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Block selective grafting of poly(vinylphosphonic acid) from aromatic multiblock copolymers for nanostructured electrolyte membranes

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Alternating aromatic multiblock copolymers have been structurally designed to enable selective lithiation and subsequent anionic graft polymerization from only one of the two block types. The multiblock copolymers were prepared by coupling polyfluoroether (PFE) and polysulfone (PSU) precursor blocks under mild conditions. The judicious combination of blocks allowed for block selective lithiation of the PSU blocks to obtain a macroinitiator for anionic polymerization of diethyl vinylphosphonate. The block selective grafting was confirmed by ¹H and ¹⁹F NMR spectroscopy. After hydrolysis to obtain poly(vinylphosphonic acid) (PVPA) side chains, mechanically stable transparent electrolyte membranes were cast from 1-methyl-2-pyrrolidinone solutions. Analysis by atom force microscopy showed that the copolymers self-assembled to form nanostructured membranes with continuous proton conducting PVPA phase domains. Calorimetry showed separate glass transition temperatures from the PFE and PVPA phases, with the latter increasing with increasing annealing temperatures as a result of anhydride formation. Fully hydrated multiblock copolymer membranes reached proton conductivities above 80 mS cm⁻¹ at 120 °C. The approach of block selective lithiation and modification of aromatic block copolymers can be used as a general strategy to prepare durable and functional nanostructured polymer membranes and materials.

Keywords: Block copolymers; Polyelectrolytes; Ionomers; Microphase separation; Water uptake; Proton conductivity; Fuel cell membranes.

1. Introduction

Phosphonated polymers are acidic, capable of hydrogen bonding and have a strong affinity for a broad variety of inorganic surfaces and metal ions. Their properties open up for a wide range of different application areas including flame-retarding additives,¹⁻² anti-corrosion³ and antimicrobial coatings⁴, dental materials,⁵⁻⁶ thermoresponsive materials⁷, and materials for water purification and proton-exchange membranes.⁸⁻¹⁰ To this end, both fluorinated¹¹⁻¹⁶ and non-fluorinated¹⁷⁻²⁵ polymers have been functionalized with phosphonic acid and studied for different purposes. Poly(vinylphosphonic acid) (PVPA) in particular contains a very high concentration of phosphonic acid units directly attached to the polymer backbone.²⁶⁻²⁷ The polymer is water soluble and shows a strong polyelectrolyte effect with only one proton per –PO(OH)₂ unit titratable.⁹ Its very high ionic content enables the preparation of proton-exchange membranes with very high ion exchange capacities (IECs). PVPA thus shows high proton conductivity, although anhydride formation leading to P-O-P bridges seriously reduces the conductivity under low relative humidity and high temperature.¹¹⁻¹³

Various block^{28,29} and graft³⁰⁻³³ copolymers, inorganic composites³⁴ as well as interpenetrating networks³⁵, based on PVPA have been prepared to circumvent the issues of water solubility and studied as membranes for fuel cells. We have previously grafted PVPA from polysulfone³¹ (PSU) and poly(phenylene oxide)³² (PPO) via anionic polymerisation. The former polymer was lithiated exclusively in positions ortho to the sulfone bridges using butyllithium, and used as polyfunctional macroinitiators for anionic polymerisation of diethyl vinylphosphonate. After hydrolysis and membrane casting, the PVPA grafted materials showed relatively high proton conductivity in the nominally dry and fully hydrated conditions in the range of 1–5 and 10–100 mS cm⁻¹, respectively.^{31,32} Very high IECs are needed to reach high proton conductivity at low water contents. However, this leads to excessive water uptake at high relative humidity which, in turn, causes swelling, dilution effects and compromises the mechanical stability of the membranes. The PVPA grafts in the PSU and PPO materials were randomly distributed along the polymer backbone, giving relatively short PSU segments inbetween the grafts. This leads to the formation of quite small and non-uniform glassy PSU phase domains in the membranes to stabilize the membrane morphology and limit the water uptake. One strategy to alleviate these issues is to only graft specific segments in the aromatic polymer,

leaving larger aromatic segments to form large glassy phase domains to stabilize the membranes (Scheme 1). Retaining the "grafting from" approach, this would require an aromatic block copolymer structure where one segment type could be selectively lithiated and grafted. Aromatic multiblock copolymers have previously been prepared by coupling of chain-end functionalised precursor segments of, e.g., PSUs and polyketones formed by polycondensation *via* nucleophilic aromatic substitutions.³⁶⁻⁴⁰ However, nucleophilic aromatic substitutions require the presence of electron-withdrawing groups, such as ketone, sulfone, and nitrile, to activate the halide atoms for substitution. With the exception of sulfone groups, these are in general incompatible with the lithiation reaction.

In the present work we have prepared multiblock copolymers by coupling PSU and polyfluoroether (PFE) precursor blocks. The latter block was prepared by polycondensation of hexafluorobenzene and bisphenol P to give a block structure where all the residual fluorine atoms were deactivated for substitution by their location in *ortho* positions to ether bridges. Accordingly, we hypothesised that this specific PFE block would remain unaffected during the addition of butyllithium. The PSU blocks of the carefully designed multiblock copolymers were selectively lithiated and grafted with diethyl vinylphosphonate. The ester functions of the grafted multiblock copolymers were hydrolysed and membranes based on the PVPA containing multiblock copolymers were evaluated by thermal analysis, microscopy, and water uptake and proton conductivity measurements to evaluate their use as electrolyte materials.

