



HAL
open science

Poly(tetrafluorostyrenephosphonic acid) – Polysulfone Block Copolymer Electrolytes

Zhecheng Shao, Arindam Sannigrahi, Patric Jannasch

► **To cite this version:**

Zhecheng Shao, Arindam Sannigrahi, Patric Jannasch. Poly(tetrafluorostyrenephosphonic acid) – Polysulfone Block Copolymer Electrolytes. *Journal of Polymer Science Part A: Polymer Chemistry*, 2013, pp.4657-4666. hal-00904746

HAL Id: hal-00904746

<https://hal.science/hal-00904746>

Submitted on 15 Nov 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Poly(tetrafluorostyrenephosphonic acid) – Polysulfone Block Copolymer Electrolytes

*Zhecheng Shao, Arindam Sannigrahi, Patric Jannasch**

Polymer & Materials Chemistry, Department of Chemistry,
Lund University P.O. Box 124, SE-221 00, Lund, Sweden

ABSTRACT: A series of ionic ABA triblock copolymers having a central polysulfone (PSU) central block and poly(2,3,5,6-tetrafluorostyrene-4-phosphonic acid) (PTFSPA) outer blocks with different lengths were prepared and studied as electrolyte membranes. PSU with terminal benzyl chloride groups was used as a bifunctional macroinitiator for the formation of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) blocks by atom transfer radical polymerization (ATRP). Selective and complete phosphonation of the PPFS blocks was achieved via a Michaelis–Arbuzov reaction using tris(trimethylsilyl)phosphite at 170 °C. Copolymer films were cast from solution and subsequently fully hydrolyzed to produce transparent flexible proton conducting PTFSPA-*b*-PSU-*b*-PTFSPA membranes with a thermal stability reaching above 270 °C under air, and increasing with the PTFSPA content. Studies of thin copolymer electrolyte membranes by tapping mode atomic force microscopy showed phase separated morphologies with continuous proton conducting PTFSPA nano scale domains. Block copolymer membranes reached a proton conductivity of 0.08 S cm⁻¹ at 120 °C under fully hydrated conditions, and 0.8 mS cm⁻¹ under 45% relative humidity at 80 °C.

KEYWORDS: polystyrene; atom transfer radical polymerization (ATRP); phosphonation; ionomers; proton-exchange membrane fuel cells

INTRODUCTION

Various polymers functionalized with phosphonic acid and its ester derivatives are interesting for use in a range of different applications including materials for dental cements,^{1,2} implants and tissue engineering,^{3,4} flame-retardants^{5,6} and fuel cell membranes.⁷⁻¹⁴ Especially the proton-exchange membrane fuel cell (PEMFC) currently attracts a great deal of interest because it has the potential to achieve higher efficiencies than current power sources at a significantly lower environmental effect.¹⁵ To this end, both fluorinated¹⁶⁻²¹ and non-fluorinated²²⁻⁴⁰ polymers have been synthesized by polymerization or by functionalization of pre-polymers. Recently Atanasov and Kerres have reported on the phosphonation of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) whereby the fluorine atom in the *para* position was substituted by phosphonic acid in a Michaelis-Arbuzov reaction with tris(trimethylsilyl)phosphite.⁴¹ Because of the presence of the fluorine atoms on the aromatic ring, the pK_a values of the resulting poly(2,3,5,6-tetrafluorostyrene-4-phosphonic acid) (PTFSPA) were calculated to be $pK_a^1 = 0.5$ and $pK_a^2 = 6.2$, which is lower than for typical arylphosphonic acids.⁴¹ PTFSPA showed a high thermal stability and a high proton conductivity at reduced relative humidity above 100 °C. However, because of its high ionic content, PTFSPA has poor film forming properties and is highly water-soluble which makes it unsuitable for direct use as an electrolyte membrane.

Water solubility of hydrophilic polymer segments can be prevented by forming hydrophilic-hydrophobic block and graft copolymers. These copolymers characteristically self-assemble because of the thermodynamic incompatibility between the ionic and nonionic polymer

segments.¹⁰ The self-assembly leads to a variety of different morphologies that contain nanostructured ion-conducting phases. Several investigators have reported on the influence of ordered ionic nanostructures on the properties of proton conducting membranes.¹¹ However, there are still quite few reports on the morphologies and the proton conducting properties of phosphonated block^{34,35,42-44} and graft³⁶⁻³⁸ copolymers.

By “clicking” PTFSPA side chains onto a PSU backbone, Dimitrov et al. very recently prepared graft copolymers which formed water non-soluble membranes with high contents of phosphonic acid.⁴⁵ In the present communication we report on the preparation and properties of the first block copolymers containing PTFSPA segments. An aromatic PSU was first prepared by polycondensation and functionalization with benzylchloride end groups. The PSU was then used as a macroinitiator for atom transfer radical polymerization (ATRP) of 2,3,4,5,6-pentafluorostyrene to form PFFS-*b*-PSU-*b*-PFFS triblock copolymers with different block ratios. Selective and complete phosphonation of the PFFS blocks was achieved with tris(trimethylsilyl)phosphite to obtain a series of PTFSPA-PSU-PTFSPA block copolymers. Solvent cast membranes of the phosphonated block copolymers were investigated by thermal analysis, microscopy, and measurements of water uptake and proton conductivity.

EXPERIMENTAL SECTION

Materials

The following reagents and solvents were used as received: copper(I) bromide (Sigma-Aldrich, 98%), 2,2'-bipyridyl (Acros, 99+%), α,α' -dibromo-*p*-xylene (Acros, 97%), *o*-xylene (Aldrich, 97%), tetrahydrofuran (Honeywell, 95%), hexane (Honeywell, 95%), tris(trimethylsilyl)phosphite (TSP, Acros, 92%), methanol (Honeywell, 95%), toluene (Sigma-

Aldrich, 99%), 2-propanol (Honeywell, 95%), diethyl ether (Sigma-Aldrich, 99%), dimethylacetamide (DMAc, Sigma-Aldrich, 99%). 4,4'-Dichlorodiphenyl sulfone (DCDPS, Aldrich, 98%) and 1,3-bis(2-(4-hydroxyphenyl)-2-propyl)benzene (bisphenol M, Aldrich, 99%) were purified by recrystallization in hot toluene. Potassium carbonate (Acros, 99+%) was dried at 120 °C overnight. 2,3,4,5,6-Pentafluorostyrene (PFS, Aldrich, 99%) was activated by passage through a column of aluminum oxide (Alfa Aesar, activated, basic, Brockmann Grade I, 58 Å) before use.

Macroinitiator Synthesis

The PSU macroinitiator was prepared in a polycondensation reaction followed by an end-group functionalization, as shown in Scheme 1. A pre-dried two-neck round bottom flask (50 mL) was firstly charged with DCDPS (2044 mg, 7.12 mmol, 1 eq.), bisphenol M (2540 mg, 7.32 mmol, 1.03 eq.), potassium carbonate (1180 mg, 8.56 mmol, 1.2 eq.), DMAc (28 mL) and toluene (8 mL) and was then equipped with a nitrogen inlet and a Dean-Stark trap. The Dean-Stark trap was filled with toluene and equipped with a condenser. The round bottom flask was kept at 160 °C for 4 h to dehydrate the reaction mixture. The toluene in the Dean-Stark trap was then removed and the temperature was raised to 175 °C. After 48 h, and the reaction mixture was diluted by adding 10 mL of DMAc, and the solution was then added drop-wise into methanol (400 mL) under vigorous stirring. The precipitate was collected by filtration and purified by stirring with a fresh portion of methanol (400 mL) overnight. After filtration, the precipitate was dried in a vacuum oven to afford a white compound **1**. (3.7 g, yield = 91%).

The end-group functionalization was carried out as follows. A round bottom flask (500 mL) was charged with **1** (3.5 g, 0.146 mmol, 1 eq.), α,α' -dibromo-*p*-xylene (1155 mg, 4.38 mmol, 30 eq.), potassium carbonate (605 mg, 4.38 mmol, 30 eq.) and THF (200 mL). The reaction mixture

was kept at 80 °C for 5 days, and was then stopped by slowly pouring the mixture into 2-propanol (1 L). The precipitate was collected by filtration, washed with water and dissolved in hot THF (200 mL). The solution was again slowly added to 2-propanol (1 L) and the precipitate was collected by filtration and washed with portions of fresh 2-propanol. The product was dried in vacuum to afford a white powder **2**. (3.4 g, yield = 92%).

