specimens annealed at 60 and 80 °C. However, the characteristic reflections of \( \alpha(110) \) and \( \alpha(111) \) appeared only after annealing at 100 °C for 30 minutes. As the samples were annealed at 120 and 140 °C, the presence of stronger \( \alpha \)-crystal plane reflections were observed. The presence of distinct peaks in WAXS data confirmed the formation of \( \alpha \)-phase during annealing. From the X-ray data, the transition of the mesophase chain bundles into monoclinic \( \alpha \)-crystals is interpreted as a two phase mechanism as proposed by Ferrero et al.\(^{22} \) It was clearly indicated that up to 80 °C, the transformation involved only rearrangement of the chain axis direction, followed by a lateral rearrangement of chains in directions normal to the chain axis. In addition to the translational motion, the transformation process may also involve a rotational mechanism to arrange 3\( \beta \) helices into position.\(^{20} \) A complete transformation to \( \alpha \)-phase is indicated at temperatures higher than 100 °C.

SAXS profiles of mesomorphic phase of the PP droplets and the transformed phase obtained during annealing are shown in Figure 6. Lorentz corrected SAXS pattern of the mesophase sample exhibited a weak but discernable correlation peak at \( s = 0.095 \text{ nm}^{-1} \) confirming a density fluctuation in these grains where dense mesophase bundles were

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**FIGURE 5** (a) WAXS patterns of the PP particles annealed at various temperatures for 30 minutes, in the presence of the PS matrix; (b) WAXS patterns of the PP particles obtained after subtraction of the PS contribution.

**FIGURE 6** SAXS patterns of annealed smectic PP droplets after subtracting PP/PS melt contribution.
separated by amorphous phase, with an average correlation length of \( \sim 10.6 \) nm. Here, \( s \) is referred to as the scattering vector and its amplitude is related to the scattering angle \( 2\theta \) and X-ray beam wavelength \( \lambda \) as \( s = 2\sin(\theta)/\lambda \). The average correlation length was not significantly affected by annealing up to \( 100 \, ^\circ\text{C} \) and increased only slightly to \( 10.9 \) nm. Higher annealing temperatures showed a stronger effect on the long spacing. When the droplets were annealed at \( 120 \) and \( 140 \, ^\circ\text{C} \), the average long spacing of \( 10.6 \) nm for the mesophase changed to \( 14.4 \) and \( 18.9 \) nm, respectively. Increased correlation length was attributed to thickening and merging of the crystals due to increased chain mobility at higher annealing temperature. The changes in the long spacings calculated from SAXS patterns are shown in Figure 7. As shown previously in the DSC thermograms, a significant fraction of mesophase was transformed into \( \alpha \)-phase at temperatures up to \( 100 \, ^\circ\text{C} \). However, the WAXS and SAXS data indicated no signs of well-developed \( \alpha \)-crystals up to this temperature. The process must involve reordering of PP chains at temperatures

![FIGURE 7 Long spacing calculated from SAXS patterns of annealed droplets, obtained from Figure 6.](image)

![FIGURE 8 AFM images of PP particle morphology annealed at various temperatures and quenched at 100 \, ^\circ\text{C}/\text{min}: (a) Without annealing; (b) Annealed at 120 \, ^\circ\text{C} for 30 mins; (c,d) grain size distribution obtained from AFM images of PP particle morphologies from (a) and (b).](image)
up to 100 °C, which transform into α-phase at temperatures greater than 100 °C due to increased chain mobility.

**Morphological Transformation**

AFM was used to investigate the morphological transformation of PP particles annealed at different temperatures. A cast thin film of the dispersed PP particles obtained by dissolving the PS in toluene was used for scanning under AFM. Representative images showing morphological features of two samples of PP particles are shown in Figure 8(a,b). The size distribution of the grains was calculated manually by determining the average size of the grain using a line intersection method. Total number of grains analyzed was between 70 and 100. The percentage size distribution of the grains is plotted in Figure 8(c,d).

