

# Intrinsically flame retardant polyamides: Research progress in the last 15 years

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## ABSTRACT

Polyamides are essential thermoplastics whose current worldwide annual production exceeds 10 million tons. They are ubiquitous and easily ignitable polymeric materials that require addition of flame retardants to comply with fire safety requirements for various applications. Flame retardant additives can be incorporated into polymer matrix as fillers or at the molecular level, implying use of reactive additives. The latter approach is less developed, but usually offers several advantages over adding flame-retardant fillers: lower additive loading used to achieve specific level of fire performance, no flame-retardant migration with time, lower corrosiveness, better polymer stability etc. Rendering polyamides intrinsically flame retardant is therefore highly desirable. In this review we survey progress in inherently flame-resistant polyamides done over the period from 2004 to 2020. The polymers are grouped according to their chemical structures: aliphatic, semiaromatic and aromatic polyamides, polyamidoimides and hybrid siloxane-polyamides. Their monomer preparation, synthesis details, thermal properties and fire performance are discussed. The minimal inclusion criterion for this review was reported fire-resistance performance: either V-1/V-0 rating achieved in UL-94 burning tests or experimental or calculated LOI above 23%.

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## 1. Introduction

Polyamides are polymers that incorporate repeating amide functionality. Based on their origin, polyamides can be divided into natural polyamides and synthetic ones that are obtained artificially. Naturally derived polyamides are better known as polypeptides, proteins and usually composed of natural aliphatic proteinogenic L-aminoacids [1]. Wool, silk, collagen,  $\beta$ -keratin, polyglutamic acid are just few examples of naturally occurring polypeptides. Nonetheless, solely wool dominates over other natural proteins in its use as fibers for consumer clothing and special textiles, e.g. train and aircraft upholstery. Wool is composed of a large variety of L-aminoacids, which renders it intrinsically flame-resistant properties. Specifically, low H-content (~6–7%) along with high amount of N (~16%) and S (~3–4%) enable increased moisture regain (up to 15%) [2,3] that leads to high ignition temperature (570°C–600 °C),

relatively low THR (20.5 kJ/g) and LOI values of 25–28% without use of FR finishes [3,4]. Furthermore, compositional and structural complexity of wool macromolecules brings about multistep thermooxidation that occurs predominantly by charring with relatively low emission of toxic gases and smoking (for untreated wool) [4]. In contrast to natural polypeptides, synthetic polyamides are usually homopolymers (polylactams, also referred to as A-B polyamides) or diacid-diamine-based polymers (or AA-BB polyamides), prepared from aliphatic and/or aromatic diamines and diacids. According to the chemical structure of a monomer used in polycondensation, the resulting synthetic polyamides are usually distinguished as aliphatic, partially aromatic, semiaromatic and aromatic, also known as aramids.

Aliphatic polyamides, or nylons, are predominantly linear polymers (PA6, PA46, PA66, PA12 etc.) derived from aliphatic monomers ( $\epsilon$ -aminocaproic acid,  $\omega$ -aminolauric acid, hexamethylenediamine, adipic acid, etc.). Therefore, macromolecular backbones in conventional artificial aliphatic PA display higher H-content, lower water absorption and higher flammability hazard as compared to polypeptides. Aliphatic polyamides are easily ignitable materials that burn completely leaving nearly no solid residues

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(except for PA66) [5]. Once ignited, bulk samples of aliphatic PAs can self-extinguish due to extensive sample shrinkage and dripping thanks to low melt viscosity of PAs. However, LOI of virgin PAs is relatively low (~20–26%) and polymer melt drips are inflamed, maintaining high fire hazard of PA materials. Combustion of PAs is accompanied by high pHRR and THR, emission of flammable small molecules and toxic gases that depend on polymer composition and temperature [5–8]. Notably, burning PAs almost do not emit vision-obscuring smoke.

Despite unsatisfactory fire performance, aliphatic PAs still dominate on the market, covering about 90% of the global demand on polyamides and thus urging research to develop FR solutions with little compromise on physical properties of the polymer as well as no complications associated with polymer-additive compatibility, additive migration, phase separation, corrosiveness to processing machinery, coloring, toxicity etc.

Partially aromatic PAs and semi aromatic PAs incorporate aromatic monomers in macromolecular backbones; thus, these polymers contain amide links directly bonded to aromatic rings (e.g. PA6T, PA6I, PA 4T/6T etc.). The amount of aromatic component in semi aromatic PAs is normally around 50%, whereas its content is not strictly set and may vary in partially aromatic polyamides, reaching as high as 85% of an aromatic monomer [5]. Replacement of aliphatic monomers with aromatic units usually results in a significant enhancement of mechanical, thermal properties and a reduction in moisture uptake, while also improving fire resistance of PA [6–9]. This can be attributed to a combination of various factors as higher  $T_g$ , reduced amount of aliphatic segments with easily oxidizable  $-\text{CH}_2\text{-NH}-$  bonds, reduced amount of flammable volatiles and increased amount of char formed upon combustion [10]. As a result, LOI of partially aliphatic polyamides are usually higher as compared to the aliphatic counterparts and correlate with the amount of aromatic monomers in the macromolecular backbone. Upon combustion, partially aromatic and semiaromatic polyamides form complex mixture of products, strongly dependent on temperature and monomers used for synthesis, and therefore combine molecules emitted upon thermooxidative decomposition of corresponding nylons and/or aramides [11]. Commercial partially aromatic PA are high-performance materials that enjoy wide range of applications, requiring superior mechanical and thermal properties compared to the aliphatic PAs. Compared to nylons, there are substantially less studies on flame retardation of partially aromatic and semiaromatic PAs, despite their widespread and increasing use combined with apparent exposure of these plastics to harsh thermal conditions [6].

Wholly aromatic PAs, or aramides, contain >85% of amide groups directly connected to aromatic rings, ensuring paramount macromolecular chain stiffness, hydrolytic stability and inherent flame retardancy among PAs [5]. Aramids are hardly ignitable, they display low THR,  $T_g$  higher than their decomposition and melting temperatures and belong to highly charring polymers [12]. Upon combustion, wholly aromatic PAs form ample char residues thanks to high density of aromatic segments in the structure, and release heavy C-rich aromatic molecules formed mostly through homo- and hydrolytic cleavage of amide bonds [13,14]. Subsequently, water content, presence of substituents grafted to monomers, as well as crystallinity may affect thermal and FR properties of aramids [14–16]. Nonetheless, wholly aromatic PAs are indispensable high-performance heat-resistant polymers used extensively in fabrication of fire-resistant clothing, firefighting equipment and other fireproof civil and military components [17]. Aramides usually do not require additional FR solutions, while many efforts are concentrated on improvement of polymer processability properties with no compromise on valuable mechanical and FR characteristics. Compared to the aliphatic polyamides, fully aromatic polyamides

are relatively expensive and require special processing conditions (processing with inorganic acids) which are suitable for bulk applications.

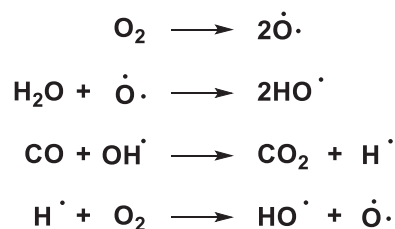
## 2. Fire and flame-retardation

Burning of organic materials is a complex phenomenon that depends on many variables: temperature, atmosphere composition, chemical composition and physicochemical properties of a burning substrate, its specific geometrical shape and surface area, etc. [18] During the burning process the substrate undergoes few distinguished phases: heating, phase transitions, degradation, decomposition, oxidation, ignition, combustion and propagation. Therefore, an overall polymer's fire performance arises from its behavior on each of these stages (Scheme 1), while it also suggests means for flame retardation [19].

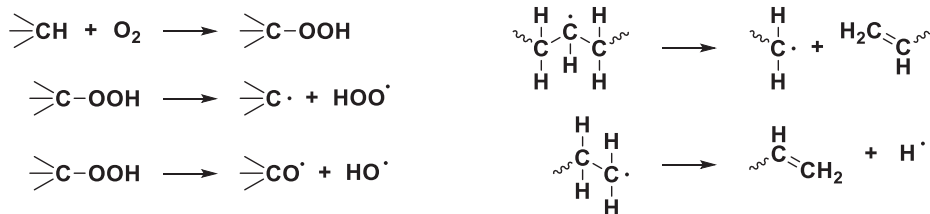
Combustion of hydrogen- and carbon-rich polymer materials (Scheme 2) with no inhibitors is accompanied with exothermic reactions happening in the gas zone of flame and at the condensed phase of a burning substrate (peroxidation, depolymerization, polymer chain scission, hydrolysis etc.), that supplies the gas zone with combustible small molecules and active radicals. Thus, fire-suppression approaches usually address processes occurring in the gas phase of the flame zone and/or at condensed phase of a burning substrate. FR acting in the gas phase are devised to scavenge reactive species that account for fire propagation. It is usually attained through either thermally induced release of radical acceptors that can recombine  $\cdot\text{H}$ ,  $\cdot\text{OH}$  reactive species and cause reaction termination; or emission of non-flammable gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  etc.) and/or solid particles that dilute gasses in the flame zone, thus increasing a flash point of the gaseous “fuel mixture”.

Old generation gas-phase active FRs usually relied on halogenated compounds that can easily emit  $\cdot\text{Hal}$  and poison fire. An evident drawback of this flame retardation approach is abundant generation of  $\text{HHal}$  as the product of radical scavenging. In addition, halogenated FRs as well as products formed upon their incineration are recognized persistent pollutants that eventually led to phasing out of these additives [20]. Modern FR solutions are mostly halogen-free and employ P-based compounds that are considered significantly less hazardous for both humans and environment [21]. Phosphorus FRs, containing P with lower oxidation number (phosphine oxides, phosphinates etc.) usually act in the gas phase, releasing flame-inhibiting  $\cdot\text{PO}$ ,  $\cdot\text{P}$ ,  $\cdot\text{HPO}$  and other radicals, and do not promote formation of ample char residues [21,22]. These additives are often used in combination with other elements to gain cooperative effect for fire suppression. For example, N-, Si-rich compounds and compounds susceptible to dehydration decompose with the release of inert gases and/or facilitate formation of a layer of solid residues that prevent a burning substrate from further thermooxidative decomposition.

The prevention of fire spread through a modification of burning substrate is usually appreciated as condensed phase mode of flame



Scheme 1. Radical reactions in the gas zone of flame.



**Scheme 2.** Radical reactions at the condensed phase of a burning substrate.

retardation. This is usually attained through formation of a mechanical barrier of solid glassy, rubbery or foamy residues with decreased flammability (P-enriched char,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ , metal oxides etc.) that protect the underlying intact polymer substrate from reactive radicals, oxygen and heat transfer. Condensed-phase active FR additives include derivatives of polyols and polyphenols as char-promoters; B-, Si- or P-based (with high oxidation number: phosphonates, phosphates etc.) compounds that tend to decompose forming solid protective layer; metal salts catalyzing char formation and incombustible fillers that hinder heat transfer.

Particularly for PAs, the vast majority of FRs solutions are non-reactive additives that are mechanically mixed with polymers during processing [19,23–25]. This popular method is inexpensive and relatively simple, enabling a widespread application in polymer industry. However, polymer-FR additive formulations usually require high FR loadings and often suffer from additive aggregation or phase segregation due to poor compatibility between small FR molecules and macromolecules, causing additive to leach over time; strong alteration of polymer properties and potentially - complications in recycling. An alternative approach to obtain FR polymers is to improve thermooxidative stability by suitable chemical modification of macromolecules themselves. Specifically, monomers with “FR substituents” can be utilized in polymerization to yield inherently flame retardant (co)polymers. This approach eliminates the mentioned issues intrinsic to formulations, except for alteration of polymer's properties – particularly important for PAs, whose properties are primarily defined by intermolecular hydrogen bonding that ensures its partial crystallinity. Nevertheless, the incorporation of FR monomers into molecular backbone was demonstrated to have a superior FR effect as compared to formulations with non-reactive additives of similar structures [26–29]. Finally, the “reactive” approach for PAs is less reported and reviewed as compared to use of small molecule additives [30]; thus, this review summarizes recent progress in development of (co)polyamides with inherent heat- and flame-resistant properties to shed more light on research performed in this field as well as indicate prospects in this area.

### 2.1. Scope and structure of the review

This review aims to survey the progress in intrinsically heat-resistant and flame-retardant (co)polyamides, in cases when this property originates from a chemical composition of macromolecules in bulk. In this review scientific literature published in English during the period since 2004 until 2020 is only considered with no emphasis of patents. The selection criteria for this review were PAs either attaining V-1/V-0 rating in UL-94 burning test or LOI values above 23%, obtained experimentally or derived from amount of char residues in TGA or MCC experiments using Van Krevelen-Hoftyzer equation:  $\text{LOI} = 17.5 + 0.4\text{CR}$ , where CR – char yield [31]. Several polymers with LOI lower than 23% were still included as benchmarks or a part of a “structural family”. Synthesis of monomers for intrinsically FR polyamides is discussed briefly. Molecular and thermal properties, as well as fire performance of FR polymers are

reported in separate tables in the end of the respective section: aliphatic PAs (Table 1, Table 2), partially aromatic PAs (Table 3), aromatic PAs (Table 4), polyamidoimides (Table 5) and polyamide-siloxane copolymers (Table 6, Table 7). The latter group of polymers was considered separately due to their specific hybrid organic-inorganic and block-copolymer nature, moreover these polymers were used for preparation of thermosetting materials.

Studies on FR additives for conventional polyamides are not considered here as they were reported in numerous reviews and book chapters [23–25,145–152]. Finally, reactive extrusion, surface modification and FR finishing for PA and wool textiles beyond the scope of this review, and can be found elsewhere [3,153–160].

## 3. Aliphatic polyamides

### 3.1. PA6 copolymers

PA6 is an important commercial thermoplastic obtained through ring-opening polymerization of  $\epsilon$ -caprolactam [7]. Few reported examples of reactive FR monomers for PA6 are mostly P-containing diacids and their salts with aliphatic diamines (see Fig. 1). They are commonly introduced as co-monomers during polycondensation and randomly distributed along macromolecular backbones. Thereby, substitutional pattern of FR co-monomers plays an important role: the presence of bulky pendants in the structure of reactive FR additives may disrupt close packing of PA6 chains, eventually deteriorating crystallinity of PA6 and its mechanical properties. Moreover, non-equal length of the aliphatic and FR co-monomers alters frequency of inter-chain hydrogen bonding, while steric hindrance and/or non-equivalence of reacting groups was reported to affect polymerization propagation, resulting in polymers with inferior crystallinity (*vide infra*).

Mourgas reported preparation and properties of FR copolyamides **1** and **2** synthesized by melt co-polycondensation of  $\epsilon$ -caprolactam and two FR organophosphorus diacids: CEPPA and DOPO-ITA [32]. The synthesized polymers contained P in the range of 0.1–0.3 wt%. Importantly, higher P-content resulted in low-molecular-weight co-polymers with lower viscosities unsuitable for processing. Co-polyamides **1** and **2** with 0.15% and 0.10 wt% of P respectively displayed properties ( $T_m$ ,  $T_c$ ,  $X_c$  and viscosity) similar to the reference unmodified PA6 and were chosen for melt-spinning and knitting inherently FR fabrics. The bulky substituents of CEPPA and DOPO-ITA did not affect hydrogen bonding in PA at low wt% loading. Fibers spun using **1** and **2** realized mechanical properties almost identical to the reference PA6 filaments. In contrast to PA6, fabrics knitted from FR fibers **1** and **2** showed excellent FR properties, achieving high LOI of 35.6% and 35.8% respectively and V-0 category according UL-94 standard. FR PAs **1** and **2** were also used as polymeric FR additives for PA6 to prepare inherently FR fabrics [161].

Liu reported preparation and characterization of FR polyamides **3** obtained via melt co-polycondensation of  $\epsilon$ -caprolactam with DOPO-ITA decane-1,10-diammonium salt at different wt% loading of the FR co-monomer. DOPO-ITA co-monomer content ranged

**Table 1**  
Preparation, selected molecular properties and DSC data of aliphatic FR PAs.

Polymer	Preparation	Form	FR content (type) <sup>a</sup>	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	Thermal properties <sup>d</sup>					Reference.
							$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$X_c$ (%)	
PA6	Hydrolytic ROP	Bulk sample	0	4.7	n/a	5.80	220.7	175.5	n/a	70.0	30.0	[32]
1	Hydrolytic ROP	Bulk sample	0.15 wt% <sup>b</sup> (CEPPA)	5.6	n/a	3.90	219.4	175.2	n/a	70.0	30.0	
2	Hydrolytic ROP	Bulk sample	0.10 wt% <sup>b</sup> (DOPO-ITA)	8.6	n/a	3.80	219.6	173.3	n/a	69.0	30.0	
PA6	Melt spun, knitted	Fabric	0	n/a	n/a	n/a	219.6	180.0	n/a	n/a	n/a	
1	Melt spun, knitted	Fabric	0.15 wt% <sup>b</sup> (CEPPA)	n/a	n/a	n/a	219.7	185.3	n/a	n/a	n/a	
2	Melt spun, knitted	Fabric	0.10 wt% <sup>b</sup> (DOPO-ITA)	n/a	n/a	n/a	219.8	183.8	n/a	n/a	n/a	
PA6	Hydrolytic ROP	Bulk sample	0	2.19	1.75	1.76	221.3	182.7	n/a	71.7	37.6	[33]
3	Hydrolytic ROP	Bulk sample	4.0 wt% (DOPO-ITA)	1.60	1.29	2.87	218.3	174.3	n/a	64.4	33.8	
3	Hydrolytic ROP	Bulk sample	5.0 wt% (DOPO-ITA)	1.51	1.22	3.12	215.0	173.0	n/a	53.7	28.2	
PA6	Melt spun, knitted	Fabric	0	n/a	n/a	n/a	223.2	n/a	n/a	73.9	38.8	
3	Melt spun, knitted	Fabric	4.0 wt% (DOPO-ITA)	n/a	n/a	n/a	220.0	n/a	n/a	67.6	35.5	
3	Melt spun, knitted	Fabric	5.0 wt% (DOPO-ITA)	n/a	n/a	n/a	216.1	n/a	n/a	58.4	30.7	
PA6	Hydrolytic ROP	Bulk sample	0	2.18	1.73	1.75	221.6	182.3	47.9	71.0	n/a	[34]
4	Hydrolytic ROP	Bulk sample	4.0 wt% (DPPO-ITA)	1.72	1.36	1.95	218.6	179.3	42.2	68.8	n/a	
4	Hydrolytic ROP	Bulk sample	0.38% <sup>c</sup> (P)									
4	Hydrolytic ROP	Bulk sample	5.0 wt% (DPPO-ITA)	1.58	1.28	2.07	217.4	176.3	38.1	62.3	n/a	
4	Hydrolytic ROP	Bulk sample	0.47% <sup>c</sup> (P)									
PA6	Hydrolytic ROP	Bulk sample	0	n/a	2.16	n/a	215.8	n/a	n/a	n/a	n/a	[35]
5	Hydrolytic ROP	Bulk sample	1.5 wt% (PTCDA)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
5	Hydrolytic ROP	Bulk sample	2.0 wt% (PTCDA)	n/a	0.70	n/a	211.3	n/a	n/a	n/a	n/a	
PA66	Melt polycondensation	Bulk sample	0	2.17	1.87	1.36	260.4	221.1	n/a	65.7	34.6	[36]
6	Melt polycondensation	Bulk sample	4.0 wt% (DPPO-ITA)	1.57	1.35	2.57	251.9	210.7	n/a	52.5	27.6	
6	Melt polycondensation	Bulk sample	5.0 wt% (DPPO-ITA)	1.32	1.11	3.25	247.6	208.8	n/a	49.7	26.1	
PA66	Interfacial polymerization	Bulk sample	0	n/a	2.4	n/a	262.0	234.0	n/a	52.2	25.3	[37]
6	Interfacial polymerization	Bulk sample	10.0 mol% (DOPO-ITA-Cl)	n/a	1.2	n/a	230.0	197.0	n/a	44.2	21.5	
6	Interfacial polymerization	Bulk sample	2.20% <sup>b</sup> (P)									
6	Interfacial polymerization	Bulk sample	1.57% <sup>c</sup> (P)									
PA66r	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[38]
7	Melt polycondensation	Bulk sample	3.0 mol.% (TRFR salt)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
7	Melt polycondensation	Bulk sample	12.45% <sup>b</sup> (P)									
7	Melt polycondensation	Bulk sample	12.26% <sup>c</sup> (P)									
PA66	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	268.0	n/a	n/a	n/a	n/a	[39]
8	Melt polycondensation	Bulk sample	9.0 wt% (BCPPO)	n/a	n/a	n/a	258.0	n/a	n/a	n/a	n/a	
PA66	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	265.8	n/a	231.3	59.6	30.6	[40]
9	Melt polycondensation	Bulk sample	5.0 wt% (NENP salt)	n/a	n/a	n/a	250.0	n/a	219.6	50.3	25.8	
PA66	Melt polycondensation	Bulk sample	0	n/a	1.40	n/a	266.0	n/a	231.0	n/a	n/a	[41]
9	Melt polycondensation	Bulk sample	5.0 wt% (NENP)	n/a	1.38	n/a	250.0	n/a	219.0	n/a	n/a	
9	Melt polycondensation	Bulk sample	6.86% <sup>b</sup> (P)									
9	Melt polycondensation	Bulk sample	6.87% <sup>c</sup> (P)									
10	Melt polycondensation	Bulk sample	5.0 wt% (BNPO)	n/a	1.35	n/a	263.0	n/a	229.0	n/a	n/a	
10	Melt polycondensation	Bulk sample	7.83% <sup>b</sup> (P)									
10	Melt polycondensation	Bulk sample	7.73% <sup>c</sup> (P)									
11	Melt polycondensation	Bulk sample	5.0 wt% (DPPD)	n/a	1.33	n/a	235.0	n/a	190.0	n/a	n/a	
11	Melt polycondensation	Bulk sample	11.94% <sup>b</sup> (P)									
11	Melt polycondensation	Bulk sample	11.97% <sup>c</sup> (P)									
12	Melt polycondensation	Bulk sample	5.0 wt% (MCPO)	n/a	1.37	n/a	262.0	n/a	224.0	n/a	n/a	
12	Melt polycondensation	Bulk sample	6.25% <sup>b</sup> (P)									
12	Melt polycondensation	Bulk sample	6.24% <sup>c</sup> (P)									
PA66	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	265.0	n/a	231.0	59.6	n/a	[42]
13	Melt polycondensation	Bulk sample	4.5 wt% (PDPPD)	n/a	n/a	n/a	235.0	n/a	190.0	48.5	n/a	
13	Melt polycondensation	Bulk sample	11.94% <sup>b</sup> (P)									
13	Melt polycondensation	Bulk sample	11.97% <sup>c</sup> (P)									
PA66	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[43]
14	Melt polycondensation	Bulk sample	2.0 wt% (CEPPA)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
14	Melt polycondensation	Bulk sample	4.0 wt% (CEPPA)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
14	Melt polycondensation	Bulk sample	6.0 wt% (CEPPA)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
PA66	Melt polycondensation	Bulk sample	0	n/a	1.11	n/a	n/a	n/a	n/a	n/a	n/a	[44]
14	Melt polycondensation	Bulk sample	10.0 wt% (CEPPA)	n/a	1.73	n/a	n/a	n/a	n/a	n/a	n/a	
PA11	Commercial	Bulk sample	0	n/a	n/a	n/a	194	150	52	44	n/a	[45]
PA11	Melt polycondensation	Bulk sample	0	n/a	n/a	n/a	160	114	39	32	n/a	
15	Melt polycondensation	Bulk sample	5.5 wt% (DOPO-ITA)	n/a	n/a	n/a	157	115	41	31	n/a	
15	Melt polycondensation	Bulk sample	0.5 wt% <sup>b</sup> (P)									
15	Melt polycondensation	Bulk sample	7.7 wt% (DOPO-ITA)	n/a	n/a	n/a	158	121	42	34	n/a	
15	Melt polycondensation	Bulk sample	0.7 wt% <sup>b</sup> (P)									
15	Melt polycondensation	Bulk sample	11.0 wt% (DOPO-ITA)	n/a	n/a	n/a	155	120	41	35	n/a	
15	Melt polycondensation	Bulk sample	1.0 wt% <sup>b</sup> (P)									

<sup>a</sup> Referred to the theoretical amount of an additive, unless otherwise indicated.

<sup>b</sup> Referred to the theoretical amount of phosphorus.

<sup>c</sup> Experimental amount of phosphorus from elemental analysis.

<sup>d</sup> derived from DSC.

