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(71) Applicant *(for all designated States except US)*: **DUPONT TEIJIN FILMS U.S. LIMITED PARTNERSHIP** [US/US]; 3600 Discovery Drive, Chester 23836, Virginia (US).

(72) Inventors; and
(71) Applicants *(for US only)*: **SANKEY, Stephen William** [GB/GB]; c/o Dupont Teijin Films UK Limited, The Wilton Centre, Wilton Site, Redcar TS10 4RF (GB). **TURNER, David** [GB/GB]; c/o Dupont Teijin Films UK Limited, The Wilton Centre, Wilton Site, Redcar TS10 4RF (GB). **COLQUHOUN, Howard** [GB/GB]; c/o The University of Reading, School of Chemistry, Food Biosciences and Pharmacy, Whiteknights, PO Box 217, Reading RG6 6AH (GB). **MEEHAN, Stephen** [GB/GB]; c/o The University of Reading, School of Chemistry, Food Biosciences and Pharmacy, Whiteknights, PO Box 217, Reading RG6 6AH (GB).

(74) Agents: **COCKERTON, Bruce Roger** et al.; Carpmaels & Ransford LLP, One Southampton Row, London WC1B 5HA (GB).

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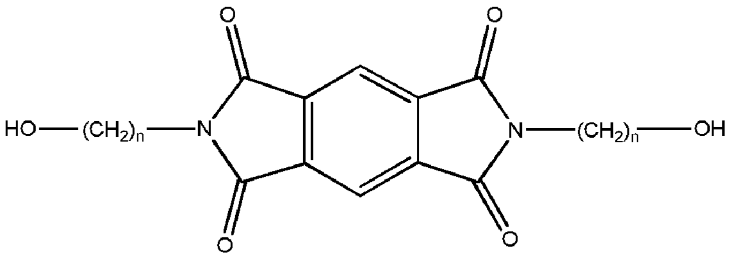
(54) Title: COPOLYESTERIMIDES DERIVED FROM N.N'-BIS-(HYDROXYALKYL)-PYROMELLITIC DIIMIDE AND FILMS MADE THEREFROM



(I)

(57) Abstract: A polyester film comprising a copolyester which comprises repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I): wherein n = 2, 3 or 4, and wherein comonomer (I) constitutes a proportion of the glycol fraction of the copolyester.

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COPOLYESTERIMIDES DERIVED FROM N,N'-BIS-(HYDROXYALKYL)-PYROMELLITIC DIIMIDE AND FILMS MADE THEREFROM

The present invention is concerned with polyesterimides and films made therefrom, and methods for their synthesis. In particular, the present invention is concerned with copolymers of aromatic carboxylic acids, particularly copolymers of poly(alkylene naphthalate)s and copolymers of poly(alkylene terephthalates), which exhibit improved heat-resistance and thermo-mechanical stability.

The glass transition temperature (T_g), crystalline melting point (T_m) and degree of crystallinity are key parameters in determining the thermo-mechanical properties of polyesters. Previous studies have succeeded in increasing the T_g of thermoplastic polymers, primarily homopolymers, but this has typically been accompanied by a corresponding increase in the T_m. Such increases in T_m can be disadvantageous because a thermoplastic polymer should also remain melt-processible (for instance in an extruder), and should preferably remain so under economic conditions (for instance, below about 320°C, preferably below about 300°C, which allows the use of conventional extrusion equipment). At higher processing temperatures, polymer extrusion requires expensive specialist equipment and a great deal of energy, and typically also results in degradation products. The melt-processing temperature should be well below (for instance, at least about 20°C below) the decomposition temperature of the polymer. In some cases, comonomers have been introduced into polymers in order to increase T_g while retaining T_m, but also resulting in convergence of the decomposition temperature and the T_m, which leads to the production of degradation products in the melt.

Many attempts have also been made to enhance the glass transition temperature of polyesters by the introduction of more rigid comonomers. However, such comonomers also disrupt the packing of the polymer chains in the crystal lattice, so that while the T_g increases, the T_m and degree of crystallinity typically both decrease as the proportion of comonomer increases, leading ultimately to amorphous materials. In order to fabricate articles from polymeric materials, it is often critical that the polymer exhibit crystallinity to achieve articles with acceptable thermo-mechanical properties.

Poly(ethylene terephthalate) (PET) is a semi-crystalline copolymer having a glass transition temperature (T_g) of 78°C and a crystalline melting point of (T_m) of 260°C. Poly(ethylene naphthalate) (PEN) is a semi-crystalline copolymer having a higher glass transition temperature (T_g = 120°C) relative to PET, although their crystalline melting points do not differ greatly (T_m = 268°C for PEN). The thermo-mechanical stability of PEN is significantly greater than that of PET. Many of the attempts made to enhance T_g by the introduction of more rigid comonomers have focussed on PET, which is significantly cheaper than PEN. There are no commercially available semi-crystalline polyesters with a T_g higher than PEN. Polyether ether ketone (PEEK) is one of the few examples of a high T_g (approximately 143-146°C) semi-crystalline thermoplastic polymer, and has been used successfully in engineering and biomedical applications. However, PEEK is suitable only for certain types of articles; for instance, it is not suitable for the manufacture of biaxially oriented films. PEEK is also very expensive and has a high crystalline melting point (approximately 350°C).

The underlying objective of the present invention is the provision of copolyester films made from a copolyester having a T_g which is higher than the corresponding base polyester, without significantly increasing the T_m to a point where the polymer is no longer melt-processible under economic conditions, particularly without significantly decreasing the degree of crystallinity of the film (in order to achieve acceptable thermo-mechanical properties), and preferably also without significantly decreasing decomposition temperature.

Thus, an object of the present invention is to provide polyesters which exhibit improved heat-resistance and thermo-mechanical stability. A further object of the present invention is to provide a thermoplastic polymer with high or increased T_g but without increasing T_m to a point where the polymer is no longer melt-processible under economic conditions (i.e. the polymer should remain melt-processible below about 320°C, preferably below about 300°C). A further object of the present invention is to provide semi-crystalline polyesters which exhibit high T_g as well as high T_m. A further object of the present invention is to increase the T_g of a polyester without significantly decreasing its T_m and/or its degree of crystallinity, and preferably without significantly decreasing its decomposition temperature.

As used herein, the term "without significantly decreasing the T_m" means that the T_m decreases by no more than 10%, preferably no more than 5%.

As used herein, the term "without significantly decreasing the degree of crystallinity", means that the polyester retains a degree of crystallinity which is commercially useful, preferably in the range of from about 10% to about 60%, preferably from about 20 to about 50%.

A further object of the present invention is to provide a copolyester having a T_g which is higher than the corresponding base polyester, without significantly decreasing its T_m and/or its degree of crystallinity and preferably without significantly decreasing its decomposition temperature.

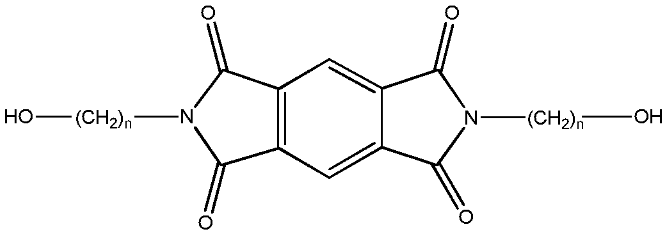
A further object of the present invention is to provide the use of a comonomer suitable for partial substitution of a monomer in a conventional polyester which increases the T_g of said polyester without significantly decreasing its T_m and/or its degree of crystallinity, and preferably without significantly decreasing its decomposition temperature.

While the objects of the invention do not exclude an increase in T_m, any increase in T_m must not be so large that melt-processing becomes uneconomical and that the T_m and decomposition temperature converge.

As used herein, the term "copolyester" refers to a polymer which comprises ester linkages and which is derived from three or more types of comonomers. As used herein, the term "corresponding base polyester" refers to a polymer which comprises ester linkages and which is derived from two types of comonomers comprising ester-forming functionalities, and which serves as a comparator for a copolyester which is derived from comonomers comprising the comonomers of the corresponding base polyester. A comonomer comprising ester-forming functionalities preferably possesses two ester-forming functionalities.

As used herein, the term “semi-crystalline” is intended to mean a degree of crystallinity of at least about 5% measured according to the test described herein, preferably at least about 10%, preferably at least about 15%, and preferably at least about 20%.

Accordingly, the present invention provides a film comprising a copolyester which comprises repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid (preferably selected from terephthalic acid and naphthalene-dicarboxylic acid), and the monomer of formula (I):



(I)

wherein n = 2, 3 or 4, and preferably wherein n = 2. The monomer of formula (I) is referred to herein as *N,N'*-bis-(hydroxyalkyl)-pyromellitic diimide (PDI). Where n = 2, the monomer is referred to as *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide.

Surprisingly, the present inventors have now found that incorporation of the specific co-monomer (I) into the polyester not only increases the T_g substantially but does so without significant detriment to the crystallinity of films made therefrom. This is achieved without significantly increasing the T_m. The copolyesters described herein are thermoplastic. Copolyesters and films made therefrom as described herein exhibit semi-crystalline properties. The copolyesters described herein can be readily obtained at high molecular weight. The copolyesters described herein can be melt-processed below 320°C (preferably below 300°C) into tough, high strength films. The copolyesters are also referred to herein as co(polyester-imide)s.

The comonomer (I) constitutes a proportion of the glycol fraction of the copolyester. In a preferred embodiment, the comonomer (I) is present in amounts of no more than about 50 mol% of the glycol fraction of the copolyester, preferably no more than about 40 mol%, preferably no more than about 30 mol%, preferably no more than about 20 mol%, preferably no more than about 15 mol%. Preferably the comonomer is present in an amount of at least about 1 mol%, more preferably at least about 3 mol%, more preferably at least about 4 mol% of the glycol fraction of the copolyester.

Where the aromatic acid is naphthalene-dicarboxylic acid, the comonomer (I) is preferably present in amounts of no more than about 15 mol%, preferably no more than about 10 mol%, preferably less than 10 mol%, preferably no more than about 9 mol%, and in one embodiment no more than about 8 mol%.

