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(54) **Solvent based enzymatic synthesis**

(57) A process for producing a polyester comprising residues of (i) at least one aliphatic dicarboxylic acid and at least one aliphatic diol or polyol or (ii) at least one aliphatic hydroxyacid comprises reacting the diacid and the diol or polyol or the hydroxyacid in the presence of a lipase and an organic solvent. Preferably the dicarboxylic acid is adipic acid and the diol is 1,4-butanediol. The hydroxyacid may have from 2 to 12 carbon atoms.

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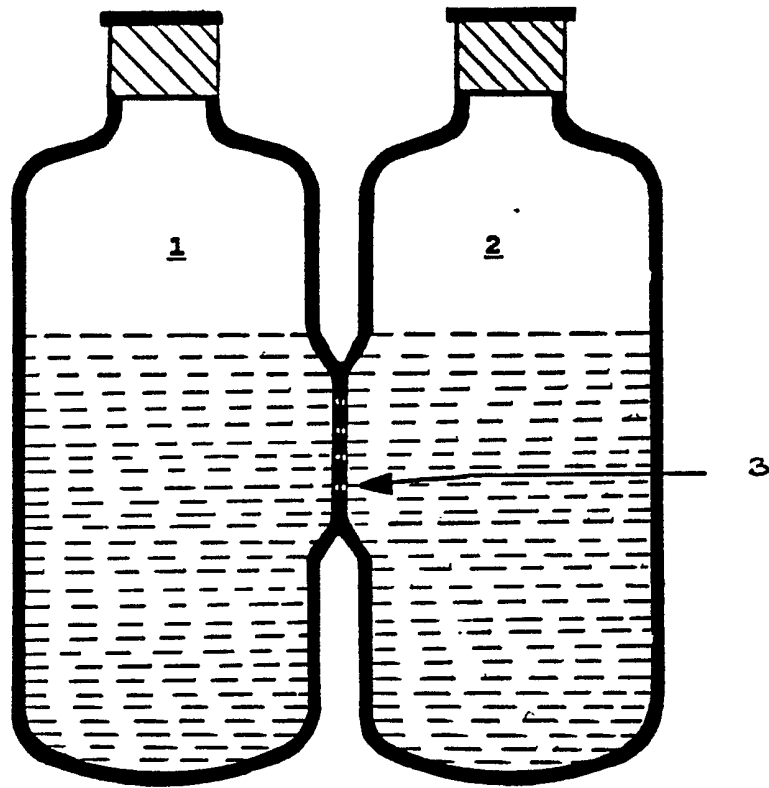


FIG.1

SOLVENT BASED ENZYMATIC SYNTHESIS

The present invention relates to a process for producing polyesters by enzyme catalysed reaction of dicarboxylic acids and diols or polyols and/or hydroxyacids
5 in the presence of a polar organic solvent.

Polyesters are well known industrial products finding applications principally as moulded articles in, for instance, the car industry. They are also of interest as the intermediates in the production of polyurethanes,
10 which are also used to form moulded articles. Polyesters are reacted with isocyanates to form polyurethanes. The characteristics of the resulting polyurethane depend at least in part on those of the polyester.

Polyesters are typically produced by chemically
15 catalysed reactions using elevated temperatures, strong acids and long reaction times. Competition between esterification, transesterification and hydrolysis limits the molecular weight of the products. Moreover, these processes are accompanied by the formation of quantities of
20 unwanted by-products, such as cyclic esters, and have the added disadvantage that the catalyst is difficult to remove. If the presence of by-products and residual catalyst is not to degrade the properties of the desired material, complex arrangements are required to prevent
25 their formation or remove them after the main reaction (see e.g. EP-A-0425201).

The present invention seeks to overcome the difficulties of chemically catalysed reactions by use of lipase enzymes. Whilst lipases have been known for some
30 time for simple esterification and transesterification

reactions (see, e.g. EP-A-0383 405) and stereoselective oligomerisations (see, e.g. Margolin A.L. et al., Tet. Letters, 28 : 1607-1610, (1987)), only limited use has been made of lipases in polyesterification. In particular

5 Wallace and Morrow, J. Polymer Science Part A, 27, 2553-2562 (1989) and Gutman, Mat. Res. Soc. Symp. Proc., 174, 217-222 (1990) have succeeded in forming polyesters of high weight average molecular weight starting from dicarboxylic acid diesters where the ester moiety is highly activated

10 (2,2,2-trichloroethyl esters) or from esters of hydroxycarboxylic acids and diesters of hydroxy dicarboxylic acids.

