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Morphology and Crystalline Structure of Inclusion Compounds Formed between Poly(ethylene glycol) and Urea*

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Abstract The poly(ethylene glycol) (PEG, with M_w 2000)-urea inclusion compound (IC) crystallized at high temperature region showed two typical orientations, flat-on and edge-on crystals. 2D-XRD and polarized FTIR spectroscopy revealed that the PEG chains within urea channels were perpendicular to the substrate in flat-on oriented crystals, while PEG chain axes were parallel to the substrate and lay along the growth direction in the edge-on crystals. FTIR absorption bands of PEG in the ICs are sensitive to orientation of the crystals. A scheme of PEG chain packing in the urea IC channel was proposed, which could explain the orientation of the crystal nucleus causing the two types of morphologies. Furthermore, functioning of PEG2000 chain end with analine had significantly influence on the morphology and orientation of the inclusion compound crystals, due to the defects caused by large terminal groups included in the urea channel.

Keywords: Poly(ethylene glycol); Urea; Inclusion compounds; Morphology; Orientation.

INTRODUCTION

Inclusion compound (IC) provides a special chance for the polymers as the guest linear chains filled in the long tunnels or channels formed by small molecules as the host structure. ICs are ideal platform to study conformation of nano-confined individual polymer chains. With various guest molecules such as *n*-alkanes[1–4] and linear polymer[5–15], urea is a widely selected host to easily form inclusion compounds. The long chain polymers are chosen from polyethers[5–7], poly(ethylene oxide) (PEO)[6, 8–13], poly(L-lactide)[14], poly-caprolactone[15], polyethylene and so on, whose extended chain conformation could be accommodated in channels with diameter of 0.55–0.58 nm formed by urea[16].

PEO-urea inclusion compound presents a different type of crystal structure from other polyethers. Suehiro and Nagano[5] found that PEO-urea crystal belongs to the trigonal system, while the general polyesters are similar to *n*-alkanes in hexagonal lattice. The detail of trigonal modification was reported by Chenite and Brisse[9] that the dimensions of unit cell are $a = b = 1.0540$ nm, $c = 0.9094$ nm and $\gamma = 120°$, and there are extra urea molecules located within the channels, which also form hydrogen bonds toward the oxygen atoms of PEO chain as well as with the other channel-forming urea molecules. This strong interaction enhances the melting point of the IC, which is nearly 10 K higher than that of pure urea[5]. The stoichiometry of trigonal PEO-urea IC was established by X-ray diffraction technique with the result of $(EO)_4$-$(urea)_9$[9]. Therefore, the PEO-urea IC with assigned crystal lattice is a suitable system to examine the influence of polymer structure on crystallization

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of inclusion compound.

Many researchers have paid more attentions on the different crystal forms of PEO-urea IC. Through different preparation methods and changing the molecular weight or proportion, PEO-urea IC could be obtained in trigonal (α)[8–10], tetragonal (β)[17, 18] and orthorhombic[13] modifications. Recently, the meta-stable tetragonal IC form was acquired from the dilute solution of PEO with high M_w of 1000000 and urea by freezing drying, reported by Ye *et al*[11]. Those demonstrate that the conformation of PEO chains varied by preparation conditions could affect the crystal structure of ICs.

Melting behavior of inclusion compounds with guest polymer chains show polymer-like characters. For example, a monotonic increase of the melting point with polymer molecular weight was observed up to 2000 for poly(ethylene glycol) (PEG) and then leveled off[5]. In addition, the terminal group like $-OCH_3$ showed a significantly influence on the melting point of PEG-UIC crystals[18]. The change on crystal thermodynamic stability is mainly due to defects caused by the density and size of the terminal group on the polymer chain.

Meanwhile, the large size terminal group was applied to control the crystal morphology of alkane/urea inclusion compounds. Using designed molecules, crystallization of hexagonal flat-plate crystals was induced and crystal growth along the channel direction was selectively inhibited[3]. Mariette and Huard[4] had analyzed the detailed crystal structure of *n*-heptane/urea ICs by X-ray diffraction at 90 K and evidenced the relative displacement along *c* axis between neighboring chains of the guest molecules.

