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C08L 71/08 (2006.01)

(56) Documents Cited:
WO 2015/198063 A1 **WO 2015/189567 A1**
WO 2015/124903 A1 **WO 2014/207458 A1**
Polymer Preprints (American Chemical Society, Division of Polymer), 1999, 40 (1), Zhou, Hong Wei et. al., pages 203-204, note particularly page 203, disclosing preparation of PEDEK-PEDEKDK copolymers, wherein Tg and Tm are studied using DSC.

(58) Field of Search:
INT CL **C08G, C08L**
Other: **CAS ONLINE, EPODOC, WPI.**

(54) Title of the Invention: **Polymeric materials**
Abstract Title: **Polyaryletherketone (PAEK) polymer materials**

(57) A polymer material, such as a polyaryletherketone (PAEK), having a repeat unit of formula (I) –O-R1-O-R3- and a repeat unit of formula (II) –O-R2-O-R3- wherein R1 and R2 are different and are both selected from phenyl, biphenyl, terphenyl, naphthyl or phenyl-ether-phenyl moieties, R3 is selected from benzophenone, 1,4-bis(benzoyl) benzene, 2,6-bis(benzoyl) naphthalene or 4,4’-bis(benzoyl) biphenyl moieties, preferably wherein the polymer has a melting temperature of less than 440°C. Also disclosed is a process for manufacture of the polymer; a pack comprising the polymer, a component comprising the polymer, a method of making the component and use of the polymer.

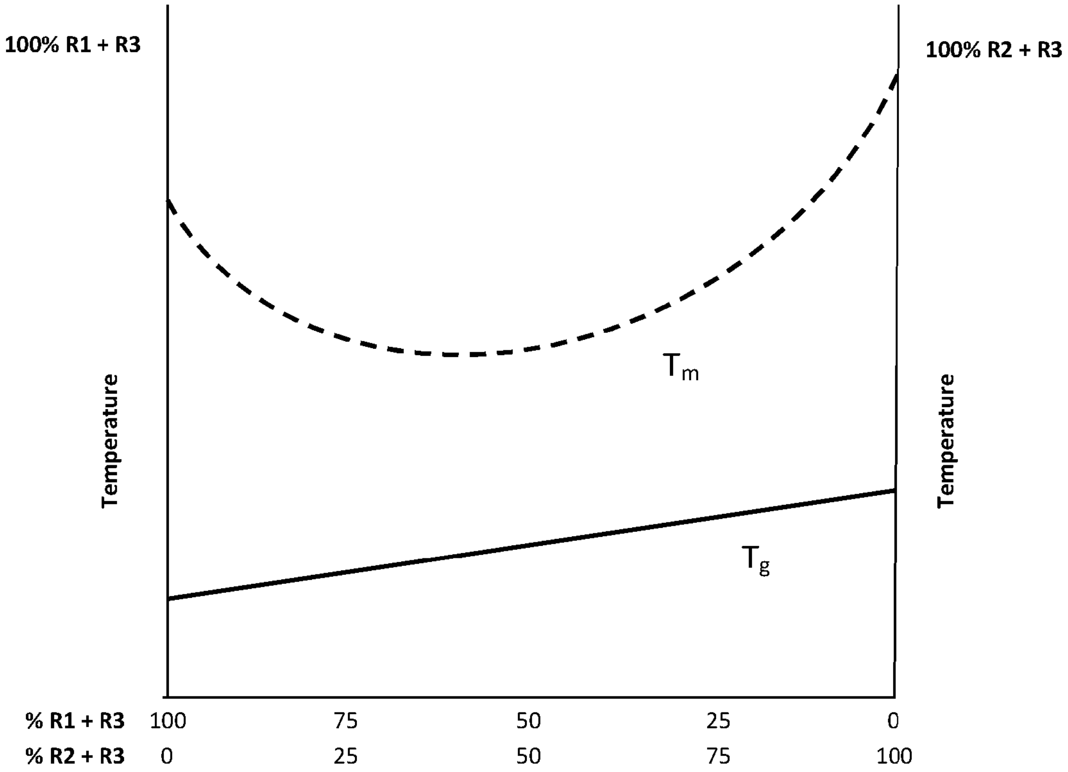

100% R1 + R3
100% R2 + R3
Temperature
Temperature
T_m
T_g
% R1 + R3
% R2 + R3
100
0
75
25
50
50
25
75
0
100

Fig 1

Polymeric Materials

This invention relates to polymeric materials. Preferred embodiments relate to high temperature polyaryletherketone (PAEK) thermoplastic materials for use in extreme environments (i.e. high temperature, high pressure, corrosive) for example, in the oil and gas industry.

There is a wide range of thermoplastic polymeric material available for use in industry, either alone or as part of composite materials. However, industry is constantly demanding materials with properties that are improved in at least some respect over existing materials.

Polyetheretherketone (PEEK) is a known and widely used polymeric material with a melt temperature (Tm) of 343°C which facilitates ease of processing. However, its glass transition temperature (Tg) of 143°C is too low for a number of demanding applications. Nonetheless, PEEK polymer is the material of choice for many commercial applications because it is highly crystalline and has outstanding chemical resistance properties.

In contrast, polyaryletherketones such as polyetherketone (PEK) and polyetherketoneetherketoneketone (PEKEKK) exhibit somewhat higher Tg values, but also have a higher Tm (Kemmish, D.J., Update on the Technology and Applications of Polyaryletherketones, Smithers, 2010, p 5) meaning that they are difficult to process using standard equipment and as a result have largely failed to gain acceptance in the marketplace.

Crystalline thermoplastics, which include polyaryletherketones, generally meet the following relationship (Billmeyer F.W., Textbook of Polymer Science, Wiley Interscience 3rd Edition, 1984):

$$Tg\ (K)/Tm\ (K) = 1/2 \text{ to } 2/3$$

Therefore the demand for a higher Tg is effectively limited by the desire to also have a polymer processing temperature that is low enough to avoid degradation of the polymer.

Sulphone co-monomers have been used to increase the Tg of PAEKs without significantly affecting the Tm. However, the presence of a sulphone group in the polymer backbone has been found to result in a polymer which is less chemically resistant since the sulphone group is more labile and its presence reduces the crystallinity, and consequently the chemical resilience, of the polymer. Additionally, it is known that under extreme conditions PAEK thermoplastics which contain the EK repeat unit (e.g. PEK, PEKEKK, etc) have been found to undergo severe degradation, thus making these materials unsuitable for such applications.

Accordingly it would be advantageous to provide a polymeric material that overcomes or at least alleviates the aforementioned problems.

