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Bridged phosphorylated diamines: Synthesis, thermal stability and flame retarding properties in epoxy resins

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ABSTRACT

The synthesis of different phosphorylated *m*-phenylenediamines is described. In this context a new synthetic pathway to 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-Cl) is reported. The reactivities of DOPO-Cl and 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOP-Cl) towards amines have been compared. Decomposition properties of the pure compounds have been determined by thermogravimetric analysis (TGA) and indicate a relationship between the chemical environment around the phosphorus atom and the thermostability of the corresponding compound. All substances were incorporated into the epoxy novolac resin system DEN438/DICY/Fenuron. Thermal as well as flame retarding properties of the cured epoxy resins have been investigated by differential scanning analysis (DSC) and UL-94 test. The changes of the glass transition temperature (T_g) and the decomposition temperature of the cured epoxy resins are small compared to the pure epoxy resin. The synthesized 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-sulfide (DOPS), diphenylphosphine sulfide (Ph2PO) and 5,5-dimethyl-1,3,2-dioxaphosphinane 2-sulfide (DDPS) derivatives exhibit a pronounced flame retardant effect in DEN438/DICY/Fenuron.

1. Introduction

The importance of polymeric materials has increased since the mid-20th century due to their multifaceted applications and properties [1–3]. Epoxy resins are a specific class of thermosets and are characterized as materials with outstanding adhesive, electrical and mechanical properties. They are widely applied for coatings, insulating materials and fiber-reinforced composites, e.g. printed wiring boards or lightweight construction materials [4–7]. However, a great drawback of epoxies is their high flammability which limits their use in applications that require high flame resistance such as electronic and electrical (E & E) applications or public transportation. Since epoxies are extensively used in such applications, the use of flame retardants is necessary [8,9]. The classical solution is the use of halogenated flame retardants, e.g. tetrabromobisphenol A (TBBA) and/or inorganic salts such as aluminium trihydroxide (ATH). However, to achieve suitable fire-protecting properties with ATH, high loadings up to 60 wt% are required, which has detrimental consequences for the mechanical properties and causes processing problems [10,11]. Although halogen-containing flame retardants are quite effective, they release corrosive and toxic substances during combustion [12,13]. That is why the development of alternative phosphorus-based flame retardants has become a challenging issue for science and industry. Various organophosphorus compounds have been incorporated into epoxy resins and have shown suitable flame retardancy results [9,14–18]. In this context, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have gained special attention due to their excellent flame retardant efficiencies. DOPO is a commercially available, reactive flame retardant. Its P–H group reacts with the oxirane moieties of the epoxy resin. Therefore, the number of epoxy functionalities available for the curing process is reduced which affects the glass transition temperature (T_g) negatively. One possibility to overcome this phenomenon is the derivatization of DOPO to achieve nonreactive flame retardants [9,19–24].

The aim of this study was to investigate the influence of the chemical environment around the phosphorus atoms on the thermal stability of the compounds that act as flame retardants. Determining this relationship is important to gain a better

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understanding of thermal decomposition, and is a fundamental issue for designing thermal stable tailor-made flame retardants in the future. Therefore six *m*-phenylenediamine derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-sulfide (DOPS), diphenylphosphine sulfide (Ph2PS) or 5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (DDPS) moieties have been synthesized. Additionally, a new synthetic approach for the synthesis of 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-Cl) via oxidation of 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOP-Cl) with oxygen was invented and the reactivity of both phosphorus chlorides was compared. Thermal stabilities of all compounds were determined by thermogravimetric analysis (TGA). Flame-retardant properties of the phosphoramidates in the epoxy resin system DEN438/DICY/Fenuron were determined using the UL-94 test.

2. Experimental

2.1. Materials

Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without further purification. Chlorodiphenylphosphine (Ph2P–Cl) was supplied by BASF SE (Germany). 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOP-Cl) was synthesized according to a previously reported procedure [27]. 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphinane (DDP-Cl) was synthesized as previously reported [24]. (9-oxa-10-phospha-phenanthrene-10-yl)-propylamine (DOPAM-3-propyl) was synthesized as described previously [28]. The epoxy resin DEN438 (DOW), DICY (Dyhard 100S) and Fenuron (Dyhard UR 300) were provided by AlzChem Trostberg GmbH (Germany).

2.2. Synthesis of N^1,N^1,N^3,N^3-tetrakis(6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl)benzene-1,3-diamine (**1**)

140 g (596 mmol) of DOP-Cl, 16.1 g (149 mmol) of *m*-phenylenediamine and 200 g (2.44 mol) of *N*-methylimidazole were used for the synthesis as previously reported [25].

Colorless solid. Yield: 126 g, 140 mmol, 93%. M.p.: 270–275 °C; ^{1}H NMR (400 MHz, CDCl3): $\delta = 7.79–6.84$ (m, 32H), 6.04–5.87 (m, 4H) ppm. ^{31}P NMR (CDCl3, 101 MHz): $\delta = 88.8–88.1$ (m, 4P), 87.7–85.8 (m, 4P) ppm. IR (KBr): $\tilde{\nu} = 3056$ (C_{aryl}–H), 1581 (C=C_{aryl}), 1473 (P–C_{aryl}), 1204, 1113 (P–O), 930 (P–O), 763, 750, 618, 474 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{54}H_{36}N_2P_4O_4$]: 900.1626, found: 900.2017 [M]$^+$.

2.3. Synthesis of 6,6′,6″,6‴-(1,3-phenylenebis(azanetriyl))tetrakis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (PDA(DOP-O)4, **2**)

50.0 g (55.5 mmol) of **1**, 68.4 g (228 mmol) of *tert*-butyl hydroperoxide and 250 ml of anhydrous toluene were used for the synthesis as previously described [25].

