

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 November 2007 (15.11.2007)

PCT

(10) International Publication Number
WO 2007/128137 A1

(51) International Patent Classification:

C07C 321/30 (2006.01) *C07D 213/50* (2006.01)
C07C 317/14 (2006.01) *C07D 271/10* (2006.01)

(21) International Application Number:

PCT/CA2007/000850

(22) International Filing Date: 3 May 2007 (03.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/798,182 8 May 2006 (08.05.2006) US

(71) Applicant (for all designated States except US): NATIONAL RESEARCH COUNCIL OF CANADA [CA/CA]; 1200 Montreal Road, Ottawa, Ontario K1A 0R6 (CA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LI, Zhao [CA/CA]; 361 King Street West, Apt. B, Cobourg, Ontario K9A 2N6 (CA). DING, Jianfu [CA/CA]; 1413 Forest Valley Drive, Ottawa, Ontario K1C 5M8 (CA). GUIVER, Michael [CA/CA]; 410 Byron Avenue, Ottawa, Ontario K1Z 6Z3 (CA).

(74) Agent: KOENIG, Hans; National Research Council of Canada, Intellectual Property Services Office, 1200 Montreal Road, EG-12, Bldg. M-58, Ottawa, Ontario K1A 0R6 (CA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLY(ARYLENE ETHER)S WITH GRAFTING CAPABILITY FROM A BISPHENOL OR BISTHIOPHENOL MONOMER

(57) Abstract: A monomer of formula (I) may be used to prepare a poly(arylene ether) of formula (II) wherein k is 1 or 2, n is a non-zero number from 0 to 1, j is 0, 1 or 2, Q is O or S, L is a leaving group, Z is F or Cl, Z' is F, Cl or an organic group, and R is hydrogen or an organic moiety. Such poly(arylene ether)s are useful as membrane materials, for example for gas separation, water desalination, and proton exchange membranes in fuel cells.



WO 2007/128137 A1

POLY(ARYLENE ETHER)s WITH GRAFTING CAPABILITY FROM A
BISPHENOL OR BISTHIOPHENOL MONOMER

Cross-reference to Related Applications

[0001] This application claims the benefit of United States provisional patent application USSN 60/798,182 filed May 8, 2006, the entire disclosure of which is herein incorporated by reference.

Field of the Invention

[0002] The present invention relates to poly(arylene ether)s with grafting capability and to monomers for preparing such poly(arylene ether)s.

Background of the Invention

[0003] As a class of high-performance engineering thermoplastic materials, poly(arylene ether)s have high glass transition temperature, high thermal stability, good mechanical properties and excellent resistance to hydrolysis and oxidation.¹ However, for some special applications, the modification of the polymer structure is frequently required in order to obtain desired properties. One objective of structure modification is to alter their chemical structure to some degree without sacrificing their excellent physical and other properties. Functionalized poly(arylene ether)s may find many applications as membrane materials for gas separation, water desalination, and more recently, for fuel cells as proton exchange membrane.²

[0004] Generally, there are two methods to functionalize poly(arylene ether) polymers. One is to chemically modify the preformed polymer after polymerization, sometimes called post-polymerization modification. Another is to use a functionalized monomer to prepare the polymer via direct copolymerization. Both methods have advantages and disadvantages. For example, the first method can lead to polymer degradation or crosslinking during the reaction. The second method may require a tedious approach for monomer synthesis.

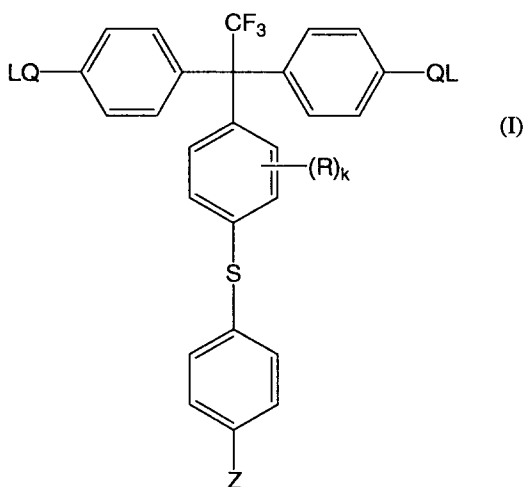
[0005] Until now, there have been few reports about the synthesis of poly(arylene ether)s with pendant activated aromatic fluorine atoms. One post-

polymerization method is to first react polysulfone with butyl lithium, then react the lithiated polysulfone with 4-fluorobenzoic acid chloride to introduce 4-fluorobenzoyl side chains to polymer main chain.^{3, 4} However, while this method is convenient, it requires stringent reaction conditions (strong basic, low temperature). This method only can be used for poly(sulfone), which is not practical for other poly(arylene ether)s. and the degree of substitution can not always be precisely controlled because of the different reactivities of electrophiles with the activated lithiated polymer. Recently, a divergent approach with an activation/condensation sequence was developed.^{5, 6} The reported monomers contain either one tertiary carbon connected with four phenyl or three phenyl and one methyl groups, which may show limited stability, especially in the presence of a strong acid.⁷

[0006] There remains a need in the art for new poly(arylene ether)s, monomers for their synthesis and methods for their synthesis.

Summary of the Invention

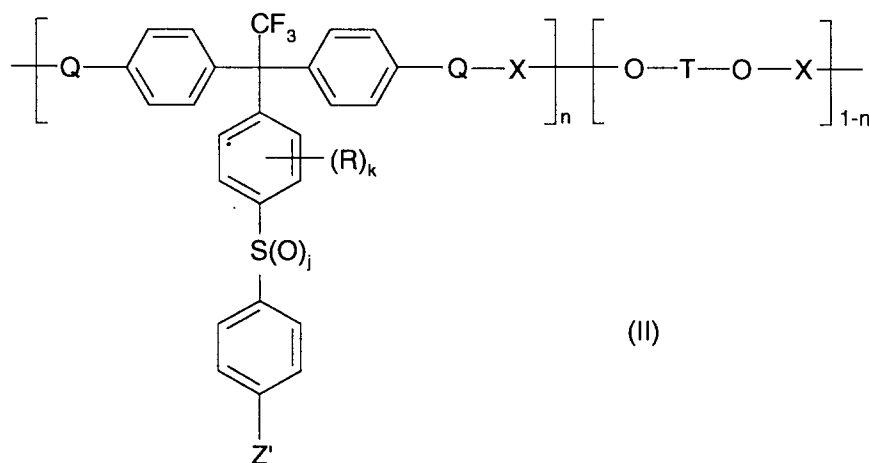
[0007] There is provided a compound of formula (I):



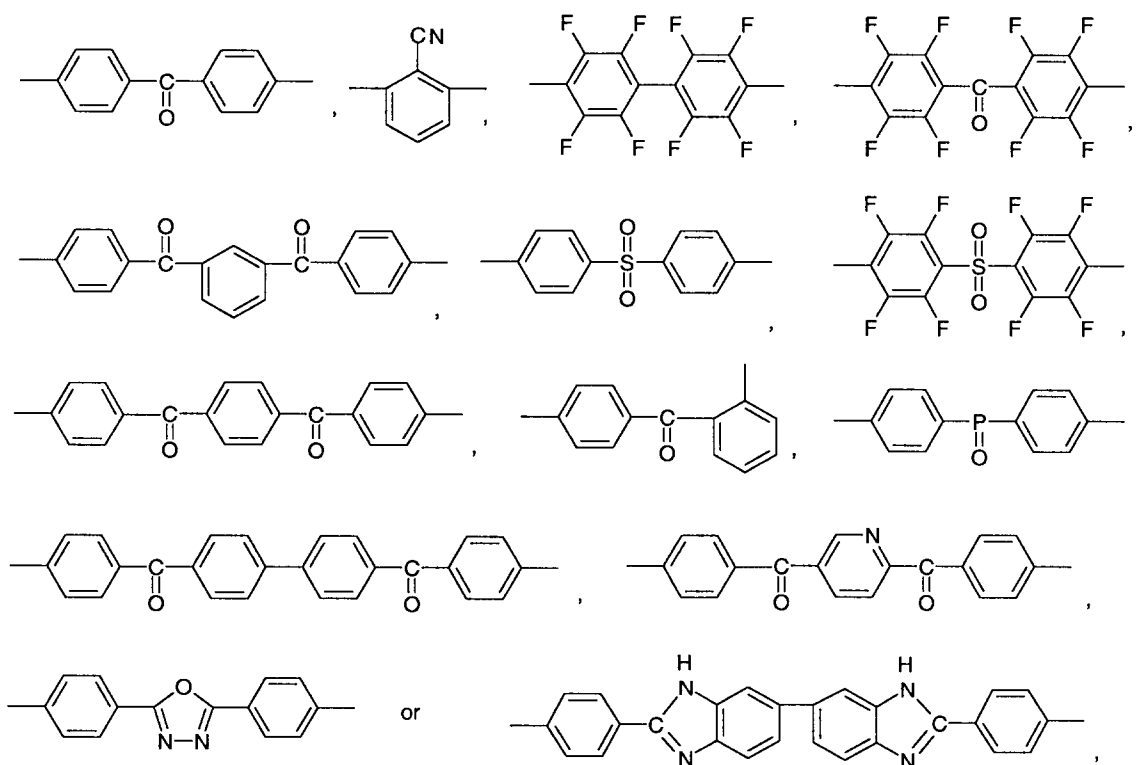
wherein: k is 1 or 2; Q is O or S; L is a leaving group; Z is F or Cl; and, R is hydrogen or an organic moiety. L is preferably hydrogen, halogen, tosylate, brosylate, mesylate or triflate. L is more preferably hydrogen. Q is preferably O. Z is preferably F. The organic moiety may be the same or different and may be, for example, substituted or unsubstituted C₁-C₈ alkyl, C₆-C₁₈ aryl, C₇-C₂₆ aralkyl, C₇-C₂₆ alkaryl, C₁-C₈ alkoxy, C₆-C₁₈ aryloxy groups. The organic moiety may be

substituted by one or more substituents, for example, halogens (e.g. F, Cl, Br, I), amines, amides, hydroxyl. The organic moiety may be, for example, methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, trifluoromethyl, phenyl, methoxy, phenoxy. In one aspect, the organic moiety may be unsubstituted C₁-C₈ alkyl groups (e.g. methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl groups). R is preferably hydrogen.

