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Novel phosphorus–silicon synergistic flame retardants: Synthesis and characterization

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Abstract

Three novel flame retardants containing both phosphorus and silicon elements in their structures, including [(1,1,3,3-tetramethyl-1,3-disiloxanediyl)di-2, 1-ethanediyl]bis(diphenylphosphine oxide) (FR-1), [(2,4,6,8-tetramethylcyclotetra-siloxane-2,4,6,8-tetrayl)tetra-2,1-ethanediyl]tetrakis[diphenylphosphine oxide] (FR-2) and 1,3,5,7,9,11,13,15-octakis(di-phenylphosphine oxide-2,1-ethanediyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (FR-3) were synthesized by a convenient pathway from the reaction of diphenylphosphine oxide (DPPO) and vinyl-terminated siloxanes under the catalysis of triethylborane. The chemical structures of the target compounds were confirmed by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR and ^{31}P NMR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and Fourier transform infrared (FT IR) measurements. Thermogravimetric analysis (TGA) results indicated that the new flame retardants possessed good thermal stability both in nitrogen and in air. FR-3 containing polyhedral oligosilsesquioxanes (POSS) moiety exhibited the best thermal properties with a 10% weight loss temperature >400 °C and a residual weight ratio >39% at 700 °C.

Keywords: Phosphorous-containing siloxanes; POSS; Flame retardant; Synergistic effect

Flame retardants (FRs) are one of the most important components for common engineering polymers, such as engineering plastics, textiles and molding compounds for electronic packaging [1]. In recent rears, various efforts have been performed in order to improve the flame retardant efficiency of the FRs. Among various methodologies, the attempts taking advantage of the synergistic effects of specific elements with flame retardant characteristics, such as boron, silicon, phosphorus, nitrogen, halogen (chlorine, bromine and iodine), antimony and bismuth have gained much attention in recent years [2–4]. Various synergistic couples, for instance, P–N, P–Si, Sb–Cl, Bi–Cl and many other combinations have been incorporated into the structures of high performance FRs [5–7]. In the synergistic systems mentioned above, the P–Si system has been proved to be of great value due to its inherent high flame retardant efficiency, good environmental compatibility and good thermal durability at elevated temperatures [8,9]. Various P–Si synergistic FRs, for instance, those containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and POSS components can usually increases the ignition resistance of common polymers significantly while maintaining the thermal stability of polymer matrixes [10,11].

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In our previous study, a series of P–Si synergistic FRs have been developed from DOPO and vinyl-terminated linear siloxanes [12]. However, the inferior hydrolysis resistance of the P–O–C bond in the DOPO ring limited their applications in moisture-sensitive areas [13].

In this communication, a class of P–Si synergistic FRs containing P–C bonds instead of P–O–C bonds was developed from diphenylphosphine oxide (DPPO) and vinyl-containing siloxanes. Compared with their DOPO analogues, the P–C bond in the phosphonate moiety in DPPO is less sensitive to moisture and would not hydrolyze in high temperature wet environments. The synthesis and characterization of the new FRs were investigated in detail.

1. Experimental

Triethylborane (as a 1 mol/L solution in hexane) and vinyl-terminated siloxanes, including 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,3,5,7-tetramethyl-1,3,5, 7-tetravinylcyclotetrasiloxane and octavinyl POSS (OVPOSS) were purchased from Sigma–Aldrich and used as received. FT IR spectra were recorded on a PE 2000 FT IR spectrometer. ^{1}H NMR and ^{13}C NMR were conducted on a Bruker AV-400 nuclear magnetic resonance spectrometer with tetramethylsilane (TMS) as the internal standard. ^{29}Si NMR and ^{31}P NMR measurements were performed on a Bruker DMX 300 spectrometer. MALDI-TOF-MS spectra were obtained on a Biflex III mass spectrometer. Differential scanning calorimeter (DSC) measurements were performed with a TA Instruments Q100 thermal analysis system.

