



(51) International Patent Classification:

C08G 65/40 (2006.01)

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/EP2017/077131

(22) International Filing Date:

24 October 2017 (24.10.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/420,751 11 November 2016 (11.11.2016) US

17164457.8 03 April 2017 (03.04.2017) EP

(71) Applicant: SOLVAY SPECIALTY POLYMERS USA, LLC [US/US]; 4500 McGinnis Ferry Road, ALPHARETTA, Georgia 30005-3914 (US).

(72) Inventors: LOUIS, Chantal; 4995 Hastings Terrace, ALPHARETTA, Georgia 30005 (US). THOMAS, David B.; 906 River Vista Dr., Atlanta, Georgia 30339 (US). EL-HIBRI, Mohammad Jamal; 320 Trowbridge Walk, Atlanta, Georgia 30350 (US). HAMMONDS, Ryan; 2600 E Madison Dr., Atlanta, Georgia 30360 (US).

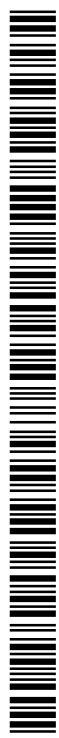
(74) Agent: BENVENUTI, Federica; Rue de Ransbeek, 310, 1120 BRUXELLES (BE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: POLYARYLEETHER KETONE COPOLYMER

(57) Abstract: The invention pertains to certain copolymers (PEDEK/PEEK), comprising a majority of " PEDEK"-type recurring units, which, thanks to the predominance of PEDEK-type units, their structural homogeneity and regularity, and absence of chlorinated end groups, possess a suitable molecular structure and crystallization behaviour so as to deliver improved mechanical properties and outstanding chemical resistance, and which are useful in numerous fields of endeavours, including notably in the oil&gas industry, and more specifically for the manufacture of parts used in oil and gas extraction systems.



WO 2018/086873 A1

Polyarylether ketone copolymer

Cross-Reference to Related Applications

[0001] This application claims priority to U.S. Provisional Application No. 62/420,751 filed November 11, 2016, and European Application No. EP 17164457.8, filed April 3, 2017, which are incorporated herein by reference in their entireties.

Technical Field

[0002] This invention pertains to novel polyarylether ketone copolymers having improved thermal and chemical resistance, to a method of making the same, and to the use thereof in oil and gas exploration and extraction.

Background Art

[0003] Polyaryl ether ketone materials are known as high performance plastics with high thermal resistance, which are used for a number of industrial applications where resistance to extreme conditions is required.

[0004] In particular, oil&gas exploration requires materials able to resist high temperature and pressure, and capable of maintaining the required performances upon prolonged exposure in the said extreme pressure and temperature conditions to aggressive chemicals present in downhole environment, including notably salt water, hydrocarbons, CO₂, H₂S, etc.

[0005] In this area, hence polyether ether ketone (PEEK), having characterizing recurring unit of formula -O-Ph-O-Ph-CO-Ph-, with Ph = para-phenylene, has found broad utility, thanks to its crystalline melting point of about 335°C enabling acceptable processing, although its glass transition temperature of about 148°C is somewhat limiting its ability to withstand continuous operations at temperatures of 150°C or beyond.

[0006] On the other side, polyaryl ether ketones (PAEKs) have been proposed, targeting increased glass transition temperatures, such as PEK (having characterizing recurring unit of formula -O-Ph-CO-Ph-), PEKK (having

characterizing recurring unit of formula -O-Ph-CO-Ph-CO-Ph-), and PEKEKK (having characterizing recurring unit of formula -O-Ph-CO-Ph-O-Ph-CO-Ph-CO-Ph-). All these PAEKs, while possessing increased T_g, are nevertheless known as more sensitive to chemicals in aggressive environments, e.g. they possess lower steam resistance, and may suffer from excessively high melting temperatures, associated hence to processing hurdles.

- [0007] In this area, copolymers comprising a mixture of units -O-Ph-O-Ph-CO-Ph- (I) and -O-Ph-Ph-O-Ph-CO-Ph- (II) have been proposed, as an attempt to provide materials possessing increased T_g over PEEK, but yet similar or even lower crystalline melting point.
- [0008] Notably, **EP 0184458 A** (ICI PLC) 6/11/1986 is directed to aromatic polyetherketones containing the repeat units: -O-Ph-O-Ph-CO-Ph- (I) and -O-Ph-Ph-O-Ph-CO-Ph- (II) in the relative molar proportions I:II of 95:5 to 60:40, preferably 90:10 to 60:40, which are disclosed as possessing similar properties as known PAEKs materials (e.g. PEK or PEEK), but enabling processing at lower temperature. A copolymer having molar proportions I:II of 50/50 was disclosed as a non-working embodiment, failing to perform adequately to the aim pursued therein.
- [0009] Similarly, **EP 0225750 A** (ICI PLC) 6/16/1987 pertains to fibrous reinforced compositions including a polyetherketone containing the repeat units: -O-Ph-O-Ph-CO-Ph- (I) and -O-Ph-Ph-O-Ph-CO-Ph- (II) in the relative molar proportions I:II of 95:5 to 60:40, preferably 95:5 to 70:30; impact properties of composite laminates processed from the melt were shown to be sensitive to the cooling conditions.
- [0010] Yet, **WO 2016/016643** (VICTREX MANUFACTURING LIMITED) 2/4/2016 discloses a polymeric material possessing mechanical and chemical resistance, notably high fracture toughness and high crystallinity, obtained by blending (A) a polyetherketone containing the repeat units: -O-Ph-O-Ph-CO-Ph- (I) and -O-Ph-Ph-O-Ph-CO-Ph- (II) in the relative molar proportions I:II of 95:5 to 50:50, preferably 95:5 to 60:40, more preferably 95:5 to 65:35; and possessing a melting point of less than 330°C; with (B) a polyarylether ketone material which can be notably PEEK or PEK.

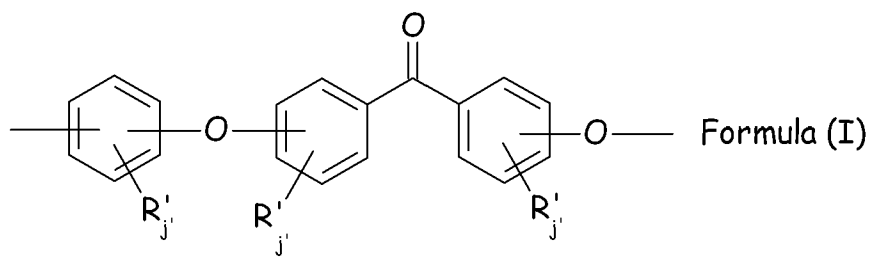
- [0011] Still, **WO 2016/042492** (GHARDA CHEMICALS LIMITED) 3/24/2016 discloses notably certain polyarylether ketones manufactured from 4,4'-difluorobenzophenone and a mixture of biphenol and hydroquinone, in molar ratios 95:5 to 5:95, as well as copolymers of PEK and PEDEK, including units of formula $-\text{Ph}-\text{CO}-\text{Ph}-\text{O}-$ and units of formula $-\text{Ph}-\text{Ph}-\text{O}-\text{Ph}-\text{CO}-\text{Ph}-\text{O}-$, in variable molar ratios, as random or block copolymers. Only these latter copolymers are actually exemplified, possessing properties similar to PEK, i.e. affected by an unfavourable ketone/ether molar ratio.
- [0012] As a whole, hence, in the past, copolymers containing a majority of repeat units $-\text{O}-\text{Ph}-\text{O}-\text{Ph}-\text{CO}-\text{Ph}-$ (I) and a minority of units $-\text{O}-\text{Ph}-\text{Ph}-\text{O}-\text{Ph}-\text{CO}-\text{Ph}-$ (II) were generally dwelt on, and recommended for use either alone or in admixture with other PAEKs.
- [0013] An isolated disclosure of a copolymer $-\text{O}-\text{Ph}-\text{O}-\text{Ph}-\text{CO}-\text{Ph}-$ (I) and $-\text{O}-\text{Ph}-\text{Ph}-\text{O}-\text{Ph}-\text{CO}-\text{Ph}-$ (II) with a molar ratio I:II of 25:75 can be nevertheless found in **US 4766197** (AMOCO CORPORATION) 8/23/1988. This document describes in its example 3 a copolymer, as above detailed, which is manufactured through nucleophilic polycondensation reacting 4,4'-difluorobenzophenone, hydroquinone and biphenol in the presence of a mixture of sodium and potassium carbonate ($\text{Na/K} \sim 20 \text{ mol/mol}$), the entire amount of which was added at the beginning of the reaction, and termination by end-capping with 4,4'-dichlorodiphenylsulfone. Further investigation carried out by the Applicant have shown that this manufacturing method, including use of carbonates at Na/K ratio of about 20, i.e. including a significant amount of more reactive K_2CO_3 , and termination through the addition of a spurious dichlorinated monomer, is such to increase probability of side reactions and generate end groups having organic chlorine bound, all structural parameters detrimentally affecting crystallization ability of the resulting polymer. Indeed, reaction chemistry and/or modifying additives have been found to significantly affect regularity of the obtained polymer structure, so that its mechanical performance were found to be poor.

[0014] There is hence a continuous quest in the art for polyaryl ether ketone polymers possessing an advantageous combination of thermal rating/thermal performances and chemical resistance, while maintaining outstanding mechanical performances, so as to provide materials suitable for being used in extremely demanding application, such as notably oil and gas exploration and extraction.

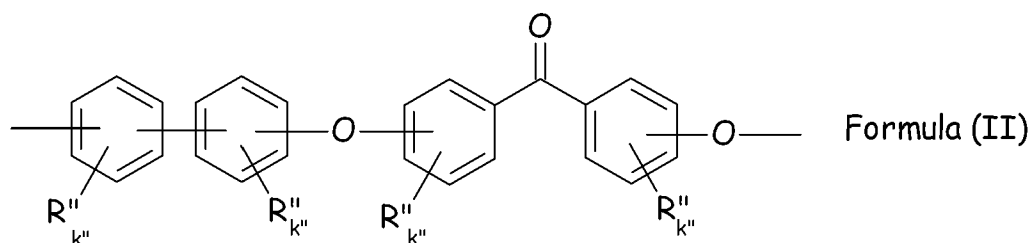
Summary of invention

[0015] It is hence a first object of the present invention a polyaryl ether ketone copolymer [copolymer (PEDEK-PEEK)] comprising:

- recurring units (R_{PEEK}) of formula (I):



- recurring units (R_{PEDEK}) of formula (II):



wherein in above formulae (I) and (II), each of R' and R'' , equal to or different from each other, is independently selected at each occurrence from a C_1 - C_{12} group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of j' and k'' , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4;

wherein the said recurring units are comprised in a molar ratio (R_{PEEK}):(R_{PEDEK}) of 45:55 to 15:85, and

wherein the said copolymer (PEDEK/PEEK):

(j) comprises an amount of chemically bound chlorine of less than

2.0 µeq/g, as determined by microcoulometry, and

(jj) possesses a narrow molecular weight distribution such that the following inequality is satisfied:

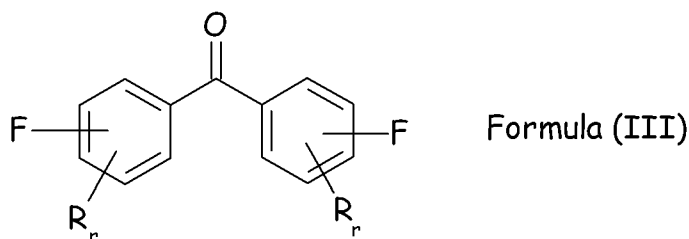
$$MV \left(\frac{\text{kN}}{\text{m}^2} \right) \leq 6.62 \cdot \left[RV \left(\frac{\text{dl}}{\text{g}} \right) \right]^{0.20}$$

Math. 1

wherein:

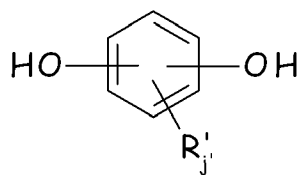
- MV is the melt viscosity measured pursuant to ASTM D3835 standard at 410°C and at a shear rate of 46.3 sec⁻¹, using a conical die having a diameter of 1.016 mm a length of 20.32 mm and a cone angle of 120°C and expressed in kN/m²; and
- RV is the reduced viscosity measured pursuant to ASTM D2857 standard at 25°C on 1.0 wt/vol % solution in concentrated H₂SO₄ (96 wt%) and expressed in dl/g.

[0016] Another object of the present invention is a method of making a copolymer (PEDEK/PEEK), as above detailed, comprising reacting at least one difluoro-derivative of formula (III):

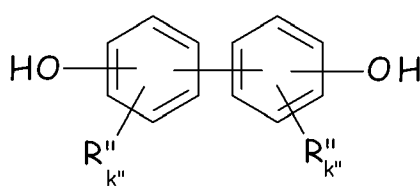


with a mixture of di-

hydroxyderivatives of formulae (IV) and (V):



Formula (IV)



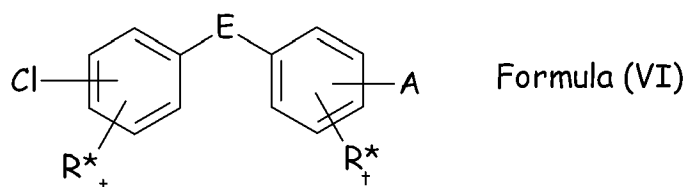
Formula (V)

in a molar ratio

(IV):(V) of 45:55 to 15:85,

wherein in above formulae (III), (IV) and (V), each of R, R' and R'', equal to or different from each other, is independently selected at each occurrence from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and

phosphonate groups; amine and quaternary ammonium groups; each of r , j' and k'' , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, in a polar organic solvent in the presence of a mixture of Na_2CO_3 and K_2CO_3 , in a molar ratio Na/K of more than 45 mol/mol, and wherein the method possibly include adding a step of adding a chlorinated compound of formula (VI):



wherein $-E-$ is a sulfone group of formula $-\text{SO}_2-$ or a ketone group of formula $-\text{C}(\text{O})-$, A is selected from Cl, F and H, each of R^* , equal to or different from each other, is independently selected at each occurrence from a C_1 - C_{12} group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of t , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, with the proviso that if said chlorinated compound of formula (IV) is added, its amount is of no more than 1 % moles with respect to the total molar amount of monomers of formula (III), (IV) and (V).

- [0017] The invention further notably pertains to the a method of making parts included in devices used for oil & gas recovery, including moulding those parts from the copolymers (PEDEK/PEEK) as above detailed.
- [0018] The Applicant has found that the method, as above detailed, is effective in delivering copolymers (PEDEK/PEEK), as above detailed, comprising a majority of "PEDEK"-type recurring units, which, thanks to the predominance of PEDEK-type units, their structural homogeneity and regularity, and absence of chlorinated end groups, possess a suitable molecular structure and crystallization behaviour so as to deliver improved mechanical properties and outstanding chemical resistance.