Colorless solid. Yield: 48.9 g, 50.7 mmol, 91%. M.p.: 176–180 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.30–8.21$ (m, 2H), 8.12–7.97 (m, 8H), 7.74–7.52 (m, 12H), 7.38–7.19 (m, 8H), 7.05–6.88 (m, 2H), 6.74–6.64 (m, 4H) ppm. ^{31}P NMR ($CDCl_3$, 101 MHz): $\delta = 8.1–7.4$ (m, 4P) ppm. IR (KBr): $\tilde{\nu} = 3062$ (vw, C_{aryl}–H), 1595 (s, C=C_{aryl}), 1477 (vs, P–C_{aryl}), 1269 (vs, P=O), 1119, 1001 (s, P–O), 981 (s, P–N), 754, 517, 425 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{54}H_{36}N_2P_4O_8$]: 964.1422, found: 964.1290 [M]$^+$.

2.4. Synthesis of 6,6′,6″,6‴-(1,3-phenylenebis(azanetriyl))tetrakis(6H-dibenzo[c,e][1,2]oxa-phosphinine 6-sulfide) (PDA(DOP-S)4, **3**)

50.7 g (56.3 mmol) of **1**, 7.21 g (225 mmol) of sulfur and 200 ml of anhydrous toluene were used for the synthesis as previously reported [25].

Colorless solid. Yield: 51.1 g, 49.6 mmol, 88%. M.p.: 177–185 °C. ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 66.1–61.9$ (m, 4P) ppm. IR (KBr): $\tilde{\nu} = 3061$ (vw, C_{aryl}–H), 1581 (m, C=C_{aryl}), 1474 (s, P–C_{aryl}), 1199, 1115 (s, P–O), 951 (vs, P=S), 915 (vs, P–N), 861, 790, 751, 717, 662 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{54}H_{36}P_4S_4O_4N_2$]: 1028.0508, found: 1028.0818 [M]$^+$.

2.5. Synthesis of N^1,N^1,N^3,N^3-tetrakis(diphenylphosphino)benzene-1,3-diamine (**4**)

54.6 g (246 mmol) of chlorodiphenylphosphine, 6.53 g (60.4 mmol) of *m*-phenylenediamine, 50.0 g (294 mmol) of triethylamine and 200 ml of anhydrous chloroform were used for the synthesis previously described [26].

Colorless solid. Yield: 42.4 g, 50.8 mmol, 93%.; M.p.: 171 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.32–7.18$ (m, 40H), 6.69 (s, 1H), 6.52 (tr, $J = 7.7$ Hz, 1H), 6.30 (d, $J = 7.9$ Hz, 2H) ppm. ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 68.8$ (s, 4P) ppm. IR (KBr): $\tilde{\nu} = 3049$ (vw, C_{aryl}–H), 1582 (s, C=C_{aryl}), 1475 (s, P–C_{aryl}), 1433 (s, P–C_{aryl}), 1246, 1150, 1091, 1025, 982, 929 (s, P–N), 853, 741, 693, 608, 491 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{54}H_{44}P_4N_2$]: 844.2455, found: 844.2528 [M]$^+$.

2.6. Synthesis of N,N′-(1,3-phenylene)bis(N-(diphenylphosphorothioyl)-P,P-diphenylphosphinothioic amide) (PDA(Ph2P-S)4, **5**)

10.0g (11.8 mmol) of **4**, 1.52 g (47.3 mmol) of sulfur and 50 ml of anhydrous toluene were used for the synthesis as previously reported [26].

Colorless solid. Yield: 7.66 g, 7.87 mmol, 67%. M.p.: 328–330 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.67$ (s, 1H), 7.98–7.82 (m, 16H), 7.30–7.17 (m, 24H), 6.65 (d, $J = 7.9$ Hz, 2H), 6.10 (t, $J = 8.1$ Hz, 1H) ppm. ^{31}P NMR (101 MHz, CDCl3): $\delta = 71.1$ (s, 4P) ppm. IR (KBr): $\tilde{\nu} = 3048$ (vw, C_{aryl}–H), 1559 (m, C=C_{aryl}), 1435 (vs, P–C_{aryl}), 1136, 1089, 970 (vs, P–N), 931 (vs, P=S), 722, 687, 650, 491 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{54}H_{44}S_4P_4N_2$]: 972.1338, found: 972.1212 [M]$^+$.

2.7. Synthesis of N^1,N^1,N^3,N^3-tetrakis(5,5-dimethyl-1,3,2-dioxaphosphinan-2-yl)benzene-1,3-diamine (**6**)

In a three-necked, round-bottomed flask 8.00 g (74.0 mmol) of *m*-phenylenediamine and 60.0 g (600 mmol) of triethylamine were dissolved in 300 ml of anhydrous chloroform under nitrogen. A solution of 54.8 g (325 mmol) of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane in 50 ml of anhydrous chloroform was added dropwise to the reaction mixture. The solution was heated at solvent reflux for one day. After cooling down to ambient temperature the reaction mixture was rinsed (3 × 300 ml) with water. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. A colorless solid was obtained.

Yield: 46.4 g, 72.8 mmol, 98%. M.p.: 120–123 °C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.27–7.19$ (m, 4H), 3.79–3.71 (m, 8H), 3.55–3.48 (m, 8H), 0.99 (s, 12H), 0.68 (s, 12H) ppm. ^{31}P NMR ($CDCl_3$, 101 MHz): $\delta = 125.0$ ppm (s, 4P) ppm. IR (KBr): $\tilde{\nu} = 3061$ (vw, C_{aryl}–H), 2964 (w, C_{alkyl}–H), 2909 (w, C_{alkyl}–H), 1581 (m, C=C_{aryl}), 1474, 1445, 1372, 1203, 1142, 1096 (vs, P–O), 967 (vs, P–N), 908, 785, 647,

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600, 555, 476 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{26}H_{44}P_4O_8N_2$]: 636.2048, found: 636.1999 [M]$^+$.

