Macromolecules **2008,** *41,* 281−284

Ionomers for Proton Exchange Membrane Fuel Cells with Sulfonic Acid Groups on the End Groups: Novel Branched Poly(ether−ketone)s

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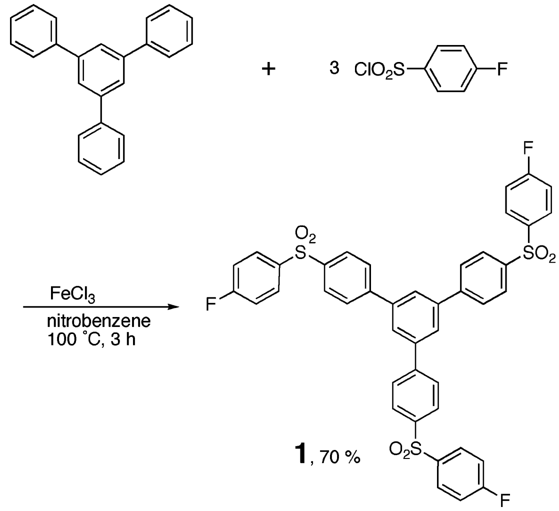
Received June 26, 2007
Revised Manuscript Received November 22, 2007

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) to convert chemical energy efficiently into electrical energy via redox reactions, have been attracting considerable attention as one of the potentially clean, quiet, and portable future power sources.[1−3] The proton exchange membrane (PEM), which acts as an electrolyte to transport protons from the anode to the cathode, is the key component of fuel cell systems. Perfluorosulfonic acid membranes, such as Nafion, are the current state-of-the-art PEM materials, because of their superior chemical and electrochemical stability, in addition to high proton conductivity with relatively low ion exchange capacity (IEC). However, perfluorosulfonic acid membranes suffer from critical drawbacks of high cost, high methanol crossover, and low proton conductivity as well as poor mechanical stability at elevated temperatures ($T > 80$ °C). This has stimulated extensive research into the investigation of promising alternatives.[2,4] The majority of current research on PEMs is based on sulfonated high-performance aromatic polymers, because of the high thermal and chemical stabilities, as well as excellent mechanical properties of the parent polymers.[5,6] These aromatic polymers, including sulfonated poly(ether−ether−ketone), one of the membranes studied extensively for PEM, usually contain sulfonic acid groups randomly distributed along polymer main chains. The model suggested by Kreuer[3] for a sulfonated poly(ether−ketone) shows less pronounced ionic/nonionic separation than that of Nafion, i.e., a morphology with narrower channels than those in Nafion, but with highly branched channels and many dead-end channels. Therefore, in general, the sulfonated polymers that have been synthesized to date require a much higher IEC in comparison with Nafion to compensate for this and to obtain conductivities comparable to that of Nafion. For example, sulfonated poly(ether−ether−ketone) required IEC of 2.45 mequiv/g to attain conductivity of 51 mS/cm,[7] and IEC of 1.52 mequiv/g for conductivity of 0.4 mS/cm.[8] High IEC usually results in high water uptake (WU) for membranes and loss of their mechanical properties.


Scheme 1. Synthesis of Branching Agent 1

We have previously reported that linear poly(sulfide−ketone) (PSK) bearing six sulfonic acid groups on each end group were successfully synthesized by regioselective post-sulfonation, and the membrane displayed relatively high proton conductivity (16 mS/cm) at very low IEC (0.48 mequiv/g).[9] The results suggested that the PSK membrane possessed better microphase-separated morphology. In these linear polymers, at the IECs required for good conductivities, the molecular weights would be too low and the required mechanical properties in the membranes would not be attainable. The required balance of IECs vs molecular weights can be attained by introducing branches into the end-capped polymers. As in the linear end-capped polymers, we would expect to have a favorable situation for segregated microdomain formation of the core polymer and the ionic end groups.

In this communication, as an expansion of our study on this new type of polymer, we report the first examples of branched wholly aromatic poly(ether−ketone)s (PEKs) bearing clusters of sulfonic acid groups only on the end groups. We designed PEKs with IECs ranging from 0.72 to 1.04, the same level as that of Nafion, by the introduction of branching using a novel trifunctional reactant and relatively short main chains. Various cross-linked PEMs have been reported for the improvement of poor dimensional stability and mechanical property of high IEC membranes.[10−13] However, only a few branched PEMs have been reported, and all of them have structures bearing randomly distributed sulfonic acid groups along the main chains and all require high IECs to attain good conductivities.[14−16]

The novel trifunctional branching agent, 1,3,5-tris(4-(4-fluorophenylsulfonyl)phenyl)benzene (**1**), was readily synthesized by Friedel−Crafts reaction of 1,3,5-triphenylbenzene with 4-fluorobenzenesulfonyl chloride in the presence of iron(III) chloride. Pure **1** was obtained in overall 70% yield and purified by recrystallization from acetic acid (Scheme 1).