According to a first aspect of the present invention, there is provided a polymeric material having a repeat unit of formula

$$\text{-O-R1-O-R3-} \qquad \text{I}$$

and a repeat unit of formula

$$\text{-O-R2-O-R3-} \qquad \text{II}$$

wherein R1 and R2 are different and are both selected from phenyl, biphenyl, terphenyl, naphthyl, or phenyl-ether-phenyl moieties, including isomers thereof, wherein R3 is selected from benzophenone, 1,4-bis(benzoyl) benzene, 2,6-bis(benzoyl) naphthalene or 4,4'-bis(benzoyl) biphenyl moieties, including isomers thereof, and wherein said polymeric material has a Tm (measured as described in Example 1 herein) of less than 440°C.

Surprisingly it has been found that the polymeric material according to the first aspect addresses the above problems because it exhibits beneficial Tg and Tm characteristics whilst also avoiding the need for sulphone groups and EK repeat units. The advantage, in terms of lower Tm and higher Tg, of the polymeric material of the first aspect is illustrated by the schematic graph shown in Figure 1. The y-axes of the graph represent temperature and the x-axis represents the molar proportion of the repeat units I and II of the polymeric material, i.e. the Tg and Tm values on the left-hand y-axis relate to a polymeric material containing repeat unit I only, whereas the Tg and Tm values on the right-hand y-axis relate to a polymeric material containing repeat unit II only. This graph indicates that the relationship between Tg and Tm is improved for a polymeric material according to the present invention that has both repeat units I and II.

In the following discussion of the invention, unless stated to the contrary, the disclosure of alternative values for the upper or lower limit of the permitted range of a parameter, coupled with an indication that one of said values is more highly preferred than the other, is to be construed as an implied statement that each intermediate value of said parameter, lying between the more preferred and the less preferred of said alternatives, is itself preferred to said less preferred value and also to each value lying between said less preferred value and said intermediate value.

Throughout this specification, the term “comprising” or “comprises” means including the component(s) specified but not to the exclusion of the presence of other components. The term “consisting essentially of” or “consists essentially of” means including the components specified but excluding other components except for materials present as impurities, unavoidable materials present as a result of processes used to provide the components, and components added for a purpose other than achieving the technical effect of the invention. Typically, when referring to compositions, a composition consisting essentially of a set of components will comprise less than 5% by weight, typically less than 3% by weight, more typically less than 1% by weight of non-specified components.

The term “consisting of” or “consists of” means including the components specified but excluding other components.

Whenever appropriate, depending upon the context, the use of the term “comprises” or “comprising” may also be taken to include the meaning “consists essentially of” or “consisting essentially of”, and also may also be taken to include the meaning “consists of” or “consisting of”.

References herein such as “in the range x to y” are meant to include the interpretation “from x to y” and so include the values x and y.

The Tm of said polymeric material (measured as described in Example 1 herein) may preferably be less than 430°C, more preferably less than 420°C, even more preferably less than 410°C, even more preferably less than 400°C, even more preferably less than 390°C, most preferably less than 385°C. The Tm may preferably be greater than 340°C, more preferably greater than 350°C, even more preferably greater than 360°C. The Tm is preferably in the range 360°C to 410°C, more preferably 360°C to 400°C, even more preferably 360°C to 385°C.

Preferably R3 is the same for both repeat unit I and for repeat unit II.

Preferably said isomers are structural isomers.

The phenylene moieties present in R3 in each repeat unit may independently have 1,4- para linkages to atoms to which they are bonded or 1,3- meta linkages. Where a phenylene moiety includes 1,3- linkages, the moiety will be in the amorphous phase of the polymer. Crystalline phases will include phenylene moieties with 1,4- linkages. In many applications it is preferred for the polymeric material to be highly crystalline and, accordingly, the polymeric material preferably includes high levels of phenylene moieties with 1,4- linkages.

In a preferred embodiment, at least 90%, more preferably at least 95%, most preferably at least 99% of the number of phenylene moieties (Ph) in the repeat unit of formulae I have 1,4- linkages to moieties to which they are bonded. It is especially preferred that each phenylene moiety in the repeat unit of formulae I and II has 1,4- linkages to moieties to which it is bonded.

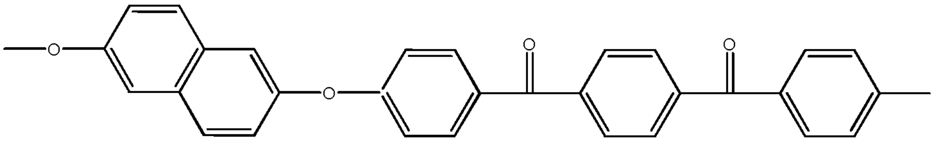
In a preferred embodiment, at least 90%, more preferably at least 95%, most preferably at least 99% of the number of phenylene moieties (Ph) in the repeat unit of formula II have 1,4-linkages to moieties to which they are bonded. It is especially preferred that each phenylene moiety in the repeat unit of formula II has 1,4- linkages to moieties to which it is bonded.

Preferably, the phenylene moieties in repeat unit of formula I are unsubstituted. Preferably, the phenylene moieties in repeat unit of formula II are unsubstituted.

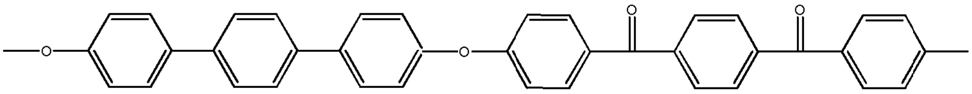
In repeat unit I R1 preferably is selected from phenyl, terphenyl, napthyl, or phenyl-ether-phenyl moieties, including isomers thereof.

In repeat unit II, R2 preferably is selected from biphenyl or terphenyl moieties, including isomers thereof.

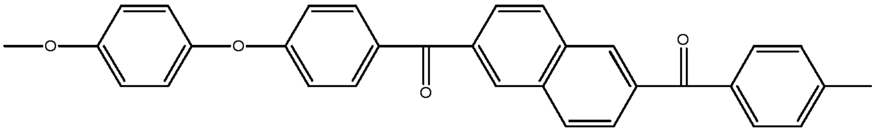
In a first preferred embodiment said repeat unit of formula I has the structure


III

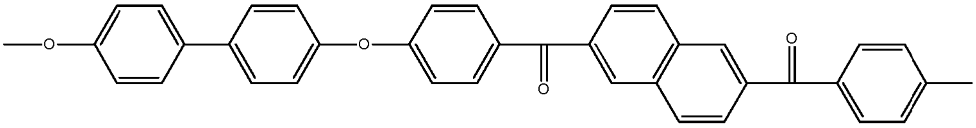
and/or said repeat unit of formula II has the structure


IV.