2. Experimental

2.1. Materials

4,4⁻(1,4-Phenylenediisopropylidene)bisphenol (Bisphenol P, Sigma-Aldrich, 99%) and 4,4⁻ dichlorodiphenylsulfone (DCDPS, Acros, 97%) were recrystallized from toluene and dried in vacuum oven at 80 °C before use. Resorcinol (RS, Acros, 98%), hexafluorobenzene (Aldrich, 99%), *n*-butyl lithium (BuLi, in hexanes, Acros, 2.5 M), 1-methyl-2-pyrrolidinone (NMP, Acros, 99%), *N*,*N*-dimethylacetamide (DMAc, Acros, 99%), dimethylsulfoxide (DMSO, Acros, 99.9%), 2-propanol (Honeywell, 98%), *n*-hexane (Scharlau, 96%), methanol (Honeywell, 98%), toluene (Fisher Scientific, HPLC grade), 1,1-diphenylethylene (DPE, Aldrich, 99%), diethyl vinylphosphonate (DEVP, Aldrich, 97%) and hydrochloric acid (Honeywell, 37%) were used as received. K₂CO₃ (Acros, 99%) was dried at 120 °C and tetrahydrofuran (THF, Fisher Scientific, Analytical reagent grade) was dried with 5 wt% molecular sieves (Acros, 4 Å, 8-12 mesh) before use. The molecular sieves were activated at 250 °C for 48 h in an oven and subsequently cooled to room temperature under vacuum.

2.2. Synthesis of PSU precursor blocks

The PSU precursor block was prepared according to Scheme 2. Hydroxy terminated oligomers were first synthesised as follows. DCDPS (13.2797 g, 46.245 mmol), RS (5.5166 g, 50.101 mmol), K₂CO₃ (7.67 g, 55.5 mmol) and DMAc (75 mL) were added to a two-neck flask (250 mL) equipped with a magnetic stirrer, a N₂ inlet and a condenser fitted with a CaCl₂ filter. The mixture was initially heated at 160 °C for 4 h and then at 175 °C for 24 h. A very low flow of N₂ was maintained throughout the polycondensation reaction. Finally, the product was precipitated in deionized water and washed several times with deionized water. The precipitate was filtered and dried under vacuum at 30 °C for 24 h (overall yield: 94%). The molecular weight was determined to be M_n = 3.8 kDa using ¹H NMR data recorded with a CDCl₃ solution.

Reactive end groups were obtained by capping the PSU oligomer with hexafluorobenzene in NMP at 80 °C. In a 100 mL two neck flask, 7.00 g oligomer (1.81 mmol) was added together with K_2CO_3 (2.45 g, 18.1 mmol), hexafluorobenzene (4.18 mL, 36.2 mmol) and NMP (50 mL). The mixture was kept at 80 °C for 24 h, before precipitating the product in 2-propanol. The product was carefully washed with deionized water and dried in a vacuum oven at 30 °C for 24 h (overall yield: 87%). This sample was designated PSU4.

2.3. Synthesis of PFE precursor blocks

Two hydroxyl terminated PFE precursor blocks with different molecular weights were prepared by a polycondensation (Scheme 2) in a three-neck 100 mL flask equipped with a magnetic stirrer, a Dean-Stark trap filled with toluene, a N₂ inlet, and a condenser fitted with a CaCl₂ filter. Bisphenol P (5.7689 g, 16.6505 mmol) and K₂CO₃ (2.69 g, 19.5 mmol) were first heated in DMAc at 110 °C for 3 h for dehydration during azeotropic removal of the toluene. The mixture was then cooled to 30 °C before adding hexafluorobenzene (1.87 mL, 16.24 mmol). The reaction temperature was kept at 50 °C for 3 h and then at 80 °C overnight. The N₂ purging was stopped after adding the hexafluorobenzene. The oligomer was precipitated in methanol and washed with deionized water. It was filtered and dried in a vacuum oven at 30 °C for 24 h (overall yield: 94%). The molecular weights of the two hydroxy terminated PFE precursor blocks were determined to be $M_n = 6.1$ and 8.0 kDa from ¹H NMR data recorded with a CDCl₃ solution. These samples were designated PFE6 and PFE8, respectively.

2.4. Synthesis of PFE-PSU multiblock copolymers

Two alternating multiblock copolymers were synthesised by coupling of the two PFE precursor blocks (PFE6 and PFE8, respectively) with the PSU4 precursor block in NMP at 80 °C during 4 h (Scheme 2). The two copolymers were designated PFEx-PSU4 where *x* is either 6 or 8 for the two PFE precursor blocks. As an example, block copolymer PFE8-PSU4 was synthesised as follows. PFE8 (8.0 kDa, 2.6959 g, 0.337 mmol) and PSU4 precursor block (3.8 kDa, 1.30 g, 0.337 mmol), K₂CO₃ (0.056 g, 0.404 mmol) and NMP (22 mL) were added to a 100 mL three-neck flask equipped with a magnetic stirrer, a N₂ inlet, and a condenser fitted with a CaCl₂ filter. The mixture was heated to 80 °C under N₂ flow. After 4 h the mixture became viscous. The multiblock copolymer was precipitated in 2-propanol and washed with deionized water. It was then filtered out and dried in a vacuum oven at 30 °C for 24 h (overall yield: 93%).

