

Poly(p-phenylene sulfone)s with High Ion Exchange Capacity: Ionomers with Unique Microstructural and Transport Features

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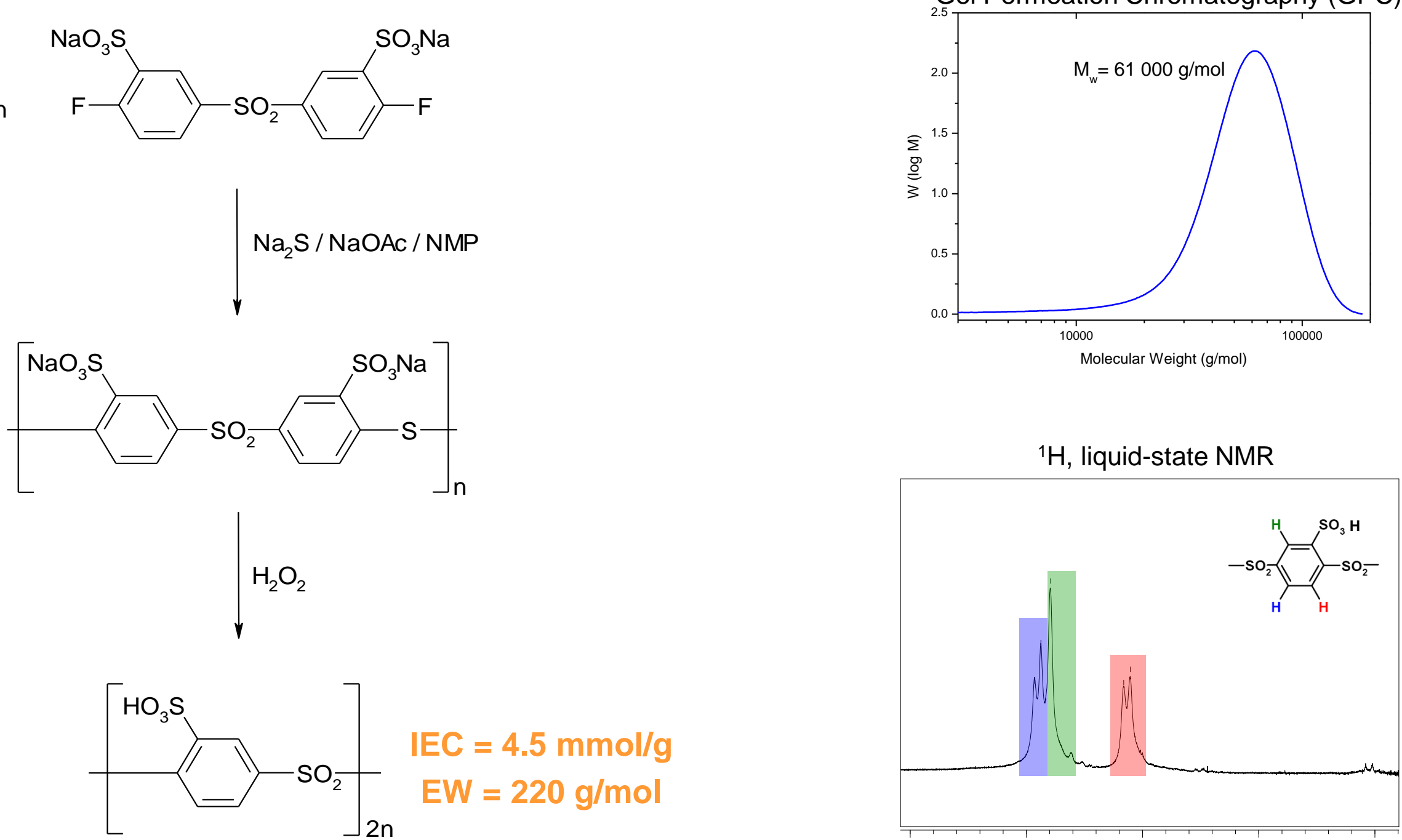
für Festkörperforschung

