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(54) Title: PREPARATION OF POLYESTERS AND ESTERS FROM COMPOUNDS CONTAINING SECONDARY HYDROXYL GROUPS		
(57) Abstract A process for preparing a polyester from a polyol containing a secondary hydroxyl group in high yield and with an improved esterification rate is described. The process comprises reacting a polyol compound containing at least one secondary hydroxyl group with a polycarboxyl compound in the presence of at least one C ₁ -C ₃ alkyltin compound. The C ₁ -C ₃ alkyltin is selected from a C ₁ -C ₃ alkyltin salt of a carboxylic acid, a C ₁ -C ₃ alkyl stannic acid, a C ₁ -C ₃ alkyltin oxide, a C ₁ -C ₃ alkyltin halide and a mixture thereof. The invention also relates to polyesters made by the above process which may be used in molded articles, fibers, coatings and adhesive formulations. The process of the invention can also be used for the preparation of an ester from a secondary alcohol. Thus, in another embodiment, the invention relates to a process for preparing esters which comprises reacting a carboxyl compound and a secondary alcohol in the presence of a catalytically effective amount of at least one C ₁ -C ₃ alkyltin catalyst as described above.		

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PREPARATION OF POLYESTERS AND ESTERS FROM COMPOUNDS CONTAINING SECONDARY HYDROXYL GROUPS

FIELD OF THE INVENTION

5 The invention relates to an improved process for the preparation of esters and polyesters from compounds having at least one secondary hydroxyl group. Esters and polyesters are prepared in high yield and with improved esterification rates in the presence of at least one C₁-C₃ alkyltin catalyst.

BACKGROUND OF THE INVENTION

10 Esters and polyesters may be prepared by direct esterification or by transesterification reactions. In direct esterification, carboxylic acids are converted into esters by reaction with an alcohol. Similarly, polyesters may be prepared from the direct esterification between dihydric or polyhydric alcohols and dicarboxylic or polycarboxylic acids or anhydrides. In a transesterification reaction, esters are prepared by
15 reacting monocarboxylic esters with monohydric alcohols and polyesters are prepared by reacting dicarboxylic esters or polycarboxylic esters with dihydric or polyhydric alcohols. The esters and polyesters prepared by either process are useful in molded articles, fibers, coatings, and adhesives.

 Tin compounds have been used as esterification catalysts in both direct esterification
20 and transesterification reactions to prepare esters and polyesters. For example, U.S. Patent Nos. 2,720,507; 3,162,616; 4,970,288 and 5,166,310 describe the preparation of polyesters in the presence of an organotin catalyst. Further, U.S. Patent Nos. 3,345,333 and 3,716,523 describe the preparation of polyesters in a two-stage process which uses a tin catalyst to increase the efficiency of the process.

25 The use of dialkyltin oxide and dialkyltin dichloride as a catalyst for the transesterification of esters of monocarboxylic acids with 1,2 and 1,3-polyols to prepare a polyol ester is described in U.S. Patent No. 5,498,751. Although the patent teaches that products with high yield and excellent purity are obtained, the process is limited to the transesterification of esters of monocarboxylic acid with 1,2- and 1,3-polyols.

30 U.S. Patent No. 4,554,344 discloses a process for the preparation of polyesters from aromatic dicarboxylic acids or derivatives thereof and diols containing vicinal

hydroxyl groups at least one of which is secondary. This patent teaches that polyesters prepared from aromatic dicarboxylic acids and diols containing vicinal hydroxyl groups having at least one secondary hydroxyl group typically have relatively low molecular weights. The low molecular weights severely limit their usefulness in the manufacture of molded articles, fibers, coatings and other shaped articles. According to this patent, the inherent viscosity and molecular weight of the polyester prepared from aromatic dicarboxylic acid and diols containing vicinal hydroxyl groups are greatly increased by using a tin catalyst. The tin catalysts include both inorganic and organic tin compounds with butylstannoic acid being particularly preferred.

10 It is well known in the art that the rate of esterification and transesterification in the preparation of esters and polyesters from monohydric, dihydric, or polyhydric alcohols in which one or more of the hydroxyl groups are secondary is much slower than when all hydroxyl groups of the alcohol are primary. Thus, there remains a need to efficiently prepare polyesters from alcohols containing at least one secondary alcohol. Such a process would result in increased reaction rates which would in turn represent lower costs in manufacturing. 15 The present invention answers this need.

SUMMARY OF THE INVENTION

It has surprisingly been discovered that esters and polyesters can be prepared in high yield and with improved esterification rates from polyols containing at least one secondary hydroxyl group when the esterification process is conducted in the presence of at least one 20 C₁-C₃ alkyltin catalyst.

Accordingly, the invention relates to an improved process for the preparation of a polyester from polyols having secondary hydroxyl groups. The process reacts at least one polyol containing at least one secondary hydroxyl group with at least one polycarboxyl 25 compound in the presence of at least one C₁-C₃ alkyltin catalyst. The C₁-C₃ alkyltin catalyst is selected from a C₁-C₃ alkyltin salt of a carboxylic acid, a C₁-C₃ alkylstannoic acid, a C₁-C₃ alkyltin oxide, a C₁-C₃ alkyltin halide and mixtures thereof.

In another embodiment the invention relates to a process for the preparation of an ester from a secondary alcohol comprising reacting at least one secondary alcohol with at 30 least one carboxyl compound in the presence of at least one C₁-C₃ alkyltin catalyst as described above.

The process of the invention can be used for the preparation of a linear high molecular weight polyester useful in molding and fiber applications. Polyesters prepared by a process of the invention may also be used as precursors in the preparation of lower molecular weight carboxylic or hydroxyl functional polyesters. The carboxylic and hydroxyl functional polyesters may be linear or optionally branched by addition of a trifunctional or polyfunctional hydroxyl or carboxyl compound. In another embodiment, polyesters prepared according to the invention are also useful in coatings and adhesive applications.

Additional objects and advantages of the invention are discussed in the detailed description which follows, and will be obvious from that description, or may be learned by practice of the invention. It is to be understood that both this summary and the following detailed description are exemplary and explanatory only and are not intended to restrict the invention.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a plot of acid number vs. time showing the effect of organotin compounds on processing IPA/AD/TMP/TMPD high solids polyester resins in the final four hours of polyesterification.

Figure 2 is a plot of natural log of acid concentration ($\text{Ln} [\text{acid}]$) vs. time showing the effect of organotin compounds on processing IPA/AD/TMP/TMPD high solids polyester resin in the final four hours of polyesterification.

Figure 3 is a plot of acid number vs. time showing the effect of organotin compounds on processing IPA/AD/TMP/PG high solids polyester resins in the final three hours of polyesterification.

Figure 4 is a plot of natural log of acid concentration ($\text{Ln} [\text{acid}]$) vs. time showing the effect of organotin compounds on processing IPA/AD/TMP/PG high solids polyester resins in the final three hours of polyesterification.

Figure 5 is a plot of acid number vs. time showing effect of organotin compounds on processing IPA/AD/TMP/NPG polyester resin in the final four hours of polyesterification.

Figure 6 is a plot of acid number vs. time showing effect of organotin compounds on processing IPA/AD/TMP/BEPD polyester resin in the final two hours of polyesterification.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a process for preparing a polyester comprising reacting at least one polyol having at least one secondary hydroxyl group and at least one polycarboxyl

compound in the presence of a catalytically effective amount of at least one C₁-C₃ alkyltin catalyst selected from a C₁-C₃ alkyltin salt of a carboxylic acid, a C₁-C₃ alkylstannoic acid, a C₁-C₃ alkyltin oxide, a C₁-C₃ alkyltin halide and mixtures thereof.

