



[Click to advertise here](#)

Chemistry Corner

## Sulfonated polymers: Simple chemistry for high-tech materials & applications

**Martin Meyer and Jorg Schrickel of CABB look at why the polymerisation of sulfonated monomers and the sulfonation of polymers are two different things**

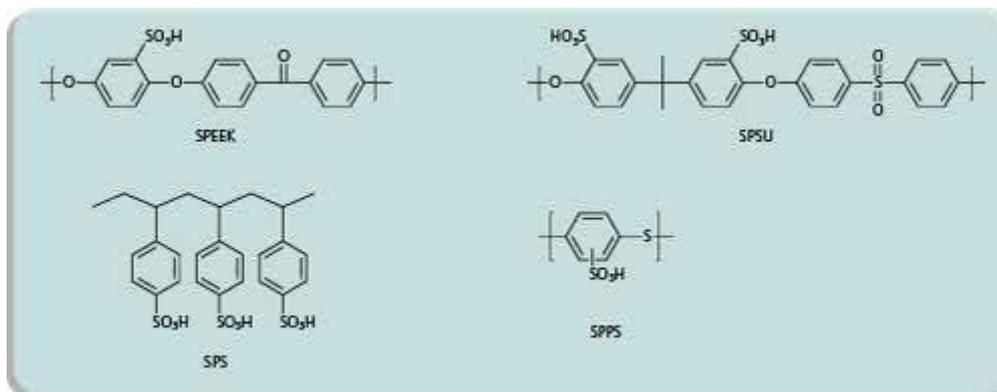
Polymers are used everywhere in modern life. In general, they are synthesised from hydrocarbons, mainly with olefins as the starting materials. Sulfur-containing carbon-based polymers, however, are rare compared to the total amount of polymer available.

Sulfur is usually incorporated in the form of sulfones, sulfonic acids, sulfonates or sulfides. The reason for introducing heteroatoms into polymers is to modify the properties of the respective polymers. Sulfonated products show different characteristics to their unsulfonated counterparts, transforming them into speciality materials suitable for highly specific applications.

Sulfonation leads to better ion conductivity, higher hydrophilicity and improved solubility of the polymer.<sup>1</sup> Applications for sulfonated polymers are found where these particular properties are needed, mainly in higher value products like membranes for fuel cells and electro dialysis, exchange resins and catalysts, surgical instruments, implants and wound healing dressings. Sulfonation is the key technology for obtaining high performance proton-conducting polymers - a prerequisite for today's fuel cell technology.

### Products

Sulfonation is facilitated by electron-rich substrates, so aromatic polymers with electron-donating substituents are preferred substrates.<sup>2,3</sup> The first reports about sulfonated polystyrene (SPS) are now nearly 80 years old.<sup>2</sup> Other frequently found sulfonated polymers are sulfonated polyetheretherketones (SPEEKs), sulfonated polyphenylenesulfides (SPPSs) and sulfonated polysulfones (SPSUs) (Figure 1).



**Figure 1 - Chemical structures of sulfonated aromatic polymers**

Sulfonated polyethylenes, notably Nafion and - formerly - Hypalon (Figure 2), are also important. Nafion is a sulfonated tetrafluoroethylene, or Teflon, polymer and was the first commercial polymer with ionic properties, or ionomer.<sup>4</sup> It is also used as a catalyst in acid-catalysed reactions.

Hypalon, a chlorosulfonated polyethylene, is somewhat different from other sulfonated polymers as sulfur dioxide and chlorine are used as reagents and results in the chlorosulfonation of the polymer.<sup>5</sup>

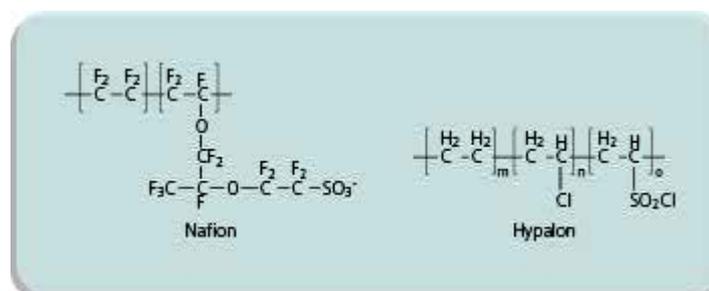
Chlorosulfonated polyethylenes are highly resistant to temperature, chemicals, ozone, weathering and moisture. Thus they are ideal for external and waterproof applications.<sup>5,6</sup>