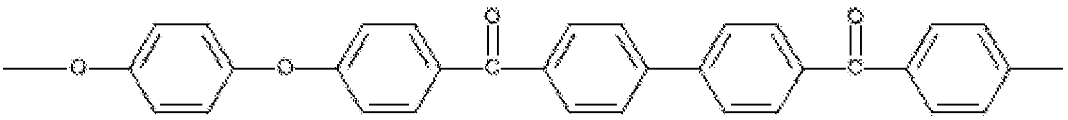
In a second preferred embodiment said repeat unit of formula I has the structure


V

and/or said repeat unit of formula II has the structure

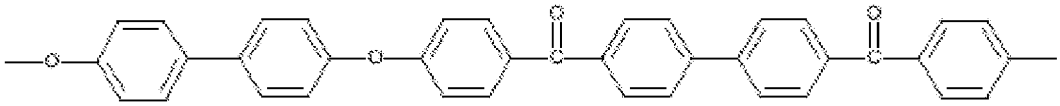

VI.

In a third preferred embodiment said repeat unit of formula I has the structure



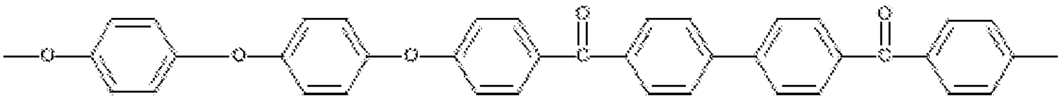
VII

and/or said repeat unit of formula II has the structure



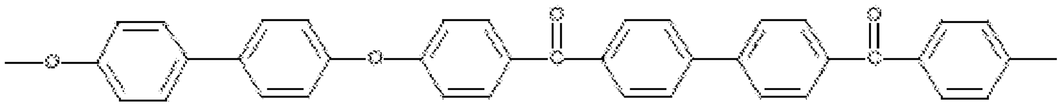
VIII.

In a fourth preferred embodiment said repeat unit of formula I has the structure



IX

and/or said repeat unit of formula II has the structure



X.

In said first preferred embodiment more preferably said repeat unit of formula I has the structure III and said repeat unit of formula II has the structure IV. In said second preferred embodiment more preferably said repeat unit of formula I has the structure V and said repeat unit of formula II has the structure VI. In said third preferred embodiment more preferably said repeat unit of formula I has the structure VII and said repeat unit of formula II has the structure VIII. In said fourth preferred embodiment more preferably said repeat unit of formula I has the structure IX and said repeat unit of formula II has the structure X.

Said polymeric material may include at least 50 mol%, preferably at least 60 mol% and even more preferably at least 65 mol% of repeat units of formula I. Said polymeric material may include less than 90 mol%, suitably 80 mol% or less of repeat units of formula I. Said polymeric material may include 50 to 90 mol%, preferably 60 to 80 mol%, more preferably 65 to 77 mol% of units of formula I.

Said polymeric material may include at least 10mol %, preferably at least 20 mol%, even more preferably at least 23 mol% of repeat units of formula II. Said polymeric material may include less than 50 mol%, preferably less than 40 mol%, more preferably less than 35 mol % of repeat units of formula II.

The sum of the mol% of units of formula I and II in said polymeric material is suitably at least 95mol%, is preferably at least 98mol%, is more preferably at least 99mol% and, especially, is about 100mol%.

The Tg of said polymeric material (measured as described in Example 1 herein) may be greater than 170°C, preferably greater than 175°C, more preferably 180°C or greater. The Tg may be less than 240°C, less than 230°C, or less than 220°C. The Tg is preferably in the range 180°C to 220°C.

In a preferred embodiment, said polymeric material has a Tg in the range 180°C-200°C, a Tm in the range 360°C to 405°C and the difference between the Tm and Tg is in the range 160°C to 225°C.

The ratio of Tg(K) / Tm(K) of said polymeric material, suitably measured as described herein, may be at least or greater than 0.67, preferably greater than 0.69, more preferably 0.71 or greater. The ratio of Tg(K)/Tm(K) may be less than 0.80, less than 0.78, or less than 0.76. The ratio of Tg(K)/Tm(K) is preferably in the range of 0.67 to 0.72, more preferably in the range of 0.70 to 0.72.

Said polymeric material may have a crystallinity of at least 25% (measured as described in Example 1 herein).

Said polymeric material suitably has a melt viscosity (MV) of at least 0.07 $kNsm^{-2}$, preferably has a MV of at least 0.08 $kNsm^{-2}$, more preferably at least 0.85 $kNsm^{-2}$. MV is suitably measured using capillary rheometry operating at 400°C at a shear rate of $1000s^{-1}$ using a tungsten carbide die, 0.5mm x 3.175mm. Said polymeric material may have a MV of less than 1.8 $kNsm^{-2}$, suitably less than 1.2 $kNsm^{-2}$ and most preferably less than 1.0$kNsm^{-2}$. Suitably the MV is in the range 0.085 – 1.0 $kNsm^{-2}$.

Said polymeric material may have a tensile strength, measured in accordance with ISO527 of at least 40 MPa, preferably at least 60 MPa, more preferably at least 80 MPa. The tensile strength is preferably in the range 80-110 MPa, more preferably in the range 80-100 MPa.

Said polymeric material may have a flexural strength, measured in accordance with ISO178 of at least 130 MPa. The flexural strength is preferably in the range 135-185 MPa, more preferably in the range 140-165 MPa.

Said polymeric material may have a flexural modulus, measured in accordance with ISO178 of at least 2 GPa, preferably at least 3GPa. The flexural modulus is preferably in the range 3.0-4.75 GPa, more preferably in the range 3.0-4.5 GPa.

Said polymeric material may be in the form of pellets or granules, wherein the pellets or granules include at least 95wt%, preferably at least 99wt%, especially about 100wt% of said polymeric material. Pellets or granules may have a maximum dimension of less than 10mm, preferably less than 7.5mm, more preferably less than 5.0mm.

Said polymeric material may be part of a composition which may include said polymeric material and a filler means. Said filler means may include a fibrous filler or a non-fibrous filler. Said filler means may include both a fibrous filler and a non-fibrous filler. A said fibrous filler may be continuous or discontinuous.

A said fibrous filler may be selected from inorganic fibrous materials, non-melting and high-melting organic fibrous materials, such as aramid fibres, and carbon fibre.