In this paper, we focus on how the polymer chain and urea organize during crystallization process, by observing morphology and orientation of the PEG-urea inclusion compound (PEG-UIC) crystals. The influence of large end groups on the PEG-UIC crystals was also examined. The orientation, crystal structure and PEG chain direction are clarified *via* a series of characterization methods, such as polarized optical microscopy (POM), digital optical microscopy, X-ray diffraction (XRD), polarizing Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and differential scanning calorimetry (DSC).

EXPERIMENTAL

Poly(ethylene glycols) with M_w of 2000 (PEG2000) was obtained from Alfa Aesar Chemical Company. Aniline-functionalized PEG2000 was synthesized according to previous literature[19, 20]. Urea and methanol were purchased from Aladdin Chemical Company and Beijing Chemical Works, respectively. Small quantity (0.05 g) of PEG was added to a dilute (7.65%, *W*/*V*) solution of urea in methanol. The solution-grown PEG-urea IC crystals were formed from the solution *via* evaporation of solvent at 20 °C overnight.

Sandwiched between two glass slides, the inclusion compound was placed on a thermal stage (Weitu, Shanghai) and melted at 150 °C. Then it was cooled down quickly to preset temperatures for isothermal crystallization, on the same hot stage. As the crystal nucleation is very slow at high temperatures, the strategy of self-seeding was adopted: Some PEG-UIC powders were placed at the edge of the melt when cooled to the isothermal crystallization temperature. The digital images during the crystallization process were captured by a CCD camera (Panasonic, Japan). To obtain qualitative birefringence information, a first order tint plate (630 nm) was inserted in the illumination path. Films prepared by this method were characterized by digital microscopy, XRD, IR and Raman spectroscopies after removing the cover slide.

The three-dimensional height distribution information along growth front was obtained using a KH-8700 instrument (Hirox, Japan) under transmission mode. 2D X-ray diffraction patterns of PEG2000-Urea inclusion compound samples were recorded on a R-Axis Spider area detector X-ray diffractometer (Rigaku, Japan) with Mo radiation and 4 kW supplied power. Polarizing FTIR was captured on a Nicolet-560 IR spectrometer, with film prepared on a calciumfluoride window about 15 mm in diameter, at a resolution of 4 cm^{-1}. DSC-60 calorimeter (Shimadzu, Japan) was employed in the calorimetric analysis of PEG-urea IC and MPEG-PPA-ureaIC. About 3 mg of samples was held in aluminum seal during each process at a heating rate of 8 K/min and an indium standard was used for calibration. The endothermic peak temperature was taken as melting point.

RESULTS

Morphology and Crystalline Structures of PEG2000-UIC (PEG-UIC)

As both the crystalline structure and morphology could be influenced by crystallization temperature, it's necessary to check their relationship at first. The effect of T_c on the crystal morphology of the PEG-UIC is shown in Fig. 1. The POM images demonstrated two typical orientations, the hexagon-like flat-on lamellae and the sword-like edge-on lamellae, prevailing at high and low super-cooling, respectively. They had the same melting temperature at around 146 °C. And there was a competition between two types of growth fronts, which depended in a clearly visible way on the crystallization temperature. When crystallization temperature was near 130 °C, the flat-on lamellae grew faster than edge-on lamellae.

