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(54) Title: POLYMER COMPOSITION

(57) Abstract: The invention pertains to a polymer composition comprising: - at least one polycondensation polymer having a heat deflection temperature (HDT) of above 80°C under a load of 1.82 MPa when measured according to ASTM D648 [polymer (P)]; at least one perfluoropolyether block copolymer [polymer (F)] comprising: A) one or more (per)fluoropolyoxyalkylene segment (chain R_i), that is to say a segment comprising recurring units having at least one catenary ether bond and at least one fluoro-carbon moiety, and B) one or more polyalkylene segment (chain R_a) comprising recurring units of formula: -(CR₁R₂-CR₃R₄)- wherein R₁, R₂, R₃, R₄, equal to or different from each other, are selected from the group consisting of H, halogens (preferably F, Cl); C₁-C₆ (hydro)carbon groups, optionally containing fluorine or other heteroatoms, preferably perfluoroalkyl or (per)fluoroalkoxyalkyl, to a process for its manufacture and to its use for manufacturing shaped articles, in particular by extrusion moulding or injection moulding techniques.



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Description**Polymer composition****Technical Field**

- [0001] This application claims priority to U.S. provisional application 61/155541, filed February 26, 2009, the whole content of which is herein incorporated by reference
- [0002] The invention pertains to a polymer composition having improved processability behaviour at high temperature and high shear rate, to a process for its manufacture and to its use for the manufacture of shaped articles.

Background Art

- [0003] High performance plastics, in particular polysulfone polymers, thanks to their attractive properties, are currently used for the manufacture of several parts and articles intended to deliver outstanding mechanical properties in severe conditions.
- [0004] Among processing technologies used for the manufacture of final parts, said polymers are often extrusion moulded; more particularly, for the manufacture of sheets and profiles, molten material is extruded from a die and pulled out through appropriate rolls or dies so as to achieve required thickness. Melt strength, i.e. tensile strength of the polymer when in molten state so as to avoid melt fractures and failures, is thus a key property. High molecular weight plastics, in particular high molecular weight polysulfones, are generally understood to comply with these requirements; nevertheless, processability of these high molecular weight materials is relatively poor, limiting throughputs and production rates.
- [0005] While processing temperature might improve melt flowability, these conditions may lead to degradation and black speck formation.
- [0006] Traditional flow modifiers, such as MFA, PFA, PTFE or LLDPE, generally require high concentrations to be effective: at these high concentrations, these additives are not compatible in the blend, so that non-homogenous mixtures are obtained, whose performance are negatively affected. Also, certain additives (e.g. LLDPE) are not thermally stable in processing conditions of said high performance plastics.

- [0007] In the past, perfluoropolyether-based additives have already been suggested for high performances plastics. In particular, **JP 63264672** (NTN-RULON INDUSTRIES) 01.11.1988 discloses a lubricating compositions for synthetic resins (e.g. polysulfone resins) comprising a perfluoropolyether compound, for improvement of wear/abrasion resistance. Also, **US 7355816** (MAXTOR CORPORATION) 08.04.2008 discloses thermoplastic polymer compositions based on high performance materials (e.g. polyetherimides, polyphenylensulfides, polysulfones) comprising PTFE and/or perfluoropolyether lubricants for reducing wear.
- [0008] Nevertheless, these perfluoropolyether additives were not investigated for their performances as melt flow modifiers and were not proven to provide any of such effects in taught compositions.
- [0009] There is thus a current shortfall in the art for flow modifiers for high performance plastics which can override above mentioned problems, which are able to withstand processing temperatures without undergoing degradation phenomena, and which can effectively improve processability and melt flow behaviour of said plastics, without negatively affecting their mechanical performances.

Disclosure of Invention

- [0010] It is thus an object of the present invention a polymer composition comprising:
- at least one polycondensation polymer having a heat deflection temperature (HDT) of above 80°C under a load of 1.82 MPa when measured according to ASTM D648 [polymer (P)];
 - at least one perfluoropolyether block copolymer [polymer (F)] comprising:
 - A) one or more (per)fluoropolyoxyalkylene segment (chain R_f), that is to say a segment comprising recurring units having at least one catenary ether bond and at least one fluorocarbon moiety, and
 - B) one or more polyalkylene segment (chain R_a) comprising recurring units of formula: $-(CR_1R_2-CR_3R_4)-$wherein R_1 , R_2 , R_3 , R_4 , equal to or different from each other, are selected from the group consisting of H, halogens (preferably F, Cl); C_1-C_6 (hydro)carbon groups, optionally containing fluorine or other heteroatoms,

preferably perfluoroalkyl or (per)fluorooxyalkyl.

- [0011] The Applicant has found that the incorporation of the polymer (F) as above detailed in said high performance plastics successfully enables achievement of improved melt flowability, significantly enhancing processability especially at low shear rates, without affecting mechanical properties of polymer (P) hosts nor undergoing decomposition/degradation phenomena at processing conditions of said polymer (P).
- [0012] The (per)fluoropolyoxyalkylene segment (chain R_f) is preferably a chain comprising recurring units (R_1), said recurring units having general formula: $-(CF_2)_k-CFZ-O-$, wherein k is an integer of from 0 to 3 and Z is selected between a fluorine atom and a C_1 - C_6 perfluoro(oxy)alkyl group.
- [0013] Chain R_f more preferably complies with formula:
 $-(CF_2CF_2O)_a(CFYO)_b(CF_2CFYO)_c(CF_2O)_d(CF_2(CF_2)_zCF_2O)_e-$,
 the recurring units being statistically distributed along the (per)fluoropolyoxyalkylene chain, wherein:
 - Y is a C_1 - C_5 perfluoro(oxy)alkyl group;
 - z is 1 or 2;
 - a', b', c', d', e' are integers ≥ 0 .
- [0014] Most preferably, chain R_f complies with formula:
 $-(CF_2CF_2O)_a(CF_2O)_b(CF_2(CF_2)_zCF_2O)_c-$, wherein:
 - z is 1 or 2;
 - a'', b'', c'' are integers ≥ 0 .
- [0015] Polymer (F) typically complies with formula:
 $T_I-O-[A-B]_z-[A-B']_{z'}-A-T_I'$ (formula I)
 wherein:
 - $A = -(X)_a-O-A'-(X')_b-$, wherein A' is a chain R_f as above detailed; X, X' , equal to or different from each other, are selected from $-CF_2-$, $-CF_2CF_2-$, $-CF(CF_3)-$; a, b , equal to or different from each other, are integers equal to 0 or 1, with the proviso that the block A linked to the end group T_I-O- has $a = 1$ and the block A linked to the end group T_I' has $b = 0$;
 - B is a segment of recurring units derived from one or more olefins having formula:
 $-[(CR_1R_2-CR_3R_4)_j(CR_5R_6-CR_7R_8)_j]-$ (formula Ia),

wherein: j is an integer from 1 to 100, j' is an integer from 0 to 100 with the proviso that $(j+j')$ is higher than 2 and lower than 100; $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8$, equal to or different from each other, are selected from halogen (preferably F, Cl); H; C_1 - C_6 groups, optionally containing F or other heteroatoms, preferably perfluoroalkyl or (per)fluorooxyalkyl, said substituents R_1 - R_8 optionally containing one or more functional groups;

- z is an integer higher than or equal to 2; z' is ≥ 0 ; z, z' are such that the number average molecular weight of the polymer (F) of formula (I) is in the range 500-500,000;
- B' is a segment otherwise complying with formula (Ia), but having at least one of the substituents R_1 to R_8 different than those in block B;
- T_1 and T_1' , equal to or different from each other, are selected from H, halogen, C_{1-3} (per)fluoroalkyls, C_{1-6} alkyls and C_1 - C_{30} functional end groups comprising heteroatoms chosen among O, S, N.

[0016] Said products can be produced by reacting (per)fluoropolyethers comprising peroxide groups with (fluoro)olefins, as detailed in patent application **WO 2008/065163** (SOLVAY SOLEXIS S.P.A.) 05.06.2008 and **WO 2008/065164** (SOLVAY SOLEXIS S.P.A.) 05.06.2008 .

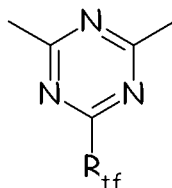
[0017] Preferably, T_1 and T_1' , equal to or different from each other, are selected from the group consisting of :

- (j) $-Y'$, wherein Y' is chain end chosen among -H, halogen, such as -F, -Cl, C_1 - C_3 perhalogenated alkyl group, such as $-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-CF_2CF_2Cl$;
- (jj) $-E_r-A_q-Y''_k$, wherein k, r and q are integers, with $q = 0$ or 1 , $r = 0$ or 1 , and k between 1 and 4, preferably between 1 and 2, E denotes a functional linking group comprising at least one heteroatom chosen among O, S, N; A denotes a C_1 - C_{20} bivalent linking group; and Y'' denotes a functional end-group.

[0018] The functional group E may comprise an amide, ester, carboxylic, thiocarboxylic, ether, heteroaromatic, sulfide, amine, and/or imine group.

[0019] Non limitative examples of functional linking groups E are notably $-CONR-$ ($R = H$, C_1 - C_{15} substituted or unsubstituted linear or cyclic aliphatic group, C_1 - C_{15} substituted or unsubstituted aromatic group); $-COO-$; $-COS-$; $-CO-$;

an heteroatom such as -O-; -S-; -NR' (R = H, C₁-C₁₅ substituted or unsubstituted linear or cyclic aliphatic group, C₁-C₁₅ substituted or unsubstituted aromatic group); a 5- or 6-membered aromatic heterocycle containing one or more heteroatoms chosen among N, O, S, the same or different each other, in particular triazines, such as



with R_{tf} being a perfluoroalkyl group, e.g. -CF₃.

[0020] The bivalent C₁-C₂₀ linking group A is preferably selected from the following classes :

1. linear substituted or unsubstituted C₁-C₂₀ alkylenic chain, optionally containing heteroatoms in the alkylenic chain; preferably linear aliphatic group comprising moieties of formula -(CH₂)_m-, with m integer between 1 and 20, and optionally comprising amide, ester, ether, sulfide, imine groups and mixtures thereof;
2. (alkylene)cycloaliphatic C₁-C₂₀ groups or (alkylen)aromatic C₁-C₂₀ groups, optionally containing heteroatoms in the alkylenic chain or in the ring, and optionally comprising amide, ester, ether, sulfide, imine groups and mixtures thereof;
3. linear or branched polyalkylenoxy chains, comprising in particular repeating units selected from : -CH₂CH₂O-, -CH₂CH(CH₃)O-, -(CH₂)₃O-, -(CH₂)₄O-, optionally comprising amide, ester, ether, sulfide, imine groups and mixtures thereof.

