Formation of banded spherulites and the temperature dependence of the band space in olefin block copolymer†

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The formation of banded spherulites, which is a representative morphological feature for polymer crystalline aggregates, has attracted great interest during the past few decades. In this study, the crystalline morphologies of a type of olefin block copolymer (OBC) at different crystallization temperatures were observed systematically. It was found that banded spherulites formed at comparatively higher temperatures and the temperature dependence of the band space in OBC-banded spherulites could be divided into two regions: it firstly increased continuously with crystallization temperature between 115 and 119 °C, while beyond 120 °C, the changing tendency of the band space became unapparent and irregular. Scanning electron microscopy and atomic force microscopy confirmed that the alternative negative and positive bands could be attributed to the alternative flat-on and edge-on lamellae in the spherulites. Through analyzing the change of lamellar thickness and long period with temperatures, we speculated that the formation of the intriguing change of band space might be ascribed to the unbalanced surface stress, which was closely correlated to the amorphous layers of the OBC lamellae. We believe that this study contributes to understanding the relationship between the crystalline structure and banding phenomenon for semi-crystalline block copolymers.

1. Introduction

Crystallization is an important physical process in polymer science, linking chain architecture with apparent properties. The formation of banded spherulites, which has been observed in some homopolymers,1–4 copolymers5–7 and polymer blends,8–10 is an interesting and representative morphological feature of polymer crystalline aggregates. It is generally believed that the rhythmic crystal growth of banded spherulites originates from a concerted twisting of ribbon-like crystalline lamellae along the radial growth direction of the spherulites.11–15 With regards to the driving force of the lamellar twisting, Keith and Padden16,17 proposed that it was the stress difference between the opposite lamellar fold surfaces that led to the continuous lamellar twisting directly. This theory is widely accepted and has already been utilized to elucidate many banding phenomena. The band space of banded spherulites, corresponding to the half-pitch length of twisted lamellae, is the morphological manifestation of the lamellar twisting frequency. According to the Keith-Padden theory,16 the twisting frequency is closely correlated to the unbalanced surface stress along the lamellae, which depends on the structures at smaller scales, e.g., molecular chirality (in case of chiral polymers), chain tilt (in case of nonchiral polymers), fold direction, chemical structure, and packing of the chemical groups on the fold surfaces.18–20 Therefore, investigation of the band space is useful to explore the influence of the chain structure and arrangement on unbalanced surface stress. To date, a lot of research has been concentrated on observing and understating the change of band space. Phillips et al.21 found that the spherulites of poly(e-caprolactone) grown at a comparatively high crystallization temperature ($T_c$) exhibited banding with a large band space in the range 50–100 μm, which increased consecutively with elevated crystallization temperatures. A similar variation tendency of the band space vs. $T_c$ was also found in polymers such as poly(lactic acid),2,9 poly(butylene succinate)22 and poly(3-hydroxybutyrate).23 The researchers concluded that the increase of band space corresponded to the decrease of surface stress, which resulted from elevated molecular mobility in the melt and improved regularity of the folding with the rise in $T_c$. Moreover, the wider band space was also correlated to the greater lamellar thickness generated by the higher crystallization temperatures, making cooperative lamellar twisting more difficult.

Recently, the banding phenomenon of semi-crystalline block copolymers has attracted great interest due to the diverse...
crystalline morphologies. With chemical bonding, the interaction between blocks becomes quite complicated and the crystalline behaviors of crystallizable blocks can be strongly influenced by the other blocks. Jiang et al.\textsuperscript{24} found that poly(ethylene oxide) (PEO) blocks induced the crystallization of PCL blocks and made banded spherulites of PCL form at a lower $T_c$ in PEO–PCL diblock copolymer. The band space increased consecutively with the rise in crystallization temperature. Ho et al.\textsuperscript{25} synthesized PS-PLLA diblock copolymer and found that the band space of the PLLA banded spherulites decreased with incorporation of the PS block, which could be attributed to the effect of PS diluents on the PLLA crystalline lamellae. The unbalanced surface stress was intensified by the existence of dangling amorphous PS chains, resulting in a higher driving force for lamellar twisting. Although investigations on banded spherulites of the block copolymer are still limited up to now, we can draw some conclusions from the pioneering works carried out so far that the significant interaction between blocks may induce diverse lamellar structures of the crystallizable component, resulting in distinct crystal morphologies for banded spherulites. Considering the structural diversity of block copolymers, it is quite essential to continue to investigate the banded spherulites for various block copolymers, which will contribute to understanding the relationship between the block architecture and corresponding crystalline morphologies.