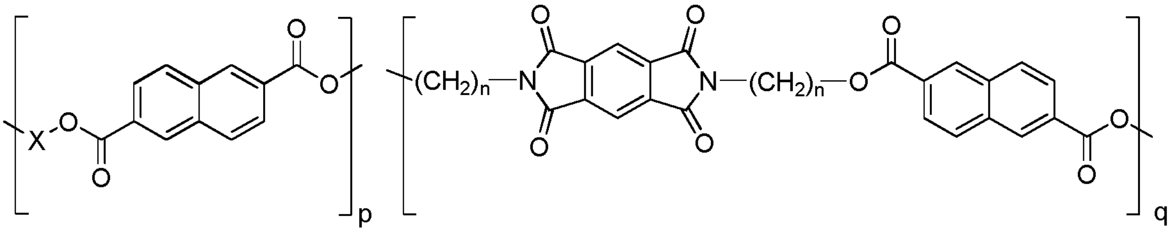
The inventors have observed that even at low molar fractions of the comonomer (I), small but valuable increases in T_g are observed. For instance, a copolyester comprising only 5 mol% comonomer (I) where $n = 2$ exhibits a significant rise in T_g, while retaining a good degree of crystallinity.

The aromatic dicarboxylic acid is preferably selected from terephthalic acid and naphthalene-dicarboxylic acid. Other aromatic dicarboxylic acids which may be used in the present invention include isophthalic acid and phthalic acid. The naphthalene-dicarboxylic acid can be selected from 2,5-, 2,6- or 2,7-naphthalene dicarboxylic acid, and is preferably 2,6-naphthalene dicarboxylic acid.

The aliphatic glycol is preferably selected from C_2, C_3 or C_4 aliphatic diols, more preferably from ethylene glycol, 1,3-propanediol and 1,4-butanediol, more preferably from ethylene glycol and 1,4-butanediol, and is most preferably ethylene glycol. The number of carbon atoms in the aliphatic glycol may be the same or different as the number (n) in the comonomer (I), but it is most preferably the same in order to retain crystallinity, particularly in order to retain crystallinity with increasing amounts of comonomer. Thus, the aliphatic glycol preferably has the formula $HO(CH_2)_mOH$, where $m = n$.

In one embodiment, the aliphatic glycol is 1,4-butanediol and n = 4. In a preferred embodiment, the aliphatic glycol is ethylene glycol and n = 2.

Copolyesters wherein the acid component is selected from 2,6-naphthalene dicarboxylic acid can be described by formula (IIa) below:



(IIa)

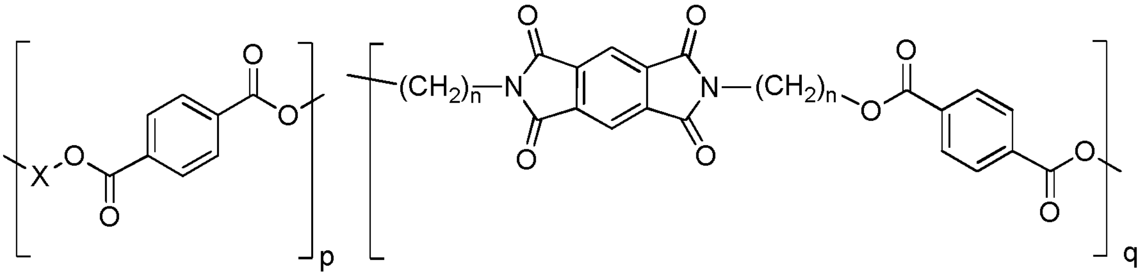
wherein:

n is as defined for formula (I);

the group X is the carbon chain of said aliphatic glycol;

and p and q are the molar fractions of the aliphatic glycol-containing repeating ester units and the monomer (I)-containing repeating ester units, respectively, as defined hereinabove (i.e. q is preferably no more than 50, and p = 100-q).

Copolyesters wherein the acid component is selected from terephthalic acid can be described by formula (IIb) below:



(IIb)

wherein n, X, p and q are as described above.

The copolyester may contain more than one type of the aforementioned aliphatic glycols, and/or more than one type of monomer of formula (I) (i.e. a plurality of types of monomer with differing values of n). Preferably, however, the copolyester comprises a single type of the aforementioned aliphatic glycols. Preferably, the copolyester comprises a single type of monomer of formula (I). Preferably, the copolyester comprises a single type of the aforementioned aliphatic glycols, and a single type of monomer of formula (I). Where the copolyester contains more than one type of said aliphatic glycols, then preferably the copolyester comprises a major aliphatic glycol fraction of a single type of said aliphatic glycols, and a minor aliphatic glycol fraction of one or more different type(s) of said aliphatic glycols, wherein said one or more different type(s) of said aliphatic glycols constitutes no more than 10 mol%, preferably no more than 5 mol%, preferably no more than 1 mol% of the total glycol fraction. Similarly, where the copolyester contains more than one type of said monomer of formula (I), then preferably the copolyester comprises a major fraction of a single type of said monomer of formula (I), and a minor fraction of one or more different type(s) of said monomer of formula (I), wherein said minor fraction of one or more different type(s) of monomer of formula (I) constitutes no more than 10 mol%, preferably no more than 5 mol%, preferably no more than 1 mol% of the total monomer (I) fraction. The copolyesters may contain minor amounts of other glycols and in a preferred embodiment such other glycols constitute no more than 10 mol%, preferably no more than 5 mol%, preferably no more than 1 mol% of the total glycol fraction, but in order to maximise performance it is preferred that the glycol fraction consists of comonomer (I) and said aliphatic glycol(s) described above.

The copolyesters described herein may contain more than one type of carboxylic acid. In this embodiment, the copolyester comprises a first aromatic dicarboxylic acid, which is preferably terephthalic acid or naphthalene-dicarboxylic acid, as described hereinabove, and one or more additional carboxylic acid(s). The additional carboxylic acid(s) is/are present in minor amounts (preferably no more than 10 mol%, preferably no more than 5 mol%, preferably no more than 1 mol% of the total acid fraction) and is/are different to said first aromatic carboxylic acid. The additional carboxylic acid(s) is/are preferably selected from dicarboxylic acids, preferably from aromatic dicarboxylic acids, for instance including terephthalic acid (where the first aromatic dicarboxylic acid is naphthalene-dicarboxylic acid), naphthalene-dicarboxylic acid (where the first aromatic dicarboxylic acid is terephthalic acid), isophthalic acid, 1,4-naphthalenedicarboxylic acid and 4,4'-diphenyldicarboxylic acid. In this embodiment, the first aromatic dicarboxylic acid may be one isomer of naphthalene-dicarboxylic acid, and the additional dicarboxylic acid(s) may be selected from other isomer(s) of naphthalene-dicarboxylic acid.

Preferably, however, the acid fraction consists of a single aromatic dicarboxylic acid as described hereinabove.

Thus, the copolyester described herein preferably contains only aliphatic glycol, an aromatic dicarboxylic acid (preferably terephthalic acid or naphthalene-dicarboxylic acid) and the monomer of formula (I) defined hereinabove.

The copolyesters described herein can be synthesised according to conventional techniques for the manufacture of polyester materials by condensation or ester interchange, typically at temperatures up to about 310°C. Polycondensation may include a solid phase polymerisation (SSP) stage. The solid phase polymerisation may be carried out in a fluidised bed, e.g. fluidised with nitrogen, or in a vacuum fluidised bed, using a rotary vacuum drier. Suitable solid phase polymerisation techniques are disclosed in, for example, EP-A-0419400 the disclosure of which is incorporated herein by reference. Thus, SSP is typically conducted at a temperature 10-50 °C below the crystalline melting point (T_m) of the polymer but higher than the glass transition temperature (T_g). An inert atmosphere of dry nitrogen or a vacuum is used to prevent degradation. In one embodiment, the copolyester is prepared using germanium-based catalysts which provide a polymeric material having a reduced level of contaminants such as catalyst residues, undesirable inorganic deposits and other by-products of polymer manufacture. Thus, according to a further aspect of the invention, there is provided a process for preparing a copolyester as defined herein, wherein said process comprises the steps of:

(i) reacting said aliphatic glycol with said aromatic dicarboxylic acid to form a bis(hydroxyalkyl)-ester of said aromatic dicarboxylic acid; and

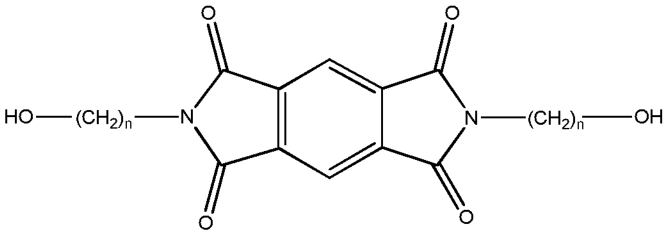
(ii) reacting said bis(hydroxyalkyl)-ester of said aromatic dicarboxylic acid with the monomer (I) under conditions of elevated temperature and pressure in the presence of a catalyst.

In one embodiment, the aliphatic glycol is reacted with the naphthalene dicarboxylic acid to form a bis(hydroxyalkyl)-naphthalate, which is then reacted with the monomer (I) in the desired molar ratios under conditions of elevated temperature and pressure in the presence of a catalyst, as exemplified in Scheme (1) hereinbelow. In a further embodiment, the aliphatic glycol is reacted with the terephthalic acid to form a bis(hydroxyalkyl)-terephthalate, which is then reacted with the monomer (I) in the desired molar ratios under conditions of elevated temperature and pressure in the presence of a catalyst, as exemplified in Scheme (2) hereinbelow.

The process of the invention described hereinabove for preparing copolyesters advantageously allows preparation of the copolyester described herein, and with high selectivity and high yield. The process advantageously also provides a stable and relatively rapid reaction, facilitating a reliable and reproducible polymerisation and allowing scale-up in a safe and economical manner, and also improves the uniformity of the product.

Surprisingly, the copolyesters exhibit an exceptionally low number of carboxyl end-groups, preferably no more than 25, preferably no more than 20, preferably no more than 15, preferably no more than 10, preferably no more than 5, and preferably no more than 1 gram equivalents/10^6g polymer, and hence exhibit excellent hydrolytic stability.