2.8. *Synthesis of 2,2′,2″,2‴-(1,3-phenylenebis(azanetriyl)) tetrakis(5,5-dimethyl-1,3,2-dioxaphosphinane 2-sulfide) (PDA(DDP-S)4, **7**)*

In a three-necked, round-bottomed flask 29.0 g (45.6 mmol) of **6** were dissolved in 150 ml of anhydrous toluene under nitrogen and 5.85 g (182 mmol) of sulfur were added to the reaction mixture. The mixture was heated at solvent reflux for 2 h. After reaching ambient temperature the colorless precipitate was collected by filtration, rinsed with toluene and dried under reduced pressure. A colorless solid was obtained.

Yield: 18.5 g, 24.1 mmol, 53%. M.p.: 244–246 °C (decomposition). ^{1}H NMR (250 MHz, DMSO-d$_6$): δ = 8.35 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.57–4.55 (m, 8H), 3.93–3.85 (m, 8H), 1.20 (s, 12H), 0.91 (s, 12H) ppm. ^{13}C NMR (101 MHz CDCl$_3$): δ = 137.5 (s, 2C), 130.7 (s, 1C), 129.9 (s, 1C), 128.9 (s, 2C), 78.3 (s, 8C), 32.1 (s, 4C), 22.3 (s, 4C), 21.1 (s, 4C) ppm. ^{31}P NMR (101 MHz, DMSO-d$_6$): δ = 57.6 (s, 4P) ppm. IR (KBr): $\tilde{\nu}$ = 2963 (m, C$_{alkyl}$–H), 2880 (vw, C$_{alkyl}$–H), 1473, 1050 (s, P–O), 1009 (s, P–N), 969 (vs, P=S), 833, 669, 472 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{26}H_{44}P_4O_8S_4N_2$]: 764.0931, found: 764.0938 [M]$^+$.

2.9. *Synthesis of N^1,N^3-bis(6H-dibenzo[c,e][1,2]oxaphosphinin-6-yl) benzene-1,3-diamine (**8**)*

A round-bottomed flask was charged with 100 g (388 mmol) of (9-oxa-10-phospha-phenanthrene-10-yl)-propylamine (DOPAM-3-propyl) and 21.0 g (194 mmol) of *m*-phenylenediamines under nitrogen. The reaction mixture was heated up to 155 °C and stirred for 24 h under reduced pressure (20 mbar) to remove the evolving *n*-propylamine. The mixture was allowed to cool to ambient temperature and dried under reduced pressure. After grinding and recrystallization from ethanol the product was dried under reduced pressure. A colorless solid was obtained.

Yield: 85.7 g, 169.8 mmol, 88%. M.p.: 70–72 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ = 8.01–7.93 (m, 4H), 7.67–7.58 (m, 4H), 7.45 (tt, *J* = 7.5 Hz, *J* = 0.9 Hz, 2H), 7.33 (td, *J* = 7.4 Hz, *J* = 1.5 Hz, 2H), 7.23–7.11 (m, 4H), 7.04–6.94 (m, 1H), 6.64–6.61 (m, 2H), 6.38–6.19 (m, 1H), 5.07 (d, *J* = 12.1 Hz, 2H, N–H) ppm. ^{31}P NMR (101 MHz, DMSO-d$_6$): δ = 68.0 (s, 1P), 67.9 (s, 1P) ppm. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{30}H_{22}N_{21}O_2P_2$]: 504.1157, found: 504.1180 [M]$^+$.

2.10. *Synthesis of 6,6′-(1,3-phenylenebis(azanediyl))bis(6H-dibenzo [c,e][1,2]oxaphosphinine 6-sulfide) (PDA(DOP-S)2, **9**)*

In a three-necked, round-bottomed flask 31.2 g (62.0 mmol) of **8** were dissolved in 120 ml of anhydrous toluene under nitrogen atmosphere and 3.89 g (122 mmol) of sulfur were added to the solution. The reaction mixture was heated at solvent reflux for 2 h. After the mixture was allowed to cool to ambient temperature the colorless precipitate was collected by filtration and washed with toluene. The crude product was recrystallized from ethanol and dried under reduced pressure. A colorless solid was obtained.