Olefin block copolymer (OBC), which is synthesized \textit{via} a chain shuttling technology in a continuous way, is a promising multi-block elastomer with good thermal stability and excellent mechanical properties.\textsuperscript{25–30} It comprises crystallizable ethylene/octene hard blocks with a low octene content, alternating with amorphous ethylene/octene soft blocks containing a high octene concentration, and has a statistical multi-block architecture with a distribution in the block length and blocks per chain. Although the hard and soft blocks of OBC are considerably different in their comonomer content, they are comparatively short and can be partially miscible in the melt. In addition, the hard blocks are long enough to form chain-folded lamellar crystals with the orthorhombic unit cell and a relatively high melting temperature.\textsuperscript{31} The lamellae can be organized into space-filling spherulites even when the crystallinity is as low as 7%, and typically the impinged spherulites exhibit straight boundaries, indicating a heterogeneous nucleation with nuclei of similar activity.\textsuperscript{29,31} This morphology resembles crystallization from a miscible melt, which is distinct from that of traditional block copolymers. During crystallization, the aggregation of hard blocks drives the segregation of the noncrystallizable soft blocks into the interlamellar regions. Different block compositions or mass ratios of hard and soft blocks can induce distinct interactions between them, leading to a diverse crystallization process and diverse final morphologies.\textsuperscript{32–34} Considering the unique architecture and crystallization behaviors of OBC, the interaction between amorphous blocks and crystallizable blocks can be more complicated compared to traditional diblock or triblock copolymers. Therefore, the influence of amorphous blocks on the lamellar structure may be quite distinctive. Khariwala et al.\textsuperscript{34} observed that OBC could form banded spherulites under certain circumstances, revealing the diversity of the crystalline morphologies. However, as far as we know, the understanding of the formation of banded spherulites for OBC is very limited, and no investigations have yet paid attention to observing the variation of band space under various crystallization conditions systematically, which conduces us to investigate the influence of crystalline structure on lamellar twisting.

In this study, we observed the crystalline morphologies of OBC at a series of crystallization temperatures and focused on the change of band space when banded spherulites form. It was quite interesting that we found the changing tendency of band space $vs. T_c$ for OBC could be divided into two regions: it firstly increased continuously with the crystallization temperature; then, when the temperature was elevated beyond a critical value, the changing tendency of the band space became irregular. The lamellar structures were observed by scanning electron microscopy and atomic force microscopy, and alternative flat-on and edge-on lamellae were clearly distinguished in the spherulites. Through analyzing the crystallization process, we speculated that the intriguing change tendency of the band space might be closely related to the change of unbalanced surface stress, which is generated by the amorphous layers of lamellae.

2. Experimental

2.1. Materials

OBC material synthesized by chain-shuttling technology is a commercial grade product produced by Dow Chemical Company. OBC has a number-average molecular weight ($M_n$) of 65 kg mol$^{-1}$ with a hard block content of approximately 49 wt% and an octene content of 1.0 mol% in hard blocks and 19.3 mol% in soft blocks (determined from $^{13}$C NMR).

2.2. Measurements and characterizations

Crystalline morphologies of OBC samples were observed using a DM2500P polarized optical microscope (POM) (Leica, Germany) with a Linkam-THMS600 hot stage. Each sample was heated to 180 °C at 20 °C min$^{-1}$ and maintained at this temperature for 5 min to allow complete melting. Samples were subsequently cooled to corresponding crystallization temperatures at 30 °C min$^{-1}$ and maintained for observation. The average band space of the banded spherulites could be measured from the average distances between several bright adjacent bands. The rotation experiments were done at the microscope stage installed with a goniometer, which is able to illustrate the lamellar twist handedness as well as to indicate whether the twist is continuous or not. During a rotation around the $Y$-axis (the light crossing the sample along the $Z$-axis), the position of the extinction rings was observed. The two polarizers were tilted between $-45^\circ$ and $45^\circ$ to the $Y$-axis, permitting an observation of the Maltese cross extinction area at $45^\circ$. The more detailed crystalline structure was observed by FEI Nova Nano SEM360 (Oregon, USA) equipped with EDX. A multimode 8 atom force microscope (AFM, Bruker, German) was also used to detect the lamellar morphologies and the peak force quantitative nanomechanical property mapping (QNM) mode was selected. Under
this mode, the formation of images is based on difference of the
moduli. Therefore, images with high resolution can be obtained
when observing the morphologies of crystallites.