2.5. Block selective grafting of PVPA

The PSU blocks of the multiblock copolymers were selectively lithiated and grafted with PVPA via anionic polymerisation of DEVP as shown in Scheme 3. The grafted multiblock copolymers were designated PFExPSU4-*g*-PVPA*y* where *y* is the content of PVPA in wt%. As an example, PFE8PSU4-*g*-PVPA57 was synthesised as follows. An amount of 0.500 g (0.456 mmol) multiblock copolymer PFE8PSU4 was dissolved in 100 mL of anhydrous THF in a round bottom glass reactor fitted with a gas inlet and outlet, a thermometer, and a rubber septum. The solution was cooled to -70 °C and degassed several times. Next, the required amount of *n*-BuLi (0.2 mL, 0.456 mmol) was added dropwise to form a yellow-orange solution. After 15 min, DPE (25 μ L, 0.228 mmol) was added. After leaving the reaction for 10 min, the required amount of DEVP (0.35 mL, 2.28 mmol) was added all at once by syringe, and the polymerization was left to proceed for 5 h at -70 °C. At the addition of the DEVP monomer the solution turned opaque and violet and the viscosity increased. The grafted multiblock copolymer was precipitated in 200 mL

of hexane and the yellow-white precipitate was filtered off and washed several times with distilled water. Finally, the copolymer was dried under vacuum during 24 h at 30 °C. The copolymer in the ester form was converted into the acid form in 37% aq. hydrochloric acid. In a typical reaction, 0.5 g of copolymer in the ester form was placed in 25 mL of the hydrochloric acid. After 24 h of reflux, the copolymer was filtered off and carefully washed with water. The copolymer was finally dried under vacuum for 24 h at 60 °C.

2.6. Polymer characterization

Size exclusion chromatography (SEC) was used to determine the molecular weight of the precursor blocks and the PFEx-PSU4 multiblock copolymers. All samples were analyzed on a Viscotek GPCmax VE-2001 equipped with ViscotekTriSEC Model 302 triple detector using two PLgel mixed-D columns from Polymer Laboratories with chloroform at an elution rate of 1 mL min⁻¹ at room temperature. Calibration was done using polystyrene standards. ¹H, ¹⁹F, and ³¹P NMR data were recorded using a Bruker DRX 400 spectrometer. All the spectra were recorded in CDCl₃ and DMSO-*d*₆ solvents at room temperature. The ratio between the integrated peak of the CH₂ protons of the phosphonic ester at $\delta = 4.1$ ppm and the integrated peaks of the aromatic protons of the main chain between $\delta = 6.8$ -8.1 ppm was used in the calculations of the PVPA content and the theoretical ion exchange capacity (IEC) of the hydrolyzed copolymers (Table 2).³¹ In the phosphonic acid units of the PVPA side chains act as monoprotic acids,^{26,31} and thus the theoretical IEC is defined as mmol P per g protonated membrane. FTIR spectra were recorded on a Bruker IFS 66 FT-IR spectrometer between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹ using 128 scans. The polymers were ground together with KBr before sample tablets were pressed.

2.7. Thermal analysis

Thermogravimetric analysis (TGA) was carried out on a Q500 TGA analyzer from TA instruments. The thermal stability of the polymers was measured under nitrogen and air, respectively, up to 600 °C at a scan rate of 10 and 1 °C min⁻¹, respectively. Initially the samples were kept at 150 °C isothermally for 10 min to remove potential water and solvent residues. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q1000 DSC to

determine the glass transition temperatures ($T_{g}s$) for all the precursors and multiblock copolymers. Samples were first heated from 50 to 300 °C and then cooled to 50 °C and finally heated to 300 °C at 10 °C min⁻¹. The reported $T_{g}s$ were determined from the second heating scan. The PFExPSU4-g-PVPAy copolymers were analyzed using the following sequence of heating scans at a rate of 20 °C min⁻¹: $0 \rightarrow 150 \rightarrow 0 \rightarrow 200 \rightarrow 0 \rightarrow 250 \rightarrow 0 \rightarrow 300$ °C. In-between the heating scans the samples were cooled at a rate of 30 °C min⁻¹. The $T_{g}s$ were evaluated from the data recorded during heating scan by identifying the inflection points.

2.8. Microscopy

The surface morphologies of the grafted copolymers were investigated by Atom Force Microscopy (AFM) in tapping mode using an XE-100 Park system. Topology and phase images were recorded at a scanning frequency of 1 Hz. No image processing was done.

