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Highly Phosphonated Polypentafluorostyrene

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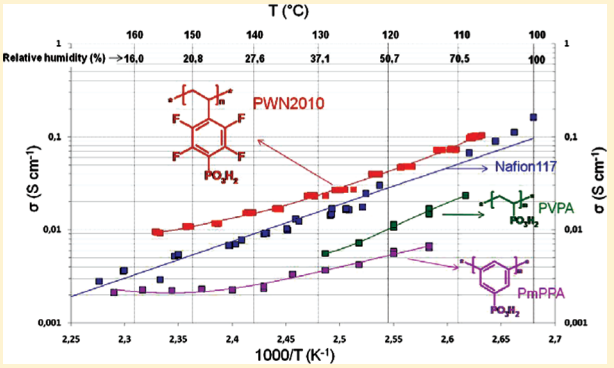
ABSTRACT: The synthesis and conductivity of highly phosphonated polypentafluorostyrene are demonstrated. Efficient postphosphonation (90%) was achieved via the classical nucleophilic aromatic substitution (S_N^{Ar}) Michaelis–Arbuzov reaction of polypentafluorostyrene (PFS) with tris(trimethylsilyl) phosphite. The contrivance is in the cumulative electron-withdrawing effect of the fluorine functions. This simultaneously facilitates the S_N^{Ar} reaction and enhances acidity of the resulting phosphonic acid. The most important consequence is a substantial increase of the H^+ conductivity being the highest one measured on phosphonated polymer: $\sigma = 0.1$ S cm^{-1} at 108 °C, $p = 10^5$ Pa water vapor pressure. This value is 4 times higher than the one for poly(vinylphosphonic acid) ($\sigma = 0.025$ S cm^{-1}) and higher than Nafion 117 ($\sigma = 0.075$ S cm^{-1}) under the same conditions. Additionally, this polymer showed outstanding resistance to oxidative and thermal treatment (T_{decomp} = 340 °C at 70% O_2 atmosphere). All this makes the phosphonated PFS a very promising candidate as polymer electrolyte for fuel cell applications.



INTRODUCTION

Highly protonogenic-functionalized polymers are considered as suitable ion conductors in fuel cell technology. Commonly sulfonated polymers attract more attention due to their better conductivity and accessibility.[1] Whereas, phosphonated polymers being amphoteric are able to conduct protons even under anhydrous conditions according to the Grotthuss mechanism.[2] Practically, however, the phosphonation of polymers is often restricted by the lack of suitable polymer precursors and anhydride formation of the obtained phosphonic acid, which lowers their conductivity. Herein, we introduce a polymer that overcomes these drawbacks.

The most widely used method for phosphonation of aromatic substances is based on nucleophilic substitution reaction between aryl halides and tri/dialkyl phosphite (Michaelis–Arbuzov and Michaelis–Becker rearrangements).[3] The most efficient approach is usually performed on aryl iodides and aryl bromides in the presence of metal containing catalysts such as Ni(II) halide salts (e.g., $NiCl_2$) or Pd(0).[4,5] However, this approach is practically not versatile and often unsuitable for effective production of highly phosphonated products. This is due to both (i) limited access to appropriate starting materials (e.g., aryl iodides), which requires additional synthetic steps, and (ii) extensive purification requirements for the metal-catalyzed systems.

On the other hand, perfluoroarylenes have already shown an ability to undergo a nucleophilic substitution reaction.[6−8] Recently, polymer-analogous postmodification of polymers containing perfluoroaromatic units has been shown to be a very efficient method for introduction of functional groups into polymers.[9,10] The authors have demonstrated the activation effect of the perfluorinated arenes on the C–F bond via "click" reaction between nucleophiles such as thiols and poly(pentafluorostyrene) (PFS). Few examples of C–P bond formation of perfluorinated arylenes with organophosphorous compounds have been found in the literature.[11−13] The preparation methods are usually based on metal–organic reagents that require additional preparation affords and dry reaction conditions. In addition, the obtained phosphonites, phosphines, and phosphanes have shown limited hydrolyzation/oxidation ability to corresponding phosphonic compounds. Direct phosphonation of perfluoroarylenes has been extensively studied only on pentafluoropyridine.[14,15] Performing the reaction in solution or neat trialkyl phosphite/sodium dialkyl phosphite has resulted in yields between 30% and 60%. The use of a catalyst (e.g., $NiCl_2$) has raised the yields above 90%. Relatively low yield (46%) has been achieved by the reaction between pentafluorophenylvinyl phosphonic acid ester and sodium diethyl phosphite.[16]

On the basis of our earlier experience with the S_N^{Ar} reaction between perfluorinated low molecular weight substances (e.g., hexafluorobenzole, octafluorotoluene, decafluorobiphenyl, and pentafluoropyridine) and polymers bearing organometallic functions (e.g., lithiated poly(ether sulfone)s),[17] we now extend our research to produce highly phosphonated high molecular weight substances. In order to achieve this goal we applied a highly versatile and efficient method for phosphonation of PFS.

