



Inclusion complex formed between poly(ethylene oxide) and thiourea



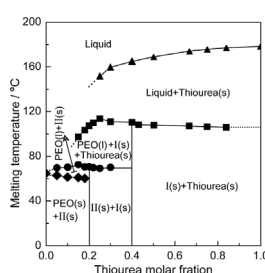
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HIGHLIGHTS

- A new PEO–thiourea complex with EO:thiourea molar ratio of 4:1 was demonstrated.
- The new complex was suggested to adopt orthorhombic modification.
- The complex probably adopts channel structure with two parallel PEO chains inside.
- Study on the stability of complex was also carried out.

GRAPHICAL ABSTRACT



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ABSTRACT

Study on the structure of PEO–thiourea binary system has been carried out by several groups, but there still remain some questions. In this study, PEO–thiourea complexes with different thiourea fractions were prepared through freeze-drying and characterized by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) microscopy and Raman scattering. A new PEO–thiourea complex with EO:thiourea molar ratio of 4:1 (form II) was demonstrated for the first time. Then the phase diagram of PEO–thiourea binary system was improved, containing two particular complexes at thiourea molar fraction of 0.4 (form I) and 0.2 (form II), respectively. Further analysis suggested that PEO–thiourea form II complex adopts orthorhombic unit cell, and probably takes channel structure with two side-by-side parallel PEO chains incorporated inside the thiourea clathrate. The form II complex is quite stable in pure state at room temperature; while gradually convert into form I by solid–solid transformation when a few form I complex serves as nucleator.

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1. Introduction

Supramolecular complexes formed between polymers and small molecules have attractive great attention over the last decades. Their particular organization structures have provided efficient perspectives to study various applications and structural properties for polymer materials, including molecular weight fractionation [1], chiral recognition [2], nucleator exploitation [3–5], pharmaceutical morphology control [6], metastable structure [7–10], etc. Besides, the guest polymer chains also guide the

host small molecules to exhibit polymer-like melting and crystallization behavior [11–13], which might open a new way to study the formation specific of polymer crystal. Among various host molecules, urea and cyclodextrin are the most often used [14]. Different polymers tend to form different structure complexes dependent on the original host structure and the stoichiometric ratio between polymer and small molecule; such as, poly(ethylene oxide) (PEO) and urea form channel and layered complexes at ethylene oxide (EO):urea molar ratios at 4:9 and 3:2, respectively; while polymers can only form channel inclusion complexes with cyclodextrins [14–19].

Analogy to urea, thiourea possesses the similar molecular and crystal structure, but higher melting temperature (i.e., ~175 °C) and larger channel diameter (i.e., ~0.8 nm). Thus, relevant study

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has been carried out. Bailey et al. reported the PEO–thiourea complex adopted an EO:thiourea molar ratio as 1:2 [20]. However, in the follow-up work, Tarnutskii et al. [21] concluded that the EO:thiourea molar ratio in the complex is 1:0.7, and Campo et al. [22] showed that the molar stoichiometry is close to 1:4 using NMR study, respectively. Recently, Pellerin group utilized electrospinning as a convenient method to prepare the host–guest complexes [16,23–25]. They succeed in obtaining pure PEO–urea β complex and determining the phase diagram of the PEO–urea binary system [16]. Similarly, they employed the electrospinning technique to prepare nanofibers of the host–guest complexes between PEO and thiourea [26]. The EO:thiourea molar ratio in complex was confirmed as 3:2 (close to 1:0.7 [21]), whose molar ratio was the same as EO:urea in PEO–urea β complex. And the PEO–thiourea complex was thus proposed to adopt a layered structure in which alternating PEO and thiourea layers were stabilized by intermolecular hydrogen-bonds. The clearer knowing on structure of PEO–thiourea complex system will help to uncover the unique characteristic of this kind of intercalates formed by weak non-covalent forces. Besides, the PEO–thiourea complex system could lead to some novel applications in different research fields, such as, solid polymer electrolyte and nonlinear optical devices [24,27].

The PEO–thiourea complex crystal (called form I hereon) takes a monoclinic unit cell with $a=0.915$ nm, $b=1.888$ nm, $c=0.825$ nm, and $\beta=92.35^\circ$. Nevertheless, there are still some questions remain. Can PEO chains form channel inclusion complex with thiourea, since thiourea takes similar molecular and crystal structure as urea? Can they form more than only one type of complex as PEO–urea system? What is more, the evidence for a possible second type of PEO–thiourea complex had been probably detected [26], but no further research has been reported yet. In this work, the PEO–thiourea with different EO:thiourea molar ratios were prepared through freeze-drying method, which is a easier path to acquire large quantitative product compared to electrospinning. The WAXD, DSC, FTIR and Raman scattering methods were employed to characterize the complexes. Results showed that a new PEO–thiourea complex formed at EO:thiourea molar ratio of 4:1. Furthermore, the phase diagram of PEO–thiourea binary system was improved and the detailed study on the structure information of new PEO–thiourea complex was carried out.