A said fibrous filler may be selected from glass fibre, carbon fibre, asbestos fibre, silica fibre, alumina fibre, zirconia fibre, boron nitride fibre, silicon nitride fibre, boron fibre, fluorocarbon resin fibre and potassium titanate fibre. Preferred fibrous fillers are glass fibre and carbon fibre.

A fibrous filler may comprise nanofibres.

A said non-fibrous filler may be selected from mica, silica, talc, alumina, kaolin, calcium sulfate, calcium carbonate, titanium oxide, ferrite, clay, glass powder, zinc oxide, nickel carbonate, iron oxide, quartz powder, magnesium carbonate, fluorocarbon resin, graphite, carbon powder, nanotubes and barium sulfate. The non-fibrous fillers may be introduced in the form of powder or flaky particles.

The filled material may be formed into a particulate form for example into pellets or granules. Pellets or granules may have a maximum dimension of less than 10mm, preferably less than 7.5mm, more preferably less than 5.0mm.

Preferably, said filler means comprises one or more fillers selected from glass fibre, carbon fibre, carbon black and a fluorocarbon resin. More preferably, said filler means comprises glass fibre or carbon fibre.

A composition or composite material as described may include 20 to 99.9wt% (e.g. 20 to 70wt%) of said polymeric material and 0.1 to 80wt% (e.g. 30 to 80wt%) of filler means. Preferred embodiments include greater than 40wt% of filler means.

The invention extends to a composite material as described per se.

According to a second aspect of the invention, there is provided a process for the manufacture of a polymeric material having a repeat unit of formula

-O-R1-O-R3- I

and a repeat unit of formula

-O-R2-O-R3- II

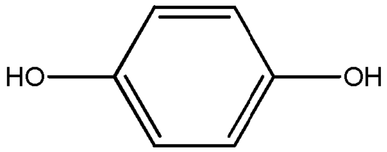
wherein R1 and R2 are different and are both selected from phenyl, biphenyl, terphenyl, naphthyl, or phenyl-ether-phenyl moieties, including isomers thereof, wherein R3 is selected from benzophenone, 1,4-bis(benzoyl) benzene, 2,6-bis(benzoyl) naphthalene or 4,4'-bis(benzoyl) biphenyl moieties and wherein said polymeric material has a Tm (measured as described in Example 1 herein)of less than 440°C, said process comprising polycondensing two different dihydroxy-containing compounds with one or more dihalogenated compound, preferably one dihalogenated compound.

Said polymeric material manufactured in the process of the second aspect may have any feature of the polymeric material of the first aspect.

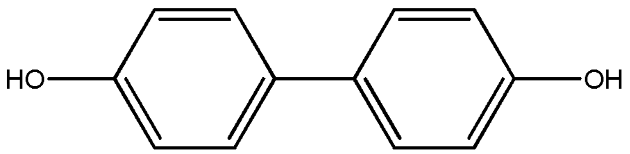
Preferably the polycondensation is carried out in the presence of a base such as an alkali metal carbonate. Preferably the alkali metal carbonate is sodium carbonate and/or potassium carbonate. Preferably the polycondensation is carried out in the presence of sodium carbonate and potassium carbonate.

Preferably, the number of moles of said one or more dihalogenated compound is equal to or, more preferably, greater than the sum of the number of moles of said dihydroxy-containing compounds.

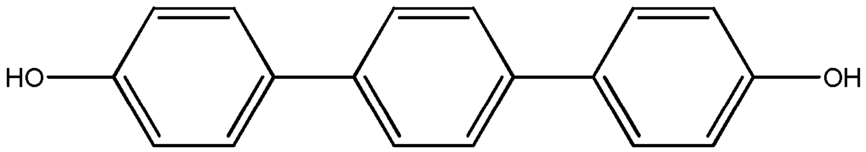
Said two different dihydroxy-containing compounds may be selected from



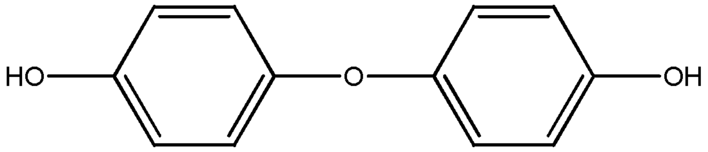
XI,



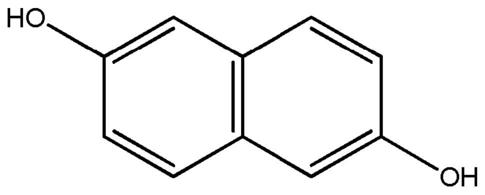
XII,



XIII,



XIV, or

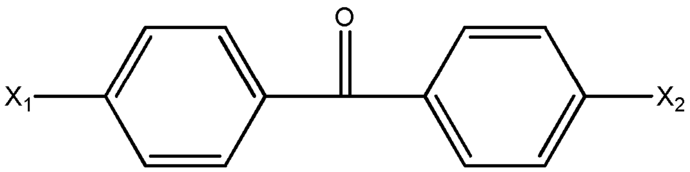


XV,

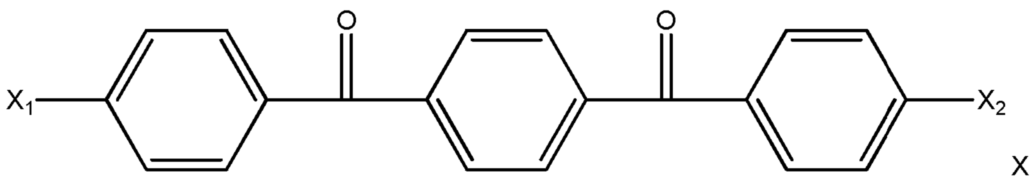
including isomers thereof.

The molar proportions of the two different dihydroxy-containing compounds selected are preferably in the range 50:50 to 80:20, more preferably in the range 65:35 to 77:23.