[0021] Examples of suitable functional groups Y'' are notably -OH , -SH, -OR',

[0022] -SR', -NH₂, -NHR', -NR'₂, -COOH, -SiR'_dQ_{3-d}, -CN, -NCO, epoxy group -(CH-CH₂-O-), 1,2- and 1,3-diols as such or as cyclic acetals and ketals (e.g., dioxolanes or dioxanes), -COR', -CH(OCH₃)₂, -CH(OH)CH₂OH, -CH(COOH)₂, -CH(COOR')₂, -CH(CH₂OH)₂, -CH(CH₂NH₂)₂, -PO(OH)₂, -CH(CN)₂, wherein R' is an alkyl, cycloaliphatic or aromatic substituted or unsubstituted group, optionally comprising one or more fluorine atoms, Q is OR', R' having the same meaning as above defined, d is an integer

between 0 and 3.

- [0023] One or more functional end-groups Y" can be linked to the group A and/or E: for instance, when A is an (alkylen)aromatic C₁-C₂₀ group, it is possible that two or more Y" groups are linked to the aromatic ring of the group A.
- [0024] More preferably, the polymer (F) complies with formula (I) here above, wherein T₁ and T₁', equal to or different from each other, are selected from the group consisting of: -H; halogen such as -F and -Cl; C₁-C₃ perhalogenated alkyl group, such as -CF₃, -C₂F₅, -CF₂Cl, -CF₂CF₂Cl; -CH₂OH; -CH₂(OCH₂CH₂)_nOH (n being an integer between 1 and 3); -C(O)OH; -C(O)OCH₃; -CONH-R_H-OSi(OC₂H₅)₃ (where R_H is a C₁-C₁₀ alkyl group); -CONHC₁₈H₃₇; -CH₂OCH₂CH(OH)CH₂OH; -CH₂O(CH₂CH₂O)_{n*}PO(OH)₂ (with n* between 1 and 3); and mixtures thereof.
- [0025] In formula I here above, block B derives from one or more olefins polymerizable by radical route; among those olefins mention can be made of tetrafluoroethylene (TFE), ethylene (E), vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), (per)fluoroalkylvinylethers, (per)fluoroalkoxyalkylvinylethers.
- [0026] Similarly, block B' derives from one or more olefins polymerizable by radical route, at least one of which is different from olefin(s) of block B. Olefins as above indicated for block B are suitable for being used for block B'.
- [0027] It is generally preferred that block B and B' (when this latter is present) comprise recurring units derived from perfluorinated olefins.
- [0028] Particularly preferred to the purpose of the invention is a polymer (F) complying with formula (I) here above, wherein z' is zero, j' is zero and each of R₁, R₂, R₃, R₄ are fluorine atoms, that is to say, wherein block B is derived from tetrafluoroethylene and block B' is absent.
- [0029] Thus, most preferred polymer (F) complies with formula:

$$T_1-O-[A-B]_z-A-T_1' \text{ (formula I)}$$
 wherein:
 - A = -(X)_a-O-A'-(X')_b-, wherein X, a and b have the meanings above defined and A' is a chain R_f of formula:

$$-(CF_2CF_2O)_{a+}(CF_2O)_{b+}(CF_2(CF_2)_zCF_2O)_{c+}-,$$

wherein: z^+ is 1 or 2; a^+ , b^+ , c^+ are integers ≥ 0 ;

- B is a segment of formula $-(CF_2-CF_2)_{j^+}-$ wherein: j^+ is an integer from 2 to 100;

- T_1 and T_1' , equal to or different from each other, are selected from the group consisting of: -H; halogen such as -F and -Cl; C_1-C_3 perhalogenated alkyl group, such as $-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-CF_2CF_2Cl$.

[0030] The polymer composition of the invention advantageously comprises polymer (F) in an amount of at least 0.05 % wt, preferably at least 0.1 % wt, most preferably at least 0.25 % wt, with respect to the total weight of polymer (F) and polymer (P).

[0031] The polymer composition of the invention advantageously comprises polymer (F) in an amount of at most 15 % wt, preferably at most 10 % wt, most preferably at most 5 % wt, even more preferably at most 2 % wt, with respect to the total weight of polymer (F) and polymer (P).

[0032] Compositions comprising polymer (F) in an amount of 0.5 to 2 % wt, with respect to the total weight of polymer (F) and polymer (P), gave particularly good results.

[0033] High performance plastics suitable for the compositions of the invention are as mentioned above polycondensation polymers that have a heat deflection temperature (HDT) of above 80°C under a load of 1.82 MPa when measured according to ASTM D648 [polymers (P)]. Typical heat deflection temperatures of certain high performance plastics are listed in Table 1.

Table 1

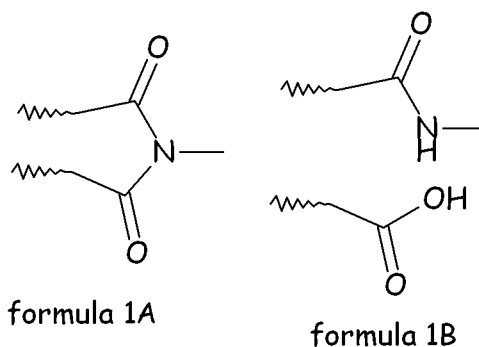
Polycondensation Polymer	Heat Deflection Temperature (°C)
Polysulfone (PSU)	174
Polyethersulfone (PES)	203
Polyphenylsulfone	204
Polyphthalamide	120
Polyamideimide	278
Liquid crystalline polymers (LCP)	180 – 310
Polyimide	360

Polyetherimide	200
Polyetheretherketone (low flow)	160
Polyetheretherketone (high flow)	171
Polyphenylene sulfide	135
Polycarbonate	132

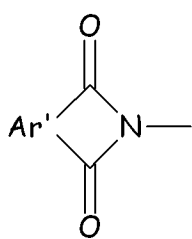
[0034] Heat deflection temperatures of polymer (P) can be determined according to ASTM D648, Method A, using a span of 4 inches. The polymer is injection moulded into plaques that are 5 inches long, 1/2 inch wide, and 1/8 inch thick. The plaques are immersed in a suitable liquid heat-transfer medium, such as oil, during the HDT test. Dow Corning 710 silicone oil, for example, can be used.

[0035] High performance plastics useful herein include, but are not limited to, aromatic polyimides (PI), in particular polyester-imides (PEI) and polyamide-imides (PAI), polyaryletherketones (PAEK), such as polyetheretherketone (PEEK) and polyetherketoneketone (PEKK), liquid crystal polymers (LCP), and aromatic sulfone polymers (SP). Preferably, the high performance polymer [polymer (P)] is an aromatic sulfone polymer (SP).

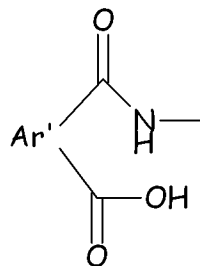
[0036] To the purpose of the present invention, "aromatic polyimide (PI)" is intended to denote any polymer comprising recurring units, more than 50 wt. % of said recurring units comprising at least one aromatic ring and at least one imide group, as such (formula 1A) or in its amic acid form (formula 1B) [recurring units (R_{PI})] :



[0037] The imide group, as such or in its corresponding amic acid form, is advantageously linked to an aromatic ring, as illustrated below :



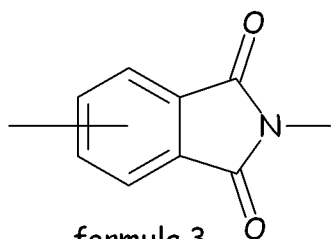
formula 2A



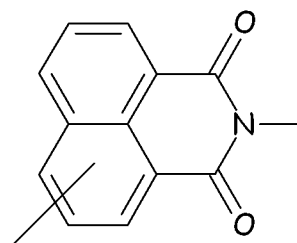
formula 2B

whereas Ar' denotes a moiety containing at least one aromatic ring.

[0038] The imide group is advantageously present as condensed aromatic system, yielding a five- or six-membered heteroaromatic ring, such as, for instance, with benzene (phthalimide-type structure, formula 3) and naphthalene (naphthalimide-type structure, formula 4).

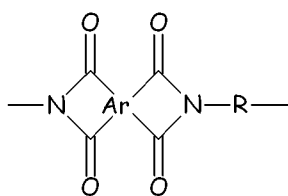


formula 3

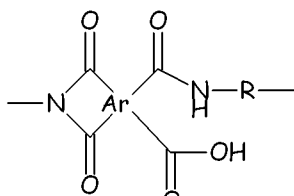


formula 4

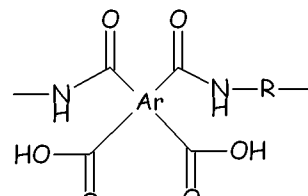
[0039] The formulae here below depict examples of recurring units (R_{PI}) (formulae 5A to 5C) :



formula 5A



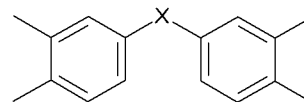
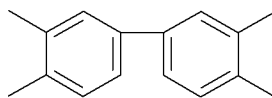
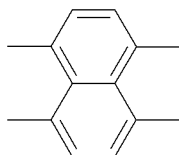
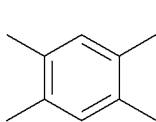
formula 5B



formula 5C

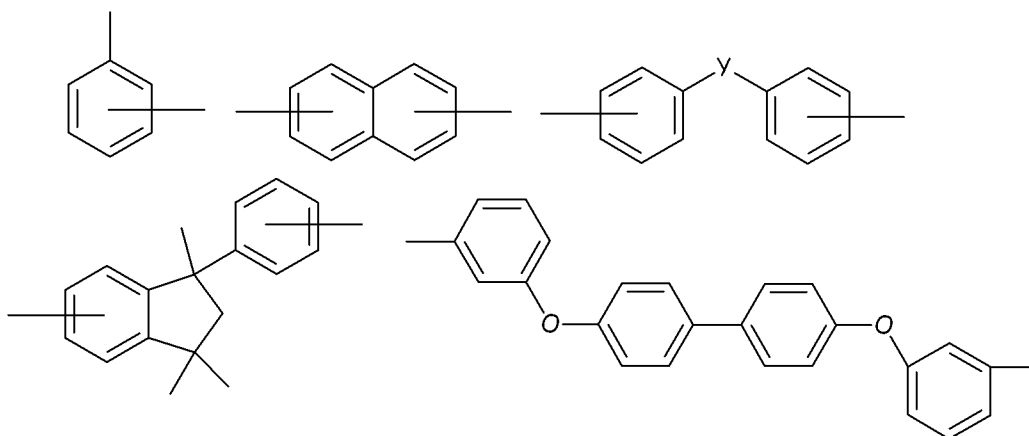
wherein :

- Ar represents an aromatic tetravalent group; typically Ar is selected from the group consisting of following structures:



and corresponding optionally substituted structures, with X being $-O-$, $-C(O)-$, $-CH_2-$, $-C(CF_3)_2-$, $-(CF_2)_n-$, with n being an integer from 1 to 5;

- R represents an aromatic divalent group; typically R is selected from the group consisting of following structures:

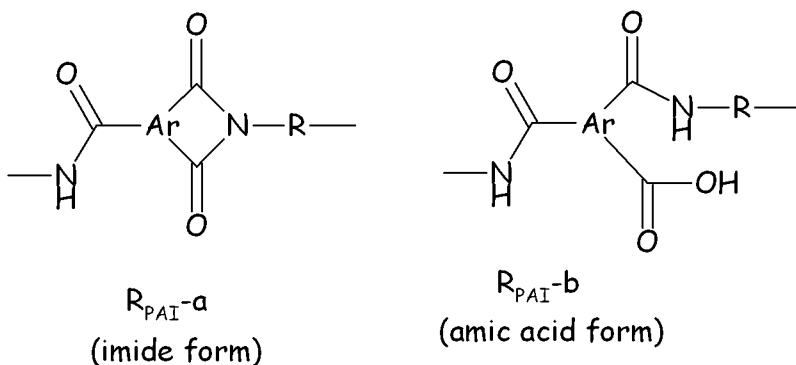


and corresponding optionally substituted structures, with Y being $-O-$, $-S-$, $-SO_2-$, $-CH_2-$, $-C(O)-$, $-C(CF_3)_2-$, $-(CF_2)_n$, n being an integer from 0 to 5.

