Process for preparing polyarylates in the presence of a diphenyl ether.

Priority: 27.08.79 US 69818

Date of publication of application: 08.04.81 Bulletin 81/14

Publication of the grant of the patent: 27.03.85 Bulletin 85/13

Designated Contracting States: AT BE CH DE FR GB IT LI NL SE

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Description

This invention is directed to a process for preparing polyarylates having a reduced viscosity of from 0.05 m²/kg (=0.5 dl/g) or greater, which process comprises reacting the diester derivative of a dihydric phenol with an aromatic dicarboxylic acid in the presence of from 10 to 60 weight percent, based on the weight of the polyarylate produced, of a diphenyl ether compound at a temperature of from 260 to 350°C and in the absence of any catalyst.

Polyarylates are polyesters derived from a dihydric phenol, particularly 2,2-bis(4-hydroxyphenyl) propane also identified as Bisphenol-A, and an aromatic dicarboxylic acid, particularly mixtures of terephthalic and isophthalic acids. These polyarylates are high temperature, high performance thermoplastic polymers with a good combination of thermal and mechanical properties. They also have good processability which allows them to be molded into a variety of articles.

Many processes have been described in the literature for the preparation of polyarylates. One such process is the diacetate process. In the diacetate process, a dihydric phenol is converted to its diester derivative which is then reacted with an aromatic dicarboxylic acid to form the polyarylate. However, heretofore, the diacetate process has been carried out by several different methods as illustrated in the following U.S. patents:

In U.S. Patent 2,595,343 issued May 6, 1952, an aromatic bisphenol is first reacted with acetic anhydride to form bisphenol diacetate which is then condensed with an aliphatic dicarboxylic acid to form a polyarylate by an acid interchange reaction. The condensation reaction is performed in the presence of an acid catalyst, such as para-toluene sulfonic acid, phosphoric acid or sulfuric acid. However, this acid exchange reaction does not yield an acceptable product when an aromatic dicarboxylic acid is substituted for the aliphatic acid.

U.S. Patent 3,225,003 issued December 21, 1965, describes the preparation of novel copolymers by reacting hydroquinone diacetate with a mixture of hexahydrophteraphalic acid and hexahydrosophthalic acid in the presence of a catalyst, such as sodium acetate, at a temperature of 230°C. The reaction is exemplified as being carried out in the presence of anhydrous sodium acetate catalyst and eutectic mixtures of biphenyl and diphenyl oxide (diphenyl ether) at 230°C in three stages for a total reaction time of about 28 hours. Thus, this process requires catalyst, long reaction times and several steps.

U.S. Patent 3,317,484 issued May 2, 1967, describes the preparation of linear aromatic polyesters by the polycondensation of diphenols, or their diacetates, with polynuclear aromatic dicarboxylic acids. The examples of this patent describe the preparation of the polyester using catalysts, such as mixtures of p-toluene sulfonic acid and antimony trioxide, or butyl orthotitanate, optionally in acetic acid. The reaction is carried out in a molten mixture of reagents and catalysts by heating these together under sub-atmospheric pressure. The patent states, but does not exemplify, that the reaction may be carried out in solution, in inert solvents, such as alpha-methyl-naphthalene, biphenyl or diphenyl oxide. Thus, this process requires catalysts as well as sub-atmospheric pressure conditions to form the polyesters.

U.S. Patent 3,329,653 issued July 4, 1967 describes the preparation of high molecular weight linear condensation polymers, such as aromatic polyesters, aliphatic polyamides, and polycarbamides. These polymers are formed at or below the melting point of the polymer by carrying out the reaction while the reacting materials are suspended in an inert non-solvent medium, with a swelling agent for the condensation polymer which also needs to be present in the reaction medium. Example 7 of this patent describes the preparation of poly[2,2-bis(4-hydroxyphenyl)propane isophthalate] by heating a mixture of 780.9 g of the diacetate of Bisphenol-A, 415.3 g of isophthalic acid, 900 g. of Apcol Incol No. 0, 25 g of sulfolane swelling agent and 2.5 g of sodium methoxide catalyst. The reaction is held in reflux for 40 hours. The patent describes, as particularly effective swelling agents, sulfolane, diphenyl ether, and quinoline. Thus, this process requires the use of large quantities of a non-solvent, a catalyst, swelling agents as well as long reaction times.

U.S. Patent 3,824,213 issued July 16, 1974, describes the preparation of halogenated aromatic polyesters by reacting in solution, an aliphatic carboxylic ester of a halogenated bisphenol, such as tetra-chlorobisphenol-A with an aromatic acid mixture of terephthalic and isophthalic acids at a temperature of 220—350°C, in the presence of a catalytically effective amount of a cobalt, nickel, or manganese salt of an aliphatic carboxylic acid. This patent describes that the esterification reaction may be conducted with said catalysts in a suitable solvent, such as a hydrocarbon, halogenated aliphatic or aromatic hydrocarbon or the like (i.e. a solvent which is inert under the reaction conditions employed). Specifically these solvents include diphenyl ether, benzophenone, dichloroethane and dichlorobenzene. This patent exemplifies that several other catalysts such as magnesium acetate are unsuitable for forming polyesters of acceptable inherent viscosities and that the particular cobalt, nickel or manganese salts, as described in this patent, are necessary to yield polyesters having an inherent viscosity of at least about 0.2, which is considered an acceptable viscosity in this patent.

U.S. Patent 3,948,856 issued April 6, 1976, describes an acid interchange polymerization process for producing an aromatic polyester by reacting substantially stoichiometric amounts of an aromatic diester with a dicarboxylic acid at a temperature of 220—350°C, in a solvent, and in the presence of a catalyst, which is a mixture of a transition metal salt of a strong inorganic acid and a transition metal salt of an
aliphatic carboxylic acid. The solvent includes diphenyl ether, halogenated diphenyl ether, diphenyl sulfone, benzophenone, polyphenyl ethers, etc.