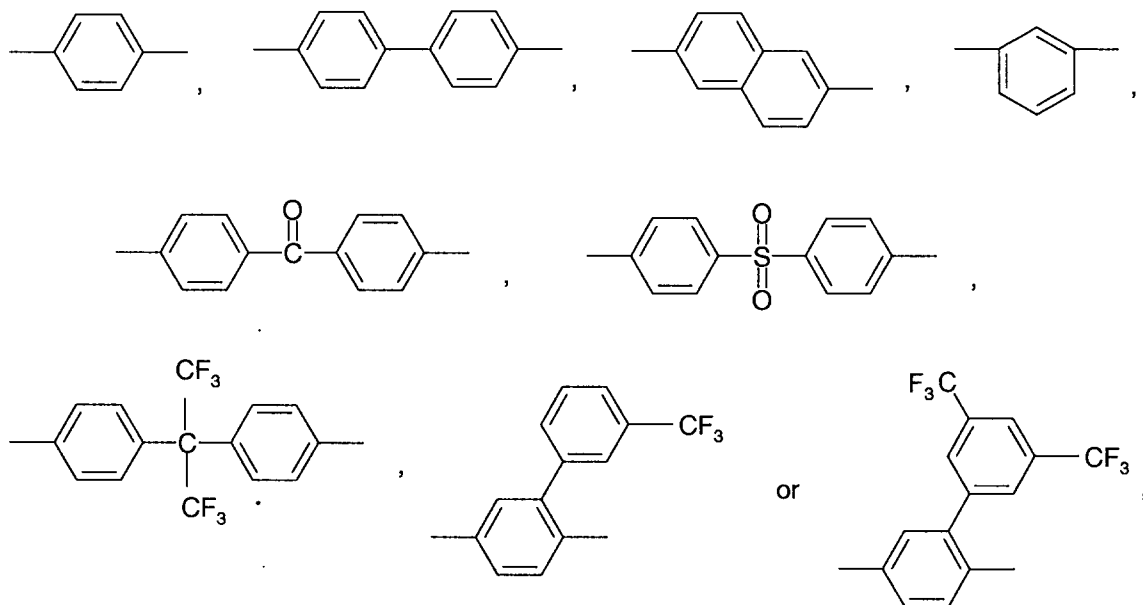
[0008] There is further provided a compound of formula (II):



wherein X is



T is



n is a non-zero number from 0 to 1, j is 0, 1 or 2, Z' is F, Cl or an organic group, and Q, R, and k are as defined above. The organic group may be, for example, a residue of a phenol or thiophenol. The organic group may have various lengths and may contain one or more functional groups. For example, the organic group may be a small molecule (e.g. having 1-100 carbon atoms), an oligomer (e.g. having 2-10,000 carbon atoms and having 2-100 repeating units) or a polymer (e.g. having over 100 repeating units). The organic group may contain one or more functional groups. In one embodiment, the functional group may be a sulfonic acid. In one embodiment, the organic group is a residue of 1-naphthyl-3,6-disulfonic acid sodium salt.

[0009] Compounds of formula (I) and (II) may be prepared as shown in Scheme 1. Compounds of formula (I) are monomers that may be used in the preparation of polymers, for example poly(arylene ether)s of formula (II).

[0010] With reference to Scheme 1, compounds of formula (I) may be prepared as follows. First, a trifluoroacetophenone (III) is reacted with a substituted thiophenol (IV) under mild conditions to form a sulfide (V). The first step is preferably conducted in the presence of an alkali carbonate (e.g. potassium carbonate or sodium carbonate), in a solvent (e.g. dimethyl acetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO) or N-

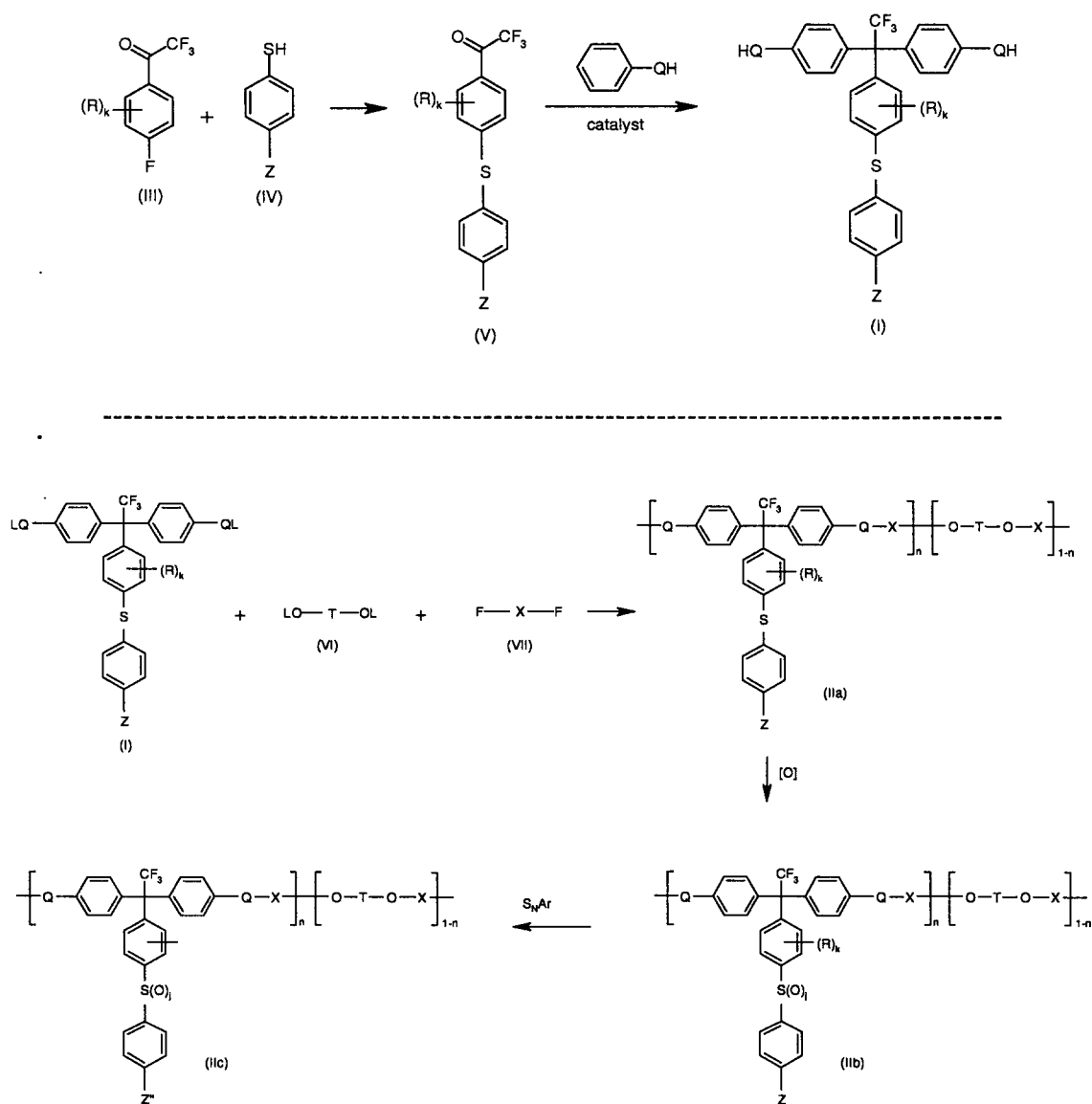
methyldipyrrolidinone (NMP)) and at an elevated temperature (e.g. 40-80 °C). Second, the sulfide (V) is condensed with two moles of phenol or thiophenol in the presence of a catalyst (e.g. triflic acid) to yield the compound of formula (I) where L is hydrogen. The second step is preferably conducted at an elevated temperature (e.g. 30-60 °C). Z, Q, R and k are as defined above. The hydrogen may then be replaced, if desired, with a different leaving group by well known reactions in the art. For example, reaction of the compound of formula (I) where L is hydrogen with tosyl chloride yields the compound of formula (I) where L is tosylate.

[0011] With reference to Scheme 1, compounds (IIa), (IIb) and (IIc) are embodiments of compound (II). A compound of formula (IIa) may be prepared by reacting a compound of formula (I) with a bisphenol (VI) and a bifluorinated arylene compound (VII). This reaction is preferably performed in a solvent (e.g. DMAc, DMF, DMSO, NMP or its mixture with toluene) at an elevated temperature (e.g. 100-165 °C) for a period of several hours (e.g. up to 5 hours). Molar percentage of pendant 4-fluoro- or 4-chlorophenyl sulfide side groups in the resulting polymer of formula (II) can be controlled by controlling the feed ratios of the bisphenol (VI) and bifluorinated arylene compound (VII). Thus in turn can be used to control the ratio of grafting to non-grafting sites in the resulting polymer.

[0012] Still with reference to Scheme 1, compounds of formula (IIb) may be prepared by subsequent oxidation of the sulfide. Any suitable oxidizing agent may be used, for example Oxone[®] (potassium peroxymonosulfate) or hydrogen peroxide. The oxidation is preferably performed in a solvent (e.g. chloroform or formic acid) at elevated temperatures.

[0013] Still with reference to Scheme 1, compounds of formula (IIc) (i.e. graft polymers) wherein Z' is an organic group may be prepared from compounds of formula (IIb) by an S_NAr reaction. The labile Z group in compounds of formula (IIb) is replaced by the organic group (Z') resulting in a polymer having the Z' group grafted thereon. Such reaction may be accomplished, for example, by reaction with a phenol or thiol, preferably in the presence of an alkali carbonate (e.g. potassium carbonate or sodium carbonate), in a solvent (e.g. DMAc, DMF, DMSO, NMP or its mixture with toluene) at an elevated temperature (e.g. 100-165

°C) for a period of many hours (e.g. up to 24 hours). Z, Q, L, R, T, X, n, and k are as defined above. In compounds of formula (IIb) and (IIc), j is 1 or 2.



Scheme 1: Synthesis of Monomers and Polymers

[0014] Polymers of formula (II) are useful as membrane materials, for example for gas separation, water desalination, and proton exchange membranes in fuel cells.

[0015] Bisphenol or bisthiophenol monomers (compounds of formula (I)) of the present invention are advantageously chemically stable and contain a masked grafting site making them useful for preparing a wide variety of thermally and chemically stable poly(arylene ether)s, which when 'unmasked', can be converted

to graft polymers. Poly(arylene ether) copolymers (compounds of formula (IIa)) of the present invention prepared from such monomers advantageously have high molecular weight with excellent thermal stability. By oxidizing the sulfide group to a sulfoxide or sulfone group in the short pendant chain of these copolymers, they can be activated for S_NAr reaction. The fluorine (or chlorine) atoms on the pendant groups of the polymer chains can be replaced with an organic group. This approach advantageously provides a novel methodology for the preparation of chemically and thermally stable functional poly(arylene ether) polymers with flexible graft side-chains.

[0016] Further features of the invention will be described or will become apparent in the course of the following detailed description.