The polyol compound employed in the process of the invention contains at least one
5 secondary hydroxyl group and preferably from about 2 to about 40 carbon atoms, more preferably from about 3 to about 26 carbon atoms. Suitable polyols include triols such as 1,2,3-trihydroxypropane (glycerol); 1,2,4-butanetriol; 1,2,6-trihydroxyhexane; and 1,3,5-cyclohexanetriol. The preferred polyol employed in the invention is a diol containing from
10 diols may be aliphatic, cycloaliphatic or aromatic, and may or may not contain unsaturation. Examples include, but are not limited to 1,2-propanediol, 1,2-butanediol, 1,4-cyclohexanediol, 2,2,4,4-tetramethylcyclobutanediol, 2,2,4-trimethyl-1,3-pentanediol or mixtures thereof. Particularly suitable diols include 2,2,4-trimethyl-1,3-pentanediol, 1,2-propanediol, and 2,2,4,4-tetramethylcyclobutanediol.

15 Polyesters containing both secondary and primary polyols may also be prepared by the process of the invention. Polyols without secondary hydroxyl groups suitable for use in the invention include aliphatic, cycloaliphatic or aromatic polyols which can be either saturated or unsaturated and contain from about 2 to about 40 carbon atoms. Preferably the polyol is a diol containing from about 2 to about 20, more preferably from about 2 to about
20 12, and still more preferably from about 2 to about 8 carbon atoms per molecule. Such diols include, but are not limited to, ethylene glycol, 1,4-butanediol, 1,3-butanediol, pentanediol, hexanediol, heptanediol, neopentyl glycol, nonanediol, decanediol, diethylene glycol, dipropylene glycol, cyclohexanedimethanol, 2-methyl-1,3-propanediol and mixtures thereof. The preferred diols containing both primary hydroxyl groups include neopentyl glycol,
25 ethylene glycol, cyclohexanedimethanol and mixtures thereof.

The polycarboxyl compound may be aliphatic, cycloaliphatic or aromatic and may or may not contain unsaturation. Also suitable are the anhydrides and lower, *e.g.*, C₁-C₈ alkyl esters thereof. Suitable aromatic polycarboxyl compounds may be derived from single ring, multiple ring and fused ring system compounds. The carboxylic acid groups may be directly
30 substituted on an aromatic ring, or part of an alkyl group that is substituted on the ring. In addition, the aromatic ring may be further substituted with one or more functional groups, *e.g.*, halogen, amino, cyano, nitro, as well as alkyl, alkoxy and alkylthio groups containing

from 1 to 20 carbon atoms. The aromatic polycarboxyl compounds preferably contain from about 7 to about 20, more preferably from about 8 to about 12 carbon atoms.

The aliphatic and cycloaliphatic polycarboxyl compounds may be derived from saturated, monounsaturated and polyunsaturated carboxylic acids. These acids may be straight or branched and may be substituted with one or more of the groups listed above as being suitable for aromatic ring substitution. The aliphatic and cycloaliphatic carboxyl compounds preferably contain from about 2 to about 40, more preferably from about 3 to about 26 carbon atoms.

Examples of suitable polycarboxyl compounds include 1,2,4-benzenetricarboxylic anhydride (trimellitic anhydride); 1,2,4-benzenetricarboxylic acid (trimellitic acid); and 1,3,5-cyclohexanetricarboxylic acid. Preferred polycarboxyl compounds are dicarboxyl compounds. Examples of suitable dicarboxyl compounds include, but are not limited to, terephthalic acid, isophthalic acid, adipic acid, 1,4-cyclohexanedicarboxylic acid, dimethylterephthalate, phthalic anhydride, maleic anhydride and mixtures thereof. Particularly suitable dicarboxyl containing compounds include terephthalic acid, isophthalic acid and adipic acid.

The mole ratio of polyol to polycarboxyl compound can be varied over a wide range. The preferred mole ratio ranges from about 0.5 to about 1.5, more preferably from about 0.8 to about 1.2.

The C_1 - C_3 alkyltin catalyst employed in the invention may be a C_1 - C_3 alkyltin salt of a carboxylic acid represented by the formula $(R)_2Sn(O_2CR^1)_2$, $RSn(O_2CR^1)_3$, or $(R)_2Sn(O_2CR^1)Y$. The R group may be the same or different and is an alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom. R^1 may be the same or different and is an alkyl group having from about 1 to about 20 carbon atoms which may be linear, branched, substituted or unsubstituted. Preferably R^1 contains from about 1 to about 12, more preferably from about 1 to about 8 carbon atoms. R^1 may also be an aryl group such as phenyl or naphthyl, an alkaryl group such as tolyl or phenylethyl or a cycloalkyl group such as cyclohexyl. Preferred aryl, alkaryl and cycloalkyl groups contain from about 3 to about 14 carbon atoms. Y is a halogen, preferably bromine or chlorine. Examples of suitable organotin salts of carboxylic acids include, but are not limited to, dimethyltin diacetate, diethyltin diacetate, dipropyltin diacetate, dimethyltin

dilaurate, methyltin trilaurate, ethyltin trilaurate, propyltin trilaurate and mixtures thereof.

A C₁-C₃ alkylstannoic acid of the formula RSn(O)OH may also be employed as the C₁-C₃ alkyltin catalyst. The R group is as defined above. Examples of suitable C₁-C₃ alkylstannoic acids include, but are not limited to methylstannoic acid, propylstannoic acid, ethylstannoic acid and mixtures thereof.

The C₁-C₃ alkyltin catalysts may also be an C₁-C₃ alkyltin oxide of the formula (R)₂SnO. R may be the same or different and is as defined above. Examples of suitable C₁-C₃ alkyltin oxides include, but are not limited to dimethyltin oxide, diethyltin oxide, dipropyltin oxide, methylethyltin oxide, methylpropyltin oxide, ethylpropyltin oxide and mixtures thereof. Preferred C₁-C₃ alkyltin oxides for use in the process of the invention include dimethyltin oxide, dimethyltin dilaurate and methylstannoic acid. The oxides can be generated in situ by hydrolyzing an appropriate C₁-C₃ alkyltin halide with a base such as ammonium hydroxide. Suitable C₁-C₃ alkyltin halides are described below.

The C₁-C₃ alkyltin catalysts useful in the process of the present invention also include C₁-C₃ alkyltin halides of the formula (R)_nSn(X)_{3-n} wherein R may be same or different and is as defined above; n is 1 or 2; and X is a halide, preferably chloride or fluoride. Examples of suitable C₁-C₃ alkyltin halides include methyltin trifluoride, dimethyltin dichloride, diethyltin dichloride, dipropyltin dichloride, methylethyltin dichloride, ethylpropyltin dichloride, methylpropyltin dichloride or a mixture thereof. The preferred C₁-C₃ alkyltin halide is dimethyltin dichloride. Under certain reaction conditions, however, the use of dichlorides may generate hydrochloric acid.

The C₁-C₃ alkyltin catalyst used in the process of the invention is present in a catalytically effective amount, preferably ranging from about 0.001 to about 3, more preferably from about 0.01 to about 1.0, and most preferably from about 0.05 to about 0.2 weight percent based upon the weight of the reactants (based on % tin in the C₁-C₃ alkyltin catalyst).

The processes of the invention are conducted under conditions sufficient to form the desired polyester. The temperature and pressure should be maintained such that the water of esterification or alcohol of transesterification are removed to give maximum reaction rate and allow the reaction to proceed to completion.

The process of the invention may be conducted as a melt of the polyol and the polycarboxyl compound under inert or nonoxidizing atmosphere using conventional polyester-forming conditions of temperature, pressure and time. The temperature of the reaction varies depending on the reactants and the desired properties of the polyester.