Triblock Copolymer Synthesis

The PPFS-PSU-PPFS triblock copolymers were synthesized by using the end-functionalized PSU as a macroinitiator for atom-transfer radical polymerization (ATRP). In a typical synthesis of a triblock copolymer, a Schlenk flask (25 mL) was first charged with **2** (500 mg, 0.02 mmol, 1 eq.). The solid was dissolved by adding *o*-xylene (2 mL) and heating to 110 °C. After cooling to room temperature, the Schlenk flask was charged with copper(I)bromide (6 mg, 0.04 mmol, 2 eq.), 2,2'-bipyridyl (13 mg, 0.08 mmol, 4 eq.) and a pre-determined amount of PFS (Table 1). The molar ratio of Br-PSU-Br:CuBr:bipyridyl was kept at 1:2:4. After three freeze-thaw cycles, the flask was kept at 110 °C for 48 h under nitrogen atmosphere. The reaction mixture was then cooled and diluted with a portion of THF (10 mL). The solution was added drop-wise to diethyl ether (250 mL) under stirring. The precipitate was collected by filtration, washed with diethyl ether and dried in vacuum to afford a white-green compound. The triblock copolymers (**3-7**) are denoted as PPFS_{*x*}-PSU₄₄-PPFS_{*y*}, where *x* and *y* are the number of repeating units in the respective blocks (*y* also represents the degree of polymerization of the PPFS blocks). The details of the synthesis of the five triblock copolymers are given in **Error! Reference source not found.**

Selective Phosphonation

In a typical phosphonation reaction, a Schlenk tube equipped with a condenser was charged with a PPFS_y-PSU₄₄-PPFS_y copolymer (500 mg) and TSP (5 mL). The Schlenk tube was kept at 170 °C for 48 h. The reaction mixture was then cooled to room temperature and diluted with THF (10 mL). The solution was then slowly added into hexane (100 mL) under stirring. The precipitate was collected by filtration, washed with fresh hexane and dried in vacuum to afford a white compound. In order to obtain the acid form of the phosphonated triblock copolymers, the samples in the ester form was dissolved in DMAc (10 mL) and treated with aqueous hydrochloride acid (0.5 M, 10 mL). The mixture was refluxed at 110 °C overnight. Water was then removed under reduced pressure and the remaining DMAc mixture was poured into 2-propanol (150 mL) under stirring. The precipitate was collected by filtration and dried under vacuum to afford a white-brown compound. Using this method, the five PPFS_y-PSU₄₄-PPFS_y copolymers (**3-7**) were phosphonated and hydrolysed to obtain the PTFSPA_y-PSU₄₄-PTFSPA_y copolymers (**3p-7p**, respectively) in the acid form.

Membrane Preparation. Phosphonated triblock copolymer membranes were cast both in the acid and ester form. The acid or ester form of **3p-7p** was dissolved with DMAc (4 mL). In both cases, the solutions were stirred at 80 °C for 30 min and then filtered through a Teflon filter onto Petri dishes (60 mm diameter), before casting the membranes in an oven at 80 °C for 2 days. The membranes were detached after immersion in deionized water, and were then treated in deionized water at 50 °C for 24 h.

Polymer and Membrane Characterization

¹H, ¹⁹F and ³¹P NMR spectroscopy was performed with a Bruker DRX400 spectrometer at 400.13 MHz using either CDCl₃ ($\delta = 7.28$ ppm) or DMSO-*d*₆ ($\delta = 2.50$ ppm) solutions of the samples. Infrared spectra were recorded on a Perkin Elmer Spectrum One model 2000 FTIR

system with a universal attenuated total reflection sampling accessory on a ZnSe/diamond composite. The size-exclusion chromatography (SEC) setup consisted of a Viscotek GPCmax VE-2001 equipped with ViscotekTriSEC Model 302 triple detector using two PLgel mixed-D columns from Polymer Laboratories. The samples were analyzed in chloroform at 1 mL min⁻¹, 30 °C, and molecular weight data were calculated using polystyrene standards.

The thermal stability of the samples was investigated by thermogravimetric analysis (TGA) between 50 and 600 °C at a heating rate of 10 °C min⁻¹ under nitrogen or at a heating rate of 1 °C min⁻¹ under air using a Q500 analyzer (TA Instruments). Prior to the TGA measurements, the sample was preheated at 150 °C for 10 min to remove any solvent residues. The temperature at 5% weight loss was taken as the degradation temperature (T_d). Samples were analyzed at 10 °C min⁻¹ under N₂ by differential scanning calorimetry (DSC) using TA Instruments Q2000. The samples were first heated from 50 to 300 °C, then cooled to 50 °C and finally heated to 300 °C. The data collected during the second heating scan were used to evaluate the glass transition temperature (T_g) which were taken as the midpoints of the transitions recorded.

Surfaces of the PTFSPA_y-PSU₄₄-PTFSPA_y membranes were analyzed by Atom Force Microscopy (AFM) in tapping mode under ambient air using an XE-100 Park System. Simultaneous topographic and phase imaging were carried out at a scanning frequency of 1 Hz. The probe was Acta-50 (25-75 N m⁻¹, 200-400 kHz, Al coating). No image processing was done.

The water uptake (W_{water}) of the membranes was calculated as:

$$W_{\text{water}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (\text{Eq. 1})$$

, where W_{wet} was the membrane weight after immersion in water for 2 days and W_{dry} was the membrane weight after keeping the samples in vacuum for 2 days. The hydration value (λ), i.e.,

the number of water molecules per acid group, was calculated by combining the water uptake data and the IEC values, as:

$$\lambda = \frac{1000}{\text{IEC} \times 18} \times W_{\text{water}} \quad (\text{Eq. 2})$$

The proton conductivity (σ , S cm⁻¹) of the membranes was measured by electrochemical impedance spectroscopy (EIS), both under fully hydrated conditions as a function of temperature and under reduced RH at 80 °C. The former measurement was performed in a sealed cell (1.4 cm × 1.4 cm × 1.0 cm) containing 0.3 mL of water with the membrane fully hydrated. A two-probe method was used in the range -20 to 120 °C with a Novocontrol high-resolution dielectric analyzer V 1.01S in the frequency range 10¹–10⁷ Hz at 50 mV. The humidity dependence of the proton conductivity from 25 to 90% RH was investigated at 80 °C by a four-probe method with a Gamry potentiostat/galvanostat/ZRA in the frequency range 10⁻¹–10⁵ Hz using a Fumatech MK3 conductivity cell. The humidity was equilibrated by deionized water in a closed system.

RESULTS AND DISCUSSION

Synthesis of Triblock Copolymers

Five different PTFSPA_y-PSU₄₄-PTFSPA_y triblock copolymers having the same central PSU block but with terminal PTFSPA blocks of different lengths were prepared as shown in **Scheme 1**. First, the hydroxy-terminated oligomeric PSU (**1**) was prepared in a K₂CO₃-mediated polycondensation of DCDPS and a carefully controlled excess of bisphenol M. The structure of the PSU was tuned for the subsequent ATRP reactions. Thus, bisphenol M was employed to obtain a PSU oligomer which was soluble in *o*-xylene, the solvent of choice for the ATRP.^{46, 47} Notably, the corresponding PSU based on 1,4-bis(2-(4-hydroxyphenyl)-2-propyl)benzene (bisphenol P) was found to be insoluble in the same solvent. The average number of repeating

units of the PSU was determined to be $x = 45$ by comparing the integral of the most electron deficient diphenyl sulfone protons H^c at 7.84 ppm with that of the phenolic protons H^a of the chain ends at 6.70 ppm (**Figure 1a**). This corresponds to an overall average molecular weight of 25 kDa. The full assignment of the aromatic protons is found in Figure 1. Using polystyrene standards, analysis by SEC gave $M_n = 36$ kDa and $M_w/M_n = 1.9$ (**Figure 2**).

The PSU oligomer was successfully functionalized by coupling α,α' -dibromo-*p*-xylene to the two phenolic chain ends to form a bidirectional macroinitiator for ATRP (**2**, **Scheme 1**). The dibromoxylene was added in a large excess to ensure complete functionalization and to prevent chain extension reactions. By comparing the integrals of signal H^l (6.82 ppm, end group protons), H^k (4.51 ppm) and H^i (5.02 ppm) in the 1H NMR spectrum, the full conversion of the phenolic end groups to bromobenzyl end groups was confirmed (**Error! Reference source not found.b**). SEC analysis showed that the peak of the PSU macroinitiator was similar in shape to that of the original PSU oligomer and had no shoulder to indicate any chain extension (**Error! Reference source not found.**).

