CHEMSYSTEMS
PERP PROGRAM

Report Abstract

Aromatics Polyamides
PERP06/07S9

March 2009

Nexant

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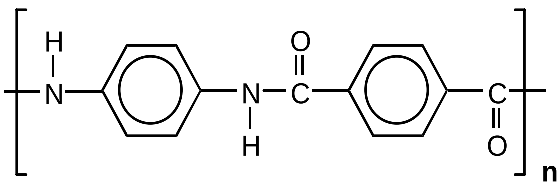
INTRODUCTION

Aromatic polyamides or polyaramids are a unique form of polyamide manufactured from an aromatic diamine and an aromatic dichloride. Today, Nexant is aware of four commercial aramid polymer products, namely:

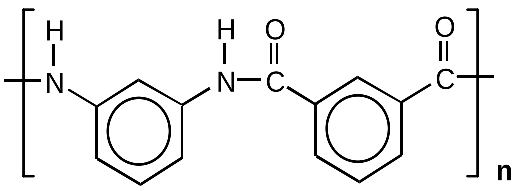
- Poly-*para*-phenylene terephthalamide
- Poly-*meta*-phenylene isophthalamide
- Co-poly-(*para*-phenylene/3,4'-oxydiphenylene terephthalamide
- Co-poly-(*para*-phenylene/4,4'-oxydiphenylene terephthalamide

The term "Polyaramid(s)" or often simply "Aramid(s)", refers to aromatic polyamides that are manufactured from specialized monomers by polycondensation. Polyaramids have exceptional performance characteristics in respect of chemical resistance and specific strength. Polyaramid properties are derived from different aspects of their molecular structure. The figure below illustrates the two most common polymers in simplified form, namely PPTA and MPIA.

Simplified Aramid Molecular Structures



Poly-paraphenylene terephthalamide (PPTA)



Poly-metaphenylene isophthalamide (MPIA)

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Major polyaramid brands such as KEVLAR®, NOMEX®, TWARON®, are household names in the plastics industry, being associated with markets where lightweight, extremely strong fibers are needed. The uses of this range of plastics range from outdoor pursuits like sailing through to ballistic protection for the military. Other brands include HERACRON®(Kolon), KAZTEX®(Kazneftekhim), TEIJINCONEX® (Teijin), NEWSTAR® (Yantai). *para*-Aramid copolymers also exist, e.g., TECHNORA®(Teijin). Aramid films and specialized aramid derivatives, e.g., SULFRON® (Teijin)

Much of the process know-how is not disclosed in patents and considerable detective work is needed to unravel the secrets of polyaramid production. Such has been the case with this study.

PROCESS CHEMISTRY

This Section of the report describes the chemistry behind the manufacture of the monomers for polyaramids as well as the polymers themselves.

Polyaramids are made via the reaction of an aromatic diamine and an aromatic dichloride. The aramid monomers can be made by different chemistries associated more with fine chemical operations. Techniques such as diazotization and photochemistry are used in some circumstances. Integration with chloralkali is beneficial. The aramid polymerization reaction takes place via polycondensation and being very rapid, requires specialized process design to ensure consistent product quality. Fiber spinning too is a highly specialized process requiring dry jet wet spinning from 100 percent sulfuric acid in the case of *para*-aramids.

The manufacture of poly-*para*-phenylene terephthalamide ("PPTA") requires three sub-processes:

- *Para*-phenylene diamine
- Terephthaloyl chloride
- Polymerization

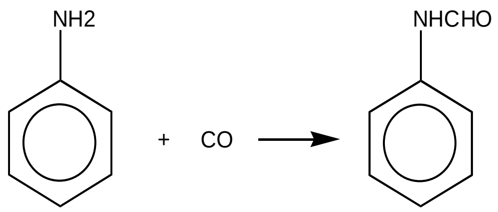
In this analysis, Nexant provides what it believes to be representative view of DuPont (in this report referred to as "First Generation") and Teijin (in this report referred to as "Second Generation") approaches to monomer and polymer production.

Para-Phenylene Diamine (PPDA)

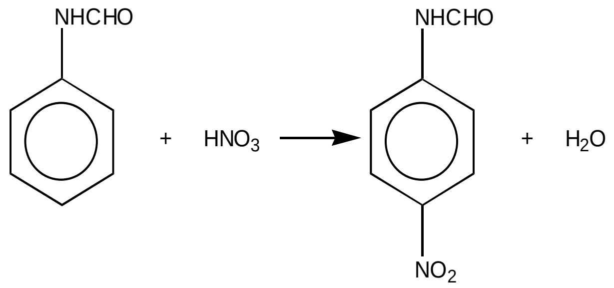
Phenylenediamines are aromatic amines with two amino groups attached to benzene. There are three isomeric phenylenediamines: *ortho*, *meta*, *para*. They are all white solids which darken upon exposure to air and they are completely soluble in hot water. Derivatives of the *para*-isomer are used extensively as antioxidants for polymers and oils, as antiozonants for rubbers and for specialty polymers such as polyamides. Both the *meta* and *para*-isomers react with benzene dicarbonyl dichlorides to give linear, fully aromatic polyamides.