- [0040] Polyimides commercialized by DuPont as VESPEL[®] polyimides or by Mitsui as AURUM[®] polyimides are suitable for the purpose of the invention.
- [0041] The recurring units (R_{PI}) of the aromatic polyimide can comprise one or more functional groups other than the imide group, as such and/or in its amic acid form. Non limitative examples of polymers complying with this criterion are aromatic polyetherimides (PEI), aromatic polyesterimides and aromatic polyamide-imides (PAI).
- [0042] To the purpose of the present invention, “aromatic polyesterimide” is intended to denote any polymer more than 50 wt. % of the recurring units comprise at least one aromatic ring, at least one imide group, as such and/or in its amic acid form, and at least one ester group [recurring units (R_{PEI})]. Typically, aromatic polyesterimides are made by reacting at least one acid monomer chosen from trimellitic anhydride and trimellitic anhydride monoacid halides with at least one diol, followed by reaction with at least one diamine.
- [0043] To the purpose of the present invention, “aromatic polyamide-imide (PAI)” is intended to denote any polymer comprising more than 50 wt. % of recurring units comprising at least one aromatic ring, at least one imide group, as such and/or in its amic acid form, and at least one amide group

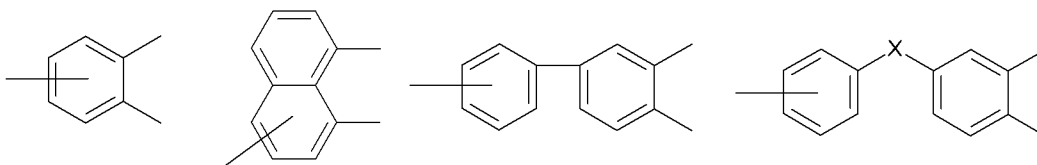
which is not included in the amic acid form of an imide group [recurring units (R_{PAI})].

[0044] The recurring units (R_{PAI}) are advantageously chosen among :



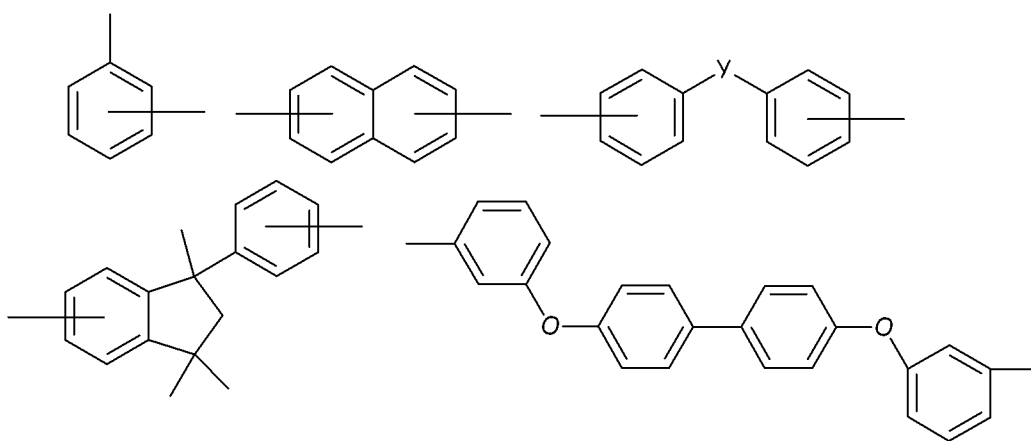
wherein :

- Ar is a trivalent aromatic group; typically Ar is selected from the group consisting of following structures:



and corresponding optionally substituted structures, with X being $-O-$, $-C(O)-$, $-CH_2-$, $-C(CF_3)_2-$, $-(CF_2)_n-$, with n being an integer from 1 to 5;

- R is a divalent aromatic group; typically R is selected from the group consisting of following structures:



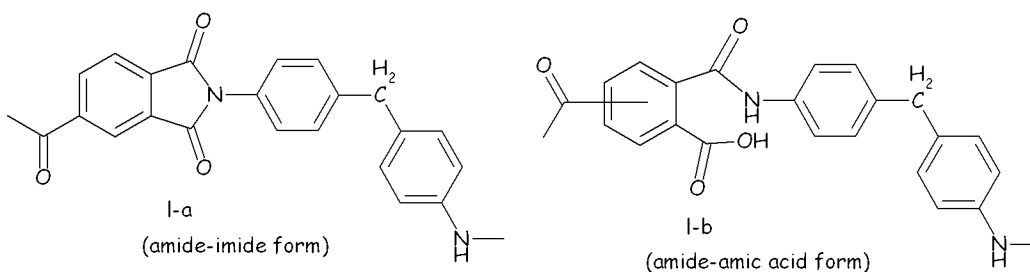
and corresponding optionally substituted structures, with Y being $-O-$, $-S-$, $-SO_2-$, $-CH_2-$, $-C(O)-$, $-C(CF_3)_2-$, $-(CF_2)_n$, n being an integer from 0 to 5.

[0045] Preferably, the aromatic polyamide-imide comprises more than 50 % of

recurring units (R_{PAI}) comprising an imide group in which the imide group is present as such, like in recurring units (R_{PAI-a}), and/or in its amic acid form, like in recurring units (R_{PAI-b}).

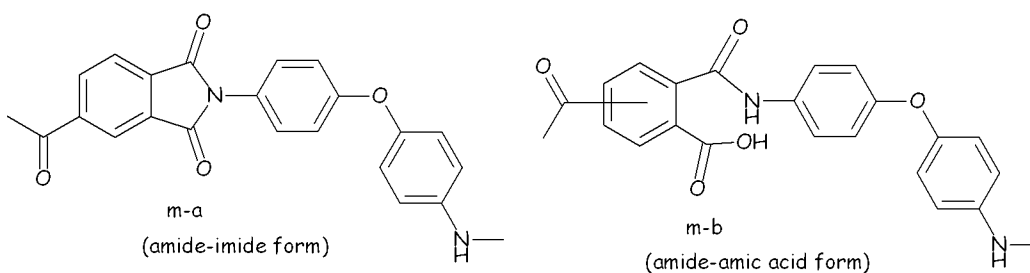
[0046] Recurring units (R_{PAI}) are preferably chosen from recurring units (l), (m) and (n), in their amide-imide (a) or amide-amic acid (b) forms:

(l)



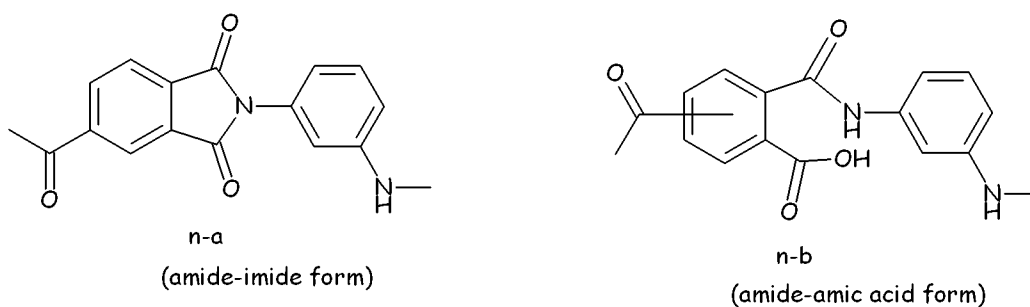
wherein the attachment of the two amide groups to the aromatic ring as shown in (l-b) will be understood to represent the 1,3 and the 1,4 polyamide-amic acid configurations;

(m)



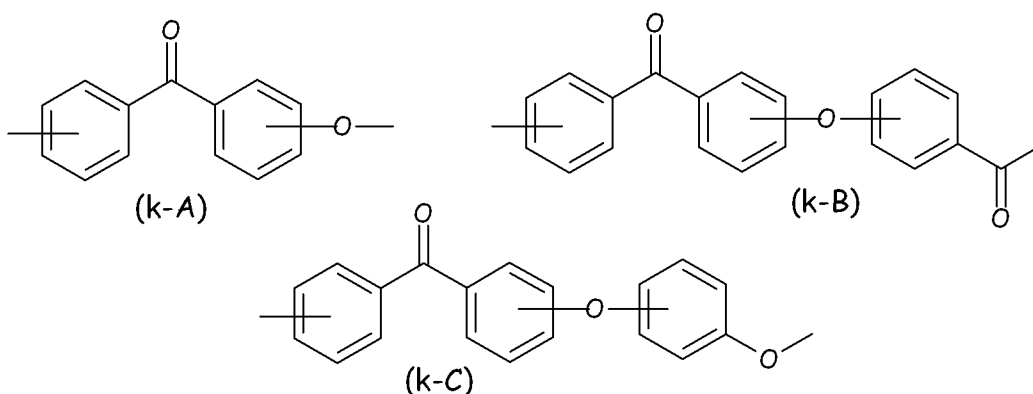
wherein the attachment of the two amide groups to the aromatic ring as shown in (m-b) will be understood to represent the 1,3 and the 1,4 polyamide-amic acid configurations; and

(n)



wherein the attachment of the two amide groups to the aromatic ring as shown in (n-b) will be understood to represent the 1,3 and the 1,4 polyamide-amic acid configurations.