The $PPFS_y$ - PSU_{44} - $PPFS_y$ triblock copolymers (**3-7**) were prepared by using the PSU macroinitiator for ATRP of PFS, employing copper(I)bromide and 2,2'-bipyridyl as the catalytic system in *o*-xylene. The polymerizations were allowed to proceed for 48 h at 110 °C, which gave monomer yields between 60 and 80% (**Table 1**). The 1H NMR spectra of the triblock copolymers indicated the expected structure (**Figure 3a**). The degree of polymerization of each of the two PPFS blocks (y) was determined by comparing the integrated values of the three broad signals H^m , H^n , and H^o at 2.04, 2.41 and 2.78 ppm, respectively, corresponding to the hydrogen atoms on the two terminal PFS backbones, with the integral of the signal at 7.84 ppm arising from the

diphenylsulfone hydrogens H^c of the central PSU block. The degree of polymerization (γ) was thus calculated as:

$$\gamma = \frac{30I_{mno}}{I_c} \quad (\text{Eq. 3})$$

, where I_{mno} is the summarized integrals of the H^m, Hⁿ and H^o signals and I_c is the integral of the H^c signal (**Figure 3a**). As seen in Figure 3b, the ¹⁹F NMR spectrum shows three peaks at -143.4, -154.3 and -161.4 ppm corresponding to the three different kinds of fluorine atoms F^p, F^q and F^r, respectively, in the PFS blocks. This further verified the success of the polymerization. SEC analysis of the block copolymers indicated higher molecular weights than the macroinitiator and no new peaks at higher elution volumes to hint any homopolymer formation (**Figure 2**).

Copolymer Phosphonation

After some optimization, the selective phosphonation of the PPFS blocks was carried out as a classic S_NAr Michaelis-Arbuzov reaction with the copolymer dissolved in the phosphonating agent TSP at 175 °C over 48 h.⁴¹ The molar ratio between PFS units and TSP was kept at 1:10 to ensure complete copolymer dissolution and phosphonation of the PPFS blocks. The triblock copolymers were insoluble in TSP below 140 °C and then gradually the powder dispersions turned to more homogenous fine white dispersions at 175 °C. After the phosphonation, the ¹⁹F NMR spectra of the copolymers showed only two broad signals at approximately -132.9 and -142.7 ppm, corresponding to F^p and F^q (**Error! Reference source not found.a**). Notably, no signals from the original non-phosphonated PPFS units were found. Complete hydrolysis of the dimethylsilyl phosphonate ester groups was readily carried out by keeping the copolymers in refluxing dilute hydrochloric acid. The subsequent ³¹P NMR analysis of the PTFSPA_y-PSU₄₄-PTFSPA_y copolymers showed just one broad signal, consistent with the phosphonic acid derivative (**Error! Reference source not found.b**).⁴¹ In addition, FTIR analysis supported the

successful phosphonation by a broad band at 2000-3750 cm^{-1} from hydrogen bonding phosphonic acid and water, and peaks at 1475, 1275 and 555 cm^{-1} arising from stretching vibrations of PO_3 and $\text{P}=\text{O}$, and bending vibrations of PO_3 , respectively (**Figure 5**).

Thermal Properties

Amorphous block copolymers containing two types of blocks typically microphase separate to display two glass transitions. DSC traces of the non-ionic triblock copolymers showed the expected two transitions at approximately $T_g = 110$ and 145 $^\circ\text{C}$, originating from the PPFS and PSU phases, respectively (**Figure 6**). These values did not change with the composition of the copolymers and were nearly identical to those measured for the PPFS homopolymer and the PSU precursor block, 105 and 144 $^\circ\text{C}$, respectively. As expected, the change in specific heat (ΔC_p) increased with the content of the respective component (**Table 2**) for all the nonionic copolymers. DSC analysis of the phosphonated triblock copolymers in both the ester and acid form showed only the T_g of the PSU phase (**Figure 6**). The PTFSPA homopolymer **8** did not show any T_g in the acid form below the degradation temperature. Ionic polymers are known to generally have a higher T_g than the corresponding non-ionic polymer because of increasing interactions as the ionic content increases. The T_g of the PSU blocks decreased gradually with the PTFSPA content, from 149 $^\circ\text{C}$ for PTFSPA₁₅-PSU₄₄-PTFSPA₁₅ **3p** to 140 $^\circ\text{C}$ for PTFSPA₁₁₃-PSU₄₄-PTFSPA₁₁₃ **7p** (**Table 2**). The value of ΔC_p increased with the content of the PSU block as expected (**Table 2**). Notably, the phosphonated copolymers **3p-7p** did not show any signs of anhydride formation like PVPA copolymers which typically show an increasing T_g with annealing temperature.^{34, 37}

The thermal stability of the precursors and the triblock copolymers were studied by TGA under air at 1 $^\circ\text{C min}^{-1}$ (**Figure 7**). The T_d values of the precursor PSU **1** and PSU macroinitiator

2 were only 5 °C apart as expected due to their structural similarity (**Table 2**). The T_d of the homopolymer PTFSPA in the acid form **8** was recorded at 335 °C, in good agreement with the literature value.⁴¹ The non-ionic triblock copolymer **4** showed a lower T_d at 289 °C which corresponded to the degradation of the PPFS blocks (T_d at ~300 °C). The phosphonated copolymer **4p** showed a gradual weight loss of 13 wt% from 200 to ~330 °C due to solvent residues, or possibly anhydride formation, before reaching the T_d of the PTFSPA blocks at 335 °C.

Membrane Preparation

Both the acid and ester form of the PTFSPA_y-PSU₄₄-PTFSPA_y (**3p-7p**) copolymers were readily soluble in polar aprotic solvents such as DMSO, DMF, DMAc and NMP. Initial attempts to directly cast copolymer membranes in the acid form using these solvents gave in most cases unstable membranes which disintegrated in contact with liquid water. This was most probably caused by the absorption of large amounts of water by the hydrophilic PTFSPA phase. Instead, membranes of the copolymers in the ester form were cast from DMAc solutions. Acidic membranes were obtained after hydrolysis in water at 50 °C for 24 h, whereafter the ester groups were completely removed. This was indicated by the loss of the ester signals at 0 ppm in the ¹H NMR spectra, corresponding to the –SiMe₃ groups. Membranes prepared from copolymers **3p-6p** in this way were water-stable, but not the ones from copolymers **7p** with the highest PTFSPA content. Thus, membranes of copolymer **3p-6p** were further characterized.

Membrane Morphology

AFM tapping mode phase images of the triblock copolymer membranes in the acid form are shown in **Figure 8**. As seen, the images display distinct structures with bright and dark regions corresponding to the PSU (hard) and PTFSPA (soft) phases, respectively, formed by the respective block. The size of the PTFSPA phase domains was estimated to be in the range

between 10 and 20 nm for copolymer **4p** and **5p**, respectively (**Figure 8**). Consequently, the AFM analysis clearly demonstrated the self-assembly of the block copolymers into phase separated morphologies on the nano level, although the DSC analysis only showed the glass transition of the PSU phase. The clear phase separation of the triblock copolymers can be expected because of the incompatibility of the ionic PTFSPA blocks and the hydrophobic PSU block. All AFM images except perhaps that of PTFSPA₁₅-PSU₄₄-PTFSPA₁₅ show morphologies with seemingly continuous proton conducting PTFSPA phase domains. In addition, all the morphologies are quite irregular and nonperiodic with poor long-range order. The formation of irregular non-periodic has been reported to be beneficial for transport properties over, e.g. periodic lamellar morphologies where the phase domains often orient parallel to the membrane surface and thus perpendicular to the direction of the proton transport.⁴⁸

Water Uptake and Proton Conductivity

The uptake of water is a fundamentally important property of PEMFC membranes that has a direct influence on the proton transport properties. Generally phosphonated polymers absorb less water molecules per acid group than the corresponding sulfonated polymers, allowing higher IEC values to be used for the former polymers. The theoretical IEC and the water uptake of the triblock copolymer membranes are summarized in **Error! Reference source not found.**. The membranes take up quite low amounts of water and, as expected, the amount increases with the IEC value. Also, the number of water molecules taken up per $-\text{PO}_3\text{H}_2$ group (λ) increases progressively with the IEC value. As already mentioned, the membrane with the highest PTFSPA content, **7p**, disintegrated in contact with water and could not be characterized further. The water uptake of the present triblock copolymers may be compared with that of PSU grafted with PTFSPA where a membrane with an IEC of 7.6 mmol g^{-1} took up 75 wt% water,

corresponding to $\lambda=11$.⁴⁵ Kerres and Atanasov measured a water uptake of 50 wt% ($\lambda=14$) at 95% RH and 30 °C for the PTFPA homopolymer.⁴¹