A Mettler DSC-821e apparatus (Mettler Toledo, Switzerland)
was used to evaluate the thermal properties of the OBC samples.
Each sample weight of about 5–8 mg was sealed in aluminum
pans and all the experiments were carried out in nitrogen
atmosphere. The lamellar thickness was calculated by Gibbs–
Thomson equation:

\[ l = \frac{2\sigma T_m^0}{\Delta H_f (T_m^0 - T_m)} \]

where \( T_m \) is the measured melting temperature for a crystalline
lamella with thickness \( l \); \( T_m^0 \) is the equilibrium melting
temperature; \( \sigma \) is the surface energy of the basal surface of
lamella; and \( \Delta H_f \) is the fusion enthalpy of the crystalline phase.

Small angle X-ray scattering (SAXS) measurements were per-
fomed with a NanoStar U system (Bruker, Germany). The power
was 3 kW, while the detection zone was from 0.2° to 2.8°. Wide
angle X-ray diffraction (WAXD) measurements were performed
using a PANalytical X’pert diffractometer (PANalytical, Nether-
lands) in a reflection mode with Ni-filtered CuKα radiation (\( \lambda =
0.154 \text{ nm} \)) under a voltage of 40 kV and a current of 40 mA.

3. Results and discussion

3.1. Banded spherulites and temperature dependence of the
band space in OBC

OBC is a novel thermoplastic elastomer that exhibits interesting
mechanical properties and attracts great attention from
researchers. In this study, we observed the morphologies of
OBC at different isothermal crystallization temperatures. As
exhibited in Fig. 1, typical spherulites without extinction bands
are found in OBC when \( T_c \) is lower than 115 °C. In contrast,
when the temperature is elevated above 115 °C, clearly visible
extinction bands emerge, which indicate that the direction of
the rotated optical axis of the molecular chains is parallel to the
incident polarized light of POM. It is generally believed that the
formation of the banded spherulite is attributed to the crystal-
line lamellar twisting along the spherulitic radius during crystal
growth. With regard to the origin of the lamellar twisting, two
main explanations are generally considered. The first one,
which is proposed by Bassett,\textsuperscript{35–37} ascribed twisting to the sum
of the screw dislocations. In this sense, lamellar twisting is
discontinuous. In the second explanation, Keith and Padden\textsuperscript{16,17}
proposed that the phenomenon results from an unbalanced
surface stress repartition, leading to continuous twisting. By
analogy between a screw and a continuously twisted lamella, a
left-handed rotation applied to a left-handed screw conducts a
visual descent of the apparent screw thread, while for a left-
handed twisted lamella, a corresponding rotation leads to a
continuous descent of the corresponding extinction rings.\textsuperscript{3,4}
Therefore, it is possible to determine the sense of twisting by
POM. Fig. 2 shows the POM micrographs of OBC when sub-
jected to a left-handed rotation. In Fig. 2b, a continuous descent
of the extinction rings is clearly seen, as underlined by the red
lines. This means that the lamellar twisting of OBC originates
from unbalanced surface stress rather than from screw
dislocations.
Furthermore, the spherulitic growth rate, as well as the band space of the OBC-banded spherulites crystallized isothermally at various crystallization temperatures, was measured. Fig. 3a exhibits the changes of the spherulite radius vs. time during isothermal crystallization at 113, 115, 118, 121 °C. The growth rate is determined by the slope of the corresponding functions. We can conclude from Fig. 3a that the growth rate always exhibited a positive correlation to $T_c$ during our experiments. The accurate band space at various crystallization temperatures was determined from the average distances between several bright adjacent bands for at least 20 spherulites, and the change of band space and corresponding error bars are plotted in Fig. 3b. As for OBC, banded spherulites only form in a narrow temperature range from 115 to 121.5 °C. With $T_c$ below 115 °C, banded spherulites quickly transformed into regular ones. The absence of extinction bands at lower $T_c$ may be related to the much higher spherulitic growth rates, which makes the cooperative lamellar twisting difficult to accomplish in an insufficient time scale. However, when $T_c$ rises beyond 122 °C, the crystallization is restrained and no spherulites form. It can be seen that the band space increases continuously from 1.8 μm of sample crystallized at 115 °C to 3.8 μm at 120 °C. The rising tendency of the band space with $T_c$ is consistent with the observation using other materials such as PCL, PLA, and PBS. However, with the temperature elevated beyond 120 °C, the temperature dependence of the band space becomes quite intriguing. It firstly decreases slightly from 3.8 μm of sample crystallized at 120 °C to 3.5 μm at 121 °C, and then increases slightly to 4.2 μm at 121.5 °C. As far as we know, a similar unapparent and irregular change tendency of the band space has not been reported by other researchers. The results indicate that the crystalline structure of OBC may be distinctive, compared with other banding materials.