1,3,5,7,9,11,13,15-Octakis(diphenylphosphine oxide-2,1-ethanediyl)pentacyclo [9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octa-siloxane (FR-3) was synthesized as follows. Into a 250-mL three-necked bottle equipped with a mechanical stirrer, a dropping funnel and a gas inlet was added diphenylphosphine oxide (DPPO) (16.16 g, 80 mmol), OVPOSS (6.31 g, 10 mmol) and tetrahydrofuran (60 mL). The mixture was stirred at room temperature in nitrogen until all of the reactants dissolved. A stoichiometric triethylborane solution in hexane (16 mL, 16 mmol) was added dropwise. After the addition, the progress of the reaction was monitored by thin layer chromatography (TLC). After the reaction was judged complete (usually after 5–6 h) by TLC, the reaction mixture was evaporated to remove the tetrahydrofuran. The resulting solid was successively washed by diethyl ether and distilled water for three times. Then, the resulting white solid was further purified by recrystallization from tetrahydrofuran to afford FR-3 (20.46 g) with a yield of 91%. Melting point: 259 °C (DSC peak temperature); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (m, 16H, –Si–CH_2–), 2.28 (d, 16H, –CH_2–P), 7.37 (m, 32H), 7.42 (m, 16H), 7.61 (m, 32H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.5, 131.8, 131.5, 130.7, 128.8, 22.7; ^{29}Si NMR (60 MHz, $CDCl_3$): δ −66.72; ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.76; FT IR (KBr): ν 3067, 3026, 2987, 2961, 1946, 1604, 1410, 1276, 1111, 1005, 970 cm^{-1}; MALDI-TOF-MS: *m/z* calcd. for $C_{112}H_{112}O_{20}P_8Si_8$ [M+Na]$^+$: 2271.4, found 2271.2.

[(1,1,3,3-Tetramethyl-1,3-disiloxanediyl)di-2,1-ethanediyl]bis(diphenylphosphine oxide) (FR-1) and [(2,4,6,8-tetramethylcyclotetrasiloxane-2,4,6,8-tetrayl)tetra-2,1-ethanediyl]tetrakis[diphenylphosphine oxide] (FR-2) were synthesized with a similar procedure as described in the synthesis of FR-3 except that 1,3-divinyl-1,1,3,3-tetramethyldisiloxane was used instead of OVPOSS for FR-1 and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane was used for FR-2.

FR-1: mp: 169 °C (DSC peak temperature); yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.08 (s, 12H, –Si–CH_3), 0.63 (d, 4H, –Si–CH_2–), 2.05 (d, 4H, –CH_2–P), 7.30 (d, 6H), 7.60 (t, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 133.0, 131.7, 130.9, 128.7, 77.1, 23.4, 8.43, −0.05; ^{29}Si NMR (60 MHz, $CDCl_3$): δ 8.63; ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.28; FT IR (KBr): ν 3052, 2958, 2899, 1483, 1437, 1410, 1318, 1255, 1183, 1150, 1120, 1091, 999, 842 cm^{-1}; MALDI-TOF-MS: *m/z* calcd. for $C_{32}H_{40}O_3P_2Si_2$ [M+Na]$^+$: 613.2, found 613.2.

FR-2: yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.06 (s, 12H, –Si–CH_3), 0.59 (d, 8H, –Si–CH_2–), 2.01 (d, 8H, –CH_2–P), 7.22 (m, 24H), 7.61 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.9, 133.5, 132.7, 132.5, 131.7, 131.3, 131.2, 130.7, 128.7, 128.1, 23.0, 22.3, 7.1, −1.1; ^{29}Si NMR (60 MHz, $CDCl_3$): δ −18.69; ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.77; FT IR (KBr): ν 3056, 2959, 2901, 1637, 1591, 1484, 1437, 1408, 1262, 1180, 1160, 1121, 1071, 918 cm^{-1}; MALDI-TOF-MS: *m/z* calcd. for $C_{60}H_{68}O_8P_4Si_4$ [M+Na]$^+$: 1175.3, found 1175.3.

2. Results and discussion

Three P–Si synergistic FRs, FR-1, FR-2 and FR-3 were synthesized with a procedure shown in Scheme 1. This procedure has been proven to be an efficient pathway for the formation of P–C bonds [14]. In our experiments, the triethylborane-induced radical addition of DPPO to vinyl-siloxanes proceeded smoothly giving rise to the