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Self-extinguishing bio-based polyamides

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A B S T R A C T

The fireproofing study of polyamide 11 (PA11), a bio-based polyamide synthesized from castor oil and marketed under the trade name Rilsan® is presented. As an interesting perspective, FR can be chemically linked to the PA backbone. In this way, we achieved the synthesis of a dicarboxylic acid from DOPO cycle (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). This phosphorus diacid derivative was able to react by polycondensation to give rise of new copolyamides (coPA) bearing phosphorus moieties attached to the PA backbone with 15,000–30,000 g/mol as molar masses. The amount of phosphorus and the viscosity of the final PA were optimized. Thermal properties such as thermogravimetry analysis (TGA) or differential scanning calorimetry (DSC) were evaluated and were shown crystallinity and degradation typical of linear PA11. UL94-V0 ranking coupled with high Oxygen Limit Indexes (LOI = 40) were also obtained. Pyrolysis-combustion flow calorimeter (PCFC) and cone calorimeter were performed to understand the mode-of-action of the new phosphorus-containing FR used to obtain self-extinguishing bio-based PA11. Lastly, the preserving of mechanical properties was highlighted.

Keywords:
Polyamide
Flame retardancy
DOPO
Flame inhibition
Bio-based monomers

1. Introduction

Polyamides (PAs) are important engineering plastics due to excellent performances such as good processability, mechanical strength and abrasion resistance. They are widely used in electronic and transportation, textiles … However, one main limitation of these polymers is their flammability. The addition of flame retardant additives allows improving their properties and uses. Phosphorus-containing compounds [1] are well recognized for their flame retardant properties, and they are increasingly becoming more popular than the halogen ones, as they release non-toxic combustion products. Furthermore, it is recognized that the migration or leaching of flame retardants exposed to high temperature or humid atmosphere may be reduced by moving from the additive to the reactive approach [2,3]. In this latter case, flame retardant species are covalently bonded to the polymer chain that inhibits their mobility within the polymer network and maintains their efficiency over the time.

The application of reactive flame retardants (FRs) involves either the design of new polymers or modification of existing polymers. This approach combined to the use of renewable resources gives environmentally friendly flame retarded polymers. Phosphorus-containing monomers with reactive functions, such as amine or carboxyl are interesting to be used in the polycondensation of PA. Some diacids [4] obtained from the fermentation of glucose and their derivatives exist and may be used as building blocks of these new phosphorus-containing FRs (PFRs).

Derivatives based on 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) are well known as attractive alternative flame retardants for various polymers. DOPO derivatives have found applications in epoxy resins [5–10], PU foams [11], polyesters and also PA[12]. Two DOPO derivatives are commercialized under the name Safire® 3000 and XP-7866® for PA66[13] because of their high thermal stability compared to other phosphorus-containing FRs. DOPO and its derivatives are known to predominantly act by a gas-phase mechanism [11,14–16] through the formation of P-O radicals [17]. Moreover, DOPO is a H-phosphinate compound that can tautomerize to its P-OH [18] form and

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can react with nucleophilic and electrophilic species. The synthesis of reactive monomer with DOPO is easy to achieve to form DOPO diacid FR. Liu et al. [19] used DOPO grafted on maleic anhydride, which reacted with the terminal hydroxyl groups of poly(butylene terephthalate) PBT matrix. An increase of polymer viscosity and good flame-retardant properties were highlighted. Zhang et al. [20] also proposed to use DOPO-MA (maleic anhydride), as a co-monomer in the synthesis of unsaturated polyester resin. Levchik & Weil [21] reported the use of reactive FR with DOPO in various polyesters and many teams [22–26] proposed different ways to obtain DOPO containing-reactive FR for flame retarded epoxy resins. Recently, Li et al. [27] grafted DOPO to SiO_2 particles to increase the thermal resistance of PA6 composites and permit the time-stability of DOPO in the polymer, but it is not clearly a reactive FR for PA. To the best of our knowledge, DOPO diacid derivatives have been reported for the first time in patent literature [28] in 1977, then in 1998 by a german team [29], and more recently some chinese patents [30–33] claimed the use of DOPO diacid derivatives to give flame retardancy properties to PA6 or PA66 by copoly-condensation. This FR reacted with a diamine monomer to form a prepolymer with a terminal amino group then the FR prepolymer was added in a polymeric medium in the presence of a catalyst at high temperature for 6–14 h. No information on the molar masses and no comprehension on flame retardancy mechanism were done.

In this present study, 3-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide-10-yl)]itaconic acid (DOPO-ITA) was synthesized and successfully used to prepare novel PA11/10-10/10-DOPOITA copolyamides with phosphorus-containing pendant groups. The mechanical, thermal and flame retardancy properties were studied and compared to those of Rilsan® [34] were investigated.

2. Experimental part

2.1. Reagents and materials

9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) was purchased from ABCR. Itaconic acid was obtained from Sigma-Aldrich. 11-aminoundecanoic acid (AC11), decane-1,10-diamine (DA10), decan-1,10-oic acid (DC10) and commercial available polyamide 11 commercial grade as reference were provided from Arkema. All the reagents were used without further purification.

Chemical structures of the prepared compounds were determined by ^{31}P NMR and ^{1}H NMR spectroscopies in a Bruker Avance 400 MHz spectrometer at room temperature in $(CD_3)_2CO$ solutions. External references were trimethylsilane (TMS) for ^{1}H NMR and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts are given in ppm. The molar masses of the polyamides were determined by gel permeation chromatography GPC (Waters Alliance 2695 and 2 columns PSS PG 100A and 1000A) that was calibrated with polymethylmethacrylate (PMMA) standard in hexafluoroisopropanol solvent at 40 °C. The potentiometric titration was made on samples in solution with a combined electrode. The viscosity analyses were achieved in meta-cresol solution. To measure the phosphorus ratio after polymerization, a portable X-Ray Fluorescence analyzer XMET 5100 was used. Analysis time was 60 s. The phosphorus content was assessed from the Kα radiation and a phosphonated epoxy resin called IL with a known phosphorus content equal to 1.75 wt% was used as reference.