The first generation approach to producing PPDA considered in this study prepares *para*-phenylenediamine by a route based on aniline, carbon monoxide, nitric acid and hydrogen as the primary reaction components.

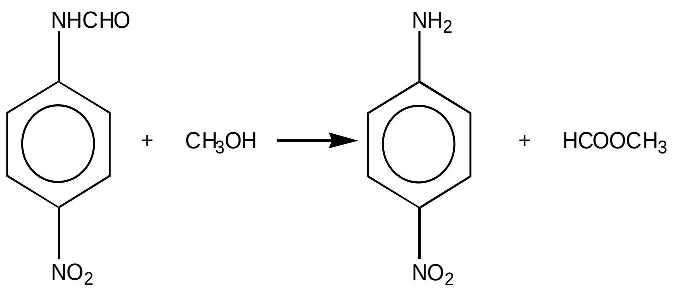
The carbonylation step proceeds as follows:



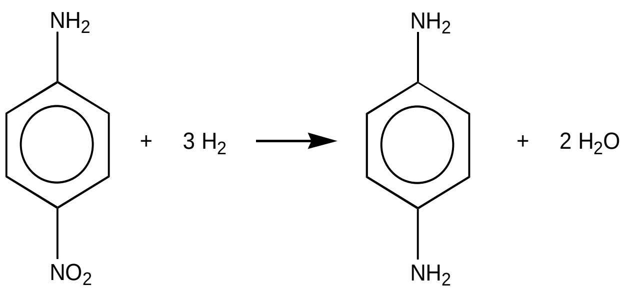
The second reaction involves nitration of the formanilide with nitric acid in combination with sulfuric acid which serves as a dehydrating agent and a solvent for the formanilide. The reaction is as follows:



The third step in the synthesis can be either hydrolysis or methanolysis. For this design, methanolysis has been chosen in accordance with the following equation:



The final step in the sequence is the catalytic hydrogenation of the nitroaniline to produce primarily *para*-phenylenediamine. Palladium on carbon catalyst is employed. The reaction is as follows:



- The second generation approach uses a rather different approach in that it exploits azo-dye chemistry. More details are given in the report.

Terephthaloyl Chloride (TDC)

Terephthaloyl chloride is a white crystalline material with a meting point circa 83°C. It is therefore stored when made in heated tanks at circa 100°C. The main raw materials in the TDC synthesis are *para*-xylene, pure terephthalic acid and chlorine.

- The chemistry for production of this chemical via first and second generation approaches are detailed in the report.

Polymerization (PPTA)

Poly-*para*-phenyleneterephthalamide is a wholly aromatic polyamide (aramid). It is produced from the starting monomers terephthaloyl chloride and *para*-phenylenediamine as described previously. This condensation polymerization reaction is carried out in the presence of an organic solvent. This process is discussed further in the report.

Other Aramid Systems

- Poly-*Meta*-Phenylene-Isophthalamide: The major brands in this market are TEIJINCONEX® and NOMEX®. As the chemistry suggests, they are made from *meta*-substituted aromatic amines and acid chlorides.
- Advanced Aramid Monomer Systems
  - Co-Poly-Para-Phenylene/3,4'-Oxydiphenylene Terephthalamide
  - Co-Poly-para-Phenylene/4,4'-Oxydiphenylene Terephthalamide

INTERMEDIATES AND POLYMERIZATION PROCESS DESIGN

Nexant has described here polyaramid technology in terms of first and second generation approaches. The first generation approach reflects Nexant's interpretation of early commercialization of aramid processes according to original DuPont designs and second generation presents a Nexant view of a technology platform closer to the Akzo/Teijin concept. A second generation technology is assumed to employ diazotization for *para*-phenylene diamine production and photochemistry/acid fusion for terephthaloyl chloride production.

Process integration is also important in the chloralkali chain as chlorine, caustic soda, hydrogen and muriatic acid are required. First generation technology also requires access to nitric and sulfuric acid processes. Nitric acid would form part of any captive aniline supply. Integration patterns can evolve over time. For example, Teijin Aramid at Delfzijl, Netherlands is co-located on a site with local monochloracetic acid production with captive chloralkali and a muriatic acid byproduct. Integration with VCM production could prove viable.

Nexant focuses on two approaches to PPTA resin (or rather powder) product. Both supporting PPDA and TCl processes are described, together with Nexant mass balance estimates. The approaches clearly reflect the very different process chemistries involved for the intermediates. Both technology platforms require considerable process integration. Both cases would benefit with close chloralkali integration as is the case with the Teijin Twaron® (formerly Akzo) facility in Delfzijl in the Netherlands.