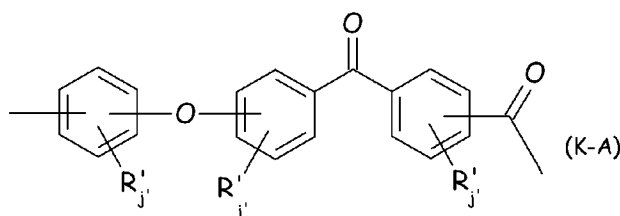
Brief description of drawings

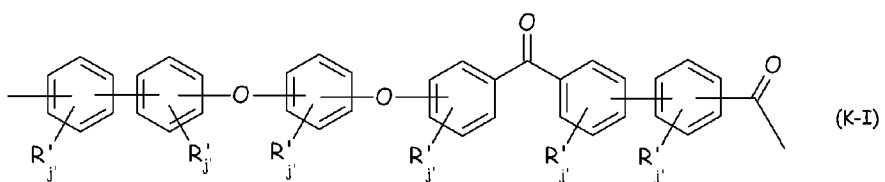
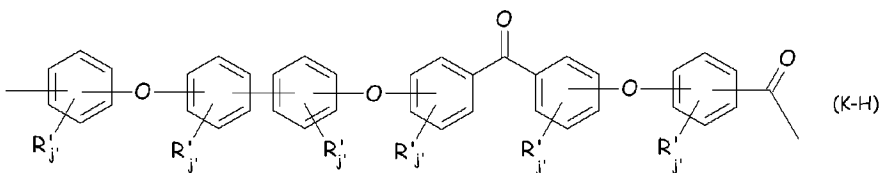
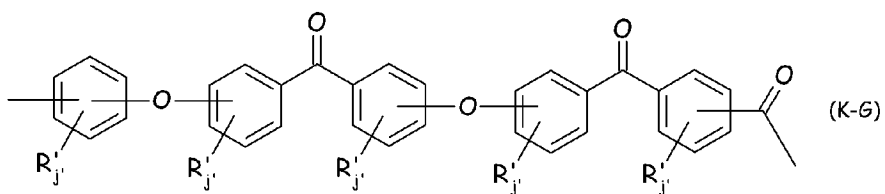
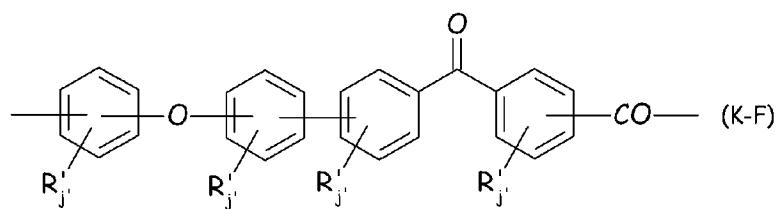
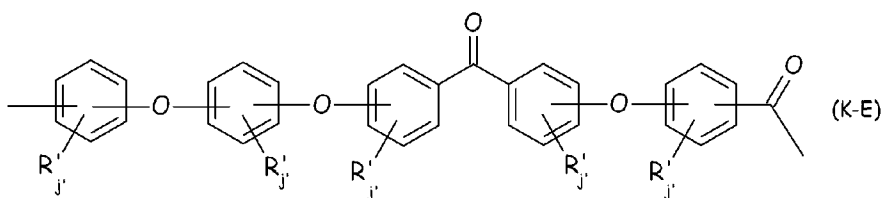
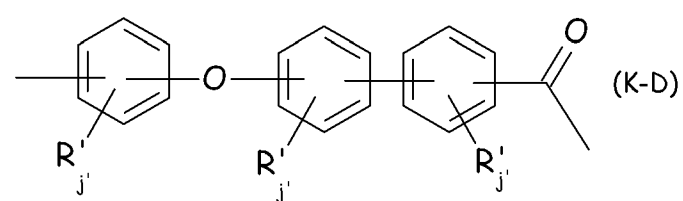
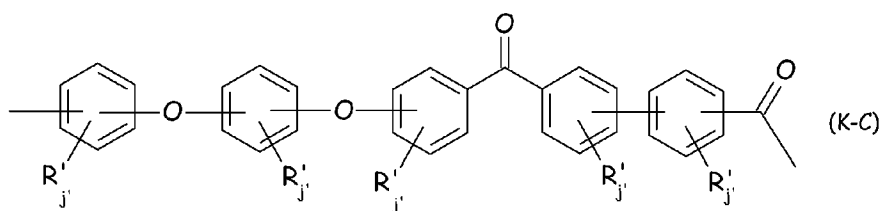
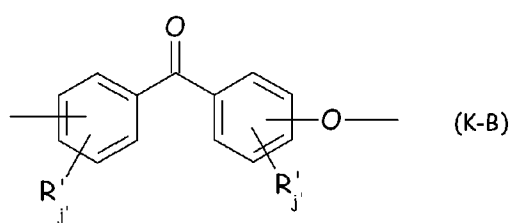
- [0019] Figure 1 schematically depicts a drilling rig equipment.
- [0020] Figure 2 is a plot of storage modulus (G' , in Pa) versus temperature ($^{\circ}\text{C}$), as determined by DMTA analysis, for copolymers (PEDEK/PEEK) of the present invention (dotted lines), and reference PEEK, PEK and PEKK materials (solid lines).

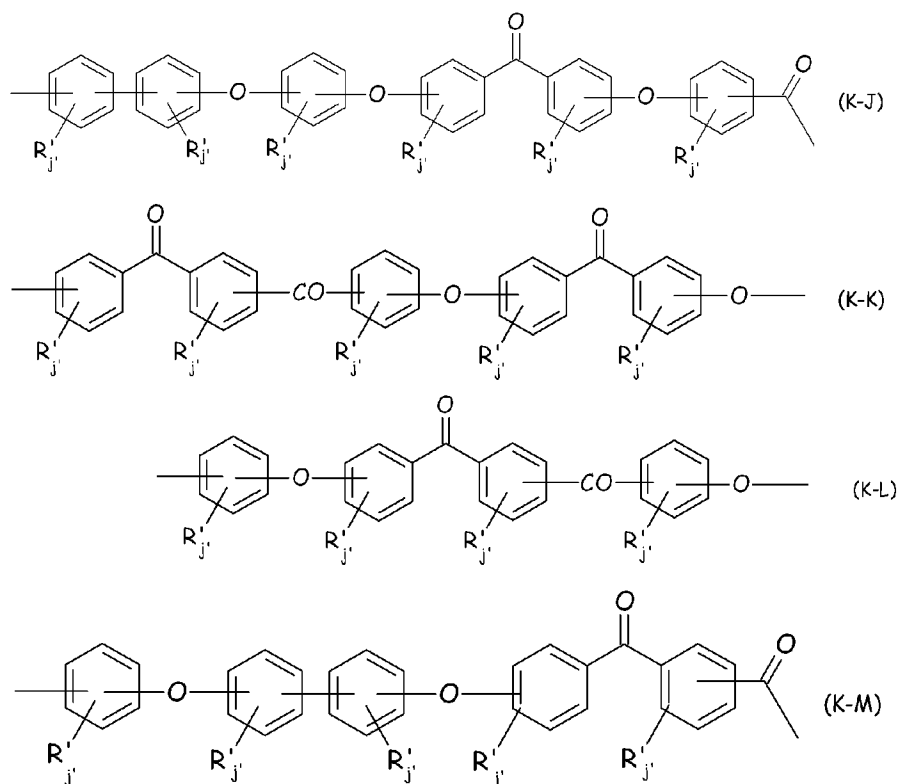
Description of embodiments

[0021] The copolymer (PEDEK/PEEK)

- [0022] The copolymer (PEDEK/PEEK) comprises recurring units (R_{PEEK}) and (R_{PEDEK}) as above detailed in molar ratio (R_{PEEK}):(R_{PEDEK}) of 45:55 to 15:85, preferably of 44:56 to 16:84, more preferably of 43:57 to 17:83, and even more preferably of 42:58 to 18:82. Copolymers (PEDEK/PEEK) which have been found particularly advantageous are those comprising recurring units (R_{PEEK}) and (R_{PEDEK}) as above detailed in molar ratio of 40:60 to 20:80.
- [0023] The copolymer (PEDEK/PEEK) of the present invention may additionally comprise recurring units (R_{PAEK}) different from recurring units (R_{PEEK}) and (R_{PEDEK}), as above detailed. In such case, the amount of recurring units (R_{PAEK}) is generally comprised between 0 and 5 % moles, with respect to the total number of moles of recurring units of copolymer (PEDEK/PEEK), while recurring units (R_{PEEK}) and (R_{PEDEK}) will be present in an amount of at least 95 % moles, with respect to the total number of moles of recurring units of copolymer (PEDEK/PEEK).
- [0024] When recurring units (R_{PAEK}) different from recurring units (R_{PEEK}) and (R_{PEDEK}) are present in the copolymer (PEDEK/PEEK) of the present invention, these recurring units (R_{PAEK}) generally comply with any of the following formulae (K-A) to (K-M) herein below:



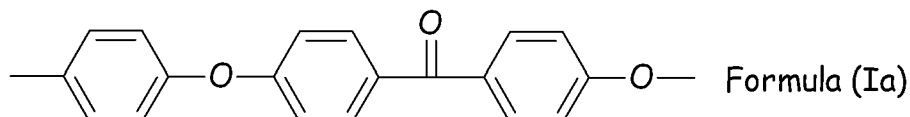




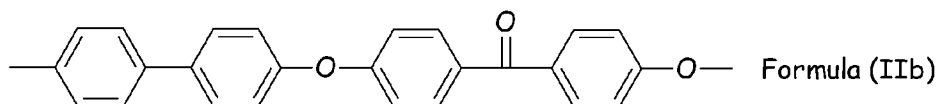
wherein in each of formulae (K-A) to (K-M) above, each of R' , equal to or different from each other, is independently selected at each occurrence from a C_1 - C_{12} group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; and each of j' , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, preferably j' being equal to zero.

- [0025] It is nevertheless generally preferred for the copolymer (PEDEK/PEEK) of the present invention to be essentially composed of recurring units (R_{PEEK}) and (R_{PEDEK}), as above detailed.
- [0026] Defects, end groups and monomers' impurities may be incorporated in very minor amounts in the copolymer (PEDEK/PEEK) of the present invention, so as to advantageously not affecting negatively the performances of the same.
- [0027] In recurring units (R_{PEEK}) of formula (I), the connections among phenyl groups are generally in the para positions of each of the phenyl rings. Further, it is generally preferred for each of j' to be zero, or in other words,

for each of the phenyl rings not to bear any further substituents in addition to the catenary ethereal or ketone bridging groups. According to these preferred embodiments, recurring units (R_{PEEK}) comply with formula (Ia):



[0028] Similarly, in recurring units (R_{PEDEK}) of formula (II), the connections among phenyl groups are generally in the para positions of each of the phenyl rings. Further, it is generally preferred for each of k'' to be zero, or in other words, for each of the phenyl rings not to bear any further substituents in addition to the catenary ethereal or ketone bridging groups. According to these preferred embodiments, recurring units (R_{PEDEK}) comply with formula (IIa):



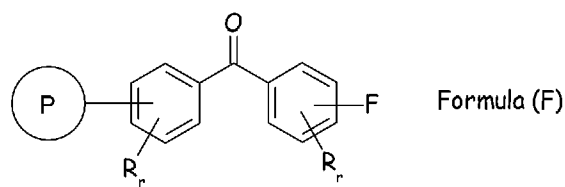
[0029] As explained above, copolymer (PEDEK/PEEK) comprises an amount of chemically bound chlorine of less than 2.0 $\mu\text{eq/g}$, as determined by microcoulometry. In other terms, copolymer (PEDEK/PEEK) is substantially deprived of chlorinated end groups.

[0030] Indeed, it is essential for copolymer (PEDEK/PEEK) to comprise spurious chlorinated end groups, e.g. those derived from chlorine-containing monomers or end-capping agents in an amount such to provide for chemically bound chlorine in an amount of less than 2.0 $\mu\text{eq/g}$, preferably less than 1.9 $\mu\text{eq/g}$, preferably less than 1.8 $\mu\text{eq/g}$.

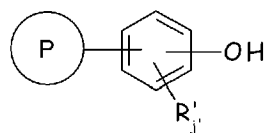
[0031] The Applicant has surprisingly found that the presence of such spurious end groups, in combination with a "disordered" structure, is such to significantly detrimentally affecting crystallization rate, so as to confer to the copolymer (PEDEK/PEEK) comprising the same lower thermal and chemical resistance.

[0032] It is hence understood that copolymer (PEDEK/PEEK) comprises a major amount of end groups selected from the group consisting of:

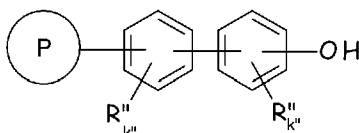
- benzo-phenone fluoride groups of formula:



- hydroxyl-containing groups of formula (OH-1) or (OH-2) or salfied groups thereof:

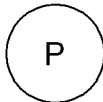


Formula (OH-1)



Formula (OH-2)

wherein in each of formulae (F), (OH-1) and (OH-2), R, R', R'', r, j' and k'' have the meanings

already defined above, and wherein the symbol  is intended to denote the polymer chain comprising recurring units (R_{PEEK}) and (R_{PEDEK}), as above detailed.

[0033] End groups of formulae (F), (OH-1) and (OH-2) preferably represent at more than 50 % moles, preferably at least 60 % moles, even more preferably at least 70 % moles, still more preferably at least 80 % moles, with respect to the total moles of end groups of the copolymer (PEDEK/PEEK).

[0034] Further, as explained above, the copolymer (PEDEK/PEEK) possesses a narrow molecular weight distribution such that the following inequality is satisfied:

$$MV \left(\frac{\text{kN}}{\text{m}^2} \right) \leq 6.62 \cdot \left[RV \left(\frac{\text{dl}}{\text{g}} \right) \right]^{0.20}$$

Math. 2

wherein:

- MV is the melt viscosity measured pursuant to ASTM D3835 standard at 410°C and at a shear rate of 46.3 sec⁻¹, using a conical die having a diameter of 1.016 mm a length of 20.32 mm and a cone angle of 120° and expressed in kN/m²; and
- RV is the reduced viscosity measured pursuant to ASTM D2857 standard at 25°C on 1.0 wt/vol % solution in concentrated H₂SO₄ (96 wt%) and expressed in dl/g.

[0035] Indeed, the Applicant has surprisingly found that when copolymers (PEDEK/PEEK) are such that:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) > 6.62 \cdot \left[RV\left(\frac{\text{dl}}{\text{g}}\right)\right]^{0.20}$$

Math. 3

these copolymers (PEDEK/PEEK) are not found to possess the advantageous thermal and chemical stability otherwise achieved through tuning of recurring units (R_{PEEK}) and (R_{PEDEK}) molar ratio and absence of spurious (chlorinated) end-groups.

[0036] Generally, the copolymers (PEDEK/PEEK) are such to preferably satisfy the following inequality:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.60 \left[RV\left(\frac{\text{dl}}{\text{g}}\right)\right]^{0.20}$$

Math. 4

more preferably to satisfy the following inequality:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.50 \left[RV\left(\frac{\text{dl}}{\text{g}}\right)\right]^{0.20}$$

Math. 5

even more preferably to satisfy the following inequality:

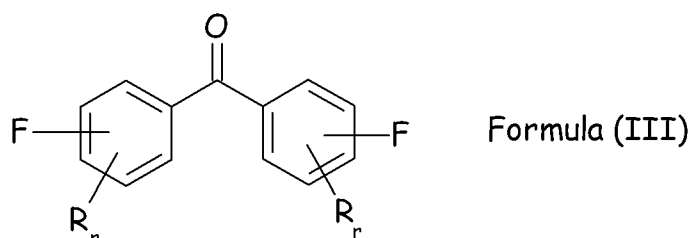
$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.40 \left[RV\left(\frac{\text{dl}}{\text{g}}\right)\right]^{0.20}$$

Math. 6

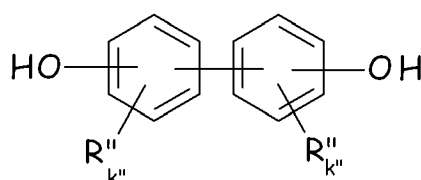
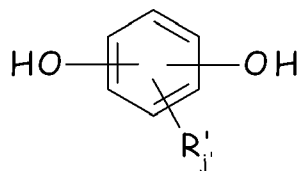
[0037] The copolymer (PEDEK/PEEK) as above detailed possesses a reduced viscosity (RV) measured as above detailed, i.e. pursuant to ASTM D2857 standard at 25°C on 1.0 wt/vol % solution in concentrated H_2SO_4 (96 wt%) and expressed in dl/g, of at least 0.2, preferably at least 0.7, more preferably at least 0.9 and/or at most 6.0, preferably at most 5.5, more preferably at most 5.0. Particularly good results were obtained with copolymers (PEDEK/PEEK) having RV of 0.9 to 5.0 dl/g.