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at 20 °C/min between −20 and 240 °C to observe the glass transition temperature determined as the inflexion value in the heat capacity jump and the residual curing, the melting and crystallization temperatures, endothermic and exothermic peaks, respectively. Thermogravimetric analyses (TGA) were carried out to determine the weight-loss temperature by heating from room temperature to 750 °C at a rate of 10 °C/min under nitrogen using a TGA Setsys Evolution from Setaram. Flammability was assessed using a Pyrolysis-combustion flow calorimeter from Fire Testing Technology (FTT UK). About 3 mg was placed in the pyrolyzer, undergoing an increase of temperature from 20 °C to 750 °C at 1 °C/s under a nitrogen flow. Pyrolytic gases were sent to a combustor heated at 900 °C under air flow ($N_2/O_2 = 80/20$). At this temperature and with 20% of oxygen, combustion was considered to be complete. Heat release rate was determined by oxygen depletion according to Huggett principle [35] (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released). PCFC analyses correspond to anaerobic pyrolysis followed by high temperature oxidation of decomposition products (complete combustion [36]). Peak of Heat Release Rate (pHRR) is the maximal value of the heat release rate. TpHRR is the temperature at pHRR. The total heat released (THR) was obtained by integration of PCFC curves. All samples were tested in triplicate. The uncertainties are typically 5 °C, 50–100 W/g and 1 kJ/g for TpHRR, pHRR and THR, respectively. Fire behavior was also studied using a cone calorimeter (Fire Testing Technology) which is a powerful tool to investigate the fire behavior of polymers. A horizontal sample sheet of 100 × 100 × 3 mm^3 was placed at 2.5 cm below a conic heater and isolated by rock wool. The samples were exposed to a 35 kW/m^2 heat flux in well-ventilated conditions (air rate 24 L/s) in the presence of a spark igniter to force the ignition. HRR was determined according to oxygen depletion (Huggett's relation) as in PCFC. This test was performed according to the ISO 5660 standard. PA11 commercial grade reference and PAx/0.5P were tested in duplicate. The limited oxygen index (LOI) and UL94 ranking were measured according to ASTM D2863 standard and according to the ISO 9772 standard on sample bars. 3 mm thickness sample bars (127 × 12.7 × 3 mm^3) were made in a standard steel mold. Dynamic Mechanical Analyses (DMA) were carried out on DMA Q800 TA instruments. Uniaxial stretching of samples was performed while heating at a rate of 2 °C.min^{-1} from −50 °C to melting point of samples, keeping frequency at 1 Hz and amplitude at 15 μm.

2.2. Synthesis of flame-retardant polyamides and melt processing

2.2.1. Synthesis of DOPO-ITA

The DOPO-ITA comonomer was synthesized according to the method used by Chang and Chang [37]. In a two-necked glass flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser, 15.03 g (0.115 mol, 1 eq) of itaconic acid and 24.97 g (0.115 mol, 1 eq) of DOPO were added. The mixture was stirred at 155 °C for 6 h. At the end, it was frozen and ground to obtain a white powder of DOPO-ITA with a 97% yield. The phosphorus ratio was 9 w% in this flame retardant product.

^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ: 2.45 (2H, H_1); 2.69 (2H, H_3); 2.98 (1H, H_2); 12.44 (2H, H_4); 7.29–8.20 (8H, $H_{aromatic}$).

^{31}P NMR (162 MHz, DMSO-d_6, ppm): δ: 35.32 and 35.75.

2.2.2. Synthesis of copolyamides by polycondensation

Reactions were carried out in a glass tube with a head equipped of mechanical stirrer and a nitrogen inlet. The reagents were added in ascending melting point and they were heated at high temperature. The temperature and the viscosity (at the molten state) of the system were continuously monitored and controlled. The polycondensation was stopped when the viscosity remained constant. The studied compositions are summarized in Table 1.

Table 1
Stoichiometric monomeric compositions of all PA polymers containing various phosphorus amounts.

Run	Polymers	%w AC11	%w DA10	%w DC10	%w DOPOITA	Theoretical w%P
1	PA-0	50.0	23	27.0	0	0
2	PA/1P	50.0	20.9	18.0	11.1	1.0
3	PAx/1P	49.1	20.5	19.4	11.0	1.0
4	PAx/0.7P	49.4	21.2	21.7	7.7	0.7
5	PAx/0.5P	49.6	21.7	23.2	5.5	0.5
6	PAx/0.4P	49.7	22.0	23.9	4.4	0.4
7	PAx/0.3P	49.7	22.2	24.7	3.3	0.3

2.2.3. Compounding

All the synthesized polyamides were dried at 100 °C, for 16 h before compounding. The polymers were prepared in a micro conical twin screw extruder Explore-DSM at 230–240 °C. After stabilization of mixture temperature at melt temperature and normal strength, the PAs were molded at 230 °C into ISO 527 1BA and ISO 178–179 dumbells for flammability test.

3. Results and discussion

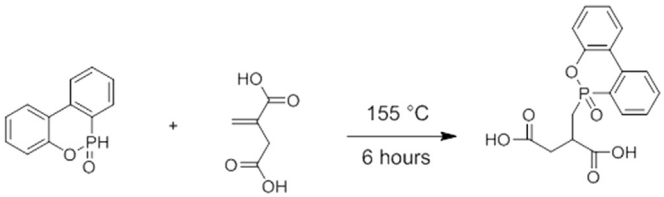
3.1. Synthesis and characterization of new phosphorus-containing polyamides

The synthesis of DOPO-ITA is shown in Scheme 1. To optimize the yield, the phosphorus-containing monomer was made in bulk conditions. DOPO and itaconic acid were added in stoichiometric conditions and stirred at 155 °C for 6 h. The product was characterized by ^{31}P and ^{1}H NMR spectroscopy. The NMR spectra are presented in Fig. 1 with DMSO-d_6 as solvent. First, the absence of signal at 5 ppm confirms the total conversion of itaconic acid in DOPOITA. Chemical shifts at 7–8 ppm result from the 8 aromatic protons of biphenyl group, while the peak centered at 12.4 ppm corresponds to the 2 carboxylic protons and H_1, H_3 and H_2 assigned to the CH_2-C, CH_2-P and CH groups are observed between 2.4 and 3.0 ppm, respectively. The ^{31}P NMR spectrum exhibits 2 single peaks at 35.2 and 35.6 ppm characteristic of the asymmetric phosphorus atom in DOPOITA structure.

New biobased PAs were synthesized by polycondensation with a mixture of 11-aminoundecanoic acid (AC11), 1,10-diaminodecane (DA10), 1,10-decanoic diacid (DC10) and DOPOITA to form PA11/10-10/10-DOPOITA. The AC11 amount represents 50% of the total weight of PA. The second part of the copolymer changes according to the phosphorus ratio, and the various proportions are summarized in Table 1. The polycondensation was carried out in a reactor monitoring the torque.

The time and the temperature of this polycondensation step are important parameters. 2 preliminary experiments were achieved on the reference mixture with 11-aminoundecanoic acid (AC11), decane-1,10-diamine (DA10), decan-1,10-oic acid (DC10) (without DOPOITA) and shown in Table 2.

The typical polycondensation of polyamides is performed at 240–250 °C for 2 h. The DOPOITA may be susceptible to high temperature degradation, so a decrease of polycondensation time was necessary. The TGA analysis of DOPOITA under nitrogen flow (Fig. S-1) shows a slight loss of weight (less than 5%) at 240 °C that may be reduced if the polycondensation temperature is decreased. The addition of few hundred ppm of acid catalyst is regularly used. It allows the significant decrease of polycondensation time (from 120 to 45 min) and a slight decrease of temperature while maintaining the same PA characteristics in terms of viscosity and end of chains. A potentiometric titration enabled to estimate the chain ends (NH_2 or COOH groups). A slight excess of acid chain ends was observed for these 2 experiments explained by the evaporation of diamine DA10, known as volatile product at high temperature under a nitrogen flux. The synthesized PA (run 1-Tables 1 and 2) with a viscosity of 1.24 dl/g, had a molar mass close to 30,000 g/mol measured by gel permeation chromatography (with PMMA standards) as shown in Fig. S-2.



