Synthesis and Properties of New Fluorinated Polymers Bearing Pendant Imidazole Groups for Fuel Cell Membranes Operating Over a Broad Relative Humidity Range

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Received 4 September 2009; accepted 25 September 2009
DOI: 10.1002/pola.23763

ABSTRACT: New alternating copolymers comprising a chlorotrifluorinated backbone and imidazole-terminated pendant ethylene oxide groups have been prepared with a view to their use as a component of proton-conducting membranes in polymer electrolyte fuel cells. A vinyl ether containing an imidazole (Imi) function protected by a benzyl group (BVI) was first synthesized in a three-step reaction. It was then copolymerized in solution with chlorotrifluoroethylene (CTFE) by conventional radical copolymerization leading to alternating poly(BVI-alt-CTFE) copolymers in good yields. Deprotection of the benzyl group under hydrogen produced a chlorotrifluorinated poly(Imi-alt-CTFE) copolymer. The polymer was subsequently used to form blend membranes with sulfonated poly(ether ether ketone) (sPEEK). The conductivity of blend membranes of poly(Imi-alt-CTFE) with sPEEK lies in the range of 4–10 mS cm^{-1} at 40–70 °C and, for blend membranes rich in poly(Imi-alt-CTFE), is little dependent on relative humidity between 30 and 100%. It is surmised that the polymer and membrane composition favor microstructural phase separation into chlorotrifluorinated polymer backbone domains and regions in which imidazole groups are clustered. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 223–231, 2010

KEYWORDS: alternating copolymers; blend membranes; blends; copolymerization; fluoropolymers; imidazole; membranes; polymer electrolyte fuel cell; sulfonated PEEK

INTRODUCTION Fluorinated polymers[1–4] exhibit remarkable properties, such as chemical, thermal, and electrical stability,[5] inertness to acids, solvents, and oils, low dielectric constant, low refractive index, low or nonflammability, high resistance to aging and oxidation, and low surface tension. These polymers show low friction coefficient and relative permittivity, and they are strongly hydrophobic. For application in a polymer electrolyte fuel cell, they must be functionalized,[6] and the choice of the protogenic group plays an important role in the proton conductivity of fuel cell separator materials. Up to now, the materials used for proton exchange membranes in fuel cell applications have relied on the presence of water as proton carrier. Although practicable at lower temperatures, water management at temperatures higher than 100 °C has a significant impact on the viability of the membrane electrode assembly and on overall operation of the system.

Over the last decade, new concepts have evolved involving alternative proton carriers. The ideal protogenic group should be amphoteric, exhibiting proton donor and acceptor properties, and showing a high degree of self-dissociation. It should also have a high dielectric constant to enhance the charge separation and be stable under fuel cell operation conditions. The relevance of these concepts has been elegantly shown by Kreuer et al.,[7] in particular, in pioneering work on imidazole–sulfonated poly(ether ether ketone) (sPEEK)-type ionomers.

Commercial perfluorosulfonic acid (PFSA) polymers, such as Nafion®, Flemion®, Aquavion®, BAM-3G®, Fumion®, Gore Select®, Dow®, 3M®, or Aciplex, are reference and emerging advanced membranes for proton exchange membrane fuel cells, being characterized by high proton conductivity and chemical stability.[8–10] Their conductivity is dependent on ambient relative humidity, and their glass transition temperature limits their use to <130 °C. In PFSA-type membranes, as in other sulfonic acid-functionalized polymers, such as PEEK, polybenzimidazole, or polysulfone,[11–14] the proton is transferred by water, and, in general, a high level of

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 223–231 (2010)

hydration is required, being around 7 (PBI-type) to 25 (PFSA-type) water molecules per sulfonic acid function. This can lead to excessive membrane swelling at high temperature, which is detrimental to membrane mechanical properties. Furthermore, maintaining a high level of hydration at high temperatures requires high pressure operation. Phosphonic acid-based systems[15] may offer the possibility of adequate proton conductivity over a broad temperature range, although the propensity to condensation by phosphonic acids at high temperature is greater than that of sulfonic acids, and the involvement of water in proton transfer at $T < 100$ °C is not avoided.

Another approach toward high-temperature proton-conducting membranes is the substitution of water by *N*-heterocycles,[16–21] such as imidazole, pyrazole, and benzimidazole. The proton conductivity is expected to be less dependent on water content, because proton transfer between heterocycles is an intrinsic property of these systems. This field was explored by Kreuer et al., and a number of model compounds were described, in which heterocycles were linked through ethylene oxide[16,17] or siloxane[18] oligomer or polymer backbones, and also by Jannasch and coworkers.[19] However, in none of the heterocycle systems prepared to date, nanophase separation could occur as for amphiphilic systems, partly because the concentration of heterocycle units has been low, but also because all polymers prepared have been built around hydrocarbon (or siloxane) backbones.

To our knowledge, no fluorinated polymer containing imidazole groups has been reported in the literature. It would be of interest to find new copolymers bearing fluorinated base units in the backbone and imidazole side functions to ensure thermal and mechanical stabilities and proton conductivity. This is the purpose of this article, which describes the synthesis of a novel monomer containing the imidazole function and its radical copolymerization with a fluoro-olefin to give a polymer with grafted imidazole along the fluoropolymer backbone. The resulting copolymers have been processed into blend membranes incorporating sPEEK, the properties of which have been investigated.

