

Synthesis of DOPO-Based Phosphonamidates and their Thermal Properties

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S Supporting Information

ABSTRACT: Synthetic strategies for the preparation of 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives are of special interest for polymer industry as well as academia involved in development of halogen-free flame retardant additives. In this work, various amino-DOPO derivatives (phosphonamidates) were synthesized by employing three different synthetic methods involving various chlorinating agents. The synthetic methods were compared with regards to purity and yield of the resulting amino-DOPO derivatives. The chlorinating agents that were used in this work are namely CCl₄, trichloroisocyanuric acid and sulfuryl chloride. Some compounds, e.g., amine substituted DOPO derivative, could be synthesized using sulfuryl chloride with a yield >94% and a purity >99%. As proof of possible future industrial scale-up, up-scaling laboratory trials at the 500 g scale were also performed for two methods. The synthesized compounds were characterized for their melting point and thermal stability by using thermogravimetric analysis and direct probe insertion mass spectrometry. In general, these amino-DOPO derivatives exhibited high thermal stability with some having stability >320 °C.

1. INTRODUCTION

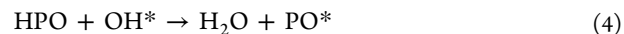
Organophosphorus compounds are ubiquitous and valuable building blocks and additives for application in miscellaneous fields in chemical industry as well as academia.¹ In academic research, they are used in organic synthesis in coordination chemistry, catalysis and biochemistry and they are also commonly used in several commercial applications such as pesticides, electrolytes or additives in polymers as lubricants or antioxidants.² because more and more halogenated flame retardants have been suspected to cause health problems³ and to be ecologically harmful⁴ and bio-accumulative⁵ the development of new organophosphorus compounds as their replacement is becoming popular and there is an immense interest of researchers as well as industry in their novel derivatives. Organophosphorus compounds can be either applied as a finishing additive⁶ or added to the polymer during its polymerization process or it is further processing.⁷ A variety of polymers, such as polyester or polyamide are processed by melt extrusion at elevated temperatures >250 °C. Therefore, flame retardant additives for such kind of polymers need to be thermally stable and unreactive at elevated processing temperatures for considerable duration of time. Furthermore it is also desirable that the melting points of such additives should also be in a similar temperature range so as to ensure good dispersion and avoid rheological problems. Among the various classes of organophosphorus flame retardant compounds, 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have attracted a lot of attention recently due to its gas-phase flame inhibition mechanism.^{2e,8} It is proposed that this gas-phase flame inhibition mechanism is similar to that of halogenated flame retardants.

A phosphorus-based flame retardant releases small low-energy radicals, such as PO*, in the gas-phase during its

decomposition.⁹ These low energy radicals can react with high energy radicals such as hydroxyl or hydrogen radicals from the decomposing polymer, as shown in eqs 1 and 2.



A subsequent reaction of HPO with H* and OH* radicals leads to a regeneration of the active PO* species. Thus, the flame retardant action of PO*, which leads to a lower release of energy/heat and subsequently a cooling down and extinguishing of the flame, can be considered as catalytic effect (eqs 3 and 4).



In addition to its good gas-phase flame inhibition effect, preliminary toxicological and ecological studies reveal that DOPO exhibits very low toxicity, which was determined by toxicity tests toward the water flea *Daphnia magna* according to OECD guideline 202.¹⁰ Thus, DOPO and its derivatives are considered as efficient and eco-friendly alternatives or replacements for toxic halogenated flame retardant additives.

In our earlier studies, we have reported that P–N bonded organophosphorus molecules such as phosphoramidate compounds show a remarkably higher flame retardant efficiency in flexible polyurethane foam matrices as compared to P–O

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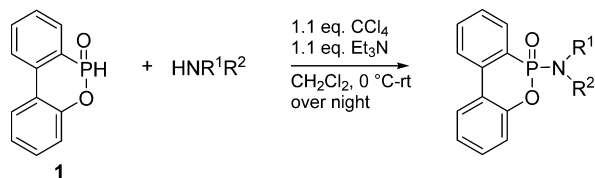
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bonded phosphate analogues.¹¹ In continuation to this preliminary work, we have further designed novel P–N bonded structures based on DOPO.^{8b} The conversion of the P–H bond of DOPO to a P–N bond leads to the desired phosphonamidate derivatives. In literature, one can find syntheses of such phosphonamidate molecules from DOPO via two common synthetic ways.