- [0047] Very preferably, the aromatic polyamide-imide comprises more than 90 wt. % of recurring units (R_{PAI}). Still more preferably, it contains no recurring unit other than recurring units (R_{PAI}). Polymers commercialized by Solvay Advanced Polymers, L.L.C., as TORLON® polyamide-imides comply with this criterion.
- [0048] The aromatic polyamide-imide can be notably manufactured by a process including the polycondensation reaction between at least one acid monomer chosen from trimellitic anhydride and trimellitic anhydride monoacid halides and at least one comonomer chosen from diamines and diisocyanates.
- [0049] Among the trimellitic anhydride monoacid halides, trimellitic anhydride monoacid chloride is preferred.
- [0050] The comonomer comprises preferably at least one aromatic ring. Besides, it comprises preferably at most two aromatic rings. More preferably, the comonomer is a diamine. Still more preferably, the diamine is chosen from the group consisting of 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, m-phenylenediamine and mixtures thereof.
- [0051] For the purpose of the invention, the term “polyaryletherketone (PAEK)” is intended to denote any polymer, comprising recurring units (R_{PAEK}), more than 50 wt. % of said recurring units are recurring units (k-A), (k-B) and/or (k-C) :

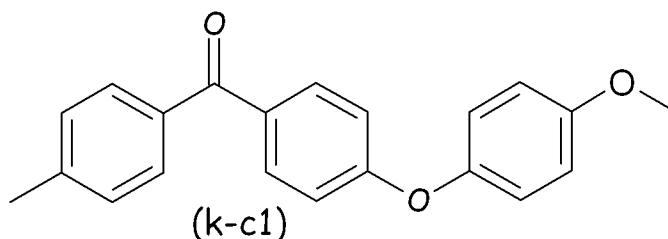


wherein the attachment of the ketone and/or ether groups to the aromatic ring as shown in (k-A), (k-B) and (k-B) will be understood to represent, independently at each occurrence, each of the possible ortho, meta and para configurations.

- [0052] Preferably at least 70 wt. %, more preferably at least 80 wt. % of the

recurring units (R_{PAEK}) of the polyaryletherketone (PAEK) suitable for the polymer composition of the invention are recurring units (k-A), (k-B) and/or (k-C). Most preferably polyaryletherketone (PAEK) comprises no recurring units other than recurring units (k-A), (k-B) and/or (k-C).

- [0053] Polyaryletherketones (PAEK) are generally crystalline aromatic polymers, readily available from a variety of commercial sources. Methods for their preparation are well known, including the processes described for example in U.S. Pat. Nos. 3,441,538, 3,442,857, 3,516,966, 4,396,755 and 4,816,556. The polyaryletherketones (PAEK) have preferably reduced viscosities in the range of from about 0.8 to about 1.8 dl/g as measured in concentrated sulfuric acid at 25° C and at atmospheric pressure.
- [0054] Preferably the polyaryletherketone (PAEK) is chosen among polyetheretherketones (PEEK) and polyetherketoneketone (PEKK).
- [0055] A polyetheretherketone (PEEK) is a polyaryletherketone (PAEK) wherein more than 50 wt. % of recurring units (R_{PAEK}) are recurring units (k-C).
- [0056] A polyetherketoneketone (PEKK) is a polyaryletherketone (PAEK) wherein more than 50 wt. % of recurring units (R_{PAEK}) are recurring units (k-B).
- [0057] Non limitative examples of commercially available polyaryletherketone (PAEK) resins suitable for the invention include the KETASPIRE[®] polyetheretherketone commercially available from Solvay Advanced Polymers and VICTREX[®] PEEK polyetheretherketone, from Imperial Chemicals, Inc., which are polymers, the recurring units of which are recurring units (k-c1) :

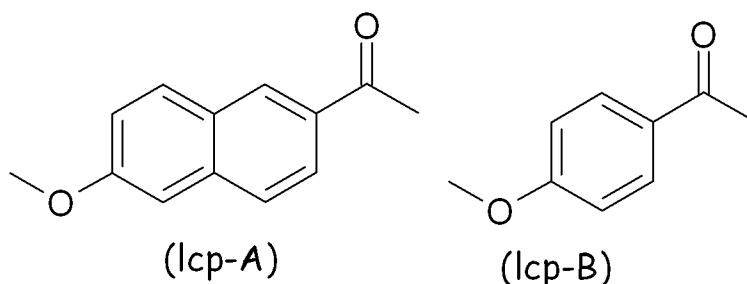


- [0058] The terms “liquid crystal polymers (LCP)” encompasses notably fully aromatic liquid crystalline polyesters.
- [0059] Fully aromatic liquid crystalline polyesters can be produced in the melt by three main processes :

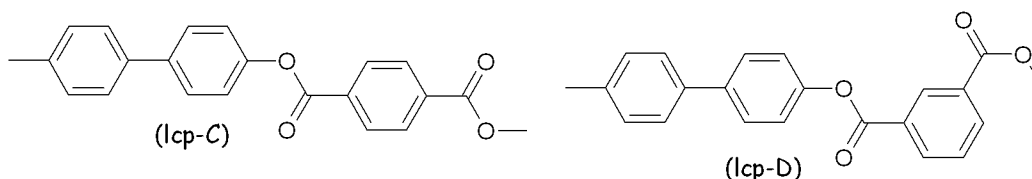
- direct esterification of optionally substituted phenols with aromatic carboxylic acids in the presence of catalysts such as titanium tetrabutryate or dibutyl tin diacetate at high temperature;
- reaction between phenyl esters of aromatic carboxylic acids with relevant optionally substituted phenols;
- acidolysis of phenolic acetates with aromatic carboxylic acids.

[0060] Non limitative examples of commercially available fully aromatic liquid crystalline polyesters are notably VECTRA® LCP from Hoechst-Celanese and XYDAR® LCP from Solvay Advanced Polymers.

[0061] VECTRA® LCP is typically synthesized from 4-hydrobenzoic acid and 6-hydroxy-2-naphtioic acid; VECTRA® LCP is a polymer the recurring units of which are recurring units (lcp-A) and (lcp-B), typically in a ratio (lcp-A)/(lcp-B) of about 25/75 :

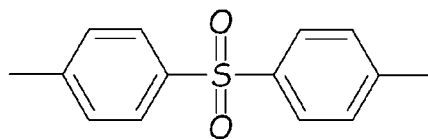


[0062] XYDAR® LCP is typically synthesized from 4-hydroxybenzoic acid, 4,4'-dihydroxy-1,1'-biphenyl, and terephthalic acid; the basic structure can be modified by using other monomers such as isophthalic acid or 4-aminobenzoic acid; XYDAR® LCP is generally a polymer the recurring units of which are recurring units (lcp-C), (lcp-D) and (lcp-B), typically in a ratio [(lcp-C)+(lcp-D)]/(lcp-B) of about 1/2 :



[0063] For the purpose of the invention, the term “polymer” is intended to denote any material consisting essentially of recurring units, and having a molecular weight above 2000.

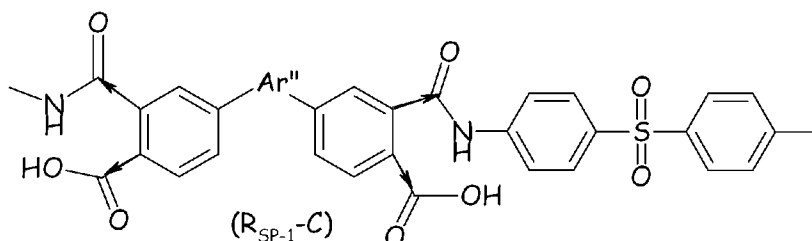
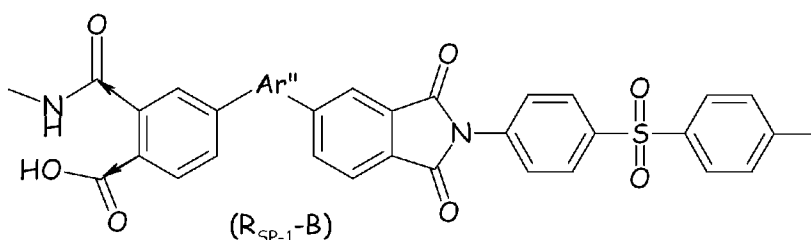
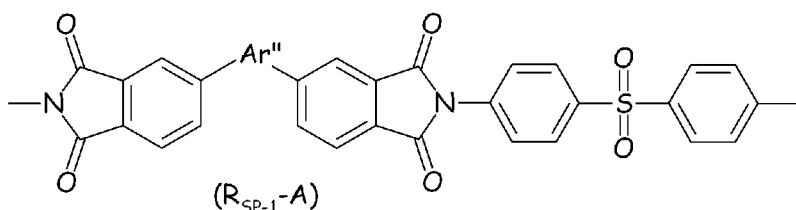
[0064] For the purpose of the invention, the expression “aromatic sulfone polymer (SP)” is intended to denote any polymer, at least 50 % wt of the recurring units thereof comprise at least one group of formula (SP) [recurring units (R_{SP})]:



Formula (SP)

[0065] The aromatic sulfone polymer (P) has a glass transition temperature of advantageously at least 150°C, preferably at least 160°C, more preferably at least 175°C.

[0066] In a first preferred embodiment of the invention, at least 50 % wt of the recurring units of aromatic sulfone polymer (SP) are recurring units (R_{SP-1}), in their imide form (R_{SP-1-A}) and/or amic acid forms [(R_{SP-1-B}) and (R_{SP-1-C})]:

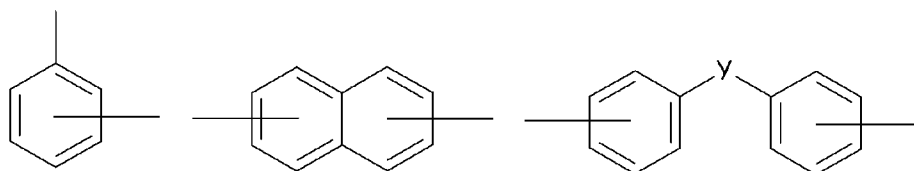


wherein :

- the \rightarrow denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged

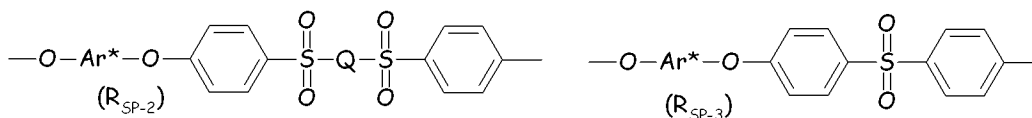
position;

- Ar'' is chosen among the following structures :



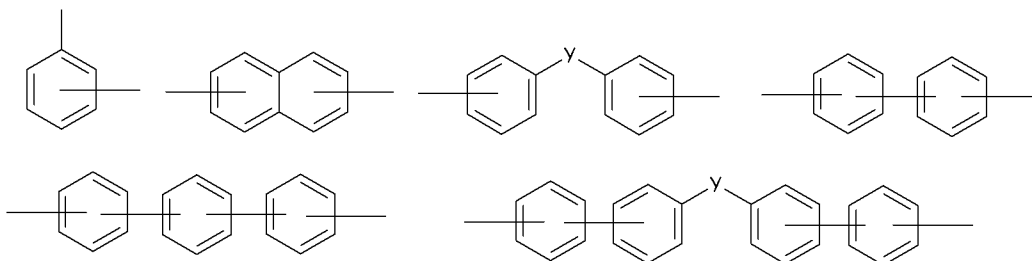
and corresponding optionally substituted structures, with Y being -O-, -C(O)-, -(CH₂)_n-, -C(CF₃)₂-, -(CF₂)_n-, with n being an integer from 1 to 5 and mixtures thereof.