EXPERIMENTAL

Materials

Imidazole, benzyl chloride, potassium hydroxide, paraformaldehyde, chloroethylvinylether, and benzyltriethylammonium chloride were provided by Aldrich, and chlorotrifluoroethylene (CTFE) and 1,1,1,3,3-pentafluorobutane were a gift from Solvay S.A. Tertiobutyl peroxypivalate was kindly given by Akzo Nobel. sPEEK was prepared from PEEK by electrophilic substitution in sulfuric acid under the controlled conditions described previously.[22]

Characterization

^{1}H and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded at room temperature on Bruker AC 400 instrument, using deuterated chloroform or acetone as the solvent and TMS and CFCl$_3$ as the references for ^{1}H and ^{19}F NMR nuclei. In the figures and discussion later, the letters s, d, t, q, and m are abbreviations for singlet, doublet, triplet, quintet, and multiplet, respectively. Coupling constants and chemical shifts are given in Hertz (Hz) and ppm. The experimental conditions to record ^{1}H and ^{19}F NMR spectra were as follows: flip angle 90°, 30°, and 30°; acquisition time: 4.5, 2.9, and 0.7 s; pulse delay: 2, 2, and 5 s; number of scans: 16, 12,000, and 64, and a pulse width of 5 μs for ^{19}F NMR.

Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus in static air with a heating rate of 10 °C min^{-1} from room temperature up to a maximum of 600 °C. Differential scanning calorimetry measurements were conducted using a TA2920 analyzer from TA Instruments DA 73085, an RCS DA cooler and Sartorius MC5 balance. Scans were recorded at a heating/cooling rate of 20 °C min^{-1} from 0 to 100 °C.

Through-plane AC conductivity measurements were performed by impedance spectroscopy using a HP4192 impedance meter in the range 5 Hz–13 MHz using an oscillating voltage of 100 mV. The locally designed conductivity measurements cell allowed the control of temperature under full humidification conditions. Measurements were performed on membrane of thickness 20 μm placed between two stainless steel electrodes of surface area 3 mm^2. In-plane (four electrode) resistance measurements were also made over the temperature range 50–90 °C and relative humidity 10–100% values, and the conductivity calculated from the relationship $\sigma = L/RdW$, where L is the distance between electrodes, d and W are the thickness and width of the sample strip, respectively. In all cases, R was derived from the low intercept of the high-frequency semicircle on a complex impedance plane with the Re (Z) axis.

Synthesis of 2-Benzyl-1-(dioxa-3,6-oct-7-ene)imidazole Monomer (3)

Synthesis of 1-Benzylimidazole (1)

In a 1-L three-necked round-bottomed flask equipped with a condenser and a magnetic stirrer were introduced 44.0 g (0.65 mol) of imidazole, 100.0 g (0.78 mol) of benzyl chloride, 60.0 g (1.07 mol) of sodium hydroxide, and 700 mL of tetrahydrofuran (THF). The solution was refluxed (70 °C) for 120 h, cooled to room temperature, and filtered to eliminate the excess of sodium hydroxide. After the solvent was removed by evaporation, the reaction mixture was diluted with 500 mL diethyl ether, extracted with water, dried with anhydrous Na$_2$SO$_4$, and finally diethyl ether was evaporated off. The desired product was obtained with more than 95% yield and was purified by recrystallization from toluene. $T_m = 72.7$ °C.[23]

^{1}H NMR (acetone-d_6, ppm) δ: 7.70 (N=CH—N, 1H); 7.30 (C$_6$H$_5$, 5H); 7.12 (m, C—H$_{\text{imidazole}}$, 1H); 7.00 (m, C—H$_{\text{imidazole}}$, 1H); 5.24 (CH$_2$, 2H).

Synthesis of 1-Benzyl-2-(hydroxymethyl)imidazole (2)

A total of 50.0 g (0.312 mol) of 1-benzylimidazole (**1**) was introduced in a 300 mL autoclave, with 15.0 g (1.5 mol) of paraformaldehyde dissolved in 150 mL of 1,4-dioxane. After the autoclave was closed, the solution was heated at 135 °C for 20 h, and the pressure reached 7 bar. After reaction, the solvent was removed under vacuum and the black oil obtained was dissolved in 400 mL of dichloromethane. The solution was washed three times with 100 mL of water, the organic phase was dried with anhydrous Na_2SO_4, and dichloromethane was removed by evaporation. The resulting product was held under reduced pressure for 2 days and recrystallized from ethyl acetate (100 mL) three times. This procedure led to 1-benzyl-2-hydroxymethylimidazole (white crystals) with 50% yield. $T_m = 154.9$ °C.[24]

^{1}H NMR ($CDCl_3$, ppm) δ: 7.30 (C6H5, 5H); 7.12 (C—H$_{imidazole}$, 1H); 7.00 (C—H$_{imidazole}$, 1H); 5.24 (CH_2, 2H); 4.61 (C**H**$_2$OH, 2H); 6.02 (OH).

Synthesis of 2-Benzyl-1-(dioxa-3,6-oct-7-ene)imidazole (3)

In a 250-mL two-necked round-bottomed flask equipped with a condenser and a mechanical stirrer, 7.5 g (38 mmol) of 1-benzyl-2-(hydroxymethyl)imidazole and 22 mL of toluene were introduced. Then, 100 mL of aqueous sodium hydroxide (20 mol L^{-1}) and 0.86 g (3.8 mmol) of benzyltriethylammonium chloride were added. Finally, 8.92 g (74.9 mmol) of 2-chloroethylvinylether (CEVE) was added, and the mixture was heated at 90 °C with a vigorous stirring. The disappearance of $Cl{-}CH_2{-}CH_2{-}O{-}CH{=}CH_2$ was monitored by ^{1}H NMR spectroscopy over a period of 24 h. Then, the solvent was evaporated under vacuum and the resulting brown liquid was dissolved in 300 mL of diethylether. The solution was washed several times with water until pH reached 7, and the organic phase was dried with anhydrous Na_2SO_4 and evaporated. A total of 9.0 g of an orange oil was obtained corresponding to 87% yield of 2-benzyl-1-(dioxa-3,6-oct-7-ene)imidazole (BVI).

