

PATENT SPECIFICATION

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(54) CATALYST FOR POLYESTERIFICATION

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of polyesters using germanium glycoloxide as catalyst.

According to the present invention we provide a process for the preparation of a linear polyester by the polycondensation of a bis(ω -hydroxyalkyl) terephthalate using as catalyst at least one germanium glycoloxide prepared by the reaction of an appropriate germanium compound with at least one vicinal diol, the vicinal diol or diols jointly being present in quantity at least equal to that required for complete reaction to form the appropriate germanium glycoloxide and subsequent submission of the product to a treatment ensuring that the germanium dioxide equivalent of the germanium present in the product is greater than 5% by weight and does not exceed 54% by weight.

By the expression "submitted to treatment" we mean that glycol is removed from the product by distillation or, when the content of germanium expressed as germanium dioxide is suitably high, that the product is cooled with separation by crystallisation of a product and the product is isolated and thereafter heated at a temperature of at least 60°C until a homogeneous liquid results and/or heated with volatilisation of glycol to achieve the desired level of content of germanium.

We believe that the product produced when a suitably high quantity of glycol is present with relation to the germanium compound is germanium tetraglycoloxide and that when submitted to treatment so as to increase the content of germanium, the product contains successively greater amounts of a polymeric form of polymeric forms of glycoloxide. We do not, however, wish to be limited by this explanation.

[Price 25p]

The bis(ω -hydroxyalkyl) terephthalate employed in the process of our invention may be prepared by any known method, examples of which are the reaction of an ester-forming derivative of terephthalic acid with a glycol and the reaction of terephthalic acid with a glycol. In these particular methods of making bis(ω -hydroxyalkyl) terephthalate a somewhat arbitrary distinction is made between the stage of preparation of the bis(ω -hydroxyalkyl) terephthalate and the polycondensation stage, and the catalyst of our invention may be added after some small degree of polycondensation has been effected to product oligomers, although the reaction mixture will at that stage consist of a major proportion of bis(ω -hydroxyalkyl) terephthalate, when this is appropriate.

In the term "polyester" we include copolyesters.

When the catalytic germanium compound is prepared by the use of a diol other than that of the polyester precursor, a small proportion of units based on the other glycol may as a result be introduced, giving a copolyester.

Examples of vicinal diols for use in the process of our invention are ethylene glycol, propan-1:2-diol and butan-1:2- (or -2:3-) diol.

Appropriate germanium compounds are those which react with glycols to give a glycoloxide. Examples of appropriate germanium compounds are germanium dioxide in the amorphous form, germanium tetrachloride, germanium tetramethoxide and ammonium germanate. Also included in this description is germanium dioxide in the hexagonal crystalline form of particle size less than 5 μ .

In the cases wherein the reaction of the germanium compound and the glycol is carried out at elevated temperature and the relative quantities of reactants are such that the resultant glycol solution of glycoloxide is of concentration greater than that of a saturated solution of glycoloxide in glycol at ambient temperature, the solution may be cooled and the solid glycoloxide which separates isolated, thus representing a method of removing unreacted glycol.

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In cases wherein the unreacted glycol is removed by volatilisation, if this proceeds beyond a certain degree the resultant glycoloxide will be obtained in the form of a syrup.

5 This syrup may either be charged as such to the reactant or reactants for the preparation of the polyesters, or may be cooled to form a solid product and thereafter reduced to an appropriate form for subsequent use, for example by powdering.

10 An advantage of the process of our invention is that by means of it polyesters may be prepared using a germanium catalyst at particularly high rates of reaction. In particular such rates of reaction are greater than are obtained when there is used as catalyst a germanium glycoloxide prepared *in situ* or prepared as a glycol solution and charged to the polyester reactants as such. In addition the derived polyesters are of superior appearance in respect of colour. In general, the higher the content of germanium in the catalytic product the higher will be its catalytic activity per unit weight of germanium.

25 We have found that the quantity of germanium glycoloxide which may usefully be employed is that corresponding to from 50 to 1,000 parts of germanium per million based on the terephthalic acid equivalent to the reactants.

30 The polyesters and copolyesters of our invention are of particular value in the manufacture of film and filaments in known manner. When used for filaments the polyester or copolyester should be of suitably high molecular weight and of linear configuration. Since the properties particularly fitting the copolyester for filament uses derive from the ω -hydroxyalkylene terephthalic units, these should constitute a useful proportion of the total structural units. We have found that a useful proportion corresponds to the condition wherein at least 75% of the structural units are units of a particular ω -hydroxyalkylene terephthalate.

