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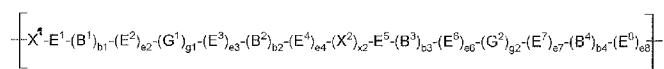
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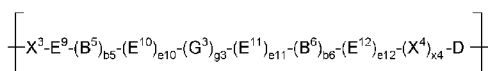
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(54) **Title:** USE OF OLIGOMERS AS COMPATIBILIZERS FOR INORGANIC PARTICLES AND COMPOSITIONS CONTAINING COMPATIBILIZER, INORGANIC PARTICLES AND POLYMER



RU-1



RU-2

(57) **Abstract:** Compositions comprising oligomers having repeating units RU-1 and RU-2 inorganic fillers and, optionally, certain polymers and the use of such oligomers for the stabilization of inorganic particles against agglomeration and coagulation.

Use of oligomers as compatibilizers for inorganic particles and compositions containing compatibilizer, inorganic particles and polymer

Cross reference to a related application. This application claims priority to European application No. 10196867.5 filed on December 23, 2010, the whole content of this application being incorporated herein by reference for all purposes.

5 The present invention relates to the use of certain oligomers as compatibilizers for inorganic particles, in particular in polymer compositions.

Inorganic particles, in this context frequently referred to as fillers, of various types are frequently used to modify or improve the properties of polymer compositions. To achieve a good dispersion of such additives in the polymeric
10 matrix, the use of so-called compatibilizers is known in the art which are added to the polymer melt during melt processing when incorporating the additives.

A specific group of inorganic particles are nanomaterials, which exhibit a very interesting spectrum of properties and find increased use as additives also for polymers. However, nanomaterials tend to coalesce and/or agglomerate
15 during processing or even already while storing same and thus the beneficial properties ascribable to the nanoparticulate structure of the particles are lost to a significant extent when adding those articles to polymeric melts.

To avoid coalescence or agglomeration of nanomaterials, the use of surfactants is known in the art. However, the typical organic surfactants are not
20 suitable when it comes to incorporation into high temperature resistant polymers like polysulfones, polyethersulfones or polyetherketones because their chemical stability is not sufficient to withstand the melt processing temperature of these polymers.

Polymers derived from the reaction of 2,6-difluoropyridine and Bisphenol-
25 A are known from J. Macromol. Sci 1992, 25, 1382ff. This reference also discloses copolymers obtained from the reaction of 1:1 mixtures of 2,6-difluoropyridine and 4,4'-difluorobenzophenone or 4,4'-difluorodiphenylsulfone with Bisphenol A.

Dieckmann et al (Polymer 40 (1999), 983) describe polysulfone oligomers
30 containing pyrazine units in the oligomer chain which are described to be useful for polymer blending or the manufacture of membranes.

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Zhao et al. (J. Mat. Sci. 1994, 623) disclose pyridine terminated polysulfone oligomers which have pyridine end groups obtained via the use of 4-hydroxypyridine as a monofunctional reactant terminating the polymerization reaction.

5 None of these references suggests or discloses to use nitrogen containing oligomers as compatibilizers or stabilizers for inorganic particles, in particular nanomaterials, to improve their dispersibility in polymer melts and to prevent coalescence or agglomeration.

10 The dispersion of inorganic particles, in particular nanomaterials, in polymeric matrices without detrimentally influencing desired properties of the respective products, in particular when high temperature resistant polymers are used as matrix, is thus not fully satisfactory solved yet.

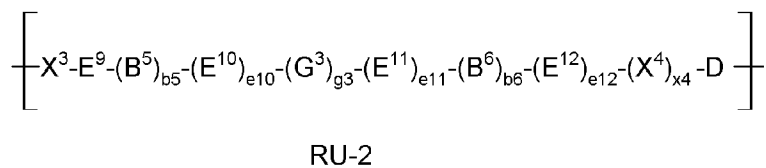
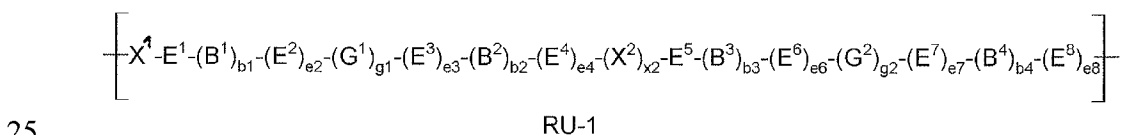
Thus it was an object of the invention to provide compositions comprising inorganic particles, certain oligomers and optionally certain polymers with
15 improved dispersion of the inorganic particles.

This object is achieved with the compositions as defined in the independent claims 1 to 3.

Preferred embodiments are set forth in the dependent claims.

20 A further embodiment of the instant invention is directed to the use of oligomers having a certain structure as defined in claim 1 to improve the incorporation of inorganic particles, preferably nanomaterials, into polymeric matrices.

The oligomer used as component a) in the compositions according to the invention comprise the repeating units RU-1 and RU-2



wherein

X^1 , X^2 , X^3 and X^4 are the same or different and are -O- or -S-,

30 E^1 to E^{12} are the same or different and represent arylene groups containing 6 to 24 carbon atoms, preferably phenylene and particular preferably 1,4-phenylene,

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B¹ to B⁶ and G¹ to G³ are the same or different and represent divalent moieties selected from -O-, -S-, -C(CH₃)₂-, -(CCF₃)₂-, -SO₂-, -CO-, C₂-C₄-alkenylene, C₂-C₄-alkynylene, -(CH₂)_n- and -(CF₂)_m-, preferably -O-, -S-, -C(CH₃)₂-, -(CCF₃)₂-, -SO₂- or -CO-, even more preferably -O-, -S-, -C(CH₃)₂-, -SO₂-

5 or -CO-,

D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

b₁ to b₆ and g₁ to g₃ are the same or different and are 0 or 1,

10 e₂ to e₄, e₆ to e₈ and e₁₀ to e₁₂ are the same or different and represent an integer in the range of from 0 to 3,

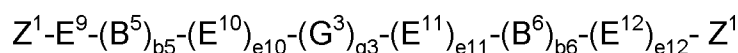
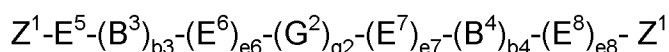
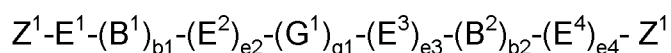
x₂ and x₄ are the same or different and are 0 or 1, and

n and m represent an integer of from 1 to 6.

15 The oligomer may comprise additional units to repeating units RU-1 and RU-2 and there may be a plurality (more than one of each type) of units RU-1 and/or RU-2 within one oligomer.

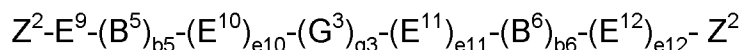
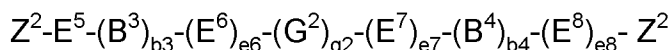
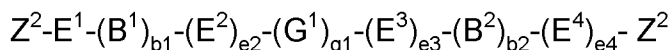
20 In certain preferred embodiments in accordance with the present invention, X³ is equal to X¹, E⁹ is equal to E¹, B⁵ is equal to B¹, b₅ is equal to b₁, E¹⁰ is equal to E², e₁₀ is equal to e₂, G³ is equal to G¹, g₃ is equal to g₁, E¹¹ is equal to E³, e₁₁ is equal to e₃, B⁶ is equal to B², b₆ is equal to b₂, E¹² is equal to E⁴, e₁₂ is equal to e₄, X⁴ is equal to X² and x₄ is equal to x₂.

Certain oligomers useful for use in accordance with the instant invention are obtainable, and are preferably obtained, by oligomerizing a mixture comprising at least one monomer from each of groups a1 to a3, wherein a1) represents compounds of formulae:



25

a2) represents compounds of formulae



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and a3) represents compounds of formula $Z^2 - D - Z^2$

wherein Z^1 is -OH or -SH or a halogen (preferably chlorine) atom, Z^2 is -OH, -SH or a halogen (preferably chlorine) atom provided that Z^1 is -OH or -SH when Z^2 is a halogen atom and Z^1 is a halogen atom when Z^2 is -OH or -SH and provided that the total number of moles of monomers with -OH or -SH end groups is substantially equal to the number of moles of monomers with halogen end groups and wherein

E^1 to E^{12} are the same or different and represent arylene groups containing 6 to 24 carbon atoms,

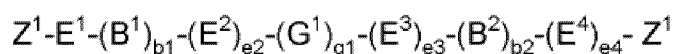
B^1 to B^6 and G^1 to G^3 are the same or different and represent divalent moieties selected from -O-, -S-, $-C(CH_3)_2-$, $-(CCF_3)_2-$, $-SO_2-$, $-CO-$, C_2-C_4 -alkenylene, C_2-C_4 -alkynylene, $-(CH_2)_n-$ and $-(CF_2)_m-$,

D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

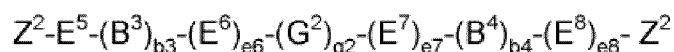
b_1 to b_6 and g_1 to g_3 are the same or different and are 0 or 1, e_2 to e_4 , e_6 to e_8 and e_{10} to e_{12} are the same or different and represent an integer in the range of from 0 to 3, and n and m represent an integer of from 1 to 6.

Certain preferred oligomers useful for use in accordance with the instant invention are obtainable, and are preferably obtained, by oligomerizing a mixture comprising

- at least one monomer compound of formula a1)



- at least one monomer compound of formula a2)



and

- at least one monomer compound of formula a3)



wherein Z^1 is -OH or -SH or a halogen (preferably chlorine) atom, Z^2 is -OH, -SH or a halogen (preferably chlorine) atom provided that Z^1 is -OH or -SH when Z^2 is a halogen atom and Z^1 is a halogen atom when Z^2 is -OH or -SH and provided that the total number of moles of monomers with -OH or -SH end groups is substantially equal to the number of moles of monomers with halogen end groups and wherein

E^1 to E^8 are the same or different and represent arylene groups containing 6 to 24 carbon atoms,

- 5 -

B^1 to B^4 , and G^1 and G^2 are the same or different and represent divalent moieties selected from -O-, -S-, $-C(CH_3)_2-$, $-(CCF_3)_2-$, $-SO_2-$, $-CO-$, C_2-C_4 -alkenylene, C_2-C_4 -alkynylene, $-(CH_2)_n-$ and $-(CF_2)_m-$,

5 D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

b_1 to b_4 , and g_1 and g_2 are the same or different and are 0 or 1,

e_2 to e_4 and e_6 to e_8 are the same or different and represent an integer in the range of from 0 to 3, and n and m represent an integer of from 1 to 6.

Two numbers, representing e.g. the number of moles of monomers, will be
10 considered to be substantially equally to each other by one skilled person typically when their ratio lies from 0.90 to 1.10, preferably from 0.97 to 1.03, more preferably from 0.99 to 1.01, and the most preferably from 0.997 to 1.003.

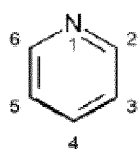
As the groups of compounds a1) and a2) are the same as useful for the
15 manufacture of the polymer component c) which may be optionally present in the compositions in accordance with the instant invention, a more detailed explanation of the meaning of the various substituents for these compounds will be given later when characterizing said polymers.

Compounds a3) when reacted with compounds of group a2) yield the
20 repeating unit RU-2 of the oligomer.

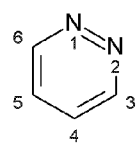
D in compound a3) is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring and may be selected from a wide variety of molecules.

