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Novel Star-shaped and Hyperbranched Phosphorus-containing Flame Retardants in Epoxy Resins

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Key Words: DOPO; DDPO; flame retardant; epoxy resins; THIC; THIC oligomer, glass transition temperature.

Abstract:

This report presents the synthesis and use of novel derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, **1**) and 5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (DDPO, **2**) as flame retardant additives for epoxy resins. DOPO- and DDPO-based compounds were synthesized *via* nucleophilic substitution with 1,3,5-tris-(2-hydroxyethyl) isocyanurate (THIC, **3**) and subsequent oxidation (Scheme 1 and 2). Another trivalent DOPO derivative recently reported by our group was obtained by transamination followed by a Michaelis-Arbuzov rearrangement (Scheme 1).^{1,2} These products were blended into two epoxy resin systems (DEN 438 and DGEBA, both cured with DICY and Fenuron) to obtain flame retardant thermosets. The flame retardancy and thermal properties of these epoxy resin systems were examined by UL 94-V, TGA and DSC analysis. Furthermore all reactions with phosphorus-containing compounds were iterated employing the THIC oligomer, which prepared *via* polycondensation of THIC (Scheme 3) using catalytic amounts of *p*-toluenesulfonic acid. In addition, Atherton-Todd reaction with the THIC oligomer was studied as a novel synthetic method for phosphorus-containing flame retardants (Scheme 4).^{3,4,5} The resulting products were utilized as flame retardants in epoxy resins and compared with the analogous monomeric compounds.

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INTRODUCTION

Epoxy resins have been commercially available for more than half a century and continue to be of increasing importance to the plastic industry as materials with excellent mechanical, adhesive and electrical properties.⁶ Hence epoxy resins have a wide range of applications, including coatings, general purpose adhesives and the fabrication of fiber reinforced composites for lightweight construction.^{7,8,9} In addition, the use of carbon fiber reinforced epoxy resins (CFRER) has been the subject of ongoing interest in the field of polymer alloys. In fact, markets for CFRER applications, such as aerospace, wind energy, printed wiring boards (PWB), transportation and leisure, are growing at a rate of more than 10 percent each year.^{10,11,12} However due to their organic nature, the inherent flammability of epoxy materials limits their use in most application that require high flame resistance, such as structural materials for aircrafts and terrestrial vehicles.¹³ Thus, modifications of the epoxy resin with a flame retardant are the focus of a great deal of research activity. As reported by several authors, the fire resistance of epoxy resin can be improved by incorporation of bromine-containing additives or by copolymerization with brominated epoxy compounds.^{14, 15} Halogenated flame retardants have shown consistent growth over the past 20 years, especially with exponential increases in the sales of computers and other electronic equipment. However, the generation of corrosive and toxic substances such as HBr or halogenated dibenzodioxines during combustion led to concerns about the exposure to halogen-containing contaminants which in turn stimulated the development of alternative methods of flame retardancy.^{16,17,18} Therefore phosphorus-based flame retardants have been investigated in an attempt to find halogen-free flame retardant solutions.^{19,20,21} Various organophosphorus compounds have been incorporated into epoxy resin systems either as additives or as reactive co-monomers.²² Commercially available phosphorus compounds such as the ExolitTM series or 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, **1**) were found to exhibit an outstanding performance as flame retardant components in diverse polymers.²³ However, additive flame retardants tend to slowly leach out of the polymer due to the lower molecular weight of such compounds, which restricts their long-term use in some applications, such as Electric & Electronic (E&E) appliances. A wide range of phosphorus-containing oligomers or polymers were reported to overcome this shortcoming.^{24, 25, 26} On the other hand reactive flame retardants like DOPO reduce the number of epoxy functionalities that can contribute to the crosslinking of the cured thermoset and thereby drastically reduce the glass transition temperature (T_g). The use of DOPO (**1**) and its derivatives as flame retardants for polymers

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3 has been widely investigated due to its high stability, good oxidation and hydrolysis
4 resistance .^{27,28,29} Additionally in the presented work, the synthesis of another heterocyclic
5 phosphorus-containing compound derived from 5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one
6 (DDPO, **2**) and 1,3,5-tris-(2-hydroxyethyl) isocyanurate (THIC, **3**) is described and its flame
7 retardancy tested.
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12 <<Insert Figure 1>>

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14 The aim of this study was to develop novel flame retardants based on the two phosphacyclic
15 compounds DOPO (**1**) and DDPO (**2**). THIC (**3**) as bridging molecule was chosen because it
16 is already used as an important and accessible raw material for the production of heat-resistant
17 wire enamels and surface coatings with extremely good mechanical properties. In addition we
18 will also present the polycondensation of THIC and novel oligomeric flame retardants derived
19 from the resulting hyperbranched alcohol. The non-reactive flame retardants were blended in
20 two resin systems, the epoxy novolac DEN 438 commercialized by DOW, and the diglycidyl
21 ether of bisphenol A (DGEBA). Both systems were cured with DICY and Fenuron as an
22 accelerator. The flame retardancy and thermal properties of both epoxy resin systems were
23 examined by UL 94-V, TGA and DSC analysis. The performance of these novel oligomeric
24 derivatives with higher molecular weight will be compared with the corresponding
25 monomeric compounds. Moreover, the influence of the molecular structure of the
26 phosphorus-containing additives on the fire behavior, thermal stabilities and T_g values of both
27 epoxy resin systems will be discussed in this paper.
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39 <<Insert Scheme 1,2,3,4>>

40 41 42 **EXPERIMENTAL**

43 44 45 **Materials and reagents**

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49 Unless stated otherwise, solvents and chemicals were obtained from commercial sources and
50 used without further purification. 2-Phenyl-phenol, phosphorus trichloride, zinc(II) chloride,
51 propylamine, methyl p-toluenesulfonate and toluene were purchased from Sigma Aldrich.
52 Hydrogen peroxide, *tert*-butyl hydroperoxide, chloroform, methylen chloride, carbon
53 tetrachloride and ethylacetate were obtained from Merck. DOPO was supplied by
54 SINOCEM and THIC by MCC-Hamburg. DGEBA was kindly donated by BASF SE. Epoxy
55 Novolac resin (DEN 438 commercialized by DOW), DICY (Dyhard 100S) and Fenuron
56 (Dyhard UR 300) were provided by AlzChem Trostberg GmbH.
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Measurements and Sample preparation

NMR spectra were recorded with a Bruker-Analytical BZH 250/52 (250 MHz). Chemical shifts are reported as δ values relative to the solvent peak. Trimethylsilane was used as a standard. All ^{31}P -NMR spectra are measured proton decoupled. All ^{13}C -NMR spectra were measured proton decoupled and phosphorus coupled. ^1H -Proton spectra were measured phosphorus coupled. Melting points are uncorrected and measured with a Büchi B-545. Differential scanning calorimeter (DSC) measurements were done using a Mettler-Toledo DSC 822 at a scan rate of 20 °C/min under nitrogen.³⁰ The measurements were performed in aluminium pots with weighted samples of 20 mg. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo TGA/SDTA 851 under nitrogen atmosphere or air.^{31,32} 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 with a Varian 660-IR (FT-IR). 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. The samples were (70 ± 1) mm long, (13 ± 1) mm wide, and had a thickness of (4 ± 1) mm.

Curing procedure and UL 94-V test

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-Getzmann GmbH at 6000 rotations *per minute in vacuo* for 20 min. After this, 2.0 phr fenuron (Dyhard UR 300) as a curing accelerator was mixed in the resin mixture with the same method for only 5 min. The formulation was transferred to an aluminum mold and cured at 110 °C for 1 hour, 130 °C for 1 hour and post-cured at 200 °C for 2 hours. All samples were allowed to cool down slowly to room temperature to avoid cracking. The cured samples were cut according to the DIN IEC 60695-11-10 norm. A burner flame is applied to the free end of the specimen for two 10 second intervals separated by the time it takes for flaming combustion to cease after the first application (T1 and T2). Two sets of 5 specimens are tested. A piece of cotton was placed under the specimen to identify burning droplets.