- 5 Preferably the temperature ranges from about 160°C to about 280°C, more preferably from about 180 °C to about 250 °C. Temperatures below about 150 °C are generally not sufficient to provide sufficient rate of reaction.

The pressure at which the reaction is carried out also varies depending on the reactants and the properties of the polyester desired. In general, the pressure ranges from
10 about 700 mm Hg to about 1,500 mm Hg. If higher molecular weight polyesters are desired the reaction should be finished at lower pressures. Depending on the molecular weight desired, the pressure of the reaction ranges from about 100 mm Hg to below about 10 mm Hg.

The process of the invention may also be conducted in a suitable solvent.

- 15 Suitable solvents include, but are not limited to aromatic hydrocarbons, ethers, sulfones, halogenated aromatic hydrocarbons, ketones, sulfolanes, sulfoxides and combination thereof. Particularly suitable solvents include toluene, xylene, diphenyl ether, dimethyl sulfolane and combinations thereof. The solvent may be a solvent for the reactants, products or both. The solvents can be employed in amounts ranging from about 40 to
20 about 95, preferably from about 45 to about 90, more preferably from about 50 to about 90 percent based on the weight of the reactants.

To control molecular weight, monofunctional compounds may be incorporated into the reaction mixture. Suitable monofunctional reactants include, but are not limited to benzoic acid, tert-butylbenzoic acid, phenylbenzoic acid, stearic acid, tert-
25 butylbenzoic acid, phenylbenzoic acid, stearic acid, tert-butylphenol, benzyl alcohol or combinations thereof. When employed the monofunctional compounds are present in amounts ranging from about 0.01 to about 10, preferably from about 1 to about 8, more preferably from about 2 to about 5 weight percent based upon the total weight of reactants.

- 30 The polyester prepared by the process of the invention can be used as precursors in the preparation of a lower molecular weight carboxylic or hydroxyl functional polyester which may be linear or optionally branched by the addition of a trifunctional or

polyfunctional branching agent as described above. When lower molecular weight carboxylic or hydroxyl functional polyesters are desired it is particularly useful to introduce a chain branching agent into the reaction mixture. Suitable chain branching agents include tri- or poly- functional reactants. The tri- or poly-functional reactant can be either hydroxyl, acid or anhydride functional. Particularly suitable tri- or poly-functional reactants include but are not limited to trimellitic anhydride, trimethylolpropane, glycerine, triethylolpropane and pentaerythritol and combinations thereof.

The polyfunctional compounds, when desired, are employed in amounts ranging from about 0.01 to about 10, preferably from about 0.1 to about 7, more preferably from about 0.1 to about 5 weight percent based upon the total weight of reactants. These polyesters are useful in coating and adhesive applications. Accordingly, the invention also relates to materials such as metals, paper and paperboard, and synthetic polymers having coated thereon one or more of the polyester compositions described above.

The C_1 - C_3 alkyltin compounds, discussed above, may also be used as catalysts in simple esterification and transesterification reactions. Thus, another embodiment of the invention relates to a method for the preparation of esters comprising reacting a carboxyl compound and a secondary alcohol in the presence of a catalytically effective amount of at least one C_1 - C_3 alkyltin catalyst.

The secondary alcohols employed in the process of the invention preferably contain from about 2 to about 40 carbon atoms. The preferred alcohol contains from about 3 to about 20 carbon atoms, preferably from about 3 to about 8 carbon atoms. Examples of suitable secondary alcohols include 2-propanol, 2-butanol, cyclohexanol and cyclohexylmethanol. The ester prepared by the process of the invention may contain a mixture of secondary alcohols and primary alcohols without a secondary hydroxyl group.

Like the polycarboxyl compound used in the preparation of polyesters, the carboxyl compound used for preparing esters may be aliphatic, cycloaliphatic or aromatic and may or may not contain unsaturation. Also suitable are the anhydrides and lower, *e.g.*, C_1 - C_8 alkyl esters thereof. Suitable aromatic carboxyl compounds may be derived from the same ring system compounds as the polycarboxyl compound described above. The carboxylic acid groups may be directly substituted on an aromatic ring, or

part of an alkyl group that is substituted on the ring. In addition, the aromatic ring may be further substituted with one or more functional groups, *e.g.*, halogen, amino, cyano, nitro, as well as alkyl, alkoxy and alkylthio groups containing from 1 to 20 carbon atoms. The aromatic carboxyl compounds preferably contain from about 7 to about 20, more preferably from about 8 to about 12 carbon atoms.

The aliphatic and cycloaliphatic carboxyl compounds may be derived from saturated, monounsaturated and polyunsaturated carboxylic acids. These acids may be straight or branched and may be substituted with one or more of the groups listed above as being suitable for aromatic ring substitution. The aliphatic and cycloaliphatic carboxyl compounds preferably contain from about 2 to about 40, more preferably from about 3 to about 26 carbon atoms.

Propionic acid, butyric acid, cyclohexanecarboxylic acid and benzoic acid are particularly preferred carboxyl compounds useful in the simple esterification and transesterification process of the invention. The preferred C₁-C₃ alkyltin catalyst for this esterification is the same as described above. The mole ratio of secondary alcohol and carboxyl compound can be varied over a wide range with a 1:1 mole ratio being particularly preferred. In some cases, however, it may be advantageous to include an excess of secondary alcohol. Like the reaction to form the polyester, the reaction may be conducted in a melt or solution.

20 EXAMPLES

The practice of the invention is disclosed in the following examples, which should not be construed to limit the invention in any way.

All reactions were carried out in 2-L flasks equipped with thermocouple, automatic stirrer, and oil heated partial condenser connected to a water cooled condenser for collection and weighing water of esterification. The reaction apparatus were computer controlled by CAMILLE® automatic data acquisition and control software to make as accurate comparison of catalyst activities as possible. All variables, such as upheat rate, column temperature, reaction temperature, and stirring rate were identical. For each example, three identical polyesters were prepared simultaneously, each containing a different organotin compound as catalyst. Reaction rates were measured by monitoring the acid number of the reaction mixture until the desired degree of reaction was achieved. First order rate constants for

Example 1 were obtained from regression analysis of plots of the natural log of acid concentration ($\text{Ln} [\text{Acid}]$) vs. time.

EXAMPLE 1

The following reactants were charged to three 2-L flasks:

5		<u>Grams</u>	<u>Moles</u>
	2,2,4-Trimethyl-1,3-propanediol (TMPD)	447.5	3.06
	Trimethylolpropane (TMP)	19.5	0.22
	Isophthalic acid (IPA)	182	1.1
	Adipic acid (AD)	160	1.1
10	Organotin catalyst	0.05 wt.% of total charge (based on % Sn in organotin catalyst)	

Three organotin catalysts were evaluated:

	<u>Reaction Flask</u>	<u>Organotin Catalyst</u>	<u>Grams</u>	<u>%Sn</u>
	1	Dibutyltin oxide	0.90	0.43
15	2	Butylstannoic Acid	0.75	0.43
	3	Dimethyltin oxide	0.60	0.43

The reaction mixtures were heated to 150 °C at a constant rate of 2 deg/min until all reactants were molten. The reaction mixtures were then heated to 215 °C at a constant rate of 2 deg/min and held at that temperature until an acid number less than 10 was obtained. The relative activities of the three organotin catalysts were determined by monitoring the acid number of the reaction mixtures during the final four hours of polyesterification. The results of acid number vs. time is shown in Table 1 and plotted in Figure 1.

