第32卷　第3期
2013年3月

中国材料进展
MATERIALS CHINA

Vol. 32　No. 3
Mar. 2013

特约专栏

DOPO-Based Flame Retardants：Synthesis and Flame Retardant Efficiency in Polymers

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Abstract: During the last decades, the importance of phosphorus-containing halogen-free flame retardants is increasing due to the good environmental sustainability of theses substances. 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives as prominent members of this group of flame retardants show excellent flame-retardant efficiency in different polymers, where they act in particular in the gas phase. Since the development of DOPO in 1972, a large number of DOPO derivatives have been investigated and synthesized in academia and industry. This review will discuss the advancements of promising DOPO-based compounds regarding their synthesis and flame retardancy in thermosets as well as in thermoplastics.

Key words: 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; flame retardant; synthesis; flame-retardant efficiency

CLC number: TQ628.4　　**Document code**: A　　**Article ID**: 1674-3962(2013)03-0144-15

基于DOPO的阻燃剂合成及其对不同高分子材料的阻燃效率

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摘　要：由于环境可持续性的需要，在过去的几十年，无卤含磷阻燃剂的重要性越来越受到社会的关注。9，10-二氢-9-氧杂-10-磷杂菲-10-氧化物(DOPO)及其衍生物作为一种无卤含磷阻燃剂，在聚合物中主要以气相阻燃的机理而表现出优异的阻燃性能。相比于卤系阻燃剂，DOPO及其衍生物在燃烧过程中所释放出的腐蚀性和毒性气体很少，因此许多反应型和添加型的DOPO衍生物得到学术界和工业界的青睐，品种越来越多。DOPO中的P-H键具有较强的反应活性，可以与含活泼双键的化合物(如苯醌、丙烯酸酯、醛类和环氧衍生物等)反应制备出反应型或添加型阻燃剂。反应型DOPO衍生物阻燃剂主要应用于热固性环氧树脂化合物(EP)的阻燃，包括基于DOPO的环氧单体和基于DOPO的胺基和酸酐固化剂，通常这类阻燃剂在环氧树脂中的磷含量达到1.5%以上就可以达到UL 94 V-0级。添加型DOPO衍生物阻燃剂主要是将DOPO中的P-H键转化为P-C，P-O或P-N键的DOPO衍生物，包括基于DOPO的三聚氰胺盐和锌盐以及将P-H键烷基化的DOPO衍生物等，通常这类阻燃剂在聚合物(如EP，PU，PA，PBT和PET等)中的磷含量达到1.0%以上就可以达到UL 94 V-0级。

关键词：DOPO；阻燃剂；合成；阻燃效率

1　Introduction

With consideration of avoiding the generation of toxic and corrosive gases as well as the release of persistent and bio accumulative substances in combustion, the trend is towards using non-halogen flame retardants[1-10]. In recent years, phosphorus-containing organic compounds have been demonstrated as effective flame retardants (FR) for thermosets as well as thermoplastics. Various organophosphorus compounds have been incorporated into epoxy resin systems either as additives or as reactive co-monomers[11-13]. Among of all phosphorus chemicals DOPO 1 (Figure 1) and its derivatives have gained the most attention due to their relative high thermal

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Received date: 2013-01-13
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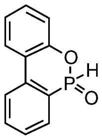
DOI: 10.7502/j.issn.1674-3962.2013.03.03

stability, high reactivity and flame-retarding efficiency[14-15].

DOPO is a phosphacyclic organic compound, made from *o*-phenylphenol and phosphorus trichloride. The first synthesis of DOPO was reported by Sanko Chemical[16] in 1972 and originally this compound was designed for Toyobo's polyester fibers and textiles. The reactive hydrogen of DOPO easily reacts with activated double bonds of benzoquinone, acrylates, aldehydes etc. or epoxides. Therefore, DOPO can be used both as precursor for a flame retardant additive and as an integrative flame retardant agent.



DOPO1

Fig. 1 Structure of 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO 1)

As a reactive phosphorus flame retardant, DOPO can be covalently incorporated into the epoxy polymer chain by a chemical addition onto the oxirane ring in the presence of a base as catalyst (Figure 2). The use of such a fusion process (preformulation) reduces the risk of flame retardant leaching out of the polymer during the polymer processing and the later application.

The flame retardancy of DOPO has been investigated in many different epoxy resin systems. Selected results are summarized in Table 1.

Compared to conventional flame retardants such as $\mathrm{Al(OH)_3}$ (ATH) or Tetrabrombisphenol A (TBBPA), DOPO provides good physical properties and requires lower loadings to reach UL 94 V0 ratings. Schartel *et al.* have thoroughly investigated the pyrolysis and fire behavior of epoxy systems based on DOPO and its derivatives. They reported that DOPO acts either exclusively in the gas phase via flame inhibition, or both in the gas phase and in the condensed phase via char formation at the same time[21-23].

A mechanistic study by Ciesielski et al. [24] supported the gas phase activity of DOPO. The authors carried out a number of thermal desorption mass spectroscopy (TDMS) experiments and proposed a mechanism for the flame retardant reactivity of DOPO (Figue 3). Additionally, they confirmed their results with density functional theory (DFT) calculations.

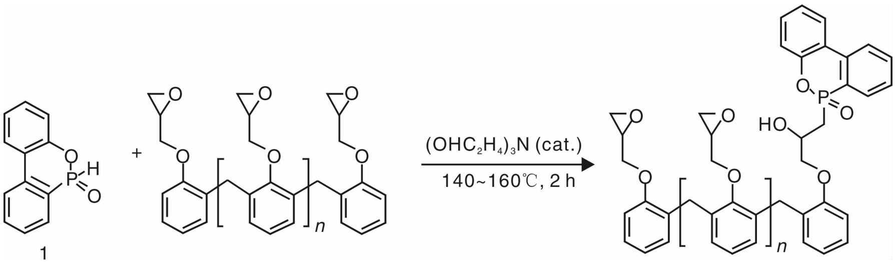


Fig. 2 Preformulation of DOPO into an epoxy novolac resin[17]

Table 1 Overview of the fire behavior and glass transition temperatures of DOPO-containing epoxy resins cured with various hardeners

Epoxy resins	Hardener	Phosphorus content, *w*/%	FR content, *w*/%	T_g/℃	UL-94[18] rating
DGEBA^a	*m*-PDA^b	0.9	6.3	–	n. r. [19]
DGEBA^a	DDS^c	1.2	8.1	–	V0[20]
DGEBA^a	DICY^d/Fenuron	2.5	24.32	135	V2
DEN 438	DICY^d/Fenuron	1.6	11.45	155	V0

Note: ^{a}DGEBA: bisphenol A diglycidyl ether; ^{b}*m*-PDA: *m*-phenylenediamine; ^{c}DDS: 4, 4'diaminodiphenylsulfone; ^{d}DICY: dicyandiamide

$\mathrm{HPO} \longrightarrow \mathrm{H}^{\cdot} + \mathrm{PO}^{\cdot}$

$\mathrm{DOPO\text{-}H}^{\cdot} \longrightarrow \mathrm{PO}^{\cdot} + \mathrm{DBF}$

$\mathrm{DOPO} \longrightarrow \mathrm{HPO}^{\cdot} + \mathrm{DBF}$

$\mathrm{DOPO} \longrightarrow \mathrm{H}^{\cdot} + \mathrm{DOPO\text{-}H}^{\cdot}$

$\mathrm{DOPO} + \mathrm{H}^{\cdot} \longrightarrow \mathrm{H_2} + \mathrm{DOPO\text{-}H}^{\cdot}$

$\mathrm{DOPO} + \mathrm{OH}^{\cdot} \longrightarrow \mathrm{H_2O} + \mathrm{DOPO\text{-}H}^{\cdot}$

$\mathrm{DOPO} + \mathrm{H}^{\cdot} \longrightarrow \mathrm{PO}^{\cdot} + \mathrm{H_2} + \mathrm{DBF}$

$\mathrm{DOPO} + \mathrm{OH}^{\cdot} \longrightarrow \mathrm{PO}^{\cdot} + \mathrm{H_2O} + \mathrm{DBF}$

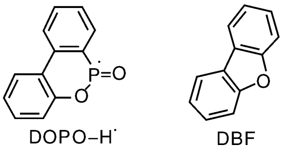


Fig. 3 Proposed mechanism for the flame retardant reactivity of DOPO 1 in the gas phase[24]

2 DOPO-derivatives as reactive flame retardants for epoxy resins

As previously mentioned, the use of a reactive flame retardant has the advantage of the permanent attachment of the flame retardant that avoids the leaching out of the flame retardants and for that reason the loss of the fire resistance. However, the incorporation of only one P-H group results in a decrease of the functionality of the epoxy resin, which leads to a detrimental impact on the material properties, e. g. reduction of the glass transition temperature (T_g). Therefore, in recent years, studies on the synthesis of new phosphorus-containing bridged flame retardants, which have no or less negative influence on the material properties, have attracted much attention.

