

# Aliphatic and Aromatic Polyamides

## Synthesis, Properties and Potential Applications

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Aliphatic as well as aromatic polyamides represent an important family of macromolecular materials, characterized by a wide range of applications. The present paper deals with some recent findings in the areas of their synthesis and characterization, respectively, also in view of future technological developments. Namely, some new synthetic approaches for the obtainment of polyamide 6 and poly(p-phenylene terephthalamide) (kevlar) as well as of some hyperbranched aramids, will be mentioned. A few relevant properties of the resultant materials, together with their potential applications, will be outlined.

In the recent past our research group has realized some new results concerning the synthesis, characterization, property evaluation and potential applications of aliphatic and aromatic polyamides, fields in which the group is active since the mid '70s. Below, we will briefly summarize the main achievements of the last few years.

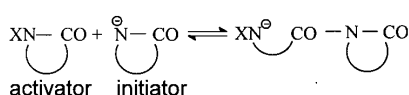
### Linear aliphatic polyamides

Aliphatic polyamides are well known and widely used polymers, due to their relevant technological properties and extensive fields of application. Among them, poly( $\epsilon$ -caprolactam) (PA6 or nylon 6) is one of the most studied and commercialized. The industrial production of the above material is based on the so-called hydrolytic process. Although this approach is an easy route to obtain PA6, alternative methods (anionic and, to a minor extent, cationic polymerization) have been studied in the past in order to overcome the problems associated with the hydrolytic process, such as high polymerization temperature (ca. 270

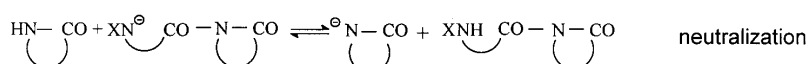
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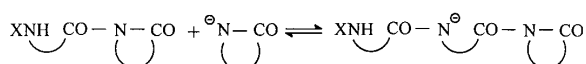
#### initiation:



X = polar group having electrophilic character



#### propagation:



followed by neutralization

Scheme 1 - Activated anionic polymerization of lactams

°C), long reaction times and relevant formation of cyclic oligomers.

Our research has been focused on the activated anionic polymerization (Scheme 1), which can be extremely fast (less than 60 s) and can take place at lower temperatures (ca. 150-200 °C). However, the anionic polymerization is characterized by strong temperature rise, due to both the exothermic character of the reaction and the high polymerization rate, with difficult heat dissipation; therefore, the process is affected by many side reactions, which strongly

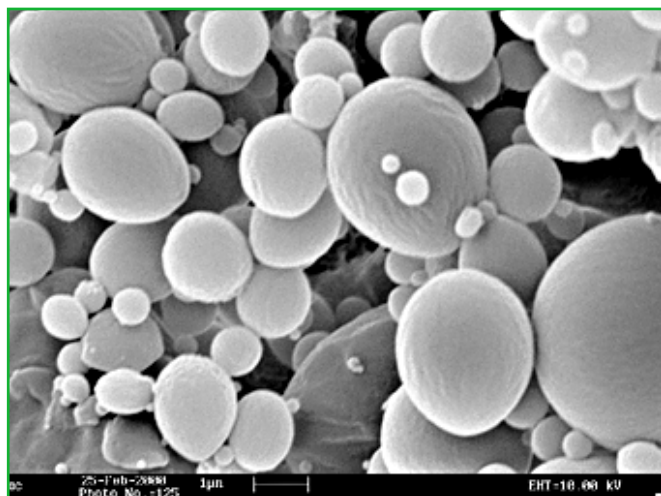


Figure 1 - SEM micrograph of powdered PA6

reduce the product quality, owing to the formation of UV-absorbing irregular structures in the polymer chains. In order to minimize this drawback, several methods based on fast dissipation of the polymerization heat have been attempted by our research group, namely by careful control of the reaction temperature. On these grounds, PA6 samples characterized by excellent structural regularity, high crystallinity, good mechanical and thermal properties have recently been obtained (see, for instance, [1]).

Among the isothermal methods studied by our research group, the suspension polymerization has produced the most interesting results. Using suitable experimental conditions, it is possible to obtain a polymer powder characterized by an almost spherical shape (Figure 1), good porosity (specific area of ca. 2 m<sup>2</sup>/g), excellent structural regularity and high crystallinity. Moreover, seeded polymerizations, using pre-formed particles of other polymer materials (polylactolactam, ABS etc.) or mineral fillers (e.g. SiO<sub>2</sub>, TiO<sub>2</sub>), have been performed. Also copolymerization with other lactams has easily been attained [2].

