Polymer Degradation and Stability 108 (2014) 12–22

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

A novel phosphorus-containing poly(1,4-cyclohexylenedimethylene terephthalate) copolyester: Synthesis, thermal stability, flammability and pyrolysis behavior

Jun-Bo Zhang, Xiu-Li Wang*, Qiu-Xia He, Hai-Bo Zhao, Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

ARTICLE INFO

Article history:
Received 16 March 2014
Received in revised form
30 May 2014
Accepted 4 June 2014
Available online 12 June 2014

Keywords:
Poly(1,4-cyclohexylenedimethylene terephthalate)
2-(6-Oxido-6H-dibenz < c,e > <1,2 > oxaphosphorin-6-yl)-1,4-hydroxyethoxy phenylene
Copolymerization
Flame retardance
Pyrolysis

ABSTRACT

Abstract: Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) is a commercialized semicrystalline high-temperature thermoplastic polyester, but its flammability restricted its applications in some fields. A third monomer, 2-(6-oxido-6H-dibenz < c,e > <1,2> oxaphosphorin-6-yl)-1,4-hydroxyethoxy phenylene (DOPO-HQ-HE), was used to synthesize an intrinsic flame-retardant copolyester through trans-esterification and polycondensation. Its chemical structure was confirmed by ^{1}H NMR and ICP-AES. The crystallization behavior of PCTDs was investigated by DSC and WAXD, and found that the introduction of DOPO-HQ-HE slightly reduced the crystallization ability of PCT. TGA results showed that the incorporation of phosphorus-containing monomer improved the thermal stability of copolyesters both in nitrogen and air. Flynn–Wall–Ozawa method was used to analyze the thermal degradation kinetics of copolyesters, and found that the apparent activation energy was enhanced. The microscale combustion calorimetry (MCC) showed that PCTDs had lower heat release rate and total heat release than PCT. The results of the limiting oxygen index (LOI), the UL-94 vertical and the cone calorimeter test indicated that DOPO-HQ-HE endowed PCTDs with flame-retardant properties to some extent. Besides this, the cone calorimeter results show that the introduction of DOPO-HQ-HE remarkably suppressed the smoke release of PCT. The pyrolysis behaviors of PCT and PCTDs were investigated by Py-GC-MS, and found that the decomposition of PCT chains usually happened at ester bond and followed the random chain scission mechanism. The introduction of DOPO-HQ-HE almost had no effect on the thermal degradation mechanism of PCT.

1. Introduction

Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), as a commercialized semicrystalline high-temperature thermoplastic polyester, was discovered and developed in 1959 by Kibler et al. [1] The melting temperatures of PCT are in the range of 251~318 °C depending on the *trans*/*cis* isomer ratio of 1,4-cyclohexylenedimethyl (CHDM) units.[2] In addition to possessing the desirable chemical resistance, thermal stability, high strength and fiber spinning properties like poly(ethylene terephthalate), PCT and its copolyesters with excellent heat resistance made them have a great potential in automotive and electronics/electrical applications. [2,3] By adjusting the composition, some properties of PCT-based copolyesters can be improved.[4–8] Usually two methods i.e. alcohol or acid modification are used to prepare PCT copolyesters. When CHDM is partially replaced by other diol, the alcohol modified PCT copolyesters (PCTG) are obtained. If terephthalic unit of PCT is partly replaced by isophthalic ones, another commercial acid modified PCT (PCTA) are gained.[9–18] However, both of the commercial PCT and its copolyesters are flammable, which restricted their usage in some fields.

In general, there are two approaches to make polyester flame retardancy. One is using additive flame retardants, which usually contain flame retardant elements, mixed with polyester. [19,20] The other is introducing reactive flame retardants into polyester's main chain via copolymerization with the monomer of polyester.[21–26] Although endowing polyester with flame retardance by addition flame retardant is convenient, the additive flame retardants always exhibit heterogeneous dispersion and poor compatibility with polyesters, which will migrate from the

---

* Corresponding authors. Tel./fax: +86 28 85410755.
E-mail addresses: xiuliwang1@163.com (X.-L. Wang), yzwang@scu.edu.cn (Y.-Z. Wang).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.06.003
0141-3910/

matrix, as well decline the physical properties of polyester. As for as reactive flame retardants are concerned, this method can solve the problems mentioned above and obtain copolyesters with inherent flame retardancy. Several phosphorus-containing reactive monomers, such as bis 4-carboxyphenyl phosphine oxide (BCPPO), 2-carboxyethyl(phenylphosphinic) acid (CEPPA), and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives, etc, have been used to prepare inherent flame-retardant copolyesters.[23,27–30]

Unfortunately, the study on the flame retardance of PCT is just at the starting stage up to now. As far as we know, there have been no any reports on the inherent flame retardance of PCT although a few patents deal with flame retardance of PCT using additive flame retardants.[31,32] For example, halogenated organic compounds, antimony compounds and functional olefins were used to improve the flame retardance of PCT's without hurting dimensional stability.[31] It was found halogenated organic compounds containing at least one imide group can also endow PCT with flame retardance.[32] In recent years, some halogen-containing flame retardants have been banned because they will release toxic and corrosive gases, such as dioxins and hydrogen halide during the combustion.[33] In addition, the common defects of adding flame retardants to polymer matrix cannot be ignored. Therefore, it is necessary to prepare halogen-free inherent flame retardant PCT.