TABLE 1

	Dibutyltin Oxide	Butylstannoic Acid	Dimethyltin Oxide
Time (hour)	Acid Number	Acid Number	Acid Number
0	62.6	52.4	55.0
0.5	50.0	40.0	31.3
1.0	39.8	28.0	17.5
1.5	30.0	21.0	10.7
2.0	23.0	12.6	5.6
2.5	17.0	9.1	4.2
3.0	12.0	n.d.*	n.d.
4.0	7.0	n.d.	n.d.

* n.d. = not determined

First order rate constants, obtained from regression analysis of $\ln [\text{Acid}]$ vs. time, for each catalyst evaluated are listed in Table 2 and plotted in Figure 2.

TABLE 2

	Dibutyltin Oxide	Butylstannoic Acid	Dimethyltin Oxide
k(hr ⁻¹)	0.57	0.71	1.05

These results show that dimethyltin oxide gives a two fold increase in esterification rate compared with dibutyltin oxide, and a fifty percent increase in reaction rate compared with butylstannoic acid, thus providing a substantial improvement prior processes.

20 EXAMPLE 2

The following reactants were charged to two 2-L flasks.

	Grams	Moles
1,2-Propanediol (propylene glycol, PG)	232.86	3.06
Trimethylolpropane (TMP)	19.5	0.22
Isophthalic acid (IPA)	182	1.1
Adipic acid (AD)	160	1.1

Organotin catalyst 0.05 wt.% of total charge (based on % Sn in organotin catalyst)

Two organotin catalysts were evaluated:

<u>Reaction Flask</u>	<u>Organotin Catalyst</u>	<u>Grams</u>	<u>%Sn</u>
5 1	Butylstannoic Acid	0.75	0.43
2	Dimethyltin oxide	0.60	0.43

The reaction mixtures were heated to 150 °C at a constant rate of 2 deg/min until all reactants were molten. The reaction mixtures were then heated to 190 °C at a constant of 2 deg/min and held at that temperature until an acid number less than 10 was
 10 obtained. The relative activities of the two organotin catalysts were determined by monitoring the acid number of the reaction mixtures during the final three hours of polyesterification. The results of acid number vs. time is shown in Table 3 and plotted in Figure 3.

TABLE 3

	Butylstannoic Acid	Dimethyltin Oxide
15 Time (hour)	Acid Number	Acid Number
	58.32	52.6
	41.4	31.7
	30.2	19.7
	22.5	13.4
20 2.0	18.5	9.6
	15.4	7

First order rate constants, obtained from regression analysis of Ln [Acid] vs. time, for each catalyst evaluated are listed in Table 4 and plotted in Figure 4.

25

TABLE 4

	Butylstannoic Acid	Dimethyltin Oxide
k(hr ⁻¹)	0.53	0.8

These results show again that the lower alkyl organotin oxide gives a fifty percent rate increase with a glycol containing a secondary hydroxyl group when compared with butylstannoic acid, thus providing a substantial improvement over prior processes.

COMPARATIVE EXAMPLE 1

5 The following reactants were charged to three 2-L flasks:

	<u>Grams</u>	<u>Moles</u>
Neopentyl glycol (NPG)	654.67	6.2853
Trimethylolpropane (TMP)	93.52	0.697
Isophthalic acid (IPA)	519.95	3.130
10 Adipic acid (AD)	457.13	3.128
Organotin catalyst	0.05 wt.% of total charge (based on % Sn in organotin catalyst)	

Three organotin catalysts were evaluated:

<u>Reaction Flask</u>	<u>Organotin Catalyst</u>	<u>Grams</u>	<u>%Sn</u>
15 1	Dibutyltin oxide	1.79	0.86
2	Butylstannoic Acid	1.50	0.86
3	Dimethyltin oxide	1.16	0.86

The reaction mixtures were heated to 150 °C at a constant rate of 2 deg/min until
 20 all reactants were molten. The reaction mixtures were then heated to 230 °C at a
 constant rate of 2 deg/min and held at that temperature until an acid number less than 10
 was obtained. The relative activities of the three organotin catalysts were determined by
 monitoring the acid number of the reaction mixtures during the final four hours of
 polyesterification. The results of acid number vs. time is shown in Table 5 and plotted in
 25 Figure 5.

TABLE 5

	Dibutyltin Oxide	Butylstannoic Acid	Dimethyltin Oxide
Time (hour)	Acid Number	Acid Number	Acid Number
0	121	73	101
0.5	58	26	36.8
1.0	29	14	16.0
1.5	14	10	10.9
2.0	11	9.4	10.6
2.75	8.6	8.6	8.7
3.75	7.5	7.5	7.0

10 The data which is summarized in Table 5, and plotted in Figure 5, show that no improvement in esterification rate is observed, regardless of the organotin catalyst, when the diol contains only primary hydroxyl groups.

COMPARATIVE EXAMPLE 2

The following reactants were charged to two 2-L flasks.

15		Grams	Moles
	2-Butyl-2-Ethyl-1,3-Propanediol (BEPD)	489.0	3.06
	Trimethylolpropane (TMP)	19.5	0.22
	Isophthalic acid (IPA)	182	1.1
	Adipic acid (AD)	160	1.1
20	Organotin catalyst	0.05 wt.% of total charge (based on % Sn in organotin catalyst)	

Two organotin catalysts were evaluated:

<u>Reaction Flask</u>	<u>Organotin Catalyst</u>	<u>Grams</u>	<u>%Sn</u>
1	Butylstannoic Acid	0.75	0.43
25	2 Dimethyltin oxide	0.60	0.43

The reaction mixtures were heated to 150°C at a constant rate of 2 deg/min until all reactants were molten. The reaction mixtures were then heated to 215°C at a constant rate of 2 deg/min and held at that temperature until an acid number less than 10 was obtained. The relative activities of the two organotin catalysts were determined by monitoring the

acid number of the reaction mixtures during the final two hours of polyesterification. The results of acid number vs. time is shown in Table 6 and plotted in Figure 6.

TABLE 6

	Butylstannoic Acid	Dimethyltin Oxide
Time (hour)	Acid Number	Acid Number
0	70.1	91.2
0.5	18.9	27.0
1	9.3	9.26
1.5	6.2	4.2

5

These results show that no improvement in esterification rate is observed when
10 the diol contains primary hydroxyl groups.

WHAT IS CLAIMED IS:

1. A process for preparing a polyester from polyols having secondary hydroxyl groups comprising the step of reacting:
 - (a) at least one polyol containing at least one secondary hydroxyl group;
 - 5 (b) at least one polycarboxyl compound selected from a polycarboxylic acid, a polycarboxylic acid anhydride, a lower alkyl ester of a polycarboxylic acid, or a mixture thereof; and
 - (c) a catalytically effective amount of at least one C₁-C₃ alkyltin compound selected from the group consisting of a C₁-C₃ alkyltin salt of a carboxylic acid; a C₁-C₃ alkylstannic acid; a C₁-C₃ alkyltin oxide; a C₁-C₃ alkyltin halide; and a mixture thereof.
- 10 2. A process according to Claim 1, wherein the mole ratio of polyol to polycarboxyl compound ranges from about 0.5 to about 1.5.
3. A process according to Claim 1, wherein the reaction is conducted as a melt of the polyol and the polycarboxyl compound.
- 15 4. A process according to Claim 3, wherein the temperature of the reaction ranges from about 160°C to about 280°C.
5. A process according to Claim 1, wherein the reaction is conducted in a solvent selected from an aromatic hydrocarbon, an ether, a sulfone, a ketone, a sulfolane, a sulfoxide and a mixture thereof.
- 20 6. A process according to Claim 1, wherein the polyol compound containing at least one secondary hydroxyl group is a diol and the polycarboxyl compound is a dicarboxyl compound.
7. A process according to Claim 6, wherein the dicarboxyl compound is terephthalic acid; isophthalic acid; adipic acid; 1,4-cyclohexanedicarboxylic acid; 25 dimethyl-terephthalate; phthalic anhydride; maleic anhydride; or a mixture thereof and the diol is 1,2-propanediol; 1,2-butanediol; 1,4-cyclohexanediol; 2,2,4,4-tetramethylcyclobutanediol; 2,2,4-trimethyl-1,3-pentanediol; or a mixture thereof.
8. A process according to Claim 1, wherein
 - (a) the C₁-C₃ alkyltin salt of a carboxylic acid has the following formula:
 - 30 (I) $(R)_2Sn(O_2CR^1)_2$
 - (II) $RSn(O_2CR^1)_3$
 - (III) $(R)_2Sn(O_2CR^1)Y$

wherein R, which can be the same or different, is a C₁-C₃ alkyl; R¹, which can be the same or different, is C₁-C₂₀ alkyl group or a C₃-C₁₄ aryl, alkaryl or cycloalkyl group; and Y is a halogen;