^{1}H NMR (acetone-d_6, ppm) δ: 7.42 (C6H5, 5H); 7.12 (CH=C**H**—NC,1H); 6.92 (NBz-C**H**=CH, 1H); 6.49 (dd, CH$_2$C**H**O, 1H); 5.30 (CH2, 2H); 4.61 (C**H**$_2$O, 2H); 4.18 (C**H**$_2$CHO, 1H); 3.99 (C**H**$_2$CHO, 1H); 3.79 (CH$_2$CHOC**H**$_2$CH$_2$O—, 2H); 3.67 (CH$_2$CHOCH$_2$C**H**$_2$O—, 2H).

Synthesis of Poly(BVI-alt-CTFE) Copolymer

The radical copolymerization of BVI with CTFE was carried out in a 0.1-L HC-276 Hastelloy autoclave equipped with a rupture disk, inlet and outlet valves, a manometer, a thermometer, and a magnetic stirrer. This vessel was left closed for 20 min and purged with 15 bar of nitrogen pressure to prevent any leak, before purging through two nitrogen-vacuum cycles to limit the presence of oxygen. A total of 10.0 g (38.7 mmol) of liquid monomer BVI, 0.210 g (1.6 mmol) of *tert*-butylperoxypivalate, and 60 mL of 1,1,1,3,3-pentafluorobutane were introduced into the autoclave. Next, the autoclave was cooled to −80 °C in an acetone/liquid nitrogen bath and 10.1 g (86.7 mmol) of CTFE was added. The autoclave was then heated to 75 °C and the pressure reached 15 bar. After 14 h of reaction, the pressure dropped to 12 bar, and the autoclave was cooled to room temperature. Unreacted CTFE was released at 0 °C, and it was determined by weighing that 49% had been converted. The solvent was evaporated under vacuum, and the resulting black viscous oil was dissolved in few milliliters of dichloromethane, and an orange-brown powder (yield 40 wt %) precipitated with 600 mL of diethylether.

^{1}H NMR (acetone-d_6, CD_3OD ppm) δ: 7.28 (C_6H_5, 5H); 6.91 (N—C**H**=C**H**—N, 2H); 5.39 (NC**H**$_2$—Ph, 2H); 4.52 (imidazole-**CH**$_2$**—O**, 2H); 4.10 (CH$_2$—C**H**OR—CF$_2$, 1H); 3.45–4.10 (O—C**H**$_2$—C**H**$_2$—O, 4H); 2.31–3.29 (C**H**$_2$—CHOR—CF2, 2H).

^{19}F NMR (acetone-d_6, CD_3OD ppm) δ: −109 (—CF$_2$—C**F**Cl—CH2, 1F); −119 (CHO—C**F**$_2$— CFCl—, 2F); −130 (—CF$_2$—C**F**Cl—C**F**Cl—CF$_2$, 2H). $T_g = 43$ °C. $T_{dec\ 10} = 226$ °C.

%C: 54.03 (calculated for alternating copolymer: 54.43); %F: 15.65 (calculated: 15.21); %Cl: 10.60 (calculated: 9.46); %N: 6.44 (calculated: 7.47).

Deprotection of Imidazole in Poly(BVI-alt-CTFE) Copolymer by Catalytic Hydrogenation

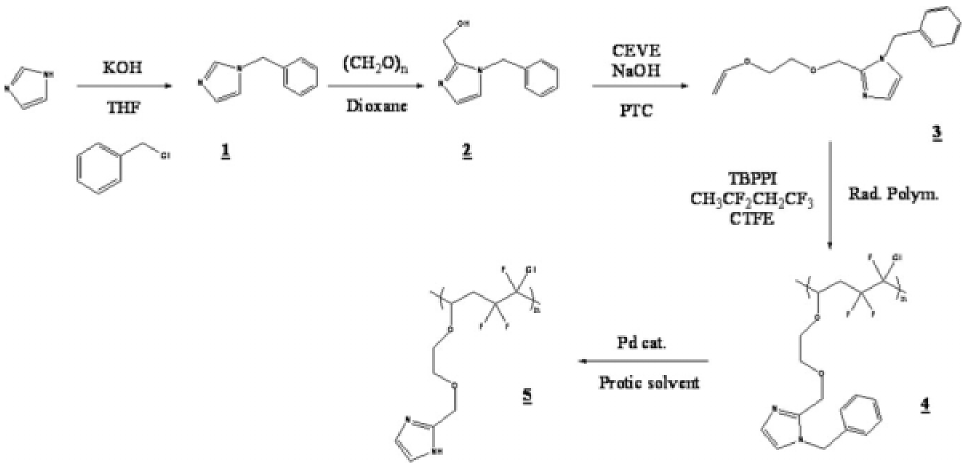
Using the same autoclave as mentioned earlier, 100 mL of acetic acid, 5.01 g of poly(BVI-alt-CTFE) copolymer, and 0.49 g (3.5 mmol) of palladium dihydroxide were introduced. The autoclave was then closed and the system was pressurized with 32 bar of hydrogen. It was heated at 70 °C for 72 h, and the pressure was maintained by addition of hydrogen each day for 6 days. The product mixture was filtered over zeolite and the solvent was removed by evaporation. The dry solid was then dissolved in 50 mL of an aqueous solution of Na_2CO_3 (5%) under reflux. The mixture was filtered, washed three times with 50 mL of distilled water, and dried under vacuum. Finally, the solid product was dissolved in 10 mL of methanol and precipitated with 400 mL of diethylether. A total of 2.05 g of an orange powder was obtained with a deprotection yield of about 75%.

^{1}H NMR (MeOH-d_6, CD_3OD ppm) δ: 7.28 (C_6H_5); 6.91 (N—C**H**=C**H**—N); 5.39 (NC**H**$_2$—Ph); 4.52 (imidazole-C**H**$_2$—O); 4.10 (CH$_2$—C**H**OR —CF$_2$); 3.45–4.10 (O—C**H**$_2$—C**H**$_2$—O); 2.31–3.29 (C**H**$_2$—CHOR—CF2).