[0038] Method of making the copolymer (PEDEK/PEEK)

[0039] Another object of the invention is a method of making a copolymer (PEDEK/PEEK), as above detailed, comprising reacting at least one difluoro-derivative of formula (III):



with a mixture of di-hydroxyderivatives of formulae (IV) and (V):

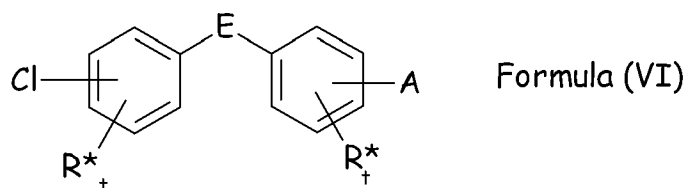


in a molar ratio

(IV):(V) of 45:55 to 15:85,

wherein in above formulae (III), (IV) and (V), each of R, R' and R'', equal to or different from each other, is independently selected at each occurrence from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of r, j' and k'', equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4,

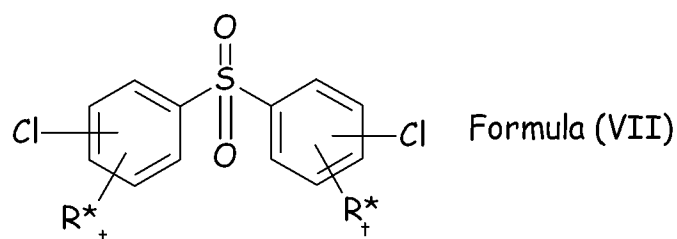
in a polar organic solvent in the presence of a mixture of Na₂CO₃ and K₂CO₃, in a molar ratio Na/K of more than 45 mol/mol, and wherein the method possibly include adding a step of adding a chlorinated compound of formula (VI):



wherein -E- is a sulfone group of formula -SO₂- or a ketone group of formula -C(O)-, A is selected from Cl, F and H, each of R*, equal to or different from each other, is independently selected at each occurrence from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of t,

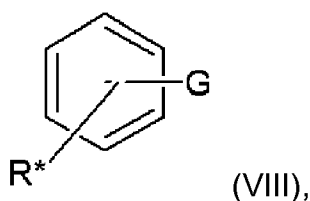
equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4,
with the proviso that if said chlorinated compound of formula (IV) is added, its amount is of no more than 1 % moles with respect to the total molar amount of monomers of formula (III), (IV) and (V)

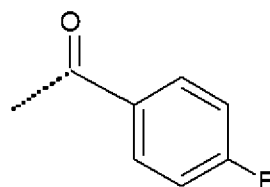
[0040] It is generally preferred for the method of the present invention that the reaction occurs in substantial absence of any chlorinated compound of formula (VII):



wherein each of R^* , equal to or different from each other, is independently selected at each occurrence from a C_1 - C_{12} group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of t , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, wherein the said expression “substantial absence” is hereby intended to mean that if the said compound of formula (VII) is present, its amount is of less than 1 % moles, preferably less than 0.8 % moles, more preferably less than 0.5 % moles, with respect to the total moles of monomers of formula (III), (IV) and (V), as above detailed.

[0041] The method of the invention may include reacting monomers of formula (III), (IV) and (V), as above detailed, in the presence of one or more compounds selected from compounds of formula (VIII) :





wherein G is OH or a group of formula: , bound to the phenyl ring of compound (VIII) through the dotted bond, and wherein R* is H or is selected from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups.

[0042] When a compound of formula (VIII) as above detailed is used, it is generally employed in an amount of at most 1.00 % moles, with respect to the total molar amounts of monomers of formula (III), (IV) and (V), as above detailed. According to these embodiment's, method may include adding required amount of compound (VIII) at the beginning of the reaction, and/or may include adding a portion or all the required amount of compound (VIII) at a later stage, after monomers of formula (III), (IV) and (V) have reacted for a certain time, and terminate the reaction after this addition.

[0043] The Applicant has advantageously found that maintaining a high Na/K ratio of more than 45 mol/mol, in combination with limiting or avoiding introduction of chlorinated compounds of formula (VI), as above detailed, is necessary for achieving the copolymers (PEDEK/PEEK) as above detailed, possessing an advantageous low content of organic chlorine and narrow molecular weight distribution, as evident from the above detailed inequality:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.62 \cdot \left[RV\left(\frac{\text{dl}}{\text{g}}\right)\right]^{0.20}$$

Math. 7

is satisfied.

[0044] In the method of the invention, Na₂CO₃ and K₂CO₃ are used in an amount such that the ratio between the total amount in moles of said Na₂CO₃ and K₂CO₃ and the total amount in moles of hydroxyl-monomers of

formulae (IV) and (V), as above detailed, i.e. the molar ratio:

$$\frac{n_{\text{Na}_2\text{CO}_3} + n_{\text{K}_2\text{CO}_3}}{n_{\text{(IV)}} + n_{\text{(V)}}}$$

Math. 8

is of advantageously at least 0.95, preferably at least 0.99, more preferably at least 1.00 mol/mol and/or advantageously at most 1.20, preferably at most 1.10, more preferably at most 1.06 mol/mol.

[0045] Generally, the Na_2CO_3 used in the method of the invention meets the particle size distribution requirements as detailed in **US 9175136** (SOLVAY ADVANCED POLYMERS LLC) 9/1/2011.

[0046] Preferred monomer (III) is 4,4'-difluorobenzophenone (DFBP). It is generally preferred to make use of DFBP comprising low amounts of certain impurities, as detailed in **US 2011213115** (SOLVAY ADVANCED POLYMERS LLC) 9/1/2011.

[0047] In the method of the present invention, monomers (III), (IV) and (V) are reacted in such an amount that the ratio between the molar amount of difluoro-monomer of formula (III) and the total molar amount of hydroxyl-monomers of formulae (IV) and (V), i.e. the molar ratio:

$$\frac{n_{\text{difluoro-monomer(III)}}}{n_{\text{hydroxyl-monomer(IV)}} + n_{\text{hydroxyl-monomer(V)}}$$

Math. 9

is of at least 0.95, preferably at least 0.99 mol/mol and/or of at most 1.05, preferably at most 1.03 mol/mol.

[0048] Preferred monomer (IV) is hydroquinone and preferred monomer (V) is 4,4'-dihydroxybiphenyl, otherwise known as 4,4'-biphenol.

[0049] Polar organic solvents possessing suitable solubilisation ability with respect to the cited monomers, and suitable thermal resistance at the polycondensation temperatures can be used. Preference is given to high boiling aprotic polar solvents; diphenylsulfone is a preferred solvent, and is generally used in the method of the present invention as solvent comprising limited amounts of impurities, as detailed in **US 9133111** (SOLVAY ADVANCED POLYMERS LLC) 8/7/2014.

[0050] It is also preferable that the monomers (III), (IV) and (V) are heated in the method of the invention at a first temperature of at least 120°C, preferably

at least 130°C, more preferably at least 140°C before being contacted with the mixture of Na₂CO₃ and K₂CO₃. According to this embodiment, the addition of the mixture of Na₂CO₃ and K₂CO₃ is done stepwise (i.e. through multiple sequential discontinuous additions) or continuously in time, e.g. through appropriate feeding systems, at a rate such that the required amount is delivered step-wise/continuously during a time period of at least 15 minutes, preferably at least 20 minutes, more preferable at least 30 minutes and/or in a manner that the addition rate is of less than 40% of total amount/minute, preferably of less than 30% of total amount/minute, more preferably of less than 20% of total amount/minute, and/or is of more than 3 % of total amount/minute, preferably of more than 5 % of total amount/minute.

- [0051] After completing addition of the mixture of Na₂CO₃ and K₂CO₃, the reaction is generally pursued by heating the resulting mixture at a temperature of at least 300°C, preferably at least 320°C, at a temperature ramp rate of less than 5°C/minute, preferably less than 3°C/minute and/or at a temperature ramp rate of more than 0.5°C/minute.
- [0052] Once achieved the final target temperature, the reaction is generally pursued for a limited period at time at this temperature, before interrupting the reaction. The polycondensation reaction is advantageously terminated by adding an additional amount of monomer (III), such that the molar ratio

$$\frac{n_{\text{difluoro-monomer(III)}}}{n_{\text{hydroxyl-monomer(IV)}} + n_{\text{hydroxyl-monomer(V)}}$$

Math. 10

as above detailed is brought in the range of 1.01 to 1.15 mol/mol, preferably in the range of 1.03 to 1.10 mol/mol.

- [0053] Composition comprising the copolymer (PEDEK/PEEK)
- [0054] The invention further pertains to a composition (C) comprising at least one copolymer (PEDEK/PEEK).
- [0055] The composition (C) may comprise copolymer (PEDEK/PEEK), as above detailed, in a weight amount of at least 10 %, at least 30 %, at least 40 % or at least 50 %, based on the total weight of the of the said composition (C). According to certain preferred embodiment's, the composition (C) comprises copolymer (PEDEK/PEEK), as above

detailed, in a weight amount of at least 70 %, based on the total weight of the said composition (C). According to other embodiment's, the composition (C) comprises the copolymer (PEDEK/PEEK), as above detailed, in a weight amount of at least 90 %, if not at least 95 %, based on the total weight of the said composition (C). Yet, embodiment's are provided wherein the composition (C) consists essentially of the copolymer (PEDEK/PEEK), as above detailed. For the purpose of the present invention, the expression "consisting essentially of" is to be understood to mean that any additional component different from the copolymer (PEDEK/PEEK), as above detailed, is present in an amount of at most 1 % by weight, based on the total weight of the composition (C), so as not to substantially alter advantageous properties of the composition.

- [0056] The composition (C) may further comprise at least one reinforcing filler. Reinforcing fillers are well known by the skilled in the art. They are preferably selected from fibrous and particulate fillers different from the pigment as defined above. More preferably, the reinforcing filler is selected from mineral fillers (such as talc, mica, kaolin, calcium carbonate, calcium silicate, magnesium carbonate), glass fiber, carbon fibers, synthetic polymeric fiber, aramid fiber, aluminum fiber, titanium fiber, magnesium fiber, boron carbide fibers, rock wool fiber, steel fiber, wollastonite etc. Still more preferably, it is selected from mica, kaolin, calcium silicate, magnesium carbonate, glass fiber, carbon fibers and wollastonite etc.
- [0057] Preferably, the filler is chosen from fibrous fillers. A particular class of fibrous fillers consists of whiskers, i.e. single crystal fibers made from various raw materials, such as Al_2O_3 , SiC, BC, Fe and Ni.
- [0058] In one embodiment of the present invention the reinforcing filler is chosen from wollastonite and glass fiber. Among fibrous fillers, glass fibers are preferred ; they include chopped strand A-, E-, C-, D-, S-, T- and R-glass fibers, as described in chapter 5.2.3, p. 43-48 of Additives for Plastics Handbook, 2nd edition, John Murphy.

- [0059] Glass fibers optionally comprised in polymer composition (C) may have a circular cross-section or a non-circular cross-section (such as an oval or rectangular cross-section).
- [0060] When the glass fibers used have a circular cross-section, they preferably have an average glass fiber diameter of 3 to 30 μm and particularly preferred of 5 to 12 μm . Different sorts of glass fibers with a circular cross-section are available on the market depending on the type of the glass they are made of. One may notably cite glass fibers made from E- or S-glass.
- [0061] Good results were obtained with standard E-glass material with a non-circular cross section. Excellent results were obtained when the polymer composition with S-glass fibers with a round cross-section and, in particular, when using round cross-section with a 6 μm diameter (E-Glass or S-glass).
- [0062] In another embodiment of the present invention the reinforcing filler is a carbon fiber.
- [0063] As used herein, the term "carbon fiber" is intended to include graphitized, partially graphitized and ungraphitized carbon reinforcing fibers or a mixture thereof. Carbon fibers useful for the present invention can advantageously be obtained by heat treatment and pyrolysis of different polymer precursors such as, for example, rayon, polyacrylonitrile (PAN), aromatic polyamide or phenolic resin ; carbon fibers useful for the present invention may also be obtained from pitchy materials. The term "graphite fiber" intends to denote carbon fibers obtained by high temperature pyrolysis (over 2000°C) of carbon fibers, wherein the carbon atoms place in a way similar to the graphite structure. Carbon fibers useful for the present invention are preferably chosen from the group composed of PAN-based carbon fibers, pitch based carbon fibers, graphite fibers, and mixtures thereof.
- [0064] The weight of said reinforcing filler is advantageously preferably below 60 % wt., more preferably below 50 % wt., even more preferably below 45 % wt., most preferably below 35 % wt., based on the total weight of the composition (C).

- [0065] Preferably, the reinforcing filler is present in an amount ranging from 10 to 60 % wt., preferably from 20 to 50 % wt., preferably from 25 to 45 % wt., most preferably from 25 to 35 % wt., based on the total weight of the composition (C).
- [0066] The composition (C) may further optionally comprise one or more than one additional ingredient (I) different from the reinforcing filler and from the copolymer (PEDEK/PEEK), as above detailed, generally selected from the group consisting of (i) colorants such as notably a dye (ii) pigments such as notably titanium dioxide, zinc sulfide and zinc oxide (iii) light stabilizers, e.g. UV stabilizers (iv) heat stabilizers (v) antioxidants such as notably organic phosphites and phosphonites, (vi) acid scavengers (vii) processing aids (viii) nucleating agents (ix) internal lubricants and/or external lubricants (x) flame retardants (xi) smoke-suppressing agents (x) anti-static agents (xi) anti-blocking agents (xii) conductivity additives such as notably carbon black and carbon nanofibrils (xiii) plasticizers (xiv) flow modifiers (xv) extenders (xvi) metal deactivators and combinations comprising one or more of the foregoing additives.
- [0067] When one or more than one additional ingredient (I) are present, their total weight, based on the total weight of polymer composition (C), is usually below 20 %, preferably below 10 %, more preferably below 5 % and even more preferably below 2 %.
- [0068] According to certain embodiments, the composition (C) comprises the copolymer (PEDEK/PEEK), as above detailed, in combination with one or more than one additional polymeric components, such as polyarylether polymers different from copolymer (PEDEK/PEEK), including e.g. PEEK, PEK, PEKK, sulfone polymers, polyaryl sulphides, and the like.
- [0069] According to other embodiments, the copolymer (PEDEK/PEEK), as above detailed, is the only polymeric component in the composition (C).
- [0070] The expression 'polymeric components' is to be understood according to its usual meaning, i.e. encompassing compounds characterized by repeated linked units, having typically a molecular weight of 2 000 or more.
- [0071] If desired, the composition (C) comprises more than 80 wt. % of the copolymer (PEDEK/PEEK), as above detailed, optionally with the proviso

that the copolymer (PEDEK/PEEK), as above detailed, is the only polymeric component in the composition (C), and comprises one or more than one reinforcing filler and/or additional ingredient (I) might be present therein.

