



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

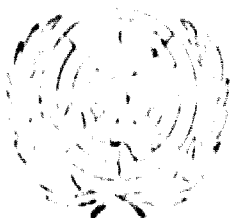
FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

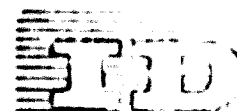
CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org



D00403



Distribution
LIMITED

ID/WG.34/31, Rev.1
17 February 1970

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

PET. SYMP. C/7

Moscow, USSR, 21 - 31 October 1969

THE PETROCHEMISTRY OF HIGH TEMPERATURE RESISTANT POLYMERS^{1/}

by

H. Mark
Polytechnic Institute of Brooklyn
Brooklyn
United States of America

S.W. Atlas
Bronx Community College
United States of America

The views and opinions expressed in this paper are those of the authors
and do not necessarily reflect the views of the secretariat of UNIDO.
This document has been reproduced without formal editing.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

Due to the recent demands in aerospace and other technological areas considerable progress has been made in the production of high temperature materials particularly for use in electrical and thermal insulation, gaskets, flexible tubing and many other items currently made from organic polymers in the form of fibres, films, webs, felts and related objects. There are essentially two synthetic methods available to achieve the principle of chain stiffening: polycondensation and polyaddition.

A. Polycondensation has the important advantage of easier control of the reaction but the disadvantage at the present time that both the monomers needed and the process itself is somewhat expensive. The following types of heat resistant polycondensation products are presently in an advanced state of development.

I. Polyimides - Aromatic polyimides are derived from aromatic diamines and aromatic dianhydrides or from aromatic compounds containing both an amide and an anhydride group. The highly inflexible nature of the C=O polymers has precluded their direct synthesis practical and successful conversion into such useful articles as fibres, films, tubes and sheets. However, recently there has been considerable progress in the synthesis and utilization of these materials; it is due to the following reasons:

- a - High molecular weight polyimides can now be prepared stepwise by use of a soluble and otherwise tractable polyamic-acid precursor, and
- b - High molecular weight polyamic-acid precursors can be prepared by low temperature polycondensation in solution.

Films, coatings, fibres and other objects are made from the polyamic-acid solutions and the soluble polyamic-acid is then converted to the polyimide. The Du Pont Company is producing a polyimide - Kapton - which exhibits excellent electrical and mechanical properties at elevated temperatures even after long periods of ageing. In addition these favourable properties are retained when subjected to the environments of high intensity β and γ radiation, high vacuum, cryogenic conditions, and hot organic solvents.



UNIDO

United Nations Industrial Development Organization

UNIDO
UNITED

11/01.31/31 SUBJECT
23 JULY 1969

ORIGINAL: ENGLISH

Interregional Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

ICP, SYMPO. 0/7

Baku, USSR, 20 - 31 October 1967

SUMMARY

THE PETROCHEMISTRY OF HIGH TEMPERATURE RESISTANT POLYMERS^{1/}

by

H. Mark
Polytechnic Institute of Brooklyn
United States of America

S.H. Atlas
Brant Community College
United States of America

Due to the recent demands in aerospace and other technological areas considerable progress has been made in the production of high temperature materials particularly for use in electrical and thermal insulation, baskets, flexible tubing and many other items currently made from organic polymers in the form of fibres, films, wools, foams and solid objects. There are essentially two synthetic routes available to achieve the principle of chain stiffening: polycondensation and polyaddition.

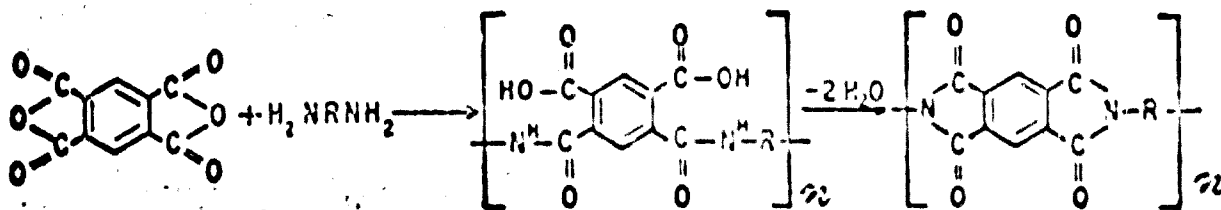
This paper describes a number of applications of these two types of process to the synthesis of heat resistant polymers.

