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A DESCRIPTION OF
VARIOUS METHODS
OF PREPARING
POLYAMIC ACIDS
AND POLYIMIDES

BDX-613-509

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ABSTRACT

Some of the reaction routes and intermediates which can be employed in the preparation of polyamic acids and polyimides are described. A tetrahydrofuran precipitation method and several other direct and indirect procedures for preparing polyamic acids and polyimides are discussed. Various curing processes for converting polyamic acids to polyimides are reviewed.

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SUMMARY

The objective of this project is to evaluate various methods of processing high temperature, high dielectric materials. This report describes several direct and indirect methods of curing polyamic acids (Paa's) and polyimides (PI's) and several unusual methods of synthesizing polyimides. The work reported has been in progress since June, 1968. There was no activity on this project at Bendix Kansas City prior to that time.

Homogeneous and heterogeneous direct methods as well as indirect methods of preparing Paa's and PI's were investigated. The direct method consisted of mixing diamines and dianhydrides in a suitable solvent such as dimethylacetamide or tetrahydrofuran to obtain various Paa solutions. By the indirect method, PI's and Paa's were prepared by way of polyamic acid triethylamine salts and polyamic acid esters. The procedures used to cure polyimide precursors included exposure of polyamic acids to heat, to monocarboxylic acid anhydrides, and to the salts of weak acids such as sodium acetate. Another method used to prepare PI's was to react diisocyanates with dianhydrides by way of polyimidolactones or diimide-dialkenes.

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DISCUSSION

SCOPE AND PURPOSE

During the past few years interest in thermo-oxidatively stable polymeric materials has grown rapidly. The polyimides (PI) are among the oldest classes of aromatic heterocyclic materials. Although PI's are superior to the polyquinoxalines, polypyrrones, and polybenzimidazoles as far as thermo-oxidative stability is concerned, they do not lend themselves readily to part fabrication. The objective of this project is to evaluate various high temperature, high dielectric materials for a number of applications such as adhesives, films, and molding compounds. This report briefly describes the preparation of polyamic acids (Paa's) and other PI intermediates and some of the methods used to cure these products.

PRIOR WORK

Although considerable work has been reported in the chemical literature on polyimide polymers, no work was initiated at Bendix Kansas City in this area prior to June, 1968.

ACTIVITY

Polyimides are intractable, insoluble, and infusible polymers. Polyimide articles must be formed by first shaping Paa's and then converting these shaped articles to the corresponding PI's by applying heat. Both direct and indirect methods of preparing Paa's are discussed below.

Direct Methods of Preparing Paa's

The two direct methods of preparing Paa's are called homogeneous and heterogeneous, and there are three variations of each.¹ The homogeneous methods involve the reaction of the diamine with the dianhydride by mixing solutions of diamine and dianhydride in an appropriate solvent. The heterogeneous methods involve (1) the addition of diamine to a solution of dianhydride; (2) the addition of dianhydride to a solution of diamine, or (3) the addition of blended diamine and dianhydride to a solvent. Work at BKC with the heterogeneous methods was discussed in a previous report,² and both the heterogeneous and homogeneous methods are thoroughly discussed elsewhere.¹ Throughout this evaluation, the latter of the three heterogeneous methods given above was used most extensively since it consistently yielded polymers of higher molecular weight, as indicated by viscosity measurements.

The Paa's and PI's obtained when the synthesis is carried out in a solvent such as dimethylacetamide (DMAc) formed complexes with the solvent.¹ This situation (Figure 1) may be avoided if the reaction is carried out in tetrahydrofuran (THF).

Figure 1. DMAc-Complexed Amic Acid

By this method, the diamine and dianhydride are both suspended (or dissolved) in sufficient THF to yield 10 to 30 percent suspensions (or solutions). These are then placed in separatory funnels and simultaneously added to enough THF with stirring to yield 5 to 25 percent suspensions of the corresponding Paa. This method of preparing Paa's yields products that do not exhibit the plasticizing effects of the solvent. These yellow to tan powders may be dried and converted to their corresponding PI by heating to at least 300°C (572°F).