RESULTS AND DISCUSSION

The synthesis of poly(4-vinyl-2,3,5,6-tetrafluorophenylphosphonic acid) (PWN2010) is done by stirring of polypentafluorostyrene (PFS) with tris(trimethylsilyl) phosphite (TSP) at

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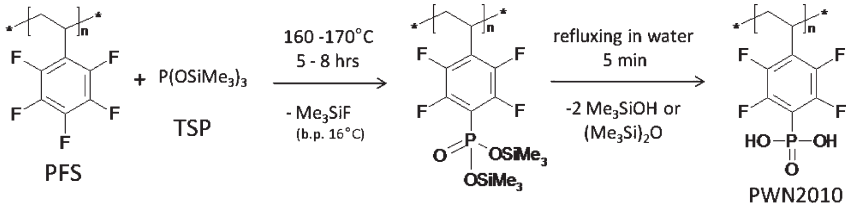
Scheme 1. Postphosphonation of PFS with TSP Followed by Complete Hydrolyzation of the Silyl Ester Derivative



T = 160−170 °C for 5−8 h (see Scheme 1). The molar ratio between PFS and TSP is kept between 2.4 and 3 to guarantee the efficient phosphonation of the aromatic rings. Reaction temperature has been slowly increased in order to monitor its influence on the reaction process. In temperature region T = 25−100 °C the reaction system is heterogeneous (solid PFS in liquid TSP). At T = 110 °C the solid PFS beads became soft and sticky (swollen by TSP) and above 150 °C dissolved completely in TSP. This behavior of PFS is provoked by both (i) its phase transition over the glass temperature (T_g = 105 °C, see discussions at TGA part below) and (ii) solvation of the phosphonated polymer segments by the TSP.

As a byproduct, trimethylsilyl fluoride (TMF with bp 16 °C) is formed, which can be detected as a gas evolution from the system starting at T = 110 °C. The gas evolution is initially slow at T = 110−150 °C and faster at T = 150−170 °C. This correlates to the transition of the reaction mixture from heterogeneous to homogeneous phase. At T = 150−170 °C the gas evolution became suddenly very fast and terminated in 1−5 min. This is probably an indication for a very fast and complete conversion of the reaction at this temperature. Nevertheless, the system is then kept at T = 170 °C for 5−8 h to ensure a full conversion. The elimination of the byproduct (TMF) from the reaction mixture rapidly shifts the reaction equilibrium toward formation of the final product. All this leads to a high reaction conversion resulting in a phosphonation degree of above 90% and quantitative yields of about 98% (see characterization methods in the Experimental Section). After the reaction is complete, the rest of the unreacted TSP was removed by vacuum distillation. The white solid residue (trimethylsily ester of PWN2010) is hydrolyzed by refluxing it in water for 5 min to the corresponding phosphonic acid derivative (PWN2010). The efficiency of the hydrolysis is due to the enhanced reactivity of the silyl esters in comparison to the most commonly used alkyl esters.[18] The completeness of hydrolysis is facilitated by the formation of trimethylhydroxysilane, which undergoes intermolecular dehydration to the corresponding hexamethyldisiloxane. This byproduct is water-insoluble and therefore can be separated from the system as an oily phase. Finally, the product is dialyzed and passed through an ion-exchange column to complete its conversion to H^+ form.

The structure of the phosphonated polymer was determined by means of ^{31}P and ^{19}F NMR (see Figure 1). The appearance of only one signal at ^{31}P NMR (see Figure 1A) and of two signals with equal integrals in ^{19}F NMR (see Figure 1B) is interpreted as a reliable indication for a mono-, para-substitution in the aromatic ring of PFS. The absence of any additional signals in ^{31}P NMR of PWN2010 is a clear evidence for suppression of the condensation process between its phosphonic acid functions, which is commonly observed for phophonated polymers (e.g., poly(vinylphosphonic acid) (PVPA)).[19] A comparison of the chemical shifts in ^{19}F NMR of both PFS and PWN2010 will be incorrect due to the different solvents used: DMSO-d_6 for PWN2010 and THF-d_8 for PFS. It is, however, noteworthy, that the three relatively weak signals in the ^{19}F NMR spectrum of PWN2010 at −110, −131, and −137 ppm are similar in shape, integral ratio (2:1:2), and distance to that of PFS. Our suspicion is that these are the signals of nonfunctionalized pentafluoro-aromatic rings. On the basis of this assumption, the degree of phosphonation is found to be 93%. This value correlates quite good with the one calculated from phosphorus content in elemental analysis (see Experimental Section). The phosphorus content in PWN2010 found is 11.32%, whereas the calculated value (for 100% phosphonation) is 12.09%. Thus, the phosphonation degree of PWN2010 based on elemental analysis is 93.2%.

Phosphonation of PFS to PWN2010 is confirmed by comparing their FT-IR spectra as well (see Figure 2). Besides the stretching vibration of the O−H of water at 3400−3800 cm^{-1}, a relatively broad signal for stretching vibration of the (P)O−H at 2500−3400 cm^{-1} is observed. This broad signal is a sign for H-bonding of the (P)O−H with the surrounding water molecules. Inter- and intramolecular H-bond formation between the phosphonic acid groups is confirmed by the broad signals at 2000−2500 and 1600−2000 cm^{-1}. Comparing to PFS spectrum, three relatively strong signals at 1476, 1276, and 554 cm^{-1} in the spectrum of PWN2010 were assigned as stretching vibration of PO_3, P═O, and bending vibration of PO_3, respectively.

The molecular weight of PWN2010 was determined by GPC (see Figure 3 and Table 1). The molecular weight of PWN2010 is higher than the one of PFS due to substitution of the PFS fluorine atom with $-PO_3H_2$. However, direct comparison of M_w value of both polymers is not possible because of the different GPC conditions applied (lack of eluent suitable for both polymers). The GPC profile of PWN2010 revealed a broad symmetrical signal with a bit of low molecular weight fraction. Although the reason for the second small fraction is unclear, we suspect (i) low molecular weight fraction of starting material (PFS) and/or (ii) degradation of the polymer at the reaction conditions. The second one is less probable because of the high thermal stability (up to 340 °C) of both PFS and PWN2010 (see discussion on TGA part below), whereas the reason for the broad molecular weight distribution is mostly inter- and intramolecular H-bond formation between the phosphonic acids and the water.