U.S. Patents 3,684,766 issued August 15, 1972, and 3,780,148 issued December 18, 1973, describe a variation of the diacetate process. In the patented processes, a prepolymer is formed from, for example, a diacate, such as Bisphenol-A diacete, and an aromatic acid in the presence of a catalyst. The prepolymer so formed is then comminuted into small particles. These particles are then contacted with a crystallizing agent to crystallize the polyester. The crystallized polyester is heated in the presence of an inert gas and under reduced pressure to increase the inherent viscosity of the polyester. However, the processes described in these patents require multi-steps including the step of crystallizing the prepolymer.

U.S. Patent 4,075,173 issued February 21, 1978, describes the preparation of copolyesters by reacting an aromatic dicarboxylic acid, a diacetate of Bisphenol-A, and an acetate of p-hydroxybenzoic acid. Various processes for producing polyarylates by the reaction of Bisphenol-A and terephthalic and isophthalic acids are reviewed in this patent. The following process for producing polyarylates, identified as route (1), is described in column 2, of the patent:

\[
\begin{align*}
\text{CH}_3\text{C-O} & \quad \text{CH}_3 \\
\text{O} & \quad \text{O-C-CO} \\
\text{O} & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{HO-C} & \quad \text{C-OH} \\
\text{O} & \quad \text{O-C-CO} \\
\text{O} & \quad \text{CH}_3 \\
\end{align*}
\]

This process is the diacetate process as described herein, or the "Acetate process" as defined in the patent.

Column 2 of the patent states:

"The route (1) is not desirable because the undesirable coloration and deterioration of polymer are particularly remarkable as disclosed in the above-mentioned literature". Further, column 3 of the patent states:

"On the other hand, the route (1), Acetate process, is economically advantageous because the materials used are cheap and the operation is simple. For example, diacetate of bisphenol-A, a monomer for Acetate process, is synthesized by merely reacting acetic anhydride and bisphenol-A. Consequently, it may be said that, if the fatal drawbacks of Acetate process, coloration and deterioration, are solved, Acetate process will become the most superior process".

Thus, the skilled workers in the field of polyarylate chemistry realize that the existing processes for producing polyarylates have one or more deficiencies, and that a need exists to develop a viable diacetate process for producing polyarylates.

In U.S. Patent 4,075,173, a copolymer was prepared by the diacetate process by a solid-state polymerization of low molecular weight polymers without using crystallizing agents. The monomers used are the diacetate of bisphenol-A, terephthalic acid and/or isophthalic acid and an acetate of p-hydroxybenzoic acid. The monomers are combined to form a prepolymer which is then converted to the desired high molecular weight polymer by solid state polymerization.

Thus, the diacetate processes for producing polyarylates by the procedures of the aforementioned U.S. Patents, and as stated in U.S. Patent 4,075,173, are generally unsuitable since they are either economically unattractive and/or produce a commercially unmarketable product. These prior art processes utilize catalysts, large amounts of solvents and generally long reaction times, high temperatures, as well as a complex series of steps, i.e. those as described in U.S. Patents 3,684,766 and 3,780,148. Thus the state of the art always contains the teaching that in order to obtain useful polyarylates catalysts have always to be used.

Therefore, a need exists for an economical and practical diacetate process for producing high molecular weight polyarylates.
In the diacetate process for producing polyarylates, problems exist which must be economically and practically solved in order to have a viable, economically attractive process. One problem when a diester derivative of a dihydric phenol is reacted with an aromatic dicarboxylic acid in the molten state is that sublimation of the diacid occurs. This disrupts the stoichiometry of the reaction and the polyarylate produced is not of acceptable molecular weight. To prevent sublimation of the diacid, several techniques have been developed. These include the use of large amounts of solvents together with a variety of catalysts and generally long reaction times in the polymerization process. However, these techniques are quite costly and do not provide an optimum process. Another problem when a diester derivative of a dihydric phenol is reacted with an aromatic dicarboxylic acid in the molten state is that the viscosity of the system increases dramatically towards the end of the reaction and therefore the reaction becomes diffusion controlled (the molecules are not close enough to insure rapid reaction) rather than kinetically controlled. Also, the polymer product is difficult to handle (i.e., removal from the reactor) due to this high viscosity.

Yet another problem in the production of polyarylates by the diacetate process is that a carboxylic acid is a by-product of the reaction of a diester derivative of a dihydric phenol with an aromatic dicarboxylic acid. In order to provide an efficient, economical process and a high molecular weight polyarylate, the acid, for example, the acetic acid has to be conveniently and efficiently removed.

It has now been discovered that polyarylate having a reduced viscosity of from 0.05 m²/kg or greater, can be efficiently and economically produced by a process which does not require the use of a catalyst or large amounts of solvent. The present process comprises reacting a diester derivative of a dihydric phenol with an aromatic dicarboxylic acid in the presence of from 10 to 60 weight percent, based on the polyarylate produced, of a diphenyl ether compound at a temperature of from 260 to 350°C. The addition of 10 to 50% of diphenyl ether as a heat transfer medium in the melt polycondensation of polyarylates is known from US—A—4,127,560. Also according to this disclosure, however, a catalyst must be used.

The utilization of from 10 to 60 percent of a diphenyl ether compound in the diacetate process of the invention prevents sublimation of the aromatic dicarboxylic acid; thus producing polyarylates of acceptable molecular weight. Also, the diphenyl ether compound provides for better removal of the acetic acid by-product. Further, an additional benefit in using a diphenyl ether compound in the amounts indicated is that the viscosity of the system is decreased. This decrease in viscosity provides a faster reaction time since better mixing of the reactants occurs which allows the reaction to proceed under kinetic control. Additionally, by using the diphenyl ether, reaction times are relatively short so that a polyarylate is produced generally in less than 10 hours at the reaction temperatures and the polyarylates produced possess lighter color, as compared to those utilizing longer reaction times. Furthermore, the present process can be carried out at atmospheric pressure and therefore avoids the use of the costly equipment which is needed by the prior art processes which carry out the diacetate process under vacuum.

