



Application Date: Nov. 12, 1946.

No. 33600/46.

Complete Specification Left: Oct. 27, 1947.

Complete Specification Accepted: April 25, 1949.

Index at acceptance:—Class 2(v), R3c8, R3d(1:2:5:6).

PROVISIONAL SPECIFICATION

Improvements in Polymers

We, JAMES GORDON NAPIER DREWITT and JAMES LINCOLN, both British subjects, of Celanese House, 22 and 23, Hanover Square, London, W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of polymers, and is especially concerned with polyesters.

According to the invention, valuable polyesters are obtained by reacting a glycol with a dicarboxylic acid containing a heterocyclic ring. In particular we use dicarboxylic acids in which two carboxylic groups are attached directly or through one or more atoms to a heterocyclic ring, the acids being such that their dimethyl esters melt at a temperature in the range 100—120° C. or higher. By this means, high melting polyesters may be obtained, the melting point in many cases being above 200° C.

The reagents may be used in such proportions and the reaction continued for such a time that a product of molecular weight sufficient to form films is obtained. Preferably the reaction conditions are such that a polymer is obtained capable of forming films and/or of forming filaments orientable by cold-drawing.

Among the heterocyclic compounds which may be used according to the present invention are thiophene-2.4- and 2.5-dicarboxylic acids, furane-2.5-dicarboxylic acid, pyrane-2.6-dicarboxylic acid, pyridine-2.5- and 2.6-dicarboxylic acids, and furane-2.5-diacrylic acid. The most suitable reagents are those in which the two carboxylic groups are attached directly to an unsaturated heterocyclic 5- or 6-membered ring in positions as remote as possible from each other. If the direct bond in such compounds is attached to a ring atom which is itself attached only to two other atoms, then the carboxylic group is substantially co-planar with the ring. Such is the case, for example in the 2.5-positions of thiophene, furane, or

pyridine, and this type of compound appears to be the best.

All the above reagents are free from functional groups other than the desired carboxylic groups, and such reagents are the preferred ones according to the present invention. However, other reagents can be used, as for example pyrrole-2.5-dicarboxylic acid, pyrazole-3.5-dicarboxylic acid, 4-methyl-pyrazole-3.5-dicarboxylic acid, 2.4.6-trimethyl-1.4-dihydro-pyridine-3.5-dicarboxylic acid, 3.5-dimethyl pyrrole-2.4-dicarboxylic acid and 5.5'-benzal-bis-(2.4-dimethyl-pyrrol-3-carboxylic acid). Such compounds as the pyrrole-2.5-dicarboxylic acid and the 3.5-dimethyl pyrrole-2.4-dicarboxylic acid may, prior to the condensation according to the present invention, be subjected alone to a preliminary condensation to form the cyclic amide, the product being then condensed with a glycol in accordance with the invention.

The above heterocyclic acids may be condensed with any suitable glycol, as for example ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, propylene glycol, β-chlor-trimethylene glycol and paraxylylene glycol. Of these, the glycols of the general formula HO(CH₂)_nOH, *n* being an integer at least 2, are the most suitable.

In carrying out polyester formation with relatively volatile glycols, the diacid can be heated, preferably in an inert atmosphere or stream of inert gas, with at least an equimolecular proportion of the glycol, and preferably with an excess, e.g. 1.25—2.5 molecular proportions of the glycol. The initial heating can be in the neighbourhood of 200° C., and subsequent heating at a temperature above the melting point of the polymer, say 220—280° C. The final heating may advantageously be carried out in a high vacuum, i.e. at an absolute pressure of less than 5 mms., and better still, less than 0.1 mm., of

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mercury. Similar considerations apply to the reaction of di-acids with non-volatile glycols but in this case it is preferred to use approximately equimoles of the two components, e.g. within 5%, or better within 2%, of the equimolar proportions.