**Table 2**  
TGA and UL-94 tests results for aliphatic FR PAs.

Polymer <sup>a</sup>	FR content, type	Cotton indicator ignited by melt drips	Flame extinction (s)	Burning distance (10 <sup>-2</sup> × m)	UL-94 rating <sup>f</sup>	LOI (%)	Thermal properties <sup>g</sup>			Reference
							T <sub>5%</sub> (°C)	T <sub>max</sub> (°C)	Char residue (%) at [T (°C)]	
PA6	0	n/a	n/a	n/a	n/a	n/a	423 <sup>h,i</sup>	n/a	1.7 [600] <sup>i</sup>	[32]
1	0.15 wt% <sup>d</sup> (CEPPA)	n/a	n/a	n/a	n/a	n/a	392 <sup>h,i</sup>	n/a	1.9 [600] <sup>i</sup>	
2	0.10 wt% <sup>d</sup> (DOPO-ITA)	n/a	n/a	n/a	n/a	n/a	409 <sup>h,i</sup>	n/a	3.1 [600] <sup>i</sup>	
PA6 <sup>b</sup>	0	n/a	n/a	n/a	n/a	23.2	n/a	n/a	n/a	[33]
1 <sup>b</sup>	0.15 wt% <sup>d</sup> (CEPPA)	no	<2	3	V-0	35.6	n/a	n/a	n/a	
2 <sup>b</sup>	0.10 wt% <sup>d</sup> (DOPO-ITA)	no	2	3–4	V-0	35.8	n/a	n/a	n/a	
PA6	0	yes	n/a	n/a	V-2 (3.2)	23.5 ± 0.2	388 <sup>h,i,j</sup>	452 <sup>i,j</sup>	0.34 [600] <sup>i,j</sup>	[33]
									0.11 [700] <sup>i,j</sup>	
									5.87 [600] <sup>i,j</sup>	
3	4.0 wt% (DOPO-ITA)	no	n/a	n/a	V-0 (3.2)	31.6 ± 0.2	375 <sup>h,i,j</sup>	422 <sup>i,j</sup>	1.03 [700] <sup>i,j</sup>	[33]
3	5.0 wt% (DOPO-ITA)	no	n/a	n/a	V-0 (3.2)	33.7 ± 0.2	372 <sup>h,i,j</sup>	420 <sup>i,j</sup>	6.43 [600] <sup>i,j</sup>	
									1.25 [700] <sup>i,j</sup>	
PA6 <sup>b</sup>	0	yes	5.3	12.3	n/a	22.1 ± 0.2	n/a	n/a	n/a	[34]
3 <sup>b</sup>	4.0 wt% (DOPO-ITA)	yes	2.1	6.1	n/a	27.1 ± 0.2	n/a	n/a	n/a	
3 <sup>b</sup>	5.0 wt% (DOPO-ITA)	no	1.7	5.2	n/a	28.4 ± 0.2	n/a	n/a	n/a	
PA6	0	yes	n/a	n/a	V-2 (3.2)	23.3 ± 0.1	380 <sup>i</sup>	450 <sup>i</sup>	0.1 [700] <sup>i</sup>	[34]
							380	453	0.1 [700]	
4	4.0 wt% (DPPPO-ITA)	no	n/a	n/a	V-0 (3.2)	30.1 ± 0.1	370 <sup>i</sup>	414 <sup>i</sup>	1.4 [700] <sup>i</sup>	
4	0.38% <sup>c</sup> (P)						373	423	2.7 [700]	[34]
4	5.0 wt% (DPPPO-ITA)	no	n/a	n/a	V-0 (3.2)	31.7 ± 0.1	369 <sup>i</sup>	413 <sup>i</sup>	1.9 [700] <sup>i</sup>	
	0.47% <sup>e</sup> (P)						369	417	3.3 [700]	
PA6	0	n/a	7.8	n/a	V-2	n/a	n/a	n/a	n/a	[35]
5	1.5 wt% (PTCDA)	n/a	2.5	n/a	V-1	n/a	n/a	n/a	n/a	
5	2.0 wt% (PTCDA)	n/a	1.9	n/a	V-1	n/a	n/a	n/a	n/a	
PA66	0	yes	n/a	n/a	V-2 (3.2)	23.7 ± 0.2	397 <sup>i,j</sup>	462 <sup>i,j</sup>	3.75 [600] <sup>i,j</sup>	[36]
									0.19 [800] <sup>i,j</sup>	
6	4.0 wt% (DPPPO-ITA)	no	n/a	n/a	V-0 (3.2)	30.5 ± 0.2	378 <sup>i,j</sup>	417 [1 stage] <sup>i,j</sup>	5.93 [600] <sup>i,j</sup>	
6								459 [2 stage] <sup>i,j</sup>	0.88 [800] <sup>i,j</sup>	[36]
6	5.0 wt% (DPPPO-ITA)	no	n/a	n/a	V-0 (3.2)	33.2 ± 0.2	371 <sup>i,j</sup>	410 [1 stage] <sup>i,j</sup>	7.05 [600] <sup>i,j</sup>	
PA66	0	n/a	n/a	n/a	no rating	21.0	344 <sup>i,k</sup>	385 [1 stage] <sup>i,k</sup>	1.16 [800] <sup>i,j</sup>	[37]
								461 [2 stage] <sup>i,j</sup>	1.6 [800] <sup>i,k</sup>	
								431 [2 stage] <sup>i,k</sup>		
6	10.0 mol% (DOPO-ITA-Cl)	n/a	n/a	n/a	V-1 (3.2)	29.5	319 <sup>i,k</sup>	483 [3 stage] <sup>i,k</sup>	7.6 [800] <sup>i,k</sup>	[37]
	2.20% <sup>d</sup> (P)							387 [1 stage] <sup>i,k</sup>		
	1.57% <sup>e</sup> (P)							416 [2 stage] <sup>i,k</sup>		
PA66	0	yes	5	n/a	V-2	24.0	n/a	n/a	n/a	[38]
7	3.0 mol.% (TRFR salt)	no	8	n/a	V-0	29.0	n/a	n/a	n/a	
	12.45% <sup>d</sup> (P)							519 [3 stage] <sup>i,k</sup>		
PA66	0	n/a	n/a	n/a	V-2 (1.6)	22.3	382 <sup>h,i</sup>	431 <sup>i</sup>	3.9 [550]	[39,46,47]
			88.0 (3.2 mm)	n/a	V-2 (3.2)		396 <sup>h</sup>	444		
							415 <sup>h,k</sup>	459 <sup>k</sup>		
8	9.0 wt% (BCPPO)	n/a	10.3 (1.6 mm)	n/a	V-0 (1.6)	27.2	431 <sup>h,m</sup>	475 <sup>m</sup>	8.9 [550]	[39,46,47]
			26.7 (3.2 mm)	n/a	V-0 (3.2)		380 <sup>h,i</sup>	433 <sup>i</sup>	10.6 [550]	
							394 <sup>h</sup>	453		
PA66	0	yes	6	n/a	V-2 (3.2)	23.0	411 <sup>h,k</sup>	464 <sup>k</sup>		[40]
9	5.0 wt% (NENP salt)	no	7	n/a	V-0 (3.2)	28.0	425 <sup>h,m</sup>	477 <sup>m</sup>		
							385	437	n/a	
PA66	0	yes	3	n/a	V-2 (n/a)	24.0	347	456 [1 stage]	n/a	[41]
9	5.0 wt% (NENP)	no	7	n/a	V-0 (n/a)	28.0	347	456	n/a	
	6.86% <sup>d</sup> (P)							480 [2 stage]		
10	5.0 wt% (BNPO)	no	6	n/a	V-0 (n/a)	26.0	385	437	n/a	[41]
	7.83% <sup>d</sup> (P)									
	7.73% <sup>e</sup> (P)									
11	5.0 wt% (DPPD)	no	5	n/a	V-0 (n/a)	29.0	338	471	n/a	[41]
	11.94% <sup>d</sup> (P)									
	11.97% <sup>e</sup> (P)									
12	5.0 wt% (MCPO)	no	6	n/a	V-0 (n/a)	27.0	410	474	n/a	[42]
	6.25% <sup>d</sup> (P)									
	6.24% <sup>e</sup> (P)									
PA66	0	yes	5	n/a	V-2 (3.2)	24.0	385	437	n/a	[42]
13	5.0 wt% (PDPPD)	no	8	n/a	V-0 (3.2)	29.0	338	471	n/a	
	11.94% <sup>d</sup> (P)									
PA66	0	yes	n/a	n/a	V-2 (3.0)	24.0	397	443 [1 stage]	1.55 [600]	[43]
14	2.0 wt% (CEPPA)	no	n/a	n/a	V-0 (3.0)	25.8	367		3.26 [600]	

(continued on next page)



Table 2 (continued)

Polymer <sup>a</sup>	FR content, type	Cotton indicator ignited by melt drips	Flame extinction (s)	Burning distance (10 <sup>-2</sup> × m)	UL-94 rating <sup>f</sup>	LOI (%)	Thermal properties <sup>g</sup>			Reference
							T <sub>5%</sub> (°C)	T <sub>max</sub> (°C)	Char residue (%) at [T (°C)]	
<b>14</b>	4.0 wt% (CEPPA)	no	n/a	n/a	V-0 (3.0)	27.0	360	404 [1 stage] 456 [2 stage] 399 [1 stage] 459 [2 stage]	3.72 [600]	[44]
<b>14</b>	6.0 wt% (CEPPA)	no	n/a	n/a	V-0 (3.0)	28.0	346	387 [1 stage] 458 [2 stage]	4.07 [600]	
PA66	0	n/a	n/a	n/a	n/a	22.0	364 <sup>l</sup> 369 389 <sup>k</sup> 406 <sup>m</sup>	432 <sup>l</sup> 440 451 <sup>k</sup> 465 <sup>m</sup>	n/a	
<b>14</b>	10.0 wt% (CEPPA)	n/a	n/a	n/a	n/a	27.0	310 <sup>l</sup> 323 339 <sup>k</sup> 354 <sup>m</sup>	435 <sup>l</sup> 439 457 <sup>k</sup> 470 <sup>m</sup>	n/a	
PA11 <sup>c</sup>	0	n/a	n/a	n/a	V-2	22.0	n/a	n/a	n/a	[45]
PA11	0	n/a	n/a	n/a	no rating	n/a	407	n/a	n/a	
<b>15</b>	5.5 wt% (DOPO-ITA)	no	n/a	n/a	V-0	28.0	393	n/a	n/a	
<b>15</b>	0.5 wt% <sup>d</sup> (P)									
<b>15</b>	7.7 wt% (DOPO-ITA)	no	n/a	n/a	V-0	n/a	n/a	n/a	n/a	
<b>15</b>	0.7 wt% <sup>d</sup> (P)									
<b>15</b>	11.0 wt% (DOPO-ITA)	no	n/a	n/a	V-0	40.0–45.0	387	n/a	n/a	
	1.0 wt% <sup>d</sup> (P)									

<sup>a</sup> a bulk sample, unless otherwise indicated.<sup>b</sup> a fabric sample.<sup>c</sup> commercial.<sup>d</sup> Referred to the theoretical amount of phosphorus.<sup>e</sup> Experimental amount of phosphorus from elemental analysis.<sup>f</sup> where available, sample thickness in cm is indicated in parentheses.<sup>g</sup> TGA data, obtained applying 10 K min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere unless stated otherwise.<sup>h</sup> temperature at the onset of the first stage of the thermal weight loss.<sup>i</sup> under air atmosphere.<sup>j</sup> Obtained applying 15 K min<sup>-1</sup> heating rate.<sup>k</sup> Obtained applying 20 K min<sup>-1</sup> heating rate.<sup>l</sup> Obtained applying 5 K min<sup>-1</sup> heating rate.<sup>m</sup> Obtained applying 40 K min<sup>-1</sup> heating rate.

from 2 to 5 wt% and resulted in polyamides with different properties [33]. Specifically, increase of the FR-additive loading decreased molecular weight of FR polymers and broadened molecular weight distribution. The authors explained the reduction of  $M_n$  with the bulkiness of DOPO-substituent that hindered polymerization, due to a decrease in reactivity of the vicinal carboxylic group that eventually hampered propagation of polymerization. As a result, mechanical properties of melt-spun fibers using FR PAs **3** were inferior to samples made of pristine PA6. On the contrary, FR PAs **3** with the highest P content (4 and 5 wt% of DOPO-ITA respectively) achieved V-0 rating according UL-94 standard and high LOI values of 31.6% and 33.7% respectively. In relation to pristine PA6, FR PAs **3** (5% of DOPO-ITA) showed lower FOT, decreased pHRR and THR by 13.93% and 24.44% correspondingly. Fabrics knitted using FR PA **3** with the highest P-content showed the best flame retardancy among other samples, attaining LOI of 28.4%. Melt dripping was not suppressed, but it did not ignite a cotton indicator.

Replacement of the DOPO-ITA salt with DPPO-based analogue (DPPO-ITA) resulted in FR PAs **4** with properties rather similar to those reported for DOPO-ITA-based FR congeners **3** [34]. Consistently, increase of P-content lead to lower molecular weight polymers, while FR properties were improved. PAs **4** containing 4 and 5 wt% of the DPPO-ITA achieved V-0 rating according in UL-94 test and the highest LOI values of 30.1% and 31.7% respectively. Finally, FR PA **4** (5 wt% of the DPPO-ITA) demonstrated decreased pHRR and THR, as compared to pure PA6. Nevertheless, comparison of MCC experiments' results for FR PAs **3** and **4** (5 wt% of the DOPO-ITA and DPPO-ITA respectively) suggested that DOPO-substituent had advantage over DPPO-based congener. Notably, DPPO-based FR co-

monomers were reported to as act as gas-phase FRs, whilst DOPO-based analogues were ascribed to perform in both gas- and condensed-phases [33,34].

Zhang reported that introduction P-free PTCDA above 1.5 wt% in polymerization of  $\epsilon$ -caprolactam results in a family of PAs **5** with improved FR properties [35]. Similarly to P-containing additives, increase of a feed fraction of PTCDA lead to a decrease in average molecular weight of a co-polyamide and disrupted regularity of hydrogen bonding, therefore leading to poorer mechanical properties as opposed to unmodified PA6. Nevertheless, addition of 2 wt % of PTCDA brought about a reduction of THR by 21.3% as compared to virgin PA6, yet none of the investigated co-polyamides could achieve V-0 rating in UL-94 vertical burning test.

### 3.2. PA66 copolymers

PA66 is another widely used aliphatic PA usually derived either through polycondensation of adipic acid or adipoyl chloride with 1,6-hexamethylenediamine or through direct melt condensation of preliminary prepared HMDAA (Scheme 3) [5,7]. Analogous synthetic approaches are used to introduce FR co-monomers into macromolecular backbone of PA6; the reactive FR additives are either P-containing diacids or diamines used as salts with corresponding organic diamides or diacids suitable for the polymerization conditions (see Figs. 2–4).

Li described preparation of FR co-polyamides **6**, employing 1,6-hexamethylenediammonium salt of DOPO-ITA as a FR additive that was co-polymerized with HMDAA [36]. The content of DOPO-ITA ranged from 2 to 5 wt%, resulting in a family of FR PA66 with different properties. Increase of DOPO-ITA fraction in the

**Table 3**

Preparation, selected molecular and thermal properties of semiaromatic FR PAs.

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties <sup>a</sup>				LOI (%) <sup>c</sup>	Reference
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
16	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	16.1	37.8	2.3	151	283	340	n/a	42.3 [800]	34.4	[48]
17	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	33.7	146.4	4.3	157	176	206	n/a	55.7 [800]	39.8	
18	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	25.6	123.2	4.8	138	207	284	n/a	43.3 [800]	34.8	
19	TPP, Py, NMP, LiCl, Δ	19.8	35.5	1.8	201	n/a	388	n/a	45.0 [700]	35.5	[49]
20	TPP, Py, NMP, LiCl, Δ	19.0	32.5	1.7	195	n/a	375	n/a	43.5 [700]	34.9	
21	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	195	n/a	410	n/a	28.0 [800]	29.0	[50]
22	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	184	n/a	427	n/a	35.0 [800]	32.0	
23	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	220	310	383	n/a	20.0 [800]	26.0	[51]
24	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	180	289	382	n/a	56.0 [600]	40.0	[52]
25	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	234	n/a	428	n/a	36.0 [800]	32.0	[53]
26	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	226	n/a	419	n/a	39.0 [800]	33.0	
27	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	211	290	336	n/a	41.0 [750]	34.0	[54]
28	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	204	284	330	n/a	29.0 [750]	29.0	
29	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	230	n/a	400	n/a	42.0 [700]	34.3	[55]
30	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	195	n/a	385	n/a	43.0 [700]	34.7	
31	Using diacylchloride, NMP, PO	n/a	n/a	n/a	n/a	195	365 <sup>b</sup>	385 <sup>b</sup>	50.0 [650] <sup>b</sup>	37.5	[56]
32	Using diacylchloride, NMP, PO	n/a	n/a	n/a	n/a	186	353 <sup>b</sup>	380 <sup>b</sup>	47.0 [650] <sup>b</sup>	36.3	
33	Using diacylchloride, NMP, Et <sub>3</sub> N	n/a	n/a	n/a	184	n/a	320 <sup>b</sup>	425 <sup>b</sup>	38.0 [600] <sup>b</sup>	32.7	[57]
34	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	n/a	n/a	n/a	65.0 [600]	43.5	[58]
34	CuI, DMEDA, K <sub>2</sub> CO <sub>3</sub> , DMF, Δ	0.46	0.56	1.21	196	n/a	364	n/a	67.4 [600]	44.5	[59]
36	CuI, DMEDA, K <sub>2</sub> CO <sub>3</sub> , DMF, Δ	n/a	n/a	n/a	260	n/a	417	n/a	61.1 [600]	41.9	
37	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	2.6	n/a	1.29	>300	n/a	372	n/a	54.5 [800]	39.9	[60]
38	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	2.4	n/a	1.23	>300	n/a	383	n/a	40.2 [800]	33.6	
39	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	2.6	n/a	1.26	>300	n/a	438	n/a	48.2 [800]	36.8	
40	Using diacylchloride TMSCl, NMP, LiCl	2.08	2.91	1.40	186	n/a	426	490	45.0 [600]	27.0 <sup>d</sup>	[61]
41	Using diacylchloride TMSCl, NMP, LiCl	2.17	2.96	1.36	181	n/a	417	478	43.0 [600]	26.5 <sup>d</sup>	
42	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	135	289	361	375	47.0 [800]	35.5	[62]
43	Using diisocyanate, TBAB, MW	n/a	n/a	n/a	124	336	365	364	45.0 [800]	35.5	
42	Using diisocyanate, DIPIB, MW	n/a	n/a	n/a	n/a	355	415	375	47.0 [800]	36.0	[63]
42	Using diisocyanate, DIPIB, Δ	n/a	n/a	n/a	135	355	410	388	47.0 [800]	36.0	
43	Using diisocyanate, DIPIB, MW	n/a	n/a	n/a	n/a	363	392	410	49.0 [800]	37.0	
43	Using diisocyanate, DIPIB, Δ	n/a	n/a	n/a	120	363	388	400	45.0 [800]	35.0	
44	Using diisocyanate, NMP, DBTDL, MW	n/a	n/a	n/a	170	283	296	n/a	27.0 [800]	28.0	[64]
44	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	200	315	380	n/a	27.0 [800]	28.3	[65]
44	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	180	315	380	n/a	27.0 [800]	28.0	[66]
46	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	135	276	293	n/a	12.0 [800]	22.0	[67]
46	Using diisocyanate, NMP, DBTDL, MW	n/a	n/a	n/a	n/a	230	282	n/a	6.0 [800]	20.0	
47	Using diisocyanate, TBAB, MW	n/a	n/a	n/a	128	n/a	n/a	n/a	n/a	n/a	
48	SNAr-polymerization, K <sub>2</sub> CO <sub>3</sub> , NMP, Δ	6.00	12.6	2.10	196, 211 <sup>a</sup>	405	n/a	432	28.3 [800]	34.0 <sup>d</sup>	[68]
49	SNAr-polymerization, K <sub>2</sub> CO <sub>3</sub> , NMP, Δ	7.90	15.6	1.97	170, 186 <sup>a</sup>	417	n/a	472	7.5 [800]	30.0 <sup>d</sup>	
50	SNAr-polymerization, K <sub>2</sub> CO <sub>3</sub> , NMP, Δ	9.40	17.2	1.83	157, 171 <sup>a</sup>	441	n/a	476	4.1 [800]	n/a	
51	SNAr-polymerization, K <sub>2</sub> CO <sub>3</sub> , NMP, Δ	1.05	2.02	1.92	146, 160 <sup>a</sup>	442	n/a	482	2.3 [800]	n/a	
52	SNAr-polymerization, K <sub>2</sub> CO <sub>3</sub> , NMP, Δ	8.6	19.9	2.31	134, 151 <sup>a</sup>	443	n/a	483	0.9 [800]	n/a	

<sup>a</sup> TGA data, obtained applying 10 K min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere unless stated otherwise.<sup>b</sup> Under air atmosphere.<sup>c</sup> Unless otherwise indicated, assessed from the respective char yield, using Van Krevelen-Hoftyzer equation: LOI = 17.5 + 0.4CR, where CR – char yield.<sup>d</sup> Experimental values.

polymer lead to a gradual decrease in average molecular weight and higher PDI, thereby bringing about lower  $T_m$ ,  $T_c$ ,  $X_c$ , and worse mechanical properties. The deterioration of the polymers properties was explained with the steric effect of DOPO-ITA on one hand and possible branching of the main PA chain on the other hand. However, the incorporation of the P-endowed diacid improved flame retardancy. The FR copolymers **6** containing 4 and 5 wt% of DOPO-ITA respectively exhibited the best FR properties, attaining high LOI values above 30% and V-0 rating in UL-94 burning test. In addition, pHRR and THR of PA **6** (5 wt% of DOPO-ITA) decreased by 19.27% and 24.66% respectively as compared to pristine PA66 samples. Notably, DOPO-ITA-endowed co-polyamides exhibited flame retardancy both in gas- and condensed phases, that correlates well results for PA6 [33].

Ge reported interfacial polymerization methodology to synthesize a similar family of FR PA66 **6** incorporating DOPO-ITA unit

[37]. A mixture of adipoyl chloride and DOPO-ITA acyl dichloride (DOPO-ITA-Cl, 2.5–10 wt%) and 1,6-hexanediamine in a biphasic system was used for polymerization. Like **6**, polymers derived through melt polycondensation, molecular weights,  $T_c$ ,  $T_m$  and  $X_c$  were lower when P-content increased. Conversely, FR properties of the final FR PAs were improved when more DOPO-ITA-Cl was added. However, none of the investigated samples attained V-0 rating in UL-94 burning test. The FR PA **6**, containing 1.57% of P (NMR-based assessment), realized the highest LOI of 29.5%, while pHRR was reduced by 47.8% as compared to the virgin PA66. FR PA **6** also generated more char residues (7.6% at 800 °C, at 20 °C/min heating rate).

Fu revealed preparation FR PA66 **7** that incorporate a “trinity” FR reactive additive. The P-containing monomer was derived in a consecutive reaction of pentaerythritol with phosphoryl chloride, followed by grafting *p*-aminobenzoic acid units [38] The FR diacid

**Table 4**  
Preparation, selected molecular and thermal properties of aromatic FR PAs.

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties (TGA data) <sup>a</sup>				LOI (%) <sup>c</sup>	Reference.
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
53	Using diisocyanate, TBAB, MW	n/a	n/a	n/a	148	376	436	427	45.0 [800]	36.3	[62]
54	Using diisocyanate, TEA, TBAB, MW	n/a	n/a	n/a	186	403	440	420	47.0 [800]	36.3	
53	Using diisocyanate, DIPIB, MW	n/a	n/a	n/a	n/a	402	446	429	58.0 [800]	41.0	[63]
53	Using diisocyanate, DIPIB, Δ	n/a	n/a	n/a	155	407	448	430	63.0 [800]	43.0	
54	Using diisocyanate, DIPIB, MW	n/a	n/a	n/a	n/a	394	428	419	50.0 [800]	37.0	
54	Using diisocyanate, DIPIB, Δ	n/a	n/a	n/a	180	391	428	417	52.0 [800]	38.0	
55	Using diisocyanate, TBAB, MW	n/a	n/a	n/a	166	n/a	n/a	n/a	n/a	n/a	[67]
56	Using diisocyanate, TBAB, MW	n/a	n/a	n/a	195	302	361	n/a	28.0 [800]	29.0	
56	Using diisocyanate, NMP, MW	n/a	n/a	n/a	n/a	250	299	n/a	28.0 [800]	29.0	
61	TPP, DIPIB, MW	n/a	n/a	n/a	202	404	455	n/a	45.0 [800]	35.5	[69]
63	TPP, DIPIB, MW	n/a	n/a	n/a	208	410	410	n/a	50.0 [800]	37.5	
70	Using diisocyanate, NMP, DBTDL, MW	n/a	n/a	n/a	180	354	385	n/a	35.0 [800]	31.0	[64]
70	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	238	363	371	n/a	29.0 [800]	29.1	[65]
70	Using diisocyanate, TBAB, DBTDL, MW	n/a	n/a	n/a	200	363	371	n/a	29.0 [800]	29.0	[66]
65	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	168	400	452	n/a	68.0 [800]	44.7	[70]
65	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	400	451	n/a	66.0 [800]	43.5	
72	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	155	348	385	n/a	56.0 [800]	39.9	
72	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	351	386	n/a	58.0 [800]	40.7	
65	DIPIB, TPP, MW	n/a	n/a	n/a	168	400	451	n/a	68.0 [800]	45.0	[71]
65	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	n/a	400	451	n/a	66.0 [800]	44.0	
72	DIPIB, TPP, MW	n/a	n/a	n/a	155	348	385	n/a	56.0 [800]	40.0	
72	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	n/a	351	386	n/a	58.0 [800]	41.0	
65	DIPIB, TPP, MW	n/a	n/a	n/a	168	400	451	n/a	68.0 [800]	44.7	[72]
65	DIPIB, TPP, Δ	n/a	n/a	n/a	n/a	408	462	n/a	69.0 [800]	45.1	
72	DIPIB, TPP, MW	n/a	n/a	n/a	155	348	385	n/a	56.0 [800]	39.9	
72	DIPIB, TPP, Δ	n/a	n/a	n/a	n/a	351	386	n/a	59.0 [800]	41.1	
73	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	201	406	434	n/a	52.0 [800]	38.3	[73]
74	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	212	459	478	n/a	54.0 [800]	39.1	
75	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	195	395	420	n/a	41.0 [800]	33.9	
76	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	196	398	422	n/a	41.0 [800]	33.9	
77	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	191	348	411	n/a	38.0 [800]	32.7	
78	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	192	387	418	n/a	38.0 [800]	32.7	
79	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	206	400	400	n/a	48.0 [800]	36.7	
80	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	195	391	391	n/a	39.0 [800]	33.1	
82	DPIB, TPP, Δ	n/a	n/a	n/a	225	n/a	n/a	n/a	n/a	70	[74]
84	DPIB, TPP, Δ	n/a	n/a	n/a	197	n/a	n/a	n/a	n/a	68	
85	DPIB, TPP, Δ	n/a	n/a	n/a	236	n/a	n/a	n/a	n/a	67	
86	DPIB, TPP, Δ	n/a	n/a	n/a	212	n/a	n/a	n/a	n/a	65	
94	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	183	300	341	n/a	54.0 [800]	39.1	[75]
95	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	185	356	385	n/a	56.0 [800]	39.9	
94	DPIB, TPP, MW	n/a	n/a	n/a	183	339	352	n/a	58.0 [800]	40.7	[76]
94	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	n/a	300	341	n/a	54.0 [800]	39.1	
95	DPIB, TPP, MW	n/a	n/a	n/a	185	315	346	n/a	42.0 [800]	34.3	
95	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	n/a	356	385	n/a	56.0 [800]	39.9	
94	DPIB, TPP, MW	n/a	n/a	n/a	183	339	352	n/a	58.0 [800]	40.7	[77]
95	DPIB, TPP, MW	n/a	n/a	n/a	185	315	346	n/a	42.0 [800]	34.3	
101	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	169	415	430	n/a	62.0 [800]	42.3	[78]
103	TPP, Py, NMP, CaCl <sub>2</sub> , MW	n/a	n/a	n/a	179	468	488	n/a	63.0 [800]	42.7	
104	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	6.9 [700] <sup>f</sup>	19.7	[79]
105	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	17.2 [700] <sup>f</sup>	23.8	
106	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.6 [700] <sup>f</sup>	18.4	
107	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	11.9 [700] <sup>f</sup>	21.7	
108	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	6.0 [700] <sup>f</sup>	19.4	
109	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4.0 [700] <sup>f</sup>	18.5	
110	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.7 [700] <sup>f</sup>	18.4	
111	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	6.3 [700] <sup>f</sup>	19.5	
112	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.3 [700] <sup>f</sup>	19.1	
113	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	7.0 [700] <sup>f</sup>	19.7	
114	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.8 [700] <sup>f</sup>	18.5	
115	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.1 [700] <sup>f</sup>	20.2	
118	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	306	390	405	n/a	46.0 [800]	35.9	[80]
						385 <sup>b</sup>	405 <sup>b</sup>				
119	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	293	380	400	n/a	50.0 [800]	37.5	
						380 <sup>b</sup>	400 <sup>b</sup>				
120	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	375	400	420	n/a	50.0 [800]	37.5	
						390 <sup>b</sup>	415 <sup>b</sup>				
121	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	345	385	415	n/a	48.0 [800]	36.7	
						365 <sup>b</sup>	400 <sup>b</sup>				
122	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	295	380	415	n/a	53.0 [800]	38.7	
						380 <sup>b</sup>	410 <sup>b</sup>				



Table 4 (continued)