DESCRIPTION OF THE INVENTION

The present invention is directed to a process for the preparation of normally solid amorphous polyarylates having a reduced viscosity of from 0.05 m²/kg or greater, which process comprises reacting a diester derivative of dihydric phenol with an aromatic dicarboxylic acid in the presence of from 10 to 60 weight percent, based on the weight of the polyarylate produced, of a diphenyl ether compound at a temperature of from 260 to 350°C in the absence of any catalyst.

The present process comprises reacting:

(a) at least one diester derivative of a dihydric phenol having the following formula:

wherein R is independently selected from an alkyl radical having from 1 to 6 carbon atoms, preferably methyl, cycloalkyl having from 4 to 7 carbon atoms, y is independently selected from alkyl groups of 1 to 4 carbon atoms, chlorine or bromine, z independently has a value of from 0 to 4, inclusive, and R' is independently selected from a divalent saturated aliphatic hydrocarbon radical, particularly alkylene or alkylidene radicals, having from 1 to 8 carbon atoms, especially C(1)(H)sub>(3), cycloalkylene or cycloalkylidene radicals having up to and including 9 carbon atoms, O, S, SO, SOsub>(2), and CO, x is 0 or 1; and
(b) at least one aromatic dicarboxylic acid.

The diester derivative of the dihydric phenol is prepared by reacting a dihydric phenol with an acid anhydride derived from acids containing from 2 to 8 carbon atoms under conventional esterification
conditions. The preferred acid anhydride is acetic anhydride. Generally, the dihydric phenol is reacted with the acid anhydride in the presence of an esterification catalyst, either in the presence or absence of a solvent.

The dihydric phenols that may be used in this invention include the following:

5 2,2-bis-(4-hydroxyphenyl)propane,
   bis-(2-hydroxyphenyl)methane,
   bis-(4-hydroxyphenyl)methane,
   bis-(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane,
   1,1-bis-(4-hydroxyphenyl)ethane,
10 1,2-bis-(4-hydroxyphenyl)ethane,
   1,1-bis-(4-hydroxy-2-chlorophenyl)ethane,
   1,1-bis-(3-methyl-4-hydroxyphenyl)ethane,
   1,3-bis-(3-methyl-4-hydroxyphenyl)propane,
   2,2-bis-(3-phenyl-4-hydroxyphenyl)propane,
15 2,2-bis-(3-isopropyl-4-hydroxyphenyl)propane,
   2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane,
   2,2-bis-(4-hydroxyphenyl)pentane,
   3,3-bis-(4-hydroxyphenyl)pentane,
   2,2-bis-(4-hydroxyphenyl)heptane,
20 1,2-bis-(4-hydroxyphenyl)-1,2-bis-(phenyl)-propane,
   4,4'-(dihydroxyphenyl)ether,
   4,4'-(dihydroxyphenyl)sulfide,
   4,4'-(dihydroxyphenyl)sulfone,
   4,4'-(dihydroxybenzenophene), and
25 hydroquinone.

These dihydric phenols may be used individually or in any combination which when reacted with an aromatic dicarboxylic acid produces polynylrate polymers that essentially do not crystallize during the reaction and recovery steps. The preferred dihydric phenol is 2,2-bis(4-hydroxyphenyl)propane.

The aromatic dicarboxylic acids that may be used in this invention include terephthalic acid, isophthalic acid, any of the naphthalene dicarboxylic acids and mixtures thereof, as well as alkyl substituted homologs of these carboxylic acids, wherein the alkyl group contains from 1 to 4 carbon atoms, and acids containing other inert substituents such as halides, alkyl or aryl ethers, and the like. Preferably, mixtures of isophthalic and terephthalic acids are used. The isophthalic acid to terephthalic acid ratio in the mixture is 20:80 to 100:0, while the most preferred acid ratio is 25:75 to 50:50. Also, from 0.5 to 20 percent of aliphatic diacids containing from 2 to 10 carbon atoms, such as adipic acid, sebacic acid, and the like may be additionally used in the polymerization reaction.

The dihydric phenols and aromatic dicarboxylic acids are selected so that the polynylrate produced remains in an essentially amorphous state during the polymerization reaction and recovery step.

The reaction of the diester derivative of a dihydric phenol with the aromatic dicarboxylic acid is carried out in the presence of from 10 to 60, preferably from 25 to 40, and most preferably, from 30 to 40 weight percent, based on the weight of the polynylrate produced, of a diphenyl ether (also known as diphenyl oxide) compound. The diphenyl ether compound may be substituted. These substituents are selected from alkyl groups, chlorine, bromine or any substituent which does not interfere with the polynylrate forming reaction or the reaction forming the diester derivative of the dihydric phenol. Additionally, the diphenyl ether compound may be used with up to 50 weight percent of conventional compounds, such as various biphenyls or any other compounds which do not interfere with the polynylrate forming reaction or the reaction forming the diester derivative of the dihydric phenol.

The amount of the diphenyl ether compound could vary during the polymerization reaction. For example, it may be advantageous to increase progressively the amount of diphenyl ether compound to maintain the reaction medium at about constant viscosity.

The reaction of the diester derivative of the dihydric phenol with the aromatic dicarboxylic acid is performed with these reactants present in the ratio of from 0.85:1.00 to 1.10:1.00, preferably from 0.98:1.02 to 1.02:0.98, diester derivative: aromatic dicarboxylic acid.