2.9. Membrane preparation

The required amount of PFExPSU4-*g*-PVPA*y* copolymer in the acid form was dissolved (5 wt%) in NMP at 100 °C. Membranes were then cast in Petri dishes at 100 °C under a continuous nitrogen flow during 24 h. The transparent and slightly yellow membranes were detached from the Petri dishes after immersion in deionized water. To remove impurities or possible solvent residues from the membranes, they were first boiled and washed several times in deionized water and then dried under vacuum at 30 °C for 24 h.

2.10. Water uptake measurements

The membranes were first thoroughly dried under vacuum for 24 h at 30 °C before measuring the weight of the dry membranes. Next, the membranes were immersed in deionized water for two days at room temperature. The surface water of the wet membranes was quickly wiped off with tissue paper before measuring the weight of the wet membranes. The water uptake (W_{water}) was then calculated as:

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

where W_{wet} and W_{dry} were the weights of the wet and dry membranes, respectively. Similarly, the temperature dependent water uptake was investigated from 20 to 100 °C under immersed conditions.

2.11. Proton conductivity measurements

The proton conductivity was measured by electrochemical impedance spectroscopy (EIS) using a Novocontrol high-resolution dielectric analyzer V 1.01S equipped with a Novocontrol temperature system. The proton conductivity (S cm⁻¹) of the membranes was measured between - 20 and 120 °C under fully hydrated conditions over the frequency range of 10^{-1} - 10^{7} Hz at 50 mV amplitude in a two-probe cell. The data was analyzed using the software WinDeta from Novocontrol to evaluate the proton conductivity.

3. Results and discussions

3.1. Multiblock copolymer synthesis

We have previously successfully grafted PSU homopolymers with PVPA side chains to prepare highly proton conducting polymers and membranes.³¹ PSU is exclusively lithiated in the aromatic *ortho* positions of the sulfone bridges and thus forms an efficient macroinitiator for anionic polymerization after reaction with DPE. In the present study, our aim was to identify and synthesize multiblock copolymers with a combination of blocks that would enable one of the block types to be selectively lithiated and grafted without affecting the other block type. To that end, two different multiblock copolymers having PFE and PSU blocks were prepared by coupling of precursor blocks under mild conditions to avoid branching and other side-reactions (Scheme 2). We assumed that the PFE under suitable conditions would be left unmodified during the lithiation and the subsequent anionic polymerisation. The PFE precursor blocks were prepared by polycondensations of bisphenol P and hexafluorobenzene, and the PSU precursor block were employed in the reactions to ensure that the precursors were terminated by hydroxyl groups and that the predetermined molecular weights were reached. The PSU precursor was quantitatively end capped with hexafluorobenzene to enable efficient coupling reactions.

Hexafluorobenzene and bisphenol P were chosen for the hydrophobic PFE block in order to avoid any reaction with BuLi during the lithiation reaction and to favor solubility in THF, the preferred solvent during the lithiation. We hypothesized that the position of the fluorine atoms *ortho* to the ether bridges in the PFE would efficiently deactivate any nucleophilic substitution reactions potentially caused by the lithiated species. Concurrently, DCDPS and RS were selected for the PSU block in order to have a high density of diaryl sulfone sites for lithiation. Moreover, the *meta* configuration induced by RS facilitates solubility in THF. In all cases, the polycondensations gave hydroxyl terminated precursor blocks with well-controlled molecular weights and solubility in THF.

Two different PFExPSU4 multiblock copolymers were prepared by varying the PFE block length (6.1 and 8.0 kDa), keeping the PSU block length constant and smaller (3.8 kDa). All the precursor blocks and the PFExPSU4 multiblock copolymers were characterized by ¹H NMR, SEC, DSC and TGA, and the data are collected in Table 1. Representative ¹H NMR spectra are shown in Fig. 1 and confirmed the structure of the respective samples. The integrals of the shifts originating from protons *a* and *c'* were used to calculate the molecular weight of the PSU precursor block (Fig. 1a), and the integrals of the signals from protons *g* and *f'* were used to calculate the molecular weights of the PFE precursor blocks (Fig. 1b).

By DSC analysis it was found that the T_g of the PFE precursor blocks increased with molecular weight (Table 1), as expected. Each of the two multiblock copolymers showed two T_{gs} to indicate microphase separation of the PFE and PSU blocks (Fig. 2). The T_{g1} of the PFE phase was approximately 10 °C higher than the respective neat precursor block, and the T_{g2} of the PSU phase was approximately the same as for the neat PSU precursor block. This may indicate a partial mixing of the PSU blocks in the PFE phase domain, and/or that the PFE chain segments were considerably constrained by the connectivity with the PSU blocks after the DSC cooling scan.