Ion-exchange capacity (IEC) is measured by both titration methods: (i) direct, where the labile protons of PWN2010 are exchanged with NaCl and the so-formed HCl is titrated against phenolphthalein, and (ii) total, where the PWN2010 is dissolved in defined excess of NaOH followed by titration of the non-neutralized rest of NaOH. This results in an IEC of 6.9 and 7.0 mmol g^{-1}, respectively. Comparing this value with the one calculated at 100% phosphonation of PFS (see Table 1), a degree of phosponation was calculated to be about 90%. This value is in good agreement with the values (93%) obtained from ^{19}F

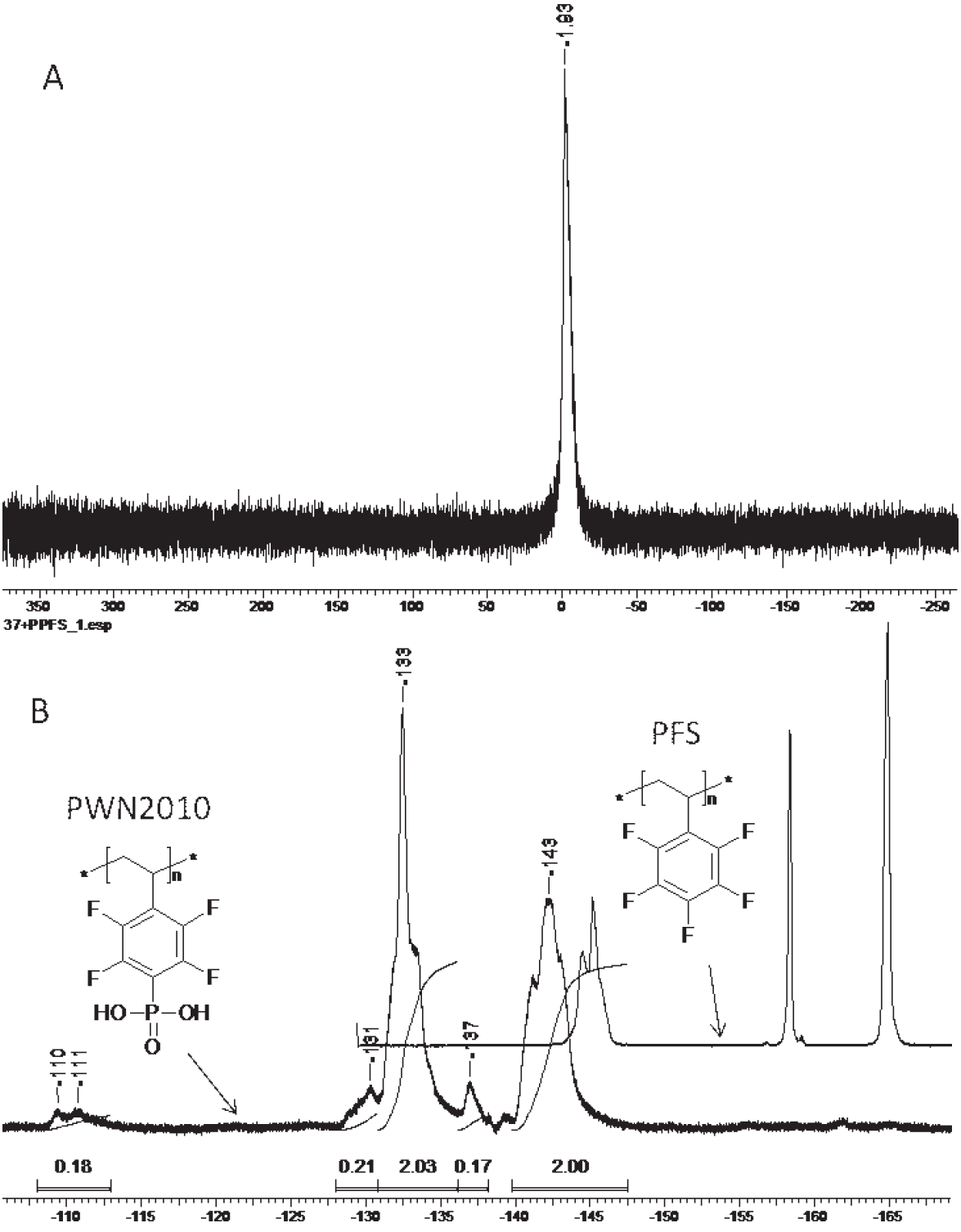


Figure 1. ^{31}P NMR of PWN2010 (A) and ^{19}F NMR of PWN2010 and PFS (B).

NMR and elemental analysis (see above). An important consequence of the practically equal value of IEC obtained by both direct and total methods is that both protons of phosphonic acid function
of PWN2010 are completely exchanged at neutral conditions (saturated NaCl solution). This means that the pK_a^2 ($-PO_3H^- \leftrightarrow -PO_3^{2-}$) is lower than 7. The values for both pK_a^1 and pK_a^2 were calculated by ACD/pK_a DB software being 0.47 ± 0.36 and 6.22 ± 0.58, respectively. Experimental determination of pK_a^1 by acid−base titration is infeasible due to inapplicability of the Nernst equation at pH values below 2.[20] The pK_a^2 = 6.2, found by titration of PWN2010 water solution with 0.1 M NaOH, is in perfect agreement with the one calculated by ACD/pK_a DB software. These pK_a values of phosphonated PFS are lower than the corresponding phosphonated polystyrene (pK_a^1 = 1.92 ± 0.1 and pK_a^2 = 7.55 ± 0.1 calculated

