Polyimide Manufacture

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FOREWORD

The detailed, descriptive information in this Chemical Process Review is based on U.S. Patents issued since 1962 and relates to the production of polyimides and closely allied substances.

This book serves a double purpose in that it supplies detailed technical information, and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant and eliminating legalistic terminology, this book becomes an advanced industrially oriented review of processes to produce a great variety of polyimides. Modified polyimides and specialty intermediates of interest are given ample discussion

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easily obtainable information.

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INTRODUCTION

Heat resistant polymers containing an imide grouping have been the subject of considerable research over the past ten years. Du Pont and General Electric have been active in the development of aromatic polyimides for high-temperature applications in the electrical industry, particularly as insulation for wire coatings and as insulation in heavy-duty electric motors. Polyimides are also being used in films, coatings, moldings, binders for glass cloth and in some high-temperature adhesive systems. Polyimide coatings were first introduced by Du Pont in the early sixties.

A number of modified polyimides have been developed and some are available, for example, polyamide-imides (Amoco) and polyester-imides (General Electric), copolyamides (Monsanto) and others.

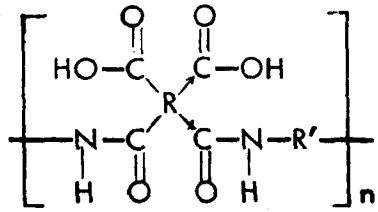
The polyimides retain good mechanical properties at temperatures of 750°F. and higher, with excellent electrical properties. Magnet wire applications consume the largest share of polyimide varnishes and enamels.

POLYAMIDE-ACIDS

GENERAL

Polyamide-Acid Process

A process described by W.M. Edwards; U.S. Patent 3,179,614; April 20, 1965; assigned to E.I. du Pont de Nemours and Company involves the preparation of polyamide-acids and their formation into shaped structures. The process involves a composition containing at least one polyamide-acid having the following structural formula:

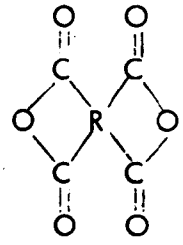


where ⟶ denotes isomerism. In any recurring unit the groups to which arrows point may exist in the polymeric structure as shown or these groups may exist in interchanged positions. Here R is an organic tetravalent radical containing at least 2 carbon atoms, no more than 2 carbonyl groups of each polyamide-acid unit being attached to any one carbon atom of the tetravalent radical; where R′ is a divalent radical containing at least 2 carbon atoms, the amide groups of adjacent polyamide-acid units each attached to separate carbon atoms of the divalent radical; and where n is an integer sufficient to provide a polyamide-acid having an inherent viscosity of at least 0.1, preferably 0.3 to 5.0, as measured as a 0.5% solution in N,N-dimethylacetamide at 30°C.

The polyamide-acids for use in the process are solids with an undefined melting point. Their infrared absorption spectra are characterized by absorption bands at ca. 3.1 microns due to the N—H bond of the amide groups, at ca. 5.8 microns due to the C=O bond of the carboxyl groups and at ca. 6.0 microns due to the C=O bond of the amide groups. The process for preparing the polyamide-acid compositions comprises reacting by mixing at least one organic diamine having the structural formula:

$$H_2N-R'-NH_2$$

where R′ is a divalent radical containing at least 2 carbon atoms, the two amino groups of the diamine each attached to separate carbon atoms of the divalent radical; with at least one tetracarboxylic acid dianhydride having the structural formula:



where R is an organic tetravalent radical containing at least 2 carbon atoms, no more than 2 carbonyl groups of the dianhydride attached to any one carbon atom of the tetravalent radical; in an organic solvent for at least one reactant, the solvent being inert to the reactants, preferably under anhydrous conditions, for a time, preferably of at least 1 minute, and at a temperature below 175°C., sufficient to provide at least 50% of the corresponding polyamide-acid.