The synthesis of 10-(2, 5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-HQ 2) was firstly reported by Nishikawa et al. [25]. DOPO-HQ was obtained by addition of 1 to p-benzoquinone in 2-ethoxyethanol with nearly quantitative yield (Fig. 4). Several years later, Wang et al[26]. reported the application of diglycol ether of DOPO-HQ for producing a flame-retardant polyester. Recently, the fire retardancy of 2 has been investigated in epoxy resins as well. Wang et al. reported[27] that the preformulation comprising DOPO-HQ and DGEBA, cured with 4, 4'-diaminodiphenylmethane (DDM), required only 2.1 % P to reach UL 94 V0 rating. In addition, compared to a pure DGEBA resin system hardened with DDS, the cured DOPO-HQ-containing systems exhibited even superior thermal stability and higher glass transition temperatures[28].

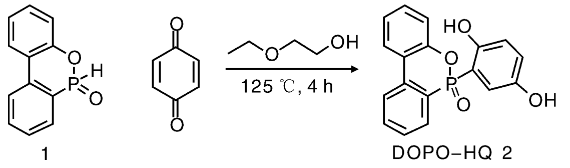


Fig. 4 Synthesis of DOPO-HQ 2[25]

Moreover, current research focuses on the synthesis of flame retardants with higher phosphorus contents via simple methods[29-31]. A novel approach for the synthesis of a series of phosphorus-containing quinone derivatives carrying two similar or different phosphorus units, exhibiting high flame-retardant potential, was recently reported by our group[32].

The synthesis is described in Figure 5. Treatment of DOPO-HQ with activated MnO_2 yielded in the quinone derivative (DOPO-BQ). DOPO-2-HQ was obtained in good yield by addition of one equivalent of DOPO to DOPO-BQ in toluene. The flammability of the DOW epoxy novolac DEN 438/DICY/Fenuron system containing DOPO-2-HQ was investigated. The cured preformulation reached UL 94 V0 rating with 2.0 % phosphorus loading. Additionally, the modification of the novolac resin system with DOPO-2-HQ slightly shifted the T_g to a higher temperature[33].

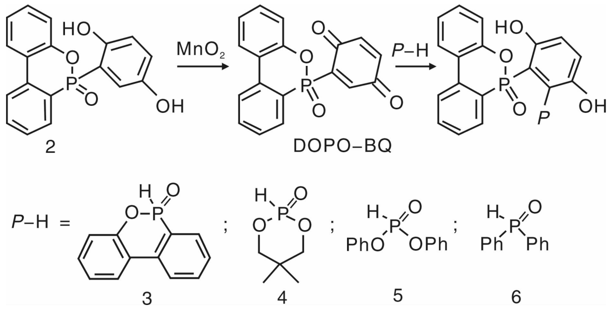


Fig. 5 Synthesis of DOPO-BQ and disubstituted p-hydroquinones: DOPO-2-HQ (3), DOPO-HQ-DDPO (4), DOPO-HQ-(PhO)$_2$PO(5) and DOPO-HQ-DPhPO (6)[32]

Various other new compounds containing at least two DOPO units were successfully synthesized by using the Pudovik reaction. For example, Liu et al. [5] prepared epoxy monomers with high phosphorus content. 2DOPO-PhOH (7) was obtained through a one-step reaction of DOPO with benzophenone derivatives. The -C-OH group formed by the nucleophilic addition of P(O)-H to the carbonyl group was reported to react further with another DOPO molecule to form the designed product *via* a condensation reaction (Figure 6). Compound 7 was used to yield a phosphorus-containing epoxy monomer followed by the reaction with epichlorohydrin and combined with bisphenol A-based epoxy resin to produce the phosphorus-containing prepolymer. The amine hardener, e. g. DDM or DICY, was used for the curing reaction of both modified epoxies. Due to the high phosphorus contents of the cured epoxy resins (4.2 % ~ 8.0 %), all samples exhibited an extremely high LOI value (between 37 and 46). Furthermore, the modified resin systems presented superior thermal stability in comparison to the phosphorus free epoxy systems.

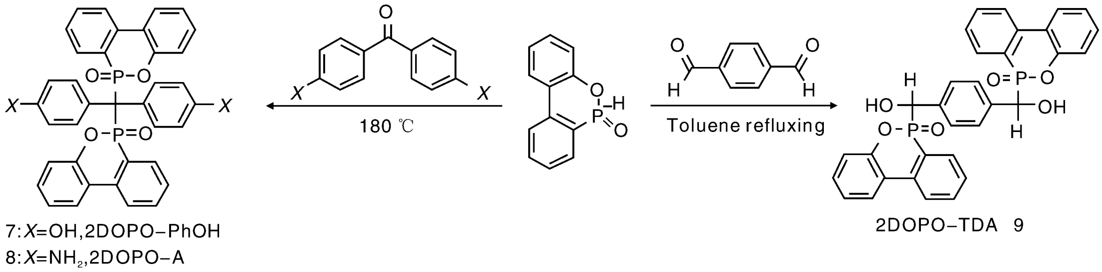


Fig. 6 Synthesis of epoxy resin monomers with high phosphorus contents[5]

2DOPO-TDA 9, the terephthal aldehyde adduct of DOPO, was also synthesized via Pudovik reaction[34]. The flame retardant epoxy novolac resin was obtained by a fusion reaction described in Figure 7[35]. In the UL 94 test, the prepolymer cured with DDM required only 1.0 % P to achieve a V0 classification. In addition, the resulting polymer exhibited a high T_g value of 189 ℃.

Kim et al[36]. pioneered the synthesis of a phosphorus-based flame retardant comprising 4 DOPO units, namely 4DOPO-bisphenol A, 10. The compound 10 was prepared via a two-step procedure (Fig. 8). The addition reaction of formaldehyde and bisphenol A followed by a high-temperature condensation reaction gave the final product 10. The intermediate product formed in the first step was purified by extraction of the reaction mixture with an organic solvent. Nevertheless, due to similar physical properties a small amount of the by-product, such as the polycondensate of formaldehyde and bisphenol A could not be removed completely. The condensation of the oligomeric by-product and DOPO was also observed. As a result the obtained compound turned out to be a combination of 10 and corresponding DOPO-based oligomers.

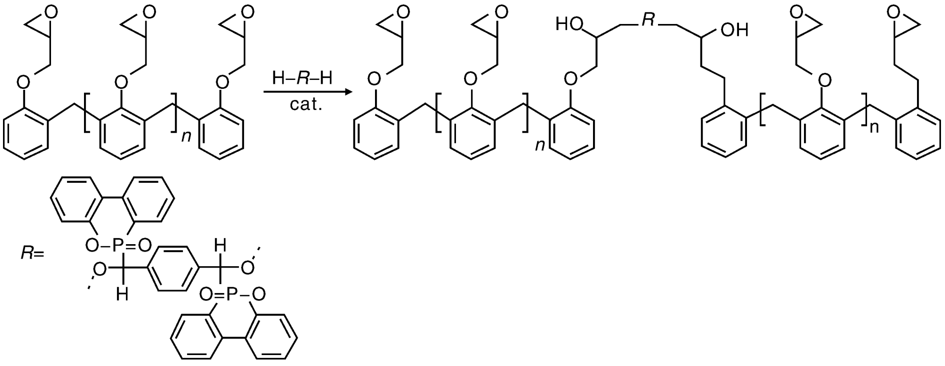


Fig. 7　The fusion reaction of 9 and DEN 438 epoxy novolac

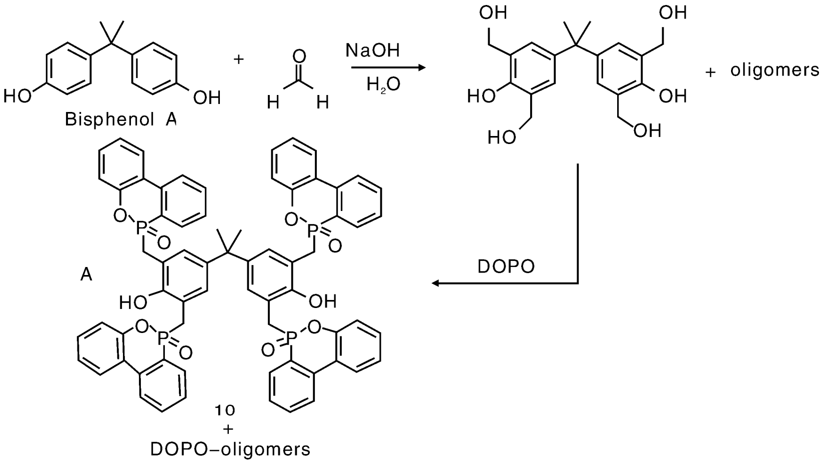


Fig. 8　Synthetic procedure to obtain 4DOPO-bisphenol A (10)[36]

A different procedure for the preparation of a similar compound was developed by the DOW chemical company around the same time[37].