The process of this invention is carried out at a temperature of from 260 to 350°C and preferably, from 275 to 295°C and in the absence of any catalyst. The present process is generally conducted in an inert atmosphere (such as argon or nitrogen). The process is preferably carried out at atmospheric pressure although higher and lower pressures may be used. Obviously, at pressures higher than atmospheric pressure, higher temperatures will result.

The polymerization reaction is conducted for a period of time sufficient to produce a polynylrate having a reduced viscosity of at least 0.05 m²/kg or greater, which time is generally less than about 10 hours. The reaction time is generally in the range of from 4 hours to 8 hours, depending on the particular polynylrate being prepared.

The polymerization reaction of this invention may be carried out batchwise or continuously and by using any apparatus desired. Moreover, the reactants may be added to the polymerization zone in any way
or order desired as long as the polymerization takes place in the presence of from 10 to 60 weight percent of a diphenyl ether compound.

The diester derivative of the dihydric phenol may be formed, in situ, by adding the dihydric phenol together with the acid anhydride, an aromatic dicarboxylic acid and a diphenyl ether compound to the reactor and the reaction carried out in a single reaction zone under combined esterification and polymerization conditions as described above. Additionally, the diester derivative of the dihydric phenol may be first prepared and then an aromatic dicarboxylic acid and a diphenyl ether compound added directly to the same reaction vessel with the polymerization being carried out under the conditions described above.

The polyarylate polymer having a reduced viscosity of at least 0.05 m²/kg is recovered in its final form by methods well known to those in the art, such as by direct devolatilization in an extruder under conditions sufficient to remove the diphenyl ether compound, coagulation, spray drying, and the like.

The polyarylates may also be prepared by first forming a polyarylate prepolymer having a reduced viscosity of from 0.01 to 0.04 m²/kg, by reacting the diester derivative of a dihydric phenol with an aromatic dicarboxylic acid in the presence of a diphenyl ether compound under the conditions described previously, for a reaction time of about 3 hours. The polyarylate prepolymer is then heated at temperatures of from 300 to 350°C to obtain a polyarylate having a reduced viscosity of from 0.05 m²/kg or greater.

Alternatively, the polyarylate prepolymer may be added directly, after its formation, to a vented extruder wherein the molecular weight is increased to form a polymer having a reduced viscosity of from 0.05 m²/kg or greater. For example, the molecular weight of polyarylate prepolymer is increased in the extruder at a temperature of from 320 to 350°C, under a vacuum of 40 to 270 Pa (0.3 to 2 mm Hg) and a residence time of from 10 to 30 minutes.

The process of this invention produces normally solid polyarylates having a reduced viscosity of from 0.05 m²/kg or greater, preferably from 0.06 to 0.08 m²/kg, as measured in chloroform (5 kg/m³ chloroform) or other suitable solvent at 25°C.

In those instances where the polyarylate is not soluble in chloroform, other solvents known in the art such as perchloroethylene, phenol/tetrachloroethane (60/40), etc. may be used. Reduced viscosities of the polyarylates measured in these solvents generally have the same range.

The polyarylates may be prepared in the presence of materials such as molecular weight regulators, antioxidants, and the like.

The polyarylates obtained by the process of this invention may be used together with the well-known additives such as plasticizers, pigments, lubricating agents, mold release agents, stabilizers, inorganic fillers, and the like. These polyarylates may also be blended with other polymers.

Examples

The following examples serve to give specific illustrations of the practice of this invention. In these examples, all parts and percentages are on a weight basis unless otherwise specified.

Example 1

Preparation of Prepolymer

The apparatus used herein consisted of a 500 cm³ round bottom flask fitted with a nitrogen inlet, mechanical stirrer, a vacuum jacketed vigreux column connected to a distillation head and collector flask. 124.8 grams of bisphenol-A diacetate, 33.2 grams of isophthalic acid, 33.2 grams of terephthalic acid, and 63 grams of diphenyl ether were added to the flask. The reaction mixture was purged with nitrogen for about 20 minutes. The reaction mixture was then heated to about 275°C by immersion of the apparatus in a heating medium. Acetic acid started to distill when the temperature reached about 260°C. The reaction was maintained at 275°C for 2 hours. The temperature was then raised to about 290—295°C and the reactants maintained at this temperature for 2 hours. No apparent distillation of acetic acid was observed during the last hour. A thick yellow product formed. This was allowed to cool to ambient temperature.

Approximately 3 grams of the product was dissolved in methylene chloride (approximately 10 percent solids) and coagulated in isopropanol. The resultant material which was in the form of a fluff was washed with isopropanol two times and then dried at 120°C (for 24 hours at <133 Pa, i.e. 1 mm Hg pressure). The reduced viscosity of this polymer was measured in chloroform (5 kg/m³) at 25°C and found to be 0.025 m²/kg.

Preparation of Polymer

To a test tube (25 by 200 mm.) fitted with a vacuum adapter, 6 grams of the prepolymer as prepared above was added. The pressure in the test tube was reduced to <53 Pa (0.4 mm Hg). After two minutes at ambient temperature, the test tube was heated to 345—350°C and the prepolymer was maintained at this temperature for 30 minutes. The test tube was allowed to cool to ambient temperature. A polymer was recovered by breaking the test tube. The polymer had a deep yellow color. The reduced viscosity of this polymer was measured in chloroform (5 kg/m³) at 25°C and found to be 0.07 m²/kg.

Table 1 shows the weight in grams of the diphenyl ether used, the weight percent of diphenyl ether used, based on the polymer produced, and the reduced viscosities of the prepolymer and polymer formed.
The procedure as described in Example 1 for forming a prepolymer and polymer was exactly repeated in Examples 2 to 6 except that in forming the prepolymer, the amounts of diphenyl ether shown in Table I were charged to the flask.

Table I shows the weight in grams of the diphenyl ether used, the weight percent of diphenyl ether used, based on the polymer produced, and the reduced viscosities of the prepolymer and polymer formed.