^{1/} The views and opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the secretariat of UNIDO.
This document has been reproduced without formal editing.
id.69-4477



The synthesis of polyimide is carried out by allowing pyromellitic dianhydride to react with an aromatic diamine in dimethyl acetamide at 25 °C to yield a soluble polyamic acid. Such a solution can be used as an enamel on a substrate or directly to cast a film which is then thermally converted to the more heat-resistant polyimide by heating at 300 °C. The thermal stability of polyimides as measured by TGA indicates a 10% weight loss in helium or air at about 600 °C. Results of isothermal weight loss experiments conducted at 450 °C in helium show only a 5% weight loss in more than 16 hours.

Synthesis of Polyimide



Soluble polyamic acid Insoluble polyimide

The DuPont polyimide products include the following materials.

<u>Form</u>	<u>Name</u>
Film	Kapton-Polyimide Film
Solid	Vespol-Precision Parts from Polymer SP
Liquid	Pyre-M. L. Enamels and varnishes
Fiber	No name yet
Polyimide/Glass	No name yet
Fabric and Roving	
Prepreg	No name yet

Kapton Polyimide Film. Kapton type II has been used successfully in applications over the temperature range -269°C to 400°C . At room temperature the properties of Kapton and Mylar polyester film are similar. However, as the temperature is increased or decreased the properties of Kapton are less affected than those of Mylar. There is no known organic solvent for the film and it is infusible and flame resistant.

Kapton can be bonded by adhesives to itself, metals, wood, plastic sheets, paper, and to other films; it can also be laminated, metalized, punched and formed. The polyimide adhesives show the excellent thermal stability of the parent polymer, but this far adhesive bonds which have been obtained had shear strengths lower than the comparable commercial epoxyphenolics. However, the polyimide bonds retained over 50% original strength after exposure at 300°C for 1000 hours, whereas all other adhesives lost all strength after only 150 hours. In the same vein polyimides retained an excess of 50% original bond strength after 24 hours at temperatures of 360°C while epoxy-phenolics had completely deteriorated after one hour at this temperature.

Applications for this polyimide film include: wire, cable and formed coil wrap, flexible printed circuits, magnet wire, transformers, capacitors, pneumatic and pressure sensitive tapes, hose and tubing. Many of these applications are based on the fact that the excellent electrical properties of Kapton such as dielectric strength and dissipation factor remain nearly constant over a wide range of temperature and frequency.

Inasmuch as Kapton has no melting point, one can combine Teflon with polyimide to give a heat-sealable structure for fabrication purposes. This combination is known as Kapton Teflon. In addition to the heat-sealable surface the coating improves the chemical resistance to bases and acids and reduces the rate of moisture permeability and of oxidative decomposition.

Vespel. The rigid solid form of the aromatic polyimide is called Polymer SF and parts made of it are sold under the trade name of Vespel in two major types: one is formulated to provide low frictional performance in seals and bearing applications; the other in devices such as brakes and clutches.

The Pyre-M.L. Enamels represent the liquid form of aromatic polyimides, which are having the greatest thermal stability, radiation, solvent and cryogenic resistance of any available enamel. These properties have been utilized in motors, generators, transformers and other machine parts which operate continuously at temperatures around 220 °C. The thermal stability and very slight tendency to give off volatile materials has led to its use in sealed relays designed for use in vacuum.

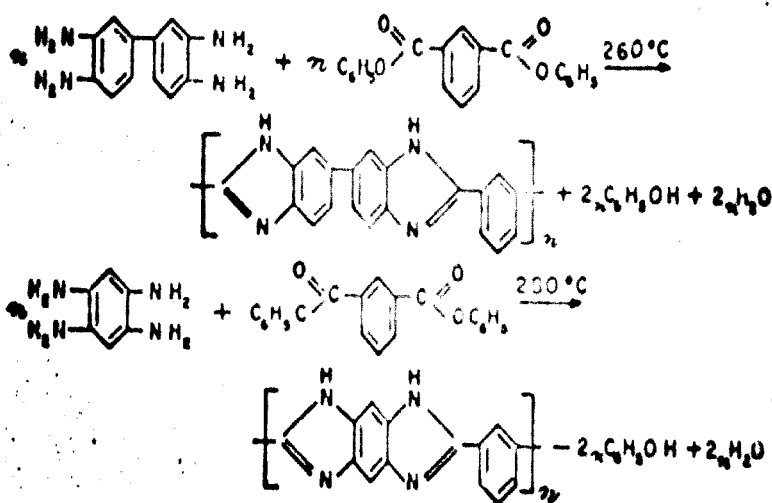
II. Polyamide - imides - Polyamide-imides are prepared by the reaction of dianhydrides with diamines containing preformed amide groups, by the reaction of trimellitic anhydride acid chloride with diamines or by the reaction of diamines with dianhydrides containing a preformed amide group. Also, a low molecular weight aromatic polyamide with amine end groups can be reacted with an aromatic dianhydride to yield a polyamide-imide.