Synthesis

Synthesis of 10-Chloro-10H-9-oxa-10-phospha-phenanthrene (DOP-Cl, **1a**): A flame dried two-neck flask with a condenser and stirring bar was charged with phosphorus trichloride (110 g, 800 mmol) and *o*-phenyl phenol (102 g, 600 mmol). After *o*-phenyl phenol was completely dissolved the reaction mixture was heated slowly to 120 °C. When no more formation of hydrochloric acid gas was detected zinc chloride (600 mg, 450 mmol) was added and the reaction mixture was heated to 150 °C and stirred over night at this temperature. The crude product was purified by distillation *in vacuo* to obtain a white solid with a yield of 115 g (490 mmol; 82%). ¹H-NMR (250 MHz, CDCl₃, δ, ppm): 7.90-7.84 (m, 2H), 7.60-7.48 (m, 2H), 7.37-7.25 (m, 2H), 7.19-7.10 (m, 2H); ¹³C-NMR (63 MHz, CDCl₃, δ, ppm): 148.0 (s, 1C), 132.7 (s, 1C), 130.2 (s, 1C), 130.0 (s, 1C), 129.2 (d, 1C), 127.9 (d, 1C), 127.7 (d, 1C), 124.8 (d, 1C), 124.6 (d, 1C), 123.9 (d, 1C), 121.4 (d, 1C), 121.0 (d, 1C); ³¹P-NMR (101 MHz, CDCl₃, δ, ppm): 134.5.

Synthesis of (9-oxa-10-phospha-phenanthrene-10-yl)-propyl-amine (DOPAM-3-propyl, **1b**): The synthesis of DOPAM-3-propyl was carried out as described in the literature using DOP-Cl (**1a**) and propylamine as reagents and *n*-hexane as solvent.³³ Propylamine was also applied as auxiliary base. The product was purified by distillation under reduced pressure. ¹H-NMR (250 MHz, DMSO-d₆, δ, ppm): 8.12-7.04 (m, 8H), 4.78 (m, 1H), 2.52 (m, 2H), 1.15 (m, 2H), 0.58 (m, 3H); ¹³C-NMR (63 MHz, DMSO-d₆, δ, ppm): 148.9 (s, 1C), 133.6 (s, 1C), 130.1 (s, 1C), 130.0 (s, 1C), 129.2 (d, 1C), 128.2 (d, 1C), 127.7 (d, 1C), 125.2 (d, 1C), 124.8 (d, 1C), 124.7 (d, 1C), 122.4 (d, 1C), 121.0 (d, 1C), 46.6 (d, 1C), 25.7 (d, 1C), 11.3 (s, 1C); ³¹P-NMR (101 MHz, DMSO-d₆, δ, ppm): 61.8; HRMS (EI) calcd for [¹²C₁₅H₁₆P₃N₁O₁]⁺ 527.2748, found 527.0907.

Synthesis of 2-Chloro-5,5-dimethyl-[1,3,2]dioxaphosphinane (DDP-Cl, **2a**): A flame dried round bottom flask with a condenser and a stirring bar was charged with phosphorus trichloride (98.9 g, 720 mmol) and cooled with an ice bath to 5 °C. 2,2-dimethyl-1,3-propanediol (72.9 g, 700 mmol) was added under vigorous stirring. The ice bath was removed as soon as the foaming stopped. The product **2** was purified by distillation *in vacuo* to obtain a colourless liquid with a yield of 104 g (617 mmol, 88%); ¹H-NMR (250 MHz, CDCl₃, δ, ppm): 4.29 (dd, *J* = 10.8 Hz, *J* = 5.8 Hz, 2H), 3.54 (tr, *J* = 10.8 Hz, 2H), 1.24 (s, 3H), 0.81 (s, 3); ¹³C-NMR (63 MHz, CDCl₃, δ, ppm): 70.8 (d, 2C), 32.8 (d, 1C), 22.6 (s, 1C), 20.1 (s, 1C);

³¹P-NMR (101 MHz, CDCl₃, δ, ppm): 147.6.

Synthesis of 1,3,5-tris(2-((6*H*-dibenzo[*c,e*][1,2]oxaphosphinin-6-yl)oxy)ethyl)-1,3,5-triazinane-2,4,6-trione (THIC-(DOP)₃, **4**):

Method 1: A flame dried three neck flask with an addition funnel and a stirring bar was charged with **3** (3.1 g, 11.9 mmol), triethylamine (7.1 ml, 51.1 mmol) and 50 ml toluene. The mixture was cooled with an ice bath to 0 °C. **1a** (8.50 g, 36.2 mmol) was dissolved in 20 ml toluene and added to the reaction mixture under stirring. The temperature was kept below 5 °C. After addition the reaction mixture was stirred at room temperature and the reaction progress was monitored by NMR spectroscopy. After completion, the white precipitate was removed by filtration and the crude product in solvent was concentrated and used without any further purification. ³¹P-NMR (101 MHz, CDCl₃, δ, ppm): 129.3.

Method 2: A flame dried two neck flask with a stirring bar was charged with **3** (16.9 g, 64.6 mmol) and **1b** (50 g, 194 mmol). The mixture was carefully heated to 100 °C and *n*-propylamine was removed *in vacuo* (20°mbar). After 4 h the temperature was raised to 150 °C and the reaction was carried out over night. The reaction progress was monitored by NMR spectroscopy. After completion, the crude product was poured into a metal bowl. The spectroscopically pure product was obtained as a pale yellow powder with the yield of 99% (54.1 g, 64.0 mmol). ¹H-NMR (250 MHz, CDCl₃, δ, ppm): 7.95-7.91 (m, 6H), 7.69-7.61 (m, 3H), 7.57-7.51 (m, 3H), 7.41-7.38 (m, 3H), 7.31-7.25 (m, 3H), 7.18-7.08 (m, 6H), 3.97-3.54 (s, 12H); ³¹P-NMR (101 MHz, CDCl₃, δ, ppm): 129.3; HRMS (EI) calcd for [¹²C₄₅H₃₆P₃N₃O₉]⁺ 855.1664, found 855.1652.

Synthesis of 1,3,5-tris (2-(6-oxido-6*H*-dibenzo[*c,e*] [1,2]oxaphosphinin-6-yl) oxy) ethyl)-1,3,5-triazinane-2,4,6-trione (THIC-(DOP)₃-O, **5**): The crude product **4** (9.67 g, 11.8 mmol) was synthesized by method 1. The reaction temperature was then elevated to 50 °C and 6 ml of a solution of *tert*-butyl hydroperoxide (1.29 g, 14.2 mmol, 3.49 mol·L⁻¹) in toluene was added under stirring to the reaction mixture. The temperature was prevented from rising above 75 °C. After addition the reaction mixture was stirred at 65 °C over night. The crude product was dried under reduced pressure at 120 °C. The spectroscopically pure product **5** was obtained as a brown solid with the yield of 60% (6.40 g, 7.08 mmol). M.p.: 82-84 °C; ¹H-NMR (250 MHz, DMSO-d₆, δ, ppm): 8.16-8.04 (m, 6H), 7.87-7.74 (m, 6H), 7.56 (dtr, *J* = 7.4 Hz, *J* = 3.4 Hz, 3H), 7.40 (dtr, *J* = 7.4 Hz, 3H), 7.30-7.22 (m, 6H), 4.18-3.96 (m, 6H), 3.77 (s, 6H); ¹³C-NMR (63 MHz, DMSO-d₆, δ, ppm): 149.6 (s, 3C), 148.6 (s, 3C), 136.6 (s, 3C),