Recently, in 2012, Wang et al.[38] published a study of an epoxy thermoset modified with a phosphorus/nitrogen containing flame retardant 11, prepared from the adduct 12 of DOPO 1 and formaldehyde with triglycidyl isocyanurate 13 (Figure 9). Epoxy resins with different contents of 11 were prepared by incorporation of the DOPO derivative 11. Thermo stabilities as well as flame retardant properties of these thermosets were investigated. In the UL 94 test, the authors archived for an epoxy resin system with a flame retardant content of 10 % the V0 classification and determined a LOI value of 35. Besides, the glass transition temperature T_g of the composites increased with increasing content of 11.

3　DOPO-derivatives as hardeners for epoxy materials

Another method to incorporate organic phosphorus moieties in epoxy resins is to modify the curing agents[39-45].

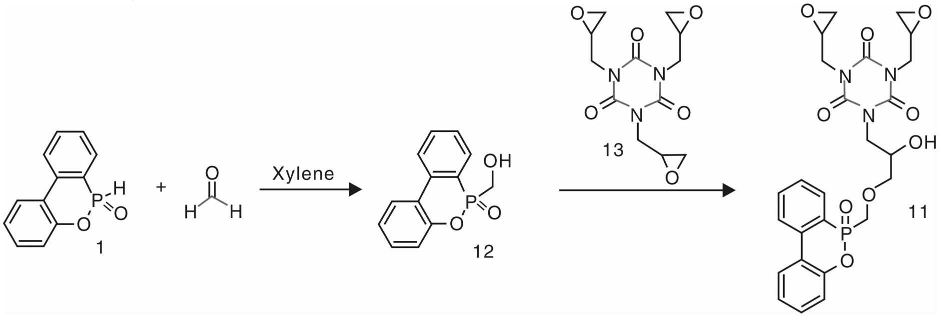
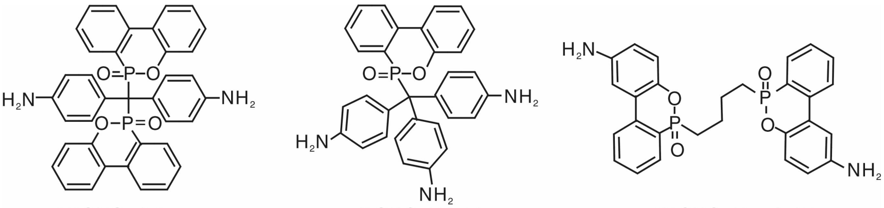


Fig. 9　Synthesis of a mono phosphorylated triglycidylisocyanurate derivative 11[38]

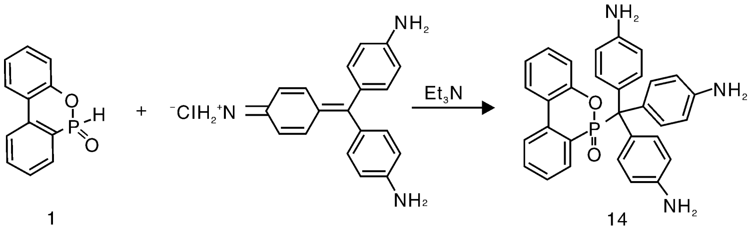
Several DOPO-based aminic hardeners have been developed[46-49]. In Figure 10 some examples of these type of hardeners are shown. The synthesis route of 8 has already been described in Figure 6. This DOPO-based diamine has proven to be an appropriate curing agent for multifunctional cresol novolac epoxy resins as well as DGEBA. Both cured resins showed high glass transition temperatures, especially the system cresol novolac/8 presented the high T_g value of 195 ℃, which is potentially useful for advanced printed circuit boards (PCBs) and electronic encapsulation[12].



2DOPO-A 8 DOPO-TA 14 2DOPO-Bu-A 15

Fig. 10 Chemical structures of DOPO-based amine curing agents 8[12], 14[48] and 15[49]

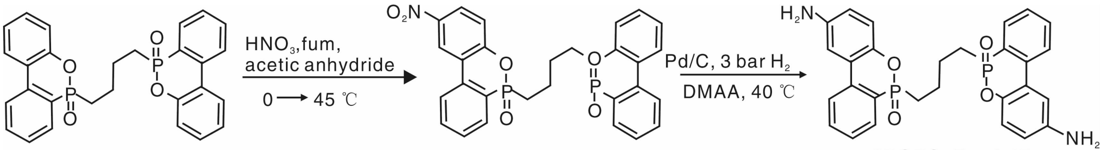
Inspired by the good results from DOPO-Triol, Lin et al.[48] developed a novel DOPO-containing triamine (DOPO-TA 14) from the nucleophilic addition of DOPO and pararosaniline chloride by using triethylamine as an acid scavenger (Figure 11). The curing behavior of 14 was investigated in DGEBA and dicyclopentadiene epoxy resin. Regarding the activation energy and onset temperature of the curing, DOPO-TA has a lower reactivity than DDM, however, it has a higher one than DDS. Both DOPO-TA cured systems possessed higher glass transition temperatures than the common curing agents and high flame retardancy.



1 14

Fig. 11 Synthesis of DOPO-TA 14[48]

The incorporation of amino groups directly to the DOPO framework was first reported by our group (Figure 12)[49]. Due to the reduced number of aromatic rings, this developed compound was proposed to exhibit a superior compatibility within the epoxy as compared to previously reported systems[12,48]. Consequently, the thermal- and mechanical properties of the DGEBA/15 system, which contained 4.5 % P, were comparable to the values of the DGEBA/DDS reference system.



2DOPO-Bu-A 15

Fig. 12 Synthesis of the diamino hardener 15[49] (DMAA = *N*, *N*-dimethylacetamide)

Apart from amines, other types of curing agents have been modified with DOPO, such as phenolic novolac and anhydrides[50]. In a study reported by Lin et al.[29], DOPO was used to produce a rigid novolac compound *via* a simple addition reactions to *para*-hydroxybenzaldehyde, followed by a polymerization using catalytic amounts of oxalic acid (Figure 13). The obtained novolac-analog compound (DOPO-PN 16) has proven to be a suitable curing agent for bisphenol-A-and o-cresol novolac-type epoxies. These results were supported by DSC and TGA measurements. High limiting oxygen index (LOI) values were found to demonstrate the good flame retardancy of the DOPO-PN-cured epoxy resin. However, with increasing phosphorus contents in the cured polymers, the T_g values decreased from 182 ℃ to 134 ℃, whereas LOI values were leveled up from 21 to 36. The same tendency could be observed for the DGEBA/16 systems.

Since the pioneer work by Endo et al.[51] on the synthesis of phosphorus-containing diacid monomers, many researchers have focused on its particular properties, paying special attention to its application in flame-retardant polyesters[52-54]. Cho et al.[50] published their studies on the aryl phosphinate anhydride (DMSA 17) as a curing agent for flame-retardant epoxy matrixes. This work revealed a facile, one-pot synthesis of phosphinate anhydride from a phospha-Michael addition of DOPO to itaconic acid, followed by a thermal dehydration (Figure 14). The curing behaviors of the obtained DMSA were investigated in DGEBA and epoxy-novolac, respectively. The same analyses were also carried out with mixtures of hexahydrophthalic anhydride (HHPA)/DMSA and phthalic anhydride (PA)/DMSA in different molar ratios. For both resin systems, the samples cured with PA showed the highest T_g values. In PA/DMSA systems the T_g decreased with increasing content of DMSA. On the contrary, in HHPA/DMSA system the T_g values increased when the DMSA contents also increased. The addition of DMSA significantly leveled up the flame retardancy of cured epoxy resins.