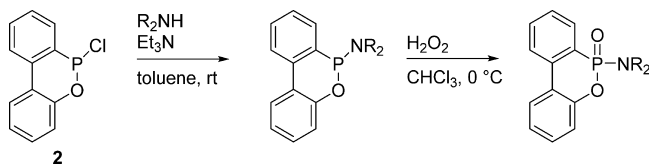
The first way involves a simple one step Atherton–Todd reaction (ATR) using CCl_4 as a chlorinating agent (Scheme 1).¹²

Scheme 1. General Scheme for Atherton–Todd Reaction for Preparation of Phosphonamidates



It is reported, for a few examples in literature, that this reaction results in the formation of DOPO-based phosphonamidates in good to excellent yields up to 87% without any additional difficult or time-consuming purification steps.^{8c–f} The major drawback of this method is the use of CCl_4 , which is relatively expensive and more importantly, it is carcinogenic and harmful to the environment. Its use as solvent and reagent in industrial chemical production is especially not attractive in Europe. Thus, a suitable replacement for CCl_4 as a chlorination agent for the conversion of a P–H bond to an intermediate P–Cl bond is desirable. The second common way of synthesizing such phosphonamidates is via a two-step reaction sequence starting from trivalent DOP–Cl 2 with subsequent H_2O_2 oxidation (Scheme 2).¹³

Scheme 2. Two-Step Reaction Procedure Involving H_2O_2 as Oxidizing Agent



Although this method avoids the use of CCl_4 , it creates other synthetic challenges such as hydrolysis or trans-esterification reactions when using H_2O_2 as an oxidizing agent.¹⁴ Furthermore, the chemical functional group tolerance is limited due to the use of a strong oxidizing agent and a multistep synthetic procedure is usually complex and results are not always reproducible.

In this work, we have evaluated two different alternative synthetic methods other than ATR for the preparation of DOPO-based phosphonamidates. We have screened two alternative chlorinating agents and compared the synthesis results (the yield and the purity of the resulting compounds) with the CCl_4 method, (Scheme 3).

The two alternative chlorinating agents used in this work are namely trichloroisocyanuric acid (TCCA) and sulfuryl chloride. Trichloroisocyanuric acid is a cheap and relatively environmentally friendly chlorinating agent. Cyanuric acid, which is the byproduct formed during the chlorination of P–H bond, can be easily isolated and recycled by rechlorination. Furthermore it is also atom economic because only 1/3rd equiv is needed for chlorination for one equivalent of P–H moiety. From a sustainable point of view, TCCA would be a very desirable chlorinating agent. The use of TCCA as an efficient and fast chlorinating agent for phosphites has been described earlier in the literature.¹⁵ Its application on phosphinites or, more specifically, on DOPO has not been reported or investigated so far. Scientific reports on using sulfuryl chloride as a chlorinating agent for phosphites are also rare.¹⁶ Furthermore, there is no report of such reactions in scales bigger than a few millimoles. The advantage of using sulfuryl chloride as a chlorinating agent would be that the only byproducts SO_2 and HCl formed during the reaction are gaseous and can thus be removed easily from the reaction mixture and trapped as salts in alkaline media. For both chlorinating agents, the intermediate DOPO–Cl (3), can either be isolated or reacted in situ with an appropriate amine to obtain the desired phosphonamidate compound. In this work, we have followed the in situ route without any isolation of DOPO–Cl (3) and further reaction with seven different amines. The choice of amines was driven by the idea to show that a certain number of chemical functionalities, such as additional ester, ether or amino groups and C–C double bonds are compatible with the reaction conditions. Furthermore, we wanted to show that it is possible to create DOPO derivatives that exhibit a wide range of thermal stabilities, melting point, and gas-phase availability, which is important for the application as flame retardant additive in different polymeric. Up-scaling laboratory trials at the 500 g scale further proves the suitability of such synthetic methods for industrial production of DOPO derivatives.