In some cases a smoother reaction can be obtained by using a solvent, for example meta-cresol, for the ingredients and the resulting polymers. In place of the di-acid, there can be used the equivalent ester-forming derivatives of the acids, for example the dialkyl or diaryl esters, the corresponding half esters, the acid chlorides, the half-ester half-acid chlorides or mixed anhydrides, e.g. with acetic acid, or a polyanhydride or a half-ester-anhydride. It is particularly desirable to use the esters where acids are used which tend to be unstable and to develop carbon dioxide under the conditions of the reaction. When using di-esters, it is of advantage to include in the reaction mixture an ester-interchange catalyst, as for example an alkali metal, magnesium or tin. Reactions with acid chlorides can be effected even at room temperature, and if desired a basic substance can be present, e.g. pyridine, to neutralise the hydrogen chloride evolved.

In a similar way the free glycol may be replaced in the process of the invention by an equivalent ester-forming reagent. Thus, for example, instead of the glycol, we may employ its mono- or di-formate or mono- or di-acetate.

If desired, mixtures of di-acids can be condensed with mixtures of glycols, or a single di-acid can be condensed with a mixture of glycols and *vice versa*, at least one of the di-acids being of the heterocyclic character described above.

The polymers of the invention are of value in coating compositions and in moulding, and, when of sufficiently high-molecular weight, can be spun into filaments. In forming filaments, the choice of the method of spinning depends in part on the properties of the polymers. Where solutions in organic solvents can readily be produced, dry spinning methods may be employed with solutions in volatile

solvents, and wet spinning methods with solutions in volatile or even comparatively non-volatile solvents. The polymers can be spun by melt spinning methods, i.e. by extruding a melt of the polymer through suitable orifices. In general, the temperature of the polymer to be extruded should be some 10—30° above the melting point of the polymer. This melting temperature may be modified to some extent by mixing the polymer with suitable proportions of plasticisers, for example sulphonamide plasticisers, phenolic plasticisers, urea and thiourea plasticisers. Such plasticisers may either be left in the products or may be partly or completely extracted therefrom.

The filaments so formed may be drawn out at comparatively low temperatures, or even at atmospheric temperature, to very fine filaments having high tenacity and good elasticity. The resulting filaments may then be used for any of the purposes to which artificial silks have in the past been applied.

While the invention is especially directed to the manufacture and application of fibre-forming polymers, it is not limited thereto and embraces the production of polymers suitable, for example, for use as softening agents, coatings and film-forming substances. Moreover, for these applications the polymers of the present invention may be mixed with other compatible fibre-forming, film-forming or lacquer substances or other ingredients, for example cellulose acetate, aceto-butyrates, butyrates and aceto-stearates, ethyl cellulose, oxyethyl cellulose, oxyethyl cellulose acetate, benzyl cellulose and other cellulose derivatives, plasticisers or softening agents, dyestuffs and pigments. Further, the invention includes the preparation of higher polymers by further condensation of low polymers obtainable from the above described components.

Dated this 11th day of November, 1946.
STEPHENS & ALLEN,
Chartered Patent Agents,
Wykeham House, Gordon Avenue,
Stammore, Middlesex.

COMPLETE SPECIFICATION

Improvements in Polymers

We, JAMES GORDON NAPIER DREWITT, a British subject, of the Works of British Celanese Limited, Spondon, near Derby, (formerly of Celanese House, 22/23, Hanover Square, London, W.1), and

JAMES LINCOLN, a British subject, of Celanese House, 22/23, Hanover Square, London, W.1, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be

particularly described and ascertained in and by the following statement:—

This invention relates to the production of polymers, and is especially concerned with polyesters.

According to the invention, valuable polyesters are obtained by reacting a glycol with a dicarboxylic acid containing a heterocyclic ring in which the two carboxylic acid groups are attached directly or through one or more atoms to the heterocyclic ring, the acid being such that its dimethyl ester melts above 100° C. and preferably at 120° C. or higher.

The reagents may be used in such proportions and the reaction continued for such a time that a product of molecular weight sufficient to form films is obtained. Preferably the reaction conditions are such that a polymer is obtained capable of forming films and/or of forming filaments orientable by cold-drawing.