**TABLE I**

<table>
<thead>
<tr>
<th>Example</th>
<th>Diphenyl Ether, Amount Used (g)</th>
<th>Reduced Viscosity of Prepolymer (m²/kg)</th>
<th>Reduced Viscosity of Polymer (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.028</td>
<td>0.041</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.022</td>
<td>0.057</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>0.028</td>
<td>0.083</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.020</td>
<td>0.089</td>
</tr>
<tr>
<td>1</td>
<td>63</td>
<td>0.025</td>
<td>0.070</td>
</tr>
<tr>
<td>6</td>
<td>435</td>
<td>0.007</td>
<td>&lt;0.020</td>
</tr>
</tbody>
</table>

The results in Table I show that without using diphenyl ether, the reduced viscosity of the polyarylate polymer produced is only 0.041 (Example 2). When diphenyl ether is used in amounts of from 5 to 35 weight percent (Examples 3 to 5 and 1), the polyarylate polymer produced has a reduced viscosity in the range of 0.057 to 0.070. However, when diphenyl ether is used in large amounts of 85 weight percent (Example 6) the polyarylate polymer produced has an unacceptable reduced viscosity of less than 0.020 m²/kg.

**Example 7**

The procedure as described in Example 1 for forming a prepolymer was exactly repeated except that 128.4 grams of bisphenol-A diacetate, 66.4 grams of isophthalic acid, and 63 grams of diphenyl ether were charged to the flask. The prepolymer formed has a reduced viscosity of 0.026 m²/kg. A homoisophthalate polymer was formed by the procedure as described in Example 1. The polymer had a reduced viscosity of 0.071 m²/kg.

**Example 8**

The procedure as described in Example 1 for forming a prepolymer was exactly repeated except that 128.4 grams of bisphenol-A diacetate, 49.8 grams of terephthalic acid, 16.6 grams of isophthalic acid and 57 grams of diphenyl ether were charged to the flask. The prepolymer formed had a reduced viscosity of 0.011 m²/kg. A polyarylate polymer was formed by the procedure as described in Example 1. The polymer had a reduced viscosity of 0.080 m²/kg.

**Example 9**

The reactor system consisted of a hot oil heated one gallon reactor fitted with a nitrogen inlet, mechanical agitator, and fractionating column (packed with ceramic saddles) connected to an overhead take-off device consisting of a condenser and a receiver.

The reactor was charged 1200 grams of Bisphenol-A diacetate, 319.1 grams of isophthalic acid, 319.1 grams of terephthalic acid and 740 grams of diphenyl ether (35 weight percent based on the polymer produced). The reactor system was purged with nitrogen for 20 minutes and then the heater turned on to raise the temperatures of the reactor to about 280°C (the oil heater was set at about 300°C). Acetic acid started to distill when the temperature reached about 260°C. Acetic acid distillation was followed by measuring the level in the receiver. After about 3.0 hours at 280°C, the power draw on the agitator began to increase which indicated a viscosity increase. The reaction was terminated after 5.5 hours at reflux by discharging the contents of the reactor under nitrogen. The reaction product was allowed to cool to room
temperature. The reaction product was ground to particles having an average size below 6.35 mm and stored in an oven at 50—60°C, for about 10—15 hours under a vacuum of 9,900 Pa (75 mm Hg). The polymer was isolated by feeding the reaction product to a single screw two vent extruder and flushing off the solvent. The barrel temperature of the extruder was 325°C, the first vent was under a vacuum of about 67 × 10^3 Pa (500 mm Hg) and the second vent was under a vacuum of about 20 × 10^3 to 27 × 10^3 Pa (15—20 mm Hg). The residence time of the polymer in the extruder was 2—5 minutes. The polymer had a reduced viscosity of 0.063 m^2/kg as measured in chloroform (5 kg/m^3) at 25°C.

Example 10

The procedure of Example 9 was exactly repeated except that 918 grams of diphenyl ether (40 weight percent based on the polymer produced) was charged to the reactor instead of 740 grams and the reaction time was 6.5 hours instead of 6.0 hours. The polymer produced had a reduced viscosity of 0.068 m^2/kg as measured in chloroform (5 kg/m^3) at 25°C.

Example 11

This Example describes the preparation of a polyarylate polymer in a one-step process starting with bisphenol-A, acetic anhydride, isophthalic and terephthalic acids, and diphenyl ether without isolating the bisphenol-A diacetate.

The reactor system, as described in Example 9, was used herein. The reactor was charged with 877.0 grams of bisphenol-A, 852.8 grams of acetic anhydride, 319.1 grams of isophthalic acid, 315.1 grams of terephthalic acid and 590 grams of diphenyl ether 30 weight percent based on the polymer produced. The reactor system was purged with nitrogen for 20 minutes and the heater turned on to raise the temperature to 150°C. The reactants were maintained at 150°C for 1.5 hours under reflux conditions. The temperature was raised to about 280°C. The removal of acetic acid by distillation was started and continued until 320 grams of acetic acid was collected. The polymerization was then carried out according to the procedure and for the times and temperatures as described in Example 9. The polymer was recovered, ground and isolated in an extruder by the procedures as described in Example 9.

The polymer had a reduced viscosity of 0.061 m^2/kg as measured in chloroform (5 kg/m^3) at 25°C.

Example 12

This Example describes the preparation of a copolymer according to the procedures of this invention.

Preparation of Prepolymer

The apparatus described in Example 1 was used herein. The 500 cm^3 round bottom flask was charged with 62.4 grams of bisphenol-A diacetate, 38.8 grams of hydroquinone diacetate, 33.2 grams of isophthalic acid, 33.2 grams of terephthalic acid and 60.0 grams of diphenyl ether (30 weight percent based on the polymer produced). The procedure described in Example 1 for forming the prepolymer was used. The prepolymer formed had a reduced viscosity of 0.033 m^2/kg as measured in chloroform (5 kg/m^3) at 25°C.