2. EXPERIMENTAL SECTION

2.1. Materials. Benzylamine, ethylenediamine, allylamine, *n*-propylamine, 2-methoxyethylamine, glycinemethylester hydrochloride, piperazine, triethylamine, methylene chloride, carbon tetrachloride, acetonitrile, sulfuryl chloride, and trichloroisocyanuric acid were purchased from Sigma Aldrich, Switzerland. All reagents and chemicals were used without further purification. DOPO was provided by Krems Chemie

Scheme 3. General Reaction Scheme for the Preparation of Phosphonamidates Using Three Different Chlorinating Agents

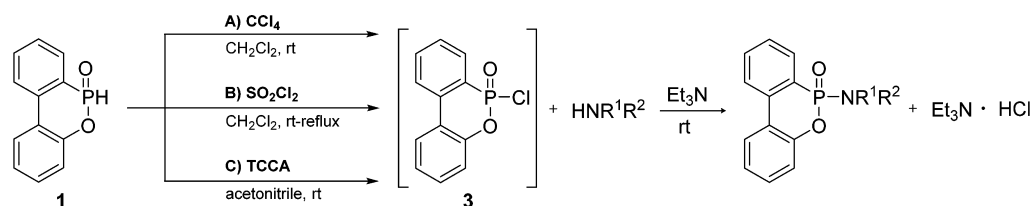


Table 1. Reaction Yield of Various Phosphonamidates

| Entry | Nu = | Product ^a | (A) CCl ₄ ^b | (B) SO ₂ Cl ₂ ^c | (C) TCCA ^d |
|-------|------|-----------------------|-----------------------------------|--|-----------------------|
| 1 | | PA-DOPO 4 | 89 | 89 | 83 |
| 2 | | AA-DOPO 5 | 88 | 88 | 61 |
| 3 | | BA-DOPO 6 | 89 | 94 | 90 |
| 4 | | MeO-DOPO 7 | 81 | 81 | 91 |
| 5 | | Gly-DOPO 8 | 30 | 84 | 59 |
| 6 | | PIP-DOPO 9 | 85 | 83 | 56 |
| 7 | | EDA-DOPO 10 | 84 | 85 | 74 |

^aFive grams of DOPO was used as reactant for each reaction; 1.1 equiv of Et₃N was used as base; (b) CH₂Cl₂ was used as solvent, 1.1 equiv of CCl₄ was used; (c) CH₂Cl₂ was used as solvent, 1.005 equiv of SO₂Cl₂ was used; (d) acetonitrile was used as solvent, 0.34 equiv of TCCA was used.

Chemical Services AG (KCCS) with a purity >97% and was used as received.

2.2. Characterization. All compounds were analyzed by gas chromatography/mass spectroscopy (GC/MS) and ¹H, ¹³C, and ³¹P NMR to ensure the purity and confirm their structure. For GC/MS analyses, a gas chromatograph coupled with mass spectrometer was used (Agilent GC6890/MS 5973). Helium was used as the carrier gas. Aliquots (1 μL) from the crimp-sealed vials were injected by use of an automated sampler. The split/splitless injection inlet was maintained at 250 °C, and samples were separated on a 30 m capillary column coated with a 0.25 μm film of (5% phenyl)methylpolysiloxane. A 10:1 split ratio was used. The temperature program consisted of an isothermal separation at 280 °C for 30 min. The NMR analyses were performed on a Bruker NMR machine. The ¹H NMR analyses were measured with a frequency of 400 MHz, while the ³¹P NMR and ¹³C NMR measurements were run at a frequency of 162 and 100 MHz, respectively. Infrared spectra were recorded on a Bio-Rad FTS-175 IR spectrometer.

The thermal stability of the DOPO-derivatives was studied using a NETZSCH TG 209 F1 instrument and a 2–5 mg sample in a nitrogen environment (50 mL/min) at a heating rate of 10 K/min from 50 to 800 °C. Three measurements were conducted for each sample system to ensure the reproducibility of the results. The presented curves are averages curve of three measurements.

Direct insertion probe mass spectrometry (DIP-MS): DIP-MS was used to evaluate the gas-phase availability and the degradation processes of these DOPO-derivatives. The sample was introduced into a quartz microcup in contact with a heating probe, the tip of which was inserted into the ionization chamber maintained at strongly reduced pressure. In this study, DIP-MS analyses were conducted for a 1–2 μgm sample of FPUF using a ThermoQuest FINNIGAN apparatus. The probe

was heated from 50 to 450 °C at a rate of 50 K/min. The final temperature was maintained for one more minute. The pressure was 10^{−6} mbar.

2.3. Experimental Procedures for Small-Scale (5 g) Reactions. Small-scale reactions using the CCl₄ method (A) were run under similar conditions as already described in literature.^{15,16} Small-scale reaction conditions for methods B and C are based on reported methods but were finally performed with major modifications. Detailed reaction procedures can be found in the Supporting Information.

