Journal of Industrial and Engineering Chemistry 27 (2015) 40–43

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Short communication

Synthesis of a novel phosphorus-nitrogen-containing intumescent flame retardant and its application to fabrics

Wei Jiang [a], Fan-Long Jin [a,b,*], Soo-Jin Park [b,*]

[a] Department of Polymer Materials, Jilin Institute of Chemical Technology, Jilin City 132022, People's Republic of China
[b] Department of Chemistry, Inha University, Nam-gu, Incheon 402-751, South Korea

ARTICLE INFO

Article history:
Received 11 November 2014
Received in revised form 9 January 2015
Accepted 11 January 2015
Available online 17 January 2015

Keywords:
Phosphorus
Nitrogen
Intumescent flame retardant
Fabrics
Flame-retardant properties

ABSTRACT

A novel phosphorus-nitrogen-containing intumescent flame retardant (IFR), ditrimethylolpropane di-*N*-hydroxyethyl phosphoramide (DDP), was successfully synthesized and used as a flame retardant for various fabrics. The chemical structure of DDP was characterized using FT-IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis. The thermal property of DDP was investigated by thermogravimetric analysis. The effect of DDP on the flame-retardant properties of fabrics was evaluated by measurement of the burning length. The optimal synthesis conditions for DDP were determined. DDP showed high flame retardancy when applied to nylon and moderate flame retardancy when applied to cotton and polyester.

Introduction

Flame retardants are used as additives to endow polymeric materials with good flame retardancy. Various forms of phosphorus-, nitrogen-, boron-, and silicon-based flame retardants have been developed and used as flame retardant coatings for polymer materials [1–8].

Intumescent flame retardants (IFRs) are mainly composed of phosphorus and nitrogen. IFRs are halogen-free, emit very low smoke or toxic gases during combustion, and display anti-dripping properties. Thus, they are not only well suited for fire rescue but also are environmentally friendly. Generally, an IFR consists of a carbonization agent, a blowing agent, and an acid source. During combustion of polymer materials, the phosphorus in IFRs forms an intumescent char layer on the surface of the materials via dehydratation of the carbonizing agent in the presence of an acid catalyst. The char layers are simultaneously expanded by the inert gas released from the blowing agent upon heating. The char layers thus form an efficient shielding and insulation layer for the underlying polymer matrix, preventing direct contact with the flame and oxygen and also form a barrier against heat transfer. The nitrogen-containing compounds produce incombustible gases without toxic smoke or fog when decomposed at high temperature. The generated gases can dilute the concentration of the oxygen near the flame and form a protective layer while being heated. The protective char layers act as very good protective barriers for polymer materials against flame and heat [9–11].

Various IFRs have been synthesized by several research groups for application as flame retardants for polymer materials. Xiang et al. [12] synthesized an IFR consisting of pentaerythritol spirobisphosphoryl-dicyandiamide that exhibited excellent flame retardancy as well as anti-dripping ability at 30 wt% IFR. Nguyen et al. [13] synthesized an environmentally friendly IFR from diethyl 4-methylpiperazin-1-ylphosphoramidate that caused the limiting oxygen index (LOI) to increase from 12 vol% to 28 vol% upon addition to printed cloth. Li et al. [14] studied the effect of a phosphorus-nitrogen IFR on the charring behavior of poly(ethylene terephthalate)/cotton blends. The results showed that the IFR was not only an effective flame retardant but also a good char-forming agent for the blends. Finally, Nguyen et al. [15] synthesized an environmentally friendly IFR from tetramethyl(6-chloro-1,3,5-triazine-2,4-diyl)bis(oxy)bis(methylene)diphosphonate and applied it to textiles. The LOI values increased from 18 vol% for the untreated fabric to 34 vol% for the IFR-treated fabric.

In this study, we present the synthesis of a novel nitrogen-phosphorus IFR, ditrimethylolpropane di-*N*-hydroxyethyl phosphoramide (DDP), and its use as a flame retardant for various

* Corresponding authors at: Inha University, Department of Chemistry, Incheon 402-751, South Korea. Tel.: +82 32 8767234/+86 432 62185319; fax: +82 32 8675604/+86 432 62185319.
E-mail addresses: jinfanlong@163.com (F.-L. Jin), sjpark@inha.ac.kr, psjin@krict.re.kr (S.-J. Park).

http://dx.doi.org/10.1016/j.jiec.2015.01.010
1226-086X/

fabrics. The chemical structure of DDP was characterized using FT-IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis. The thermal property of DDP was studied by thermogravimetric analysis (TGA), and the effect of DDP on the flame-retardant properties of the fabrics was evaluated by measurement of the burning length.

Experimental

Materials

Ditrimethylolpropane (Di-TMP), phosphoryl chloride ($POCl_3$), and 2-aminoethanol used in this study were supplied from Haite Chem., Tianjin Guangfu Chem., and Tianjin Chemical Reagent Co., China, respectively. 1,4-Dioxane and boric acid, respectively used as solvent and catalyst, were purchased from Tianjin Guangfu Chem.

Synthesis of IFR

(1) Synthesis of ditrimethylolpropane diphosphorus chloride (DDC). Specific amounts of Di-TMP, $POCl_3$, and 1,4-dioxane were added to a 250 ml glass flask equipped with a mechanical stirrer, thermometer sensor, and circumference condenser. The mixture was gradually heated to 50 °C and reacted for 5 h. After the reaction, 1,4-dioxane and unreacted $POCl_3$ were removed by distillation in a vacuum oven to yield a highly viscous, light-yellow liquid.