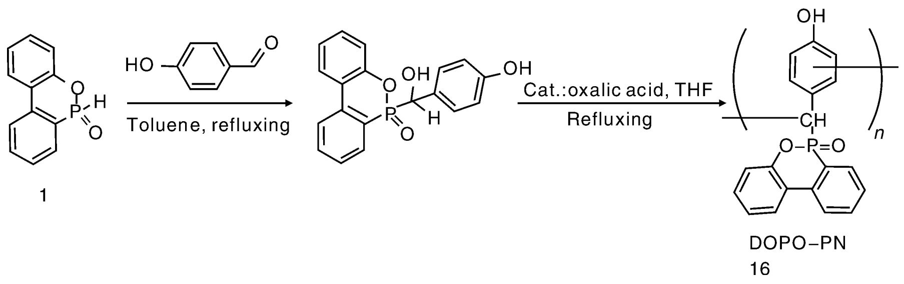


Fig. 13　Synthesis of DOPO-PN 16

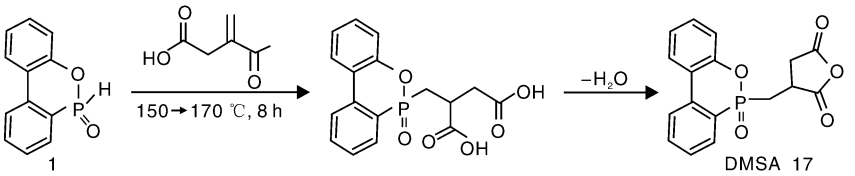


Fig. 14　Synthesis of aryl phosphinated anhydride 17[50]

4　DOPO derivatives as additive flame retardants

An alternative approach to get a DOPO derivative into polymers, instead of introducing it via a chemical reaction described above, is to blend the polymer with a non-reactive or additive DOPO compound. Two disadvantages of additives in polymers are their tendency to leach out of the bulk material as well as their plasticizer effect. For avoiding these drawbacks, DOPO based additives should have a salt or polymer-like structure or at least a high molecular weight[55]. As mentioned before, DOPO is a reactive compound and can act as an acid. Furthermore its thermal degradation starts at approximately 200 ℃[56]. Therefore, it cannot be used as an additive without derivatization. Later on, a number of different reactions to obtain derivatives of DOPO and of course their use as flame retardants are described.

4.1　Salt and salt-like DOPO additives

Described DOPO salt additives often have a nitrogen-containing cation and a DOPO-based anion[57-60]. For the synthesis of such compounds, DOPO 1 has to be oxidized into its corresponding acid DOPO-OH 18 which can be easily done by using hydrogen peroxide as oxidant[61]. In a second step DOPO-OH 18 and an organic typically nitrogen-containing base such as melamine (Mel, 19) are mixed together to provide a corresponding DOPO salt. Figure 15 shows an example of a DOPO salt additive 20 where DOPO-OH 18 was treated with melamine 19 at elevated temperature in water as solvent to get[H Mel][DOPO – O] 20[61].

The authors blended [H Mel][DOPO – O] 20 into a novolac epoxy resin with or without synergist and hardened with DICY/Fenuron to investigate the flame retardancy of 20. The composites reached the V0 classification in the UL-94 test with a phosphorus content of 1.0 % and even less in combination with synergists. Moreover, the additive 20 and the mixture of additive and synergist showed just a slightly influence on the glass transition temperature (Table 2)[62].

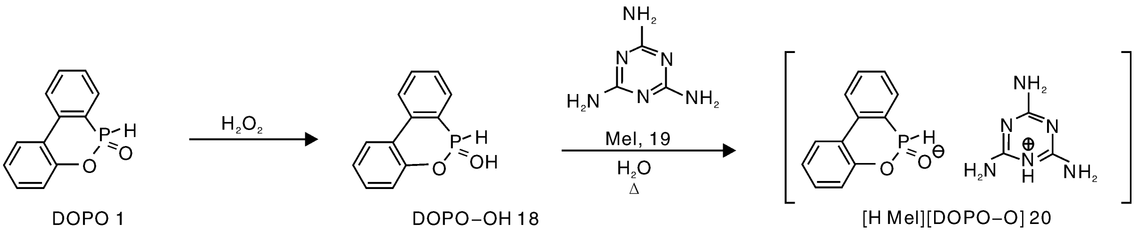


Fig. 15　Two step Synthesis of 20: In the first step DOPO 1 is oxidized with hydrogen peroxide to the corresponding acid DOPO-OH 18. Treatment of 18 with melamine (19) at elevated temperature yielded the salt 20[61]

A further compound has to be mentioned in this context namely zinc DOPO (ZnDOPO 21). In 2006, Just et al.[63]

Table 2　Required loading of the salt 17 to achieve UL 94-V0 in DEN 438 cured with DICY/Fenurone[62]

Flame retardant	UL 94 (4 mm)	P content, *w*/%	FR content, *w*/%	T_g /℃
–	n. c.	–	–	182
20	V0	1.0	11.6	174
20 + 30 % boehmite	V0	0.8	7.0	171
20 + MPP (1:1)	V0	0.9 + 0.7	5.2 + 5.2	179

Note: MMP: melaminepolyphosphate; boehmite: Al(O)OH; T_g measured by Differential Scanning Calorimetry (DSC) reported a simple synthesis of this salt-like substance 21, from the reaction of a zinc salt with DOPO 1 in the presence of a base (Fig. 16). The exact structure of the product 21, which represents a coordination polymer, was by crystal structure analysis (Fig. 17). ZnDOPO 21 can be oxidized to the corresponding coordination polymer ZnDOPO-O 22, according to Figure 14. Due to its high thermostability above 400 ℃, ZnDOPO 21 was blended with and without melamine cyanurate (MC) into polyamide 6 (PA6), an engineering plastic and showed in both cases good results concerning flame retardancy. As an example, a PA6 blend with 7.5 % 21 and 7.5 % MC reached the UL V0 classification[64].

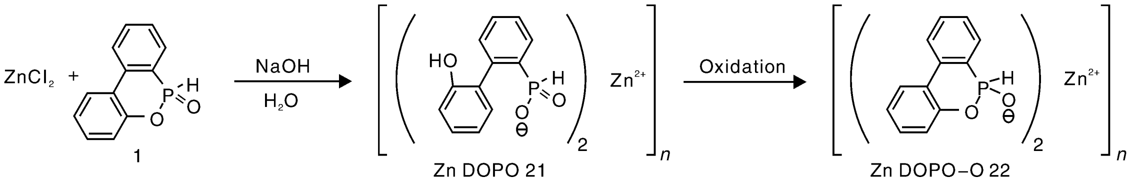


Fig. 16 Synthesis of the coordination polymers ZnDOPO 21 and ZnDOPO-O 22 starting with zinc chloride and 1 to obtain 21 followed by an oxidation to 22[63-64]

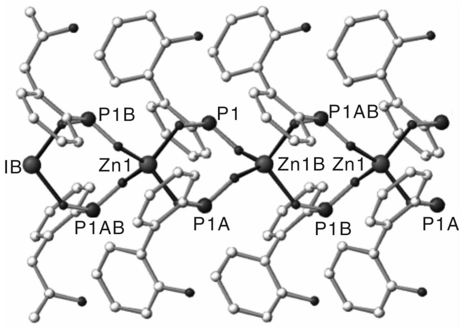


Fig. 17 Crystal structure of ZnDOPO 21[63]

4.2 Organic derivatives of DOPO

In the following section, selected organic DOPO derivatives are discussed where the P-H group of DOPO 1 was formally converted into a P-C, P-O or P-N group. This transformation is important to block the reactivity and to increase the thermal stability of the DOPO compounds.

DOPO-methyl 23, an efficient flame retardant for flexible, low density polyurethane foam was investigated by König et al. [65]. They obtained 23 from a Arbuzov reaction of the trivalent DOPO species 24 in the presence of a catalytic amount of methylsulfate, according to Dittrich et al. [66] and Artner et al. [49]. The precursor 24 was prepared from DOPO 1, methanol, orthoformiate and HCl (Figure 18). Additionally, the authors synthesized low density, flexible polyurethane foams that contained different amounts of 23 to study the burning behavior and the material properties of these foams. The results of this research indicate that 23 has a good compatibility with the polyurethane foams. Furthermore, 23 shows a good flame-retardant effect. König et al. [65] figured out that 23 mainly acted in the gas phase by diluting the burnable gaseous product of the decomposed polymer and by functioning as radical scavenger, as described earlier. The latter effect was determined by TG-MS and cone calorimeter experiments.