Brief Description of the Drawings

[0017] In order that the invention may be more clearly understood, embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

[0018] Fig. 1 is a graph of GPC curves of (A) PAESf-T-10, (B) after oxidation using Oxone[®] for 16 h in reflux chloroform, and (C) after oxidation using H_2O_2 ;

[0019] Fig. 2 is ^1H NMR spectra of polymers (A) PAESf-T-100, and (B) PAESf-S -100 (see Scheme 3 for proton labels);

[0020] Fig. 3 are ^{19}F NMR spectra of copolymers (A) PAESf-T-67, and (B) PAESf-S-67 (see Scheme 3 for labels);

[0021] Fig. 4 are ^{13}C NMR spectra of homopolymers (A) PAESf-T-100, and (B) PAESf-S-100;

[0022] Fig. 5 is a ^1H - ^{13}C HSQC spectrum of polymer PAESf-S-100;

[0023] Fig. 6 is a ^1H - ^{13}C HMBC spectrum of polymer PAESf-S -100;

[0024] Fig. 7 is a graph depicting the relationship between T_g and pendant group content X;

[0025] Fig. 8 is a graph depicting the relationship between 5% weight loss temperature and pendant group content X; and,

[0026] Fig. 9 is a graph of temperature dependence of the proton conductivity of PEASf-SS-80 and Nafion[®]-117 at 100% RH.

Description of Preferred Embodiments

[0027] Methods and Materials

[0028] *Measurements:*

[0029] The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector. THF was used as eluant and the μ -Styragel columns were calibrated by polystyrene standards. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) using a TA instruments DSC 2920 at heating rate of 10 °C/min, calibrated with melting transition of indium. The reported data were taken from the second heating scan. The thermal gravimetric analysis (TGA) was performed using a TA instruments TGA 2950 at heating rate of 20 °C/min under a nitrogen atmosphere (60 mL/min). MS data was obtained using a Prince capillary electrophoresis system coupled to an API3000 mass spectrometer via a microspray interface. A sheath solution of 1 μ L/min isopropanol/methanol (2:1) was used, with 30 mM ammonium acetate dichloromethane/methanol (3:1) as the running buffer.

[0030] NMR spectra were recorded in DMSO-d₆ using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for ¹H, 376.29 MHz for ¹⁹F and 100.58 MHz for ¹³C. ¹H and ¹⁹F NMR and 2D spectra were obtained using a 5 mm indirect detection probe. A 5 mm broadband probe was used for acquiring 1D ¹³C NMR spectra. CFC1₃ was used as an internal standard (0 ppm) for the ¹⁹F NMR measurements. Signals from DMSO-d₆ were used as the reference for ¹H (2.50 ppm) and ¹³C NMR (39.43 ppm) measurement. The 2D ¹H-¹H correlated spectroscopy (COSY), ¹H-¹³C heteronuclear single quantum coherence (HSQC) and ¹H-¹³C heteronuclear multiple bond correlation (HMBC) spectra were

recorded to assist assignment of all NMR signals. Coupling constants of $^1J_{\text{CH}} = 150$ Hz and $^3J_{\text{CH}} = 7.5$ Hz were used for HSQC and HMBC experiment.

[0031] *Materials:*

[0032] Hexafluorobisphenol A (6F-BPA), 4, 4'-difluorodiphenyl sulfone (DFS), anhydrous dimethyl acetamide (DMAc), 1-Naphthol-3,6-disulfonic acid disodium salt (N36DS) were purchased from Sigma-Aldrich Ltd. 6F-BPA and DFS were purified by recrystallization in toluene before use. DMAc and N36DS were used as received. 4-Fluoro-2,2,2-trifluoroacetophenone (F3FAP), trifluoromethanesulfonic acid (triflic acid) and 4-fluorothiophenol (FTP) were purchased from Oakwood Products Inc. and used as received. Anhydrous K_2CO_3 were purchased from EMD and used as received. Phenol was purchased from Anachemia Ltd. and used as received.

[0033] *Synthesis of monomer:*

[0034] *4-((4-fluorophenyl)thio) phenyl trifluoromethyl ketone (FTP3FK)*

[0035] A mixture of F3FAP (25.0 g, 130 mmol), FTP (18.34 g, 143.15 mmol), K_2CO_3 (10.8 g, 78.1 mmol) and DMAc (300mL) were stirred under nitrogen for 24 h at 60 °C. Then the mixture was poured into 1 L of water and extracted with 500 mL diethyl ether. The organic phase was further washed with water and the solvent was removed by a rotary evaporator. The yellowish oily product was purified by chromatographic column (using 1/4 v/v hexanes/ethyl acetate). Yield: 96%. ^1H NMR (DMSO- d_6 , ppm) 7.93-7.95 (d, $J=8.4$ Hz, 2H), 7.68 (m, 2H), 7.41 (t, 2H), 7.28(d, $J=8.4$ Hz, 2H); ^{19}F NMR (DMSO- d_6 , ppm) -70.0(s, 3F), -110.1 (m, 1F). MS (m/z): 318.1 ($[\text{M}+\text{NH}_4]^+$). FT-IR (diamond plate, cm^{-1}): 1711 (C=O), 835 (Ar).

[0036] *1,1-bis(4-hydroxyphenyl)-1-(4-((4-fluorophenyl) thio) phenyl)-2,2,2-trifluoroethane (3FBPT)*

[0037] FTP3FK (18.0 g, 60.0 mmol) and phenol (22.6 g, 240 mmol) were added to a round bottom flask. The system was purged with nitrogen three times before heating to 45 °C to form a homogeneous solution. Then triflic acid (2.34 g, 15.6 mmol) was added and the solution was stirred at 60 °C for 1 h until a pale

yellowish solid formed. The product was washed with boiling water three times and recrystallized from toluene to give a white solid. Yield: 94%. ^1H NMR (DMSO- d_6 , ppm) 9.63 (s, 2H), 7.52 (dd, 2H), 7.29(t, 2H), 7.18(d, $J=8.8\text{Hz}$, 2H), 7.00 (d, $J=8.8\text{Hz}$, 2H), 6.80(d, $J=8.8\text{Hz}$, 4H), 6.74(d, $J=8.8\text{Hz}$, 4H); ^{19}F NMR (DMSO- d_6 , ppm) -57.9(s, 3F), -112.5(m, 1F). MS (m/z): 488.2 ($[\text{M}+\text{NH}_4]^+$). FT-IR (diamond plate, cm^{-1}): 3400 (-OH), 820 (Ar).

[0038] *Synthesis and oxidization of Poly(arylene ether sulfone):*

[0039] The following procedure represents a typical polymerization that gave the polymer, PAESf-T-67 shown in Scheme 3. 6F-BPA (0.673 g, 2.0 mmol), 3FBPT (1.882 g, 4.0 mmol), K_2CO_3 (1.66 g, 12.0 mmol), DMAc (40 mL) and toluene (20 mL) were added into a 100 mL three-necked round bottom flask equipped with a Dean-Stark trap and a nitrogen inlet. The system was purged with nitrogen and a slow flow of nitrogen was maintained during the entire reaction period. The mixture was heated with continuous stirring. After reaction at 140 °C for 2 h, water and toluene were removed by azeotropic distillation at 150 °C. The system was then cooled to RT and DFS (1.526 g, 6.0 mmol) was added. The temperature was increased to 165 °C and the mixture was stirred at this temperature for 4 h. The solution was filtered before being precipitated into 500 mL methanol. The resulting white polymer product, in the form of fiber, was then filtered and dried under vacuum at 60 °C overnight. Yield: 93%; GPC: $M_n=58700$, $M_w=111000$, $\text{PDI}=1.90$; ^1H NMR (DMSO- d_6 , ppm): 7.84-8.00 (Ar- SO_2 -Ar), 7.42-7.58 (Ar-S-Ar), 7.32-7.42 (Ar-O-Ar), 6.90-7.30 (m, Ar); ^{19}F NMR (DMSO- d_6 , ppm): -57.8 (s, 3F), -62.9 (s, 3F), -112.0 (m, 1F).

[0040] In a typical oxidization procedure, polymer PAESf-T-67 (3.0 g) was added into 130 mL formic acid and 13 mL 30% hydrogen peroxide were added dropwise at 40 °C. The heterogeneous dispersion was stirred vigorously for 1.5 h before being filtered and washed with methanol. The white polymer powder was then dried under vacuum at 60 °C overnight to give polymer PAESf-S-67 containing sulfone in the pendant group. Yield: 99%; GPC: $M_n=55800$, $M_w=103000$, $\text{PDI}=1.85$, ^1H NMR (DMSO- d_6 , ppm): 7.86-8.18 (Ar- SO_2 -Ar), 7.30-7.50 (m, Ar), 7.00-7.10 (Ar-O-Ar), 7.10-7.28 (m, Ar); ^{19}F NMR (DMSO- d_6 , ppm): -57.7 (s, 3F), -62.9 (s, 3F), -103.7 (m, 1F).

[0041] *Preparation of Sulfonated Polymer, PAESf-SS-X*

[0042] The following represents a typical procedure to attach sulfonated phenol to the pendant group of the polymers. PAESf-S-80 (0.854 g, 1.0 mmol *para*-fluorine atom), N36DS (0.697 g, 2.0 mmol), K₂CO₃ (0.276 g, 2.0 mmol), 30 mL DMAc and 10 mL toluene were added into a nitrogen flushed reactor which was equipped with a Dean-Stark trap. The mixture was heated at 140 °C for 2h before water and toluene were removed at 150 °C. The reaction was continued at 160°C for 16h before the solution was filtered. The solution was precipitated into diethyl ether and the precipitate was washed with distilled water before being dried under vacuum overnight at 60 °C. Yield: 95%; ¹H NMR (DMSO-d₆, ppm): 8.23 (s, H-Ar-SO₃H), 7.90-8.10 (m, Ar-SO₂-Ar), 7.84 (d, *J*=8.4Hz, H-Ar-SO₃H), 7.75 (d, *J*=8.4Hz, H-Ar-SO₃H), 7.30-7.49 (m, Ar), 7.02-7.28 (m, Ar); ¹⁹F NMR (DMSO-d₆, ppm): -57.6(s, 2F), -62.9 (s, 1F). FT-IR (diamond plate, cm⁻¹): 3500 (-SO₃H), 1296, 1121 (-SO₃H).