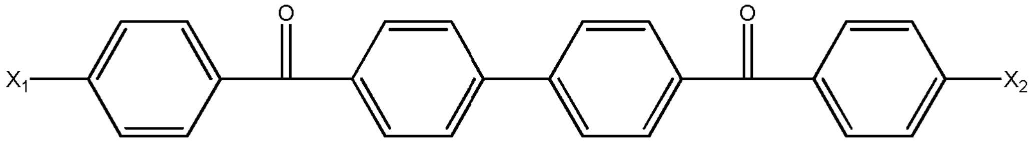
Said one or more, preferably one, dihalogenated compound may be selected from



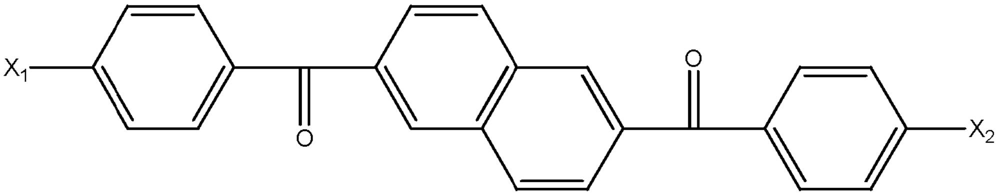
XVI,



XVII,



XVIII, or



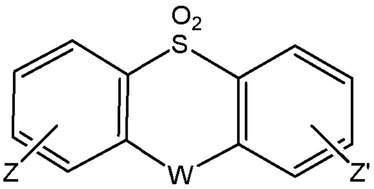
XIX,

including isomers thereof, wherein X_1 and X_2 independently represent halogen atoms preferably selected from chlorine and fluorine atoms. Preferably X_1 and X_2 represent fluorine atoms.

Preferably, the number of moles of said dihalogenated compound is equal to or greater than the sum of the number of moles of said dihydroxy-containing compounds.

Preferably, at least 95wt%, more preferably at least 99wt% of the total weight of said two different dihydroxy-containing compounds and said one or more, preferably one, dihalogenated compound consists of two different dihydroxy-containing compounds selected from formulae XI to XV, including isomers thereof, and dihalogenated compounds selected from formulae XVI to XIX, including isomers thereof. Preferably said two different dihydroxy-containing compounds and said one or more, preferably one, dihalogenated compound consist of two different dihydroxy-containing compounds selected from formulae XI to XV, including isomers thereof, and dihalogenated compounds selected from formulae XVI to XIX, including isomers thereof.

Said process is preferably carried out in the presence of a solvent. The solvent may be of formula



where W is a direct link, an oxygen atom or two hydrogen atoms (one attached to each benzene ring) and Z and Z', which may be the same or different, are hydrogen atoms or phenyl groups. Examples of such aromatic sulphones include diphenylsulphone, dibenzothiophen dioxide, phenoxanthin dioxide and 4-phenylsulphonyl biphenyl. Diphenylsulphone is a preferred solvent.

The process is preferably carried out under substantially anhydrous conditions. In the process, said two different dihydroxy-containing compounds and said one or more, preferably one, dihalogenated compound are suitably contacted in the presence of said solvent, especially diphenylsulphone. Polymerisation is suitably effected at a temperature within the range 150-400°C. In the process, the reactants are suitably heated up to a maximum temperature which may be greater than 300°C, for example in the range 300°C to 370°C. Preferably, however, prior to reaching the maximum temperature, the reagents may be held at one or more temperatures lower than the maximum temperature. For example, the process may involve holding the reagents at a temperature within the range 160-200°C for at least 20 minutes; and/or may involve holding the reagents at a temperature within the range 210 to 300°C for at least 20 minutes.

The process of the second aspect is preferably for manufacturing a polymeric material of the first aspect.

The invention extends, in a third aspect, to a pack comprising a polymeric material, preferably in the form of powder, pellets and/or granules, as described in the first aspect or manufactured in the process of the second aspect.

Said pack may include at least 1kg, suitably at least 5kg, preferably at least 10kg, more preferably at least 14kg of said polymeric material. Said pack may include 1000kg or less, preferably 500kg or less of said polymeric material. Preferred packs include 10 to 500kg of said polymeric material.

Said pack may comprise packaging material (which is intended to be discarded or re-used) and a desired material (which suitably comprises said polymeric material). Said packaging material preferably substantially fully encloses said desired material. Said packaging material may comprise a first receptacle, for example a flexible receptacle such as a plastics bag in which said desired material is arranged. The first receptacle may be contained within a second receptacle for example in a box such as a cardboard box.

The invention extends, in a fourth aspect, to a component which comprises, preferably consists essentially of, a polymeric material according to the first aspect or manufactured in the process according to the second aspect. Said component may be an injection moulded component or an extruded component. Said component preferably includes at least 10g (e.g.

at least 100g or at least 1kg) of said polymeric material. Said component preferably includes at least 10g (e.g. at least 100g or at least 1 kg) of said polymeric material of said first aspect.

The invention extends, in a fifth aspect, to a method of making a component as described which comprises selecting a polymeric material according to the first aspect and melt-processing, for example by injection moulding or extrusion, said polymeric material to define the component. The component may be as described in the fourth aspect.

According to an sixth aspect of the present invention there is provided the use of the polymeric material according to the first aspect or obtained via the process according to the second aspect, the pack according to the third aspect, or the component according to the fourth aspect in automotive, aerospace, medical, electronic, oil and/or gas applications.

It will be appreciated that optional features applicable to one aspect of the invention can be used in any combination, and in any number. Moreover, they can also be used with any of the other aspects of the invention in any combination and in any number. This includes, but is not limited to, the dependent claims from any claim being used as dependent claims for any other claim in the claims of this application.

The reader’s attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

Specific embodiments of the invention will now be described, by way of example:

Example 1 - Differential Scanning Calorimetry of Polyaryletherketone

The Glass Transition Temperature (Tg), the Cold Crystallisation Temperature (Tn), the Melting Temperature (Tm) and Heat of Fusions of Nucleation (ΔHn) and Melting (ΔHm) for the polymers were determined using the following differential scanning calorimetry (DSC) method using a Mettler Toledo DSC1 Star system with FRS5 sensor.

A dried sample of each polymer was compression moulded into an amorphous film, by heating 7g of polymer in a mould at 400°C under a pressure of 50bar for 2 minutes, then quenching in cold water producing a film of dimensions 120 x120mm, with a thickness in the region of 0.20mm. A 8mg plus or minus 3mg sample of each film was scanned by DSC as follows:

Step 1	Perform and record a preliminary thermal cycle (1st cycle) by heating the sample from 30°C to 450°C at 20°C /min.
Step 2	Hold for 5 minutes.
Step 3	Cool at 20°C/min to 30°C and hold for 5mins.
Step 4	Re-heat from 30°C to 450°C at 20°C/min (2nd cycle), recording the Tg, Tn, Tm, ΔHn and ΔHm.

From the DSC trace resulting from the scan in step 4, the onset of the Tg was obtained as the intersection of the lines drawn along the pre-transition baseline and a line drawn along the greatest slope obtained during the transition. The Tn was the temperature at which the main peak of the cold crystallisation exotherm reaches a maximum. The Tm was the temperature at which the main peak of the melting endotherm reach maximum.

