The preparation, thermal properties and fire property of a phosphorus containing flame retardant polystyrene copolymer

Yu Sun¹,², Yachen Wang²,³, Li Liu²,³, Tianyuan Xiao⁴

¹ College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, People’s Republic of China
² Heilongjiang Province Key Laboratory of Polymeric Composite Material, Qiqihar University.
³ College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, People’s Republic of China
⁴ College of Light Industry and Textile, Qiqihar University, Qiqihar 161006, People’s Republic of China

Abstract: In this paper, DOPO acrylate, 6-oxido dibenzo [ca][1,2] oxaphosphinin-6-yl) methyl acrylate (DOPOAA), was synthesized, and the copolymer of styrene (St) and DOPOAA was prepared by emulsion polymerization in different ratios. After that, the chemical structures of the DOPOAA and copolymers were different compositions were verified by Fourier transform infrared (FT-IR) spectroscopy and ¹H nuclear magnetic resonance (¹H-NMR) spectroscopy. The results proved that DOPOAA copolymer was well synthesized. On top of that, the thermal properties and flame retardant behaviors of DOPO-containing monomers and copolymers were observed by thermogravimetric analysis and microscale combustion calorimetry tests. Thermogravimetric analysis (TGA), it was found out that the T₅₀ of copolymer was lower than that of PS, but the residual at 700°C was higher than that of PS. The results of microscale combustion calorimetry (MCC) tests showed that the rate of the heat release of the copolymer was lower than that of PS, during thermal decomposition, and the amount of limiting oxygen index (LOI) of the copolymer rose with the molar fraction of DOPOAA. These data indicate that copolymerization of the phosphorus-containing flame retardant monomer, DOPOAA, into PS segment can effectively improve the thermal stability and flame retardancy of the copolymer.

Keywords: Emulsion Polymerization; Flame Retardancy; DOPO Derivate; Polystyrene; Copolymer

1. Introduction

Polystyrene (PS) is a very crucial thermoplastic and widely used in many applications [1, 2], such as automotive, housing, computer, packaging and injection molding [3-5] due to its great mechanical properties and chemical stability. However, PS is extremely flammable and is accompanied by a large amount of smoke. Therefore, there has been a lot of research to alter its unsatisfactory fire performance and promote its fire retardancy [6].

In the past, halogenated compounds were added into polymers as flame retardants. Although halogenated compounds are effective, they often produce a lot of toxic gases and fumes when the polymer burns, which will not only damage human health, but also pollute the environment. Instead, researchers began to use compounds such as nitrogen [7, 8], phosphorus [9, 10, 11], boron [12], which are environment friendly as flame retardant. Phosphorus-containing flame retardants have received more attention [13, 14].

In 1972, Sato successfully synthesized 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and synthesizing of reactions. Since then, DOPO has been widely used in the field of polymer flame retardant. It can be easily modified, due to its weak P-H bond, with other organic compounds to generate a series of products.
Increasing regulatory pressure. At high temperature, these materials are converted to volatile toxic dioxins (J. Hazard. Mater., 2016, 304, 26-39).

Moreover, and more importantly, when items containing organohalogen flame retardants are discarded in a landfill, the additives are leached into the environment. As a consequence, human exposure and consequent disease formation is widespread (Environ. Res., 2019, 168, 420-427; Chemosphere, 2002, 46, 579-582).
synthesizing many derivatives and improving flame retardant property thermal stability and fire behavior [15, 16]. In addition, researchers have also modified DOPO derivatives by different flame retardancy elements, such as P-N [17-19], P-Si [20-22], P-N-S [23,24] for its better fire behavior. For PS, the frequently used means to ameliorate the flame retardancy is to add flame-retardants. However, because of the poor compatibility with polymer matrix and other disadvantages of DOPO and its small molecule derivatives, their further application was limited in the flame retardant field [25-27]. Compared with the small molecule phosphorus-containing flame retardants, flame retardant which could enter the PS small molecule structure show better stability and flame retardancy. Some phosphorus-containing flame retardant monomer containing C-C bond copolymerized with PS to make the flame retardant improved [28, 29]. In this article, DOPO acrylate, DOPOAA, was synthesized as a flame retardant monomer and copolymerized with PS to improve the properties of PS. The thermal stability and flammability of the copolymer were improved by polymerization of DOPOAA into the chain segment of PS. Flame retardant effect of DOPOAA in condensed phase and gas phase was proved by TGA and microcalorimetry.

2. Materials and Methods

The structure and properties of monomers and copolymers were studied by $^1$H-NMR, FT-IR spectroscopy, TGA, MCC analysis and LOI test. $^1$H-NMR measurement was tested by a Bruker AV600 NMR spectrometer. In 500 MHz, ODOPM was dissolved in DMSO-D$_6$, and the internal standard for $^1$H-NMR spectra was tetramethylsilane. FTIR spectroscopy was conducted by a Perkin Elmer Spectrum Two FT-IR spectrometer with the wavenumber set from 500 to 4000 cm$^{-1}$. The sample and potassium bromide were mixed and ground and pressed to sheets for testing. The thermal stability experiment was performed on a TA Instruments Q8000 SA thermogravimetric analyzer from room temperature to 700 °C at the heating rate of 20 °C/min under nitrogen atmosphere. MCC analysis was conducted using the FAA-PCFC microcalorimeter. Some of samples was heated up to 700 °C from room temperature at the heating rate of 1 °C/s. The combustion furnace was averaged up to 900 °C and oxygen flow rate was 20 mL/min. LOI test values were obtained by a Chengde Dajia LF-3 oxygen index meter following the standard of GB/T2406.2-2009. The size of the sample was 70 x 6.5 x 3.2 mm$^3$.

Scheme 1 shows the synthesis of ODOPM (30.31). A mixture of DOPO and 200 mL toluene were added into the three-necked, 500 mL glass flask with a funnel, a condenser, a thermometer, and a magnetic stirrer, then were heated to 80 °C under stirring. After that, 26.7 g of paraformaldehyde was fed in the flask for three batches at half an hour. This mixture was reacted for six hours at 95 °C to get the products. After that, the mixture was obtained by filtration, and then was washed several times with toluene and dried under reduced pressure to constant weight. The yield was 91%.

![Scheme 1. The synthesis route of DOPO acrylate/Styrene Copolymer](image-url)