- [0072] The composition (C) can be prepared by a variety of methods involving intimate admixing of the at least one copolymer (PEDEK/PEEK), as above detailed, optionally the reinforcing filler and optionally additional ingredient (I) desired in the polymeric material, for example by dry blending, suspension or slurry mixing, solution mixing, melt mixing or a combination of dry blending and melt mixing.
- [0073] Typically, the dry blending of copolymer (PEDEK/PEEK), as detailed above, preferably in powder state, optionally the reinforcing filler and optionally additional ingredient (I) is carried out by using high intensity mixers, such as notably Henschel-type mixers and ribbon mixers so as to obtain a physical mixture, in particular a powder mixture of the at least one copolymer (PEDEK/PEEK), optionally the reinforcing filler and optionally additional ingredient (I).
- [0074] Alternatively, the intimate admixing of the at least one copolymer (PEDEK/PEEK), optionally the reinforcing filler and optionally additional ingredient (I) desired in the composition (C), is carried out by tumble blending based on a single axis or multi-axis rotating mechanism so as to obtain a physical mixture.
- [0075] Alternatively, the slurry mixing of the copolymer (PEDEK/PEEK), optionally the reinforcing filler and optionally additional ingredient (I) is carried out by first slurrying said copolymer (PEDEK/PEEK), as above detailed, in powder form, optionally the reinforcing filler and optionally additional ingredient (I) using an agitator in an appropriate liquid such as for example methanol, followed by filtering the liquid away, so as to obtain a powder mixture of the at least one copolymer (PEDEK/PEEK), optionally the reinforcing filler and optionally additional ingredient (I).
- [0076] In another embodiment, the solution mixing of the copolymer (PEDEK/PEEK), as detailed above, optionally the reinforcing filler and optionally additional ingredient (I) using an agitator in an appropriate

solvent or solvent blends such as for example diphenyl sulfone, benzophenone, 4-chlorophenol, 2-chlorophenol, meta-cresol. Diphenyl sulfone and 4-chlorophenol are most preferred.

- [0077] Following the physical mixing step by one of the aforementioned techniques, the physical mixture, in particular the obtained powder mixture, of the at least one copolymer (PEDEK/PEEK), optionally the reinforcing filler and optionally additional ingredient (I) is typically melt fabricated by known methods in the art including notably melt fabrication processes such as compression molding, injection molding, extrusion and the like, to provide shaped articles, including notably part(s) of an oil and gas recovery article or a finished oil and gas recovery article, as explained below in more detail.
- [0078] So obtained physical mixture, in particular the obtained powder mixture can comprise the copolymer (PEDEK/PEEK), the reinforcing filler, as detailed above, and optionally, other ingredients (I) in the weight ratios as above detailed, or can be a concentrated mixture to be used as masterbatch and diluted in further amounts of the copolymer (PEDEK/PEEK), as above detailed, the reinforcing filler, as detailed above, and optionally, other ingredients (I) in subsequent processing steps. For example, the obtained physical mixture can be extruded into a stock shape like a slab or rod from which a final part can be machined. Alternatively, the physical mixture can be compression or injection molded into a finished part of the oil and gas recovery article or into a stock shape from which a finished part of the oil and gas recovery article can be machined.
- [0079] It is also possible to manufacture the composition of the invention by further melt compounding the powder mixture as above described. As said, melt compounding can be effected on the powder mixture as above detailed, or directly on the copolymer (PEDEK/PEEK), as above detailed, the reinforcing filler, as detailed above, and optionally, other ingredients (I). Conventional melt compounding devices, such as co-rotating and counter-rotating extruders, single screw extruders, co-kneaders, disc-pack processors and various other types of extrusion equipment can be used. Preferably, extruders, more preferably twin screw extruders can be used.

[0080] If desired, the design of the compounding screw, e.g. flight pitch and width, clearance, length as well as operating conditions will be advantageously chosen so that sufficient heat and mechanical energy is provided to advantageously fully melt the powder mixture or the ingredients as above detailed and advantageously obtain a homogeneous distribution of the different ingredients. Provided that optimum mixing is achieved between the bulk polymer and filler contents, it is advantageously possible to obtain strand extrudates of the composition (C) of the invention. Strand extrudates of the composition (C) can be chopped by means e.g. of a rotating cutting knife after some cooling time on a conveyer with water spray. Thus, for example composition (C) which may be present in the form of pellets or beads can then be further used for the manufacture of shaped articles, notably of different shape and size.

[0081] **Shaped articles**

[0082] The copolymer (PEDEK/PEEK) and/or composition (C), as above detailed, can be processed by usual melt processing techniques, including notably extrusion molding, injection molding, compression molding, so as to provide shaped articles.

[0083] According to certain embodiment's shaped articles are under the form of substantially bidimensional articles, e.g. parts wherein one dimension (thickness or height) is significantly less than the other two characterizing dimensions (width and length), such as notably films and sheets.

[0084] According to other embodiment's, shaped articles are provided as three-dimensional parts, e.g. substantially extending in the three dimensions of space in similar manner, including under the form of complex geometries parts, e.g. with concave or convex sections, possibly including undercuts, inserts, and the like.

[0085] According to certain embodiments, shaped articles made from the copolymer (PEDEK/PEEK) and/or composition (C), as above detailed, are provided as part(s) of oil and gas recovery article(s).

[0086] **Use of the copolymer (PEDEK/PEEK) in O&G**

[0087] The invention further pertains to a method of making parts included in devices used for oil & gas recovery, including shaping those parts from the

copolymers (PEDEK/PEEK) or from any composition comprising the same. Shaping can be achieved through any melt processing technique, including notably extrusion molding, injection molding, compression molding, and the like.

- [0088] An oil and gas recovery article including at least one part made from a copolymer (PEDEK/PEEK), as above detailed, or from a composition comprising the same is still another object of the present invention.
- [0089] To the purposes of the invention, the term “oil and gas recovery article” is intended to denote any article that is designed to conveniently be used in oil and gas recovery applications, in particular in HP/HT conditions.
- [0090] For the sake of clarity, the term “part of an oil and gas recovery article” is intended to denote a piece or portion which is combined with others to make up the whole oil and gas recovery article. The external coating of an oil and gas recovery article falls thus within this scope. Thus, the at least one part of the oil and gas recovery article according to the present invention, can be a coating.
- [0091] Representative examples of oil and gas recovery applications, but not limited to, include (i) drilling and completion of deep, higher temperature, higher pressure oil and gas wells, as notably described in U.S. Pat. No. **US 5662170** the entire disclosure of those are incorporated herein by reference, (ii) an oil and gas recovery method as traditionally subdivided in three stages, namely a primary oil recovery stage, a secondary or assisted oil recovery and a tertiary or enhanced oil recovery stage (iii) gas and oil gathering treatment applications, (iv) complex transportation of gas and oil from said deep, higher temperature, higher pressure wells to refineries and the like.
- [0092] All these applications as herein mentioned above, are well familiar to the skilled person, and should be understood under their common meaning.
- [0093] As non limitative examples of oil and gas recovery articles useful in the present invention are drilling systems; drilling rigs; compressor systems, as notably described in published U.S. Pat. Appl. **US 2010239441** , the entire disclosure of which is incorporated herein by reference; pumping systems; motor systems, sensors, such as reservoir sensors; control

systems, such as temperature and/or pressure; stimulation and flow control systems; liner hanger systems, as notably described in U.S. Pat. No. **US 6655456** , the entire disclosure of which is incorporated herein by reference; packer systems, as notably described in U.S. Pat. No. **US 7874356** , the entire disclosure of which is incorporated herein by reference; pipe systems, valve systems, tubing systems, casing systems, and others.

- [0094] All these systems as herein mentioned above, are well familiar to the skilled person, and should be understood under their common meaning.
- [0095] By the term “drilling rig” is meant a structural housing equipment that is used to drill oil wells, or natural gas extraction wells, and may comprise a single article or comprise two or more components. Typically components of said drilling rig include, but not limited to, mud tanks, shale shakers, mud pumps, drill pipes, drill bits, drilling lines, electric cable trays.
- [0096] As non limitative examples of pumping systems useful in the present invention are jet pump systems, submersible pumping systems, in particular electric submersible pumps, as notably described in U.S. Pat. No. **US 6863124** the entire disclosure of which is incorporated herein by reference, beam pumps.
- [0097] As non limitative examples of motor systems useful in the present invention are mud motor assemblies, as notably described in U.S. Pat. No. **US 2012234603** , the entire disclosure of which is incorporated herein by reference.
- [0098] As non limitative examples of pipe systems useful in the present invention, mention can be made of pipes including rigid pipes and flexible pipes, flexible risers, pipe-in-pipe, pipe liners, subsea jumpers, spools, umbilicals.
- [0099] Typical flexible pipes have been described by way of example in **WO 01/61232** , U.S. Pat. No. **US 6123114** and U.S. Pat. No. **US 6085799** ; the entire disclosure of those are incorporated herein by reference. Such flexible pipes can notably be used for the transport of fluids where very high or very different water pressure prevails over the length of the pipe, and for example can take the form of flexible risers which run from the ocean floor up to equipment at or in the vicinity of the

ocean surface, and they can also generally be used as pipes for the transport of liquids or gases between various items of equipment, or as pipes laid at great depth on the ocean floor, or as pipes between items of equipment close to the ocean surface, and the like.

[00100] Preferred pipe systems are pipes, flexible risers and pipe liners.

[0101] By the term “valves” is meant any device for halting or controlling the flow of a liquid, gas, or any other material through a passage, pipe, inlet, outlet, and the like. As non limitative examples of valve systems useful in the present invention, mention can especially be made of choke valves, thermal expansion valves, check valves, ball valve, butterfly valve, diaphragm valve, gate valve, globe valve, knife valve, needle valve, pinch valve, piston valve, plug valve, poppet valve, spool valve, pressure reducing valve, sampling valves, safety valve.

[0102] The at least one part of the oil and gas recovery articles according to the present invention may be selected from a large list of articles such as fitting parts; such as seals, in particular sealing rings, preferably backup seal rings, fasteners and the like; snap fit parts; mutually moveable parts; functional elements, operating elements; tracking elements; adjustment elements; carrier elements; frame elements; films; switches; connectors; wires, cables; bearings, housings, compressor components such as compressor valves and compressor plates, any other structural part other than housings as used in an oil and gas recovery articles, such as for example shafts, shells, pistons.

[0103] In particular, the copolymer (PEDEK/PEEK) is very well suited for the production of seals, fasteners, cables, electrical connectors, housing parts of oil and gas recovery articles.

[0104] In one preferred embodiment, the at least one part of the oil and gas recovery article according to the present invention, is advantageously an oil and gas recovery housing, a seal, an electrical connector or a cable.

[0105] A cable can be notably wires electrically connecting the different parts within an oil and gas recovery article, for example connecting different electrical connectors, connecting tools to connectors, instruments or other tools, connecting instruments to connectors, other instruments or tools,

connecting a power source to connectors, instruments or tools. A cable can also advantageously be used for carrying a signal to computer systems.

- [0106] In a particularly preferred embodiment, the cable is a coated wire.
- [0107] By "oil and gas recovery housing" is meant one or more of the back cover, front cover, frame and/or backbone of an oil and gas recovery article. The housing may be a single article or comprise two or more components. By "backbone" is meant a structural component onto which other components of the oil and gas recovery article, are mounted. The backbone may be an interior component that is not visible or only partially visible from the exterior of the oil and gas recovery article.
- [0108] Typical fasteners have been described by way of example in **WO 2010/112435**, the entire disclosure of those are incorporated herein by reference, and include, but not limited to, threaded fasteners such as bolts, nuts, screws, headless set screws, scrivers, threaded studs and threaded bushings, and unthreaded fastener, such as notably pins, retaining rings, rivets, brackets and fastening washers and the like.
- [0109] Sealing of components of oil and gas recovery articles is important and it can be said that seals are used in all types of oil and gas recovery articles, as well as those used in parts of oil and gas recovery articles which remains in the well after completion, testing and production of the well. Thus the seals need to resist to these extreme conditions, as mentioned above, in substantially indefinite time. It is worthwhile mentioning that seals besides electronics can be considered as the most vulnerable parts of oil and gas recovery articles.
- [0110] In one embodiment of the present invention, the at least part of an oil and gas recovery article is a seal system, wherein said seal system is selected from a group consisting of a metal seal, an elastomeric seal, a metal-to-metal seal and an elastomeric and metal-to-metal seal.
- [0111] Seal systems are typically used in drill bits, motor systems, in particular mud motors, reservoir sensors, stimulation and flow control systems, pump systems, in particular electric submersible pumps, packers, liner hangers, tubing's, casings and the like.

- [0112] Representative examples of seal systems, are, without limitation, seal rings such as notably C-rings, E-rings, O-rings, U-rings, spring energized C-rings, backup rings and the like; fastener seals; piston seals, gask-O-seals; integral seals, labyrinth seals.
- [0113] In a particularly preferred embodiment, the at least one part of the oil and gas recovery article according to the present invention, is a seal ring, preferably a backup seal ring.
- [0114] The weight of the copolymer (PEDEK/PEEK), based on the total weight of oil and gas recovery article, is usually above 1 %, above 5 %, above 10 %, preferably above 15 %, above 20 %, above 30 %, above 40 %, above 50 %, above 60 %, above 70 %, above 80 %, above 90 %, above 95 %, above 99 %.
- [0115] The oil and gas recovery article may consist of one part, i.e. it is a single-component article. Then, the single part preferably consists of the copolymer (PEDEK/PEEK) or of any composition thereof.
- [0116] Alternatively, the oil and gas recovery article may consist of several parts. The case being, either one part or several parts of the oil and gas recovery article may consist of the copolymer (PEDEK/PEEK) or of any composition thereof. When several parts of the oil and gas recovery article consist of copolymer (PEDEK/PEEK) or of any composition thereof, each of them may consist of the very same copolymer (PEDEK/PEEK) or of any composition thereof; alternatively, at least two of them may consist of different copolymer (PEDEK/PEEK) or of any composition thereof.
- [0117] Another objective of the present invention is to provide a method for the manufacture of the above described part of the oil and gas recovery article. Such method is not specifically limited. The copolymer (PEDEK/PEEK) or a composition comprising the same, as above detailed, may be generally processed by injection molding, extrusion molding, compression molding, or other shaping technologies.
- [0118] In one embodiment of the present invention, the method for the manufacture of the above described part of the oil and gas recovery article or oil and gas recovery article includes the step of compression molding or

injection molding and subsequent solidification of the copolymer (PEDEK/PEEK) or of the composition comprising the same.

- [0119] In another embodiment, the method for the manufacture of the above described part of the oil and gas recovery article or oil and gas recovery article includes the step of coating.
- [0120] For example, the copolymer (PEDEK/PEEK) or the composition comprising the same can be applied to a wire as a coating by using any suitable coating method, preferably by extrusion coating around a wire to form a coated wire.
- [0121] Techniques for manufacturing wire coatings are well known in the art.
- [0122] In another embodiment of the present invention, the method for the manufacture of the above described part of the oil and gas recovery article or the oil and gas recovery article, as described above includes the machining of a standard shaped structural part in a part having any type of size and shape. Non limiting examples of said standard shaped structural part include notably a plate, a rod, a slab and the like. Said standard shaped structural parts can be obtained by extrusion molding, compression molding or injection molding of the copolymer (PEDEK/PEEK) or of the composition comprising the same.
- [0123] **Method of recovering oil and/or gas using the copolymer (PEDEK/PEEK)**
- [0124] According to another aspect of the present invention, it is hereby provided a method for recovering oil and/or gas including using at least one oil and gas recovery article as defined above.
- [0125] The method of the invention is advantageously a method for recovering oil and/or gas from a subterranean formation including using said oil and gas recovery article.
- [0126] The subterranean formations can be advantageously deeply buried reservoir, wherein temperatures close to 300C at a depth of more than 6,000 meters and pressures of over 1,500 bar can be encountered: the said oil and gas articles of the invention possess all the requisites and properties for being qualified to withstand this below-ground inferno over long periods of time.

[0127] The method of the invention may advantageously comprises at least one of the operations selected from the group consisting of :

1. drilling at least one borehole for exploring or exploiting an oil and/or gas reservoir in a subterranean formation using at least one oil and gas recovery article as defined above;
2. completing at least one well using at least one oil and gas recovery article as defined above;
3. transporting oil and/or gas from an oil and/or gas reservoir in a subterranean formation to the ground level.

[0128] The operation of drilling boreholes for exploring or exploiting oil and/or natural gas reservoirs generally includes the use of drilling rig equipment, which is an embodiment of the oil and gas recovery article as defined above.