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3 134.5 (s, 3C), 131.3 (s, 3C), 130.3 (s, 3C), 129.2 (s, 3C), 126.2 (s, 3C), 125.5 (s, 3), 125.1 (s,
4 3C), 122.4 (s, 3C), 121.8 (s, 3C), 120.2 (s, 3C), 62.6 (s, 3C), 42.6 (s, 3C); ³¹P-NMR (101
5 MHz, DMSO-d₆, δ, ppm): 11.4; FT-IR ν (KBr, cm⁻¹): 3064 (w, C_{aryl}-H), 2065 (w, C_{alkyl}-H),
6 1695 (vs, C=O), 1596 (m, P-C_{aryl}), 1582 (w, P-C_{aryl}) 1456 (vs, P-O), 1271 (vs, P=O), 1204,
7 1034, (P-O), 928, 757, 602, 517, 413; HRMS (EI) calcd for [¹²C₄₅H₃₆P₃N₃O₁₂]⁺ 903.1512,
8 found 903.1606.
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16 Synthesis of 1,3,5-tris (2- (6-oxido-6*H*-dibenzo[*c,e*][1,2]oxaphosphinin-6-yl) ethyl)-1,3,5-
17 triazinane-2,4,6-trione (THIC-(DOP)₃-C, **6**): The product THIC-(DOP)₃ (**4**) was synthesized
18 by method 2. A flame dried round bottom flask with thermometer and a stirring bar was
19 charged with *p*-toluenesulfonic acid methylester (27.9 mg, 15 mmol) and **4** (50.0 g,
20 57.4 mmol). Under a gentle steam of argon the temperature was raised to 180 °C and kept at
21 that temperature for another 24 hours to yield the corresponding THIC-(DOP)₃-C (99%,
22 49.5 g, 56.8 mmol). ¹H-NMR (250 MHz, CDCl₃, δ, ppm): 7.88-7.02 (m, 24H), 4.08-3.72 (m,
23 6H), 2.50-2.23 (m, 6H); ¹³C-NMR (63 MHz, DMSO-d₆, δ, ppm): 149.5 (s, 3C), 148.6 (s, 3C),
24 136.6 (s, 3C), 134.5 (s, 3C), 131.3 (s, 3C), 130.3 (s, 3C), 129.2 (s, 3C), 126.2 (s, 3C), 125.5 (s,
25 3C), 125.1 (s, 3C), 122.4 (s, 3C), 121.8 (s, 3C), 120.2 (s, 3C), 62.6 (s, 3C), 42.6 (s, 3C); ³¹P-
26 NMR (101 MHz, CDCl₃, δ, ppm): 34.7; HRMS (EI) calcd for [¹²C₄₅H₃₆P₃N₃O₉]⁺, 855.7025,
27 found 855.5347.
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39 Synthesis of 1,3,5-tris (2- ((5,5-dimethyl-1,3,2-dioxaphosphinan-2-yl) oxy) ethyl)-1,3,5-
40 triazinane-2,4,6-trione (THIC-(DDP)₃, **7**): A flame dried three neck flask with a condenser and
41 an addition funnel was charged with **3** (25.8 g, 98.9 mmol) and 100 mL dry chloroform.
42 Triethylamine (30 g, 300 mmol) was added and the reaction mixture was cooled to 0 °C. The
43 addition funnel was charged with **2a** (50g, 297 mmol) and 150 mL dry chloroform. The DDP-
44 Cl solution was added carefully under vigorous stirring and the reaction temperature was not
45 allowed to exceed 5 °C. After addition the reaction was kept at room temperature for 2 hours
46 and monitored by NMR spectroscopy. The crude product was washed three times with 100
47 mL of brine. The organic phase was dried with magnesium sulfate and the solvent was
48 removed *in vacuo* to obtain colourless oil with the yield of 98% (63.7 g, 96.9 mmol). ¹H-NMR
49 (250 MHz, CDCl₃, δ, ppm): 4.15-3.96 (m, 18H), 3.22 (d_{tr}, *J* = 10.6 Hz, 6H), 1.16 (s, 9H), 0.69
50 (s, 9H); ¹³C-NMR (63 MHz, CDCl₃, δ, ppm): 148.8 (3C), 68.8 (6C), 59.6 (d, *J* = 20.3 Hz, 3C),
51 43.5 (d, *J* = 4.8 Hz, 3C), 32.7 (d, *J* = 5.0 Hz, 3C), 22.7 (3C), 22.4 (3C); ³¹P-NMR (101 MHz,
52 CDCl₃, δ, ppm): 123.7; HRMS (EI) calcd for [¹²C₂₄H₄₂P₃N₃O₁₂]⁺ 657.1981, found 657.1883.
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3 Synthesis of 1,3,5-tris (2-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl) oxy) ethyl)-
4 1,3,5-triazinane-2,4,6-trione (THIC-(DDP-O)₃, **8**): A 500 mL 2 three neck flask with a
5 condenser and an addition funnel was charged with **7** (63.0 g, 95.8 mmol) and 200 mL ethyl
6 acetate. A hydrogen peroxide solution (102 g, 283 mmol, 10% in ethyl acetate) was carefully
7 added at 5 °C. The reaction temperature was not allowed to exceed 10 °C. After the addition
8 was complete the reaction was stirred at room temperature for 5 hours. After completion the
9 reaction mixture was washed three times with brine. The organic phase was separated and
10 dried with magnesium sulfate. After filtration the solvent was removed *in vacuo* to obtain a
11 colourless solid with a yield of 73% (48.6°g, 68.9°mmol). ¹H-NMR (250 MHz, CDCl₃, δ,
12 ppm): 4.30 (dd, *J* = 9.3 Hz, *J* = 4.9 Hz, 6H), 4.21-4.17 (m, 6H), 4.07-4.11 (m, 6H), 3.82 (dd, *J*
13 = 21.4 Hz, 11.3 Hz, 6H), 1.18 (s, 9H), 0.83 (s, 9H); ¹³C-NMR (63 MHz, CDCl₃, δ, ppm):
14 149.0 (s, 3C), 77.8 (d, *J* = 6.7 Hz, 6C), 63.4 (d, *J* = 5.4 Hz, 3C), 42.7 (d, *J* = 5.7 Hz, 3C), 32.0
15 (d, *J* = 5.7 Hz, 3C), 21.6 (s, 3C), 20.1 (s, 3C); ³¹P-NMR (101 MHz, CDCl₃, δ, ppm): -6.2;
16 FT-IR ν (KBr, cm⁻¹): 2971 (w, C_{alk}-H), 2892, (w, C_{alk}-H), 1696 (vs, C=O), 1463 (vs, P=O),
17 1303 (vs, P-O), 1287, 1067 (s, P-O), 1042, 1008 (vs, P-O), 986, 916, 855, 819, 762, 623, 511,
18 491, 474; HRMS (EI) calcd for [¹²C₂₄H₄₂P₃N₃O₁₅]⁺ 705.1829, found 705.1747.
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33 Synthesis of THIC oligomer (**9**):

34 Under a gentle steam of argon **3** (113.1 g, 522.9 mmol) and *p*-toluenesulfonic acid hydrate as
35 catalyst (0.15 g, 0.8 mmol) were fed into a 1 L four-necked round bottom flask equipped with
36 a KPG stirrer, thermometer and a vacuum distillation bridge. The reaction mixture was melted
37 at 160 °C under argon atmosphere. The temperature was then elevated to 185 °C and the
38 reaction mixture was stirred at this temperature for 3 hours. The condensed water formed
39 during the reaction was distilled off under reduced pressure (50 mbar) to shift the
40 polycondensation. The reaction system was refilled with argon and 0.06 g catalyst added to
41 the mixture. After addition the reaction was stirred at 185 °C for another 8 hours. The
42 condensed water was removed again at 20 mbar and 0.03 g catalyst was added. The mixture
43 was heated to 193 °C and the polycondensation then monitored by NMR spectroscopy. After
44 the desired polymerisationsgrad was achieved, the reaction was quenched by decreasing the
45 reaction temperature to room temperature. The hazel solid was collected, pulverized and used
46 without further purification (yield, 99 %, 111.6°g, 75.5°mmol). ¹H-NMR (250 MHz, DMSO-
47 d₆, δ, ppm): 4.76 (s, 8H), 3.53-3.87 (m, 36H), 3.40-3.62 (m, 36H), ¹³C-NMR (63 MHz,
48 DMSO-d₆, δ, ppm): 149.1-149.4 (18C), 66.7, 57.8 (18C), 44.6, 41.5 (18C).
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3 Synthesis of THIC_n-(DOP)_m-O (**10**): Under a gentle steam of argon **1** (60.7 g, 280 mmol), **9**
4 (50.0 g, 33.8 mmol) and 500 ml dry chloroform were fed into a 1 L three-necked round
5 bottom flask equipped with a stirrer and an addition funnel. The reaction mixture was cooled
6 down to -5 °C under stirring and the solid was slowly dissolved. A solution of triethylamine
7 (28.3 g, 280 mmol) and carbon tetrachloride (42.8 g, 280 mmol) in 100 ml chloroform was
8 added in a drop wise manner under vigorous stirring and the reaction temperature was not
9 allowed to exceed 5 °C. After addition the reaction mixture was maintained at room
10 temperature over night and monitored by NMR spectroscopy. The reaction mixture was
11 concentrated under reduced pressure and the residue was washed thoroughly three times with
12 water. The organic phase was dried with magnesium sulfate and the solvent was removed *in*
13 *vacuo* to obtain a white solid with a yield of 65% (67.0 g, 22.0 mmol). ¹H-NMR (250 MHz,
14 DMSO-d₆, δ, ppm): 8.15-7.23 (m, 64H), 4.73 (s, 1OH), 4.17-3.48 (m, 72H); ¹³C-NMR (63
15 MHz, DMSO-d₆, δ, ppm): 149.5-148.8, 136.7 134.4, 131.2, 130.15, 129.1, 126.1, 128.9,
16 126.1, 125.4, 125.0, 124.9, 123.1, 122.4, 122.2, 120.1, 66.7, 62.7 42.40, 41.62; ³¹P-NMR (101
17 MHz, DMSO-d₆, δ, ppm): 10.8.

