Fully Sulfonated Graft Copolymer Blends - a Structure-Property Relationship Study

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Background

Previous studies of partially sulfonated Poly(vinylidene difluoride-*co*-chlorotrifluoroethylene)-*g*-poly(styrene sulfonic acid) [P(VDF-*co*-CTFE)-*g*-SPS] showed that when the ion exchange capacity (IEC) is controlled by varying the graft length, graft density (GD) and degree of sulfonation (DS) water sorption was decreased without compromising on proton conductivity at low GD[1]. The ion content was observed to greatly influence phase separation and ionic aggregation. The presence of unsulfonated PS however, reduced the connectivity between ionic domains. Blends of partially sulfonated P(VDF-*co*-CTFE)-*g*-SPS with PVDF displayed only minor changes in water sorption and conductivity over a range in IEC as the additional PVDF incorporated into the domains of the perfluorinated backbone of the graft ionomers[2].

Analytical techniques

- Nuclear magnetic resonance spectroscopy (NMR)
- Transmission electron microscopy (TEM)
- Gravimetry
- Titration
- Dynamic vapor sorption (DVS)
- AC Impedance Spectroscopy

Conclusions

Fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS formed interconnected ionic clusters increasing in size by graft length, yet they partially dissolved in water. When blended with PVDF the fluorous segments incorporate into each other and the interconnected network is maintained, with the addition of macrophase in-plane ionic channels at high PVDF content. At equal IEC water swelling was lower than for fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS and higher than for partially sulfonated one. As expected DVS showed a strong dependence on a high RH of the blends compared to similar IEC fully sulfonated pure graft copolymer. Interestingly the proton conductivity of the blends were higher than both partially and fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS. The performance of the fully humidified 25:75 blend series looks especially promising.

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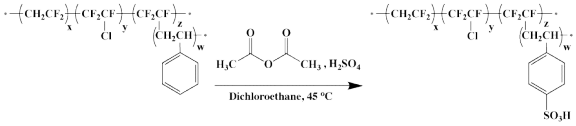
Objectives

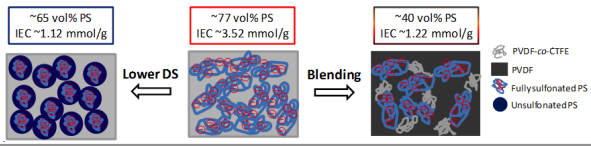
The aim with the current study is to investigate fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS of various graft lengths blended with PVDF. A fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS of similar IEC as the blends is included in order to compare the various systems: partially[3] and fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS, and PVDF blends of the fully sulfonated system.

Synthetic strategy

Complete sulfonation of the PS grafts was obtained in two consecutive reactions.



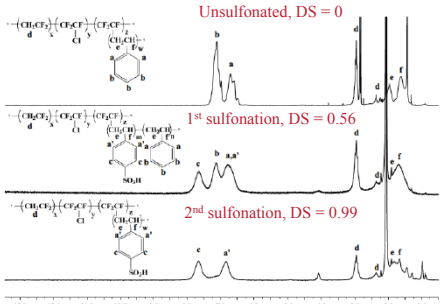
The polymers were blended with PVDF, thereby tuning IEC. Membranes properties of these are compared to those obtained by tuning IEC by varying DS.



Nomenclature

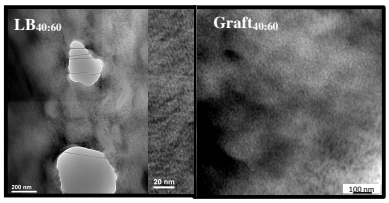
S = short grafts
M = medium grafts
L = long grafts
B = blend
$_{40:60}$ = SPS:PVDF ratio
$_{25:75}$ = SPS:PVDF ratio
Graft = reference P(VDF-co-CTFE)-g-SPS

^{1}H NMR

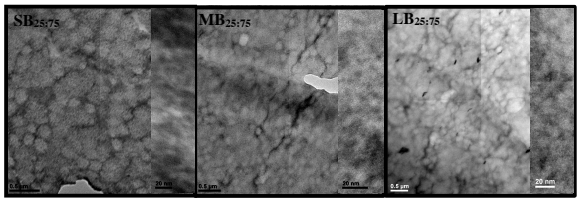


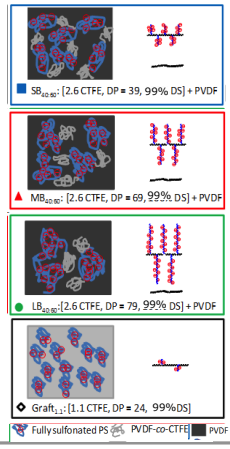
TEM

- The graft copolymer blends show interconnected ionic networks.
- In addition they have in-plane macrochannels.
- The domain morphology seems fairly independent of grafts lengths.



