



Phosphonium sulfonates as flame retardants for polycarbonate



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ABSTRACT

Phosphonium sulfonates (PhSs) as flame retardants have been synthesized from organic sulfonates and triphenylphosphine as starting materials. The PhSs revealed good thermal stability and efficient flame retardancy for polycarbonate (PC). The LOI values increased with the increase of PhS-1 contents to PC and reached 33.7 when the PhS-1 content is 10 phr, and the V-0 rating can be achieved when only 5 phr PhSs are added. The cone calorimeter analysis indicated that the HRR and THR were reduced with the addition of PhSs to the PC matrix. The PhS bearing alkene group revealed highest LOI values and lowest peak HRR (pHRR) values for PC. The morphology of the residual chars after LOI test and the element content of the chars after CONE test were also investigated by SEM and EDX.

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1. Introduction

Polycarbonate (bisphenol-A, PC) as one of important engineering plastics is broadly applied in a wide variety of areas by virtue of its excellent features, such as good hardness, outstanding impact strength and glass-like transparency, dimensional and thermal stability, and excellent compatibility with several polymers [1,2]. Because of relatively high tendency to charring and low heat of combustion, PC by itself shows certain flame retardancy. However, more strict flame retardant modification of PC is often required in many fields, especially in electronic and electrical applications [3,4].

Organic phosphorus compounds are one class of most promoting flame retardants (FRs) for replacement of traditional halogenated FRs for polymeric materials. Thanks to the good flame retardancy and environmental friendliness for organic phosphorus FRs, a great number of flame retardants containing phosphorus atom have been developed and applied them to a wide range of polymeric materials [5]. Among them, triphenyl phosphate (TPP), bisphenol-A bis (diphenyl phosphate) (BDP) and resorcinol bis (diphenylphosphate) (RDP) are three typical phosphate fire retardant, widely used in the fire retardancy of PC and PC blends (PC/ABS etc) [6]. However, it is well known that the relatively low initial degradation temperature of the traditional phosphates fire

retardant deteriorated some properties of PC composites [3,4]. Therefore, the development of new organic phosphorus FRs for PC with advantages of high flame retardancy and high thermal stability is highly appealing. Phosphonium salts are widely used in corrosion inhibitors, lubricants, catalysts, solvents or supports in organic reactions, and electrolytes for various electrochemical devices due to their high thermal and air stability, low viscosity, good electrical conductivity, low vapor pressure, and favorable compatibility in polymers [7–22]. Most recently, a type of oligomeric siloxane containing triphenylphosphonium phosphate (SiPP) as a new FR was developed. The FR, SiPP revealed excellent thermal stability (over 300 °C) and showed efficient flame retardancy for PC. However, the synthesis of SiPP is relatively complicated and the molecular weight is not so easy to control [5].

FRs containing sulfur atom have also been applied to different polymer matrix in recent decades [23–41]. Especially, it has been found that alkali or earth alkali metals salts with aryl-sulfonates, such as potassium diphenylsulfone sulfonate (KSS), sodium trichlorobenzene sulfonate (STB), potassium perfluorobutane sulfonate (KPFBS), reveal self-extinguishing performance for PC. It is also reported that blending aromatic sulfonates to PC could lead to higher concentrations of CO₂ and dilution of combustion products as well as faster crosslinking and char formation [3,41].

Herein phosphonium sulfonates (PhSs) as flame retardants for PC will be disclosed. The PhSs can be readily synthesized, and show high thermal stability, which can meet the need of almost all polymer processing. The PC/PhS composites show efficient flame retardancy based on Limiting Oxygen Index test and Cone calorimeter analysis.

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2. Experimental

2.1. Materials

Polycarbonate (PC) was purchased as made in Dow Chemical Co. with a density of 0.918 g/cm³ and a melt index (GB 368283) of 20 g/10 min. Paratoluensulfonyl chloride (PTSC), sodium hydride, benzyl alcohol, but-3-en-1-ol, butan-1-ol, triphenylphosphine were purchased from Aladdin Industrial Co., Ltd. Organic solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene tetrafluoro-ethylene (ETFE) was supplied by Dongyue Group Ltd.

2.2. Synthesis of phosphonium sulfonates (PhS)

2.2.1. Synthesis of PhS-1

2.2.1.1. Synthesis of benzyl 4-methylbenzenesulfonate. To a suspension of sodium hydride (2.88 g, 0.12 mol) in THF (200 mL) was added benzyl alcohol (10.4 mL, 0.1 mol) dropwise under ice bath. The reaction mixture was stirred under room temperature for 10 min. And then, a solution of paratoluensulfonyl chloride (19.06 g, 0.1 mol) in THF (200 mL) was added dropwise under ice bath. Then the reaction mixture was stirred under room temperature for 12 h. The reaction was quenched by water in 0 °C, and extracted by ethyl acetate. The obtained organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica to give benzyl 4-methylbenzenesulfonate (20.46 g, 78%).

2.2.1.2. Synthesis of benzyltriphenylphosphonium 4-methylbenzenesulfonate (PhS-1). A solution of benzyl 4-methylbenzenesulfonate (19.67 g, 0.075 mol) and triphenylphosphine (19.67 g, 0.075 mol) in toluene (300 mL) was stirred under 85 °C for 10 h. After the reaction mixture was cooled to room temperature, the resulted precipitate was filtered and washed with ethyl ether (100 mL × 3) to give desired product benzyltriphenylphosphonium 4-methylbenzenesulfonate (PhS-1) (35.42 g, 90%) as a white solid.