Indirect Methods of Preparing PI's

Polyimides may also be prepared by indirect methods. The use of triethylamine salts (Figure 2) of Paa's is such a method.³ These salts can be prepared by mixing equal volumes of THF and Paa solutions in DMAc. This solution is then slowly added, as it is vigorously mixed, to five times (by volume) as much diethylether. After the usually green Paa precipitates, it is washed several times with anhydrous diethylether. The Paa is dried in a vacuum oven at 80°C (176°F) and less than 10 millimeters pressure for 8 hours. The lumps of Paa which are obtained are ground and dried for an additional 2 hours under the same conditions.

Figure 2. Triethylamine Amic Acid Salt

An equivalent number of moles of triethylamine as an aqueous 0.25N solution is then mixed with the isolated Paa prepared by the aforementioned method. This mixture is stirred for approximately 12 hours to obtain a homogeneous solution of the Paa triethylammonium salt. This water-soluble polyamic acid derivative may be converted to its corresponding PI by applying heat or by reaction with monocarboxylic acid anhydrides.

Another indirect method of preparing PI's is by way of diamine salts of pyromellitic acid diesters.⁴ This method was confirmed in the laboratory at Bendix using the following method. One mole of pyromellitic dianhydride (PMDA) was refluxed in 500 milliliters of absolute ethanol for 24 hours. The precipitate was isolated by filtration, and 4.6 parts of the obtained diacid diester and 3.0 parts of bis(4-aminophenyl) methane (PCH₂P) were mixed in a 50:50 ethanol-water solution under a nitrogen atmosphere. When this mixture was refluxed, a purple-grey powder was obtained which was infusible, insoluble, and intractable. Upon heating to a temperature above 300°C (572°F), the isolated powder turned brown and evolved ethanol, indicating that imidization was occurring.

More processible products are reportedly obtained when long-chain aliphatic diamines (Figure 3) are used in lieu of the aromatic diamines.⁴

Figure 3. Tetramethylenediammonium Amic Acid Salt

The solution of the aliphatic diamine salts of pyromellitic acid diesters may be heated until all the volatiles are removed and a molten residue obtained. It is reported that this product may then be compression molded at 200°C (392°F) to obtain a thin, tough, cold-drawable film which is completely soluble in meta-cresol and which manifests an inherent viscosity of 0.8.⁴ Diamines which reportedly yield usable products are listed below.

Tetramethylenediamine

Hexamethylenediamine

Nonamethylenediamine

4,4 Dimethylheptamethylenediamine

2,11-Dodecanediamine

The above method could be very useful in molding PI parts if the application does not call for extreme thermal exposures (above 500°F); however, the aliphatic groups in the polymer make it more susceptible to thermal oxidation. These PI's are, therefore, thermally inferior to those of a fully aromatic nature.

PI's may also be prepared from polyamide esters.⁵ These intermediates were prepared in our laboratory by way of the lithium salt of poly (p, p'-methylene) (bisphenylene)-3,3'-benzophenonedicarboxylamide-4,4(dicarboxylate). This lithium salt was prepared by adding 300 ml of 0.23 N lithium acetate in a 20:80 mixture of glacial acetic acid-DMAc solution to 100 ml of a 24 percent solution of bis(4-aminophenyl) methane (PCH₂P)/benzophenonetetracarboxylic dianhydride (BTDA) in DMAc and stirring for approximately one

hour. During this period, the clear solution turned from dark amber to a transparent bright yellow. A bright yellow suspension, which was the lithium salt of PCH₂P/BTDA, was then observed. This reaction, which was prompted by the addition of acetic anhydride, was exothermic and the temperature increased to approximately 40°C (104°F). The addition of acetic anhydride to the solution apparently catalyzes the reaction by removing the carboxyl hydrogen of the Paa and leaving the resulting carboxylate anion readily available to react with the lithium cation. The lithium salt was converted to the poly(diallyester-diamide) (Figure 4) by slowly adding four 6.5 ml aliquots of allyl bromide to the solution with stirring. The result was a dark brown low-viscosity solution.

Figure 4. Amic Acid Allyl Ester

It was found in the laboratory at Bendix that the poly(diester-diamide) is best isolated by precipitation methods using 0.001 N potassium hydroxide (KOH). This was carried out by slowly adding 1500 ml of 0.001 N KOH to 500 ml of the reaction mixture with stirring and using a dropping funnel. A caramel-colored precipitate was obtained. The precipitate was stirred for 60 minutes and immediately washed with cold cyclohexane. The washed precipitate [poly(diester-diamide)] was dried in a vacuum oven for 8 hours at 40°C (104°F).