### Properties & applications

The properties of the final sulfonated polymer are heavily influenced by the degree of sulfonation. The introduction of sulfonic acid groups leads to an increase in hydrophilicity, proton conductivity and transforms the polymers to ionomers. At higher degrees of sulfonation, however, swelling increases and the mechanical stability is reduced.<sup>3</sup> At higher temperatures, the polymer starts to decompose, due to desulfonation.<sup>7</sup>

One of the most important properties that changes by the introduction of sulfonic acid groups is their ionic character. Compared to unsulfonated compounds, the introduction of a sulfonic acid group leads to proton and cation conductivity. This makes the material ideal for membranes like proton exchange membrane fuel cells (PEMFCs). Here, the flow of protons from anode to cathode can be enhanced by using a sulfonated polymer.<sup>7</sup>

Nafion shows high proton conductivity at low operating temperature together with a high chemical and thermal stability.<sup>7,8,9</sup> These properties permit a broad range of applications from membranes in PEMFCs and chloroalkaline electrolysis, humidification or the drying of gases to acidic catalysts.



**Figure 2 - Sulfonated aliphatic polymers**

Poly(ether ketones) offer a high chemical and thermal stability as well as good mechanical properties.

SPEEK show high ion and proton conductivities and low methanol permeability, making it a good material for direct methanol fuel cells (DMFCs) and other membrane applications.<sup>4,10</sup>

Similar to poly(ether ketones) are polysulfones (PSUs), which also possess the characteristics for PEMs. The conductivity of SPSUs is much lower than Nafion's but it can be increased with a higher temperature and degree of sulfonation.<sup>10</sup>

Poly(ether)sulfones are also used as membranes in other areas like food technology, medicine or process water filtration. Especially for medical applications, the polymers used have to be sterilisable, stable against disinfectants and biocompatible.

These requirements are fulfilled by sulfonated polyethersulfones with a low degree of sulfonation.<sup>11</sup> Attention has to be paid on the degree of sulfonation as the solubility increases with the amount of sulfonic acid groups present in the polymer.<sup>12</sup>

Polystyrene sulfonates in the form of their sodium and calcium salts have applications as pharmaceuticals in the treatment of hyperkalaemia, which is an abnormally high potassium level in blood serum.<sup>13</sup>

Sulfonated polymers are also present in wound dressings. Wound healing is facilitated when the wound is kept moist and clean. Dressings are available as hydrogels that contain insoluble polymers with hydrophilic sites, which can interact with aqueous solutions. They can be charged with active substances and are hence used as transporters for therapeutic agents to prevent infections. These agents can be drugs or metals. They are introduced during manufacture or by swelling and diffuse into the wound over time.<sup>14,15</sup>

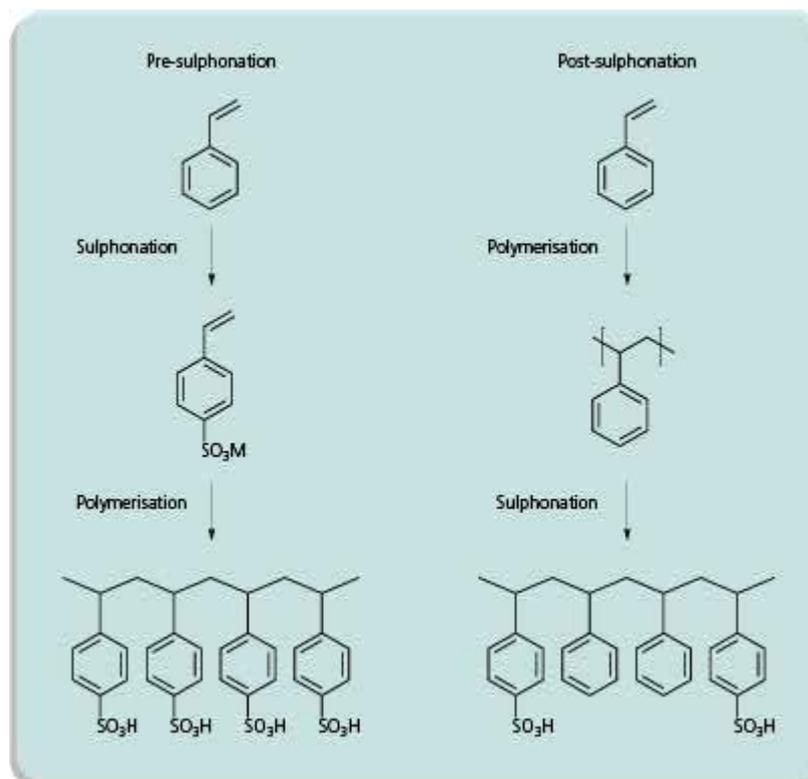
Reduced adhesion, as exhibited by sulfonated membranes, is frequently a desirable property for medical devices. The sulfonation of parts used for medical devices with gaseous sulfur trioxide (SO<sub>3</sub>) and subsequent neutralisation reduces the adhesion to biological fluids and thus improves its resistance. These parts are made of polyesters and can be used for syringes, dialysis and other applications.<sup>16</sup> Similar results are achieved by coating a respective material with a sulfonated polymer.<sup>17</sup>