[0067] In a second preferred embodiment of the invention, at least 50 % wt of the recurring units of aromatic sulfone polymer (SP) are recurring units (R_{SP-2}) and/or recurring units (R_{SP-3}) :



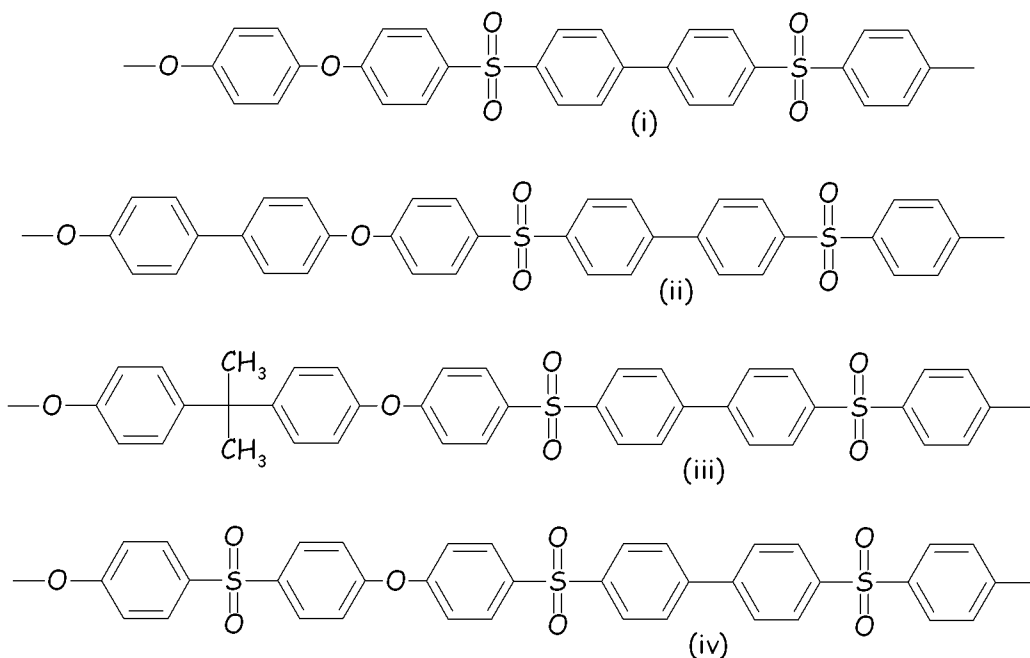
wherein :

- Q and Ar*, equal or different from each other and at each occurrence, are independently a divalent aromatic group; preferably Ar* and Q equal or different from each other and at each occurrence, are independently selected from the group consisting of the following structures :



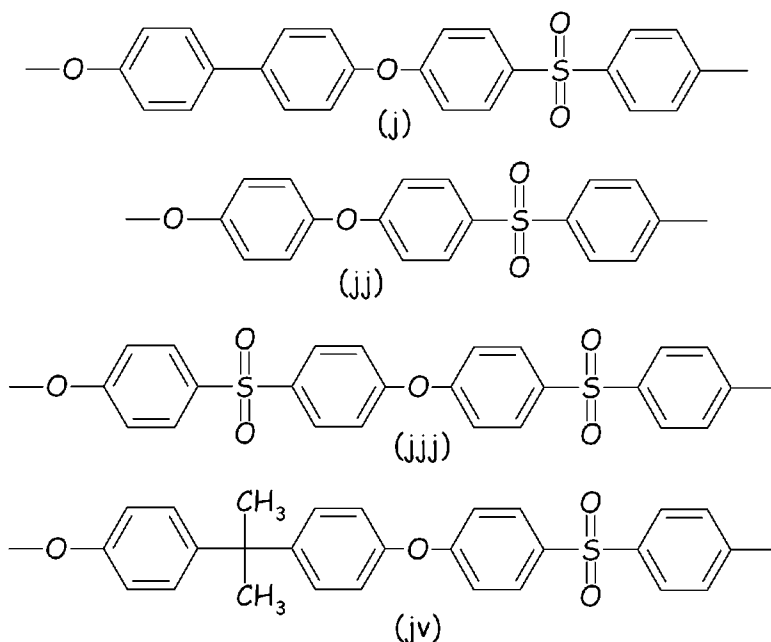
and corresponding optionally substituted structures, with Y being -O-, -CH=CH-, -C≡C-, -S-, -C(O)-, -(CH₂)_n-, -C(CF₃)₂-, -C(CH₃)₂-, -SO₂-, -(CF₂)_n-, with n being an integer from 1 to 5 and mixtures thereof; and mixtures thereof.

[0068] Recurring units (R_{SP-2}) are preferably chosen from :



and mixtures thereof.

[0069] Recurring units ($R_{\text{SP-3}}$) are preferably chosen from :



and mixtures thereof.

[0070] Aromatic sulfone polymer (SP) according to the second preferred embodiment of the invention comprises at least 50 % wt, preferably 70 % wt, more preferably 75 % wt of recurring units ($R_{\text{SP-2}}$) and/or ($R_{\text{SP-3}}$), still more preferably, it contains no recurring unit other than recurring units ($R_{\text{SP-2}}$) and/or ($R_{\text{SP-3}}$).

[0071] Good results were obtained with aromatic sulfone polymer (P) the

recurring units of which are recurring units (ii) (polybiphenyldisulfone, herein after), with aromatic sulfone polymer (P) the recurring units of which are recurring units (j) (polyphenylsulfone, hereinafter), with aromatic sulfone polymer (P) the recurring units of which are recurring units (jj) (polyetherethersulfone, hereinafter), with aromatic sulfone polymer (P) the recurring units of which are recurring units (jjj) and, optionally in addition, recurring units (jj) (polyethersulfone, hereinafter), and with aromatic sulfone polymer (P) the recurring units of which are recurring units (jv) (polysulfone, hereinafter).

- [0072] Polyphenylsulfone is notably available as RADEL[®] R PPSU from Solvay Advanced Polymers, L.L.C. Polysulfone is notably available as UDEL[®] PSF from Solvay Advanced Polymers, L.L.C. Polyethersulfone is notably available as RADEL[®] A PES from Solvay Advanced Polymers, L.L.C.
- [0073] Preferably, aromatic sulfone polymer (SP) is chosen among the group consisting of polybiphenyldisulfone, polysulfone, polyphenylsulfone, polyethersulfone, copolymers and mixtures thereof.
- [0074] Optionally, the polymer composition of the invention can further comprise fillers, lubricating agents, flow modifiers, heat stabilizer, anti-static agents, extenders, reinforcing agents, organic and/or inorganic pigments like TiO₂, carbon black, antioxidants, flame retardants, smoke-suppressing agents.
- [0075] Among flame retardants, mention can be made of PTFE; suitable PTFE are described notably in **WO 2007/065867** (SOLVAY) 14.06.2007 and **WO 2007/065880** (SOLVAY) 14.06.2007 .
- [0076] Additional flow modifiers can also be used in combination with polymer (F); among them mention can be notably made of fluoroelastomers and of thermoplastic tetrafluoroethylene (TFE) –perfluoroalkylvinylethers (PAVE) copolymers, in particular a TFE-perfluoromethylvinylether copolymer, like those commercially available under trade name HYFLON[®] from Solvay Solexis.
- [0077] The composition of the invention can advantageously comprise at least one filler chosen from reinforcing fillers, structural fibers and mixtures thereof. Structural fibers may include glass fiber, carbon or graphite fibers, and fibers formed of silicon carbide, alumina, titania, boron and the like,

and may include mixtures comprising two or more such fibers. Reinforcing fillers which can also be used in the composition of the invention include notably pigments, flake, spherical and fibrous particulate filler reinforcements and nucleating agents such as talc, mica, titanium dioxide, potassium titanate, silica, kaolin, chalk, alumina, mineral fillers, and the like. The reinforcing fillers and structural fibers can be used alone or in any combination.

[0078] Another aspect of the present invention concerns a process for manufacturing the polymer composition as above described, which comprises mixing :

- at least one polymer (P);
- at least one polymer (F).

[0079] Advantageously, the process of the invention comprises mixing by dry blending and/or melt compounding polymer (P) and polymer (F).

[0080] Preferably, polymer (P) and polymer (F) are mixed by melt compounding.

[0081] Advantageously, polymer (P) and polymer (F) are melt compounded in continuous or batch devices. Such devices are well-known to those skilled in the art.

[0082] Examples of suitable continuous devices to melt compound the polymer composition of the invention are notably screw extruders. Thus, polymer (P) and polymer (F) and, optionally, other ingredients, are advantageously fed in powder or granular form in an extruder and the composition is extruded into strands and the strands are chopped into pellets.

[0083] Optionally, fillers, lubricating agents, flow modifiers, heat stabilizer, anti-static agents, extenders, reinforcing agents, organic and/or inorganic pigments like TiO_2 , carbon black, antioxidants, flame retardants, smoke-suppressing agents may be added to the composition during the compounding step.

[0084] Preferably, polymer (P) and polymer (F) are melt compounded in a twin-screw extruder.

[0085] The composition can be further processed following standard methods for injection moulding, extrusion, thermoforming, machining, and blow moulding. Solution-based processing for coatings and membranes is also

possible. Finished articles comprising the composition as above described can undergo standard post-fabrication operations such as ultrasonic welding, adhesive bonding, and laser marking as well as heat staking, threading, and machining.

[0086] Another object of the invention is a shaped article comprising the polymer composition as above described.

[0087] Advantageously, the article is an injection moulded article, an extrusion moulded article, a shaped article, a coated article or a casted article. Preferably it is an extrusion moulded article, like notably a sheet or a film.

[0088] The articles according to the invention can be fabricated by processing the composition as above described following standard methods.