Preparation of Copolymer

A copolymer was formed from the prepolymer by the procedure as described in Example 1. The amorphous copolymer formed was not soluble in chloroform. The reduced viscosity of the copolymer was 0.079 m^2/kg as measured in p-chlorophenol (2kg/m^3) at 49°C.

Claims

1. A process for preparing a polyarylate having a reduced viscosity of from 0.05 m^2/kg (chloroform, 5 kg/m^3, 25°C) or greater, which comprises reacting:
(a) at least one diester derivative of a dihydric phenol having the following formula:

\[
\begin{align*}
\text{O} & \quad \text{R-C-O} \\
& \quad \begin{array}{c}
\text{(y)}_z \\
\text{(y)}_z \\
\end{array} \\
& \quad \text{R'} \quad \text{O-C-R} \\
\end{align*}
\]

wherein R is independently selected from an alkyl radical having from 1 to 6 carbon atoms or cycloalkyl having from 4 to 7 carbon atoms, y is independently selected from alkyl groups of 1 to 4 carbon atoms, chlorine or bromine, z independently has a value of from 0 to 4, inclusive, and R' is independently selected from a divalent saturated aliphatic hydrocarbon radical having 1 to 8 carbon atoms, a cycloalkylene or cycloalkylidene radical having up to and including 9 carbon atoms, O, S, SO, SO_2, and CO; x is 0 or 1; with
(b) at least one aromatic dicarboxylic acid, in the presence of from 10 to 60 weight percent, based on the polyarylate produced, of a diphenyl ether compound, at a temperature of from 260 to 350°C said reaction being carried out in the absence of any catalyst.
2. A process as defined in claim 1 wherein the dihydric phenol has the following formula:

\[
\begin{align*}
\text{CH}_3 - \text{CO} - \left( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right) \text{O} - \left( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right) \text{O} - \text{C-CH}_3
\end{align*}
\]

3. A process as defined in claim 1 wherein the diphenyl ether is substituted with alkyl groups, chlorine, bromine, or any substituent which does not interfere with the polyarylate forming reaction.

4. A process as defined in claim 1 wherein the polyarylate produced has a reduced viscosity of from 0.5 to 0.8.

5. A process as defined in claim 1 wherein the diphenyl ether is present in an amount of from 25 to 40 weight percent.

6. A process as defined in claim 1 wherein the temperature is between 275°C to 295°C.

7. A process for preparing a polyarylate having a reduced viscosity of from 0.05 m²/kg or greater which process comprises reacting:
   (a) an acid anhydride derived from an acid containing from 2 to 8 carbon atoms; said anhydride being preferably acetic anhydride;
   (b) at least one dihydric phenol having the following formula:

\[
\begin{align*}
\text{HO} - \left( \begin{array}{c}
\text{R'} \\
\text{x}
\end{array} \right) \text{OH}
\end{align*}
\]

wherein \( y \) is independently selected from alkyl groups of 1 to 4 carbon atoms, chlorine or bromine, \( z \) independently has a value of from 0 to 4, inclusive, \( R' \) is independently selected from a divalent saturated hydrocarbon radical having 1 to 8 carbon atoms, a cycloalkylene or cycloalkylidene radical having up to and including 9 carbon atoms, O, S, SO, SO₂ and CO; \( x \) is 0 or 1; and
   (c) at least one aromatic dicarboxylic acid, characterized in that the said reaction is carried out in the presence of from 10 to 60 weight percent, based on the polyarylate produced, of a diphenyl ether compound, at a temperature of from 260 to 350°C and in the absence of any catalyst.

8. A process as defined in claim 7 wherein the dihydric phenol has the following formula:

\[
\begin{align*}
\text{HO} - \left( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right) \text{CH}_3 - \left( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right) \text{OH}
\end{align*}
\]

wherein each \( z \) is preferably 0.

9. A process as defined in claim 1 or 7 wherein the aromatic dicarboxylic acid is a mixture of isophthalic acid and terephthalic acid, in a ratio which is preferably of 20:80 to 100:0.

10. A process for preparing a polyarylate having a reduced viscosity of from 0.05 m²/kg or greater, which process comprises the following steps:

i. forming a polyarylate prepolymer having a reduced viscosity of from 0.01 to 0.04 m²/kg by reacting:
(a) at least one diester derivative of a dihydric phenol having the following formula:

wherein R is independently an alkyl radical having from 1 to 6 carbon atoms or cycloalkyl having from 4 to 7 carbon atoms, y is independently selected from alkyl groups of 1 to 4 carbon atoms, chlorine, or bromine, z independently has a value of from 0 to 4, inclusive, and R' is independently selected from a divalent saturated aliphatic hydrocarbon radical having 1 to 8 carbon atoms, a cycloalkylene or cycloalkylidene radical having up to and including 9 carbon atoms, O, S, SO, SO_2, and CO; x is 0 or 1; with
(b) at least one aromatic dicarboxylic acid, in the presence of from 10 to 60 weight percent, based on the polyarylate produced, of a diphenyl ether compound at a temperature of from 260 to 350°C, and in the absence of any catalyst and.

II. heating the prepolymer so formed at a temperature of from 300 to 350°C for a period of time sufficient to form the polyarylate having a reduced viscosity of from 0.05 m²/kg or greater, preferably said heating being carried out in a vented extruder under vacuum.

