



EXPLANATION OF SYNTHESIS METHODS AND FUNCTIONS OF AROMATIC POLYAMIDES

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ABSTRACT

This article presents the preparation and properties of aromatic polyamides as well as the fibers and films made from these polymers. Particular focus is placed on the polymers that have achieved commercial status, namely, poly (m- phenylene isophthalamide), poly (p- phenylene terephthalamide), and copoly (p- phenylene/- diphenyl ether terephthalamide). The production processes of the corresponding monomers for these three polymers are described in detail, analyzing both laboratory and commercial- scale processes for the preparation of the polymers in the form of fibers and films. We describe herein the state of the art following the last 8 years of research into aromatic polyamides, wholly aromatic polyamides or aramids. These polymers belong to the family of high performance materials because of their exceptional thermal and mechanical behavior. Commercially, they have been transformed into fibers mainly for production of advanced composites, paper, and cut and fire protective garments.

Keywords: -Synthesis, Polyamides, Material, Phenylene, Aromatic

I. INTRODUCTION

Polyamides are polymers containing the amide group (–CO–NH–) in their repeating unit. They can be found both in nature (proteins, silk, wool, etc.) and in synthetic compounds (aliphatic polyamides or nylons, and aromatic polyamides or aramids). Wholly aromatic polyamides are synthetic polyamides in which at least 85% of the amide groups are bound directly to two aromatic rings, according to the definition of the U.S. Federal Trade Commission.

The main properties of wholly aromatic polyamides include thermal and chemical stability and the potential for high strength and modulus. Most of the aromatic polyamides do not melt or melt above 350°C and exhibit great chemical resistance and low flammability. These properties arise from the high chain rigidity derived from the aromatic character of the polymer backbone.

Aromatic polyamide fibers can have very high strength and modulus, and these properties persist at high temperatures. These outstanding characteristics qualify them to be classified as high-performance materials, having higher specific strength and modulus than steel or glass due to their low density. Furthermore, aromatic polyamides were used recently to replace ceramics and metals. However, the rigidity of the polymer backbone is also responsible for the insolubility of the aramids, limiting the expansion of their applications.

Historically and commercially, polyamides, occupy an important place in the world of polymers. Early work dealt with polyamides, with emphasis on the commercial development of synthetic fiber and plastic, known commonly as nylons.

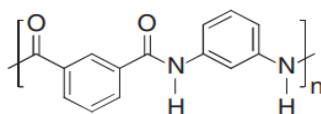
Wholly aromatic polyamides (aramids) belong to the class of high-performance heat-resistant material. For example, Kevlar (poly-p-phenylene terephthalamide) and Nomex® (poly(p-phenylene isophthalamide)), commercially known, are composed of phenylene units linked via an amide group and exhibit high crystallinity. Thus, they are useful as ultrahigh-strength/high-modulus fibers. These polyamides exhibit a number of excellent properties such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties as fibers. However, the applications of these aramids have generally been hampered by the high crystallinity and limited solubility.

Aromatic polyamides, wholly aromatic polyamides, or the shorter form aramids, stand for synthetic polyamides comprised >85% by amide groups (–CO–NH–) bound directly to two aromatic rings.

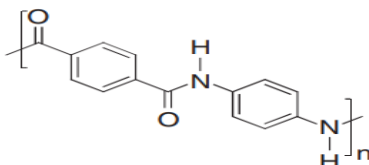
These polymers are categorized as high-performance materials because of their outstanding mechanical strength and superior high thermal resistance.

They are spun into fibers for advanced fabrics such as advanced sport and work protective clothing, bullet-proof body armor, advanced composites in armament and aerospace industries, in composites as asbestos substitutes, high-temperature insulation paper, to name but a few.

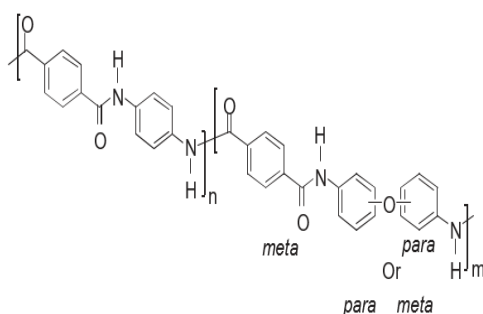
II. AROMATIC POLYAMIDES



Poly (m-phenylene isophthalamide) MPIA



Poly(p-phenylene terephthalamide) PPTA



Scheme 1. Chemical structures of MPIA, PPTA, and ODA/PPTA.

Owing to their special characteristics, aramids are being used as functional and cutting-edge materials for applications in thermal- and mechanical-resistant materials for personal protective garments, sensing, and extraction, materials with electrochromic properties, membranes for transport applications or optically active materials.

III. SYNTHESIS METHODS

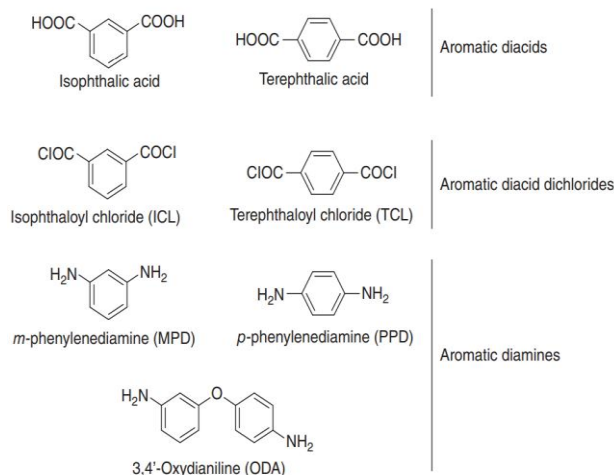
Aromatic polyamides are prepared in solution according to two methods:

- (1) reaction between diacid chlorides and diamines at low temperatures and
- (2) by direct condensation of aromatic diacids with diamines at high temperatures (Yamazaki-Higashi method). In both cases, polar aprotic solvents such as hex methyl phosphor amide

(HMPA), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA) are used.