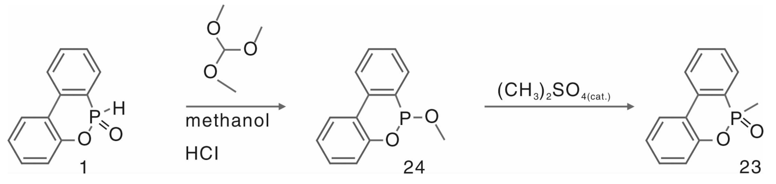


Fig. 18 Synthesis of DOPO-methyl 23 from the trivalent compound 24, prepared from DOPO 1[49,65-66]

Angell et al. [67] reported the synthesis of an ethylene bridged DOPO derivative $DOPO_2$-ethylene 25. It results from the nucleophilic reaction of the potassium salt of DOPO with dichloroethane prepared by treating DOPO 1 with potassium *tert*-butoxide according to Figure 19a. They also successfully incorporated 25 into epoxy resins and prepared laminates. UL-94 tests with and without synergists were performed of these laminates. The results indicated a good flame retardant effect and are summarized in Table 3. Afterwards, Yao et al. [68] described a one-step procedure to obtain 25 from DOPO and ethylene glycol catalyzed by sodium iodide (Figure 19b).

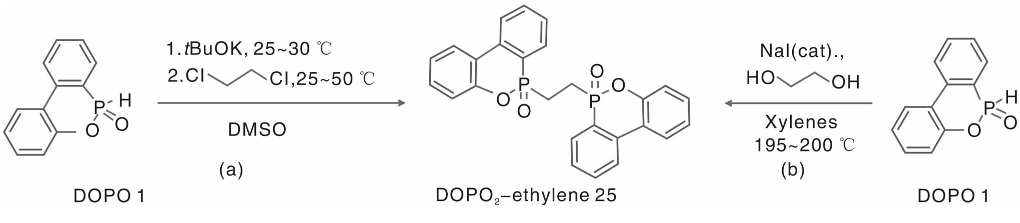


Fig. 19 Two synthetic strategies starting with DOPO 1 to obtain $DOPO_2$-ethylene 25: (a) DOPO 1 was transformed into a potassium salt via potassium-*tert*-butoxide that was treated in a second step with dichloroethane to lead the final product 25. (b) in a one-pot reaction 25 was obtained from DOPO 1, ethylene glycol and sodium iodide as catalyst[67-68]

In 2007, Artner et al.[49] already synthesized a similar bridged DOPO compound $DOPO_2$-butylene 26 with a butylene instead of an ethylene spacer between the two DOPO moieties. Their synthetic approach was a transesterification of the trivalent DOPO compound 27 with butanediol to 25, followed by an Arbuzov rearrangement in the presents of *para*-toluenesulfonic acid as catalyst to obtain the final product 26 (Figure 20). However, the authors have not done any tests regarding flame retardancy. This synthetic route could also be used for the preparation of 25 starting from 27 and ethylene glycol[69].

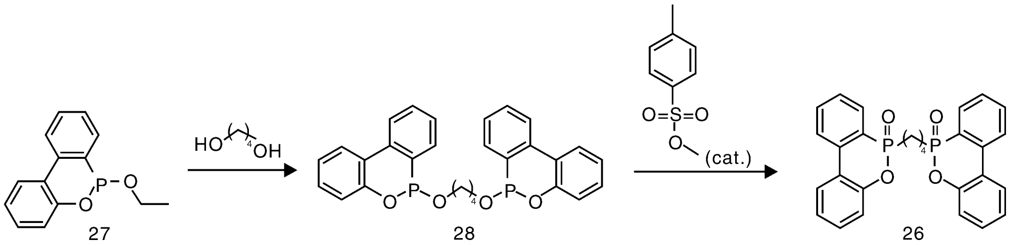


Fig. 20 Synthesis of $DOPO_2$-butylene 26 published by Artner and coworkers. The product was obtained from a Arbuzov reaction of the corresponding trivalent phosphorus species 28, prepared from the transesterification of 27 and butanediol[49]

Table 3 Results of UL 94 tests of $DOPO_2$-ethylene 25 in epoxy resins[67]

Epoxy resin	Flame retardant	UL 94 (0.94 mm)	P content, *w*/%	T_g /℃
DEN 438-EK 85/ Durite SD-1702	none	n. c	0	163 ~ 172
DEN 438-EK 85/ Durite SD-1702	25	V0	4.0	126 ~ 131
DEN 438-EK 85/ Durite SD-1702	25	V1	3.0	136 ~ 140
NPCN-703/ Durite SD-1702	none	n. c	0	198
NPCN-703/ Durite SD-1702	25 6.6 % +6.6 % MMP +30 % silica	V0	1.76	179

Note: MMP: melamine polyphosphate; T_g measured by Differential Scanning Calorimetry (DSC)

A study of Perret et al.[70] published in 2011, pointed out that the treatment of pentaerythrol tetraacrylate (TAEP 29) with DOPO 1 and triethylamine as catalyst gave the corresponding tetra DOPO derivative (DOPP 30) via analogue Michael Addition (Figure 21). The authors blended DOPP 30 into commercially available epoxy resins for aircraft applications RTM6 as well as in carbon fiber reinforced RTM6 and investigated the fire behaviors and mechanical properties. Additionally, they proposed thermal decomposition pathways and figured out that DOPP 30 acted in the gas phase by flame inhibition and in the condensed phase through charring. The results of UL-94 tests are listed in Table 4 and demonstrate efficient flame retardancy.

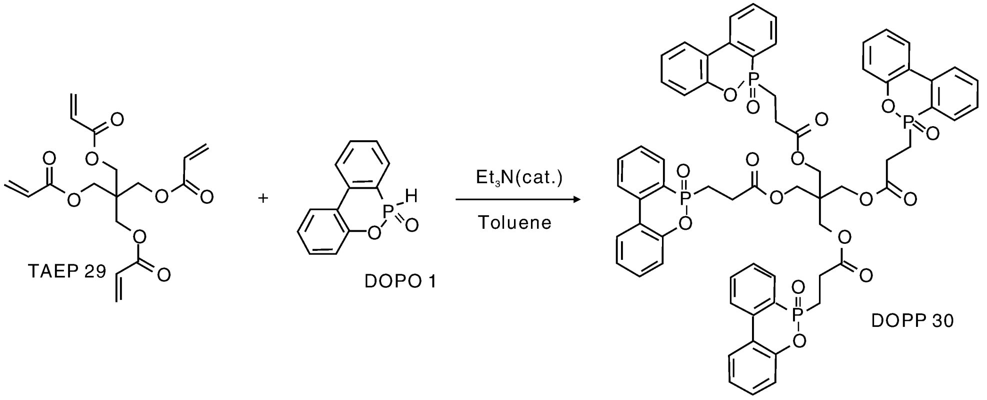


Fig. 21 Synthesis of DOPP 30 via analogue Michael Addition of DOPO 1 to TAEP 29 in the presence of triethylamine as catalyst[70]

Table 4 Results of UL 94 tests of DOPP 30 in RTM6[70].

Epoxy resin	Flame retardant	UL 94 (3.0 mm)	P content, *w*/%	FR content, *w*/%	T_g /℃
RTM6	none	HB	0	0	229
RTM6	DOPP 30	V1	2.0	19.6	191
RTM6-CF	none	HB	0	0	215
RTM6-CF	DOPP 30	V0	0.6	5.9	190

Note: T_g measured by dynamics mechanical analysis (DMA)

A further approach to achieve a DOPO based flame retardant was done by Zang et al.[71]. They obtained a star like THIC-DOPO compound 31 from its corresponding derivative (THIC-O-DOP, 32) via Arbuzov reaction catalyzed with para-toluenesulfonic acid methylester (Figure 22e). The precursor 32 can be synthesized with two different methods. Both use THIC 33 as starting material. In the first one, 33 is coupled with DOP-Cl 34, a precursor of the DOPO synthesis[16], by nucleophilic substitution in the presence of a base (Figure 21a). In the second one 33 is converted into 32 using DOPAM-3-propyl 35, prepared from DOPO itself and n-propylamine, according to Figure 21c. To evaluate the flame retardancy of THIC-DOPO 31 and its effect on the material properties, the final product 31 was blended into epoxy resins. For example, the THIC-DOPO 31 containing epoxy resin (DEN 438/DICY/Fenuron) reached the UL 94 V0 classification with a phosphorus content of 1.0 percent (Table 5).