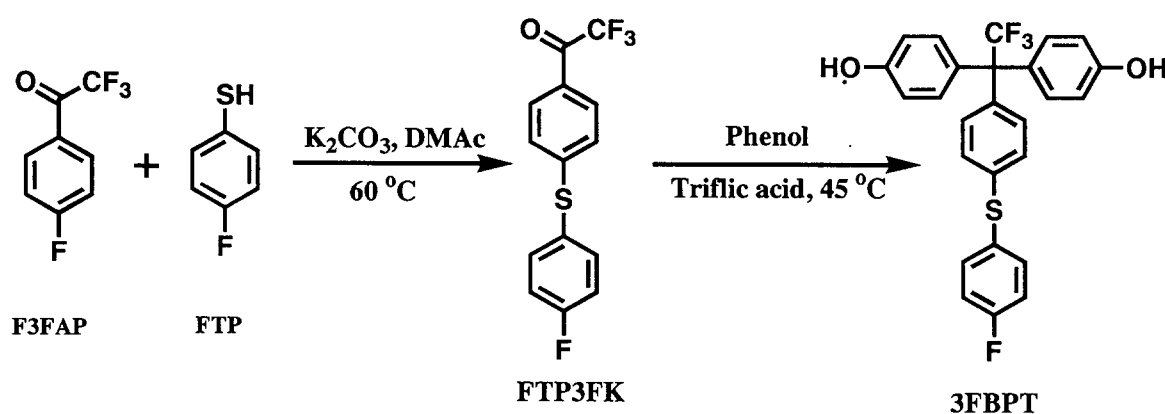
[0043] *Membrane casting and characterization:*

[0044] Polymer PAESf-SS-80 membranes were cast from DMAc solutions (10 wt%) in a custom-built flat glass dish at 50 °C under slow nitrogen flow for 2 days. The resulting membranes in the salt form were then soaked in 2N HCl for 2 days to exchange the ion and obtain the protonated form, before soaking and washing thoroughly with deionized water several times. The ion exchange capacity (IEC) was determined by titration with 0.025N NaOH. Water uptake was measured as previously reported.⁸ A four-probe conductivity cell from BekkTech was used for proton conductivity measurement. Membranes samples were cut into strips that were 1.0 cm wide, 2.0 cm long, and about 100 μm thick prior to mounting in the cell. The cell was placed in deionized water in a temperature controlled stainless steel chamber. Impedance measurements were made using Solartron SI1260 impedance/gain-phase analyzer by a four-probe ac impedance technique. The scan frequency was between 100 to 10⁷ Hz at a maximum perturbation amplitude of 100 mV.⁸

[0045] *Discussion:*

[0046] *Monomer synthesis:*

[0047] As shown in Scheme 2, the synthesis of monomer 3FBPT comprises two steps. First, the fluoride of F3FAP was displaced with FTP using K_2CO_3 under mild conditions.⁶ The resulting FTP3FK was then condensed with two moles of phenol to produce the bisphenol, 3FBPT using the superacid catalyst triflic acid.⁹ The overall yield of the two step reactions was above 90% and the proposed structure was confirmed by ^1H and ^{19}F NMR spectra. This bisphenol monomer contains a 1,1,1-trifluoroethylidene group as the linkage for the two phenol units in the molecule, which was shown to provide excellent stabilities in a monomer with a similar structure, 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane.^{9, 10}



Scheme 2. Synthesis of 3FBPT monomer.

[0048] *Polymerization and oxidization:*

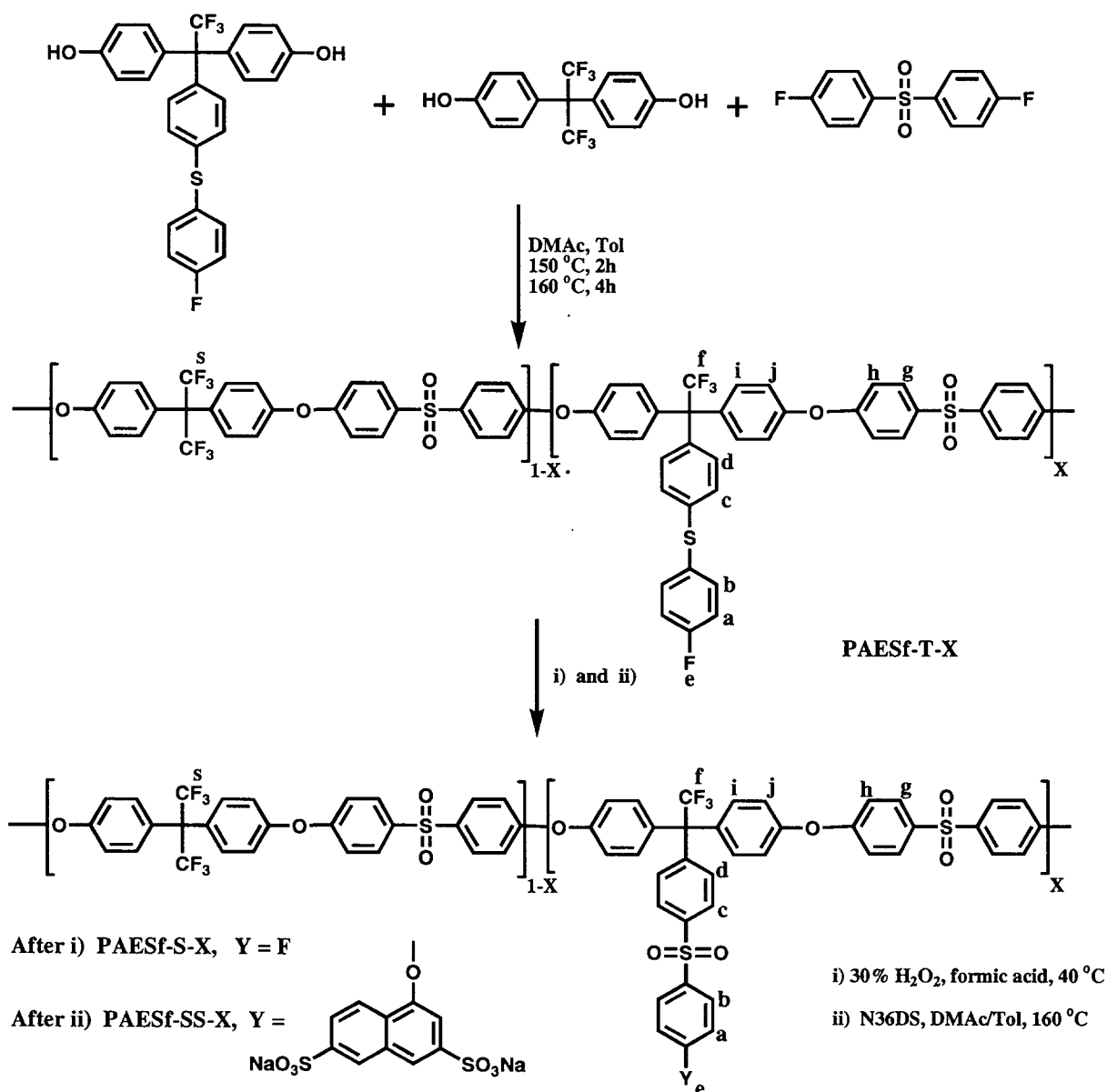
[0049] Poly(arylene ether sulfone)s containing pendant 4-fluorophenyl sulfide groups (PAESf-T-X) were synthesized by the S_NAr polycondensation using various feed ratios of 3FBPT/6F-BPA, so that polymers with different molar percentage of pendant group (Scheme 3) have been obtained. Their characterization results are listed in Table 1 and the polymers are named as PAESf-T-X or PAESf-S-X, where PAESf represents Poly(arylene ether sulfone), T (thio) represents 4-fluorophenyl sulfide pendant group and S (sulfone) represents 4-fluorophenyl sulfone pendant group. X is the molar percent of 3FBPT in total bisphenol monomers. The polymerization reactions proceeded smoothly and no crosslinking was evident when the system was carefully purged with nitrogen and the temperature was well controlled by oil bath (less than 170 °C). GPC results (Table 1, Fig. 1) showed that high molecular weight polymers ($M_n > 50,000$ g/mol) were obtained and the polydispersity index is around 2, which is consistent with

the results of a typical polycondensation reaction. All these demonstrate the much higher selectivity of the reaction to the activated para-fluorine on the sulfonyl phenyl group than to *para*-fluorine on the pendant phenyl sulfide group during the nucleophilic substitution. It was found that higher temperature (above 170 °C) or longer reaction time (longer than 5 h) would lead to some crosslinked gel-like polymer remaining attached on the glassware, indicating that the comparative selectivity decreased when the temperature was higher than 170 °C. In this case, GPC analysis showed a shoulder peak in the high molecular weight region of the main peak.

Table 1. Characterization of polymer PAESf-T-X and PAESf-S-X.

Polymer Sample	χ^a	χ^b	Molecular Weight ^c ($\times 10^4$ mol/g)		PDI ^c	T_g	T_d^d
			M_n	M_w			
PAESf-T-10	0.10	0.10	14.0	26.2	1.87	203.4	508.1
PAESf-T-20	0.20	0.20	6.92	11.9	1.72	196.9	505.6
PAESf-T-33	0.33	0.33	19.5	44.8	2.30	198.1	508.2
PAESf-T-40 ^e	0.40	0.41	12.3	37.3	3.03	197.2	499.2
PAESf-T-67	0.67	0.67	5.87	11.1	1.90	190.1	499.0
PAESf-T-80	0.80	0.80	6.56	12.3	1.88	226.6	507.5
PAESf-T-100	1.0	-	5.57	9.47	1.70	186.6	509.4
PAESf-S-10	0.10	0.10	13.3	24.8	1.87	-	516.4
PAESf-S -20	0.20	0.20	6.43	10.9	1.69	206.6	508.41
PAESf-S -33	0.33	0.34	18.9	41.4	2.19	-	500.1
PAESf-S -40 ^e	0.40	0.40	11.9	33.3	2.81	216.0	508.0
PAESf-S -67	0.67	0.67	5.58	10.3	1.85	219.7	513.7
PAESf-S -80	0.80	0.80	6.29	11.6	1.84	226.6	507.5
PAESf-S -100	1.0	-	5.02	7.56	1.51	226.6	507.5
PAESf-SS -80	0.80	0.80	-	-	-	264.1	374.4

- Molar ratio of 3FBPT in total bisphenol monomers.
- Molar ratio measured from ^{19}F NMR spectrum.
- Measured by GPC using THF as solvent. The small molecular weight cyclic polymer peak was not included for calculation of M_n , M_w and PDI.
- 5% weight loss temperature in nitrogen atmosphere.
- Some branching and crosslinking detected.



Scheme 3. Synthesis of PAESf-T-X, PAESf-S-X and PAESf-SS-X.

[0050] The pendant 4-fluorophenyl sulfide groups of these polymers were oxidized, initially using Oxone[®] for this purpose.⁵ It was found that the sulfide group could be oxidized completely to sulfone using excess Oxone[®] in refluxing chloroform solution overnight. However, substantial polymer degradation was detected under these conditions, as indicated by the GPC curves in Fig. 1B. Shorter reaction times with Oxone[®] lead to incomplete oxidization. A second method was developed using hydrogen peroxide in heterogeneous polymer formic

acid suspension.¹² ^{19}F and ^1H NMR confirms the success of complete oxidization, which occurred without accompanying polymer degradation as shown by almost identical GPC curves (Fig. 1C).