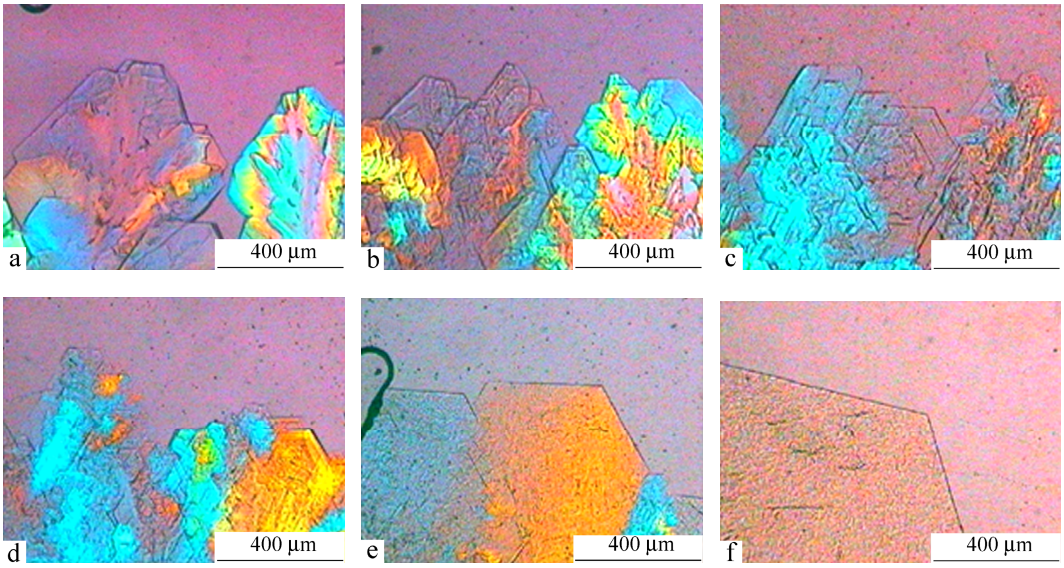


Fig. 1 The influence of crystallization temperature on the morphologies of PEG-UIC:
(a) T_c = 141 °C, (b) T_c = 138 °C, (c) T_c = 136 °C, (d) T_c = 134 °C, (e) T_c = 132 °C and (f) T_c = 131 °C

To control the type of crystal morphology in melt and solve randomness of nucleation with two-component system, crystallization temperatures were in high-temperature region, under the melting temperature less than 20 K. With flat-on oriented growth front in Fig. 1(a to f), we noted a morphology development influenced by crystallization temperature, from hexagon-like faceted to wide and smooth growth front. Under the cross polarized microscope with a first order tint plate, the thick front grew slowly and exhibited strong birefringence at high temperature as 141 °C. As cooled down, there were lots of screw dislocations (Fig. 1c) arising near the growth front, at temperature range of 137–135 °C. The growth front changed to wider and smoother with increasing degree of undercooling, with included angle of 120° as well. It grew fast obviously due to the high degree of undercooling. Flat-on crystals prevailed at low crystallization temperatures and edge-on crystals appeared more frequently at high temperatures. It's different to the general way of polymer crystallization. In the latter, flat-on lamellae prevail at high crystallization temperatures.

As the optical micrograph couldn't provide the quantitative information of thickness directly, we measured the sample thickness by 3D-digital microscope. The height of lamellae is around 50 μm, captured by optical confocal three-dimensional imaging. The large thickness of lamellae of PEG-Urea inclusion complex exhibited the similar crystallization behavior as small molecules. Before removing the cover slide, the sample in Fig. 2 was prepared at 128 °C, represented the wide and smooth flat-on type front, like Fig. 1(f).

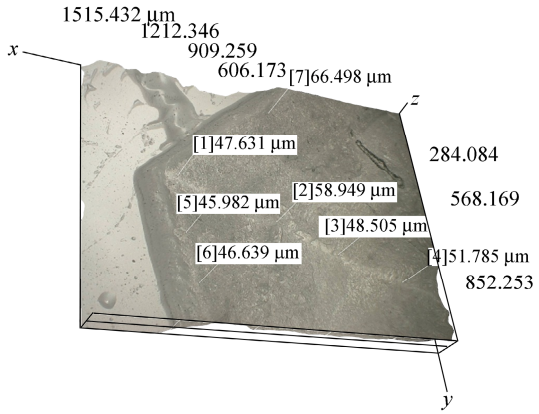


Fig. 2 3D digital microscope image of flat-on growth front

To reveal the microscopic crystalline structure of the two types of morphology in PEG2000-Urea ICs, two-dimensional XRD study was performed, with the results shown in Fig. 3. The patterns of flat-on (Fig. 3c) and

