

Conformation transition and molecular mobility of isolated poly(ethylene oxide) chains confined in urea nanochannels

Hai-Mu Ye ^a, Min Peng ^b, Jun Xu ^{a,*}, Bao-Hua Guo ^a, Qun Chen ^b, Tian-Liang Yun ^{c,d}, Hui Ma ^{c,d}

^a Institute of Polymer Science & Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

^b Physics Department and Shanghai Key Laboratory for Functional Magnetic Resonance Imaging, East China Normal University, Shanghai 200062, China

^c Department of Physics, Tsinghua University, Beijing 100084, China

^d Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

Received 6 July 2007; received in revised form 17 October 2007; accepted 23 October 2007

Available online 26 October 2007

Abstract

Inclusion compounds formed from host small molecules and guest polymers have provided a novel platform to study the behavior of isolated polymer chains confined in nanochannels. In this article, the PEO chain conformation in the metastable poly(ethylene oxide) (PEO)–urea inclusion compound (IC) and its transition was characterized via a combination of different analytical methods. Based on the FTIR and Raman spectroscopy results, PEO chains in the metastable tetragonal IC are tentatively assigned to the *tgg'* conformation. The structural changes of the metastable tetragonal IC to the stable trigonal form were observed via *in situ* FTIR and *ex situ* WAXD. The transformation is a kinetic solid–solid process and can even occur at room temperature. The activation energy of about 222 kJ/mol indicates that the transition occurred via cooperative disruption of several hydrogen bonds. Measurement of the laboratory frame spin-lattice relaxation time T_1 (^{13}C) shows that molecular motions of the nanoconfined PEO chains are more intensive than the neat crystalline PEO but weaker than those of the neat amorphous PEO. Second harmonic generation microscopy demonstrates that the trigonal IC exhibits stronger nonlinear optical activity than the tetragonal IC. The intermolecular hydrogen bonding is attributed to the driving force for the transformation of the metastable tetragonal IC into the stable trigonal form.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Inclusion compound; Chain conformation; ^{13}C spin-lattice relaxation time

1. Introduction

More attention has been paid on the nanoconfined polymer chains because they show distinct different conformations from the bulk polymers. It will be of particular interest when each strand of polymer chains is separately confined in the nanochannels formed by another component. Extensive studies [1–5] have focused on reeling of polymers into the preformed nanotubes. However, since the process leads to dramatic decrease of the entropy of the polymers, special

interaction of the polymer chains with the confining environment is necessary to obtain negative ΔG of the system. Due to the low diffusion coefficient of macromolecules into the nanochannels, the load capacity is usually unsatisfying [6]. Furthermore, it is quite a challenge to obtain nanochannels with narrow size distribution. On the contrary, the crystalline inclusion compounds (ICs) [1,7–10] formed from spontaneous assembly of polymers and small molecules provide a new method for observing the behaviors of isolated nanoconfined polymer chains. The ICs can be obtained in sufficient amount so that the common analytical methods are feasible to characterize the material structures. Various ICs of polymers and small molecules, such as urea [9–17], perhydrotriphenylene [1,18] and cyclodextrin [1,2,4], have been reported, in

* Corresponding author. Tel./fax: +86 10 6278 4550.

E-mail address: jun-xu@mails.tsinghua.edu.cn (J. Xu).

which the included polymer chains are confined by the nano-channels composed of the small molecules, or the host clathrates. In the polymer–urea inclusion compounds, the polymer chains are extended and separated from neighboring chains by the channels of about 5.5 Å diameter [1,19]. Among them, the PEO–urea IC has attracted much interest due to the following reasons: first, there are at least two types of crystal modifications; second, melt crystallization is allowed because the melting temperature is lower than the degradation temperature; third, hydrogen bonding is a key factor affecting the crystallization behavior.