[0089] The invention will be now described in more details with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

[0090] **Preparative example 1: Preparation of the polymer (F) additive**

In a 1 litre glass flask, 600 g of GALDEN[®] HT230 perfluoropolyether solvent and 300 g of perfluoropolyether comprising peroxide moieties of formula: $X_O-O(CF_2CF_2O)_r(CF_2O)_s(O)_t-X_O'$ wherein X_O and X_O' are: $-CF_3$ (29%), $-CF_2Cl$ (13%), $-CF_2CF_2Cl$ (20%), $-COF$ (24%), $-CF_2COF$ (14%), with number average molecular weight = 5.8×10^4 , $r/s=1.25$ and $t/(r+s)=0.077$, corresponding to a PO [defined as g of active oxygen /100 g of perfluoropolyether peroxide] equal to 1.3, were introduced.

The reaction mixture was heated under stirring under nitrogen flow (1 NI h⁻¹) up to 190°C, temperature starting at which tetrafluoroethylene (TFE) was continuously fed (flow rate = 8.5 NI h⁻¹).

The mixture was maintained under stirring at 190°C for 1.5 hours, then brought to 200°C and maintained at this temperature for 1.5 hours and finally, heated at 210°C for one hour. After having fed TFE so as to achieve a molar ratio between TFE fed and peroxidic moieties initially present of 7, monomer feeding was stopped and temperature increased up to 230°C for 3 hours. The mixture was then cooled to room temperature to yield a homogeneous solution. Said solution was again heated at 180°C and treated with nitrogen saturated with water (10 NI h⁻¹) for 4 hours, then

with anhydrous nitrogen (10 NI h^{-1}) for 30 minutes and finally with fluorine (4 NI h^{-1}) for 7 hours. Solvent GALDEN[®] HT230 was removed under vacuum (10^{-1} mbar) until a maximum temperature of 230°C , yielding 330 g of a product which was characterized by ^{19}F -NMR analysis as complying with formula: $\text{Q-O-[A-B]}_z\text{-A-Q'}$ (I) wherein

Q, Q' are $-\text{CF}_3$ (70% mol), $-\text{CF}_2\text{Cl}$ and $-\text{CF}_2\text{CF}_2\text{Cl}$ (30% mol),

B is $-\text{[CF}_2\text{-CF}_2\text{]}_j$ wherein j has a number average value equal to 6.7;

A is $-\text{CF}_2\text{O-[(CF}_2\text{O)}_n(\text{CF}_2\text{CF}_2\text{O)}_m(\text{CF}_2\text{CF}_2\text{CF}_2\text{O)}_p(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O)}_q\text{)]-(CF}_2\text{)}_b$ with values of $m/n = 1.08$, $p/n = 0.014$, $q/n = 0.020$; $(p+q)/(p+q+n+m) = 0.016$, wherein $b = 0$ when A is linked to Q', $b = 1$ in all the other cases.

The percentage by weight of the perfluorocarbon segments B in the compound of formula (I) was found to be equal to 21.4%. The number average molecular weight of the polymer resulted equal to 6.4×10^4 , from which an average value of the index $z = 20$ was calculated.

The DSC analysis showed a T_g equal to -113°C . The analysis at DSC shows a melting ΔH of 3.1 J/g in the temperature range between 50 and 200°C . The obtained polymer was found to have by TGA analysis a loss by weight of 1 % at 305°C and of 2% at 362°C .

[0091] **General description of the compounding process:**

[0092] A dry blend of RADEL[®] R PPSU or UDEL[®] PSF with the desired amount of polymer (F) additive (or other comparative additives) was first prepared by tumble blending. The preblended mixture was then fed into a Berstorff 25 mm twin screw extruder. The barrel temperatures of the extruder were maintained at $300\text{-}350^{\circ}\text{C}$ to give an adequate melt temperature. The screw speed was typically set at 180 rpm. The melt was extruded through a single hole die and the polymer strands were cooled using a water bath prior to pelletization. Composition, physical and mechanical properties of the RADEL[®] - R- based and UDEL[®] -based blends are summarized in table 2 and 3, respectively.

[0093] **Capillary Rheology Test Method (viscosity):**

[0094] The viscosity of a melt was measured as a function of shear rate at several temperatures using an LCR-7000 Capillary Rheometer.

[0095]

Table 2

Run ⁽¹⁾		Ex. 2C	Ex. 3	Ex. 4	Ex. 5C	Ex. 6C	Ex. 7C
additive	type	-	Ex. 1	Ex. 1	PFA ⁽²⁾	MFA ⁽³⁾	FKM ⁽⁴⁾
	(%wt)	-	1 %	2 %	2 %	2 %	2 %
Physical and mechanical properties							
MFR ⁽⁵⁾	dg/min	17.5	18.4	18.8	18.1	18.2	18.0
VR ₄₀ ⁽⁶⁾		1.51	1.81	1.79	1.76	1.79	1.74
viscosity ⁽⁷⁾	Pa.s	887	700	672	683	706	693
T.S. _y ⁽⁸⁾	kpsi	10.9 ±0.1	10.7± 0.1	10.7±0. 1	10.8±0. 1	10.7±0. 1	10.5±0. 1
ε _y ⁽⁹⁾	%	7.8±0. 1	7.7±0 .1	7.7±0.1	7.6±0.3	7.7±0.2	7.7±0.1
T.S. _b ⁽¹⁰⁾	kpsi	9.4±0. 5	9.3±0 .2	8.8±0.3	10.4±0. 9	9.2±0.8	9.0±0.6
ε _b ⁽¹¹⁾	%	61±8	61±3	36±20	78±15	49±20	49±14
E ⁽¹²⁾	kpsi	318±2	315± 2	315±4	320±8	315±4	311±3
I.S. ⁽¹³⁾	ft.lb/in	2.26± 0.08	2.75± 0.23	2.27±0. 11	2.49±0. 13	2.68±0. 07	3.30±0. 29

[0096] (1) All compositions based on RADEL[®] R PPSU; (2) HYFLON[®] PFA P7010; (3) HYFLON[®] MFA 1041; (4) TECNOFLON[®] NM FKM; (5) Melt flow rate at 365°C, under a piston load of 5.0 kg; (6) ratio of melt viscosity after 40 min heating at 410°C at a shear rate of 46 s⁻¹ over melt viscosity after 10 minutes at 410°C at same shear rate (VR₄₀); (7) melt viscosity determined at a shear rate of 46 s⁻¹ after 10 min heating at 410°C; (8) Tensile strength at yield; (9) elongation at yield; (10) tensile strength at break; (11) elongation at break; (12) tensile modulus; (13) Izod Impact Strength measured on specimens with a notch of 0.003'.

[0097]

Table 3

Run ⁽¹⁴⁾		Ex. 8C	Ex. 9
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additive	type	-	Ex. 1
	(%wt)	-	2 %
Physical and mechanical properties			
MFR ⁽⁵⁾	dg/min	6.9	6.9
VR ₄₀ ⁽⁶⁾		1.18	1.10
viscosity ⁽⁷⁾)	Pa.s	427	439
T.S. _y ⁽⁸⁾	kpsi	10.8±0.1	10.9±0.1
ε _y ⁽⁹⁾	%	5.7±0.1	5.6±0.1
T.S. _b ⁽¹⁰⁾	kpsi	7.3±0.1	7.8±0.3
ε _b ⁽¹¹⁾	%	33±16	61±17
E ⁽¹²⁾	kpsi	353±2	366±5
I.S. ⁽¹⁵⁾	ft.lb/in	1.058±0.04	1.24±0.06

[0098] (14) All compositions based on UDEL[®] PSF; (5)-(12): as in table 1; (15) Izod Impact Strength measured on specimens with a notch of 0.001'.

[0099] **General description of Sheet Extrusion Equipment:**

[0100] After compounding the blended polymers were extruded through a sheet die to assess their utility in profile extrusion. The materials were extruded using a Sterling single screw extruder (2.5 inch screw diameter with 25:1 Length/Diameter ratio) through a 14 inch wide "T"- type die. The sheet (thickness ~ 4 mm) was run through a 3 roll cooling stack with hot oil temperature controlled rolls prior to being cut to a desired length. The thickness of the sheet was controlled by adjusting the height of the die. Results obtained for RADEL[®] R PPSU-based compositions comprising additive from Ex. 1 are summarized in table 4.

[0101]

Table 4

Run	Additive	Extruder	Extruder power	Pressure	Calendering Roll
	(% wt)	(rpm)	(Amps)	(psi)	(rpm)
Ex. 10C	none	~ 25	10	1540-1710	21.5
Ex. 11	2 %	~ 25	7.5	570-850	19

Ex. 12	2 %	~ 180	8.5	500-700	19
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[0102] Data embedded here above well demonstrate a dramatic improvement in processability when adding the polymer (F) additive to RADEL[®] R material.

[0103] Same test was repeated but targeting thinner sheets (thickness ~ 2 mm). Results obtained for RADEL[®] R PPSU-based compositions comprising additive from Ex. 1 are summarized in table 5.

[0104]

Table 5

Run	Additive	Extruder	Extruder power	Pressure
	(% wt)	(rpm)	(Amps)	(psi)
Ex. 13C	none	~ 40	> 20(*)	> 2000(*)
Ex. 14	1 %	~ 40	10	500-600
Ex. 15	0.5 %	~ 40	10	500-600

[0105] (*) The pressure and extruder power increased steadily until the maximum pressure limit was reached after about 5 minutes.

[0106] These data have demonstrated that while it is not possible to manufacture RADEL[®] R PPSU sheets of above mentioned thickness in these conditions without the use of an additive, as little as 0.5 % wt of polymer (F) enables achievement of outstanding processability.

[0107] **Spiral Flow Description**

[0108] Spiral flow is a technique commonly used to assess the rheology of injection moulding materials. According to this technique, a molten sample of blends as above described was injected at a fixed pressure into cavity of fixed cross section that radiated outward in a spiral direction from a central injection point. The length that the polymer melt flowed around the spiral prior to solidification gave an empirical measure of the rheological properties of the material. We used a Toyo 50 ton injection moulding pressure to generate data summarized in table 6. The equipment was setup to deliver pressures of 10000 or 25000 psi into a spiral mould of 3/16 inch by 1/8 inch cross section.

[0109]

Table 5

Run	Additive		Spiral flow length (inches)	
	type	(%wt)	At 10 kpsi	At 25 kpsi
Ex. 16C	none		4.9	12.1
Ex. 17	Ex. 1	1 %	5.6	12.1
Ex. 18	Ex. 1	2 %	5.8	12.8
Ex. 19C	MFA	2 %	5.8	12.8
Ex. 20C	PFA	2 %	5.8	12.5
Ex. 21C	FKM	2 %	5.4	12.8

[0110] Data provided here above show that the material containing polymer (F) added to RADEL® R PPSU flows better under injection molding conditions, because a longer flow length is achieved before the polymer solidifies in the spiral mould.