2.4. Experimental Procedures for Synthesis of EDA-DOPO (10) at 500 g Scale. CCl₄ Method. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (**1**) (500 g, 2.31 mol), triethylamine (353 mL, 2.54 mol), and ethylene diamine (73.5 mL, 1.1 mol) are dissolved in 2 L of dichloromethane, stirred, and cooled to 0 °C. After the solution has been cooled down, carbon tetrachloride (246 mL, 2.54 mol) is added dropwise at a rate that the reaction temperature does not exceed 15 °C. After all CCl₄ has been added, the solution is allowed to warm up to room temperature and stirring is continued overnight. The desired product precipitates from the solution together with triethylamine hydrochloride as a white solid. Subsequently, the reaction mixture is filtered and all solid material is collected. The precipitate is washed with water (3 × 1 L) to remove triethylamine hydrochloride from the mixture. The resulting white solid is washed twice with acetone (500 mL each) and then dried in vacuum at 50 °C until no more water and acetone is left. Finally, the pure product (**10**) is isolated as a 1:1 mixture of diastereomers with a yield of 85% (457 g, 0.93 mol).

SO₂Cl₂ Method. A 3 L three-neck-flask equipped with a reflux condenser, dropping funnel, and gas washing bottle (filled with sodium hydroxide solution) is filled with a solution of 500 g (2.31 mol) of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (**1**) in 1.5 L of CH₂Cl₂ under a

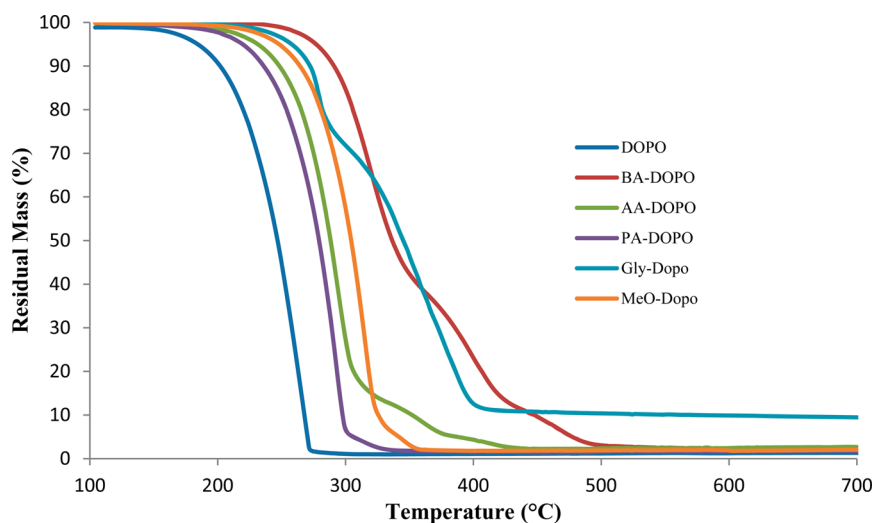


Figure 1. Thermogravimetric Analysis (TGA) curves of mono-DOPO derivatives 4–8 in comparison with DOPO 1.

nitrogen atmosphere. The mixture is kept at room temperature with an external water bath cooling while sulfonyl chloride (187.5 mL, 2.32 mol) is added dropwise. An immediate gas evolution of HCl and SO₂ can be observed. After complete addition (~3 h), the reaction mixture is heated to reflux until no more gas evolution can be observed (about 3–4 h). Afterward, the reaction mixture is cooled to room temperature and a solution of ethylene diamine (73.5 mL, 1.1 mol) together with triethylamine (353 mL, 2.54 mol) in 500 mL of CH₂Cl₂ is added dropwise at a rate that the reaction temperature of the reaction mixture does not exceed 30 °C. Subsequently, the reaction mixture is stirred overnight at room temperature. The white precipitate that contains triethylamine hydrochloride as well as EDA-DOPO (**10**) is separated by filtration. The filtercake is washed several times with deionized water (3 × 1 L) to remove triethylamine hydrochloride and two times with 500 mL of acetone. The resulting solid is dried in vacuum to give 445 g (0.91 mol, 83%) EDA-DOPO (**10**) as a 1:1 mixture of diastereomers in sufficient purity.