[0051] *NMR spectra:*

[0052] ^1H NMR

[0053] ^1H NMR spectra of homopolymer PAESf-T-100 and PAESf-S-100 are shown in Fig. 2; all the proton signals were unambiguously assigned from 1D and 2D C-H correlation NMR spectra. As expected, the ortho-sulfonyl protons appear at higher frequencies due to deshielding from the sulfone groups. On the other hand, the electron rich proton atoms such as those ortho to ether linkage appear at lower frequencies. The integration ratios are as expected from the molecular structures of polymers.

[0054] ^{19}F NMR

[0055] ^{19}F NMR of copolymer PAESf-T-67 is shown in Fig. 3A; the three sharp signals at -57.8, -62.9, -112.0 ppm belong to Ff, Fs and Fe respectively as labeled in Scheme 3. After oxidization, the fluorine signal on the phenylsulfide group at -112.0 ppm shifts to -103.7 ppm (Fig. 3B) due to the formation of phenylsulfone group. In addition, a small signal (inset in Fig. 3) was also detected at -108.3 ppm, which is believed to arise from the partially oxidized product, phenylsulfoxide group. The relative intensity of this signal is less than 5% compared with the fluorine signal on the phenylsulfone group.

[0056] ^{13}C NMR

[0057] The ^{13}C NMR spectra of the copolymers are very complicated due to the large number of the different carbons present. Therefore only the spectra of homopolymer, PAESf-T-100 and PAESf-S-100 are presented in Fig. 4 as examples. These two polymers contain 18 different carbon atoms each, and HSQC and HMBC spectra (Figs. 5 and 6) have been applied for assignment of all these carbon peaks.

[0058] Useful information can be extracted simply from studying the ^{13}C NMR spectrum of PAESf-S-100 (Fig. 4B). Since $^1J_{\text{CF}}$ is usually about 200-310 Hz,¹¹ the doublet at 164.4 and 166.9 ppm ($^1J_{\text{CF}}=253.2\text{Hz}$) can be assigned to Ce, and this assignment was confirmed by $^3J_{\text{Ce-Hb}}$ correlation in HMBC. For the same reason, the quartet at 122.9, 125.7, 128.6 and 131.4 ppm ($^1J_{\text{CF}}=285.6\text{Hz}$, last signal overlapped with other large signal at 131 ppm) can be assigned to Cf. $^2J_{\text{CF}}$ is expected near 20-50 Hz, the doublet at 117.1 ppm ($^2J_{\text{CF}}=23.0\text{Hz}$) and the quartet at 63.7 ppm ($^2J_{\text{CF}}=23.5\text{Hz}$) can be assigned to Ca and Ck respectively.

[0059] The ^1H - ^{13}C HSQC spectrum of this polymer is shown in Fig. 5, Cb, Cc, Cg, Cd, Ch can be easily assigned based on their correlation signals via $^1J_{\text{CH}}$. The ^1H - ^{13}C HMBC spectrum of this polymer is shown in Fig. 6 and the correlation signals via $^3J_{\text{CH}}$ is yielded. From the correlation $^3J_{\text{Ck-Hi}}$ with Ck, Hi signal can now be distinguished from Hj as labeled in Fig. 2B. All the other carbon, such as Ci, Cj, Cp, Cm, Cl, Cr, Co, Cq, Cn can all be assigned from their correlation with the corresponding protons three bonds away.

[0060] In the same manner, all of the signals in the ^{13}C NMR spectrum of PAESf-T-100 can be assigned as indicated in Fig. 4 using the ^1H - ^{13}C HSQC and HMBC analysis (spectra not shown). It is interesting that Hi and Hj signals in PAESf-T-100 overlapped with each other (Fig. 2A), but their counterpart signals in the oxidized product were distinctly separated as shown in Fig. 2B, even though the oxidation occurred at the position several bonds away. An explanation for this could be from the anisotropic effect of the sulfone group through space on Hi and Hj.

[0061] *Thermal analysis:*

[0062] Thermal analyses for most of the polymers with either sulfide or sulfone linkage in the pendant group were carried out as summarized in the data in Table 1. All the polymers have T_g between 180 °C to 230 °C. Interestingly, as the content of pendant group increased, the T_g of the polymer with the sulfide linkage showed a linear decrease, while the T_g of the polymer with the sulfone linkage had a linear increase (Fig. 7). The best-fit straight lines for the two sets of data crossed at the Y axis, where only one T_g should be present, representing the

homopolymer of 6F-BPA with DFS. The difference between the T_g of homopolymer PAESf-T-100 and PAESf-S-100 is 40 °C. This data was unexpected and surprising since these two polymers have the same main-chain structure. Theoretical calculation by a semiempirical equation¹² shows that the difference should be about 27 °C. Compared with sulfide, the higher polar sulfone side groups can form stronger inter-molecular interactions. In addition the sulfone group is less flexible than sulfide to offer a higher steric hindrance effect.

[0063] TGA experiments show that all the polymers have excellent thermal stabilities and the 5% weight loss temperature in nitrogen is around 500 °C. There is also some trend between this temperature and monomer ratio. As shown in Fig. 8, all the sulfone side-chain copolymers show better thermal stability than their sulfide counterparts by about 10 °C. As the molar ratio of the pendant group increases from 10% to 100%, the 5% weight loss temperature decreased nearly 10 °C, for both PAESf-T-X and PAESf-S-X copolymers.

[0064] *Sulfonated side chain attachment.*

[0065] To demonstrate the reactivity of the fluorine atom on the pendant group of the sulfone polymer, PAESf-S-80 was further reacted with a phenol compound N36DS. A preliminary ^1H and ^{19}F NMR study showed that more than 85% of fluorine reacted with this phenol. This ionomer (PAESf-SS-80) is soluble in DMAc and formed transparent, flexible and tough membranes after solution casting, which implies that no crosslinking or degradation occurred during the side-group attachment reaction. A titration experiment shows this membrane had an IEC of 1.52 meq/g that agrees well with the theoretical calculation (1.57 meq/g). The equilibrium water uptake at 20 °C is 52%, which means the number of water molecules per sulfonic acid groups (λ) is equal to 18. The proton conductivity, perhaps the most critical property of proton exchange membranes, is shown in Fig. 9. For comparison, the data from Nafion[®] 117 is also shown in the same figure. PAESf-SS-80 has a very similar proton conductivity compared with Nafion 117 throughout the whole measured temperature range (20-95 °C). This result is promising considering the novel sulfonated side chain grafted structure. More detailed studies of these series of polymers are still underway.

[0066] It should be noted that this bisphenol monomer, 3FBPT is a universal monomer which can be used for preparation of other kinds of poly(arylene ether) polymers by condensation polymerization, and we are currently investigating these polymer systems as potential PEM materials. The pendant 4-fluorophenyl sulfide group serves as a masked reactive site for further S_NAR reaction. The fluorine in this group is easily activated for reaction with any functional phenolic or similar compounds by converting the sulfide to sulfone.¹⁴ These functional phenolic or similar compounds could be small molecules, oligomers or polymers containing one phenol group and some other functional groups.

[0067] *References:* The disclosures of the following references are incorporated herein by reference in their entirety.

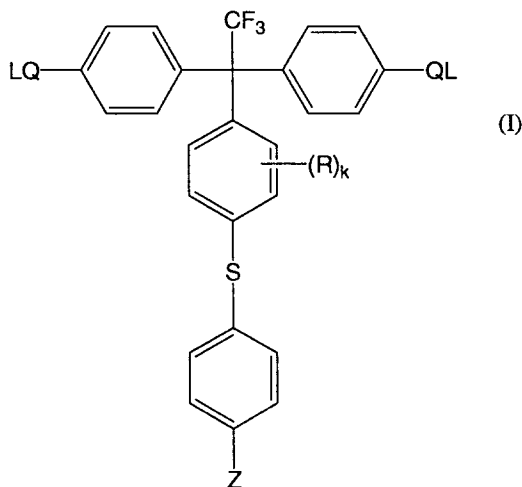
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14. Bloom, P. D.; Sheares, V. V. *Macromolecules*, 2001, *34*, 1627.

[0068] Other advantages that are inherent to the structure are obvious to one skilled in the art. The embodiments are described herein illustratively and are not meant to limit the scope of the invention as claimed. Variations of the foregoing embodiments will be evident to a person of ordinary skill and are intended by the inventor to be encompassed by the following claims.

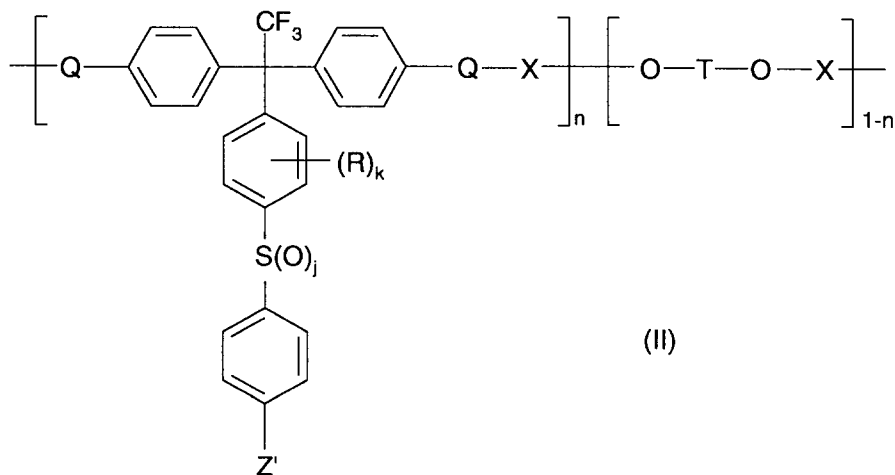
Claims:

1. A compound of formula (I):

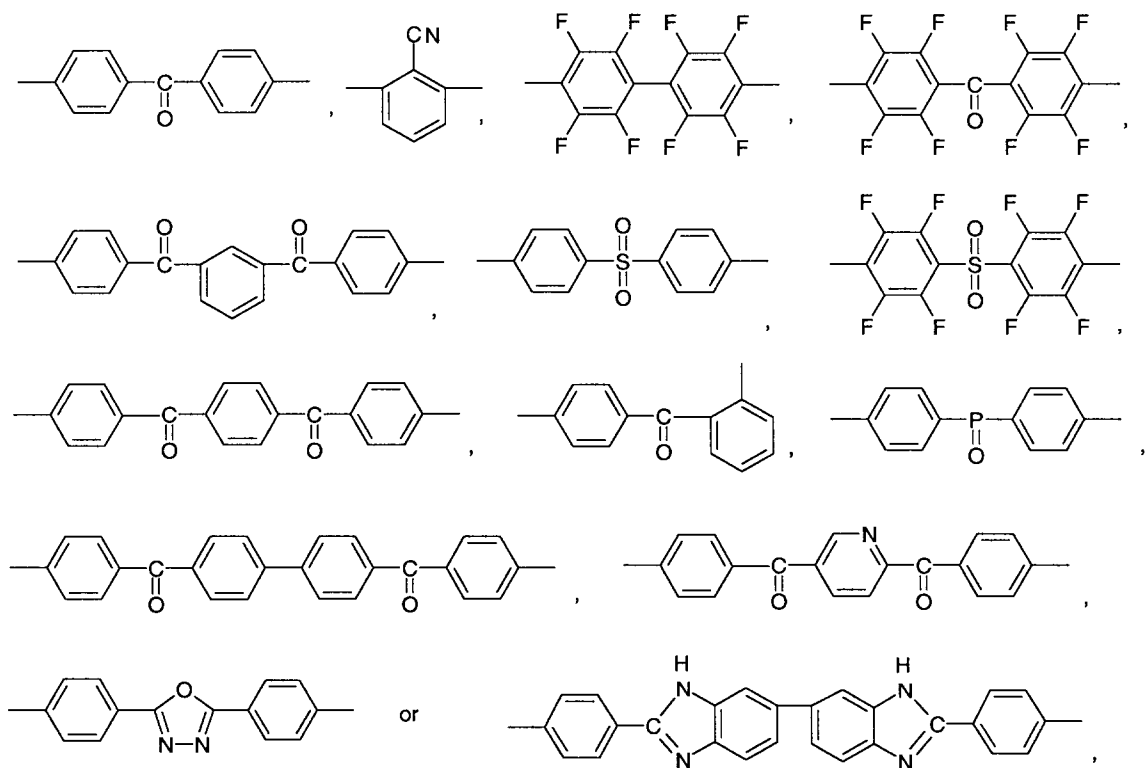


wherein: k is 1 or 2; Q is O or S; L is a leaving group; Z is F or Cl; and, R is hydrogen or an organic moiety.

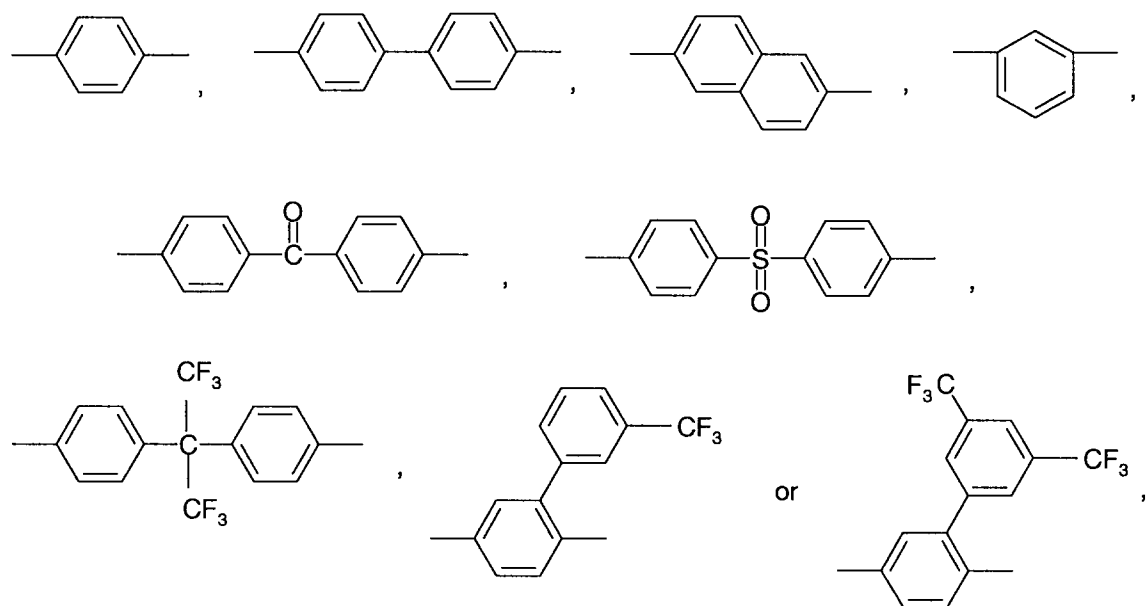
2. The compound of claim 1, wherein L is hydrogen.
3. The compound of claim 1 or 2, wherein Q is O.
4. The compound of any one of claims 1 to 3, wherein Z is F.
5. The compound of any one of claims 1 to 4, wherein R is hydrogen.
6. A compound of formula (II):



wherein X is



T is



n is a non-zero number from 0 to 1,

j is 0, 1 or 2,

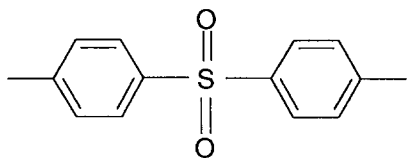
Z' is F, Cl or an organic group,

Q is O or S,

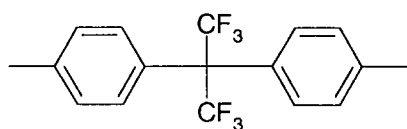
R is hydrogen or an organic moiety, and

k is 1 or 2.

7. The compound of claim 6, wherein Q is O.
8. The compound of claim 6 or 7, wherein Z' is F or an organic group.
9. The compound of claim 8, wherein the organic group is a residue of a phenol or thiophenol.
10. The compound of claim 8, wherein the organic group contains a sulfonic acid functional group.
11. The compound of claim 8, wherein the organic group is 1-naphthyl-3,6-disulfonic acid sodium salt.
12. The compound of any one of claims 6 to 11, wherein R is hydrogen.
13. The compound of any one of claims 6 to 12, wherein j is 1 or 2.
14. The compound of any one of claims 6 to 13, wherein X is

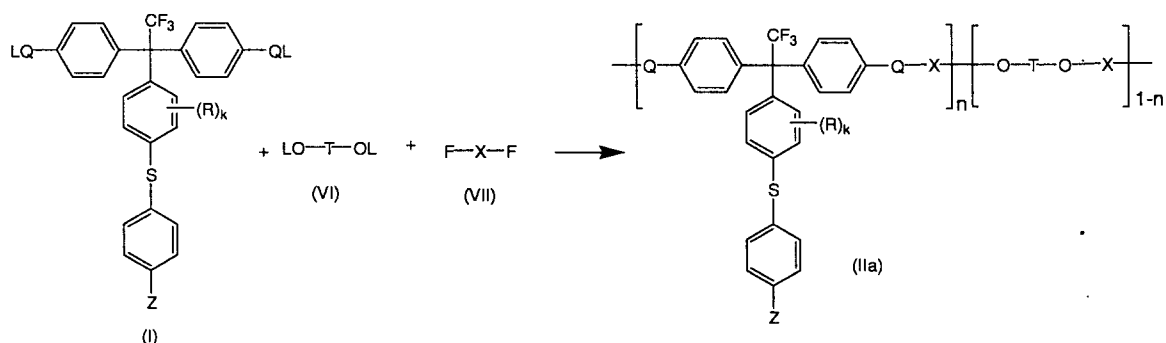


15. The compound of any one of claims 6 to 14, wherein T is

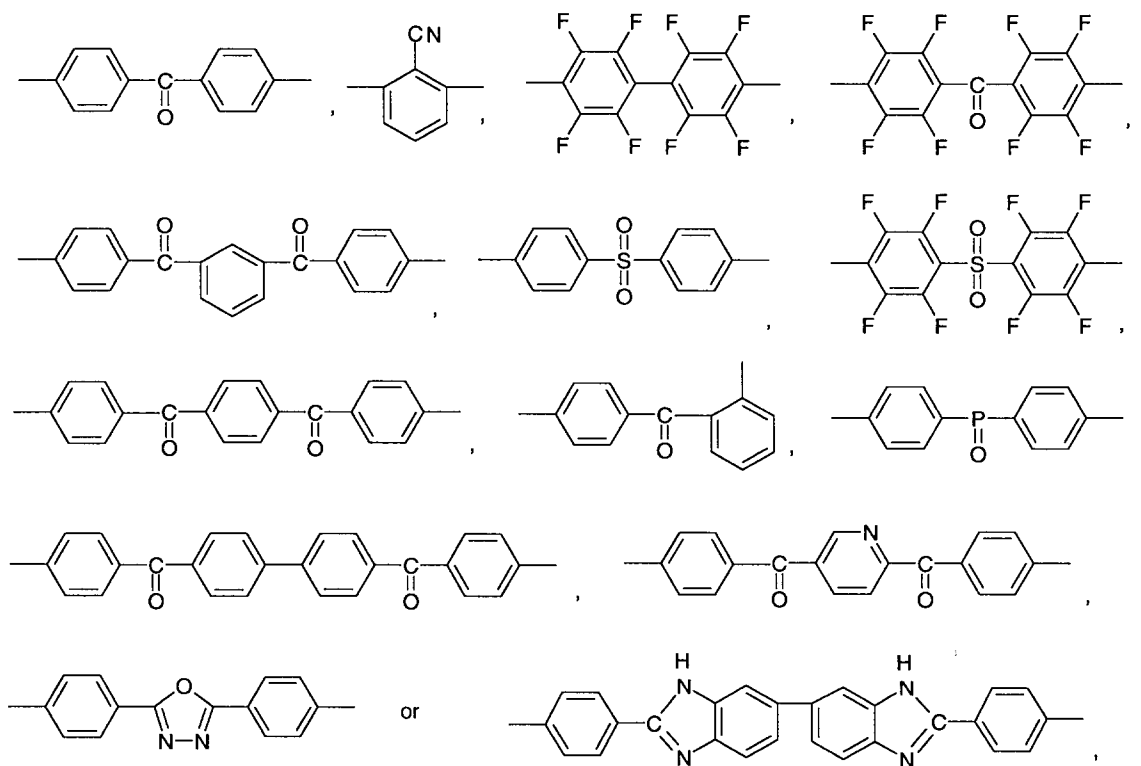


16. A membrane comprising a compound as defined in any one of claims 6 to 15.

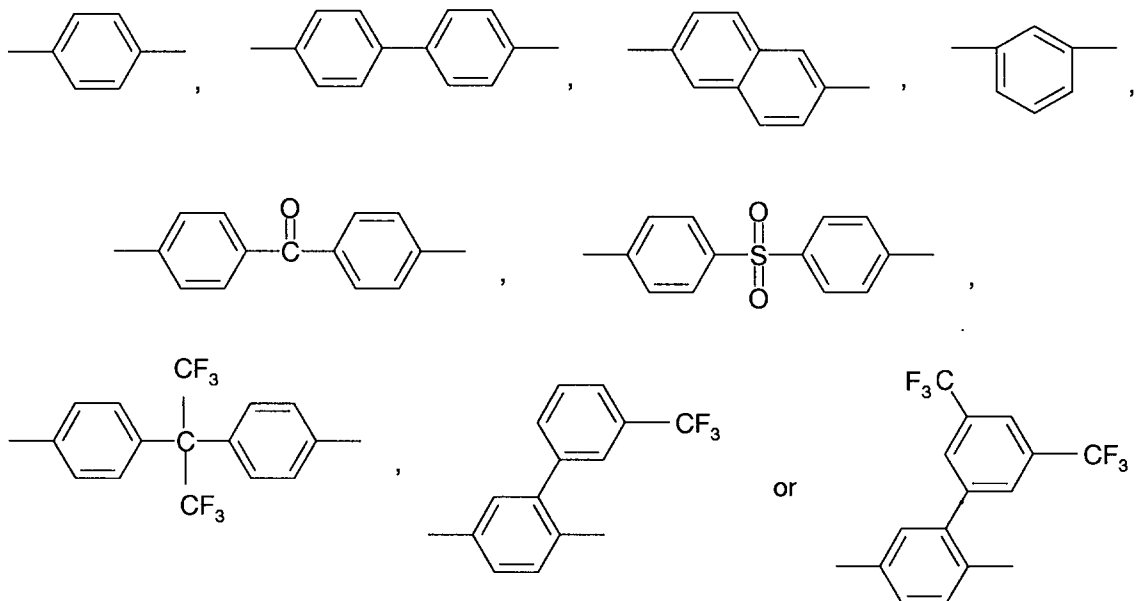
17. Use of a membrane as defined in claim 16 for gas separation, water desalination or proton exchange.
18. Use of a membrane as defined in claim 16 for proton exchange in a fuel cell.
19. A process comprising