A first group of preferred divalent moieties D includes pyridylenes,
pyridazinylenes, pyrimidinylenes, pyrazinylenes, imidazolylenes,
25 benzimidazolylenes, pyrazolylenes, 1-H-indazolylenes, purinylenes, isoquinolylenes, quinolylenes, phthalazinylenes, naphthyridinylenes, quinoxalinylenes, quinazolininylenes, cinnolyninylenes, pteridinylenes, 4aH-carbazolylenes, carbazolylenes, beta-carbolinylenes, phenanthridinylenes, acridinylenes, phenanthrolinylenes and phenazinylenes. The respective
30 structures of the basic ring systems of divalent moieties D are reproduced below:

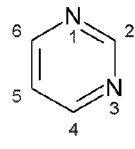
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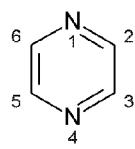
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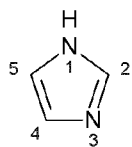
pyridazine



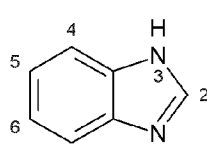
pyrimidine



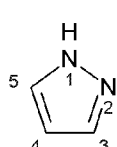
pyrazine



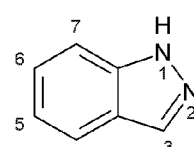
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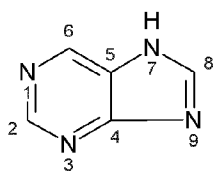
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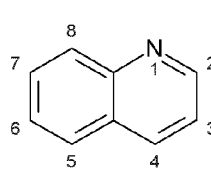
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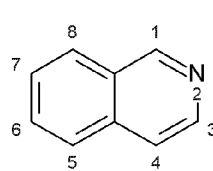
1-H-indazole



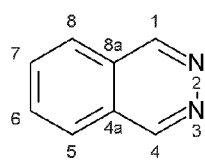
purine



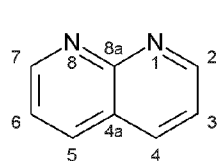
quinoline



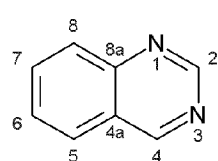
isoquinoline



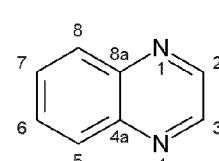
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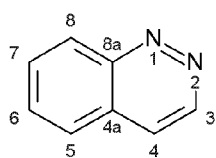
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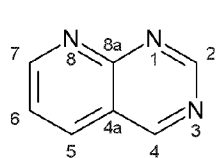
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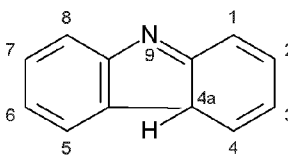
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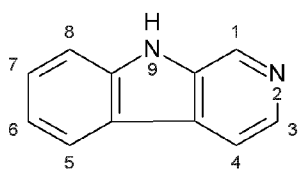
cinnoline



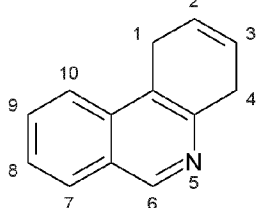
pteridine



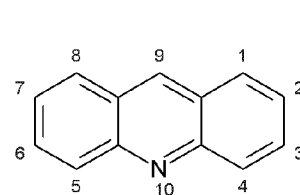
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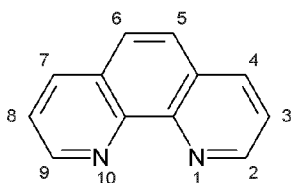
beta-Carboline



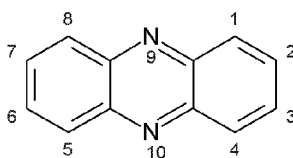
phenanthridine



acridine



1,10 - phenanthroline



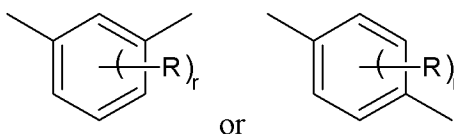
phenazine

The two linkages of the divalent moiety D are preferably in meta- or para position to each other when located at the same ring of the ring system or, if located at different rings in such an arrangement that the geometric structure obtained is similar to a meta- or para- substitution.

5 Out of the foregoing structures 2,6-pyridylene, 2,6-pyrazinylene, 2,4-pyridylene, 2,5-pyridylene, 2,5-pyrazinylene, 2,4-pyrimidinylene, 2,5-pyrimidinylene, 4,6-pyrimidinylene, 3,5-pyridazinylene, 3,6-pyridazinylene and mixtures thereof are more preferred. Most preferred out of this group are 2,6-pyridylene, 2,4-pyridylene, 2,5-pyridylene, and mixtures thereof.

10 The nitrogen containing heterocyclic ring in moiety D may also be attached to another divalent ring or ring system which forms part of the oligomer main chain.

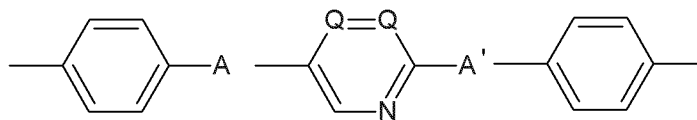
As an example only, such divalent ring may be a 1,4-phenylene or a 1,3-phenylene ring or another arylene system having 6 to 24 carbon atoms. In
15 the case of 1,3-phenylene or 1,4-phenylene, the following structures result :



with R representing a monovalent ligand derived from the basic ring systems for moiety D as outlined above and r being 1 or 2.

Preferred moieties of this type are moieties where R represents a pyridinyl, pyrimidinyl, pyrazinyl or a pyridazinyl substituent.
20

Another example of suitable moieties D are the following:



wherein A and A' may be the same or different and represent a chemical bond, -CO-, -SO₂-, -C(CH₃)₂- or -C(CF₃)₂- and wherein each Q independently may be a
25 carbon or a nitrogen atom.

The foregoing examples for nitrogen-containing moieties D are merely given for illustrative purposes; other suitable moieties D are apparent to the skilled person in the art.

A particularly preferred oligomer for use in the compositions in accordance
30 with the instant invention can be obtained from the copolymerization of a dichloropyridine, in particular 2,5 or 2,6-dichloropyridine or a dichloropyrimidine, 4,4'-dichlorodiphenylsulfone and 4,4'-dihydroxydiphenyl.

The reaction conditions for preparing the oligomer are similar to the conditions used for the synthesis of polyethersulfones, which are known to the skilled person. In principle the monomers can be introduced at the same time into the reaction system together with a suitable base like e.g. potassium carbonate. The dihydroxy monomer reacts with the potassium carbonate while releasing carbon dioxide and water thus yielding a potassium diphenolate, which then reacts with the halogen end groups of the other monomers.

Without a suitable monofunctional monomer terminating the polymerization, high molecular weight polymers would be obtained as described in US 4,803,258. Accordingly, a monofunctional monomer is used in addition with the difunctional monomers. In the case of the preferred oligomer described above, the preferred monofunctional monomer is phenylphenol which has the closest structural similarity to 4,4'-dihydroxydiphenyl as a monofunctional monomer. As a general rule it can be said that it is preferred to use monofunctional monomers resembling as close as possible the difunctional monomers for chain termination and molecular weight regulation.

The use of monofunctional monomers to control the molecular weight in polycondensation reactions is known per se and the skilled person knows that by choosing the amount and type of monofunctional monomer he can adjust the degree of polymerization and thus the molecular weight of the product obtained. By determining the end group type in the oligomer chains (which can be achieved through NMR spectroscopy) it is possible to check the degree of polymerization which desirably is close or equal to 100 %. This eliminates the risk of uncontrolled increase of molecular weight during incorporation of the oligomer in the melt.

While in principle it is also possible to control the molecular weight through the molar ratio of the difunctional monomers, this is not the preferred way. By using difunctional monomers the resulting oligomer should at the end of the polymerization have only one type of end groups, namely the end groups derived from the monomer which has been used in excess.

However, such endgroups are still reactive and can, for example react with the end groups of the polymer which forms the polymer matrix into which the oligomer together with inorganic particles are preferably incorporated. Thus, again the risk of uncontrolled reaction of the oligomer is present which is undesirable as this might detrimentally influence the properties of the oligomer.

For estimating the molecular weight of the oligomer dependent on the amount of monofunctional monomer, the following equation can be used :

$$DP_n = (N_a/N_b + 2 n_a/N_a + 1)/(N_a/N_b + 2 n_a/N_a + 1 - 2(N_a/N_b) \times (N_i - N)/N_i$$

wherein DP_n is the number average degree of polymerization, N_a is the number of moles of dihydroxy monomers, N_b is the number of moles of dihalogen monomers, n_a is the number of moles of monofunctional monomer, N_i is the number of molecules at the start of the oligomerization and N is the number of molecules at time t of the oligomerization (thus $(N_i - N)/N_i$ defines the degree of conversion from the monomers to the oligomer).

Based on the foregoing equations and the desired degree of oligomerization the skilled man can adjust the relative amounts of the reactants easily.

The number of units RU-2 per oligomer can be adjusted through the ratio of the respective monomers used. Assuming a comparable reactivity of the heteroaromatic monomers used to obtain repeating unit RU-2 one can easily adjust the amount of the respective monomers and estimate the amount of units per oligomer chain. If the reactivity of the monomers is significantly different one has to take into account the different reactivity to steer and control the number of units RU-2 per oligomer chain.

As well known to the skilled person, oligomers are substances composed of few constitutional units which are respectively linked to each other (*ολιγος*, or *oligos*, is Greek for "a few"). The oligomer used in accordance with the present invention complies usually with the IUPAC definition for an "oligomer", as notably made available on p. 25, definition 1.3.55 of French Standard ("norme française enregistrée") NFT 50-100, entitled "*Plastiques – Vocabulaire bilingue français-anglais*", released in April 1980. According to NFT 50-100 standard, an oligomer is a substance composed of molecules containing a few of one or more species of atoms or groups of atoms (constitutional units) respectively linked to each other, and the physical properties of the oligomer vary with the addition or removal of one or a few of the constitutional units from its molecules. This clearly contrasts with the definition of the term "polymer" as provided on p. 26, definition 1.3.58 of the same standard, whereby a polymer is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or more of the constitutional units. So, the

IUPAC definition does not specify an absolute degree of polymerization or molecular weight or solution viscosity that distinguishes an oligomer from a polymer, but instead introduces a structure-property definition that is perhaps the most meaningful definition of an oligomer, as reported on p. 432 of

5 “Encyclopedia of Polymer Science and Engineering”, vol. 10, Wiley Ed., 1987.

The oligomer used in accordance with the instant invention can be selected from the group consisting of dimers; trimers; tetramers; higher oligomers the number of repeating units of which is 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 or 35
10 respectively, and mixtures thereof ; and mixtures thereof.

The oligomer used in accordance with the instant invention has usually a number average degree of oligomerization DP_n , as determined by NMR, in the range of from about 2 to about 35. Its DP_n is preferably of at least about 6, more preferably of at least about 9, and still more preferably of at least about 12 ;
15 besides, it is preferably of at most about 30, more preferably of at most about 25 and still more preferably of at most about 20. Any range obtainable by associating any lower limit as above defined with any upper limit as above defined forms part of the present invention and any subranges thereof are to be considered as if they had been explicitly written out. Excellent results were
20 obtained with oligomers of which the DP_n ranged from about 14 to about 17 l/g.

The oligomer used in accordance with the instant invention has usually an intrinsic viscosity in the range of from 0.013 l/g to 0.045 l/g, measured at a temperature of 25°C in N-Methyl-2-pyrrolidone (NMP) solvent. Its intrinsic viscosity is preferably of at least 0.016 l/g, more preferably of at least 0.019 l/g,
25 and still more preferably of at least 0.022 l/g; besides, it is preferably of at most 0.040 l/g, more preferably of at most 0.035 l/g and still more preferably of at most 0.030 l/g. Any range obtainable by associating any lower limit as above defined with any upper limit as above defined form part of the present invention and any subranges thereof are to be considered as if they had been explicitly
30 written out. For example, certain suitable ranges for the intrinsic viscosity of the oligomer used with the present invention are from 0.016 l/g to 0.040 l/g, from 0.019 l/g to 0.035 l/g, from 0.019 l/g to 0.040 l/g, from 0.022 l/g to 0.035 l/g, and from 0.015 l/g to 0.032 l/g. Excellent results were obtained with oligomers the intrinsic viscosity of which ranged from 0.024 l/g
35 to 0.027 l/g.

The intrinsic viscosity of the oligomer can be measured as follows. Five solutions of the oligomer in NMP solvent are prepared at concentrations of 2 g/l, 3.5 g/l, 5 g/l, 6.5 g/l and 8 g/l. The dissolution of the oligomer in NMP solvent is performed at 50°C during 24 hours, under magnetic agitation. The relative viscosity measurements are made on the oligomer solution maintained at 25°C ± 0.5°C, using a Ubbelohde viscometer of type 1 (as described in ISO 1628-1 standard, table 1, with the Ubbelohde conforming to ISO 3105:1994, table B.4). The relative viscosities at 2 g/l, 3.5 g/l, 5 g/l, 6.5 g/l and 8 g/l are calculated as follows : $\eta_{rel} = t/t_0$ wherein t is the efflux time of the solution and t_0 is the efflux time of the solvent. The corresponding reduced viscosities (expressed in l/g) are calculated as follows: $\eta_{red} = (\eta_{rel} - 1)/c$ wherein c is the concentration in g/l. The corresponding inherent viscosities (expressed in l/g) are calculated as follows : $\eta_{inh} = \ln \eta_{rel}/c$ wherein c is the concentration in g/l. The reduced viscosities and the inherent viscosities are extrapolated at zero concentration by linear regression (method of least squares), using e.g. the linear regression function of Microsoft® Office Excel software 2003 (English Professional edition). Let us denote $\eta_{red)c=0}$ and $\eta_{inh)c=0}$ respectively the reduced and inherent viscosities extrapolated at zero concentration. The intrinsic viscosity $[\eta]$ (expressed in l/g) is arbitrarily defined as the mean arithmetic value (the sum divided by 2) of the above two extrapolated viscosities:

$$[\eta] = (\eta_{red)c=0} + \eta_{inh)c=0})/2.$$

The method is advantageously in full accordance with the ISO 1628-1 method, except that : (i) the concentrations are expressed in g/l (instead of kg/m³ or g/cm³, as provided by ISO 1628-1), and the reduced viscosities are expressed in l/g (instead of m³/kg) ; (ii) as already above mentioned, the temperature of the oligomer solution is maintained at 25°C ± 0.5°C during the measurement (instead of ± 0.05°C, as provided by ISO 1628-1) ; (iii) as also above mentioned, $[\eta]$ is the mean arithmetic value of $\eta_{red)c=0}$ and $\eta_{inh)c=0}$ (instead ISO 1628-1 provides that $[\eta]$ can be otherwise defined, notably as $[\eta] = \eta_{inh)c=0}$).

