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Incorporation of polyethylene glycol into polyethylene terephthalate towards blue emitting co-polyester

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ABSTRACT

In this work, fluorescent *co*-polyester was prepared by incorporating polyethylene glycol (PEG) segment into backbone of polyethylene terephthalate (PET). The crystalline structures and fluorescence properties of obtained PET-PEG copolymers were systematically studied. It was found that the crystalline behaviour of PET was significantly alternated after incorporation of flexible PEG segment, meanwhile the ultrasmall sized carbon dots with blue emitting luminescence can be obtained from incorporated PEG segment, which contributed to the fluorescence property of resultant PET-PEG *co*-polyester solution and fiber.

1. Introduction

As the most typical thermoplastic polymer in polyester family, polyethylene terephthalate (PET) has been widely applied in various fields such as packaging, textile, and engineering composites due to its cost effectiveness, excellent moisture/gas barrier properties, mechanical strength, and good processability [1–3]. However, the applications of traditional PET polymers are limited because of low toughness which is derived from their rigid backbone molecular structures. Meanwhile, the optofunctionalization of PET would be of great importance for their potential application in advanced optoelectric devices, where transparent PET thermoplastics are currently employed as flexible substrate [4,5].

Carbon dots (CDs) have witnessed increasing research attentions owing to their unique superiorities such as low cytotoxicity, biocompatibility, and photoluminescence properties, etc [6–9]. Since the first report in 2004, CDs have been extensively used in the fields of bio-imaging, biochemical sensor and photo-catalysis [10–12]. Generally, the diverse protocols for CDs synthesis can be simply classified into two groups of top-down and bottom-up methods, respectively [11]. Although these investigates have made significant progress for the CDs synthesis, multiple steps and surface passivation treatment for improving the water solubility and fluorescence properties of obtained CDs are still involved in many protocols.

Herein, we discovered that fluorescent CDs can be obtained by direct thermal decomposition of polyethylene glycol (PEG) without using any surface passivation agent in nitrogen atmosphere above 250 °C. More interestingly, we found that the highly transparent PET-PEG copolymers showing intense blue emission under UV light illumination can be synthesized by incorporating PEG segment into the backbone of PET, where fluorescent CDs are *in-situ* formulated and dispersed in obtained PET-PEG copolymers. Finally, the crystalline behaviour and fluorescence properties of obtained PET-PEG copolymer were systematically characterized with differential scanning calorimetry, polarized microscope and X-ray diffractometer as well as steady state and microscope coupled fluorescence spectroscopy.

2. Experimental

2.1. Materials

Pure terephthalic acid (PTA), ethylene glycol (EG), isophthalic acid (IPA) and Sb_2O_3 were purchased from the Sinopec Yangzi petrochemical company (China), polyethylene glycol (average molecular weight of 1000) was obtained from Sanyo chemical industries (Japan), while phenol and 1, 1, 2, 2-tetrachloroethane were acquired from Sigma Aldrich (China).

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2.2. Preparation of PET-PEG copolymers

PET-PEG copolymers were synthesized via the step polymerization of PTA, IPA, EG and PEG. Specifically, 13 kg EG, 20 kg PTA and 480 g IPA were put into a 100 L pilot reactor protected by nitrogen, refluxed at 230 °C with pressure at 2.7 bars under constant stirring for 2.5 h. Next, the produced water was separated from vaporized EG using a fractionating column and subsequently removed. Afterward, 4.2 kg PEG (previously dried in a vacuum oven at 120 °C for 1.5 h) and 10.2 g Sb_2O_3 as a catalyst were added into the reactor at atmospheric pressure. The temperature was then elevated to 280 °C and the reaction continued under high vacuum for 3.5 h, after which the melt was cooled in water to obtain the PET-PEG copolymers.

2.3. Confirmation of carbon dots(CDs) formation via thermal decomposition of PEG

As the carbon precursor, 30 g PEG was added into a 100 mL three-neck flask equipped with a magnetic stirrer, followed by heating at 280 °C and under nitrogen protection for a period of 3.5 h. Meanwhile, samples were extracted at different time intervals and diluted with pure water for further measurements.

2.4. Characterization

The UV-Vis absorption and steady state fluorescence spectra of the as-prepared CDs and the PET-PEG copolymers were recorded with a PerseeTU1901 UV-Vis spectrophotometer and a Hitachi F-4600 fluorescence spectrophotometer, respectively. The luminescence images of the copolymers were captured using a fluorescence microscopy (Eclipse TE2000-U, Nikon), while the hyperfluorescence spectroscopy was acquired from a microscope coupled fluorescence spectroscopy system of Ideaoptics co. Ltd. The crystalline behaviour of the PET and PET-PEG copolymers were characterized by means of a polarizing microscope (PLM, MP41, MShot), a X-ray diffractometer (XRD, Shimadzu XRD-7000) operating at 40 kV and 30 mA using Cu-Kα radiation wavelength of 1.5406 Å, and a differential scanning calorimeter (DSC, Q100, TA), while their thermal stability was evaluated using a thermogravimetric analyzer (TGA, Q50, TA).