3.2. Selective grafting of multiblock copolymers

The PFExPSU4 multiblock copolymers were used as macroinitiators for anionic graft polymerization of DEVP (Scheme 3). The aim was to selectively and densely graft the PSU blocks with PVPA side chains to obtain multiblock copolymers having continuous phases with very high local concentrations of proton conducting phosphonic acid groups. After lithiation of the multiblock copolymers, DPE was added to form the active initiator sites for the polymerization of DEVP at -70 °C. We have previously used the same strategy to polymerize

DEVP to prepare block²⁸ and graft^{31,32} copolymers. After the polymerizations, the ester functions were hydrolyzed by reflux in aq. HCl. In this way, five different grafted multiblock copolymers were made with PVPA contents ranging from 57 to 82 wt% (Table 2). The phosphonated copolymers in both the ester and the acid forms were characterised by ¹H, ¹⁹F, ³¹P NMR and IR spectroscopy. Before hydrolysis, the signals of the CH₂ and CH₃ protons of the phosphonic ester were found by ¹H NMR at $\delta = 4.1$ ppm and at $\delta = 1.2$ ppm, assigned as *b* and *a*, respectively, in Fig. 3a. The CH and CH₂ protons from the poly(diethyl vinylphosphonate) chains were confirmed by the presence of two broad signals between $\delta = 1.3-1.7$ ppm (see Fig. 3a).

One of the crucial points of the present work was to selectively graft the PSU blocks with PVPA without affecting the PFE blocks. BuLi is very reactive and there is a risk that the fluorine atoms of the PFE block may be substituted in connection with the grafting reactions. In order to ensure that the lithiation and the subsequent grafting were selective, we analyzed the copolymers before and after grafting by ¹⁹F NMR spectroscopy. As expected, the solubility greatly changed after the grafting which complicated the analysis. The hydrophobic PFExPSU4 copolymers were readily soluble in CDCl₃, while the hydrophilic PFExPSU4-g-PVPA_V copolymers in the ester form easily dissolved in DMSO- d_6 . The former copolymers just barely dissolved in DMSO- d_6 after ultrasonication and heating at 100 °C for 2 h. Fig. 4a shows the expected single sharp signal at $\delta = -154.3$ ppm from the PFExPSU4 copolymers in CDCl₃ to indicate that all the fluorine atoms were chemically equivalent. The same sample shows a much broader asymmetrical signal at $\delta = -155.3$ ppm in DMSO- d_6 , most probably because of the limited solubility (Fig. 4b). After grafting, the spectra recorded in DMSO- d_6 showed a single symmetrical rather broad signal at δ = -155.3 ppm, again indicating that all the fluorine atoms were equivalent (Fig. 4c). Thus, the fluorine signal was not shifted after the grafting which indicated that PFE was not affected by the grafting reactions. In addition, multiple signals in the ¹⁹F NMR spectra would be expected if some of the fluorine atoms had been displaced. We concluded that the PSU blocks were selectively lithiated and grafted while the PFE blocks were left unmodified. In this context it should be mentioned that a corresponding multiblock copolymer having PFE blocks based on decafluorobiphenyl, instead of hexafluorobenzene, was not possible to lithiate selectively under the same conditions and multiple signals were found in the ¹⁹F NMR spectrum. In contrast to the PFE blocks based on hexafluorobenzene, all the fluorine atoms in PFE blocks based on

decafluorobiphenyl are not placed ortho to ether bridges, and are thus not deactivated for nucleophilic substitution during the lithiation.

The quantitative hydrolysis of the diethyl phosphonate ester groups was indicated by the disappearance of the characteristic signals of the phosphonic ester in the ¹H NMR spectra of the hydrolyzed products (Fig. 3c). Based on this result, it was possible to calculate the IEC from the spectra and these IEC values are collected in Table 2 for all five grafted multiblock copolymers. In comparison with the ³¹P NMR signal arising from the diethyl ester derivatives at $\delta = 32.9$ ppm (Fig. 3b), the hydrolyzed copolymers showed a slightly lower chemical shift at $\delta = 29.2$ ppm (Fig. 3d). The latter shift was attributed to the diacid form of the phosphonate units.³¹ In some cases a small signal at $\delta = 21$ ppm was observed in the ³¹P NMR spectra of the hydrolyzed copolymers. This signal confirmed the presence of anhydrides produced through condensation of the phosphonic acid groups to form P-O-P bonds.

Representative FTIR spectra of the PFExPSU4 multiblock copolymers and the PFExPSU4-*g*-PVPA*y* multiblock copolymers in both the ester and acid forms are presented in Fig. 5. Before analysis, the PFExPSU4-*g*-PVPA*y* multiblock copolymers were dried in a vacuum oven at 30 °C overnight to remove traces of water. The P=O stretching is usually found to absorb at 1320-1200 cm⁻¹.³¹ The FTIR spectrum of the grafted copolymer in the ester form (Fig. 5b) showed four new bands in comparison with those identified in the spectrum of the ungrafted copolymer in Fig. 5a. The bands at 1052 and 1023 cm⁻¹, as well as the band at 778 cm⁻¹, were assigned to (P)-O-C absorptions of the ester group, and the band at 952 cm⁻¹ was ascribed to P-O-(C) vibrations. As shown in Fig. 5c, these bands disappeared after hydrolysis, and the (P)-O-H bending vibration at 990 cm⁻¹ and a broad (P)-O-H stretching band at 2300 cm⁻¹ appeared for the acidic copolymers (not shown). Thus, the FTIR spectra confirmed the successful hydrolysis of the phosphonate ester groups.