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32 Synthesis of THIC_n-(DDP)_m-O (**11**) and THIC_n-(DOP)_m-C (**12**): The synthesis of **11** and **12**
33 were carried out as described above in the synthesis of corresponding monomers **5** and **6**.

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35 **11**: white powder with 68% yield; ¹H-NMR (250 MHz, DMSO-d₆, δ, ppm): 4.06-3.87 (m,
36 84H), 3.56 (m, 22H), 1.12 (m, 24H), 0.80 (m, 24H); ¹³C-NMR (63 MHz, DMSO-d₆, δ, ppm):
37 149.2, 66.7, 63.1, 63.0, 60.1, 32.0, 21.2, 19.6); ³¹P-NMR (101 MHz, DMSO-d₆, δ, ppm): - 7.1.

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40 **12**: white powder with 82% yield; ¹H-NMR (250 MHz, DMSO-d₆, δ, ppm): 8.14 (m, 19H),
41 7.78 (m, 18H), 7.55-7.24 (m, 28), 3.70-3.67 (m, 36H), 3.39 (m, 36H); ¹³C-NMR (63 MHz,
42 DMSO-d₆, δ, ppm): 148.7, 134.9, 133.9, 129.9, 129.1, 126.0, 125.3, 124.7, 122.0, 120.5, 66.6,
43 41.6; ³¹P-NMR (101 MHz, DMSO-d₆, δ, ppm): 33.3.

44 45 46 47 48 49 RESULTS AND DISCUSSION

50 51 52 53 Synthesis of monomers

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60 As mentioned above, the use of THIC as a bridge molecule was borne out of consideration of
its good thermal and mechanical properties. The coupling reaction between the THIC and
phosphorus compounds were described in Scheme 1 and 2. For the synthesis of compound **5**
and **8** we started the reactions from DOP-Cl **1a** and DDP-Cl **2a** separately, which bonded

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3 themselves with THIC via nucleophilic substitution. The trivalent DOPO derivative **4** was
4 used without further purification for the next step, whereas DDPO based compound **7** was
5 isolated in near quantitative yields. Subsequently **4** was oxidized by tert-butyl hydroperoxide
6 in toluene and the desired product **5** dried at 120 °C under reduced pressure. The oxidation of
7 **7** was achieved by using hydrogen peroxide in ethyl acetate. Another kind of DOPO derivate
8 was also presented herein, the synthesis of which has been performed as a two-step procedure.
9 In the first step, **1b** is transformed into the corresponding phosphonite **4** by reaction with
10 THIC in the presence of n-propylamine. The second step was carried out via Michaelis-
11 Arbuzov rearrangement using catalytic amounts of *p*-toluenesulfonic acid methylester at
12 180°C. The targeted phosphinate was isolated in good yields.
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23 Thermal degradation behaviors of the synthesized flame retardants

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26 The obtained phosphorus compounds were analyzed *via* thermogravimetric analysis with a
27 heating rate of 4 °C/min under an inert atmosphere. The presented results are shown in
28 Figure 2 and 3. THIC-(DOP)₃-O (**5**) and THIC_n-(DOP)_m-O (**10**) decomposed in a single step
29 reaction with a high initial degradation temperature at a weight loss of 5% around 330 °C
30 (T_{d,5%}). Both flame retardants decompose gradually where the mass loss is attributed to the
31 elimination of phosphorus containing hydrocarbons. The initial char residue found after
32 850 °C was 13.9% for compound THIC-(DOP)₃-O (**5**) and 10.8% for compound THIC_n-
33 (DOP)_m-O (**10**). **10** indicates a comparable thermal stability to the corresponding monomer **5**.
34 However, the degradation steps of THIC-(DOP)₃-C (**6**) and THIC_n-(DOP)_m-C (**12**) occurred
35 near 292 °C and 300 °C. Therefore THIC_n-(DOP)_m-C (**12**) proved to be more thermally stable
36 than THIC-(DOP)₃-C (**6**) (Figure 3). In this case the thermal stability increased with the
37 molecular weight. Both compounds leave very little charred residue at 800 °C (less than 5%).
38 Contrary to the DOPO derivatives, both DDPO-based flame retardants THIC-(DDP)₃-O (**8**)
39 and THIC_n-(DDP)_m-O (**11**) presented a two-step thermal degradation with high initial char
40 residue (25.5% for **8** and 24.7% for **11**) after 800 °C. The TGA analysis of the DDPO
41 derivatives is displayed in Figure 4 where the initial mass loss of about 5% is associated with
42 the loss of solvent traces. In the first degradation step from 270 °C to 370 °C, both
43 compounds decompose gradually with 60% mass loss which is attributed to the elimination of
44 phosphorus containing hydrocarbons.
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The chemical environment around the phosphorus differs from molecule **5** to **6**.
THIC-(DOP)₃-O (**5**) has a 30 °C higher temperature at 5% weight loss in TGA *versus*

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3 THIC-(DOP)₃-C (**6**) because of the more thermally stable phosphorus-oxygen bond (Figure 2
4 and 3). This observation is confirmed in the literature by the investigation of dissociation
5 energies of oxygen-phosphorus bonds (86 kcal/mol) and carbon-phosphorus bonds
6 (65 kcal/mol).³⁴ However, the same tendency of was not observed for the oligomers **10** and **12**.
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10 <<Insert Figure 2,3,4>>
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12 13 14 **Thermal degradation behaviors of fire retardant epoxy resins** 15

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17 Informations regarding the thermal stability and the thermal degradation behavior of the cured
18 epoxy resins were also evaluated using TGA analysis under nitrogen atmosphere. The TGA
19 data of the selected samples and the neat resins are summarized in Table 1 and 2.
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21 All DEN 438/DICY/Fenuron samples presented in Table 1 show the minimum phosphorus
22 concentrations necessary to achieve the V0 rating in the UL 94-V test. In contrast to the neat
23 resin, the degradation temperature of the resins containing DDPO-based flame retardants (**8**
24 and **11**) decreased significantly from 342 °C to 305 °C. This behavior is probably due to the
25 volatility and instability of DDPO derivatives at high temperatures. The influence of DOPO
26 derivatives (**5**, **6**, **10**, and **12**) on the thermal stability of the resins was much weaker, as the
27 onset values remained above 320 °C. The char yield of applied additives showed only
28 negligible differences, which ranged from 29.4% to 34.2% (Table 1).
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30 The addition of both DDPO derivatives (**8** and **11**) to the DGEBA/DICY/Fenuron system
31 resulted in a noticeable increase of the char yield. This is indicative for the presence of a
32 condensed phase fire retardance mechanism for these epoxy systems (Table 2). However, the
33 monomeric compound (**8**) exhibited a better char forming property (char yield: 24.8% at
34 900 °C) compared to the corresponding oligomer (**11**, char yield 18.7%). No significant
35 change was observed when DOPO-based derivatives were added.
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48 49 50 51 **DSC analysis** 52