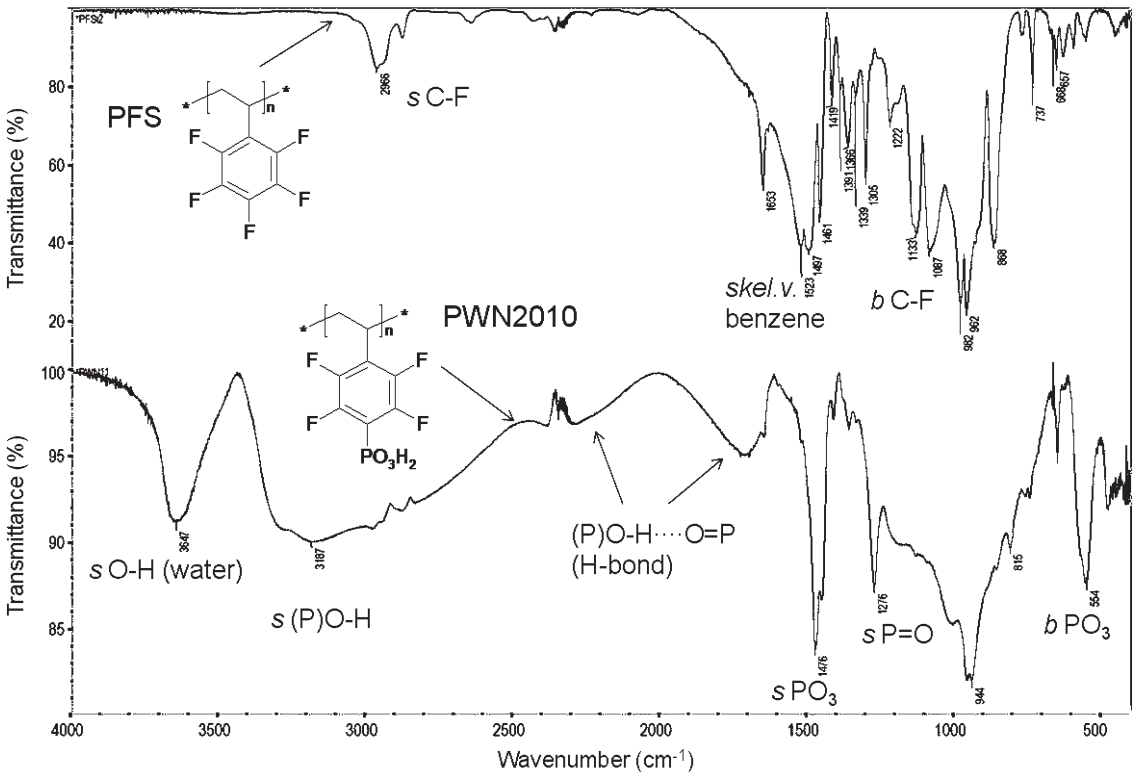


Figure 2. FT-IR spectra (KBr pellet) of PFS and PWN2010.

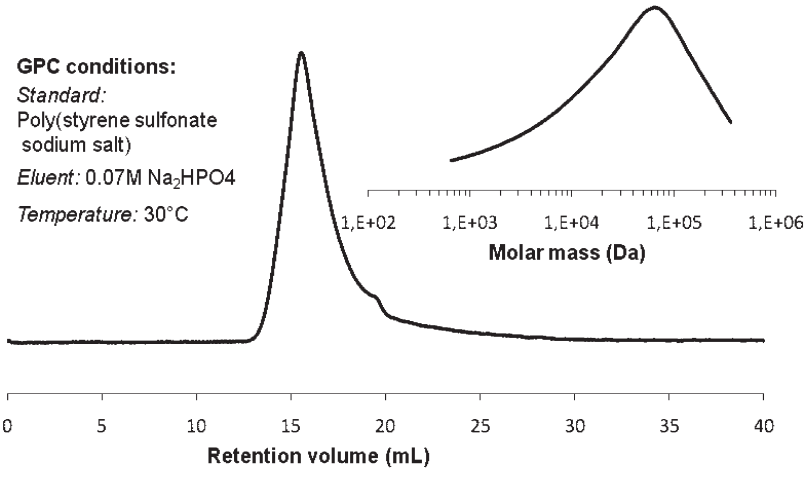


Figure 3. SEC traces of PWN2010. Molar mass profile is shown in the intercept.

Table 1. Characteristics of Both PFS and PWN2010

	GPC			IEC [mmol g^{-1}]		TGA	DSC	water uptake[c]	
polymer	M_n	M_w	PD	calcd	found	T_{decomp} [°C]	T_g [°C]	[wt %]	$[\lambda]^d$
PFS	30 200	59 000[a]	1.92	0		285	105.5	0	0
PWN2010	9 000	67 000	7.5	7.8[b]	7.0	340	>330	18	2.5

[a] Value is received from the supplier (Monomer Polymer & Dajac Laboratories, USA). [b] Calculation is based on 100% substitution (1 $-PO_3H_2$/aromatic ring). [c] Value at RH = 50%, T = 30 °C. [d] $\lambda = [H_2O]/[-PO_3H_2]$.