(b) the C₁-C₃ alkylstannoic acid has the formula RSn(O)OH wherein R is
5 defined above;

(c) the C₁-C₃ alkyltin oxide has the formula (R)₂SnO wherein R, which may be the same or different, is defined above; and

(d) the C₁-C₃ alkyltin halide has the formula (R)_nSn(X)_{3-n} wherein R, which may be the same or different, is defined above; n is 1 or 2; and X is a halide.

10 9. A process according to Claim 8, wherein

(a) the C₁-C₃ alkyltin salt of a carboxylic acid is dimethyltin diacetate, diethyltin diacetate, dipropyltin diacetate, dimethyltin dilaurate, methyltin trilaurate, ethyltin trilaurate, propyltin trilaurate or a mixture thereof;

(b) the C₁-C₃ alkylstannoic acid is methylstannoic acid, propylstannoic acid,
15 ethylstannoic acid or a mixture thereof;

(c) the C₁-C₃ alkyltin oxide is dimethyltin oxide, diethyltin oxide, dipropyltin oxide, methylethyltin oxide, ethylpropyltin oxide, methylpropyltin oxide or a mixture thereof; and

(d) the C₁-C₃ alkyltin halide is methyltin trifluoride, dimethyltin dichloride,
20 diethyltin dichloride, dipropyltin dichloride, methylethyltin dichloride, ethylpropyltin dichloride, methylpropyltin dichloride or a mixture thereof.

10. A process according to Claim 9, wherein

(a) the C₁-C₃ alkyltin salt of a carboxylic acid is a dimethyltin diacetate;

(b) the C₁-C₃ alkyl stannoic acid is a methylstannoic acid;

25 (c) the C₁-C₃ alkyltin oxide is dimethyltin oxide; and

(d) the C₁-C₃ alkyltin halide is dimethyltin dichloride.

11. A process according to Claim 10, wherein the C₁-C₃ alkyltin compound is dimethyltin oxide.

12. A polyester prepared by the process according to Claim 1.

30 13. A process for preparing an ester from an alcohol having a secondary hydroxyl group comprising the steps of reacting:

(a) at least one secondary alcohol;

(b) at least one carboxyl compound selected from a carboxylic acid, a carboxylic anhydride or a lower alkyl ester of a carboxylic acid; and

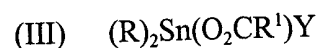
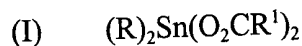
(c) a catalytically effective amount of at least one C₁-C₃ alkyltin compound selected from the group consisting of a C₁-C₃ alkyltin salt of a carboxylic acid, a C₁-C₃ alkyl stannic acid, a C₁-C₃ alkyltin oxide, a C₁-C₃ alkyltin halide; and a mixture thereof.

14. A process according to Claim 13, wherein the secondary alcohol is 1,2,3-trihydroxypropane; 1,2,4-butanetriol; 1,2,6-trihydroxyhexane; 1,3,5-cyclohexanetriol; or a mixture thereof and the carboxyl compound is 1,2,4-benzenetricarboxylic anhydride; 1,2,4-benzenetricarboxylic acid; 1,3,5-cyclohexanetricarboxylic acid; or a mixture thereof.

15. A process according to Claim 13, wherein the reaction is conducted in a solvent selected from an aromatic hydrocarbon, an ether, a sulfone, a ketone, a sulfolane, a sulfoxide and a mixture thereof.

16. A process according to Claim 13, wherein

(a) the C₁-C₃ alkyltin salt of a carboxylic acid has the following formula:



wherein R, which can be the same or different, is a C₁-C₃ alkyl; R¹, which can be the same or different, is a C₁-C₂₀ alkyl group or a C₃-C₁₄ aryl, alkaryl or cycloalkyl group; and Y is a halogen;

(b) the C₁-C₃ alkylstannic acid has the formula RSn(O)OH wherein R is defined above;

(c) the C₁-C₃ alkyltin oxide has the formula (R)₂SnO wherein R, which may be the same or different, is defined above; and

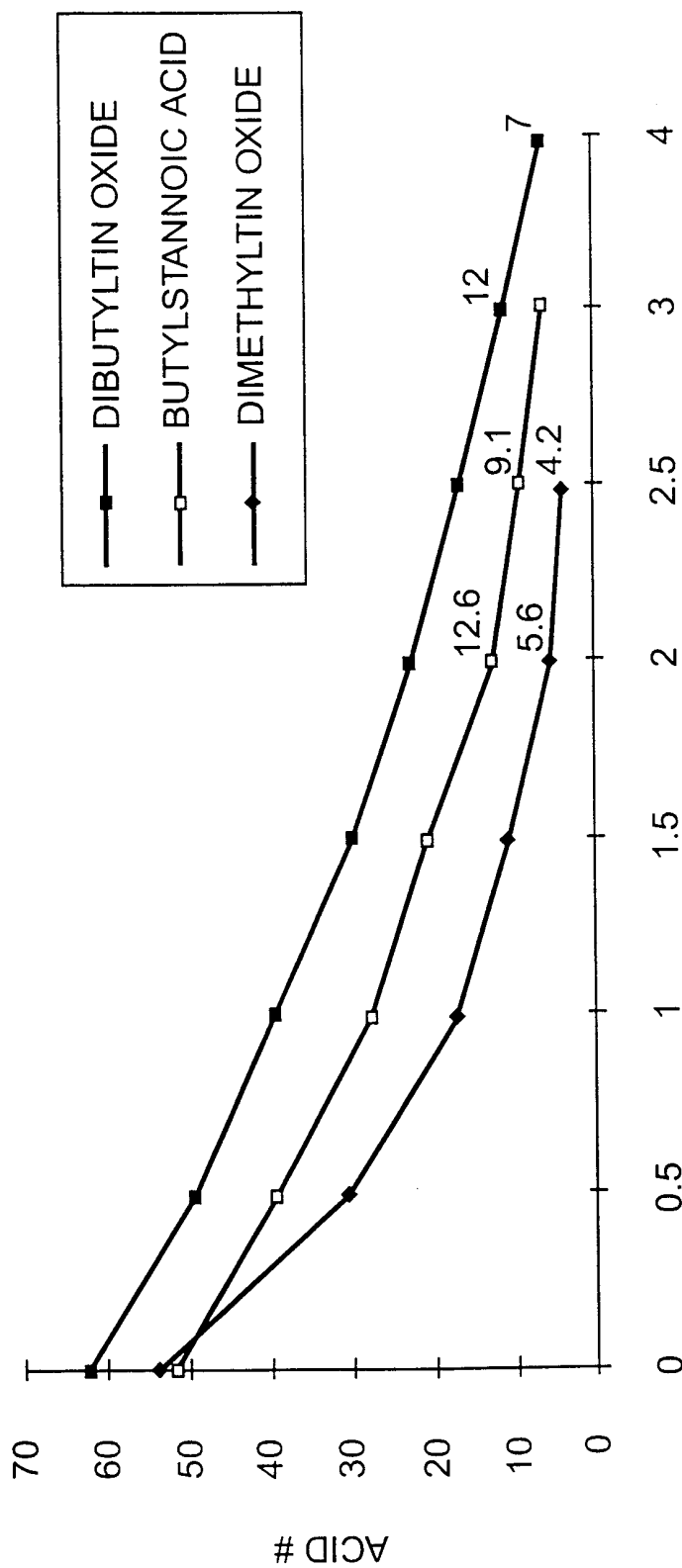
(d) the C₁-C₃ alkyltin halide has the formula (R)_nSn(X)_{3-n} wherein R, which may be the same or different, is defined above; n is 1 or 2; and X is a halide.