Scheme 1. Synthesis of phosphonated telechelic diacid DOPOITA.

After focusing on the polycondensation conditions, the addition of DOPOITA was conducted with 11 wt%-insertion. A first test (run 2-Tables 1 and 3) allowed obtaining a PA with an intrinsic viscosity equal 0.46 dl/g.

The potentiometric titration is shown in Fig. 2. Without DOPOITA, the acidity was higher than the basicity because of the slight evaporation of DA10. Meanwhile, this phenomenon allowed obtaining PA with suitable molar masses. With the addition of 11% of DOPOITA (run 2-Tables 1 and 3), the tendency was changed, the basicity was far superior to acidity (empty circle and square-Fig. 2) due to a decrease of the acidic ends of chain. Then an excess of DC10 was added to permit the increase of molar mass. On PAx/1P (run 3-Tables 1 and 3), equilibrium between acidic and basic functions was found leading to an increase of the intrinsic viscosity observed. The increase of Mn is significant: from 5300 g/mol for PA/1P to 8000 g/mol for PAx/1P (runs 2 and 3-Table 3). Nevertheless, the addition of 11% of DOPOITA decreases the molar mass and the intrinsic viscosity of the final oligomer PAx/1P in comparison to PA-0 reference and may be explained by secondary terminal reaction. The presence of a short diacid monomer in the copolymerization and more especially the itaconic acid with 4 carbons that carried this reaction was described by Hoey et al. [38] or Vakili et al. [39] in polymer applications. The imidification reaction was possible between an amine and a diacid as shown in Scheme 2. At high temperature, water was eliminated and the cyclisation of imide was achieved, leading to chain growth limitation.

Five DOPOITA-containing PAs with various phosphorus amounts were synthesized in the same conditions: at 220 °C in the presence of catalyst and a slight excess of DC10. The reaction time was studied by the measurement of the torque in the polymerization reactor and adapted to the DOPOITA ratio.

Fig. 3 shows the torque data versus polymerization time at high temperature. The torque required to stir a molten polymer is an indirect measurement of the molecular weight of polymer, because it is proportional to the intrinsic viscosity of the polymer. In the first hundred minutes, the torque was stable, then it was increasing until a falling phase indicating the end of polymerization and this time increased with the DOPOITA ratio. The presence of DOPOITA

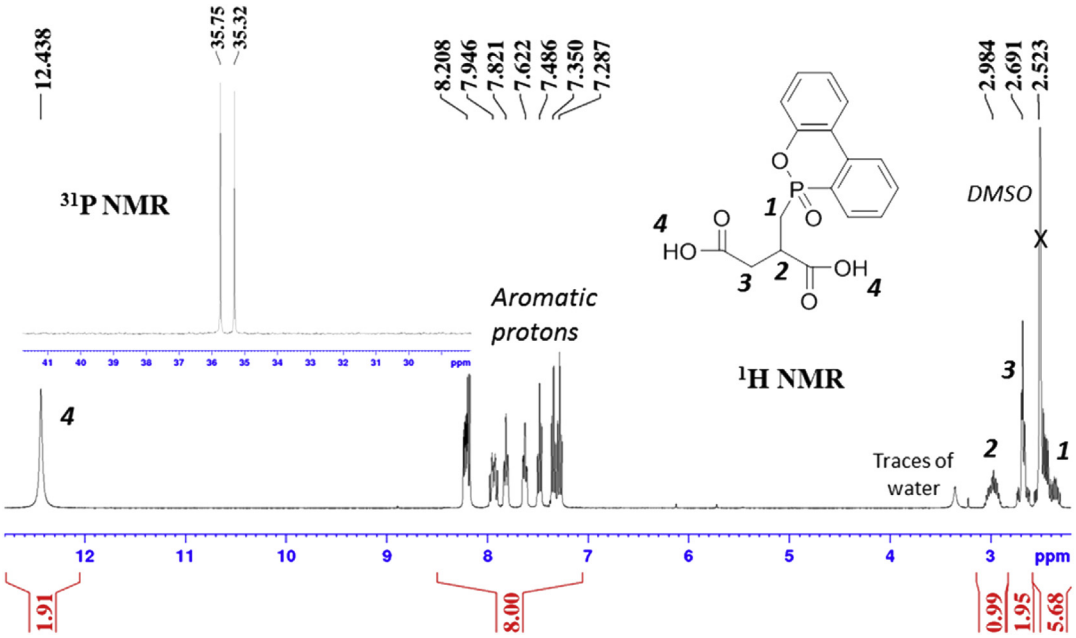


Fig. 1. NMR spectra of DOPOITA: (A) ^{1}H NMR and (B) ^{31}P NMR in DMSO-d_6 solvent.

Table 2
Influence of the catalyst and temperature on polycondensation of PA-0 (corresponding to a PA11/10-10 copolyamide).

Run	Temperature (°C)	Catalyst	Time (min)	Viscosity (dl/g)	Basicity/Acidity
0	240	No	120	1.30	0.032/0.085
1	220	600 ppm of acid catalyst	45	1.24	0.025/0.091

Table 3
Viscosities and molar masses of various synthesized copolyamides (with 11-aminoundecanoic acid (AC11), decane-1,10-diamine (DA10), decan-1,10-oic acid (DC10) and DOPOITA as monomers).

Run	Polymers	Viscosity (dl/g)	Molar Mass (g/mol)
1	PA-0	1.24	30,200
2	PA/1P	0.46	5300
3	PAx/1P	0.54	8000
4	PAx/0.7P	0.66	NC[a]
5	PAx/0.5P	0.79	16,200
6	PAx/0.4P	0.92	NC[a]
7	PAx/0.3P	1.07	NC[a]

[a] NC: not calculated.

decreased the reactivity and the molar mass obtained for the final PA. The addition of DC10 in excess in these 5 experiments allowed obtaining a suitable equilibrium between acidic and basic functions (Fig. 2) on these final PA.

The intrinsic viscosities of final copolyamides are summarized in Fig. 4. The tendency of intrinsic viscosity of PA-DOPOITA copolymers is similar to the torque obtained at the end of the polymerization. It can be seen that the intrinsic viscosity continuously decreases when DOPOITA is added until 0.54 dl/g for the PAx/1P with 11% of DOPOITA (run 3-Table 3). Above a viscosity value of 0.8 dl/g, the copolyamide is considered to have good characteristics for injection molding grade. Regarding the molar masses of new PA, the addition of 5% of DOPOITA (i.e. 0.5%wP) leads to a copolyamide with an intermediate molar mass of 16,200 g/mol (Fig. S-2) and a viscosity close to 0.8 dl/g (run 5-Table 3). This is a suitable compromise for the introduction of efficient phosphorus percentage and a molar mass allowing the PA injection molding.