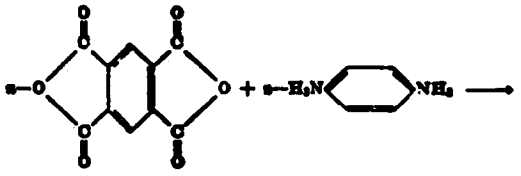
One purpose of the process is to provide a composition that can be shaped into useful objects. For this purpose, it has been found that a composition containing a polymeric component made up of at least 50% of the polyamide-acid will suffice for all combinations of diamine/dianhydride reaction products. However, for polyamide-acids prepared from some combinations of diamine and dianhydride, the polymeric components of shapeable compositions may contain less than the specified minimum of 50%.

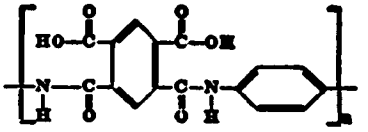
Furthermore, in determining a specific time and a specific temperature for forming the polyamide-acid of a specified diamine and a specified dianhydride, several factors must be considered. The maximum permissible temperature will depend on the diamine used, the dianhydride used, the particular solvent, the percentage of polyamide-acid desired in the final composition and the minimum period of time that one desires for the reaction. For most combinations of diamines and dianhydrides falling within the definitions given above, it is possible to form compositions of 100% polyamide-acid by conducting the reaction below 100°C.

However, temperatures up to 175°C. may be tolerated to provide shapeable compositions, the polymeric portion of which contains at least 50% of the polyamide-acid. The particular temperature below 175°C. that must not be exceeded for any particular combination of diamine, dianhydride, solvent and reaction time to provide a reaction product composed of at least 50% of the polyamide-acid will vary but can be determined by a simple test by any person of ordinary skill in the art. However, to obtain the maximum inherent viscosity, i.e., maximum degree of polymerization, for any particular combination of diamine, dianhydride, solvent, etc., and thus produce shaped articles such as films and filaments of optimum toughness, it has been found that the temperature throughout the reaction should be maintained below 60°C., preferably below 50°C.

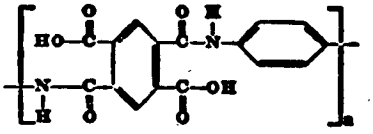
After shaping the composition composed predominantly of the polyamide-acid, preferably still in the solvent, into a useful article, e.g., filament, film, tube, rod, etc., and

drying the article, it is preferred to convert the polyamide-acid to another polymer to modify the properties of the shaped structure. Thus, the polyamide-acid may be converted by heat treatment or chemical treatment to the corresponding polyamide. The following illustration is typical of the reactions in the examples and should serve as a guide to the polyamide-acid obtained in each example. The reactions in this illustration involves para-phenylene diamine (PPD) and pyromellitic dianhydride (PMDA).

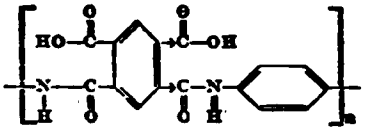




and/or



The fact that the carboxyl groups on each recurring unit may be meta or para to each other, as shown above, indicates the isomeric nature of the recurring unit. This isomerism is depicted most simply by the arrows in the following structural formula of the polyamide-acid product:



In the examples, the polyamide-acid compositions were prepared by reacting at least one diamine with a dianhydride in the presence of N,N-dimethylacetamide, N,N-dimethylformamide, pyridine, N-methylcaprolactam or dimethyl sulfoxide as solvents. The reactions, unless otherwise stated, were carried out under a dry nitrogen atmosphere. The temperature of the reaction in most of the examples was not permitted to rise above 50°C.

The presence of the polymer, the polyamide-acid, in the final composition was determined by infrared absorption spectra. The appearance of bands representing —NH and —COOH groups and the lack of bands representing anhydride and free amino groups served to characterize the polyamide-acids. The preparations of some of the important ingredients used in the examples are given below. The meta-phenylene diamine used was colorless and had a melting point of 62° to 63°C. It was prepared by first bubbling air through a melt of the commercially available product followed by fractional distillation.