The present invention relates to an enzymatic polyesterification process which not only avoids the

15 disadvantages of earlier chemical and enzymatic techniques but remarkably affords polyesters of high weight average molecular weight, and very narrow dispersity whilst also being extremely pure in terms of freedom from unwanted by-products.

20 The present invention provides a process for producing a polyester comprising as repeating units residues of

(i) at least one aliphatic hydroxycarboxylic acid

25 or

(ii) at least one aliphatic dicarboxylic acid and at least one aliphatic diol or polyol

30 which process comprises reacting the hydroxy acid or the

diacid and the diol or polyol in the presence of a lipase and in the presence of an organic solvent. Optionally a diacid and diol or polyol may be reacted with an aliphatic hydroxycarboxylic acid.

5 The diol, polyol, hydroxyacid and dicarboxylic acid used in the process of the present invention preferably have from 2 to 12 carbon atoms.

 Most preferably the dicarboxylic acid is adipic acid.

10 The diol is preferably 1,4-butanediol or diethylene glycol. Diethylene glycol has a lower activity so that, when diethylene glycol is used, it may be necessary to carry out the reaction either at higher temperature, in which case the dispersity is relatively wide or at low
15 temperature for a long period. Most preferably the diol is 1,4-butanediol.

 The polyol has at least three hydroxyl groups of which at least two must be non-sterically hindered primary or secondary hydroxyl groups. Tertiary hydroxyls
20 and sterically hindered primary and secondary hydroxyls are unlikely to react under the conditions of the present invention but provide branch points when subsequently reacted with isocyanates. Suitable polyols include triols, especially glycerol, which generally results in a linear
25 polymer as the enzyme preferentially esterifies the primary hydroxyls, the secondary hydroxyl being sterically hindered, but branched products may be obtained using certain enzymes. Pentaerythritol generally does not react in the present process. Similarly, hydroxy acids must have
30 a non-sterically hindered primary or secondary hydroxyl.

Preferred hydroxy acids are hydroxy-straight chain aliphatic carboxylic acids.

At high dilution certain hydroxy carboxylic acids tend to form lactones and it is therefore preferred that, when such hydroxyacids are used in the present process, they are used only in high concentration in order to avoid the unwanted lactonisation reaction.

Because of the low temperatures used in the present process compared with those of conventional chemically catalysed polyesterifications, it is possible to use diacids and hydroxyacids, such as oxalic acid, lactic acid and glycolic acid, which decarboxylate at elevated temperatures and thereby produce polyesters not generally accessible by previous methods.

In one embodiment the polyesters produced by the present process may consist of repeating units of one or more hydroxyacids.

In alternative embodiments the polyesters produced by the present process may comprise or consist of repeating units of a diacid and a diol; a diacid and a polyol; a diacid, a diol and a polyol; a diacid, a diol and a hydroxy acid; a diacid, a polyol and a hydroxy acid or a diacid, a diol, a polyol and a hydroxy acid.

The reactive carboxylic acid groups and reactive hydroxy groups of the reactants are generally present in substantially equal numbers. The reaction may be carried out with a stoichiometric imbalance, but this generally results in a product having a lower weight average molecular weight than if the reactants are used in equimolar amounts. However, in particular aspects of the

invention, the proportions may be adjusted slightly such that a polyester having terminal acid units or terminal hydroxy units is obtained. Polyesters having terminal acid units are useful in a variety of coating compositions

5 whereas those with terminal hydroxy units may be used as the soft segments in production of polyurethanes. In particular it is preferred that the acid groups and hydroxyl groups are present in a molar ratio of 1:1 to 1:1.1 such that a hydroxyl-terminated product is obtained.