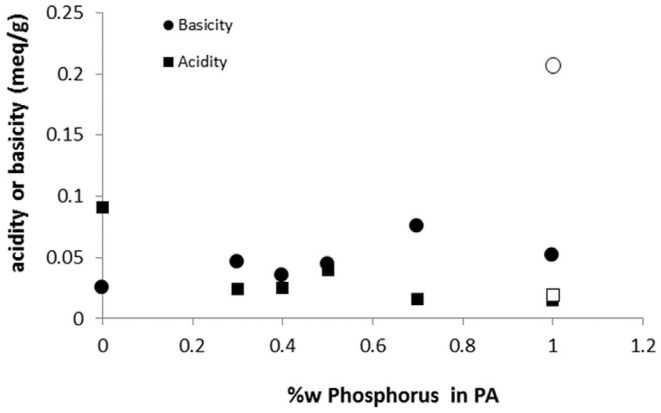
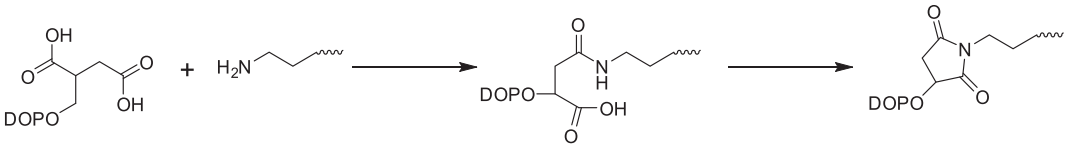


Fig. 2. Measurement of Acidity (square) and Basicity (circle) of each PA (versus $\%_wP$) at the end of polycondensation (full circle and square = run with an excess of DA10 and empty circle and square = run with ideal molar stoichiometry of acid and amine function (run 2-Table 1)).

Moreover, to confirm the phosphorus amount, an elementary analysis by X-ray fluorescence was carried out. The results are shown in Fig. 5. A good correlation between the theoretical phosphorus contents and the measured ones was obtained for all samples. For this study, the evolution of phosphorus content was respected and allows evaluating its influence on flame retardant properties.



Scheme 2. Imidification reaction between DOPOITA and an amino derivative.

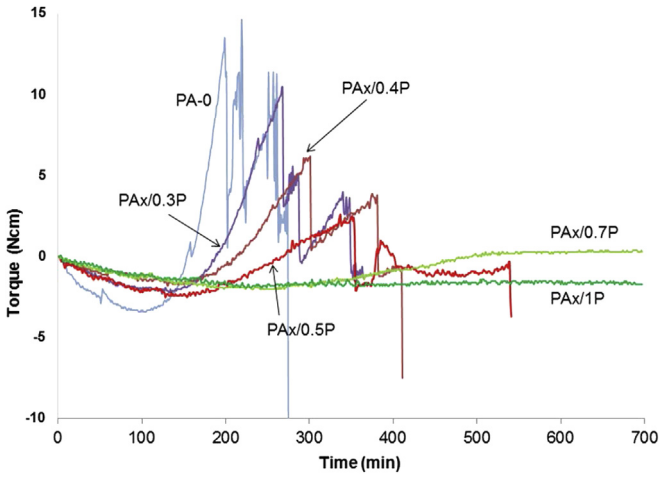


Fig. 3. Variation of torque versus the time of various synthesized copolyamides (with 11-aminoundecanoic acid (AC11), decane-1,10-diamine (DA10), decan-1,10-oic acid (DC10) and DOPOITA as monomers).

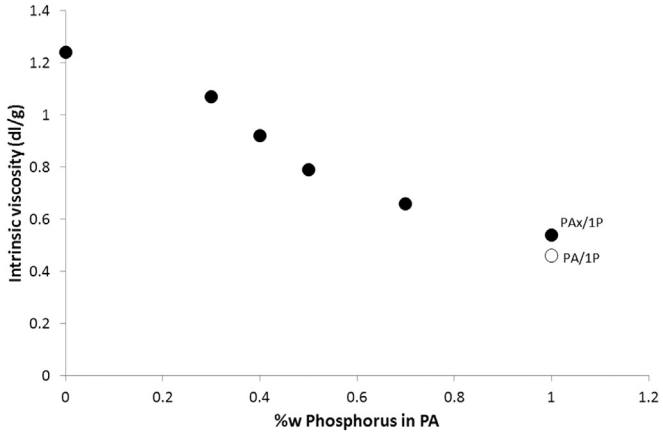


Fig. 4. Viscosity of final PA versus the phosphorus content (full circle = run with an excess of DA10 and empty circle = run with ideal molar stoichiometry of acid and amine functions (run 2-Table 1)).

3.2. Thermal and flame retardancy properties

Aliphatic PA including PA11 are semi-crystalline polymers. The crystalline fraction has a strong influence on the mechanical properties, so the differential scanning calorimetry (DSC) was employed to highlight this part. Fig. 6 shows some DSC 2nd heating curves obtained at 20 °C/min rate. A baseline shift associated with the glass transition (Tg around 40 °C, except for PA11 commercial grade at 52 °C) was detected in all curves (Table 4), that was followed by a multiple melting endotherm (main peak at Tm = 158 °C in synthetized samples). The enthalpy associated with melting is the same in all cases (33 ± 2 J g^{-1}) and lower than for PA11 commercial grade. A multiple melting process has been observed in

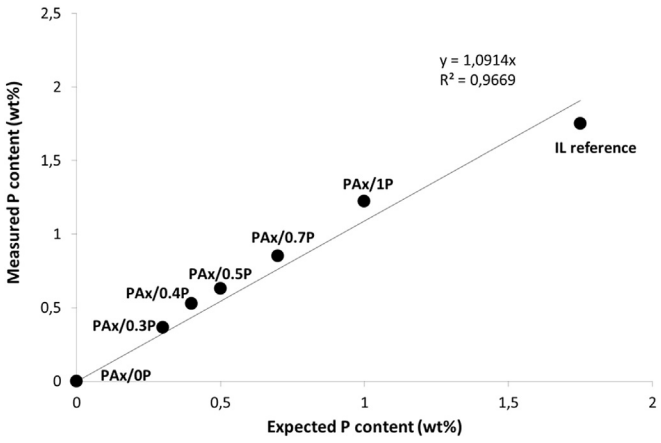


Fig. 5. Measured phosphorus contents versus the expected ones.