Abstract

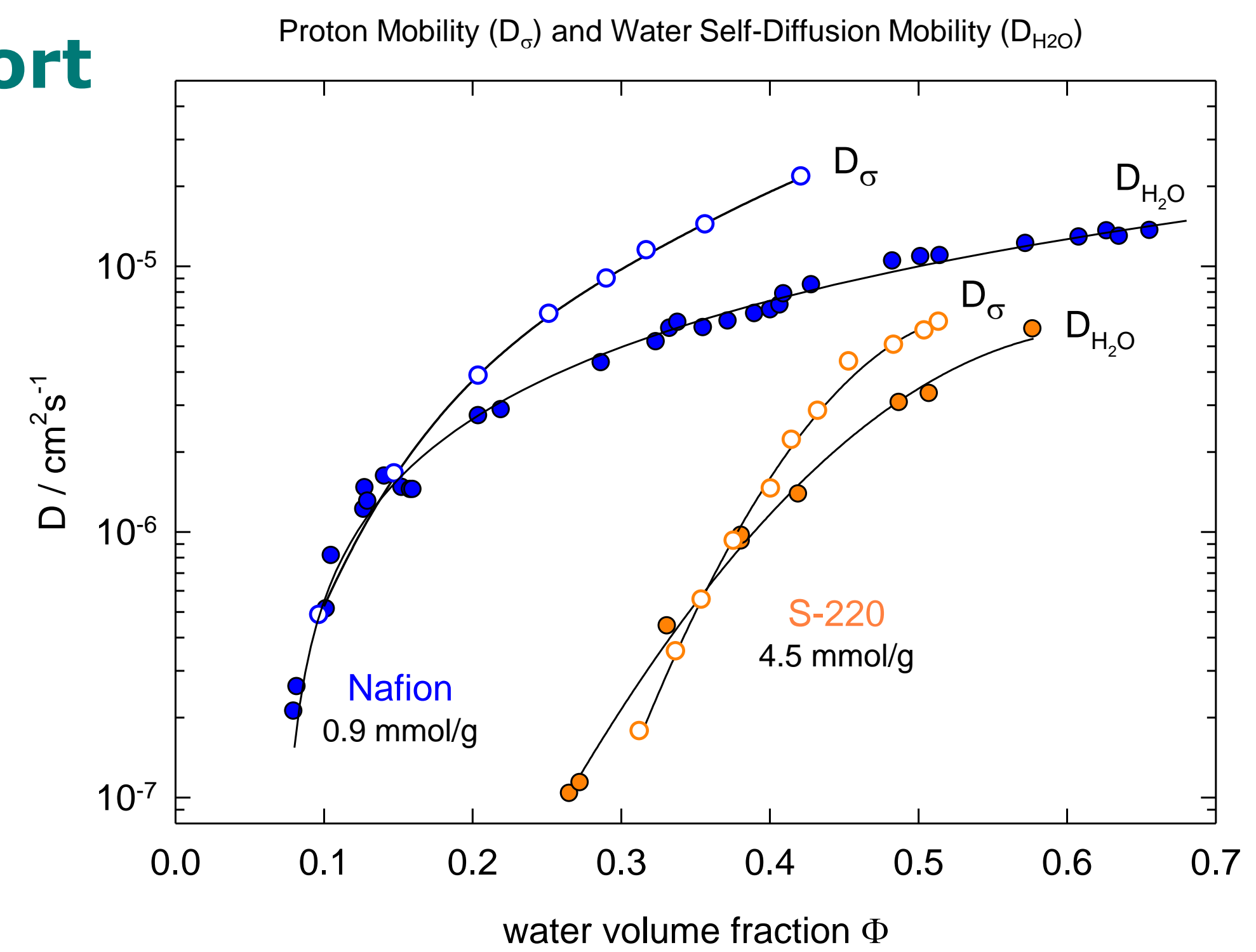
Poly(phenylene) ionomers which contain merely sulfone units ($-\text{SO}_2-$) connecting the phenyl rings and in which each phenyl ring is sulfonated ($-\text{SO}_3\text{H}$) have been characterized with respect to their hydrolytic stability, microstructural and transport properties. The high degree of sulfonation leads to the development of a microstructure characterized by very narrow hydrated, hydrophilic domains which are well connected on larger scales. These features together with high absolute

water uptakes at given relative humidities and the high charge carrier concentration corresponding to the high ion exchange capacity ($\text{IEC} \sim 4.5 \text{ meq./g}$) result in very high proton conductivities but also low water transport coefficients (water diffusion and presumably also electroosmotic drag and permeation). Compared to the transport properties of Nafion, these trends increase with increasing water content and temperature. Under the same conditions sulfonated poly(p-phenylene sulfone)s show very high hydrolytic stability.