Polymer	Synthesis	M <sub>n</sub> (10 <sup>4</sup> × g mol <sup>-1</sup> )	M <sub>w</sub> (10 <sup>4</sup> × g mol <sup>-1</sup> )	PDI	T <sub>g</sub> (°C)	Thermal properties (TGA data) <sup>a</sup>				LOI (%) <sup>e</sup>	Reference.
						T <sub>5%</sub> (°C)	T <sub>10%</sub> (°C)	T <sub>max</sub> (°C)	Char residues (%) at [T (°C)]		
123	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	265 <sup>c</sup> 265 <sup>b,c</sup>	n/a	n/a	58.0 [700]	40.7	[81]
124	From 114: DMSO, Cs <sub>2</sub> CO <sub>3</sub>	n/a	n/a	n/a	n/a	265 <sup>c</sup> 260 <sup>b,c</sup>	n/a	n/a	51.0 [700]	37.9	
125	From 115: NaBH <sub>4</sub> , DMA	n/a	n/a	n/a	n/a	255 <sup>c</sup> 260 <sup>b,c</sup>	n/a	n/a	59.0 [700]	41.1	
126	From 115: malononitrile, DMF	n/a	n/a	n/a	n/a	280 <sup>c</sup> 280 <sup>b,c</sup>	n/a	n/a	58.0 [700]	40.7	
127	From 115: NH <sub>2</sub> OH·HCl, DMF	n/a	n/a	n/a	n/a	255 <sup>c</sup> 255 <sup>b,c</sup>	n/a	n/a	60.0 [700]	41.5	
128	From 115: NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> O, DMF	n/a	n/a	n/a	n/a	260 <sup>c</sup> 260 <sup>b,c</sup>	n/a	n/a	47.0 [700]	36.3	
129	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	2.0	4.4	2.20	208	370	400	n/a	44.0 [800]	35.1	[82]
130	TBAB, TPP, Δ	n/a	n/a	n/a	248	496	502	n/a	59.0 [800]	41.1	[83]
131	TBAB, TPP, Δ	n/a	n/a	n/a	223	418	448	n/a	53.0 [800]	38.7	
132	TBAB, TPP, Δ	n/a	n/a	n/a	234	439	476	n/a	54.0 [800]	39.1	
133	TBAB, TPP, Δ	n/a	n/a	n/a	240	465	492	n/a	56.0 [800]	39.9	
134	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.8 [890] <sup>f</sup>	18.5	[84]
135	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	25.8 [890] <sup>f</sup>	27.3	
136	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.8 [890] <sup>f</sup>	18.5	
137	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	21.7 [890] <sup>f</sup>	25.7	
138	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.2 [890] <sup>f</sup>	18.3	
139	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	6.2 [890] <sup>f</sup>	19.5	
140	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	35.6 [890] <sup>f</sup>	31.2	
141	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	10.4 [890] <sup>f</sup>	21.2	
142	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.6 [890] <sup>f</sup>	19.2	
143	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.1 [890] <sup>f</sup>	19	
144	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	36.8 [890] <sup>f</sup>	31.7	
145	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	23.6 [890] <sup>f</sup>	26.4	
146	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	24.4 [890] <sup>f</sup>	26.8	
147	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	18.8 [890] <sup>f</sup>	24.5	
148	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	19.5 [890] <sup>f</sup>	24.8	[85]
149	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	11.7 [890] <sup>f</sup>	21.8	
150	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	33.5 [890] <sup>f</sup>	30.4	
151	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	20.3 [890] <sup>f</sup>	25.1	
152	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	27.8 [890] <sup>f</sup>	28.1	
153	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	30.9 [890] <sup>f</sup>	29.4	
154	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	32.2 [890] <sup>f</sup>	29.4	
155	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	29.0 [890] <sup>f</sup>	25.6	
156	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	30.9 [890] <sup>f</sup>	29.4	
157	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	15.2 [890] <sup>f</sup>	23.1	
158	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	34.5 [890] <sup>f</sup>	30.8	
159	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	27.2 [890] <sup>f</sup>	27.9	
160	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	18.7 [890] <sup>f</sup>	24.5	
161	Using diacylchloride, dioxane, H <sub>2</sub> O)))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	33.2 [890] <sup>f</sup>	30.3	
162	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	275	424	444	n/a	53.0 [800]	39	[86]
163	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	377	412	n/a	59.0 [800]	41	
164	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	396	434	n/a	65.0 [800]	43	
165	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	384	401	n/a	53.0 [800]	39	
166	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	170	380	410	n/a	45.0 [800]	35.5	[87]
167	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	175	370	400	n/a	57.0 [800]	40.3	
168	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	180	360	390	n/a	44.0 [800]	35.1	
169	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	180	375	400	n/a	53.0 [800]	38.7	
170	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	160	380	410	n/a	58.0 [800]	40.7	
171	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	170	370	408	n/a	63.0 [800]	42.7	
172	TPP, Py, DMF, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	175	380	410	n/a	59.0 [800]	41.1	
173	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	323	525	553	n/a	57.0 [800]	39	[88]
174	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	520	550	n/a	54.0 [800]	43	
175	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	320	514	551	n/a	53.0 [800]	41	
176	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	332	496	524	n/a	49.0 [800]	43	
177	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	318	511	549	n/a	52.0 [800]	44	
178	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	316	500	551	n/a	60.0 [800]	40	
179	TPP, Py, NMP, LiCl, Δ	2.73	4.93	1.81	240	n/a	390	n/a	58.0 [700]	40.7	[49]
180	TPP, Py, NMP, LiCl, Δ	2.64	5.02	1.90	268	n/a	402	n/a	58.0 [700]	40.7	
181	TPP, Py, NMP, LiCl, Δ	2.56	4.81	1.88	247	n/a	338	n/a	49.0 [700]	37.1	
182	TPP, Py, NMP, LiCl, Δ	2.56	4.81	1.88	247	n/a	390	n/a	66.3 [700]	44.0	
183	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	264	n/a	438	n/a	41.0 [800]	34.0	[50]
184	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	277	n/a	467	n/a	55.0 [800]	39.0	
185	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	254	n/a	455	n/a	51.0 [800]	38.0	
186	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	269	n/a	480	n/a	61.0 [800]	42.0	

(continued on next page)

Table 4 (continued)

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties (TGA data) <sup>a</sup>				LOI (%) <sup>e</sup>	Reference.
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
187	TPP, TBAB, $\Delta$	n/a	n/a	n/a	n/a	174	315	n/a	61.0 [800]	41.9	[89]
188	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	304	n/a	n/a	n/a	n/a	25.2	[90]
189	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	325	n/a	n/a	n/a	n/a	35.8	
190	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	304	n/a	n/a	n/a	n/a	33.6	
191	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	43.5	
192	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	36.8	
193	Using diacylchloride, dioxane, $\text{H}_2\text{O}$ ))	n/a	n/a	n/a	200	n/a	n/a	n/a	n/a	41.5	
188	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	24.4	
189	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	29.5	
190	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	23.5	
191	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	20.3	
192	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	21.5	
193	Doping with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , DMSO	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	24.2	
194	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	285	n/a	460	n/a	53.0 [700]	38.7	[55]
195	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	275	n/a	435	n/a	52.0 [700]	38.3	
196	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	300	n/a	480	n/a	61.0 [700]	41.9	
197	TPP, Py, NMP, $\text{CaCl}_2$ , $\Delta$	1.82	3.55	1.95	154	200	296	416	42.3 [800]	34.4	[91]
198	TPP, Py, NMP, $\text{CaCl}_2$ , $\Delta$	n/a	n/a	n/a	165	350	380	n/a	39.4 [800]	32.0 <sup>g</sup>	[92]
										33.0	
199	Using diacylchloride, NMP, Py	n/a	n/a	n/a	n/a	270–275	295–300	n/a	11.0 [600]	20.0 <sup>g</sup>	[93]
200	Using diacylchloride, NMP, Py	n/a	n/a	n/a	n/a	345–350	375–380	n/a	25.0 [600]	29.0 <sup>g</sup>	
201	Using bisiodide, CO, Pd-cat., DBU, DMAC	4.12	7.35	1.78	254	499	510	n/a	55.6 [800] <sup>c</sup>	41.0 <sup>g</sup>	[94]
						465 <sup>d</sup>	515 <sup>d</sup>		7.7 [800] <sup>d</sup>		
202	Using bisiodide, CO, Pd-cat., DBU, DMAC	4.65	7.81	1.50	250	481	508	n/a	62.3 [800]	44.0 <sup>g</sup>	
						460 <sup>d</sup>	498 <sup>d</sup>		4.6 [800] <sup>d</sup>		
203	Using bisiodide, CO, Pd-cat., DBU, DMAC	4.03	6.98	1.73	245	475	506	n/a	52.1 [800]	39.0 <sup>g</sup>	
						448 <sup>d</sup>	497 <sup>d</sup>		2.1 [800] <sup>d</sup>		
204	Using bisiodide, CO, Pd-cat., DBU, DMAC	3.97	7.14	1.80	237	478	503	n/a	59.8 [800]	42.0 <sup>g</sup>	
						463 <sup>d</sup>	498 <sup>d</sup>		2.3 [800] <sup>d</sup>		
205	Using bisiodide, CO, Pd-cat., DBU, DMAC	4.21	7.42	1.76	256	464	517	n/a	61.6 [800]	42.0 <sup>g</sup>	
						459 <sup>d</sup>	500 <sup>d</sup>		1.4 [800] <sup>d</sup>		
206	Using diacylchloride, NMP, $\text{Et}_3\text{N}$	n/a	n/a	n/a	209	n/a	370 <sup>d</sup>	455 <sup>d</sup>	43.0 [600] <sup>d</sup>	34.7	[57]
207	Using diacylchloride, NMP, $\text{Et}_3\text{N}$	n/a	n/a	n/a	218	n/a	385 <sup>d</sup>	470 <sup>d</sup>	48.0 [600] <sup>d</sup>	36.7	
208	Using diacylchloride, NMP, PO	n/a	n/a	n/a	203	n/a	392 <sup>d</sup>	410 <sup>d</sup>	54.0 [650] <sup>d</sup>	39.1	[56]
209	Using diacylchloride, NMP, PO	n/a	n/a	n/a	210	n/a	409 <sup>d</sup>	432 <sup>d</sup>	56.0 [650] <sup>d</sup>	39.9	
210	CuI, DMEDA, $\text{K}_2\text{CO}_3$ , DMF, $\Delta$	0.62	0.87	1.41	259	n/a	465	n/a	69.3 [600]	45.2	[59]
212	CuI, DMEDA, $\text{K}_2\text{CO}_3$ , DMF, $\Delta$	0.64	1.20	1.87	276	n/a	476	n/a	72.1 [600]	46.3	
211	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	n/a	n/a	n/a	n/a	n/a	<100	n/a	82.0 [600]	50.3	[58]
212	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	n/a	n/a	n/a	n/a	n/a	<100	n/a	70.0 [600]	45.5	
214	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	n/a	n/a	n/a	286	350	435	n/a	56.0 [800]	40.0	[51]
215	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	n/a	n/a	n/a	264	321	404	n/a	42.0 [800]	34.0	
216	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	260	392	450	n/a	59.0 [600]	41.0	[52]
217	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	258	391	454	n/a	62.0 [600]	42.0	
218	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	269	419	473	n/a	70.0 [600]	45.0	
219	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	316	n/a	476	n/a	57.0 [800]	40.0	[53]
							450 <sup>d</sup>				
220	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	305	n/a	460	n/a	46.0 [800]	36.0	
							433 <sup>d</sup>				
221	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	330	n/a	492	n/a	63.0 [800]	43.0	
							466 <sup>d</sup>				
222	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	308	387	450	n/a	63.0 [750]	43.0	[54]
223	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	287	301	360	n/a	55.0 [750]	40.0	
224	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	299	339	401	n/a	59.0 [750]	41.0	
225	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	264	295	343	n/a	48.0 [750]	37.0	
162	Using diacylchloride, DMAC	n/a	n/a	n/a	n/a	432	452	n/a	50.0 [800]	38.0	[95]
						419 <sup>d</sup>	445 <sup>d</sup>		9.0 [800] <sup>d</sup>		
226	Using diacylchloride, DMAC	n/a	n/a	n/a	n/a	416	448	n/a	58.0 [800]	41.0	
						427 <sup>d</sup>	462 <sup>d</sup>		n/a [800] <sup>d</sup>		
227	Using diacylchloride, DMAC	n/a	n/a	n/a	n/a	444	463	n/a	56.0 [800]	40.0	
						451 <sup>d</sup>	482 <sup>d</sup>		1.0 [800] <sup>d</sup>		
228	Using diacylchloride, DMAC	n/a	n/a	n/a	n/a	449	472	n/a	60.0 [800]	42.0	
						451 <sup>d</sup>	480 <sup>d</sup>		n/a [800] <sup>d</sup>		
229	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	n/a	420	455	n/a	62.0 [800]	42.0	[96]
						420 <sup>d</sup>	450 <sup>d</sup>				
230	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	n/a			n/a	61.0 [800]	42.0	

Table 4 (continued)

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{gmol}^{-1}$ )	$M_w$ ( $10^4 \times \text{gmol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties (TGA data) <sup>a</sup>				LOI (%) <sup>e</sup>	Reference.
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
						425	460				
						430 <sup>d</sup>	465 <sup>d</sup>				
<b>231</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	n/a	370	410	n/a	47.0 [800]	36.0	
						365 <sup>d</sup>	410 <sup>d</sup>				
<b>232</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	n/a	410	445	n/a	52.0 [800]	38.0	
						415 <sup>d</sup>	445 <sup>d</sup>				
<b>233</b>	Using diacylchloride TMSCl, NMP, LiCl	2.20	3.29	1.49	226	n/a	475 <sup>d</sup>	535	68.0 [600] <sup>d</sup>	27.5 <sup>g</sup>	[61]
<b>234</b>	Using diacylchloride TMSCl, NMP, LiCl	2.61	3.48	1.33	245	n/a	489 <sup>d</sup>	539	72.0 [600] <sup>d</sup>	27.5 <sup>g</sup>	
<b>235</b>	TPP, Py, NMP, $\text{CaCl}_2$ , $\Delta$	n/a	n/a	n/a	n/a	285	426	n/a	61.0 [700]	41.9	[97]
<b>236</b>	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	2.66	4.42	1.19	>300	n/a	502	n/a	73.6 [800]	46.9	[60]
<b>237</b>	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	2.53	3.11	1.23	>300	n/a	428	n/a	66.7 [800]	44.1	
<b>238</b>	TPP, Py, NMP, $\text{CaCl}_2$ , LiCl, $\Delta$	3.30	4.46	1.35	>300	n/a	488	n/a	71.3 [800]	46.0	
<b>239</b>	Using diacylchloride, DMAC, Py	0.31	0.51	1.67	157	n/a	439	n/a	38.0 [700]	32.7	[98]
<b>240</b>	Using diacylchloride, DMAC, Py	0.41	0.70	1.73	159	n/a	442	n/a	48.0 [700]	36.7	
<b>241</b>	Using diacylchloride, DMAC, Py	0.33	0.59	1.78	178	n/a	461	n/a	50.0 [700]	37.5	
<b>242</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	253	n/a	737	n/a	51.0 [900]	37.9	[99]
<b>243</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	251	n/a	698	n/a	43.0 [900]	34.7	
<b>244</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	267	n/a	715	n/a	44.0 [900]	35.1	
<b>245</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	272	n/a	733	n/a	54.0 [900]	39.1	
<b>246</b>	TPP, Py, NMP, LiCl, $\Delta$	n/a	n/a	n/a	274	n/a	744	n/a	56.0 [900]	39.9	

<sup>a</sup> TGA data, obtained applying 10 K min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere unless stated otherwise.

<sup>b</sup> Under O<sub>2</sub> atmosphere.

<sup>c</sup> Temperature at the onset of the first stage of the thermal weight loss.

<sup>d</sup> Under air atmosphere.

<sup>e</sup> Unless otherwise indicated, assessed from the respective char yield, using Van Krevelen-Hoftyzer equation  $\text{LOI} = 17.5 + 0.4\text{CR}$ , where CR = char yield.

<sup>f</sup> Obtained applying 20 K min<sup>-1</sup> heating rate.

<sup>g</sup> Experimental values.

was designed to increase char formation and emission of non-flammable gases upon combustion. In fact, FR PA **7** was obtained using as low as 3 wt% of the corresponding FR 1,6-hexamethylenediammonium salt (TRFR salt) and was rated V-0 in UL-94 vertical burning test, owing to the formation of ample porous char that prevented polymer from dripping when burning. The PA **7** improved LOI by 5% in comparison to pure PA66.

Yang reported preparation and thermal properties of FR PA66 **8** using BCPPO 1,6-hexanediammonium salt as a reactive FR additive [39]. In the initial studies, the amount of BCPPO varied from 1.5% to 9 wt%. The increase of FR monomer content decreased the  $T_m$  and  $T_c$  of **8** due to interruption of intermolecular hydrogen bonding periodicity. Only FR PA **8** with the highest P-content (9 wt% of BCPPO) could attain reproducible V-0 rating in UL-94 burning test and improved LOI of 27.2% (22.3% for unmodified PA66) to. Remarkably, FR PA **8** with 9 wt% of BCPPO displayed FR performance similar to a formulation of PA66 with 10% MERP (80 wt% red phosphorus and 20 wt% melamine cyanurate). Further studies on thermal properties of BCPPO-based FR PAs revealed a three-stage decomposition mechanism: initial P–C bond cleavage ( $E_a = 75$  kJ/mol) that generates prime thermolysis intermediates, followed by decomposition of PA segments and final carbonization [46,47]. The former stage was unique for FR PA **8**, while two latter stages were characteristic for both pure and FR PAs. Furthermore, the corresponding  $E_a$  for FR polymers were 50 kJ/mol (middle thermolysis stage) and 46 kJ/mol (late thermolysis stage) higher than that for pristine PA66, suggesting better protective properties of a char layer for FR PAs with BCPPO units [47].

Lyu reported series of designed phosphinamide and phosphonamide-based reactive additives (diacids and diamines)

used as co-monomers for inherently FR PA66 **9–13** [41,42]. All co-monomers, except NENP, were derived from phenylphosphonic dichloride through one-step synthesis procedures followed by polycondensation with HMDAA. The first screening study disclosed that introduction of 5 wt% of NENP, BNPO, DPPD or MCPO additives resulted in inherently FR polymers **9–12** that passed UL-94 burning test achieving V-0 rating. Notably, melt dripping was observed only for burning **10** specimen, but it did not ignite a cotton indicator, while other FR PAs formed ample char, which prevented melt dripping. All specimens made of FR copolymers self-extinguished within 3–7 s after the first ignition and displayed LOI >26%.

Further study confirmed that 5 wt% loading of NENP prepolymer is essential to achieve V-0 classification in UL-94 burning test, while lower FR co-monomer feed fraction resulted in worse fire performance of FR PAs **9** [40]. MCC experiments confirmed that PA **9** with the highest P-content displayed better fire performance: pHRR and THR of the FR polymer **9** decreased by 33.3% and 22.8% respectively as compared to unmodified PA66. However, increase in the amount of FR additive lead to a decrease of  $T_m$ ,  $T_g$ ,  $X_c$  and mechanical properties of FR PAs **9**.

Short ( $n = 2$ ) and longer ( $n = 5$ ) oligomeric FR diamines were obtained from phenylphosphonic dichloride and *p*-phenylene diamine and used as co-monomers to prepare FR PA66 **12** and **13** (5 wt% and 4.5 wt% of the respective reactive FR additive) [41,42]. Both polymers attained V-0 rating in UL-94 burning test and exhibited high LOI of 29%. Increase of PDPPD content in FR polymer **13** lead to a significant reduction in  $T_{5\%}$ ,  $T_m$  and  $T_g$ , while it was essential for improvement of fire performance [42]. Thus, MCC experiments clearly demonstrated that increase of P-content in FR PAs reduces pHRR, THR and TSP. Importantly, synthetic protocols for FR monomers were not supported with unequivocal data on

**Table 5**  
Preparation, selected molecular and thermal properties of PAI.

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties <sup>a</sup>				LOI (%)	Reference
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
247	Using diacylchloride, NMP, Py	n/a	n/a	n/a	n/a	270–275	295–300	n/a	41.0 [600]	21.0 <sup>f</sup>	[100]
248	Using diacylchloride, NMP, Py	n/a	n/a	n/a	n/a	340–345	420–425	n/a	69.0 [600]	29.0 <sup>f</sup>	
250	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	305–310	380–385	n/a	54.9 [800]	39.5	[101]
251	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	305–310	370–375	n/a	54.8 [800]	39.5	
254	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	177	390	400	n/a	40.8 [800]	33.8	[102]
255	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	180	390	410	n/a	45.5 [800]	35.7	
256	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	195	360	400	n/a	38.9 [800]	33.1	
257	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	205	375	410	n/a	43.0 [800]	34.7	
258	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	185	340	390	n/a	40.3 [800]	33.6	
259	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	175	330	380	n/a	45.1 [800]	33.5	
261	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	220	310–315	355–360	n/a	55.1 [800]	40.0	[103]
262	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	240	285–290	350–355	n/a	51.5 [800]	38.0	
265	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	180	344	355	n/a	46.3 [800]	36.0	[104]
266	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	256	532	550	n/a	46.0 [800]	35.9	[105]
267	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	277	550	570	n/a	51.0 [800]	37.9	
268	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	272	544	567	n/a	49.0 [800]	37.1	
269	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	244	511	541	n/a	43.0 [800]	34.7	
270	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	246	518	546	n/a	42.0 [800]	34.3	
271	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	249	526	544	n/a	44.0 [800]	35.1	
272	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	229	498	512	n/a	39.0 [800]	33.1	
273	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	n/a	418	640	17.0 [800]	37.0 <sup>g</sup>	[106]
274	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	201	n/a	410	600	18.0 [800]	41.0 <sup>g</sup>	
275	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	205	n/a	390	670	15.0 [800]	39.0 <sup>g</sup>	
276	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	n/a	370	610	18.0 [800]	38.0 <sup>g</sup>	
277	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	215	n/a	390	590	22.0 [800]	40.0 <sup>g</sup>	
278	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	207	n/a	390	640	16.0 [800]	40.0 <sup>g</sup>	
279	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/a	n/a	420	650	25.0 [800]	28.0	[107]
280	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	180	n/a	425	620	24.0 [800]	27.0	
281	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	174	n/a	385	630	22.0 [800]	26.0	
282	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	n/o	n/a	450	600	30.0 [800]	30.0	
283	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	185	n/a	465	580	22.0 [800]	26.0	
284	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	175	n/a	420	580	19.0 [800]	25.0	
287	TBAB, TPP, MW	n/a	n/a	n/a	n/a	364 <sup>b</sup>	402 <sup>b</sup>	n/a	47.0 [800] <sup>b</sup>	36.3	[108]
288	TBAB, TPP, MW	n/a	n/a	n/a	n/a	332 <sup>b</sup>	378 <sup>b</sup>	n/a	38.0 [800] <sup>b</sup>	32.7	
289	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	192	370	410	n/a	43.0 [800]	34.0	[109]
290	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	177	380	390	n/a	45.5 [800]	35.0	
294	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	212	365	400	n/a	47.0 [800]	36.0	
297	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	428 <sup>b</sup>	503 <sup>b</sup>	536 <sup>b</sup>	71.3 [800] <sup>b</sup>	46.0	[110]
298	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	431 <sup>b</sup>	461 <sup>b</sup>	483 <sup>b</sup>	57.4 [800] <sup>b</sup>	40.4	
299	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	437 <sup>b</sup>	453 <sup>b</sup>	492 <sup>b</sup>	60.0 [800] <sup>b</sup>	41.5	
300	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	413 <sup>b</sup>	446 <sup>b</sup>	481 <sup>b</sup>	53.4 [800] <sup>b</sup>	38.9	
301	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	421 <sup>b</sup>	499 <sup>b</sup>	521 <sup>b</sup>	63.1 [800] <sup>b</sup>	42.7	
302	TPP, Py, NMP, CaCl <sub>2</sub> , LiCl, Δ	n/a	n/a	n/a	n/a	476 <sup>b</sup>	537 <sup>b</sup>	539 <sup>b</sup>	75.9 [800] <sup>b</sup>	47.9	
303	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	4.60	8.30	1.80	196	n/a	400 <sup>c</sup>	n/a	44.0 [700] <sup>c</sup>	35.1	[111]
304	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	4.45	7.80	1.75	187	n/a	375 <sup>c</sup>	n/a	39.0 [700] <sup>c</sup>	33.1	
305	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	4.35	7.45	1.71	192	n/a	392 <sup>c</sup>	n/a	43.0 [700] <sup>c</sup>	34.7	
306	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	4.55	7.60	1.67	190	n/a	386 <sup>c</sup>	n/a	41.0 [700] <sup>c</sup>	33.9	
307	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	332 <sup>b</sup>	398 <sup>b</sup>	n/a	46.8 [800] <sup>b</sup>	36.2	[112,113]
310	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	326 <sup>b</sup>	417 <sup>b</sup>	n/a	45.4 [800] <sup>b</sup>	35.6	
311	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	294 <sup>b</sup>	325 <sup>b</sup>	n/a	34.0 [800] <sup>b</sup>	31.1	[114]
312	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	290 <sup>b</sup>	318 <sup>b</sup>	n/a	28.0 [800] <sup>b</sup>	28.7	
315	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	220	325	n/a	46.0 [800]	35.9	[115]
316	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	255	320	n/a	45.0 [800]	35.5	
317	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	250	315	n/a	42.0 [800]	34.3	
318	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	245	322	n/a	40.0 [800]	33.5	
317	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	255 <sup>b</sup>	330 <sup>b</sup>	n/a	30.0 [800] <sup>b</sup>	29.5	[116]
318	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	260 <sup>b</sup>	321 <sup>b</sup>	n/a	37.0 [800] <sup>b</sup>	32.3	
319	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	276 <sup>b</sup>	360 <sup>b</sup>	n/a	44.8 [800] <sup>b</sup>	35.4	[117]
319	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	260 <sup>b</sup>	301 <sup>b</sup>	n/a	39.1 [800] <sup>b</sup>	33.1	[118]
320	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	197	257	n/a	52.9 [800]	38.6	[119]
321	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	326 <sup>b,d</sup>	346 <sup>b,d</sup>	n/a	52.0 [800] <sup>b,d</sup>	38.3	[120]
322	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	352 <sup>b,d</sup>	381 <sup>b,d</sup>	n/a	49.0 [800] <sup>b,d</sup>	37.0	[121]
323	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	166	390	410	n/a	30.5 [800]	29.6	[122]
326	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	171	370	400	n/a	34.9 [800]	31.4	
328	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	194	380	390	n/a	33.5 [800]	29.9	
329	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	100	263	293	n/a	28.0 [800] <sup>b</sup>	28.7	[123]
330	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	46	256	293	n/a	41.0 [800] <sup>b</sup>	33.9	
331	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	43	226	259	n/a	33.0 [800] <sup>b</sup>	30.7	
333	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	270–275	335–340	n/a	60.0 [600]	33.0 <sup>f</sup>	[124,125]
336	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	300–305	365–370	n/a	62.1 [600]	32.0 <sup>f</sup>	
337	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	310–315	345–350	n/a	60.0 [600]	31.0 <sup>f</sup>	

Table 5 (continued)

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties <sup>a</sup>				LOI (%)	Reference
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\text{max}}$ (°C)	Char residues (%) at [T (°C)]		
339	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	161	350	370	n/a	31.5 [800]	30.0	[126]
341	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	157	340	380	n/a	29.7 [800]	29.0	
344	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	173	310	370	n/a	33.0 [800]	30.0	
346	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	1.20	4.40	3.70	n/a	305	370	n/a	62.1 [600]	33.0	[127]
347	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	1.40	4.90	3.50	n/a	280	305	n/a	61.5 [600]	34.0	
351	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	1.30	4.20	3.20	n/a	280	330	n/a	64.9 [600]	32.0	
352	Using diacylchloride, NMP, PO	n/a	n/a	n/a	381	372	390	422	47.0 [600]	36.3	[128]
353	Using diacylchloride, NMP, PO	n/a	n/a	n/a	380	315	391	413	46.0 [600]	35.9	
354	Using diacylchloride, NMP, PO	n/a	n/a	n/a	385	358	398	423	51.0 [600]	37.9	
355	Using diacylchloride, NMP, PO	n/a	n/a	n/a	425	364	412	450	56.0 [600]	39.9	
356	Using diacylchloride, NMP, PO	n/a	n/a	n/a	398	362	402	437	52.0 [600]	38.3	
357	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	397	429	n/a	49.0 [800]	37.1	[129]
358	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	401	431	n/a	51.0 [800]	37.9	
359	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	411	462	n/a	54.0 [800]	39.1	
360	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	416	465	n/a	55.0 [800]	39.5	
361	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	425	471	n/a	58.0 [800]	40.7	
362	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	404	440	n/a	53.0 [800]	38.7	
363	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	147	257	312	347	51.0 [600]	37.9	[130]
364	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	198 <sup>d</sup>	302 <sup>d</sup>	370 <sup>d</sup>	55.0 [800] <sup>d</sup>	39.5	[131]
365	TBAB, TPP, Δ	n/a	n/a	n/a	n/a	238 <sup>b,d</sup>	301 <sup>b,d</sup>	n/a	41.0 [800] <sup>b,d</sup>	33.9	[132]
366	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	2.30	5.20	2.20	142	294	390	452 <sup>e</sup>	29.8 [800]	29.4	[133]
367	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	220	270	n/a	51.4 [800]	38.1	[134]
368	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	330	390	n/a	42.1 [700]	34.4	[135]
372	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	n/a	n/a	n/a	n/a	245	383	n/a	37.0 [700]	32.3	
374	TPP, Py, NMP, CaCl <sub>2</sub> , Δ	2.41	5.36	2.22	127	211	271	432 <sup>e</sup>	40.2 [800]	33.5	[136]
375	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	—	n/a	424	667	16.0 [800]	24.0	[137]
376	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	209	n/a	440	757	15.0 [800]	24.0	
377	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	—	n/a	448	592	12.0 [800]	22.0	
378	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	204	n/a	450	749	12.0 [800]	22.0	
379	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	—	n/a	430	699	26.0 [800]	26.0	
380	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	203	n/a	449	795	28.0 [800]	28.0	
381	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	202	n/a	478	660	34.0 [800]	34.0	
382	TPP, Py, NMP, LiCl, Δ	n/a	n/a	n/a	—	n/a	455	570	32.0 [800]	32.0	
383	Using diacylchloride, DMAC	4.75	7.94	1.67	290	n/a	534	616	50.0 [650]	49.0	[138]
384	Using diacylchloride, DMAC	4.84	8.04	1.66	292	n/a	544	619	54.0 [650]	53.0	
385	Using diacylchloride, DMAC	4.56	7.75	1.70	288	n/a	522	601	46.0 [650]	45.0	
386	Using diacylchloride, DMAC	4.47	7.89	1.72	286	n/a	517	592	44.0 [650]	44.0	
387	NMP, then Ac <sub>2</sub> O, Py, Δ	n/a	n/a	n/a	242	428	n/a	n/a	59.0 [600] <sup>c</sup>	41.1	[139]
388	NMP, then Ac <sub>2</sub> O, Py, Δ	n/a	n/a	n/a	227	385	n/a	n/a	57.0 [600] <sup>c</sup>	40.3	
389	NMP, then Ac <sub>2</sub> O, Py, Δ	n/a	n/a	n/a	230	415	n/a	n/a	58.0 [600] <sup>c</sup>	40.7	
390	DMAC, then casting and Δ	4.73	7.47	1.58	245	n/a	540	563	46.7 [800] <sup>b</sup>	36.2	[140]
391	DMAC, then casting and Δ	4.85	7.62	1.57	261	n/a	550	570	52.2 [800] <sup>b</sup>	38.8	
392	DMAC, then casting and Δ	4.49	7.18	1.60	232	n/a	530	551	52.6 [800] <sup>b</sup>	38.1	
393	DMAC, then casting and Δ	4.30	6.93	1.61	220	n/a	520	544	49.7 [800] <sup>b</sup>	37.4	

<sup>a</sup> TGA data, obtained applying 10 K min<sup>−1</sup> heating rate under N<sub>2</sub> atmosphere unless stated otherwise.<sup>b</sup> Obtained applying 20 K min<sup>−1</sup> heating rate.<sup>c</sup> Under air atmosphere.<sup>d</sup> Under Ar atmosphere.<sup>e</sup> Data obtained in MCC measurements.<sup>f</sup> Experimental values.<sup>g</sup> Assessed values do not correspond to the reported char yield.

identification and characterization of new compounds, while microphotographs of char residues of burnt PAs **9** and **13** looked similar [42,40].