The anionic suspension polymerization can be successfully compared to the hydrolytic process for the production of powdered PA6. The latter process, which does not allow to directly obtain PA6 powder, needs a cryogenic grinding step to cut the polymer pellets. Besides other drawbacks, partly sintered pieces of polymer with rather low surface area are obtained by the above grinding method.

The anionic suspension polymerization of  $\epsilon$ -caprolactam is influenced by several parameters, such as type of suspending medium, reaction temperature, mixing apparatus, monomer concentration, catalytic system etc. By a careful control of all mentioned variables, a fine powder of PA6 is obtained, almost entirely free of UV-absorbing structural defects (optical density values are as low as 0.04), as a consequence of the minimization of side reactions. As shown in Table 1, the products obtained by hydrolytic, anionic suspension and anionic isothermal (bulk)

Table 1 - OD<sub>max</sub> values of PA6 obtained from several polymerization processes ( $\lambda_{\text{max}} \approx 270\text{-}280 \text{ nm}$ )

Polymerization process	OD <sub>max</sub>
hydrolytic	0.04
bulk anionic (quasi-adiabatic, fast)	0.50
bulk anionic (isothermal, fast)	0.04
suspension anionic (fast)	0.04

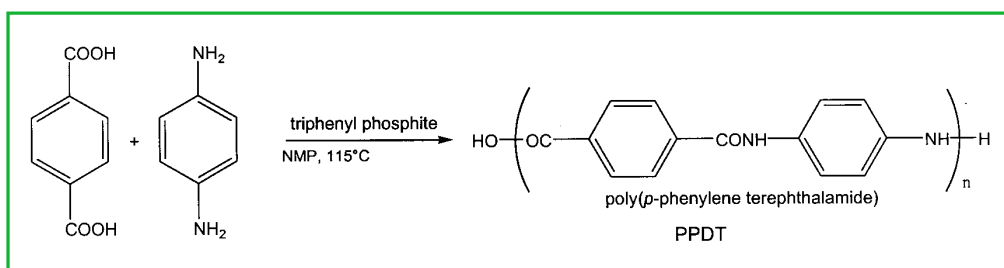
Table 2 - PA6 high polymer yield in fast anionic suspension polymerization at 155 °C

Monomer concentration in the suspension medium (wt-%)	Yield (%)
7	39
8	58
9	69
10	77
14	86
20	93

processes are characterized by the same OD values. On the contrary, the polymer obtained by *quasi-adiabatic* bulk polymerization (cast nylon) is highly UV-absorbing and not suitable for many industrial applications.

When the various reaction parameters are considered in more detail, it comes out that, by appropriate choice of the type of suspension medium, it is possible to modify both the particle surface characteristics and the average particle size. The high polymer yield is strongly influenced by monomer concentration in the suspending medium (Table 2). The maximum concentration, which still allows to minimize particle coalescence maintaining isothermal conditions, is ca. 20 %, with a monomer conversion only a few % lower than that obtained by the isothermal bulk method (ca. 97 %). As verified in the bulk polymerization studies [1], the catalytic system strongly affects PA6 molecular weight. By changing type and amount of the activator, it is possible to finely tune polymer molecular weights in a much wider range as compared to hydrolytic PA6.

Among the reaction parameters, type and rate of mixing are particularly important for limitation of the coalescence phenomenon. The system we have settled seems to be very effective for the obtention of a finely powdered polymer in short times and good yields. Potential applications in several fields are currently explored, taking advantage of both the almost spherical shape and the polymer porosity.



Scheme 2 - Direct synthesis of an aromatic polyamide in presence of triphenyl phosphite as the condensing agent

**Table 3 - Matrix effect. Intrinsic viscosities of some poly(*p*-phenylene terephthalamide) (PPDT) samples as compared to those of kevlar fibers**

	Matrix polymer	$[\eta]^a$ (dL/g)
kevlar (commercial fibers) <sup>b</sup>	none	6-7
PPDT-1 <sup>c</sup>	none	11.0
PPDT-2 <sup>c</sup>	PVP K90 <sup>d</sup>	14.2
PPDT-3 <sup>c</sup>	PVP K10 <sup>e</sup>	5.4

<sup>a</sup> in 96% sulfuric acid, at 25 °C

<sup>b</sup> synthesized by using terephthaloyl chloride

<sup>c</sup> synthesized by using terephthalic acid (direct synthesis)

<sup>d</sup> MW = 360,000

<sup>e</sup> MW = 10,000

### Linear aromatic polyamides

Aromatic polyamides (aramids) represent one the most important families of macromolecular compounds used as high performance materials. Because of the very high modulus, some of them are commonly employed when excellent mechanical properties and low specific weight are requested. In addition, they show good resistance to heating and flame. Kevlar, twaron, nomex are some of the most relevant trade-names in this class.