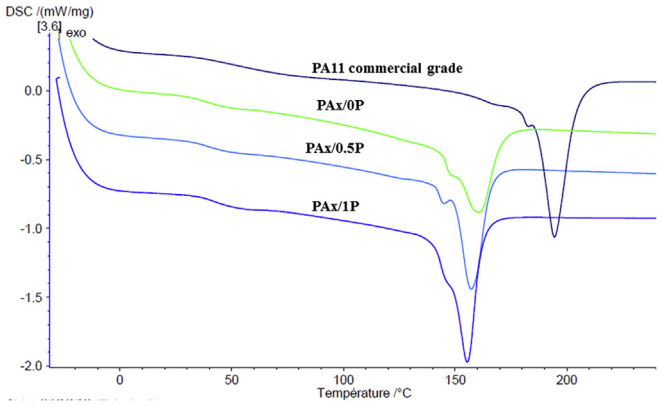


Fig. 6. DSC 2nd heating curves (20 °C/min rate).

PA11 commercial grade and previously reported for linear Nylon 11 [40]. Two distinct morphological structures are present where form I is thermodynamically preferred while form II is kinetically preferred [41]. The present results show that this complex melting behavior is also common to our copolyamides with or without DOPOITA. Only one peak of crystallization was observed between 114 °C and 121 °C for synthetized copolyamides and at 150 °C for PA11 commercial grade. The slight shift of Tc for synthetized PA is influenced to the amount of DOPOITA in the copolymer.

In the whole, compared to PA11 commercial grade (Tm = 194 °C according to literature value [42]), our copolymers exhibit lower Tm, Tc and Tg and lower degree of crystallinity. But there is no significant difference between copolyamides with different DOPOITA contents.

Thermogravimetric analysis was carried out for all polyamides under nitrogen. Fig. 7 exhibits the thermograms of PA-0, PAx/0.5P, and PAx/1P (runs 1, 3 and 5-Table 3). It can be noted that the thermal stability is slightly reduced when DOPOITA was incorporated. The temperatures at 5% of mass loss are 407 °C, 393 °C, and

Table 4
Main data from DSC analysis.

Materials	Glass transition temperature (°C)	Crystallization temperature (°C)	Melting temperature (°C)	Enthalpy of fusion (J.g-1)
PA11 commercial grade	52	150	194	44
PA-0	39	114	160	32
PAx/0.3P	41	116	158	31
PAx/0.4P	40	116	157	34
PAx/0.5P	41	115	157	31
PAx/0.7P	42	121	158	34
PAx/1P	41	120	155	35

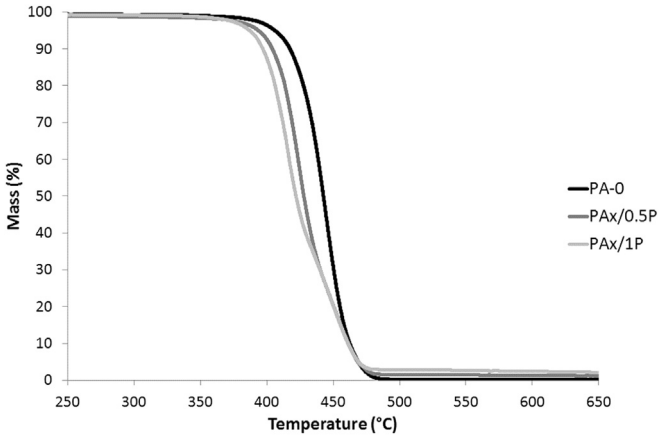


Fig. 7. TGA thermograms of PA-0, PAx/0.5P and PAx/1P under nitrogen flow.

387 °C for PA-0, PAx/0.5P, and PAx/1P, respectively. The same decreasing tendency is maintained when considering the temperature at 50% of mass loss (422–442 °C). Nevertheless the weight loss stabilizes at similar temperature (around 480 °C) for all the polyamides. The residue content is negligible (<3%) in all cases. These results are in good agreement with literature [17]. Indeed, DOPO is known to limit the decrease in thermal stability which is usually observed when adding phosphorus-containing flame retardants. Moreover, DOPO is believed to act mainly in gaseous phase with little efficiency as char promoter.

UL94 and LOI are two common tests used to assess the flame retardancy of polymers. In both tests, PAx sample is exposed to a flame for a short time. Then, flame inhibition (which is the main mode-of-action reported for DOPO) is particularly efficient. Moreover, melt flow helps reaching good ratings by removing fuels far from flame, especially for UL94 test. Lower viscosity of PAx can promote melt flow.

Table 5 summarizes the UL94 rating for commercially available PA11 commercial grade and polyamides synthesized with various DOPOITA contents. Phosphorus-free polyamides exhibit no rating in UL94. The incorporation of a small amount of DOPOITA enables reaching V2 rating. For higher phosphorus contents (0.5 wt% and more), the materials are V0-rated which is the highest rating. Significant dripping is observed but drips are non-flaming (see movie in supporting information). The dripping evidences the role of melt flow as discussed above. The instantaneous flame-out of drips also confirms the activity of DOPO in gas phase, i.e. it acts as flame inhibitor. It is interesting to note that PAx/0.5P allows reaching high level of flame retardancy while maintaining suitable viscosity for processing.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.polymdegradstab.2016.09.022.

LOI was measured for phosphorus-free commercial reference, PAx/0.5P and PAx/1P. Due to the small amount of prepared specimen, LOI was roughly assessed, especially for the latter. LOI values were 22, 28 and 40–45 for PA11 commercial grade, PAx/0.5P, and PAx/1P respectively. Such an increase is particularly impressive compared to previous results reported in literature [43]. Fig. 8 compares the relative increase in LOI versus the phosphorus content for various polymers containing phosphorus groups in their macromolecules [43]. Relative increase (ΔLOI) is calculated as follows:

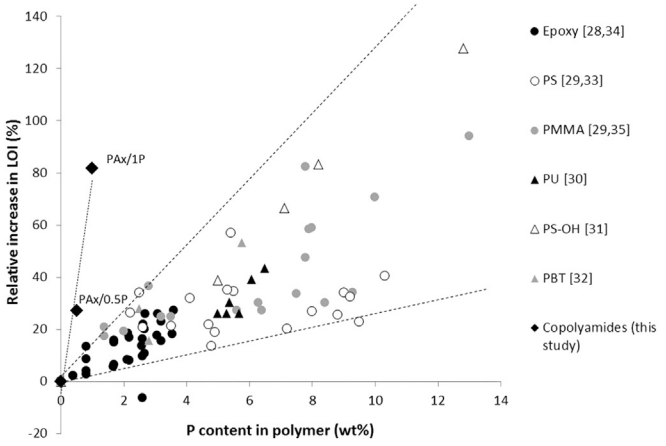


Fig. 8. Relative increase in LOI versus phosphorus content for various phosphorus-containing polymers (from Ref. [43]) and for PA of this study.

Table 5
Main data from pyrolysis-combustion flow calorimeter (PCFC) analysis and UL94 rating (pHRR for Heat Release Rate, THR for Total Heat Release).

