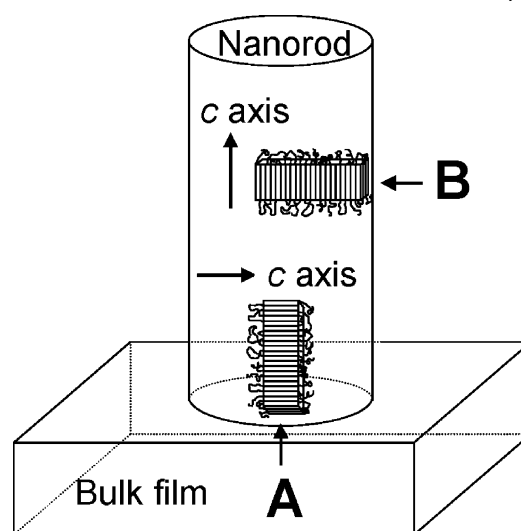


Orientation of Syndiotactic Polystyrene Crystallized in Cylindrical Nanopores

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Syndiotactic polystyrene (sPS) nanorods with different diameters have been prepared by using anodic aluminum oxide templates, and the orientation of the sPS crystals in the nanorods has been investigated by FT-IR spectroscopy. It is found that the *c* axis of the β' crystals preferentially oriented perpendicular to the axis of the nanorod, and the degree of orientation is lower as the diameter of the nanorod decreases. This unexpected result is attributed to nuclei formed at the surface of the nanopores and their subsequent growth, in addition to the preferential growth compatible with the pore direction by the nuclei formed in the bulk film and in the nanorods.



Introduction

In recent years, crystallization of polymers under cylindrical confinement of organic^[1–5] or inorganic^[6–13] templates has been widely investigated. Strong phase-separated crystalline–amorphous diblock copolymers have been employed to construct hexagonal nanocylindrical structures to investigate the crystallization of the crystallizable blocks confined in the continuous amorphous matrix. It was found that crystallites confined in nanocylindrical domains resulted from phase separation in block copolymer films exhibit a preferred orientation,^[1,2] and the orientation of the crystallites, defined by the chain direction with respect to the axial direction of the nanocylinder, depends on the crystallization temperature,

which changes from random to a uniformly perpendicular orientation when the crystallization temperature is elevated.^[2] However, the diameters of the cylindrical domains are generally in the range of 5–20 nm^[2,3] as controlled by the phase segregation strength and molecular weights of the two blocks, which makes it difficult to investigate the effects of the diameter of the cylinder on the crystallization under confinement over a broader range. Inorganic templates such as anodic aluminum oxide (AAO) membranes have been employed recently to study the morphology of polymers under cylindrical confinement.^[6–12] The thermal stability and mechanical rigidity of the inorganic materials provide a strictly constrained environment compared to the glassy matrix in the diblock copolymers and avoid the breakdown of the nanocylindrical confinement. The AAO templates consist of well-ordered straight separated cylindrical pores, and the pore diameter is easily controlled by the oxidization conditions, which makes them ideal for the investigation of polymers confined in pores with diameters ranging from micrometers to nanometers. Recently polymer crystallization

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in AAO templates has been investigated by several groups.^[7–12] In general the crystals in the nanopores crystallized at low supercooling temperatures exhibit a perpendicular orientation because of the kinetic selection of crystal growth processes.^[7–9] For poly(vinylidene difluoride) (PVDF), homogeneous nucleation was found to dominate in the separated nanostructures, while for the nanorods in connection with bulk, the crystal orientation in the nanorods is dominated by the bulk owing to the kinetic ‘gate effect’.^[8] In addition, polyethylene (PE) crystallization in nanopores was found to be controlled by the nucleation rather than the growth of the crystallites.^[9,10] The dependence of crystal orientation in the nanopores on the pore diameter was qualitatively assessed by Monte Carlo simulations^[14] and X-ray diffraction (XRD),^[9] and it was reported that the perpendicular orientation increases as the pore diameter decreases owing to stronger confinement effects of the smaller pores.

In our previous work, we investigated the crystallization of syndiotactic polystyrene (sPS) in AAO templates by FT-IR spectroscopy, and found that at low supercooling temperatures, in nanorods, the sPS exhibit a perpendicular orientation and lower degree of crystallinity,^[11] and a mixed crystallinity of α and β' forms upon cooling.^[12] In this work, we analyze the orientation of sPS crystals by FT-IR spectroscopy and measure the orientation function quantitatively in nanorods of different diameters, and explore how the diameter can affect the orientation of the crystals under cylindrical confinement.