Claims

1. A polymer composition comprising:

- at least one polycondensation polymer having a heat deflection temperature (HDT) of above 80°C under a load of 1.82 MPa when measured according to ASTM D648 [polymer (P)];

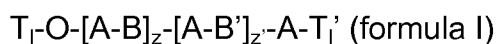
- at least one perfluoropolyether block copolymer [polymer (F)] comprising:

A) one or more (per)fluoropolyoxyalkylene segment (chain R_f), that is to say a segment comprising recurring units having at least one catenary ether bond and at least one fluorocarbon moiety, and

B) one or more polyalkylene segment (chain R_a) comprising recurring units of formula: $-(CR_1R_2-CR_3R_4)-$

wherein R_1 , R_2 , R_3 , R_4 , equal to or different from each other, are selected from the group consisting of H, halogens (preferably F, Cl); C_1 - C_6 (hydro)carbon groups, optionally containing fluorine or other heteroatoms, preferably perfluoroalkyl or (per)fluorooxyalkyl.

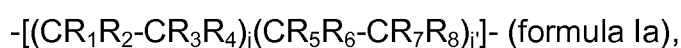
2. The polymer composition of claim 1, wherein polymer (F) complies with formula:



wherein:

- $A = -(X)_a-O-A'-(X')_b-$, wherein A' is a chain comprising recurring units (R_1), said recurring units having general formula: $-(CF_2)_k-CFZ-O-$, wherein k is an integer of from 0 to 3 and Z is selected between a fluorine atom and a C_1 - C_6 perfluoro(oxy)alkyl group; X , X' , equal to or different from each other, are selected from $-CF_2-$, $-CF_2CF_2-$, $-CF(CF_3)-$; a , b , equal to or different from each other, are integers equal to 0 or 1, with the proviso that the block A linked to the end group T_1-O- has $a = 1$ and the block A linked to the end group T_1' has $b = 0$;

- B is a segment of recurring units derived from one or more olefins having formula:



wherein: j is an integer from 1 to 100, j' is an integer from 0 to 100 with the proviso that $(j+j')$ is higher than 2 and lower than 100; R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , equal to or different from each other, are selected from halogen ; H; C_1 - C_6

groups, optionally containing F or other heteroatoms, preferably perfluoroalkyl or (per)fluorooxyalkyl, said substituents R_1 - R_8 optionally containing one or more functional groups;

- z is an integer higher than or equal to 2; z' is ≥ 0 ; z, z' are such that the number average molecular weight of the polymer (F) of formula (I) is in the range 500-500,000;

- B' is a segment otherwise complying with formula (Ia), but having at least one of the substituents R_1 to R_8 different than those in block B;

- T_1 and T_1' , equal to or different from each other, are selected from H, halogen, C_{1-3} (per)fluoroalkyls, C_{1-6} alkyls and C_1 - C_{30} functional end groups comprising heteroatoms chosen among O, S, N

3. The polymer composition of claim 2, wherein polymer (F) complies with formula:

$T_1-O-[A-B]_z-A-T_1'$ (formula I)

wherein:

- $A = -(X)_a-O-A'-(X')_{b-}$, wherein X, a and b have the meanings above defined and A' is a chain R_f of formula:

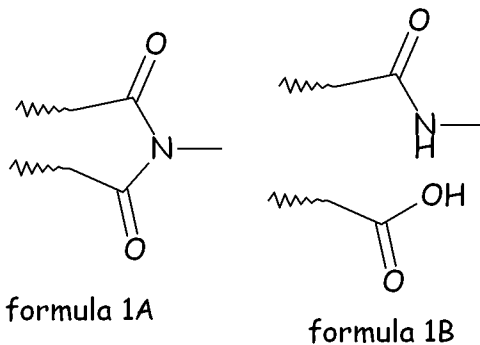
$-(CF_2CF_2O)_{a+}(CF_2O)_{b+}(CF_2(CF_2)_{z+}CF_2O)_{c+-}$,

wherein: z^+ is 1 or 2; a^+, b^+, c^+ are integers ≥ 0 ;

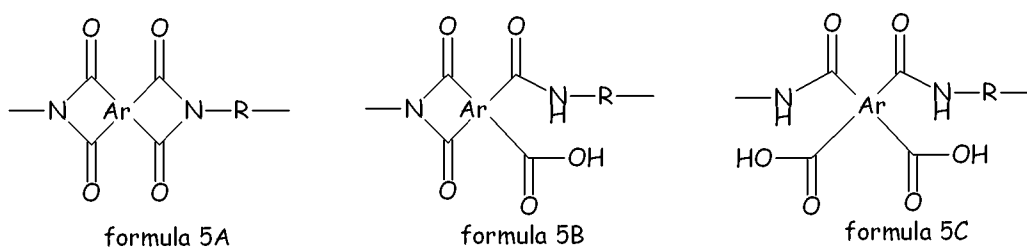
- B is a segment of formula $-[(CF_2-CF_2)_{j+}]_-$ wherein: j^+ is an integer from 2 to 100;

- T_1 and T_1' , equal to or different from each other, are selected from the group consisting of: -H; halogen such as -F and -Cl; C_1 - C_3 perhalogenated alkyl group, such as $-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-CF_2CF_2Cl$.

4. The polymer composition of anyone of claims 1 to 3, wherein polymer (P) is selected among aromatic polyimides (PI), polyaryletherketones (PAEK), , liquid crystal polymers (LCP), and aromatic sulfone polymers (SP).
5. The polymer composition of claim 4, wherein polymer (P) is an aromatic polyimide (PI) comprising recurring units, wherein more than 50 wt. % of said recurring units comprising at least one aromatic ring and at least one imide group, as such (formula 1A) or in its amic acid form (formula 1B) [recurring units (R_{PI})]:

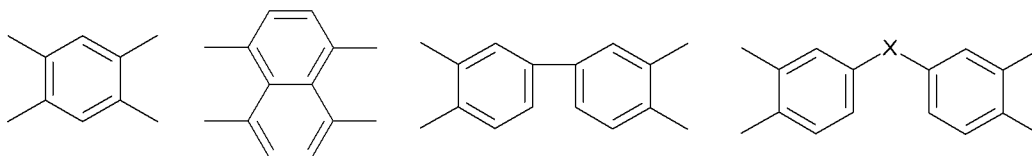


and wherein said recurring units (R_{PI}) are selected from formulae 5A to 5C :



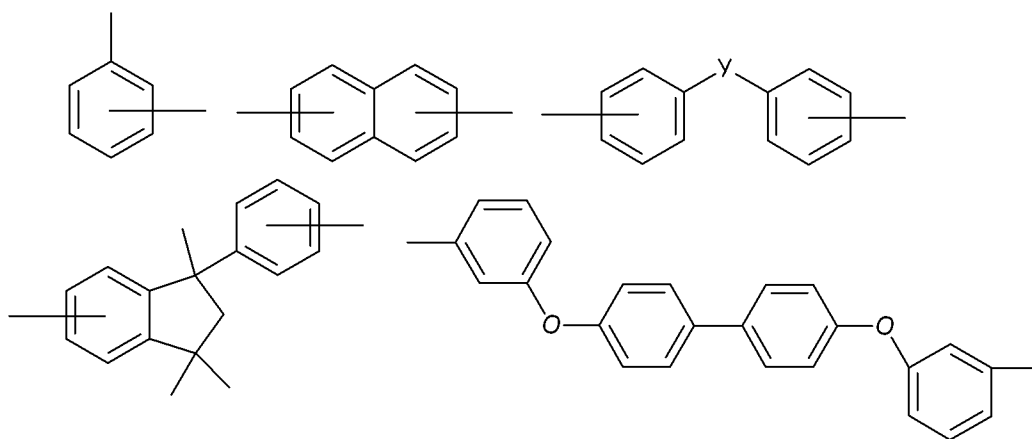
wherein :

Ar represents an aromatic tetravalent group; typically Ar is selected from the group consisting of following structures:



and corresponding optionally substituted structures, with X being $-O-$, $-C(O)-$, $-CH_2-$, $-C(CF_3)_2-$, $-(CF_2)_n-$, with n being an integer from 1 to 5;

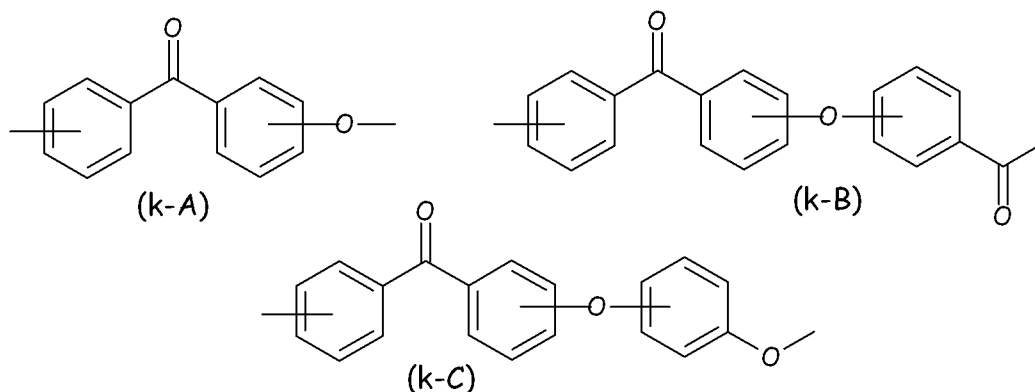
R represents an aromatic divalent group; typically R is selected from the group consisting of following structures:



and corresponding optionally substituted structures, with Y being $-O-$, $-S-$, $-SO$

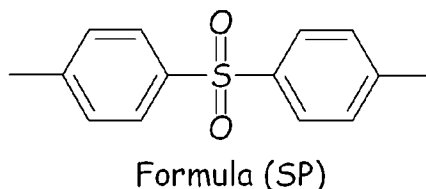
2^- , $-\text{CH}_2^-$, $-\text{C}(\text{O})^-$, $-\text{C}(\text{CF}_3)_2^-$, $-(\text{CF}_2)_n$, n being an integer from 0 to 5.