3.2. Lamellar morphologies in banded spherulites

The lamellar morphologies of OBC spherulites can be distinctly seen by FE-SEM. As exhibited in Fig. 4, when crystallized at 115 or 120 °C, OBC-crystalline lamellae grow helically from the center of the banded spherulites and show a slightly wavy lamellar morphology, which can be ascribed to crystalline
lamellar twisting.\(^6\) Periodic concerted regular rings can be clearly distinguished, alternating with rings formed by edge-on lamellae (pointed by the red imaginary lines) and flat-on lamellae.\(^{40,41}\) Comparing Fig. 4b with 4d, the distance between the adjacent rings formed by the edge-on lamellae is obviously larger when crystallizing at 120 °C, which is approximately consistent with the POM observations. Fig. 4d exhibits the magnification of the local region in Fig. 4c. It can be seen that there is no apparent boundary between the rings formed by the flat-on and edge-on lamellae, suggesting the twisting of lamellae may be continuous.

To further examine the crystalline lamellar texture in the spherulites, AFM micrographs in peak force QNM mode were scanned. This mode maps and distinguishes according to the nanomechanical properties, including modulus and adhesion, while simultaneously imaging the sample topography at a high resolution.\(^{42-44}\) As the modulus of the crystalline and amorphous phase of OBC is completely different, the contour profiles of the lamellae can be clearly observed. Moreover, the probe touches the sample intermittently and the forces applied to the sample can be precisely controlled for this mode. In this way, the damage to the samples is reduced to a great extent, which is important to obtain better images and to enable continuous scanning. Fig. 5a and b present the surface topography of regular spherulites isothermally crystallized at 110 °C. The organization of lamellae is rather disordered and no obvious periodic arrangement can be distinguished. In this condition, the crystallization of OBC completes quite quickly and typical spherulites develop instead of banded spherulites, which is consistent with the POM observation in Fig. 1. In contrast, the lamellar packing in Fig. 5c and d is quite ordered (lamellar packing in different regions is exhibited in Fig. S1 in ESI†). Fig. 5c catches the transition region from the edge-on lamellae to flat-on lamellae (from the upper-right corner to the lower-left corner) of OBC isothermally crystallized at 115 °C. It can be noted that the change of lamellar crystals from an edge-on to flat-on orientation appears to be gradual on the spherulite surface, and no obvious boundary can be distinguished. This phenomenon further demonstrates that the twisting of the lamellae is continuous. Compared with Fig. 5c, the period of edge-on lamellae is longer in Fig. 5d. The lamellae are well-organized and directed toward the same growth direction on the spherulite surface.