[0129] Figure 1 schematically depicts drilling rig equipment. In this equipment a drill pipe or string (#5) acts as a conduit for a drilling fluid; it is generally made of joints of hollow tubing connected together and stood in the derrick vertically. A drill bit (#7) device is attached to the end of the drill string; this bit breaks apart the rock being drilled. It also contains jets through which the drilling fluid exits. The rotary table (#6) or a top drive (not shown) rotates the drill string along with the attached tools and bit.

[0130] A mechanical section or draw-works section (#13) contains the spool, whose main function is to reel in/out the drill line to raise/lower the travelling block.

[0131] A mud pump (#11) is used to circulate drilling fluid through the system; the mud is suctioned from the mud tank or mud pit (#9) which provides a reserve store of drilling fluid. The mud flows through the conduit #14 and through the drill pipe (#5) down to the bit (#7). Loaded with drill cuttings it flows upwards in the borehole and is extracted through the conduit (#12) back to the mud pit. A shale shaker (#10) separates drill cuttings from the drilling fluid before it is pumped back down the borehole.

[0132] The equipment can further comprise devices installed at the wellhead to prevent fluids and gases from unintentionally escaping from the borehole (not shown).

- [0133] Any of the components of the drilling rig as above detailed maybe an oil and gas recovery article, as above detailed, i.e. may comprise at least a part comprising the copolymer (PEDEK/PEEK) or any composition thereof, as above defined.
- [0134] The operation b) of completing a well is the operation comprehensive of all the preparation or outfitting operations required for bringing in operations a geologic formation from the wellbore. This principally involves preparing the bottom of the hole to the required specifications, running in the production tubing and its associated down hole tools and controlling devices as well as perforating and stimulating as required. Sometimes, the process of running in and cementing the casing is also included. In all these single operations, articles comprising at least one part comprising the copolymer (PEDEK/PEEK) or any composition thereof, as above detailed, can be used.
- [0135] The invention will be now be described with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the present invention.
- [0136] **Examples**
- [0137] The following Examples demonstrate the synthesis of copolymers (PEDEK-PEEK), their thermal properties and their chemical resistance to sweet salt water environment.
- [0138] **Raw materials**
- [0139] **PAEK:**
- [0140] KETASPIRE® KT-820 P (KT-820P herein after) is an aromatic polyetheretherketone (PEEK) polymer available from Solvay Specialty Polymers USA, LLC.
- Cypek® FC (PEKK FC, herein after) and HT (PEKK HT, herein after) are aromatic polyetherketoneketones (PEKK) available from Solvay S.A.
- Arlon® 2000 is an aromatic polyetherketone (PEK, herein after) available from Green, Tweede & Company, USA.
- [0141] Hydroquinone Photo-Grade was procured from Eastman.
- [0142] 4,4'-biphenol, polymer grade, was procured from SI, USA.

- [0143] 4,4'-difluorobenzophenone, polymer grade, was procured from Jintan, China.
- [0144] Diphenyl sulfone (polymer grade) was procured from Provion (99.8% pure).
- [0145] Sodium carbonate, light soda ash, was procured from Solvay S.A., France.
- [0146] Potassium carbonate with a $d_{90} < 45 \mu\text{m}$ was procured from Armand products.
- [0147] Lithium chloride was procured from Acros
- [0148] **Determination of reduced viscosity**
- [0149] Reduced viscosity (RV) was measured pursuant to ASTM D2857 standard at 25 °C on 1.0 wt/vol% solutions in concentrated H_2SO_4 (96 wt% minimum), using a Cannon –Fenske capillary, size 200.
- [0150] **Determination of the chlorine content in polymer by microcoulometry**
- [0151] Using forceps, a clean, dry combustion boat was placed onto a microbalance, and the balance was zeroed. One to five mg of polymer sample was weighed into said dried combustion boat and weight was recorded to 0.001 mg. The combustion boat and sample were placed in the introduction port of a ThermoGLAS 1200 Total Organic Halogen Analyzer, and the port was capped. The sample weight was entered into the sample weight field on the instrument computer. The sample analysis cycle was then started. The sample was burned in a mixture of argon and oxygen and the combustion products were passed through concentrated sulfuric acid scrubber to remove moisture and byproduct. Hydrogen chloride and oxychlorides from the combustion process were absorbed into the cell acetic acid solution from the gas stream. Chloride entered the cell was titrated with silver ions generated coulometrically. Percent chlorine in the sample was calculated from the integrated current and the sample weight. The resulting percent chlorine value was converted to chlorine end group concentration in microequivalents per gram.
- [0152] **Determination of the glass transition temperature, melting temperature and heat of fusion**
- [0153] The glass transition temperature T_g was determined by the mid-point method and the melting temperature T_m was determined as the peak

temperature of the melting endotherm on the 2nd heat scan in differential scanning calorimeter (DSC) according to ASTM D3418-03, E1356-03, E793-06, E794-06. Details of the procedure as used in this invention are as follows: a TA Instruments DSC Q20 was used with nitrogen as carrier gas (99.998% purity, 50 mL/min). Temperature and heat flow calibrations were done using indium. Sample size was 5 to 7 mg. The weight was recorded ± 0.01 mg. The heat cycles were:

- 1st heat cycle: 30.00°C to 450.00°C at 20.00°C/min, isothermal at 450.00°C for 1 min;
- 1st cool cycle: 450.00°C to 30.00°C at 20.00°C/min, isothermal for 1 min;
- 2nd heat cycle: 30.00°C to 450.00°C at 20.00°C/min, isothermal at 450.00°C for 1 min.

The melting temperature T_m was determined as the peak temperature of the melting endotherm on the 2nd heat scan.

The crystallinity level of the molded plaque was determined measuring the enthalpy of fusion, as determined on the 1st heat scan of the DSC of the plaque and was taken as the area over a linear baseline drawn from above the T_g to a temperature above end of the endotherm.

[0154] **Determination of the melt viscosity**

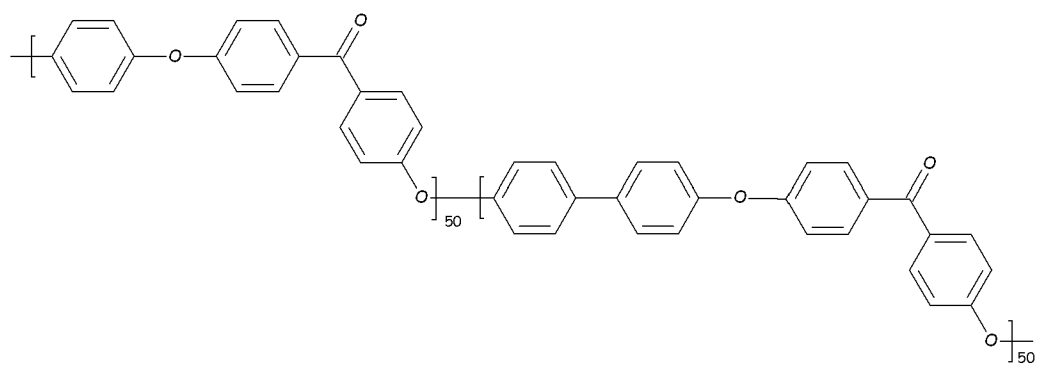
[0155] The melt viscosity was measured using a capillary rheometer pursuant to ASTM D3835 standard. Readings were taken after 10 minute dwell time at 410 °C and a shear rate of 46.3 s⁻¹ using a tungsten-carbide die with the following characteristics : diameter = 1.016 mm, length = 20.32 mm, cone angle = 120°

[0156] **Comparative Example D : preparation of PEDEK-PEEK copolymer 50/50**

[0157] In a 1000 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 288.96 g of diphenyl sulfone, 28.718 g of hydroquinone, 48.415 g of 4,4' biphenol and 114.258 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

[0158] The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 57.044 g of Na₂CO₃ and 0.359 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320 °C at 1°C/minute. After 2 minutes at 320 °C, 13.616 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.887 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 4.539 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 150 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The reduced viscosity of the copolymer, measured at 1 wt/vol% in 96% H₂SO₄ at 25°C, as above detailed, was found to be 1.25 dL/g.

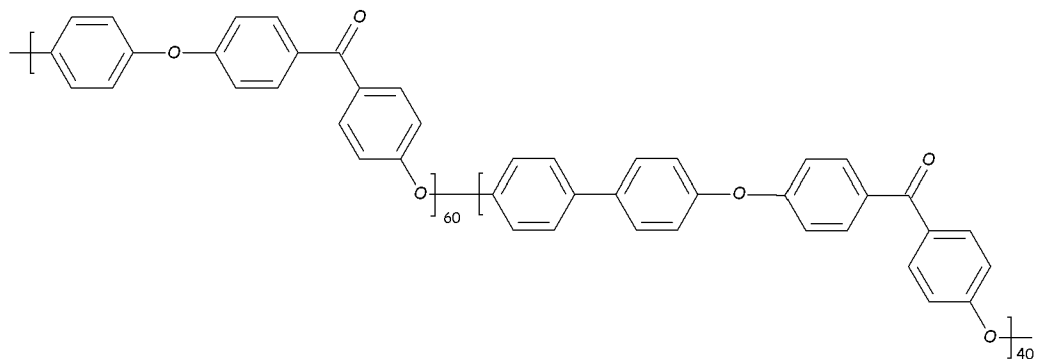
[0159] **Comparative Example E : preparation of PEDEK-PEEK copolymer 40/60**

[0160] In a 1000 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 287.65 g of diphenyl sulfone, 35.123 g of hydroquinone, 39.477 g of 4,4'-biphenol and 116.455 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen

(containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 58.141 g of Na₂CO₃ and 0.366 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320 °C at 1°C/minute. After 2 minutes at 320 °C, 13.878 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.904 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 4.626 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

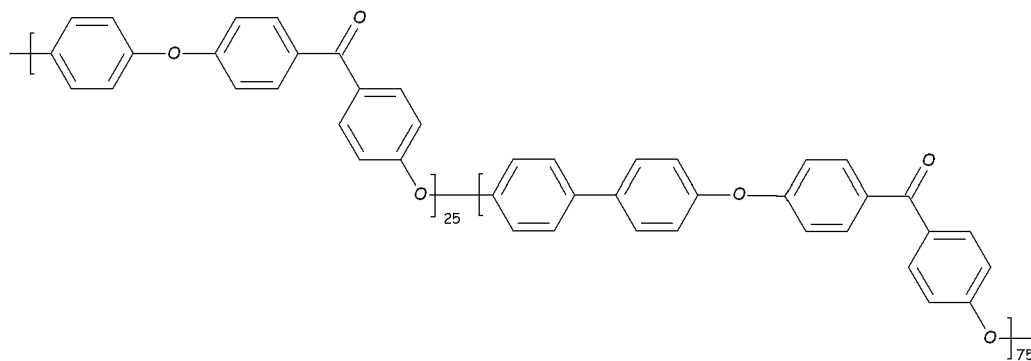
The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 160 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The reduced viscosity of the copolymer, measured at 1 wt/vol% in 96% H₂SO₄ at 25°C, as above detailed, was found to be 1.35 dL/g.

[0161] Comparative Example F : preparation of PEDEK-PEEK copolymer 75/25 following example 3 of US4766197

[0162] The procedure as detailed in example 3 of US 4766197 was repeated at the 0.45 mol scale and yielded 133 g of a white powder, having molecular structure schematized as follows:



The reduced viscosity of the copolymer, measured at 1 wt/vol% in 96% H_2SO_4 at 25°C, as above detailed, was found to be 3.13 dL/g. The melt viscosity measured by capillary rheology at 410°C, 46 s⁻¹, as above detailed, was found to be higher than 15.0 kN-s/m². The polymer exhibited a chlorine content by microcoulometry of 17.1 µeq/g = 610 wtpm Cl.

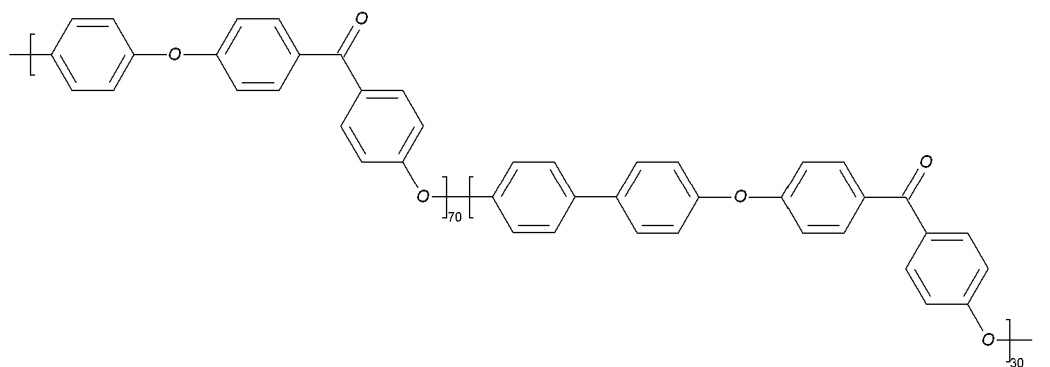
[0163] **Comparative example G : preparation of PEDEK-PEEK copolymer 30/70**

[0164] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 129.80 g of diphenyl sulfone, 18.942 g of hydroquinone, 13.686 g of 4,4'-biphenol and 54.368 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 26.876 g of Na₂CO₃ and 0.1524 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320 °C at 1°C/minute. After 10 minutes at 320 °C, 6.415 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.418 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 2.138 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a

2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 73 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



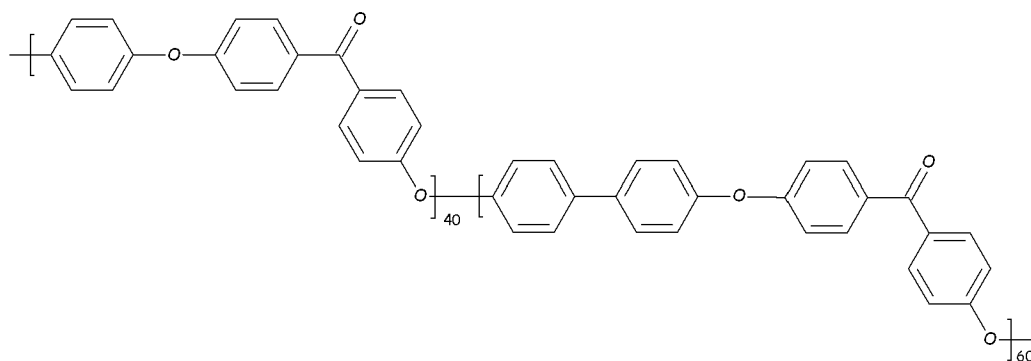
The melt viscosity, measured by capillary rheology at 410°C, 46 s⁻¹ was found to be 0.16 kN-s/m².

[0165] **Example 1 : preparation of PEDEK-PEEK copolymer 60/40**

[0166] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 127.70 g of diphenyl sulfone, 9.894 g of hydroquinone, 25.103 g of 4,4'-biphenol and 50.130 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 25.097 g of Na₂CO₃ and 0.155 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320 °C at 1°C/minute. After 2 minutes at 320°C, 5.892 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.384 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.964 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120°C under vacuum for 12 hours yielding 74 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The melt viscosity, measured by capillary rheology at 410°C, 46 s⁻¹ was found to be 0.18 kN-s/m².