The product was found to be soluble in diethylether, tetrahydrofuran, and dioxane. It was also partially soluble in solvents such as acetone and methyl alcohol. Several different esters of PCH₂P/BTDA were synthesized. Among these were the allyl-, benzyl-, methyl-, ethyl-, hexyl-, and the para-nitrobenzyl esters. Examples of usable halides are methyl bromide, ethyl bromide, ethyl iodide, and other lower alkyl chlorides, bromides, and iodides. The allyl-, methyl-, and the benzyl-esters appear to lend themselves most readily to this process for preparing PI's while from the standpoint of reactivity, the preferred halide is the bromide. The iodides react faster, but it is reported that their products are difficult to isolate and the by-products are often undesirable; the chlorides provide the cleanest reaction, but their low reactivity causes the reaction to be quite sluggish.⁵

Poly(diamide-diester)s prepared in the manner described may be converted to their corresponding PI's by heating to temperatures in excess of 150°C (302°F) with the evolution of the corresponding alcohol.⁵

Another indirect method of preparing Paa's involves basic catalysis of the reaction using such bases as potassium hydroxide or salts of a strong base and a weak acid such as sodium acetate or potassium carbonate.⁷ With this process, the imide was formed by reacting the diester of a tetracarboxylic acid with a diamine in the presence of sodium acetate. The reaction was carried out in the laboratory in the manner described below.

One mole of BTDA was esterified with N-hexyl alcohol by refluxing 2 moles of the alcohol in the presence of a suitable catalyst (CaO). A mixture of 1 mole of bis(4-aminophenyl) methane and 0.1 mole of sodium acetate was prepared and dissolved in approximately 2 liters of DMAc. This solution was added to the dihexyl ester with stirring and then refluxed for at least 8 hours. The result was a yellow slurry composed of a yellow precipitate and an orange liquid. The precipitate was allowed to settle and the supernatant liquid was decanted. The precipitate was washed alternately with acetone and water for at least six successive times and finally with acetone. The precipitate was then filtered and placed in a vacuum oven equipped with a dry ice/acetone trap and dried under reduced pressures at 80°C (176°F) for 24 hours. The yellow solid that was obtained was insoluble but fusible when processed properly. It could be compression molded or extruded when heated to at least 366°C (691°F) while under pressures on the order of 1,500 psi. This process resulted in a void-free, hard usable part.

During this investigation, attempts were made to similarly catalyze Paa's by heating them with sodium acetate, but no significant improvement in the character of the resulting polymers was noted. The major advantage in preparing PI's by this method was that a more processible polymer was obtained. It is believed that the sodium acetate may catalyze the formation of intermediate anhydride groups.⁷ That is, when heated, the ester pairs eliminate their corresponding alcohol and form the corresponding aromatic anhydride. The aromatic anhydride then reacts readily with the diamine which is present, forms the Paa's which are unstable at the heating temperature, and, in turn, forms their PI's immediately. This sequence of events (Equation 1) would allow formation of more processible polymers of higher molecular weight before subsequent imide formation could cause insolubility to occur.

Equation 1.

Another possible reaction mechanism is based on possible transamidization in the case where the amine replaces the alcohol. Still another possibility involves the reaction of the acetate anion with the ester group to form the corresponding anhydride. In any event, the ultimate product is more processible (extrudable) than are the polyimides prepared by conventional methods.

Other Methods of Preparing PI's

PI's may also be prepared by reacting dianhydrides with diisocyanates or from polyiminolactones or from diimide-dialkenes. In the reaction between diisocyanates and dianhydrides, the reactants are mixed and then heated to temperatures in the order of 200°C (392°F) to effect an appreciable reaction rate.^{10, 11, 12, 13}

This reaction produces PI materials with the evolution of carbon dioxide, as shown in Equation 2.

Equation 2.