Yield: 49.73 g, 87.1 mmol, 92%. M.p.: 233–235 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ = 8.82 (d, *J* = 12.7 Hz, 2H), 8.09 (dd, *J* = 14.5, 7.8 Hz, 4H), 7.73–7.66 (m, 4H), 7.51–7.41 (m, 4H), 7.30 (td, *J* = 7.5 Hz, 2.9 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.87–6.73 (m, 2H), 6.46 (dd, *J* = 7.9, 1.0 Hz, 2H) ppm. ^{13}C NMR (63 MHz, CDCl$_3$): δ = 149.2 (d, *J* = 8.7 Hz, 2C), 141.1 (d, *J* = 3.9 Hz, 2C), 135.2 (d, *J* = 6.4 Hz, 2C), 133.3 (s, 1C), 130.9 (s, 2C), 129.1 (s, 2C), 129.2 (s, 2C), 128.8 (s, 2C), 127.8 (d, *J* = 138 Hz, 2C), 126.0 (s, 2C), 125.2 (s, 2C), 124.8 (d, *J* = 10.4 Hz, 2C), 123,1 (d, *J* = 12.4 Hz, 2C), 120.8 (d, *J* = 5.6 Hz, 2C), 113.4 (d, *J* = 7.9 Hz, 2C), 110.1 (s, 1C) ppm. ^{31}P NMR (101 MHz, DMSO-d$_6$): δ = 61.5 (s, 1P), 61.4 (s, 1P) ppm. IR (KBr): $\tilde{\nu}$ = 3244 (br, N–H), 3066 (wv, C$_{aryl}$–H), 1606 (s, C$_{aryl}$–P), 1595 (s, C=C$_{aryl}$), 1581, 1558, 1496 (vs, C=C$_{aryl}$), 1473, 1446.3, 1429, 1412, 1371, 1254 (m, C–O), 1240, 1166, 1148, 1118, 1041, 1002 (s, P–O), 956 (s, P=S), 915, 886, 788, 717, 703, 583, 436 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{30}H_{22}P_2N_2S_2O_2$]: 568.0598, found: 568.0601 [M]$^+$.

2.11. *Synthesis of 6,6′-(1,3-phenylenebis(azanediyl))bis(6H-dibenzo [c,e][1,2]oxaphosphinine 6-oxide) (PDA(DOP-O)2, **10**)*

In a three-necked, round-bottomed flask 5.40 g (50.0 mmol) of *m*-phenylenediamine and 11.62 g (115 mmol) of anhydrous triethylamine were dissolved in 250 ml of anhydrous chloroform under nitrogen. After cooling to a temperature of 5 °C, a solution of 25.1 g (100.0 mmol) of 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide in 150 ml of anhydrous chloroform was added dropwise to the reaction mixture. The stirring was continued for 18 h at solvent reflux. Afterwards the formed, colorless precipitate was collected by filtration and rinsed with chloroform (250 ml). The obtained colorless solid was dried under reduced pressure.

Yield: 19.3 g, 36.0 mmol, 72%. M.p.: 250–260 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.59 (dd, *J* = 9.1, 3.0 Hz, 2H), 8.27–8.03 (m, 4H), 7.84–7.16 (m, 12H), 6.94–6.84 (m, 1H), 6.79–6.60 (m, 1H), 6.55–6.39 (m, 2H) ppm. ^{13}C NMR (76 MHz, DMSO-d$_6$): δ = 149.8–149.4 (m, 2C), 141.6 (s, 2C), 136.6–136.0 (m, 2C), 133.7–133.4 (m, 2C), 131.2–130.4 (m, 2C), 130.0–129.4 (m, 4C), 129.1–128.5 (m, 2C), 126.3–125.9 (m, 2C), 125.3–124.6 (m, 4C), 124.1–124.0 (m, 1C), 122.6–122.4 (m, 2C), 120.9–120.4 (m, 2C), 112.2–111.9 (m, 2C), 109.2–108.7 (m, 1C) ppm. ^{31}P NMR (122 MHz, DMSO-d$_6$): δ = 7.92 (s, 1P), 7.88 (s, 1P) ppm. IR (KBr): $\tilde{\nu}$ = 3161 (s, N–H), 3026 (w, C$_{aryl}$–H), 1608 (s, P–C$_{aryl}$), 1477 (s, C=C$_{aryl}$), 1446, 1191 (vs, P=O), 1118 (m, P–O), 939, 783, 758, 600, 517 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{30}H_{22}P_2O_4$]: 536.1055, found: 536.1029 [M]$^+$.

2.12. *Synthesis of 10-Chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-Cl)*

In a three-necked, round-bottomed flask 130 g (553 mmol) of 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOP-Cl) were heated to 140 °C under nitrogen. Under vigorous stirring dry oxygen was passed into the reaction mixture for 24 h. The crude product was purified by distillation under reduced pressure (2 mbar). A colorless solid was obtained.

Yield: 99.4 g, 398 mmol, 72%. B.p. 165 °C (2 mbar). M.p.: 113–116 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.10–7.90 (m, 3H), 7.77 (ddt, *J* = 8.1, 7.4, 1.4 Hz, 1H), 7.56 (tdd, *J* = 7.5, 4.4, 1.0 Hz, 1H), 7.44 (ddt, *J* = 8.0, 7.4, 1.6 Hz, 1H), 7.38–7.31 (m, 1H), 7.30–7.23 (m, 1H) ppm. ^{13}C NMR (76 MHz, CDCl$_3$): δ = 149.0 (d, *J* = 9.7 Hz, 1C), 135.9 (d, *J* = 8.5 Hz, 1C), 134.8 (d, *J* = 2.8 Hz, 1C), 131.2 (s, 1C), 129.7 (d, *J* = 10.6 Hz, 1C), 128.9 (d, *J* = 16.9 Hz, 1C), 126.0 (d, *J* = 1.2 Hz, 1C), 125.5 (d, *J* = 1.7 Hz, 1C), 125.1 (d, *J* = 164.0 Hz, 1C), 124.5 (d, *J* = 13.0 Hz, 1C), 122.1 (d, *J* = 13.5 Hz, 1C), 120.5 (d, *J* = 7.4 Hz, 1C) ppm. ^{31}P NMR (121 MHz, CDCl$_3$): δ = 20.0 (s, 1P) ppm; IR (ATR): $\tilde{\nu}$ = 3070 (w, C$_{aryl}$–H), 1609, 1595 (m, P–C$_{aryl}$), 1581, 1475 (m, C=C$_{aryl}$), 1450, 1431, 1237 (vs, P=O),1237, 1189 (s, P–O), 1155, 1082, 927, 778, 753 cm^{-1}. HR-MS (EI, *m*/*z*) calc. for [$^{12}C_{12}H_8ClPO_2$]: 249.9950, found: 249.9967 [M]$^+$.