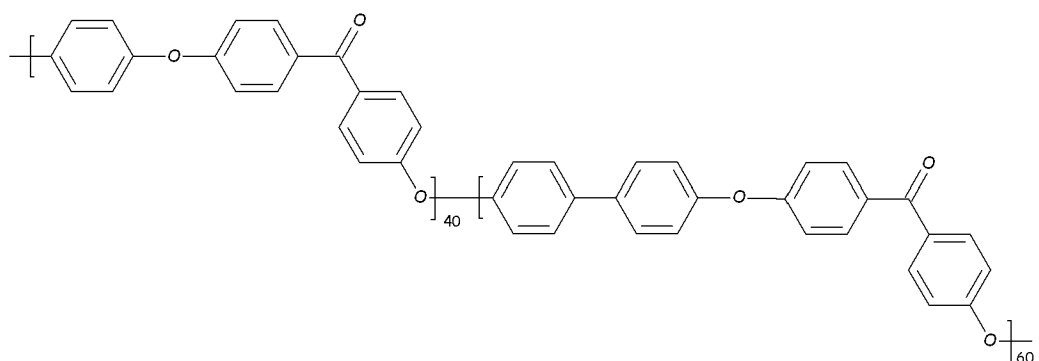
[0167] **Example 2 : preparation of PEDEK-PEEK copolymer 60/40**

[0168] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 127.95 g of diphenyl sulfone, 9.940 g of hydroquinone, 25.138 g of 4,4' biphenol and 50.273 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 24.325 g of Na₂CO₃ and 0.1244 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 320 °C at 1°C/minute. After 2 minutes at 320 °C, 5.892 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.384 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.964 g of 4,4'-difluorobenzophenone were added

to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 74 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The melt viscosity measured by capillary rheology, as above detailed, at 410 °C, 46 s⁻¹ was found to be 1.85 kN-s/m².

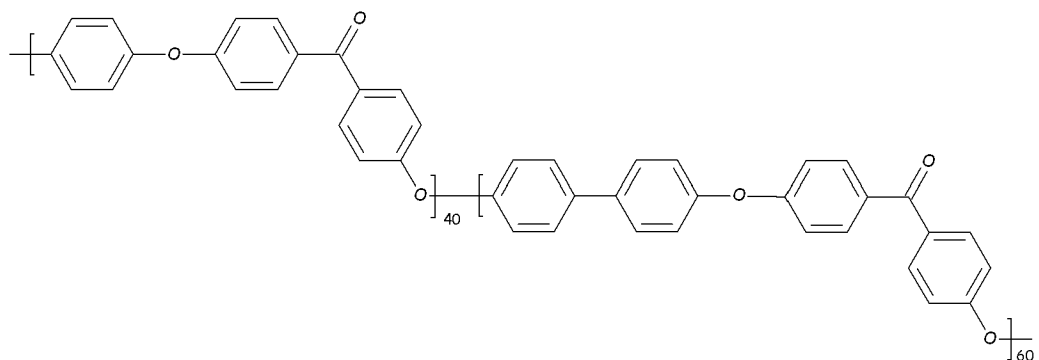
[0169] **Example 3 : preparation of PEDEK-PEEK copolymer 60/40**

[0170] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 145.87 g of diphenyl sulfone, 9.940 g of hydroquinone, 25.138 g of 4,4' biphenol and 49.831 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 24.682 g of Na₂CO₃ and 0.1555 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 340 °C at 1°C/minute. After 20 minutes at 340 °C, 5.892 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After

5 minutes, 0.384 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.964 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 75 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The melt viscosity, measured by capillary rheology as above detailed, at 410 °C, 46 s⁻¹, was found to be 1.89 kN-s/m².

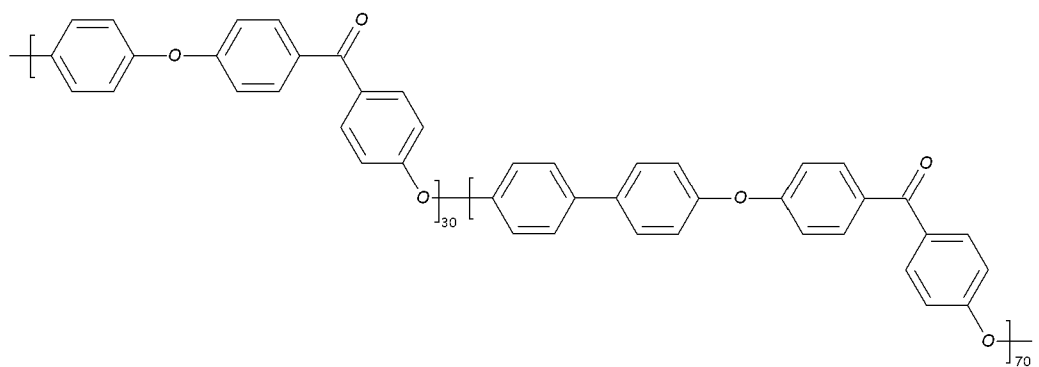
[0171] **Example 4 : preparation of PEDEK-PEEK copolymer 70/30**

[0172] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 145.87 g of diphenyl sulfone, 7.290 g of hydroquinone, 28.676 g of 4,4' biphenol and 48.580 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 24.134 g of Na₂CO₃ and 0.152 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 340 °C at 1°C/minute. After

2 minutes at 340 °C, 5.761 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.375 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.920 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 75 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The melt viscosity measured by capillary rheology, as above detailed, at 410 °C, 46 s⁻¹, was found to be 2.04 kN-s/m².

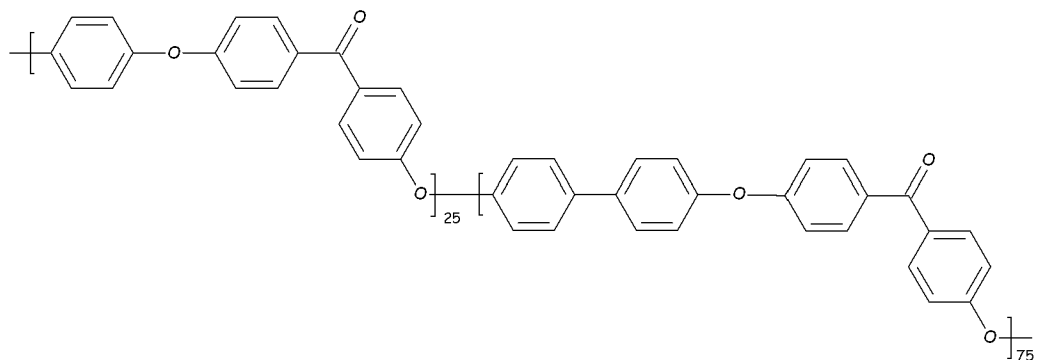
[0173] **Example 5 : preparation of PEDEK-PEEK copolymer 75/25**

[0174] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 212.00 g of diphenyl sulfone, 4.226 g of hydroquinone, 21.442 g of 4,4'-biphenol and 33.853 g of 4,4'-difluorobenzophenone. The flask content was evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 16.812 g of Na₂CO₃ and 0.106 g of K₂CO₃ was added via a powder

dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 340 °C at 1°C/minute. After 7 minutes at 340 °C, 3.928 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.651 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.309 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 53 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The reduced viscosity of the material measured as above detailed was 3.50 dL/g. The melt viscosity measured by capillary rheology, as above detailed, at 410 °C, 46 s⁻¹ was found to be 8.75 kN-s/m². The polymer was found to possess a chlorine content by microcoulometry of 0.7 µeq/g = 25 wtppm Cl.

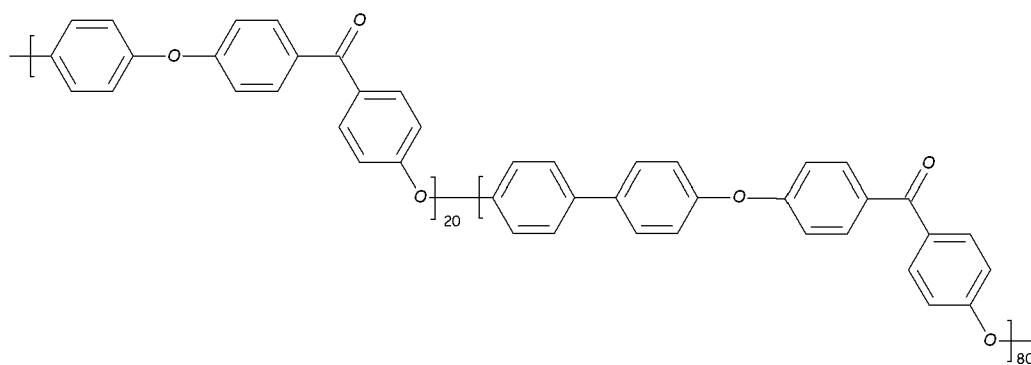
[0175] **Example 6 : preparation of PEDEK-PEEK copolymer 80/20**

[0176] In a 500 mL 4-neck reaction flask fitted with a stirrer, a N₂ inlet tube, a Claisen adapter with a thermocouple plunging in the reaction medium, and a Dean-Stark trap with a condenser and a dry ice trap were introduced 156.09 g of diphenyl sulfone, 3.291 g of hydroquinone, 22.196 g of 4,4'-biphenol and 32.902 g of 4,4'-difluorobenzophenone. The flask content was

evacuated under vacuum and then filled with high purity nitrogen (containing less than 10 ppm O₂). The reaction mixture was then placed under a constant nitrogen purge (60 mL/min).

The reaction mixture was heated slowly to 150 °C. At 150 °C, a mixture of 16.345 g of Na₂CO₃ and 0.103 g of K₂CO₃ was added via a powder dispenser to the reaction mixture over 30 minutes. At the end of the addition, the reaction mixture was heated to 340 °C at 1°C/minute. After 120 minutes at 340 °C, 3.901 g of 4,4'-difluorobenzophenone were added to the reaction mixture while keeping a nitrogen purge on the reactor. After 5 minutes, 0.254 g of lithium chloride were added to the reaction mixture. 10 minutes later, another 1.300 g of 4,4'-difluorobenzophenone were added to the reactor and the reaction mixture was kept at temperature for 15 minutes.

The reactor content was then poured from the reactor into a SS pan and cooled. The solid was broken up and ground in an attrition mill through a 2 mm screen. Diphenyl sulfone and salts were extracted from the mixture with acetone and water at pH between 1 and 12. The powder was then removed from the reactor and dried at 120 °C under vacuum for 12 hours yielding 53 g of a white powder. The structure of the obtained copolymer can be sketched, in terms of repeat units, as follows:



The melt viscosity measured by capillary rheology at 410 °C, 46 s⁻¹, as above detailed, was found to be 5.33 kN-s/m².

[0177] **Assessment of thermal performance of copolymers (PEDEK-PEEK)**

[0178] A 102 mm x 102 mm x 3.2 mm plaque was prepared from each of the copolymers obtained as detailed in examples and comparative examples above by compression molding under conditions matching the melting

temperature of the composition:

For copolymers of examples 0 to 2, the molding conditions were :

1. preheat at 420°C,
2. 420°C/15 minutes, under 2000 kg-f
3. 420°C/2 minutes, under 2700 kg-f
4. cool down to 320°C over 20 minutes, under 2000 kg-f
5. 50 minute-hold at 320°C, under 2000 kg-f
6. 25 minute-cool down to 30°C, under 2000 kg-f.

The plaques so obtained were annealed under air at 275°C for 3 hours.

[0179] For the other copolymers and PAEK polymers of comparison, the temperatures of the steps 2, 3 and 5 were modified as specified in the table herein below :

[0180]

Table 1

Polymer from Example:	T in steps 2 & 3 (°C)	T in step 5 (°C)	Annealing T (°C)
0-2	420	320	275
3-5, F	440	330	275
A	440	No intermediate step 5	None
B-C-G-H	400	No intermediate step 5	None
D-E	420	270	250

[0181] The crystallinity level of specimens taken from plaques of copolymers (PEDEK-PEEK) was determined by DSC (one heat cycle, 20 °C /min up to 450 °C), assuming 130 J/g for 100% crystalline material.

[0182] Rectangular test samples (1.2 cm x 5.1 cm) were prepared from these molded plaques and were dried at 120°C under vacuum for 12 hours.

Said test specimens were then analyzed by Dynamic Mechanical Analysis (DMTA) on a TA ARES G2 rheometer under torsion mode (10 rad/s; 0.05% strain) from 50 to 350°C at 5.0°C/min, in order to measure the storage modulus (G' in Pa) at different temperatures, ranging from 50 up to 310°C, as shown in the following Table and presented in the graph of Figure 2. The data shows that the copolymers (PEDEK-PEEK) of the invention present a better retention of properties at 165°C, as shown by higher percentage values of ratio $G'(165^\circ\text{C})/G'(140^\circ\text{C})$ than PEEK and PEKK or copolymers PEEK-PEDEK with less than 60% moles of PEDEK-type units (Comp. ex D and E). Compositions are endowed with mechanical performances retention with temperature similar to PEK or even superior to PEK (ex. 3-5). The higher retention of properties at higher temperature is unexpected based on the T_g alone (compare Ex. 0 vs Comp. D): while copolymer (PEDEK-PEEK) of Ex. 0, having PEDEK/PEEK molar ratio of 60/40 has substantially similar T_g to copolymer of comparative Ex. D, having PEDEK/PEEK molar ratio of 50/50, this latter copolymer has a much inferior retention of mechanical properties with temperature, showing a $G'(165^\circ\text{C})/G'(140^\circ\text{C})$ percent ratio of only 15 %, which is significantly worse than the outstanding value of 41 % demonstrated by the copolymer of the present invention.

[0183]

Table 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
PEDEK/PEEK (mol/mol)	60/40	60/40	60/40	70/30	75/25	80/20
T_g (°C)	158	163	164	162	173	173
T_m (°C)	365	360	356	381	372	385
RV (dL/g)	1.18	4.20	4.35	1.07	4.85	1.55
MV (kN/m ²)	0.18	1.85	1.89	2.04	8.75	4.41

	6.84	8.82	8.88	6.71	9.08	7.23
Inequality respected	Y	Y	Y	Y	Y	Y
G' (GPa) at 140°C	1.47	1.32		1.34	1.38	1.25
G' (GPa) at 165°C	0.602	0.642		0.948	1.13	0.935
G'(165°C)/ G'(140°C) (%)	41	49	N/A	71	82	75

[0184]

Table 3

	Ex. A	Ex. B	Ex. C	Ex. D	Ex. E	Ex. F	Ex. H
PEDEK/PEEK or nature of polymer	PEK	PEKK -FC	KT- 820P	50/50	40/60	75/25	PEKK -HT
T _g (°C)	159	157	151	159	157	173	157
T _m (°C)	373	341	336	349	336	373	359
RV (dL/g)			1.07	1.25	1.35	3.13	0.93
MV (kN/m ²)	0.31	0.30	1.25	0.32	0.55	>15	0.16
	n.d.	n.d.	n.d.	6.92	7.03	8.32	6.52

Inequality respected				Y	Y	N	Y
G' (GPa) at 140°C	2.19	1.67	1.51	1.21	1.12	n.d.	1.93
G' (GPa) at 165°C	1.16	0.538	0.377	0.186	0.028	n.d.	0.732
G'(165°C)/ G'(140°C) (%)	53	32	25	15	2.5	n.d.	38

[0185] **Evaluation of chemical resistance of compression molded samples**

[0186] The 102 mm x 102 mm x 3.2 mm compression molded plaques of all the copolymers (PEDEK-PEEK) and PAEKs as detailed above were machined into Type V ASTM tensile specimens and these specimens were subjected to tensile testing according to ASTM method D638 at 0.05 inch/minute and at room temperature (i.e. 23°C); results are the average of iterations on 3 specimens. Further, 3 Type V tensile bars of each polymer were exposed to a sweet salt water and hydrocarbon mixture in a 600 mL Inconel pressure vessel (154 mL heptanes + 44 mL cyclohexane + 22 mL toluene + 36 mL aq 15 wt% KCl solution) at 300 °C for 7 days under nitrogen. At the end of this exposure time, the specimens were wiped and the weight after and before exposure were compared. **Tables below** summarize the weight gain, appearance of the bars and mechanical properties measured before and after exposure. EB is the elongation at break; TS_y is the tensile strength at yield and TS_b is the tensile strength at break; EY is the elongation at yield and TM is the tensile modulus. The retention of strength is calculated as follows :

[0187]

$$\% \text{ retention strength} = 100 \times \left(\frac{\text{strength at yield (or at break if no yield) after exposure}}{\text{strength at yield (or at break if no yield) before exposure}} \right).$$

[0188]

Table 4

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
PEDEK/PEEK	60/40	60/40	60/40	70/30	75/25	80/20
T _g (°C)	158	163	164	162	173	173
T _m (°C)	365	360	356	381	372	385
RV (dL/g)	1.18	4.20	4.35	1.07	4.85	1.55
MV (kN/m ²)	0.18	1.85	1.89	2.04	8.75	4.41
% crystallinity plaque	34.0	24.9	20.5	42.0	28.4	35.8
Before exposure						
EB (%)	4.5	2.7	67	2.0	34	19
TS _y (psi)	13400	-	11800	-	12100	12100
TS _b (psi)	13200	9070	11600	8650	12000	7000
EY (%)	4.3	-	4.8	-	6.2	5.3
TM (kpsi)	545	404	382	496	449	385
After exposure						
EB (%)	1.5	2.0	9.9	1.5	20	1.0
TS _y (psi)	-	-	9590	-	9880	-

TS _b (psi)	7560	8460	7680	6880	9810	5280
EY (%)	-	-	3.0	-	21	-
TM (kpsi)	577	519	577	627	500	576
% retention TS	56	93	81	80	82	44
% retention EB	33	74	15	75	59	5
% weight gain (wt%)	6.7	7.1	7.1	5.2	7.3	6.0
Appearance*	○	○	○	○	○	○

[0189] Appearance: ○ = unchanged; ● = discoloured; and/or enbrittled; and/or molten; and/or voids; ◐: some deformation.