In our laboratories we have developed an alternative method for their synthesis, leading to materials characterized by molecular weights higher than those of the aforementioned commercial products. This means that the aramids obtained by our route are characterized by better mechanical properties and, in general, can provide a wider spectrum of applications. This goal has been achieved by two different approaches, both based on the *direct* synthesis. With the term *direct* it is meant that the polymerization reactions are performed by polycondensation (usually in solution) of aromatic diamines and aromatic dicarboxylic acids (Scheme 2), the latter being used instead of their activated derivatives, namely their chlorides, as commonly carried out in the industrial process. Acyl chlorides are extremely reactive and, therefore, difficult to obtain, purify and store. As a consequence, relatively high production costs characterize these materials. On the contrary, a carboxylic acid is not an air-sensitive compound and does not undergo any significant degradation reaction during its storage and use, with relevant cost benefits. Furthermore, as already mentioned, by our method it is possible to increase molecular weights and reach values much higher than those known so far for these polymeric compounds (Table 3) [3,4].

In this respect, a further modification of our original method has been successfully studied: the influence of a second polymer (matrix effect), dissolved in the reaction medium in which the above reactants are allowed to react. We have observed that, when poly(*N*-vinylpyrrolidone) (PVP) is used as a polymer matrix, the MW values of the resultant aramid are strongly influenced by those of the PVP itself (Table 3). Namely, by using high MW PVP it is possible to synthesize aromatic polyamides characterized by MWs even higher than those mentioned above. On the contrary, if PVP MW is sufficiently low, the same comes out for the corresponding aramide. In other words, the addition of a specific polymer matrix makes

possible to predetermine some of the molecular characteristics of the resultant aromatic polyamide [5]. The role of the matrix polymer is strongly enhanced by our *direct* synthesis, much more than by the acyl chloride route [6].

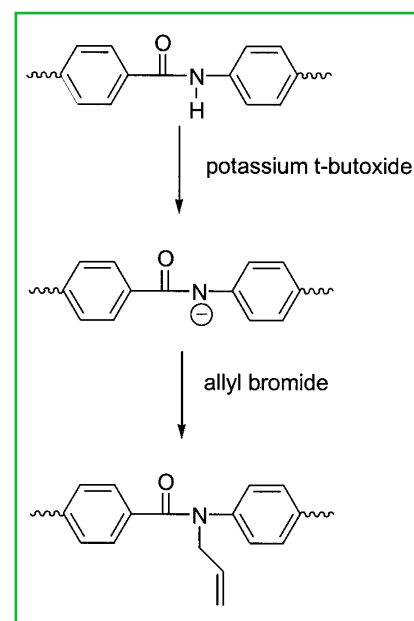
Finally, we have recently developed a functionalization method (*N*-allylation) of aramids (Scheme 3), which gives derivatized aramids soluble in several organic solvents, thus allowing an easy evaluation of their molecular weight distribution by SEC [7]. Indeed, in the past the SEC technique has not been commonly employed for this kind of polymers, as most of them are soluble only in concentrated sulfuric acid.

### Hyperbranched (HB) aramids

In recent years the synthesis of dendrimers opened a new and wide field of research in polymer chemistry. In fact, it has been found that this new class of macromolecular compounds is characterized by unique features, which attracted the interest also of the industrial world. Their almost globular shape and the high number of functional end groups strongly enhance their solubility in common solvents and lower their solution and melt viscosity. In addition, a suitable derivatization of their end groups opens many new perspectives of application for the polymer. By this way, dendrimers can be employed as catalysts, drug carriers, dissolving agents, additives to reduce viscosity, unimolecular micelles etc. However, dendrimers are characterized by high production costs because of their time-consuming route of synthesis, with many reaction and purification steps following each other in order to obtain extremely pure and defect-free structures.