^{19}F NMR (MeOH-d_6, CD_3OD ppm) δ: −109 (—CF$_2$—C**F**Cl—CH2, 1F); −119 (CHO—C**F**$_2$— CFCl—, 2F); −130 (—CF$_2$—C**F**Cl—C**F**Cl—CF$_2$, 2H). T_g 38 °C.

Membrane Preparation

Poly(Imi-alt-CTFE) copolymer (30 wt %) was added to *N*-methylpyrrolidinone (NMP) giving a suspension, to which aqueous lithium chloride (3 mol L^{-1}) was added. The same preparation was carried out with sPEEK (15 wt %), and the copolymer suspension was slowly added in sPEEK suspension under strong stirring. The suspensions were heated at 120 °C to yield a dark brown solution that was treated with ultrasound for 1 h to increase the melting of polymer chains. The solution was filtered to separate any insoluble material, and water was evaporated by heating under vacuum. It was cast on to a heated glass plate with a doctor blade and transferred to a vacuum oven, where solvents were removed by heating at 110 °C for 10 h. The resultant film was removed from the glass support either by immersion in water or in aqueous hydrochloric acid (1 mol L^{-1}), when the acid form membrane could be recovered directly. Any



SCHEME 1 Synthesis of poly(BVI-alt-CTFE) copolymer by direct copolymerization and imidazole deprotection. PTC, CEVE, TBPPI, and CTFE represent phase transfer catalysis, 2-chloroethyl vinyl ether, tertiobutyl peroxypivalate, and chlorotrifluoroethylene, respectively

residual solvent and lithium ions [13] were eliminated by washing the membrane in HCl (1 mol L^{-1}) at 100 °C for 2 h, then in deionized water at 100 °C for 2 h.

RESULTS AND DISCUSSION

The poly(BVI-alt-CTFE) copolymer was prepared according to a five-step reaction (Scheme 1). This novel copolymer first requires the synthesis of the nonfluorinated imidazole-terminated vinylic ether monomer (three steps), that is then directly copolymerized with CTFE. The deprotection of imidazole groups by catalytic hydrogenation in a final step leads to the desired fluorinated copolymers bearing pendant imidazole functions.

Synthesis of 2-Benzyl-1-(dioxa-3,6-oct-7-ene)imidazole Monomer 3

The novel imidazole-containing vinyl-ether **3** was synthesized in a three-step reaction (Scheme 1). Imidazole was initially protected with a benzyl group, then condensed with paraformaldehyde, and the resulting hydroxymethyl-protected imidazole submitted to nucleophilic substitution with commercially available CEVE. The first step of protection of the imidazole group led to quantitative yield of product **1**, which was purified by recrystallization from toluene. Protection of imidazole was required to avoid any grafting onto nitrogen during the substitution step and then any transfer to the acid proton during radical copolymerization. The ^{1}H NMR spectrum of compound **1** shows a characteristic singlet centered at 5.24 ppm assigned to the methylene of the benzyl group. A multiplet centered at 7.30 ppm corresponds to the aromatic protons of the phenylene group. Finally, two signals attributed to the imidazole protons are distinguished at 7.00 and 7.12 ppm.

The second step is the condensation[25] of molecule **1** with a large excess of paraformaldehyde. This hydroxymethylation leads to compound **2** bearing a hydroxymethyl group on the position adjacent to the two imidazole nitrogen atoms. Compound **2** was purified by recrystallization from ethyl acetate in 50% yield. The ^{1}H NMR spectrum was similar to that of intermediate **1** with an additional signal at 4.61 ppm assigned to $\mathbf{CH_2}$—OH. The last step was the nucleophilic substitution of **2** with CEVE. This reaction was carried out by phase-transfer catalysis and led to desired monomer **3** in 87% yield. This monomer was also characterized by ^{1}H NMR, the spectrum of which (Fig. 1) shows the vinyl protons centered at 4.04 ppm for terminal CH_2 and 6.49 ppm for the adjacent CH proton (CH_2=C**H**), the methylene groups adjacent to the oxygen atoms giving signals at 3.79 and 3.67 ppm. The overall yield of **3** was 44% relative to starting imidazole.

Direct Radical Copolymerization of BVI with CTFE

The proton conductivity being expected here, as in other polymer electrolytes, to depend on the number of charge carriers, it was an important aim here to incorporate a sufficient number of imidazole-containing groups within the final copolymer. It was known from previous work that the radical copolymerization of vinyl ether (electron-donating monomer) with CTFE (electron-withdrawing monomer) leads to alternating copolymers.[4] Radical copolymerization of **3** with CTFE was carried out using various sets of experimental conditions. These reactions were performed in solution with different initial molar ratios C_0 $\{C_0 = [\mathrm{In}]_0/([\mathrm{CTFE}]_0 + [\mathrm{BVI}]_0)\}$. The results are summarized in Table 1. In initial experiments, reaction was carried out with a C_0 of 1% using different solvents. This first set of experiments clearly demonstrated that $C_4F_5H_5$ only is appropriate as solvent and good yields (about 50%) were achieved. Indeed, experiments were repeated in acetonitrile instead but only low yields could be reached. This may be explained by higher solubility of the fluorinated monomer as well as the corresponding copolymers. Indeed, the concentration of CTFE incorporated into the copolymers always remained higher than that of BVI. However, whatever the experimental parameters used, alternating copolymers were formed having near to 50% of BVI units. However, a few excess in CTFE conversion was observed, characterized by CTFE-CTFE diades at the ^{19}F NMR analysis (signal centered at 127 ppm). Entry 4 confirms this observation and also shows that the use of a greater amount of BVI entails a drop in monomer conversion. The system pressure also seems to be an important parameter too, Entry 2 is the experiment using the most quantity of fluorinated gas (higher pressure), which results to a

