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Thermal degradation comparison of polypropylene glycol and its complex with β-cyclodextrin

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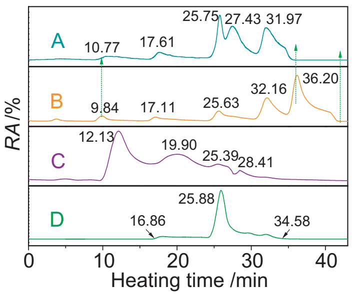
ABSTRACT

In this paper, the difference in thermal degradation behavior between polypropylene glycol (PPG) and its complex of β-cyclodextrin was carefully compared by a gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS) as well as *in situ* Fourier transformation infrared spectroscopy and thermogravimetric (TG) analyses. The present data revealed a very interesting phenomenon that there was a variation in the order of thermal stability of PPG and its complex between the conditions of TG and GC-TOF-MS. In addition, the relative abundances of released fragments in the inclusion complex were changed with different programmed temperatures in GC-TOF-MS measurements. We believe that this work will provide a better understanding on the degradation behavior of polypseudorotaxanes.

Graphical abstract:



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1. Introduction

In the past three decades the construction and characterization of supramolecules based on cyclodextrins (CDs) with organic molecules [1–3] or inorganic ions [4–6] have been studied extensively. Some of them have been applied to many fields including foods, cosmetics and pharmaceutical industries [7–10]. Polypseudorotaxanes formed by CDs and polymers have attracted a great deal of attention of researchers from 1990s [11–14], because they can be functionalized as target-specific carriers, photo-responsive gels, gene deliveries and so on [15–18].

Thermal stability is one of the most important properties of CD complexes [19,20]. Also, there are a number of studies on the relationship between heating temperatures and mass changes of polypseudorotaxanes of CDs and polymers based on thermogravimetric (TG) analysis [21,22], as well as on the correlation between heating temperatures and energy changes associated with various phase transitions based on differential scanning calorimetry (DSC) analysis [23,24]. Most of them give us an indication that there is an active interplay between CDs and polymers against thermal degradation. In recent years, the relationship between temperatures and decomposition fragments was widely used to investigate the decomposition behavior of polymers [25–27], but very few studies have focused on the decomposition behaviors of CD

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polypseudorotaxanes based on the relationship between heating temperatures and decomposed fragment properties based on a gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF-MS). Very recently, we found that the thermal release of complexed organic molecules or adducted inorganic salts changed the decomposition model of β-CD [19,28], and that the presence of β-CD led to the change of thermal decomposition of adducted inorganic guests [29]. These urge us to pose the questions as follows: 1) How do polymers alter the decomposition behavior of β-CD? 2) Can thermal stabilities of polymers bound by β-CD be enhanced by intermolecular interactions? 3) Can and how do different heating programs in GC-TOF-MS measurements influence the thermal behaviors of CD polypseudorotaxanes? 4) Is there a variation in the order of thermal stability of a polymer and its complex between the conditions of TG and GC-TOF-MS?

The present work attempts to answer these questions. Initially, a polypseudorotaxane formed by β-CD and polypropylene glycol (PPG) was prepared. Its molecular formula was determined to be PPG–(β-CD)$_5$ based on ^{1}H nuclear magnetic resonance (NMR) measurement and element analysis. [30] And the interaction between the protons in the cavity of β-CD and the protons in the PPG chain was observed by 2D NMR spectroscopy. Next, *in situ* Fourier transformation infrared (FTIR) spectra and TG profiles were used to estimate the difference in thermal stabilities of β-CD and PPG–(β-CD)$_5$. Finally, GC-TOF-MS experiments with programmed temperature rise were performed using a standard direct insertion probe for samples in the case of two different heating programs, *i.e.*, Programs A and B (see Table 1). Program A was adopted in this study to make a direct comparison in thermal degradation behaviors between β-CD and its polypseudorotaxane under the same conditions. Program B was selected to investigate the influence of different initial temperatures at the same heating rates between heating programs on the thermal degradation of the inclusion complex.

2. Experimental section

2.1. Materials

PPG (*M*n 1000) was kindly donated by Ms. X. W. Wang. β-CD was obtained from Shanghai Chemical Reagent Company and recrystallized twice from deionized water. All other reagents and chemicals used were of analar grade or general purpose.