The Heats of Fusion for Nucleation (ΔHn) and Melting (ΔHm) are obtained by connecting the two points at which the cold crystallisation and melting endotherm(s) deviate from the relatively straight baseline. The integrated areas under the endotherms as a function of time yields the enthalpy (mJ) of the particular transition, the mass normalised Heats of Fusion are calculated by dividing the enthalpy by the mass of the specimen (J/g).

If a nucleating peak is present on the second heating cycle (step 4), the nucleating exotherm may be subtracted from the melting endotherm, and the resulting crystallinity calculated. Assuming a heat of fusion of 130 joules/g for the crystalline material present, the degree of crystallinity may be calculated as:

$$\%X\ (\%\ \text{crystallinity}) \frac{= \text{area} \times 100}{130}$$

<u>**Example 2 – Preparation of PEDEKDK:PEEKDK Copolymer With 25:75 Molar Ratio**</u>

A 1 litre reaction flask equipped with a ground glass lid, stirrer, stirrer guide, nitrogen inlet and outlet was charged with 4,4'-bis(4-fluorobenzoyl)biphenyl (60.96g, 0.153 mol), 1,4-dihydroxybenzene (12.39g, 0.1125 mol), 4,4'dihydroxybiphenyl (6.98g, 0.0375 mol) and diphenylsulphone (302.76g, 1.387 mol) and purged with nitrogen whilst agitating the powder mixture for 1 hour. The contents were then heated under a nitrogen blanket to 180°C to form an almost colourless solution. Whilst maintaining a nitrogen blanket in the reaction vessel, dried sodium carbonate 15.98g, 0.151mol) and potassium carbonate (0.41g, 0.003 mol), both sieved through a screen with a mesh size of 500µm, were added. The temperature of the reaction vessel and its contents was raised to 200°C over a period of 20 minutes and maintained at this temperature for 20 minutes, with the reaction product remaining in solution at this stage. The temperature was then further raised to 220°C over a period of 40 minutes and maintained at his temperature for 10 minutes. The temperature was then further raised to 330°C over a period of 110 minutes and maintained at this temperature for a further 2 hours, or until the desired MV was reached, as determined by the torque rise on the stirrer. The required torque rise was determined from a calibration graph of torque rise versus MV. The reaction mixture was then poured into a foil tray, allowed to cool, and washed with 2.5 litres of acetone and then warm water at 70 - 80°C until the conductivity of the waste water was <2µS. The resulting polymer powder was dried in an air oven at 140°C for 12 hours.

Example 3 – Preparation of PEDEKDK:PEEKDK Copolymer With 50:50 Molar Ratio

The same procedure set out in Example 2 was followed except that the amounts of the dihydroxy-containing compounds used were as follows:
1,4-dihydroxybenzene (8.26g, 0.075 mol), 4,4'dihydroxybiphenyl (13.97g, 0.075 mol).

Tg and Tm Results

The Tg and Tm values for the polymers prepared in Examples 2 and 3 and for the commercially available Victrex (RTM) PEEK 450G polymer (available from Victrex Manufacturing Ltd) were determined using the method of Example 1 and are shown in Table 1 below.

Polymer	**Tg (K (°C)) from 2nd cycle**	**Tm (K (°C))**	**Tg/Tm (Tm from 2nd cycle)**
PEDEKDK:PEEKDK 25:75 molar ratio	453.7 (180.5)	672.0 (398.8) and 698.0 (424.8) (both 1st cycle), 676.8 (403.6) (2nd cycle)	0.670
PEDEKDK:PEEKDK 50:50 molar ratio	455.4 (182.2)	666.2 (393.0) and 710.9 (437.7) (both 1st cycle) 670.8 (397.6) and 701.0 (427.8) (both 2nd cycle)	0.679 (based on first Tm detected)
Victrex (RTM) PEEK 450G	416 (143)	616 (343)	0.675

Table 1: Tg and Tm values for two polymers according to the present invention and a commercially available polymer

Table 1 shows that the two copolymers according to the present invention exhibit vastly improved (higher) Tg values when compared with the commercially available Victrex (RTM) PEEK 450G polymer. Moreover, the Tm values of these copolymers are low enough to enable the copolymers to be processed using standard equipment. In addition, these two copolymers exhibit Tg/Tm ratios that are either lower than (in the case of PEDEKDK:PEEKDK 25:75 molar ratio) or higher than (in the case of PEDEKDK:PEEKDK 50:50 molar ratio) the commercially available Victrex (RTM) PEEK 450G polymer.

The invention is not restricted to the details of the foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A polymeric material having a repeat unit of formula

-O-R1-O-R3- I

and a repeat unit of formula

-O-R2-O-R3- II

wherein R1 and R2 are different and are both selected from phenyl, biphenyl, terphenyl, naphthyl, or phenyl-ether-phenyl moieties, including isomers thereof, wherein R3 is selected from benzophenone, 1,4-bis(benzoyl) benzene, 2,6-bis(benzoyl) naphthalene or 4,4'-bis(benzoyl) biphenyl moieties, including isomers thereof, and wherein said polymeric material has a Tm (measured as described in Example 1 herein) of less than 440°C.

2. The polymeric material according to claim 1, wherein said polymeric material has a Tm (measured as described in Example 1 herein) of less than 430°C, preferably less than 420°C, even more preferably less than 410°C, even more preferably less than 400°C.

3. The polymeric material according to claim 1 or claim 2, wherein said polymeric material has a Tm (measured as described in Example 1 herein) of greater than 340°C, preferably greater than 350°C, more preferably greater than 360°C.

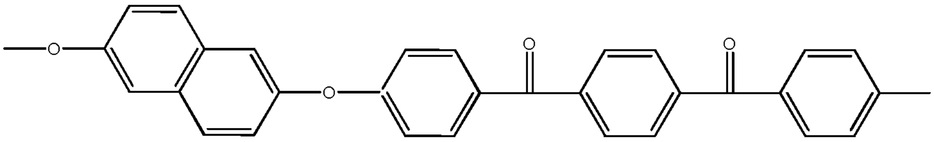
4. The polymeric material according to any preceding claim, wherein R3 is the same for both repeat unit I and for repeat unit II.

5. The polymeric material according to any preceding claim, wherein at least 90% of the number of phenylene moieties in the repeat unit of formula I have 1,4-linkages to moieties to which they are bonded, and wherein at least 90% of the number of phenylene moieties in the repeat unit of formula II have 1,4-linkages to moieties to which they are bonded.