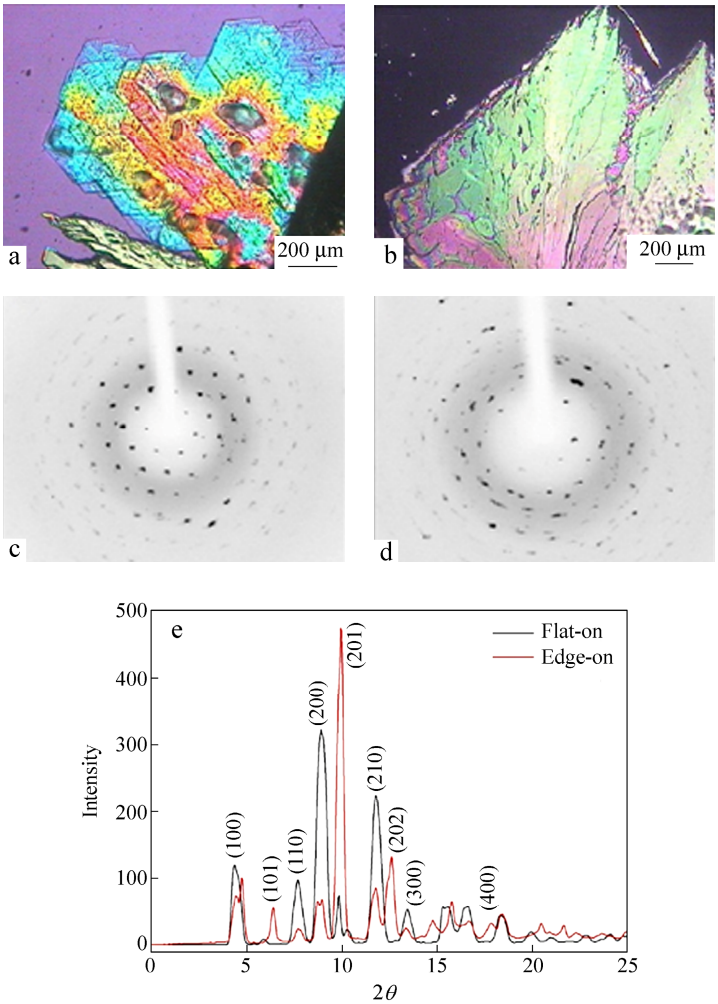


Fig. 3 POM images (a, b), 2D-XRD patterns (c, d) and XRD patterns (e) of flat-on and edge-on orientations of PEG-UIC

edge-on (Fig. 3d) oriented crystals are quite different. The flat-on crystal with typical hexagonal diffraction spots indicates that the urea channels are perpendicular to film plane. Chenite and Brisse[9] reported the crystalline structure in the trigonal form of PEO-urea complexes, in which the urea host molecules formed pseudo-hexagonal channels in a honeycomb-like pattern, which were the same to the diffraction of our flat-on lamellae. Meanwhile, the channels are filled with poly(ethylene oxide) chains along *c* axis. Consequently, the flat-on oriented lamellae could show the urea hexagonal channels and PEG molecules perpendicular to the substrate. In contrast, the pattern of edge-on crystals was not as simple as the flat-on crystals. Maybe not all edge-on lamellae was parallel to the substrate strictly and they tilted with small angles easily, so the pattern of edge-on crystals was supposed to be a combination of simple spots.

Figure 3(e) shows the XRD curves of the integrated two-dimensional XRD data. The flat-on crystals had stronger peaks at 2θ of 7.65°, 8.91° and 11.79°, corresponding to (110), (200) and (210) planes, respectively. The characteristic peaks at 6.39°, 9.95° and 12.6° due to (101), (201) and (202) planes, indicate presence of crystal planes containing *c* axis in the edge-on crystals. From the XRD diffraction, we could clearly confirm the orientation of urea channels in the c direction in the two types of crystals.