Analytical Data for EDA-DOPO (10**).** m.p.: 272 °C. ¹H NMR (DMSO-*d*₆) δ (ppm): 8.13–8.22 (m, 4H), 7.72–7.86 (m, 4H), 7.56 (m, 2H), 7.40–7.49 (m, 2H), 7.32 (q, *J* = 6.5 Hz, 2H), 7.20 (m, 2H), 5.79 (m, 2H), 2.91 (bs, 4H). ¹³C NMR (DMSO-*d*₆) δ (ppm): 149.4 (d, *J* = 7.3 Hz), 149.3 (d, *J* = 7.1 Hz), 136.0, 135.9, 132.7, 130.3, 129.5 (d, *J* = 3.6 Hz), 129.3 (d, *J* = 3.6 Hz), 128.4 (d, *J* = 2.2 Hz), 128.3 (d, *J* = 2.5 Hz), 125.4 (d, *J* = 1.6 Hz), 125.2 (d, *J* = 162 Hz), 124.3, 124.1 (d, *J* = 3.5 Hz), 124.0 (d, *J* = 3.5 Hz), 122.0, 121.8, 120.1 (d, *J* = 5.4 Hz), 120.0 (d, *J* = 5.0 Hz), 41.8, 41.7. ³¹P NMR (DMSO-*d*₆) δ (ppm): 15.7, 15.6. IR (ATR) ν (cm^{−1}): 3159 (m), 2877 (w), 1598 (w), 1476 (m), 1446 (m), 1196 (s), 1146 (m), 1116 (s), 922 (s), 747 (s), 711 (m). MS (ESI) *m/z* (%): 488 (100). HR-MS (ESI-TOF) calcd for [M + 1] C₂₆H₂₃N₂O₄P₂ *m/z*, 489.1128; found, 489.1129

3. RESULTS AND DISCUSSION

3.1. Comparison of Different Chlorinating Agents.

Seven different DOPO-based phosphonamidates were synthesized using three different chlorinating agents for the conversion of the P–H bond of DOPO into an intermediate P–Cl bond and subsequent reaction of the DOPO-Cl 3 derivative with respective amines. It can be seen from Table 1

that the appropriate amino-DOPO derivatives 4–10 could be synthesized in moderate to excellent yields depending on the chosen method and amines. In general, method B provided the highest yields consistently whereas methods A and C are not efficient for all compounds. Using amines like benzylamine or propylamine bearing no additional functional group, all methods provide good to excellent yields up to 94% (Figure 1, entry 3, method B).

In the case of glycine methylester, entry 5, product **8** was isolated in moderate yields of 30% and 59%, respectively, using method A and C. In contrast, method B was more efficient and led to a yield of 84% of **8**. Moreover the yields of **5**, **9**, and **10** were only moderate to good when method C was used. Lower yields for method C could be explained by a possible unfavorable interaction of cyanuric acid with the corresponding amine such as complex formation and subsequent precipitation. The reason for these lower yields was not investigated in more detail. Furthermore, the chlorination reaction of DOPO with TCCA is quite exothermic even at a small scale and thus, for this method, no reactions larger than 5 g was performed. The two bis-DOPO compounds **9** and **10** could be isolated in very good yields between 83 and 85% when method A or B was applied.

The preparation of DOPO-based phosphonamidates using CCl₄ has been described earlier for few compounds in lab scale experiments. However, to the best of our knowledge, no synthesis on a scale of >1 mol, with regard to DOPO, has been reported so far. As described earlier in the section 2, EDA-DOPO was prepared at the 500 g scale (based on DOPO weight). It is observed that both methods A and B work comparably well and provide the desired final product in a yield of 85% for method A and 83% for method B. Due to a precipitation of the product from the reaction mixture, the work up and isolation of the desired compounds is quite easy and efficient. These results indicate that both methods could be appropriate for up-scaling of such phosphonamidate compounds. As CCl₄ is toxic and a proven carcinogen and its use is restricted in many countries, SO₂Cl₂ seems to be an efficient and attractive alternative reagent for the preparation of phosphonamidate compounds from phosphinites.

3.2. Thermal Stability. All synthesized amino-DOPO derivatives were analyzed for their thermal stability using TGA. The TGA data could be useful in determining the