3.3. Characterizations of the isothermal crystallization process

The band space of banded spherulites is the morphological manifestation of the lamellar twisting frequency. The investigation on band space is important to understand the relationship between the unbalanced surface stress and the lamellar structure. As for OBC-banded spherulites, the temperature dependence of the band space is quite intriguing. In general, the changing tendency of the band space vs. \(T_c\) in OBC can be divided into two regions: it firstly increases continuously with crystallization temperatures from 115 to 119 °C; while beyond 120 °C, the changing tendency of the band space becomes...
unapparent and irregular. The results of the first region are in agreement with the observation for other materials, which can be attributed to the decrease of surface stress and the increase of lamellar thickness. However, the irregular changing tendency of the band space beyond 120 °C is difficult to comprehend.

In order to examine whether the change of band space is influenced by the crystal forms, WAXD patterns of OBC films under different crystallization conditions were recorded. As shown in Fig. 6, all the samples exhibit two similar peaks. The strong diffraction peak located at 21.6° corresponds to the (110) reflection, while the weak diffraction peak located at approximately 24.1° can be attributed to the (200) reflection of the
polyethylene crystal.\textsuperscript{44,45,46} The results indicate that the crystallization conditions have little impact on the formation of crystal forms, and the changing of the band space is not correlated to the crystal forms for OBC.

The melting curves of OBC isothermally crystallized at different temperatures are shown in Fig. 7, while the melting parameters are summarized in Table 1. No abrupt change of melting behaviors could be found when the temperature increased from 113 to 115 °C, during which the crystalline morphology transformed from regular spherulites to banded ones. This indicates that the formation of banded spherulites may have little influence on the melting behaviors of OBC. We can conclude from the results that the lamellar thickness increases successively as $T_c$ rises, which makes lamellar twisting more difficult and is beneficial to generate larger band space. No abnormal change tendency of lamellar thickness can be seen with temperatures elevated beyond 120 °C. Therefore, we conjecture that the irregular temperature dependence of the band space is not directly induced by variation of the lamellar thickness. We notice in Table 1 that the melting fusion ($\Delta H_m$) of OBC almost remains constant with $T_c$ below 120 °C. However, once the $T_c$ is elevated beyond 120 °C, $\Delta H_m$ drops dramatically and the crystallizable components decrease correspondingly. The abrupt change of $\Delta H_m$ at 120 °C corresponds to the abnormal changing of the band space, indicating that the band space may be correlated to the increased amorphous component.

SAXS analysis was utilized to detect the crystalline arrangement of OBC. After the Lorentz correction, one scattering peak from the lamellar structure can be seen, as shown in Fig. 8. As demonstrated by Crist,\textsuperscript{47} the average structural period of the lattice (long period) can be calculated using the first scattering maximum under such conditions. It was found that the q value at the scattering peak decreased slightly from that of the samples crystallized at 113 °C to the sample at 117 °C, with the corresponding long period increasing from 25.9 to 28.2 nm. Moreover, when $T_c$ further rises to 120 °C, the long period increases dramatically to 34 nm. Assuming a simple two phase model of the semicrystalline OBC, since the lamellar thickness increases gradually with temperature, the abrupt increase of the long period at 120 °C can be attributed to the thickness change of the amorphous layer. With a dramatically reduced degree of crystallinity beyond 120 °C, the length of the amorphous blocks increases, which then arrange into a thicker amorphous layer.

Considering the above mentioned results, we speculate that the intriguing changing of the band space beyond 120 °C may be correlated to the elevated surface stress brought about by the amorphous layer. It has been reported in previous investigations that for diblock copolymers comprising crystallizable and amorphous blocks, the random coiled amorphous chains, dangling from the crystalline lamella surface via chemical junction, can be regarded as the origin for the amplification of the steric hindrance effect,\textsuperscript{6,41} which is similar to the chirality effect. This leads to an increase in the unbalanced stress and a decrease in the band space compared with homopolymers. In order to understand the unusual banding phenomenon, we should take the architecture of OBC into consideration. OBC has a statistical multi-block architecture alternating with crystallizable and amorphous blocks. It exhibits a distribution in block length and blocks per chain. Therefore, one lamella may comprise several crystallizable hard blocks.\textsuperscript{46,48} In this sense, the amorphous soft blocks between two crystallizable blocks can distribute either between two adjacent lamellae or along the fold surface. When crystallization temperatures are elevated beyond 120 °C, some original crystallizable blocks lose their crystalline ability and the length of the amorphous blocks increases correspondingly. This generates a greater steric hindrance effect for OBC lamellae and thus induces a larger unbalanced surface stress. Moreover, with longer soft blocks arranged into amorphous layers, thicker amorphous layers form and the regularity of folding may be reduced to some extent, leading to larger unbalanced surface stress as well. Therefore, with improved unbalanced surface stress and increased lamellar thickness, the change of band space becomes irregular beyond 120 °C. However, as the architecture of OBC is quite complicated, the quantitative calculation of the unbalanced surface stress is difficult, which is under our further investigation.