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54 The influence of the fire retardant additives on the glass transition temperatures (T_g) for both
55 resin systems was investigated by DSC (Table 3 and 4). In general, the addition of the novel
56 flame retardants to both epoxy resin systems slightly shifted the T_g to a lower temperature.
57 DDPO or DOPO species were connected by THIC bridges that possess a rigid and star-like
58 geometry (Scheme 1, 2 and 4). As we predicted, the star-shaped geometry of these compounds
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3 had only moderate plasticizing effect on the cured epoxy resins. This is confirmed by our
4 previous work in this field.² In addition, due to their non-reactive character the presented
5 flame retardants do not reduce the effective number of epoxy groups in the uncured resin. The
6 impact on the T_g was similar for both monomeric and oligomeric compounds.
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10 <<Insert Table 3,4>>

11 12 13 **UL 94-V ratings**

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17 The effect of the synthesized compounds on the flame retardancy of both epoxy resin systems
18 was evaluated using the UL 94 vertical burning test. The UL 94-V results are given in Table 3
19 and 4 together with the corresponding T_g values of the cured resin samples. The loading of
20 DOPO- and DDPO-based flame retardants was kept at a maximum of 2.5wt% phosphorus.
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24 As shown in Table 3, DOPO derivatives showed very high flame retardancy in DICY and
25 Fenuron cured novolac resin DEN 438, as all samples were rated UL 94-V0 with phosphorus
26 contents below 1.7% in the formulation. DDPO derivatives achieved UL 94-V0 rating with
27 2.5wt% phosphorus concentration. Furthermore, it was found that THIC_n-(DOP)_m-O (**10**)
28 exhibited a slightly decreased fire-retardant efficiency compared to THIC-(DOP)-O (**5**).
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32 Depending on the chemical environment around the phosphorus of the flame retardant and on
33 the resin applied, phosphorus can act both in the condensed-phase and in the gas-phase. The
34 fire retardancy mechanism of DOPO and its derivatives is explained usually as a gas phase
35 mechanism. During combustion DOPO or its derivatives release phosphorus containing
36 radicals which are able to scavenge the H- and OH-radicals in the gas phase.³⁵ In addition, the
37 gas phase mechanism dominates generally in DEN438/DICY/Fenuron system. Novolac resins
38 have a high functionality, which leads to an increasing in crosslink densities and eventually an
39 improving on thermal resistance. On the other hand, because of its inherent high heat-
40 resistance, THIC is believed to act as a char forming additive. As seen in Table 3, monomeric
41 flame retardants are more suitable for the DEN 438 systems. THIC-(DOP)₃-O (**5**) and THIC-
42 (DOP)₃-C (**6**) gave a UL 94-V0 classification at a phosphorus content of 1.5% and 1.0%
43 whereas the oligomeric THIC_n-(DOP)_m-O (**10**) and THIC_n-(DOP)_m-C (**12**) achieved the V0
44 rating at a phosphorus content of 1.7% and 1.3% respectively. This can be explained by fact
45 that the increased amount of THIC groups in the oligomer contributes to the condensed phase
46 activity of those compounds. Subsequently the effective number of gas phase active
47 phosphorus groups is reduced. **Since novolac resins demand a gas phase active flame**
48 **retardant, it is evident that the monomeric compounds (5) and (6) are more suitable for this**
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3 system. Furthermore, the flame retardancy of (6) and (12) is more efficient than (5) and (10).
4 This observation can be explained by the oxidation states of phosphorus, which lower
5 oxidation states relate to higher fire-retardant efficiency. It is also confirmed by our previous
6 studies.³⁶ Flame retardants (6) and (12) are both phosphinates therefore indicating an
7 increasing gas phase action compared to the phosphonate flame retardants (5) and (10).
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10 In the case of the DDPO derivatives, THIC-(DDP)₃-O (8) as well as THIC_n-(DDP)_m-O (11)
11 only moderated fire-retardant properties were found. Both flame retardants required 2.5%
12 phosphorus to achieve V0 in the novolac resin. Therefore, DDPO is not the optimal flame
13 retardant for the used epoxy novolac resins.
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16 The fire retardant efficiency of the synthesized compounds was also investigated in the
17 DGEBA/DICY/Fenuron system. As seen in Table 4, both DOPO and DDPO derivatives
18 exhibit satisfactory fire resistance in this epoxy system. In the case of DOPO derivatives, the
19 oligomeric THIC_n-(DOP)_m-O (10) and THIC_n-(DOP)_m-C (12), an improved flame retardancy
20 was observed when compared to the monomeric compounds (2.5% P for compound 5 (V2)
21 and 2.5% P for compound 10 (V0), 2.5% P for compound 6 (V2) and 2.0% P for compound
22 12 (V0). As mentioned above, THIC bridges between the phosphorus compounds are
23 expected to enhance their properties in condensed phase. Moreover, DGEBA distinguishes
24 itself from the epoxy novolac by its lower functionality, which crucially reduces the T_g and
25 thermal stability of the neat epoxy resin. Hence, it is expected that an increased amount of
26 THIC groups in the compound will result in higher fire retardant efficiency for
27 DGEBA/DICY/Fenuron.
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30 However, in the case of THIC_n-(DDP)_m-O (11) and THIC-(DDP)-O (8) the monomeric
31 compound was found to be a better flame retardant (2.5% P for compound 8 (V0) and 2.5% P
32 for compound 11 (n.c.)). With increasing molecular weight the content of DDPO species
33 decreases while the content of THIC groups increases. This leads to the assumption that the
34 contribution of DDPO to the condensed phase mechanism is more than the contribution of
35 THIC.
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52 CONCLUSION

53 In summary, novel star-shaped or hyperbranched fire resistant compounds based on DDPO
54 and DOPO were synthesized and blended into two epoxy resins systems, based on DGEBA
55 and the novolac resin DEN 438. Both resins were cured by the same hardener (DICY) under
56 acceleration by Fenuron. The thermal behavior of the pure phosphorus compounds and the
57 flame retardant containing epoxy resins were investigated by TGA analysis. TGA
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3 measurements indicated that the use of THIC proved to be beneficial for the thermal stability
4 of the new compounds. All derivatives were more thermally stable than pure DOPO and
5 DDPO. This can be explained by the influence of the molecular weight of the compounds and
6 the different bond strengths between the THIC and DOPO or DDPO. The influence of the
7 additives on the T_g values were also studied using DSC analysis. Due to the star-shaped
8 geometry of these flame retardants no strong deterioration of the T_g was observed. The most
9 efficient flame retardant additives presented show a beneficial influence on the flame-
10 retardant efficiency compared to DDPO and DOPO themselves. Especially for the monomeric
11 DOPO derivative **6** in DEN 438/DICY/Fenuron the UL 94-V0 ratings was achieved with
12 1.0% phosphorus content (9.2 wt% flame retardant) in the resin. In the case of
13 DGEBA/DICY/Fenuron the oligomeric DOPO derivative **12** accomplished the best flame
14 retardant efficiency with about 2% phosphorus content. Furthermore, the chemical
15 environment around the phosphorus atom has a crucial influence on the flame retardant
16 properties. In DEN 438 phosphinates (**6** and **12**) exhibit a better flame retardancy compared to
17 the corresponding phosphonates (**5** and **10**). The same observation was also found in the
18 DGEBA system with flame retardant **12** being more efficient than flame retardant **10** and can
19 be explained by the different preferred and provided fire retardancy mechanism of each resin
20 system and type of flame retardant.
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37 Acknowledgements

38 The authors are very grateful to colleagues from our group that contributed to the work
39 presented here, in particular Mrs Lenzner for all the DSC and TGA measurements, Mrs
40 Silbernagel and Ms Schmelcher for performing the UL 94-V tests and Mrs Rakotomalala for
41 inspiring discussions and support.
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Figures