10 The enzyme used in the process of the present invention may be bound on an inert carrier, for instance polymers such as an anion exchange resin, an acrylic resin or a polypropylene, polyester or polyurethane resin, or may be used in free form. When the enzyme is bound on an inert
15 carrier it can easily be removed from the reaction mixture (e.g. by filtration) without the need for complicated purification steps. Preferably the enzyme is recovered from the reaction mixture and re-used. Suitable enzymes are commercially available lipases. A preferred enzyme for
20 use in the present process is the lipase derived from Mucor miehei, for example Lipozyme IM-20, available from Novo Industri AS, in which the enzyme is bound to a macroporous anion exchange resin. The enzyme may be obtained commercially by recombinant DNA techniques having the
25 native sequence or genetically engineered modifications thereof although it may be extracted from the organism if desired. Other suitable lipases can be identified by simple trial-and-error experimentation within the ability of those skilled in the art.

30 The amount of enzyme used is not critical and

is generally limited by economic considerations. Too little enzyme will result in a slow reaction whereas too much enzyme simply increases the costs unnecessarily. With Lipozyme IM-20 (14% by weight lipase from Mucor miehei on
5 macroporous anion exchange resin having an activity of about 30,000 Lipase Units/g; Novo Industri AS) it has been found convenient to use from 1 to 20% by weight of supported enzyme based on the total weight of monomers, preferably 9 to 15% by weight of enzyme. This corresponds
10 to 0.1 to 3%, preferably 1% to 2.5% free enzyme. However with free enzyme it is preferred to use the Mucor miehei lipase (activity 10,000 Lipase Units/g) at 12 to 40% by weight based on the total weight of monomers preferably 20 to 25% by weight.

15 The process of the present invention is carried out in the presence of an organic solvent. Suitable solvents are inert to the reaction, do not inactivate the enzyme and are sufficiently immiscible with water to prevent dehydration of the enzyme. Alkane solvents are
20 suitable. Polar solvents and especially ether solvents such as aliphatic or alicyclic ethers have been found to be convenient and preferred solvents are straight or branched chain alkyl ethers. Generally the ether has from 4 to 12 carbon atoms, for example diisopropyl ether and diethyl
25 ether.

Diethyl ether has a relatively high water absorption capacity, which may lead to lipase dehydration under desiccated conditions. Its volatility and flammability also mean that careful handling is required.
30 Preferably diisopropyl ether is used.

The process is generally carried out at from 10°C to 60°C, preferably 40 to 45°C. Above 60°C, the reaction becomes more difficult to manage on a commercial scale because most suitable solvents evaporate, but
5 solvents may be used which have higher boiling and flash points and the reaction may then be carried out above 60°C. Below 10°C the reaction is very slow and the reaction takes an uneconomically long time to go to complete conversion of the monomers.

10 The process is generally carried out at atmospheric pressure. The water produced by the reaction is generally removed during or after the reaction. When the lipase derived from Mucor miehei is used the water is generally removed during the reaction; although the lipase
15 requires at least a partial monolayer of water molecules to maintain an active conformation, it does not function well in the presence of large excesses of water. Furthermore, the water liberated by the polycondensation reaction will rehydrolyse the product esters in the presence of a lipase,
20 so the reaction will reach equilibrium at less than 70% conversion of starting materials unless the water is removed.

The water may be removed by using a desiccant whose affinity for water is greater than that of the
25 solvent when anhydrous. Suitable desiccants include molecular sieves, such as 4A° molecular sieves, for example in pellet form. The desiccant may be present in the reaction mixture throughout the course of the reaction. Alternatively the desiccant may be added later
30 (particularly when using more water-tolerant enzymes) or

dosed at intervals during the reaction.

When the lipase used is bound to a support precautions should be taken to avoid physical damage to the supported enzyme due to abrasion between the molecular
5 sieves and the enzyme support. Furthermore, direct contact between the desiccant and the enzyme may result in dehydration and thus deactivation of the enzyme. These problems may be avoided by carrying out the reaction in a two chamber apparatus where the two chambers communicate
10 via a semipermeable membrane or other porous means for separating the enzyme from the desiccant, such as a perforated glass wall for instance a sintered glass frit. The supported enzyme is placed in one chamber and the desiccant in the other. This allows the desiccant be
15 agitated without the risk of abrasive damage to and dehydration of the enzyme.