Chen described the preparation of FR PAs **14**, using CEPPA as a reactive FR additive [43]. The content of CEPPA ranged from 2% to 6%, rendering all FR PAs **14** excellent FR properties. All FR PAs passed UL-94 burning test, attaining V-0 rating and with no melt dripping. LOI values incremented with amount of CEPPA added and were the highest (LOI = 28.0%) for FR polymer **14**, containing 6 wt% of the reactive FR additive. In addition, increase of CEPPA content in the macromolecules decreased the decomposition temperature and improved char formation with continuous dense surface.

Tan reported a study on thermolysis of a similar FR PA **14** incorporating 10 wt% of CEPPA [44]. Thermolysis results were

analyzed and rationalized using Flynn-Wall-Ozawa and Coast-Redfern methods. Like BCPPO-based co-polyamides, thermal degradation of FR PA **14** with 10 wt% of CEPPA displayed three distinct stages related to different decomposition rates and scenarios, while pure PA66 displayed only a two-stage thermal decomposition. The prime and the middle stages of FR PA **14** thermolysis were assigned to dissociation of P–C bonds with lower thermal stability as compared to C–C bonds. Therefore, PA **14** with 10 wt% of CEPPA demonstrated a decreased  $E_a$  of decomposition: 148.3 kJ/mol and 139.1 kJ/mol for the respective two stages vs 142.8 kJ/mol and 262.3 kJ/mol for pure PA66. The third stage of thermolysis of FR PA **14** resulted in a noticeable increase of  $E_a$  that attained a peak value of 454 kJ/mol followed by a fast  $E_a$  decline. This behavior was accounted for char layer formation that gave rise to



**Table 6**  
Preparation, selected molecular and thermal properties of polyamide-siloxane copolymers.

Polymer	Synthesis	$M_n$ ( $10^4 \times \text{g mol}^{-1}$ )	$M_w$ ( $10^4 \times \text{g mol}^{-1}$ )	PDI	$T_g$ (°C)	Thermal properties <sup>a</sup>				LOI (%)	Ref.
						$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\max}$ (°C)	Char residues at [T (°C)](%)		
<b>394</b>	Novozyme-435, neat, $\Delta$ , then vacuum	1.10	1.54	1.4	n/a	302 <sup>b,c</sup>	n/a	n/a	0.4 [1200] <sup>c</sup>	n/a	[141]
<b>395</b>	Novozyme-435, neat, $\Delta$ , then vacuum	1.29	1.94	1.5	n/a	277 <sup>b,c</sup>	n/a	n/a	8.8 [1200] <sup>c</sup>	n/a	
<b>396</b>	Novozyme-435, neat, $\Delta$ , then vacuum	1.53	2.30	1.5	n/a	285 <sup>b,c</sup>	n/a	n/a	6.7 [1200] <sup>c</sup>	n/a	
<b>397</b>	Novozyme-435, neat, $\Delta$ , then vacuum	1.60	2.72	1.7	n/a	403 <sup>b,c</sup>	n/a	n/a	1.4 [1200] <sup>c</sup>	n/a	
<b>398</b>	Novozyme-435, neat, $\Delta$ , then vacuum	n/a	n/a	n/a	n/a	n/a	n/a	508 <sup>d,e</sup>	13.17 [800] <sup>d,e</sup>	n/a	[142]
<b>399</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 20 wt %	n/a	n/a	n/a	n/a	n/a	n/a	522 <sup>d,e</sup>	20.73 [800] <sup>d,e</sup>	n/a	
<b>400</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 20 wt %	n/a	n/a	n/a	n/a	n/a	n/a	523 <sup>d,e</sup>	18.85 [800] <sup>d,e</sup>	n/a	
<b>401</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 20 wt %	n/a	n/a	n/a	n/a	n/a	n/a	500 <sup>d,e</sup>	15.05 [800] <sup>d,e</sup>	n/a	
<b>398</b>	Novozyme-435, neat, $\Delta$ , then vacuum	1.10	1.47	1.34	n/a	378 <sup>b,d</sup>	n/a	n/a	3.7 [1200] <sup>f</sup>	n/a	[143]
<b>402</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 10 wt %	n/a	n/a	n/a	n/a	386 <sup>b,d</sup>	n/a	n/a	8.3 [1200] <sup>f</sup>	n/a	
<b>403</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 10 wt %	n/a	n/a	n/a	n/a	357 <sup>b,d</sup>	n/a	n/a	10.9 [1200] <sup>f</sup>	n/a	
<b>403</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; diacyl chloride 10 wt %	n/a	n/a	n/a	n/a	n/a	n/a	n/a	9.3 [1200] <sup>f</sup>	n/a	
<b>404</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 10 wt %	n/a	n/a	n/a	n/a	379 <sup>b,d</sup>	n/a	n/a	7.4 [1200] <sup>f</sup>	n/a	
<b>405</b>	CHCl <sub>3</sub> /Acetone; $\Delta$ ; dianhydride 10 wt %	n/a	n/a	n/a	n/a	376 <sup>b,d</sup>	n/a	n/a	2.3 [1200] <sup>f</sup>	n/a	
<b>403<sup>g</sup></b>	ROP, then esterification and transesterification	1.79	3.34	1.86	48	386	n/a	434	12.4 [700]	28.3	[144]

<sup>a</sup> TGA data, obtained applying 10 K min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere unless stated otherwise.

<sup>b</sup> temperature at the onset of the first stage of the thermal weight loss.

<sup>c</sup> Heating rate was not indicated.

<sup>d</sup> Under air atmosphere.

<sup>e</sup> Obtained applying 20 K min<sup>-1</sup> heating rate.

<sup>f</sup> data obtained in MCC experiments.

<sup>g</sup> Referred to the champion copolymer that attained V-0 UL-94 rating.

superior FR properties of FR PA **14** compared to pristine PA66. Interestingly, FR PA **14** with 10 wt% of CEPPA attained LOI of 27%, that is 1% lower compared to FR PA **22** containing 6 wt% of CEPPA [43].

### 3.3. PA11 copolymers

PA11 is an important biobased niche PA that is derived from castor oil, thereby enabling polymer synthesis in more sustainable manner. PA11 has a lower amide frequency which results in lower  $T_g$ ,  $T_m$ ,  $T_c$ , Young and flexural modules as compared to PA6 and PA66. In contrast to PA6 and PA66, “more aliphatic” structure of PA11 accounts for lower water absorption and higher dimensional stability [7]. Expectedly, similar approaches in development and use of FR reactive monomers can be foreseen, yet scarcely reported.

**Table 7**  
MCC data of polyamide-siloxane copolymers.

Polymer	Cross-linker (amount)	THR (kJ g <sup>-1</sup> )	HRC (J g <sup>-1</sup> K <sup>-1</sup> )	Reference
<b>395</b>	n/a	27.0	120	[141]
<b>396</b>	n/a	28.0	90	
<b>397</b>	n/a	31.0	96	
<b>398</b>	n/a	24.0	213	
<b>399</b>	n/a	18.1	190	[142]
<b>400</b>	5% pyromellitic dianhydride	16.3	177	
<b>400</b>	10% pyromellitic dianhydride	19.7	177	
<b>400</b>	15% pyromellitic dianhydride	18.7	144	
<b>400</b>	20% pyromellitic dianhydride	11.6	100	[143]
<b>400</b>	25% pyromellitic dianhydride	19.6	133	
<b>400</b>	30% pyromellitic dianhydride	20.7	134	
<b>401</b>	20% 3,3',4,4'-biphenyltetracarboxylic dianhydride	21.3	209	
<b>402</b>	20% 4,4'-oxydiphthalic anhydride	16.0	160	
<b>399</b>	n/a	20.2	310	
<b>403</b>	10% isophthalic acid	15.9	132	
<b>404</b>	10% terephthalic acid	25.2	165	
<b>404</b>	10% terephthaloyl chloride	24.5	180	
<b>405</b>	10% malonic acid	19.1	248	
<b>406</b>	10% glutaric acid	23.4	293	

Negrell described preparation and characterization of FR PAs **15**, synthesized from 11-aminoundecanoic acid, decane-1,10-diamine, decane-1,10-dioic acid and DOPO-ITA reactive FR additive that was copolymerized in the concentration range of 3.3 wt% to 11.1 wt% (equivalent to 0.3–1.0 wt% of P) (see Fig. 5) [45]. As a result, increase of a feed fraction of DOPO-ITA lead to a decrease in intrinsic viscosity, molecular weight,  $T_g$ ,  $T_m$  and  $T_c$  of the FR polymers, similarly to trends in FR PA66-type polymers. The deterioration of properties was rationalized with a competing imidization reaction: DOPO-ITA may form cycloimides in presence of amine end-groups at elevated temperatures, thus limiting polymer chain growth and therefore decreasing molecular weight of FR PAs **15** (see Scheme 4, Table 1). In addition, shorter polymerization times were suggested to avoid thermal degradation of DOPO-ITA. Noteworthy, presence of residual amount of phosphoric acid, used as polycondensation catalyst, was also reported to cause branching of PA11 [162].

Expectedly, higher phosphorus content in FR PAs **15** brought about superior FR properties as compared to pristine commercial and in-house synthesized reference PA11. FR PAs **15** containing more than 0.5 wt% of P were rated as V-0 materials in UL-94 burning test. Melt dripping was not suppressed, but drips were non-flaming. Similarly, LOI values were also improved for P-containing co-polymers. Unusually high LOI of 40–45% measured for FR polymer **15** with 1 wt% of P was admitted to be roughly assessed. Finally, MCC experiments demonstrated that the presence of 0.5 wt % of P in FR PA **15** allows to reduce pHRR and THR by only 8.3% and 12.1% respectively (as compared to commercial PA11 sample).

## 4. Aliphatic, semiaromatic and partially aromatic polyamides

As compared to conventional aliphatic nylons and their copolymers with reactive aromatic FR additives, PAs incorporating aromatic monomers (aliphatic, semiaromatic and partially aromatic) usually display higher intrinsic thermal robustness and flame retardancy, thanks to the presence of higher number of aromatic segments in the polymer structure. Fine-tuning of thermal,

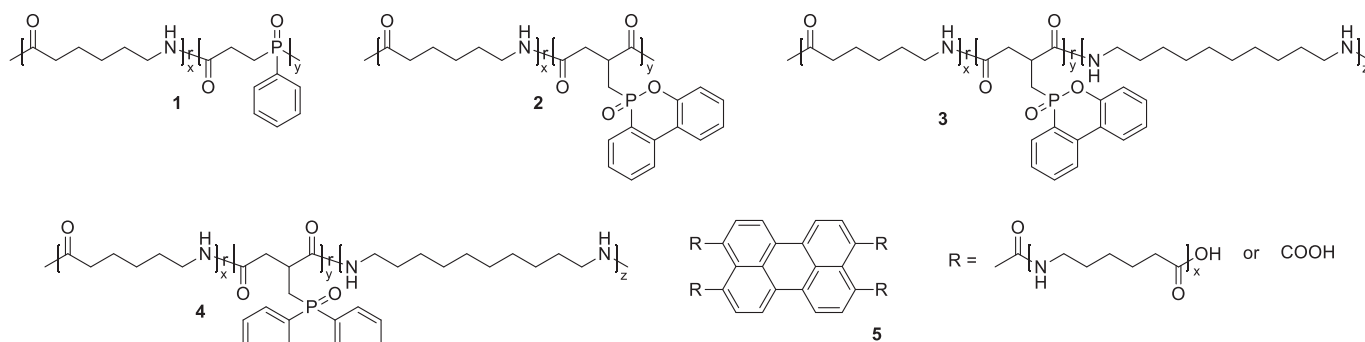


Fig. 1. PA6 FR copolymers.

mechanical, optical properties, solubility and fire performance is possible through length of aliphatic chains (amide frequency); balance between aliphatic and aromatic monomers or use of araliphatic units; introduction of heteroatoms, functional groups and/or side-substituents along macromolecular backbones. Thus, judicious chemical design often affords polymers with prominent thermal and fire properties that do not require addition of extra FR additives. PAs containing aromatic monomers are vastly AABB-type polyamides and are derived from diacids, diamines or their analogues (see Fig. 6).

Various substituted aromatic diamines based on 2,4,6-triphenylpyridine core were synthesized and used in direct polycondensation with aliphatic diacids of different length to deliver a family of related semiaromatic FR PAs: **16–20**. Nazari and Shabani reported the synthesis and properties FR PAs **16–18** composed of -Cl, -Br and -NMe<sub>2</sub>-endowed 4,4'-(4-phenylpyridine-2,6-diyl) dianilines and adipic acid segments [48]. The diamine monomers were derived from cyclization of 4-nitroacetophenone with 4-substituted benzaldehydes in presence of ammonium acetate followed by complete reduction of nitro-groups. Halogen-substituted polymers **16** and **17** exhibited similar *T<sub>g</sub>* of ~150 °C, while *N,N*-dimethylamine-endowed analogue displayed *T<sub>g</sub>* ca. 20 °C lower, that was rationalized with the bulkiness and flexibility of the substituent. In contrast, thermal stability (*T<sub>5%</sub>*, *T<sub>10%</sub>*) followed a different trend increasing in the row **16, 18, 17**, while a reverse trend for char yield (800 °C, N<sub>2</sub>-atmosphere) was observed, i.e. the highest for Br-modified PA **17**. LOI values were assessed based on char yield and were above 34%. Therefore, the polymers **16–18** were classified as self-extinguishing polymers. In addition, in good agreement with char formation trend FR PAs **16–18** demonstrated low PHRR of 111.7; 66.6 and 92.5 W/g respectively, while THR for FR PAs **16–18** was 14.7; 11.6 and 15.7 kJ/g accordingly.

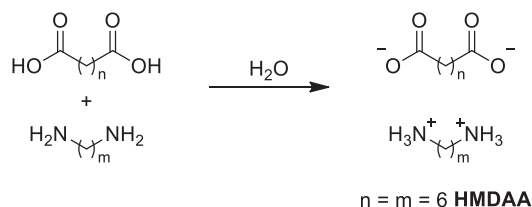
Amininasab reported thermally stable semiaromatic PAs **19** and **20** obtained through a direct polycondensation of adipic acid with two isomeric aromatic diamines based on 2,4,6-triphenylpyridine core endowed with a bulky xanthene pendant group [49]. The fluorochrome synthon was prepared via a condensation reaction of two equivalents of 2-naphthol and one equivalent terephthaldehyde

and used further to construct the photoactive diamine following a similar protocol as reported for **16–18** monomers. Direct polycondensation with adipic acid resulted in amorphous polyamides **19** and **20**, displaying excellent thermal robustness with *T<sub>g</sub>* of 195 °C and 201 °C and *T<sub>10%</sub>* of 388 °C and 375 °C respectively – the highest values among other related macromolecules. Finally, PAs **19** and **20** formed ample CR (measured at 700 °C under N<sub>2</sub> atmosphere) and therefore displayed high calculated LOI above 35%.

In an earlier work, Amininasab reported the synthesis of thermally stable semiaromatic PA **21** and **22** with bulky xanthene pendant bonded to imidazole core [50]. The designed diamines were obtained through a multi-step convergent protocol, involving preparation of the xanthene synthon as for **19** and **20**, as well as derivatized benzil precursor with terminal nitro-groups. Thus, the imidazole core was constructed in Debus-Radziszewski reaction followed by the reduction of terminal nitro-groups. Direct polycondensation with adipic acid afforded target PAs **21** and **22** that were amorphous and well soluble in polar aprotic solvents, including pyridine. The polymers showed low water uptake less than 3.95% and good thermal properties with *T<sub>g</sub>* of 195 °C and 184 °C respectively, and no significant mass loss up to 410 °C. PAs **21** and **22** formed 28–35% of CR and therefore demonstrated high calculated LOI. Finally, polymers **19–22** exhibited rather similar thermal behavior.

A number of structurally related thermally robust semiaromatic PAs **23–28** with 4,5-diphenylimidazole bulky pendants were reported in series of works [51–54]. All aromatic polyamides featured alike diamine motif derived via SNAr reaction of 2-(2-chloro-5-nitrophenyl)-4,5-diphenyl-1H-imidazole with various bisphenols, followed by reduction of nitro groups. The resulting designed aromatic diamines were directly polycondensed with adipic or sebacic acids affording PAs **23–28**. All PAs were amorphous and well-soluble in polar amide solvents, DMSO as well as pyridine, THF and *m*-cresol. Furthermore, PAs **23–28** were thermally robust polymers with high *T<sub>g</sub>* in the range of 180–234 °C and *T<sub>10%</sub>* beyond 330 °C. Notably, cardo PA **25** with only C–C bonds at node C-atom displayed superior thermal properties as compared to PA **24**, based on phenolphthalein containing three C–C and one C–O linkage. Better thermal properties were also observed for cardo PA **26** compared to the acyclic congeners **23, 27, 28** with similar acid monomers. All polymers formed ample CR and thus exhibited high calculated LOI values.

Ghaemy and Alizadeh reported thermally stable semiaromatic **29, 30** and aromatic (*vide infra*) PAs, containing a bulky carbazole substituent grafted to a diamine monomer [55]. The designed diamine was obtained through a 4-step linear synthetic protocol, including SNAr reaction between 1-fluoro-4-nitrobenzene with carbazole, followed by complete reduction of –NO<sub>2</sub>-group and its



Scheme 3. General synthesis of diammonium dicarboxylate prepolymers.

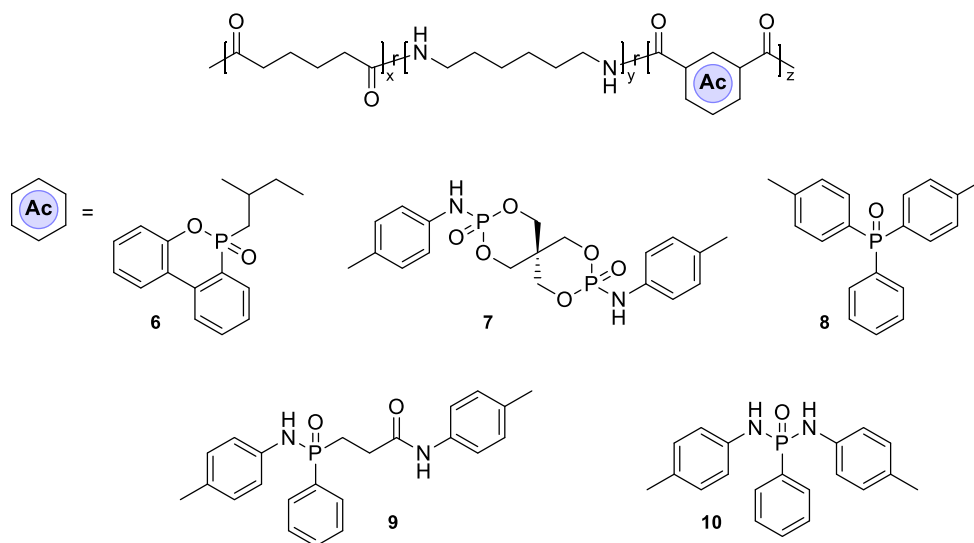


Fig. 2. PA66 FR copolymers.

acylation with 3,5-dinitrobenzoyl chloride. The resulting molecule was reduced further to provide the desired diamine that was used in direct polycondensation with adipic or sebacic acid, yielding thermally resistant and fully amorphous semiaromatic PAs **29** and **30**. The polymers were well soluble in amide solvents, DMSO and pyridine. In addition, macromolecules **29** and **30** demonstrated high  $T_g$  of 230 °C and 195 °C respectively, and  $T_{10\%}$  above 385 °C. Expectedly, PA **29** with higher amide frequency was superior in thermal properties, while both polymers formed similar amount of CR and therefore displayed comparable assessed LOI.

Mehdipour-Ataei and Ehsani described the preparation of thermally robust nicotinamide-based semiaromatic **31** and **32** and aromatic (*vide infra*) poly (etheramides) composed of pyridine-based diamine and adipic or sebacic acid respectively [56]. The diamines with etheramide linkages were synthesized in two-step process: acylation of 2,6-diaminopyridine with 6-chloronicotinoyl chloride followed by SNAr with 5-aminonaphthalen-1-ol. The semiaromatic PAs were designed to combine high thermal stability with good solubility thanks to polar pyridines constituting the monomer. PAs **31** and **32** displayed  $T_g$  of 195 °C and 186 °C and  $T_{10\%}$  of 365 °C and 353 °C respectively. Elongation of the aliphatic acid chain lead to slight decrease of  $T_g$ ,  $T_{10\%}$ , lower char yield (measured at 650 °C under air atmosphere) and assessed LOI. Specifically, PA **31** yielded 50% of solid residues with LOI of 37.5%, while PA **32** formed 47% of char residues and exhibited LOI of 36.3%

In a different work, Mehdipour-Ataei reported the synthesis and thermal properties of semiaromatic **33** and aromatic (*vide infra*) polyester-amides incorporating quinoline heterocycle [57]. The heteroaromatic diamines with internal ester linkage were derived via a 2-step protocol from 8-hydroxy-5-nitroquinoline and 4-nitrobenzoyl chloride, followed by reduction of nitro groups and polycondensation with commercial diacyl chlorides. PA **33** displayed high  $T_g$  of 184 °C and  $T_{10\%}$  of 320 °C, forming ample CR and exhibiting high calculated LOI of 32.7%.

Quinoxaline-containing semiaromatic **34–36** and aromatic (*vide infra*) PAs were obtained via two different methodologies: either conventional polycondensation and/or Ullmann-coupling polymerization between commercial diamides and 2,3-bis-(4-bromophenyl)-quinoxaline, synthesized via 1-step cyclisation of *o*-phenylenediamine with 4,4'-dibromobenzil [58,59]. Conventional polymerization protocol required the preparation of the designed diamine - 4,4'-(quinoxaline-2,3-diyl)dianiline, derived from benzoin through 4-step linear protocol: consecutive condensation with urea; nitration affording 4,4'-dinitrobenzil; its condensation with *o*-phenylenediamine and reduction of terminal nitro-groups. PA **34** was prepared by exploiting both methods that yielded PAs of different thermal properties. Specifically, the product of conventional polycondensation displayed very low  $T_{10\%}$  (not reported explicitly), while the product of Ullmann coupling showed  $T_{10\%}$  of 335 °C and  $T_g$  of 196 °C. Nevertheless, PAs **34** formed 65–67% of CR, regardless of the protocol used. Furthermore, Ullmann-type polymerization protocol enabled PA **36** with rigid multicyclic structure (see Fig. 7), obtained using 2,5-piperazinedione and inaccessible via conventional polycondensation process. The resulting polymer **36** was less soluble in polar aprotic solvents yet displayed superior thermal properties as compared to acyclic **34** and was rather similar to congener aramides, obtained similarly. Unfortunately, data reported for the semiaromatic PAs do not allow adequate comparison of the synthetic methods and polymers' properties.

Mondal and Das reported thermally resistant semiaromatic PAs **37–39** and aramids (*vide infra*) containing bulky 2,6-diaminotriptycene [60]. The designed aromatic diamine was synthesized via a 2-step protocol, including double nitration of triptycene core followed by reduction of terminal nitro-groups. Further direct polycondensation with commercial diacids with even number of C-atoms in aliphatic chain yielded semiaromatic PAs **37–39** that were well-soluble in polar amide solvents, DMSO and pyridine.

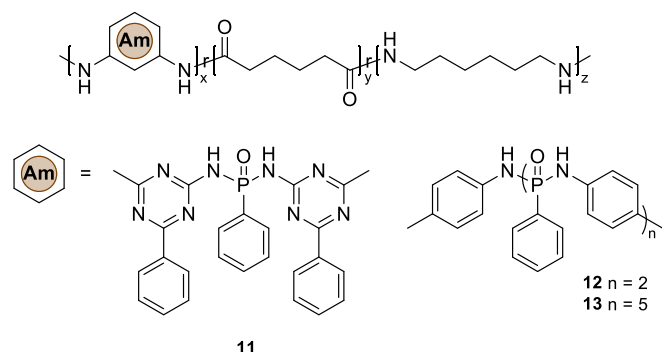


Fig. 3. PA66 FR copolymers containing phenylphosphorodiamidate reactive additives.

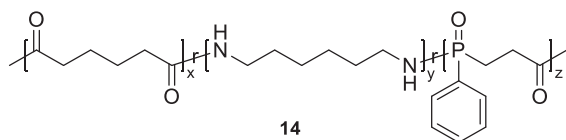


Fig. 4. PA66 FR copolymer containing CEPPA.

In addition, the polymers **37–39** displayed high thermal robustness with no significant thermal degradation up to 372 °C. Notably, the thermal stability of the macromolecules improved upon elongation of the aliphatic chain of the monomers and was the highest for **39**. In addition, PAs **37–39** formed >40.2% of char residues (measured at 800 °C under N<sub>2</sub> atmosphere) and exhibited high assessed LOI in the range of 33.6–39.3%.

Mehdipour-Ataei et al. investigated organometallic semi-aromatic PAs **40** and **41**, based on ferrocene [61]. The ferrocene diamine monomer was synthesized via consecutive preparation of 1,1'-ferrocene dicarboxylic acid and its amidation with 4,4'-(pyridine-2,6-diylbis (oxy))dianiline. Combination of multiple ether bonds, bulky ferrocenyl unit, and polar heterocycles gave rise to good solubility in polar aprotic solvents and imparted high thermal stability. Specifically, polymers **40** and **41** exhibited  $T_g$  of 181 °C and 186 °C accordingly and a high  $T_{10\%}$  above 417 °C. Moreover, both PAs realized 43–45% of solid residues (measured at 600 °C under air atmosphere) and LOI in the range of 26.5–27.0% that were 5.5% higher as compared to ferrocene-free semiaromatic analogues. Related ferrocene-based PAs with either higher aliphatic content in macromolecules or expanded  $\pi$ -system of aromatic monomers are also known and were reported to exhibit LOI in the range of 25.5–28.5%, yet no details on LOI was provided for the specific polymers [163,164].