[0190]

Table 5

	Ex. A	Ex. B	Ex. C	Ex. D
PEDEK/PEEK or nature	PEK	PEKK-FC	KT-820P	50/50
T _g (°C)	159	157	151	159
T _m (°C)	373	341	336	349
RV (dL/g)				1.25
MV (kN/m ²)	0.31	0.30	1.25	
% crystallinity plaque	48.9	33.6	34.0	27.8
Before exposure				
EB (%)	4.7	3.2	15	6.0

TS _y (psi)	-	-	13700	9320
TS _b (psi)	14300	17200	11800	8730
EY (%)	-	-	5.0	4.9
TM (kpsi)	633	648	540	456
After exposure				
EB (%)	0.4	0.08	17	1.9
TS _y (psi)	-	-	-	-
TS _b (psi)	3280	434	10500	4610
EY (%)	-	-	-	-
TM (kpsi)	846	700	586	491
% retention TS	23	3	77	49
% retention EB	9	3	113	32
% weight gain (wt%)	1.2	3.8	8.3	8.3
Appearance*	○	●	◐	○

[0191] *Apparence: ○ = unchanged; ●= discoloured; and/or enbrittlened; and/or molten; and/or voids; ◐: some deformation.

[0192]

Table 6

	Ex. E	Ex. F	Ex. G	Ex. H
PEDEK/PEEK or nature	40/60	75/25	30/70	PEKK-HT
T _g (°C)	157	173	153	157

T _m (°C)	336	373	296	359
RV (dL/g)	1.35	3.13	0.93	
MV (kN/m ²)		>15.0	0.16	0.93
% crystallinity plaque	26.1	28.0	24.4	40.0
Before exposure				
EB (%)	39	29	12	2.0
TS _y (psi)	11500	12100	12500	-
TS _b (psi)	10900	11800	10400	11500
EY (%)	5.1	5.9	5.1	-
TM (kpsi)	450	470	169	643
After exposure				
EB (%)	4.5	0.61	N/A**	0.26
TS _y (psi)	5200	-	N/A**	-
TS _b (psi)	4450	3150	N/A**	1810
EY (%)	4.3	-	N/A**	-
TM (kpsi)	455	562	N/A**	1070
% retention TS	45	26	N/A**	1.6
% retention EB	12	2	N/A**	13
% weight gain (wt%)	9.1	7.1	N/A**	1.7
Appearance*	●	●	●	●

- [0193] *Apparence: ○ = unchanged; ● = discoloured; and/or enbrittlened; and/or molten; and/or voids; ◐: some deformation; **N/A: determination after exposure were impossible as the specimen has completely molten.
- [0194] The data shows that the copolymers (PEDEK-PEEK) of the invention present a better chemical resistance to the mixture simulating oil extraction muds and fluids than PEK or PEKK FC or HT, as shown by the higher retention of strength and of elongation at break. It also shows that copolymers with a ratio of PEDEK/PEEK units higher than 55/45 exhibit a better chemical resistance than the ones with a ratio of 50/50 or lower (Comp. Ex. D and E and G). The copolymers according to the invention possessing low amount of organic chlorine and possessing ordered structure and narrow molecular weight distribution (so as to comply with the MV vs RV parameters inequality mentioned above) exhibits a higher flow than the copolymers described in **US 4766197** and a better retention of properties after exposure to chemicals (see ex. 4 vs Comp. Ex. F).
- [0195] **Evaluation of thermooxidative stability of compression molded samples**
- [0196] 2 compression molded Type V tensile bars of each sample were exposed to air at 300 °C for 500 h and the tensile properties measured after exposure. Results are summarized in the Table below.
- [0197]

Table 7

	Ex. 1	Comp. Ex A (PEK)	Comp. Ex. B (PEKK FC)
PEDEK/PEEK	60/40		
Tg (°C)	158	159	157
Tm (°C)	365	373	341
MV (kN/m ²)	0.18	0.31	0.30
Unexposed bars			

% crystallinity plaque	34.0	48.9	31.4
EB (%)	4.5	6.7	3.2
TS _y (psi)	13400	17044	17044
TS _b (psi)	13200	16117	16
EY (%)	4.3	6.3	-
TM (kpsi)	545	648	648
Exposed bars			
EB (%)	5.2	5.4	3.4
TS _y (psi)	14951	-	
TS _b (psi)	14900	17300	15800
EY (%)	5.4	-	-
TM (kpsi)	511	623	541
% retention strength	111	102	93
% retention elongation at break	121	80	106

[0198] The data shows that the copolymers (PEDEK-PEEK) of the invention maintain their mechanical properties after exposure to air.

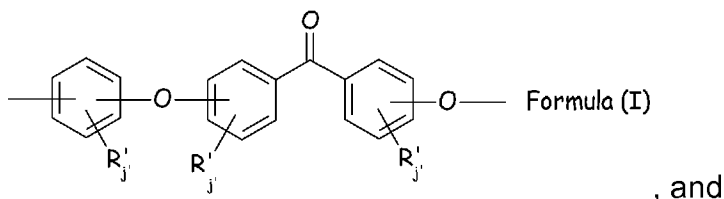
[0199] Overall, the data shows that the copolymers (PEDEK-PEEK) present a higher thermal performance than PEEK or PEKK FC (higher $G'(165^{\circ}\text{C})/G'(140^{\circ}\text{C})$ ratio) and a better chemical resistance in oil and gas applications than PEK or PEKK FC or HT, offering a unique combination of properties, solely when the molar ratio PEDEK/PEEK is higher than 55/45 and when the structure is sufficiently ordered and deprived of spurious end groups, as required in the claimed materials.

- [0200] This unique combination of properties is particularly advantageous to the aim of using these materials for the manufacture of parts used in devices intended for Oil & gas exploration and extraction.
- [0201] 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.

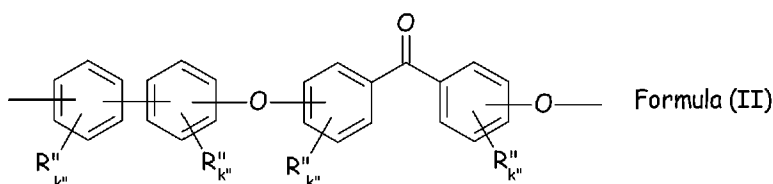
Claims

Claim 1. A polyaryl ether ketone copolymer [copolymer (PEDEK-PEEK)] comprising:

- recurring units (R_{PEEK}) of formula (I):



- recurring units (R_{PEDEK}) of formula (II):



wherein in above

formulae (I) and (II), each of R' and R'' , equal to or different from each other, is independently selected at each occurrence from a C_1 - C_{12} group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of j' and k'' , equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4; wherein the said recurring units are comprised in a molar ratio (R_{PEEK}):(R_{PEDEK}) of 45:55 to 15:85, and

wherein the said copolymer (PEDEK/PEEK):

(j) comprises an amount of chemically bound chlorine of less than 2.0 $\mu\text{eq/g}$, as determined by microcoulometry, and

(jj) possesses a narrow molecular weight distribution such that the following inequality is satisfied:

$$MV \left(\frac{\text{kN}}{\text{m}^2} \right) \leq 6.62 \cdot \left[RV \left(\frac{\text{dl}}{\text{g}} \right) \right]^{0.20}$$

Math. 15

wherein:

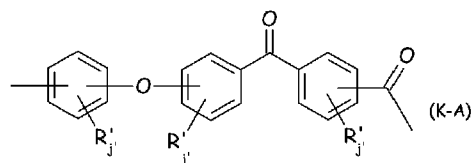
- MV is the melt viscosity measured pursuant to ASTM D3835 standard at 410°C and at a shear rate of 46.3 sec^{-1} , using a conical die having a diameter of 1.016 mm a length of 20.32 mm and a cone angle of 120°C and expressed

in kN/m²; and

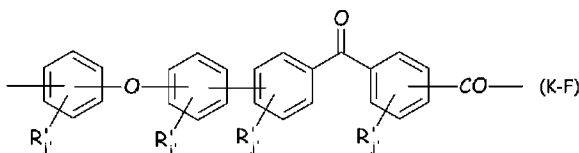
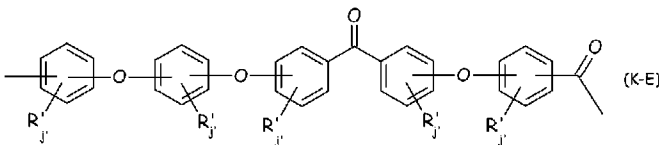
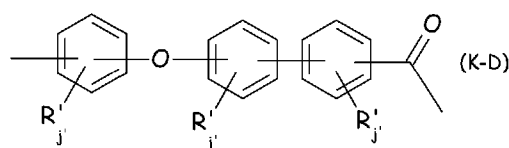
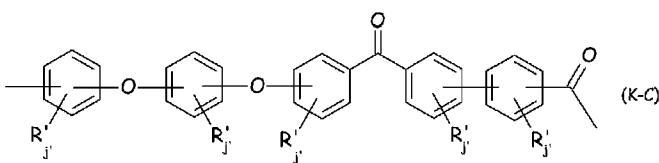
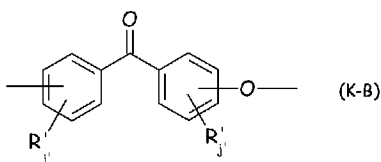
- RV is the reduced viscosity measured pursuant to ASTM D2857 standard at 25°C on 1.0 wt/vol % solution in concentrated H₂SO₄ (96 wt%) and expressed in dl/g.

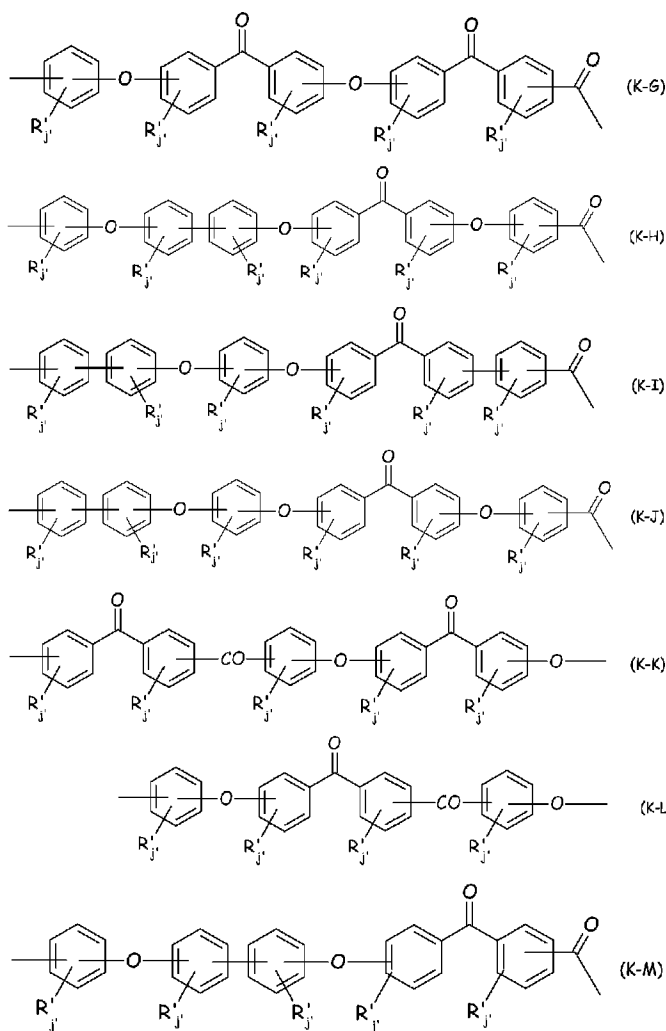
Claim 2. The copolymer (PEDEK/PEEK) of claim 1, comprising recurring units (R_{PEEK}) and (R_{PEDEK}) in molar ratio (R_{PEEK}):(R_{PEDEK}) of 44:56 to 16:84, more preferably of 43:57 to 17:83, and even more preferably of 42:58 to 18:82, and most preferably of 40:60 to 20:80.

Claim 3. The copolymer (PEDEK/PEEK) of claim 1 or 2, said copolymer additionally comprising recurring units (R_{PAEK}) different from recurring units (R_{PEEK}) and (R_{PEDEK}), wherein the amount of recurring units (R_{PAEK}) is preferably comprised between 0 and 5 % moles, with respect to the total number of moles of recurring units of copolymer (PEDEK/PEEK), and/or wherein said recurring units (R_{PAEK}) preferably comply with any of the following



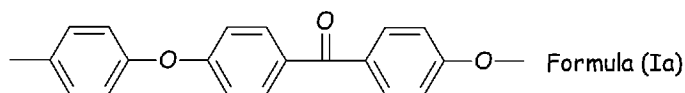
formulae (K-A) to (K-M) herein below:





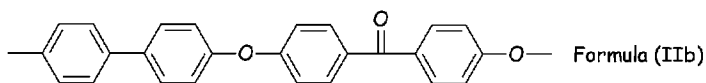
wherein in each of formulae (K-A) to (K-M) above, each of R', equal to or different from each other, is independently selected at each occurrence from from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; and each of j', equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, preferably j' being equal to zero.

Claim 4. The copolymer (PEDEK/PEEK) of anyone of the preceding claims, wherein in recurring units (R_{PEEK}) of formula (I), the connections among phenyl groups are generally in the para positions of each of the phenyl rings and/or each of j' is zero, and preferably wherein recurring units (R_{PEEK}) comply with



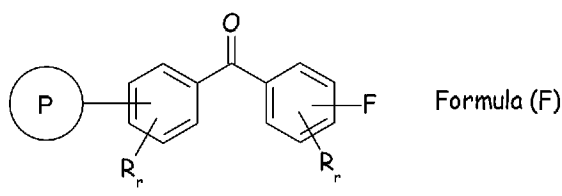
formula (Ia):

Claim 5. The copolymer (PEDEK/PEEK) of anyone of the preceding claims, wherein in recurring units (R_{PEDEK}) of formula (II), the connections among phenyl groups are generally in the para positions of each of the phenyl rings and/or each of k'' is zero, and preferably wherein recurring units (R_{PEDEK}) comply with formula (IIa):

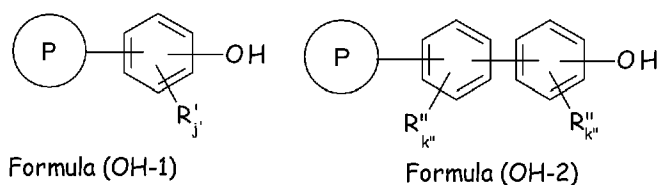


Claim 6. The copolymer (PEDEK/PEEK) of anyone of the preceding claims, said copolymer comprising a major amount of end groups selected from the group consisting of:

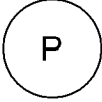
- benzo-phenone fluoride groups of formula:



- hydroxyl-containing groups of formula (OH-1) or (OH-2) or salified groups thereof:



wherein in each of formulae (F), (OH-1) and (OH-2), R , R' , R''' , r , j' and k'' have the meanings as

defined in Claim 1, and wherein the symbol  is intended to denote the polymer chain comprising recurring units (R_{PEEK}) and (R_{PEDEK}), and wherein end groups of formulae (F), (OH-1) and (OH-2) preferably represent at more than 50 % moles, preferably at least 60 % moles, even more preferably at least 70 % moles, still more preferably at least 80 % moles, with respect to the total moles of end groups of the copolymer (PEDEK/PEEK).