The Anoco AI polymer is a material composed of amide and imide groupings. It is based on ANOCO trimellitic anhydride and provides excellent electrical and mechanical properties as well as outstanding thermal resistance. It is being used in laminates, adhesives, moldings, coatings, and films for high temperature applications. The molecular weight and molecular weight distribution of this polymer is controlled to give optimum performance in coating applications such as magnet wire and capacitors. Enamels can be prepared by dissolving AI polymer in suitable solvent blends. The wire coating is dried and cured at high temperatures to form a tough heat resistant film.

The basic structure of Westinghouse's Doryl resins comprises diphenyl oxide units bonded with methylene bridges. The functional group forming these bridges is generally an alkoxy-methyl group reacting with a ring hydrogen on an already substituted ring under the influence of Lewis acids in liquid or solid form. Homopolymers and copolymers have been made. The resulting materials are used as varnishes, dry-type transformers, binders in glass and carbon cloth laminates and as varnish in electrical equipment for extreme service performance.

III. Polybenzimidazole - These polymers are synthesized by reacting an aromatic tetramine with the diphenyl ester of an aromatic diacid. This reaction is carried out at about 260 °C evolving phenol and water as volatile constituents. In certain cases curing is carried out at temperatures as high as 400 °C.

Synthesis of a Poly(benzimidazole)



The polybenzimidazole adhesive from diaminobenzidine and diphenyl ortho-phthalate is very stable up to 500 °C and loses only about 20% of its weight at 900 °C in helium at a heating rate of 2.5° per minute. In the presence of air, however, thermal degradation is much more rapid.

A number of polybenzimidazoles have been prepared. All the polymers prepared were colored, ranging from yellow to dark brown; they are characterized by superior hydrolytic stability and a high degree of thermal stability. Polybenzimidazole adhesives have not only exhibited high initial lap shear strengths comparable to those of epoxy-phenolics but like polyimides they are vastly superior on exposure to elevated temperatures.

B. Polyaddition - As soon as the principles for high heat resistance of organic polymers were established by polycondensation products, work also started on polyaddition reactions. Their main disadvantage is the difficulty to obtain well controlled, high molecular weights but once such a reaction is worked out at least under simple conditions and, most important, the monomers are inexpensive.

Rigid molecules of this type are based on aromatic chains such as polyparaphenylenes which cannot fold even at high temperatures because rotation about the carbon-carbon single bond between the para-combined phenylene rings can only lead to different angles between the places of consecutive rings but not to a kink or bend in the main chain. In fact, representatives of this species are rigid, high melting, possess a pronounced tendency to crystallize and are insoluble.

Already 20 years ago Dr. George Goldfinger published a paper on the synthesis and characterization of poly-p-phenylene. He used the Wurtz-Fitting reaction of 1,4-dichlorobenzene with metallic sodium in dioxane and obtained a benzene-soluble fraction which did not melt up to 500 °C. However, the molecular weight of this polymer was only around 2500.

The latest and best synthesis of poly-p-phenylene was prepared by straightforward polymerization of benzene. Kovacic and his associates have found that benzene polymerizes in a system consisting of Lewis acid catalyst-co-catalyst-oxidizing agent. In the presence of aluminum chloride-ferric chloride, benzene was polymerized under mild reaction conditions (temperatures 35-50 °C, 15 minutes) to a brown solid with 60% yield.

Recently another method has been developed by a group of chemists at the Monsanto Chemicals, Ltd. in England. They have succeeded to obtain linear poly-phenylene by the thermal decomposition of aromatic sulphonyl chlorides. These results a mixture of o-, m- and p- substitution. For instance 75% of mixed terphenyls were obtained by decomposing benzene sulphonyl chloride (1 mol.) in biphenyl (15 moles) at 225 °C. An efficient catalyst is cuprous chloride.