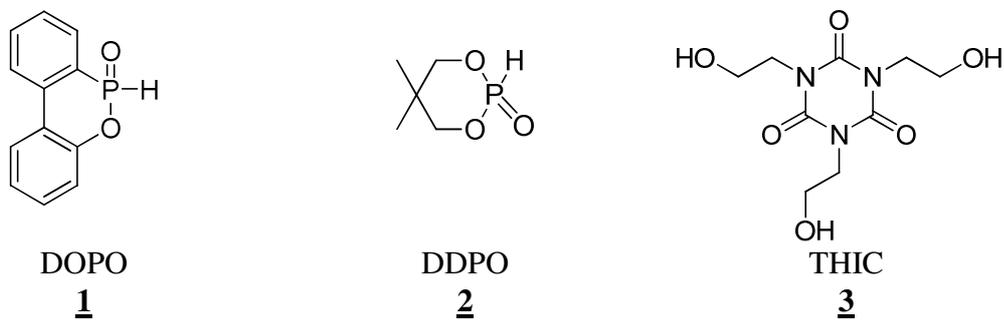
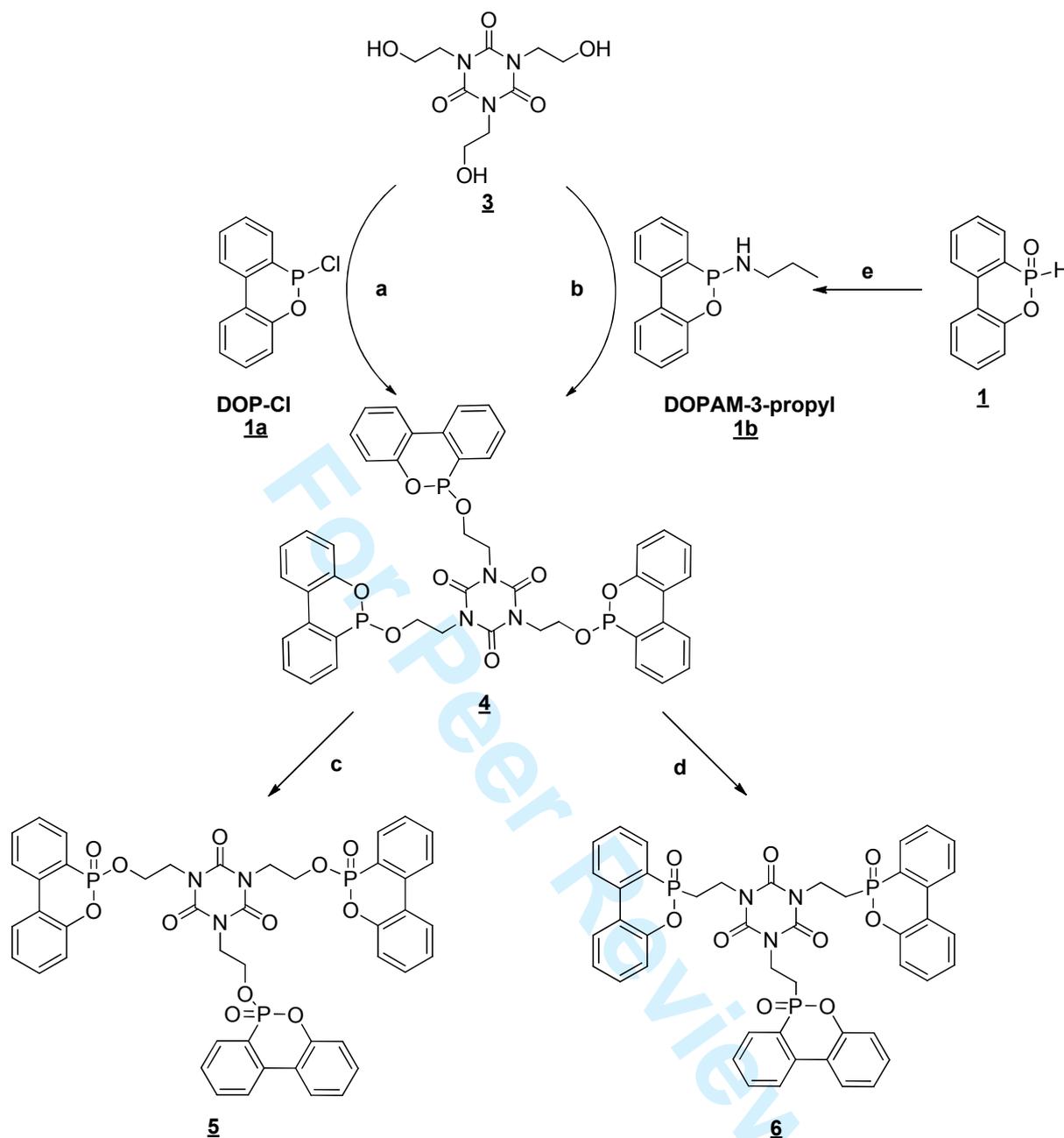
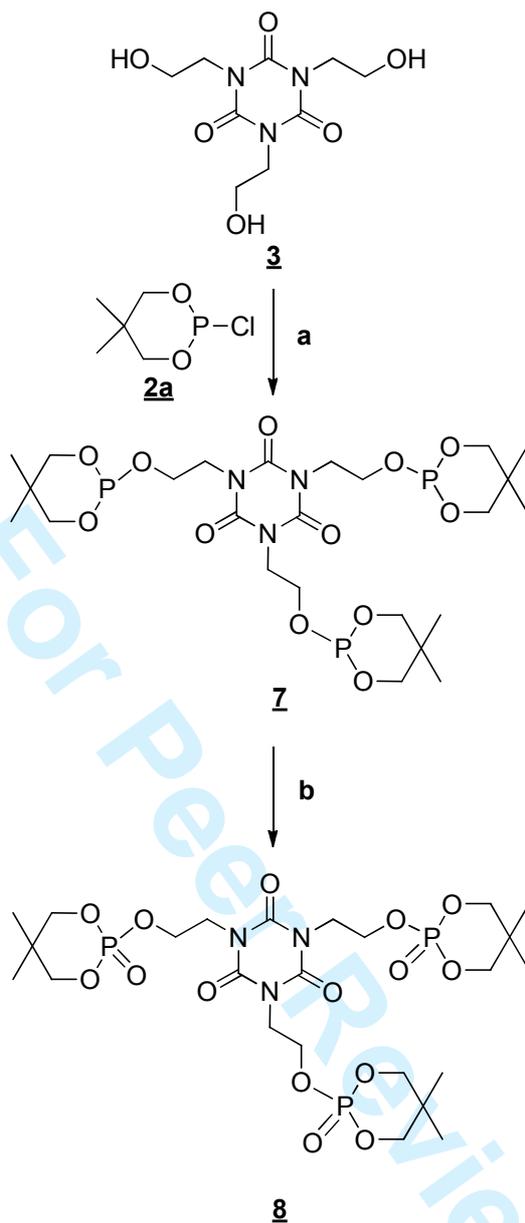


Figure 1. Organophosphorus compound **1** and **2** as well as star shaped-linker **3**.



