



Melting behavior of inclusion complex formed between polyethylene glycol oligomer and urea



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ABSTRACT

Inclusion complexes formed from host small molecules and guest polymers have provided a novel platform to study both the physical properties of isolated polymer chains and crystallization behavior of host molecules. In this report, we have studied the crystalline structure, melting behavior and infrared information of inclusion complexes formed between polyethylene glycol oligomers and urea molecules. The effect of molecular weight and terminal group of guest PEG oligomer on the melting behavior of inclusion complex is presented. FTIR spectra reveal that terminal –OH of PEG is hydrogen-bonded to urea in inclusion complex, while the terminal –OCH₃ is free. The melting behaviors of complexes are interpreted using either Gibbs–Thomson equation for lamellar crystals with definite channel length or Flory equation for crystals with infinite channel length and included defects. The results show that the interaction between terminal –OH in PEG chain and urea induces larger interfacial free energy or stronger defect effect, compared to the terminal –OCH₃ in the inclusion complexes, which results in the particular order of melting point: $T_m(\text{DPEG500UIC}) > T_m(\text{MPEG550UIC}) > T_m(\text{HPEG600UIC})$.

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1. Introduction

Inclusion complex (IC) formed between polymer (as guest) and small molecules (as host) has provided a usual and efficient method to study different applications and structural properties in polymer science. Complex formation can be used for polymer fractionation [1], chiral recognition [2], nucleant exploitation [3–6], crystallization behavior [7–11], and study of metastable structure [12–16], etc. Among various host molecules, urea is widely selected due to its rather easy feasibility to obtain IC with different polymers. In polymer-urea ICs, polymer chains are reported to adopt extended conformation and be isolated from neighboring chains in urea channels of about 5.5 Å diameter [17,18], which are constructed by the crystalline network of hydrogen-bonded urea molecules. The crystal modification of urea channel is often independent of different polymer chains, shown as either trigonal or tetragonal modification [19,20].

Polyethylene glycol (PEG) (or polyethylene oxide (PEO)) is often chosen as guest polymer to study the IC with urea as host molecules, because of its easy preparation, adjustable molecular weight as well as a narrow molecular weight distribution. PEG-urea IC (PEGUIC) could be obtained through different methods, including coprecipitation [21,22], electrospinning [16,20,23], and freeze drying [15]. The first preparation of PEGUIC was reported in 1964 by Tadokoro [24]. Then the detail of trigonal (α) modification of PEGUIC was reported by Chenite and Brisse that the cell dimensions are $a = b = 10.52 \text{ \AA}$, $c = 9.26 \text{ \AA}$, $\gamma = 120^\circ$, and the stoichiometry is $(\text{EO})_4\text{-(urea)}_9$ [19]. And an orthorhombic modification was suggested with $a = 19.07 \text{ \AA}$, $b = 8.62 \text{ \AA}$, and $c = 7.73 \text{ \AA}$ recently by Liu et al. based on the pure β form complex with the stoichiometry of $(\text{EO})_3\text{-(urea)}_2$ [20]. The β modification complex is stable when it is pure [16], while the β to α transition could take place at different temperatures when the sample is prepared through melt-quenched process [15,16,20]. Another crystal form was reported as tetragonal modification: The cell dimensions are $a = b = 7.30 \text{ \AA}$, $c = 19.51 \text{ \AA}$, and the stoichiometry is $(\text{EO})_1\text{-(urea)}_1$ [21].

During the formation of IC, polymer chains are isolated and play a role as crystallization guide, which results in the appearance of some polymer-like character for urea. For example, a steep rise of the melting point of PEGUIC with molecular weight was observed for PEG up to 2000 and then the increase became significantly slow and finally leveled off [21]. PEOUIC formed spherulitic structure

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during the melt-crystallization process [14,15], which was rather different from the needle-like morphology for pure urea crystal. Terminal groups of polymer chain play important roles in thermal behavior and other properties, especially for oligomer. For instance, Cheng and co-workers carried out systematic work on the terminal group effect on the crystallization behavior of PEG oligomer, and revealed many details of the metastable crystal phase and structure transition kinetics [25]. Zhang et al. showed that the steric hindrance of terminal group could be used to control the banded spacing of poly(L-lactide) spherulite [26]. Therefore, it is worth studying the terminal group of guest PEG effect on the crystal structure of host urea, which would help to further understand its properties.

In this paper, we characterized a series of PEG oligomer-urea ICs, and considered both molecular weight and terminal group effect of PEG on IC. It was found that the dependence of PEGUIC melting point on guest PEG molecular weight shows polymer-like behavior and the melting point of IC is also significantly affected by the terminal group of PEG oligomer.

2. Materials and methods

2.1. Materials and sample preparation

PEG oligomers with different molecular weights (M_n ranged from 400 to 10,000 g/mol) and terminal groups were purchased from Sigma–Aldrich Company (USA) and Alfa Aesar Company (Tianjin, China). Urea and other reagents were bought from Aladdin Chemical Company (Shanghai, China). PEG oligomers with two terminal –OH groups, one terminal –OH group and the other terminal –OCH₃ group, and two terminal –OCH₃ groups were abbreviated as HPEG, MPEG and DPEG, respectively.