Fourier transforms infrared (FTIR) and Raman spectroscopy are utilized to reveal the PEG conformation in the crystals. Polarized infrared spectroscopy is sensitive to crystal orientation. Figure 4 shows the polarized FTIR spectroscopy of two type lamellae with polarizing angle of 0° and 90°. Our results show that the edge-on crystals (Fig. 4a) with growth direction parallel to the polarization direction possess stronger absorption at 1341, 1247, 1079 and 945 cm^{-1} , while the flat-on crystals (Figs. 4c and 4d) demonstrate stronger absorption at 1359, 1277 and 954 cm^{-1}. The absorption bands at 1341, 1247, 1079 and 945 cm^{-1} are hardly observed in the flat-on crystals. In literature, the bands at 1359, 1277, 1247, 945 cm^{-1} are assigned to CH_2 wagging, CH_2 twisting, CH_2 rocking and CH_2 rocking of the *gauche* conformation, respectively. The bands at 1341 and 954 cm^{-1} are assigned to CH_2 wagging and CH_2 rocking of the *trans* conformation, respectively[11]. Our results are a bit different from such assignment and demonstrated that the bands depend strongly on the orientation of the crystals.

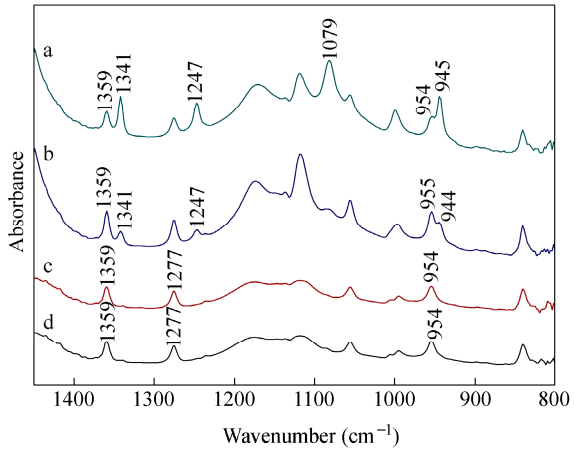


Fig. 4 Polarized FTIR spectroscopy of PEG-UIC:
(a) edge-on crystals with polarizing angle of 0°, (b) edge-on crystals with polarizing angle of 90°, (c) flat-on crystals with polarizing angle of 0° and (d) flat-on crystals with polarizing angle of 90°

The polarizing angle with the electric vector of polarized beam along the growth direction was referred to as 0°, then changed to the perpendicular direction by rotating the polarizer 90° and tested again. Marentette and Brown[21] had examined the pure PEO orientated film in detail. They found that the vibrations at 1359 cm^{-1} and 1277 cm^{-1} are perpendicular to the PEO chain axis, while the bands at 1341, 1247 and 947 cm^{-1} are parallel to the PEO chain axis, respectively. No matter what's the polarizing angle, the polarization direction is always perpendicular to chain axis in flat-on orientation. But in edge-on PEG-UIC crystals, the parallel vibrations are

stronger at polarizing angle of 0°, from which we could infer that the PEG chains are filled in the urea channels along the growth direction.

Morphology and Crystalline Structures of Inclusion Compound Formed between p-Phenyl-amine Terminated PEG 2000 and Urea (MPEG-PPA-UIC)

During the crystallization process, polymer chains play a role as guide in the inclusion compounds. To examine the effect of chain ends, we replaced one terminal group of PEG2000 with *p*-phenyl-amine.

Figure 5 shows the terminal group effect on the morphology and crystal structure of MPEG-PPA-Urea ICs. While the POM image of MPEG-PPA-UIC is different from that of PEG-UIC, the crystal structure obtained *via* WAXD was closed to PEG-UIC's. The special morphology of hexagonal axialite with branches was quite different from that of PEG-Urea ICs. The areas between the six main growing axes have strong orientation individually. With the growth front keeping in the hexagon like flat-on type, the crystals are more similar to edge-on crystals because of the anisotropy and the branches however. Sometimes a strand of fiber even appeared and crossed the mother crystal. We supposed that flat-on crystal grows as a thin template and edge-on crystals grow on the template further, filling the space between the flat-on lamellae and cover slide. The weak six-fold symmetrical ring pattern in Fig. 5(b) corresponds to the six sectors of hexagonal axialite. And the XRD diffractogram of MPEG-PPA-UIC basically shared the characteristic diffraction peaks in the edge-on oriented PEG-UIC crystals.