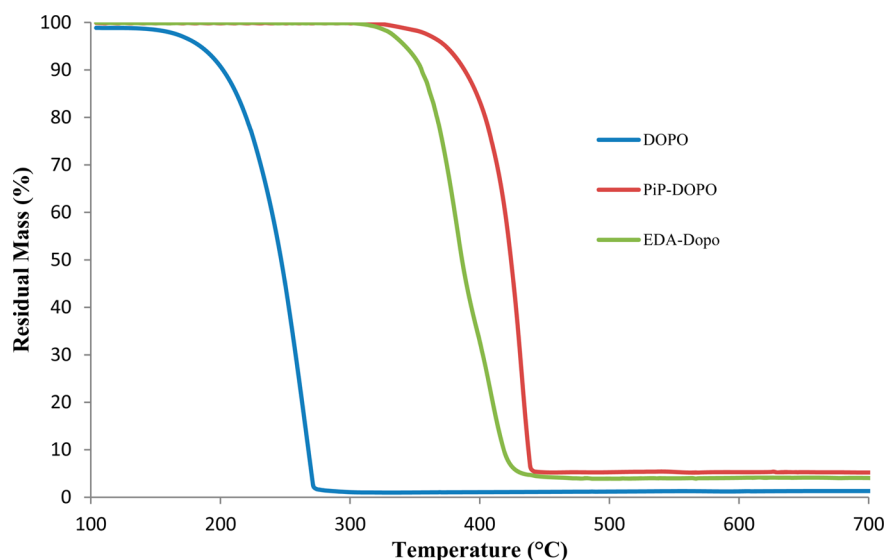


Figure 2. TGA curves of bis-DOPO derivatives **9** and **10** in comparison with DOPO (**1**).

suitability or possible further application of such compounds as flame retardant additive in different polymeric systems.

The TGA thermograms of mono-DOPO derivatives **4–8** and unmodified DOPO are shown in Figure 1. It can be seen that the DOPO derivatives exhibit a significantly higher thermal stability as compared to DOPO itself. The onset of decomposition of DOPO starts at 237 °C whereas its derivatives **4–8** are stable at this temperature. Thus, by suitable choice of amine one can develop DOPO derivatives, which are thermally more stable and suitable for different polymers. BA-DOPO (**6**) has the highest thermal stability among the investigated mono-DOPO derivatives. This higher thermal stability might be explained by a beneficial π – π interaction of the aromatic systems of DOPO and the additional benzyl group, which could lead to a formation of more stable and less volatile conformers. The onset temperature of its decomposition was determined to be at 298.9 °C. **7** and **8** exhibit a comparable thermal stability of about 287.2 and 294.5 °C, respectively. **4** and **5** seem to be the least stable of the investigated compounds with onset temperatures of 260 and 261 °C, respectively. Among these mono-DOPO derivatives Gly-DOPO (**8**) is the only compound to leave a significant amount of residue at 700 °C, which is about 9.32%. The thermal decomposition of this compound proceeds via a two-step mechanism. There is a relatively rapid and steep mass loss of about 20% (~220–280 °C) and after that the mass loss rate is significantly reduced until the final residue of 9.32% is reached. This residue and the slower mass loss rate in the second stage (~290–400 °C) could be explained by intermolecular condensation reactions of either the free N–H group or the α -carbon (type of Claisen Condensation) of one molecule with the ester group of another molecule.

The GA data of the two bis-DOPO derivatives (**9** and **10**) are presented in Figure 2. One can see that these compounds are thermally more stable than DOPO and other DOPO compounds **4–8**. The onset of the degradation of EDA-DOPO (**10**) was measured to be 352 °C. PiP-DOPO is even more stable with an onset temperature of 414 °C. A certain amount of residue was also detected for both compounds **9** and **10**, 4.07% and 5.2%, respectively. The high thermal stability of **9** and **10** could be explained by a higher steric demand of these

compounds. The two biphenyl moieties in these compounds can shield and protect the relatively labile P–N bond and thus guarantee a higher thermal stability. To elucidate this hypothesis, we have carried out quantum chemical calculations. Therefore, the geometry was optimized employing the dispersion corrected ω B97xd functional and 6-311g+ basis set as implemented in the Gaussian09 suite of programs.¹⁷ This method is known to predict X-ray structures with relatively small statistical errors for the overall geometry as well as selected bond length.¹⁸ Figure 3 shows the calculated structures

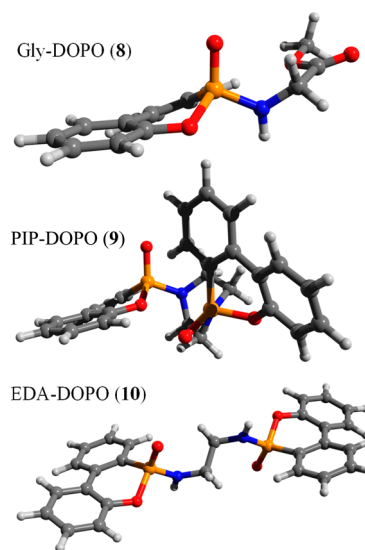


Figure 3. Computed structures of Gly-DOPO (**8**), PiP-DOPO (**9**), and EDA-DOPO (**10**).