The pyromellitic dianhydride used was obtained as white crystals by sublimation of the commercial product through silica gel at 220° to 240°C. and 0.25 to 1 mm. mercury pressure. N,N-dimethylformamide and N,N-dimethylacetamide were prepared by fractional distillation from phosphorous pentoxide; the fraction distilling at 47.5°C. and 17 mm. pressure being N,N-dimethylformamide and the fraction distilling at 73°C. and 30 mm. pressure

being N,N-dimethylacetamide, which were used as solvents in the examples.

Example 1: 12.4 g. (0.115 mol) of meta-phenylene diamine was dissolved in 100 ml. N,N-dimethylacetamide. Pyromellitic dianhydride, 25.0 g. (0.115 mol) was added portionwise with agitation. During the entire operation (40 minutes) the reaction vessel was cooled by tap water (15°C.) circulating through an outer jacket. The last portion of dianhydride was added with 15 ml. N,N-dimethylacetamide, then an additional 85 ml. of N,N-dimethylacetamide was added to give a viscous solution containing 15.4% by weight polymer. The inherent viscosity of the polyamide-acid was 1.7 (as measured as a 0.5% solution in N,N-dimethylacetamide at 30°C.). The viscous solution was cast onto a glass plate and dried at 120°C. in a forced-draft oven for 60 minutes. A tough, flexible polyamide-acid film was obtained.

Example 2: A polyamide-acid from para-phenylene diamine and pyromellitic dianhydride was prepared following the procedure described in Example 1. 6.2 g. (0.0575 mol) of the diamine, 12.5 g. (0.0575 mol) of the anhydride and 120 ml. of N,N-dimethylacetamide were used. The viscous solution containing 12.8% by weight of the polymer was cast onto a glass plate to form a tough, flexible polyamide-acid film.

Example 3: Benzidine, 2.01 g. (0.011 mol), was dissolved in 10 ml. of N,N-dimethylformamide. Pyromellitic dianhydride, 2.37 g. (0.011 mol), was added portionwise with stirring. During addition, the solution was diluted by adding 10 ml. of N,N-dimethylformamide at three separate times. With the last portion of dianhydride was added 10 ml. of N,N-dimethylformamide to give a viscous casting solution containing 8.1% by weight of polymer. The reaction was carried out at a temperature maintained at 15°C. It was allowed to continue for 45 minutes, at which time a noticeable increase in viscosity indicated substantial completion of the reaction. Tough polyamide-acid films were made by casting the solution onto glass plates by drying at 80°C. in a vacuum for 60 minutes. The inherent viscosity of the polyamide-acid was 2.0 (as measured as 0.5% solution in N,N-dimethylformamide at 30°C.).

Example 4: Meta-phenylene diamine, 0.7 g. (0.0065 mol) and 0.75 g. (0.0065 mol) hexamethylene diamine were dissolved in 30 ml. of N,N-dimethylformamide. Pyromellitic dianhydride, 2.84 g. (0.01304 mol) was added portionwise with agitation. During the polymerization (60 minutes) the reaction vessel was cooled by tap water (15°C.) circulating through an outer jacket. The polymerization was considered to be substantially complete as indicated by the perceptible increase in viscosity.

A solution containing 12% polymer by weight was obtained. The viscous solution was cast onto a glass plate with a doctor knife having 15 mil opening and was dried in a vacuum at 60°C. for 60 minutes. The film was stripped from the glass plate and dried additionally for 15 hours at room temperature under a dry nitrogen atmosphere. The inherent viscosity was 0.34 (as measured as a 0.5% solution of the film in 97/3 N,N-dimethylformamide/lithium chloride at 30°C.). The resultant polyamide-acid film displayed the following properties:

Tensile modulus (psi)	229,000
Elongation (percent)	0.9
Tensile strength (psi)	2,100

Example 5: 4,4'-diaminodiphenylmethane, 1.98 g. (0.010 mol) and 0.38 g. (0.00325 mol) hexamethylene diamine were dissolved in 30 ml. of N,N-dimethylformamide. Pyromellitic dianhydride, 2.87 g. (0.01325 mol) was added portionwise with agitation. During the polymerization (60 minutes) the reaction vessel was cooled by tap water (15°C.) circulating through an outer jacket. The polymerization was considered to be substantially complete as indicated by the perceptible increase in viscosity