Molecular weight and architecture of branched **PEK 5** can be controlled by the design of the average block length (n) and number of branches (m) in **5** (Scheme 2). While the molecular weight of **5** affects the IEC of sulfonated **5** that, in turn, generally affects proton conductivity, the architecture of **5** may affect the morphology of sulfonated **5**. This can also affect proton conductivity. In this study, we attempted to synthesize branched polymers **5** ($m = 2$, 3) with relatively short average block

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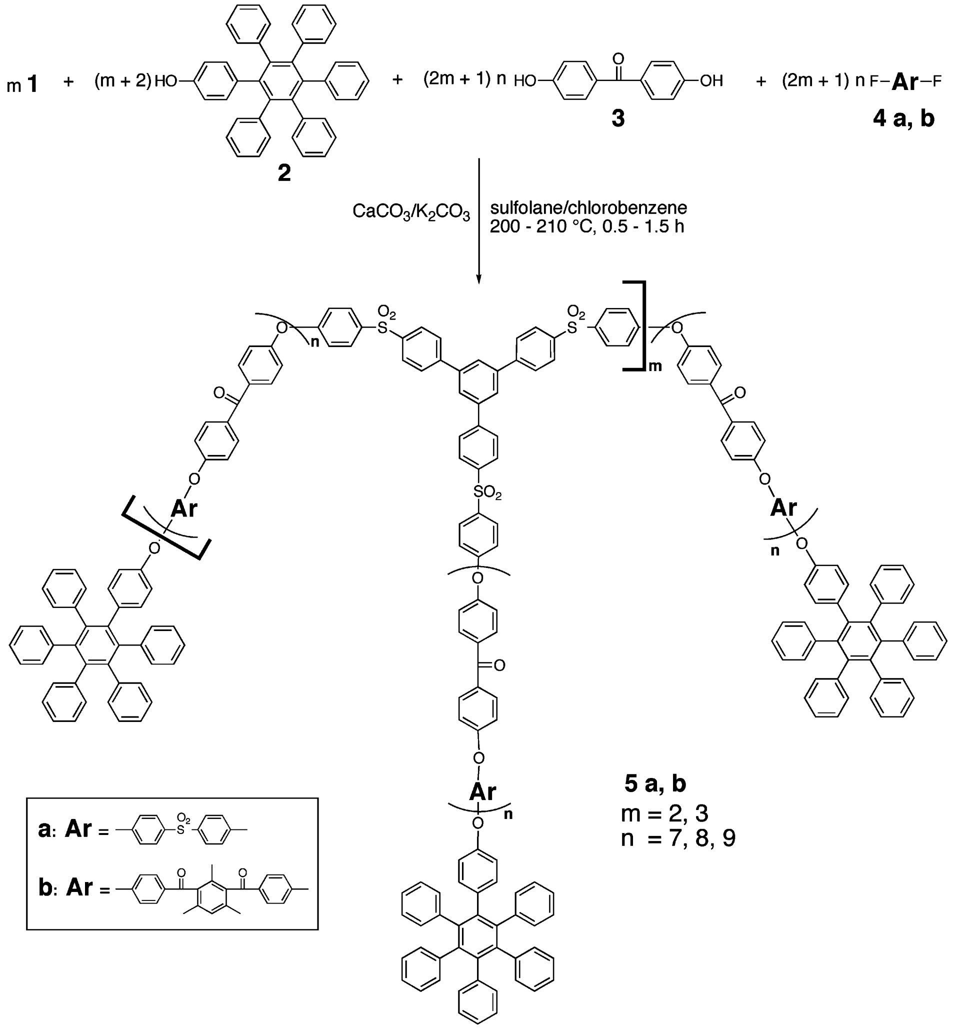
10.1021/ma071422x CCC: $40.75

