

# Tailoring Schiff base cross-linking by cyano group toward excellent flame retardancy, anti-dripping and smoke suppression of PET



Jia-Ning Wu, Zi-Hao Qin, Lin Chen, Bo-Wen Liu, Xiu-Li Wang\*, 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

### Keywords:

Cyano group  
Schiff base  
Cross-linking  
PET  
Flame retardancy  
Anti-dripping

## ABSTRACT

To improve the flame retardant efficiency of aromatic Schiff base (BA), and adjust the crosslinking temperature of imine groups, a cyano group, an electron-drawing group has been introduced into the chemical structure of aromatic Schiff base to obtain a third monomer for poly(ethylene terephthalate) (PET), named as dimethyl-5-[(2-cyanobenzylidene)amino]-isophthalate (CBAA). Thermogravimetry-differential scanning calorimetry (TG-DSC) and dynamic rheological results prove that the PET-based copolyester containing CBAA (CBAA<sub>n</sub>PETs) can cross-link at higher temperature than that containing BA, which will not affect the preparing and processing of PET. DSC and wide angle x-ray diffraction (WAXD) results demonstrate CBAA<sub>n</sub>PETs remain good crystallization ability. Owing to the two types of cross-linking reactions, i. e. the reactions between Schiff base (–CH=N–) and cyano group (–C≡N), and among –CH=N– units, CBAA plays an important role in solid phase as well as gaseous phase endowing CBAA<sub>n</sub>PETs with excellent flame retardancy. With a low CBAA content (only 6.7 mol%), the copolyesters self-extinguish in 5 s with no melt drips in UL-94 vertical test, and its LOI value also increases to 31.0%. The peak heat release rate and total smoke release of the copolyesters obtained from cone calorimetry also observably decrease.

## 1. Introduction

To endow poly(ethylene terephthalate) (PET) with good flame retardancy, anti-dripping and smoke suppression properties simultaneously, many efforts have been made [1–14]. One of the most efficient methods is incorporating “smart self-cross-linking” monomer into PET chains [4,9,11]. These monomers can, at a temperature range above the processing temperature while below the decomposition temperature, form stable cross-linked networks, which further increase the melt viscosity of the copolyesters and promote the char formation, thus endowing the copolyesters with good flame retardancy, anti-dripping and smoke suppression performances.

In our previous work [11], based on the above concept, a kind of aromatic Schiff base (BA) monomer was designed and used to prepare PET-based copolyesters (BA<sub>n</sub>PETs). The obtained results show that, at a proper temperature, the imine units of BA can cross-link and form char during combustion, thus endowing BA<sub>n</sub>PETs with highly efficient flame retardancy and anti-dripping performance [11]. Because of the high reactivity of the cross-linking reaction among the imine groups, the low cross-linking temperature of BA<sub>n</sub>PETs leads to a narrow processing

window and generates tiny cross-linked networks during polycondensation. Compared with neat PET, the peak heat release rate (PHRR) and total heat release (THR) of BA<sub>n</sub>PETs show no significant decrease in cone calorimetry. Thus, a new third monomer, which can not only obviously improve the combustion behaviors of PET, but also possess more suitable cross-linking temperature should be used. Considering the low cost and convenient synthesis process of Schiff base, the new functional monomer still is designed based on aromatic Schiff base. It is expected via introducing some special functional groups into the chemical structure of BA, the cross-linking temperature and the combustion behaviors of PET-based copolyesters can be adjusted.

An electron-drawing group, cyano group, which can reduce the reactivity of cross-linking reaction among imine groups, will cross-link and cyclize at about 300 °C resulting in triazine ring structure formation [15,16]. This triazine group will further lead to char formation during combustion and release inert gas during thermal decomposition to dilute the combustible gas [17,18]. Therefore, in the present work, we designed a cyano-containing monomer dimethyl-5-[(2-cyanobenzylidene)amino]isophthalate (CBAA) and introduced it into PET chains via melt polycondensation. The cross-linking behaviors, rheological

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [xiuliwang1@163.com](mailto:xiuliwang1@163.com) (X.-L. Wang), [yzwang@scu.edu.cn](mailto:yzwang@scu.edu.cn) (Y.-Z. Wang).

performance, thermal properties, flame retardancy and flame-retardant mechanism of the copolyesters were studied in detail.