17. A process according to Claim 16, wherein

(a) the C₁-C₃ alkyltin salt of a carboxylic acid is dimethyltin diacetate, diethyltin diacetate, dipropyltin diacetate, dimethyltin dilaurate, methyltin trilaurate, ethyltin trilaurate, propyltin trilaurate or a mixture thereof;

- (b) the C₁-C₃ alkyl stannic acid is methylstannic acid, propylstannic acid, ethylstannic acid or a mixture thereof;
- (c) the C₁-C₃ alkyltin oxide is dimethyltin oxide, diethyltin oxide, dipropyltin oxide, methylethyltin oxide, methylpropyltin oxide, ethylpropyltin oxide or a mixture thereof; and
- (d) the C₁-C₃ alkyltin halide is methyltin trifluoride, dimethyltin dichloride, diethyltin dichloride, dipropyltin dichloride, methylethyltin dichloride, ethylpropyltin dichloride, methylpropyltin dichloride or a mixture thereof.
18. A process according to Claim 17, wherein
- 10 (a) the C₁-C₃ alkyltin salt of a carboxylic acid is a dimethyltin diacetate;
- (b) the C₁-C₃ alkyl stannic acid is a methylstannic acid;
- (c) the C₁-C₃ alkyltin oxide is dimethyltin oxide; and
- (d) the C₁-C₃ alkyltin halide is dimethyltin dichloride.
19. A process according to Claim 18, wherein the C₁-C₃ alkyltin compound is
- 15 dimethyltin oxide.

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FINAL FOUR HOURS OF POLYESTERIFICATION

FIG. 1

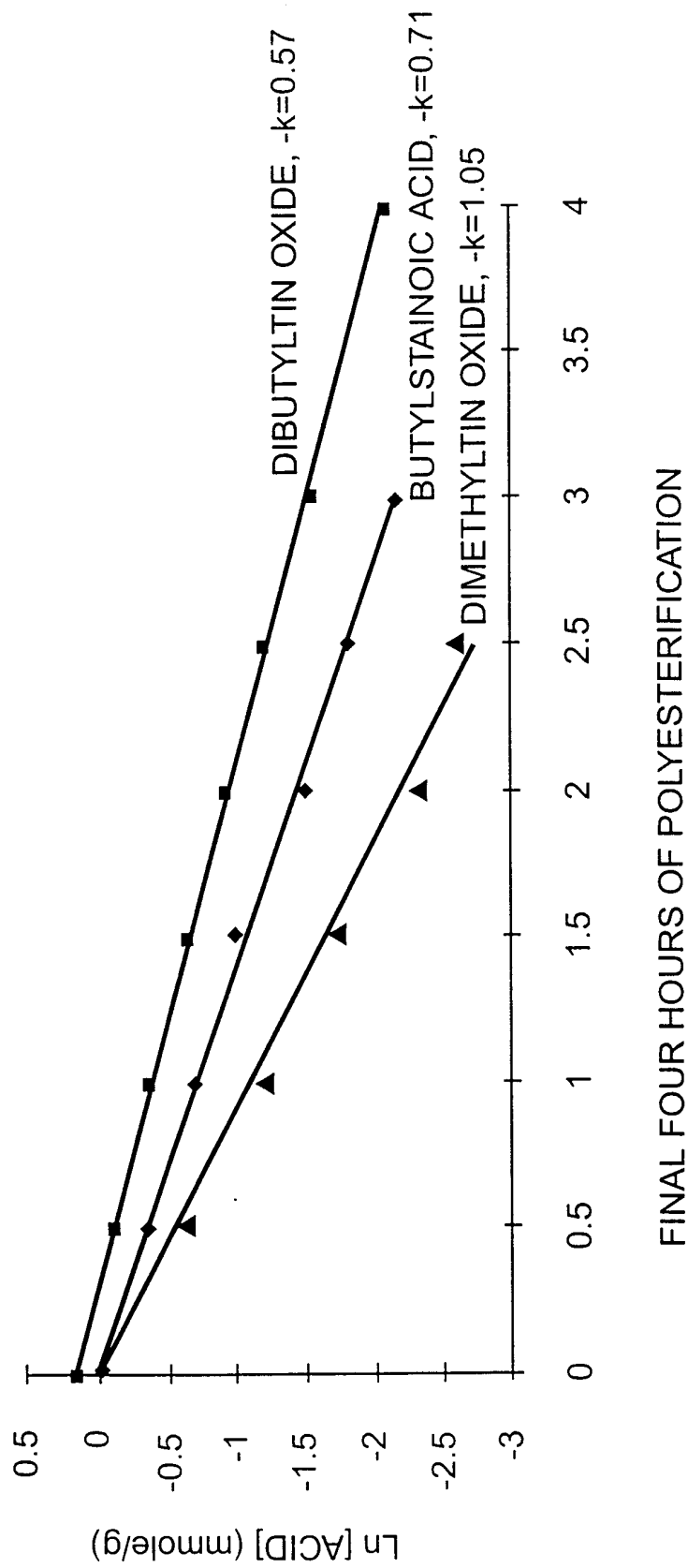
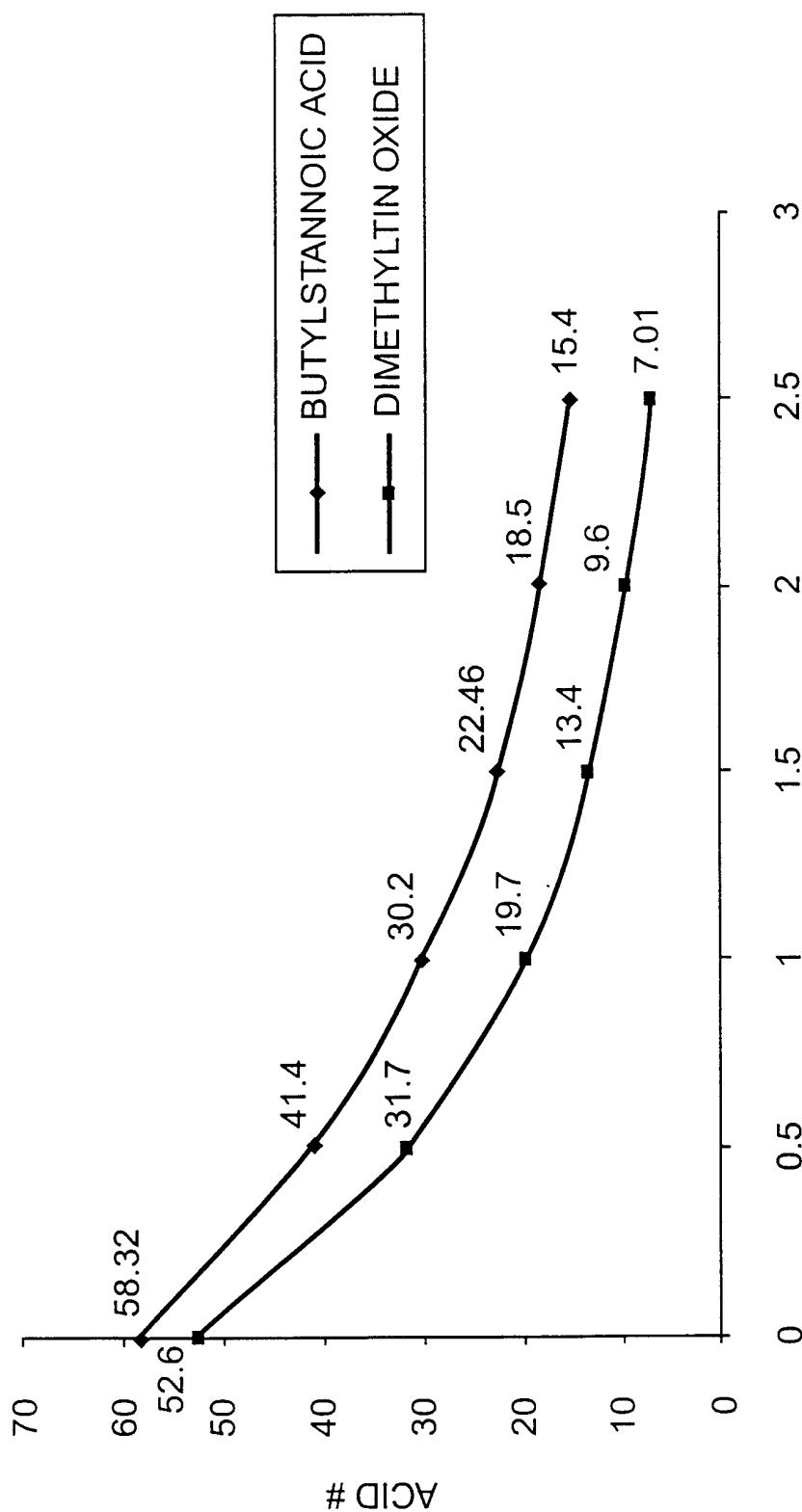