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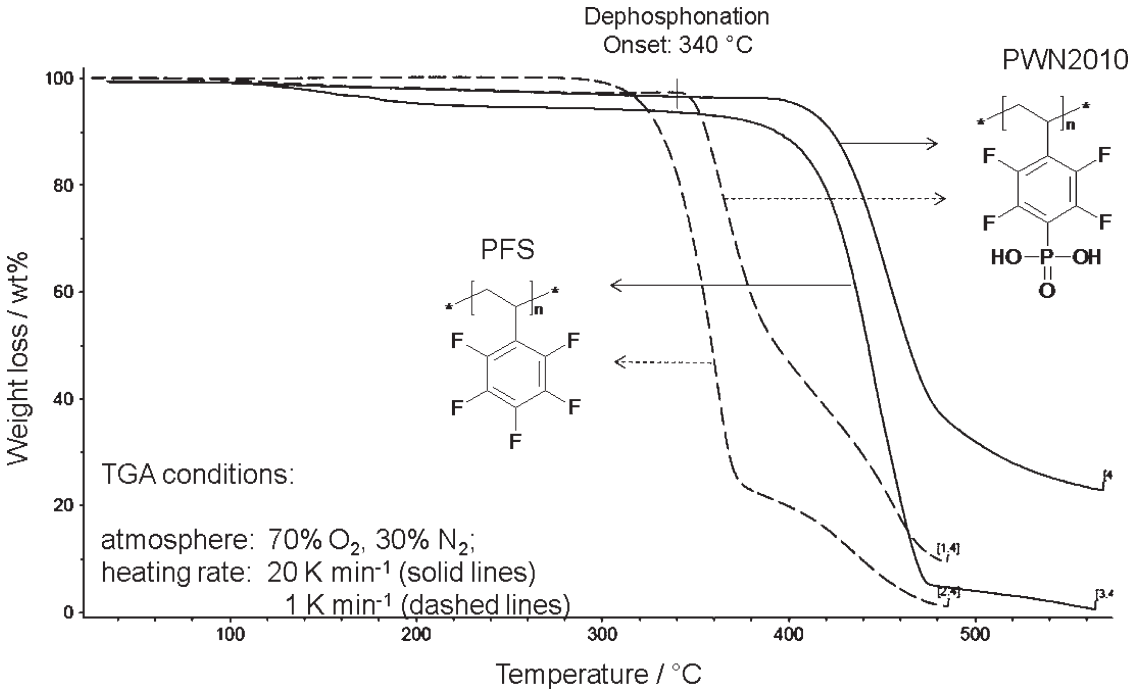

Figure 4. Thermogravimetric analysis of PWN2010 and PFS (solid lines: 20 K min^{-1}; dashed lines: 1 K min^{-1}).

by ACD/pK_a DB). This substantial decrease of pK_a values is mostly due to the collective negative induction effect of fluorine functions next to the phosphonic acid.

The resistance to heat of PWN2010 was examined by thermogravimetric analysis (TGA, see Figure 4 and Table 1). PWN2010 showed a thermal stability up to T = 349 °C, at which temperature the 5% barrier of CO_2 (at 2250−2400 cm^{-1}) transmission at IR detector, coupled with the TGA measurement, was overcome. This decomposition temperature is even higher than the one of PFS (T_{decomp} = 285 °C), which is a consequence of the generally flame-retarding effect of phosphorus-containing polymers.[21] Dephosphonation of PWN2010 at about 340 °C was detected as an appearance of stretching vibrations of PO_3 at ∼1050 cm^{-1} by the IR detector coupled to the gas outlet of the TGA instrument (see Figure 2). TGA performed at two different heating rates revealed a difference of 60−85 °C in decomposition temperature of PWN2010 and PFS. The increase of resistance to heat at higher heating rate is attributed to kinetic restrictions on the decomposition process, whereas thermodynamics controls the processes at low heating rate. Importantly, the absence of a "water step" at about 100−120 °C in both temperature profile of PWN2010 is a positive sign of suppressed condensation reaction between phosphonic groups of a near proximity.

Differential scanning calorimetry (DSC) of both PFS and PWN2010 revealed evanescence of glass transition (T_g) in case of PWN2010, whereas T_g = 105 °C was found for PFS (see Figure 5). The absence of glass transition of highly functionalized polymers is commonly observed for polymers functionalized with polar groups such as phosphonic and sulfonic acids.[22,23] Higher saturation of the polymer scaffold with polar functions correlates with a higher T_g observed.[22] The strong electron-withdrawing effect of the sulfonic acid group can affect some polarizable backbone functionality as in sulfone or ketone bridges and thus rapidly increase the rigidity of the polymer backbone.[23] Apparently, in this case, phosphonation cannot influence the inherent chain rigidity due to the minority of the negative induction effect on polymer backbone rotation. However, through its amphoteric properties the phosphonic acids can undergo intra- and intermolecular proton exchange between the neighboring functional groups. This will introduce additional electrostatic forces and H-bonding, which will strongly restrict the free segmental and rotational motion of the polymer chain. Therefore, PWN2010 is a rather stiff and brittle material in absence of plasticizers such as water or phosphoric acid.

Instead of T_g in the DSC profile of PWN2010, an exothermic phase transition with an onset at 332 °C is observed (see Figure 5). This relatively sharp semipeak seems not to refer to thermal disintegration of the polymer (compare TGA and DSC profile both at heating rate 20 °C min^{-1} in Figures 4 and 5), rather than a crystallization phase transition (T_c). Since segmental motion is a requirement for polymer crystallization, the T_g of PWN2010 is presumably immediately followed by T_c. However, the appearance of an endothermic glass transition is overcompensated by the exothermic crystallization due to the commonly much lower ΔC_p of glass transition in compared to that of crystallization.

The hydration isotherms at T = 30 °C of PWN2010 and Nafion 117 are compared in Figure 6. The water uptakes of both are generally increased with an increase of the RH (see Figure 6A). A relatively steep increase of water uptake of above 80% RH is attributed to an overwhelming effect of the water osmosis on the polymer's inherent interactions, e.g., entanglement, ionic attraction, and H-bonding. The hydration isotherm behavior and values of PWN2010 are similar to that of analogous highly phosphonated polymers, e.g., PVPA.[19] However, the water uptake in wt % of PWN2010 largely exceeds the one of Nafion 117, whereas the numbers of the water molecules per functional group (λ) of PWN2010 and Nafion 117 are similar (see Figure 6B). The fact that λ of both polymers is roughly equal refers to enhanced acidity of PWN2010 (see discussion of PWN2010 acidity above). In conclusion, the absolute higher water uptake of PWN2010 is due to its higher number of functional groups at similar λ with Nafion 117. It is worth noting