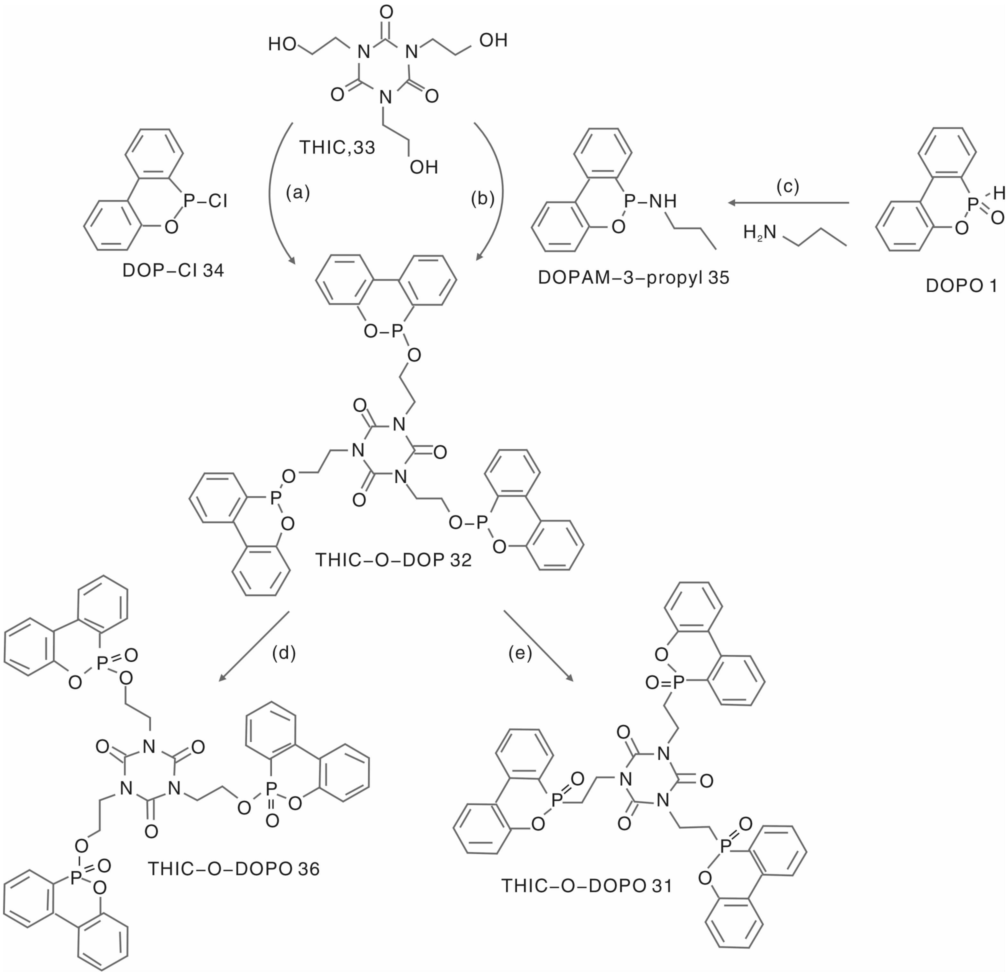


Fig. 22 Synthesis of DOPO-THIC based flame retardants THIC-O-DOPO 36 and THIC-DOPO 31 starting with THIC 33. To obtain these compounds the following reactions were performed: (a) nucleophilic substitution of THIC 33 with DOP-Cl 34, (b) conversion of THIC 33 with DOPAM-3-propyl 35, (c) reaction of DOPO 1 with n-propylamine, (d) oxidation of THIC-O-DOP 32 with tert-butyl hydroperoxide, and (e) Arbuzov reaction of THIC-O-DOP 32 catalyzed by p-toluenesulfonic acid methylester[71]

Table 5 Results of UL 94 tests of THIC based flame retardants 31 and 37 in DEN 438[71]

Epoxy resin	Flame retardant	UL 94 (4.0 mm)	P content, w/%	T_g /℃
DEN 438-EK/DICY/ Fenuron	none	n. c.	0	182
DEN 438-EK/DICY/ Fenuron	THIC-DOPO 31	V0	1.0	169
DEN 438-EK/DICY/ Fenuron	THIC$_n$-DOPO 37	V0	1.3	178

Note: T_g measured by Differential Scanning Calorimetry (DSC)

Zang et al. [71] also reported the synthesis of a corresponding oligomer THIC$_n$-DOPO 37, which was first prepared by Just et al. [72]. To achieve 37, THIC$_n$ 38 was treated with DOPAM-3-propyl 35, followed by an Arbuzov reaction. THIC$_n$ 38 was obtained from the polycondensation reaction of THIC 32 (Figure 23). The oligomeric compound 37 exhibited after incorporation in epoxy resins similar flame retardant behaviors to 37, but the glass transition temperatures of the epoxy resins were higher, see Table 5.

A commercially available polymeric flame retardant with DOPO in the side-chain is 40 also known as Ukanol-FR80. In an analogue Michael Addition DOPO 1 and itaconic acid (ICA, 41) were converted into the addition product ICA-DOPO 42, which was first synthesized by Endo et al. [74] in 1975. In 2009, Glauner et al. [73] published a method where the DOPO containing acid 39 was treated with ethylene glycol to obtain the monomer 43. In a polycondensation reaction 43 was transformed into the final product 40 (Figure 24). First, 40 was applied as flame retardant for polyamide fibers especially polyamide 6 (PA6) and polyester fibers especially polyethylene terephthalate (PET). Later on, Wermter et al. [75] reported the application as flame retardants for poly-butylene terephthalate (PBT), glass fiber reinforced PA6 and thermoplastic copolyester elastomer (TPE-E).

An interesting approach to get a monomer with high phosphorus content was published by Müller et al[76]. in 2004. The addition of two equivalents of DOPO with acetylenedicarboxylic acid 44 to 45 in the presence of aluminium triisopropylate or mercury (II) sulfate as catalyst gave 45. Afterwards, the authors synthesized a monomer 46, prepared from the acid 45 and ethylene glycol. The monomer 46 was used for the copolymerization with the diglycol ester of terephthalic acid 47 (Figure 25). In the copolymer the DOPO moieties are directly connected to the polymer backbone. However, the authors did not mention any test results concerning flame retardancy.

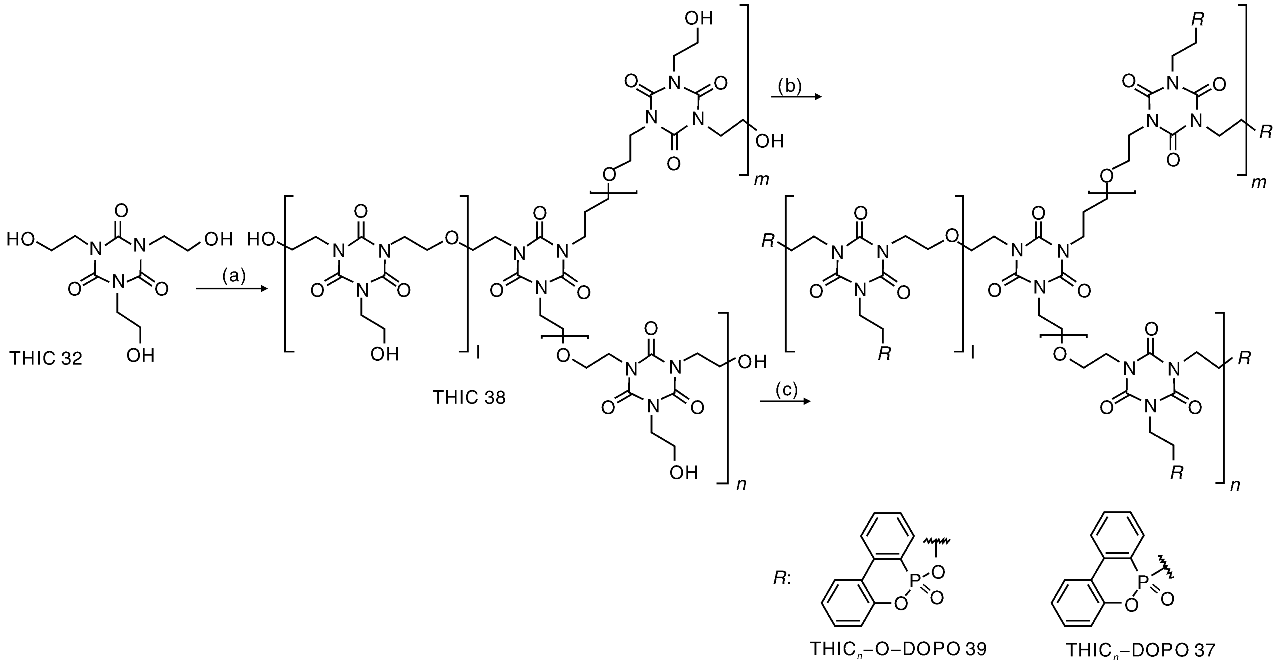


Fig. 23 Synthesis of the oligomeric flame retardants THIC$_n$-O-DOPO 39 and THIC$_n$-DOPO 37 with THIC 32 as starting material: (a) THIC 32 was transformed by polycondensation to THIC$_n$ 38, which acts as precursor for both oligomers 37 and 39. (b) The polycondensate 38 was converted into THIC$_n$-O-DOPO 39 by Atherton-Todd reaction. (c) The precursor 38 was treated with DOPAM-3-propyl 35 followed by an Arbuzov reaction to obtain THIC$_n$-DOPO 37[71]