The ratio of the number of repeating units RU-1 to repeating units RU-2 may be selected from a broad range, preferably of from 0.5:1 to 1000:1, more preferably of from 1:1 to 500:1 and even more preferably of from 5:1 to 50:1.

These ratios represent the average number ratio of the respective units in a sample of oligomer of a given weight as determined by appropriate analytical methods. As such sample comprises a significant number of molecules, the

specific content of the repeating unit RU-1 or RU-2 in a specific single oligomer molecule may be even outside the ranges given before.

As an exemplary method of determining the content and ratio of repeating units RU-1 and RU-2 the amount of nitrogen in the sample may be determined and, if only one nitrogen-containing monomer has been used in the synthesis, this allows to calculate the number of nitrogen-containing molecules in the sample and thus the average content of repeating units RU-2 in the oligomer if the molecular weight of the oligomer as a whole has been determined, e.g. by an estimation method as outlined above.

The average degree of polymerization (number of repeating units overall) determined in accordance with the formula given above, of the oligomer is typically in the range of from 1 to 100, preferably of from 1 to 50.

Besides the repeating units RU-1 and RU-2 the oligomer may comprise additional repeating units different from RU-1 and RU-2. Oligomers comprising at least 80 wt. %, preferably at least 90 wt. % and even more preferably at least 95 wt. % of repeating units RU-1 and RU-2 have proved to be particularly suitable. Oligomers consisting of repeating units RU-1 and RU-2 are most preferred.

The oligomer described hereinbefore and defined in the claims is suitable for a wide variety of inorganic particles and can stabilize dispersions of such particles against gelation, agglomeration and coagulation. Accordingly, the nature of the inorganic particle is not subject to specific limitations, but can be chosen from a wide variety of respective products known to the skilled person and commercially available. Only by example dispersions of fibrous particles like glass or carbon fibres can be stabilized as well as dispersions of spherical particles or particles having even different geometrical shapes.

A group of particles the dispersions of which can particularly benefit are nanomaterials which are also known to the skilled person in a great variety and which are available from a number of sources.

Any particles have three characteristic dimensions ("length", "width" and "height"). Nanomaterials are particles characterized in that at least one of their three characteristic dimensions is in the sub-micrometer range.

Certain nanomaterials, herein referred to as nanoplatelets, have one and only one characteristic dimension, namely their thickness, in the sub-micrometer range. The number average thickness of nanoplatelets can be determined by electronic microscopy, possibly coupled with image analysis software. Since the

thickness of a given platelet may vary to some extent all over the length of its section, the individual thickness of any platelet subject to measurement will be obtained by length-averaging the individual local thicknesses all over the length of the section of the platelet ; then, the number average thickness of the
5 nanoplatelets is calculated by number-averaging the individual thicknesses of each of the nanoplatelets that have been subject to measurement. For the purpose of the present invention, the number average thickness of the nanoplatelets as above defined will be qualified as their “average diameter”.

Certain other nanomaterials, herein referred to as nanofibers, have two and
10 only two characteristic dimensions in the sub-micrometer range, their third characteristic dimension (commonly named, “length”) being in contrast greater, and quite often even much greater than 1 μm ; since the two characteristic dimensions in the sub-micrometer range are generally substantially equal to each other, these ones are conveniently translated into a single parameter, namely a
15 “diameter”. The average diameter of such nanofibers can also be determined by electronic microscopy, possibly coupled with image analysis software. The average diameter will be obtained by number-averaging the individual diameters of each of the nanofibers that have been subject to measurements; as for said individual diameter, the Feret diameter of the section of the fiber of
20 consideration can be used.

Still certain other nanomaterials, herein referred to as nanoparticles, have their three characteristic dimensions in the sub-micrometer range. Then, the term “average particle diameter” when used herein will refer to the D_{50} median diameter computed on the basis of the intensity weighed particle size distribution
25 as obtained by the so called Contin data inversion algorithm. Generally said, the D_{50} divides the intensity weighed size distribution into two equal parts, one with sizes smaller than D_{50} and one with sizes larger than D_{50} . In general the average particle diameter is determined according to the following procedure. First, if needed, the nanoparticles are isolated from a medium in which they may
30 be contained (as there are various processes for the manufacture of nanoparticles, the products may be available in different forms, e.g. as neat dry particles or as a suspension in a suitable dispersion medium. The neat particles are then used for the determination of the particle size distribution preferably by the method of dynamic light scattering. In this regard the method as described in ISO Norm
35 Particles size analysis – Dynamic Light Scattering (DLS), ISO 22412:2008(E) is recommended to be followed. This norm provides i.a. for instructions relating to

instrument location (section 8.1.), system qualification (section 10), sample requirements (section 8.2.), measurement procedure (section 9 points 1 to 5 and 7) and repeatability (section 11). Measurement temperature is usually at 25°C and the refractive indices and the viscosity coefficient of the respective dispersion medium used should be known with an accuracy of at least 0.1 %.

After appropriate temperature equilibration the cell position should be adjusted for optimal scattered light signal according to the system software. Before starting the collection of the time autocorrelation function the time averaged intensity scattered by the sample is recorded 5 times. In order to eliminate possible signals of dust particles moving fortuitously through the measuring volume an intensity threshold of 1.10 times the average of the five measurements of the average scattered intensity may be set. The primary laser source attenuator is normally adjusted by the system software and preferably adjusted in the range of about 10,000 cps. Subsequent measurements of the time autocorrelation functions during which the average intensity threshold set as above is exceeded should be disregarded. Usually a measurement consists of a suitable number of collections of the autocorrelation function (e.g. a set of 200 collections) of a typical duration of a few seconds each and accepted by the system in accordance with the threshold criterion explained above. Data analysis is then carried out on the whole set of recordings of the time autocorrelation function by use of the Contin algorithm available as a software package, which is normally included in the equipment manufacturer's software package.

Advantageously, the particles used in accordance with the present invention are nanomaterials.

Advantageously, the particles used in accordance with the present invention have an average diameter of less than 1 µm, preferably of less than 500 nm and very preferably of less than 250 nm. Most preferred particles or nanoparticles have an average diameter of less than 150 nm, in particular of less than 50 nm.

Examples of inorganic particles, in particular examples of nanomaterials, useful for the present invention are vermiculite, bentonite, hectorite, montmorillonite and mica as examples for clays, carbon and graphite nanopowders, various metals, various oxides, hydroxides, nitrides, carbides, phosphates, and borates of metals like Al, Mg, Fe, Ti, Zn, Nb, Bi, rare earth metals and heavy metals which are commercially available e.g. from Aldrich

Chemical Corporation in a great variety. Carbon nanotubes as well as carbon nanofibers are also amongst the suitable particles.

In accordance with the present invention, the inorganic particles are commonly used to modify and improve the properties of polymeric compositions, e.g. the fire resistance, the conductivity, the colour etc. In case of nanomaterials in particular, it is undesired that such particles agglomerate or coagulate during incorporation into the polymer matrix which is usually achieved through the melt i.e. at higher temperatures. Such agglomeration or coagulation detrimentally influences the desired properties of the end product.

A preferred group of inorganic particles, which can be stabilized against agglomeration or coagulation during incorporation into the melt of polymers are core shell particles comprising a core essentially consisting of an UV absorbing inorganic oxygen containing metal compound selected from the group consisting of ZnO, TiO₂, CeO₂ and/or TiOF₂, and a shell essentially consisting of SiO₂, MgF₂, CaF₂ and/or SrF₂ wherein the atomic ratio of the metal atom in the core to the metal atom in the shell is in the range of from 0.1:1 to 1.7:1, and the average particle diameter of the core shell particles is less than or equal to 150 nm.

Various techniques have been developed and described in the literature to synthesize nanoparticulate core shell particles. A successful synthesis has to ensure a complete coverage of the core particles with the shell material. Precipitation, grafted polymerization, micro emulsion, reverse micelle sol-gel condensation or layer-by-layer adsorption techniques can be mentioned as suitable methods to achieve the desired structure.

According to one approach core and shell particles are synthesized separately and in a second step, the shell particles are anchored to the core particles by appropriate procedures. According to a preferred embodiment of this approach, the surface of the core particles is modified with bifunctional molecules to enhance the coverage of shell material on their surface. Through the bifunctionality of the modifying agents core and shell particles are bonded together.

According to a similar approach, described in Langmuir, 2003, 19, 6993-7000 colloidal particles are functionalized on their surface with polyvinyl pyrrolidone (PVP), an amphiphilic non-ionic polymer.

It is also possible to make core shell nanoparticles without functionalizing the core particles with chemicals. For example, opposite electrical charges can

be developed on the core and shell particles which are then coupled together by electrostatic attraction (Adv. Funct. Mat. 2004, 14, 1089-1095).

A preferred approach for the synthesis of the core shell particles in accordance with the instant invention is the so-called controlled precipitation.

5 The synthesis of the shell particles is carried out in the presence of the core particles. The core particles act as nuclei and hydrolysed shell material gets condensed on these cores. Through the concentration of the reactants and the amount of core shell particles the shell thickness can be controlled.

10 In another technique, known as so-called layer-by layer technique alternating layers of anionic particles and cationic particles are deposited on a surface modified template molecule by heterocoagulation. Such methods lead to the formation of homogeneous and dense coatings.

The reactants for the aforementioned processes can be produced in a “top-down” process from larger particles (i.e. grinding) or a “bottom-up” process
15 from smaller particles (atoms, molecules). Nanophase Technologies Corporation USA has developed a vapour phase plasma synthesis referred to as Physical Vapour Synthesis (PVS) and NanoArcTM Synthesis (NAS). According to this method, metals or metal oxides (as powders or as solid rods) are fed into a reactor where plasma energy is used to generate a vapour at high temperature. A
20 reactant gas such as oxygen (air) is added. Immediately afterwards, the vapour is cooled at a controlled rate and nanoparticles are formed.

Due to their non-porous structure and controlled surface chemistry, nanoparticles synthesized by the vapour phase plasma process are easy to disperse in liquid media, and the resulting dispersions are highly stable, low
25 viscosity compositions (even at higher concentrations) and therefore easy to handle. Chemically there is a wide variety of nanoparticles that can be manufactured using the described methods. Examples are ZnO as well as CeO₂ particles for UV protection.

A concise review on the manufacture of nanoshell particles is given in
30 Kalele et al., Current Sci. Vol. 91, No. 8, (2006).

Atou et al., Physica E 16, 2003, 179-189 discloses a method for the preparation of silicon oxide layers on TiO₂ particles and Siddiquey et al., Applied surface sci. 255 (2008), 2419-2424 describe the silica coating of CeO₂ nanoparticles by a fast microwave irradiation method.

35 WO 2008/019905 mentioned hereinbefore also describes methods for the manufacture of nanoparticulate core shell particles.

The principles of the aforementioned methods for specific products can be applied to other core shell particles having a different core and/or a different shell.

Thus, suitable methods for the manufacture of the nanoparticulate core shell particles are known per se and described in the literature so that further details are not necessary here.

The atomic ratio of the metal atom of the core to the metal atom in the shell of the aforementioned preferred core shell particles (Si for this purpose considered to be a metal) is in the range of from 0.1:1 to 1.7:1, preferably of from 0.2:1 to 1.1:1, most preferably in the range of from 0.25:1 to 0.8:1. By using the known specific density of the materials this atomic ratio translates into a certain thickness ratio of core and shell and by using the molecular weight of the core and shell materials the respective mass percentages can be easily calculated.

When selecting the atomic ratio in the aforementioned range unexpected beneficial properties are observed when such core shell particles are used as additives for polymer compositions. The combination of particle size and atomic ratio of the metals in core and shell in accordance with the instant invention improves dispersability of the materials in polymer matrices combined with improved end-use properties of the polymer materials such as homogeneity and transparency.

Surprisingly, the most preferred atomic ratio is rather independent from the shell metal, i.e. the nature of the shell metal (or shell compound) is less important for the optimum atomic ratio than the core metal. Thus, it has been found that a very preferred range of atomic ratios for ZnO as core material is in the range of from 0.4:1 to 0.9:1, most preferred in the range of from 0.5:1 to 0.8:1 (always atomic ratio core:shell metal atom) for any of the shell materials SiO₂, MgF₂, CaF₂ and SrF₂. If ZnO is replaced by TiO₂, the preferred range is from 0.15:1 to 0.45:1 and particularly preferred of from 0.15:1 to 0.35:1. For CeO₂ as core the preferred ratios are 0.3:1 to 0.75:1 and most preferred of from 0.4:1 to 0.7:1. Finally, for TiOF₂ the most preferred ranges are 0.3:1 to 0.7:1, especially 0.4:1 to 0.6:1.