Mallakpour reported the preparation and thorough synthetic optimization of polymerization conditions that enable optically active thermally robust semiaromatic PAs **42–47** (see Fig. 8) and aramides (*vide infra*) [62–67]. The polymers were obtained through polymerization between commercially available diisocyanates and designed structurally alike amide-endowed diacids. The diacids were prepared via multistep protocols, including consecutive imidization of L-aminoacids with phthalic or 1,8-naphthalic anhydride, followed by formation of a chloroanhydride that was further grafted to 5-aminoisophthalic acid either directly or via 4-aminobenzoyl bridge. The authors reported how different polymerization conditions affect properties of resulting semiaromatic PAs **42–47**. Specifically, an effect of ammonium or imidazolium ILs as a reaction medium, different catalysts, conventional and MW-assisted heating was disclosed. Thermally robust PAs **42** and **43** contained 1,8-naphthalimide substituent and hexamethylene or isophorone diamine monomers respectively. These polymers displayed  $T_g$  in the range of 120–135 °C and  $T_{5\%}$  above 289 °C. Notably, polymerization performed in molten DIPIB provided **42** and **43** with superior thermal properties, compared to the same polymers isolated from a reaction in TBAB. In contrast to the solvent effect,

variation in heating method almost did not affect thermal properties of the resulting PAs. As compared to **42** with linear aliphatic monomer, isophorone-based PA **43** displayed lower  $T_g$  and higher  $T_{5\%}$ , while both polymers formed ample CR in the range of 45–47%, leading to very high calculated LOI >35%. Difference in temperatures of thermal decomposition of **42** and **43** was rationalized in a study of kinetic parameters. Specifically, both Coast-Redfern and Dharwarkar-Kharkhanawala methods gave comparable results:  $E_a$  was in range of 60.7–64.6 kJ/mol and 57.6–71.8 kJ/mol for **42** and **43** respectively and corresponded to TGA results. PAs **44** and **46** contained hexamethylenediamine repeating units and side phthalimide-endowed substituents of different bulkiness that were grafted to the aromatic diacid. The polymers **44**, **46** demonstrated inferior  $T_g$ ,  $T_{5\%}$  and two times lower thermal decomposition  $E_a$  of 30.5 kJ/mol (Coast-Redfern method) as compared to **42** with a compact 1,8-naphthalimide entity. Moreover, **44** and **46** formed less CR and therefore displayed lower calculated LOI. Unfortunately, thermal properties of other isophoronediamine-based polymers were not disclosed in detail.

Zhang reported the synthesis and study of series of semi-aromatic polyetheramides **48–52** containing diamine segments with different even number of carbon atoms in the aliphatic chain (see Fig. 9) [68]. The polymers were prepared using S<sub>N</sub>Ar polymerization between aryl fluorides with internal amide functionality and 1,1-bis(4-hydroxyphenyl)-1-phenylethane. Elongation of the aliphatic segments in the monomers lead to gradual decrease of  $T_g$  and water absorption. On the contrary, thermal stability ( $T_{5\%}$ ,  $T_{max}$  and  $E_a$  of thermal decomposition) increased with increasing the number of methylene units in aliphatic chains. Specifically,  $T_{5\%}$  grew from 405 °C to 443 °C and  $E_a$  rose from 180.1 kJ/mol to 203.6 kJ/mol (estimated using Kissinger method). Notably,  $E_a$  of thermal decomposition for **48–52** is significantly higher than values reported for aliphatic and other semiaromatic co-PAs. Semiaromatic polymers **48** and **49** showed superior flame retardancy and improved char formation (28.3% and 7.5% respectively) as compared to **50–52** and commercial PA9T. In addition, **48** and **49** demonstrated the highest LOI values of 34% and 30% and were rated as V-1 and V-2 materials respectively in UL-94 vertical burning test. Both polymers displayed no melt dripping, and the authors referred PAs **48** and **49** as intrinsically FR polymers. However, PAs **50–52** with longer aliphatic segments were fully combustible.

## 5. Aramides

Along with semiaromatic PAs **42–47**, Mallakpour reported the preparation and properties of aramids **53–56** and **67**, **70** obtained from the similar derivatives of 5-aminoisophthalic acid and commercial aromatic diisocyanates (see Fig. 10) [62–67]. Expectedly, aramids displayed better thermal properties as compared to the semiaromatic counterparts, demonstrating  $T_g$  and  $T_{5\%}$  in the range of 148–238 °C and 250–407 °C respectively, that is on average higher in relation to **42–47**. Notably, similar to the semiaromatic PAs, aramids isolated from reactions performed in ILs showed superior thermal properties, compared to the products from

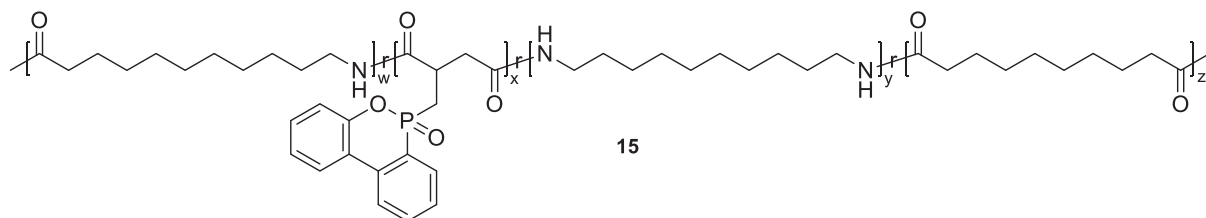
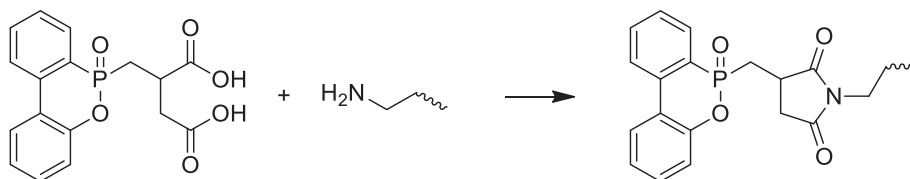
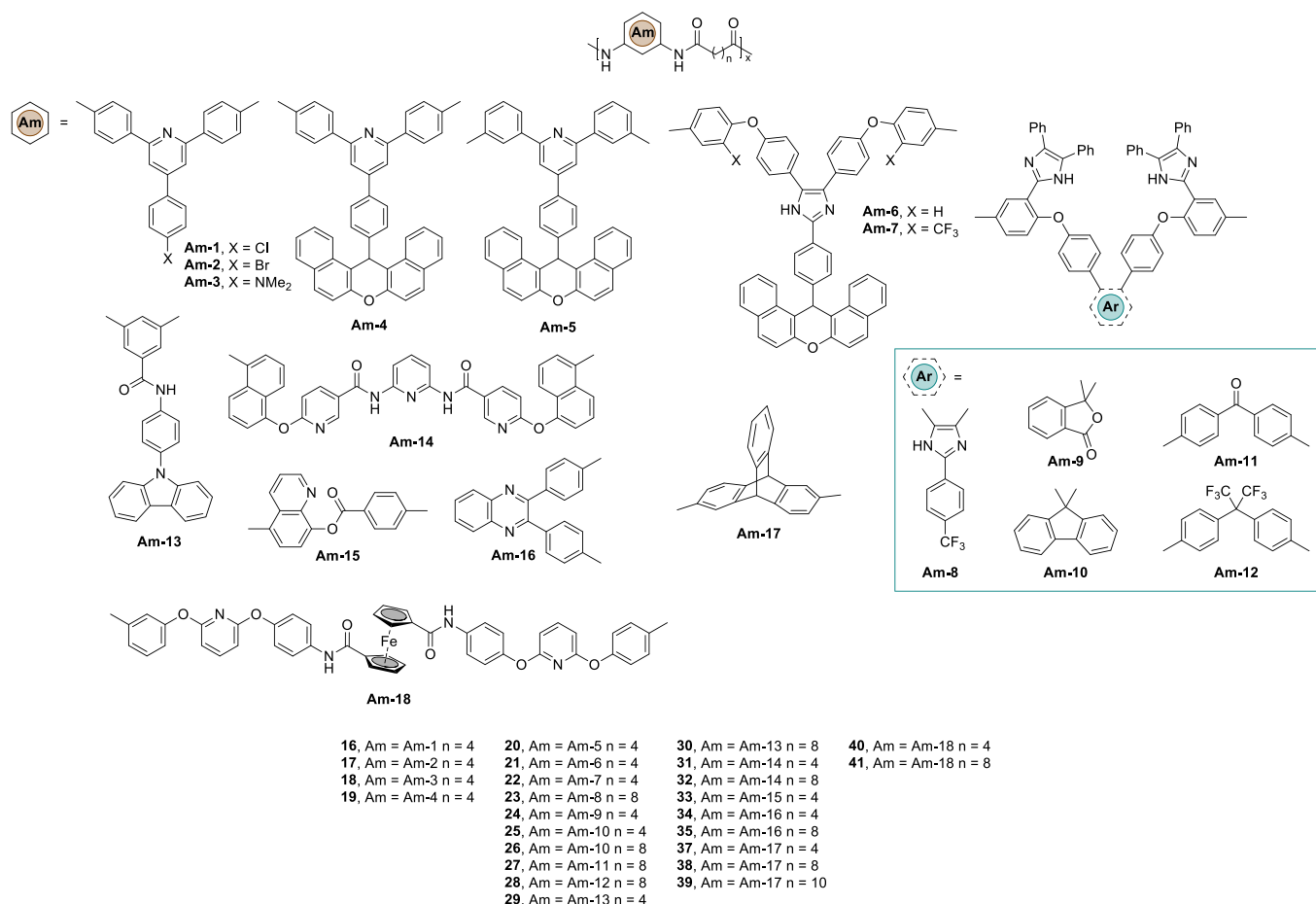


Fig. 5. PA11 FR copolymer containing DOPO-ITA.



**Scheme 4.** Competing imidification reaction between DOPO-ITA and an amine end-group.



**Fig. 6.** Chemical structures of FR semiaromatic PAs.

polymerizations carried out in NMP. Moreover,  $E_a$  of thermal decomposition of **53**, **54** and **70** was higher, yet significantly discrepant values were reported. The elevated  $E_a$  for PA **53** was attributed to either homolytic cleavage of Ph-CH<sub>3</sub> bond in 2,4-diaminotoluene monomer resulting in highly cross-linked structures resistant to further decomposition, or enhanced intermolecular hydrogen bonding due to +I effect of the methyl affecting electronic properties of proximal amide-groups. However, the significant discrepancy of ~110 kJ/mol for **53** was not discussed. In addition, char yields for PAs containing 2,4-diaminotoluene were in the same range as for other aramids, despite hypothesized extensive crosslinking. Lastly, PA **54** displayed overall  $E_a$  of thermal decomposition ranging from 54.4 kJ/mol [62] to 131.8 kJ/mol [63], while aramid **57** had even higher  $E_a$  of 153.6 kJ/mol [65].

Further works by Mallakpour, Dinari and Rafiee described the development of methodologies for synthesis of structurally related PAs **57–95**, based on derivatives of 5-aminoisophthalic acid endowed with other bulky chiral imide-containing substituents,

while the polyamides were obtained through direct polycondensation of the diacids with aromatic diamines [69–77]. The chiral pendants were derived following a similar protocol as for the substituents of **42–47** followed by its grafting to the amino-group of 5-aminoisophthalic acid via an amide linkage. The designed diacid monomers were polycondensed with a number of aromatic diamines to deliver families of thermally stable aramids **57–95**. The polymerization optimization included the use of ILs and MW-assisted reactions studied in comparison with a conventional polycondensation method in aprotic solvents [70–72,76]. Despite different polymerization protocols, resulting aramids showed minor differences in properties, suggesting an advantage of IL and/or MW-assisted heating to substitute hazardous solvents and shorten polymerization times. For example, aramids **65** and **72** showed similar thermal properties with a  $T_g$  of 168 °C and 155 °C respectively and no significant thermal decomposition up to 348 °C. Similarly, PAs **94** and **95** with ethanoanthracene entity also showed little differences in thermal properties with no evident dependence



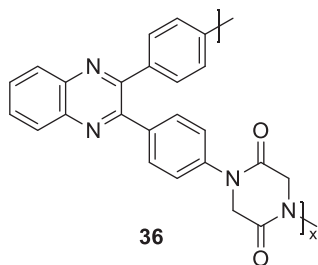


Fig. 7. FR semiaromatic PA containing quinoxaline and 2,5-piperazinedione cycles.

of the polymers properties on polymerization method employed [76]. The families of the reported PAs demonstrated high  $T_g$  ranging from 155 °C to 236 °C and no significant decomposition up to 315–459 °C. Moreover, the polymers formed >38% of char residues (measured at 800 °C under  $N_2$  atmosphere), thus displaying high calculated LOI above 32.7%. Thermal decomposition of PAs **65**, **72**, **82** and **84** was investigated in TGA experiments with different heating rates to derive kinetic parameters of thermal degradation using Coats-Redfern equation [70,74]. The studied aramids displayed an overall  $E_a$  of thermal degradation in the range of 52.1–78.5 kJ/mol. Furthermore, the authors rationalized the thermal oxidative degradation of **82** and **84** that was best described by random nucleation mechanism with one nucleus on individual particle. Lastly, all polymers were readily soluble in  $H_2SO_4$ , amide solvents and DMSO, thanks to bulky substituents that prevented close interaction and formation of hydrogen bonds among macromolecules.

Rafiee reported synthesis and properties of photoactive aramids **96–103** containing acetoxynaphthalene moiety, grafted to the amino-group of 5-aminoisophthalic acid via 4-aminobenzoyl bridge [78]. The designed diacid monomer was synthesized via a 5-step procedure from 3-hydroxynaphthalene-2-carboxylic acid and introduced into MW-assisted polycondensation with a number of commercial and one bulky designed aromatic diamine (*vide infra* for synthesis) that furnished a family of thermally stable fluorescent polymers. Two selected aramids **101** and **103** were characterized in DSC and TGA experiments, exhibiting  $T_g$  of 169 °C and 176 °C respectively and no significant thermal degradation up to 415 °C. Moreover, the polymers formed 62–63% of char residues (measured at 800 °C under  $N_2$  atmosphere), and as a result demonstrated high calculated LOI above 42.3%. The selected representative results expectedly contrasted with the thermal stability of related macromolecules **104–117** that contained smaller isomeric *m*- and *p*-acetoxypheyl-based substituents and no 4-

aminobenzoyl bridge [79]. The related designed diacylchlorides were obtained following a 4-step protocol, including acetylation of isomeric hydroxybenzoic acids, its grafting to the amino group of 5-aminoisophthalic acid followed by conversion of carboxyls to carbonyl chlorides. Aramids **104–117** were synthesized as NP using commercial aromatic diamines in dioxane-water mixture under ultrasonic irradiation. Except for **105**, polymers **104** and **106–117** formed noticeably less char in the range of 3.8–11.9%, therefore exhibiting LOI below 23.8% typical for readily combustible materials with no flame retardancy. Importantly, the aramids **104–117** were tested in the form of NP, therefore flame resistance of bulk samples may differ significantly.

Gómez-Valdemoro reported synthesis and properties of triazole containing aramids **118–122** designed for  $Hg^{2+}$  extraction from aqueous media, nevertheless displaying advantageous heat-resistant properties thanks to rigid N-rich heteroaromatic backbone with aptitude for hydrogen-bond formation (see Figs. 10 and 11) [80]. A 1,2,4-triazole unit was either grafted as a side substituent or integrated into a macromolecular backbone. In the first case, diethyl-5-aminoisophthalate was converted to diethyl-5-(3-benzoylthioureido)isophthalate followed by reaction with hydrazine monohydrate to form 1,2,4-triazole heterocycle and subsequent ester hydrolysis. In the latter case, a similar synthetic concept was used to prepare an amino acid monomer: 4-(3-(4-nitrobenzoyl)thioureido)benzoate was reacted with hydrazine monohydrate to form the heterocycle followed by conversion of terminal ester- and nitro-groups into free carboxylic acid and amine respectively. Additionally, the excess amino acid was also reacted with isophthaloyl chloride to furnish a new symmetric elongated diacid with two internal amide bonds. The short diacid monomer with side triazole substituent was condensed with *m*- or *p*-phenylenediamine, yielding **118** and **119** respectively. The amino acid was either homo- or co-polymerized with isophthalic acid and *m*-phenylenediamine to form **120** and **121**. Finally, the elongated diacid monomer was directly polycondensed with *m*-phenylenediamine, forming **122**. Presence of polar N-rich heterocycles and amide bonds in the structure resulted in very high water uptake above 10%. Nevertheless, aramides **118–121** displayed excellent heat robustness with very high  $T_g$  in the range of 293–375 °C and exhibited no decomposition up to 365 °C that was almost insensitive to atmosphere used. Moreover, the polyamides formed >46% of char residues (measured at 800 °C under  $N_2$  atmosphere), therefore exhibiting high LOI above 35% and thus classified as self-extinguishing materials.

Estévez reported synthesis and properties of thermally stable aramids **123–128** that incorporate chromophore and fluorophore fluorene-based substituents [81]. The photoactive fluorene-based monomer was obtained conjugating the amino group of 5-

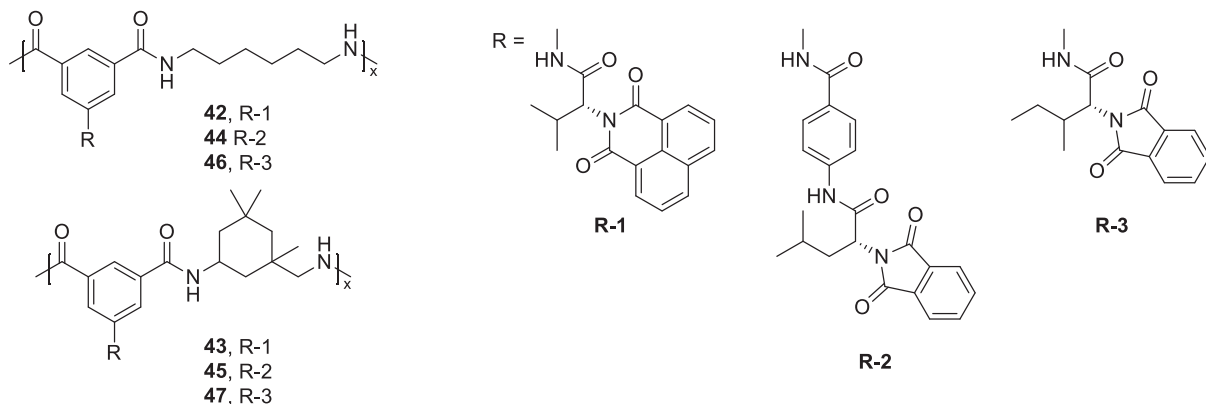


Fig. 8. FR semiaromatic PAs containing derivatives of 5-aminoisophthalic acid.

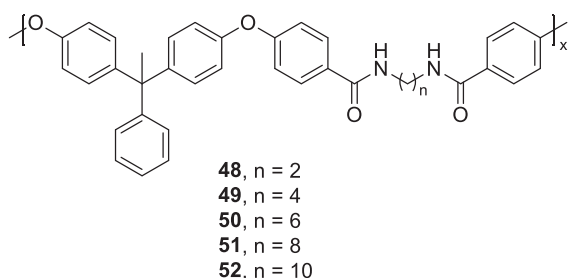


Fig. 9. Semiaromatic polyetheramides containing 1-bis(4-hydroxyphenyl)-1-phenylethane unit.

aminoisophthalic acid with 9H-fluoren-2-yl isocyanate and introduced into copolymerization with *m*-phenylenediamide, substituting 10% of isophthalic acid. The resulting aramid **123** was converted to **124** via post-polymerization oxidation of fluorenes' methylene. Similarly, the preparation of other photoactive macromolecules **125–128** implied modification of fluorenone-endowed **124**, exploiting reactivity of the cyclic carbonyl group. All PAs were readily soluble in amide solvents, DMSO and demonstrated high water uptake of 8.3–9.4%. Finally, aramids **123–128** demonstrated good thermal resistance up to 255 °C regardless of the atmosphere used and formed >47% of char residues (measured at 700 °C under N<sub>2</sub> atmosphere), resulting in high assessed LOI above 36.3%.

Thanks to affordability of cyanuric chloride and temperature-dependent stepwise substitution of Cl-atoms in it, S-triazine is a widely used heteroaromatic platform which allows to graft up to

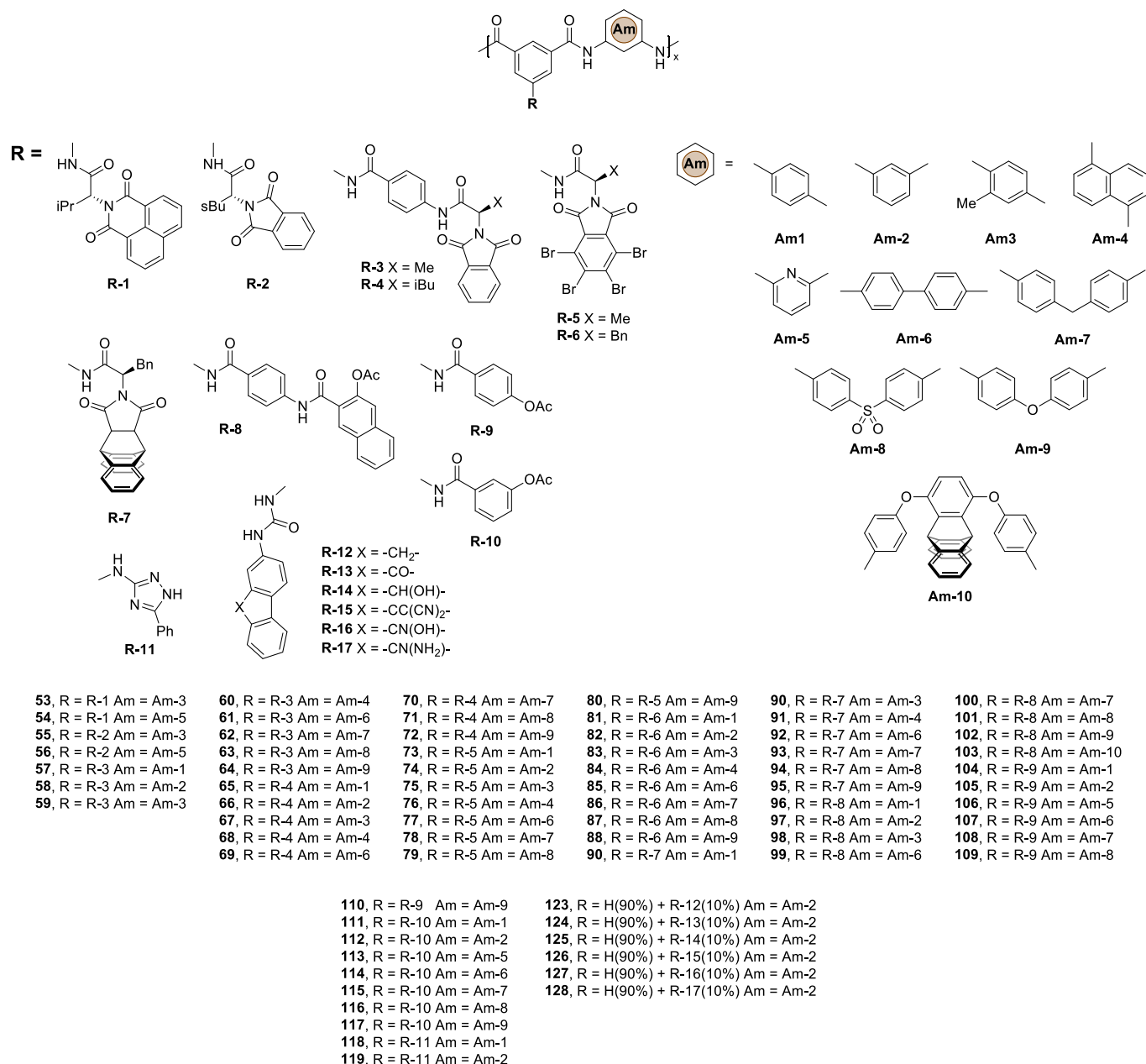


Fig. 10. FR aromatic PAs containing derivatives of 5-aminoisophthalic acid.

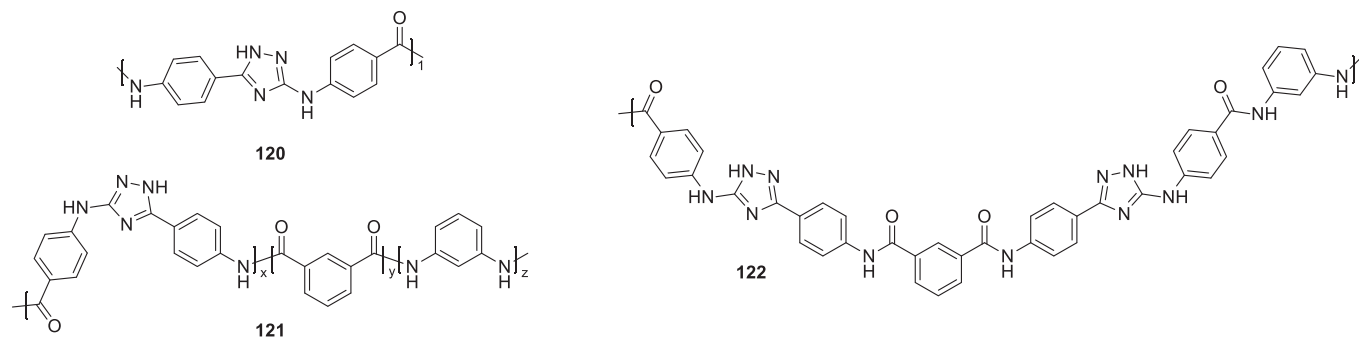
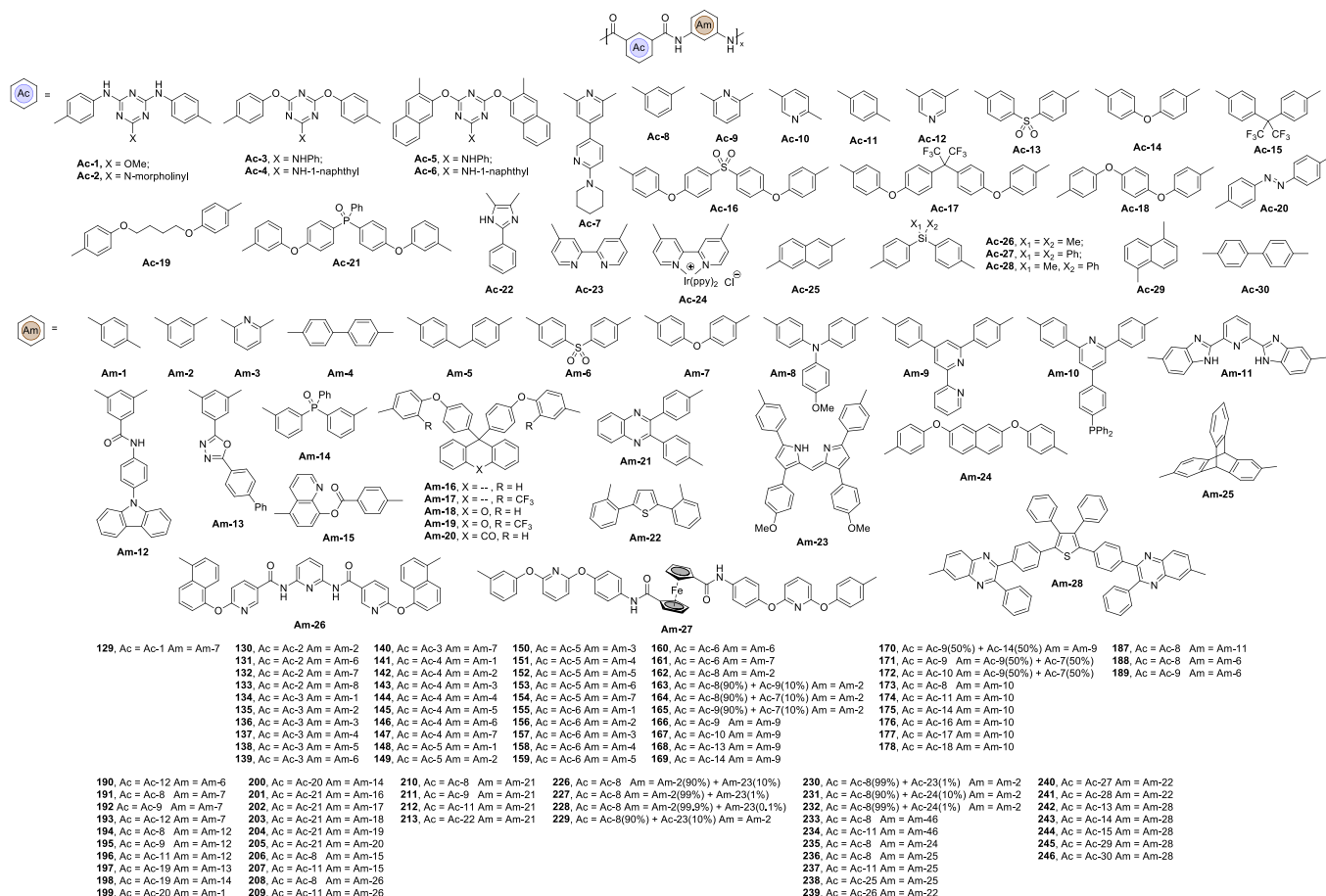


Fig. 11. FR aramids containing triazole units.

three reactive nucleophiles ( $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{OH}$ ,  $-\text{SH}$  etc.) in *meta*-relation. S-triazine core was used in synthesis of diacid monomers for preparation of series of heat resistant aramids **129–161** (see Fig. 12). The synthesis of the monomers included consecutive reactions of cyanuric chloride with one equivalent of a monofunctional nucleophile (morpholine, aniline or 1-naphthylamine) followed by reaction with two equivalents of amino- or hydroxyl-carboxylic acid [82–85]. The resulting designed N-rich aromatic diacids were used in polycondensation with several aromatic diamides either directly, thus delivering PAs **129–133**, or converted to the corresponding acyl chlorides in order to prepare polymer NP of **134–161**, analogously to **104–117**. Aramids **129–133** demonstrated

high thermal robustness, displaying  $T_g$  beyond 208 °C and no significant thermal decomposition up to 370 °C [82,83]. Moreover, the aramids formed ample char residues ranging from 44% to 59% (measured at 800 °C under  $\text{N}_2$  atmosphere), thus resulting in high calculated LOI above 35.1%. Additionally, aramid **129** was studied in MCC experiments and revealed pHR of 111 W/g and THR of 8.2 kJ/g. Further reinforcement of **129** with CPN nanofiller improved thermal parameters and fire performance [82].