According to a further aspect of the present invention, there is provided a copolyester comprising repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I):



(I)

wherein n = 2, 3 or 4;

wherein comonomer (I) constitutes a proportion of the glycol fraction of the copolyester; and wherein said copolyester is obtainable by the process described herein and/or exhibits a carboxyl end-group content of no more than 25, preferably no more than 20, preferably no more than 15, preferably no more than 10, preferably no more than 5, and preferably no more than 1 gram equivalents/10^6g polymer.

The copolyesters described herein are particularly suitable for use in applications involving exposure to high temperatures and applications which demand high thermo-mechanical performance. One advantage of the copolyesters described herein over PEEK is that they exhibit T_g values approaching those of PEEK, but with a T_m which is significantly lower.

Surprisingly, the present inventors have found that incorporation of the specific co-monomer (I) into an aromatic polyester (preferably a terephthalate or naphthalate polyester) not only increases the T_g substantially but does so without significant detriment to the crystallinity of films made therefrom. This is achieved without significantly increasing the T_m. Films made from the copolyesters described herein exhibit unexpectedly excellent semi-crystalline properties. Semi-crystalline films of the invention exhibit a degree of crystallinity of at least about 5%, preferably at least about 10%, preferably at least about 15%, preferably at least about 20%, and preferably at least about 25%, measured according to the density method described herein. Thus, the present invention provides films wherein the aromatic dicarboxylic acid (or the first dicarboxylic acid as defined herein) is naphthalene dicarboxylic acid and the degree of crystallinity of the film is at least about 5% (preferably 10%, preferably 15%, preferably 20%, preferably 25%) as calculated from the film density and on the basis of the density of 0% crystalline polyethylene naphthalate (PEN) being 1.325 g/cm^3 and the density of 100% crystalline PEN being 1.407 g/cm^3; and further provides films wherein the aromatic dicarboxylic acid (or the first dicarboxylic acid as defined herein) is terephthalic acid and the degree of crystallinity of the film is at least about 5% (preferably 10%, preferably 15%, preferably 20%, preferably 25%) as calculated from the film density and on the basis of the density of 0% crystalline polyethylene terephthalate (PET) being 1.335 g/cm^3 and the density of 100% crystalline PET being 1.455 g/cm^3.

The film of the present invention is preferably an oriented film, preferably a biaxially oriented film. Biaxially oriented films in particular are useful as base films for magnetic recording media, particularly magnetic recording media required to exhibit reduced track deviation in order to permit narrow but stable track pitch and allow recording of higher density or capacity of information, for instance magnetic recording media suitable as server back-up/data storage, such as the LTO (Linear Tape Open) format. The film (preferably biaxially oriented film) of the present invention is also particularly suitable for use in electronic and opto-electronic devices (particularly wherein the film is required to be flexible) where thermo-mechanically stable backplanes are critical during fabrication of the finished product, for instance in the manufacture of electroluminescent (EL) display devices (particularly organic light emitting display (OLED) devices), electrophoretic displays (e-paper), photovoltaic (PV) cells and semiconductor devices (such as organic field effect transistors, thin film transistors and integrated circuits generally), particularly flexible such devices.

The copolyester comprising repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I) defined hereinabove is preferably the major component of the film, and makes up at least 50%, preferably at least 65%, preferably at least 80%, preferably at least 90%, and preferably at least 95% by weight of the total weight of the film. Said copolyester is suitably the only polyester used in the film.

Formation of the film may be effected by conventional extrusion techniques well-known in the art. In general terms the process comprises the steps of extruding a layer of molten polymer at a temperature within an appropriate temperature range, for instance in a range of from about 280 to about 300°C, quenching the extrudate and orienting the quenched extrudate. Orientation may be effected by any process known in the art for producing an oriented film, for example a tubular or flat film process. Biaxial orientation is effected by drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties. In a tubular process, simultaneous biaxial orientation may be effected by extruding a thermoplastics polyester tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation. In the preferred flat film process, the film-forming polyester is extruded through a slot die and rapidly quenched upon a chilled casting drum to ensure that the polyester is quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate in at least one direction at a temperature above the glass transition temperature of the polyester. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. Forward stretching of the extrudate is conveniently effected over a set of rotating rolls or between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. Stretching is generally effected so that the dimension of the oriented film is from 2 to 5, more preferably 2.5 to 4.5 times its original dimension in the or each direction of stretching. Typically, stretching is effected at temperatures higher than the T_g of the polyester, preferably about 15 °C higher than the T_g. Greater draw ratios (for example, up to about 8 times) may be used if orientation in only one direction is required. It is not necessary to stretch equally in the machine and transverse directions although this is preferred if balanced properties are desired.

A stretched film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional support at a temperature above the glass transition temperature of the polyester but below the melting temperature thereof, to induce the desired crystallisation of the polyester. During the heat-setting, a small amount of dimensional relaxation may be performed in the transverse direction (TD) by a procedure known as “toe-in”. Toe-in can involve dimensional shrinkage of the order 2 to 4% but an analogous dimensional relaxation in the process or machine direction (MD) is difficult to achieve since low line tensions are required and film control and winding becomes problematic. The actual heat-set temperature and time will vary depending on the composition of the film and its desired final thermal shrinkage but should not be selected so as to substantially degrade the toughness properties of the film such as tear resistance. Within these constraints, a heat set temperature of about 150 to 245°C (typically at least 180°C) is generally desirable. After heat-setting the film is typically quenched rapidly in order induce the desired crystallinity of the polyester.

In one embodiment, the film may be further stabilized through use of an in-line relaxation stage. Alternatively the relaxation treatment can be performed off-line. In this additional step, the film is heated at a temperature lower than that of the heat-setting stage, and with a much reduced MD and TD tension. The tension experienced by the film is a low tension and typically less than 5 kg/m, preferably less than 3.5 kg/m, more preferably in the range of from 1 to about 2.5 kg/m, and typically in the range of 1.5 to 2 kg/m of film width. For a relaxation process which controls the film speed, the reduction in film speed (and therefore the strain relaxation) is typically in the range 0 to 2.5%, preferably 0.5 to 2.0%. There is no increase in the transverse dimension of the film during the heat-stabilisation step. The temperature to be used for the heat stabilisation step can vary depending on the desired combination of properties from the final film, with a higher temperature giving better, i.e. lower, residual shrinkage properties. A temperature of 135 to 250 °C is generally desirable, preferably 150 to 230 °C, more preferably 170 to 200 °C. The duration of heating will depend on the temperature used but is typically in the range of 10 to 40 seconds, with a duration of 20 to 30 seconds being preferred. This heat stabilisation process can be carried out by a variety of methods, including flat and vertical configurations and either "off-line" as a separate process step or "in-line" as a continuation of the film manufacturing process. Film thus processed will exhibit a smaller thermal shrinkage than that produced in the absence of such post heat-setting relaxation.

The film may further comprise any other additive conventionally employed in the manufacture of polyester films. Thus, agents such as anti-oxidants, UV-absorbers, hydrolysis stabilisers, cross-linking agents, dyes, fillers, pigments, voiding agents, lubricants, radical scavengers, thermal stabilisers, flame retardants and inhibitors, anti-blocking agents, surface active agents, slip aids, gloss improvers, prodegradents, viscosity modifiers and dispersion stabilisers may be incorporated as appropriate. Such components may be introduced into the polymer in a conventional manner. For example, by mixing with the monomeric reactants from which the film-forming polymer is derived, or the components may be mixed with the polymer by tumble or dry blending or by compounding in an extruder, followed by cooling and, usually, comminution into granules or chips. Masterbatching technology may also be employed. The film may, in particular, comprise a particulate filler which can improve handling and windability during manufacture, and can be used to modulate optical properties. The particulate filler may, for example, be a particulate inorganic filler (e.g. metal or metalloid oxides, such as alumina, titania, talc and silica (especially precipitated or diatomaceous silica and silica gels), calcined china clay and alkaline metal salts, such as the carbonates and sulphates of calcium and barium).

The thickness of the film can be in the range of from about 1 to about 500 μm, typically no more than about 250 μm, and typically no more than about 150 μm. Particularly where the film of the present invention is for use in magnetic recording media, the thickness of the multilayer film is suitably in the range of from about 1 to about 10 μm, more preferably from about 2 to about 10 μm, more preferably from about 2 to about 7 μm, more preferably from about 3 to about 7 μm, and in one embodiment from about 4 to about 6 μm. Where the film is to be used as a layer in electronic and display devices as described herein, the thickness of the multilayer film is typically in the range of from about 5 to about 350 μm, preferably no more than about 250 μm, and in one embodiment no more than about 100 μm, and in a further embodiment no more than about 50 μm, and typically at least 12μm, more typically at least about 20 μm.

According to a further aspect of the invention, there is provided an electronic or opto-electronic device comprising the film (particularly the biaxially oriented film) described herein, particularly electronic or opto-electronic devices such as electroluminescent (EL) display devices (particularly organic light emitting display (OLED) devices), electrophoretic displays (e-paper), photovoltaic (PV) cells and semiconductor devices (such as organic field effect transistors, thin film transistors and integrated circuits generally), particularly flexible such devices.

According to a further aspect of the invention, there is provided a magnetic recording medium comprising the film (particularly the biaxially oriented film) described herein as a base film and further comprising a magnetic layer on one surface thereof. The magnetic recording medium includes, for example, linear track system data storage tapes such as QIC or DLT, and, SDLT or LTO of a further higher capacity type. The dimensional change of the base film due to the temperature/humidity change is small, and so a magnetic recording medium suitable to high density and high capacity causing less track deviation can be provided even when the track pitch is narrowed in order to ensure the high capacity of the tape.

The following test methods were used to characterise the properties of the novel compounds disclosed herein.

(i) **Glass transition temperature (T_g); temperature of cold crystallisation (T_{cc}), crystalline melting point (T_m)** and **degree of crystallinity (X_c)** were measured by differential scanning calorimetry (DSC) using a Universal V4.5A machine (TA Instruments). Unless otherwise stated, measurements were made according to the following standard test method and based on the method described in ASTM E1356-98. The sample was maintained under an atmosphere of dry nitrogen for the duration of the scan (approx. 1.5 to 3 hours). The sample (4-6 mg) was heated from 20°C to 300°C at a rate of 20°C/min, held at 300°C for 5 minutes, and then cooled to 20°C at a rate of 20°C/min, and then heated from 20°C to 350°C at 10°C/min. The thermal properties were recorded on the second heating scan.