Among the heterocyclic dicarboxylic acids which may be used according to the present invention are thiophene-2.4- and 2.5-dicarboxylic acids, furane-2.5-dicarboxylic acid, 1.4-pyrane-2.6-dicarboxylic acid, pyridine-2.5- and 2.6-dicarboxylic acids and furane-2.5-diacrylic acid. The most suitable reagents are those in which the two reactive groups are attached directly to an unsaturated heterocyclic ring in positions as remote as possible from each other. If the direct bond in such compounds is attached to a ring atom which is itself attached only to two other atoms, then the carboxylic group is substantially co-planar with the ring. Such is the case, for example in the 2.5-positions of thiophene, furane, or pyridine, and this type of compound appears to be the best.

All the above reagents are free from functional groups other than the desired carboxylic groups, and such reagents are the preferred ones according to the present invention. However, other reagents can be used, as for example pyrrole-2.5-dicarboxylic acid, pyrazole-3.5-dicarboxylic acid, 4-methyl-pyrazole-3.5-dicarboxylic acid, 2.4.6-trimethyl-1.4-dihydro-pyridine-3.5-dicarboxylic acid, 3.5-dimethyl pyrrole-2.4-dicarboxylic acid and 5.5'-benzal-bis-(2.4-dimethyl-pyrrole-3-carboxylic acid). Such compounds as the pyrrole-2.5-dicarboxylic acid and the 3.5-dimethyl-pyrrole-2.4-dicarboxylic acid may, prior to the condensation according to the present invention, be subjected alone to a preliminary condensation to form the cyclic amide, the product being then condensed with a glycol in accordance with the invention.

The above heterocyclic acids may be condensed with any suitable glycol, as for

example ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, propylene glycol, β -chlor-trimethylene glycol and para-xylene glycol. Of these, the glycols of the general formula $\text{HO}(\text{CH}_2)_n\text{OH}$, n being an integer at least 2, are the most suitable.

In carrying out polyester formation with relatively volatile glycols the di-acid can be heated, preferably in an inert atmosphere or stream of inert gas, with at least an equimolecular proportion of the glycol, and preferably with an excess, e.g. 1.25—2.5 molecular proportions of the glycol. The initial heating can be in the neighbourhood of 200° C., and subsequent heating at a temperature above the melting point of the polymer, say 220—280° C. The final heating may advantageously be carried out in a high vacuum, i.e. at an absolute pressure of less than 5 mms., and better still, less than 1 mm., of mercury. Similar considerations apply to the reaction of di-acids with non-volatile glycols, but in this case it is preferred to use approximately equimoles of the two components, e.g. within 5%, or better within 2%, of the equimolar proportions.

In some cases a smoother reaction can be obtained by using a solvent, for example meta-cresol, for the ingredients and the resulting polymers. In place of the di-acid, there can be used the equivalent ester-forming derivatives of the acids, for example the dialkyl or diaryl esters, the corresponding half esters, the acid chlorides, the half-ester half-acid-chlorides or mixed anhydrides, e.g. with acetic acid, or a poly-anhydride or a half-esteranhydride. It is particularly desirable to use the esters where acids are used which tend to be unstable and to develop carbon dioxide under the conditions of the reaction. When using di-esters, it is of advantage to include in the reaction mixture an ester interchange catalyst, as for example an alkali metal, magnesium or tin. Reactions with acid chlorides can be effected even at room temperature, and if desired a basic substance can be present, e.g. pyridine, to neutralise the hydrogen chloride evolved.

In a similar way the free glycol may be replaced in the process of the invention by an equivalent ester-forming reagent. Thus, for example, instead of the glycol, we may employ its mono- or di-formate or mono- or di-acetate.

If desired, mixtures of di-acids can be condensed with mixtures of glycols, or a single di-acid can be condensed with a mixture of glycols and *vice versa*, at least one of the di-acids being of the heterocyclic character described above.