Fiber spinning requires dissolution in 100 percent sulfuric acid for *para*-aramids under tightly controlled conditions. For spinning *meta*-aramids more common solvents such as NMP and DMAC can be used. Dry jet wet spinning (originally a Monsanto concept) is used to create aramid fibers with the desirable properties the market requires. Post-treatments are also performed to tailor fiber properties. At the time of writing new spinning technology is even being developed to improve fiber properties.

In summary, this section discusses technology designs related to:

- Para-Phenylene Diamine first and second generation process designs
- Terephthaloyl Chloride first and second generation process designs
- Polymerization first (theoretical) and second generation process designs
- Spinning process design
  - The primary challenge of the spinning process is to ensure that the alignment of the liquid crystal polymers is maintained as the PPTA dope is forced through the spinnerets, extended and drawn so that the ensuing fiber properties meet specifications.
- Process Integration for first and second generation approaches

PROCESS ECONOMICS

Cost of Production Estimates for the following have been evaluated for production of:

- *para*-Phenylene Diamine by Second Generation approach: Diazotization/Hydrogenation
- *para*-Phenylene Diamine by First Generation approach: Carbonylation/Nitration/Methanolysis/Hydrogenation
- Terephthaloyl Chloride by Second Generation approach: Photochlorination/Acid Fusion
- Terephthaloyl Chloride by First Generation approach: Chlorination with Thionyl Chloride
- Poly-*para*-Phenylene Terephthalamide by Polycondensation and Solvent Recovery – Second Generation approach
- Poly-*para*-Phenylene Terephthalamide by Polycondensation and Solvent Recovery – First Generation approach
- Second Generation Fiber by Dry Jet Wet Spinning
- First Generation PPTA Fiber by Dry Jet Wet Spinning

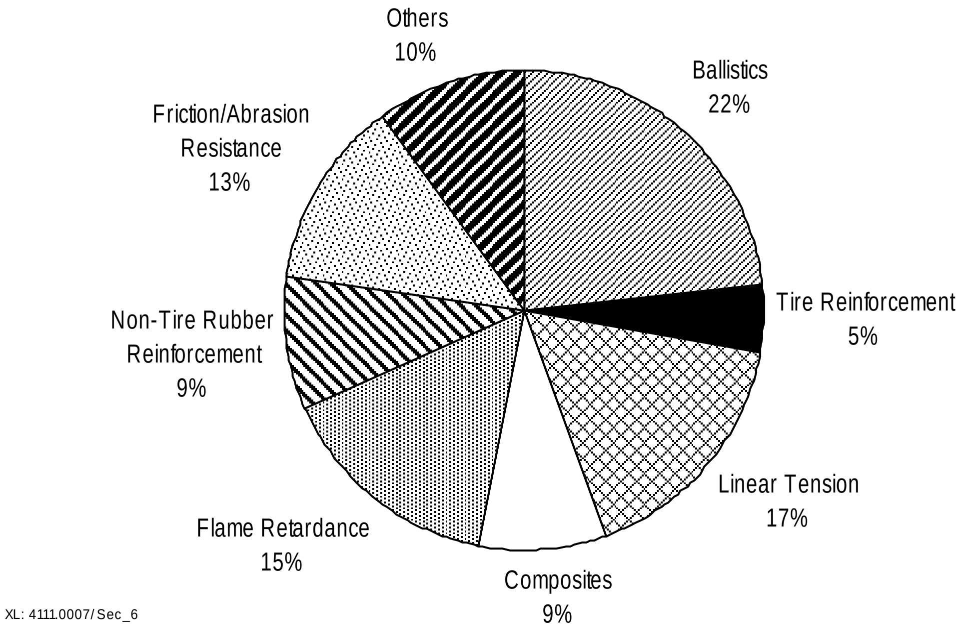
COMMERCIAL STATUS

The focus of Nexant's PERP program is on technology in a commercial context. Therefore, Nexant has included here a brief review of aramid applications and markets. The market information provided is based on Nexant estimates, taking into account material available in the public domain.

Whilst the market is concentrated on developed economies, Asia has seen a surge in demand in recent years, driven in part by local production. Strong demand growth across all applications is driving major expansion programs. The Figure below gives an indication of global polyaramid demand for 2007.

Global Polyaramid Demand by Major End-Use, End 2007

para- and meta-forms, Nexant estimates



Topics discussed in this section include:

- Polymer Properties
- Major Applications
  - The properties of polyaramid fibers and films are sufficiently different from those of the products that preceded them that many new uses and applications have been developed. Applications are summarized according to general market groupings, specifying the type of fiber or film used but not necessarily the specific product.
- Market Overview
  - Supply, Demand projections are discussion and estimated plant capacities where available are given.
  - Producer Profiles – DuPont, Teijin Aramid, and others.
  - Global Supply/Demand Issues- Nexant has developed empirical supply demand balances for polyaramids on a global basis. These are indicative market estimates only.

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