Key parameters of the polymerization reaction include anhydrous conditions and high purity of the solvents and monomers, the monomer stoichiometry, stirring intensity, monomer concentration, and temperature.

Also, to increase the solubility by decreasing the strength of the interchange hydrogen bonds during the synthesis procedure, LiCl and/or CaCl₂ salts can be added to the reaction.



Scheme 2. Monomers used in the synthesis of commercial aramids.

For polymers that remain soluble in the polymerizing medium, such as MPIA in NMP, the reaction is rapid, even at low temperatures. For those that do not remain soluble, the choice of solvent becomes very important. More powerful solvents can produce polymers with higher molecular weights. Lower temperatures can also delay the precipitation of the polymer.

IV. SYNTHESIS OF FUNCTIONAL AROMATIC POLYAMIDES WITH CONTROLLED STRUCTURE

For the sake of simplicity, it is generally assumed that all the functional groups of the monomers and growing polymer chains present same or similar reactivity. Under this assumption, conventional polycondensation reactions occur on a step-growth manner according to Carother's equation and Flory's statistical description.

The control over the molecular mass and the polymer end groups is difficult, and thus the molecular mass distribution approaches a value of 2 at high conversion.

However, when monomers with evident unequal reactivity are employed, or when a change of reactivity is induced in one functional group by reaction and bond formation during

polymerization of other functional group, the polymer growth do not obey these conventional rules.

In order to synthesize a polymer with controlled molecular mass, a narrow molecular mass distribution and defined chain-end functional groups, the condensation should proceed in a chain-growth polymerization manner instead of step-growth polycondensation. This is the case for so-called living polymerization.

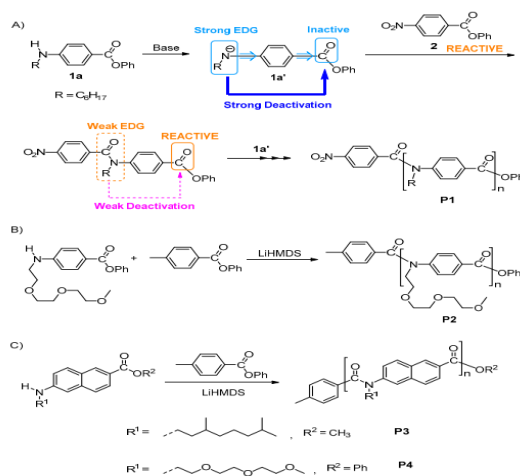
- **Chain-Growth Polycondensation**

Some experimental results showed that it is possible to obtain high molecular mass condensation polymers even at low conversions, contrary to Flory's and Carother's predictions.

This opened the way to chain-growth polycondensation. Yokoyama and Yokosuka published a detailed review of chain-growth polycondensation, and a more recent review about the latest developments in the field.

Polyether's and aromatic polyamides are prepared using the unequal reactivity induced by activation of the end groups of the polymer chains.

They found that the polycondensation of phenyl 4-(octylamino) benzoate **1a** (Scheme 1A, P1) and the initiator phenyl 4-nitrobenzoate **2** in the presence of a base yielded well defined aramids with low polydispersity ($M_w/M_n \leq 1.1$, where M_n and M_w are number-average and weight-average molecular masses, respectively).



Scheme 2 Aromatic polyamides with controlled polydispersity and mass obtained by chain-growth polycondensation. (A) polycondensation of phenyl 4-(octylamino)benzoate and the initiator phenyl 4-nitrobenzoate; (B) polycondensation of a monomer that bears a TEG sidechain; (C) polycondensation of 2,6-positions substituted naphthalene's.

The resonance effects also work in the 1,5- or 2,6-positions of naphthalene, so Mikami et al. extended their work using this type of monomers (Scheme 1C, P3–P4). Well defined polymers were obtained using the monomer with a 3,7-dimethyloctyl pendant group, whereas the monomer with the TEG moiety gave both chain-growth and step-growth polyamides, with self-condensation, because an insufficient deactivation of the electrophilic ester moiety, rendering polymers with Mn lower than the expected theoretical value

V. CONCLUSION

1, 6-Bis (4-aminophenoxy) naphthalene (1, 6-BAPON) was prepared in high purity and high yield in two steps starting from 1, 6-dihydroxynaphthalene and p -chloronitrobenzene. High molecular weight aromatic polyamides could be directly synthesized from diamine 1, 6-BAPON and various aromatic dicarboxylic acids by means of triphenyl phosphite and pyridine. Almost all the resultant polyamides showed an amorphous nature and good solubility, and they could be solution-cast into transparent, flexible, and tough films. The polymer films had excellent tensile properties and high T_g s and thermal stability. Thus, the present polyamides are considered to be new, promising, soluble, high-temperature materials.

The demand of commercial aramid fibers derived from the spun of MPDI, ODA/PPTA and PPTA, is strong, e.g., 100–120 thousands of tons expected for PPTA in 2020, with an expected annual growth range of 7–9% [6]. This fact is mainly related to the application of the fibers in protective clothing, advanced composites and heat and fire resistant insulation paper. The advanced composites and heat and fire resistant insulation paper.

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