Claim 7. The copolymer (PEDEK/PEEK) of anyone of the preceding claims, possessing a narrow molecular weight distribution such that the following inequality is satisfied:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.60 \left[RV\left(\frac{\text{dl}}{\text{g}}\right) \right]^{0.20}$$

Math. 16

preferably the following inequality:

$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.50 \left[RV\left(\frac{\text{dl}}{\text{g}}\right) \right]^{0.20}$$

Math. 17

more preferably the following inequality:

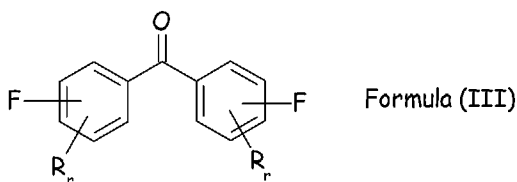
$$MV\left(\frac{\text{kN}}{\text{m}^2}\right) \leq 6.40 \left[RV\left(\frac{\text{dl}}{\text{g}}\right) \right]^{0.20}$$

Math. 18

wherein:

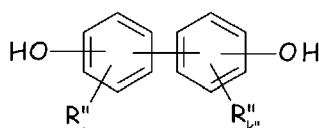
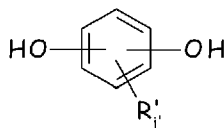
- MV is the melt viscosity measured pursuant to ASTM D3835 standard at 410°C and at a shear rate of 46.3 sec⁻¹, using a conical die having a diameter of 1.016 mm a length of 20.32 mm and a cone angle of 120°C and expressed in kN/m²; and
- RV is the reduced viscosity measured pursuant to ASTM D2857 standard at 25°C on 1.0 wt/vol % solution in concentrated H₂SO₄ (96 wt%) and expressed in dl/g.

Claim 8. A method of making the copolymer (PEDEK/PEEK) according to anyone of the preceding claims, comprising reacting at least one difluoro-derivative of formula (III):



with a mixture of di-hydroxyderivatives of

formulae (IV) and (V):



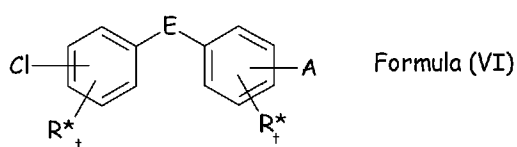
in a molar ratio (IV):(V) of of 45:55

to 15:85,

wherein in above formulae (III), (IV) and (V), each of R, R' and R'', equal to or different from each other, is independently selected at each occurrence from a

C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of r, j' and k", equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4,

in a polar organic solvent in the presence of a mixture of Na₂CO₃ and K₂CO₃, in a molar ratio Na/K of more than 45 mol/mol, and wherein the method possibly include adding a step of adding a chlorinated compound of formula (VI):



wherein –E– is a

sulfone group of formula –SO₂– or a ketone group of formula –C(O)–, A is selected from Cl, F and H, each of R*, equal to or different from each other, is independently selected at each occurrence from a C₁-C₁₂ group optionally comprising one or more than one heteroatoms; sulfonic acid and sulfonate groups; phosphonic acid and phosphonate groups; amine and quaternary ammonium groups; each of t, equal to or different from each other, is independently selected at each occurrence from 0 and an integer of 1 to 4, with the proviso that if said chlorinated compound of formula (IV) is added, its amount is of no more than 1 % moles with respect to the total molar amount of monomers of formula (III), (IV) and (V).

Claim 9. The method of claim 8, wherein Na₂CO₃ and K₂CO₃ are used in an amount such that the ratio between the total amount in moles of said Na₂CO₃ and K₂CO₃ and the total amount in moles of hydroxyl-monomers of formulae (IV) and (V), i.e. the molar ratio:

$$\frac{n_{\text{Na}_2\text{CO}_3} + n_{\text{K}_2\text{CO}_3}}{n_{\text{(IV)}} + n_{\text{(V)}}}$$

Math. 19

is of at least 0.95, preferably at least 0.99, more preferably at least 1.00 mol/mol and/or at most 1.20, preferably at most 1.10, more preferably at most 1.06 mol/mol.

Claim 10. The method of claim 8 or 9, wherein monomer (III) is 4,4'-difluorobenzophenone (DFBP), and/or wherein monomer (IV) is hydroquinone and/or wherein monomer (V) is 4,4'-dihydroxybiphenyl.

Claim 11. The method of anyone of claims 8 to 10, wherein monomers (III), (IV) and (V) are reacted in such an amount that the ratio between the molar amount of difluoro-monomer of formula (III) and the total molar amount of hydroxyl-monomers of formulae (IV) and (V), i.e. the molar ratio:

$$\frac{n_{\text{difluoro-monomer(III)}}}{n_{\text{hydroxyl-monomer(IV)}} + n_{\text{hydroxyl-monomer(V)}}$$

Math. 20

is of at least 0.95, preferably at least 0.99 mol/mol and/or of at most 1.05, preferably at most 1.03 mol/mol.

Claim 12. A composition (C) comprising the copolymer (PEDEK/PEEK) of anyone of claims 1 to 7, at least one reinforcing filler and optionally one or more than one additional ingredient (I) different from the reinforcing filler and from the copolymer (PEDEK/PEEK), generally selected from the group consisting of (i) colorants such as notably a dye (ii) pigments such as notably titanium dioxide, zinc sulfide and zinc oxide (iii) light stabilizers, e.g. UV stabilizers (iv) heat stabilizers (v) antioxidants such as notably organic phosphites and phosphonites, (vi) acid scavengers (vii) processing aids (viii) nucleating agents (ix) internal lubricants and/or external lubricants (x) flame retardants (xi) smoke-suppressing agents (x) anti-static agents (xi) anti-blocking agents (xii) conductivity additives such as notably carbon black and carbon nanofibrils (xiii) plasticizers (xiv) flow modifiers (xv) extenders (xvi) metal deactivators and combinations comprising one or more of the foregoing additives.

Claim 13. A shaped article comprising the copolymer (PEDEK/PEEK) of anyone of claims 1 to 7 and/or the composition (C) of claim 12, said shaped article being preferably a substantially bidimensional article, such as a film or a sheet.

Claim 14. An oil & gas recovery article comprising at least a part made from the copolymer (PEDEK/PEEK) of anyone of claims 1 to 7 or from the composition (C) of claim 12.

Claim 15. A method for recovering oil and/or gas including using at least one oil and gas recovery article according to Claim 14.

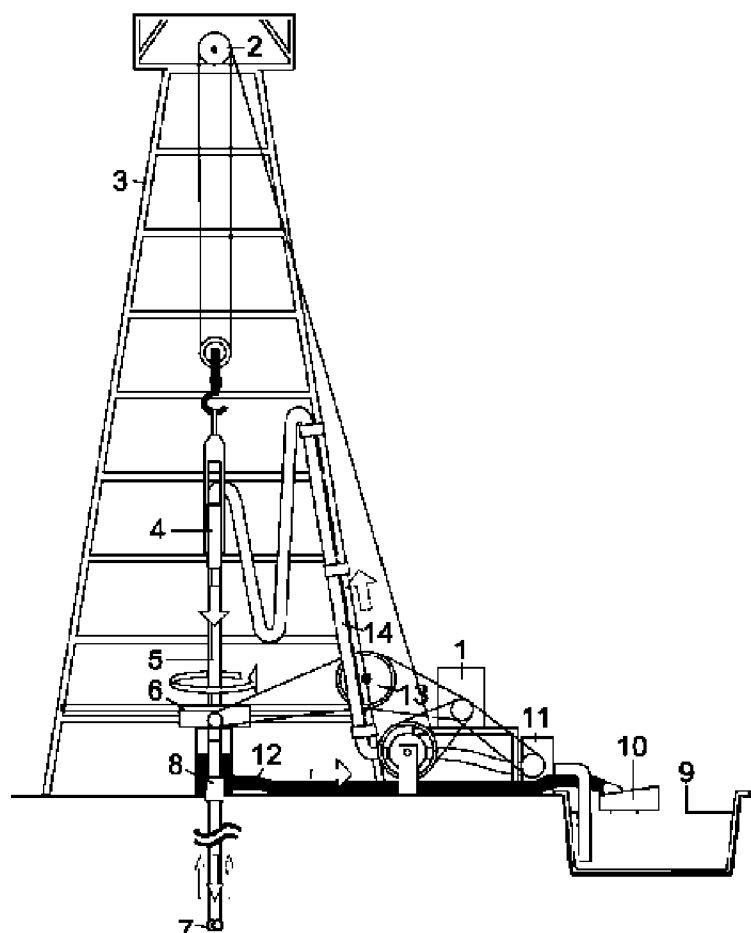


Fig. 1

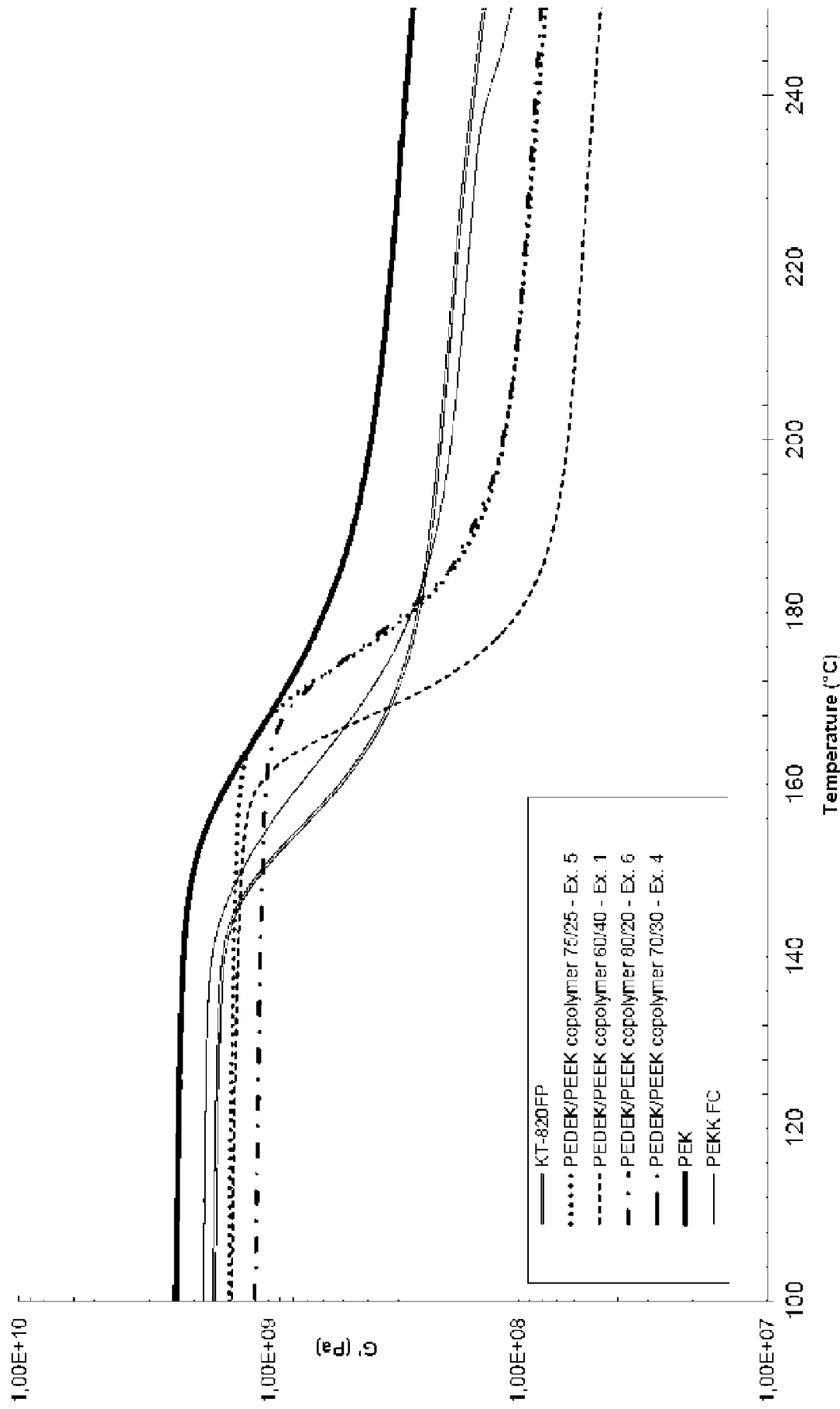


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077131

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G65/40
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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 766 197 A (CLENDINNING ROBERT A [US] ET AL) 23 August 1988 (1988-08-23) cited in the application example 3	1-14
Y	----- WO 2009/021918 A1 (SOLVAY ADVANCED POLYMERS LLC [US]; LOUIS CHANTAL [US]; SRINIVASAN SATC) 19 February 2009 (2009-02-19) examples 1-3 claim 2 page 4, line 24 - page 5, line 3	1-14
A	----- WO 2016/156825 A1 (VICTREX MFG LTD [GB]) 6 October 2016 (2016-10-06) example 1 claims 1-31 ----- -/-	15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent 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

22 November 2017

Date of mailing of the international search report

30/11/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Popescu, Teodora

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077131

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/001327 A1 (VICTREX MFG LTD [GB]) 8 January 2015 (2015-01-08) claims 1-30 examples 1-15 -----	15
A	BENNETT G S ET AL: "THE SYNTHESIS AND CHARACTERIZATION OF NOVEL THERMOTROPIC LIQUID CRYSTALLINE POLY(ARYL ETHER KETONE)S", POLYMER ENGINEERING AND SCIENCE, BROOKFIELD CENTER, US, vol. 34, no. 10, 1 May 1994 (1994-05-01), pages 781-793, XP000498378, ISSN: 0032-3888, DOI: 10.1002/PEN.760341002 figure 1 -----	1-14
A	WO 2016/042492 A2 (GHARDA CHEMICALS LTD [IN]) 24 March 2016 (2016-03-24) cited in the application claims 1-10 tables 1-3 examples 1-14 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/077131

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 4766197	A	23-08-1988	JP	S63150322 A		23-06-1988
			US	4766197 A		23-08-1988

WO 2009021918	A1	19-02-2009	CN	101809063 A		18-08-2010
			EP	2178946 A1		28-04-2010
			TW	200922970 A		01-06-2009
			US	2011224399 A1		15-09-2011
			US	2014163192 A1		12-06-2014
			WO	2009021918 A1		19-02-2009

WO 2016156825	A1	06-10-2016	GB	2538848 A		30-11-2016
			WO	2016156825 A1		06-10-2016

WO 2015001327	A1	08-01-2015	EP	3016992 A1		11-05-2016
			GB	2517578 A		25-02-2015
			US	2016177031 A1		23-06-2016
			WO	2015001327 A1		08-01-2015

WO 2016042492	A2	24-03-2016	CN	107108826 A		29-08-2017
			EP	3194460 A2		26-07-2017
			US	2017190835 A1		06-07-2017
			WO	2016042492 A2		24-03-2016