Experimental Part

The AAO templates with a 200 nm pore diameter were purchased from Whatman, while AAO templates with 32 and 80 nm pore diameters were prepared by a two-step anodization process using oxalic acid as the electrolyte following the literature procedure.^[15] Figure 1(a,c,e) show scanning electron microscopy (SEM) images of the top view of the AAO templates with the three different pore diameters, respectively.

sPS pellets (Dow Questra F-2250, $\overline{M}_w = 2.6 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2$) was used as received. A transparent amorphous sPS film with a thickness of $\sim 180 \mu\text{m}$ was obtained by compression molding several sPS pellets at 300°C and quickly quenching the film in ice water. An alumina membrane was placed on top of the sPS film, and the assembly was heated at 300°C for 1.5 h under a nitrogen atmosphere so that the sPS melt was drawn into the membrane pores by capillary force. The assembly was cooled from the molten state to 255°C and annealed for 2 h, and then quenched in ice water to freeze the structure formed at high temperatures. All the samples experienced identical processing conditions.

The morphology of the AAO templates and the sPS nanorods was investigated using an FEL XL30FESEM field emission scanning electron microscope. The template/polymer assembly was immersed in a sodium hydroxide aqueous solution for 12 h to remove the AAO template, to leave an array of sPS nanorods

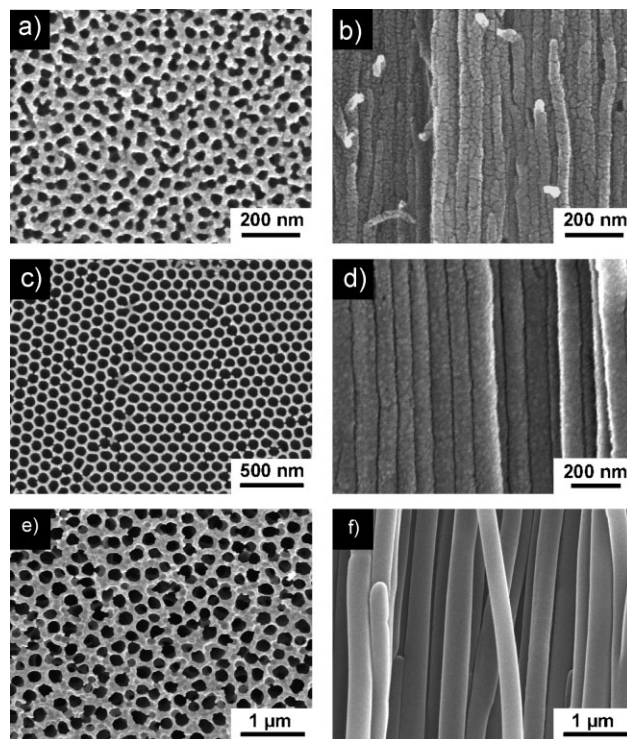


Figure 1. FE-SEM images of the AAO templates and the nanorods: (a, c, and e) the top view of the AAO templates with diameters of 32, 80, and 200 nm; (b, d, and f) the cross sections of the nanorod arrays with diameters of 32, 80, and 200 nm.

protruding from the sPS film. Thin slices of the cross section of an sPS film with protruding nanorods were cut under an optical microscope using a razor blade.

Infrared measurements were performed on a Bruker IFS 66V/S FT-IR spectrometer in connection with a Bruker Hyperion 3000 IR microscope equipped with a narrow band MCT detector operating in the transmission mode. Polarized spectra were collected with a gold wire grid polarizer (Specac) mounted between the sample and the detector optics. Each IR spectrum was collected at 2 cm^{-1} resolution with 512 scans. The growth direction of the nanorods was defined as the reference direction, and the infrared beam passing through the sample at normal incidence was polarized parallel or perpendicular to the reference direction accordingly.^[11] The orientation of the sPS crystals (which are orthorhombic) was defined by the c axis (which is the chain direction) with respect to the axial direction of the nanorod. Curve fitting was performed using the Levenberg Maquardt Least Squares Algorithm routine of the OPUS software package. The orientation function F can be determined from the infrared dichroism through Equation (1):^[16]

$$F = \frac{3\langle \cos^2 \theta \rangle - 1}{2} = \frac{R - 1}{R + 2} \frac{R_0 + 2}{R_0 - 1} \quad (1)$$