Materials	Phosphorus content (wt%)	UL94 rating	Temperature at pHRR (°C)	pHRR (W/g)	THR (kJ/g)
PA11 commercial grade	0	V2	477	678	32.3
PA-0	0	No rating	460	721	31.6
PAx/0.3P	0.3	V2	458	654	31.3
PAx/0.4P	0.4	V2	454	663	31.6
PAx/0.5P	0.5	V0	451	722	31.4
PAx/0.7P	0.7	V0	447	636	31.2
PAx/1P	1	V0	446	653	30.8

$$\Delta LOI = \frac{LOI_{P-containing\ polymer} - LOI_{P-free\ polymer}}{LOI_{P-free\ polymer}} \times 100$$

Where $LOI_{P\text{-}containing\ polymer}$ and $LOI_{P\text{-}free\ polymer}$ stand for the LOI values of the polymer containing phosphorus derivative and of the free polymer that does not contain any phosphorus compound, respectively. It must be precised that the efficiency of phosphorus does not depend only on the phosphorus content but also on the nature of the groups containing phosphorus. Then the data summarized in Fig. 8 must be considered with caution.

It is clear that the relative increase in LOI at similar phosphorus content is much higher for the materials analyzed in this work than for other polymers previously studied [44–51]. The reason why such a significant increase is observed in this present study may be related to the mode-of-action of DOPO. As already noted, flame inhibition is very efficient to improve the flame retardancy when the material is exposed to a flame for a short time.

Table 6 also summarizes the main data from PCFC analyses for all studied copolyamides. In standard conditions, combustion is complete in PCFC test. Then, flame inhibition is not effective. Moreover, TGA has already shown that DOPO does not promote charring. As a consequence, pHRR and THR does not significantly change when incorporating an increased DOPOITA content. Only the thermal stability is slightly impacted: the temperature of pHRR decreases continuously from 460 to 447 °C when phosphorus content increases from 0 to 1 wt%. Once again, this is in agreement with TGA results discussed above.

Cone calorimeter tests were performed on PA11 commercial grade and PAx/0.5P at heat flux of 35 kW/m^2. Keep in mind that PAx/0.5P is a good compromise because it contains a high enough phosphorus amount to reach V0 at UL94 test while maintaining acceptable viscosity. Table 5 and Figs. 9–11 summarize the main data obtained from these tests. The incorporation of DOPOITA has limited (or negligible) influence on the heat release rate (HRR). pHRR is rather constant. While DOPO mainly acts as flame inhibitor and not as char promoter, residue amount is very low but the effective heat of combustion decreases moderately. As a consequence, THR is decreased. Time-to-ignition (TTI) increases slightly when incorporating DOPOITA, as expected for a flame inhibitor. Nevertheless, the uncertainty on TTI is high and this point needs to be checked in further work.

Other data give additional information about the mode-of-action of DOPO in cone calorimeter test. First, ignition for PAx/0.5P is preceded by several flashes in cone calorimeter test, which typically corresponds to flame inhibition. Flame inhibition is also generally accompanied by a significant increase in smoke and CO production. Figs. 10 and 11 display the smoke production rate (SPR) and the CO/CO_2 ratio for both polymers during cone calorimeter test (for CO/CO_2 ratio, the values are only accurate between 100 and 300 s, i.e. when mass loss is fast enough). As expected PAx/0.5P exhibits higher SPR and CO/CO_2 ratio than PA11 commercial grade does. These observations confirm that DOPO acts as a flame inhibitor.

As explained above, DOPO acts as flame inhibitor and plasticizer (enhancing the melt flow). The flame retardancy depends on a complex combination of various modes-of-action and this combination is different from one test to another one. Flame inhibition and melt flow are both involved in UL94 test [52] while dripping is prevented in cone calorimeter. The performances of DOPO as flame retardant are then worse in the latter test than in the former. Other FR systems act similarly by flame inhibition and melt flow. For example, diazenes and disulfides are two classes of radical generators efficient to flame retard polypropylene [53,54]. Nevertheless, it can be noted that these systems generally do not improve significantly the LOI [54], in contrast with our results.

Similarly, melamine cyanurate also acts in polyamides by enhancing melt flow and reducing the effective heat of combustion. In this case, the decrease in EHC is not due to flame inhibition but to dilution of fuels by non-combustible gases [55]. Melamine cyanurate allows polyamide 6 reaching V0 rating at UL94 test and high LOI at relative low content (8 wt%) but is rather ineffective in cone

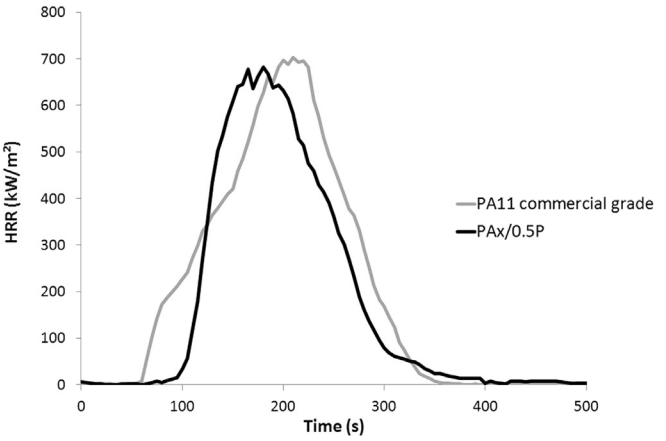


Fig. 9. Heat release rate (HRR) versus time curves for PA11 commercial grade and PAx/0.5P in cone calorimeter tests at 35 kW/m^2.

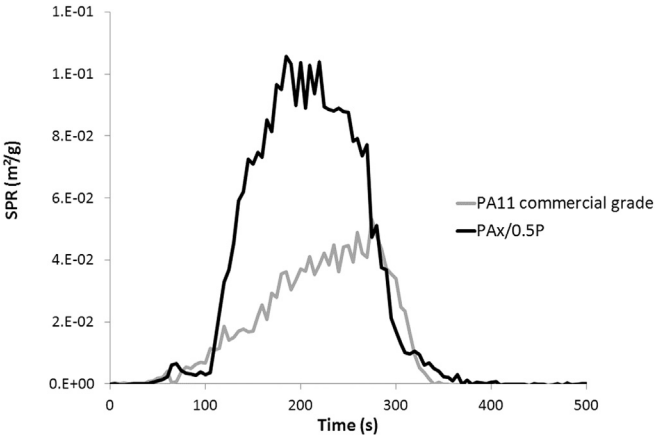


Fig. 10. Smoke production rate curves for PA11 commercial grade and PAx/0.5P in cone calorimeter tests at 35 kW/m^2.

Table 6
Results of cone calorimeter tests at 35 kW/m^2 of irradiance.