The temperature dependence of the proton conductivity of the triblock copolymer membranes in the fully hydrated state is shown in **Error! Reference source not found.** As seen, the conductivity increased with the IEC and water uptake. The proton conductivity of all the membranes also increased sharply between -20 and 20 °C because of the melting of ice. Membrane **6p** showed the highest conductivity, 0.08 S cm⁻¹ at 120 °C, and membrane **3p** the lowest with 0.001 S cm⁻¹ at the same temperature. This may be compared with the PTFSPA grafted PSU which also reached 0.08 S cm⁻¹ at 120 °C, although at a significantly higher IEC (7.6 mmol g⁻¹).⁴⁵

The proton conductivity under reduced humidity (RH) at 80 °C is given in **Error! Reference source not found.** for the three membranes with the highest PTFSPA content. As expected, the proton conductivity decreased with the RH, and the values for membrane **6p** decreased from 0.08 S cm⁻¹ under full humidification, to 5×10^{-3} S cm⁻¹ at 90% RH and further to 5×10^{-5} S cm⁻¹ at 25% RH. The much lower conductivity of membrane PTFSPA₄₆-PSU₄₄-PTFSPA₄₆ **4p** in relation to PTFSPA₆₂-PSU₄₄-PTFSPA₆₂ **5p** indicated that the former membrane had a morphology with a significantly lower percolation at low RH for the proton transport. Membrane **6p** reached a conductivity of approx. 10^{-3} S cm⁻¹ at 50% RH (80 °C) which may be compared with a conductivity of 0.04 S cm⁻¹ at 50% RH (120 °C) measured for the PTFSPA homopolymer.⁴¹

CONCLUSIONS

A series of block copolymers containing PTFSPA blocks have been prepared for the first time. PTFSPA blocks with different molecular weights were successfully polymerized by ATRP from a difunctional macroinitiator to form PPFS_y-PSU₄₄-PPFS_y triblock copolymers. The PPFS blocks were selectively and quantitatively phosphonated by displacing the aromatic fluorine atom in the *para* position by using TSP. Electrolyte membranes derived from the block copolymers were found to be phase separated and nanostructured, and showed a high thermal stability under air. If the PTFSPA content was too high, the membranes became unstable in liquid water. Still, a membrane containing 4.2 mmol g⁻¹ was stable and reached a proton conductivity of 0.08 S cm⁻¹ at 120 °C under fully hydrated conditions, and 0.8 mS cm⁻¹ under 45% RH at 80 °C. The results also showed that PTFSPA has a low tendency to form anhydrides at high temperatures which significantly promotes the proton conductivity. This work opens up for the controlled synthesis of new of PTFSPA block copolymers with alternative architectures and block types, provided that the copolymers become reasonably soluble in TSP during the phosphonation. Copolymers containing PTFSPA should be interesting for a number of different applications because of the properties emanating from their high acidity and fluorinated character.

Supporting Information

DSC traces of the triblock copolymer **3-7** and their phosphonated acid form **3p-7p** were shown in the supporting information.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2010-2013) under the call ENERGY-2010-10.2-1: Future

Emerging Technologies for Energy Applications (FET) under contract 256821 QuasiDry. We thank Dr. Tobias Halthur for help with the AFM experiments.

REFERENCES

1. J. Ellis, M. Anstice, A. D. Wilson, *Clin. Mater.* **1991**, 7, 341-346.
2. G. O. Adusei, S. Deb, J. W. Nicholson, *Dent. Mater.* **2005**, 21, 491-497.
3. J. Tan, R. A. Gemeinhart, M. Ma, W. M. Saltzman, *Biomaterials* **2005**, 26, 3663-3671.
4. R. A. Gemeinhart, C. M. Bare, R. T. Haasch, E. J. Gemeinhart, *J. Biomed. Mater. Res., Part A* **2006**, 78A, 433-440.
5. M. Banks, J. R. Ebdon, M. Johnson, *Polymer* **1994**, 35, 3470-3473.
6. D. D. Jiang, Q. Yao, M. A. McKinney, C. A. Wilkie, *Polym. Degrad. Stab.* **1999**, 63, 423-434.
7. T. Bock, H. Möhwald, R. Mülhaupt, *Macromol. Chem. Phys.* **2007**, 208, 1324-1340.
8. . Lafitte, P. Jannasch, in *Advances in Fuel Cells, Vol. Volume I* (Eds.: K. D. K. T.S. Zhao, N. Trung Van), Elsevier Science, **2007**, pp. 119-185.
9. A. Rusanov, P. Kostoglodov, M. M. Abadie, V. Voytekunas, D. Likhachev, in *Fuel Cells II, Vol. 216* (Ed.: G. Scherer), Springer Berlin Heidelberg, **2008**, pp. 125-155.
10. T. J. Peckham, S. Holdcroft, *Adv. Mater.* **2010**, 22, 4667-4690.
11. J. Roziere, D. J. Jones, *Annu. Rev. Mater. Res.* **2003**, 33, 503-555.

12. C. H. Park, C. H. Lee, M. D. Guiver, Y. M. Lee, *Prog. Polym. Sci.* **2011**, *36*, 1443-1498.
13. P. Jannasch, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 96-102.
14. M. Schuster, T. Rager, A. Noda, K. D. Kreuer, J. Maier, *Fuel Cells* **2005**, *5*, 355-365.
15. F. de Bruijn, *Green Chem.* **2005**, *7*, 132-150.
16. R. Tayouo, G. David, B. Ameduri, *Eur. Polym. J.* **2010**, *46*, 1111-1118.
17. R. Tayouo, G. David, B. Ameduri, J. Roziere, S. Roualdes, *Macromolecules* **2010**, *43*, 5269-5276.
18. B. J. Liu, G. P. Robertson, M. D. Guiver, Z. Q. Shi, T. Navessin, S. Holdcroft, *Macromol. Rapid Commun.* **2006**, *27*, 1411-1417.
19. C. Stone, T. S. Daynard, L. Q. Hu, C. Mah, A. E. Steck, *J. New Mater. Electrochem. Syst.* **2000**, *3*, 43-50.
20. S. V. Kotov, S. D. Pedersen, W. M. Qiu, Z. M. Qiu, D. J. Burton, *J. Fluorine Chem.* **1997**, *82*, 13-19.
21. M. Yamabe, K. Akiyama, Y. Akatsuka, M. Kato, *Eur. Polym. J.* **2000**, *36*, 1035-1041.
22. H. R. Allcock, M. A. Hofmann, C. M. Ambler, S. N. Lvov, X. Y. Y. Zhou, E. Chalkova, J. Weston, *J. Membr. Sci.* **2002**, *201*, 47-54.
23. Y. Z. Meng, S. C. Tjong, A. S. Hay, S. J. Wang, *Eur. Polym. J.* **2003**, *39*, 627-631.
24. K. Miyatake, A. S. Hay, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3770-3779.
25. T. Rager, M. Schuster, H. Steininger, K. D. Kreuer, *Adv. Mater.* **2007**, *19*, 3317-3321.

26. B. Lafitte, P. Jannasch, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 273-286.
27. J. Parvole, P. Jannasch, *J. Mater. Chem.* **2008**, *18*, 5547-5556.
28. E. Abouzari-Lotf, H. Ghassemi, A. Shockravi, T. Zawodzinski, D. Schiraldi, *Polymer* **2011**, *52*, 4709-4717.
29. S. I. Lee, K. H. Yoon, M. Song, H. G. Peng, K. A. Page, C. L. Soles, D. Y. Yoon, *Chem. Mater.* **2012**, *24*, 115-122.
30. K. D. Papadimitriou, A. K. Andreopoulou, J. K. Kallitsis, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2817-2827.
31. H. Steininger, M. Schuster, K. D. Kreuer, A. Kaltbeitzel, B. Bingol, W. H. Meyer, S. Schauff, G. Brunklaus, J. Maier, H. W. Spiess, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1764-1773.
32. M. Schuster, K. D. Kreuer, H. Steininger, J. Maier, *Solid State Ionics* **2008**, *179*, 523-528.
33. A. Kaltbeitzel, S. Schauff, H. Steininger, B. Bingol, G. Brunklaus, W. H. Meyer, H. W. Spiess, *Solid State Ionics* **2007**, *178*, 469-474.
34. R. Perrin, M. Elomaa, P. Jannasch, *Macromolecules* **2009**, *42*, 5146-5154.
35. T. Wagner, A. Manhart, N. Deniz, A. Kaltbeitzel, M. Wagner, G. Brunklaus, W. H. Meyer, *Macromol. Chem. Phys.* **2009**, *210*, 1903-1914.
36. P. R. Sukumar, W. C. Wu, D. Markova, O. Unsal, M. Klapper, K. Mullen, *Macromol. Chem. Phys.* **2007**, *208*, 2258-2267.
37. J. Parvole, P. Jannasch, *Macromolecules* **2008**, *41*, 3893-3903.