A solution containing 14.5% polymer by weight was obtained. The viscous solution was cast onto a glass plate with a doctor knife having 15 mil opening and was dried in a vacuum at 60°C. for 60 minutes. The film was stripped from the glass plate and dried additionally for 15 hours at room temperature under a dry nitrogen atmosphere. The inherent viscosity was 0.44 (as measured as a 0.5% solution of the film in 97/3 N,N-dimethylformamide/lithium chloride at 30°C.). The polyamide-acid film displayed the following properties:

Tensile modulus (psi)	402,000
Elongation (percent)	11.3
Tensile strength (psi)	8,300

Example 6: A polyamide-acid was prepared from 4,4'-diaminodiphenylmethane and pyromellitic dianhydride as follows: In a three-necked 250 cc round-bottomed flask equipped with stirrer, addition funnel, and nitrogen inlet tube were placed 9.91 g. (0.05 mol) 4,4'-diaminodiphenylmethane and 10.91 g. (0.05 mol) pyromellitic dianhydride which had been sublimed through a silica gel onto a stainless steel screen. The stirrer was started and 83.3 g. N,N-dimethylformamide which had been distilled from pyromellitic dianhydride was added to give a polyamide-acid solution. The reaction was conducted at room temperature (23°C.) and during the reaction the temperature did not rise more than 5° to 10°C. The resulting polyamide-acid was found to have an inherent viscosity of 1.70.

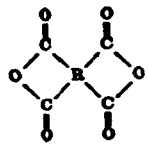
To the solution prepared as above was added 83 cc N,N-dimethylformamide and the solution, containing 10.5% by weight of the polyamide-acid, was then spun through a flat-faced spinneret having five holes, each 0.005 inches in diameter, into a water bath at room temperature. The fibers were stretched to twice their original lengths immediately following the coagulating bath and were wound up at 27 yards/minute. After air drying, the polyamide-acid fibers were found to have a tenacity of 1.1 g./denier, an elongation of 6.5% and an initial tensile modulus of 44 g./denier.

Reaction with Acid Anhydrides

In a process described by A.L. Endrey; U.S. Patent 3,179,630; April 20, 1965; assigned to E.I. du Pont de Nemours and Company polyimides are prepared by reacting at least one organic diamine having the structural formula:

$$H_2N-R'-NH_2$$

where R' is a divalent radical containing at least 2 carbon atoms, the two amino groups of the diamine each attached to separate carbon atoms of the divalent radical; with at least one tetracarboxylic acid dianhydride as shown on the following page, in which formula the R is a tetravalent radical containing at least 2 carbon atoms, no more than 2 carbonyl



groups of the dianhydride attached to any one carbon atom of the tetravalent radical; in an organic solvent for at least one of the reactants, the solvent being inert to the reactants, preferably under anhydrous conditions, for a time and at a temperature below 175°C. sufficient to form n mols of a polyamide-acid, each mol containing m amide-acid linkages and then converting the polyamide-acid to the polyimide by treating the polyamide-acid composition with n times m mols of a lower fattv monobasic acid anhydride, preferably acetic anhydride.

Although the stoichiometric equivalent, based on the polyamide-acid, of the anhydride alone is operable in the process, it is preferred to have some of the tertiary amine, preferably pyridine, present as well. The ratio of the tertiary amine to anhydride may vary from zero to almose infinite mixtures with a 1:1 ratio being the most commonly used with tertiary amines having the activity of pyridine. The amine functions as a catalyst for the action of the cyclizing agent, the anhydride. Besides acetic anhydride, other operable lower fatty acid anhydrides include propionic, butyric, valeric, mixed anhydrides of these with one another and with anhydrides of aromatic monocarboxylic acids, e.g., benzoic acid, naphthoic acid, etc. and with anhydrides of carbonic and formic acids, as well as aliphatic ketenes (ketene and dimethyl ketene). The preferred anhydrides are acetic anhydride and ketene. The preparations of some of the important ingredients used in the examples are given below.