In a preferred embodiment of the invention, the process is carried out in two steps. The first step comprises reacting the acid and hydroxy component(s) in the
20 presence of a lipase and a polar organic solvent to produce a mixture of oligomers. The resulting mixture is isolated and residual starting materials and low molecular weight products, for example having a molecular weight of less than 600 Da, are removed. The oligomeric mixture is then
25 subjected to a second enzymatic esterification process in which the reaction conditions need not be the same as those of the first esterification.

Generally the starting materials have a much greater solubility in aqueous solvents than the product
30 esters. Therefore, the residual starting materials and low

molecular weight products may be removed by partitioning the products of the first polymerisation step between an aqueous solvent, such as water, and an organic solvent, such as ethylacetate.

5 Preferably the product of the esterification reaction is washed with an aqueous solution of a weak base, for example aqueous sodium bicarbonate. When the reaction is carried out in more than one step, the product is washed with aqueous base only after the final step.

10 The reaction time for each esterification step is generally 24 to 84 hours, preferably 70 hours.

 The process of the present invention generally enables the production of high weight average molecular weight polyesters, for instance up to or higher than
15 2.5 kDa, especially up to or higher than 4 kDa. The polyester produced by the process of the present invention generally has a minimum weight average molecular weight of 300 Da, preferably 600 Da, more preferably 1000 Da and most preferably 4 kDa. The weight average molecular weight of
20 the polyester is measured using gel permeation chromatography.

 The polyesters produced by the process of the present invention generally comprise from 3 to 25 monomer units, preferably from 5 to 20 monomer units and most
25 preferably from 15 to 20 monomer units. Generally it has an acid number of from 0 to 50, preferably from 0 to 25 and more preferably from 0.5 to 10. Most preferably the polyester has an acid number of about 1.

 The polyesters produced by the process of the
30 invention generally have a dispersity of 1.5 or less,

preferably 1.3 or less most preferably 1.1. The dispersity is calculated as follows:

$$\begin{array}{l} \text{Dispersity, } d = \frac{\text{Weight Average Molecular Weight}}{\text{Number Average Molecular Weight}} \end{array}$$

and the number and weight average molecular weights may be obtained by conventional methods which are well known to those skilled in the art.

The process of the present invention may further comprise reacting the resulting polyesters having hydroxy terminal groups with at least one isocyanate to produce polyurethanes. Generally the enzyme used during the polyesterification is removed from the polyester before the reaction of the polyester with isocyanate. This prevents the enzyme and its support from interfering with the polyester/isocyanate reaction. Generally water produced during the polyesterification is removed before reaction with isocyanate.

The polyesters produced by the process of the invention, by virtue of their narrow dispersity, have sharp melting points (unlike previously produced materials with wide dispersity) and impart to the polyurethanes excellent physical properties such as desirable combinations of hardness and flexural and tensile strength.

The polyesters and polyurethanes produced by the process of the present invention find uses as shaped articles and foams, particularly for motor vehicles.

The invention will now be described with reference to the Figures of the accompanying drawings in

which:

Fig.1 shows a two-chamber apparatus for
conducting the process of the invention.

The following Example illustrates the invention
5 and is not intended to limit the scope thereof.

2

•

2 hours; allow to cool under vacuum
immediately before use.

Heat a glass syringe (capacity not less than 50 cm³) to
5 100°C for a minimum of 30 minutes and allow to cool in a
desiccator immediately before use.

Preheat a suitable constant-temperature bath to 40°C.

10 APPARATUS

The apparatus is a two-chamber reaction vessel as shown in
Fig.1 comprising two chambers (1) and (2) separated by and
communicating via a porous glass panel (3) having holes of,
15 for instance, 1 mm diameter.

PROCEDURE

Place adipic acid (approximately 10 g) and a magnetic
20 follower in chamber (1) of the 2-chamber reactor.