As for melamine-based **130–133**, congener PAs **134–161** were well soluble in polar amide solvents, DMSO, and exhibited good thermal stability. However, char yield of these polymers strongly varied: from 3.2% to 36.8% (measured at 890 °C under  $\text{N}_2$



atmosphere), suggesting that TGA of polymers in form of NP may bring about strong scattering in results of char yield (similarly to **104–115**). Thus, the calculated LOI of aramids **134–161** were in the range of 18.3–31.7% [84,85].

Pyridine is another heteroaromatic unit used to support diamine or di-acid functionalities and therefore widely employed in the synthesis of heat-resistant aramids. Unlike similar carbocyclic analogues, pyridine is a polar electron-deficient heterocycle capable of providing an additional H-bond accepting site which may strongly influence the thermal properties of a polymer. Oppositely, pyridine can also provide a lone pair of electrons for coordination of metal species, thereby suitable for application in synthesis of hybrid functional materials. Beside the simplest commercially available pyridine dicarboxylic acids and diamines, researchers have also reported the preparation of designed pyridine monomers.

Barrio-Manso described synthesis and properties of the simplest pyridine-containing aramid **163** and congener macromolecules **164** and **165** combining bipyridine with piperidine as building blocks for the synthesis of aromatic diacid monomer [86]. The aromatic PAs were obtained through direct polymerization and studied in comparison with readily available carbocyclic aramid **162** - poly [*N,N'*-(1,3-phenylene)isophthalamide]. In addition to good thermal stability, the designed heteroaromatic polymers **163** and **164** displayed fluorescence and were used for sensing of Cr(VI), Fe (III) and Cu(II) thanks to the presence of coordinating N-atoms. The bulky rod-like monomers were derived from 4-hydroxypyridine-2,6-dicarboxylic acid via multistep protocol, including a Pd-catalyzed cross-coupling. Introduction of the bulky rod-shaped pendant substituent did not improve solubility of **163**, **164** and slightly affected the thermal decomposition temperatures (increase of  $T_{5\%}$ ) as compared to the substituent-less macromolecule **163**, that demonstrated  $T_{5\%}$  ca. 50 °C lower than for **162**. All aramids formed char residues in the range of 53–65% (measured at 800 °C under  $N_2$  atmosphere) and demonstrated high assessed LOI of 39–43% and therefore rendering polymers as self-extinguishing materials.

Koomareh and Souri reported a family of thermally resistant bipyridine-based homo- and co-polyamides **166–172**, where the heterocycles were integrated into the structure of bulky star-shaped aromatic diamines [87]. The designed heteroaromatic monomers were obtained following 4-step protocol and using Kröhnke reaction to construct bipyridine fragment from 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridin-1-ium and 1,3-bis(4-nitrophenyl)prop-2-en-1-one, followed by the reduction of the terminal nitro-groups. Thereafter, the monomers were directly polycondensed with commercial diacids and *p*-phenylenediamine to yield (co)aramids exhibiting crystallinity, yet soluble in polar amide solvents, DMSO and  $H_2SO_4$ . Additionally, aramids **166–172** displayed high  $T_g$  in the range of 160–180 °C in conjunction with thermal stability up to 360 °C. Notably, homoaramids **167** and **168** with the “elongated” and flexible diacid monomers displayed the highest  $T_g$ . Lastly, the polymers formed 44–63% of char residues (measured at 800 °C under  $N_2$  atmosphere) resulting in high calculated LOI above 35.1%.

Zhang reported a family of heat resistant aramids **173–178** based on a related bulky 2,4,6-triphenylpyridine diamine monomers, additionally endowed with triphenylphosphine substituent [88]. The designed diamines were obtained following Hantzsch pyridine synthesis methodology from 4-nitroacetophenone and 4-(diphenylphosphino)-benzaldehyde with subsequent reduction of nitro-groups to amino-groups. In addition, few aromatic diacids with internal ether groups were prepared from commercial phenols and 4-fluorobenzonitrile. Subsequent direct polycondensation of the diamine with various commercial and in-house made aromatic diacids delivered amorphous aramids **173–178** with good solubility in polar aprotic solvents including pyridine and less polar

*m*-cresol and  $CHCl_3$ . Moreover, the polymers demonstrated excellent thermal robustness with very high  $T_g$  in the range of 316–332 °C and no significant mass loss up to 496 °C. Lastly, polyamides **173–178** formed 49–60% of char residues (measured at 800 °C under  $N_2$  atmosphere) resulting in high calculated LOI in the range of 39–43%. Notably, PA **186** containing a sulfone-group exhibited the lowest decomposition temperature and the highest char yield that was attributed to easier thermal degradation of less stable  $-SO_2-$  bridge.

Along with semiaromatic polymers **19–22**, Amininasab reported aramids **179–186**, endowed with a photoactive xanthene substituent, grafted to heterocyclic star-shaped platforms (see Fig. 13) [49,50]. PAs **179–182** were derived from isomeric designed diamides with 2,4,6-triphenylpyridine core and xanthene pendant through a direct polycondensation with terephthalic and dipicolinic acid [49]. The obtained polymers **179–182** were soluble in fewer solvents, than **19** and **20**, including polar amide solvents, DMSO and only partially soluble in pyridine and *m*-cresol. Yet, aramids **179–182** displayed high thermal robustness with  $T_g$  in the range of 218–268 °C,  $T_{10\%}$  above 338 °C, ability to form ample char residues >49% (measured at 700 °C under  $N_2$  atmosphere) and exhibit LOI >37%. Remarkably, PA **182** exhibited a superior char yield of 66.3%, however this phenomenon was not rationalized. In addition, to the individual PAs, the authors also reported the preparation of electrospun blends of PAN with 10 wt% and 30 wt% of **179**, however the polymer formulations displayed inferior thermal stability compared to the unmodified PAN or **179**. Aramids **183–186** with xanthene unit grafted to imidazole core displayed superior thermal stability compared to **179–182** [50]. The  $T_g$  of the polymers was in the range of 254–277 °C and  $T_{10\%}$  beyond 438 °C. However, the char yield and LOI of **183–186** were almost in the same range as for congener **179–182**: i.e. 41–61% (measured at 800 °C under  $N_2$  atmosphere) and 34–42% respectively. Comparison of thermal parameters of **183–186** do not suggest any evident dependence or correlation of thermal properties of the macromolecules with aromatic diacid used.

Abdolmaleki and Molavian reported the synthesis and properties of N-rich amorphous aramid **187** by incorporating a designed heteroaromatic diamine based on 2,6-bis(2-benzimidazol-2-yl)pyridine [89]. The monomer was synthesized via 3-step protocol from 1,2-phenylenediamine and 2,6-pyridinedicarboxylic acid followed by nitration and reduction of the terminal nitro groups. Subsequent direct polycondensation of the diamine with isophthalic acid in TBAB afforded the coordinating macromolecule **187**. Aramid **187** displayed moderate thermal stability with  $T_{5\%}$  of 174 °C, while it formed ample char residues of 61% (measured at 800 °C under  $N_2$  atmosphere) and therefore exhibited high calculated LOI of 41.9%. The coordinating capacity of **187** was exploited to support and stabilize Co NP, used for catalysis. The nanofiller slightly improved char yield and LOI.

Hassan reported synthesis and properties of aramids **188–193** in their native and Cu(II)-doped forms, studying dielectric properties of resulting hybrid materials [90]. The polymers were obtained as NP from commercial aromatic diamines and aromatic diacylchlorides, followed by doping of the macromolecules with  $Cu(OAc)_2$  in DMSO. The authors investigated the kinetic parameters for thermal decomposition and calculated LOI of 25.2–43.5% for pristine aramids **188–193**. Lower LOI of 20.3–29.5% was obtained for Cu-doped polymers. However, the latter values were derived from char yield obtained at 700 °C and not 500 °C as determined for native **188–193**.

Similar to semiaromatic PA **29** and **30**, aramids **194–196** contained diamine with a carbazole-pendant group [55]. The resulting aramids derived from direct polycondensation with commercial

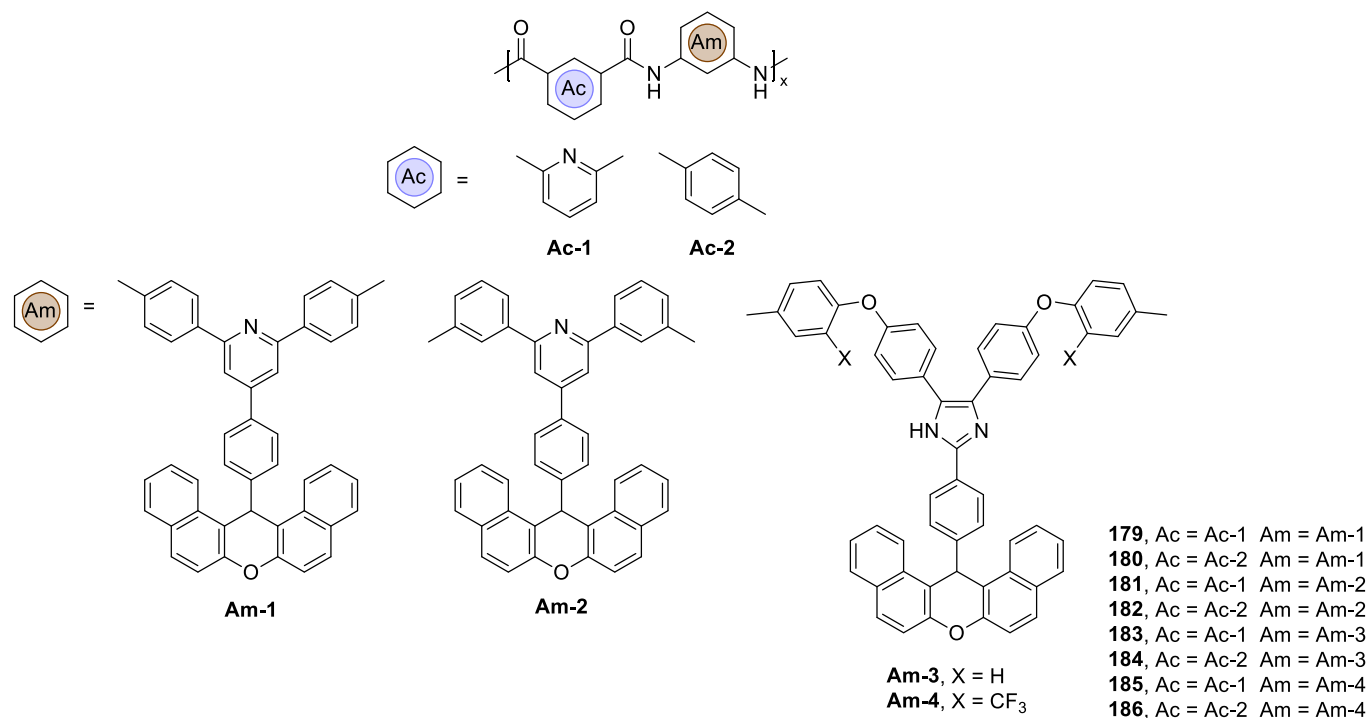


Fig. 13. FR aramids containing optically-active xanthene pendant.

aromatic diacids demonstrated good solubility in polar amide solvents, DMSO and pyridine. In addition, aromatic PAs **194–196** showed high  $T_g > 275^\circ\text{C}$  and no significant thermal decomposition up to  $435^\circ\text{C}$ . Moreover, the formation of ample char for **194–196** (measured at  $700^\circ\text{C}$  under  $\text{N}_2$  atmosphere) ensured high assessed LOI in the range of 38.3–41.9% for the polymers.

FR aramids **197** and **198** incorporated similar 4,4'-(butane-1,4-diylbis (oxy)dibenzoic acid and different designed aromatic diamides. Faridi et al. described aramid **197** with bulky rigid rod-like diamine containing 1,3,4-oxadiazole unit synthesized via a 5-step protocol and utilizing 3,5-dinitrobenzoyl chloride as the key precursor for the diamine [91]. Direct polycondensation of the designed monomers afforded **197** with  $T_g$  of  $154^\circ\text{C}$  and  $T_{5\%}$  of  $200^\circ\text{C}$ . Moreover, the aramid **197** formed ample char residues of 42.3% (measured at  $800^\circ\text{C}$  under  $\text{N}_2$  atmosphere) and therefore exhibited high assessed LOI of 34.4%. The aramid **197** was also reinforced with ZnO NP that slightly improved  $T_g$ ,  $T_{5\%}$ , char yield and LOI of the polymer.

The triphenylphosphineoxide-based aramid **198** was obtained through direct polycondensation of the designed monomers [92]. The engineered phosphorus-based diamine was prepared in a two-step protocol, including nitration of triphenylphosphine oxide followed by reduction of terminal nitro-groups. In relation to **197**, aramid **198** demonstrated superior  $T_g$  and  $T_{5\%}$  of  $165^\circ\text{C}$  and  $350^\circ\text{C}$  respectively, while char yield and LOI were on par with the P-free polymer. Specifically, **198** formed 39.4% of char residues and exhibited high assessed LOI of 33%, that corresponded well to the experimental value of 32%. Reinforcement of **198** with an organo-modified clay improved fire resistance and thermal parameters of the polymer.

Faghihi and Hagibeygi reported another triphenylphosphine oxide-based aramid **200** incorporating 4,4'-azobisbenzoic acid monomer [93]. The diacid with azo-bridge was obtained by a reductive coupling of 4-nitrobenzoic acid in alkaline solution of glucose followed by conversion of the product to the corresponding

diacylchloride used for polycondensation with aromatic diamines. The P-containing polymer **200** was studied in comparison with a congener P-free aramid **199**, which was synthesized from *p*-phenylenediamine and exhibited inferior thermal properties and fire performance. Specifically, **200** demonstrated  $T_{5\%}$  of  $\sim 70^\circ\text{C}$  higher than that for **199** and exhibited LOI of 29%, while LOI of **199** was only 20%, typical for easily combustible materials.

Wei reported unconventional approach for the preparation of aramids **201–205** which incorporated triphenylphosphine oxide unit, cardo groups and ether linkages [94]. The synthesis of aromatic polymers was realized in a heterogeneous Pd-catalyzed carbonylation-polycondensation, employing bis(4-(3-iodophenoxy)phenyl)phenylphosphine oxide, designed diamines with cardo groups and CO in the presence of  $\text{PdCl}_2$  complexed on the surface of magnetic NP. Thus, the phosphine oxide formally constituted an aromatic diacid. The resulting aramids were well soluble in polar aprotic amide solvents, DMSO, pyridine and partially - in less polar THF. Moreover, the aramids **201–205** high thermal stability, displaying  $T_g$  of  $237–256^\circ\text{C}$  and  $T_{5\%}$  in the range of  $475–499^\circ\text{C}$ . In addition, all polymers formed ample char residues above 52.1% residues (measured at  $800^\circ\text{C}$  under  $\text{N}_2$  atmosphere), resulting in high assessed LOI  $> 39\%$ .

In different works, Mehdi-pour-Ataei reported synthesis and thermal properties of aromatic polyester-amides **206**, **207** by incorporating quinoline and **208**, **209** containing multiple pyridine units [56,57]. The hetaramides were obtained through similar polycondensation of commercial diacylchlorides with designed diamines (*vide supra* for synthesis). The synthesized PAs were well soluble in polar amide solvents, DMSO and *m*-cresol. Moreover, the aramids **206–209** displayed  $T_g$  above  $203^\circ\text{C}$  and  $T_{10\%}$  higher than  $370^\circ\text{C}$ , while char yield in the range of 43–56% brought about high assessed LOI beyond 34.7%. Notably, aramids **208** and **209** contained bigger pyridine monomers and displayed superior thermal robustness, as compared to **206** and **207** with compact quinolone-based diamines.



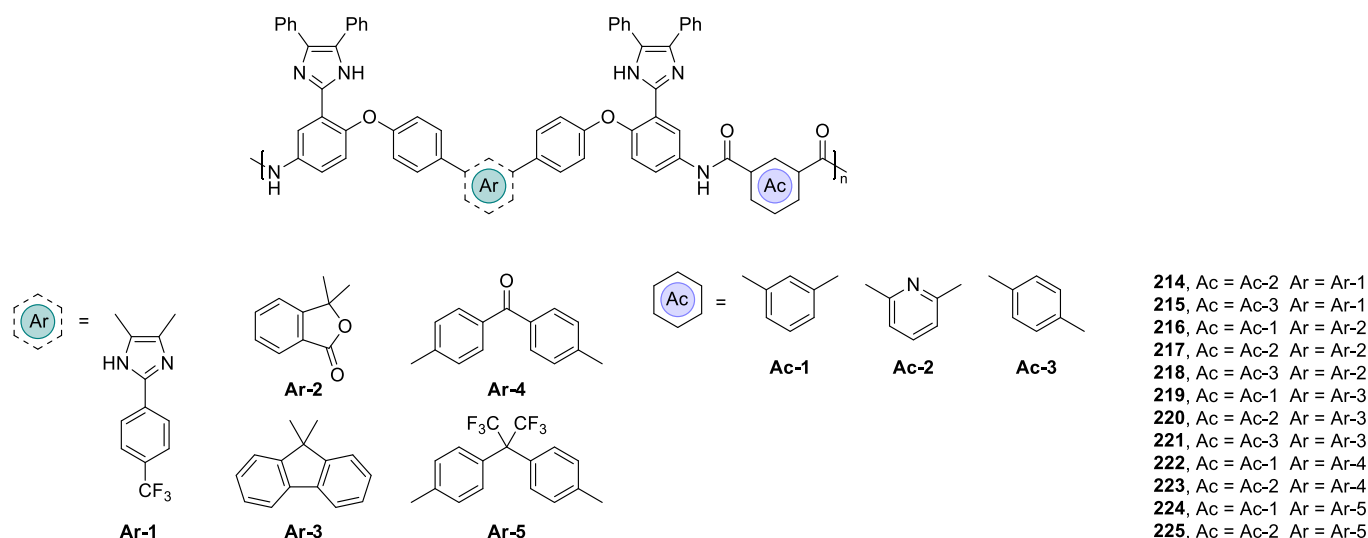


Fig. 14. FR aramids containing 4,5-diphenylimidazole side-substituents.

Like semiaromatic PAs **33–36**, quinoxaline-containing aramids **210–213** were obtained via two different methodologies, using commercial diacids and diamides respectively [58,59]. The resulting aramids displayed significantly differing  $T_{10\%}$  and char yield, depending on polymerization protocol. Specifically polycondensation products **211** and **212** demonstrated 10% mass loss at temperatures  $<100$  °C, while the macromolecules **210** and **212** obtained in cross-coupling polymerization exhibited high  $T_{10\%}$  above 460 °C. However, char residues for the synthesized aramids were less dependent on the preparation method and were in the range of 69.3–82.0% (measured at 600 °C under  $N_2$  atmosphere), and ensuring high calculated LOI  $>45\%$ .

Synthesis of families of structurally related thermally robust aramids **214–225** with 4,5-diphenylimidazole bulky pendant groups were reported in series of works along with analogous semiaromatic PAs **23–28** (see Fig. 14) [51–54]. The aramids were obtained through direct polycondensation method and were well soluble in polar amide solvents, DMSO, pyridine and, in some cases, in THF, *m*-cresol or  $CHCl_3$ . All aramids displayed  $T_g$  in the range of 258–330 °C and no significant thermal degradation up to 295 °C. Notably, except for **214**, all aramids incorporating dipicolinic acid displayed the lowest  $T_g$  and  $T_5\%$  (or  $T_{10\%}$ ) as compared to carbocyclic congeners. All aromatic PAs formed ample char residues  $>42\%$  and therefore exhibited high assessed LOI  $>34\%$ .

Trigo-López described the preparation of thermally stable intrinsically colored aramids **226–228**, that incorporate azadi-pyrromethene chromophore [95]. The designed diamine dye-core was prepared via three-step protocol and copolymerized at 0.1–10 wt% with *m*-phenylenediamine and isophthaloyl chloride to approach properties of poly-(*m*-phenylene isophthalamide). The resulting colored aramids were well soluble in polar amide solvents, DMSO, and displayed similar water uptake of 7% as the reference aramid **162**, studied for comparison. In addition, the incorporation of the heteroaromatic chromophore did not have influence on thermal properties as compared to **162**. The polymers **226–228** displayed  $T_5\%$  beyond 416 °C, high char yield above 56% and therefore assessed LOI  $>40\%$ .

Miguel-Ortega described pyridine-containing aramids **229** and **230** used for synthesis of hybrid luminescent materials **231** and **232**, bearing Ir(III) cyclometalated species [96]. Copolyamides were structurally related to poly-(*m*-phenylene isophthalamide), but

incorporated 10% or 1% of 2,2'-bipyridine-4,4'-dicarboxylic acid as a binding site for Ir. Pristine copolyamides displayed no significant thermal decomposition up to 425 °C, regardless the atmosphere used, and formed  $>60\%$  of char residues (measured at 800 °C under  $N_2$  atmosphere). Coordination of Ir (ppy)<sub>2</sub>Cl species led to a significant decrease in  $T_5\%$ , char yield and as a result lower assessed LOI of 36.0–38.0%. Moreover, the incorporation of polar bipyridine entities and ionic Ir species lead to increased water uptake of 15%, 17% for pristine **229** and **230** and 21%, 18% for hybrid **231** and **232** respectively.

Two other organometallic aramids **233** and **234** containing ferrocene entities were reported together with semiaromatic counterparts **40** and **41** [61]. Expectedly, the aromatic PAs displayed superior thermal properties as compared to **40** and **51** and more char residues. Both aramids **233** and **234** exhibited high experimental LOI of 27.5%

Mirsamiei and Faghihi reported wholly aromatic PA **235** endowed with flexible ether linkages [97]. The designed diamine with flexible ether bonds was obtained in  $S_NAr$  reaction of 2,7-dihydroxynaphthalene with 1-fluoro-4-nitrobenzene followed by reduction of terminal nitro-groups. Afterwards, direct polymerization with isophthalic acid afforded thermally robust **235**, displaying  $T_5\%$  of 285 °C and  $T_{10\%}$  of 426 °C. Moreover, aramid **235** formed ample char of 61% (measured at 700 °C under  $N_2$  atmosphere) and therefore exhibited high calculated LOI of 41.9%. Addition of MWCNT filler strongly improved  $T_5\%$  and had little positive effect on char yield formation and calculated LOI.

Triptycene-based aramids **236–238** were synthesized along with semiaromatic PAs **37–39** [60]. The designed diamine was polycondensed directly with commercial aromatic carbocyclic diacids, yielding fully aromatic PAs soluble in polar amide solvents, DMSO and pyridine. In addition, the polymers **236–238** displayed high thermal robustness with no significant thermal degradation up to 428 °C. Notably, **236** with isophthalic acid monomer exhibited the superior thermal stability among with all triptycenediamine-based PAs. Moreover, polymers **236–238** formed  $>66.7\%$  of char residues (measured at 800 °C under  $N_2$  atmosphere), thus exhibiting high assessed LOI in the range 44.1–46.9%.

Jessop reported synthesis and properties of oligoamides **239–241** incorporating designed thiophene- and diphenylsilane-containing monomers [98]. Aromatic 2,2'-(thiophene-2,5-diyl)

dianiline was prepared using 1-step Suzuki-Miyaura cross coupling, while the Si-endowed dicarbonyl chlorides were obtained via 3-step procedure. The latter included lithiation of *p*-bromotoluene followed by a reaction with different dichlorosilanes, oxidation of terminal Me-substituents and conversion of the corresponding carboxylic groups into carbonyl chlorides. Consecutive polycondensation afforded short oligomers of 6–11 repeating units that were well soluble in polar aprotic solvents  $\text{CHCl}_3$ , and THF. Despite short chains, the compounds displayed promising thermal properties:  $T_g$  in the range of 157–178 °C,  $T_{10\%}$  beyond 439 °C and char residue above 38% (measured at >600 °C under  $\text{N}_2$  atmosphere), and LOI >32%.

Salunkhe reported the preparation and properties of other FR aramids **242–246** composed of thiophene-quinoxaline aromatic diamines and aromatic diacid monomers [99]. The designed diamines were synthesized via 5-step procedure followed by direct polycondensation with commercial aromatic diacids. The introduction of polar heterocycles and bulky phenyl pendant groups into the macromolecular backbone lead to a good solubility of the PAs **242–246** in polar aprotic solvents, including DMAC, NMP, Py and less polar *m*-cresol. The polymers were amorphous and hydrophobic, attaining water contact angle up to 82° (for films made of **244**). In addition, the polyamides demonstrated excellent thermal properties, typical for aramides. Specifically, the polymers **242–246** displayed very high  $T_{10\%}$  above 698 °C and  $T_g$  in the range of 251–274 °C, depending on the rigidity of a diacid moiety. Furthermore, upon heating to 900 °C in  $\text{N}_2$  atmosphere all aramids decomposed to yield high amount of char residues in the range of 43–56% and therefore high calculated LOI >34.7%. Notably, aramids **245** and **246** containing more rigid diacids displayed superior thermal properties.

## 6. Polyamidoimides

Polyamidoimides represent an important class of hybrid polymers with high mechanical, thermal and chemical resistance. They combine properties of two parental polymers: polyamides and polyimides. The presence of amide linkers imparts improved processability, while retaining excellent polymer strength that is intrinsic to polyimides. A judicious choice of monomers affects polymer properties and may further improve solubility, processability, thermal properties and confer inherent flame-retardancy.

Polyamidoimides contain at least two different functional groups as polymer-forming bonds (amide and imide groups). Thus, the preparation of monomers implies introduction of either amide or imide bond into the structure beforehand, while the second remaining type of the bonding is formed during the subsequent polycondensation reaction.

Reaction between two equivalents of trimellitic anhydride and primary diamines is a common way to prepare diacid monomers containing bisimide functionality (see Fig. 15). Since PAI considered in this section are aramids, polymerization reaction is identical to aromatic PA, requiring activation of the functional groups.