3.3. Thermal properties

The thermal stability of all the multiblock copolymers was analyzed up to 600 °C under nitrogen at a heating rate of 10 °C min⁻¹, as well as under air at 1 °C min⁻¹. Fig. 6a shows representative TGA curves of a PFE-PSU multiblock copolymer and grafted copolymers derived from this

copolymer in the ester and acid form. The ungrafted multiblock copolymers showed decomposition temperatures (T_{ds}) at approx. 450 °C. All the grafted copolymers in the ester form initially lost weight because of absorbed water. The first degradation step began at around 250 °C and was due to the decomposition of the ester groups by the formation and loss of ethylene. The magnitude of the weight loss was directly proportional to the PDEVP content of the samples, as previously noted for other copolymers.^{31,41} The second main degradation step between 400 and 500 °C was assigned for the cleavage of the C–P bond and degradation of the PVPA chain.¹⁸ For all the grafted copolymers in the acid form, an initial weight loss was observed above 150 °C attributed to the loss of water and formation of P–O–P anhydride bonds. This was in accordance with previous findings.^{26,27,31,32}

Fig. 6b shows the TGA curves of the grafted multiblock copolymers with different PVPA contents ranging from 57 to 82 wt% under air at 1 °C min⁻¹. The initial weight loss (less than 1%) above 150 °C was assigned to the reversible condensation of the phosphonic acid, as discussed already. The small weight increases observed above 300 °C are most probably due to oxygen uptake in connection with the formation of phosphates as the phosphonic acid is degraded, and has been reported previously.^{31,32} The main degradation step was noted above 350 °C for all PFExPSU4-*g*-PVPA*y* samples and was attributed to the degradation of PVPA side chains. From Fig. 6b, it is clearly visible that the magnitude of the weight loss above 350 °C decreased with increasing PVPA content, which is mainly attributed to the flame-retardant property of the phosphonic acid.⁴² The *T*_ds for all the PFExPSU4-*g*-PVPA*y* copolymer samples in the acid form are collected in the Table 3.

All the multiblock polymer samples were analyzed by DSC to evaluate the glass transitions. Block copolymers having two immiscible amorphous blocks usually microphase separate and show two separate glass transitions. As mentioned previously, the PFE6PSU4 and PFE8PSU4 copolymers displayed two glass transitions to indicate phase separation between the blocks (Fig. 2). The grafted copolymers in the acid form showed two glass transition temperatures, one at $T_g = 131$ °C from the PFE block and the other T_g was found to increase with increasing annealing temperature during a temperature cycling with successively higher temperatures, as shown in Fig. 7. This glass transition originated from the PVPA phase for which the T_g increased because of an increased level of anhydride formation with the temperature. The

anhydride formation leads to intra- and intermolecular crosslinks which decreases the segmental mobility of the PVPA side chains leading to increased values of $T_{g.}^{26-28,32}$ As expected, no glass transition from the PSU phase was detected for the acidic copolymers because of the dense grafting with PVPA.

3.4. Multiblock copolymer membrane morphology

PVPA grafted multiblock copolymer membranes were cast in the acid form from NMP solutions at 100 °C. The morphologies of the membrane surfaces that faced the air during the casting were analyzed by tapping mode AFM analysis. Fig. 8 shows phase and topography images of two membranes. It is evident from the images that the grafted multiblock copolymers were distinctly phase separated and nanostructured. The soft PVPA phase domains appear as dark areas while the hard hydrophobic phases appear as the brighter areas in the images. From Fig. 8 it is seen that the PVPA phase domain seemed to be continuous and that the size of the PVPA phase domain increased with the PVPA content, as expected. The size of the PVPA phase domains was estimated to be in the range between 10 to 20 nm for copolymer PFE8PSU4-*g*-PVPA82.

3.5. Water uptake and proton conductivity

The water uptake is a very important parameter that determines both the mechanical properties and the level and mechanism of the proton conductivity in both sulfonated and phosphonated membranes. Typically, sulfonated membranes absorb more water molecules per acid group compared to phosphonated membranes, allowing higher IECs of the latter membranes to be used. Membranes based on the PFE6PSU4-*g*-PVPA75 and PFE8PSU4-*g*-PVPA82 copolymers were not stable in water at room temperature because of their high IEC, 6.9 and 7.7 mmol P g⁻¹, respectively. Fig. 9a shows the variation of the water uptake and λ value between 20 and 100 °C for the other phosphonated membranes in the acid form. As expected, the water uptake increased with the temperature and the IEC value. At 20 °C, the water uptake of PFE6PSU4-*g*-PVPA68 was 75 wt% but increased excessively to 176 wt% at 100 °C. Membrane PFE8PSU4-*g*-PVPA57 showed a moderate increase of the water uptake with temperature and reached a value of 95% at 100 °C. Membranes PFE8PSU4-*g*-PVPA57 and PFE8PSU4-*g*-PVPA59 had a very similar structure and PVPA content and both absorbed 45% water at 20 °C. However, at 100 °C the latter membrane absorbed approximately 50% more water than the former membrane. The water uptake of the phosphonated membrane corresponded to $\lambda = 10-16$ water molecules per phosphonic acid unit at 100 °C (Fig. 9b). This can be compared to $\lambda = 27$ for Nafion[®] NRE212. In comparison, a previously studied PSU with randomly placed PVPA grafts along the backbone, containing 57 wt% PVPA (IEC=5.3 mmol g⁻¹), took up 125 wt% water under immersed conditions at 20 °C.³¹ Moreover, a poly(phenylene oxide) randomly grafted with PVPA (65 wt% PVPA, IEC=6.0 mmol g⁻¹) had a water uptake of 111 wt% at 100% RH and 25 °C.³² This is considerably more than for the present grafted multiblock copolymer membranes with similar PVPA content. Consequently, the grafted block copolymer architecture provides morphologies which restrict the water uptake much more efficiently than randomly grafted copolymers.