Gradually add 1,4-butanediol to the same chamber until the
diol mass corresponds precisely to the molar quantity of
acid. Flush the air from the reactor with dry nitrogen.
Use the cooled syringe to transfer anhydrous diisopropyl
25 ether (150 cm³) under nitrogen into the reactor so that the
solvent level lies above the communication holes and the
potential substrate concentrations are between 0.4 and 0.5

mol dm³. Add the immobilised lipase to chamber (1), then reflush the apparatus with nitrogen, and seal with both gas spaces being connected externally with each other and with a flexible reservoir (balloon) containing nitrogen.

- 5 Partially immerse the apparatus in the preheated constant-temperature bath (40°C). Add activated 4Å molecular sieves (20-30g) to chamber (2), reseal the reactor and commence gentle magnetic agitation of chamber (1).

- 10 After 70 hours, remove the apparatus from the bath and filter the diisopropyl ether solution. Thoroughly rinse out the sieves, immobilised lipase, and undissolved materials with tetrahydrofuran (200 cm³) and combine the filtered rinsings with the existing filtrate. Evaporate
- 15 the solution to dryness at not more than 50°C and dissolve the resulting oil in ethyl acetate (200 cm³). Wash with deionised water (2 x 200 cm³), dry over anhydrous magnesium sulphate, filter, and evaporate to dryness. Place the oily residue in the (cleaned) reactor with fresh diisopropyl
- 20 ether, immobilised lipase and activated molecular sieves precisely as before, and agitate gently under nitrogen for a further 70 hours.

Drain off the ethereal solution. Rinse the solids with

- 25 tetrahydrofuran (8 x 25 cm³) and evaporate the filtered rinsings to dryness. Dissolve the resulting white solid in ethyl acetate (200 cm³) and stir vigorously with an equal

volume of saturated aqueous sodium bicarbonate solution for
2 hours. Separate the organic phase, wash with equal
volumes of deionised water and saturated aqueous sodium
chloride solution, dry over anhydrous magnesium sulphate,
5 filter, and evaporate to a soft white crystalline solid.

The course of the polycondensation reaction can be
monitored qualitatively by thin layer chromatography, as
there is an approximate correlation between retention
10 factor and molecular size. The most suitable eluant for
the adipic acid/1,4-butanediol system is a 10:1 (volume)
mixture of dichloromethane and ethanol, with which the diol
appears at R_f 0.18 and the ester products in the range R_f
0.26-0.70, progressively higher with chain growth although
15 resolution is not sufficient to allow identification of
individual oligomers. The diol and products stain blue
when visualised with p-anisaldehyde and heat.

The presence of lower ester products in the reaction
20 residues, most notably the three- and five-component
hydroxy terminated oligomers, was confirmed through
multistage column chromatography. Despite the chemical
similarity and mutual solubility of the oligomers, which
make complete separation difficult to achieve, product
25 fractions containing one dominant species can be obtained,
allowing identification by conventional spectroscopic
means. Cross-referencing of the chromatographic data from

each fraction then gives the retention factors of each component, from which their present in or absence from subsequent reaction residues can readily be assessed.

5 The lower weight product fractions were characterised by infrared and proton NMR spectroscopy, mass spectrometry and gel permeation chromatography. IR can give little indication of chain length (other than some variation in the relative intensity of the hydroxyl absorption), but
10 will clearly show the significant end groups. The most important diagnostic features are, for hydroxyl, a strong absorption around 3450 cm^{-1} (O-H stretch); for carboxyl, a very broad absorption in the range $2400\text{--}3600\text{ cm}^{-1}$ (O-H stretch) and a broadening of the carbonyl (C=O stretch)
15 absorption to below 1720 cm^{-1} .