38. M. Ingratta, M. Elomaa, P. Jannasch, *Polym. Chem.* **2010**, *1*, 739-746.
39. R. W. Lindström, A. Oyarce, L. G. Aguinaga, D. Ubeda, M. Ingratta, P. Jannasch, G. Lindbergh, *J. Electrochem. Soc.* **2013**, *160*, F269-F277.
40. B. Lafitte, P. Jannasch, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 269-283.
41. V. Atanasov, J. Kerres, *Macromolecules* **2011**, *44*, 6416-6423.
42. A. Kumar, W. Pisula, D. Markova, M. Klapper, K. Mullen, *Macromol. Chem. Phys.* **2012**, *213*, 489-499.
43. D. Markova, A. Kumar, M. Klapper, K. Mullen, *Polymer* **2009**, *50*, 3411-3421.
44. C. G. Cho, S. H. Kim, Y. C. Park, H. Kim, J. W. Park, *J. Membr. Sci.* **2008**, *308*, 96-106.
45. I. Dimitrov, S. Takamuku, K. Jankova, P. Jannasch, S. Hvilsted, *Macromol. Rapid Commun.* **2012**, *33*, 1368-1374.
46. K. Jankova, S. Hvilsted, *Macromolecules* **2003**, *36*, 1753-1758.
47. K. Jankova, P. Jannasch, S. Hvilsted, *J. Mater. Chem.* **2004**, *14*, 2902-2908.
48. E. M. W. Tsang, Z. Zhang, Z. Shi, T. Soboleva, S. Holdcroft, *J. Am. Chem. Soc.* **2007**, *129*, 15106-15107.

FIGURE LEGENDS

SCHEME 1 Synthetic pathway to phosphonated triblock copolymers **3p-7p** via polycondensation, ATRP, selective phosphonation and hydrolysis ($x = 45$; $y = 15-113$).

FIGURE 1 ^1H NMR spectra of the PSU oligomer **1** (a) and the functionalized PSU macroinitiator **2** (b) recorded in CDCl_3 .

FIGURE 2 SEC traces of PSU oligomer **1** (a), macroinitiator **2** (b) and triblock copolymer **7** (c).

FIGURE 3 ^1H NMR (a) and ^{19}F NMR (b) spectra of triblock copolymer **5** in CDCl_3 .

FIGURE 4 ^{19}F NMR (a) and ^{31}P NMR (b) spectra of phosphonated triblock copolymer **5p** in $\text{DMSO}-d_6$.

FIGURE 5 FTIR spectra of PSU oligomer **1** (a), triblock copolymer **5** (b) and **5p** in the acid form (c).

FIGURE 6 DSC traces of PSU oligomer **1** (a), macroinitiator **2** (b), triblock copolymer **4** (c), and triblock copolymer **4p** in the ester (d) and acid form (e), recorded during heating at $10\text{ }^\circ\text{C min}^{-1}$. The glass transitions are indicated by thin lines.

FIGURE 7 TGA traces of PSU oligomer **1** (a), macroinitiator **2** (b), homo PTFSPA **8** in the acid form (c), triblock copolymer **4** (d) and **4p** in acid form (e), as recorded during heating at $1\text{ }^\circ\text{C min}^{-1}$ under air.

FIGURE 8 AFM tapping mode images of thin triblock copolymer membranes in the acid form. Phase (a) and topography (b) images of $\text{PTFSPA}_{46}\text{-PSU}_{44}\text{-PTFSPA}_{46}$ **4p**, and phase (c) and topography (d) images of $\text{PTFSPA}_{62}\text{-PSU}_{44}\text{-PTFSPA}_{62}$ **5p**.

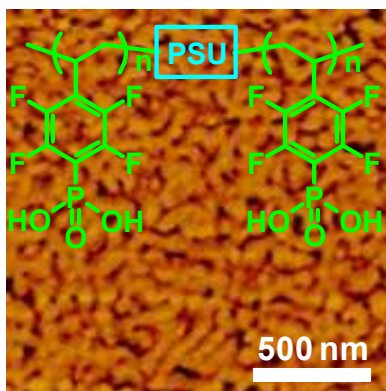
FIGURE 9 Proton conductivity of block copolymer membranes as a function of temperature under fully hydrated conditions as measured by EIS using a two-probe method.

FIGURE 10 Proton conductivity of block copolymer membranes at $80\text{ }^\circ\text{C}$ as a function of RH, as measured by EIS using a four-probe method.

Graphical abstract

Poly(tetrafluorostyrenephosphonic acid) block copolymers for proton conducting electrolyte membranes

*Zhecheng Shao, Arindam Sannigrahi, Patric Jannasch**



Polysulfone (PSU) with terminal benzyl chloride groups was used as a bifunctional macroinitiator for atom transfer radical polymerization of 2,3,4,5,6-pentafluorostyrene. The fluorostyrene blocks of the ABA triblock copolymers were selectively and quantitatively phosphonated with tris(trimethylsilyl)phosphite and hydrolysed to form poly(2,3,5,6-tetrafluorostyrene-4-phosphonic acid). Solvent cast copolymer membranes had a high thermal stability, and showed a nanophase separated morphology and a quite high proton conductivity at 80 mS cm^{-1} at $120 \text{ }^\circ\text{C}$ under fully hydrated conditions.

TABLE 1 Synthetic and structural data of triblock copolymers **3-7**.

Triblock copolymer	Sample #	PFS monomer added ^a (g)	PPFS content ^b (wt%)	Copolymer $M_n^b \times 10^{-3}$ (g mol ⁻¹)	Polymer yield ^b (%)
PPFS ₁₅ -PSU ₄₄ -PPFS ₁₅	3	0.27	18	31	79
PPFS ₄₆ -PSU ₄₄ -PPFS ₄₆	4	0.61	42	43	76
PPFS ₆₂ -PSU ₄₄ -PPFS ₆₂	5	0.93	49	49	66
PPFS ₇₂ -PSU ₄₄ -PPFS ₇₂	6	1.17	53	53	75
PPFS ₁₁₃ -PSU ₄₄ -PPFS ₁₁₃	7	2	64	69	57

^aAll ATRP's were initiated by 500 mg macroinitiator **1** with 2 mL *o*-xylene added, and took place during 48 h. ^bCalculated from ¹H NMR results.

TABLE 2 Thermal data of the precursors and the phosphonated copolymers in the acid form.

Sample	Sample #	MW ^c (kDa)	$T_{d5\%}$ ^a (°C)	T_{gPSU} ^b (°C)	$T_{gPPFS}/T_{gPTFSPA}$ A (°C)	ΔC_{pPPFS} J (g K) ⁻¹	ΔC_{pPSU} J(g K) ⁻¹
PSU ₄₄	1	25	358	144	-	-	0.227
Br-PSU ₄₄ -Br	2	25	363	144	-	-	0.250
PPFS ₁₅ -PSU ₄₄ -PPFS ₁₅	3	31	274	145	n.d.	n.d.	0.328
PPFS ₄₆ -PSU ₄₄ -PPFS ₄₆	4	43	289	145	110	0.064	0.230
PPFS ₆₂ -PSU ₄₄ -PPFS ₆₂	5	49	270	145	109	0.085	0.105
PPFS ₇₂ -PSU ₄₄ -PPFS ₇₂	6	53	283	144	110	0.084	0.066
PPFS ₁₁₃ -PSU ₄₄ -PPFS ₁₁₃	7	64	294	145	107	0.154	0.052
PTFSPA	8	-	335	-	n.d.	n.d.	-
PTFSPA ₁₅ -PSU ₄₄ -PTFSPA ₁₅	3p	33	243	149	n.d.	n.d.	0.402
PTFSPA ₄₆ -PSU ₄₄ -PTFSPA ₄₆	4p	49	256	145	n.d.	n.d.	0.105
PTFSPA ₆₂ -PSU ₄₄ -PTFSPA ₆₂	5p	56	269	145	n.d.	n.d.	0.121
PTFSPA ₇₂ -PSU ₄₄ -PTFSPA ₇₂	6p	62	274	141	n.d.	n.d.	0.083
PTFSPA ₁₁₃ -PSU ₄₄ -PTFSPA ₁₁₃	7p	78	297	140	n.d.	n.d.	0.018