Preparation



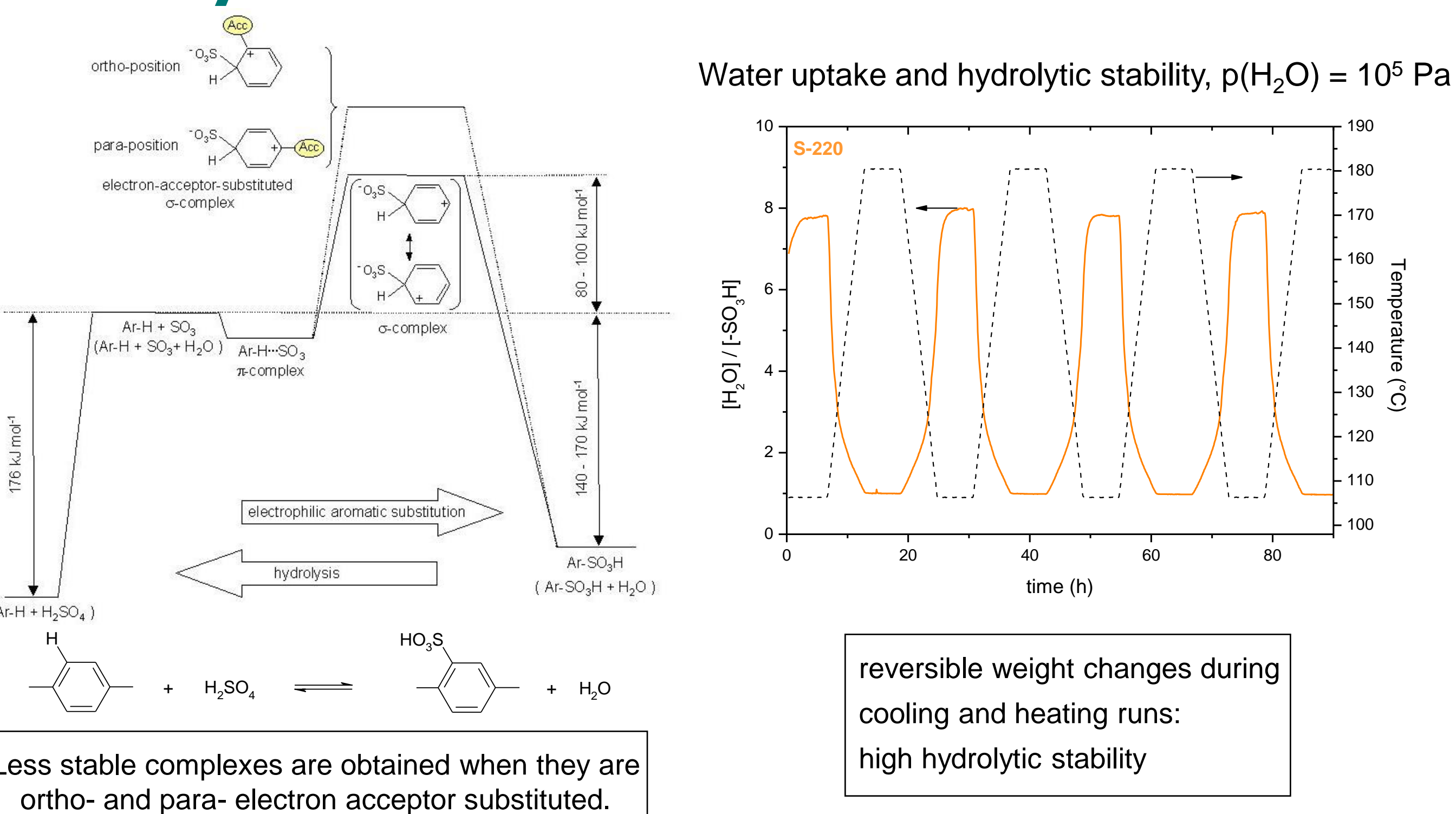
Transport



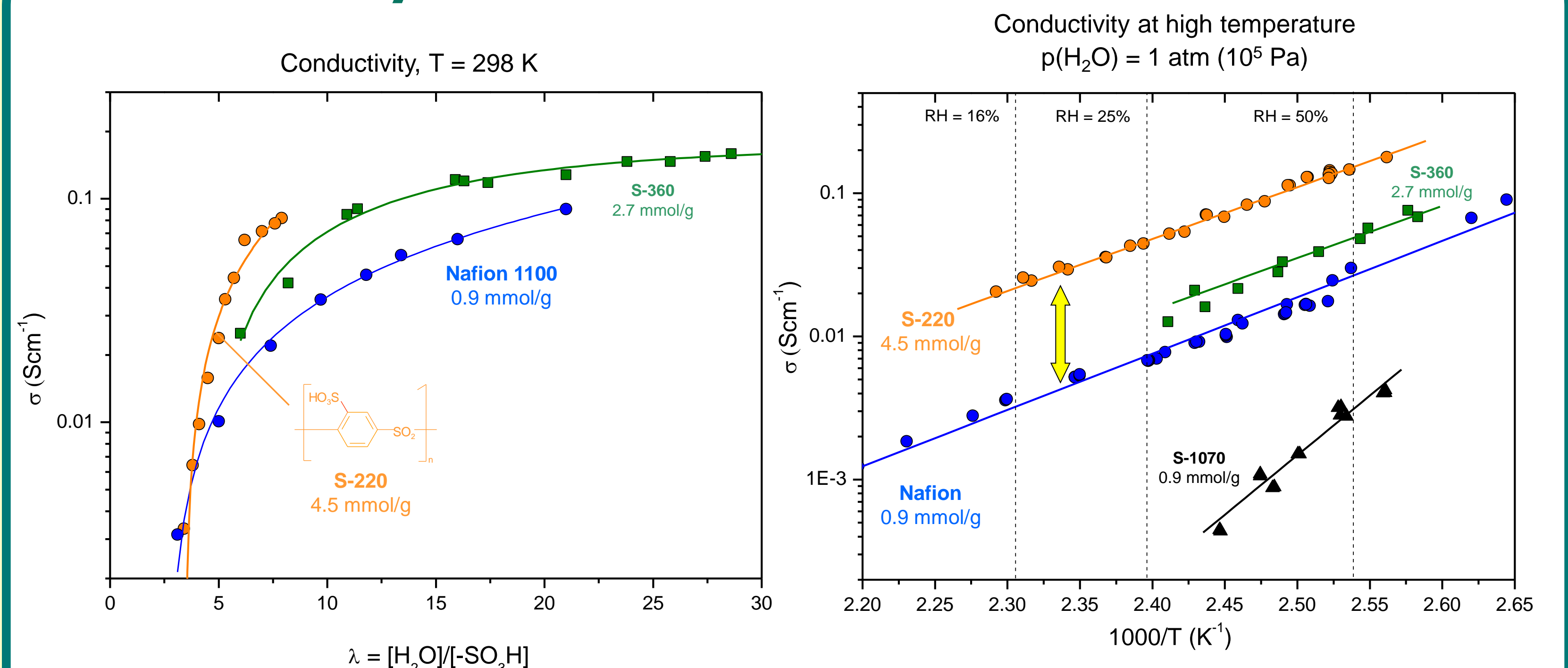
Low water diffusion coefficient of the sulfonated poly(p-phenylene sulfone)s even at high degrees of hydration as a consequence of the very narrow water structures

At room temperature and high water content D_σ hardly exceeds the water diffusion coefficient, meaning that there is no significant conductivity contribution from structure diffusion (Grotthuss mechanism)