The value of T_g was taken as the extrapolated onset temperature of the glass transition observed on the DSC scan (heat flow (W/g) against temperature (°C)), as described in ASTM E1356-98.

The values of T_{cc} and T_m were taken from the DSC scan as the temperature at which peak heat flow was observed in the respective transitions.

Herein, the degree of crystallinity was measured for samples which have been annealed at 200°C for 2 hours, unless otherwise stated. The annealing of the sample was conducted during a DSC heating cycle according to the following test method and based on the method described in ASTM E1356-98, using a 5mg sample and the equipment noted above. The full heating cycle for these crystallinity measurements was as follows:

(i) Heated from 20 to 300°C at 20°C/min
(ii) Held at 300°C for 5 minutes
(iii) Cooled to 20°C at 20°C/min
(iv) Heated to 200°C at 20°C/min
(v) Held at 200°C for 120 min

(vi) Cooled to 20°C
(vii) Heated from 20 to 400°C at 10°C/min.

The thermal properties were recorded on the final heating scan.

The degree of crystallinity (X_c) was calculated according to the equation:

$$X_c = \Delta H_m / \Delta H_m^{\circ}$$

wherein:

ΔH_m = experimental enthalpy of fusion calculated from the integral of the melting endotherm;

ΔH_m° = theoretical enthalpy of fusion of the corresponding poly(alkylene-carboxylate) homopolymer (i.e. without the co-monomer of formula (I)) at 100 % crystallinity. Thus, for copolyesters of the present invention comprising repeating units derived from ethylene glycol, naphthalene-dicarboxylic acid and the co-monomer of formula (I), ΔH_m° is the theoretical enthalpy of fusion of a 100% crystalline PEN polymer (103 J/g), and for copolyesters of the present invention comprising repeating units derived from ethylene glycol, terephthalic acid and the co-monomer of formula (I), ΔH_m° is the theoretical enthalpy of fusion of a 100% crystalline PET polymer (140 J/g), as defined in the literature (B. Wunderlich, *Macromolecular Physics*, Academic Press, New York, (1976)).

(ii) **Inherent viscosity** (η_{inh}) was determined at 25 °C for 0.1 % w/v solutions of the polymer in $CHCl_3$/TFA (2:1) using a Schott-Geräte CT-52 auto-viscometer, with capillary No. 53103. Inherent viscosities were calculated as:

$$\eta_{inh} = \ln[(t_2/t_1)/c]$$

wherein:

η_{inh} = Inherent Viscosity (dL/g)
t_1 = Flow time of solvent (s)
t_2 = Flow time of the polymer solution (s)
c = Concentration of the polymer (g/dL)

Preferably, the inherent viscosity of the copolyesters described herein is at least 0.7 dL/g. Such viscosities are readily obtainable using SSP techniques.

(iii) **Carboxyl end-group content** (gram equivalents/10^6g polymer) was determined by ^{1}H-NMR spectroscopy at 80°C in d_2-TCE using an Eclipse +500 spectrometer.

(iv) **Degree of crystallinity of the film** was measured via measurement of density. The density of the film samples was measured using a calibrated calcium nitrate/water density column controlled at a constant 23°C using a water jacket using the following method. Two 860 ml calcium nitrate solutions of known densities were prepared, filtered and degassed in vacuo for 2 h before being pumped simultaneously into a graduated column tube under hydrostatic equilibrium. The two calcium nitrate solutions of known density are low and high concentration solutions which form a range of densities within the column to encompass the expected densities for the semi-crystalline films of the present invention (corresponding to a degree of crystallinity of from about 0 to about 60%, as defined by the literature densities for the 0 and 100% homopolymers, as noted below for the PET and PEN homopolymers). The concentration of each solution is thus selected on the basis of the aromatic dicarboxylic acid in the polymer (or where more than one dicarboxylic acid is used, on the basis of the first aromatic dicarboxylic acid as defined herein), and the solutions used were as follows.

PET: Low concentration solution: 1.28 g/cm^3 (240.80 g calcium nitrate; 860mL water; 1.71 M molar concentration with respect to calcium nitrate).
High concentration solution: 1.43 g/cm^3 (369.80 g calcium nitrate; 860mL water; 2.62 M calcium nitrate).

PEN: Low concentration solution: 1.32 g/cm^3 (275.20 g calcium nitrate; 860mL water; 1.95 M calcium nitrate).
High concentration solution: 1.41 g/cm^3 (352.60 g calcium nitrate, 860mL water; 2.50 M calcium nitrate).

The density column was calibrated using eight pips of known density which were washed in calcium nitrate solution before being placed in the graduated column. For each pip placed in the column, the volume height of the column was recorded upon reaching a constant level of suspension (after 4 to 5 hours). Separate measurements were taken for each pip to generate a calibration plot of volume height against density. The measurement method was repeated for each film specimen (dimensions 3x5mm) and three specimens were used for each film sample to generate a mean of the measured volume height, from which the measured density ($\rho_{recorded}$) was obtained from the calibration plot. The degree of crystallinity (χ_c) was then calculated for each sample using Equation (1):

$$\chi_c(\%) = 100\left(\frac{\rho_{recorded} - \rho_{amorphous}}{\rho_{crystalline} - \rho_{amorphous}}\right) \qquad (1)$$

where

χ_c = degree of crystallinity (%)

$\rho_{recorded}$ = recorded density of polymer (g cm^{-3})

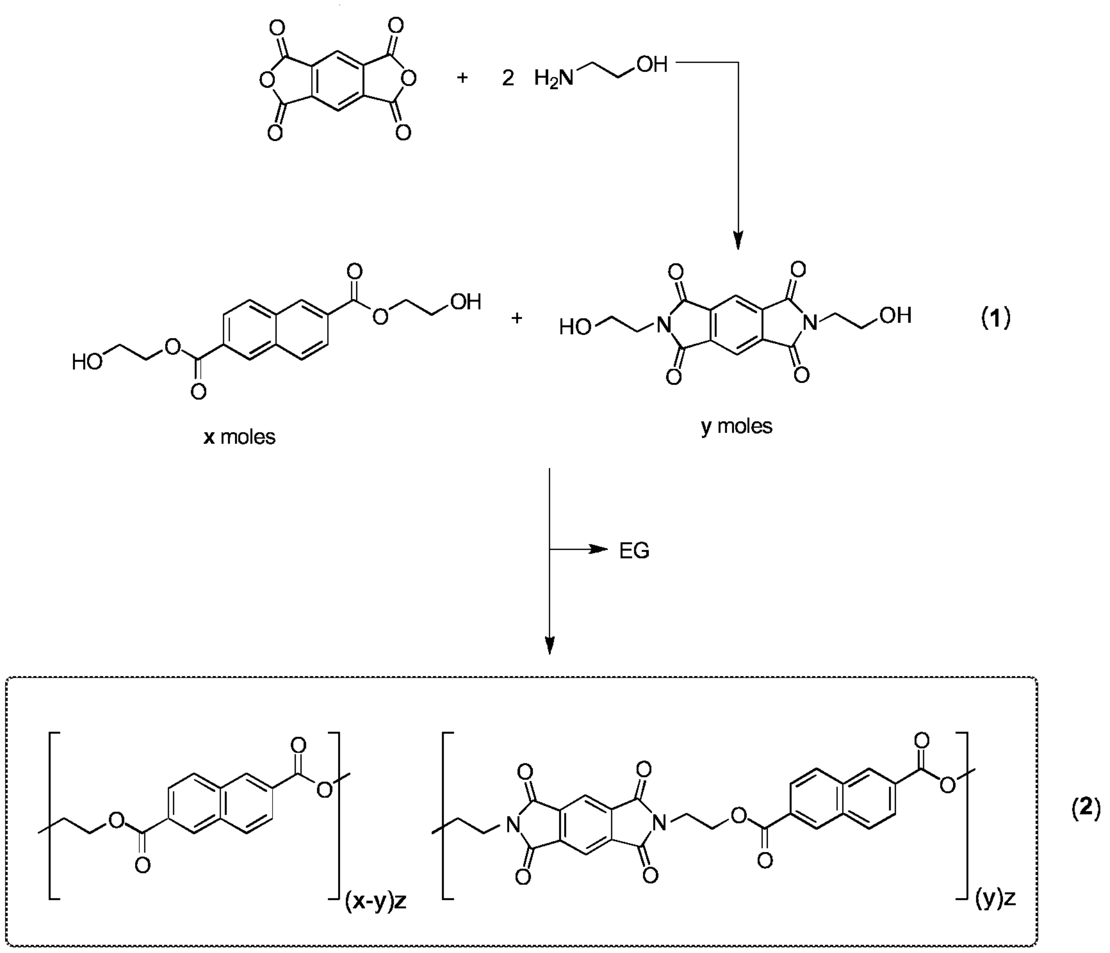
$\rho_{amorphous}$ = known density of amorphous homopolymer (0% crystallinity)

$\rho_{crystalline}$ = known density of 100% crystalline homopolymer.