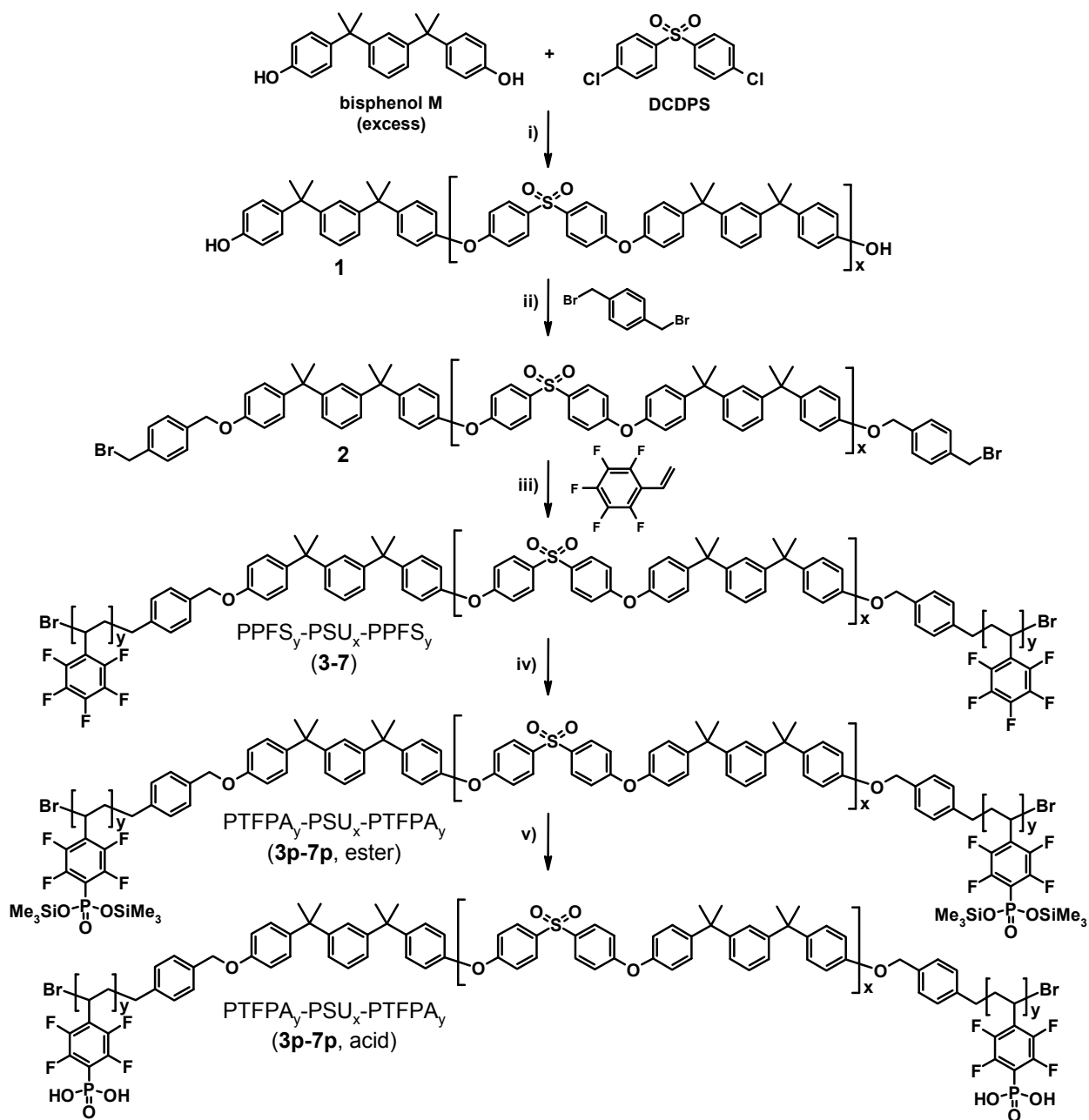
^aRecorded under air at 1 °C min⁻¹. ^bRecorded under nitrogen at 10 °C min⁻¹. ^cCalculated from NMR data. n.d. = not detected

TABLE 3 IEC, water uptake and proton conductivity of phosphonic acid membranes under fully hydrated conditions.

Phosphonated triblock copolymers	Sample #	Theoretical IEC ^b (mmol g ⁻¹)	Water uptake ^c (wt%)	[H ₂ O]/[-PO ₃ H ₂] (λ) ^c	σ at 120 °C (S cm ⁻¹)
PTFSPA ₁₅ -PSU ₄₄ -PTFSPA ₁₅	3p	1.4	1	0.8	0.001
PTFSPA ₄₆ -PSU ₄₄ -PTFSPA ₄₆	4p	3.2	5	1.7	0.028
PTFSPA ₆₂ -PSU ₄₄ -PTFSPA ₆₂	5p	3.8	7	2.0	0.028
PTFSPA ₇₂ -PSU ₄₄ -PTFSPA ₇₂	6p	4.2	25	6.6	0.008
PTFSPA ₁₁₃ -PSU ₄₄ -PTFSPA ₁₁₃ ^a	7p	5.0	-	-	-

^aUnable to form water-stable membranes. ^bDetermined from NMR data. ^cImmersed at 25 °C.

SCHEME 2



Key: (i) K₂CO₃, DMAc, 175 °C, 48 h; (ii) K₂CO₃, THF, 80 °C, 120 h; (iii) CuBr, bipy, *o*-xylene, 110 °C, 48 h; (iv) P(OSiMe₃)₃, 170 °C, 24 h; (v) HCl/H₂O, DMAc, 100 °C, 24 h.

