Phosphonated & sulfonated poly(pentafluorostyrene)

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![Chemical structures](image-url)
• Phosphonated poly(pentafluorostyrene) (PWN2010)
  • Synthesis & Characterization
  • Conductivity (EIS)
  • Structure (SAXS)
  • Anhydride formation (phosphonic acid condensation)
  • Resistance to radical attack (Fentons test)

• Emulsion polymerization of pentafluorostyrene
  • Molecular weight (GPC)

• Sulfonated poly(pentafluorostyrene) (sPFS)
  • Synthesis & Characterization
  • Resistance to heat (TGA)
  • Hydration isotherms (water uptake)
  • Conductivity (EIS)
Phosphonation of PFS

\[
\begin{align*}
\text{PFS} & \quad (\text{commercial}) \\
\text{Characteristics:} & \\
\text{• phosphonation above } & 90 \% \\
\text{• molecular weight } M_w & = 67 \text{ kDa} \quad (M_w \text{ (PFS)} = 59 \text{ kDa}) \\
\text{• IEC} & = 7 \text{ mmol g}^{-1} \quad (\text{calc. } 7.8 \text{ mmol g}^{-1}) \\
\text{• } pK_a & = 0.5 \quad (\text{Polystyrene-PO}_3\text{H}_2: \quad pK_a = 1.9) \\
\text{• resistance to heat up to } & 340 \ ^\circ \text{C} \\
\text{• } T_g & \text{ above } 340 \ ^\circ \text{C}
\end{align*}
\]

Yield: 98%
water soluble powder

Atanasov & Kerres *Macromolecules* 2011, 44, 6416
* H. Steininger *Phys. Chem. Chem. Phys.*, 2007, 9, 1764
SAXS

Intensity (a.u.)

q (Å⁻¹)

q0 = 0.27 Å⁻¹

q1 = 0.557 Å⁻¹

PWN 2010, 84% RH

N117 Ambient RH

d = 2p/q = 23 Å
**31P solid-state NMR**

**Drying:** 50 °C, p = 1 mbar, a week

**Observing:** Single resonance

**Reason:** free phosphonic function

**Conclusion:**

Inability of PWN2010 to undergo self-condensation at 50 °C

**Annealing:** 250 °C, p = 1 atm, 5 hrs

**Observing:** Shoulder in the main resonance

**Reason:** formation of new phosphorous species

**Conclusion:**

PWN2010 formed anhydride at 250 °C (confirmed by FTIR)
Integration:
acid : anhydride = 58 : 42

Experimental spectrum of PWN annealed at 250 °C

PVPA

Anhydride > 90%

difference

acid form

anhydride form

<table>
<thead>
<tr>
<th>PWN</th>
<th>Weightloss [wt%]</th>
<th>$M_w$ / kDa</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before FT</td>
<td>-</td>
<td>67</td>
<td>7.4</td>
</tr>
<tr>
<td>After 24h FT</td>
<td>0</td>
<td>137</td>
<td>3.2</td>
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<tr>
<td>After 48h FT</td>
<td>0</td>
<td>106</td>
<td>2.8</td>
</tr>
<tr>
<td>After 96h FT</td>
<td>2</td>
<td>105</td>
<td>2.8</td>
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</tbody>
</table>

Fenton test of PWN2010

PWN after 24, 48 and 96h Fenton test

PWN before Fenton test

Molecular weight (g mol$^{-1}$)
### Emulsion polymerization of PFS

- Initiator: \( \text{K}_2\text{S}_2\text{O}_8 \)
- M/H\(_2\text{O} \) = 1/2
- M/SDS = 50/1
- Temperature: \( T = 80 \rightarrow 94 \degree \text{C} \) for 1 h
- React. Time: 2 h

<table>
<thead>
<tr>
<th>Name</th>
<th>( M_n ) calc kDa</th>
<th>( M_n ) exp kDa</th>
<th>( M_w ) exp kDa</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS*</td>
<td>-</td>
<td>25</td>
<td>105</td>
<td>4.2</td>
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<tr>
<td>1</td>
<td>100</td>
<td>312</td>
<td>716</td>
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<tr>
<td>2</td>
<td>100</td>
<td>260</td>
<td>780</td>
<td>3.0</td>
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<tr>
<td>3</td>
<td>100</td>
<td>140</td>
<td>440</td>
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<tr>
<td>4</td>
<td>30</td>
<td>110</td>
<td>295</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*commercial
Characteristics:

• sulfonation 100 %
• IEC = 3.4 mmol g⁻¹ (calc. 3.9 mmol g⁻¹)
• pKₐ = - 2 (PSSA: pKₐ = - 0.5)
• resistance to heat up to 270 °C
• molecular weight is unknown: sPFS is partially soluble only in DMSO
Temperature / °C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Defuncional. [°C]</th>
<th>Degradation [°C]</th>
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</thead>
<tbody>
<tr>
<td>PαMSSA</td>
<td>201</td>
<td>381</td>
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<tr>
<td>PSSA</td>
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<td>382</td>
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<td>sPFS</td>
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<td>351</td>
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<tr>
<td>tPFS</td>
<td>325</td>
<td>478</td>
</tr>
<tr>
<td>PFS</td>
<td>-</td>
<td>402</td>
</tr>
<tr>
<td>PWN 2010</td>
<td>340</td>
<td>391</td>
</tr>
</tbody>
</table>
The absolute higher water uptake of sPFS and PWN2010 is due to its higher number of functional group in compare to Nafion117.
Conductivity at 1 atm water pressure

Temperature (°C)

Conductivity (S cm⁻¹)

160
140
120
100

1

0,1

0,1

0,01

0,01

0,001

2,25

2,95

2,45

2,55

2,65

1000/T (K⁻¹)

sPSO₂-220

sPFS


Nafion117

PWN2010
Phosphonated poly(pentafluorostyrene) with phosphonation degree above 90% is obtained

- The high conductivity ($\sigma = 0.1 \ \text{S cm}^{-1}$ at 110 °C):
- Lamellar structuring (SAXS).
- The reduced formation of anhydrides ($^{31}$P MAS NMR)
- Resistance to radical attack.

Poly(pentafluorostyrene) was obtained by emulsion polymerization

- Molecular weight (GPC): up to 800 kDa
- Control over molecular weight

Sulfonated poly(pentafluorostyrene) is obtained with 100% sulfonation degree.

- Ion conductivity ($\sigma = 50 \ \text{mS cm}^{-1}$ at 150 °C) is making this material one of the best ion-conducting polymer.
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