¹H NMR (400 MHz, CDCl₃), σ 7.77–7.58 (m, 18H), 7.12–6.93 (m, 6H), 5.09 (d, J = 14.4 Hz, 2H), 2.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃), σ 144.4, 138.3, 134.8, 134.8, 134.3, 134.2, 131.4, 131.4, 130.1, 130.0, 128.8, 128.7, 128.3, 128.2, 127.2, 126.1, 118.2, 117.4, 30.3, 29.8, 21.2.

³¹P NMR (161 MHz, CDCl₃), σ 24.3.

2.2.2. Synthesis of PhS-2

2.2.2.1. Synthesis of but-3-en-1-yl 4-methylbenzenesulfonate. But-3-en-1-ol (8.57 mL, 0.1 mol) was added to a suspension of sodium hydride (2.88 g, 0.12 mol) in THF (200 mL) dropwise under ice bath. The reaction mixture was stirred under room temperature for 10 min. After that, a solution of paratoluensulfonyl chloride (19.06 g, 0.1 mol) in THF (200 mL) was added dropwise in ice bath. Then the reaction mixture was stirred under room temperature for 12 h. The reaction was quenched by water in 0 °C, and extracted by ethyl acetate. The obtained organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica to give but-3-en-1-yl 4-methylbenzenesulfonate (16.52 g, 73%).

2.2.2.2. Synthesis of but-3-en-1-yltriphenylphosphonium 4-methylbenzenesulfonate (PhS-2). A solution of but-3-en-1-yl 4-methylbenzenesulfonate (15.84 g, 0.07 mol) and triphenylphosphine (18.36 g, 0.07 mol) in xylene (300 mL) was stirred under 140 °C for 10 h. After the reaction mixture was cooled to room temperature, petroleum ether was added to the reaction mixture, and white solid was precipitated out. After standing for a while, the

resulted precipitate was filtered and washed with ethyl ether (100 mL × 3) to give desired product but-3-en-1-yltriphenylphosphonium 4-methylbenzenesulfonate (PhS-2) (30.78 g, 90%) as a white solid.

¹H NMR (400 MHz, CDCl₃) σ 7.86–7.65 (m, 17H), 7.09 (d, J = 7.6 Hz, 2H), 5.98–5.88 (m, 1H), 5.04–4.96 (m, 2H), 3.81–3.74 (m, 2H), 2.46–2.37 (m, 2H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃), σ 144.2, 138.5, 135.1, 135.0, 134.9, 134.9, 133.7, 133.6, 130.5, 130.3, 128.3, 126.2, 118.7, 117.9, 117.1, 26.6, 26.6, 21.6, 21.3, 21.1.

³¹P NMR (161 MHz, CDCl₃), σ 24.5.

2.2.3. Synthesis of PhS-3

2.2.3.1. Synthesis of butyl 4-methylbenzenesulfonate. To a suspension of sodium hydride (2.88 g, 0.12 mol) in THF (200 mL) was added butan-1-ol (9.15 mL, 0.1 mol) dropwise under ice bath. The reaction mixture was stirred under room temperature for 10 min. And then, a solution of paratoluensulfonyl chloride (19.06 g, 0.1 mol) in THF (200 mL) was added dropwise in ice bath. Then the reaction mixture was stirred under room temperature for 12 h. The reaction was quenched by water in 0 °C, and extracted by ethyl acetate. The obtained organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica to give butyl 4-methylbenzenesulfonate (17.12 g, 75%).

2.2.3.2. Synthesis of butyltriphenylphosphonium 4-methylbenzenesulfonate (PhS-3). A solution of butyl 4-methylbenzenesulfonate (15.98 g, 0.07 mol) and triphenylphosphine (18.36 g, 0.07 mol) in xylene (300 mL) was stirred under 145 °C for 10 h. After the reaction mixture was cooled to room temperature, petroleum ether was added to the reaction mixture, and white solid was precipitated out. After standing for a while, the resulted precipitate was filtered and washed with ethyl ether (100 mL × 3) to give desired product butyltriphenylphosphonium 4-methylbenzenesulfonate (PhS-3) (29.53 g, 86%) as a white solid.

¹H NMR (400 MHz, CDCl₃) σ 7.84–7.65 (m, 17H), 7.08 (d, J = 8.0 Hz, 2H), 3.68–3.60 (m, 2H), 2.31 (s, 3H), 1.65–1.51 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃), σ 144.5, 138.4, 134.8, 134.8, 133.6, 133.5, 130.4, 130.3, 128.2, 126.2, 119.0, 118.1, 24.6, 24.5, 23.7, 23.5, 21.8, 21.3, 21.3, 13.7.

³¹P NMR (161 MHz, CDCl₃), σ 24.5.

2.3. PC/PhS composites preparation

PC and PhS was dried before processing, and the processing was done in general condition. PC, PhS and anti-dripping agent (Ethylene tetrafluoro-ethylene (ETFE)) were mixed in a Haake Rheocord 90 internal mixer (Haake, Bersdorff, Germany) at 220 °C for 10 min. The obtained mixtures were subsequently pressed into sheets of 3 mm to obtain samples that contained corresponding synthesized PhS. The compositions of PC/PhS composites are summarized in Table 1. The composites were denoted using the

Table 1
PC/PhS composites content.

Sample	PC content (phr)	PhS content (phr)	ETFE content (phr)
PC	100	0	0.1
PC/PhS-1 (5 phr)	100	5	0.1
PC/PhS-1 (7.5 phr)	100	7.5	0.1
PC/PhS-1 (10 phr)	100	10	0.1
PC/PhS-2 (5 phr)	100	5	0.1
PC/PhS-3 (5 phr)	100	5	0.1

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