The aforementioned core shell particles in accordance with the instant invention are particularly suitable as UV absorbers and stabilizers against UV degradation in polymer compositions. Due to their inorganic nature they show a very high thermal stability, which enables their respective use in polymer

compositions comprising high temperature resistant polymers which have to be processed at temperatures often in excess of 200°C. At such temperatures organic UV absorbers often show undesirable decomposition.

5 The oligomer described hereinbefore is particularly suitable to stabilize the aforementioned core shell particles when incorporating same into polymer melts at high temperatures as the oligomer is stable and does not undergo decomposition at these high temperatures which differentiates same from other commonly known surfactants.

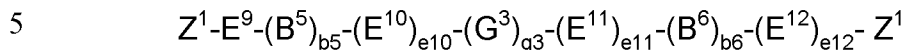
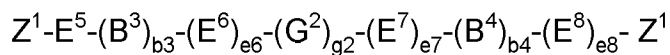
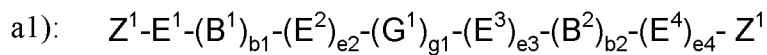
10 A further preferred group of inorganic particles which are mentioned by way of example only are the so called flame retardants, which provide a better fire resistance to polymer compositions and products made therefrom, which is an indispensable requirement in certain areas of application like interior parts in aircrafts or parts used in or in the vicinity of electrical installations. Only by way of example, zinc borate may be expressly mentioned here, which is a well known
15 fire retardant for polymer compositions and which is also available in nanoparticulate form.

As mentioned hereinabove, the compositions comprising inorganic particles and the oligomer described hereinbefore are particularly suitable for the incorporation into matrices of high temperature resistant polymers through melt
20 processing. Due to the high thermal stability of the oligomer, same are stable during these conditions which is advantageous compared to known organic surfactants commonly used in such applications which show degradation which leads to undesired effects.

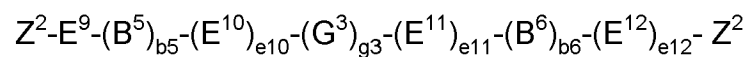
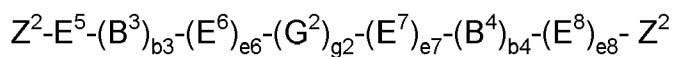
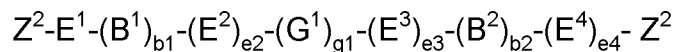
For compatibility reasons it is most preferred to tailor the oligomer based
25 on the structure of the polymer into which the inorganic particle and oligomer are incorporated, i.e. to use an oligomer comprising - apart from the repeating unit RU-2 which differentiates the oligomer from the polymer, repeating units RU-1 which are the same or similar to the repeating units of the polymer. However, it is also possible to deviate from this principle.

30 Thus, according to another preferred embodiment of the instant invention, the compositions of the invention comprise, in addition to components a) and b), at least one polymer selected from the group consisting of polyarylene polyethers obtainable by polymerizing at least one monomer of group a1) and at least one monomer of group a2) as defined above:

- 19 -

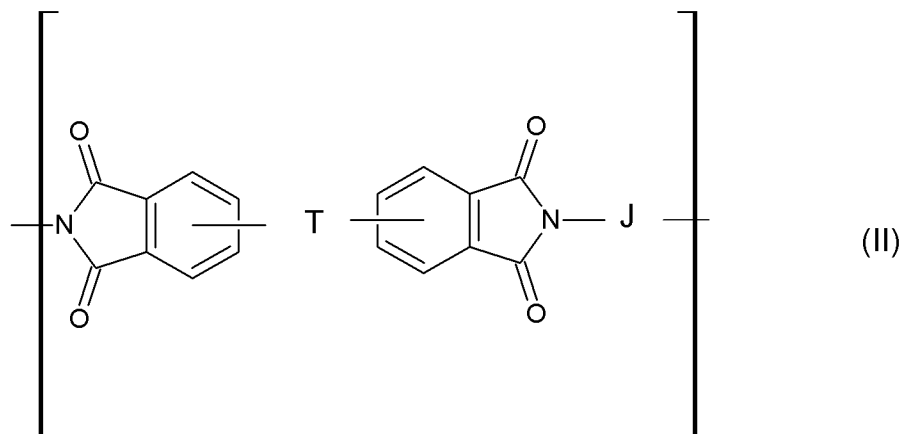


a2):



, or

polyetherimides having recurring units of formula II



10 wherein

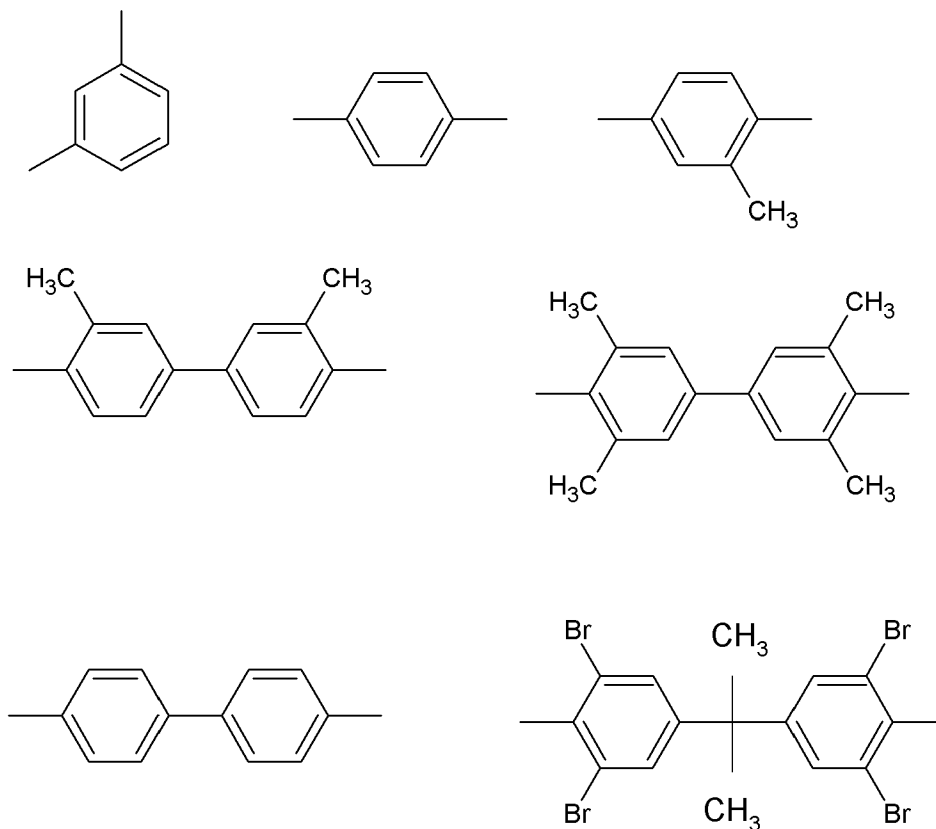
T is -O- or a substituent -O-Z-O-,

the two linkages are formed at the 3,3', 3,4', 4,3' or 4,4' positions,

Z is a divalent organic moiety selected from the group consisting of

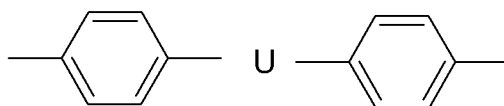
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a1) a divalent organic moiety selected from the group consisting of



and

b1)

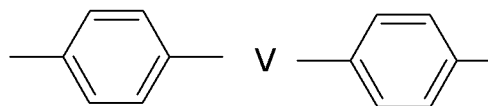


5

wherein U is a divalent moiety selected from the group consisting of $-C_yH_{2y}-$, $-CO-$, $-SO_2-$, $-O-$ and $-S-$, y being an integer of from 1 to 5,

and J is a divalent organic moiety selected from the group consisting of

- 10 i) aromatic hydrocarbylene groups or halogenated hydrocarbylene groups having from 6 to 20 carbon atoms,
 ii) alkylene groups having from 2 to 20 carbon atoms or cycloalkylene groups having from 3 to 20 carbon atoms, and
 iii)



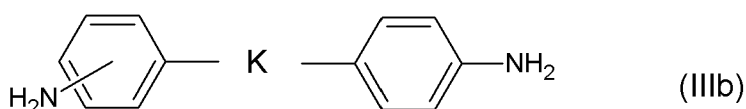
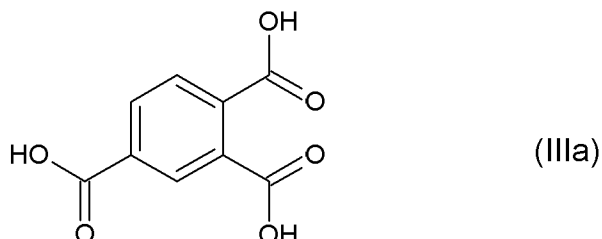
15

wherein V is a divalent group selected from the group consisting of $-S-$, $-O-$, $-CO-$, $-SO_2-$ and $-C_xH_{2x}-$ with x being an integer of from 1 to 5,

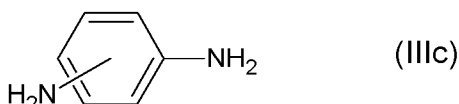
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or

polyamideimides obtainable from the reaction of tricarboxylic acid derivatives IIIa and aromatic diprimary amines IIIb and IIIc



wherein K is selected from the group consisting of -O-, -S-, -CO-, -SO₂-, -C(CH₃)₂- and wherein the amino group in the indicated left ring is in m- or p-position to the bridging substituent K,



wherein the amino groups are in m- or p-position to each other.

Polyarylene polyethers obtainable by polymerizing monomers a1) and a2) are known to the skilled person and available as commercial products in a wide variety.

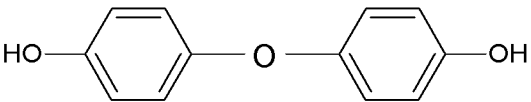
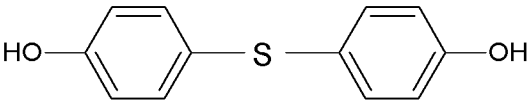
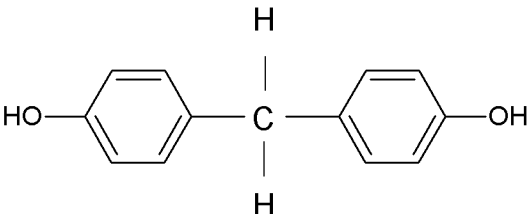
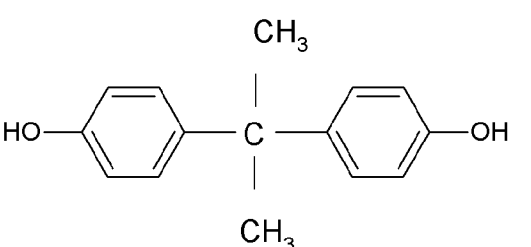
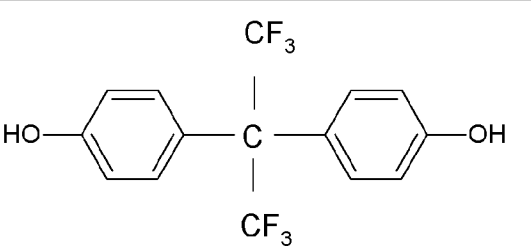
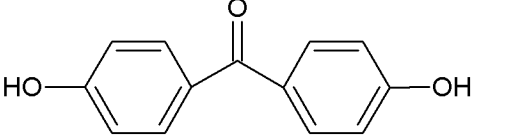
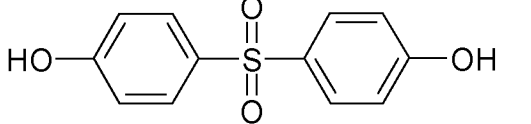
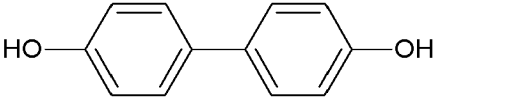
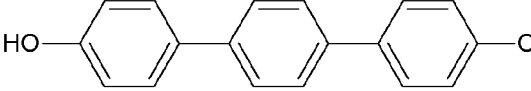
E¹ to E¹² may be the same or different and represent an arylene group containing 6 to 24 carbon atoms. Preferred examples of such arylene groups are phenylene or naphthylene groups, phenylene groups being particularly preferred.

B¹ to B⁶ and G¹ to G³ are the same or different and represent divalent moieties selected from -O-, -S-, -C(CH₃)₂-, -(CCF₃)₂-, SO₂-, -CO-, C₂-C₄-alkenylene, C₂-C₄-alkynylene, -(CH₂)_n- and - (CF₂)_m- where n and m individually represent an integer of from 1 to 6.