where θ is the angle between the chain axis and the nanorod axis (reference axis); R is the infrared dichroic ratio defined as $R = A_{\parallel}/A_{\perp}$, A_{\parallel} and A_{\perp} being the absorbances with the infrared beam polarized parallel and perpendicular to the direction of the long axis of the nanorods, respectively, and $R_0 = 2 \cot^2 \alpha$, where α is the

angle between the chain axis and the transition moment associated with the infrared band used for the orientation measurements. For measuring uniaxial orientation, the orientation function F ranges from -0.5 to 1 . A perfect parallel orientation leads to $F=1$, while a perfect perpendicular orientation gives $F=-0.5$, and a random orientation is indicated by $F=0$. Three 200 nm samples and two 80 and 32 nm samples each were analyzed, and the average and standard deviation were reported.

Results and Discussion

Nanorods of 32, 80, and 200 nm diameters were obtained by wetting the membrane pores with sPS melt by capillary force. Figure 1(b,d,f) show the SEM micrographs of the sPS nanorod arrays. FT-IR measurements^[11] were then applied to investigate the morphology of the sPS nanorods. Careful analysis of the spectra in the 940 – 820 cm^{-1} region, which are shown in Figure 2, reveals that for all the nanorods and the bulk, besides the amorphous bands at 905 and 841 cm^{-1} ,^[17] the characteristic bands of the β -crystalline phase at 911 and 858 cm^{-1} are present uniquely, while the 901 and 851 cm^{-1} bands associated with the α form crystals are absent, which indicates that sPS crystallizes into a β' form in all these nanorods and in the bulk at ~ 255 $^{\circ}\text{C}$, as was reported previously.^[11,12] The polarized FT-IR spectra of sPS nanorods with different diameters and the bulk as reference in the perpendicular and parallel

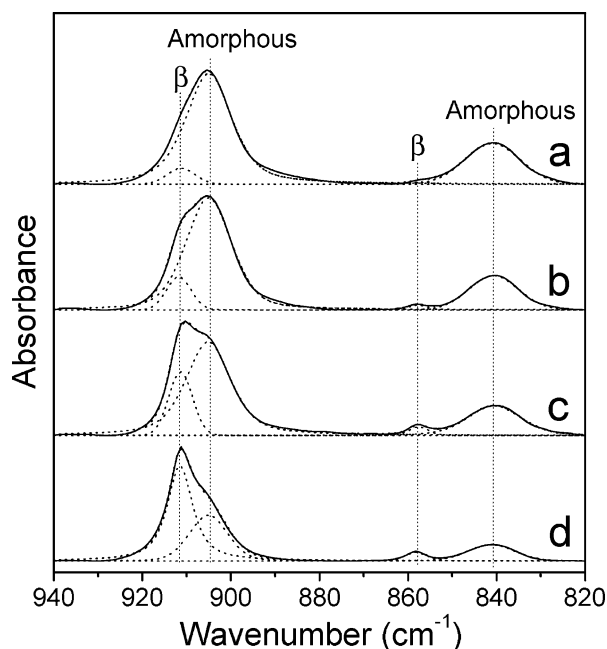


Figure 2. Infrared spectra of the sPS in the region of 940 – 820 cm^{-1} for a) 32 nm nanorods, b) 80 nm nanorods, c) 200 nm nanorods, and d) the bulk film. The dash lines are the deconvoluted peaks, and the dotted lines are the fitted curves.

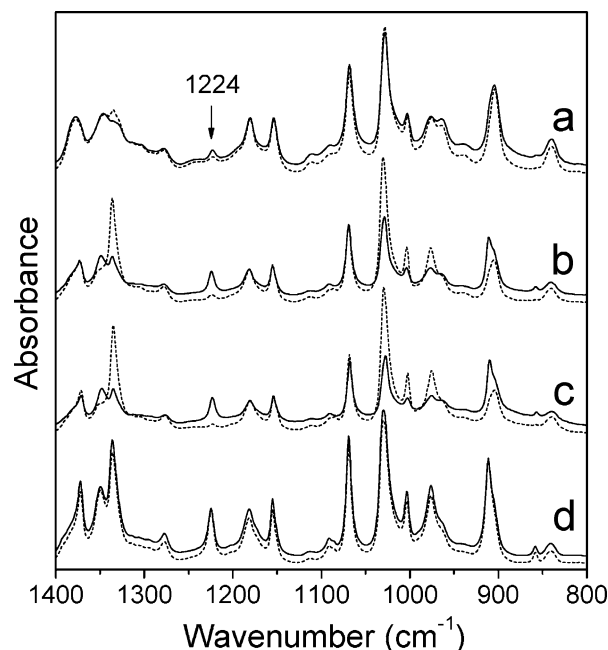


Figure 3. Polarized infrared spectra of the sPS for a) 32 nm nanorods, b) 80 nm nanorods, c) 200 nm nanorods, and d) the bulk film: perpendicular polarization (—), parallel polarization (–).