2.13. *Formulation and curing of the flame retardant epoxy resin*

The flame retardant additives and 6.0 phr DICY (Dyhard 100S) as curing agent were combined with the pure epoxy resin at 80 °C and mixed in a Dissolver DISPERMAT from VMA-GetzmannGmBH at

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Table 1
Formulation of the composites.

Flame retardant	DEN438 [%]	DICY [%]	Fenuron [%]	P [%]	FR [%]
PDA(DOP-O)2 **10**	80.04	5.22	1.74	1.5	12.9
PDA(DOP-S)2 **9**	79.31	5.17	1.72	1.5	13.8
PDA(DOP-O)4 **2**	81.23	5.30	1.77	1.5	11.6
PDA(DOP-S)4 **3**	80.50	5.25	1.75	1.5	12.4
PDA(Ph2P-S)4 **5**	81.15	5.29	1.76	1.5	11.0
PDA(DDP-S)4 **7**	83.45	5.44	1.81	1.5	9.3

6000 rotations per minute under reduced pressure for 20 min. Afterwards, 2.0 phr fenuron (Dyhard UR 300) as a curing accelerator was mixed in the resin mixture with the same method for 5 min. The formulation was transferred into an aluminum mold and cured at 110 °C for 1 h, 130 °C for 1 h and post-cured at 200 °C for 2 h. All samples were allowed to cool slowly to room temperature to avoid cracking. The formulations of the thermosets are listed in Table 1.

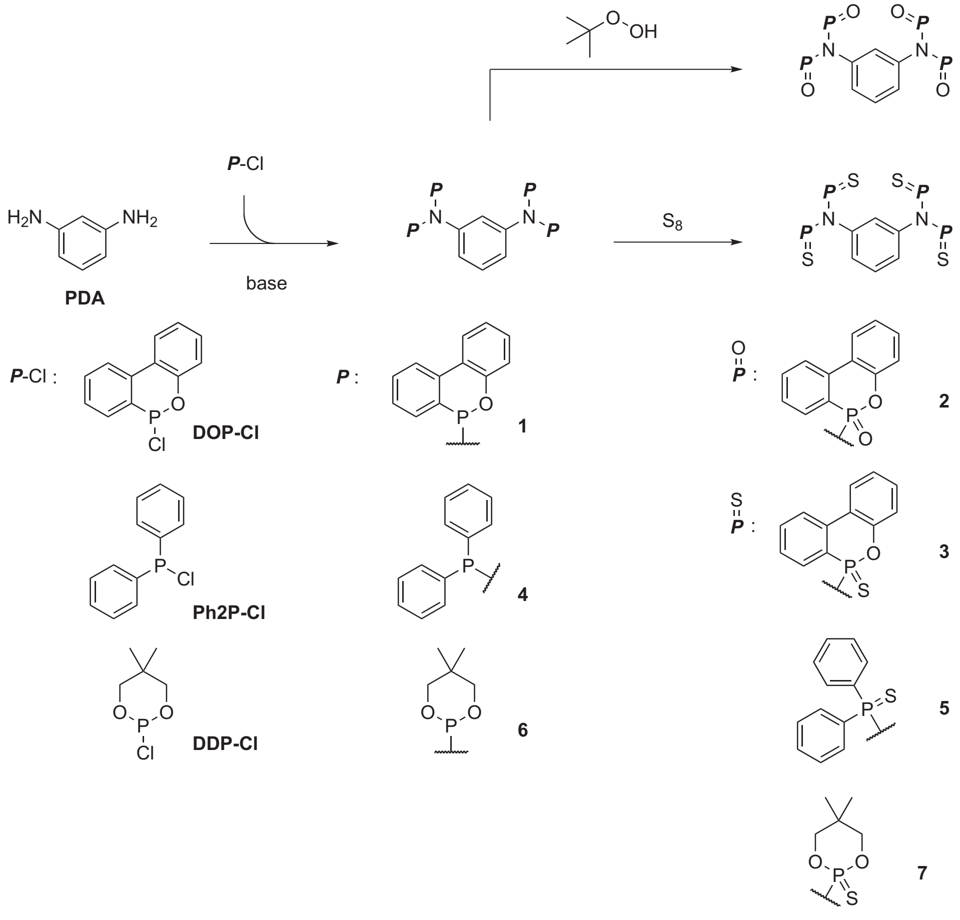
2.14. Characterizations

NMR spectra were recorded using a Bruker - Analytical BZH 250/52 (250 MHz), a Bruker – Nanobay 300 (300 MHz) or a Varian Inova-400 (400 MHz) spectrometer. Chemical shifts are reported as δ values relative to the solvent peak. All ^{31}P NMR spectra are measured proton-decoupled. All ^{13}C NMR spectra were measured proton-decoupled and if mentioned phosphorus-coupled. ^{1}H-Proton spectra were measured phosphorus-coupled. All ^{31}P NMR spectra are available in the supporting information. Melting points are uncorrected and measured using a Büchi B-560. High-resolution mass spectrometry (HR-MS) analyses were performed on a MicroMass GCT (time of flight (TOF); electron ionization (EI), 70 eV). IR spectra were recorded using a Varian 660-IR (FT-IR). Differential scanning calorimetry (DSC) was accomplished using a Mettler–Toldeo DSC 822 at a scan rate of 20 °C/min under nitrogen. The samples were contained in aluminium pots with weighted samples of 20 mg. Thermogravimetric analysis (TGA) was performed using a Mettler–Toledo TGA/SDTA 851 at a scan rate of 10 °C/min under a nitrogen atmosphere. The UL-94 vertical burning classification was accomplished using an ATLAS HVUL 2 burning chamber according to DIN IEC 60695-11-10 with a 50 W burner flame [29]. The samples were (70 ± 1) mm long, (13 ± 1) mm wide, and had a thickness of (4 ± 1) mm.