6. The polymer composition of claim 4, wherein polymer (P) is a polyaryletherketone (PAEK) polymer, comprising recurring units (R_{PAEK}), wherein more than 50 wt. % of said recurring units are recurring units (k-A), (k-B) and/or (k-C) :

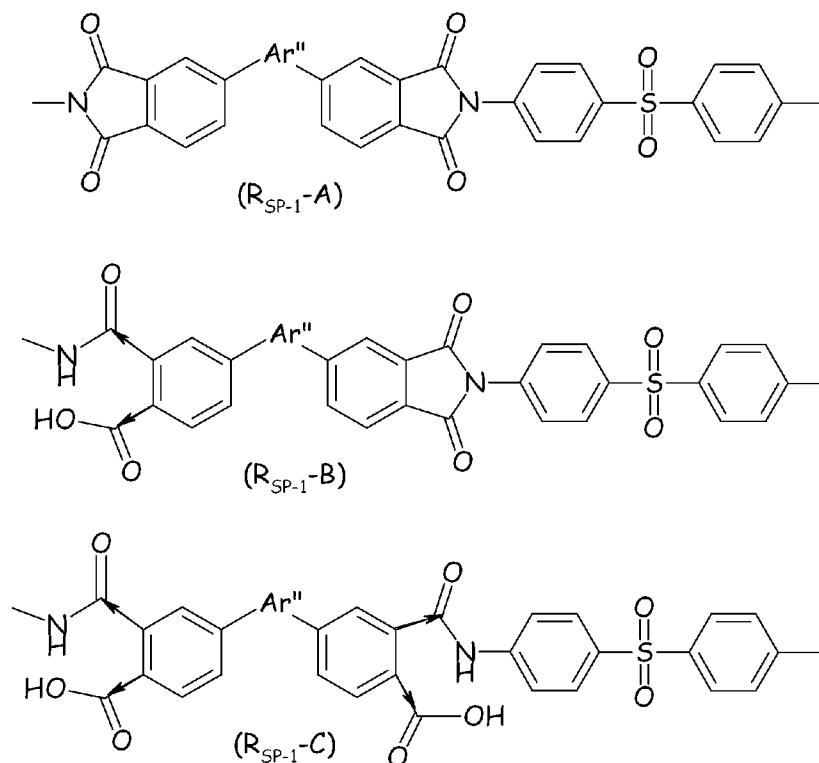


wherein the attachment of the ketone and/or ether groups to the aromatic ring as shown in (k-A), (k-B) and (k-B) will be understood to represent, independently at each occurrence, each of the possible ortho, meta and para configurations.

7. The polymer composition of claim 4, wherein polymer (P) is an aromatic sulfone polymer (SP), wherein at least 50 % wt of the recurring units thereof comprise at least one group of formula (SP) [recurring units (R_{SP})]:



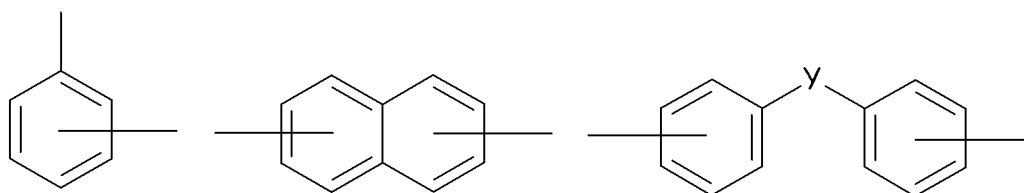
8. The polymer composition of claim 7, wherein at least 50 % wt of the recurring units of aromatic sulfone polymer (SP) are recurring units ($R_{\text{SP-1}}$), in their imide form ($R_{\text{SP-1-A}}$) and/or amic acid forms [$(R_{\text{SP-1-B}}$) and ($R_{\text{SP-1-C}}$)]:



wherein :

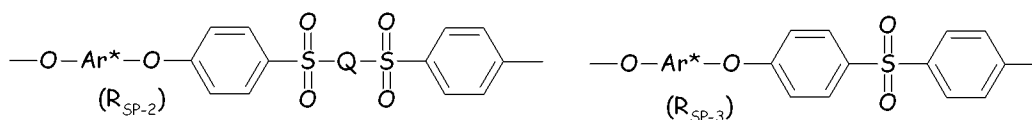
the \rightarrow denotes isomerism so that in any recurring unit the groups to which the arrows point may exist as shown or in an interchanged position;

Ar'' is chosen among the following structures :



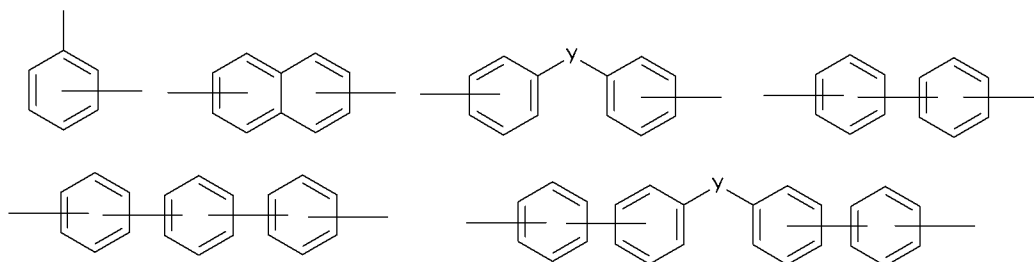
and corresponding optionally substituted structures, with Y being $-O-$, $-C(O)-$, $-(CH_2)_n-$, $-C(CF_3)_2-$, $-(CF_2)_n-$, with n being an integer from 1 to 5 and mixtures thereof.

9. The polymer composition of claim 7, wherein at least 50 % wt of the recurring units of aromatic sulfone polymer (SP) are recurring units (R_{SP-2}) and/or recurring units (R_{SP-3}) :



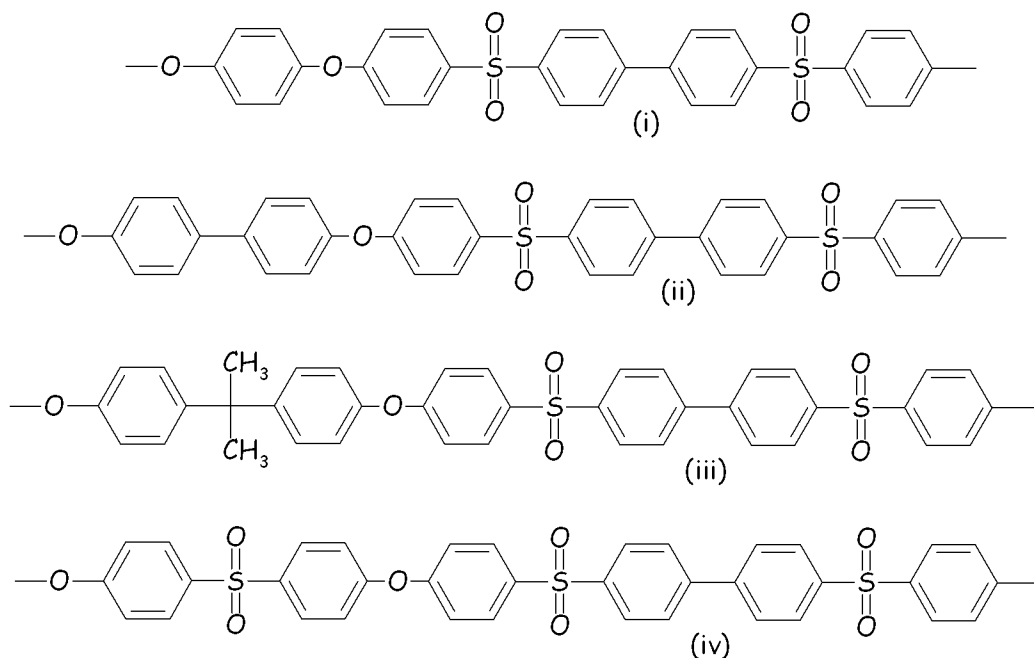
wherein :

- Q and Ar*, equal or different from each other and at each occurrence, are independently a divalent aromatic group; preferably Ar* and Q equal or different from each other and at each occurrence, are independently selected from the group consisting of the following structures :

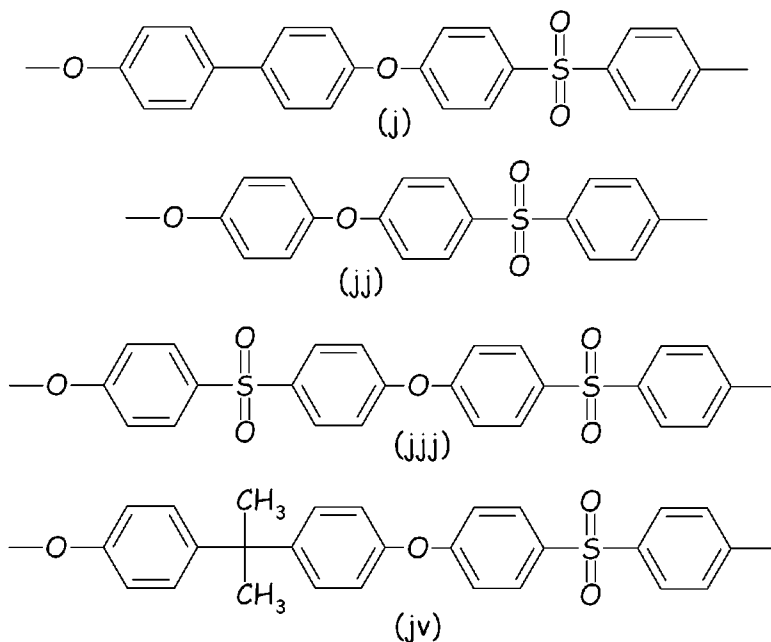


and corresponding optionally substituted structures, with Y being -O-, -CH=CH-, -C≡C-, -S-, -C(O)-, -(CH₂)_n-, -C(CF₃)₂-, -C(CH₃)₂-, -SO₂-, -(CF₂)_n-, with n being an integer from 1 to 5 and mixtures thereof; and mixtures thereof.

10. The polymer composition of claim 9, wherein recurring units (R_{SP-2}) are chosen from :



and mixtures thereof, and wherein recurring units (R_{SP-3}) are chosen from :



and mixtures thereof.

11. A process for manufacturing the polymer composition according to anyone of claim 1 to 10, which comprises mixing :
 - at least one polymer (P);
 - at least one polymer (F).
12. The process of claim 11, wherein polymer (P) and polymer (F) are mixed by melt compounding.
13. A shaped article comprising the polymer composition according to anyone of claim 1 to 10.
14. The article of claim 13, selected among an injection moulded article, an extrusion moulded article, a shaped article, a coated article or a casted article.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/052199

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G65/323 C08G65/40 C08L71/02 C08L81/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08L

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.
Y	WO 2008/116939 A2 (SOLVAY ADVANCED POLYMERS LLC [US]; EL-HIBRI MOHAMMAD JAMAL [US]; RYAN) 2 October 2008 (2008-10-02) tables 1,2 page 30, line 33 - page 31, line 3 claims	1-14
Y	WO 2008/065163 A1 (SOLVAY SOLEXIS SPA [IT]; AVATANEIO MARCO [IT]; GUARDA PIER ANTONIO [IT]) 5 June 2008 (2008-06-05) cited in the application claim 29 examples	1-14

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

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

14 April 2010

Date of mailing of the international search report

21/04/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/052199

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008116939 A2	02-10-2008	CN 101679741 A	24-03-2010
		EP 2142599 A1	13-01-2010
		EP 2142600 A2	13-01-2010
		WO 2008129059 A1	30-10-2008
WO 2008065163 A1	05-06-2008	EP 2089443 A1	19-08-2009