Faghihi described the use of bis(3-aminophenyl)phenylphosphine oxide for preparation of FR PAI **247** and **248** [100]. The phosphorus-containing aromatic diamine monomer (*vide supra* **198** for the monomer synthesis) was polymerized with a designed imide-based diacid derived from commercial 4,4'-oxydianiline. The polycondensation of the monomers afforded PAIs **247** and **248**, that were well soluble in polar aprotic solvents while also resistant to thermal decomposition up to 270 °C and 340 °C respectively, and forming high amount of CR 41% and 69% of solid residues respectively (measured at 600 °C under  $\text{N}_2$  atmosphere). Moreover, LOI values were measured to be 21% for **247** and 29% for **248**, suggesting that replacement of a short *p*-phenylenediamine unit with P-

containing monomer might be beneficial for thermal stability and FR properties of the PAIs.

In other publications Faghihi reported synthesis and properties of series of related araliphatic polyetheramidoimides **249–264** containing linear aliphatic spacers of different length [101–103]. Ether-endowed flexible diamine “bridges” were synthesized starting from 4-nitrophenol and desired  $\alpha,\omega$ -dihaloalkanes, followed by reduction of terminal nitro-groups to amino-groups and their conversion into the corresponding designed imide-endowed diacids. Polycondensation of the resulting monomers with commercial aromatic diamines afforded hybrid FR polyetheramidoimides that were soluble or partly soluble in polar aprotic solvents. Some selected polymers were studied in TGA experiments and demonstrated high thermal stability, displaying  $T_{5\%}$  in the range of 285–390 °C. However, almost no correlation between thermal stability and number of carbon atoms in aliphatic linkers was observed for a series of polymers with isomeric aminophenylsulfones **251**, **256**, **261** and **251**, **257**, **262** reported systematically. Interestingly,  $T_g$  values for **256**, **261** were reported to be lower as compared to **257**, **262** containing longer aliphatic bridges. All polymers formed ample amount of char residues above 38.9% (measured at 800 °C under  $\text{N}_2$  atmosphere), therefore ensuring high assessed LOI values in the range of 33.1–40.0%.

Fully aromatic polyetheramidoimides were reported in a series of publications and mostly varied with a structure of a bridging unit connecting two imide cycles. These bridges are usually prepared via  $\text{S}_\text{N}\text{Ar}$  reaction between a phenol and an activated arylhalides, while one entity necessarily bears a masked amine functionality used further in imidization reaction. Expectedly, structure and functional groups embodied in the connecting unit can affect properties of the resulting macromolecules.

Shabaniyan and Hajibeygi reported aromatic polyetheramidoimide **265**, containing bisphenol A entity as a flexible ether linker [104]. The corresponding diacid monomer was derived from 4-fluoronitrobenzene and bisphenol A in  $\text{S}_\text{N}\text{Ar}$  reaction, followed by reduction of terminal nitro groups and formation of the corresponding imide-endowed diacid monomer. Interestingly, the aromatic congener **265** exhibited rather similar thermal properties as compared to the polymers with aliphatic linkers, despite its fully aromatic backbone. Specifically, polyetheramidoimide **265** displayed  $T_{5\%}$  of 344 °C,  $T_g$  of 180 °C and formed 46.3% of solid residues (measured at 800 °C under  $\text{N}_2$  atmosphere). Reinforcement of **297** with  $\text{Fe}_3\text{O}_4$  NP affected these parameters, mainly increasing  $T_g$ , char yield and the calculated LOI value.

Rafiee reported the preparation and properties of aromatic polyetheramidoimides **266–272** with bulky triptycene-based ether linker [105]. Diacid monomer synthesis was realized following similar concept as for **265**, whilst initial 1,4-dihydroxytriprycene scaffold was constructed via a Diels-Alder reaction between anthracene and *p*-benzoquinone. Direct polycondensation of commercial diamines and tailored triptycene diacid delivered amorphous polyetheramidoimides **266–272** with excellent solubility in polar organic solvents, which was ascribed to the presence of bulky triptycene group, preventing packing and hydrogen bonding among macromolecules. Moreover, all polyetheramidoimides displayed very high thermal stability without significant mass loss up to 500 °C;  $T_g$  in the range of 229–277 °C and formed >39% of solid residues (measured at 800 °C under  $\text{N}_2$  atmosphere). Notably, **267** and **268** demonstrated the best thermal stability and the highest char yield. Finally, assessed LOI values were above 33.1%, rendering the polyetheramidoimides **266–272** as self-extinguishing materials.

Thiruvassagam and Vijayan reported the synthesis and properties of series of fully aromatic polyetheramidoimides **273–284** based on benzophenone or diphenylsulfone central cores

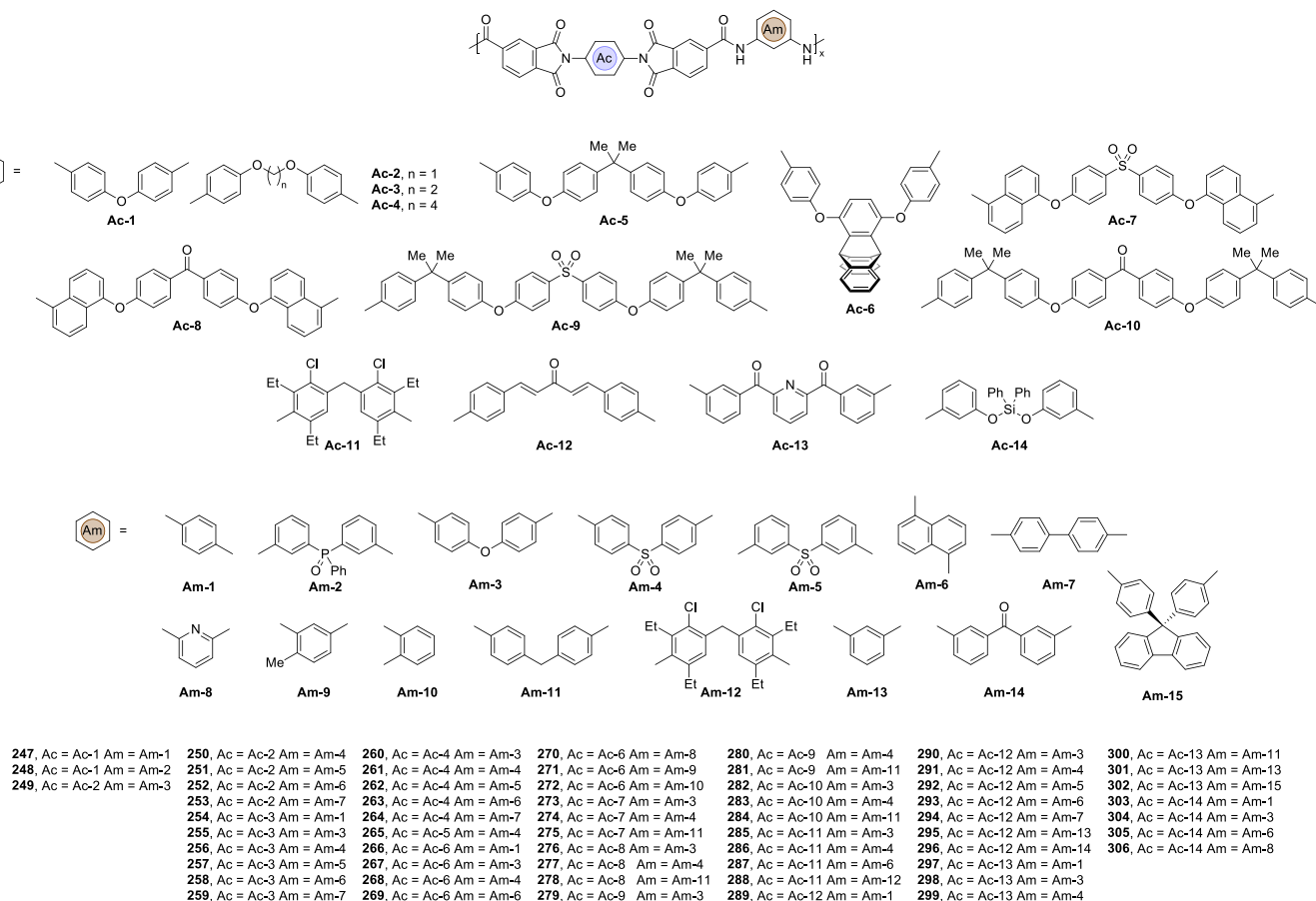


Fig. 15. Chemical structures of FP PAI.

[106,107]. Synthesis of symmetric imide-containing diacid monomers was accomplished via  $S_NAr$  reaction between 4,4'-dichlorodiphenyl sulfone or 4,4'-difluorobenzophenone and a selected aminophenols, followed by condensation with trimellitic anhydride. Polycondensation of commercial diamines and synthesized multifunctional diacid furnished series of poly-amidoimides **273–284** with improved solubility in polar aprotic solvents. Notably, polymers **273**, **276**, **279** and **282** incorporating 4,4'-oxydianiline unit were fully amorphous, exhibiting the best solubility among the investigated polyetheramidoimides. Moreover, all polymers demonstrated high thermal stability, without significant mass loss up to 370 °C and  $T_g$  in the range of 174–215 °C. Notably, macromolecules **279–284** with diphenylisopropylidene bridge showed superior properties compared to naphthalene-endowed **273–278**. In addition, investigated polyetheramidoimides formed 15–30% of char residues (measured at 800 °C under  $N_2$  atmosphere) and therefore realized assessed LOI values up to 30%.

Mallakpour and Zeraatpisheh described environmentally benign synthesis of PAI **285–288** [108]. The imide-containing diacid monomer was prepared using commercial 4,4'-methylenebis(3-chloro-2,6-diethylaniline) and trimellitic anhydride. The resulting diacid was polymerized with several commercial aromatic diamines, under MW-irradiation and using molten tetrabutylammonium bromide as a replacement of conventional solvents. Polymers **285–288** displayed good solubility in polar aprotic solvents and  $H_2SO_4$ . In addition, two PAI **287** and **288** were studied in TGA experiments and demonstrated good thermal stability up to 332 °C. Moreover, formation of >38% of solid residues (measured at

800 °C under  $N_2$  atmosphere) ensured high assessed LOI values above 32%.

Faghihi reported synthesis and characterization of thermally stable PAI **289–296**, containing dibenzylideneacetone repeating subunit [109]. The imide-containing aromatic diacid monomer was synthesized following a three-step protocol: consecutive condensation of 4-nitrobenzaldehyde with acetone, reduction of terminal nitro-groups followed by cyclic imide formation using trimellitic anhydride. The resulting monomer was further used in the polycondensation reaction with commercial diamines, yielding PAI **289–296** soluble in polar aprotic solvents and  $H_2SO_4$ . Three polymers **289**, **290** and **294** were also studied in TGA and DSC experiments and demonstrated good thermal stability. Specifically, these PAI showed high  $T_g$  in the range of 177–212 °C and no significant mass loss up to 365 °C. In addition, the investigated dibenzylideneacetone-based polymers formed solid residues above 42% (measured at 800 °C under  $N_2$  atmosphere), thus manifesting high calculated LOI over 34%.

Parhami described the preparation and properties of PAIs **297–302** by incorporating polar 2,6-dibenzoylpyridine units [110]. The heterocyclic diacid monomer was derived from 2,6-pyridinedicarbonyl dichloride in double Friedel-Crafts reaction with benzene, followed by consecutive double nitration, reduction of nitro-groups and imidization with trimellitic anhydride. Polycondensation of commercial diamines with the tailored heterocyclic diacid resulted in a hybrid and mostly amorphous PAIs **297–302** that were well soluble in polar aprotic solvents, while also soluble in *m*-cresol and pyridine upon heating. Moreover, all polymers demonstrated excellent thermal stability with almost no

mass lost up to 413 °C. Aromatic nature of polymers favored formation of ample char >53.4% (measured at 800 °C under N<sub>2</sub> atmosphere) and very high assessed LOI values over 38.9%. Notably, cardo PAI **302** displayed the best thermal and FR properties.

Jalalian reported the preparation and properties of silicon-endowed PAI **303–306** [111]. Si-bridged symmetric imide-based diacid monomer was derived from dichlorodiphenylsilane reacted with 3-aminophenol. Polycondensation of the designed diacid with four commercial aromatic diamines delivered PAI **303–306**. Polymers were well soluble in polar aprotic solvents and in *m*-cresol upon heating and showed some crystallinity. Furthermore, PAI **303–306** displayed high *T<sub>g</sub>* values in the range of 187–196 °C and excellent thermal robustness with no significant thermal decomposition up to 375 °C. In addition, the hybrid aromatic polymers formed ample solid residues above 39% (measured at 700 °C under air atmosphere), thus manifesting high assessed LOI value and self-extinguishing behavior. Remarkably, PAI **304** containing 4,4'-oxydianiline monomers demonstrated the poor thermal robustness and formed the least char.

Trimellitic anhydride is a versatile molecular platform and is used to graft affordable  $\alpha$ -aminoacids. This facile condensation provides asymmetric chiral imide-endowed diacid monomers, which allows the introduction of functionalized side-substituents along macromolecular backbone, break regularity of monomer connection and therefore increase solubility of PAI (see Fig. 16). This approach was investigated in a series of works by Mallakpour S. and co-authors.

Chiral PAI **307–310** were obtained from trimellitic imide-based araliphatic diacids and L-DOPA-endowed designed aromatic diamine [112,113]. The diamine was prepared via 2-step protocol, exploiting similar chemistry as for monomers for PAs **29, 30** and **194–196** (*vide supra*). The synthesis included amidation of L-DOPA

with 3,5-dinitrobenzoyl chloride, followed by a reduction or nitro-groups. Further polycondensation of the designed monomers was performed using MW-heating and resulted in chiral PAI **307–310** that were soluble in H<sub>2</sub>SO<sub>4</sub> and polar aprotic solvents, including pyridine. Two PAI **307** and **310** were characterized in TGA experiments and demonstrated thermal stability up to 326 °C. The investigated PAI formed 46.8% and 45.4% of char residues (measured at 800 °C under N<sub>2</sub> atmosphere) respectively, and therefore demonstrated high calculated LOI >35%.

Structurally similar PAIs **311–314** contain more compact 2-aminothiazole pendant group instead of L-DOPA [114]. Polycondensation reaction of the designed monomers afforded a family of the related chiral PAIs that were soluble in H<sub>2</sub>SO<sub>4</sub> and polar aprotic solvents, including pyridine and *m*-cresol at room temperature. Thermal studies of **311** and **312** revealed no significant thermal decomposition up to 290 °C. PAIs **311** and **312** formed 34% and 28% of solid residues (measured at 800 °C under N<sub>2</sub> atmosphere), and therefore exhibited high calculated LOI above 28%.

Replacement of the amide-containing pendant groups with a directly connected benzimidazole group at aromatic diamine monomers resulted in PAI **315–318** with the least thermal-robustness [115,116]. The designed diamine monomer was obtained through 2-step protocol, that included direct condensation of 1,2-phenylenediamine and 3,5-dinitrobenzoyl chloride with Eaton's reagent. Subsequently, direct polycondensation of several synthesized imide-based diacids with the aromatic diamine yielded the desired polymers **315–318**. These PAI demonstrated *T<sub>5%</sub>* in the range of 220–260 °C, depending on the substituent of the parental amino acid used and polymerization protocol. Despite their moderate thermal stability, PAI **315–318** formed 30–46% of char residues (measured at 800 °C under N<sub>2</sub> atmosphere), thus demonstrating high LOI >29%.

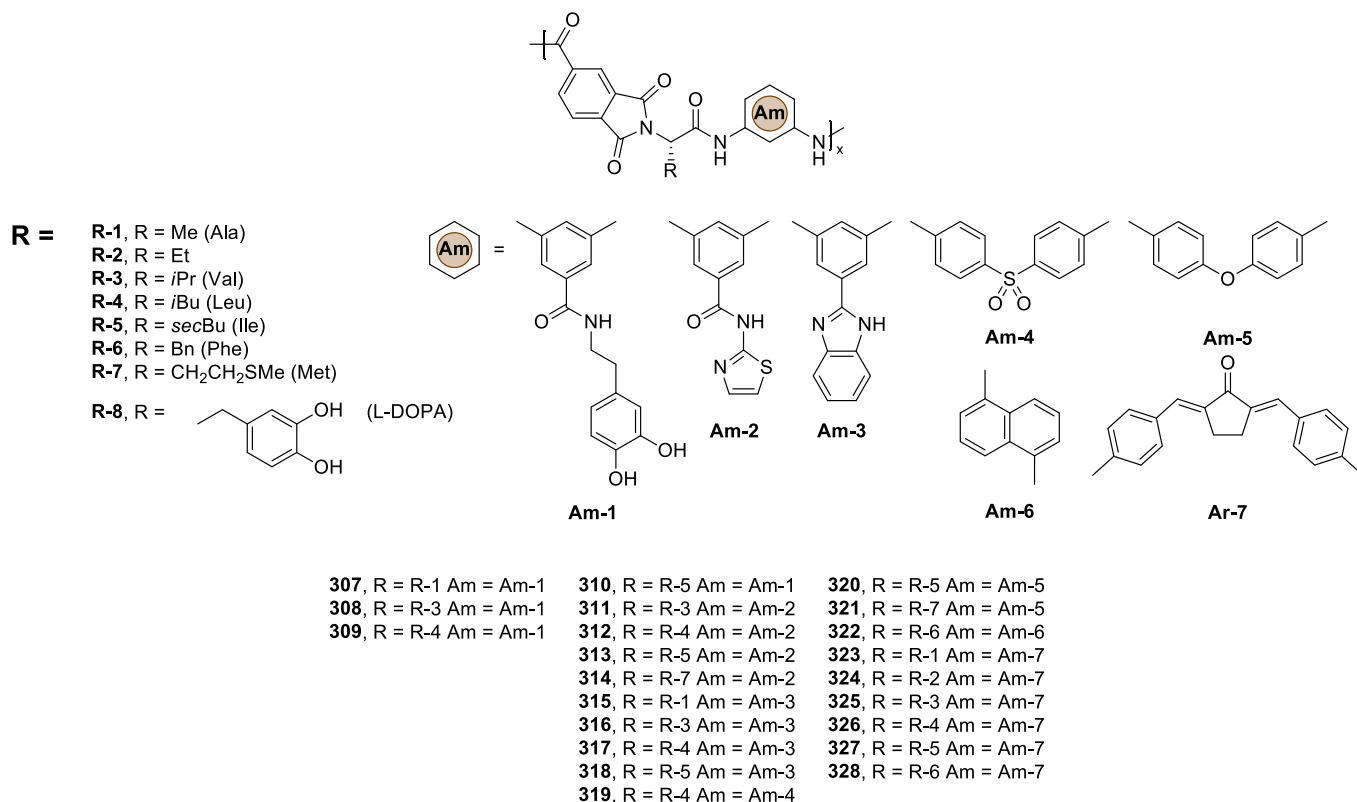


Fig. 16. FR PAI based on conjugates of trimellitic acid with L-aminoacids.



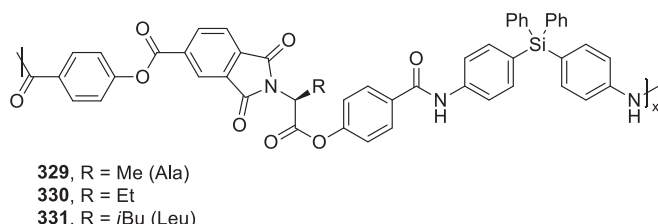


Fig. 17. FR PAI containing tetraphenylsilane-based diamine monomer.

The aramid **319** was obtained through polycondensation of *L*-leucine based imidodiacid and commercial 4,4'-diaminodiphenylsulphone [117,118]. Despite similar synthetic protocols used, **319** demonstrated slightly different decomposition temperatures:  $T_{5\%}$  of 276 °C or 260 °C and  $T_{10\%}$  of 360 °C or 301 °C. Moreover, scattering in char yield results was also demonstrated and had similar trend with the decomposition temperatures: 44.8% and 39.1%. Nonetheless, **319** formed ample char that ensures high assessed LOI values above 39%. The polymer **319** was reinforced with organo-modified ZrO<sub>2</sub> NP that slightly improved char yield and LOI.

Mallakpour and Barati described PAI **320** that was obtained in polycondensation of *L*-isoleucine based imidodiacid with a commercial 4,4'-oxydianiline [119]. The polymer demonstrated no significant thermal decomposition up to 197 °C and formed ample char residues of 52.9%, thus ensuring high assessed LOI of 38.6%. PAI **320** was also reinforced with organo-modified TiO<sub>2</sub> nanofiller that improved thermal resistance of the polymer.

Interestingly, structurally related PAI **321** containing *L*-methionine exhibited significantly higher thermal resistance [120]. Specifically, **321** displayed  $T_{5\%}$  of 326 °C, while formed 52.0% of char residues, similarly to **320**. Thus, high calculated LOI of 38.3% was achieved. Further reinforcement of **321** with organo-modified SiO<sub>2</sub> nanofiller improved thermal stability of the polymer and char formation.

Mallakpour and Khadem reported the preparation of PAI **322** via polycondensation of *L*-phenylalanine-based imidodiacid with commercial 1,5-diaminonaphthalene [121]. PAI **322** showed high  $T_{5\%}$  of 353 °C and formed ample char residues of 49%, therefore giving rise to high calculated LOI of 37%. Introduction of organo-modified  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> filler only moderately increased the  $T_{5\%}$  and  $T_{10\%}$  of **322** with little improvement in the char formation and LOI.

Hajibeygi reported the synthesis and properties of photosensitive intrinsically colored PAI **323–328**, based on diamines with an expanded  $\pi$ -system [122]. Several imide-containing diacid monomers were obtained from *L*-aminoacids with hydrophobic side chains, while the photosensitive amine monomer was synthesized in a two-step reaction including double condensation of 4-nitrobenzaldehyde with cyclopentanone, followed by reduction of the terminal nitro-groups. Polycondensation of the designed monomers afforded a family of PAI that were soluble in H<sub>2</sub>SO<sub>4</sub> and polar aprotic solvents. Moreover, three selected polymers **323**, **326** and **328** were characterized in TGA experiments and displayed excellent thermal stability: no significant thermal decomposition was observed up to 370 °C. In addition, PAI **323**, **326** and **328** demonstrated  $T_g$  in the range of 166–194 °C and formed ample char above 30% (measured at 800 °C under N<sub>2</sub> atmosphere) and exhibited high assessed LOI >29.6%.

Tagle described the synthesis and properties of PAI **329–331** composed of Si-based diamines and imide-based diacid monomers extended with ester functionalities (see Fig. 17) [123]. The designed diamine was obtained from 4-bromo-*N,N*-bis(trimethylsilyl)aniline via consecutive metalation, reaction with diphenyldichlorosilane

and completed with deprotection of terminal amino groups. The designed ester-imide diacids were derived from selected *L*-aminoacids reacted with trimellitic anhydride, followed by the conversion of free carboxylic groups into carbonyl chlorides and their coupling with 4-hydroxybenzoic acid. Polycondensation of the designed monomers resulted in PAI **329–331** that were well soluble in polar aprotic organic solvents, including *m*-cresol, but displayed moderate thermal stability. Thus, PAI **329–331** exhibited  $T_{5\%}$  in the range of 226–263 °C, while elongation of the alkyl side substituents had negative effect on their thermal stability, including  $T_g$ . Nonetheless, all PAI formed ample char residues above 28% (measured at 800 °C under N<sub>2</sub> atmosphere), and exhibited high assessed LOI value > 28.7%.

Faghihi reported systematic preparation and thermal characterization of semiaromatic chiral FR PAI **332–345** synthesized from with *L*-amidoacids grafted to a bridged cycloaliphatic core via imide linkers and designed aromatic diamines: bis(3-aminophenyl)phenylphosphine oxide or 1,5-bis(4-aminophenyl)penta-1,4-dien-3-one (see Fig. 18) [124–126]. The diacid monomers with bis-imide functionalities were prepared from commercial bicyclooctenetetracarboxylic dianhydride and selected *L*-aminoacids. The respective diamines were synthesized like monomers for polymers **198** and **323–328** but using acetone as a starting enolizable ketone (*vide supra*). Further polycondensation of the designed monomers resulted in a thermally stable chiral PAI **332–345**. All polymers were soluble in DMSO and H<sub>2</sub>SO<sub>4</sub>, while PAI **339–345** displayed better solubility in other polar aprotic solvents (amide solvents) as compared to the triphenylphosphine oxide-containing **332–338**. In addition, selected PAI were investigated in TGA experiments and displayed  $T_{5\%}$  above 250 °C. Moreover, the studied polymers formed ample solid residues in the range of 60–65% (measured at 600 °C under N<sub>2</sub> atmosphere) and exhibited high LOI in the range of 29–33%.

Like the rigid aliphatic bicyclooctenetetracarboxylic dianhydride, aromatic pyromellitic dianhydride was widely employed to synthesize bisimide-containing diacid monomers from affordable *L*-aminoacids. For example, families of chiral polyamides **346–351**, **352–356** and **357–362** were derived from proteinogenic amino acids and tailored aromatic diamines: bis(3-aminophenyl)phenylphosphine oxide (*vide supra* PA **198** for the monomer synthesis), 3,5-diamino-*N*-(4-hydroxyphenyl)benzamide (*vide supra* PA **307–314** for similar monomers synthesis) and 5-(1H-benzo [d] imidazole-2-yl)benzene-1,3-diamine (*vide supra* PA **315–318** for the monomer synthesis) [127–129]. Subsequent polycondensation between the designed monomers resulted in PAIs **346–362** that were well-soluble in DMSO. PAIs **352–362** displayed very low crystallinity and good solubility also in other polar aprotic and amide solvents. Moreover, polymers with bulky amide- and benzimidazole-pendants displayed superior thermal stability and no significant mass loss up to 315 °C, as compared to triphenylphosphineoxide-based polymers **346–351** which displayed  $T_{5\%}$  in the range of 250–305 °C. Notably, thermal stability ( $T_{5\%}$  and  $T_{10\%}$ ) for alanine and phenylalanine-based polymers increased in rows: **346**, **352**, **357** and **351**, **356**, **361**, suggesting that grafting a benzimidazole side-substituent may improve thermal stability of the pyromellitic-based PAIs. All PAIs formed ample solid residues over 38.9% and therefore displayed high assessed LOI >33%. Additionally, water uptake for polyamides **352–356** was in the range 4.4–4.8%, higher than that for typical aramides due to the presence of hydroxyl group on the diamine monomer.