Proton NMR not only provides confirmation of the oligomer end groups, but can also be used to estimate the number of repeat units. The signals found in this system are a
20 multiplet at $1.66\text{--}1.68\text{ ppm}$ (central, or β , methylenes), a labile singlet at $1.70\text{--}2.10\text{ ppm}$ (hydroxyl), a multiplet at $2.33\text{--}2.34\text{ ppm}$ (methylene adjacent to carbonyl), a triplet at $3.66\text{--}3.70\text{ ppm}$ (methylene adjacent to hydroxyl), a triplet at $4.10\text{--}4.14\text{ ppm}$ (methylene adjacent to ester
25 oxygen) and a broad and labile singlet at 7.00 ppm (combined hydroxyl and carboxyl). The chain length may be determined from the relative intensity of an end group

signal. In a free acid residue, the hydroxyl singlet is often concealed within the chain methylene multiplet and the carboxyl singlet, if seen, is liable to exaggeration because of hydrogen bonding to traces of water, so the most
5 reliable signal for use as a scaling factor is the CH_2OH triplet at around 3.68 ppm. With all-hydroxy termination, for example, this must have a proton number of four, so the sum of the integrations can be translated into the total hydrogen content of the molecule, which equals $26 + 16n$
10 where n is the number of repeat units (or, in the case of a mixture of similar oligomers, the number average degree of polymerisation). This technique is useful for low oligomers of four units or fewer; with longer chains the inaccuracy in the integrations usually leads to an
15 uncertainty in n greater than one.

Unambiguous confirmation of oligomer identity is provided by mass spectrometry. Using chemical ionisation by ammonia bombardment, molecular ions are found in combination with
20 hydrogen and ammonium, that is, at $M+1$ and $M+18$, up to a molecular weight of 600-700 Daltons, above which the chains tend to fragment.

The principal technique used for analysis of the
25 polycondensation residues was gel permeation chromatography. The sample is dissolved in tetrahydrofuran and the solution passed through a column packed with a

polymer gel. Components are separated according to their molecular volume, the smaller substances tending to divert into the pores and thus follow a longer route than large molecules which pass directly through the interstices. The
5 elution of the various components is monitored by a differential refractometer and a plot produced of intensity against retention time, expressed as distance on the chart paper. The relationship of retention factor to molecular size is logarithmic, hence substances in the lower size
10 range are very well resolved and give rise to peaks which can be individually identified, whilst resolution decreases with greater size and signals eventually coalesce at a point determined by the maximum pore dimension of the column. Where the constituents of the sample are
15 structurally similar, molecular weight can be regarded as proportional to molecular volume for practical purposes.

Above the region where oligomers can be individually characterised, the condensation products have been
20 classified into molecular weight ranges by comparison of the retention factors of the measured elution peaks with those of polyethylene glycol reference standards. The data

on which analysis of the residues is based are as follows:

	<u>Species</u>	<u>Retention factor/cm (± 0.1)</u>		<u>Molecular mass/Daltons</u>
		50Å Column	500Å Column	
5	Tetrahydrofuran	16.5	18.9	72
	Diethylene glycol	16.0		106
	1,4-butanediol (B)	15.7	18.2	90
10	Adipic acid (A)	14.5	17.6	146
	AB	14.0	17.2	218
	BAB	13.6	16.8	290
	PEG 440	13.3		440
	B(AB) ₂	12.6		490
15	PEG 600	12.6		600
	B(AB) ₃	12.2		690
	PEG 960	12.0		960
	PEG 1450	11.6		1450
	PEG 4250		13.0	4250
20	PEG 7100		12.1	7100

Gel permeation chromatography was performed by Baxenden Chemicals Ltd. using Waters 440 series chromatographic equipment with THF as the mobile phase. The columns, manufactured by Polymer Laboratories Ltd., were of dimensions 600 x 7.5 mm and packed with PL gel, a highly crosslinked spherical polystyrene/divinylbenzene material of particle size 10 μ m and pore size 50Å (or 500Å where specified). The detector was a Waters model 401 differential refractometer, and estimates of molecular weight average were made by a BBC model B microcomputer from a calibration against commercial PEG samples.

Estimates of the number average and weight average molecular weights, M_n and M_w , of the product mixtures are computer-generated by calibration against commercial PEG standards and have been corrected to the known mass of residual starting material (in most cases, adipic acid, MW 146). These figures are calculated from approximate relationships and thus have lower intrinsic accuracy than direct comparisons of retention, but nonetheless they provide a convenient measure of experimental results. The confidence band of the corrected averages is estimated at $\pm 10\%$.