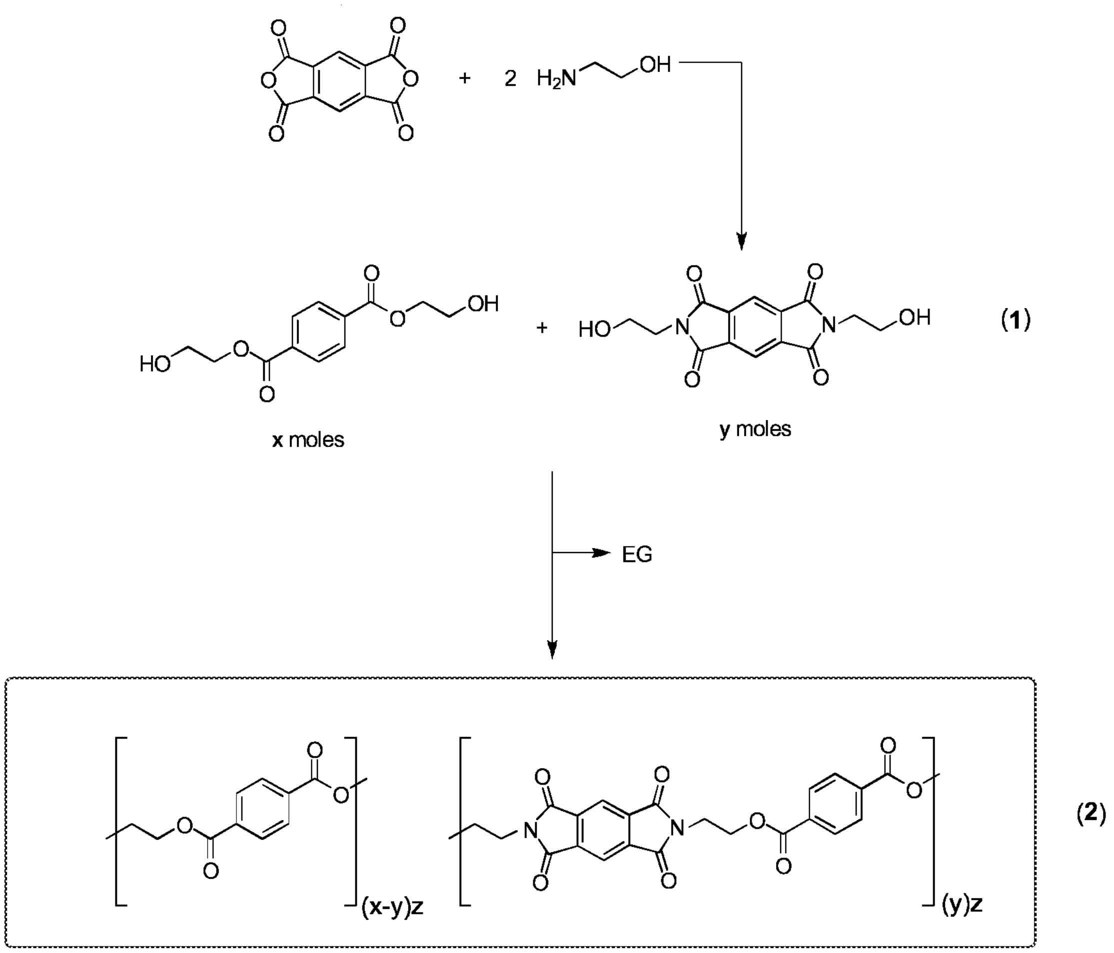
The invention is further illustrated by the following examples. It will be appreciated that the examples are for illustrative purposes only and are not intended to limit the invention as described above. Modification of detail may be made without departing from the scope of the invention.

EXAMPLES

Reaction schemes to prepare copolyesters of the present invention are shown in Schemes 1 and 2 below.

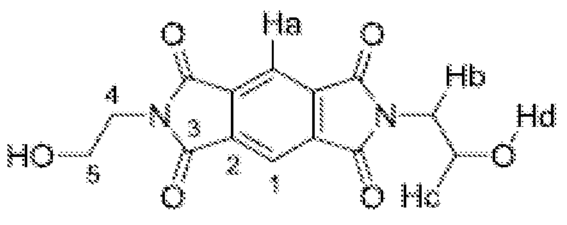


Scheme 1. Synthesis of comonomer **1** and its copolymerisation with bis(hydroxyethyl 2,6-naphthalate) to give a family of co(polyester-imide)s (**2**) (where z in Scheme 1 is the degree of polymerisation of the overall copolymer).



Scheme 2. Synthesis of comonomer **1** and its copolymerisation with bis(hydroxyethyl 2,6-terephthalate) to give a family of co(polyester-imide)s (**2**) (where z in Scheme 1 is the degree of polymerisation of the overall copolymer).

Example 1: *Synthesis of (monomer 1)*



Ethanolamine (1.70mL, 27.56 mmol) was added to a mixture of pyromellitic dianhydride (3.01 g, 13.80 mmol), DMAc (25mL) and toluene (15mL). The reaction mixture was then refluxed overnight, using a Dean-Stark apparatus to azeotropically distil off the co-produced water. The reaction mixture was cooled to room temperature and poured into water (~400mL) upon which a white precipitate formed. The suspension was stirred for

6 h, filtered, and the solid was washed with water and MeOH and dried under vacuum at 100 °C overnight to produce 3.72g of *N,N'*-bis-(2-hydroxyethyl)-pyromellitic diimide as an off-white powder (yield: 89%; mp (DSC): 283°C; MS *m/z*= 327.0589 [M+Na], calculated 327.0545, ^{1}H NMR (400 MHz, DMSO) δ(ppm) 8.22 (4H, m, H_{b+c}), 7.97 (2H, d, J = 8.16 Hz, H_a), 4.85 (2H, t, J = 12.0 Hz, H_f), 3.67 (4H, t, J = 11.3 Hz, H_d), 3.59 (4H, m, H_f); ^{13}C NMR (100 MHz, DMSO) δ (ppm)167.48 (C_{7+8}), 144.00 (C_1), 137.17 (C_3), 132.75 (C_4), 131.42 (C_6), 123.53 (C_2), 121.68 (C_5), 57.90 (C_9), 40.42 (C_{10}); IR (ν_{max}cm^{-1}) 3385, 3034, 2947, 2883, 1771, 1697, 1394, 1362, 1132).

Examples 2 to 11: synthesis of the copolyesters

Two series of novel linear poly(ester-imide)s were synthesised, by polycondensation between either bis-(2-hydroxyethyl)-terephthalate (BHET) or bis-(2-hydroxyethyl)-2,6-naphthalate (BHEN) and the comonomer of formula (I). Copolymers containing varying amounts of co-monomer were obtained using Sb_2O_3 or GeO_2 as catalyst. Transesterification was carried out under vacuum at 190-200°C over ca. 30-90 minutes, followed by a polycondensation stage at 290- 300 °C. The polymers were soluble in TFA and/or HFIP, and in mixtures of either TFA or HFIP with $CHCl_3$. Re-precipitation in MeOH gave white or off-white polymer beads which were isolated by filtration, washed with methanol and dried.

The general polyesterification procedure, illustrated for PET, is as follows: bis(2-hydroxyethyl) terephthalate (BHET, 5.01 g, 19.71 mmol) and Sb_2O_3 (1.50 mg, 4.12x10^{-3} mmol) were charged to a Schlenk tube fitted with a rubber-sealed stirrer guide and a glass stirrer rod. The reaction mixture was heated to the trans-esterification temp (Temp 1) over 30 minutes by use of a tube furnace under an inert nitrogen atmosphere and held for 20-30 minutes. A stirring rate of 300 rpm was then applied via a mechanical stirrer and the reaction mixture heated to the polycondensation temperature (Temp 2) over 40 min. A vacuum between 0.1 and 1 torr was gradually applied over 1-2 minutes and the temperature was maintained for a period (Soak Time) until the stirring rate dropped to 250-260 rpm as a result of the increasing viscosity of the reaction mixture. At this point, nitrogen was purged through the system, the stirrer was removed and the mixture was allowed to cool. The reaction tube was cut and the lower section, containing the polymer, was broken up. The polymer was dissolved away from the tube fragments and from the stirrer-rod in a solution of $CHCl_3$/TFA (2:1) (~50 mL),and the glass was filtered off. The resulting brown solution was concentrated in *vacuo* to ~15mL and beads were formed by precipitation in MeOH (~120mL). The polymer beads were filtered, washed with MeOH (2 x 15mL) and dried in a vacuum oven overnight at 120°C for PET (150°C for PEN). The corresponding conditions for PEN are shown in Table 1 below.

Table 1

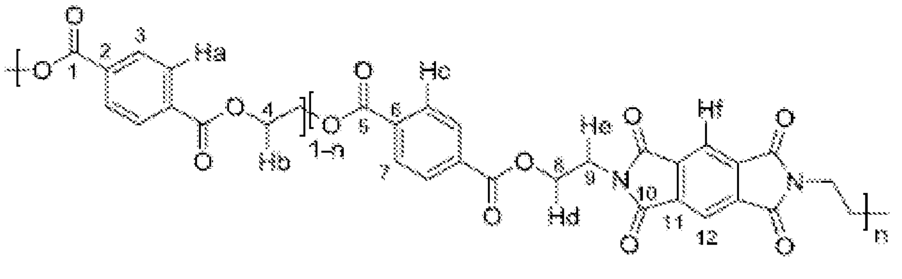
Monomer (g)	Monomer Mass (mg)	Catalyst	Catalyst Mass (mg)	Temp 1 (°C)	Temp 2 (°C)	Vacuum (torr)	Soak Time (min)
BHET	5.01	Sb_2O_3	1.5	190	290	0.4	60
BHEN	5.00	GeO_2	5.1	200	300	0.8	110

Replacement of varying amounts of BHET by comonomer (I), as shown in Table 2 below, provided copolyesters of PET with varying mole fractions of comonomer (I).

Table 2

Ex.	mol (%)	BHET (g)	PDI (g)	Sb_2O_3 (mg)	Temp 1 (°C)	Temp 2 (°C)	Vacuum (torr)	Soak Time (min)
2	5	4.7518	0.2996	1.6	190	290	0.6	50
3	10	4.5006	0.5994	1.7	190	300	0.7	45
4	15	4.2503	0.8981	1.6	190	290	0.6	45
5	20	2.4003	0.7187	1.0	190	290	0.7	30
6	25	2.2508	0.8979	1.0	190	290-310	0.5	30

The analytical results for the PET copolyesters are as follows.



Example 2: PETcoPDI-5

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.40 (s, H_f), 8.17 (s, H_a), 8.10 (s, H_c), 4.84 (s, H_b), 4.70 (s, H_d), 4.29 (s, H_e), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 167.85

(C_1), 166.98 (C_{10}), 137.09 (C_{11}), 133.31 (C_2), 133.11 (C_6), 130.05 (C_3), 119.33 (C_{12}), 63.92 (C_4), 63.50 (C_8), 37.67 (C_9), Tg = 88 °C, Tcc = 170 °C, Tm = 243 °C, Tc = 156 °C, η_{inh} = 0.58 dL g^{-1}.