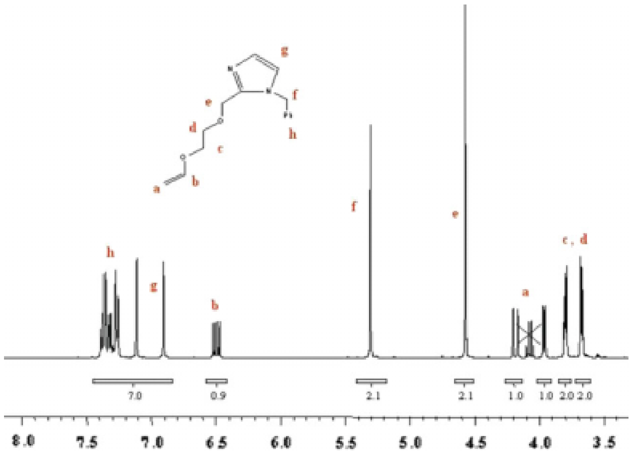


FIGURE 1 ^1H NMR spectrum of 1-benzyl-2-(vinyloxyethyloxymethyl)imidazole (BVI) in acetone-d_6 (presence of residual alcohol).

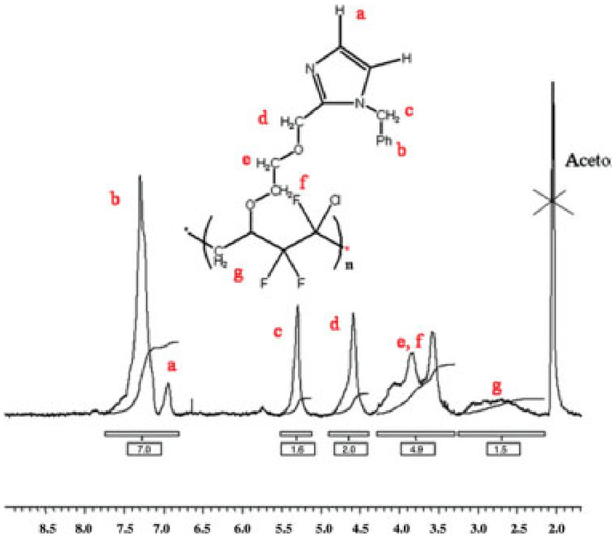


FIGURE 2 ^1H NMR spectrum of poly(BVI-alt-CTFE) copolymer in deuterated DMF.

mass yield higher than all the other experiments. The ^1H NMR spectrum of the sample of entry 1 is given in Figure 2. The copolymers precipitate during the course of copolymerization, which may not be favorable to reach high-molecular-weight polymer. The determination of polymer molecular weight was impeded by the insolubility of the resulting copolymer in any organic solvent commonly used for GPC analysis (DMF, THF) probably due to a chemical affinity between the polymer and the chromatographic column. A low molecular weight would seem to be indicated by the T_g value of about 40 °C, because high-molecular-weight fluoropolymers usually exhibit higher T_g values.[4] TGA (Fig. 3) shows that weight loss on heating in air occurs in two main steps. The first, at around 230 °C, is characteristic of the degradation of the heterocycle BVI units. After a weight loss of around 50%, a plateau is observed between 350 and 500 °C, and thereafter the fluorinated units begin to degrade.

Deprotection of the Imidazole Group

Removal of the protecting benzyl group is required to regenerate the imide group on imidazole. Deprotection by hydrogenation is more difficult on a nitrogen-containing heterocycle than on an aliphatic amine (e.g., on the amine function of an α-aminated acid) and needs more drastic conditions. The literature[26–28] describes different methods for removal of benzyl groups supported on the nitrogen atom in position 1 of imidazole. The most used method is catalytic hydrogenation in the presence of a palladium catalyst. Different palladium-based catalysts can be used for this reaction with various efficiencies: Pd/C (5%) < Pd/C (10%) < $Pd(OH)_2$/C (15–20%). Various parameters influence the result of the reaction such as temperature or hydrogen pressure. This reaction is often carried out at room temperature for aliphatic amines but, generally, higher temperature is required in the case of heterocycles (50–80 °C). (The hydrogen pressure is most of the time higher than 30 bar for nitrogen-containing heterocycles). The nature of the solvent is also crucial, alcohols being good solvent media for hydrogenation, whereas acidification of the medium (HCl or CH_3COOH) is known to favor benzyl group reduction. A series of experiments were performed so as to identify the conditions allowing the highest yield of deprotected copolymer (Table 2). Experiments 5–8 have clearly failed to deprotect the imidazole group, at all reaction temperatures, solvents, and hydrogen partial pressures used. Methanol is inappropriate as a

TABLE 1 Radical Copolymerization of BVI (0.5 mol L^{-1}) with Chlorotrifluorethylene at 75 °C Initiated by *tert*-Butylperoxypivalate (In)

Entry	Mole Percent of BVI in the Feed (%)	C_0[a] (%)	Mass Yield[b] (%)	BVI Unit in Copolymer[c] (%)	T_g[d] (°C)	T_{10}[e] (°C)	T_{50}[e] (°C)
1	30	1.0	45	48	43	226	362
2	20	2.0	50	47	42	217	345
3	30	0.5	40	48	39	228	359
4	50	1.0	31	47	42	224	347

[a] $C_0 = [In]_0/([BVI]_0 + [CTFE]_0)$.

[b] $m(\text{copolymer})_{\text{expt}}/m(\text{copolymer})_{\text{calculated max.}}$

[c] Calculated from elemental analyses using nitrogen values.

[d] T_g: glass transition determined by DSC.

[e] T_{10} and T_{50}: 10 and 50% decomposition, respectively, determined by TGA, under air.