Scheme 2. Synthesis of Branched PEK 5 with Hexaphenylbenzene Moieties as End Groups



lengths (n = 7, 8, 9), respectively. 1-(4-Hydroxyphenyl)-2,3,4,5,6-pentaphenylbenzene (**2**) was employed as the end group bearing a number of pendant phenyl rings to provide a number of post-sulfonation sites. We designed soluble, chemically stable, and wholly aromatic blocks by the introduction of at least 1 strong electron-withdrawing group, such as a ketone group or sulfonyl group, on each phenyl ring for efficient post-sulfonation of only the polymer end groups in **5**. First, polycondensation of **3** and **4a** was carried out in the presence of **1** and **2** by conventional methods using K_2CO_3 as base. Only low molecular weight **5a** (m = 3, n = 9), that gave a brittle cast film, was obtained in this case. It is known that fluoride anions are formed during polycondensation and can cleave ether linkages in PEK and poly(ether−sulfone) (PES).[17,18] It has been reported that the use of a mixture of $CaCO_3$ and K_2CO_3 as base suppresses the side reaction for the synthesis of PEK and PES, because fluoride ions are precipitated from the reaction system as insoluble CaF_2.[19,20] Therefore, the polycondensation of **3** and **4a** was carried out in the presence of K_2CO_3 and $CaCO_3$: **2** and **3** were heated in the presence of K_2CO_3 (0.104 equiv) and $CaCO_3$ (1.04 equiv) in sulfolane/chlorobenzene at 160−180 °C for 0.5 h to remove water by azeotropic distillation, followed by the addition of **1** and **4a** to the reaction system, and heating at 200−210 °C for 0.5 h. The desired high molecular weight polymer **5a** (m = 3, n = 9) was obtained in 99% yield as a white powder, that gave a strong cast film from its chloroform solution. The ^{1}H NMR spectrum of **5a** (m = 3, n = 9) clearly confirmed its end-capped structure and the incorporation of the branching moiety. Polymers **5a** (m = 3, n = 8, 7 and m = 2, n = 9, 8) were synthesized by the same method used for **5a** (m = 3, n = 9). Polymers **5b** (m = 3, n = 9, 8 and m = 2, n = 9) were readily synthesized by basically the same procedure for **5a**, except that a prolonged reaction time (1.5 h) was required to complete the reaction, because of relatively low reactivity of **4b** compared with **4a**. Polymer **5a** and **5b** all showed good solubility in various organic solvents such as dichloromethane, and strong cast films were obtained from their chloroform solution.

Stability of the main chain of **5** under sulfonation conditions was examined using unend-capped linear **5** prepared by the same procedure for branched **5**, except that the reaction was carried out in the absence of **1** and **2**. No difference was observed in their ^{1}H NMR and IR spectra, and GPC profiles before and after the treatment under sulfonation conditions for linear **5**, indicating its excellent stability, i.e., neither sulfonation nor chain cleavage occurred.

Sulfonation of end groups in branched **5a** was attempted by reaction with chlorosulfonic acid (10 equiv for each phenyl ring on the end groups) in dichloromethane at room temperature for 2 d. The sulfonyl chloride intermediate **6a** was then hydrolyzed with 3% basic aqueous solution, followed by acidification with conc. HCl aqueous solution (Scheme 3). An aliquot of **6a** was converted into the corresponding sulfonamide **8a** by reaction with *tert*-butylamine in the presence of pyridine in NMP (Scheme 3) to determine by ^{1}H NMR the number of sulfonic acid groups introduced in **7a**. The introduction of 6 *tert*-

Scheme 3. Sulfonation of Branched PEK 5 Bearing Hexaphenylbenzene Moieties as End Groups