### The process

The sulfonation reaction can take place at the monomer before polymerisation (pre-sulfonation) or at the finished polymer (post-sulfonation). This has a direct influence on the degree of sulfonation and the resulting properties of the sulfonated polymer (Figure 3).

Pre-sulfonation is in general linked with the co-polymerisation of a different, unsulfonated monomer. In the case of a post-sulfonation the degree of sulfonation depends on the type of reagent, substrate, reaction time and temperature. This leads to a statistical distribution of the sulfonic acid groups within a bandwidth.<sup>2</sup>

When sulfonated monomers are polymerised or co-polymerised with other monomers, the exact degree of sulfonation and the substitution pattern can both be controlled in a much better way and no chemical treatment after polymerisation is necessary. Depending on the desired properties of the sulfonated polymer and hence the degree of sulfonation, one or the other method can be applied.



**Figure 3 - Sulfonation before & after polymerisation**

Most post-sulfonation processes are conducted in a homogeneous way and are thus limited by the solubility of the polymer. In general, polymers are soluble in strong acids and chlorinated organic solvents in low concentrations. In processes which employ concentrated sulfuric acid as a solvent, the acid can act as a sulfonation agent at the same time.<sup>2</sup>

The disadvantages of post-sulfonation are the difficulty in controlling the degree of sulfonation, the low solubility of the polymer and its possible degradation if strong reagents are used. Further disadvantages of homogeneous sulfonation are the high solvent volumes, due to the high dilutions needed, and the separation of the sulfonated polymer from the reaction mixture.<sup>2</sup>

Homogeneous sulfonation, however, allows the use of less reactive reagents, like complexes of  $\text{SO}_3$  with amines or phosphates (see below), with the advantage that cross-linking and degradation can be significantly reduced compared to more reactive conventional reagents. The best compromise between reactivity, reaction conditions and the desired degree of sulfonation must be determined in trials.

The low solubility of the polymers in homogeneous sulfonation can be overcome by heterogeneous sulfonation, which is carried out using polymer beads and gaseous or liquid  $\text{SO}_3$  or other liquid reagents. Under certain conditions, concentrated sulfuric or chlorosulfonic acid are used as reagents for the solid polymer. With an increasing degree of sulfonation, the polymer dissolves in these acids.<sup>2</sup>

### The reagents

Polymers can be sulfonated with a large range of various reagents, which differ with regards to reactivity and selectivity, potential of side-reactions and economics. Sulfuric acid, fuming sulfuric acid,  $\text{SO}_3$  and chlorosulfonic acid are conventional, inexpensive and highly reactive reagents (Figure 4).

- **Strong reagents**  
Sulfur trioxide, (fuming) sulphuric acid, chlorosulphuric acid
- **Milder reagents**  
Acetyl sulfur trioxide complexes, alkylphosphate sulphur trioxide complexes
- **Polymer-bound reagents**  
Poly-2-vinylpyridine sulfur trioxide

**Figure 4 - Sulfonation reagents**

However, the strength of these agents can cause various side-effects, like chain cleavage, unwanted cross-linking and an unreproducible degree of sulfonation due to possible phase separation of polymer chains from the reaction mixture.<sup>10</sup> Individual problems are that fuming sulfuric acid produces water as a by-product, which inhibits the sulfonation reaction and favours desulfonation.<sup>2</sup> In reactions with concentrated sulfuric acid as a solvent, the quenching of the reaction mixture on water leads to the precipitation of the sulfonated polymer.<sup>18</sup>