A first preferred group of polymers of this structure is generally referred to as polysulfones or polyethersulfones, which are commercially available from various sources. The common feature of these groups of polymers is at least one diphenyl sulfone group as part of the repeating unit, i.e. one of the monomers used is derived from a diphenylsulfone, preferably from 4,4'-dihydroxy- or 4,4'-dichlorodiphenylsulfone.

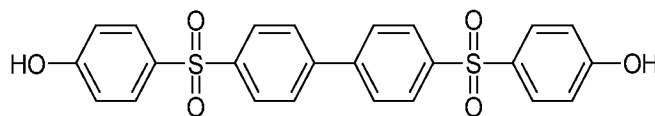
A preferred group of co-monomers for the copolymerization with 4,4'-dichlorodiphenylsulfone is indicated in below table as dihydroxy monomers.

Table 1

4,4'-dihydroxydiphenyl oxide	
4,4'-dihydroxydiphenylsulfide	
4,4'-dihydroxydiphenylmethane	
2,2'-bis(p-hydroxyphenyl)propane	
2,2'-bis(p-hydroxyphenyl)perfluoropropane	
4,4'-dihydroxybenzophenone	
4,4'-dihydroxydiphenylsulfone	
Hydroquinone	
4,4'-dihydroxydiphenyl	
1,4-bis(4-hydroxyphenyl)benzene	

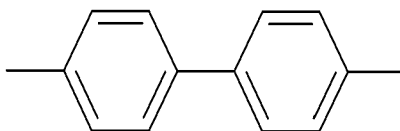
2,2'-Bis(p-hydroxyphenyl)propane (also frequently referred to as Bisphenol A) and 4,4'-dihydroxydiphenylsulfone and mixtures thereof are a first group of particularly preferred comonomers from the above table, yielding products commonly referred to as PSU and PES and commercially available i.a. from Solvay Advanced Polymers LLC. under the tradenames Udel[®] and Radel[®].

A further preferred monomer is 4,4'-bis(4''-hydroxybenzenesulfonyl)diphenyl of formula



In all the foregoing monomers the hydroxy groups can in principle be substituted by SH-groups, thus yielding the respective polyarylene polythioethers.

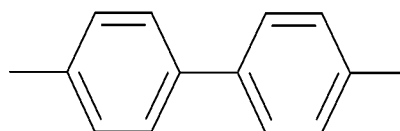
Another preferred group of polymers are the so called poly(biphenylethersulfones), which for the purpose of this invention are intended to denote polycondensation polymers of which more than 50 % of the recurring units are recurring units containing at least one optionally substituted p-biphenylene group



at least one ether group ($-O-$) and at least one sulfone group ($-SO_2-$).

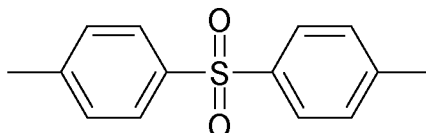
The biphenylene unit may be unsubstituted, or it may be substituted by one or more substituents ; the substituent(s) may be notably chosen from halogen atoms, C_1 - C_{12} alkyls, C_1 - C_{24} alkylaryls, C_1 - C_{24} aralkyls, C_6 - C_{18} aryls, and C_1 - C_{12} alkoxy groups ; preferred substituents are halogen atoms, in particular fluorine atoms.

Usually, more than 50 % of the recurring units of the poly(biphenyl ether sulfone) are recurring units of one or more formulae containing at least one p-biphenylene group :



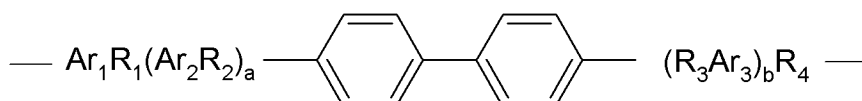
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as above detailed, and at least one diphenyl sulfone group:



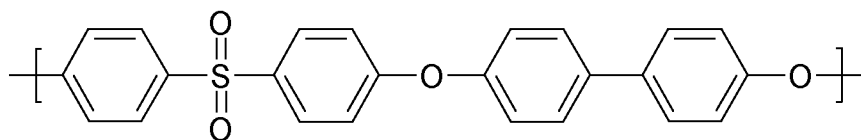
Each of the phenylene units of the diphenyl sulfone group may be,
 5 independently from each other, unsubstituted, or they may be substituted by one or more substituents ; the substituent(s) may be notably chosen from halogen atoms, C₁-C₁₂ alkyls, C₁-C₂₄ alkylaryls, C₁-C₂₄ aralkyls, C₆-C₁₈ aryls, and C₁-C₁₂ alkoxy groups ; preferred substituents are halogen atoms, in particular fluorine atoms.

10 Preferably, the poly(biphenyl ether sulfone) has one or more recurring units having the following formula :

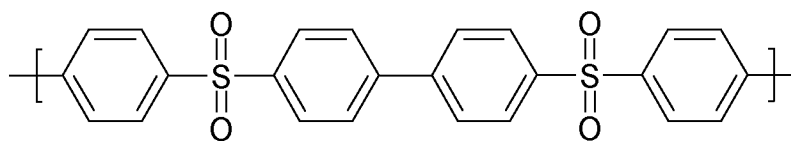


where R₁ through R₄ are any of —O—, —SO₂—, —S—, or —CO—, with the proviso that at least one of R₁ through R₄ is —SO₂— and at least one of R₁ through R₄ is —O— ;
 15 Ar₁, Ar₂ and Ar₃ are arylene groups containing 6 to 24 carbon atoms, and are preferably phenylene or p-biphenylene ; and a and b are either 0 or 1.

More preferably, the recurring units of the poly(biphenyl ether sulfone) are chosen from the following formulae 2 to 6 (in this order below)

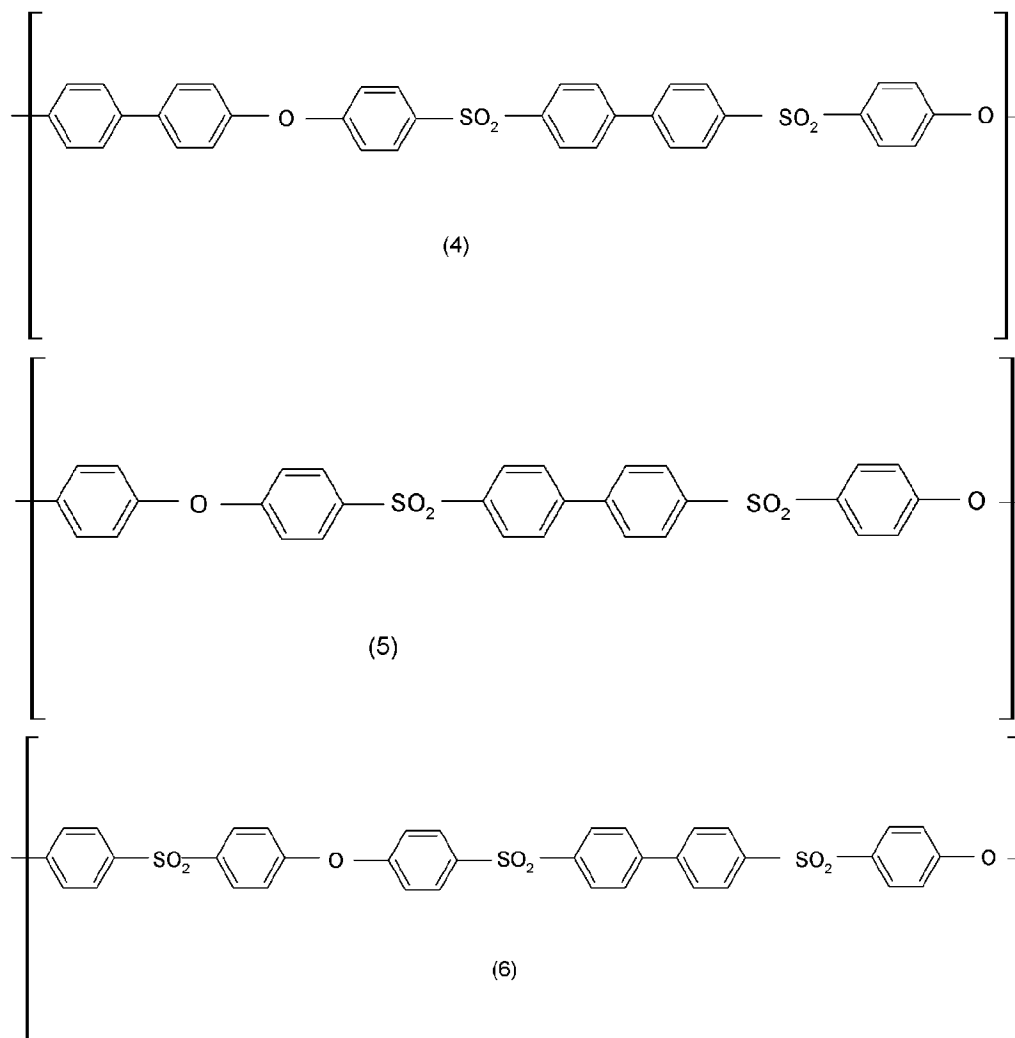


(2)



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- 25 -



Still more preferably, the recurring units of the poly(biphenyl ether sulfone) are selected from the poly(biphenyl ether sulfone)s of formulas (2) or (4) above or a mixture of the recurring units of formula (4) and formula (6) described above.

Preferably, the poly(biphenyl ether sulfone) consists of recurring units of formulae (4) and (6) where the recurring unit (6) is present in an amount of from 10 to 99 %, preferably between 50 and 95 %, based on the total number of the recurring units (4) and (6).

The poly(biphenyl ether sulfone) may be a poly(biphenylether diphenylsulfone) polycondensation polymer of which more than 50 % of the recurring units are recurring units of condensed molecules of a dihydroxybiphenyl group and a diphenyl sulfone group. A poly(biphenyl ether sulfone) that has recurring units of the first formula (2), i.e., condensed units of

4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone provides, in general, the best overall balance of cost and toughness.

A poly(biphenyl ether sulfone) that has recurring units of formula (4) or mixtures of recurring units of formulae (4) and (6) provides a poly(biphenyl ether sulfone) with an especially high glass transition temperature. A
5 poly(biphenyl ether sulfone) that includes a mixture of recurring units of formulae (4) and (6) may provide substantially the same level of physical and chemical properties of a poly(biphenyl ether sulfone) that consists of recurring units of formula (4), but at a somewhat more attractive cost.

10 The poly(biphenyl ether sulfone) may be a homopolymer, a random copolymer, an alternating copolymer or a block copolymer. The, a poly(biphenyl ether sulfone) random copolymer, a poly(biphenyl ether sulfone) alternating copolymer, and a poly(biphenyl ether sulfone) block copolymer.

The poly(biphenyl ether sulfone) of the invention may have a block
15 structure wherein a first repeating unit and a second repeating unit appear in an irregular but predictable repeating or recurring manner, e.g., in blocks. For example, a block may contain at least two of the same recurring units or a combination of different recurring units bonded together wherein the bonded recurring units appear at intervals in the poly(biphenyl ether sulfone). The
20 poly(biphenyl ether sulfone) may be a copolymer in a block form having first blocks made up of recurring units consisting of only one type of biphenyl group and only one type of diphenyl sulfone, and second blocks that contain one or more recurring units that consist of biphenyl and/or diphenyl sulfone units that are different from the biphenyl and/or diphenyl sulfone units of the first block of
25 recurring units. The poly(biphenyl ether sulfone) may contain polymerized blocks of a first recurring unit that are randomly distributed among groups of randomly polymerized second recurring units.

The poly(biphenyl ether sulfone) may be a copolymer that is a random copolymer having at least two different recurring units appearing randomly in
30 the polymer chain. In an embodiment of the invention the poly(biphenyl ether sulfone) has at least three different repeating or recurring units that are distributed randomly throughout the poly(biphenyl ether sulfone).

The poly(biphenyl ether sulfone) may contain portions of random structures and portions of block structures. The random portion of the
35 poly(biphenyl ether sulfone) is a portion wherein different sulfone units are randomly distributed between recurring units having biphenyl-containing units

(e.g., derived from dihydroxybiphenyl molecules) that may be the same or different.

The poly(biphenyl ether sulfone) may have a structure that is from 0 to 100 wt. % random and from 0 to 100 wt. % block where wt. % is % by weight based on the total weight of the poly(biphenyl ether sulfone) (co)polymer. Preferably, when in co-polymer form, the poly(biphenyl ether sulfone) has from 20 to 80 wt. % random structure and from 80 to 20 wt. % block structure, more preferably from 30 to 70 wt. % random structure and from 70 to 30 wt. % block structure, more preferably from 40 to 60 wt. % random structure and from 60 to 40 wt. % block structure, most preferably the polysulfone co-polymer has about 50 wt. % random structure and about 50 wt. % block structure.