PP particles formed at 44 °C by homogeneous nucleation into the mesophase showed a granular or nodular morphology, Figure 8(a). Grain size distribution was in a range of 15–32 nm, Figure 8(c). Granular morphology is a characteristic feature of the mesophase, which was previously seen in quenched PP films. Although the sizes of the grains in quenched PP ranged from 10 nm to 25 nm, it is generally accepted that the granular morphology is a unique signature of the mesophase of PP. Average grain size larger than the correlation length obtained from the SAXS pattern of the mesophase showed the existence of a density fluctuation and, hence, more than one mesophase bundle in one grain or nodule. It is also possible that the size distribution may be smaller than the measured grain size. Recent study evaluated the effect of AFM tip geometry on the measurement of the size of polymer domains in quenched PP.

A standard silicon tip and a high resolution tungsten probe were used to measure the size of PP grains within a range of 5–25 nm. It was shown that the true size of the polymer domains measured using silicon tip was about 5–10 nm larger than that obtained using a tungsten probe. The granular morphology of polymers has often been discussed as a precursor to the actual lamellae formation during the crystallization process. Strobl also observed similar granular morphology in isothermal crystallization of polymers. The crystallization process was proposed as a multistep process, where polymer chains first form a metastable blocky structure in the melt, which then merge to form a long lamellar structure. It must be noted that the internal structure of these blocks is different than the mesophase structure in PP grains. In contrast, Sirota conceptually argued the granular structure as the indicator of the transient mesophase, which stabilizes to a higher-density crystalline form through volume contraction. Structural transformation of the mesophase into an ordered α-phase may provide some insights into the crystallization process from this observed granular morphology.

Morphology of the droplets remained granular when annealed at temperatures ranging from 60 to 140 °C. The grain size distribution was not significantly affected at 60, 80, and 100 °C and the average size remained in the 10–35 nm range. Figure 8(b) revealed a small increase in the grain size to 15–45 nm during the annealing of particles at 120 °C, Figure 8(d).

The solid state transition of the mesophase to α-phase did not involve the formation of lamellar structures at
temperatures up to 140 °C. Only small changes in the granular morphology were noted in the AFM images. However, the DSC and X-ray data suggested transformation of a significant fraction of mesophase bundles into z-phase. The initial structure consisted of 6–8 nm bundles of 31 helices separated by 10.6 nm long spacing, Figure 9(a). During annealing, internal chain rearrangement led to the formation of ordered z-phase crystals by translational and rotational motion of the chains. Due to limited chain mobility at the annealing temperatures, no significant changes in the morphology were observed. The hierarchical structure of the transformed phase is described in Figure 9(b).

High Temperature Annealing

Morphological and structural changes that occurred after the transformation to z-phase were further investigated at higher annealing time and temperature. Annealing of the PP particles close to the peak melting temperature was carried out at 160 °C for 2 hours and the particles were cooled slowly at 10 °C min⁻¹ to room temperature. Additionally, annealing at 140 °C for a longer duration of 2 hrs was also performed. The cooling and heating thermograms obtained after subtraction of the PS contribution are shown in Figure 10. The cooling thermogram obtained after annealing at 140 °C did not show any changes in the heat flow indicating an absence of any transition during cooling, while the cooling thermogram of PP particles annealed at 160 °C for 2 hrs showed two exotherms, at 140 °C and 43 °C.