FIG. 2



FINAL THREE HOURS OF POLYESTERIFICATION

FIG. 3

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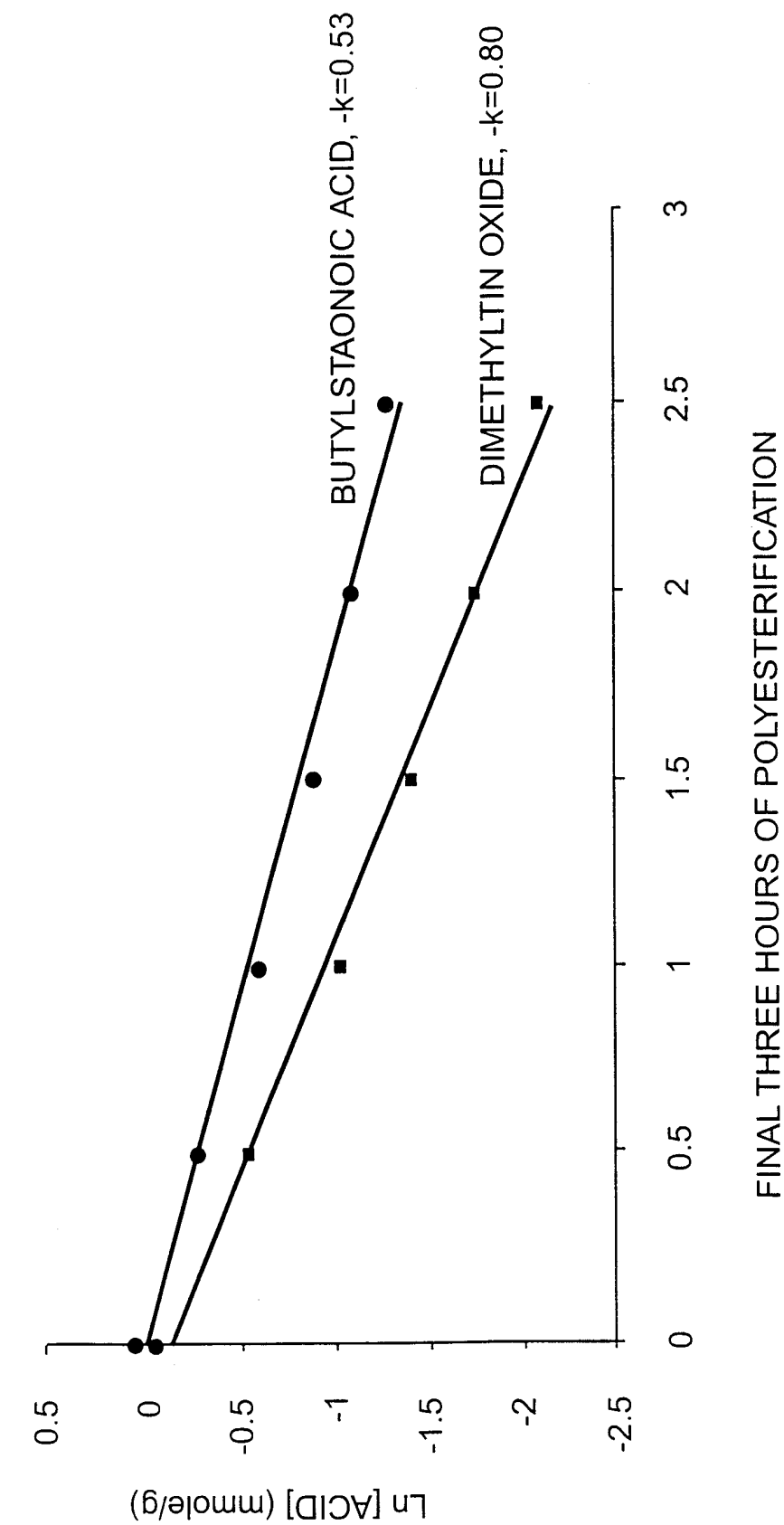