Stability



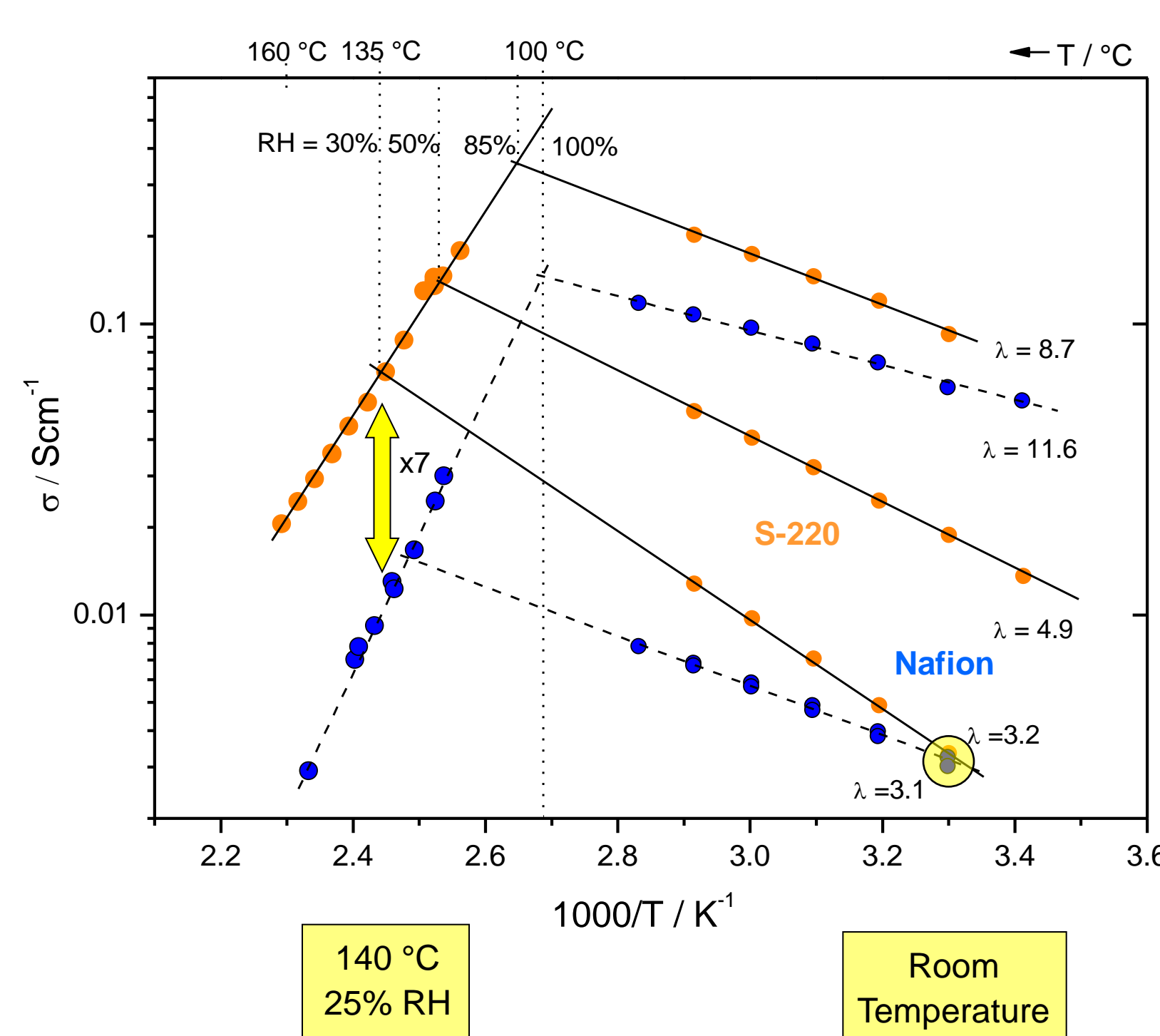