The pyromellitic dianhydride used was obtained as white crystals by sublimation of the commercial product through silica gel at 220° to 240°C. and 0.25 to 1 mm. mercury pressure. N,N-dimethylformamide and N,N-dimethylacetamide were prepared by fractional distillation from phosphorus pentoxide; the fraction distilling at 47.5°C. and 17 mm. pressure being N,N-dimethylformamide and the fraction distilling at 73°C. and 30 mm. pressure being N,N-dimethylacetamide.

Test Descriptions: Tensile Strength, Elongation and Tensile Modulus — These measurements are determined at 23°C. and 50% relative humidity. They are determined by elongating the film sample (samples were cut with a Thwing-Albert Cutter which cut samples 1/4" wide) or filament at a rate of 100% per minute until the sample breaks. The force applied at the break in pounds/square inch (psi) is the tensile strength for films; in g./denier (gpd) is tenacity for filaments.

The elongation is the percent increase in the length of the sample at breakage. Initial tensile modulus in psi or gpd is directly related to film or filament stiffness. It is obtained from the slope of the stress-strain curve at the elongation of 1%; both tensile strength and initial tensile modulus are based upon the initial cross-sectional area of the sample.

Degree of Toughness — This is determined by subjecting a film 1 to 7 mils thick to a series of creasing actions by folding the film through 180° and creasing, followed by folding through 360° and creasing, to complete one cycle. The number of creasing cycles which the film withstands before breaking at the crease line is referred to as the "degree of toughness". If a film cannot be creased without breaking, it has a degree of toughness of 0, and if a film breaks on the second cycle, its degree of toughness is 1, and so on. The degree of toughness for films of the process must be at least 3.

Retention of Degree of Toughness — This test is used for determining the effect of heat on the retention of toughness. It involves heating the polymer at 360°C. for 20 minutes under nitrogen, and determining loss of toughness caused by such heating. The retention of the degree of toughness must also be at least 3.

Example 1: Meta-phenylenediamine, 6.2 g., was dissolved in 50 ml. of dimethylacetamide. The solution was cooled (water jacket ca. 15°C.) and 12.5 g. of pyromellitic dianhydride was added portionwise with stirring. 25 ml. of dimethylacetamide was added to give a polyamide-acid solution containing 20.8% polymer, by weight. Films were cast with a doctor knife having a 10 mil opening and dried at 120° to 130°C. for 30 minutes. Inherent viscosity of the polymer solution as measured in a 0.5% solution of DMA was 0.91. The film was soaked overnight in a mixture of 180 ml. of benzene, 120 ml. pyridine and 50 ml. of acetic anhydride. The film was dried at 160°C. in vacuum for 2 hours to give strong, tough, flexible film. Its infrared spectra indicated a polyimide film had been obtained.

Example 2: Benzidine, 16.9 g., was dissolved in 100 ml. of dimethylformamide. Pyromellitic dianhydride, 20.0 g., was added portionwise with stirring and cooling (water jacket ca. 15°C.). A viscous solution was formed and was further diluted with 150 ml. of dimethylformamide to give a polyamide-acid solution containing 13.5% polymer, by weight. Inherent viscosity as measured in a 0.5% solution of dimethylformamide was 1.8. The polymer solution was cast with a doctor knife having a 15 mil opening into films and dried at 120°C. under draft for 20 minutes. The films were soaked in a mixture of 230 ml. benzene, 200 ml. pyridine and 100 ml. acetic anhydride for at least 20 hours. The films were then dried at 180°C. in a vacuum for 2 hours to give tough, flexible polyimide films.

Example 3: 4,4'-diamino-diphenyl propane, 10.35 g., and pyromellitic dianhydride, 10.0 g., were weighed into a beaker and mixed. The solid mixture was added to 75 ml. of dimethylformamide with stirring with cooling (water jacket ca. 11°C.). After the solids had dissolved, the solvent solution obtained had an inherent viscosity as measured in a 0.5% solution of DMA of 0.74. The polyamide-acid solution was diluted with 50 ml. of dimethylformamide and then 5.5 ml. of triethylamine was added.