(2) Synthesis of ditrimethylolpropane diphosphate ester (DDE). DDC was dissolved in 1,4-dioxane and a specific amount of distilled water was added to the solution. The mixture was gradually heated to 72 °C and reacted for 1.5 h. Subsequently to distillation of 1,4-dioxane, a highly viscous, light-yellow liquid was obtained.

(3) Synthesis of ditrimethylolpropane di-*N*-hydroxyethyl phosphoramide (DDP). DDE was dissolved in 1,4-dioxane and specific amounts of 2-aminoethanol and boric acid were added to the solution. The mixtures was gradually heated to 70 °C and reacted for 4 h. Subsequently, 1,4-dioxane and the unreacted 2-aminoethanol were removed by distillation in a vacuum oven to generate a highly viscous, light-yellow liquid (yield: 90.3%).

FT-IR (KBr): 3260 cm^{-1} (OH), 1378 cm^{-1} (P═O), 1054 cm^{-1} (P–O–C), 2964 cm^{-1} (CH_3), 2884 cm^{-1} (CH_3), 2930 cm^{-1} (CH_2), 1173 cm^{-1} (C–O–C).

^{1}H NMR (DMSO-d_6): δ = 3.55–357 ppm (CH_2–O), 3.09–3.25 ppm (CH_2–NH), 2.81 ppm (OH), 1.20–1.23 ppm (P–NH), 0.74–0.79 ppm (CH_3).

^{31}P NMR (DMSO-d_6) δ = 8.7 ppm (singlet peak).

Elemental analysis: C, 41.11; H, 8.21; N, 5.18; O, 33.60. Calculated for $C_{18}H_{42}N_2O_{11}P_2$: C, 41.22; H, 8.02; N, 5.34; O, 33.59.

Fabric ttreatment

A 300 g portion of DDP was placed into 1000 ml of distilled water and stirred for 30 min. Fabrics cut to dimensions of 90 × 350 mm^2 were immersed in the DDP solution to give a wet

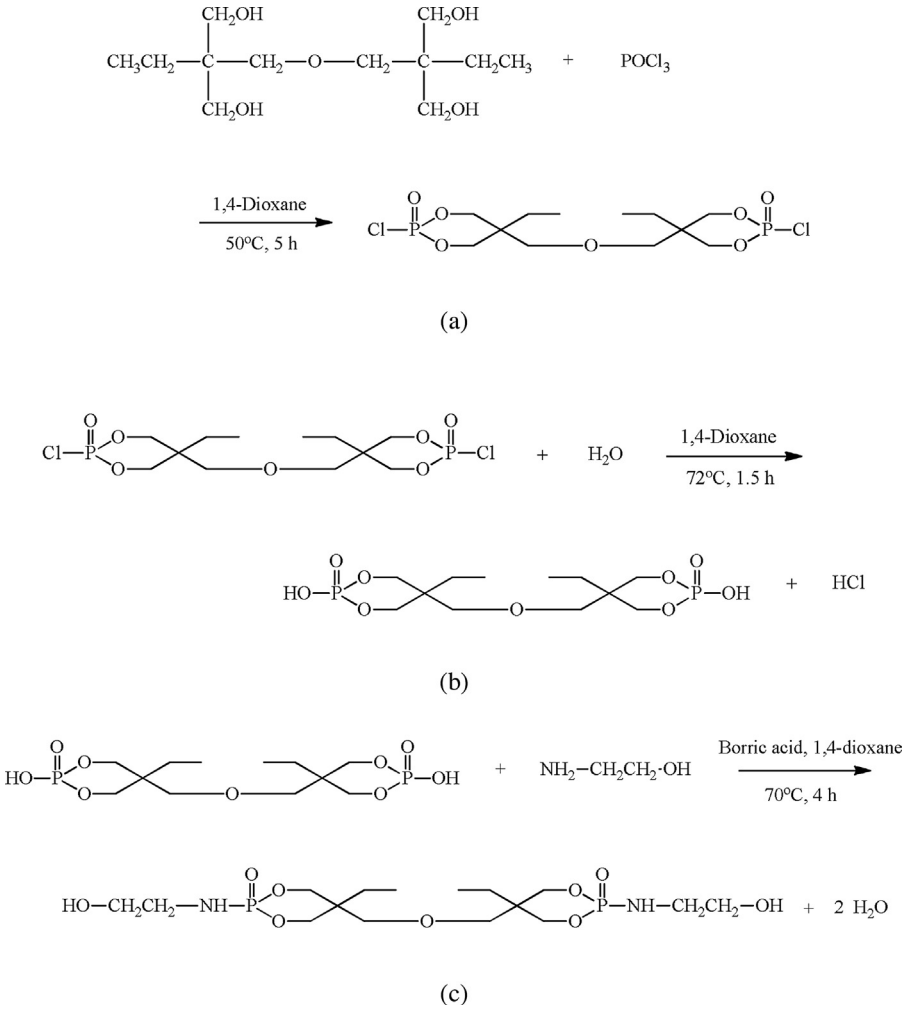

Fig. 1. Schematic outline for synthesis of DDP: (a) esterification reaction, (b) hydrolysis reaction, (c) amination reaction.