2. Materials and methods

2.1. Materials

Four types of PEO with weight-average molecular weights of 1000, 4000, 20,000, and 400,000 g/mol were purchased from Sigma–Aldrich Company. Thiourea and urea, analytical reagent grade, were obtained from Aladdin Industrial Inc. The PEO–(thio)urea complexes were prepared from dilute aqueous solution of PEO and (thio)urea (about 1% in total, w/v) using a freeze drier after the solution had been frozen in a -20°C refrigerator for 24 h. The film samples for morphology study were prepared through solution spin-coating method at a speed of 2000 rpm. All obtained complexes were kept in drying oven before use.

2.2. Methods

NETZSCH-204F1 calorimeter was utilized for the thermal analysis of samples. Sample about 3.0 mg was held in aluminum seal during each process at a heating rate of $10^\circ\text{C}/\text{min}$ or other rate, and indium and zinc standards were used for calibration. The endothermic peak temperature was taken as melting point. WAXD measurements were carried out on a Bruker AXS D8 Advance powder diffractometer using Cu $K\alpha$ ($\lambda=0.154$ nm) radiation. The 2θ

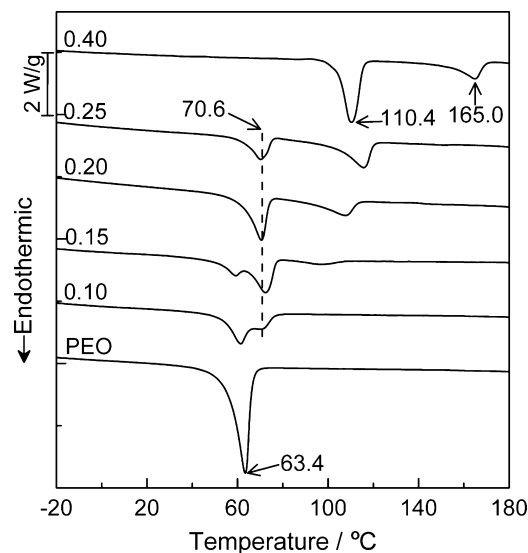


Fig. 1. DSC thermograms of PEO and PEO–thiourea complex with various thiourea molar fractions.

scanning was carried out from 8° to 30° with a step interval of 0.01° at a scanning rate of $2^\circ/\text{min}$. FTIR spectra were recorded on a Nicolet-560 IR spectrometer by signal averaging over 32 scans at a resolution of 4 cm^{-1} in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. A Renishaw RM-2000 micro-Raman spectrometer was used to obtain the Raman scattering spectra of the samples at the excitation wavelength of 633 nm. The spectrometer operates in 180° backscattering geometry and utilizes a grating of 1800 lines/mm. The resolution is 1 cm^{-1} . The Raman spectrum was obtained via six accumulations of the backscattering light, each lasting for 30 s. The laser power irradiated on the sample was 4.7 mW. Polarized optical microscopy (POM, Leica DM2500P) and atomic force microscopy (AFM, Veeco Multimode-IIIa) were utilized to characterize the morphologies of complexes, respectively.

3. Results and discussion

3.1. Formation of PEO–thiourea complexes

The DSC thermograms of PEO–thiourea complexes with various thiourea molar fractions were measured at a heating rate of $10^\circ\text{C}/\text{min}$. Complexes with thiourea molar fractions ranged between 0.4 and 1.0 displayed the similar results as Liu's research [26] and the data were not shown here; while the complexes with thiourea molar fractions lower than 0.4 displayed quite different phenomena, as shown in Fig. 1. The endothermic peaks at ~ 110 and 165°C for complex with thiourea molar fraction of 0.4 are response to the melting of form I complex and the recrystallized thiourea. With decreasing thiourea fraction, a new remarkable endothermic peak at $\sim 70^\circ\text{C}$ appeared, slightly higher than the melting point of neat PEO (i.e., 63.4°C), which suggested the formation of a new type of PEO–thiourea complex that was different from previous form I. With further decreasing thiourea fraction, a melting peak attributed to the excess PEO at around 63.4°C was detected, suggesting the endothermic peak at $\sim 70^\circ\text{C}$ was indeed due to the melting of PEO–thiourea complex. Fig. 2 shows that the melting enthalpy of peak at $\sim 70^\circ\text{C}$ gradually increases when the thiourea molar fraction decreases from 0.4 to 0.2; then it changes to decrease with further decreasing thiourea molar fraction. The melting enthalpy reaches a maximum value of 71.6 J/g at thiourea molar fraction of 0.2. Thus, the new type of PEO–thiourea complex is right corresponding to a EO:thiourea molar ratio of 4:1, which is different from

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