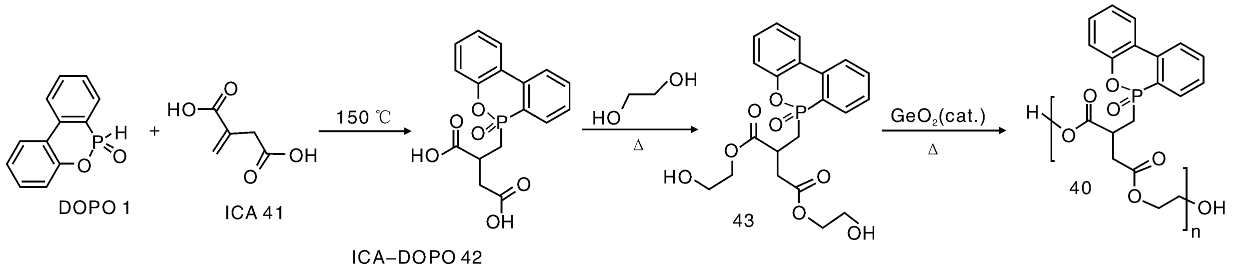


Fig. 24 Synthesis of the commercially available DOPO containing polymer Ukanol-FR80 40. In an analogue Michael Addition DOPO 1 and itaconic acid 41 were converted into ICA-DOPO 42, followed by a condensation reaction with ethylene glycol to obtain 43. The monomer 43 was polymerized to the final product 40[73-74]

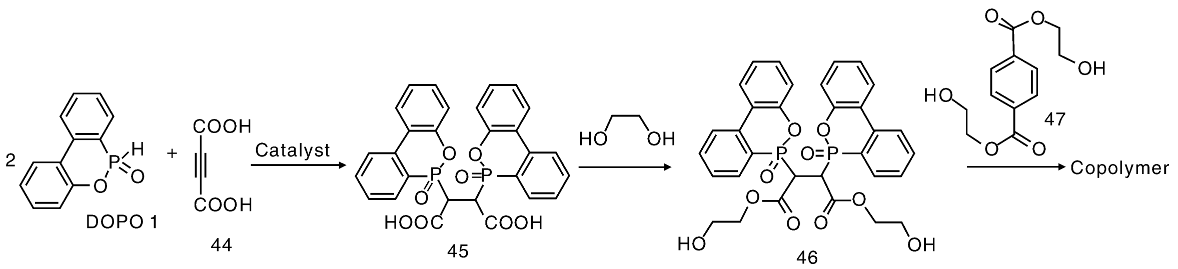


Fig. 25 Synthesis of the acid 45 prepared from DOPO 1 an acetylenedicarboxylic acid 44 by addition reaction. The acid 45 was treated with ethylene glycol to get the corresponding monomers 46, which were copolymerized with bis (2-hydroxyethyl) terephthalate 47 in the presence of a catalyst[76]

In a study by Brehme et al.[77], the fire behaviors and mechanical properties of a blend of polybutylene terephthalate (PBT) with a DOPO containing polyester 48 were determined and compared to corresponding PBT/aluminium diethyl-phosphinate composites. The flame retardant 48 was first synthesized by Pospiech et al. [78] from the polycondensation reaction of the diglycole ether of DOPO-HQ 49 and dimethylterephthalate 50, according to Figure 26. The PBT/48 blend reached the UL 94 V2 classification with a phosphorus content of 1.5 % (flame retardant content: 26 %) and did not show a negative effect on the tensile strength.

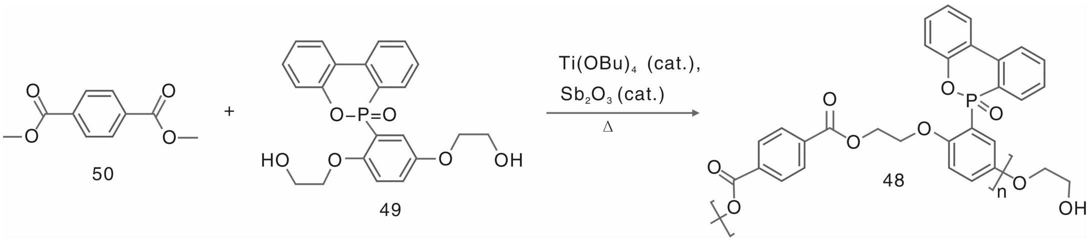


Fig. 26 Synthesis of the DOPO containing polyester 48 prepared from the polycondensation reaction of 49 and 50 in the presence of a catalyst[77-78]

The reaction, reported by Chang et al. [79], of DOPO-HQ 2 with phenylphosphonic dichloride 51 gave a polymer 52 with a high phosphorus content of 13.8 % (Figure 27). In this case the phosphorus containing units are in the polymer chain as well as in the side chain. The authors studied also the flame retardant effect of 52 in different polymer systems by UL 94 tests and determined the LOI values. In Table 6, the results of these tests are shown and indicate excellent flame retardancy for PET, epoxy resin and unsaturated polyester.

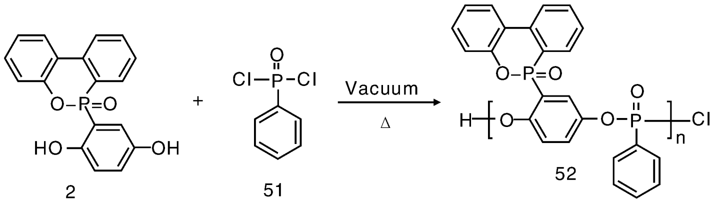


Fig. 27 Synthesis of a polymeric flame retardant 52 with a high phosphorus content, prepared from DOPO-HQ 2 and the dichloride 51 via a polycondensation reaction[79]

Table 6 Table 6. Results of UL 94 tests and LOI values of the polymeric flame retardant 52 in different polymer systems[79]

Polymer system	Flame retardant	P content, w/%	UL 94 (3.2 mm)	LOI
PET	none	0	–	21.6
PET	Polymer 52	0.77	V0	32.4
ER, glycerol epoxy resin/polyamide 651	Polymer 52	0	–	20.4
ER, glycerol epoxy resin/polyamide 651	Polymer 52	0.70	V0	32.6
Unsaturated polyester (USPE, 191)/styrene/BPO	Polymer 52	0	–	20.8
Unsaturated polyester (USPE, 191)/styrene/BPO	Polymer 52	0.28	V0	28.6

Bauer[80] published a synthesis of a DOPO-based methacrylate monomer 53, prepared from 12 and methacryloyl chloride 54 in the presence of a base (Figure 28). Afterwards the monomer 53 was copolymerized with methacrylate 55 to obtain a polyacrylate that passed the UL 94 HB test in contrast to the pure polymethacrylate.

With this last discussed example, the section of P-C derivatives of DOPO is completed. The next presented examples are DOPO derivatives where the P-H group was formally converted into a P-O group.

Wagner et al. [81] reported a synthesis of a DOPO resorcinol derivative 56, prepared via an Atherton-Todd reaction[82], which is a multi-purpose tool to obtain organophosphorus derivatives from amines and alcohols[83], of resorcinol 57 and 1, according to Figure 29. Ratotomalala et al. [55] pointed out that 56 is an effective flame retardant in novolac based epoxy resin with a low influence on the glass transition temperature, see Table 7.