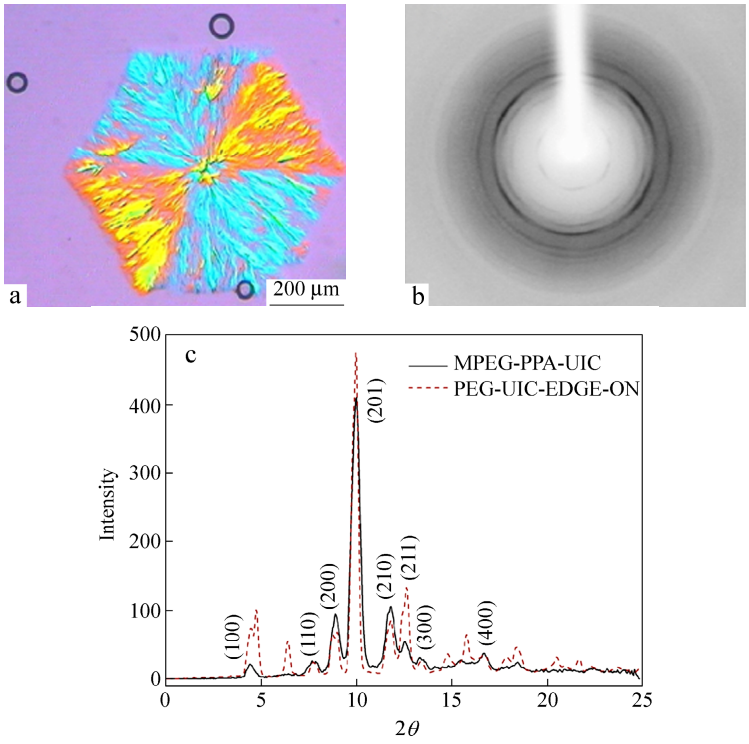


Fig. 5 POM image (a), 2D-XRD pattern (b) and XRD patterns (c) of MPEG-PPA-UIC crystallized at 129 °C

To further assign the crystal orientation, the polarized IR was measured. The vibrations at 1341, 1247 and 944 cm^{-1} belonging to the edge-on crystals were observed, which could confirm the edge-on orientation of the crystals. What's more, there was no obvious difference between the spectroscopy with polarizing angle of 0° and 90°, indicating that the edge-on crystals are randomly oriented. Consequently, we suggested that MPEG-PPA-Urea ICs are a mixture of flat-on and edge-on orientation, based on the above results.

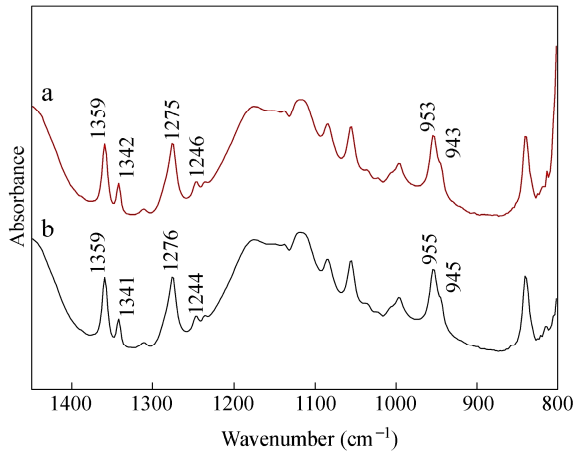


Fig. 6 Polarized IR spectroscopy with polarizing angle of 0° (a) and 90° (b) of MPEG-PPA-UIC

The terminal group shows little influence on the crystal structure, but the thermal behavior is significantly affected by the *p*-phenyl-amine terminal group. The melting curves of MPEG-PPA-UIC and PEG-UIC are presented in Fig. 7. During heating process, the single melting peak of the former appears at around 136 °C, and the substitution of —OH by —PPA only reduces the value of T_m by 4 K. Nevertheless, the melting enthalpy is considerably influenced by the terminal group. Specifically, the melting enthalpy of MPEG-PPA-UIC and PEG-UIC is 164.3 J/g and 224.9 J/g, so the terminal –PPA group makes the inclusion complex containing more defects and thus less stable.