wherein X is



T is



n is a non-zero number from 0 to 1,

L is a leaving group,

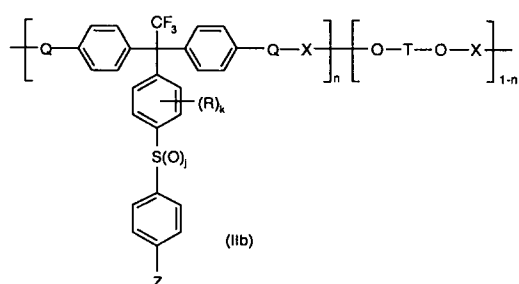
Z is F or Cl,

Q is O or S,

R is hydrogen or an organic moiety, and

k is 1 or 2.

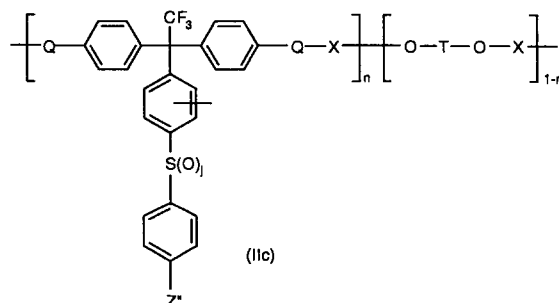
20. The process of claim 19 or 20, further comprising oxidizing the compound (IIa) to a compound (IIb):



wherein j is 1 or 2.

21. The process of claim 20, wherein the oxidizing is accomplished with hydrogen peroxide.

22. The process of claim 20 or 21, further comprising converting the compound (IIb) to a compound (IIc) by nucleophilic aromatic substitution:



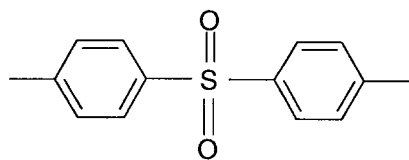
wherein Z' is an organic group.

23. The process of claim 22, wherein the organic group is a residue of a phenol or thiophenol.

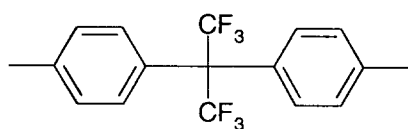
24. The process of claim 23, wherein the residue contains a sulfonic acid functional group.

25. The process of any one of claims 19 to 24, wherein L is H, Z is F, Q is O and R is hydrogen.

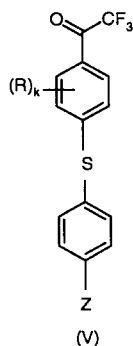
26. The process of claim 25, wherein X is



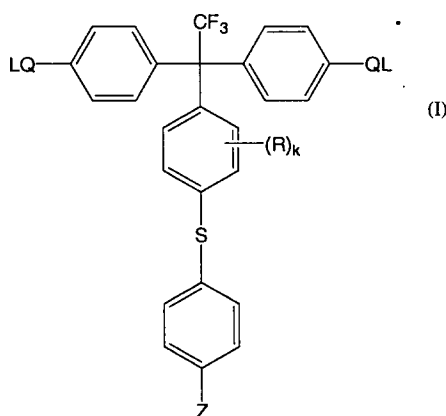
and T is



27. A process comprising reacting compound (V):



with phenol in the presence of a catalyst to produce compound (I):

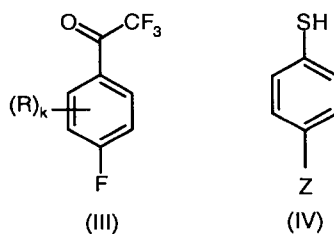


wherein: k is 1 or 2; Q is O or S; L is hydrogen; Z is F or Cl; and, R is hydrogen or an organic moiety.

28. The process of claim 27, wherein Q is O, Z is F and R is hydrogen.

29. The process of claim 27 or 28, wherein phenol and compound (V) are reacted in a molar ratio of 2:1.

30. The process of any one of claims 27 to 29, further comprising producing compound (V) by reacting compound (III) with compound (IV):