SO<sub>3</sub> is one of the most reactive inorganic compounds.<sup>19</sup> Sulfonation reactions can be carried out using liquid SO<sub>2</sub>, which is the best solvent for SO<sub>3</sub>, but it can be used in gaseous form as well, especially for sulfonating polymer in solid form.<sup>20</sup>

Sulfonation reactions of polymers with chlorosulfonic acid result in the formation of one equivalent of HCl as a by-product, which has to be neutralised and disposed of. This limits its commercial application. The reaction runs unhomogeneously but this can be overcome by the addition of DMF as co-solvent.<sup>8,10</sup>

Milder sulfonation agents are trimethylsilyl chlorosulfonate (TMSCS), acetylsulfate or complexes from SO<sub>3</sub> with amines or trialkyl phosphates. They permit milder reaction conditions and generally lead to fewer side reactions like degradation or cross-linking.<sup>2,21</sup>

Polymer-bound SO<sub>3</sub>, in the form of poly-2-vinylpyridine SO<sub>3</sub>, may act as a mild reagent for some heterogeneous applications where the polymer is dissolved and the reagent is solid. An advantage is that the polymer carrier can easily be separated from the product by filtration, then cleaned and reloaded with SO<sub>3</sub> for repeated use.<sup>22</sup>

## Summary

Sulfonated polymers show different properties compared to their unsulfonated counterparts. The most interesting characteristics are their ion-conductive properties. They are used in high performance applications ranging from ion exchange resins and membranes to pharmaceutical intermediates, implants and medical patches. Much effort is being put in at this moment into research on membranes and solid electrolytes for fuel cells.

Sulfonated polymers can be prepared by pre- or post-sulfonation, by heterogeneous or homogeneous reactions or via copolymerisation. The reagents, substrates and reaction conditions determine the degree of sulfonation, which itself influences the properties of the sulfonated polymer.

## References

- 1 N. N. Fathima, R. Aravindhan, D. Lawrence, U. Yugandhar, T.S.R. Moorthy & B.U. Nair, *J. Sci. Ind. Res.* **2007**, 66, 209-219
- 2 F. Kucera & J. Jancar, *Polymer Engineering and Science* **1998**, 38, 783-792
- 3 S.M.J. Zaidi, *The Arabian Journal for Science and Engineering* **2003**, 28, 183-194

- 4 S.M.J. Zaidi & T. Matsuura, *Polymer Membranes for Fuel Cells*, Springer, **2009**
- 5 WO 2009/123993 A1, **2009**
- 6 US 5559182 A, **1996**
- 7 J.S. Lee, N.D. Quan, J.M. Hwang, S.D. Lee, H. Kim, H. Lee & H.S. Kim, *J. Ind. Eng. Chem.* **2006**, 12, 175-183
- 8 M.A. Hickner, H. Ghassemi, Y.L. Kim, B.R. Einsla & J.E. McGrath, *Chem. Rev.* **2004**, 104, 4587-4611
- 9 S.-L. Chen, A B. Bocarsly & J. Benziger, *Journal of Power Sources* **2005**, 152, 27-33
- 10 K. G. Reed, *The Development & Implementation of High-throughput Tools for Discovery & Characterization of Proton-Exchange Membranes*, Dissertation, Georgia Institute of Technology, **2009**
- 11 US 5879554 A, **1999**
- 12 K. Ohlrogge & K. Ebert, *Membranen: Grundlagen, Verfahren und industrielle Anwendungen*, Wiley-VCH, **2006**
- 13 US 2007/0248564 A1, **2007**
- 14 US 6306419 B1, **2001**
- 15 US 2006/0292208 A1, **2006**
- 16 US 2010/0099792 A1, **2010**
- 17 EP 1358896 A1, **2003**
- 18 DE 10007272 A1, **2000**
- 19 E.E. Gilbert, *Chem. Rev.* **1962**, 62, 549-589
- 20 G.Y. Kim, R. Salovey & J.J. Aklonis, *Polym. Bulletin* **1990**, 23, 543-547
- 21 A. Dyck, D. Fritsch & S.P. Nunes, *Journal of Applied Polymer Science* **2002**, 86, 2820-2827
- 22 US 3057855 A1, 1962, EP 0103538 A2, **1984**

**From Online Issue: February 2013**

---

[Privacy Policy](#) | [Terms & Conditions](#)

©Quartz Business Media Ltd. 2013