## 2. Experimental section

### 2.1. Materials

5-amino-isophthalic acid dimethyl ester (98.0%) was purchased from Lideshi Chemical Technology Co., Ltd., Beijing, China. 2-Formylbenzonitrile (98.0%) was available from Best Reagent Co., Ltd., Chengdu, China. Dimethyl terephthalate (DMT, CP), zinc acetate (99.5%) and antimony trioxide ( $\text{Sb}_2\text{O}_3$ , AR) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anhydrous methanol, anhydrous ethanol, ethylene glycol (EG), phenol and 1,1,2,2-tetrachloroethane were all obtained as reagent grade from Chengdu Chemical Industries Co., Ltd., Chengdu, China. All reagents were used without further purification.

### 2.2. Synthesis of dimethyl-5-[(2-cyanobenzylidene)amino]isophthalate (CBAA)

Under nitrogen atmosphere, 2-formyl-benzonitrile (0.2 mol) and anhydrous methanol (250 mL) were mixed together in a 500 mL four-necked round bottom flask and heated to reflux. After that 0.2 mol 5-amino-isophthalic acid dimethyl ester was added into the mixture and stirred with high-speed for 8 h. Finally, the mixture was cooled down to room temperature, filtrated and recrystallized to obtain the final product (khaki powder). The corresponding synthetic route is depicted in Scheme 1.

Yield: 80%. FTIR (KBr, shown in Figure S1): the two absorption peaks at  $2231\text{ cm}^{-1}$  and  $1626\text{ cm}^{-1}$  are attributed to  $\text{-C}\equiv\text{N}$  and  $\text{-CH}=\text{N-}$ , respectively.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm, shown in Figure S2): 8.9 (1H,  $\text{-CH}=\text{N-}$ ), 8.6 (1H, Ar-H), 8.1 (2H, Ar-H), 7.8–7.6 (4H, Ar-H) and 3.98 (6H,  $\text{-OCH}_3$ ).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm, shown in Figure S3): 165.8 (1H,  $\text{-CH}=\text{N-}$ ), 157.5 (2C,  $\text{O-C=O}$ ), 151.2 (1C, Ar-H), 137.5–126.2 (11C, Ar-H), 116.7 (1C,  $\text{-C}\equiv\text{N}$ ), 113.5 (1C, Ar-H) and 52.6 (2C,  $\text{-OCH}_3$ ). From element analysis, the actual content of N, C and H is 8.39%, 68.14% and 5.18%, respectively, which is basically consistent with the theoretical value (shown in Table S1).

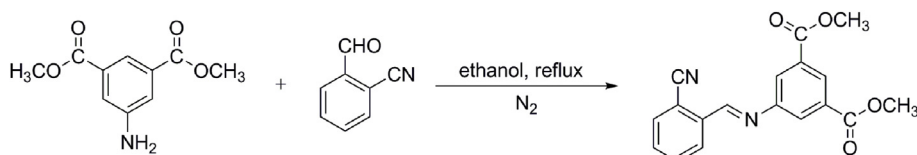
### 2.3. Polymerization of $\text{CBAA}_n\text{PETs}$

Scheme 2 shows the preparing process for CBAA-containing PET-based copolyesters, which is as same as  $\text{BA}_n\text{PETs}$  according to our previous work [11]. The copolyesters are named as  $\text{CBAA}_n\text{PETs}$ , where n denotes the molar content of CBAA per hundred mole of DMT ( $\text{CBAA:DMT} = n:100$  in mol), not the block length or repeating units. The yield of  $\text{CBAA}_n\text{PETs}$  is among 90.0–93.0%.

### 2.4. Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FTIR 170SX spectrometer by the KBr disk method with the wavenumber ranging from 500 to  $4000\text{ cm}^{-1}$ .

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of monomer and copolyesters were obtained from Bruker Avance 400 MHz NMR instrument, and the solid  $^{13}\text{C}$  MAS NMR spectra of copolyesters were performed on Bruker Avance 500 MHz NMR instrument.



Scheme 1. Synthetic route of CBAA.

The intrinsic viscosities  $[\eta]$  of PET and copolyesters were determined with an Ubbelohde viscometer at  $25^\circ\text{C}$  with a concentration of  $0.5\text{ g dL}^{-1}$  in 50/50 (v/v) of phenol/1,1,2,2-tetrachloroethane solution.

Cross-linking behavior of  $\text{CBAA}_{15}\text{PET}$  was examined using a Netzsch simultaneous TG-DSC (449 C). Under nitrogen atmosphere, all samples were heated from  $40^\circ\text{C}$  to  $500^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ .

Dynamic oscillatory rheological behaviors of all samples (parallel plates, 25 mm in diameter and 1 mm in thickness) were measured with an Advanced Dynamic Rheometric Expansion System (TA, Discovery HR-2) at a fixed frequency of 1 Hz. Temperature scanning tests were in the range from  $270^\circ\text{C}$ ,  $245^\circ\text{C}$ ,  $240^\circ\text{C}$ ,  $230^\circ\text{C}$  to  $310^\circ\text{C}$  for PET,  $\text{CBAA}_5\text{PET}$ ,  $\text{CBAA}_{10}\text{PET}$ ,  $\text{CBAA}_{15}\text{PET}$ , respectively. Time scanning tests were performed at a fixed  $280^\circ\text{C}$  for 10 min.

Differential scanning calorimetry (DSC) analysis was studied on a TA Q200 DSC calibrated with pure indium standards. In tests,  $5.0 \pm 0.5\text{ mg}$  samples were placed in aluminum pans under a nitrogen flow of  $50\text{ mL min}^{-1}$ . PET,  $\text{CBAA}_5\text{PET}$ ,  $\text{CBAA}_{10}\text{PET}$  and  $\text{CBAA}_{15}\text{PET}$  were firstly heated at  $280^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $240^\circ\text{C}$  and  $230^\circ\text{C}$ , respectively, and maintained for 3 min. Then all samples were cooled down to  $40^\circ\text{C}$  at a cooling rate of  $10^\circ\text{C min}^{-1}$  (marked as cooling scans) and subsequently reheated to  $280^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  (marked as 2nd heating scans).

Wide angle x-ray diffraction (WAXD) measurements were performed on a Philips X'Pert X-ray diffractometer at room temperature using a Cu-K $\alpha$  radiation and scanning from  $10^\circ$  to  $40^\circ$  with a scan rate of  $2^\circ\text{ min}^{-1}$ .

A Netzsch 209 F1 thermal analyzer was used to study the thermal stabilities of all samples, under nitrogen and air atmosphere, respectively. The specimens were heated from  $40^\circ\text{C}$  to  $700^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  heating rate. The samples have been tested for at least three times and experiment error was about  $\pm 2\%$ .

According to the standard ASTM D 2863-97, limiting oxygen index (LOI) tests were carried out with a HC-2C oxygen index flammability gauge with a dimensional size of  $130 \times 6.5 \times 3.2\text{ mm}^3$ . Underwriters Laboratory 94 vertical burning (UL-94) tests were performed on a CZF-2 apparatus with a dimensional size of  $130 \times 13 \times 3.2\text{ mm}^3$ . The results of each sample were obtained from at least five measurements.

Cone calorimetric tests were measured with a FTT (UK) calorimeter according to the standard ISO 5660-1 at a  $50\text{ kW m}^{-2}$  heat flux. All samples used dimensions of  $100 \times 100 \times 3.2\text{ mm}^3$ . The average values of each sample were obtained from at least four measurements, and the experiment error was about  $\pm 10\%$ .

Scanning electron microscopy (SEM) images of residual char after cone tests were collected using a Jeol JSM-5900LV spectrometer under a 10 kV acceleration voltage. Before tests, samples were over gilded by an Eiko IB-3 ion coater instrument.

X-ray photoelectron spectroscopies (XPS) were recorded by a XSAM 800 spectrometer (Kratos Co., UK), using Al K $\alpha$  excitation radiation ( $1486.6\text{ eV}$ ).

The pyrolysis behaviors of PET and  $\text{CBAA}_{15}\text{PET}$  were characterized with pyrolysis gas chromatography and mass spectrometry (Py-GC-MS) tests using a Pyroprobe (CDS5200) filled with helium. Samples (about  $300\text{ }\mu\text{g}$ ) were heated from room temperature to  $500^\circ\text{C}$  at a rate of  $1000^\circ\text{C min}^{-1}$  and maintained for 20 s. The pyrolyzer was linked with Dani Master GC-TOF-MS Systems under helium. The heating program of the capillary column GC (DN-1701 FAST  $10\text{ m} \times 0.10\text{ mm} \times 0.10\text{ mm}$ ) was as follows: the samples firstly held at  $45^\circ\text{C}$  for 2 min, then the

Download English Version:

<https://daneshyari.com/en/article/7818786>

Download Persian Version:

<https://daneshyari.com/article/7818786>

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