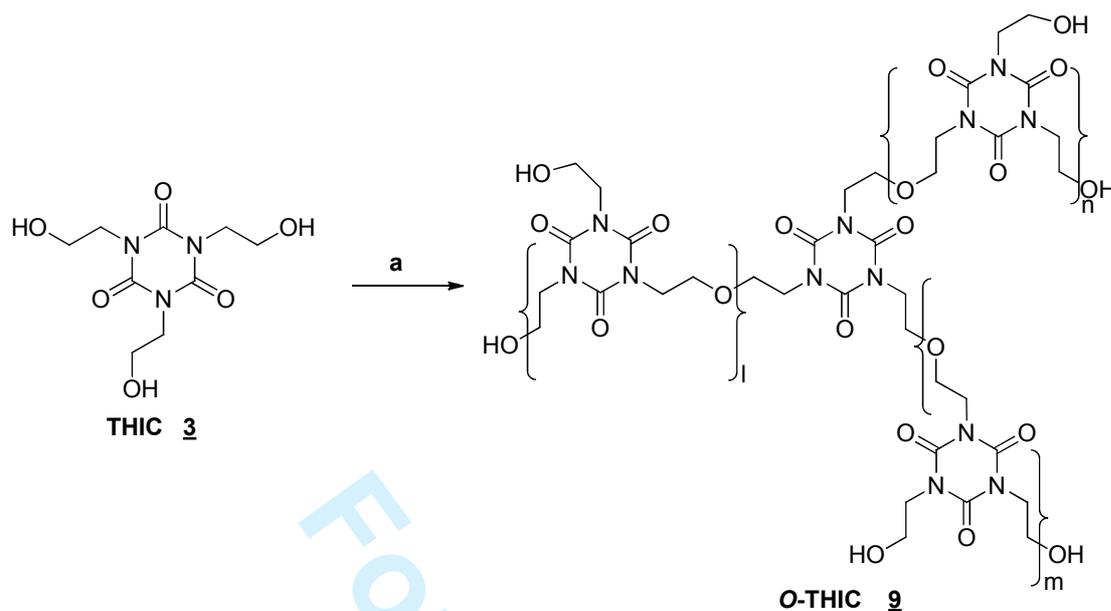
Scheme 1. Synthesis of DOPO and THIC based flame retardants **5** and **6**.¹

Reaction conditions (a): triethylamine, chloroform, 0 °C; (b): 130 °C, 2 mbar; (c): *tert*-butyl hydroxide, toluene, 80 °C; (d): cat.: *p*-toluenesulfonic acid methylester, 180 °C; (e)³⁷: *n*-propylamine, *n*-heptane, 45 ~ 53 °C.



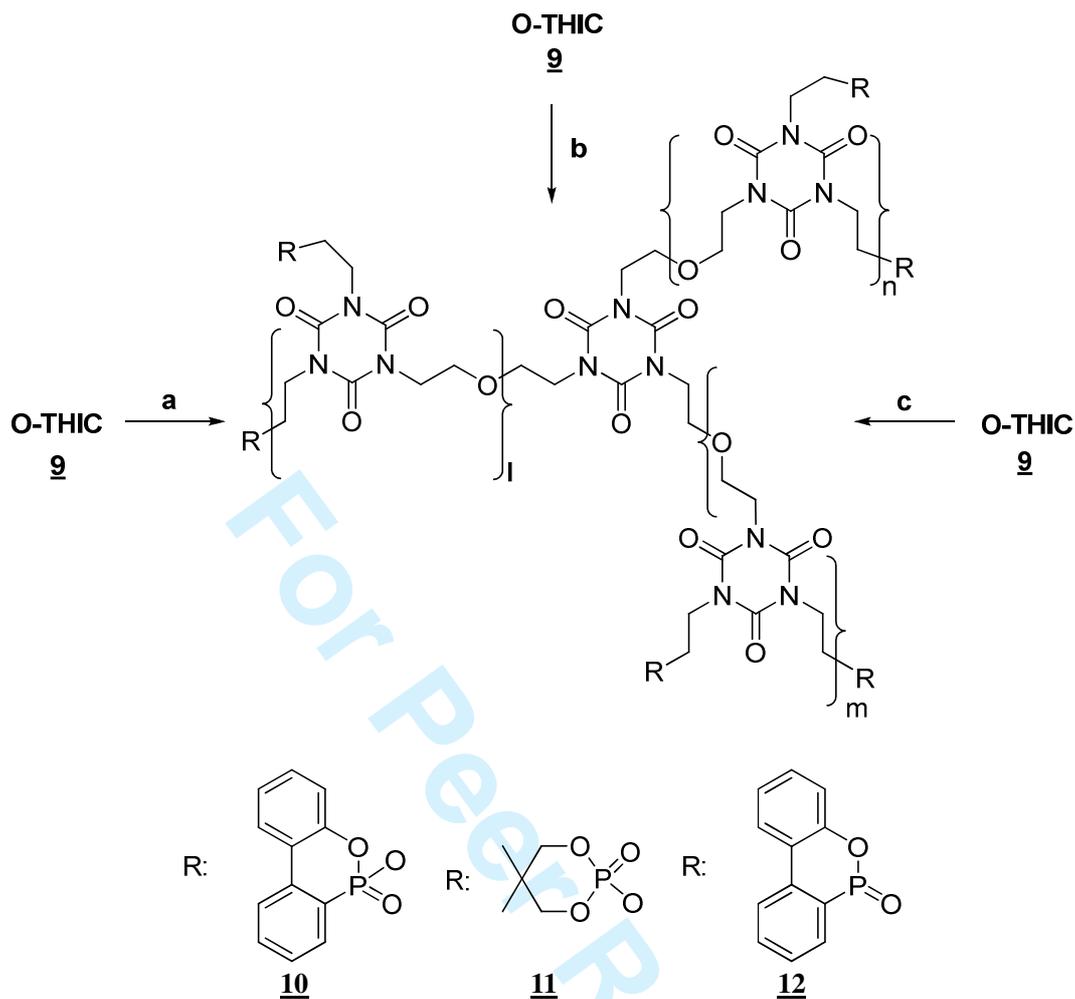
45 **Scheme 2.** Synthesis of DDPO-based flame retardant **8**.

46 Reaction conditions (a): DDP-Cl (**2a**), triethylamine, chloroform, 0 °C; (b): hydrogen
47 peroxide in ethyl acetate, ethyl acetate, 10 °C.
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Scheme 3. Polycondensation reaction to yield THIC-oligomer **9**.

Reaction condition (**a**): *p*-toluenesulfonic acid hydrate, reduced pressure, 185-193 °C.



Scheme 4. Synthesis of THIC oligomer flame retardants **10**, **11** and **12**.

- a** DOPO (**1**), triethylamine, carbon tetrachloride, chloroform, 0 °C
b i: DDP-Cl (**2a**), triethylamine, chloroform, 0 °C
 ii: hydrogen peroxide in ethyl acetate, ethyl acetate, 10 °C
c i: DOPAM-3-propyl, 130 °C, 2 mbar
 ii: *p*-toluenesulfonic acid methylester, 180 °C

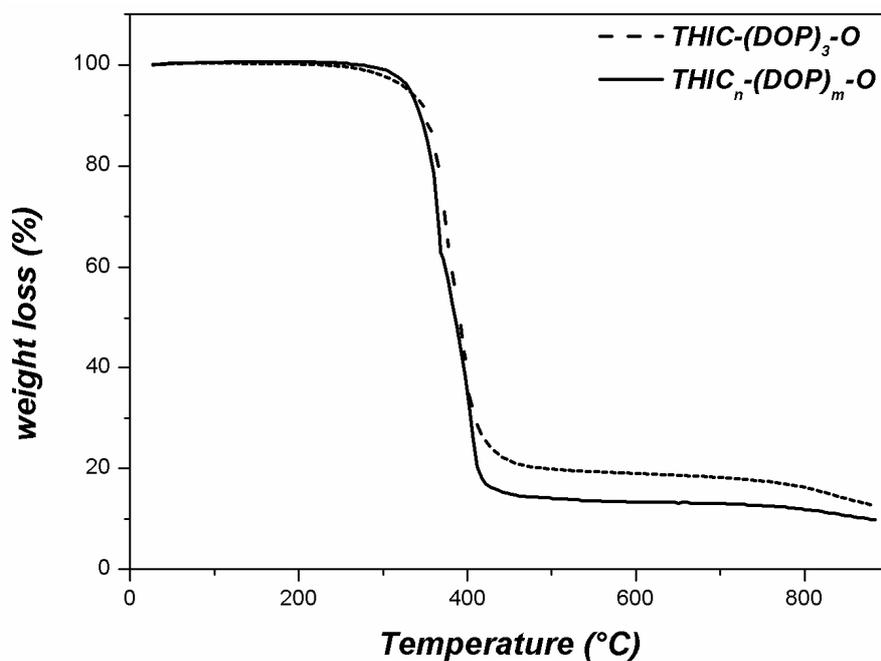


Figure 2. TGA traces of THIC-(DOP)₃-O (**5**) and THIC_n-(DOP)_m-O (**10**) under a nitrogen atmosphere (**5**: $T_{d,5\%} = 333$ °C, **10**: $T_{d,5\%} = 333$ °C).