RESULTS

Using Lipozyme IM-20 (a product of Novo Industri A/S, 3g) as the immobilised lipase, a sample of poly(1,4-butanediol adipate) having the narrow dispersity of 1.11 and a number-average degree of polymerisation of 20 has been produced by this method. The yield corresponded to 24% of the combined initial starting material mass.

CLAIMS

1. A process for producing a polyester comprising residues of (i) at least one aliphatic dicarboxylic acid and at least one aliphatic diol or polyol or (ii) at least one
5 aliphatic hydroxyacid which process comprises reacting the diacid and the diol or polyol or the hydroxyacid in the presence of a lipase and an organic solvent.

2. A process according to claim 1 wherein the dicarboxylic acid has from 2 to 12 carbon atoms.

10 3. A process according to claim 2 wherein the dicarboxylic acid is adipic acid.

4. A process according to any one of the preceding claims wherein the diol has from 2 to 12 carbon atoms.

15 5. A process according to claim 4 wherein the diol is 1,4 butanediol.

6. A process according to any one of the preceding claims wherein the reactive carboxylic acid groups and reactive hydroxyl groups of the reactants are present in a
20 molar ratio of 1:1 to 1:1.1.

7. A process according to any one of the preceding claims which comprises reacting a diacid, a diol or polyol and a hydroxyacid in the presence of a lipase and in the presence of a polar organic solvent.

25 8. A process according to any one of the preceding claims wherein the hydroxyacid has from 2 to 12 carbon atoms.

9. A process according to any one of the preceding claims wherein the lipase is derived from Mucor

miehei.

10. A process according to claim 9 wherein the lipase is Lipozyme IM-20.

11. A process according to any one of the
5 preceding claims wherein the solvent is a straight or branched alkyl ether having from 4 to 12 carbon atoms.

12. A process according to claim 11 wherein the ether is isopropyl ether.

13. A process according to any one of the
10 preceding claims wherein the reaction is conducted at a temperature from 10 to 60°C.

14. A process according to claim 13 wherein the reaction is conducted at a temperature from 40 to 45°C.

15. A process according to any one of the
15 preceding claims wherein the water produced by the reaction is removed from the reaction vessel.

16. A process according to claim 15 wherein the water is removed using a desiccant.

17. A process according to claim 16 wherein the
20 desiccant is a molecular sieve.

18. A process according to any one of the claims 15 to 17 wherein the reaction is carried out in a two chamber reaction vessel.

19. A process according to any one of the
25 preceding claims which comprises
(a) reacting the diacid and the diol or polyol or the hydroxyacid in the presence of a straight or branched chain ether,
(b) removing residual starting materials and products having a

molecular weight less than 600 Da, and

(c) subjecting the resulting oligomeric mixture to a further polyesterification reaction.

20. A process according to any one of the
5 preceding claims which further comprises washing the reaction product with an aqueous solution of a weak base.

21. A process according to any one of the preceding claims wherein the polyester has a weight average molecular weight of from 600 to 5000 Da.

10 22. A process according to claim 21 wherein the polyester has a weight average molecular weight of from 1000 to 4500 Da.

23. A process according to any one of the preceding claims wherein the polyester has a dispersity of 1.5
15 or less.

24. A process according to claim 23 wherein the polyester has a dispersity of 1.3 or less.

25. A process according to claim 24 wherein the polyester has a dispersity of 1.1 or less.

20 26. A process according to any one of the preceding claims which further comprises reacting the polyester with isocyanate to form a urethane polymer.

27. A process substantially as described in Example 1.

25 28. A polyester or polyurethane obtainable by the process as claimed in any one of the preceding claims.

29. A polyester or polyurethane produced by the process as claimed in any one of the preceding claims.

30. A shaped article comprising a polyester or

polyurethane as claimed in claim 28 or 29 or produced by the process as claimed in any one of claims 1 to 27.

ents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9324594.2
Relevant Technical Fields (i) UK Cl (Ed.L) C3R (RPC) (ii) Int Cl (Ed.5) C08G 63/82 Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI, WPIL, EDOC, CLAIMS	Search Examiner A J RUDGE Date of completion of Search 21 FEBRUARY 1994 Documents considered relevant following a search in respect of Claims :- ALL

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