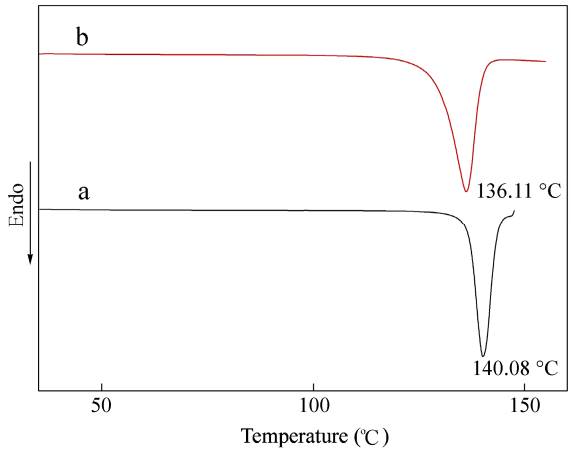


Fig. 7 DSC thermograms of PEG-UIC (a) and MPEG-PPA-UIC (b) at a heating rate of 8 K/min

DISCUSSION

For polymer-urea inclusion compounds, it is well known that the host walls of honeycomb-like channels are built with hydrogen-bonded urea molecules and the channels are filled with the guest chain. For PEG-urea system, the extra urea molecules are located within the channels, which also form hydrogen bonds toward the oxygen atoms of PEG chain as well as with the other channel-forming urea molecules[9]. Mariette and Huard had paid more attention on the phase ordering of *n*-heptane/urea as an aperiodic inclusion compound, and found the offset between guest molecules in adjacent channels was non-zero by X-ray diffraction[19]. Similar to alkanes, the long-chain molecular guest in urea honeycomb-like network couldn't be stacked in a layer-by-layer pattern.

In our work, through various characterization techniques on the two kinds of lamellae with typical morphologies in PEG2000-urea ICs, we can infer the orientation of crystal structure and the spatial relationship between PEG chain axis in urea channel and the growth direction. The large thickness of lamellae implies that the PEG chains are included in the IC channel end by end, leading to large size of crystal along *c* axis, which is similar to alkanes/urea inclusion compounds. The XRD honeycomb-like patterns show that the urea hexagonal channels are perpendicular to the substrate in the flat-on oriented lamellae. Meanwhile, the PEG molecular chains with $(ttg)_n$ conformation are perpendicular to the substrate in the flat-on lamellae, evidenced by the characteristic vibrations in IR spectra. What's more, the parallel vibrations sensitive to polarizing angle of polarized IR demonstrate the PEG chains axes are parallel to the substrate and even lie along the growth direction in the edge-on oriented crystals, which is distinctly different from polymer crystallization that the polymer chains in edge-on lamellae are generally normal to the growth direction.

Some single crystals of PEG-UIC were observed at 139 °C, as revealed in Fig. 8. The color of crystals depends on thickness and orientation. Based on the polarizing optical microscopic images in Fig. 1(a), the edge-on crystals have much stronger birefringence than the flat-on crystals with the same thickness. Consequently, we could distinguish the two types of crystals by color and shape. In Fig. 8, the grey hexagonal single crystal (indicated by arrow A) is a typical flat-on oriented crystal and the long rod-like ones (indicated by arrow B) are edge-on crystals. As not all crystals are parallel or perpendicular to the substrate strictly and they may tilt with small angles, there are lots of crystals with various shapes shown in Fig. 9. For instance, the light blue single crystal (indicated by arrow C) is an edge-on crystal with growth direction of [010] in the plane of substrate.