Dimer of polyethylene glycol monomethyl ether (Di-MPEG) was synthesized from MPEG oligomer and succinyl chloride with a molar ratio of 2:1. Reaction product was purified by recrystallization from benzene using cold petroleum ether as precipitator. Gel permeation chromatography (TDA302, Viscotek) showed that two MPEG oligomers were well linked by succinyl chloride, and the polydispersity index of the synthesized products was below 1.10.

ICs were obtained using coprecipitation method: 1.0 g PEG oligomer was added to 100 ml urea saturated methanol solution at 0 °C. It was subsequently heated to 50 °C for 10 min to get a homogeneous solution. White precipitate (IC formed between PEG and urea) appeared several hours after the solution was slowly cooled to 0 °C, and it was collected by vacuum filtration and put in a vacuum oven at 40 °C for 4 days to remove residual methanol. The ICs composed of different types of PEG oligomers were termed as HPEGUIC, MPEGUIC, DPEGUIC and Di-MPEGUIC according to the different PEG oligomers. The single crystal of PEGUIC was slow grown from dilute solution, and thin film sample was prepared through spin-coating method.

2.2. Differential scanning calorimetry

A DSC-60 calorimeter (Shimadzu, Japan) was used to analyze thermal properties of PEGs and PEGUICs. Sample about 2.0 mg was sealed in an aluminum crucible, and heated with a rate of 10 °C/min under nitrogen atmosphere. The temperature and melting enthalpy values were calibrated using zinc and indium as standard substance.

2.3. X-ray diffraction

Wide angle X-ray diffraction was performed on a D8 Advance diffractometer (Bruker, USA) using a Ni-filtered Cu $K\alpha$ target. The

scanning range (2θ) was from 10° to 50° with a step of 0.02°, and the scanning rate was 4°/min.

2.4. Fourier transform infrared spectroscopy

FTIR spectra were recorded on a Nicolet-560 IR spectrometer (USA) by signal averaging over 32 scans at a resolution of 4 cm^{-1} . The scanning wavenumber ranged from 4000 to 400 cm^{-1} . To reveal the change of IC during heating process, temperature-dependent FTIR was performed with a heating accessory.

3. Results and discussion

3.1. Structure of the ICs

Fig. 1 shows the diffractograms of different PEGUICs. All samples display the same diffraction peaks, which can be assigned to the α modification of PEGUIC (or PEOUIC) [15,19,21,23]. The peak positions of 2θ at 13.6°, 16.7°, 19.3°, 21.6°, 25.8° and 27.4° correspond to crystal planes of (101), (110), (200), (102), (112) and (202), respectively. These results indicate that neither terminal group nor molecular weight (M_n not less than 400) affects crystal modification of IC obtained via this co-solvent precipitation process. It is similar to the previous paper published by Chenite and Brisse, they reported that molecular weight did not affect the crystal modification [19]. However, it is different from the work by Suehiro et al. [21] and Vasanthan et al. [22] that the crystal modification of PEGUIC changes from trigonal to tetragonal as the molecular weight decreases. The difference might be caused by different preparation conditions: Suehiro et al. obtained the specimens at a much lower temperature.

FTIR is a powerful tool to reveal conformation of polymer chains. It has been widely used to distinguish the α and β modifications of PEGUIC [15,20,22]. The FTIR spectra of HPEG400UIC, MPEGUIC, DPEG500UIC and HPEG1000UIC are shown in Fig. 2. The spectra of other PEGUICs are almost the same, so the data are not shown here. The results show that all ICs adopt the α modification and PEG chains take 4_1 helical conformation, (*tgt*)₄. Characteristic absorption bands at 1360, 1277, 1248, 945 cm^{-1} are assigned to CH₂ wagging, CH₂ twisting, CH₂ rocking, CH₂ rocking and C–O–C deformation perpendicular to the chain axis, respectively; the absorption bands at 1342 and 953 cm^{-1} are assigned to CH₂ wagging, CH₂ twisting and rocking conformation parallel to the chain axis [27,28].

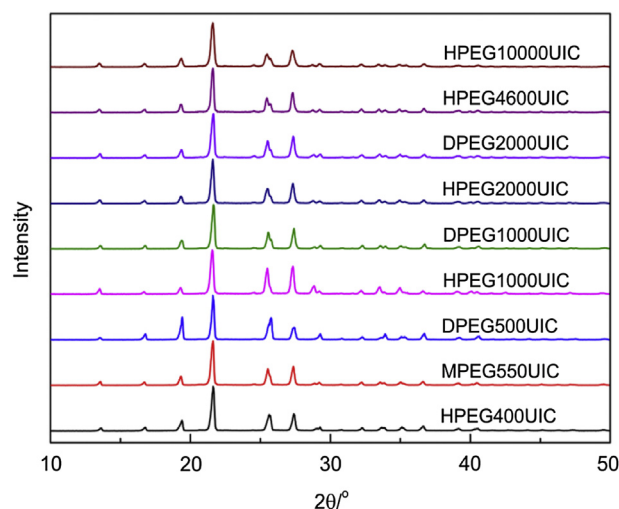


Fig. 1. WAXD diffractograms of different PEGUICs.

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