Patentansprüche

1. Verfahren zur Herstellung eines Polyarylates mit einer reduzierten Viskosität von 0,05 m²/kg (Chloroform, 5 kg/m², 25°C) oder größer, welches umfaßt die Umsetzung:
(a) mindestens eines Diesterderivats eines zweiwertigen Phenols der folgenden Formel:

worin R unabhängig ausgewählt ist unter einem Alkylrest mit 1 bis 6 Kohlenstoffatomen oder Cycloalkyl mit 4 bis 7 Kohlenstoffatomen, y unabhängig ausgewählt ist unter Alkylresten mit 1 bis 4 Kohlenstoffatomen, Chlor oder Brom, z unabhängig einen Wert von 0 bis 4 einschließlich hat und R' unabhängig ausgewählt ist unter einem zweiwertigen gesättigten aliphatischen Kohlenwasserstoffrest mit 1 bis 8 Kohlenstoffatomen, einem Cycloalkyl- oder Cycloalkylidenrest mit bis zu und einschließlich 9 Kohlenstoffatomen, O, S, SO, SO_2 und CO; x 0 oder 1 ist; mit:
(b) mindestens einer aromatischen Dicarbonsäure in Gegenwart von 10 bis 60 Gew.-%, bezogen auf das produzierte Polyarylat, einer Diphenylether-Verbindung bei einer Temperatur von 260 bis 350°C, wobei die Reaktion in Abwesenheit eines Katalysators durchgeführt wird.

2. Verfahren, wie in Anspruch 1 definiert, worin das Diesterderivat eines zweiwertigen Phenols die folgende Formel hat:

3. Verfahren, wie in Anspruch 1 definiert, worin der Diphenylether mit Alkylgruppen, Chlor, Brom oder einem beliebigen Substituenten, der die Polyarylat-Bildungsreaktion nicht beeinträchtigt, substituiert ist.
4. Verfahren, wie in Anspruch 1 definiert, worin das produzierte Polyarylät eine reduzierte Viskosität von 0,5 bis 0,8 hat.


6. Verfahren, wie in Anspruch 1 definiert, worin die Temperatur zwischen 275 bis 293°C liegt.

7. Verfahren zur Herstellung eines Polyyarylats mit einer reduzierten Viskosität von 0,05 m²/kg oder größer, welches umfaßt die Umsetzung:
   (a) eines von einer Säure, die 2 bis 8 Kohlenstoffatome enthält, abgeleiteten Säureanhydrids; welches Anhydrid vorzugsweise Acetanhydrid ist;
   (b) mindestens eines zweiwertigen Phenols der folgenden Formel:

   ![Diagramm](image)

   worin \( y \) unabhängig ausgewählt ist unter Alkylgruppen mit 1 bis 4 Kohlenstoffatomen, Chlor oder Brom, \( z \) unabhängig einen Wert von 0 bis 4 einschließlich hat, \( R' \) unabhängig ausgewählt ist unter einem zweiwertigen gesättigten Kohlenwasserstoffrest mit 1 bis 8 Kohlenstoffatomen, einem Cycloalkyl- oder Cycloalkylidenrest mit bis zu und einschließlich 9 Kohlenstoffatomen, O, S, SO, SO₂ und CO; x 0 oder 1 ist; und
   (c) mindestens einer aromatischen Dicarbonsäure, dadurch gekennzeichnet, daß die Reaktion durchgeführt wird in Gegenwart von 10 bis 60 Gew.-%, bezogen auf das produzierte Polyarylät, einer Diphenylether-Verbindung bei einer Temperatur von 260 bis 350°C und in Abwesenheit eines Katalysators.

8. Verfahren, wie in Anspruch 7 definiert, worin das zweiwertige Phenol die folgende Formel hat:

   ![Diagramm](image)

   worin jedes \( z \) vorzugsweise 0 ist.

9. Verfahren, wie in Anspruch 1 oder 7 definiert, worin die aromatische Dicarbonsäure ein Gemisch von Isophthalsäure und Terephthalsäure in einem Verhältnis von vorzugsweise 20:80 bis 100:0 ist.

10. Verfahren zur Herstellung eines Polyarylats mit einer reduzierten Viskosität von 0,05 m²/kg oder größer, welches umfaßt die folgenden Schritte:
   I. Bildung eines Polyarylät-Prepolymers mit einer reduzierten Viskosität von 0,01 bis 0,04 m²/kg durch Umsetzen:
     (a) mindestens eines Diesterderivats eines zweiwertigen Phenols der folgenden Formel:

   ![Diagramm](image)

   worin \( R \) unabhängig ein Alkyrest mit 1 bis 6 Kohlenstoffatomen oder Cycloalkyl mit 4 bis 7 Kohlenstoffatomen ist, \( y \) unabhängig ausgewählt ist unter Alkylgruppen mit 1 bis 4 Kohlenstoffatomen, Chlor oder Brom, \( z \) unabhängig einen Wert von 0 bis 4 einschließlich hat und \( R' \) unabhängig ausgewählt ist unter einem zweiwertigen gesättigten aliphatischen Kohlenwasserstoffrest mit 1 bis 8 Kohlenstoffatomen, einem 11
Cycloalkylen- oder Cycloalkylidenrest mit bis zu und einschließlich 9 Kohlenstoffatomen, O, S, SO, SO₂ und CO; x 0 oder 1 ist; mit 
(b) mindestens einer aromatischen Dicarbonsäure in Gegenwart von 10 bis 60 Gew.-%, bezogen auf 
das produzierte Polyarylat, einer Diphenylether-Verbindung bei einer Temperatur von 260 bis 350°C und in 
Abwesenheit eines Katalysators und 
II. Erhitzen des so gebildeten Prepomers auf eine Temperatur von 300 bis 350°C für eine ausreichende 
Zeitspanne, um das Polyarylat mit einer reduzierten Viskosität von 0,05 m²/kg oder größer zu bilden, wobei 
das Erhitzen vorzugsweise in einem Entgasungseextruder unter Vakuum durchgeführt wird.