The PI materials which are formed by the reaction described above are usually foams. Some success has been recorded in the area of free-rise foams,¹² but little success has been made in the area of molded foams.¹³ The free-rise foams which are prepared are characterized by very brittle open cells and dark-brown to amber color. Although these foams exhibit the usual thermal stabilities of PI's, they lack in physical strength.^{10, 11} The molded PI foams prepared in this manner have the same characteristic brittleness and coloration, but their cell structure is not uniform.¹³

To prepare PI's from polyimidelactones, Paa's are treated with N, N-disubstituted carbodiimides such as N, N-diphenylcarbodiimide in a highly polar aromatic solvent such as DMAc to form the corresponding polyimidelactone.¹⁴ The polyimidelactone is then converted to the corresponding PI by heat or by treatment with triethylammonium acetate¹⁴ as shown in Equation 3.

To 0.005 mole of Paa is added 0.01 mole of N, N-dicyclohexylcarbodiimide. With moderate stirring the mixture becomes yellow and then gels. The yellow precipitate is less soluble than the Paa in the polar aprotic solvent and is isolated by adding a strong base. The yellow precipitate is heated to yield the corresponding PI.¹⁴ The polyimidelactone may also be used as an intermediate to several other PI precursors. Among these are polyamide-esters by treatment with alcohols,¹⁵ polyamide-amides by treatment with ammonia, amines, or diamines;¹⁸ or polytetrazole acid by treatment with hydrazoic acid.¹⁷

Another reported method of preparing PI's which offers a processible product is by way of cyclopentane diallylimide.¹⁸ By this process, cyclopentane dianhydride is reacted, as shown in Equation 4, with an excess of allylamine in xylene in a 2-liter, 3-neck flask equipped with a stirrer, condenser, and a Dean Stark trap. The mixture is refluxed until the theoretical amount of water is obtained and the cyclopentane diallylimide is precipitated from the xylene solution by cooling.¹⁸

Equation 3.

Equation 4.

It is reported that when the diallyl diimide is melted at 100°C (212°F), mixed with 2 percent t-butylperbenzoate, and then poured into a mold at 120°C (248°F) a tough hard product is obtained after the material has cured for 72 hours at 125°C (257°F).

Methods of Curing Paa's

Among the numerous ways that PI's may be cured are the following:

By heating;

By exposure to monocarboxylic acid anhydrides; and

By treating with bases or salts of weak acids.

The conventional method for curing Paa's to PI's is to heat the shaped Paa to approximately 300°C (572°F). The direct heating method has proven to be the best. This method is thoroughly discussed elsewhere. ^{1, 3, 4, 5, 6}

The use of chemical means to cure Paa's to PI's is usually accomplished by steeping a shaped Paa article in a mixture of monocarboxylic acid anhydride, a tertiary amine, and a nonpolar organic solvent. A typical example of such a process is as follows. ⁷ To a portion of a solution containing 0.01 mole of polyamic acid, 0.03 mole of acetic anhydride and 0.01 mole of pyridine are added at room temperature. It is reported that when this mixture is thoroughly blended and doctored with a 30.0 mil knife onto a glass plate a highly swollen Paa film results when the material is maintained at 30°C (80°F) for 24 hours. The gel film is then maintained at 60°C (140°F) for at least 60 minutes after which it is dried under restraint on a frame for one hour at 300°C (572°F). A stiff, tough, strong film is then obtained.

It is reported that several different amines and anhydrides may be used to catalyze imidization. ⁷ Among these are the following:

pyridine;

isoquinoline;

3, 4-lutidine;

3, 5-lutidine;

4-methylpyridine;

3-methylpyridine;

4-isopropylpyridine;

N-methylbenzyl pyridine;

N, N-dimethyldodecyl amine;

benzoic acid anhydride;

o-, m-, and p-toluic acids;
m- and p-ethyl benzoic acids;
nitrobenzoic acid;
halobenzoic acids;
naphthoic acids; and
many others.

Earlier work at Bendix showed this method of curing Paa's and PI's to be interesting but inconvenient.^{2, 8} Since the resulting films had to be heated in the same manner as those prepared in conventional processes, the catalyzed imidization offers no significant advantage.

ACCOMPLISHMENTS

The following methods of preparing polyamic acids and other PI intermediates were evaluated and the results discussed.

Tetrahydrofuran (THF) Precipitation Methods

Trialkylammonium Salts of Polyamic Acids

Dialkyl- and Diarylesters of Paa's

Lithium Salts of Paa's

Diamine Salts of Paa Diesters

FUTURE WORK

Future work on this project will include the evaluation of the thermal, electrical, and mechanical properties of the various Paa and PI's described in this report.

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