	TTI (s)	pHRR (kW/m^2)	THR (kJ/g)	Residue amount (%)	EHC (kJ/g)
PA11 commercial grade	87	747	34.0	0	34
PAx/0.5P	96	685	29.9	1.9	30.4

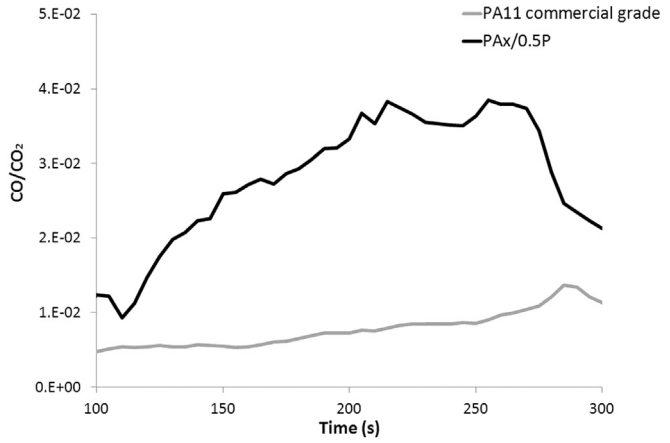


Fig. 11. CO/CO_2 ratio for PA11 commercial grade and PAx/0.5P in cone calorimeter tests at 35 kW/m^2.

calorimeter test [56].

It must be noted that these flame retardants are more effective for thin specimens for which melt flow is a dominant mode-of-action. Indeed, the melt flow is generally not fast enough for thick specimens. Hence we can expect that our new copolyamides meet the requirements for use as thin parts.

3.3. Thermo-mechanical properties

Beside their flammability, the mechanical and thermomechanical performances of new self-extinguishing bio-based coPA were compared to commercially available PA11 commercial grade because of the importance of their daily end use.

Fig. 12 exhibits the dynamic mechanical analysis curves of commercial reference, reference PA-0, and PAx/0.5P. All these 3 samples showed similar mechanical transition temperature around 60 °C, the slight difference came from the presence of a unique type of segment with 11 carbons for commercial PA11 commercial grade. The negative influence of DOPOITA on the molar mass can be evidenced on the modulus E': at room temperature, a decrease of 200 MPa and 160 MPa is observed in comparison respectively to commercial PA11 and synthetized PA-0. The addition of flame retardants with 10–20% ratio into polyamides led to the same observations [57,58]. The introduction of DOPOITA not only provides an improvement in flame retardancy but also leads to the worsening of mechanical performance. Despite these changes, the same type of applications may be targeted.

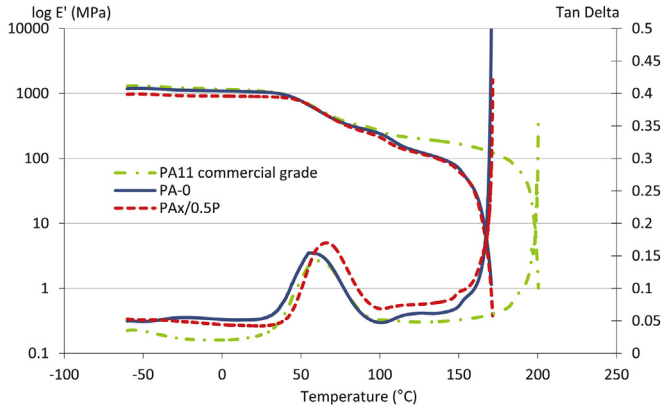


Fig. 12. Dynamic mechanical analyses of 3 polyamides: PA11 commercial grade as the commercial reference, synthesized copolyamide without DOPOITA (PA-0) and synthesized copolyamide with 0.5 wt% of phosphorus (PAx/0.5P)).

4. Conclusion

New copolyamides containing various contents of a new phosphorus monomer (DOPOITA) have been prepared and characterized. Incorporation of DOPOITA lowers the viscosity and the molar mass. However, new phosphorus-containing copolyamides were synthesized with suitable molar masses around 15,000 g/mol. The crystallinity of all samples was preserved. Fire tests suggest that the presence of at least 5 wt% of DOPO (corresponding to 0.5 wt% of phosphorus) yielded to a flame inhibition effect leading to V-0 rating at UL94 test. Cone calorimeter test confirmed that DOPO acts as a flame inhibitor. Copolyamide containing 0.5 wt% of phosphorus exhibits flame retardancy and maintained suitable viscosity and mechanical properties.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymdegradstab.2016.09.022.

References

[1] S.V. Levchik, E.D. Weil (Eds.), Developments in Phosphorus Flame Retardants, Woodhead Publishing Ltd., 2008, pp. 41–66.
[2] C.A. Wilkie, A.B. Morgan (Eds.), Fire Retardancy of Polymeric Materials, second ed., CRC Press, 2010, p. 823.
[3] H. Vahabi, R. Sonnier, L. Ferry, Polym. Int. 64 (2015) 313–328.
[4] F.H. Isikgor, C.R. Becer, Polym. Chem. 6 (2015) 4497–4559.
[5] D. Sun, Y. Yao, Polym. Degrad. Stab. 96 (2011) 1720–1724.
[6] J. Hu, J. Shan, D. Wen, X. Liu, J. Zhao, Z. Tong, Polym. Degrad. Stab. 109 (2014) 218–225.
[7] B. Schartel, A.I. Balabanovich, U. Braun, U. Knoll, J. Artner, M. Ciesielski, M. Doering, R. Perez, J.K.W. Sandler, V. Altstaedt, T. Hoffmann, D. Pospiech, J. Appl. Polym. Sci. 104 (4) (2007) 2260–2269.
[8] P. Mueller, Y. Bykov, M. Doering, Polym. Adv. Technol. 24 (2013) 834–840.
[9] X. Wang, Y. Hu, L. Song, W. Xing, H. Lu, P. Lv, G. Jie, Polymer 51 (2010) 2435–2445.
[10] P. Wang, F. Yang, L. Li, Z. Cai, Polym. Degrad. Stab. 129 (2016) 156–167.
[11] A. Koenig, E. Kroke, Fire Mater. 36 (2012) 1–15.
[12] A. Buczko, T. Stelzig, L. Bommer, D. Rentsch, M. Heneczkowski, S. Gaan, Polym. Degrad. Stab. 107 (2014) 158–165.
[13] E.D. Weil, S.V. Levchik, Flame Retardants for Plastics and Textiles, Hanser Publications, Cincinnati, USA, 2010.
[14] Z. Bai, L. Song, Y. Hu, X. Gong, R.K.K. Yuen, J. Anal. Appl. Pyrolysis 105 (2014) 317–326.
[15] S. Brehme, B. Schartel, J. Goebbels, O. Fischer, D. Pospiech, Y. Bykov, M. Döring, Polym. Degrad. Stab. 96 (5) (2011) 875–884.
[16] M. Sato, M. Yokoyama, Eur. Polym. J. 16 (1980) 79–83.
[17] B. Schartel, Materials 3 (2010) 4710–4745.
[18] K.A. Salmeia, S. Gaan, Polym. Degrad. Stab. 113 (2015) 119–134.
[19] P. Liu, M. Liu, C. Gao, F. Wang, Y. Ding, B. Wen, S. Zhang, M. Yang, J. Appl. Polym. Sci. 130 (2013) 1301–1307.
[20] C. Zhang, S.M. Liu, J.Q. Zhao, J.Y. Huang, Polym. Bull. 70 (2013) 1097–1111.
[21] S.V. Levchik, E.D. Weil, Polym. Int. 54 (2005) 11–35.
[22] Yang, S.; Wang, J.; Huo, S.; Cheng, L.; Wang, M., Polym. Degrad. Stab. 2015, 115 (Copyright (C) 2016 American Chemical Society (ACS). All Rights Reserved.), 63–69.
[23] B. Schartel, U. Braun, A.I. Balabanovich, J. Artner, M. Ciesielski, M. Doering, R.M. Perez, J.K.W. Sandler, V. Altstaedt, Eur. Polym. J. 44 (2008) 704–715.
[24] G. Lligadas, J.C. Ronda, M. Galia, V. Cadiz, J. Polym. Sci. Part A Polym. Chem. 44 (2006) 6717–6727.
[25] B. Szolnoki, A. Toldy, P. Konrad, G. Szebenyi, G. Marosi, Period. Polytech. Chem. Eng. 57 (2013) 85–91.
[26] S.Q. Ma, X.Q. Liu, Y.H. Jiang, L.B. Fan, J.X. Feng, J. Zhu, Sci. China Chem. 57 (2014) 379–388.
[27] M. Li, Y. Zhong, Z. Wang, A. Fischer, F. Ranft, D. Drummer, W. Wu, J. Appl. Polym. Sci. 133 (2016) 42932–42942.