6. The polymeric material according to any preceding claim, wherein in repeat unit I, R1 is selected from phenyl, terphenyl, napthyl, or phenyl-ether-phenyl moieties, including isomers thereof; and/or

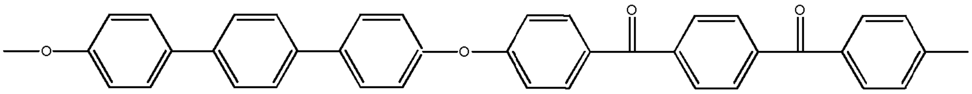
wherein in repeat unit II, R2 is selected from biphenyl or terphenyl moieties, including isomers thereof.

7. The polymeric material according to any preceding claim, wherein said repeat unit of formula I has the structure



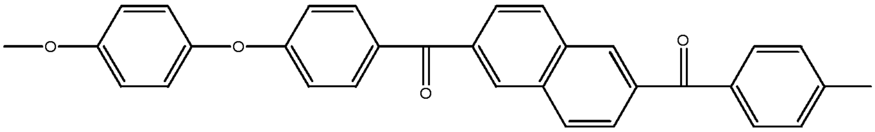
III

and/or said repeat unit of formula II has the structure



IV.

8. The polymeric material according to any of claims 1 to 6, wherein said repeat unit of formula I has the structure



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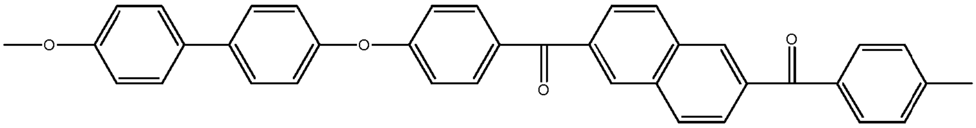
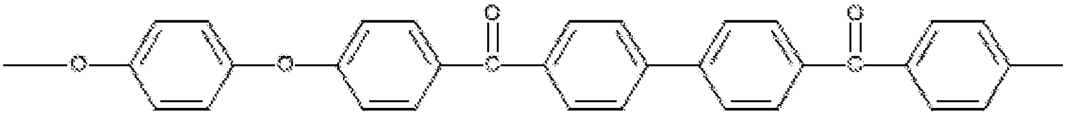
and/or said repeat unit of formula II has the structure



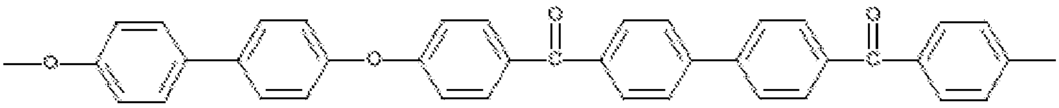
VI.

9. The polymeric material according to any of claims 1 to 6, wherein said repeat unit of formula I has the structure



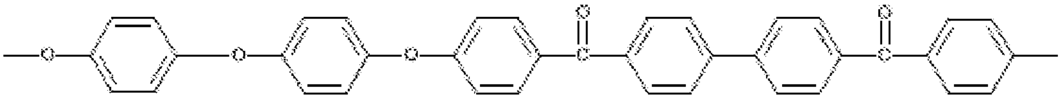
VII

and/or said repeat unit of formula II has the structure



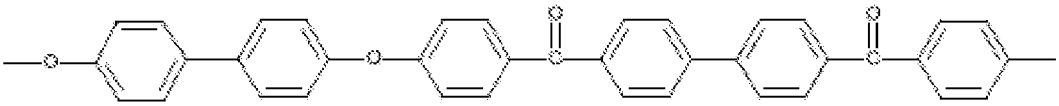
VIII.

10. The polymeric material according to any of claims 1 to 6, wherein said repeat unit of formula I has the structure



IX

and/or said repeat unit of formula II has the structure



X.

11. The polymeric material according to any preceding claim, wherein said polymeric material includes 50 to 90 mol% of units of formula I, preferably 60 to 80 mol% of units of formula I, more preferably 65 to 77 mol% of units of formula I.

12. The polymeric material according to any preceding claim, wherein said polymeric material includes at least 20 mol%, but less than 40 mol% of repeat units of formula II; preferably at least 23 mol%, but less than 35 mol % of repeat units of formula II.

13. The polymeric material according to any preceding claim, wherein the sum of the mol% of units of formulas I and II in said polymeric material is at least 99 mol%.

14. The polymeric material according to any preceding claim, wherein said polymeric material has a Tg (measured as described in Example 1 herein) in the range 170°C to 240°C, preferably in the range 180°C to 220°C.

15. The polymeric material according to any preceding claim, wherein said polymeric material has a Tg (measured as described in Example 1 herein) in the range 180°C to 220°C, a Tm (measured as described in Example 1 herein) in the range 360°C to 405°C, and a Tg(K)/Tm(K) ratio of at least 0.67.

16. The polymeric material according to any preceding claim, wherein said polymeric material has a crystallinity of at least 25% (measured as described in Example 1 herein).

17. The polymeric material according to any preceding claim, wherein said polymeric material is part of a composition which includes said polymeric material and a filler means.

18. The polymeric material according to claim 17, wherein said filler means comprises one or more fillers selected from glass fibre, carbon fibre, carbon black and a fluorocarbon resin.

19. A process for the manufacture of a polymeric material having a repeat unit of formula

-O-R1-O-R3- I

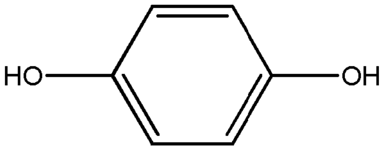
and a repeat unit of formula

-O-R2-O-R3- II

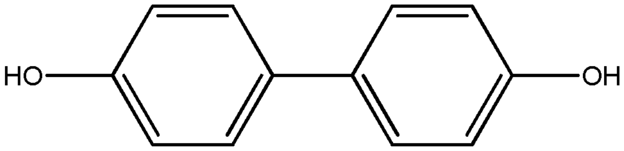
wherein R1 and R2 are different and are both selected from phenyl, biphenyl, terphenyl, naphthyl, or phenyl-ether-phenyl moieties, including isomers thereof, wherein R3 is selected from benzophenone, 1,4-bis(benzoyl) benzene, 2,6-bis(benzoyl) naphthalene or 4,4'-bis(benzoyl) biphenyl moieties and wherein said polymeric material has a Tm (measured as described in Example 1 herein) of less than 440°C, said process comprising polycondensing two different dihydroxy-containing compounds with one or more dihalogenated compound, preferably one dihalogenated compound.

20. The process according to claim 19, wherein the number of moles of said one or more dihalogenated compound is equal to or, preferably, greater than the sum of the number of moles of said dihydroxy-containing compounds.