45 Our invention is of particular value in the preparation of polyesters based on ethylene terephthalate.

A suitably high molecular weight for filament formation is above about 8,000 which corresponds to Viscosity Ratio 1.33 as measured at 1% solution in orthochlorophenol at 25°C.

50 Other additives commonly employed in polyester manufacture may be added in the amounts commonly used. Examples of such additives are phosphorus compounds, delustrants, optical whiteners, dyeing assistants and coloured materials.

60 In order that the nature of the process of our invention may be the more clearly understood, we give hereinafter some examples of its application. In these examples all parts and percentages are by weight. Example 1 is for comparison purposes only.

65 In each example titanium dioxide was added

before the start of the polycondensation stage in such amount as to yield a final polyester containing 0.5% by weight of titanium dioxide.

The details of the conditions of reaction are given under individuals Examples; the reaction times, properties of polyesters and type and amount of catalysts are compared in the Table.

Example 1

Dimethyl terephthalate (100 parts) and ethylene glycol (71 parts) were reacted under ester-interchange conditions using manganous acetate tetra hydrate (352 parts per million on dimethyl terephthalate) as catalyst. When the reaction was complete as judged by the evolution of the theoretically obtainable amount of methanol, the catalyst was deactivated by the addition of phosphorous acid (0.015 parts) and agitation at 22°C for 5 minutes. To the resultant reaction mixture was added amorphous germanium dioxide (0.02 parts) as a slurry in ethylene glycol (0.50 parts) and the polycondensation was carried out at a temperature of 290°C and vacuum of 0.3 mm Hg.

Example 2

Dimethyl terephthalate and ethylene glycol were reacted in the amounts and according to the conditions described in Example 1, with the exception that the amorphous germanium dioxide was reacted with ethylene glycol (0.20 parts) by heating at the boil with removal of water of reaction by volatilisation.

Example 3

Dimethyl terephthalate and ethylene glycol were reacted in the amounts and according to the conditions described in Example 1, with the exception that the germanium catalyst was added as a germanium glycoloxide concentrate (645 p.p.m on dimethyl terephthalate).

The germanium glycoloxide concentrate was made by the reaction of amorphous germanium dioxide with 10 times its weight of glycol and distillation of the excess glycol to give the germanium content of the product corresponding to that given in the Table.

Example 4

Example 3 was repeated with the exception that the germanium glycoloxide concentrate (690 p.p.m on dimethyl terephthalate) was obtained by the reaction of 1 part by weight of amorphous germanium dioxide with 20 parts by weight of ethylene glycol at the boil, cooling and isolation of the product which crystallised out. The germanium content is shown in the Table.

Example 5

Example 3 was repeated with the exception that the germanium glycoloxide (425 p.p.m on dimethyl terephthalate) was further concentrated by distillation of ethylene glycol to give the germanium content as indicated in the Table.

Example 6

Example 3 was repeated with the exception that the germanium glycoloxide (490 p.p.m on dimethyl terephthalate) was prepared from the crystalline hexagonal form of the dioxide.

5 The following two examples show the advantage of using the concentrated glycoloxide solution when high viscosity polymer is required.

Example 7

Example 2 was repeated and the melt viscosity was taken to its maximum.

Example 8

Example 7 was repeated with exception that a germanium glycoloxide concentrate (526 p.p.m on dimethyl terephthalate) was used as catalyst.

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TABLE

Example	Germanium dioxide (p.p.m. based on dimethyl terephthalate)	Conc. of germanium in the glycoloxide (exp'd as % w/w GeO_2)	Viscosity Ratio	Reaction Time	Colour		
					L	Y	L-Y
1	200	—	1.675*	105	79	21	58
2	200	10	1.836	90	81	17	64
3	200	31	1.817	75	81	12	69
4	200	29	1.815	58	81	14	67
5	200	47	1.836	69	80	15	65
6	180	37	1.815	85	79	18	61
7	200	10	1.807*	140	—	—	—
8	200	37	1.903	120	—	—	—

*The melt viscosity of the reaction mixture ceased to increase at the time stated.