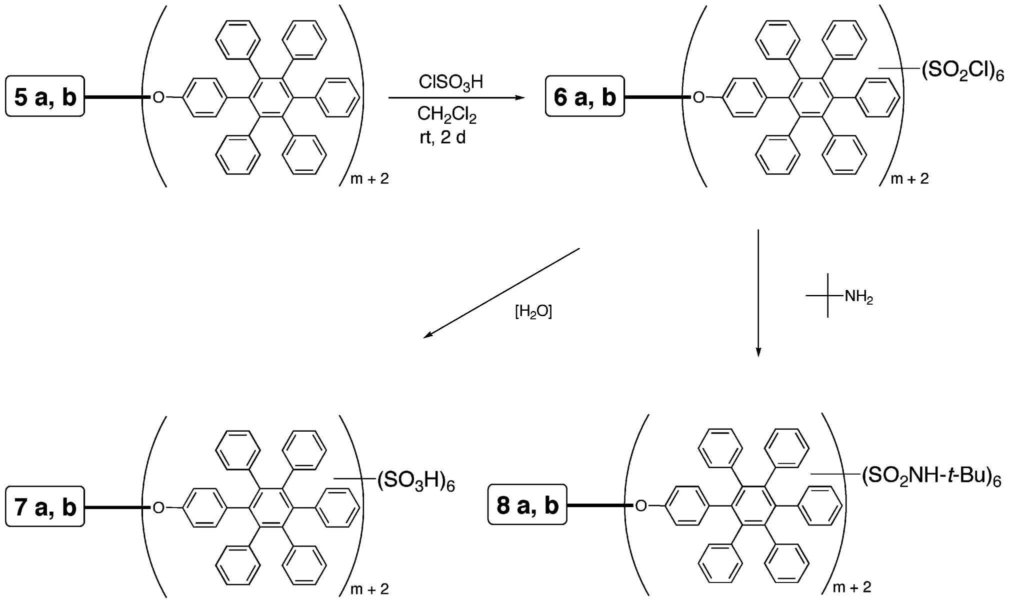


Table 1. Properties of Branched Sulfonated PEK 7

membrane	m	n	M_w(MWD)[a]	designed (calcd[b]) IEC (mequiv/g)	T_{d5}[c] (°C)	T_g[d] (°C)	T_g[e] (°C)	WU[f] (%)	λ[g] (H_2O/SO_3H)	$\sigma_{RT/100\%\ RH}$[h] (mS/cm)	$\sigma_{80°C/80\%\ RH}$[i] (mS/cm)
7a	3	9	46 000 (5.1)	0.86 (0.90, 0.89[j])	529	202	206	18	10.8 (10.9[k])	40	8.0
		8	39 000 (5.6)	0.95 (0.87, 0.76[j])	504	199	208	28	17.7 (20.3[k])	55	16
		7	74 000 (8.8)	1.04 (1.07, 1.03[j])	521	202	216	36	18.5 (19.2[k])	78	11
	2	9	67 000 (5.0)	0.96 (0.96)	471	204	210	25	14.7	65	11
		8	80 000 (5.5)	1.05 (1.09)	517	207	221	43	22.1	91	29
7b	3	9	140 000 (6.4)	0.72 (0.76)	456	215	221	17	12.4	41	12
		8	120 000 (7.4)	0.79 (0.79)	456	215	222	20	13.9	40	14
	2	9	110 000 (6.6)	0.80 (0.92)	459	214	223	21	12.7	44	22
Nafion$_{n-117}$				0.91[l]				33[m]	20.2[m]	98	34

[a] M_w and *MWD* of pre-sulfonated **PEK** (**5**), measured by GPC. [b] Calculated from the ^{1}H NMR spectrum of the corresponding sulfonamide (**8**). [c] 5% weight loss temperature. [d] T_g of **PEK** (**5**). [e] T_g of sulfonated **PEK** (**7**). [f] Water uptake, measured by TGA after a few weeks for **7a** (m = 3, n = 8), and 3 or 4 d for the others at room temperature. [g] Hydration number, calculated using IEC determined by ^{1}H NMR spectrum. [h] Proton conductivity at room temperature with 100 % RH. [i] Proton conductivity at 80 °C with 80 % RH. [j] Measured by titration. [k] Calculated using IEC determined by titration measurement. [l] Reported value. [m] Obtained from ref 21.

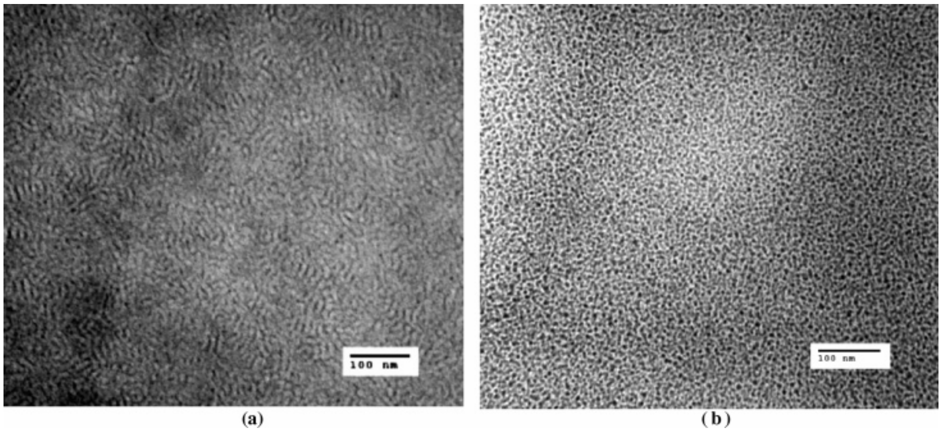


Figure 1. TEM micrographs of **PEK** and Nafion: (a) **PEK 7a** (m = 3, n = 8); (b) Nafion.