1/7

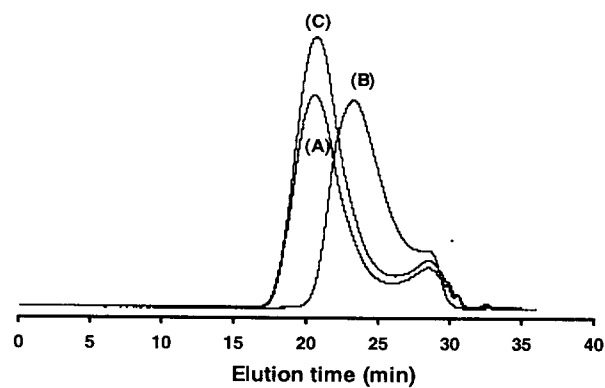


Fig. 1

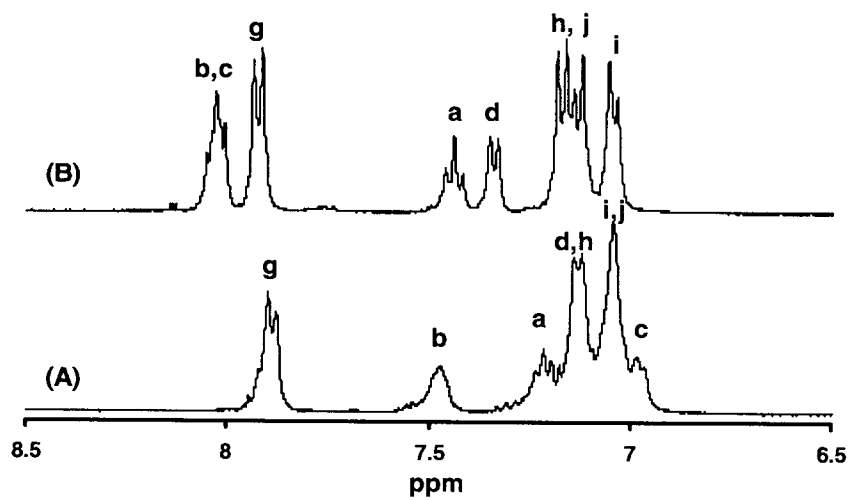


Fig. 2

2/7

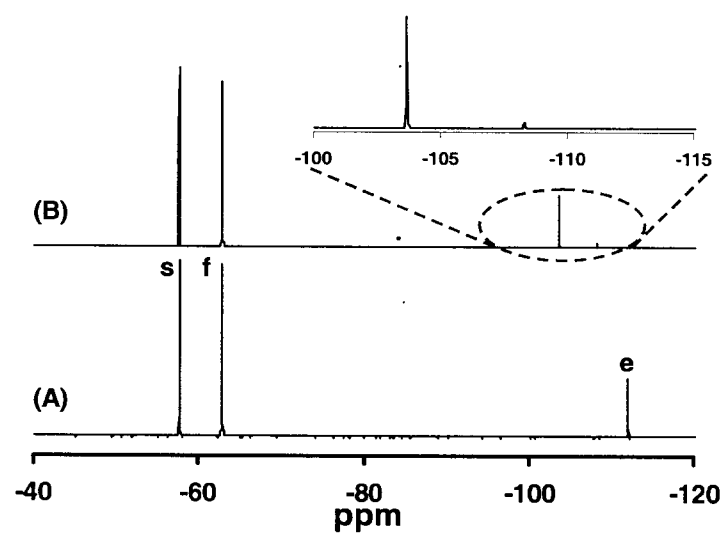


Fig. 3

3/7

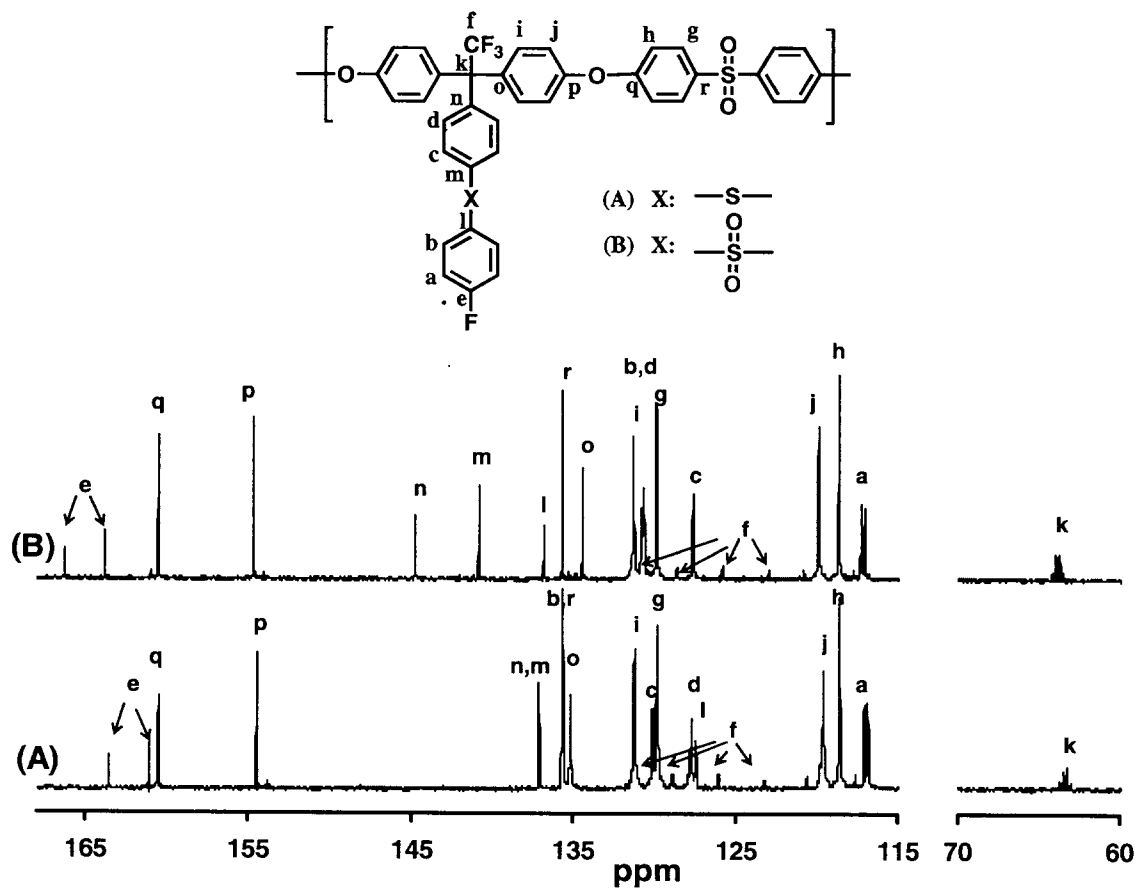


Fig. 4

4/7

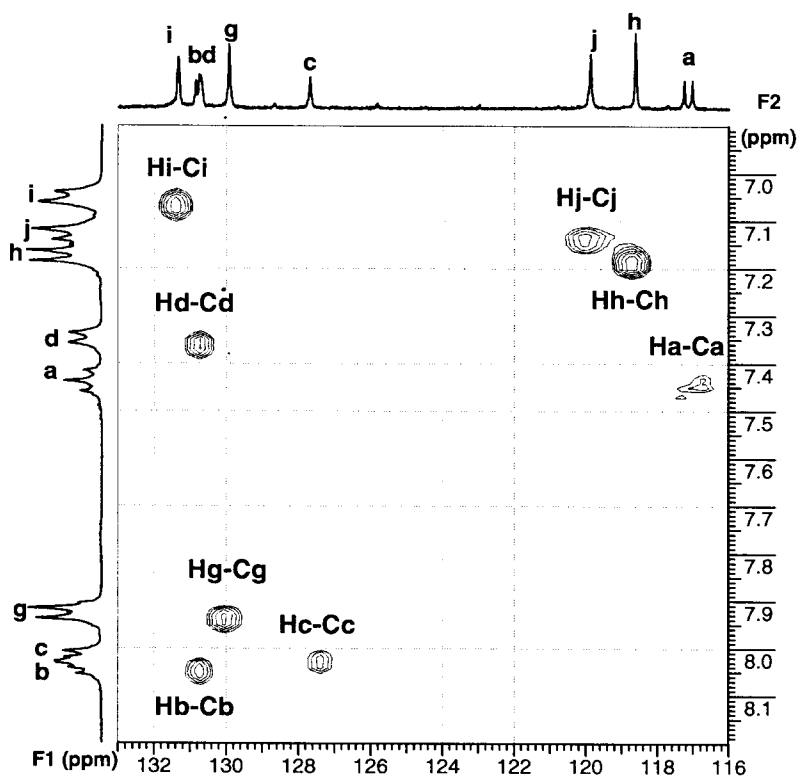


Fig. 5

5/7

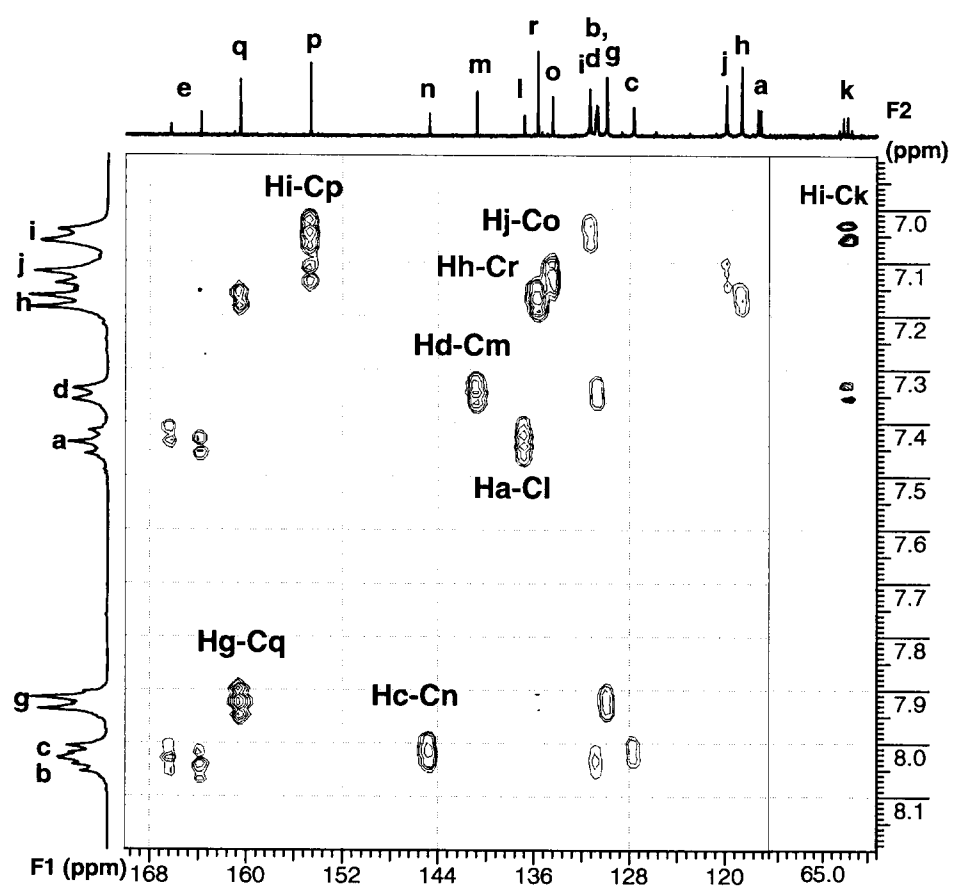


Fig. 6

6/7

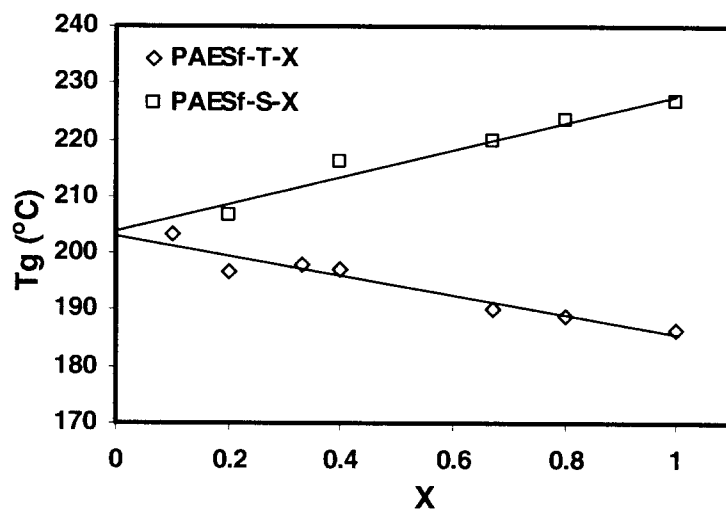


Fig. 7

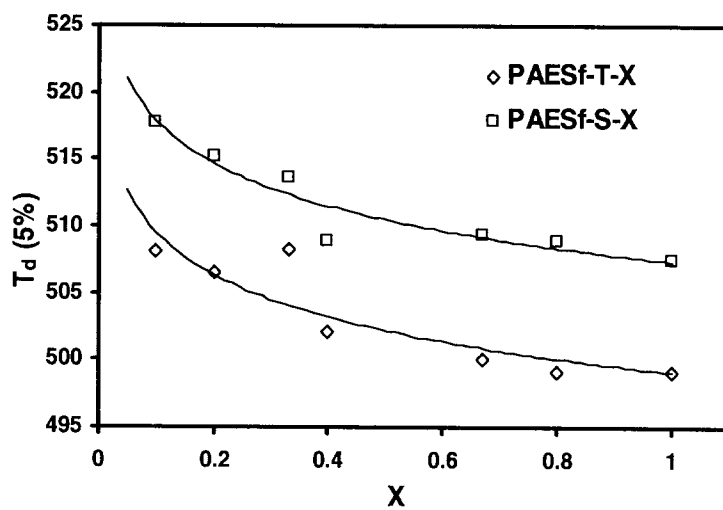


Fig. 8

7/7

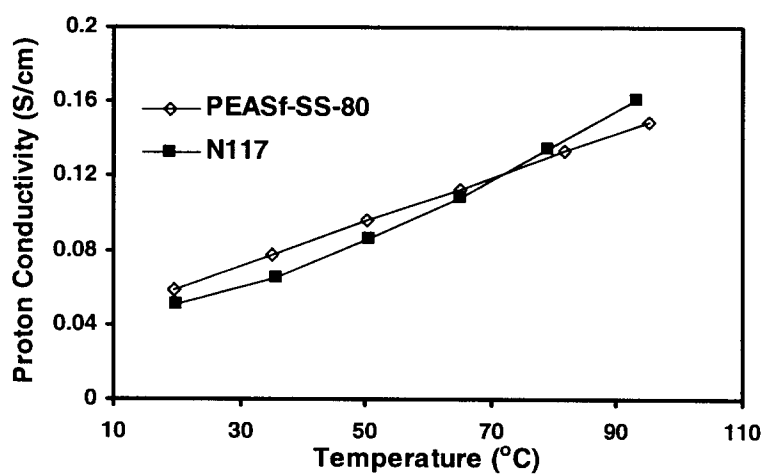


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2007/000850

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C07C 321/30** (2006.01) , **C07C 317/14** (2006.01) , **C07D 213/50** (2006.01) , **C07D 271/10** (2006.01)

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)

C07C 321/30 (2006.01) , **C07C 317/14** (2006.01) , **C07D 213/50** (2006.01) , **C07D 271/10** (2006.01)

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

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

STN structure search, Canadian Patent Database, Delphion

Keywords: bisphenol, polyarylene ether

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	LI, Z. et al. "A Novel Bisphenol Monomre with Grafting Capability and the Resulting Poly(arylene ether sulfone)s" Macromolecules, 6 September 2006 (06-09-2006), vol 39, pages 6990-6996.	1-30
A	Martinez, C. A. et al. "Synthesis of dendritic poly(arylene ether)s from a linear polymer core" Polymer 2002, vol 43, pages 3843-3855.	1-30

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

☐ See patent family annex.

* Special categories of cited documents :	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

04 July 2007 (04-07-2007)

Date of mailing of the international search report

10 September 2007 (10-09-2007)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer

Sandra Nevill 819- 934-6732