The random/block structure ratio of the poly(biphenyl ether sulfone) may be determined by using ^1H and ^{13}C NMR spectroscopy techniques. Specifically, 2D NMR spectroscopy including ^1H - ^1H COSY, ^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC and 1D- ^1H and ^{13}C NMR techniques are suitable.

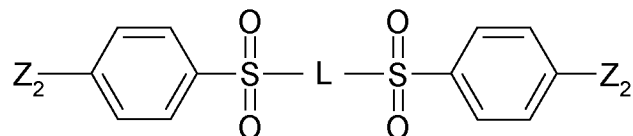
Preferably more than 70 %, more preferably more than 80 % of the recurring units of the poly(biphenyl ether sulfone) are recurring units consisting of a diphenyl sulfone group and a biphenyl group such as the recurring units of formulas (1)-(6). Still more preferably, essentially all of the recurring units of the poly(biphenyl ether sulfone) are recurring units having a diphenyl sulfone group and a biphenyl group such as the recurring units of formulas (1)-(6). Most preferably, all of the recurring units of the poly(biphenyl ether sulfone) are recurring units having a diphenyl sulfone group and a biphenyl group, such as the recurring units of formulas (1)-(6).

Excellent results are in general obtained when the poly(biphenyl ether sulfone) is a poly(biphenylether sulfone) homopolymer, e.g., a polymer wherein all, or substantially all, of the recurring units are of formula (2). RADEL[®] R poly(biphenylether sulfone) from Solvay Advanced Polymers, L.L.C. is an example of such a poly(biphenylether sulfone) homopolymer that is commercially available.

In some applications where the poly(biphenyl ether sulfone) is subjected to very high temperature, excellent results are obtained when the poly(biphenyl ether sulfone) is a homopolymer of recurring units of formula (4), i.e., a polymer wherein all, or substantially all, of the recurring units are of formula (4). In such high temperature applications, excellent results are also obtained when the

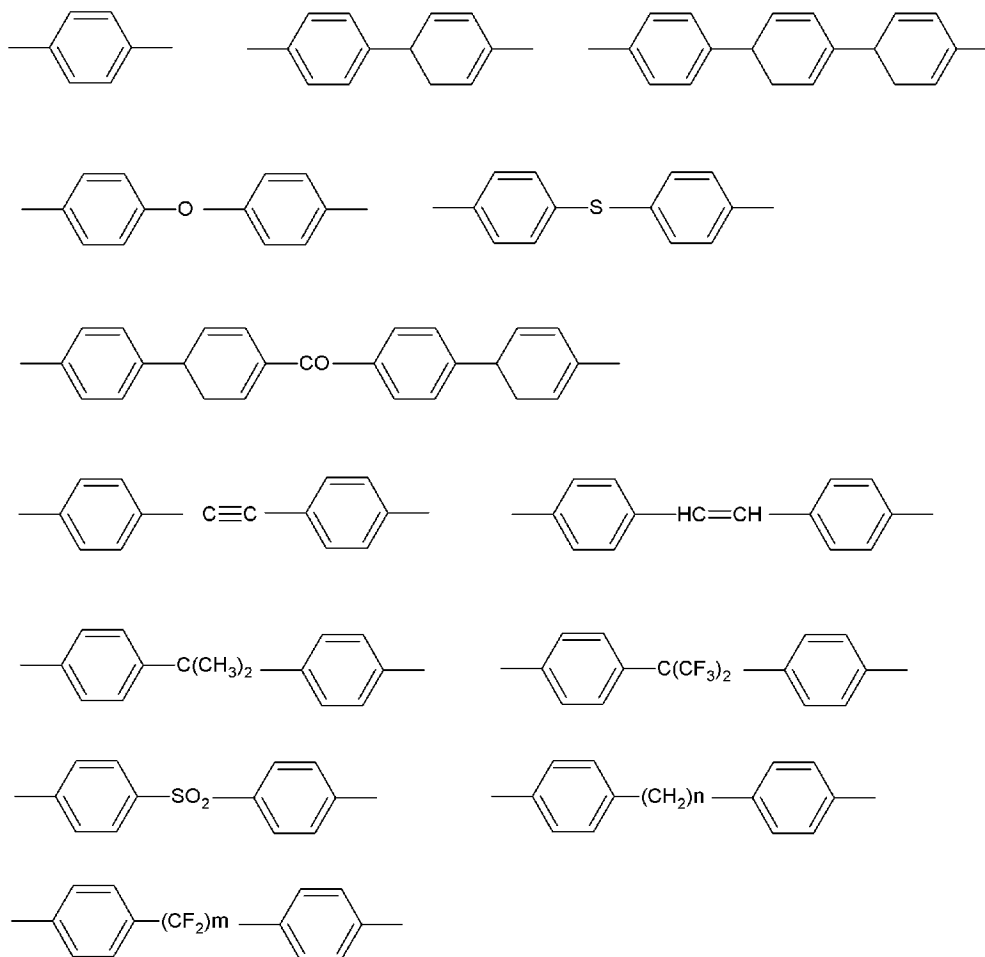
poly(biphenyl ether sulfone) is a copolymer of which all, or substantially all, of the recurring units are of formulae (4) and (6).

Another preferred group of polyarylene polyethers are polymers obtainable by using monomers of the formula



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wherein Z_2 is a halogen atom, preferably a chlorine atom, and L is a group chosen from the following structures :

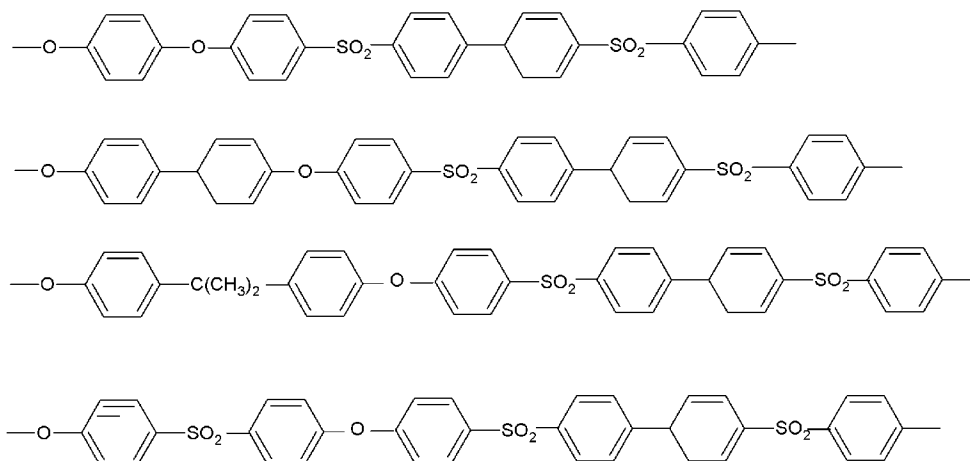


and n and m are independently an integer of from 1 to 6.

10

In the presence of the appropriate dihydroxy-contg. comonomers, for example with p-hydroquinone, 4,4'-biphenol, bisphenol A, 4,4'-dihydroxydiphenylsulfone and bisphenol A, the polyarylene polyethers yield respectively e.g. the following repeating units or mixtures thereof :

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which may be mentioned as preferred examples of this group of polymers.

As can be easily recognized, the first two polymers and the last polymer depicted above correspond respectively to the polymers with repeating units (5),
 5 (4) and (6) as shown above.

The compositions of the invention can comprise one and only one poly(biphenyl ether sulfone). Alternatively, they may comprise two, three, or even more than three poly(biphenyl ether sulfone)s. Mixtures of certain poly(biphenyl ether sulfone)s are preferred. For example a mixture consisting
 10 of (i) at least one poly(biphenyl ether sulfone) of which more than 50 % of the recurring units, preferably essentially all the recurring units, and still more preferably all the recurring units are of formula (2) described above, (ii) at least one poly(biphenyl ether sulfone) of which more than 50 % of the recurring units, preferably substantially all of the recurring units, and still more preferably all the
 15 recurring units are of formula (4) described above, and, optionally, in addition (iii) at least one other poly(biphenyl ether sulfone) different from the poly(biphenyl ether sulfone)s (i) and (ii), where % is based on the total number of the recurring units.

Preferred poly(biphenyl ether sulfones) are those where substantially all, if
 20 not all, the recurring units are of formula (2), and those where substantially all, if not all, the recurring units are of formula (4).

Still more preferably, the composition is a binary mixture of poly(biphenyl ether sulfone)s consisting of (i) one poly(biphenyl ether sulfone) of which all the recurring units are of formula (2), and (ii) one poly(biphenyl ether sulfone) of
 25 which all the recurring units are of formula (4).

Still more preferred are mixtures mixtures consisting of (i) at least one poly(biphenyl ether sulfone) of which more than 50 wt. % of the recurring units

are of formula (2), preferably consisting essentially of recurring units of formula (2), and still more preferably consisting of recurring units of formula (2), and (ii) at least one poly(biphenyl ether sulfone) of which more than 50 % of the recurring units are of formula (4) and (6), preferably consisting essentially of recurring units of formula (4) and (6), and still more preferably consisting of recurring units of formulae (4) and (6), wherein the amount of the recurring units (6) contained in the mixture, based on the total weight of the recurring units (4) and (6), is between 10 and 99 %, and preferably between 50 and 95 %, and, optionally, in addition (iii) at least one other poly(biphenyl ether sulfone) different from the poly(biphenyl ether sulfone)s (i) and (ii).

Preferred poly(biphenyl ether sulfone)s include the RADEL[®] R polyphenylsulfones available from Solvay Advanced Polymers, e.g., RADEL R-5000, RADEL R-5100, RADEL R-5500, and RADEL R-5800.

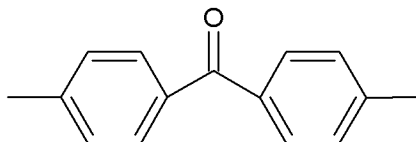
The weight average molecular weight of the poly(biphenyl ether sulfone) may be in any range that is suitable for practical processing, e.g., injection moulding, extrusion, sheet forming, etc., under melt or thermoforming conditions to provide moulded, formed and/or extruded articles having desirable physical and mechanical properties as well as good optical properties. The weight average molecular weight of the poly(aryl ether sulfone)s suitable generally ranges from about 30,000 to about 100,000, more preferably 40,000 to 80,000, more preferably 60,000 to 75,000, as measured by gel permeation chromatography using methylene chloride as a solvent and polystyrene calibration standards according to ASTM D-5296-05. The melt flow rate of the poly(biphenyl ether sulfone) is preferably low. For example, a melt flow rate of from 2-40 g/10 min is preferred, more preferably from 6-35 g/10 min, more preferably from 8-30 g/10 min, more preferably from 10-25 g/10 min, and most preferably from 14-28 g/10 min. Melt flow rate is reported as measured under the conditions of ASTM D 1238 at a temperature of 365°C and a load of 5 kg. Melt flow rates of greater than 15 g/10 min may also be used.

The glass transition temperature for the poly(biphenyl ether sulfone) generally is in the range of from about 180 to about 270°C, preferably 190-240°C, more preferably 200-230°C, more preferably 205-225°C, more preferably 210-220°C.