butylsulfonamide groups on each end group was readily confirmed by the integral ratio of protons on methyl group and all aromatic protons in the ^{1}H NMR spectrum of **8a**. This indicated that selective and quantitative sulfonation occurred exclusively on the end groups in **5a** as in the sulfonation of linear **PSK**s bearing the same end groups.[9] IEC of **7a**s was calculated using the number of sulfonamide groups from the ^{1}H NMR spectrum of **8a**, and also titration was performed to directly measure IEC of selected **7a**s. Both the calculated IECs agreed well with the designed IEC (Table 1). **7b**s were readily synthesized by the same procedure used for **7a**. The characteristic IR absorption $\nu_{S=O}$ of the sulfonic acid group was observed at 1042 cm^{-1} for **7**s. All **7**s were soluble in polar solvents such as DMSO, and strong membranes were cast from their DMSO solution in sulfonic acid form or sodium salt form.

The T_gs of **7a** and **7b** were higher than those of **5a** and **5b**, respectively, due to the introduction of polar sulfonic acid groups (Table 1). In contrast to aromatic membranes reported up to now, PEMs **7** with the same level of IECs (0.76−1.09 mequiv/g) as Nafion (0.91 mequiv/g) showed the same level of conductivity as Nafion. The PEMs **7** with these much lower IECs (0.76−1.09 mequiv/g) achieved more than 2 orders of magnitude higher proton conductivities (40−91 mS/cm), than the above-mentioned sulfonated poly(ether−ether−ketone)s (0.4 mS/cm with 1.52 mequiv/g).[8] These results suggest significant phase-separated microstructure in these membranes, as discussed below together with the results of transmission electron microscopy (TEM) analyses. Polymer **7a** ($m = 2$, $n = 8$) showed the best conductivity both at room temperature and 80 °C of all **7**s synthesized in this study, along with the highest IEC and highest hydration number (λ) of all **7**s. The results in Table 1 show that, as expected, the polymers **7b** containing the diketone unit **b** have lower IECs than those containing the diphenylsulphone moiety **a** because of the higher mass associated with **b**. The conductivities of the ionomers **7a** increased as the IEC, WU and λ increased. The number of branches per se in the polymers seemed not to affect the conductivities, e.g., **7a** ($m = 3$, $n = 7$) and **7a** ($m = 2$, $n = 8$) showed similar conductivities.

TEM analysis was performed on 60−100 nm thick slices of Pb^{2+} stained polymers **7a** ($m = 3$, $n = 9$, 8, and 7). Figure 1 shows the TEM results for **7a** ($m = 3$, $n = 8$) and Nafion for comparison. The dark domains represent ionic clusters due to Pb^{2+} staining, and lighter regions represent nonionic domains. Significantly phase-separated, and worm-like, highly connected morphologies were observed for all these polymers ($m = 3$, $n = 9$, 8, and 7) and Nafion. The size of the ionic clusters of all **7a**s was uniform and smaller (2−3 nm in diameter) than those of Nafion (5−10 nm in diameter). There is little evidence for dead end channels or larger spheroidal clusters as seen in previously reported ionomers. The high connectivity could then be the principal reason for the attainment of the relatively high conductivities, comparable to Nafion, at IEC levels similar to Nafion. No significant difference in morphology was observed between **7a** ($m = 3$, $n = 9$) with λ around 10 H_2O/SO_3H and **7a**s ($m = 3$, $n = 8$, and 7) with λ around 20 H_2O/SO_3H.

In conclusion, we have described the successful synthesis of the first examples of branched **PEK** polymers bearing sulfonic acid groups on the end groups. At the same level of IEC as Nafion, they showed proton conductivities comparable to that of Nafion. TEM analysis showed significantly phase-separated, and worm-like, highly connected morphology in the membranes. Further investigations on this class of polymers are ongoing in our laboratory.

Acknowledgment. This research was financially supported by a Natural Sciences and Engineering Research Council of Canada (NSERC) partnership grant funded by NSERC, National Research Council of Canada, and Dupont Canada.

Supporting Information Available: Text giving detailed experimental procedures and characterization of **1**, **5**, **7**, and **8** and a figure showing the ^1H NMR specrtum of **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA071422X