### 3.4. Further verification of the temperature dependence of band space with another OBC

As mentioned above, the intriguing temperature dependence of band space in OBC-banded spherulites may be closely correlated to the amorphous layers of the OBC lamellae. If this hypothesis is the case, a similar banding phenomenon may also be found in other OBCs with different octene contents as well as...
molar ratios between hard and soft blocks. In order to verify our speculation, we took another OBC (OBC-A) and observed its crystalline morphologies at different crystallization temperatures. OBC-A has a $M_n$ of 67 kg mol$^{-1}$, the hard block content is about 36 wt% while the octene content is 1.9 mol% in hard blocks and 21.8 mol% in soft blocks. As shown in Fig. 9, the extinction rings of OBC-A begin to emerge at 113 °C, which is lower than the original OBC. This may be attributed to the crystallization of OBC-A being comparatively slower. The detailed changes of the band space and the corresponding error bars in OBC-A-banded spherulites are shown in Fig. 10. It can be seen that OBC-A exhibits a similar changing tendency of the band space as the former type of OBC. The band space firstly increases continuously with the crystallization temperature; then, when the temperature is elevated beyond 119 °C, the changing tendency becomes irregular. Considering the different crystal forms of the two types of OBC (Fig. S2 in ESI†), it is difficult to compare the band space between them. Therefore, we focus on exploring the change of band space with temperatures.

The change of band space in OBC-A-banded spherulites corresponds to the change in melting fusion as well. It is shown in Table 2 that the $\Delta H_m$ of OBC-A almost remains constant below 120 °C; while with $T_c$ elevated beyond 119 °C, $\Delta H_m$ drops dramatically. The results are in consistence with that of the original OBC, indicating that the intriguing temperature dependence of band space is not limited to a special type of OBC and the banding phenomenon is closely correlated to its unique multi-block architecture.

4. Conclusions

In this study, we investigated the crystalline morphologies of OBC, and found that OBC could form banded spherulites under certain crystalline conditions. It is quite interesting that distinct from the rising tendency of the band space vs. $T_c$ as observed in many materials, the temperature dependence of the band space in OBC-banded spherulites can be divided into two regions: it firstly increases continuously with the crystallization temperature between 115 and 119 °C; while beyond 120 °C, the changing tendency of the band space becomes irregular. Lamellar morphologies in banded spherulites were observed by SEM and AFM, which confirmed that the concentrated bands could be attributed to the alternative flat-on and edge-on lamellae. According to the characterizations of the crystallization process, we speculate that the irregular temperature dependence of the band space beyond 120 °C is closely correlated to the increase of unbalanced surface stress. The amorphous blocks of OBC may

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<th>Table 2</th>
<th>Melting parameters of OBC-A isothermally crystallized at different temperatures</th>
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<td>$T_c$/°C</td>
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<tr>
<td>Melting temperature/°C</td>
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<td>Melting fusion/J g$^{-1}$</td>
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Fig. 9 POM micrographs of OBC-A isothermally crystallized at different temperatures.

Fig. 10 Changes of band space vs. $T_c$ for OBC-A.
influence the surface stress through a steric hindrance effect and through changing amorphous layers of lamellae. However, quantitative calculation of unbalanced surface stress is quite complicated and under our further investigation. A similar changing tendency of band space is observed in OBC-A as well, confirming that the banding phenomenon is not limited to just a special type of OBC and is closely correlated to the unique multi-block architecture. We believe this study is beneficial to understanding the morphologies of banded spherulites for block copolymers, and prompts that the crystalline character of specific materials should be considered when exploring the banding phenomenon.

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Notes and references

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