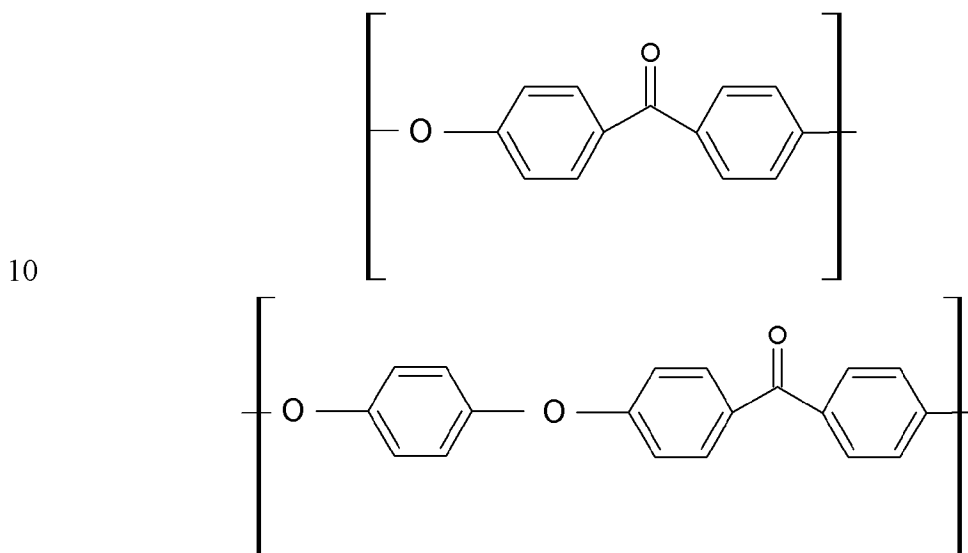
Another group of high temperature resistant polymers are the so-called polyetherketones which comprise similar structural units as the various

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polysulfones described above, but comprising at least one diphenyl ketone group as shown below :



These polymers are generally further characterized through their sequence of -CO- and -O- bridging units between the phenylene rings. Thus, PEK is a polyetherketone having alternating -CO- and -O- groups bridging the aromatic benzenic rings and PEEK is a polymer where two -O- groups are followed by a -CO- group. PEK and PEEK are thus characterized by the following structures

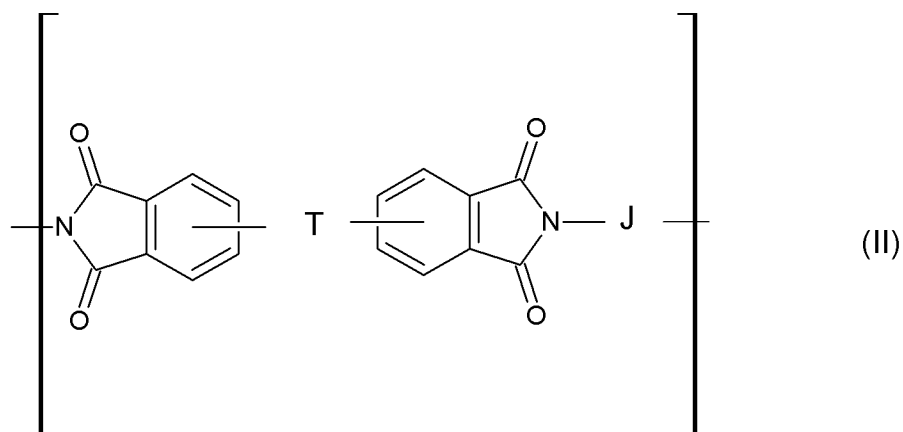


The skilled man is familiar with this nomenclature of polyetherketones and knows which monomers to choose to achieve the desired polymer structure.

Copolymers having repeating units described hereinbefore for polysulfones and repeating units described hereinbefore for polyether ketones are also possible in many variations.

A further group of polymers for the polymer compositions in accordance with the instant invention are the so called polyether imides characterized by the general formula II

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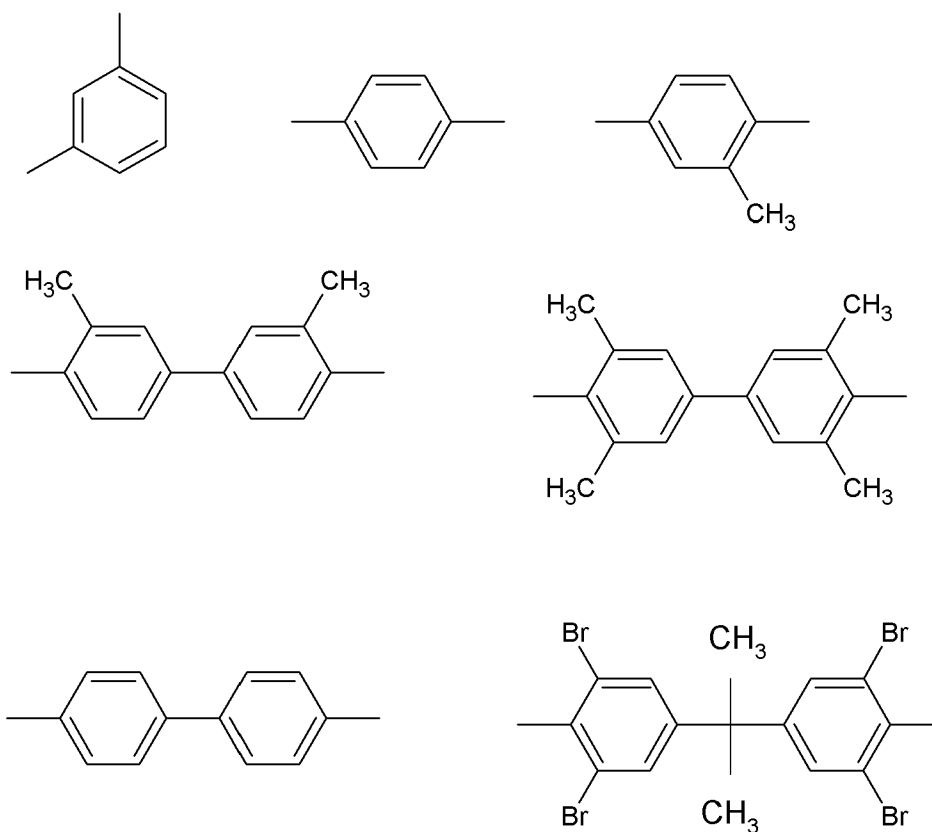
wherein

T is -O- or a substituent -O-Z-O-,

the two linkages are formed at the 3,3', 3,4', 4,3' or 4,4' positions,

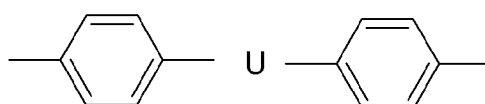
5 Z is a divalent organic moiety selected from the group consisting of

a) a divalent organic moiety selected from the group consisting of



and

b)

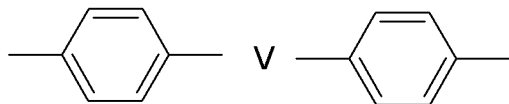


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wherein U is a divalent moiety selected from the group consisting of $-C_yH_{2y}$, $-CO-$, $-SO_2-$, $-O-$ and $-S-$, y being an integer of from 1 to 5,

and J is a divalent organic moiety selected from the group consisting of

- i) aromatic hydrocarbylene groups or halogenated hydrocarbylene groups having from 6 to 20 carbon atoms,
- ii) alkylene groups having from 2 to 20 carbon atoms or cycloalkylene groups having from 3 to 20 carbon atoms, and
- iii)

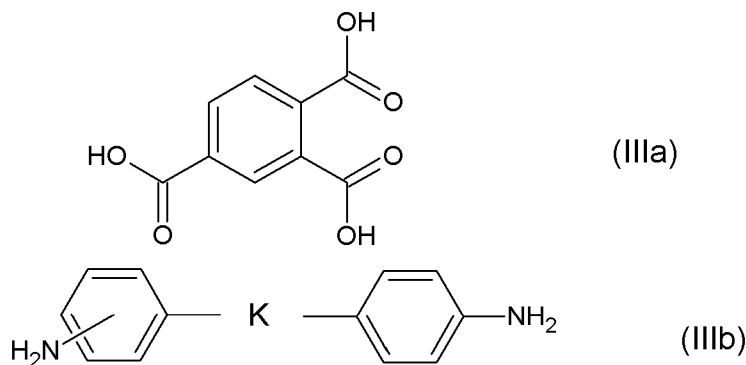


- wherein V is a divalent group selected from the group consisting of $-S-$, $-O-$, $-CO-$, $-SO_2-$ and $-C_xH_{2x}-$ with x being an integer of from 1 to 5.

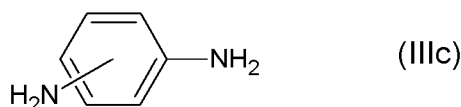
Polymers of this type are commercially available under the tradename Ultem[®] and appropriate methods for the manufacture of such polymers are described in the literature, e.g. in EP 605197 so that further details are not necessary here.

Still another group of polymers suitable are so called polyamide imides which are generally obtainable by the reaction of derivatives of tricarboxylic acids with aromatic diamines or diisocyanates.

- Preferred polyamide imides are obtainable from the reaction of derivatives of tricarboxylic acid IIIa and aromatic diprimary amines IIIb and IIIc



- wherein K is selected from the group consisting of $-O-$, $-S-$, $-CO-$, $-SO_2-$, $-C(CH_3)_2-$ and wherein the amino group in the indicated left ring is in m- or p-position to the bridging substituent K,



wherein the amino groups are in m- or p-position to each other.

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The compositions in accordance with the invention contain the oligomer in an amount of from 1 to 300 wt.-%, preferably of from 10 to 200 wt.-% and especially preferred of from 10 to 150 wt.-%, based on the weight of component b). The amount of component b) in compositions comprising components a) to c) is generally in the range of from 0.5 to 50 wt.-%, preferably of from 1 to 40 wt.-% and most preferred of from 2 to 20 wt.-%, based on the weight of component c).

According to a further embodiment of the invention, the compositions comprise a fluid. Preferably the fluid is a polymer in the molten state or a solvent capable of dissolving oligomer a) in an amount of at least 10 g/l at a temperature of 25°C. Compositions comprising a polymer in the molten state may be obtained by melting the polymer by heating it above the melting point or by other suitable methods known to the skilled person. As the oligomer, as outlined above, has preferably a structural similarity to the polymer used, compositions of this type enable a particularly good dispersion of the oligomer/particle composition in the polymer.

The same effect may be achieved, if a solvent for the oligomer as outlined above is used instead or in addition to a polymer in the molten state. Depending on the structure of the oligomer the skilled person is able to select an appropriate solvent so that a detailed description is not necessary here.

A further aspect of the invention is the use of the oligomer as defined in claim 1 and described hereinbefore for the stabilization of inorganic particles, in particular nanomaterials, against agglomeration and coagulation. The stabilized particles show an increased stability against agglomeration and coagulation during storage or during incorporation into polymer matrices.

A last aspect of the instant invention relates to the use of the oligomer as defined in claim 1 and described in more detail hereinbefore in the melt processing of polymeric compositions comprising the polymer described in more detail hereinbefore and inorganic particles. In this embodiment the oligomer can either be added separately to the melt comprising polymer and the oligomer can be mixed with the inorganic particles prior to adding same to the polymer melt.

By selecting the inorganic particles, the polymer and the oligomer one can tailor the properties of the end product in a broad range, e.g. with regard to transparency of final products (where the core shell particles described in more detail hereinbefore have proved advantageous) or flame retardancy (where zinc borate has proven advantageous).

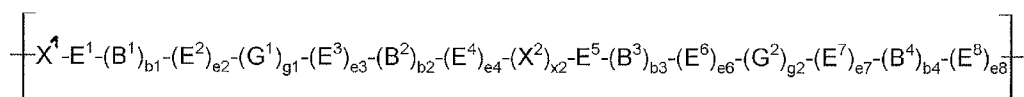
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Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

CLAIMS

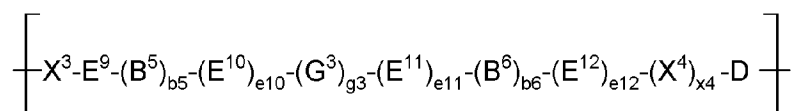
1. Compositions comprising

- a) 1 to 300 wt.-%, based on the weight of component b), of at least one oligomer comprising repeating units RU-1 and RU-2



5

RU-1



RU-2

wherein

X^1 , X^2 , X^3 and X^4 are the same or different and are -O- or -S-

10 E^1 to E^{12} are the same or different and represent arylene groups containing 6 to 24 carbon atoms,

B^1 to B^6 and G^1 to G^3 are the same or different and represent divalent moieties selected from -O-, -S-, $-C(CH_3)_2-$, $-(CCF_3)_2-$, $-SO_2-$, $-CO-$, C_2-C_4 -alkenylene, C_2-C_4 -alkynylene, $-(CH_2)_n-$ and $(CF_2)_m-$,

15 D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

b_1 to b_6 and g_1 to g_3 are the same or different and are 0 or 1,

e_2 to e_4 , e_6 to e_8 and e_{10} to e_{12} are the same or different and represent an integer in the range of from 0 to 3,

x_2 and x_4 are the same or different and are 0 or 1, and

20 n and m represent an integer of from 1 to 6,

and

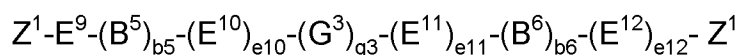
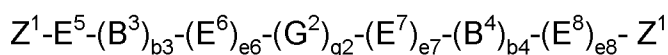
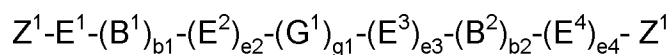
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b) inorganic particles.