A portion of the casting dope containing the triethylamine was poured into a mixture of acetic anhydride (50 ml.) and pyridine (120 ml.) in a Waring Blendor and stirred for 30 minutes. A yellow precipitate was obtained. The reaction appeared to be complete within 5 minutes. The precipitate was filtered, washed with benzene, and dried at 120°C. in a vacuum for 120 minutes. The infrared spectra of the powder showed it to be a polyimide powder.

Example 4: 4,4'-diamino-diphenyl sulfide, 10.0 g., was dissolved in 75 ml. of dimethylformamide. Pyromellitic dianhydride, 10.15 g., was added portionwise with stirring and cooling over a period of 15 minutes to give a viscous solution of the polyamide-acid thereof. The last part of the dianhydride was added with 25 ml. of dimethylformamide. Films were cast with a doctor knife having a 15 mil opening and dried under nitrogen in a forced draft oven at 120°C. for 10 to 15 minutes. The inherent viscosity of the polyamide-acid solution was 1.2, as measured in a 0.5% solution of DMF. The films were soaked in a 13/1/1 cyclohexane/acetic anhydride/pyridine mixture. After three days the solution was poured off, the films were rinsed with dioxane and steeped in dioxane for one hour. The films were then dried at 120°C. for 15 minutes and then heated at 300°C. for 15 minutes. The physical properties of the films at 23°C. were:

Initial modulus	290,000 psi
Elongation	7.8 percent
Tensile strength	9,500 psi

The film was then heat treated at 380°C. for one minute with the resulting physical properties:

Initial modulus	260,000 psi
Elongation	10.8 percent
Tensile strength	10,400 psi

Example 5: A polyamide-acid solution was prepared by mixing and stirring the following, with exclusion of moisture, for 18 hours at room temperature:

	Parts
Meta-phenylenediamine	5.407
Pyromellitic dianhydride	10.906
Dimethylacetamide	47.15
Pyridine	32.78

A portion of the viscous solution was removed, diluted with dimethylacetamide to 0.5%, and the inherent viscosity determined at 30°C. The value was found to be 1.94. The solution was spun through a spinneret having 100 holes of 0.003 inch diameter each into a bath of acetic anhydride at room temperature. Bath travel was 3 feet. Filaments were removed from the bath around a roll at 32 feet per minute and then to another roll at 54 feet per minute to give a 1.7 draw ratio. The filaments were then extracted in water for one hour and dried. Physical properties of the resulting filaments were tenacity, 1.3 g./denier, elongation, 45%; initial tensile modulus, 30 g./denier. When the windup on the second roll was 70 feet per minute (draw ratio of 2.2X) the filaments had tenacity, 2.2 g./denier; elongation, 22%; initial tensile modulus, 43 g./denier.

Example 6: By the procedure of Example 5, a polyamide-acid solution was prepared as shown on the following page.

	Parts
4,4'-diamino-diphenyl methane	9.913
Pyromellitic dianhydride	10.906
Dimethylacetamide	47.08
Pyridine	49.15

The inherent viscosity was 1.4. Spinning was from a spinneret having 27 protruded holes of 0.005 inch diameter each. Filaments were obtained in the manner described in Example 5 using roll speeds, draw ratios and having the physical properties shown below.

	1st Roll (feet/minute)	2nd Roll (feet/minute)	Draw Ratio (times)	T/E/M_i
A	8.5	9.0	1.05	0.95/71/22
B	8.5	16.5	1.94	1.5/27/29
C	9.5	15.5	1.63	1.3/37/27
D	20.0	31.0	1.55	1.4/29/31
E	29.5	35.0	1.19	1.5/29/32

T is tenacity in g./denier, E is percent elongation and M_i is initial tensile modulus in g./denier. Heating the filaments of B at 300°C. for 5 minutes improved the properties to 3.0/28/50. Further stretching the filaments of C an additional 2.2 times improved the properties to 3.4/26/65.