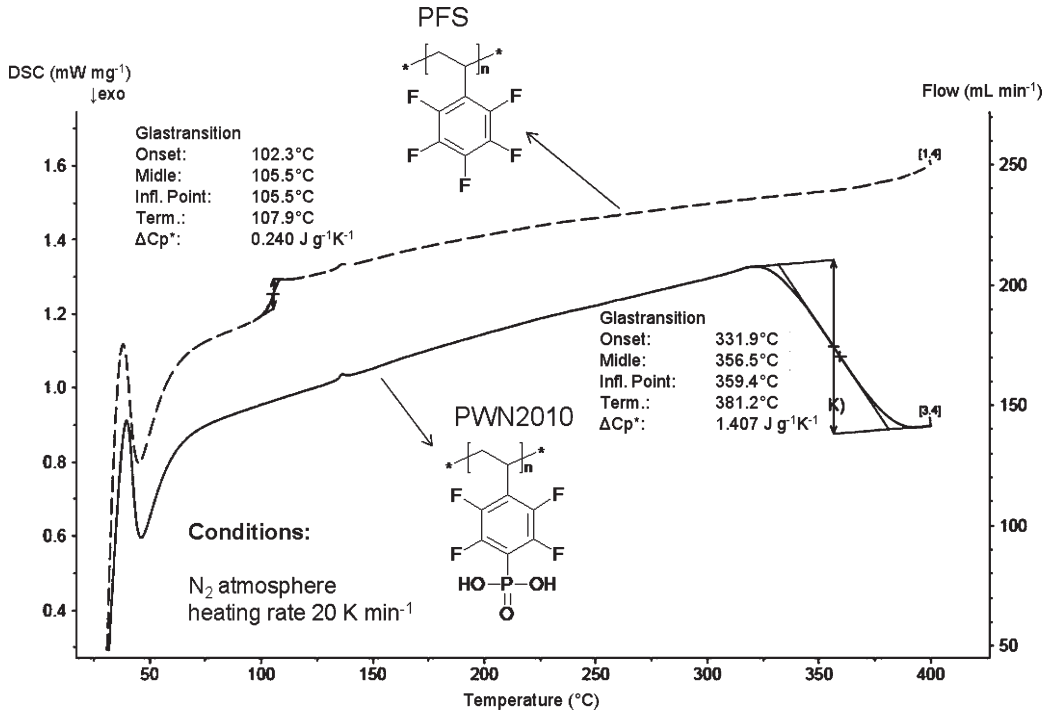

Figure 5. DSC of PWN2010 (solid line) and PFS (dashed line).

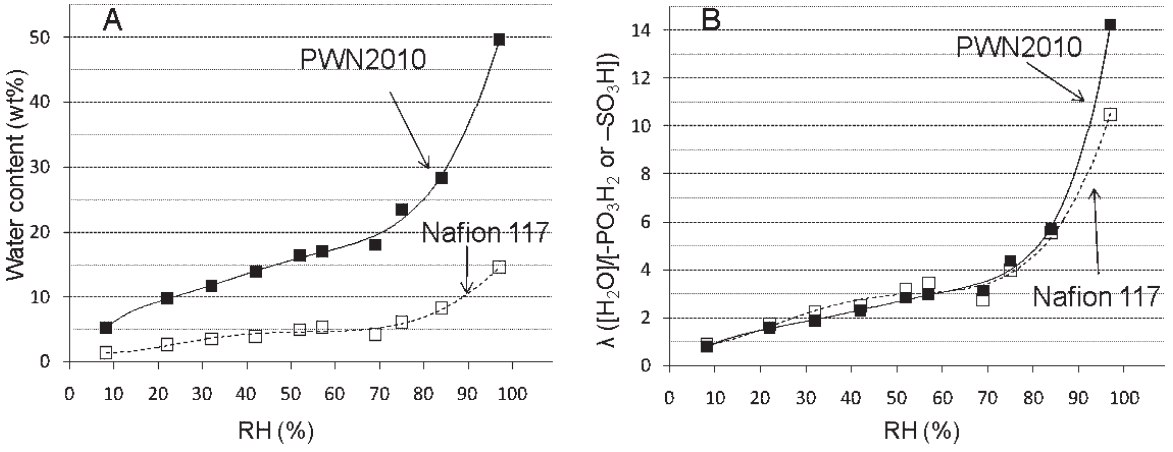

Figure 6. Hydration isotherms of PWN2010 (■) and Nafion 117 (□) given as water content in wt % (A) and λ (B) as a function of relative humidity (RH) at 30 °C.

that the hydration isotherms of PWN2010 did not show any hysteresis. This contributes to our thesis for suppressed condensation reaction between the phosphonic acids for this material (see discussions to TGA and ^{31}P NMR data above).

This higher hydration ability of PWN2010 has implications for the water-based conductivity. The conductivity of PWN2010, measured at 1 atm water vapor pressure (see Figure 7), was found to be by a factor of 4−10 higher than similar phosphonated polymers such as PVPA and poly(methaphenylene phosphonic acid) (PmPPA). It is even higher than the conductivity of Nafion 117, being up to 2 times larger at T = 155 °C. This makes PWN2010 the best ion-conducting polyelectrolyte based on phosphonated polymer at the conditions given in Figure 7. Similar to PmPPA, PWN2010 showed reduced dependence of the conductivity from the water content at higher temperatures (T = 135−155 °C). This is due to the opposing effect of increase with temperature activation, which overcomes the drying-out effect on conductivity. Hysteresis of conductivity with temperature was not observed excluding formation of phosphonic anhydrides at these conditions. The overall enhancement of the conductivity of PWN2010 is presumably based on higher acidity of the phosphonic acid in surrounding of fluorine functions. This leads subsequently to an increase of the water uptake and water retention in the polymer scaffold, which are the most decisive factors for building ion percolation phases into the conductive materials. Of course, suspicion about the positive effect of microstructuring of the material as well as relatively free rotational backbone of polystyrene based polymers in comparison to polyphenylenes, polysulfones, and poly(ether ketone)s are feasible but need to be experimentally supported in the near future.