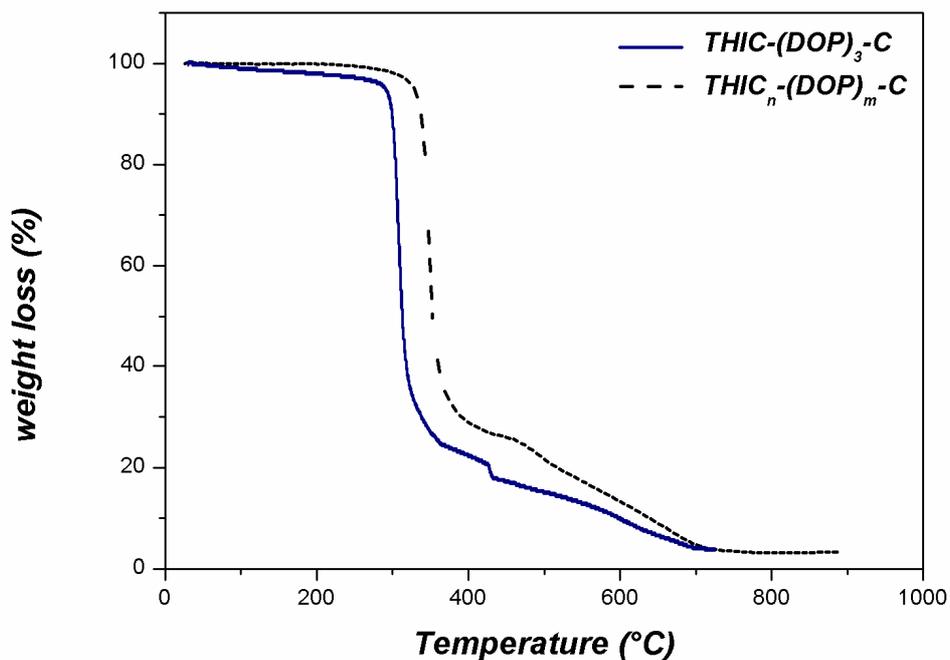


Figure 3. TGA curves of THIC-(DOP)₃-C (**6**) and THIC_n-(DOP)_m-C (**12**) under a nitrogen atmosphere (**6**: $T_{d,5\%} = 292$ °C, **12**: $T_{d,5\%} = 330$ °C).

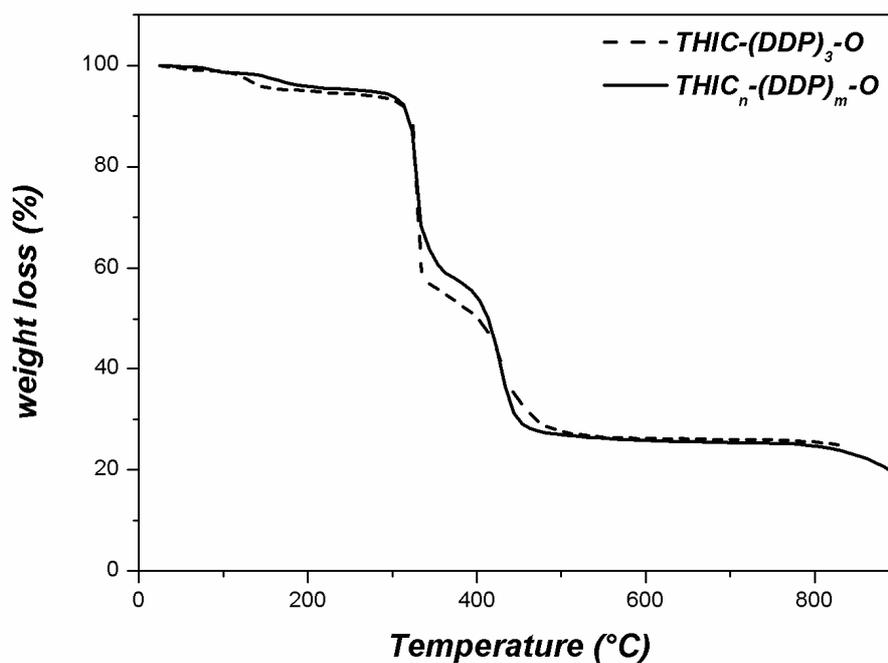


Figure 4. TGA curves of THIC-(DDP)₃-O (**8**) and THIC_n-(DDP)_m-O (**11**) under a nitrogen atmosphere (**8**: $T_{d,5\%} = 181$ °C, **11**: $T_{d,5\%} = 247$ °C).

Tables

Table 1. Thermogravimetical data of DEN 438/DICY/Fenuron containing flame retardant that achieved UL-94 V0 classification.

Substance in DEN 438 /DICY/Fen.	neat epoxy resin	<u>5</u>	<u>10</u>	<u>6</u>	<u>12</u>	<u>8</u>	<u>11</u>
$T_{d,5\%}^{a)}$ (°C)	342	320	330	340	340	305	317
$T_{max}^{b)}$ (°C)	420	380	390	410	410	350	390
P (%)	-	1.5	1.7	1.0	1.3	2.5	2.5
Char yield 900°C (%)	29.4 ^{c)}	32.0	30.1	29.4	28.0	34.2	33.1

a) Temperature for decomposition of 5% mass loss.

b) Temperature of maximum rate of mass loss.

c) Data for the pure n.c.-rated epoxy sample cured with DICY and Fenuron.

Table 2. Thermogravimetric data of DGEBA/DICY/Fenuron containing flame retardant that analyzed by UL-94-V classification.

Substance in DGEBA/DICY/Fen.	neat epoxy resin	<u>5</u>	<u>10</u>	<u>6</u>	<u>12</u>	<u>8</u>	<u>11</u>
$T_{d,5\%}^a$ (°C)	350	308	302	321	340	298	310
T_{max}^b (°C)	410	390	365	388	405	345	350
Char yield 900°C (%)	10.5 ^{c)}	12.6	12.8	11.6	12.3	24.8	18.7
P (%)	-	2.5	2.0	2.5	2.0	2.5	2.5
UL-94 ratings	n.c.	V2	V0	V2	V0	V0	n.c.

a) Temperature for decomposition of 5% mass loss.

b) Temperature of maximum rate of mass loss.

c) Data for the pure n.c.-rated epoxy sample cured with DICY and Fenuron.

Table 3. T_g values and UL 94-V ratings of DEN 438/DICY/Fenuron samples.

Flame retardant	DEN 438 (%)	DICY (%)	Fenuron (%)	%P	%N	%FR	T_g (°C)	UL-94 ratings
-	92.60	5.55	1.85	-	-	-	182	n.c.
DOPO	82.25	4.65	1.65	1.6	-	11.45	155	V0
5	79.08	4.74	1.57	1.5	0.7	14.61	176	V0
10	75.63	4.54	1.51	1.7	1.4	18.30	179	V0
6	84.07	5.04	1.68	1.0	0.4	9.21	169	V0
12	78.29	4.70	1.57	1.3	1.2	15.45	178	V0
DDPO	79.48	4.77	1.59	3.0	-	14.16	158	V0
8	75.02	4.50	1.50	2.5	1.1	18.98	173	V0
11	67.65	4.06	1.35	2.5	2.6	26.93	175	V0

Table 4. T_g values and UL 94-V ratings of DGEBA/DICY/Fenuron samples.

Flame retardant	DGEBA (%)	DICY (%)	Fenuron (%)	%P	%N	%FR	T_g (°C)	UL-94 ratings
-	92.60	5.55	1.85	-	-	-	136	n.c.
DOPO	76.44	4.58	1.53	2.5	-	17.45	110	V2
5	70.08	4.20	1.40	2.5	1.1	24.32	135	V2
10	62.79	3.77	1.26	2.5	2.5	32.19	136	V0
6	71.28	4.28	1.42	2.5	0.9	23.02	120	V2
12	69.70	4.18	1.39	2.0	1.9	24.72	129	V0
DDPO	81.66	4.90	1.63	2.5	-	11.80	127	n.c.
8	75.02	4.49	1.49	2.5	1.1	18.98	138	V0
11	67.65	4.06	1.35	2.5	2.6	26.93	134	n.c.

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