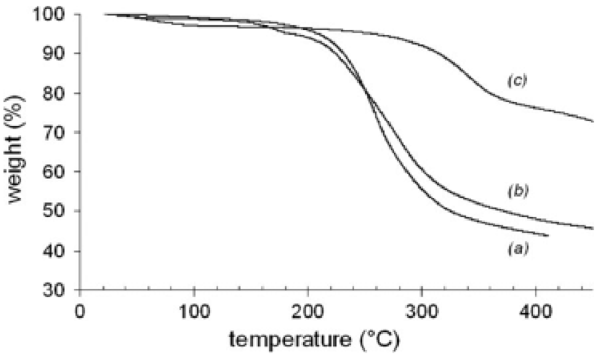


FIGURE 3 Thermogravimetric analysis of protected (a) and deprotected (b) copolymer poly(Imi-alt-CTFE) and of blend membrane ImiCTFE-sPEEK-73 (c). Heating rate 10 °C min^{-1} in air.

solvent, with a poor yield, even after 2 days using a Pd/C catalyst. When the reaction time and the pressure were increased and acetic acid used as a solvent (Experiment 9), deprotection occurred in 50% yield. The use of $Pd(OH)_2$ at higher hydrogen pressure and higher temperature (Experiment 10) led to 74% deprotection of imidazole, as determined from the ^1H NMR analysis of the final product. Deprotection yield was calculated using integration as follows:

$$1 - \frac{I_{5.39}}{I_{4.52}},$$

where $I_{5.39}$ and $I_{4.52}$ represent the integrals of the signals centered at 5.39 and 4.52 ppm in the ^1H NMR spectra, respectively. The resonance corresponding to the methylene protons of the benzyl group centered at 5.39 ppm disappeared, whereas a second signal appears at 4.52 ppm corresponding to the methylene protons adjacent to the imidazole function. The resulting copolymer (**5**) is characterized by a chlorotrifluorinated backbone, in which CTFE units alternate with a pendant imidazole group linked to the backbone through a flexible ethylene oxide spacer; this copolymer is referred to as poly(Imi-alt-CTFE).

Finally, assessment of the solubility of the copolymers in various solvents showed that the unprotected copolymers are soluble in solvents such as DMF, DMSO, or NMP after addition of a lithium salt.

Properties of Poly(Imi-alt-CTFE)sPEEK Blend Membranes

Charge defects are needed for proton conduction in any system based on nitrogen-containing heterocycles. In this case, an increase in charge carrier concentration was brought about by blending the above poly(Imi-alt-CTFE) copolymer with sPEEK.[22] Membrane compositions were chosen to have different proportions of poly(Imi-alt-CTFE) copolymer to sPEEK, one membrane series being richer in poly(Imi-alt-CTFE), a second richer in sPEEK. Mass ratios were, respectively, 70:30 and 30:70 in membranes ImiCTFE-sPEEK-73 and ImiCTFE-sPEEK-37, corresponding to mole ratios of imidazole to sulfonic acid groups of 3.00 and 0.77, respectively (concentrations of sulfonic acid groups of 0.52 and 0.91 meq g^{-1}).

TGA of the ImiCTFE-sPEEK-73 blend membrane (Fig. 3) shows that there is no loss of weight in air until >250 °C. This is higher than for the poly(Imi-alt-CTFE) copolymer, and the thermal stability has thus been improved by blending, probably due to proton transfer from the sulfonic acid groups to imidazole and concomitant ionic crosslinking. Observation by SEM coupled with EDX analysis indicates the membrane composition to be homogenous with true blend formation between the s-PEEK and poly(Imi-alt-CTFE) copolymer components (Fig. 4).

The proton conductivity at 65 °C of the ImiCTFE-sPEEK-73 and ImiCTFE-sPEEK-37 membranes is shown in Figure 5 in the relative humidity range 10–90%. Interestingly, the two membranes show rather distinct behavior. The conductivity of membrane ImiCTFE-sPEEK-37 (higher proportion of sPEEK) has a strong dependence on RH, as is observed for dense membranes of sPEEK alone.[22] At 65 °C, the conductivity value increases by six orders of magnitude from 5×10^{-5} mS cm^{-1} at 10% RH to 15 mS cm^{-1} at 90% RH. In contrast, the conductivity of membrane ImiCTFE-sPEEK-73 (higher proportion of ImiCTFE) is significantly less

TABLE 2 Catalytic Removal of Benzyl Groups on Poly(BVI-alt-CTFE) Copolymer under H_2 Pressure

Exp.	Catalyst	Temp. (°C)	*P* (bar)	Solvent	Time (h)	Yield (%)
5	Pd/C (10%)	55	1	MeOH	40	–
6	Pd/C (10%)	60	10	MeOH	48	–
7	Pd/C (10%)	70	20	MeOH	48	–
8	Pd/C (10%)	70	25–30	MeOH	48	–
9	Pd/C (10%)	70	34	CH_3CO_2H	120	50
10	$Pd(OH)_2$ (10%)	70	34	CH_3CO_2H	120	74
11	$Pd(OH)_2$ (10%)	90	31	CH_3CO_2H	120	75
12	$Pd(OH)_2$ (40%)	90	34	CH_3CO_2H	120	77
13	$Pd(OH)_2$ (40%)	70	34	CH_3CO_2H	120	75