Polymer 360 is 3M's thermoplastic molding resin capable of structural use at elevated temperatures; it consists of linear macromolecules composed of biphenyl and phenyl units linked together by oxygen or sulfur atoms. The polymer is characterized by the following data:

Specific gravity	1.36
Glass Transition Temp.	550 °F
Colour	clear
Water absorption, 24 hours	1.4%
Flammability	self-extinguishing

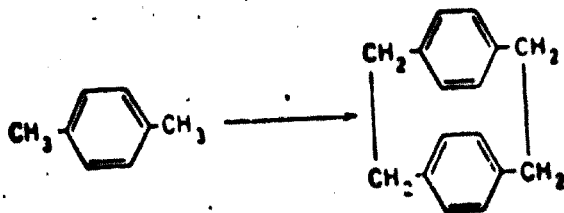
The poly (xylylenes) belong to a class of linear polymers containing methylene and phenylene groups with two methylene groups between connective units. The melting points of the isomers are as follows:

poly-o-xylylene	110 °C
poly-m-xylylene	60 °C
poly-p-xylylene	400 °C

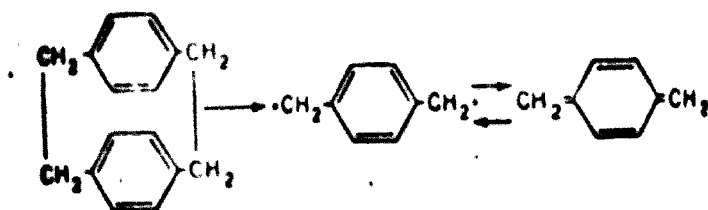
which shows that only the para isomer is of practical interest.

Parylene is the generic name for members of this thermoplastic polymer series as they are being produced by the Union Carbide Corporation. One representative is Parylene N, a completely linear, high crystalline poly-para-xylylene. Parylene C and D, two other members of the series contain one viz. two chlorine atoms in each aromatic ring; they are somewhat less crystalline than Parylene N.

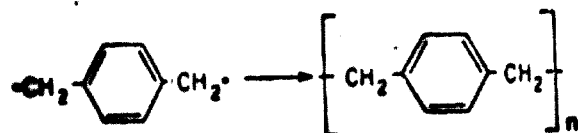
The parylenes are formed by vapor phase polymerization of para-xylylene or substituted para-xylylenes; the first step of the synthesis is the dimerization of p-xylylene at about 950 °C in the presence of steam, yielding di-p-xylylene which after several steps of purification is a white stable,



crystalline powder. This dimer is pyrolyzed at 550 °C in a sublimation chamber to yield a monomeric biradical and dimethylenequinone.



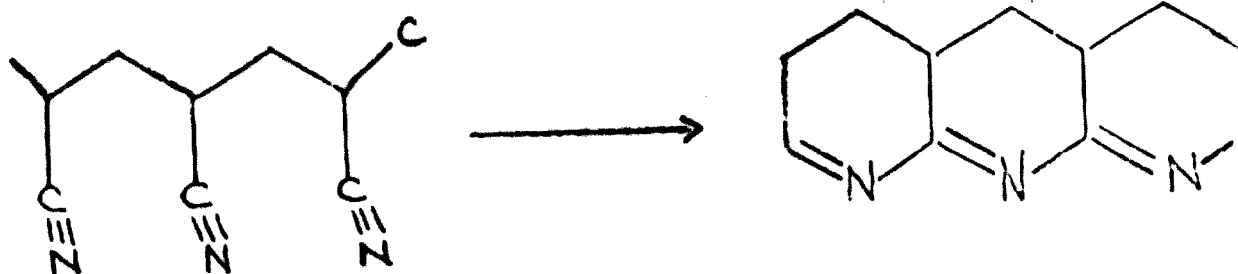
Cooling of the monomer to a temperature below 50 °C results in immediate polymerization with the formation of linear poly-p-xylylene,



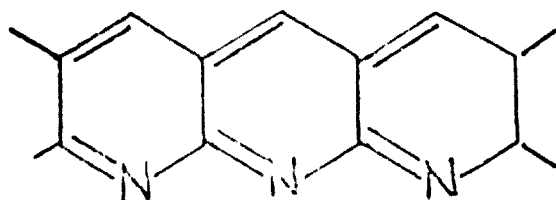
which has a molecular weight of about 500,000.

The electrical properties depend on the substitution on the aromatic ring. Parylene N itself can be classed as a particularly valuable dielectric material because of its unusually low dissipation factor over a wide range of frequencies. The chlorine containing parylenes have higher dielectric constants and high dissipation factors.