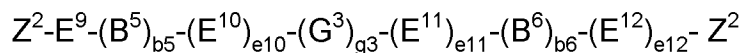
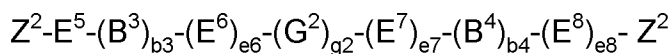
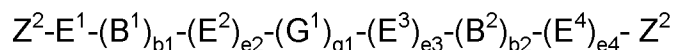
2. Compositions comprising

- a) 1 to 300 wt. %, based on the weight of component b), of at least one oligomer obtainable by oligomerizing a mixture comprising at least one monomer from each of groups a1 to a3 :

a1) compounds of formulae



a2) compounds of formulae



- 10 a3) compounds of formula Z^2-D-Z^2

wherein Z^1 is -OH or -SH or a halogen atom, Z^2 is -OH, -SH or a halogen atom provided that Z^1 is -OH or -SH when Z^2 is a halogen atom and Z^1 is a halogen atom when Z^2 is -OH or -SH and provided that the total number of moles of monomers with -OH or -SH end groups is substantially equal to the number of moles of monomers with halogen end groups,

and wherein

E^1 to E^{12} are the same or different and represent arylene groups containing 6 to 24 carbon atoms,

B^1 to B^6 and G^1 to G^3 are the same or different and represent divalent moieties selected from -O-, -S-, -C(CH₃)₂-, -(CCF₃)₂-, -SO₂-, -CO-, C₂-C₄-alkenylene, C₂-C₄-alkynylene, -(CH₂)_n- and -(CF₂)_m-,

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D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

b_1 to b_6 and g_1 to g_3 are the same or different and are 0 or 1,

5 e_2 to e_4 , e_6 to e_8 and e_{10} to e_{12} are the same or different and represent an integer in the range of from 0 to 3, and

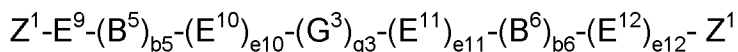
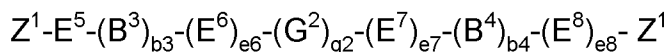
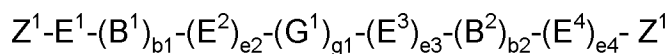
n and m represent an integer of from 1 to 6,

and

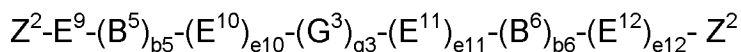
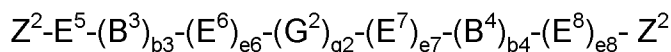
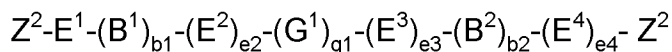
b) inorganic particles.

3. Compositions in accordance with claim 1 or 2, further comprising

10 c) at least one polymer selected from the group consisting of polyarylene polyethers obtainable by polymerizing at least one monomer of group a1)



and at least one monomer of group a2)



15 wherein

Z^1 is -OH or -SH or a halogen atom, Z^2 is -OH, -SH or a halogen atom provided that Z^1 is -OH or -SH when Z^2 is a halogen atom and Z^1 is a halogen atom when Z^2 is -OH or -SH and provided that the total number of moles of monomers with -OH or -SH end groups is substantially equal to the number of
20 moles of monomers with halogen end groups,

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and wherein

E^1 to E^{12} are the same or different and represent arylene groups containing 6 to 24 carbon atoms,

5 B^1 to B^6 and G^1 to G^3 are the same or different and represent divalent moieties selected from -O-, -S-, -C(CH₃)₂-, -(CCF₃)₂-, -SO₂-, -CO-, C₂-C₄-alkenylene, C₂-C₄-alkynylene, -(CH₂)_n- and -(CF₂)_m-,

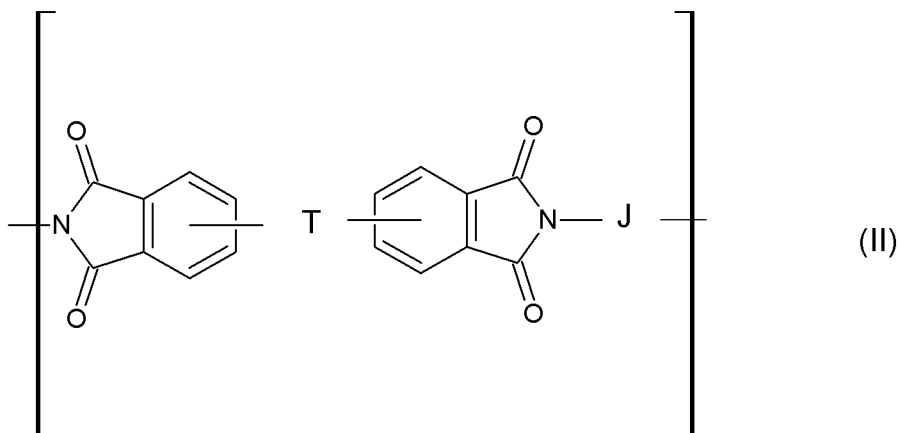
D is a divalent moiety comprising at least one nitrogen-containing heterocyclic ring,

b_1 to b_6 and g_1 to g_3 are the same or different and are 0 or 1,

10 e_2 to e_4 , e_6 to e_8 and e_{10} to e_{12} are the same or different and represent an integer in the range of from 0 to 3,

n and m represent an integer of from 1 to 6, or

polyetherimides having recurring units of formula II



15 wherein

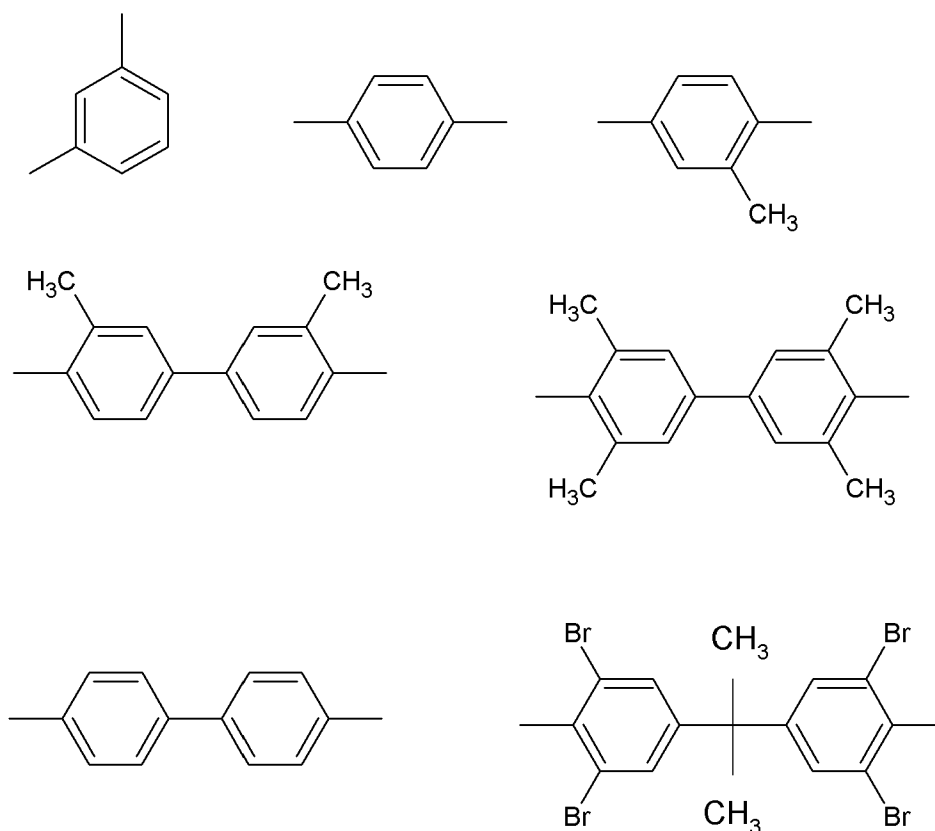
T is -O- or a substituent -O-Z-O-,

the two linkages are formed at the 3,3', 3,4', 4,3' or 4,4' positions,

Z is a divalent organic moiety selected from the group consisting of

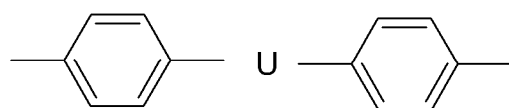
a1) a divalent organic moiety selected from the group consisting of

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and

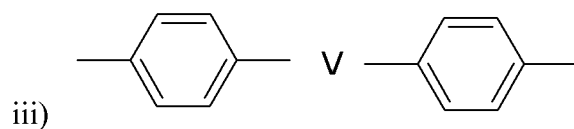
b1)



5 wherein U is a divalent moiety selected from the group consisting of $-C_yH_{2y}$, $-CO-$, $-SO_2-$, $-O-$ and $-S-$, y being an integer of from 1 to 5,

and J is a divalent organic moiety selected from the group consisting of

- i) aromatic hydrocarbylene groups or halogenated hydrocarbylene groups having from 6 to 20 carbon atoms,
- 10 ii) alkylene groups having from 2 to 20 carbon atoms or cycloalkylene groups having from 3 to 20 carbon atoms, and



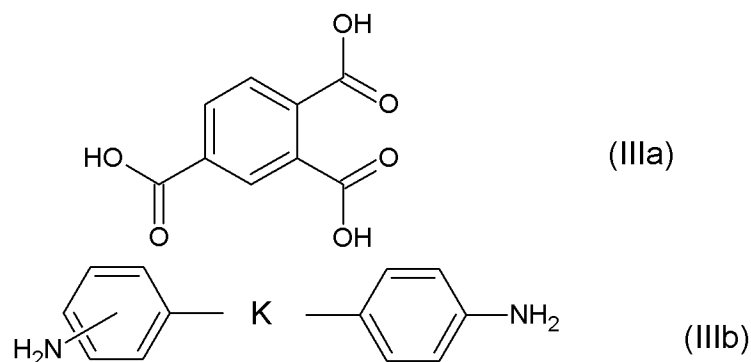
iii)

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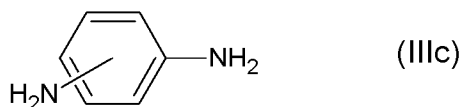
wherein V is a divalent group selected from the group consisting of $-S-$, $-O-$, $-CO-$, $-SO_2$ and $-C_xH_{2x}$ with x being an integer of from 1 to 5,

or

polyamideimides obtainable from the reaction of tricarboxylic acid
 5 derivatives IIIa and aromatic diprimary amines IIIb and IIIc



wherein K is selected from the group consisting of $-O-$, $-S-$, $-CO-$, $-SO_2-$,
 10 $-C(CH_3)_2-$ and wherein the amino group in the indicated left ring is in m- or p- position to the bridging substituent K,



wherein the amino groups are in m- or p-position to each other and wherein
 the amount of inorganic particles b), based on the weight of the polymer c),
 is in the range of from 0.5 to 50 wt. %.

15 4. Compositions in accordance with any of claims 1 to 3, further comprising a fluid.

5. Compositions in accordance with claim 4, wherein the fluid is a polymer in the molten state.

20 6. Compositions in accordance with claim 4, wherein the fluid is a solvent selected from the group consisting of organic solvents capable of dissolving oligomer a) in an amount of at least 10 g/l at a temperature of 25°C.

7. Compositions in accordance with any of claims 1 to 6, comprising nanoparticles as component b).

8. Compositions in accordance with any of claims 1 to 7, comprising as component b) core shell particles comprising a core essentially consisting of an UV absorbing inorganic oxygen containing metal compound selected from the group consisting of ZnO, TiO₂, CeO₂ and/or TiOF₂, and a shell essentially
5 consisting of SiO₂, MgF₂, CaF₂ and/or SrF₂.

9. Compositions in accordance with claim 8, wherein the atomic ratio of the metal atom in the core to the metal atom in the shell is in the range of from 0.1:1 to 1.7:1, and the average particle diameter of the core shell particles is less than or equal to 150 nm.

10. Compositions in accordance with any of the preceding claims, wherein the oligomer has an intrinsic viscosity in the range of from 0.016 l/g to 0.040 l/g, measured at a temperature of 25°C in N-Methyl-2-pyrrolidone solvent.

11. Compositions in accordance with any of the preceding claims, comprising as component a) an oligomer wherein D in the repeating units RU-2
15 is selected from the group consisting of 2,4-pyridylene, 2,5-pyridylene, 2,6-pyridylene and mixtures thereof, X₁ and X₂ are oxygen atoms, E, E' and E'' are and B and G are -O-, -S-, -C(CH₃)₂-, -SO₂- or -CO-.

12. Use of the oligomer as defined in claim 1, 2 or 10 for the stabilization of inorganic particles.

13. Use of the oligomer as defined in claim 1, 2 or 10 for the stabilization of the inorganic particles contained in the compositions according to any one of claims 4 to 6.

14. Use in accordance with claim 12 or 13, wherein the inorganic particles are nanoparticles.

15. Method for preparing compositions in accordance with claim 3 which comprises mixing the polymer with the inorganic particles and the oligomer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/073399

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/04 C09C3/08
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)
C08K C09C

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

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

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.
X	WO 2008/002867 A2 (GEN ELECTRIC [US]; CHAN KWOK PONG [US]; ODLE ROY RAY [US]; WHITE JAMES) 3 January 2008 (2008-01-03) page 9; compound 1i page 11; compound II page 12; compound IV page 18; compound 2d page 23; compound XXII page 37; compound XI example 5; compound 5 example 14; compound 14 example 19; compound 19 example 58; compound 31 page 97; example 62 claims 3-11,17,19,20,23,27 ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

18 January 2012

Date of mailing of the international search report

31/01/2012

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Authorized officer

Russell, Graham

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/073399

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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