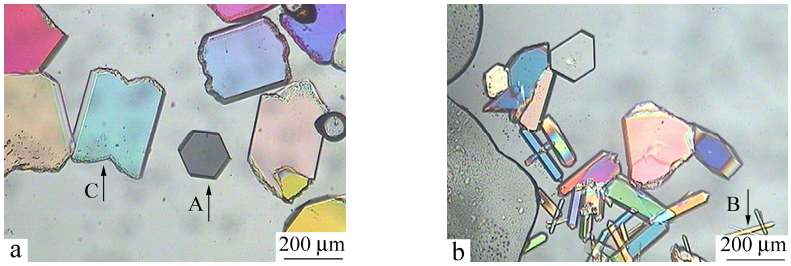


Fig. 8 POM images of single crystals of PEG-UI crystallized at 139 °C
Arrow A indicates a hexagonal flat-on crystal. Arrow B indicates rod-like edge-on crystals. Arrow C indicates the symmetrical shaped edge-on crystal.

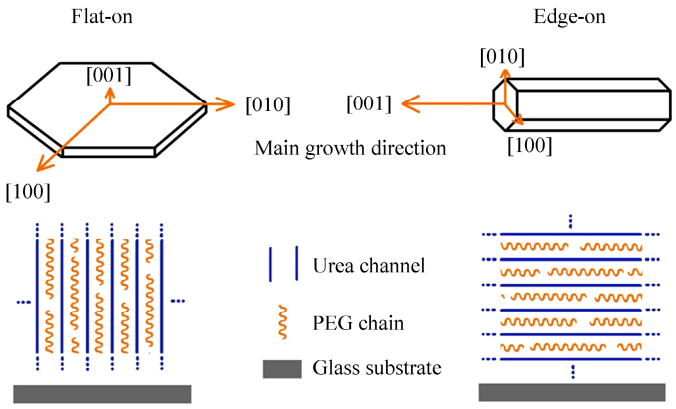


Fig. 9 Schematic illustration of crystalline structure of PEG-UIC showing different orientations

Based on the aforementioned results, a schematic illustration of crystal growth of PEG2000-urea inclusion compounds is presented in Fig. 9. The two-dimensional illustration shows the relationship between the chain axis of PEG molecules in urea channels and substrate. The flat-on crystal grows along [100] or [010] axis mainly,

forming flat-plate due to the limited height between two glass slides. Moreover, the edge-on crystal nucleus prefers to grow along [001], namely *c* axis. If the plane (110) is parallel to the substrate strictly, the needles can be observed in the melt.

Inclusion of PEG chain ends in the urea channel leads to a large size of crystal along *c* axis. The guest polymer chains play a role as crystallization guide and the melting point can be adjusted by changing the molecules or terminal group[18]. After introduction of chain end with larger size, there are more defects now, This results in depressed melting point and decreasing size of IC crystals along *c* axis. However, the *p*-phenyl-amine end group with size of 0.5 nm can still be accommodated in the urea channel with diameter of 0.55–0.58 nm[16]. Thus the thickness of crystal along *c* axis is still much larger than the single chain length. To obtain single layer IC crystals with thickness equal to the polymer chain length, we may need much bulkier terminal groups.

CONCLUSIONS

PEG2000-urea ICs crystallized at a high temperature region has two typical orientations, the flat-on and edge-on lamellae, depending on the orientation of the crystal nucleus. 2D-XRD diffraction and polarized FTIR demonstrate that the PEG chains within urea channels are perpendicular to the substrate in flat-on crystals and are parallel to the substrate and lie along the growth direction in the edge-on crystals. For PEG2000 chains with analine end, there are more defects in ICs. This results in depressed melting point and decreasing size of IC crystals along *c* axis. In addition, the morphology of inclusion compounds changed as well. In the studied temperature range, edge-on lamellae were observed all the time which deservers further study. A scheme of PEG chain packing in the urea IC channel is proposed, in which PEG2000 chains with helical conformation were packed end by end in the channel formed by urea. Consequently, the crystal size along *c* axis is much larger than the individual PEG chain length.

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