Another important way to arrive at chains made up of condensed aromatic rings is the synthesis of so called "ladder" polymers. The first ladder polymer was prepared by exposing polyacrylonitrile to elevated temperatures which cause the formation of rows of fused six membered rings by electron pair displacement:



This process involves stiffening, insolubility, and discolouration. Further heating leads to the evolution of H_2 and to aromatization,



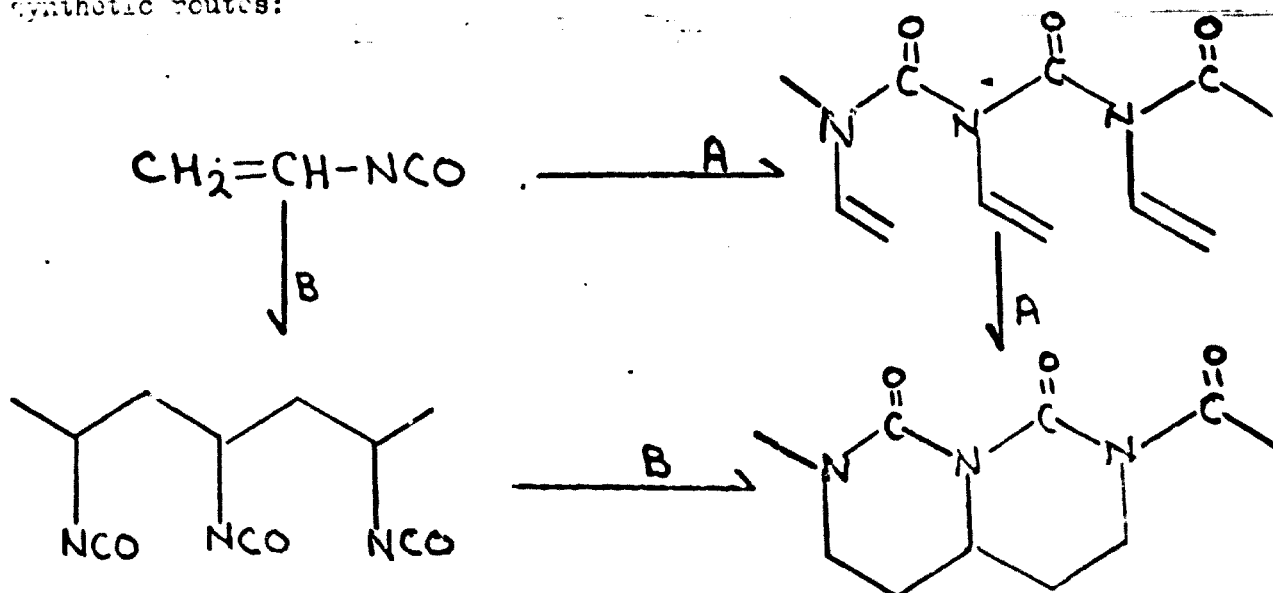
whereby a black, completely infusible and insoluble material is obtained which in its structure, corresponds to linear graphite in which one carbon atom of every ring has been replaced by a nitrogen.

Black Orlon, a pyrolyzed polyacrylonitrile in fibre form, withstood exposure to temperatures of 700 - 800 °C with an open flame with essentially no loss in properties. Various polydiene ladder polymers have been prepared.

Pluton B is a member of a family of new carbon based fibres manufactured by the GM Co. Pluton B does not melt when exposed to high temperatures, but rather sublimates or vaporizes at a rate dependent upon the surrounding atmosphere and exposure temperature. The excellent high temperature stability and resistance to corrosion materials indicate a stability of Pluton B in such areas as high temperature thermal insulation, packing and gasketing, and corrosive fluid filtration.

Ladder polymers from vinyl isocyanate

These structures have been prepared via the following two-step synthetic routes:



The isocyanato and vinyl groups can be polymerized under quite different conditions. The N-vinyl-1-nylon, prepared by anionic polymerization by using sodium cyanide in N-N DMF, was cyclized to the ladder polymer with azobisisobutyronitrile and U.V. light (Pathway A). Polyvinyl isocyanate, which can be prepared by the uncatalyzed polymerization of vinyl isocyanate in dilute solutions, was cyclized by treatment with x-rays (Pathway B). The products from both routes were identical and, based on chemical and spectral data, appeared to be ladder polymers of the structure shown in the slide.





16.

3.

72