In related work, W.R. Hendrix; U.S. Patent 3,179,632; April 20, 1965; assigned to E.I. du Pont de Nemours and Company describes a process for preparing polyimides by treating polyamide-acids with aromatic monocarboxylic acid anhydrides such as benzoic anhydride. The following example illustrates the process.

Example: In a nitrogen atmosphere, 4.0000 g. (0.0199 mol) of 4,4'-diamino diphenyl ether and 4.3400 g. (0.0199 mol) of pyromellitic dianhydride were placed in a 250 ml. flask equipped with mechanical stirrer. 47.2 g. of N,N-dimethylacetamide was added with stirring as the mixture was maintained under a nitrogen atmosphere. The reaction was conducted at room temperature (23°C.) and stirring was continued for three hours. N,N-dimethylacetamide was added to the viscous solution to give a 15% by weight polyamide-acid solution.

To a portion of the solution containing 0.01 mol of the polyamide-acid was added at room temperature 0.03 mol of benzoic anhydride and 0.01 mol of isoquinoline. After thorough mixing, the reaction mixture was doctored with a 30 mil knife onto a glass plate at 30°C. This gel film was maintained at 30°C. for 60 minutes. A strong, highly swollen gel film of polyimide resulted. After drying for one hour at 300°C. under restraint on a frame, the film was stiff, tough and strong.

In related work, W.M. Edwards; U.S. Patent 3,179,634; April 20, 1965; assigned to E.I. du Pont de Nemours and Company describes a similar process for preparing aromatic polyimides.

Nicotinic Acid Anhydride as a Converting Agent

J.A. Kreuz; U.S. Patent 3,541,057; November 17, 1970; assigned to E.I. du Pont de Nemours and Company describes a process which provides for converting polyamide-acid to a polyimide by subjecting the polyamide-acid (preferably in the form of a shaped structure, e.g., a film structure) to the action of an anhydride converting agent, e.g., nicotinic acid anhydride. The following examples illustrate the process.

Example 1: A solution of 1.35 g. of nicotinic anhydride in 10 ml. of N,N-dimethylacetamide was mixed with 10 g. of a 15% by weight solution in N,N-dimethylacetamide of the polypyromellitamide-acid of cumene diamine. The polymer solution became orange in a few minutes and was allowed to remain in a dry box overnight. A thin film was cast with a 1.5 mil Bird Applicator and the solvent was evaporated under nitrogen and vacuum. Infrared examination of this film showed it to be composed of a combination of the corresponding poly-n-imide and poly(iminolactone).

Example 2: Two 10 g. portions of a 10.9% solid solution of the polypyromellitamide-acid of bis(4-aminophenyl) ether were placed in containers in a constant temperature bath at 33°C. and each was mixed with a different chemical converting reagent. One sample was admixed with 0.68 ml. of acetic anhydride, 0.67 ml. of beta-picoline and 3.7 ml. of N,N-dimethylacetamide. To the other sample was added 1.19 g. of nicotinic anhydride and 5 ml. of N,N-dimethylacetamide. The sample containing the acetic anhydride/beta-picoline gelled in 10 minutes, whereas the sample containing nicotinic anhydride was flowable after 2.5 hours. Both cyclized the polymer to polyimide.

Example 3: To 30 g. of a 15% by weight solution in N,N-dimethylacetamide of the polypyromellitamide-acid of bis(4-aminophenyl) ether was added 4.90 g. of nicotinic anhydride dissolved in a minimum amount of N,N-dimethylacetamide. The resulting viscous solution was poured onto a thin release sheet of tetrafluoroethylene polymer supported by a metal sheet, and having a 10 mil spacer of tetrafluoroethylene around the edge (spacers of other thicknesses can also be used, depending on the film thickness desired); on top of this is placed another release sheet of tetrafluoroethylene, and finally another metal sheet. The whole assembly was pressed at 100°C. at 30 tons pressure (high pressure used only to insure good contact for heat transfer) for 9 minutes to convert the viscous polyamide-acid solution to a gel polyimide film. This film was extracted with benzene and dried to give a film of the polypyromellitimide of bis-(4-aminophenyl) ether.