WAXS patterns of the annealed particles showed strong z (110), z (040), z (130), z (111), z (041) reflections indicating the presence of well developed z-phase crystals, Figure 11. It is suggested that when the droplets were annealed at 160 °C, a small fraction of the transformed mesophase did not melt and remained in the crystalline phase. The transformed and unmelted z-PP served as nucleating sites for
molten amorphous PP chains, leading to the formation of α-crystals by self seeded heterogeneous nucleation during slow cooling of the droplets at 10 °C min⁻¹. The resulting crystallization exotherm at 140 °C during cooling was 30°C higher than the bulk crystallization temperature of 110 °C, Figure 10(a). A small exotherm observed at 43 °C was attributed to the mesophase nucleation of a small fraction of droplets that were completely melted at 160 °C during annealing. It is speculated that a large number of nuclei surfaces with high activation energy were present in a single droplet during the crystallization process, resulting in the crystallization of a large fraction of droplets into monoclinic crystals. The subsequent heating thermogram showed a melting peak at 183 °C, 20°C higher than the regular α-melting peak, Figure 10(b). SAXS data revealed the presence of increased long spacing to 22.8 and 20.2 nm when the droplets were annealed at 140 and 160 °C, respectively, Figure 12.

Morphology of the droplets at 140 °C resulted in the formation of larger grains in a size range of 25–70 nm at a higher annealing time of 2 hrs, Figure 13(a,c). Merging of the grain boundaries is thought to be responsible for the increased grain size during the transformation. This annealing temperature is still lower than the onset of PP melting, which prevented melting of PP droplets as described earlier. We speculate that at this temperature, the higher chain mobility resulted in diffusion of the grain boundaries, which have higher interfacial energy than the bulk of the grain. When the droplets were annealed at 160 °C for 2 hrs, the resulting morphology after slow cooling showed the presence of short lamellae of lengths 40–100 nm and thicknesses of 20–30 nm, Figure 12(b,d). Long spacing of 20.2 nm in the SAXS results correlated well with the average interlamellar distance. The absence of bulk heterogeneous nuclei during the cooling process prevented any preferential growth, resulting in random
lamellae. The lamellar structures occasionally showed the presence of surface undulations, which may have resulted due to volume contraction during the crystallization process.

In this step of transformation at higher annealing temperatures, the increased grain size and the presence of x-reflections confirmed significant chain rearrangement, possibly due to higher chain mobility to form ordered x-phase crystals. As the annealing was carried out for longer times, close to the melting temperature, merging of the grain boundaries and stronger x-reflections were observed. Absence of any lamellar structures suggested the presence of bundled crystals even in the larger grains observed at 140 °C. The hierarchical structures, thus, evolved during this step are shown in Figure 14(a). Further annealing of the droplets at 160 °C led to partial melting of the transformed phase. The subsequent crystallization of PP droplets resulted in the formation of short anisotropic lamellae, Figure 14(b). Based on the morphological and structural changes, the transformation process was viewed as a two step process. The route for transformation involved the rotational and translational movements of 31 helices in the first step, followed by rearrangement of the chains to produce ordered x-crystals.

CONCLUSIONS

Structural transformation of homogeneously nucleated metastable mesophase of PP particles was successfully investigated. Submicron size droplets produced from 12 nm PP layers formed mesophase in the absence of any heterogeneous nuclei. Mesophase of the droplets transformed into x-phase during heating. This transformation was studied by annealing the PP particles. It was observed that the transformation did not involve melting of the mesophase during heating and the solid state transition was confirmed from AFM images.

A two step process for the structural transformation was proposed. In the first step, mesomorphic granular morphology and X-ray data indicated that the mesophase transformation involved translational and rotational motions of the PP chains. In the second step of transformation, as the annealing time and temperature increased, the merging of the grain boundaries was attributed to increased chain mobility and to higher surface energy at the grain interfaces than the bulk of the grain. This was confirmed by increased grain size distribution and the presence of strong x-crystal reflections. Results confirmed the thermodynamic feasibility of the transition without melting of the mesophase of PP. Structural transformation involved rearrangement of the polymer chains into more ordered crystals, without any preferred orientation, in the absence of heterogeneous nuclei. In addition to the transformation of the crystal structure, the transformed mesophase induced some growth at the local scale resulting in increased x-phase crystallinity. Annealing by partially melting PP droplets resulted in short lamellae through self-seeding without any preferred orientation due to the absence of directed growth.
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