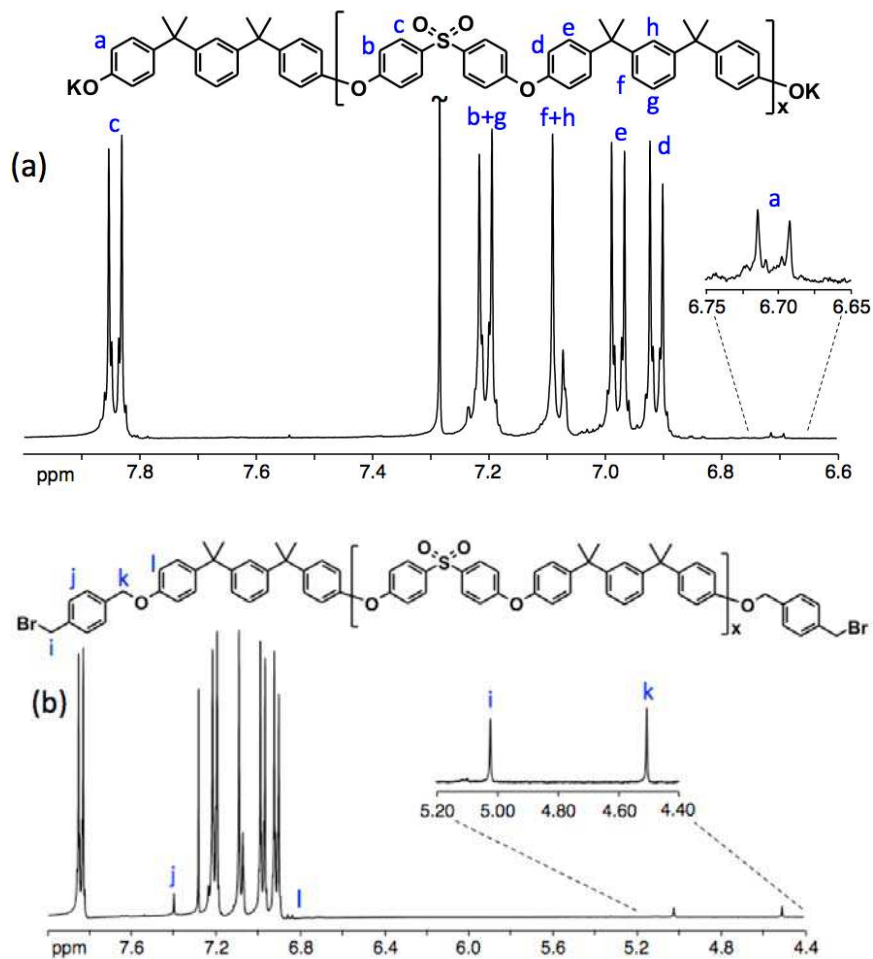


FIGURE 11

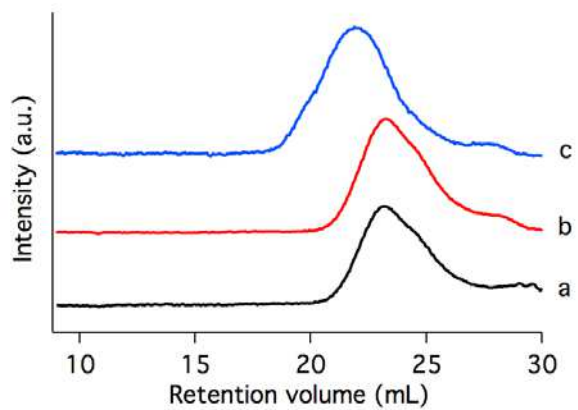


FIGURE 12

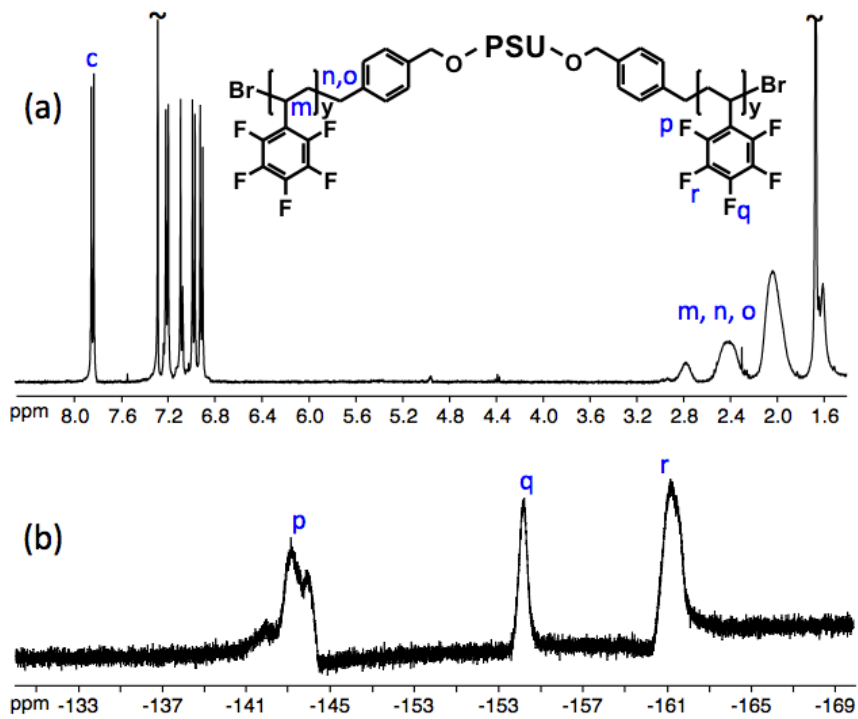


FIGURE 13

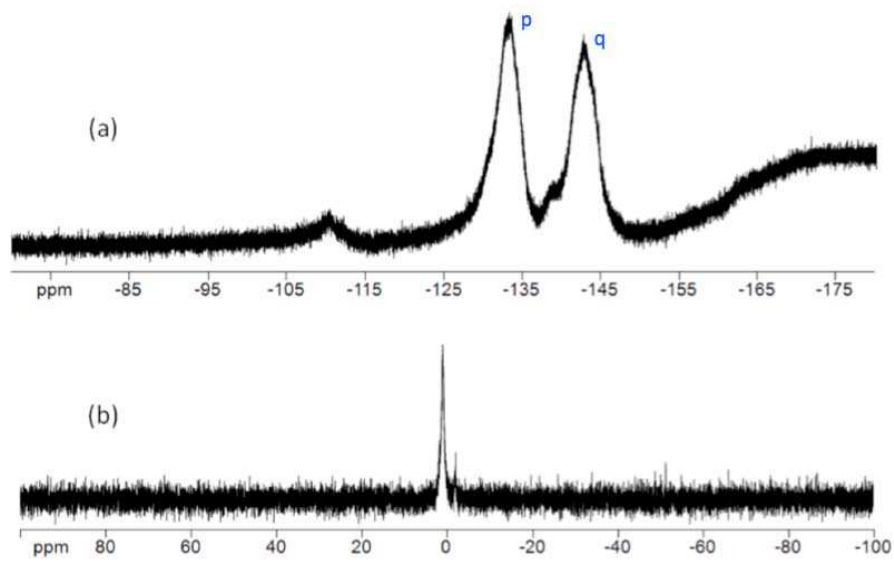


FIGURE 14

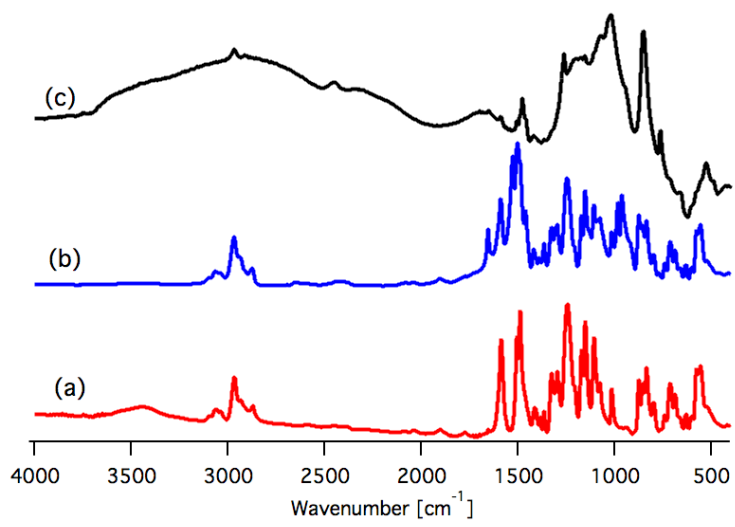


FIGURE 15

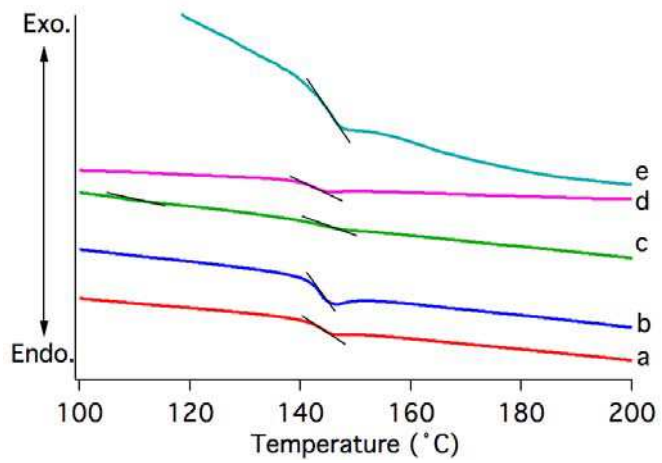


FIGURE 16

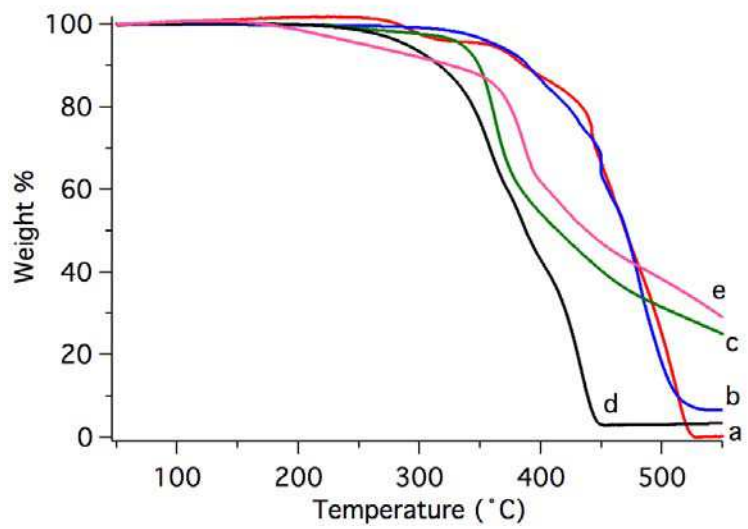


FIGURE 17

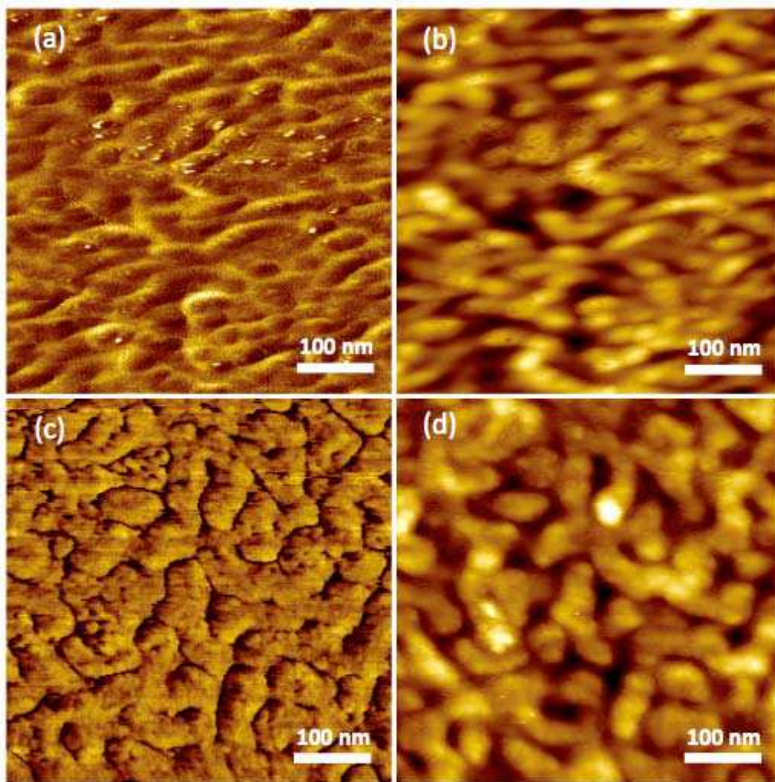


FIGURE 18

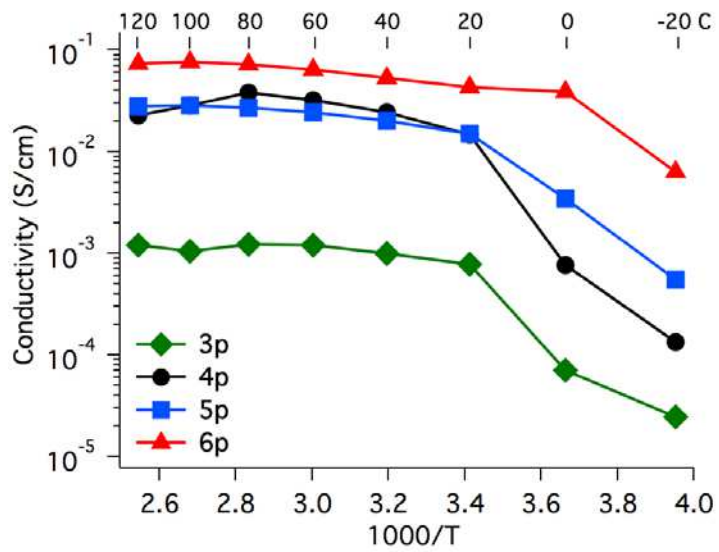


FIGURE 19

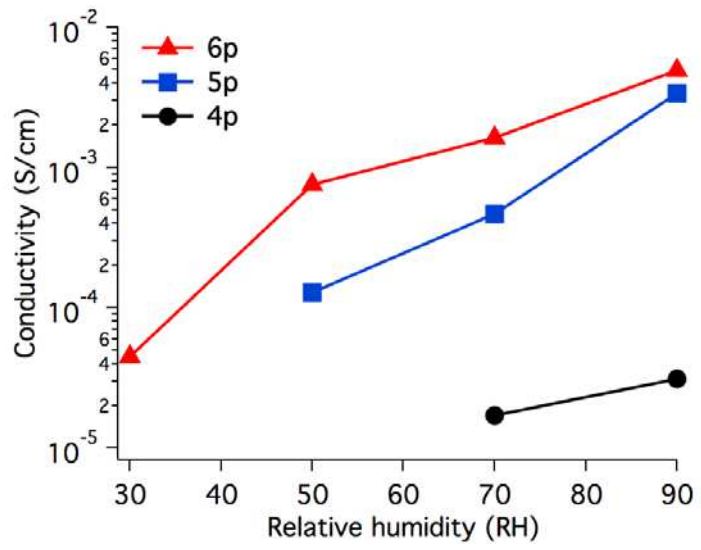


FIGURE 20

Supporting Information

Poly(tetrafluorostyrenephosphonic acid) block copolymers for proton conducting electrolyte membranes