Although theoretically proposed already by Flory, HB dendritic macromolecules have been synthesized only since the end of the '80s. Their structure is similar to that of dendrimers with the important exception of being more or less rich of defects. This is due to the one-step procedure commonly used for their synthesis which, in analogy to the synthesis of linear polymers, gives a mixture of macromolecules having different MWs. Nevertheless, most of the relevant properties of dendrimers are present also in HB polymers. It is obvious that the latter ones are, in general, strongly preferred because of their much lower cost of production.

Our group is active in the synthesis, characterization and evaluation of potential applications of HB aramids. As a natural development of our studies on linear aramids, our interest for HB



**Scheme 3 - *N*-allylation of an aromatic polyamide. The resultant product is characterized by easy solubility in common organic solvents [7]**

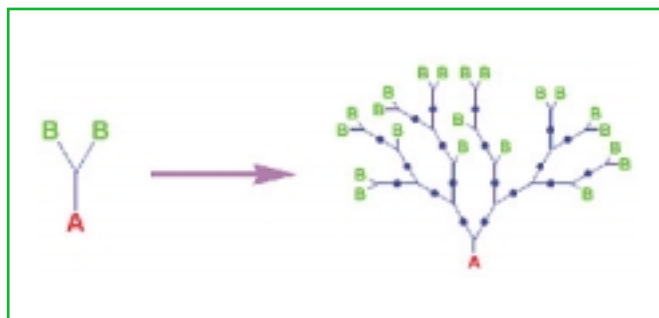


Figure 2 - Schematic representation of the one-step synthesis of a dendritic hyperbranched polymer from an  $AB_2$ -type monomer

aramids has been principally focused on kevlar-type structures, namely their synthesis, characterization and applications. The synthesis of HB aramids is performed by polymerization of  $AB_2$  monomers or  $A_2+B_3$  reagent pairs. The former ones are aromatic compounds having one amino and two carboxylic acid groups (or *vice versa*) on the same molecule. The resultant HB polymers (Figure 2) belong to the wide class of dendritic macromolecules. In fact, they have a tree-like structure, with a core molecule (which bears the only remaining A group), from which a number of branches grows. At the other ends of the macromolecule (the "leaves" of the tree-like structure), a relatively high number of B groups are placed (the number of B groups is almost the same as the polymerization degree). As a general consideration, it must be noted that this kind of systems does not crosslink and can easily be dissolved in both organic and inorganic media.

The second class of HB polymers studied by our group is that derived by the polymerization reaction of  $A_2+B_3$  reagent pairs. Because of their non tree-like structure, they cannot be included in the class of dendritic macromolecules, unlike polymers derived from  $AB_2$  monomers, but we can certainly refer to them as HB macromolecular compounds.

As can be seen in Figure 3, the number of both A and B end groups in these structures is relevant and related to MW of the polymer. As a consequence, the possibility of reaching gel point (crosslinking) for sufficiently high conversions has to be taken in consideration. On the other hand, non-crosslinked structures (sol fractions), in analogy to the aforementioned dendritic ones, are completely soluble in common organic solvents and can easily be derivatized to HB aramids containing suitable functional end groups.

#### HB aramids from $AB_2$ monomers

Polymerization reactions have been performed using the above *direct* synthesis (with minor modifications). Unlike their linear counterparts, these macromolecular compounds are easily soluble at room temperature in aprotic polar solvents [8], such as dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone, dimethylsulfoxide (whereas kevlar is soluble only in concentrated sulfuric acid). This makes easier their characterization and processability, joined to lower costs pertaining to plant maintenance and safety. A comparison between HB and linear aramids having the same MW reveals that the former ones have much lower solution viscosity. Moreover, desirable features, such as heat and flame resistance, are still kept. This suggests the possibility of using HB aramids as additives to linear aromatic polyamides in order to improve their processability. Furthermore, solubility in the above organic solvents allows for the easy preparation of