Ammonium Salts of Polyamide-Acids

A.L. Endrey; U.S. Patent 3,242,136; March 22, 1966; assigned to E.I. du Pont de Nemours and Company describes the preparation of ammonium salts of aromatic polyamide-acids and a process for the conversion to polyimides. The following examples illustrate the process.

Example 1: 4,4'-diamino-diphenyl propane, 10.35 g., and pyromellitic dianhydride, 10.0 g., were weighed into a beaker and mixed. The solid mixture was added to 75 ml. of dimethylformamide with stirring with cooling (water-jacket ca. 11°C.). After the solids had dissolved, the solvent solution obtained had an inherent viscosity as measured in a

0.5% solution of DMA of 0.74. The polyamide-acid solution was diluted with 50 ml. of dimethylformamide and then 5.5 ml. of triethylamine was added. A portion of the casting dope containing the triethylamine was poured into a mixture of acetic anhydride (50 ml.) and pyridine (120 ml.) in a Waring Blendor and stirred for 30 minutes. A yellow precipitate was obtained. The reaction appeared to be complete within 5 minutes. The precipitate was filtered, washed with benzene, and dried at 120°C. in a vacuum for 120 minutes. The infra red spectra of the powder showed it to be a polyimide powder.

Example 2: Meta-phenylenediamine, 8.7 g., and 3.7 g. of para-phenylenediamine and 25.0 g. of pyromellitic dianhydride were weighed into a flask and mixed. The solid mixture was added portionwise to 100 ml. of dimethylformamide with stirring, while the solution was cooled (water jacket ca. 15°C.). The last portion was added with 50 ml. of dimethylformamide to give a polyamide-acid solution containing 20.6% polymer, by weight. Inherent viscosity as measured in a 0.5% solution of DMA was 1.5.

To a 110 g. portion of the polymer solution was added 9.5 ml. of triethylamine and 50 ml. of dimethylformamide. The polymer started to precipitate and then to this mixture 4.5 ml. of acetic anhydride and 7.5 ml. of pyridine and 10 ml. of acetic acid were added to give a yellow, viscous solution after some stirring. A portion of the polyamide-acid solution was cast with a doctor knife having a 10 mil opening and dried at 120° to 130°C. for 15 minutes. The films were then converted to the corresponding polyimide by soaking in a large excess of pyridine-acetic anhydride (3/2 by volume) mixture for 12 hours. The films were dried for one hour at 120°C., then for one hour at 250°C. in a vacuum. The films were then heat treated at 380°C. (in air) for 5 minutes to provide tough, flexible films.

Example 3: To 10 g. (0.002 mol) of a dimethylacetamide solution of the polyamide-acid of pyromellitic dianhydride and bis(4-aminophenyl) ether (10% solids, inherent viscosity of 2.03) was added 1 ml. (0.004 mol) of tri-n-butylamine with stirring. A 5 mil doctor knife was used to cast a film on a glass plate after which the glass plate was placed in an oven at 130°C. for 3 minutes to remove excess solvent. The film was clamped on a frame and heated at 200°C. for 45 minutes. An infrared spectrum of the resulting 0.20 mil film showed that the normal imide band at 13.75 microns was very intense proving that the product was a polyimide.

Examples 4 to 5: Tertiary amine salt films were prepared by respectively mixing the stoichiometric amounts of triethylamine and tri-n-butylamine with weighed portions of the 10% solution of polyamide-acid of Example 3; casting films with a 10 mil doctor knife; and finally, drying the films at 110° for 10 minutes. These films, together with an ordinary film of polyamide-acid, were clamped on frames and gradually heated to 200°C. The films were held at this temperature for 1 hour. The properties of the resulting films are given in the table below.

Example	Tensile Modulus	Tensile Strength	Elongation
Control	423,700	12,700	5.2
4	415,400	12,700	5.6
5	322,200	9,800	4.3