FIG. 4

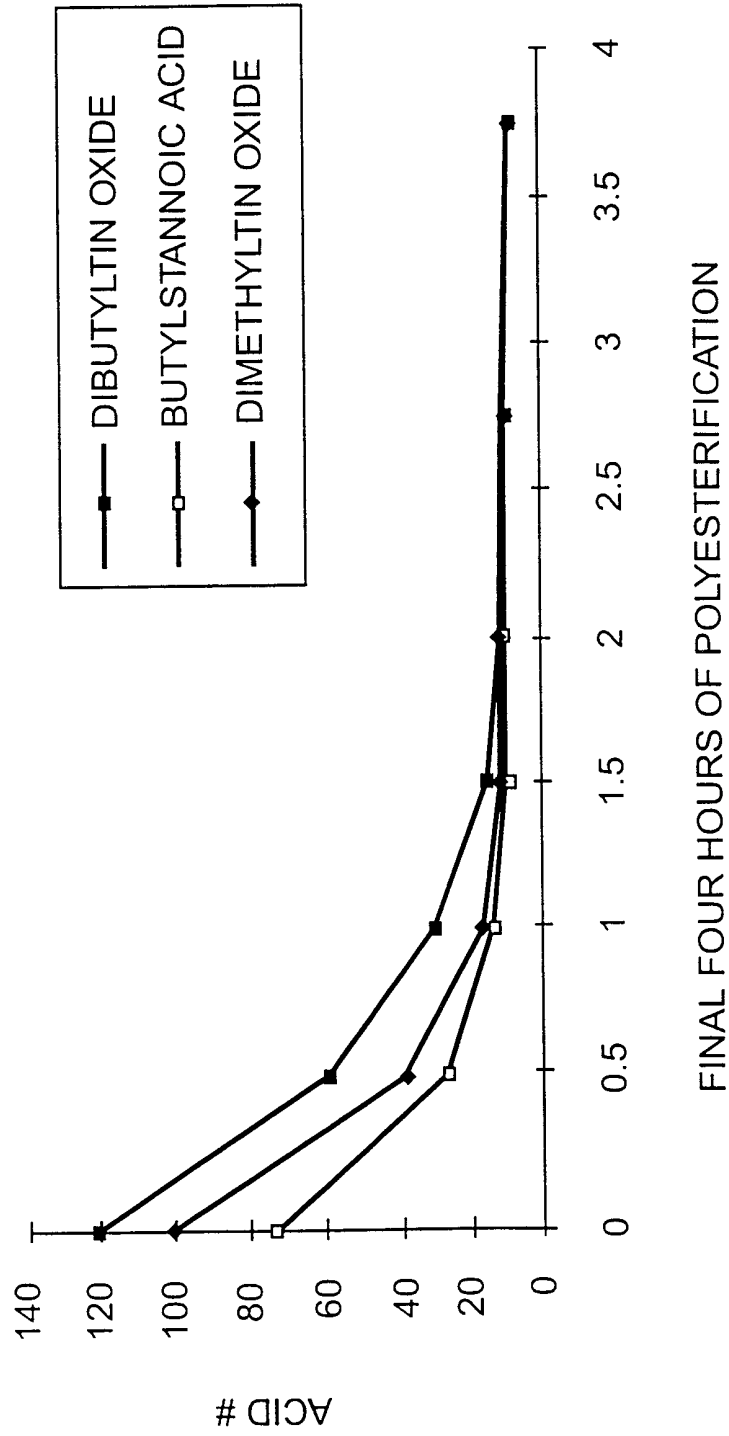
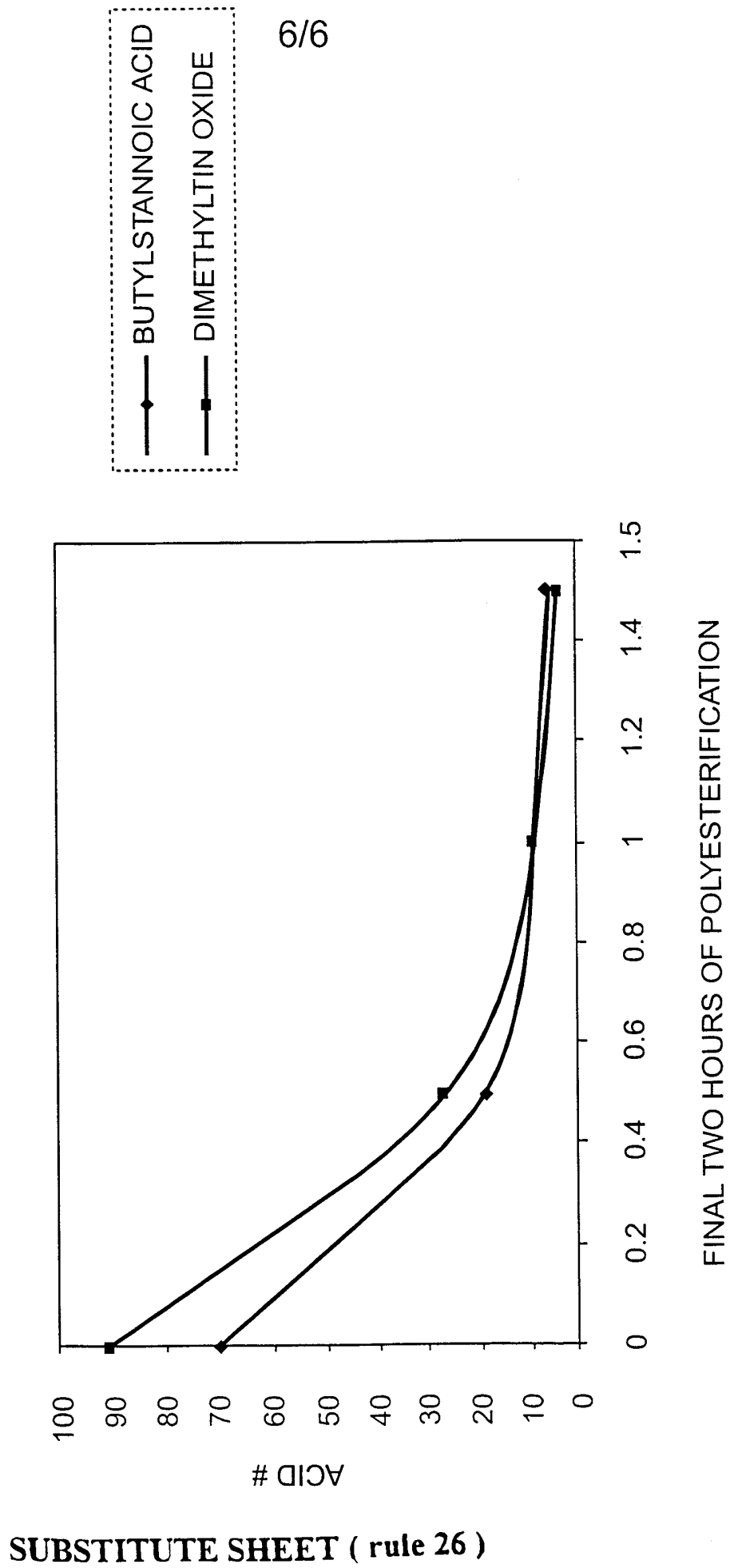


FIG. 5



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FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/25578

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08G63/85 C07C67/03 C07C67/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 85, no. 12, 20 September 1976 Columbus, Ohio, US; abstract no. 78908, XP002100474 see abstract & JP 51 061595 A (ADEKA ARGUS CHEMICAL CO., LTD.) 28 May 1976 ---	1-4, 6-12
X	EP 0 799 816 A (CPS CHEM CO INC) 8 October 1997	13, 16-19
Y	see claims 1-7; examples 1,6 see page 5, line 14 - page 8, line 5 & US 5 498 751 A cited in the application ---	15
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

20 April 1999

Date of mailing of the international search report

06/05/1999

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INTERNATIONAL SEARCH REPORT

Internati	Application No
PCT/US 98/25578	

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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	see claim 1; example 1; see column 3, line 25 - column 5, line 58 ---	15
X	US 4 554 344 A (JACKSON JR., WINSTON J. ET AL) 19 November 1985 cited in the application see claims 1,2; example 1 see column 2, line 9 - line 63 ---	1-4,6,7, 12
X	US 4 970 288 A (W.A. LARKIN ET AL.) 13 November 1990 cited in the application see claims 1,4; example see column 4, line 47 - column 6, line 4 see column 8, line 9 - line 19 ---	1-4,6-12
P,X	R. BACALOGLU ET AL.: POLYMER ENGINEERING AND SCIENCE, vol. 38, no. 6, June 1998, pages 1014-1022, XP002100473 see page 1014 - page 1015 see page 1018 - page 1021 ---	1-4,6,8, 12
A	DATABASE WPI Section Ch, Week 8745 Derwent Publications Ltd., London, GB; Class A23, AN 87-317617 XP002100475 & JP 62 225521 A (TORAY IND INC) , 3 October 1987 see abstract ---	1,8-10
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