directions are presented in Figure 3. From these spectra, it can be seen that the perpendicular bands at 1334 , 1028 , and 1004 cm^{-1} in the parallel spectra are stronger than the corresponding ones in the perpendicular spectra, and the parallel bands at 1224 , 911 , and 858 cm^{-1} in the parallel spectra are weaker, which indicates that the c axis of the crystals (i.e., the chain direction) in the nanorods of 32, 80, and 200 nm diameters all tend to orient perpendicular to the long axis of the nanorod, in agreement with literature results.^[7–9] The 1224 cm^{-1} band was then used to analyze the orientation of the β' form crystals quantitatively because this band is associated with an all-*trans* planar zig-zag backbone conformation and has a transition dipole moment parallel to the chain axis.^[18] Using Equation (1), the values of the orientation functions F for the crystalline chains in the nanorods of 200, 80, and 32 nm diameters were derived, which were -0.40 ± 0.03 , -0.33 ± 0.04 , and -0.11 ± 0.06 , respectively. These numbers suggest that the degree of orientation of the sPS chains in the crystals decreases as the nanorod diameter decreases, which is contrary to the trend reported for the results of Monte Carlo simulation^[14] and experiments^[9] of PE crystallized in AAO templates, where as the pore diameter decreased the degree of orientation was found to increase qualitatively as indicated by the narrowing of the full width at half maximum of the X-ray diffraction peaks.

It was reported that for polymers in nanorods in connection with a bulk film, when the assembly is

crystallized at low supercooling temperatures, the bulk will crystallize first and influence the crystallization of the polymer in the nanorods greatly.^[8] The crystals formed at the interfaces between the AAO template and the bulk films act as nuclei to initiate the crystallization of the polymer in the nanopores. The preferred crystal orientation in the nanopore is then determined by selection of growth directions compatible with the cylindrical confinement imposed by the pore geometry, and the crystals formed will have an obvious perpendicular orientation.^[8] Based on this mechanism, it can be expected that the degree of orientation of the crystals in the nanopores would be higher in smaller pores. On the other hand, it has been reported that with the bulk film completely removed after the polymer has filled the pores in the AAO template, the crystallization temperature of the polymer in isolated nanorods is significantly lower than that in the bulk, and crystallization of the polymer in the isolated state is more likely initiated by homogeneous nucleation.^[8,10] That is, the separated nanopores have divided the bulk into numerous isolated nanorods and thus provide an appropriate circumstance for homogeneous nucleation, just as the nucleation in PE nanospheres^[19] and poly(ethylene oxide) nanodroplets.^[20] It must be pointed out that the degree of orientation derived by IR is an average for the crystalline domains in the numerous nanorods in the array. Our previous work showed that homogeneous nucleation could happen in sPS nanorods of 32 nm diameter, but only at temperatures much lower than the crystallization temperature (255 °C) in this study. Even if homogeneous nucleation has taken place here, it would lead to a higher degree of orientation in nanopores of smaller diameter because of the stronger confinement by the pores to the growth of the crystals, as a previous study on PE crystallization in AAO templates has indicated.^[9] Thus, the above two mechanisms for polymer crystallization in AAO templates, both of which have been reported so far in the literature,^[8,9] i.e., selection growth compatible with the pore direction from heterogeneous nuclei in the bulk film and crystals grown from homogeneous nuclei formed in the nanopores, would predict a higher degree of orientation in a nanocylinder of smaller diameter. Since the trend we observed, i.e., the degree of orientation decreases when the pores become smaller, was the opposite to that expected based on the above two mechanisms, an additional crystallization mechanism must be responsible. Furthermore, because of the confinement of the nanopores, the crystallinity in smaller pores is lower than that in the larger ones.^[11,12] This indicates that the crystallization of the polymer in the smaller nanopores initiated by the nuclei formed in the bulk film is much more difficult, i.e., it is more difficult for the crystals in the bulk film to grow into smaller nanopores, which leaves more crystallizable chain segments in smaller pores than in the larger ones.