3. Results and discussion

3.1. Synthesis of the tetraphosphorylated m-phenylenediamines 2, 3, 5 and 7

The two-step synthesis of the compounds **2**, **3** and **5** [25,26] and the novel compound **7** is summarized in Scheme 1. The first step was the reaction of *m*-phenylenediamine (PDA) with a corresponding phosphorus chloride **DOP-Cl**, **Ph2P–Cl** or **DDP-Cl** via nucleophilic substitution in the presence of a base to form the intermediates **1**, **4** or **6**, respectively.



Scheme 1. Synthesis of the tetraphosphorylated compounds **2**, **3**, **5** and **7**.

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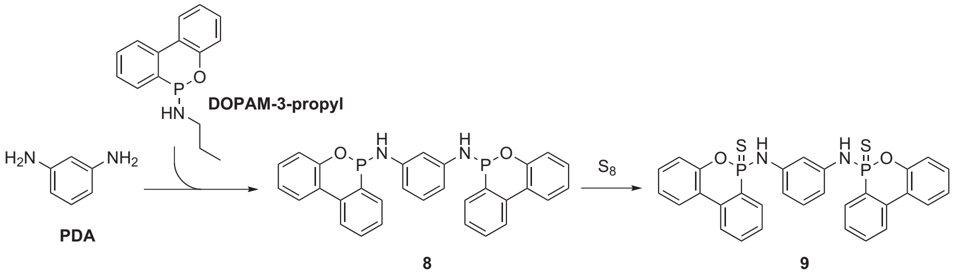
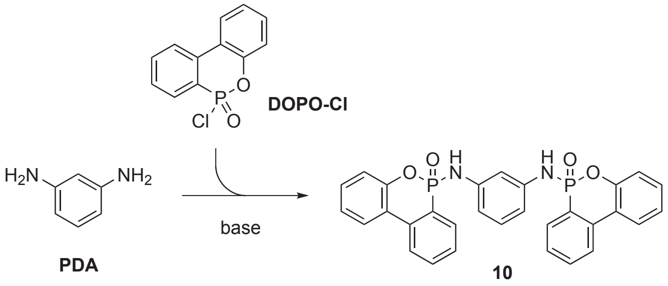
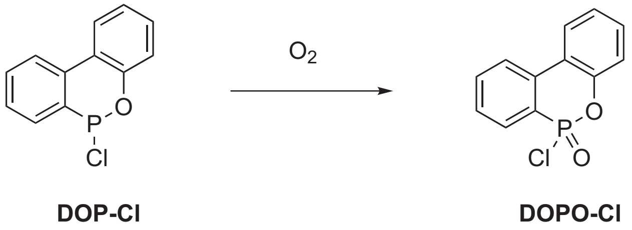


Scheme 2. Two step synthesis to obtain the phosphorylated diamine **9**.



Scheme 3. Synthesis of the phosphorylated diamines **10** starting from **PDA** and **DOPO-Cl**.



Scheme 4. New synthetic pathway to **DOPO-Cl** via oxidation of **DOP-Cl** with oxygen.

In a second step, the diphosphonamidite **1** was oxidized with *tert*-butyl hydroperoxide or thionated with elemental sulfur to the *m*-phenylene bridged diphosphonamidate **2** or di(thiophosphon)amidate **3**, respectively [25]. The di(thiophosphin)amide **5** was obtained by thionation of **4** with sulfur [26]. Di(thiophosphor)amidate **7** was also prepared by the oxidation of the diphosphoramidite **6** with sulfur.

3.2. Synthesis of the m-phenylenediamine phosphonamidates *9* and *10* as well as *DOPO-Cl*

The thiophosphonamidate **9** was prepared by a two-step procedure (Scheme 2). First, **PDA** and **DOPAM-3-propyl** were transformed via a condensation reaction under reduced pressure to the phosphonamidite **8**, in a fashion analog to an earlier procedure [30]. Afterwards, **8** was thionated with sulfur to the final thiophosphonamidate **9**.

The phosphonamidate **10** was obtained in one step via nucleophilic substitution of **PDA** with **DOPO-Cl** in the presence of a base, as illustrated in Scheme 3. The electrophile **DOPO-Cl** was prepared by an oxidation reaction of **DOP-Cl** (an intermediate of the industrial DOPO synthesis [27]) with oxygen (Scheme 4). In contrast *o*-phenylphenol and phosphoryl chloride were used as reactants in an earlier reaction pathway [31].

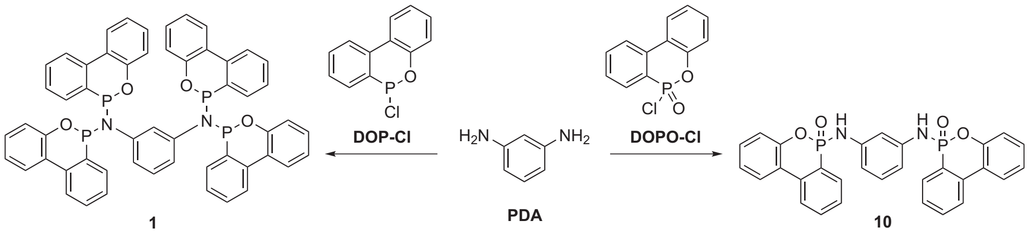
DOPO-Cl is a postulated intermediate in the Atherton–Todd reaction (ATR), which usually yields phosphonamidates with primary amines [32,33]. In analogy to the ATR, the reaction of two equivalents **DOPO-Cl** with **PDA** provided only the phosphonamidate **10**, Scheme 5. An excess of **DOPO-Cl** did not result in the diphosphonamidate **2**. In contrast, the reaction of four equivalents **DOP-Cl** with **PDA** gave selectively the diphosphonamidite **1** (Scheme 5) which could be transformed to the diphosphonamidate **2** via oxidation, Scheme 1.