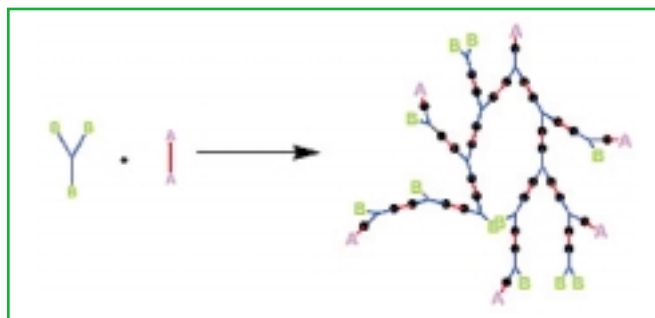


Figure 3 - Schematic representation of a non-dendritic hyperbranched polymer from an  $(A_2+B_3)$ -type reagent pair

solid films. At present, a thorough study on properties and applications of these materials is under way and is reported in detail elsewhere [9,10]. Because of their unique structure, rich of rigid cavities (comparable to those of zeolites), new and interesting film properties and applications can already be foreseen. We have also found [9] that these HB polymers can give liquid crystalline solutions in some of the above organic solvents (Figure 4), a further feature which can be potentially appealing, not only from an academic point of view. Furthermore, thermotropic LC behaviour is present in the solid films cast from the above solutions.

As mentioned above, HB polymers have many of the properties of their dendrimeric counterparts. However, for specific applications a *quasi* defect-free dendritic structure can be requested. On the basis of what very recently appeared in literature [11], we are trying to synthesize *quasi*-dendrimeric amide structures by polycondensation of our  $AB_2$  monomers in a one-pot reaction. The above method, linked to a new condensation agent replacing triphenyl phosphite, permits the obtaining of HB aramids with an amount of defects much lower than that found for the typical recipes used so far in direct synthesis. If the positive results can be extended also to our systems, this innovative approach could provide an interesting and economical way to obtain *quasi*-dendrimeric aramids on industrial scale.



Figure 4 - Mesophasic behaviour of an HB aramide in NMP solution (ca. 60wt-%)



**Table 4 -  $\alpha$ -amylase linked to different HB aramids and kinetic data of its bioactivity [14]**

Sample code	Reagent pair or monomer	Immobilized enzyme/aramide (w/w)	$k_m^a$ (mg/mL)	$V_{max}$ ( $\Delta A s^{-1}$ )	$k_{cat} 10^{-3}$ ( $s^{-1}$ )
AB <sub>2</sub>	A <sub>2</sub> +B <sub>3</sub>	0.80	19	0.18	85.1
Y1	A <sub>2</sub> +B <sub>3</sub>	0.70	16	0.07	49.3
Y8	A <sub>2</sub> +B <sub>3</sub>	0.82	26	0.10	39.2
AB6	AB <sub>2</sub>	0.72	6	0.02	11.4
V17	AB <sub>2</sub>	0.72	8	0.03	18.9
V14	AB <sub>2</sub>	0.62	13	0.03	10.0
V13	AB <sub>2</sub>	0.86	3	0.01	5.1
Y22	AB <sub>2</sub>	0.81	4	0.02	7.5
V15	AB <sub>2</sub>	0.70	5	0.01	5.1
Y34	A <sub>2</sub> +B <sub>3</sub>	0.58	2	0.01	4.7
Y33	A <sub>3</sub> +B <sub>2</sub>	0.60	4	0.02	14.9
AB50	A <sub>2</sub> +B <sub>3</sub>	0.78	2	0.01	3.5
$\alpha$ -amylase (free enzyme)			6	0.41	140.4

<sup>a</sup> Michaelis-Menten constant is expressed as starch-RBB concentration (mg/mL)

#### HB aramids from A<sub>2</sub>+B<sub>3</sub> reagent pairs

A relevant part of our research is currently devoted to the direct polycondensation of commercial aromatic diamines with commercial aromatic tricarboxylic acids (the corresponding study related to the polymerization of dicarboxylic acids with triamines is also in progress and will be presented soon). Some HB aramids of this family have been synthesized and characterized [10,12,13].

In order to avoid the formation of a crosslinked fraction, polymerizations are stopped before reaching the gel point, i.e. at relatively low conversion. The properties of the obtained materials are very attractive. This is particularly true after an appropriate derivatization of the many carboxylic end groups which remain onto or near the surface of the obtained HB macromolecule. In particular, they have been used for the immobilization of enzymes, such as  $\alpha$ -amylase.

In Table 4, kinetic data of  $\alpha$ -amylase bioactivity are reported for various HB aramids of both (A<sub>2</sub>+B<sub>3</sub>)- and AB<sub>2</sub>-type, synthesized in our laboratory [14]. The results show that the HB aramid acts as an effective rigid support for the enzyme, the activity of the latter being almost an order of magnitude higher than that of commercial products, with advantages in terms of both needed volumes and costs.

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