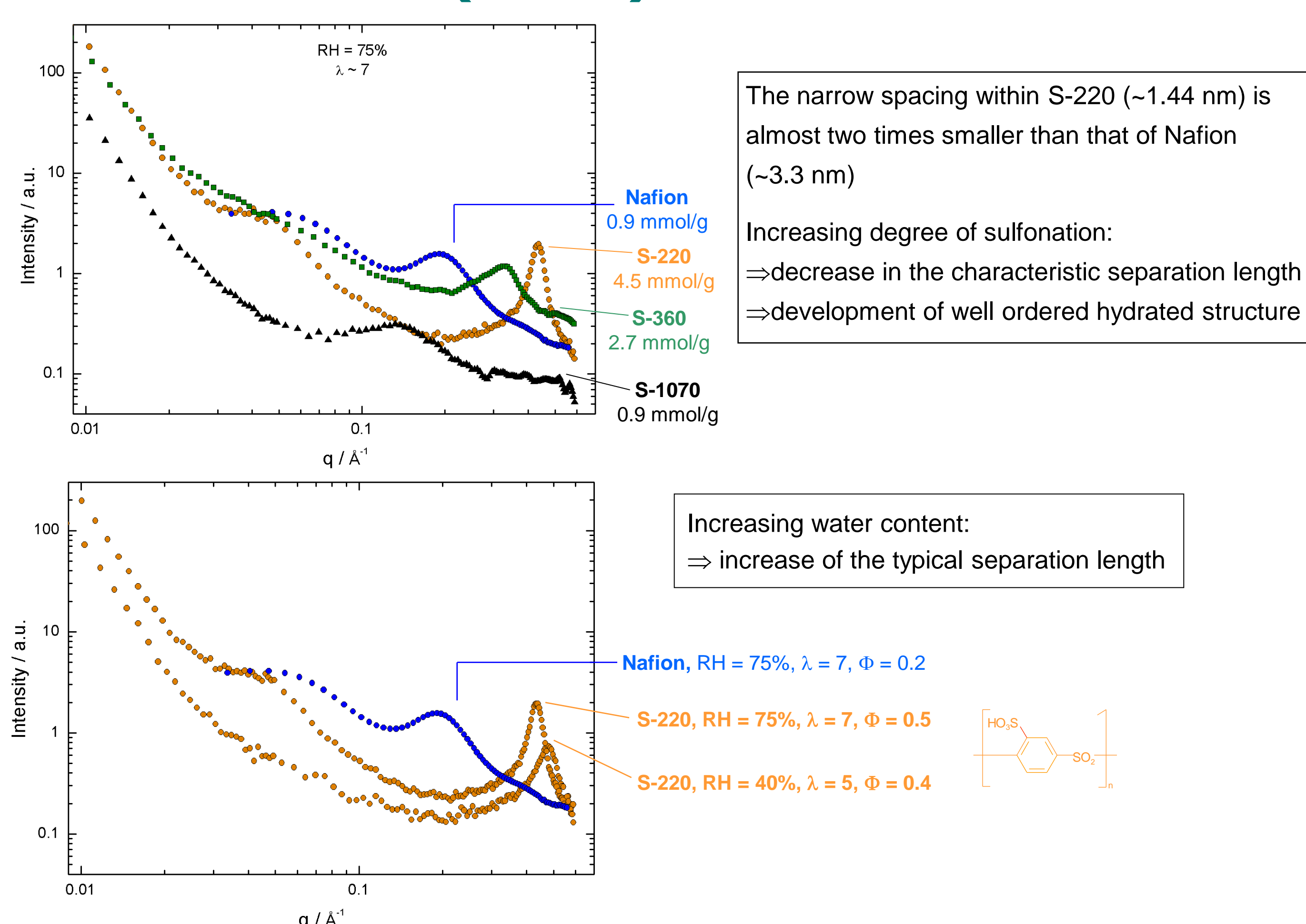
Conductivity