of Gly-DOPO (**8**), PiP-DOPO (**9**) and EDA-DOPO (**10**). Only the lowest energy conformers that were found are depicted. It becomes evident that steric shielding of the O=P group is more pronounced in **9** compared to **8** and **10**. The CH₂ group of the piperazine ligand (**9**) efficiently shields the backside of the O=P functional group. This might lead to, for example, a reduced reactivity of the O=P moiety toward nucleophilic attack and thus to a larger stability. However, it

does not explain the increased stability of EDA-DOPO (**10**) compared with Gly-DOPO (**8**). Hence, we attribute this finding to association between neighboring molecules in the solid phase, e.g., intermolecular forces. Both the higher shielding and the better organized structure in the solid phase supports a higher thermal stability. The corresponding melting points, onset temperatures, and residues of all compounds are presented in Table 2.

Table 2. Onset Temperatures and Residual Mass Determined by TGA and Melting Points

| compound | T_{Onset} (°C) | M_{residual} at 700 °C (%) | T_{melting} (°C) |
|----------|-------------------------|-------------------------------------|---------------------------|
| 1 | 237 | 1.4 | 119–121 °C |
| 4 | 260 | 1.8 | 127 °C |
| 5 | 261 | 2.6 | 95 °C |
| 6 | 299 | 2.4 | 156 °C |
| 7 | 287 | 2.1 | 113 °C |
| 8 | 295 | 9.3 | 126 °C |
| 9 | 414 | 5.2 | >300 °C |
| 10 | 352 | 4.1 | 272 °C |

The high thermal stability and melting points of compounds **9** and **10** could indicate that these compounds might be suitable and compatible with the processing conditions of polymers that are processed at elevated temperatures >250 °C such as polyesters or polyamides. It can be additionally seen from Table 2 that the synthesized DOPO derivatives cover a wide range of melting areas. In contrast to the high melting bis-DOPO compounds, the mono compounds melt in a range between 95 and 156 °C. Due to such thermal characteristics, these products could be interesting for application in lower melting polymers such as polyethylene, polypropylene, or polyamide 12.

3.3. DIP-MS measurements. The availability of a flame retardant in the gas-phase is an important criterion, which determines its efficacy and suitability for a polymeric system. It is usually assumed that the flame retardant should decompose and release active species in the gas phase at a temperature that is close to the degradation temperature of the polymer matrix. Thus, DIP-MS measurements were performed on the synthesized DOPO derivatives to evaluate the availability of the phosphorus species in gas phase at different temperatures. The total ion chromatogram of the mono-DOPO derivatives is presented in Figure 4. Measurements with similar conditions on polyether-based polyurethane foams can be found in literature.^{7c}

Like observed in TGA thermograms, DOPO (**1**) decomposes or volatilizes earlier as compared to its derivatives **4**–**8**. It starts to volatilize and decompose at around 2 min, which corresponds to a temperature of about 150 °C. The maximum decomposition rate is at around 2.5 min and, after 3 min, no more DOPO or its decomposition fragments can be detected. Compounds **4** and **5** start to volatilize at around 2.5 min and can be detected over a relatively wide temperature range of about 50 °C. After 4 min, no more **4**, **5**, and their fragments can be detected. It was also noted in the TGA measurements that **7** and **8** volatilize and decompose in a similar temperature range. They can be detected starting from about 2.5 min and the maximum intensity can be observed at 4.1 and 4.2 min, respectively. After 5 min, no more fragments of these compounds can be detected. As expected from the TGA measurements, **6** volatilizes and decomposes later than the other compounds. **6** and its decomposition fragments can be detected from 3.5 until 5.5 min, which corresponds to a temperature range of about 225 to 325 °C.

Both bis-DOPO derivatives **9** and **10** volatilize and degrade at very high temperatures. EDA-DOPO (**10**) and fragments of its decomposition can only be detected later than 7 min (Figure 5), which corresponds to a temperature of more than 350 °C. Only a very small amount of EDA could be detected below this temperature. Significant amounts of EDA-DOPO can be observed between 9 and 10 min (temperature of 450 °C). PIP-DOPO (**9**) is even more stable and less volatile because it cannot be detected in the gas phase before 8.5 min (Figure 5).

Thus, PIP-DOPO (**9**) may be useful for polymers that degrade at higher temperatures such as 400–500 °C. Extracted MS data from TICs of the DOPO derivatives are given in the Supporting Information.