2.2. Preparation and characterization of PPG–(β-CD)$_5$

The polypseudorotaxane PPG–(β-CD)$_5$ was prepared using magnetic stirring method with a 1:10 initial molar ratio of PPG (100 mg, 0.1 mmol) and β-CD (1.135 g, 1 mmol). The mixed solution of 200 ml was stirred for 1 h at 353 K and continued to stir for 48 h at room temperature. A white precipitate was obtained and washed thoroughly with small amount of ethanol and deionized water. The solid sample was dried under vacuum at 383 K for 8 h. The result of ^{1}H NMR measurement indicated that the host–guest stoichiometric ratio in the complex is 5:1, which is in accordance with the result of elemental analysis. [30] Further, there are two prominent cross-signals related to the protons of PPG and the intracavity protons of β-CD. One is the NOE cross-peak between the H-5 protons of β-CD and the CH$_3$ protons of PPG, and the other is the cross-peak between C-2–OH and C-3–OH of β-CD and the CH and CH$_2$ protons of PPG. These results suggest that the PPG chain has traversed the cavity of β-CD. (Supporting information). The better thermal stability of PPG–(β-CD)$_5$ than free β-CD is confirmed by *in situ* FTIR spectroscopy. First, the hydroxyl groups band in free β-CD appearing at 3397 cm^{-1} disappears at 548 K, but the strong and broad absorption band of hydroxyl groups in PPG–(β-CD)$_5$ appearing at 3376 cm^{-1} gradually decreases in intensity with the increase of temperature, and disappears at 568 K and above. This difference means a stronger hydrogen bond interaction occurring in PPG–(β-CD)$_5$ than in free β-CD. A similar difference for the absorption peak at 2934 cm^{-1} also is observed. The findings show that the presence of PPG indeed changes the intensity of some covalent bonds (O–H, C–H) in β-CD molecules due to the non-covalent interaction between them. Second, the bending vibration of O–H centered around 1638 cm^{-1} in PPG–(β-CD)$_5$ only appears at 298 and 373 K, but in free β-CD it still can be observed even at 523 K. This indicates that the vibration mode of O–H has been limited to a lower temperature after inclusion, strongly suggesting that the decomposition mechanism of β-CD is altered by the presence of PPG. Third, in PPG–(β-CD)$_5$, the vibration bands of C–O and C–O–C at 1029, 1080 and 1157 cm^{-1} still exist even at the temperature of 573 K while these bands in free β-CD disappear at 543 K. In a word, the thermal stability of PPG–(β-CD)$_5$ is enhanced in comparison with that of free β-CD (Supporting information).

Table 1
Heating Programs for PPG–(β-CD)$_5$.

Step	Temperature range (/K)		Heating rate/K·min^{-1}	Retained time/min
	A	B		
1	303	573	0	3
2	303–363	573–633	80	5
3	363–463	633–733	80	6
4	463–553	733–823	80	7
5	553–653	823–873	80	5
6	653–773	–	100	3

2.3. Instruments and methods

Two-dimensional rotating frame nuclear Overhauser effect spectroscopy (ROESY) experiment was performed on a Bruker AV400 spectrometer at 400 MHz with DMSO-d_6 as solvent to seek evidence for any direct chemical exchange between host and guest protons. A Bruker standard sequence was applied to make an observation of an intermolecular nuclear Overhauser effect (NOE) between β-CD and PPG. The data consisted of 16 scans collected over 1024 complex points and for a spectral width of 4085 Hz. A mixing time of 200 ms, a 90° pulse width of 12.5°μs at 1 dB power attenuation, an acquisition time of 0.167 s, and a repetition delay of 2.0 s were used. The data were zero-filled to 2048 × 512 points and processed by applying a $\pi/2$ shifted *Q*-sine window in both dimensions.

TG measurements were made on a Shimadzu TGA-50 thermogravimetric analyzer at a constant heating rate of 10 K min^{-1} under a nitrogen atmosphere with a gas flow of 25 mL min^{-1}.

In situ FTIR spectra were recorded on a Bruker Equinox 55 spectrometer in KBr pellets in the range 400–4000 cm^{-1}, high-temperature controller was made by Harrick Scientific Products.

GC-TOF-MS experiments with programmed temperature operations were carried out on a Micromass GCT-MS spectrometer with a heating unit. The detailed description about the heating program A was reported in a recent paper [19]. With the exception of the initial temperature, there were no difference in heating rates and retain times at each corresponding step between the two heating programs.

3. Results and discussion

3.1. TG profile analyses of β-CD, PPG and PPG–(β-CD)$_5$

Fig. 1 shows the mass loss curves of β-CD, PPG and PPG–(β-CD)$_5$ versus temperatures at a constant heating rate of 10 K min^{-1} as well as the theoretical curve of PPG–(β-CD)$_5$ based on the experimental data of free PPG and free β-CD.