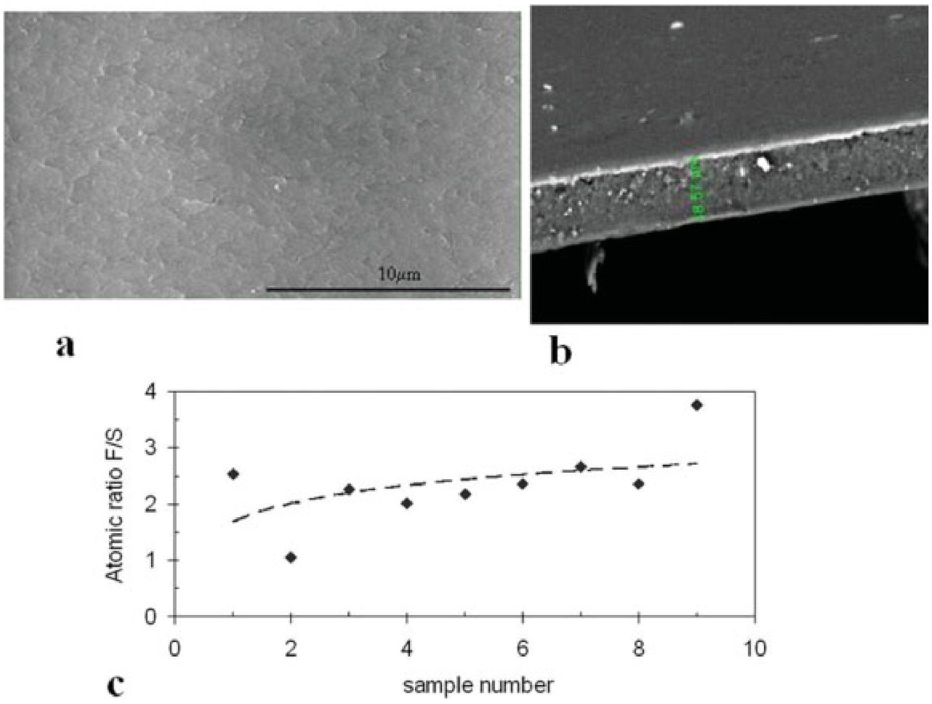


FIGURE 4 SEM micrograph of the surface (a) and edge (b) of blend membrane ImiCTFEsPEEK73 and atomic ratio of fluorine to sulfur from EDX analysis across the membrane thickness (c). [Color figure can be viewed in the online issue, which is now available at www.interscience.wiley.com.]

dependent on the relative humidity, and the values at low RH are higher. Thus, the conductivity at 30% RH is 4 mS cm^{-1} and at 50–90% RH is in the range 8–10 mS cm^{-1}. This is a central result, because it responds at least in part to the application-driven need for proton-conducting materials having low dependence of the conductivity on the degree of ambient humidity. The results can be directly related to the proportion of pendant imidazole functionalities in the membranes, which determines the dominant proton-conduction mechanism occurring in each sample. Although a mechanistic study is not the objective of this work, it can be expected that in ImiCTFE-sPEEK-73 (higher concentration of imidazole) a mechanism that does not depend on membrane water content is more prevailing than in ImiCTFE-sPEEK-37, where water-assisted proton transport is predominant.

The conductivity of membrane ImiCTFE-sPEEK-73 in the temperature range 40–90 °C at 25 and 100% RH is shown in Figure 6. At 25 and 100% RH, the conductivity is about 0.5 and 6 mS cm^{-1} respectively, between 50 and 70 °C. Above 70 °C, however, the conductivity takes a sharp downturn in both cases. These observations were reproducible on membranes incorporating poly (Imi-alt-CTFE) copolymer prepared from different batches. As the drop in conductivity above 70 °C is observed at both low and high relative humidities, it is considered not to be due to any influence of water-assisted proton transport, that is, to membrane dehydration. A more likely explanation is that a change in membrane microstructure occurs above 70 °C, which is unfavorable to proton transfer and transport. A strong thermal event was indeed detected for ImiCTFE-s-PEEK73 at 68 °C (Fig. 7). Application of the Fox-Flory equation[29] ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$) gives a calculated T_g value for the blend of 70.6 °C. On the basis of these observations, we conclude that microstructure of ImiCTFE-sPEEK-73 is modified above 70 °C and that this new structure creates a barrier to proton transport.

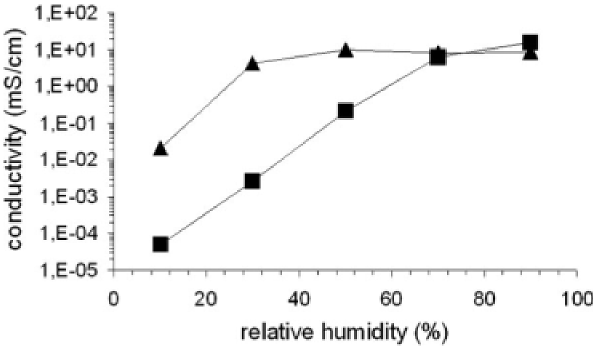


FIGURE 5 Dependence of proton conductivity at 65 °C of blend membranes ImiCTFEsPEEK73 (▲) and ImiCTFEsPEEK37 (■) on relative humidity.

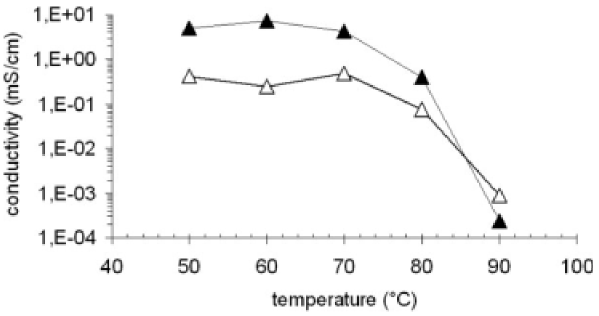


FIGURE 6 Temperature dependence of the proton conductivity of blend membrane ImiCTFEsPEEK73 at 100 (▲) and 25% (△) relative humidity.