*Zhecheng Shao, Arindam Sannigrahi, Patric Jannasch**

Polymer & Materials Chemistry, Department of Chemistry, Lund University

P.O. Box 124, SE-221 00, Lund, Sweden

E-mail: patric.jannasch@chem.lu.se

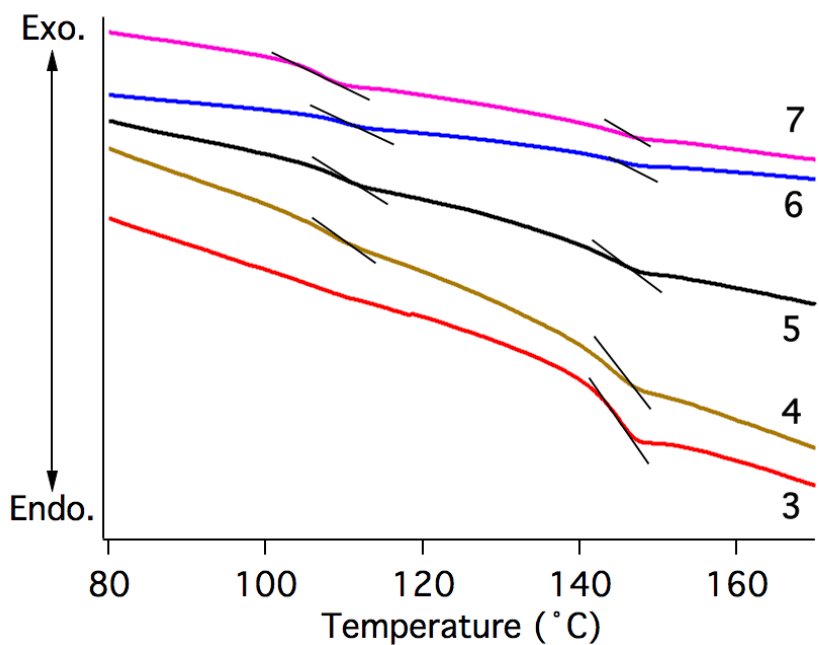


Figure S1 DSC traces of triblock copolymers (**3-7**) recorded during heating at $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen. The glass transitions are indicated by thin lines.

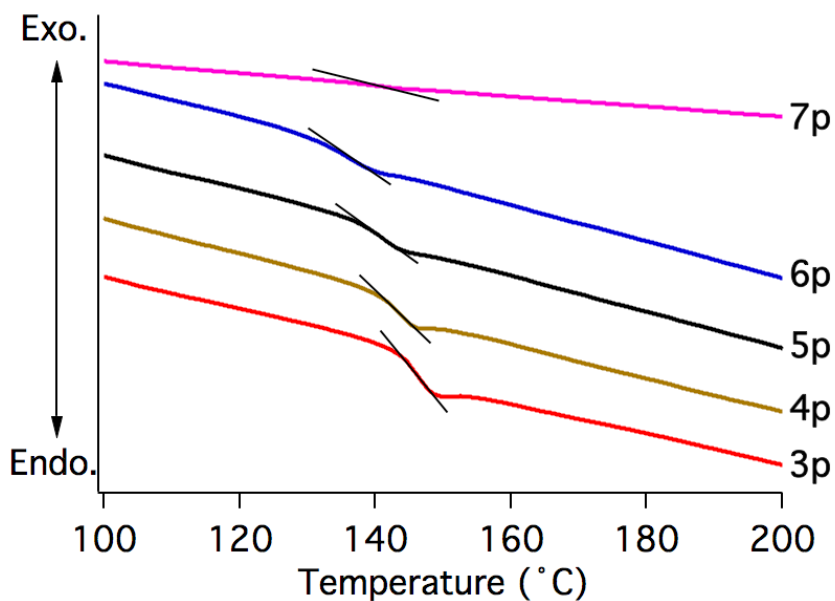


Figure S2 DSC traces of phosphonated triblock copolymers (**3p-7p**) recorded during heating at $10\text{ }^{\circ}\text{C min}^{-1}$. The glass transitions are indicated by thin lines.