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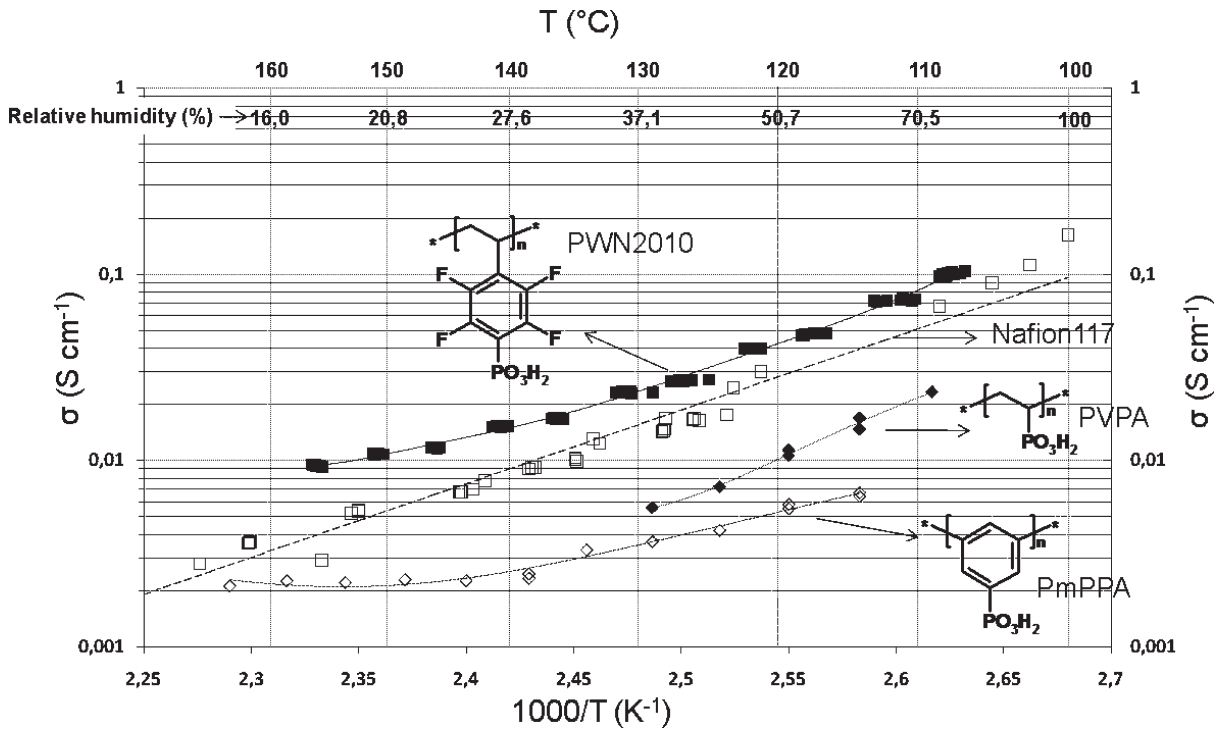

Figure 7. Conductivity of PWN2010 as a function of temperature at water partial pressure of $p(H_2O)$ = 1 atm (10^5 Pa). Conductivities of Nafion 117, PVPA, and PmPPA, measured at the same conditions and setup, are given as comparison after permission from the authors of ref 24.

CONCLUSIONS

A new polystyrene-based polymer containing simultaneously fluorinated and phosphonated aromatic rings is obtained. The polymer is produced after postphosphonation of poly(pentafluorostyrene), achieving a degree of mono-, para-phosphonation of about 90−93%. The thermal analysis revealed stability of up to 340 °C with glass transition above 300 °C. This polymer showed enhanced water attraction with hydration number similar to sulfonated systems (e.g., Nafion). The lack of any additional signals in the ^{31}P NMR spectrum, hysteresis at conductivity and hydration isotherms, and distinguishable water failure at T = 100−340 °C in the thermogravimetric analysis are our grounds for assuming suppression or inability for formation of anhydrides between phosphonic acids of the polymer. All this together with the conductivity being well above the best phosphonic acid based polyelectrolytes is making this material applicable in fuel cell technology. Our major suspicion for the beneficial effect on fuel cell relevant properties (e.g., conductivity and water uptake) of this material is in the enhanced by the neighboring fluorine function acidity of the phosphonic acid functions.

EXPERIMENTAL SECTION

Materials. PFS and TSP were purchased by ABCR and Aldrich, respectively, and used as received. All the other chemicals are used in HPLC grade quality.