The proton conductivity of the phosphonated membranes was measured from -20 °C to 120 °C under fully hydrated conditions in water (Fig. 10). In order to remove possible impurities and/or residual solvent, the membranes were first boiled in deionized water, and then washed several times with deionized water before being dried under vacuum at 30 °C for 24 h. The membranes were finally immersed in deionized water before the conductivity measurements. As seen in Fig. 10, the conductivity of Nafion[®] NRE212 increased sharply between -20 and 0 °C because of the melting of the absorbed water and reached high values at higher temperatures. At -20 °C, the conductivity of the phosphonated membranes exceeded that of the Nafion membrane. For the phosphonated membranes, the conductivity increased less sharply than Nafion between -20 and 20 °C. The level of conductivity then followed the same trend as the water uptake. Consequently, membrane PFE6PSU4-g-PVPA68 showed the highest conductivity and reached 85 mS cm⁻¹ at 120 °C. The previously studied PSU with randomly placed PVPA grafts (57 wt% PVPA, IEC=5.3 mmol g⁻¹) showed a conductivity of 79 mS cm⁻¹ under fully hydrated conditions at 120 $^{\circ}C^{31}$, while the poly(phenylene oxide) randomly grafted with PVPA (65 wt% PVPA, IEC= 6.0 mmol g^{-1}) showed 78 mS cm⁻¹ under the same conditions.³² Thus, the grafted multiblock copolymers exceeded the proton conductivity of the randomly grafted polymers at a significantly lower water content.

4. Conclusions

In the present work, we have selectively lithiated the PSU blocks of PFE-PSU multiblock copolymers without affecting the PFE blocks. The multiblock copolymers were then used as macroinitiators for anionic graft polymerization of DEVP from the lithiated PSU blocks. The block selective grafting was made possible because of the careful choice of the PFE block. By using of hexafluorobenzene as the dihalide monomer in the polycondensation, all the fluorine atoms of the resulting tetrafluorobenzene rings in the PFE were deactiviated for substitution because of the position ortho to the ether bridges to the bisphenol residues. This allowed for an efficient lithiation of the PSU block without affecting the PFE block. After hydrolysis of the DEVP monomer residues to obtain PVPA grafts, the multiblock copolymers showed phase separation with separate T_{gs} of the PFE blocks and the PVPA grafts, respectively. Moreover, AFM showed that the membranes derived from the grafted copolymers were nanostructured with seemingly continuous PVPA phase domains. The membranes had high thermal stability and reached high proton conductivity. At an IEC of 6.3 mmol P g⁻¹ the membranes reached a conductivity of 85 mS cm⁻¹ under fully hydrated conditions. In comparison to the previous studies of PSU and PPO grafted with PVPA, the current grafted multiblock copolymers reached similar proton conductivity, but at a significantly lower water content. This is an advantage for their use as electrolyte membranes. The tendency of PVPA to form anhydrides was found to increase with the temperature, which is still an issue under hot and dry conditions. In light of the numerous possibilities to introduce functional groups via lithiation chemistry, the approach of block selective lithiation and modification can be used as a general strategy to prepare durable and functional nanostructured polymer membranes and materials.

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Scheme 1. Molecular structure of a grafted homopolymer (upper) and a selectively grafted multiblock copolymer (lower) containing PVPA (green), PSU (blue) and PFE (red) segments.



Scheme 2. Synthetic pathway to PFE-PSU multiblock copolymers via coupling reactions of hydroxy terminated PFE and pentafluorophenyl terminated PSU precursor blocks under mild conditions (*x* denotes the molecular weight of the PFE block in kDa).



Scheme 3. Selective lithiation and grafting of the PSU blocks of the multiblock copolymers *via* anionic polymerization of DEVP, followed by cleavage of the ester functions to obtain the PVPA side chains (*y* denotes the PVPA content of the multiblock copolymer in wt%)



Fig. 1 ¹H NMR spectra of the PSU4 (a) and PFE8 (b) precursor blocks, as well as of multiblock copolymer PFE8PSU4 (c). All the spectra were recorded with polymers dissolved in CDCl₃.



Fig. 2 DSC traces of precursor blocks PFE6 (a), PFE8 (b), and PSU4 (c), and multiblock copolymer PFE6PSU4 (d) and PFE8PSU4 (e). The multiblock copolymers show separate T_{gs} (T_{g1} and T_{g2}) to indicate phase separation. Data was recorded during heating at 10 °C min⁻¹ and the glass transitions are indicated by thin lines.



Fig. 3 ¹H NMR (left) and ³¹P NMR (right) spectra of the grafted multiblock copolymer PFE8PSU4-*g*-PVPA59 carrying phosphonated side chains in the ester form (a, b) and in the acid form (c, d), respectively. Data were collected using DMSO- d_6 solutions.