Up to now, three crystalline modifications have been observed in PEO–urea ICs, which depend on the crystallization condition. The IC formed from solution took a trigonal crystal structure [13,20], in which PEO segments adopted an approximate 4_1 helix conformation; while recrystallization from melt produced a hexagonal form [13]. The ethylene oxide oligomer (PEG)–urea inclusion compounds were found to crystallize in two crystalline modifications, tetragonal and hexagonal form. The tetragonal form contained eight molecules of urea and eight ethylene oxide units in a unit cell, which transformed into the trigonal form on heating [15]. Bogdanov et al. [14,21] studied both the solid and molten states of PEO–urea IC via infrared spectroscopy and observed the transformation of the metastable IC into the stable form when heated to 85–90 °C; however, the crystalline structure and the chain conformation in the metastable form have not been assigned yet. Solid state ^{13}C NMR has been applied to determine the mobility of polymer chains in the trigonal PEO–urea IC. The measured spin-lattice relaxation time showed that the included polymer chains demonstrated higher mobility than the bulk crystalline polymer chains [1,13].

Though much work has been carried out on PEO–urea IC, however, there are still some items unsolved, e.g. the PEO conformation, the chain mobility in the metastable crystalline modification and the details of the transition of the crystal modification have not yet been clarified. In addition, urea has been found to show nonlinear optical (NLO) behavior; nonetheless, the NLO behavior of the polymer–urea complex has not been reported so far.

In the present work, the crystalline structure, PEO conformation, kinetics of the transition process and the PEO mobility in the metastable tetragonal ICs are clarified via a combination of different methods, such as polarized optical microscopy (POM), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, wide angle X-ray diffraction (WAXD) and solid state ^{13}C NMR. Furthermore, second harmonic generation (SHG) microscopy was introduced to characterize the nonlinear optical property of the different crystal modifications of the ICs for the first time.

2. Experimental part

2.1. Sample preparation

PEO with Mw of about 1×10^6 was obtained from Shanghai Lianshen Chemical Company. The solution-grown PEO–

urea IC crystals were obtained from the dilute (0.5%, w/v) water solution of PEO and urea using a freezing drier after the solution had been frozen in a -20 °C refrigerator. There were no water molecules in the ICs, since the ICs prepared from freeze drying showed the same IR spectra as the samples cocrystallized from the supersaturated methanol solution.

2.2. POM

The inclusion compound was melted between two clean glass slides at 160 °C and held for 2 min, then transferred quickly to a thermal stage preset at a fixed temperature for isothermal crystallization. After impingement of the spherulites and no observable changes occurred, the digital images of the spherulites were captured with a computer controlled charge coupled detector (Tota, Japan). To obtain qualitative information of birefringence, a first order tint plate (530 nm) was inserted into the illumination path.

2.3. DSC

DSC-60 calorimeter (Shimadzu, Japan) was employed in the calorimetric analysis of pure PEO, urea and PEO–urea IC. Sample about 3 mg was held in aluminum seal during each process at a heating rate of 10 °C/min and an indium standard was used for calibration. The endothermic peak temperature was taken as melting point.

2.4. X-ray diffraction

Wide angle X-ray diffractions of the disk-shaped samples of about 5 mm in diameter and 0.5 mm in thickness were recorded at ambient conditions on a BRUKER D8 Advance instrument using Ni-filtered Cu $K\alpha$ radiation. The supplied power was 3 kW. The scanning was carried out with 2θ from 2° to 50° with a step of 0.02°, and the diffraction peak positions of the sample were calibrated from the pattern of aluminum.

2.5. FTIR

The PEO–urea IC film was sandwiched between KBr windows. 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 4000–400 cm^{-1} . To reveal the details of transformation of the crystals, *in situ* FTIR study was carried out. The thin film sandwiched between KBr windows was placed in a manually controlled heater. The tetragonal PEO–urea ICs were kept at a fixed temperature for a long period of time and the FTIR spectrum was recorded for every 2 or 3 min.

2.6. Raman spectroscopy

A Renishaw RM-2000 micro-Raman spectrometer was used to obtain the Raman spectra of the samples at the excitation wavelength of 633 nm. The spectrometer operates in 180°

Download English Version:

<https://daneshyari.com/en/article/5185703>

Download Persian Version:

<https://daneshyari.com/article/5185703>

[Daneshyari.com](https://daneshyari.com)