21. The process according to claim 19 or claim 20, wherein said two different dihydroxy-containing compounds may be selected from



XI,



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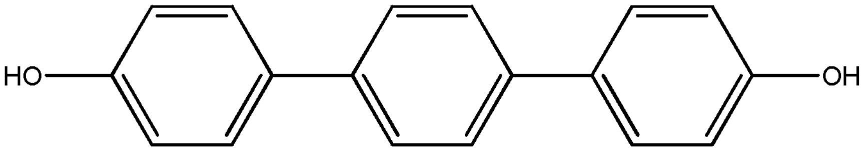

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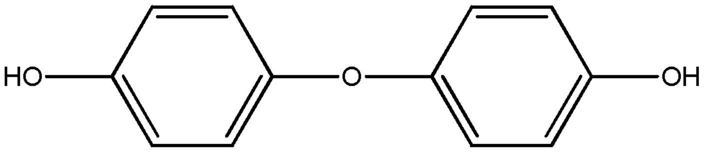
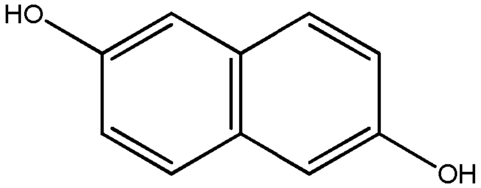


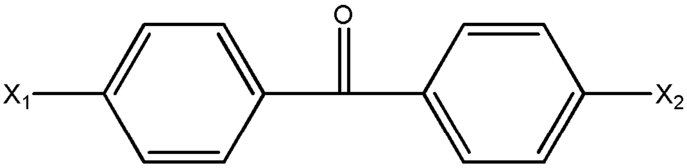
XIV, or



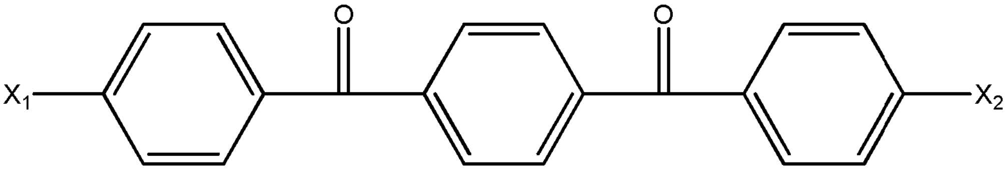
XV,

including isomers thereof.

22. The process according to any of claims 19 to 21, wherein said one or more, preferably one, dihalogenated compound is selected from



XVI,



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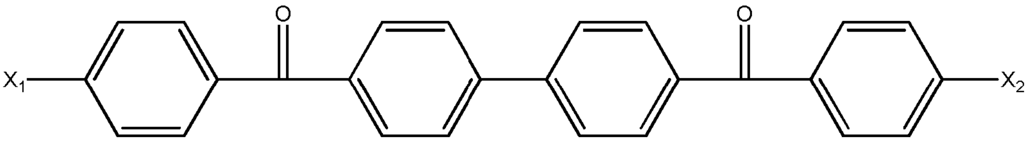
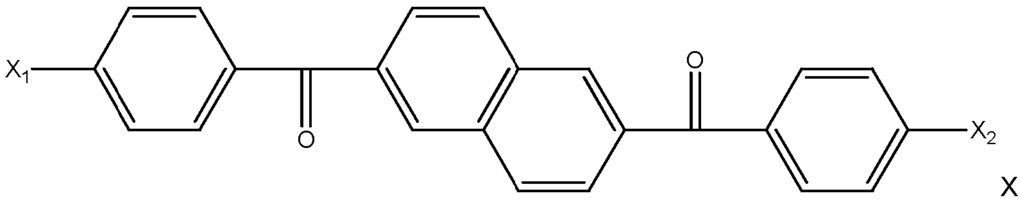


XVIII, or



XIX,

including isomers thereof, wherein X_1 and X_2 independently represent halogen atoms preferably selected from chlorine and fluorine atoms. Preferably X_1 and X_2 represent fluorine atoms.

23. A pack comprising a polymeric material, preferably in the form of powder, pellets and/or granules, as described in any of claims 1 to 18 or manufactured in the process of any of claims 19 to 22.

24. A component which comprises, preferably consists essentially of, a polymeric material according to any of claims 1 to 18 or manufactured in the process according to any of claims 19 to 22.

25. A method of making a component according to claim 24 which comprises selecting a polymeric material according to any of claims 1 to 18 and melt-processing, for example by injection moulding or extrusion, said polymeric material to define the component.

26. Use of the polymeric material according to any of claims 1 to 18 or obtained via the process according to any of claims 19 to 22, the pack according to claim 23, or the component according to claim 24 or obtained via the method according to claim 25, in automotive, aerospace, medical, electronic, oil and/or gas applications.

27. A polymeric material, process for the manufacture of a polymeric material, pack, component, method of making a component or use substantially as described herein.

Intellectual
Property
Office

Application No:	GB1518393.2	**Examiner:**	Dr Albert Mthupha
Claims searched:	1-27	**Date of search:**	22 July 2016

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-2, 4-6, 11-14, 16-27.	WO2014/207458 A1 (VICTREX), see whole document, note particularly page 1 lines 31-37, page 2 line 30-page 3 line 2, line 8-page 4 line 1.
X	1-2, 4-6, 11-13, 16-27.	WO2015/198063 A1 (VICTREX), see whole document, note particularly page 3 lines 2-11, line 37, page 9 line 19-page 10 line 20, page 11 lines 2-6, and example 1.
X	1-2, 4-6, 11-13, 16-27.	WO2015/189567 A1 (VICTREX), see whole document, note particularly the Abstract, page 1 lines 29-36, page 2 line 30-page 4 line 3, line 9, lines 16-19, lines 25-36, and example 1.
X	1-2, 4-6, 11-13, 16-27.	WO2015/124903 A1 (VICTREX), see whole document, note particularly page 4 line 20-page 6 line 8, lines 20-22, page 7 line 16, and example 1.
X	1-6, 9-11, 14-15, 19-22, 27.	Polymer Preprints (American Chemical Society, Division of Polymer), 1999, 40 (1), Zhou, Hong Wei et. al., pages 203-204, note particularly page 203, disclosing preparation of PEDEK-PEDEKDK copolymers, wherein Tg and Tm are studied using DSC.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

C08G; C08L

The following online and other databases have been used in the preparation of this search report

CAS ONLINE, EPODOC, WPI.

International Classification:

Subclass	Subgroup	Valid From
C08G	0065/40	01/01/2006
C08G	0061/10	01/01/2006
C08L	0071/08	01/01/2006