Fig. 4 ¹⁹F NMR spectra of multiblock copolymer PFE8PSU4 recorded in CDCl₃ (a) and DMSO-d₆ (b), and of the grafted multiblock copolymer PFE8PSU4-*g*-PVPA82 in the ester form recorded in DMSO- d_6 (c).



Fig. 5 FTIR spectra of multiblock copolymers PFE6PSU4 (a), and PFE6PSU4-*g*-PVPA68 in the ester (b) and acid (c) form.



Fig. 6 TGA curves of (a) multiblock copolymers PFE8PSU4, PFE8PSU4-*g*-PVPA57 in the ester and acid form, respectively (recorded at 10 °C min⁻¹ under nitrogen), and (b) TGA curves of PFExPSU4-*g*-PVPA*y* samples in the acid form with PVPA contents ranging from 57 to 82 wt% (recorded at 1 °C min⁻¹ under air).



Fig. 7 DSC heating traces of grafted multiblock copolymer PFE8PSU4-g-PVPA59 showing the successively increasing T_g of the PVPA phase during the scan sequence: $0 \rightarrow 150 \rightarrow 0 \rightarrow 200 \rightarrow 0 \rightarrow 250 \rightarrow 0 \rightarrow 300$ °C at 20 °C min⁻¹. The T_g of the PFE phase remains constant at approx. 150 °C (T_g s indicated by arrowheads).



Fig. 8 Tapping mode AFM phase images of PFE8PSU4-*g*-PVPA57 (a) and PFE8PSU4-*g*-PVPA82 (b) surfaces, respectively. The hard PFE and soft PVPA phases appear as bright and dark areas, respectively. The corresponding topography images are shown in part c and d, respectively.



Fig. 9 The water uptake (a) and λ (b) for the phosphonated multiblock copolymer membranes as a function of temperature under immersed conditions. The data of Nafion[®] NRE212 was added for reference.



Fig. 10 Proton conductivity data measured under fully hydrated conditions for the phosphonated multiblock copolymer membranes using EIS. The data of Nafion[®] NRE212 was added for reference.

 Table 1. Multiblock copolymer data.

			PFE	PSU	PFExPSU4 copolymer		
Multiblock copolymer	PFE precursor block MW ^a	PSU precursor block MW ^a	precursor block T_a^b	precursor block T_a^b	T_{g1}^{b}	T_{g2}^{b}	$T_d^{\ c}$
	(kDa)	(kDa)	(°C)	(°C)	(°C)	(°C)	(°C)
PFE6PSU4	6.1 (5.0)	3.8 (5.7)	115	174	128	171	465
PFE8PSU4	8.0 (8.2)	3.8 (5.7)	143	174	153	176	456

^aMolecular weight calculated from NMR data and values in parenthesis calculated from SEC data using polystyrene standards. ^bDetermined by DSC. ^c Temperature for 5% weight loss at 10 ^oC min ⁻¹ under N₂.

Table 2. Grafted multiblock copolymer data.

Grafted	Precursor multiblock copolymer	Ratios of the reactants	DEVP cor	ntent (wt%)	PVPA content (wt%)	IEC ^b
multiblock copolymer		DEP:DEVP:PSU (mmol)	by ¹ H NMR	by TGA ^a		(mmol P g ⁻¹)
PFE6PSU4-g-PVPA68	PFE6PSU4	0.23:4.6:0.47	76	74	68	6.3
PFE6PSU4-g-PVPA75	PFE6PSU4	0.23:8.8:0.47	82	83	75	6.9
PFE8PSU4-g-PVPA57	PFE8PSU4	0.23:2.0:0.46	66	52	57	5.2
PFE8PSU4-g-PVPA59	PFE8PSU4	0.23:2.2:0.46	68	47	59	5.4
PFE8PSU4-g-PVPA82	PFE8PSU4	0.23:9.0:0.46	88	84	82	7.7

^aDetermined via the weight loss at 350 °C recorded by TGA under nitrogen. ^bCalculated from ¹H NMR data.

Table 3. Grafted multiblock copolymer membrane properties.

Copolymer	PVPA content (wt%)	T_{d}^{a} (°C)	IEC ^b (mmol P g ⁻¹)	W _{water} c (wt%)	$\lambda_{20}{}^o{}_C{}^d$	σ^{e} (mS cm ⁻¹)
PFE6PSU4-g-PVPA68	68	264	6.3	74	6.5	85
PFE6PSU4-g-PVPA75	75	246	6.9	-	-	-
PFE8PSU4-g-PVPA57	57	332	5.2	46	4.8	20
PFE8PSU4-g-PVPA59	59	292	5.4	45	4.7	39
PFE8PSU4-g-PVPA82	82	310	7.7	-	-	-

^a Temperature for 5% weight loss under air at 1 °C min⁻¹; ^b Calculated from ¹H NMR data; ^c Determined at 20 °C under immersed conditions; ^d Number of absorbed water molecules per phosphonic acid group at 20 °C; ^e Measured under immersed conditions at 120 °C.