3. Results and discussion

Initially, PEG was employed to enhance the toughness of PET thermoplastics by incorporating into polymer backbone structure.

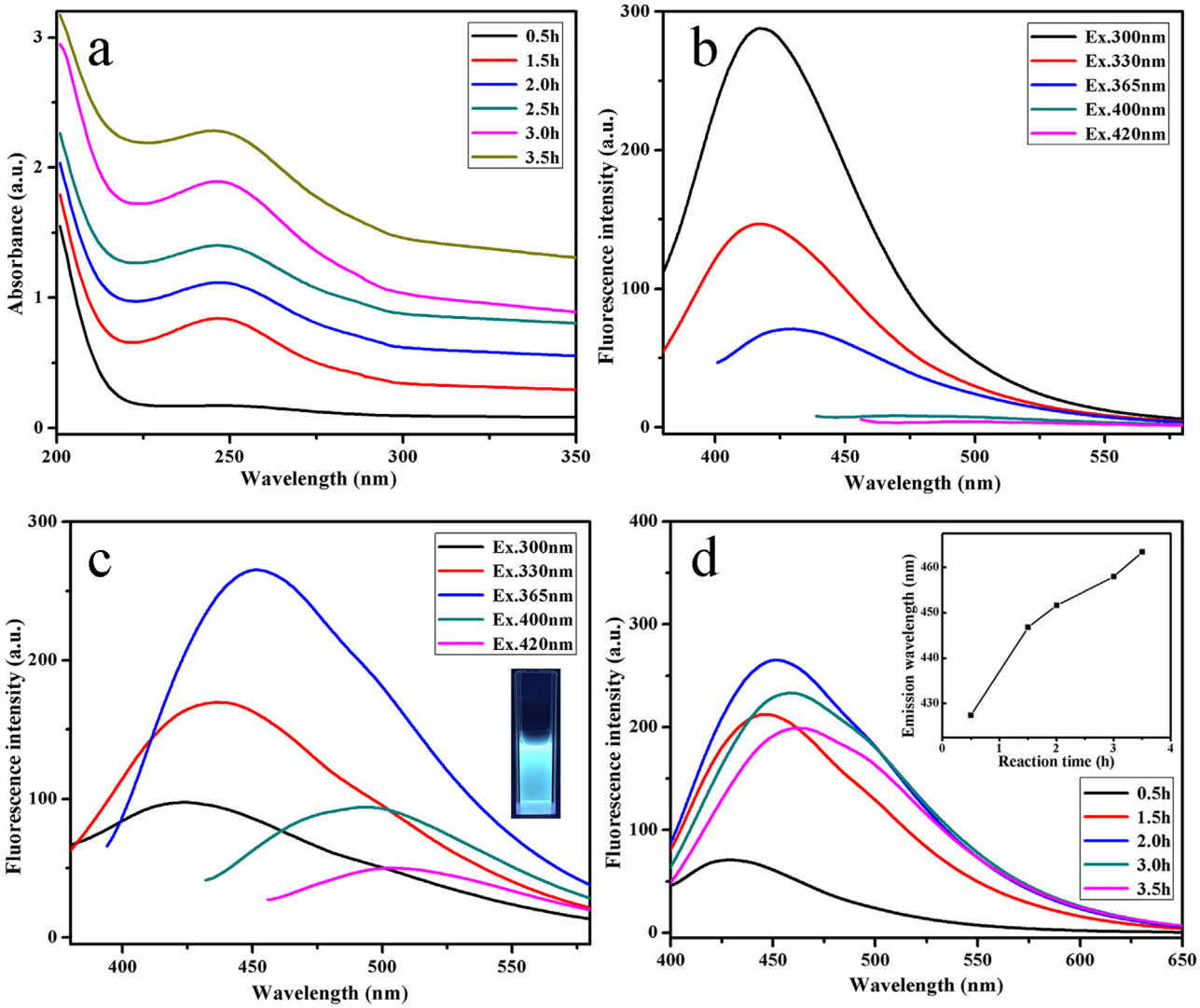

Fig. 1. UV-Vis absorption spectra of CDs obtained for different refluxing time (a), the fluorescence emission spectra excited at different wavelengths of CDs obtained after refluxing for 0.5 h (b) and 2.0 h (c), shown in inset was a cuvette containing CDs solution under 365 nm illumination, the emission spectra (excited at 365 nm) of synthesized CDs obtained at different reaction time, shown inset was the variation of the emission wavelength versus reaction time (d).