10 Revendications

1. Procédé de préparation d’un polyarylate ayant une viscosité réduite de 0,05 m²/kg (chloroforme, 5 
kg/m³, 25°C) ou davantage, qui consiste à faire réagir:
   (a) au moins un diester d’un phénol dihydroxylique répondant à la formule suivante:

   \[
   \begin{align*}
   &R - O - C - O - (y) \quad (y) \\
   &R' - O - C - R
   \end{align*}
   \]

   dans laquelle R est choisi indépendamment entre un radical alkyle ayant 1 à 6 atomes de carbone ou 
cycloalkyle ayant 4 à 7 atomes de carbone, y est choisi indépendamment entre des groupes alkyle ayant 1 à 
4 atomes de carbone, le chlore ou le brome, z a indépendamment une valeur de 0 à 4 inclus, et R’ est choisi 
indépendamment entre un radical hydrocarboné aliphatique saturé divalérent ayant 1 à 8 atomes de carbone, 
um radical cycloalkylène ou cycloalkylidené ayant jusqu’à et y compris 9 atomes de carbone, O, S, SO, SO₂ 
cou CO₂; x 0 ou 1; avec 
(b) au moins un acide dicarboxylique aromatique en présence de 10 à 60% en poids, sur la base du 
polyarylate produit, d’un éther de diphényle, à une température de 260 à 350°C, ladite réaction étant 
conduite en l’absence de tout catalyseur.

2. Procédé tel que défini dans la revendication 1, dans lequel le diester est un phénol dihydroxylique de 
forme suivante:

   \[
   \begin{align*}
   &CH₃ - CO - O - (y) \quad (y) \\
   &CH₃ - C - O - CH₃
   \end{align*}
   \]

3. Procédé tel qui défini dans la revendication 1, dans lequel l’éther de diphényle est substitué avec des 
groupes alkyle, du chlore, du brome ou tout substituant qui n’interfère pas avec la réaction de formation du 
polyarylate.

4. Procédé tel que défini dans la revendication 1, dans lequel le polyarylate produit a une viscosité 
réduite de 0,5 à 8.

5. Procédé tel que défini dans la revendication 1, dans lequel l’éther de diphényle est présent en une 
quantité de 25 à 40% en poids.

6. Procédé tel que défini dans la revendication 1, dans lequel la température est comprise entre 275 et 
295°C.

7. Procédé de préparation d’un polyarylate ayant une viscosité réduite de 0,05 m²/kg ou davantage, 
procédé qui consiste à faire réagir:
   (a) un anhydride d’acide dérivé d’un acide contenant 2 à 8 atomes de carbone; ledit anhydride étant 
avantageusement l’anhydride acétique;
0 026 684

(b) au moins un phénol dihydroxylique ayant la formule suivante:

\[
\text{HO-} \begin{array}{c}
\text{(y)}_z \\
\text{R'}
\end{array}
\begin{array}{c}
\text{(y)}_z \\
\text{OH}
\end{array}
\text{CH}_3
\]

dans laquelle y est choisi indépendamment entre des groupes alkyle ayant 1 à 4 atomes de carbone, le chlore ou le brome, z a indépendamment une valeur de 0 à 4 inclus, R' est choisi indépendamment entre un radical hydrocarboné saturé divalent ayant 1 à 8 atomes de carbone, un radical cycloalkylène ou un radical cycloalkylidène ayant jusqu'à et y compris 9 atomes de carbone, O, S, SO, SO₂ et CO; x a la valeur 0 ou 1; et

c) au moins un acide dicarboxylique aromatique, caractérisé en ce que ladite réaction est conduite en présence de 10 à 60% en poids, sur la base du polyarylate produit, d'un éther de diphenyle, à une température de 260 à 350°C, et en l'absence de tout catalyseur.

8. Procédé tel que défini dans la revendication 7, dans lequel le phénol dihydroxylique répond à la formule suivante:

\[
\text{HO-} \begin{array}{c}
\text{(y)}_z \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{(y)}_z \\
\text{CH}_3
\end{array}
\text{OH}
\]

où chaque indice z a de préférence la valeur 0.

9. Procédé tel que défini dans la revendication 1 ou 7, dans lequel l'acide dicarboxylique aromatique est un mélange d'acide isophthalique et d'acide téréphthalique, dans un rapport qui va avantageusement de 20:80 à 100:0.

10. Procédé de préparation d'un polyarylate ayant une viscosité réduite de 0,05 m²/kg ou davantage, procédé qui comprend les étapes suivantes:
   I. formation d'un polyarylate prépolymère ayant une viscosité réduite de 0,01 à 0,04 m²/kg, en faisant réagir:
   (a) au moins un diester d'un phénol dihydroxylique répondant à la formule suivante:

\[
\text{R-C-O-} \begin{array}{c}
\text{(y)}_z \\
\text{R'}
\end{array}
\begin{array}{c}
\text{(y)}_z \\
\text{O-C-R}
\end{array}
\]

dans laquelle R représente indépendamment un radical alkyle ayant 1 à 6 atomes de carbone ou cycloalkyle ayant 4 à 7 atomes de carbone, y est choisi indépendamment entre des groupes alkyle ayant 1 à 4 atomes de carbone, le chlore ou le brome, z a indépendamment une valeur de 0 à 4 inclus, et R' est choisi indépendamment entre un radical hydrocarboné aliphatique saturé divalent, ayant 1 à 8 atomes de carbone, un radical cycloalkylène ou cycloalkylidène ayant jusqu'à et y compris 9 atomes de carbone, O, S, SO, SO₂ et CO; x a la valeur 0 ou 1; avec

(b) au moins un acide dicarboxylique aromatique, en présence de 10 à 60% en poids, sur la base du polyarylate produit, d'un éther de diphenyle à une température de 260 à 350°C, et en l'absence de tout catalyseur, et

II. chauffage du prépolymère ainsi formé à une température de 300 à 350°C pendant une période suffisante pour former le polyarylate ayant une viscosité réduite de 0,05 m²/kg ou davantage, le dit chauffage étant avantageusement conduit sous vide dans une extrudeuse à purge d'air.