Example 3: PETcoPDI-10

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.40 (s, 2H_f), 8.17 (s, 2H_a), 8.09 (m, 2H_c), 4.84 (s, 4H_b), 4.70 (s, 4H_d), 4.29 (s, 4H_e), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 167.84 (C_1), 166.91 (C_{10}), 137.09 (C_{11}), 133.32 (C_2), 133.12 (C_6), 130.05 (C_3), 119.33 (C_{12}), 63.92 (C_4), 63.49 (C_8), 37.66 (C_9), Tg = 96°C, Tcc = 158°C, Tm = 232°C, Tc = 159°C, η_{inh} = 0.69 dL g^{-1}.

Example 4: PETcoPDI-15

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.40 (s, 2H_f), 8.17 (s, 2H_a), 8.08 (m, 2H_c), 4.83 (s, 4H_b), 4.70 (s, 4H_d), 4.29 (s, 4H_e), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 167.80 (C_1), 166.93 (C_{10}), 137.08 (C_{11}), 133.31 (C_2), 133.10 (C_6), 130.04 (C_3), 119.33 (C_{12}), 63.92 (C_4), 63.51 (C_8), 37.65 (C_9), Tg = 106 °C, Tcc = 171 °C, Tm = 247 °C, Tc = 176 °C, η_{inh} = 1.02 dL g^{-1}.

Example 5: PETcoPDI-20

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.39 (s, 2H_f), 8.17 (s, 2H_a), 8.08 (d, 2H_c), 4.83 (s, 4H_b), 4.70 (s, 4H_d), 4.29 (s, 4H_e), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 167.85 (C_1), 166.93 (C_{10}), 137.08 (C_{11}), 133.30 (C_2), 133.09 (C_6), 130.04 (C_3), 119.34 (C_{12}), 63.92 (C_4), 63.51 (C_8), 37.64 (C_9), Tg = 102 °C, η_{inh} = 0.45 dL g^{-1}.

Example 6: PETcoPDI-25

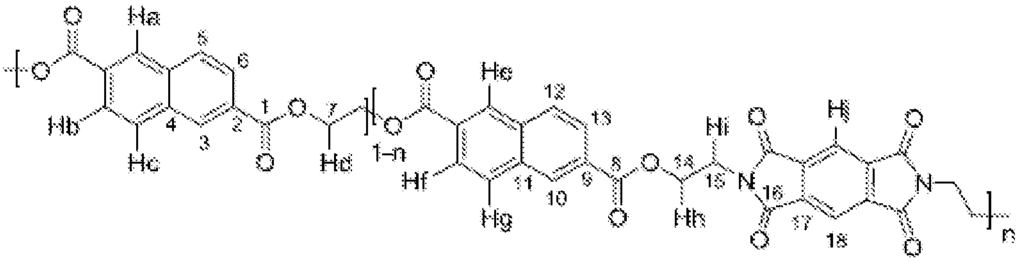
^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.39 (s, 2H_f), 8.17 (s, 2H_a), 8.08 (d, 2H_c), 4.84 (s, 4H_b), 4.70 (s, 4H_d), 4.29 (s, 4H_e), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 167.69 (C_1), 166.87 (C_{10}), 137.10 (C_{11}), 133.35 (C_2), 133.14 (C_6), 130.04 (C_3), 119.28 (C_{12}), 63.89 (C_4), 63.47 (C_8), 37.67 (C_9), Tg = 97 °C, η_{inh} = 0.30 dL g^{-1}, IR (ν_{max} cm^{-1}) 2956, 1717, 1457, 1405, 1388, 1340, 1263, 1251, 1119, 1102.

Replacement of varying amounts of BHEN by comonomer (I), as shown in Table 3 below, provided copolyesters of PEN with varying mole fractions of comonomer (I).

Table 3

Ex.	Mol (%)	BHEN (g)	PDI (g)	GeO_2 (mg)	Temp 1 (°C)	Temp 2 (°C)	Vacuum (torr)	Soak Time (min)
7	5	4.7506	0.2995	4.9	200	300	2.0	90
8	10	4.5009	0.5000	4.8	200	300	1.2	90
9	15	4.2503	0.8981	4.8	200	300	2.3	90
10	20	3.9998	1.0003	4.7	200	300	1.6	90
11	25	3.7502	1.2498	4.9	200	300	2.1	80

The analytical results for the PET copolyesters are as follows.



Example 7: PENcoPDI-5

^{1}H NMR (500 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.70 (s, H_a), 8.62 (s, H_e), 8.40 (s, H_j), 8.14 (d, J = 8.5 Hz, H_b), 8.06 (d, J = 8.5 Hz, H_c), 8.02 (m, H_g), 7.94 (s, H_f), 4.92 (s, H_d), 4.74 (s, H_h), 4.32 (s, H_i), ^{13}C NMR (125 MHz, $CDCl_3$:TFA (2:1)) 168.87 (C_1), 166.98 (C_{16}), 137.14 (C_{17}), 135.01 (C_4), 134.87 (C_{11}), 131.59 (C_3), 130.25 (C_5), 128.46 (C_2), 128.17 (C_9), 125.84 (C_6), 125.70 (C_{13}), 119.36 (C_{18}), 64.00 (C_7), 63.47 (C_8), 37.78 (C_9), Tg = 130 °C, Tm = 256 °C, η_{inh} = 0.49 dL g^{-1}.

Example 8: PENcoPDI-10

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.71 (s, $2H_a$), 8.60 (m, $2H_e$), 8.40 (s, $2H_j$), 8.13 (d, J = 8.4 Hz, $2H_b$), 8.05 (d, J = 8.8 Hz, $2H_c$), 8.02 (s, $2H_f$, $2H_g$), 4.91 (s, $4H_d$), 4.74 (s, $4H_h$), 4.32 (s, $4H_i$), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 168.89 (C_1), 166.98 (C_{16}), 137.10 (C_{17}), 134.98 (C_4), 131.58 (C_3), 130.23 (C_{5+12}), 128.40 (C_2), 128.14 (C_9), 125.79 (C_6), 125.68 (C_{13}), 119.36 (C_{18}), 64.00 (C_7), 63.45 (C_8), 37.74 (C_9), Tg = 136 °C, η_{inh} = 0.52 dL g^{-1}.

Example 9: PENcoPDI-15

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.71 (m, $2H_a$), 8.60 (m, $2H_e$), 8.40 (s, $2H_j$), 8.14 (d, J = 8.4 Hz, $2H_b$), 8.03 (m, $2H_c$, $2H_f$, $2H_g$), 4.91 (s, $4H_d$), 4.74 (s, $4H_h$), 4.32 (s, $4H_i$), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 168.91 (C_1), 166.99 (C_{16}), 137.10 (C_{17}), 134.98 (C_4), 131.58 (C_3), 130.22 (C_5), 128.39 (C_2), 128.10 (C_9), 125.78 (C_6), 125.64 (C_{13}), 119.37 (C_{18}), 63.98 (C_7), 63.45 (C_8), 37.76 (C_9), Tg = 144 °C, η_{inh} = 0.47 dL g^{-1}.

Example 10: PENcoPDI-20

^{1}H NMR (400 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.71 (m, $2H_a$), 8.60 (m, $2H_e$), 8.40 (s, $2H_j$), 8.14 (d, J = 8.8 Hz, $2H_b$), 8.03 (m, $2H_c$, $2H_f$, $2H_g$), 4.91 (s, $4H_d$), 4.74 (s, $4H_h$), 4.32 (s, $4H_i$), ^{13}C NMR (100 MHz, $CDCl_3$:TFA (2:1)) 168.90 (C_1), 166.98 (C_{16}), 137.11 (C_{17}), 134.98 (C_4), 131.58 (C_3), 130.23 (C_5), 128.40 (C_2), 128.12 (C_9), 125.79 (C_6), 125.65 (C_{13}), 119.45 (C_{18}), 63.99 (C_7), 63.45 (C_8), 37.82 (C_9), Tg = 148 °C, η_{inh} = 0.46 dL g^{-1}.

Example 11: PENcoPDI-25

^{1}H NMR (500 MHz, $CDCl_3$:TFA (2:1)) δ (ppm) 8.73 (m, $2H_a$), 8.62 (m, $2H_e$), 8.42 (s, $2H_j$), 8.16 (d, J = 10.45 Hz, $2H_b$), 8.06 (m, $2H_c$, $2H_f$, $2H_g$), 4.95 (s, $4H_d$), 4.76 (s, $4H_h$), 4.34 (s, $4H_i$), ^{13}C NMR (500 MHz, $CDCl_3$:TFA (2:1)) 168.81 (C_1), 166.98 (C_{16}), 137.11 (C_{17}), 134.98 (C_4), 134.94 (C_{11}), 131.59 (C_3), 131.55 (C_{10}), 130.24 (C_{5+12}), 128.43 (C_2), 128.14 (C_9), 125.83 (C_6), 125.68 (C_{13}), 119.35 (C_{18}), 64.00 (C_7), 63.48 (C_8), 37.76 (C_9), Tg = 151 °C, η_{inh} = 0.45 dL g^{-1}, IR (ν_{max} cm^{-1}) 2956, 1717, 1387, 1339, 1278, 1257, 1182, 1132, 1091.

The experimental data for the Examples are summarised in Table 4 below. The control samples are pure PET or PEN, synthesised in accordance with the procedure described for Examples 2 to 11, but without the inclusion of the comonomer. The enthalpy of fusion and degree of crystallinity data in Table 4 were obtained using the standard (non-annealing) DSC process.

Table 4

Example	Polymer	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	Xc (%)	Viscosity (gdL^{-1})
Control	PET	75	-	257	44	31	0.80
2	PETcoPDI-5	88	170	243	23	16	0.58
3	PETcoPDI-10	96	158	232	13	-	0.69
4	PETcoPDI-15	106	171	247	4	-	1.02
5	PETcoPDI-20	102	-	245	2	-	0.45
6	PETcoPDI-25	97	-	-	-	-	0.3
Control	PEN	119	191	267	36	35	0.67
7	PENcoPDI-5	130	224	256	4.9	5	0.49
8	PENcoPDI-10	136	-	-	-	-	0.52
9	PENcoPDI-15	144	-	-	-	-	0.47
10	PENcoPDI-20	148	-	-	-	-	0.46
11	PENcoPDI-25	151	-	-	-	-	0.45

Examples 12, 13 and 14

Three PEN copolymers (referred to herein as PENcoPDI-5, PENcoPDI-10 and PENcoPDI-16) comprising 5, 10.3 and 16.4 mol%, respectively, of monomer (I) were manufactured on a larger scale (using a 5 gallon reactor) using the synthetic methods described above, then dried overnight (8 hours at 150°C), and biaxially oriented films manufactured therefrom. The amount of comonomer (I) in the copolymer was determined by NMR. A 100% PEN film was also prepared as a control.