The polymers of the invention are of value in coating compositions and in moulding, and, when of sufficiently high molecular weight, can be spun into filaments. In forming filaments, the choice of the method of spinning depends in part on the properties of the polymers. Where solutions in organic solvents can readily be produced, dry spinning methods may be employed with solutions in volatile solvents, and wet spinning methods with solutions in volatile or even comparatively non-volatile solvents. The polymers can be spun by melt spinning methods, i.e. by extruding a melt of the polymer through suitable orifices. In general, the temperature of the polymer to be extruded should be some 10—30° above the melting point of the polymer. This melting temperature may be modified to some extent by mixing the polymer with plasticisers, for example sulphonamide plasticisers, phenolic plasticisers, urea and thiourea plasticisers. Such plasticisers may either be left in the products or may be partly or completely extracted therefrom.

The filaments so formed may be drawn out at comparatively low temperatures, or even at atmospheric temperature, to very fine filaments having high tenacity and good elasticity. The resulting filaments may then be used for any of the purposes to which artificial silks have in the past been applied.

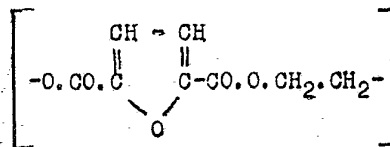
While the invention is especially directed to the manufacture and application of fibre-forming polymers, it is not limited thereto and embraces the production of polymers suitable, for example, for use as softening agents, coatings and film-forming substances. Moreover, for these applications the polymers of the present invention may be mixed with other compatible fibre-forming, film-forming or lacquer substances or other ingredients, for example cellulose acetate, aceto-butyrate, butyrate and aceto-stearate, ethyl cellulose, oxyethyl cellulose, oxyethyl cellulose acetate, benzyl cellulose and other cellulose derivatives, plasticisers or softening agents, dyestuffs and pigments. Further, the invention includes the preparation of higher polymers by further condensation of low polymers obtainable from the above described components.

The following examples illustrate the invention, all parts being by weight:—

EXAMPLE 1.

18.4 parts (1 mole) of furane-2.5-dicarboxylic acid dimethyl ester (M.P. 109—110° C.) were mixed with 10 parts (about 1.6 moles) of ethylene glycol, and 0.025 parts of sodium dissolved in 8 parts of methanol and a small quantity of magnesium ribbon added. The mixture was

first heated at 160° C. for half an hour using a water-cooled reflux condenser and then for a further hour with an air-cooled reflux. At this stage the product was a crystalline mass with a melting point of under 120° C. The condenser was removed and the mass heated for 2 hours at 220° C. with the polymerising vessel open to the atmosphere. The vessel was then connected to a high vacuum pump and a hydrogen bubbling apparatus was fitted and the heating was continued with a stream of hydrogen bubbling through the molten mass and under an absolute pressure of 3 mms. of mercury, first at 190° C. for 2 hours and finally at 220° C. for 3 hours. The product had a melting point of 205—210° C. and readily yielded filaments from a melt. It showed on analysis a carbon content, on an ash-free basis, of 52.83%. The theoretical value for the infinite polymer



is 52.75%.

EXAMPLE 2.

Equal parts of furane-2.5-dicarboxylic acid and ethylene glycol (molar ratio 1:2.52) were refluxed for 3 hours at 180° C., the reflux condenser removed and heating continued for a further 4 hours at 210° C. A vacuum pump was then connected and heating continued for a further 7 hours at the same temperature and under an absolute pressure of 2 mms. of mercury. The resulting polymer had properties very similar to those of the product produced according to Example 1.

EXAMPLE 3.

15 parts (1 mole) of thiophene-2.5-dicarboxylic acid dimethyl ester (recrystallised from methanol, M.P. 152° C.), 7.5 parts (about 1.6 moles) of ethylene glycol, a solution of 0.025 parts of sodium in 8 parts of methanol and a small quantity of magnesium ribbon were heated for 40 minutes at 160° C. under a water-cooled reflux in an atmosphere of hydrogen and then for 3 hours under an air-cooled reflux. The condenser was then removed and heating continued at 230° C. for 3 hours and then for a further 7 hours under an absolute pressure of 2—3 mms. of mercury with a temperature rising from 170° C. to 200° C. The product, melting point 180—190° C., readily gave fibres and had a carbon content, on an ash-free basis, of 49.14%. Theory for the infinite polymer