These results demonstrate a different reactivity of **DOPO-Cl** as compared to that of **DOP-Cl.**

3.3. Thermal stability of the compounds

The TGA curves for compounds **3**, **5** and **7** are displayed in Fig. 1. The three compounds had clearly different degradation temperatures depending on the phosphorus moieties. Substance **7** (a DDPS derivative) showed a degradation temperature of approximately 250 °C, whereas **5** (a Ph2PS derivative) decomposed at about 300 °C and **3** (a DOPS derivative) started to degrade at 350 °C or above. All three compounds were tetraphosphorylated, thionated with sulfur and differ in the chemical environment around the phosphorus atom. These results suggest a strong relationship between the chemical environment of the phosphorus and the degradation temperature of the molecule and can be summarized in the following order of thermal stability of the phosphorus substituents:

DDPS << Ph2PS << DOPS.



Scheme 5. Different reactivity of **DOP-Cl** and **DOPO-Cl** towards **PDA**.

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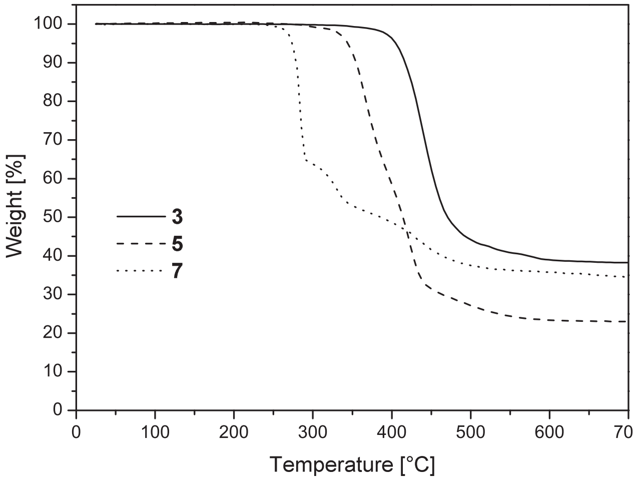

Fig. 1. TG curves of the compounds **3** (a DOPS derivative), **5** (a Ph2PO derivative) and **7** (a DDPS derivative) under nitrogen.

In Fig. 2, the TGA curves for compounds **2**, **3**, **9** and **10** are shown and illustrate that the diphosphonamidates **2** and **3** decompose at much higher temperatures than phosphonamidates **9** and **10**. Each DOPS derivative (**3** and **9**) had a slightly higher decomposition temperature than the corresponding DOPO compounds (**2** and **10**). The differences were less pronounced for **2** and **3** (decomposition temperature approximately 350 °C) than for **9** and **10**.

The char yields at 700 °C of **2**, **3**, **5**, **7**, **9** and **10** ranged from 20 to 40 wt.%, as shown in Figs. 1 and 2.

3.4. *Glass transition temperatures and thermal stability of the epoxy resins*

The glass transition temperatures (T_g) of the prepared epoxy resins are listed in Table 2. Because of the rod-like geometry of all prepared substances, marginal changes in the T_g of the cured epoxy resins were observed, indicating a low plasticizer effect of the compounds. This is consistent with results from previous work [30].

The TGA curves of the cured epoxy resins measured under nitrogen atmosphere are shown in Fig. 3. The corresponding values of the decomposition temperature at 5% weight loss and the char yield at 850 °C are listed in Table 2. All incorporated substances decreased the decomposition temperature of the epoxy resin. The char yield of the thermosets with the blended amines increased compared to the neat epoxy resin and ranged from about 30% (neat epoxy resin) to approximately 40 wt.% (thermoset of **7**). The high char yield of thermoset **9** leads to the assumption that the DDPS derivative **7** acts mainly in the condensed phase, in contrast to the DOPO (**2** & **10**), DOPS (**3** & **9**) and Ph2PS (**5**) derivatives. A previous study with flame retardants containing 5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (DDPO) moieties (an oxygen derivative of DDPS) supports this assumption [24]. Contrary to the DDPS derivate the DOPO (**2** & **10**), DOPS (**3** & **9**) and Ph2PS (**5**) derivatives increased the char not as strong as, so that a gas phase mechanism is assumed to be dominating during combustion for these types of compounds. This is also supported by previous studies [9,19,24].

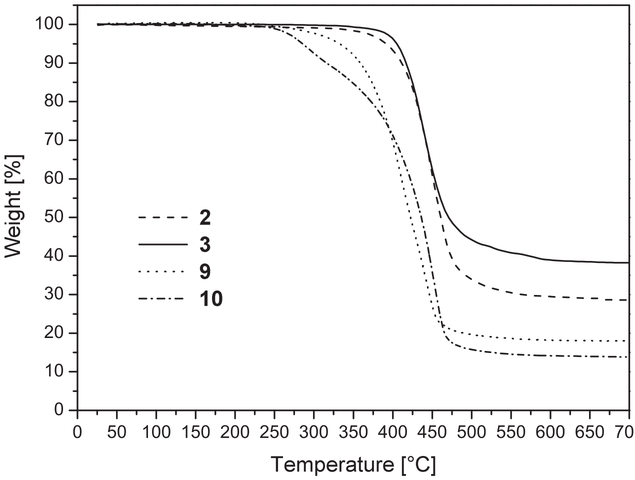

Fig. 2. TG curves of the compounds **2**, **3**, **9** and **10** under nitrogen.