In the studies on the crystallization of poly(δ -valerolactone) homopolymer confined within PS matrices^[4] and on the simulation of polymer crystallization under confinements,^[21] it was reported that the nucleation occurred predominantly at the domain interface. Previous studies by diffuse neutron-scattering^[22,23] and molecular simulations^[24] have demonstrated that flat walls may induce a preferentially parallel orientation for polymer chains in contact with these walls. Highly ordered polymer chains will deposit on the wall surfaces of the template^[13,25] and ease the formation of nuclei with the *c* axis (chain axis) parallel to the walls of the pores.^[13] Therefore, the nuclei formed at the interface of the nanorods and the templates will have a preferential orientation with the chain parallel to the long axis of the nanorod. We believe that this kind of surface nucleation has taken place during the sPS crystallization in AAO templates we have studied and is responsible for the decrease in the perpendicular orientation with the pore diameter, because while the nuclei formed in the volume of the nanorods should have a random orientation, only the nuclei formed at the surface may have a preferred orientation.

We then propose the following mechanism for the crystallization of sPS in the AAO templates at low supercoolings as schematically illustrated in Figure 4. There are two kinds of nuclei formed in the process. For the nuclei formed in the bulk film, because of the 'gate effect' imposed by the nanopores, only part of them can grow

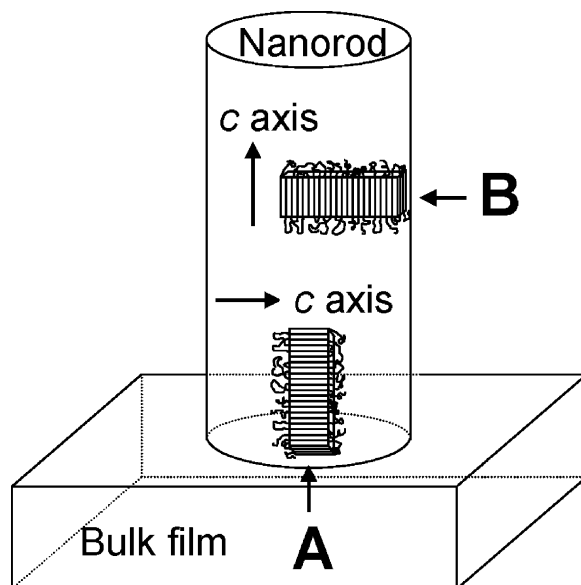


Figure 4. Schematic illustration of sPS crystallites developed in the cylindrical nanopores from (A) a perpendicular nucleus formed at the interface of the nanorod and the bulk, and (B) a parallel nucleus formed at the interface of the nanorod and nanopore wall. The contribution by the latter becomes more important when the pores become smaller.

into the pores to form crystals with a perpendicular or near perpendicular orientation. The other type is the nuclei formed at the internal surface of the nanopores which have a parallel orientation and can grow into crystals with a parallel orientation, which would decrease the degree of orientation along the perpendicular direction. As the pore diameter decreases, the surface-to-volume ratio increases, and the contribution by the surface-induced parallel nuclei and subsequent parallel crystals also increases. This increase in parallel crystals dominates the competition and outweighs the increase in perpendicular crystals as a result of the 'gate effect', and the net result is that the degree of perpendicular orientation decreases with the pore diameter.

Conclusion

We have investigated the orientation of crystalline sPS in the cylindrical nanopores with diameters of 32, 80, and 200 nm. For these nanorods crystallized from melts at low supercooling (255 °C) and then quenched, β' crystals were produced exclusively regardless of the diameter of the nanopores, and the c axis of the β' crystals was preferentially perpendicular to the long axis of the nanorods. However, the perpendicular orientation was found to decrease as the pore diameter decreased, which is the opposite to what was predicted based on previous studies where either kinetic selection growth from heterogeneous nuclei in the bulk film, or crystal growth from homogeneous nuclei formed in the nanopores, dominates the crystallization process. We attribute this unusual result to the additional contribution by the parallel nuclei formed at the walls of the nanopores, which at this stage appears to be the only logical explanation to the experimental data we obtained. This result suggests that the wall surface of the nanopores can play an important role in the crystallization of polymers in the AAO templates, especially when the pores are small and the specific surface area becomes a significant factor to be considered.

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