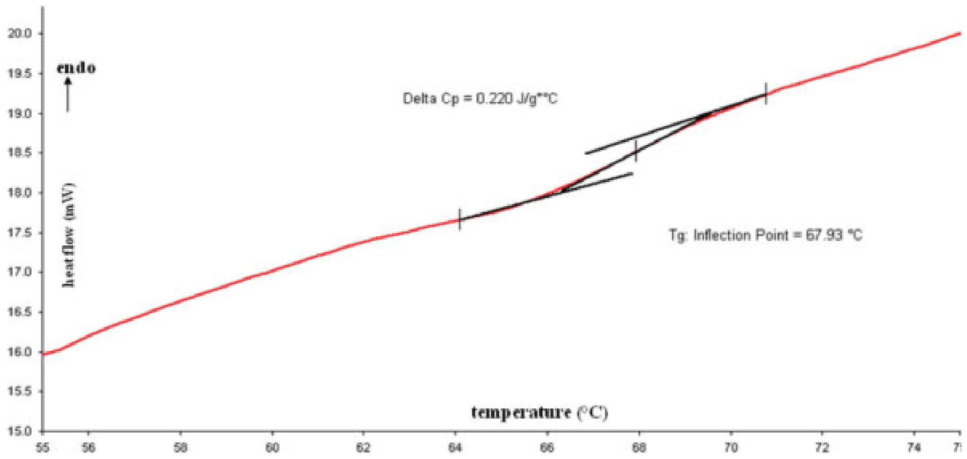


FIGURE 7 Differential scanning calorimetry of blend membrane ImiCTFEsPEEK73. [Color figure can be viewed in the online issue, which is now available at www.interscience.wiley.com.]

Although no direct information is available, some suggestions can be put forward to interpret these observations. The different characters of the CTFE backbone of the polymer and the imidazole-terminated and hydrocarbon-based ethylene oxide pendant chains are expected to lead to a phase-separated microstructure within the cast membranes, in which imidazole groups will be clustered together into imidazole-rich domains. The sPEEK component of the blend will also be associated with these domains, both through nonspecific interactions between the hydrocarbon chains, but more particularly through hydrogen bonding between the sulfonic acid and imidazole groups. This configuration is clearly favorable to proton transfer and transport. Above 70 °C, the loss in conductivity can be interpreted in terms of a thermally induced rearrangement within the membrane that is possibly due to disruption of the hydrogen bonded network as a result of flow of the fluorinated polymer backbone. Whatever the physical origin of the loss of conductivity above 70 °C, it is a reversible phenomenon, because the low temperature conductivities are almost completely recovered when the membrane is cooled, Figure 8. It is possible that a higher polymer molecular weight could help to maintain the low-temperature membrane microstructure and endeavors continue in this direction.

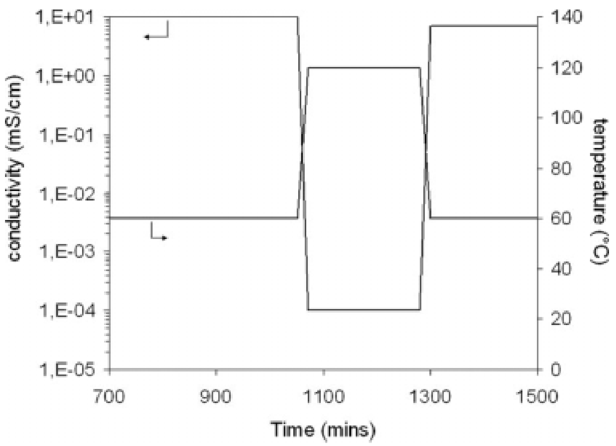


FIGURE 8 Temperature dependence (60–120 °C) of conductivity of blend membrane ImiCTFEsPEEK73 at 80% relative humidity showing reversibility of thermally induced phenomenon at 70 °C.

The recent literature provides several examples of imidazole- or benzimidazole-functionalized species bound, for example, to polyoxoethylene spacers[16,17] or as functional units on a hydrocarbon or siloxane polymer chain.[18] Although the Imi-POE-Imi systems have related proton-conduction properties, such "model compounds" of short chain length have no film-forming ability. The propensity of the imidazole and sulfonic acid groups in the present ImiCTFE-sPEEK system to cluster into confined domains is a property of the membrane, and in this sense, the properties exhibited by model (molecular) compounds cannot be directly related to those developed by a polymer membrane system. In other recent work, polymeric benzimidazole- or imidazole-functionalized polymers have been developed, the conductivities of which have been described as in the range of 10^{-7} S cm^{-1} when measured under anhydrous conditions.[19] In comparison with these studies, we have increased the density of heterocycle moieties in the polymer chains, while using a flexible pendant group, both factors tending to encourage clustering of imidazole units in the membrane. In addition, we have introduced an acidic polymer as proton "dopant" to promote a higher degree of dissociation. Unlike the phosphoric acid doping of polybenzimidazole,[30] or the polyphosphoric acid doping of imidazole-functionalized poly(diphenyl phenylene) oxide,[31] the sPEEK used in the blend membranes of this work does not suffer any risk of elution under conditions when liquid water is present.

CONCLUSIONS

The poly(Imi-alt-CTFE) copolymers prepared here for the first time associate a CTFE backbone with pendant imidazole groups linked through ethylene oxide groups. This composition favors microstructural phase separation of the polymer backbone regions giving chemical stability on the one hand, and pendant group regions providing proton-conduction properties on the other. It is expected that PEO and imidazole groups form clusters in the same way as the sulfonic acid groups in PFSA Nafion®-type membranes. No weight loss in TGA was observed below 230 °C for the poly(Imi-alt-CTFE) copolymers and the T_g is about 40 °C.

Polymer blend membranes of poly(Imi-alt-CTFE) and sPEEK can be formulated in various compositions, and all compositions have high proton conductivity above 70% RH. At lower RH values, only those membranes with higher poly(Imi-alt-CTFE) content retain a conductivity of 4–10 mS cm^{-1}, whereas membranes with a high concentration of sPEEK have lower conductivity at low RH, even though the concentration of proton charge carriers is higher. The conductivity decreases above 70 °C, and it is believed that this is due to a thermally induced structural rearrangement.

The authors acknowledge the award of doctoral funding (to G. Frutsaert) by the CNRS Direction aux Entreprises and Peugeot-Citroën S.A.

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