Ahmadi reported polymers **363** and **364** with catechol side-substituents derived from *L*-DOPA grafted to a pyromellitic core via imide linkage [130,131]. Polycondensation of the designed diacid with commercial aromatic diamines afforded **363** and **364**, showing no significant mass loss up to 257 °C and 184 °C



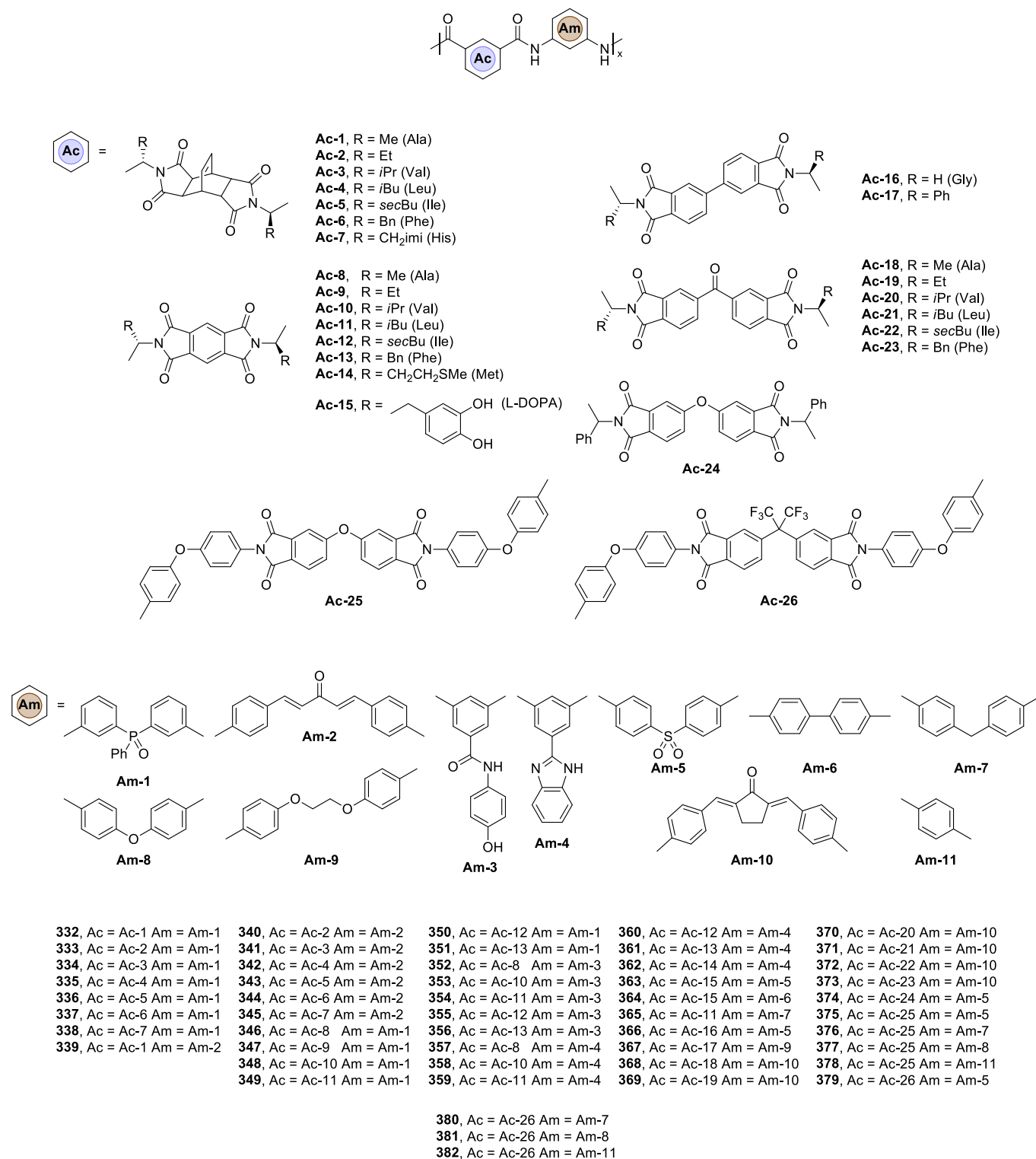


Fig. 18. Chemical structures of FR PAI.

respectively. In addition, PAI **363** and **364** formed ample char residues: 51.0% (measured at 600 °C under N<sub>2</sub> atmosphere) and 55.0% (measured at 800 °C under N<sub>2</sub> atmosphere) accordingly; thus ensuring high calculated LOI above 37%. Both polymers were further reinforced with inorganic fillers, that improved their resistance to thermolysis and increased char yield.

Mallakpour and Derakhshan reported preparation and properties of PAI **365** synthesized from L-leucine grafted to a pyromellitic core via amide linkage and commercial 4,4'-diaminodiphenylmethane [132]. The polymer demonstrated no significant thermal decomposition up to 238 °C and formed 41.0% of char residues (measured at 800 °C under Ar atmosphere), therefore providing

high calculated LOI of 33.9%. Reinforcement of **365** with organo-modified TiO<sub>2</sub> nanofiller slightly improved char yield.

Hajibeygi and Shabanian reported the preparation and properties of thermally robust PAI **366** [133]. The diacid monomer was prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride and glycine, and was polycondensed with 4,4'-diaminophenylsulfone to yield **366**. The polymer exhibited  $T_g$  of 142 °C and no thermal decomposition up to 294 °C. Furthermore, **366** formed 29.8% of char residues (measured at 800 °C under N<sub>2</sub> atmosphere), and ensured high calculated LOI of 29.4%. Fire performance of **366** was evaluated in MCC experiments: pHRR of 252 W/g and THR of 15.8 kJ/g were obtained. Incorporation of organo-modified clay further improved  $T_g$ ,  $T_{5\%}$  and boosted char formation, while had little effect on fire performance.

Structurally related to **366**, PAI **367** was derived from phenyl-glycine grafted to 3,3',4,4'-biphenyltetracarboxylic dianhydride and the diamine obtained as for PAI **249–264** (*vide supra*) [134]. Polycondensation of the tailored monomers afforded PAI **367**, that showed no significant thermal degradation up to 220 °C, while formed more char residues by 21.6% as compared to **366**. Thus, calculated LOI of 38.1% was obtained. PAI **367** was reinforced with organo-modified clay filler, that improved thermal stability of the polymer and promoted char formation.

Faghihi reported the preparation and properties of chiral photosensitive PAIs **368–373** composed of designed monomers [135]. The family of imide-endowed diacid monomers was synthesized by grafting proteinogenic L-aminoacids to 3,3',4,4'-benzophenonetetracarboxylic dianhydride core. Polycondensation of the tailored diacids with photosensitive diamine (*vide supra* PA **323–328** for the monomer synthesis) resulted in a family of chiral polymers **368–373** that were well soluble in polar aprotic solvents. Thermal properties of two selected polymers **368** and **372** were studied and revealed  $T_{5\%}$  of 330 °C and 245 °C accompanied with the formation of 34.3% and 32.3% of solid residues respectively (measured at 700 °C under N<sub>2</sub> atmosphere).

Hajibeygi described synthesis, thermal properties and fire performance of PAI **374** [136]. The diacid monomer was derived from flexible 4,4'-oxydiphthalic anhydride and phenylglycine, and subsequently polycondensed with 4,4'-diaminophenylsulfone to yield **374**, that displayed  $T_g$  of 127 °C and no thermal decomposition up to 211 °C. The polymer **374** formed 40.2% of char residues (measured at 800 °C under N<sub>2</sub> atmosphere) and therefore ensured high calculated LOI of 33.5%. In addition, fire performance of **375** was studied in MCC experiments: pHRR of 250 W/g and THR of 13.5 kJ/g were achieved.

Thiruvagasam and Venkatesan reported the synthesis and properties of fully aromatic processable PAI **375–382** with good insulating properties and high thermal stability [137]. The polymers were derived from designed imide-endowed diacids and commercial diamines. Tailored diacids were prepared from either 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoropropylidene) diphthalic anhydride condensed with 4-(4-aminophenoxy)benzoic acid. Subsequent polycondensation between the chosen monomers delivered a family of PAI **375–382** displaying good solubility in H<sub>2</sub>SO<sub>4</sub> and polar aprotic solvents. Notably, the polymers **379–382**, containing hexafluoropropylidene bridges displayed lower crystallinity and better solubility in THF, *m*-cresol and pyridine in contrast to **375–378**. All PAIs demonstrated high thermal stability with  $T_{10\%}$  from 424 °C and char yield in the range of 12–40% (measured at 800 °C under N<sub>2</sub> atmosphere). Importantly, fluorine-containing macromolecules **379–382** showed overall superior thermal properties and LOI of 22–34%.

To the best of our knowledge, the preparation of imide-endowed diamines is rarely reported despite apparent simplicity of the reaction and its similarity to the preparation of imide-containing diacid

monomers. A family of PAI **383–386** is example of polymers where the imide unit was embodied into amine monomer (see Fig. 19) [138].

The designed multifunctional aromatic diamine monomer was synthesized from trimellitic anhydride chloride, that was reacted with KSCN followed by a treatment with 4-nitroaniline to simultaneously form thiourea and imide functionalities. The final step in the monomer preparation involved the reduction of two terminal nitro-groups. Direct polycondensation of the monomers yielded FR PAIs **383–386** displaying high  $T_g$  in the range of 286–292 °C and  $T_{10\%}$  above 517 °C. In addition, all PAIs formed ample char residues >44% of initial mass (measured at 650 °C, N<sub>2</sub> atmosphere) and high assessed LOI of 44–54%. The authors attributed good FR properties and excellent thermal stability of PAI **383–386** to the introduction of the thiourea-based monomer.

An alternative way to synthesize PAI macromolecules involves the preparation of terminal diamines containing inner amide functionality. Lateral diamines are used in a two-step reaction with carboxylic acid dianhydrides, firstly forming polyamic acids via ring-opening polyaddition followed by cycloimidation (see Fig. 20). To the best of our knowledge, the following polymerization technique is used seldom as compared to the conventional polyamidation methods.

Mehdipour-Ataei described the preparation and FR properties of nicotinic-based poly (amide-ether-imide)s **387–389** [139]. The multifunctional diamine monomer was prepared from 2,6-diaminopyridine following two-step procedure, that included amidification with 6-chloronicotinoyl chloride followed by nucleophilic aromatic substitution with 5-amino-1-naphthol. Afterwards, polycondensation with three aromatic bis-anhydrides delivered aramides **387–389** of very low crystallinity. The solubility of polymers was about 1.3–1.7 g/dL in polar aprotic solvents and in *m*-cresol. In addition, the PAI displayed high  $T_g$  in the range of 227–242 °C and  $T_{10\%}$  beyond 385 °C. Moreover, the aramides **387–389** formed ample char residues (measured at 600 °C under air atmosphere), therefore ensuring high assessed LOI values in the range of 40.3–41.1%. Besides excellent thermal resistance, the aramids demonstrated water absorption values below 1.2%.

Ghulam reported the preparation and properties of PAI **390–393** using a diamine monomer with diphenylsulfone core and embedded amide groups [140]. The tailor-made diamine was synthesized through 2-step protocol starting from 4,4'-diaminophenylsulfone reacted with 4-nitrobenzoyl chloride followed by reduction of side nitro-groups into amines. Polycondensation of the crafted diamine with selected commercial carboxylic dianhydrides resulted in PAI **390** and **391**, which exhibited a crystalline morphology, while polymers **392** and **393** were fully amorphous. Despite the morphological differences, all polyamides

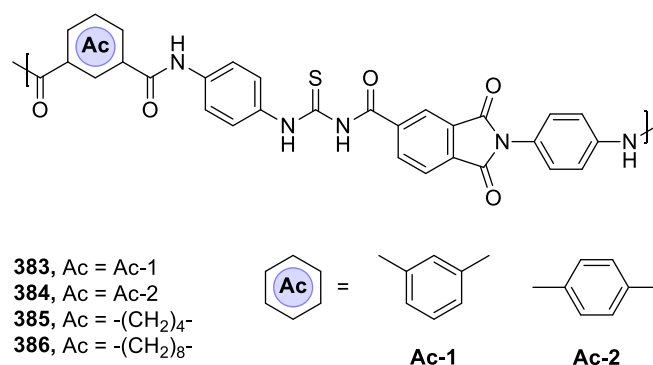


Fig. 19. FR PAI based on an imide-containing diamine.

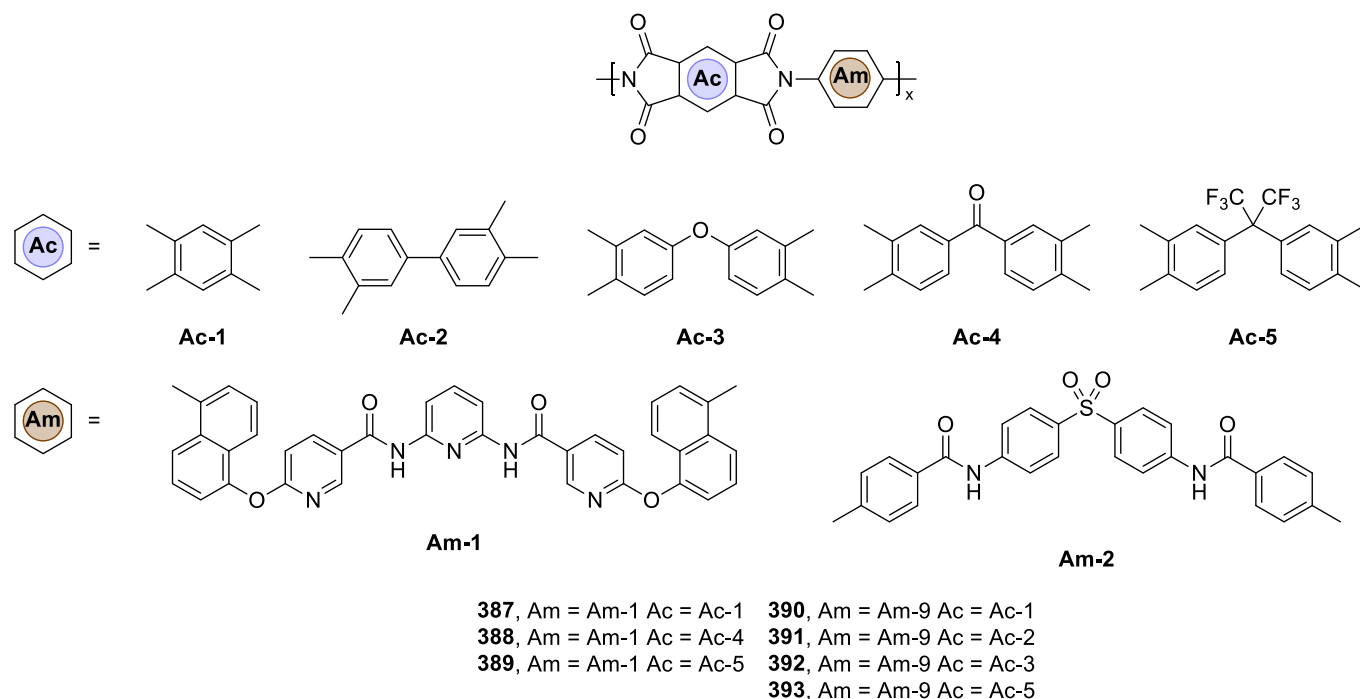


Fig. 20. FR PAI obtained in a two-step condensation of amines with acid dianhydrides.

demonstrated good solubility in polar aprotic solvents and low water uptake in the range of 0.14–0.27%. Moreover, PAI **390–393** displayed  $T_g$  of 220–261 °C and high thermal stability without significant mass loss up to 520 °C. In addition, the investigated polymers formed solid residues above 46% of the initial mass (measured at 800 °C under  $N_2$  atmosphere), thus exhibiting calculated LOI over 36%.

## 7. Polyamide-siloxane copolymers

Kumar reported environmentally benign enzyme-assisted preparation of hybrid organic-inorganic polymers by incorporating polydimethylsiloxane and polyamide fragments (see Fig. 21) [141]. Lipase-assisted (lipase B from *Candida antarctica*) transamidation between aminopropyl-terminated polydimethylsiloxane and selected esters furnished hybrid polymers **394–397** under mild reaction conditions. The hybrid polyamides demonstrated good thermal stability and flame retardant properties. Specifically, PAs **394–396** with aliphatic diacids realized  $T_{onset}$  in the range of

277–302 °C, while polymer **397** incorporated 5-hydroxyisophthalic acid monomer and exhibited the highest  $T_{onset}$  of 402 °C. Notably, PAs **394–397** left less than 9% of solid residues when heated up to 1200 °C. Low amount of solid residues was rationalized with the formation of cyclic siloxane compounds  $[SiO(CH_3)_2]_n$  where  $n = 3–6$ , rather than silica particles upon thermal decomposition in an inert atmosphere. In addition, MCC experiments revealed very low HRC in the range of  $100 J g^{-1} K^{-1}$  for aliphatic PAs **394–396** and  $200 J g^{-1} K^{-1}$  for **397**, indicating relatively low flammability comparable with Kevlar or polyether-ether-ketone.

In further studies, Mosurkal explored crosslinking of a related hybrid PA **398** composed of 5-aminoisophthalic acid monomer and polydimethylsiloxane-based diamine (see Fig. 22) [142]. Hardening of **398** was realized by reacting available amino-group with commercially available dianhydrides or diacylchlorides. The use of 20% of pyromellitic dianhydride crosslinkers was optimal for hardening the polymer and rendering it insoluble in common organic solvents, as well as achieving the lowest THR of 11.6 kJ/g and HRC of  $100 J/(g \cdot K)$ . Importantly, a type of a crosslinker and its

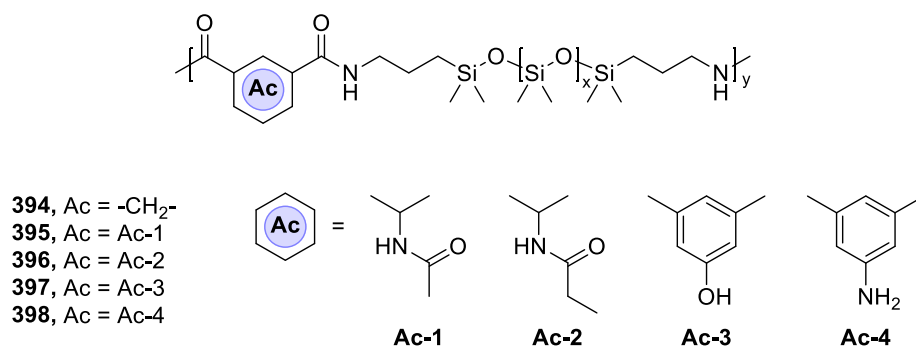


Fig. 21. Linear FR polyamide-siloxane copolymers.

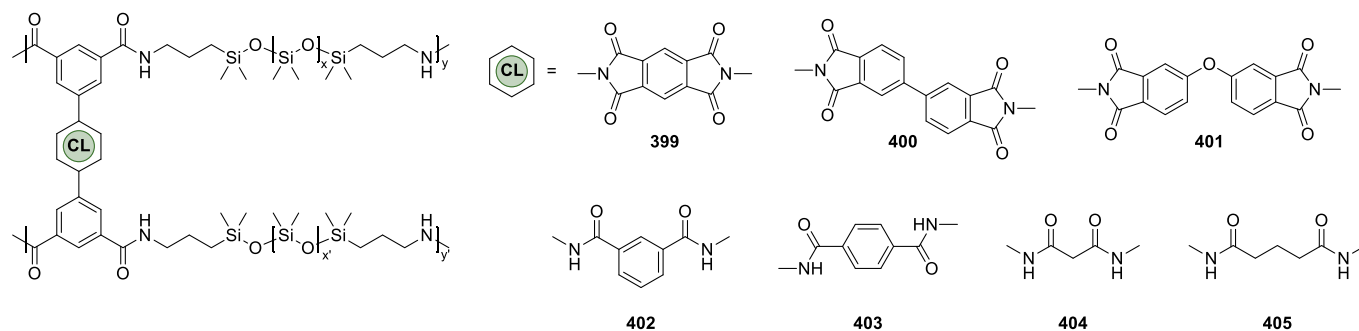


Fig. 22. Cross-linked FR polyamide-siloxanes.

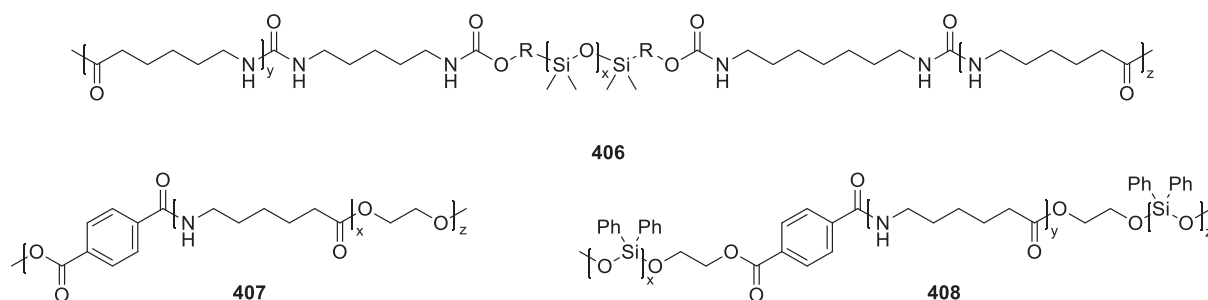


Fig. 23. PA6-siloxane FR copolymers and reference polyetheramide.

amount had a pronounced effect on the thermal and flame retardant properties of the final material. Specifically, all cross-linked polyamide-siloxanes **399–401** decomposed at lower temperatures (decomposition temperatures at 20 wt% loss) and formed more residual char (measured at 800 °C, under air atmosphere) as compared to the parental macromolecule **398**. In addition, polymers **399** and **400** exhibited significant reduction in HRC, as opposed to **401** that performed even worse than virgin non-cross-linked PA **398**.

The use of isomeric benzenedicarboxylic and aliphatic diacid crosslinkers for **398** resulted in polymers **402–405** with improved FR properties that, however, could not surpass metrics of the champion FR PA **399** (20 wt% of the pyromellitic dianhydride cross-linker) [143]. Similarly to **399–401**, the choice of a cross-linking precursor affected thermal properties of the final thermoset too. For example, the use of terephthaloyl chloride instead of terephthalic acid resulted in lower char yield, THR and HRC for the thermoset polymer **403**. Importantly, properties of the unmodified **398** in both studies, as well as the loading of crosslinkers were significantly different [142,143].

Song reported the preparation and properties of a hybrid organic-inorganic copolymer **406** composed of monomer-cast PA6 with 1–7% of polydimethylsiloxane (see Fig. 23) [165]. The grafting of PA6 to siloxane chains was realized using reactive isocyanate terminal groups of the polydimethylsiloxane macromolecules. The resulting hybrid PAs **406** exhibited  $T_m$  and  $T_c$  similar to pure PA6 ( $T_m$  of 219.7 and  $T_c$  of 173.4), despite the incorporation of flexible hydrophobic inorganic part. Contrarily, the thermal stability of **406** and pHRR decreased, when the content of PDMS in the polymer increased. For example, the incorporation of 3% of inorganic chains led to pHRR reduction by 28.7% from 654 kW m<sup>-2</sup> for pure PA6 to 466 kW m<sup>-2</sup> for the hybrid.

Finally, all siloxane conjugated displayed superior hydrophobic properties and decreased crystallinity.

Fan reported preparation of hybrid FR polymers containing PA6 and polydiphenylsiloxane (PDPS) chains which are bonded together with ethylene glycol and terephthalate linkers [144]. The synthesis included stepwise ring-opening polymerization of  $\epsilon$ -caprolactam in the presence of terephthalic acid, followed by esterification with ethylene glycol. Afterwards, ethylene-glycol terminated esters were either self-condensed, furnishing a reference PAs with ester linkers **407**, or copolymerized with various amount of PDPS in the presence of zinc acetate to yield hybrid FR PAs **408**. The authors reported that the introduction of ester and siloxane into macromolecule chains did not have strong effect on crystallinity and  $T_g$  of polymers, therefore ensuring values similar to pure PA6 ( $T_g$  of 47 °C). The increase in the amount of ethylene glycol decreased  $T_m$  by ~20–50 °C,  $T_{5\%}$  by ~10–30 °C and  $T_{max}$  by ~35–60 °C for PDPS-free polyamides **407** in comparison to the benchmark PA6. Contrarily, variation in polydiphenylsiloxane ratio in **408** with fixed amount of ethylene glycol linkers resulted in polymers with similar  $T_m$ ,  $T_{5\%}$  and  $T_{max}$ , that were slightly lower than that for PA6. The authors note that the incorporation of glycol units in the polymer brought some positive FR effect, however only the presence of PDPS was essential to attain V-0 rating in UL-94 test, improve LOI and to reduce pHRR, THR substantially, as compared to pure PA6 or **407**. Specifically, the champion hybrid PA **408** attaining V-0 rating in UL-94 burning test demonstrated significant reduction in pHRR by 454 kW/m<sup>2</sup> and in THR by 21.2 MJ/m<sup>2</sup> as compared to the performance of unmodified PA6 in cone calorimeter tests. Notably, polydiphenylsiloxane in conjunction with ethylene glycol units were rationalized to act both in gas and condensed phase, forming ample Si-enriched char and non-flammable volatile cyclic siloxanes.

## 8. Conclusion and outlook

In this review we have surveyed developments in heat resistant and intrinsically flame-resistant polyamides that have been published since 2004 to 2020. PAs remain to be a very important class of thermoplastics that urge researchers to develop novel non-hazardous and efficient reactive FR additives as co-monomers that do not compromise mechanical properties of the polymers and render them fire-safe even at low loadings. Despite the advantage of the method and the abundance of Nylons, halogen-free FR co-monomers for aliphatic polyamides remain at a development stage, scarce and still relatively expensive for high-volume production. They are mainly represented by few P-containing monomers, based on CEPPA, DOPO- and DPPO-containing structures. Use of other P-containing monomers, their fire performance and effect on aliphatic PAs properties remains largely unknown. Moreover, significant effort must be undertaken to make FR monomers competitive compared to the non-reactive additives used in PAs nowadays: metal salts of alkylphosphinic acids, MCA, red phosphorus etc.

Some engineering and heavy-duty PAs are partially aromatic or semiaromatic PAs, that are often exposed to elevated temperatures during their life cycle. In most of the cases, these polymers require improvement in their fire performance as well as processability. Use of external non-reactive FR fillers may not be desirable for melt processing that occurs at higher temperatures (by ~100 °C) than for aliphatic PAs. Thus, incorporation of reactive FRs may be an optimal approach to address these challenges. Existing literature in this domain often describe novel macromolecules, but fails to address FR monomers. Moreover, reported design of novel fire-resistant polymers focusses mainly on solubility of macromolecules, while detailed melt properties and fire performance is rarely investigated and reported. Published data are often incomplete, limited or indirect: fire-performance of developed polymers is rarely supported by common fire experiments (UL-94 tests, experimental LOI, MCC, cone calorimetry etc.). Thus, development of FR monomers for engineering PAs and processable aramids and exhaustive data generation for fire performance of new macromolecules remain critical.

## Declaration of competing interest

The authors declare no conflict of interest.

## Glossary of abbreviations and units

)))	ultrasonication
Ac	acetyl
BCPPO	bis(4-carboxyphenyl)phenyl phosphine oxide
BNPO	bis-(4-carboxyanilino)phenylphosphamide
Bu	butyl
CEPPA	(2-carboxyethyl)phenylphosphinic acid
CR	char residues
DBTDL	dibutyltin dilaurate
DBU	1,8-diazabicyclo[5.4.0]undec-7-en
DCM	dichloromethane
DIPIB	1,3-diisopropylimidazolium bromide
DMAC	N,N-dimethylacetamide
DMEDA	1,2-dimethylethylenediamine
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DOPO-ITA	3-[10-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-10-yl)]itaconic acid.
DPIB	1,3-dipropylimidazolium bromide
DPPD	poly-N-aniline-phenyl phosphoramidate

DPPO	diphenylphosphine oxide
DPPO-ITA	2-((diphenylphosphoryl)methyl)succinic acid
DSC	differential scanning calorimetry
$E_a$	activation energy
Et	ethyl
FOT	flame out time
FR	flame retardant
Hal	halogen
HMDAA	1,6-hexamethylenediamonium adipate
IL	ionic liquid
L-DOPA	L-3,4-dihydroxyphenylalanine
LOI	limiting oxygen index
MCA	melamine cyanurate
MCC	microscale combustion calorimeter
MCPO	bis-N-benzoguanamine-phenyl posphamide
Me	methyl
$M_n$	number-average molecular weight
MW	microwave
$M_w$	mass average molecular weight
MWCNT	Multiwalled carbon nanotube
$M_\eta$	viscosity-average molecular weight\
NENP	4-(3-(((4-carboxyphenyl)amino) (phenyl)phosphoryl)propanamido)benzoic acid
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
PA	polyamide
PAN	polyacrylonitrile
PDI	polydispersity index
Ph	phenyl
pHRR	peak heat release rate
PO	propylene oxide
ppy	2-phenylpyridine
Pr	propyl
PTCDA	perylene-3,4,9,10-tatercarboxylic dianhydride
Py	pyridine
ROP	ring-opening polymerization
$S_NAr$	nucleophilic aromatic substitution
$T_{10\%}$	temerature for 10% gravimetric mass loss
$T_{5\%}$	temerature for 5% gravimetric mass loss
TBAB	tetrabutylammonium bromide
$T_c$	crystallization temperature
TEA	triethylamine
$T_g$	glass-transition temperature
TGA	thermogravimetric
THF	tetrahydrofuran
THR	total heat release
$T_m$	melting temperature
$T_{max}$	tempereture at maximum weight loss
TMSCl	trimethylsilylchloride
TPP	triphenylphosphite
TSR	total smoke production
TTI	time to ignition
$X_c$	degree of crystallinity
$\Delta H_m$	fusion enthalpy

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