Phosphous-containing monomer for synthesizing PCT copolyester is difficult to choose because of a higher boiling point of CHDM. Based on our previous work,[34] we chose DOPO derivative named 2-(6-oxido-6H-dibenz < c,e > <1,2 > oxaphosphorin-6-yl)-1,4-hydroxyethoxy phenylene (DOPO-HQ-HE), which possesses relatively high decomposition temperature and high reaction activity, to prepare a series of flame-retardant PCT copolyesters. The chemical structures, thermal transition behaviors, thermal degradation kinetics, pyrolysis, and combustion behaviors of the obtained copolyesters have been studied in this paper.

2. Experimental

2.1. Materials

Dimethyl-p-phthalate (DMT, CP) was purchased from Sinopharm chemical Reagent Co., Ltd. 1, 4-Cyclohexanedimethanol (99%) was purchased from Aladdin chemistry Co., Ltd. and the ratio of cis to trans is 30:70. Tetrabutyl titanate was purchased from Kelong Chemical Reagent Factory (Chengdu, China). Before using, tetrabutyl titanate was dissolved into anhydrous toluene to prepare a 0.2 g/mL solution. 2-(6-Oxido-6H-dibenz < c,e > <1,2 > oxaphosphorin-6-yl)-1,4-hydroquinone (DOPO-HQ) was prepared according our previous work.[35] Other materials were commercially available and used as received.

2.2. Synthesis of DOPO-HQ-HE

DOPO-HQ-HE was prepared according to the literature.[35] ^1H NMR (d-DMSO; δ, ppm): 7.0–8.3 (Ar–H), 4.0 ($-C\underline{H}_2CH_2OH$), 3.7 ($-C\underline{H}_2OH$), 3.6 ($-C\underline{H}_2CH_2OH$), 2.9 ($-C\underline{H}_2$-OH), 4.5 (–OH) and 4.9 (–OH).

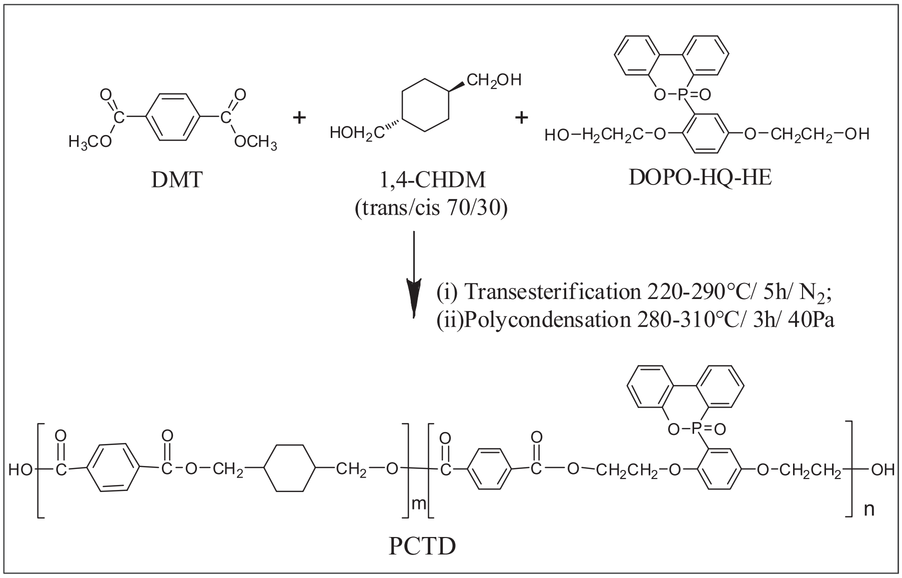
2.3. Synthesis of phosphorus-containing PCT (PCTD)

Phosphorus-containing PCT (PCTD) was synthesized by direct polymerization of DMT, CHDM and DOPO-HQ-HE, in which tetrabutyl titanate (400 ppm) was used as a catalyst (Scheme 1). Two-step reaction was carried out on a laboratory scale polymerization reactor. The first-step reaction was the transesterification of CHDM and/or DOPO-HQ-HE with DMT at 220~285 °C for 5 h under nitrogen atmosphere, in which the ratio of DMT to alcohol was fixed at 1:1.05. The second-step was the polycondensation processed at 290~310 °C, in which the pressure was slowly reduced to 40 Pa over 30 min and isothermally held for 2–4 h. Finally, the reactor was cooled to room temperature under vacuum. Samples containing 0, 5, 10 and 20 mol% DOPO-HQ-HE (DOPO-HQ-HE: CHDM) are coded as PCT, PCTP5, PCTP10, and PTTP20, respectively.

2.4. Characterization

NMR spectra (^1H, 400 MHz) were performed in a Bruker AVANCE AV II-400 NMR instrument. CF_3COOD was used as a solvent. About 20 mg of sample was dissolved in 0.5 ml solvent for testing.

Intrinsic viscosites [η] of PCTPs were measured at 25 °C with an Ubbelohde viscometer in 50/50 (v/v) of phenol/1,1,2,2-



Scheme 1. Synthesis routes of PCTDs.