Instruments. NMR spectra were recorded on a Bruker Avance 400 spectrometer at a resonance frequency of 250 MHz for ^{1}H, 62.9 MHz for ^{13}C, 235 MHz for ^{19}F, and 101.2 MHz for ^{31}P NMR at RT. Molecular weights and molecular weight distributions were determined by GPC in water on Waters pump model 515, eluent: 0.07Na_2HPO_4, detectors: RI ERC-101 and UV−vis Soma S-3702 (270 nm), temperature: 30 °C, standard: PSSNa, concentration: 1.000 g/L, flow rate: 1.0 mL/min, columns: MCX, MCX 10 E7 and MCX 1000. FTIR spectra were detected as KBr pellet on a Nicolet 6700 FTIR instrument. Ion-exchange capacities (IEC_{direct} and IEC_{total}) were determined by titration. PWN2010 was immersed in saturated sodium chloride solution for 24 h to convert it into the Na form. The exchanged H^+ ions were then titrated with 0.1 M NaOH to the equivalent point (IEC_{direct}). After that a defined excess of NaOH was added and this solution was back-titrated with 0.1 M HCl (IEC_{total}). The thermal stability of the polymers and membranes was determined by thermogravimetry (TGA, Netzsch, model STA 449C) with a heating rate of 20 °C min^{-1} and 1 °C min^{-1} under an atmosphere enriched with oxygen (65−70% O_2, 35−30% N_2). The outlet with the released products was continuously analyzed by FTIR spectrometer (Nicolet Nexus FTIR spectrometer) to determine the onset of splitting-off phosphonic acid function by the stretching vibration at 1050 cm^{-1}. The glass transition temperatures (T_g) were determined by differential scanning calorimetry (Netzsch DSC 204 F1). Polymers were dried at T = 110 °C in vacuum (1×10^{-3} mbar) for 20 h prior to the thermal analysis. Water hydration isotherms at T = 30 °C were determined by equilibrating polymer samples in desiccators with different saturated salt solutions for particular relative humidity. The hydration kinetics of the PWN2010 was slower compared to that of Nafion, requiring equilibration times of about 5−7 days. The water uptake was determined by quickly weighing the samples after equilibration on an external balance and comparing the weight to that of the dried polymer sample ($p = 10^{-3}$ mbar, T = 110 °C, 24 h). With w_{wet} and w_{dry} being the weights of the wet and the dry samples, the water uptake is calculated by wt % = $100 \times (w_{wet} - w_{dry})/w_{dry}$. The number of water molecules per phosphonic acid λ is given by $\lambda = [(w_{wet} - w_{dry})EW]/(w_{dry}M_{water})$, where EW is equivalent weight of the polymer and M_{water} is the molecular weight of water. Conductivity measurements in pure water vapor ($p(H_2O)$ = 10^5 Pa) were carried out in a double-wall temperature-controlled glass chamber with an open outlet at temperatures between T = 110 and 160 °C. Liquid water was continuously evaporated by a heater and injected into the chamber with a constant flow rate using a digital peristaltic

pump (Ismatec). Inside the chamber pressed pellets of PWN2010 polymer powder (diameter 6 mm and total thickness of 2−3 mm) were placed in a notched cylindrical glass tube with a charcoal-coated electrode at the bottom. The second electrode was pressed from the top onto the pellet by a screw in order to ensure optimal contact. The specific conductivity $\sigma = l/(A \times R)$, where l is the distance between the electrodes, A the area of the pellet, and R the resistance derived from the high-frequency intercept of the complex impedance with the real axis.

Phosphonation of Polypentafluorostyrene. All the glassware was dried (400 °C, argon flow) prior to use. PFS (6.817 g, 0.0351 mol) and TSP (20.96 g, 0.0702 mol) were introduced into a round-bottom flask equipped with magnetic stirrer, reflux condenser, argon in-/outlet system, and an oil bath. Mixture was stirred and the system was heated to 170 °C (heating rate: 3.5 °C min^{-1}) for 8 h. At T = 25−100 °C the mixture was heterogenic (large beads of PFS in liquid TSP); at T = 110−150 °C PFS beads became soft and stacked to a large heavy ball; T = 150−170 °C reaction mixture homogenized to a clear solution. Gas evolution was detected at T = 110−170 °C, more intensively at T = 150−170 °C. After the reaction was complete, the rest of TSP was distilled off the mixture. The white solid rest was refluxed in water for 5 min, resulting in a viscous clear mixture. After cooling down, the oily phase was separated from the water phase in a separation funnel. The water phase was then concentrated and dialyzed (dialyzing tubes MWCO 10 000 g mol^{-1}) for 3 days exchanging to fresh water twice a day. Afterward, the water solution was passed through a proton-exchange column (H-form), and the water was evaporated. The product, obtained as a white solid, was dried at 120 °C, $p = 5 \times 10^{-3}$ mbar for 18 h. Yield: 8.8 g (98%). ^{1}H NMR (250 MHz, DMSO-d_6, δ): 2.0 (bp, 2H), 3.0 (bp, 1H), 11.0 (bp, 2H). ^{13}C NMR (62.9 MHz, DMSO-d_6, δ): 32.69, 121.58, 142.98, 146.84. ^{19}F NMR (ext. stand. trifluorotoluene, 235 MHz, DMSO-d_6, δ): −133 (bp, 2F), −143 (bp, 2F). ^{31}P NMR (ext. stand. 85% H_3PO_4, 101.2 MHz, DMSO-d_6, δ): −1,93 (bp, 1P). GPC (eluent: water; standard: PSSNa): M_w 67 kg mol^{-1}, MWD. 7.8. FT-IR (KBr): 3800−3400, 3400−2500, 2000−1600, 1476, 1276, 1200−700, 653, 554, 481. TGA (heating rate 1 K min^{-1}; O_2/N_2 = 70/30): $T_{decomposition}$ = 349 °C, $T_{dephosphonation}$ = 340 °C. Elemental analysis (%) calcd for $C_8H_5F_4O_3P$: C 37.52, H 1.97, P 12.09; found: C 36.65, H 2.31, P 11.32. (calcd of phosphonation degree based on phosphorus ontent is 93.2%). IEC [mmol g^{-1}]: calcd 3.9 ($-PO_3H^-$), 7.8 ($-PO_3^{2-}$), found 6.9 ($-PO_3H^-$), 7.0 ($-PO_3^{2-}$); 90% phosphonation. Conductivity (water vapor $p = 10^5$ Pa): 0.1 S cm^{-1} (T = 108 °C), 0.01 S cm^{-1} (T = 150 °C).

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