Table 7 Results of UL 94 tests of the flame retardants 56, 58 and 60 in DEN 438[55,84]

Epoxy resin	Flame retardant	UL 94 (4.0 mm)	P content, w/%	T_g /℃
DEN 438/DICY/ Fenuron	none	n. c.	0	182
DEN 438/DICY/ Fenuron	56	V0	1.6	175
DEN 438/DICY/ Fenuron	60	V0	1.0	164
DEN 438/DICY/ Fenuron	58	V2	1.2a)	182

Note: (a) Higher phosphorus loadings could not be achieved due to limited solubility of the additive 58 in the resin;[84] T_g measured by Differential Scanning Calorimetry (DSC)

In 2008, Ciesielski et al. [84] published a synthetic route to a DOPO functionalized bisphenol A derivative 58. They treated bisphenol A 59 with DOPAM-3-propyl 35 to receive a trivalent compound 60. The followed oxidation of 60 with hydrogen peroxide gave the desired product 58 (Figure 30). Additionally, the two phosphorylated products 60 and 58 were incorporated into DEN 438/DICY and UL 94 tests of the obtained composites were performed. The trivalent additive

60 reached UL 94 V0 with a phosphorus content of 1.0 %, whereas the pentavalent species 58 achieved a V2 classification with a phosphorus loading of 1.2 %, see table 7. The result, that a trivalent compound has a higher flame retardancy effect than a pentavalent one, was also supported by other examples given in the study by the authors.

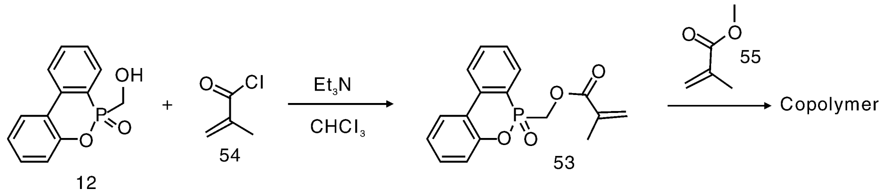


Fig. 28 Synthesis of the DOPO compound 53, prepared from the alcohol 12 and methacryloyl chloride 54. Afterwards, the monomer 53 was copolymerized with methyl methacrylate 55[80]

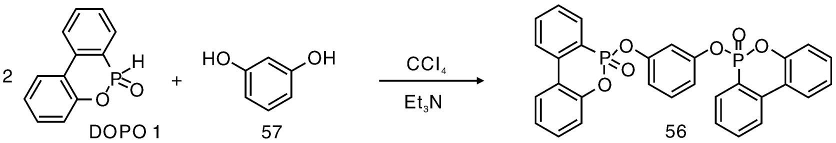


Fig. 29 Synthesis of the DOPO derivative 56 by Atherton-Todd reaction of resorcinol 57 and DOPO 1[81]

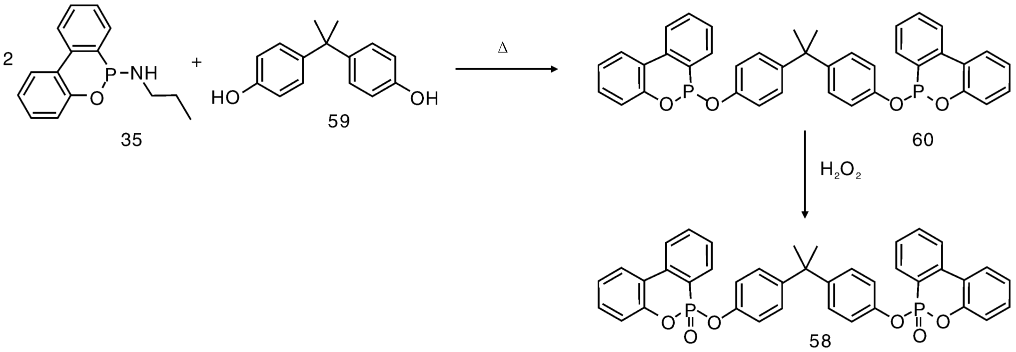


Fig. 30 Synthesis of a DOPO compound 58, prepared by the oxidation of the corresponding trivalent species 60 that was obtained by treatment of bisphenol A 59 with two equivalents of 35[84]

Above an approach of Zang et al.[71] concerning THIC based DOPO derivatives with P-C bonds has been discussed in detail. The authors also synthesized a compound, where the DOPO moieties are connected via a P-O bond to the THIC core using a similar synthetic route (Figure 22). To obtain THIC-O-DOPO 36, the corresponding trivalent derivative 32 was oxidized with *tert*-butyl hydroperoxide, according to Figure 22. Furthermore, the oligomer 39 was prepared from the polycondensate 38 and DOPO 1 via Atherton-Todd reaction (Figure 23). The molecular compound 36 and the oligomeric compound 39 were blended into a novolac epoxy resin and UL 94 tests of the composites were performed. Both reached the V0 classification with a phosphorus content of 1.5 % and 1.7 %, respectively, see Table 8.

The oligomer 39 was also blended with melamine polyphosphate (MMP) as synergist (12 % 39 and 8 % MMP) into glass fiber reinforced polyamide 66 (PA66) (glass fiber content 30 %) and reached the UL V0 classification[64]

Above several P-C and P-O DOPO derivatives were presented. The next discussed examples are P-N derivatives of DOPO 1.

Table 8 Results of UL 94 tests of THIC based flame retardants 33 and 36[71].

Polymer system	Flame retardant	UL 94	P content, w/%	T_g /℃
DEN 438/DICY/ Fenuron	none	n. c.	0	182
DEN 438/DICY/ Fenuron	THIC-DOPO 36	V0	1.5	176
DEN 438/DICY/ Fenuron	THICn-DOPO 39	V0	1.7	179

Note: T_g measured by DSC

The synthesis of a phosphorylated diaminodiphenylmethane derivative 61, prepared from DDM and DOPAL-3-prolyl 35, was published by Cieslielski et al. (Figure 31)[84].

The trivalent compound 61 was incorporated into DEN 438, cured with DICY and reached the UL V0 classification with a phosphorus content of 0.84 %. The T_g of the modified epoxy resin was insignificantly lower than the one of the unmodified DEN 438 (180 ℃ vs. 182 ℃).

In 2012, Dumitrascu et al.[85] published a synthesis of a polymeric derivative 62 via the radical polymerization reaction of the monomer 63 with AIBN as radical initiator (Figure 32). The precursor 63 was prepared by the Atherton-Todd reaction of 1 and vinylanilin 64. The homopolymer 62 has a high thermal degradation temperature of 416 ℃. However, the authors have not performed any tests concerning flame retardancy.

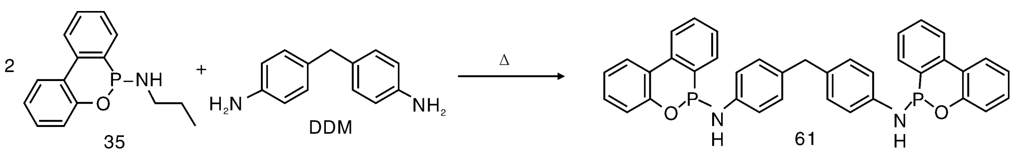


Fig. 31 Synthesis of the DOPO derivative 61, prepared from DOPO-3-propyl 35 and DDM[84]

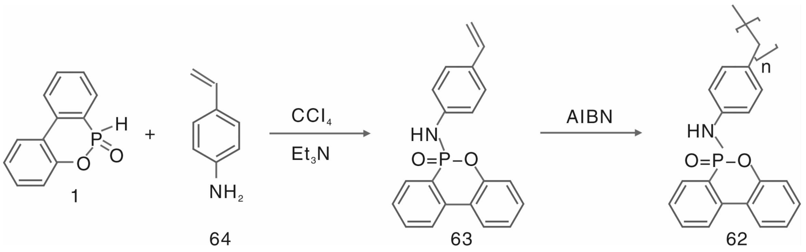


Fig. 32 Synthesis of a DOPO containing homopolymer 62, prepared from the radical polymerization of 63 with AIBN as radical initiator. 63 was obtained by Atherton-Todd reaction of DOPO 1 and 64[85]

5 Conclusion

Since the development of DOPO as an effective organophosphorus, halogen-free flame retardant, that releases less corrosive and toxic gases during combustion compared to halogen-containing flame retardants, a large number of reactive and non-reactive DOPO derivatives have been invented in academia and industry. For instance, DOPO-based amine- and anhydride-like hardeners as well as epoxy resins, which do not affect or in some cases even increase the material properties of the resulting composites such as the glass transition temperature, were synthesized and investigated. Furthermore, DOPO additives, which have an excellent compatibility to a number of polymers like epoxy resins, polyurethanes and engineering plastics (PA, PBT, PET), could be prepared. As a beneficial result of this tendency, various synthetic methods are now available to create "tailor made" DOPO based flame retardants to substitute the halogenated ones in the future.

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