Each polymer was fed to an extruder (single screw; screw speed approx. 80rpm) at a temperature in the range of 275 to 300°C. A cast film was produced, which was electrostatically pinned and threaded around the casting drum and over the top of the forward draw onto a scrap winder. Once settled, cast samples are collected at a range of casting drum speeds (2, 3 and 5 m\min) to give a range of thicknesses. The cast films are subsequently drawn using a Long Stretcher (supplied by T.M. Long Co., Somerville, New Jersey). The Long Stretcher comprises a hydraulically operated stretching head mounted inside a heated oven with a liftable lid. The operation of the stretching mechanism is based upon the relative motion of two pairs of draw bars (one fixed and one moveable, mounted normally to one another). The draw bars are attached to hydraulic rams which control the amount (draw ratio) and speed (draw rate) of the imposed stretching. On each draw bar are mounted pneumatic sample clips attached to a pantograph system. A sample loading system is used to position samples within the pneumatic clips. A cast sample cut to a specific size (11.1x11.1cm) is located symmetrically on a vacuum plate attached to the end of an arm. The arm is run into the oven and the sample lowered so that it is between the clips. The clips are closed using nitrogen pressure to hold the film and the loading arm withdrawn. The oven is heated to a specified temperature by two plate-heaters. The lid is lowered and air heaters rapidly bring the sample up to a specified temperature. After a suitable preheat time (30 seconds), the draw is manually initiated by the operator. A draw rate of approximately 2.54cm/second was used. Simultaneous biaxial draw in perpendicular directions is used in these examples. The processing conditions are given in Table 5 below.

Table 5

Sample ID	**Approx Draw Ratio**	**Air Heater Temp (°C)**	**Plate Heater Temp (°C)**
Control: 100%PEN	3.5x3.5	155	150
Ex.12: PENcoPDI-5	3.5x3.5	155	150
Ex.13: PENcoPDI-10	3.5x3.5	168	160
Ex.14: PENcoPDI-16	3.5x3.5	165	160

The films produced on the Long Stretcher are then crystallised using the Laboratory Crystallisation Rig and held at specified temperatures for specified times (as presented in Tables 6 to 9 below). In this equipment, samples are clamped in a frame which is dropped pneumatically and held between heated platens for a specific time before being rapidly quenched by dropping into iced water.

Crystallinity of film samples was calculated using the density method described herein on the basis of the following literature data for known values for PEN density and crystallinity:

Density of 0% crystallinity PEN = 1.325 g/cm^3

Density of 100% crystallinity PEN = 1.407 g/cm^3

The density and crystallinity results for the films are shown in Tables 6 to 9 below.

Table 6: PEN control film

Sample	Crystallisation conditions	Density	%Crystallinity
1	None	1.346	25.88
2	2s @ 220°C	1.360	42.67
3	10s @ 220°C	1.361	43.82
4	100s @ 220°C	1.362	45.35
5	2s @ 230°C	1.363	45.74
6	10s @ 230°C	1.362	45.60
7	100s @ 230°C	1.366	49.37
8	2s @ 240°C	1.362	44.82
9	10s @ 240°C	1.362	45.21
10	100s @ 240°C	1.361	43.32

Table 7: PENcoPDI-5 film (Example 12)

Sample	Crystallisation conditions	Density	%Crystallinity
1	None	1.3537	35.03
2	2s @ 200°C	1.3516	32.49
3	10s @ 200°C	1.3624	45.57
4	100s @ 200°C	1.3639	47.47
5	2s @ 210°C	1.3627	45.96
6	10s @ 210°C	1.3635	46.94
7	100s @ 210°C	1.3631	46.41
8	2s @ 220°C	1.3613	44.21
9	10s @ 220°C	1.3622	45.38
10	100s @ 220°C	1.3641	47.66
11	2s @ 225°C	1.3613	44.31
12	10s @ 225°C	1.3622	45.33
13	100s @ 225°C	1.3643	47.96
14	2s @ 230°C	1.3559	37.74
15	10s @ 230°C	1.3629	46.24
16	100s @ 230°C	1.3627	45.92
17	2s @ 240°C	1.3581	40.42

Table 8: PENcoPDI-10 film (Example 13)

Sample	Crystallisation Conditions	Density(g\cm3)	%Crystallinity
1	None	1.3637	47.17
2	2s @ 180^{0}C	1.3577	39
3	10s @ 180^{0}C	1.3608	43.71
4	100s @ 180^{0}C	1.3672	51.41
5	10s @ 190^{0}C	1.3592	41.69
6	10s @ 200^{0}C	1.3637	47.15

Table 9: PENcoPDI-16 film (Example 14)

Sample	Crystallisation Conditions	Density(g\cm3)	%Crystallinity
1	None	1.3590	41.5
2	10s @ 180^{0}C	1.3594	41.97
3	10s @ 190^{0}C	1.3625	45.71

The data in Tables 7, 8 and 9 demonstrate that the copolymers of the present invention can be manufactured into crystalline biaxially oriented films under typical stenter conditions used on a conventional film-line, and that films manufactured in this way exhibit excellent crystallinity. With the higher amounts of comonomer present in Examples 13 and 14, the manufacture of biaxially oriented crystalline films is suitably conducted at relatively lower heat-set (crystallisation) temperatures in the stenter.

Examples 15 and 16

Two PET copolymers (referred to herein as PETcoPDI-12 and PETcoPDI-16) comprising 12.5 and 16.7 mol%, respectively, of monomer (I) were manufactured on a larger scale (using a 5 gallon reactor) using the synthetic methods described above for Example 12. The amount of comonomer (I) in the copolymer was determined by NMR. The copolymer PETcoPDI-12 exhibited a Tg of 108°C and a Tm of 240°C. The copolymer PETcoPDI-16 exhibited a Tg of 103°C and a Tm of 257°C. The polymers were dried overnight as described above and biaxially oriented films manufactured therefrom as described above. A 100% PET film was also prepared as a control. The processing conditions are given in Table 10 below.

Table 10

Sample	Draw Ratio	Air Heater Temp (°C)	Plate Heater Temp (°C)	Draw Speed (cm\sec)	Preheat Time (sec)
Control: 100%PET	3.5x3.5	100	100	2.54	30
Ex.15: PETcoPDI-12	3.5x3.5	120	120	5.08	30
Ex.16: PETcoPDI-16	3.5x3.5	110	108	5.08	25

Crystallinity of film samples was calculated using the density method described herein on the basis of the following literature data for known values for PET density and crystallinity:

Density of 0% crystallinity PET = 1.335g/cm^3

Density of 100% crystallinity PET = 1.455 g/cm^3

The density and crystallinity results for the films are shown in Tables 11, 12 and 13 below.

Table 11: 100% PET Control Film

Sample	Crystallisation Conditions	Density(g\cm3)	%Crystallinity
1	None	1.3529	14.94
2	2s @ 220°C	1.3944	49.48
3	10s @ 220°C	1.3969	51.57
4	100s @ 220°C	1.3913	46.93
5	2s @ 230°C	1.3903	46.06
6	10s @ 230°C	1.3888	44.85
7	100s @ 230°C	1.3910	46.66
8	2s @ 240°C	1.3597	20.59
9	10s @ 240°C	1.3959	50.74
10	100s @ 240°C	Melted	Melted

The PET control film exhibited a crystallinity of 14.94% for the non-heat-set biaxially oriented film, and this increased to about 50% after additional crystallisation during heat-setting. At 240°C the film samples started to melt during crystallisation.

Table 12: PETcoPDI-12 Film (Example 15)

Sample	Crystallisation Conditions	Density(g\cm^3)	%Crystallinity
1	None	1.3669	26.60
2	2s @ 220^{0}C	1.3735	32.08
3	10s @ 220^{0}C	1.3716	30.54
4	100s @ 220^{0}C	1.3743	32.79
5	2s @ 230^{0}C	1.3717	30.55
6	10s @ 230^{0}C	1.3713	30.23
7	100s @ 230^{0}C	1.3717	30.55
8	2s @ 240°C	Melted	Melted
9	10s @ 240°C	Melted	Melted
10	100s @ 240°C	Melted	Melted

Table 13: PETcoPDI-16 Film (Example 16)

Sample	Crystallisation Conditions	Density(g\cm^3)	%Crystallinity
1	None	1.3681	27.62
2	2s @ 220^{0}C	1.3890	45.01
3	10s @ 220^{0}C	1.3884	44.47
4	100s @ 220^{0}C	1.3871	43.45
5	2s @ 230^{0}C	1.3901	45.94
6	10s @ 230^{0}C	1.3875	43.75
7	100s @ 230^{0}C	1.3922	47.70
8	2s @ 240^{0}C	1.3903	46.09
9	10s @ 240^{0}C	1.3832	40.10
10	100s @ 240^{0}C	1.3898	45.65

The data in Tables 12 and 13 demonstrate that the copolymers of the present invention can be manufactured into crystalline biaxially oriented films under typical stenter conditions used on a conventional film-line, and that films manufactured in this way exhibit excellent crystallinity. Because of the lower melting point of Example 15, the manufacture of biaxially oriented crystalline films is suitably conducted at relatively lower heat-set (crystallisation) temperatures in the stenter.

Example 17

The PENcoPDI-5 copolyesterimide was manufacture using solid state polymerisation techniques, using a starting polymer prepared in a manner similar to that described for Example 7 above. A polymer sample weighing approximately 5 g was placed in a Schlenk tube within a hot block. The sample was then heated at 200 °C for 16 h *in vacuo* (< 0.1 mbar). After the SSP procedure, the higher molecular weight polymer was analysed by DSC to measure the crystallinity of the polymer directly after SSP (i.e. without erasing its thermal history), which demonstrated that the final polymer exhibited a ΔH_m of 46.56 J g^{-1} and a crystallinity of 45%.