[28] S. Endo, T. Kashihara, A. Osako, T. Shizuki, T. Ikegami, Flame-resistant Polyesters, JP52047891A, 1977.
[29] H. Rieckert, J. Dietrich, H. Keller, U. Guenther, Method for Preparing DOP-its-Adduct and its Application, DE19711523A1, 1998.
[30] T. Hu, X. Tang, K. Yang, W. Wang, K. Deng, Q. Jiang, Nylon Resin with High Flame Retardance and Good Mechanical Properties, and Preparation Method Thereof, CN103694468A, 2014.
[31] X. Du, X. Feng, W. Xiao, X. Wu, L. Jiang, Method for Preparing Halogen-free Flame-retardant Nylon 66 Polymer, CN104211954A, 2014.
[32] J. Yang, Y. Yang, Preparation Method of Organophosphorus-Copolymerized Flame Retardant Polyamide, CN104231262A, 2014.
[33] X. Tang, T. Hu, K. Yang, W. Wang, K. Deng, Q. Jiang, Preparation of Highly Flame-retardant Nylon Resin, CN103819666A, 2014.
[34] Arkema Group http://www.rilsan.com/en/.
[35] C. Huggett, Fire Mater. 4 (1980) 61–65.
[36] F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, Mater. Sci. Eng. 63 (2009) 100–125.
[37] S.-J. Chang, F.-C. Chang, J. Appl. Polym. Sci. 72 (1) (1999) 109–122.
[38] G.B. Hoey, C.T. Lester, J. Am. Chem. Soc. 73 (1951) 4473–4474.
[39] M.R. Vakili, S. Zahmatkesh, T. Jafarizadeh, M.J. Panahiyan, Polym. Bull. 68 (2012) 85–94.
[40] S. Gogolewski, Colloid Polym. Sci. 257 (1979) 811–819.
[41] L. Li, C.Y. Li, C. Ni, L. Rong, B. Hsiao, Polymer 48 (2007) 3452–3460.
[42] L. Martino, L. Basilissi, H. Farina, M.A. Ortenzi, E. Zini, G. Di Silvestro, M. Scandola, Eur. Polym. J. 59 (2014) 69–77.
[43] R. Sonnier, L. Ferry, J.-M. Lopez-Cuesta, RSC Polym. Chem. Ser. 11 (2014) 252–270.
[44] A. Schaefer, S. Seibold, O. Walter, M. Doering, Polym. Degrad. Stab. 93 (2008) 557–560.
[45] J.R. Ebdon, D. Price, B.J. Hunt, P. Joseph, F. Gao, G.J. Milnes, L.K. Cunliffe, Polym. Degrad. Stab. 69 (2000) 267–277.
[46] Y.-L. Liu, G.-H. Hsiue, C.-W. Lan, Y.-S. Chiu, J. Polym. Sci. Part A Polym. Chem. 35 (1997) 1769–1780.
[47] Y.-L. Liu, G.-H. Hsiue, Y.-S. Chiu, R.-J. Jeng, C. Ma, J. Appl. Polym. Sci. 59 (1996) 1619–1625.
[48] R. Sablong, R. Duchateau, C.E. Koning, D. Pospiech, A. Korwitz, H. Komber, S. Starke, L. Haeussler, D. Jehnichen, M. Auf der Landwehr, Polym. Degrad. Stab. 96 (2011) 334–341.
[49] Q. Tai, L. Song, Y. Hu, R.K.K. Yuen, H. Feng, Y. Tao, Mater. Chem. Phys. 134 (2012) 163–169.
[50] U. Braun, A.I. Balabanovich, B. Schartel, U. Knoll, J. Artner, M. Ciesielski, M. Doering, R. Perez, J.K.W. Sandler, V. Altstaedt, T. Hoffmann, D. Pospiech, Polymer 47 (2006) 8495–8508.
[51] M. Cochez, M. Ferriol, J.V. Weber, P. Chaudron, N. Oget, J.L. Mieloszynski, Polym. Degrad. Stab. 70 (3) (2000) 455–462.
[52] F. Kempel, B. Schartel, J.M. Marti, K.M. Butler, R. Rossi, S.R. Idelsohn, E. Onate, A. Hofmann, Fire Mater. 39 (2015) 570–584.
[53] M. Aubert, C.-E. Wilen, R. Pfaendner, S. Kniesel, H. Hoppe, M. Roth, Polym. Degrad. Stab. 96 (2011) 328–333.
[54] W. Pawelec, A. Holappa, T. Tirri, M. Aubert, H. Hoppe, R. Pfaendner, C.-E. Wilen, Polym. Degrad. Stab. 110 (2014) 447–456.
[55] S.V. Levchik, E.D. Weil, Polym. Int. 49 (2000) 1033–1073.
[56] S. Tang, L.-j. Qian, Y. Qiu, N. Sun, J. Appl. Polym. Sci. 131 (2014) 40558/1–40558/8.
[57] F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, Mater. Sci. Eng. R Rep. 63 (3) (2009) 100–125.
[58] S. Zhang, W. Tang, X. Gu, P. Jiang, J. Sun, D. Sophie, S. Bourbigot, M. Casetta, J. Appl. Polym. Sci. 133 (20) (2016) 43370–43380.