4. CONCLUSION

Seven different DOPO-based phosphonamidates were successfully synthesized in moderate to excellent yields. Three different synthesis methods were used and compared with each other regarding yields of the products and also capability for up-scaling trials. Methods **A** (CCl_4) and **B** (SO_2Cl_2) were, in general, more efficient than method **C** (TCCA) due to higher yields and easier handling of the reaction process. Unlike in the case of the TCCA method, the reaction is not exothermic for CCl_4 and SO_2Cl_2 methods and thus EDA-DOPO (**10**) was prepared at the 500 g scale (>2 mol) in the lab. Such synthetic methods for synthesis of phosphonamidates could be suitable for future scale-up at the industrial level. The thermal stabilities and volatilities (gas phase availability) of the synthesized

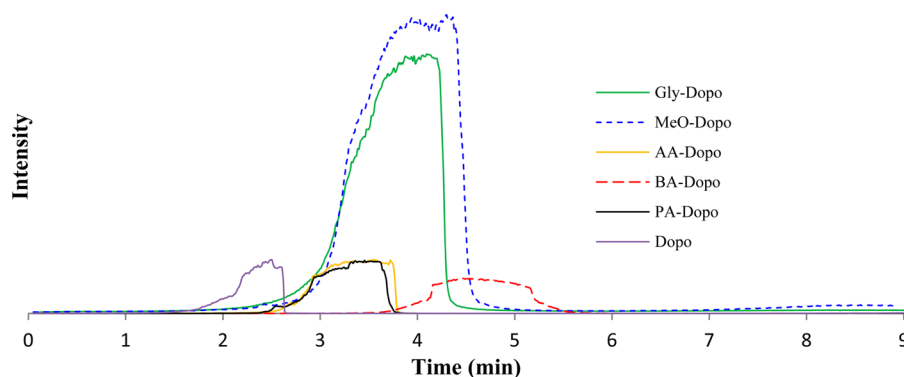


Figure 4. Total ion Chromatogram (TIC) of mono-DOPO derivatives **4**–**8** in comparison with DOPO (**1**).

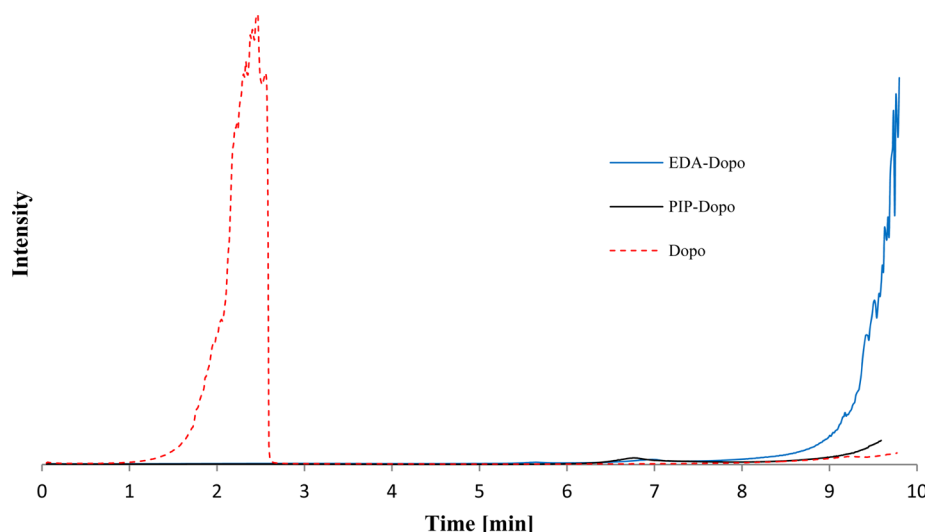


Figure 5. Total ion Chromatogram (TIC) of bis-DOPO derivatives **9** and **10** in comparison with DOPO (**1**).

compounds were investigated by TGA and DIP-MS. All DOPO derivatives were much more thermally stable than unmodified DOPO. Among mono-DOPO derivatives, BA-DOPO (**6**) exhibits the highest thermal stability and is only superseded by bis-DOPO derivatives **9** and **10**. These compounds exhibit a thermal stability greater than $>300\text{ }^{\circ}\text{C}$, which makes them interesting as flame retardant additives for application in for polymer which have high melt processing temperatures ($\sim 250\text{--}300\text{ }^{\circ}\text{C}$)

■ ASSOCIATED CONTENT

Supporting Information

General procedures of all small scale reactions and analytical data including copies of NMR and DIP-MS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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