20 L and Y refer to Luminance and Yellowness determined using a "Colormaster" differential colorimeter manufactured by the Manufacturers Engineering Equipment Corporation. A high value for L-Y accompanied by a high value of L is a measure of superior visual appearance.

25 WHAT WE CLAIM IS:—

1. A process for the preparation of a pre-formed catalyst for the polycondensation stage in the preparation of a polyester wherein at least one germanium glycoloxide is prepared by the reaction of an appropriate germanium compound with at least one vicinal diol, the vicinal diol or diols jointly being present in quantity at least equal to that required for complete reaction to form the appropriate germanium glycoloxide and subsequent submission of the product to a treatment ensuring that the germanium dioxide equivalent of the germanium present in the product is greater than 5% by weight and does not exceed 54% by weight.

2. A process for the preparation of a catalyst according to Claim 1 or 2 wherein the germanium compound reacted with the diol is germanium dioxide in the amorphous form, germanium dioxide in the hexagonal crystalline form of particle size less than 5 microns, germanium tetrachloride, germanium tetramethoxide or ammonium germanate.

3. A process according to any of Claims 1 or 2 wherein the diol is ethylene glycol, propan-1:2-diol, butan-1:2:-diol or butan-2:3-diol.

4. A process according to any of Claims 1 or 2 wherein the diol is ethylene glycol.

5. A catalyst for the polycondensation stage in the preparation of a polyester, prepared according to the process of any of Claims 1, 2, 3 or 4.

6. A process for the preparation of a polyester using as catalyst in the polycondensation stage the catalyst of Claim 5.

7. A process according to Claim 6 wherein the polyester is poly(ethylene terephthalate).

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Example 6

Example 3 was repeated with the exception that the germanium glycoloxide (490 p.p.m on dimethyl terephthalate) was prepared from the crystalline hexagonal form of the dioxide.

The following two examples show the advantage of using the concentrated glycoloxide solution when high viscosity polymer is required.

Example 7

Example 2 was repeated and the melt viscosity was taken to its maximum.

Example 8

Example 7 was repeated with exception that a germanium glycoloxide concentrate (526 p.p.m on dimethyl terephthalate) was used as catalyst.

TABLE

Example	Germanium dioxide (p.p.m. based on dimethyl terephthalate)	Conc. of germanium in the glycoloxide (exp'd as % w/w GeO_2)	Viscosity Ratio	Reaction Time	Colour		
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5	200	47	1.836	69	80	15	65
6	180	37	1.815	85	79	18	61
7	200	10	1.807*	140	—	—	—
8	200	37	1.903	120	—	—	—

*The melt viscosity of the reaction mixture ceased to increase at the time stated.

L and Y refer to Luminance and Yellowness determined using a "Colormaster" differential colorimeter manufactured by the Manufacturers Engineering Equipment Corporation. A high value for L—Y accompanied by a high value of L is a measure of superior visual appearance.

WHAT WE CLAIM IS:—

1. A process for the preparation of a pre-formed catalyst for the polycondensation stage in the preparation of a polyester wherein at least one germanium glycoloxide is prepared by the reaction of an appropriate germanium compound with at least one vicinal diol, the vicinal diol or diols jointly being present in quantity at least equal to that required for complete reaction to form the appropriate germanium glycoloxide and subsequent submission of the product to a treatment ensuring that the germanium dioxide equivalent of the germanium present in the product is greater than 5% by weight and does not exceed 54% by weight.

2. A process for the preparation of a catalyst according to Claim 1 or 2 wherein the germanium compound reacted with the diol is germanium dioxide in the amorphous form, germanium dioxide in the hexagonal crystalline form of particle size less than 5 microns, germanium tetrachloride, germanium tetramethoxide or ammonium germanate.

3. A process according to any of Claims 1 or 2 wherein the diol is ethylene glycol, propan-1:2-diol, butan-1:2-diol or butan-2:3-diol.

4. A process according to any of Claims 1 or 2 wherein the diol is ethylene glycol.

5. A catalyst for the polycondensation stage in the preparation of a polyester, prepared according to the process of any of Claims 1, 2, 3 or 4.

6. A process for the preparation of a polyester using as catalyst in the polycondensation stage the catalyst of Claim 5.

7. A process according to Claim 6 wherein the polyester is poly(ethylene terephthalate).



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8. A polyester prepared according to the process of Claim 6 or 7.

9. Filaments or films prepared from a polyester according to Claim 8.

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