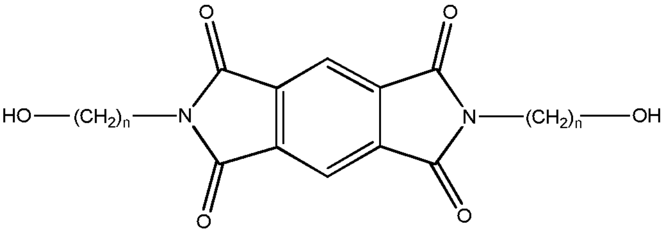
The carboxyl end-group contents of the polymer were also analysed, and the values are presented in Table 14 below. As noted herein, the copolyesters described herein exhibit a surprisingly low carboxyl end-group content, and SSP accentuates this characteristic.

Table 14: Carboxyl end-group content

Sample	COOH end groups (gram equivalents/10^6g polymer)	
	Pre-SSP	**Post-SSP**
PEN control	22.96	13.12
PEN*co*PDI5	3.83	Not detected

CLAIMS

1. A polyester film comprising a copolyester which comprises repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I):



(I)

wherein n = 2, 3 or 4, and wherein comonomer (I) constitutes a proportion of the glycol fraction of the copolyester.

2. A film according to claim 1 wherein the monomer (I) is present in a range of from about 1 to about 50 mol% of the glycol fraction of the copolyester.

3. A film according to any preceding claim wherein the aliphatic glycol is selected from C_2, C_3 or C_4 aliphatic diols.

4. A film according to any preceding claim wherein the aliphatic glycol is ethylene glycol.

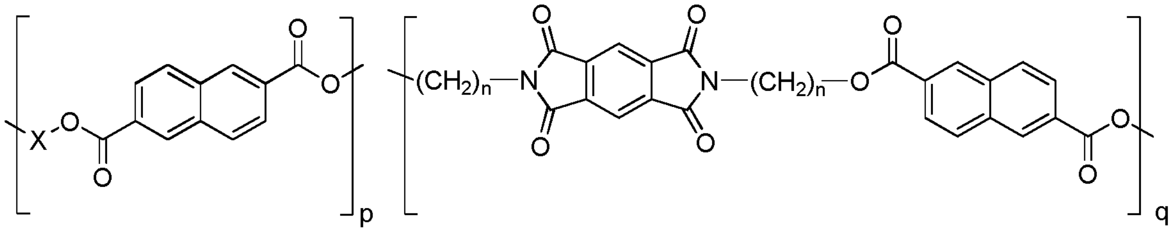
5. A film according to any preceding claim wherein the number of carbon atoms in the aliphatic glycol is the same as the number (n) in comonomer (I).

6. A film according to any preceding claim wherein n = 2.

7. A film according to any preceding claim wherein the aromatic dicarboxylic acid is selected from naphthalene dicarboxylic acid and terephthalic acid.

8. A film according to any preceding claim wherein the aromatic dicarboxylic acid is 2,6-naphthalene dicarboxylic acid.

9. A film according to any of claims 1 to 8 wherein the copolyester has formula (IIa):



(IIa)

wherein:

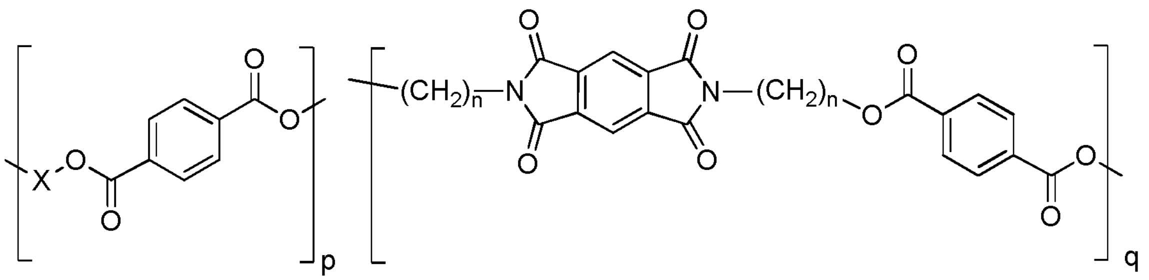
n = 2, 3 or 4;

the group X is the carbon chain of said aliphatic glycol; and

p and q are the molar fractions of the aliphatic glycol-containing repeating ester units and the monomer (I)-containing repeating ester units, respectively.

10. A film according to claim 9 wherein the monomer (I) is present in amounts of from about 3 to about 15 mol%, preferably in amounts of no more than about 10 mol%, of the glycol fraction of the copolyester.

11. A film according to any of claims 1 to 7 wherein the copolyester has formula (IIb):



(IIb)

wherein:

n = 2, 3 or 4;

the group X is the carbon chain of said aliphatic glycol; and p and q are the molar fractions of the aliphatic glycol-containing repeating ester units and the monomer (I)-containing repeating ester units, respectively.

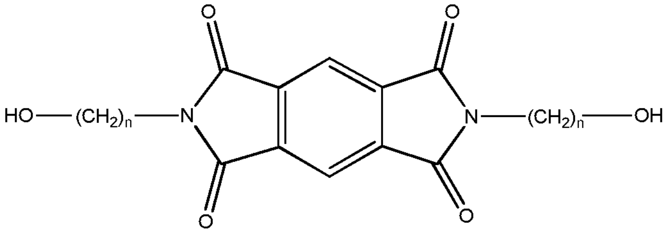
12. A film according to claim 11 wherein the monomer (I) is present in a range of from about 1 to about 30 mol%, preferably from about 3 to about 15 mol%, of the glycol fraction of the copolyester.

13. A film according to any preceding claim wherein the copolyester exhibits a carboxyl end-group content of no more than 25, and preferably no more than 1 gram equivalents/10^6g polymer.

14. A film according to any preceding claim wherein the film is an oriented film, particularly a biaxially oriented film.

15. A film according to any preceding claim wherein said aromatic dicarboxylic acid is naphthalene dicarboxylic acid and the degree of crystallinity of the film is at least about 10% as calculated from the film density and on the basis of the density of 0% crystalline polyethylene naphthalate (PEN) being 1.325 g/cm^3 and the density of 100% crystalline PEN being 1.407 g/cm^3; or wherein said aromatic dicarboxylic acid is terephthalic acid and the degree of crystallinity of the film is at least about 10% as calculated from the film density and on the basis of the density of 0% crystalline polyethylene terephthalate (PET) being 1.335 g/cm^3 and the density of 100% crystalline PET being 1.455 g/cm^3.

16. A process for preparing a copolyester comprising repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I):



(I)

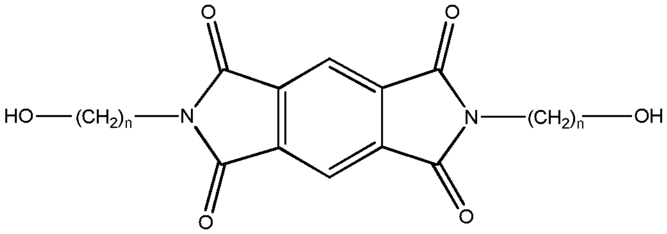
wherein n = 2, 3 or 4, wherein comonomer (I) constitutes a proportion of the glycol fraction of the copolyester, wherein said process comprises the steps of:

(i) reacting said aliphatic glycol with said aromatic dicarboxylic acid (preferably naphthalene dicarboxylic acid or terephthalic acid) to form a bis(hydroxyalkyl)-ester of said aromatic dicarboxylic acid (preferably bis(hydroxyalkyl)-naphthalate or bis(hydroxyalkyl)-terephthalate);

(iii) reacting said bis(hydroxyalkyl)-ester of said aromatic dicarboxylic acid with the monomer (I) under conditions of elevated temperature and pressure in the presence of a catalyst.

17. A process according to claim 16 wherein said aromatic dicarboxylic acid is naphthalene dicarboxylic acid and said bis(hydroxyalkyl)-ester is bis(hydroxyalkyl)-naphthalate, or wherein said aromatic dicarboxylic acid is terephthalic acid and said bis(hydroxyalkyl)-ester is bis(hydroxyalkyl)-terephthalate).

18. A copolyester comprising repeating units derived from an aliphatic glycol, an aromatic dicarboxylic acid, and the monomer of formula (I):



(I)

wherein n = 2, 3 or 4;

wherein comonomer (I) constitutes a proportion of the glycol fraction of the copolyester; and

wherein said copolyester is obtainable by the process according to claim 16 or 17 and/or exhibits a carboxyl end-group content of no more than 25, and preferably no more than 1 gram equivalents/10^6g polymer.

19. A process according to claim 16 or 17 or a copolyester according to claim 18 wherein the copolyester is as defined in any of claims 2 to 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/051740

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G63/685 C08J5/18 C08G73/16
ADD.

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)
C08G C08J

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	page 2, line 58 - page 3, line 10; examples 2, 3, 5h, 5i; tables II, III -----	8-10,14, 15
X	US 4 605 728 A (TUNG WILLIAM C T [US]) 12 August 1986 (1986-08-12)	16-19
A	column 1, line 16 - column 1, line 19; examples 1-4 -----	1-15
X	US 2005/171326 A1 (EDWARDS WALTER L [US] ET AL) 4 August 2005 (2005-08-04)	1-7,13, 14,18,19
A	paragraph [0128] - paragraph [0193]; claims 26, 36, 37, 42; examples 2-4; tables 2-4 -----	8-12, 15-17
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search 13 August 2014	Date of mailing of the international search report 21/08/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Enescu, Cristina

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 050 789 A1 (MITSUI CHEMICALS INC [JP]) 22 April 2009 (2009-04-22) paragraph [0033] - paragraph [0089]; claims 1, 18, 21; examples 2, 7-10, 13, 24; tables 1, 2 -----	1-19
A	LEE W-F ET AL: "VARIOUS PROPERTIES OF DIIMIDE-DIACID-MODIFIED SATURATED POLYESTERS", JOURNAL OF APPLIED POLYMER SCIENCE, WILEY, US, vol. 52, no. 1, 4 April 1994 (1994-04-04), pages 69-75, XP000464460, ISSN: 0021-8995, DOI: 10.1002/APP.1994.070520108 page 69, right-hand column, line 26 - page 73, left-hand column, line 25; figure 3; examples 6-9; tables I, III -----	1-19

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Information on patent family members

International application No
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