At low water content S-220 and Nafion have similar proton conductivity. At high water content ($\lambda \sim 10$) S-220 conductivity is about 3 times higher. The reasons for higher conductivity are higher absolute water content and higher concentration of protonic charge carriers

Under conditions similar to those relevant for PEM fuel cell, even the half-sulfonated poly(p-phenylene sulfone), S-360, has conductivity higher than Nafion

Microstructure (SAXS)



Conclusions and Outlook

Highly sulfonated poly(p-phenylene sulfone) are shown to combine high hydrolytic stability with very high proton conductivity. This is the result of the very high charge carrier concentration (IEC up to 4.5 meq/g) and the very high water uptakes for a given relative humidity leading to the development of a well connected aqueous channel like structure facilitating the long range transport of water and hydrated species. Locally, it

consists of very narrow structures retarding the water diffusion. However, the polymer with the highest IEC is water soluble and brittle in the dry state. The preparation of membranes with highly sulfonated poly(p-phenylene sulfone) polymer as main constituent (e.g. as part of blends, interpenetrating networks, complexes, copolymers) is in progress in our group.

References

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- [2] M. Schuster, C. C. de Araujo, V. Atanasov, H. T. Andersen, K.-D. Kreuer, J. Maier, *Macromolecules*, 42, 3129 (2009).
- [3] C. C. de Araujo, K. D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, and J. Maier, *PCCP*, 11, 3305 (2009).

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