Table 2
Thermal properties and results of the UL-94 test.[a]

Flame retardant	$T_{d5\%}$ [°C]	Char @ 850 °C [%]	T_g [°C]	UL-94V rating (4 mm)
None	337	28.6	181	n. c.
PDA(DOP-O)2 **10**	332	31.4	186	V1
PDA(DOP-S)2 **9**	323	29.7	181	V0
PDA(DOP-O)4 **2**	318	32.6	183	V0
PDA(DOP-S)4 **3**	312	31.7	174	V0
PDA(Ph2P-S)4 **5**	326	30.6	176	V1
PDA(DDP-S)4 **7**	311	36.7	170	n. c.

[a] Flame retardant contents are listed in Table 1.

3.5. *Flame retardant properties of the epoxy resins*

The flame retardant properties of the cured epoxy resins were evaluated using the UL-94 vertical burning test (Table 2). All samples were prepared with a constant phosphorus content of 1.5 percent. The cured epoxy resins containing flame retardants **2**, **3,** and **9** respectively showed excellent flame retardant efficiencies and passed the V0 classification in the UL-94 test. Also the cured epoxy resins containing **5** and **10** illustrated that the incorporated compounds acted as flame retardants (V1 classification in the UL-94 test).

Usually, the epoxy novolac resin system DEN438/DICY/Fenuron requires a gas phase active flame retardant [9,24]. Since the compounds **2**, **3**, **5**, **9** and **10** show a good flame retardancy effect in this specific epoxy resin system, the earlier mentioned assumption, that

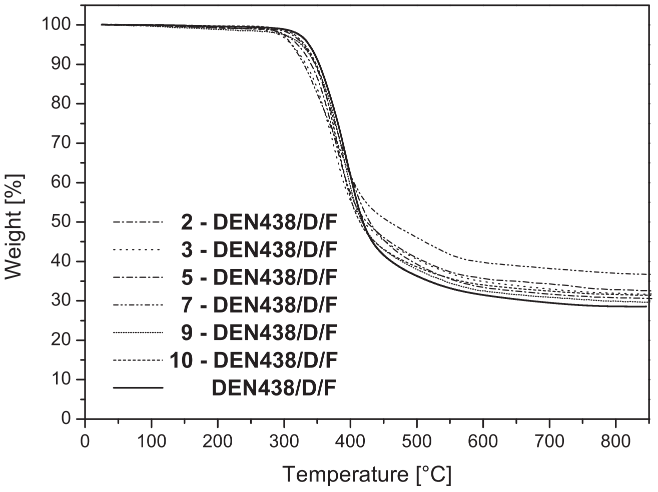

Fig. 3. TG curves of the cured epoxy resins system DEN438/DICY (D)/Fenuron (F) containing the compounds **2**, **3**, **5**, **7**, **9** or **10**, respectively under nitrogen.

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DOPO (**2** & **10**), DOPS (**3** & **9**) and Ph2PS (**5**) derivatives mainly act in the gas phase, is supported. This finding is also confirmed by a previously study that showed an outstanding flame retardant efficiency of comparable gas phase active substances in the same epoxy novolac resin system DEN438/DICY/Fenuron [19].

Only the cured epoxy resin containing **7** did not show a flame retardant effect and could not be classified according to the UL-94 specification.

A possible explanation for this result is that in the case of **7** (a DDPS derivative) a condensed phase mechanism is dominating as suggested in 3.4. Since the epoxy novolac resin system DEN438/DICY/Fenuron demands a gas phase active system, the phosphorous content of 1.5 percent in the thermoset of the potential condensed phase active compound **7** was too low for an efficient flame retardant effect. A previous study supports this assumption. It reveals, that at least a phosphorus content of 3.0 percent is required for a V0 classification in the UL-94 test using DDPS as flame retardant in the epoxy novolac resin system DEN438/DICY/Fenuron [19].

4. Conclusion

Six organophosphorus compounds **2**, **3**, **5**, **9** and **10** were synthesized. **DOPO-Cl** was obtained via oxidation of **DOP-Cl** with oxygen and showed a different reactivity compared to **DOP-Cl**: **DOPO-Cl** forms phosphonamidates with primary amines. In contrast, **DOP-Cl** provides diphosphonamidites with primary amines which can be transformed via oxidation to the corresponding diphosphonamidates or di(thiophosphin)amidates. The advantages of diphosphonamidates compared to phophonamidates are their higher decomposition temperatures, higher phosphorus contents and higher molecular weight.

The substances **2**, **3**, **5**, **7**, **9** and **10** were successfully incorporated into the epoxy novolac resin system DEN438/DICY/Fenuron. In the case of the tetraphosphorylated amines **3**, **5** and **7**, a relationship between the chemical environment around the phosphorus atom and the thermal stability of the corresponding compound was confirmed by TGA measurements of the pure substances. All cured epoxy resins of the introduced amines exhibited slight changes in the T_g and decomposition temperature compared to that of the neat epoxy resin. Except **7** (n.c.), all compounds showed a flame retardancy effect determined using the UL-94 test with a phosphorus content of 1.5 percent. **2**, **3** and **9** reached the V0 classification, in contrast to those containing **5** and **10** which were classified as V1.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymdegradstab.2014.04.002.

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