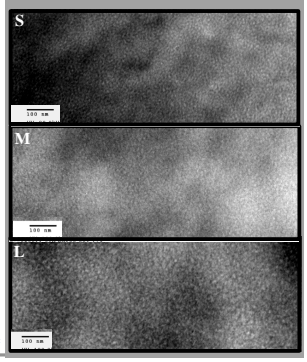
Dark domains are lead acetate stained -SO_3H. Bright domains are hydrophobic backbone and grafts.



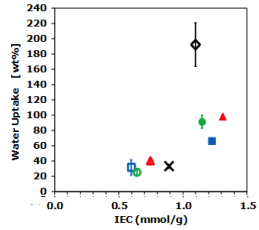


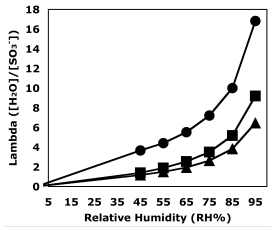
Perspective

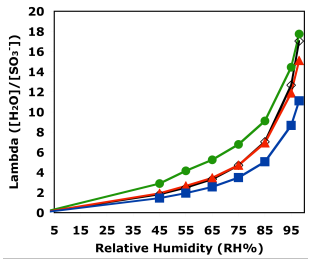
TEM of the pure graft copolymers show interconnected ionic domains. The longer the sidechains the larger the ionic domains.



Water sorption







Immersed / RT

- Fully sulfonated P(VDF-*co*-CTFE)-*g*-SPS partially dissolved.
- 40:60 blends showed water uptakes 50% lower than Graft$_{40:60}$.
- 25:75 blends showed water uptakes close to Nafion.

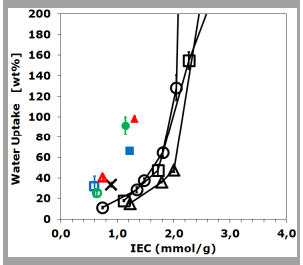
DVS

- The longer pure graft copolymers exhibited higher water sorption.
- 40:60 blends showed similar hygroscopic behaviour as Graft$_{40:60}$

■ S ▲ M ● L ■ $SB_{40:60}$ ▲ $MB_{40:60}$ ● $LB_{40:60}$ □ $SB_{25:75}$ △ $MB_{25:75}$ ○ $LB_{25:75}$ ◇ $Graft_{40:60}$ × Nafion 117

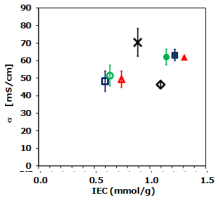
Perspective

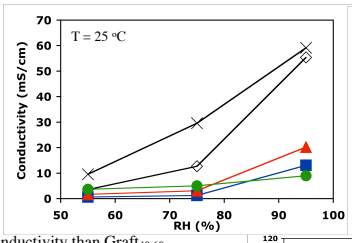
Water uptake of blends is higher than for equivalent IEC-value partially sulfonated P(VDF-*co*-CTFE)-*g*-SPS.

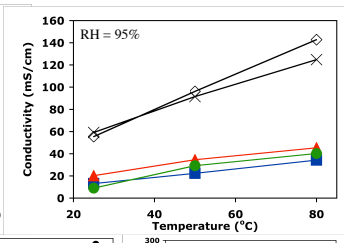


□ S △ M ○ L -partially sulfonated

Proton conductivity





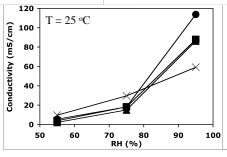


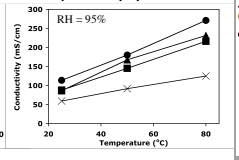
Immersed / RT

- 40:60 blends have 37% higher conductivity than Graft$_{40:60}$.
- 25:75 blends have same conductivity as Graft$_{40:60}$.

Conductivity as f(RH, T)

- 40:60 blends show lower conductivity than Graft$_{40:60}$ at reduced RH and elevated temperatures.
- The conductivity of the pure graft copolymers surpass Nafion at 80% RH / 25 °C.

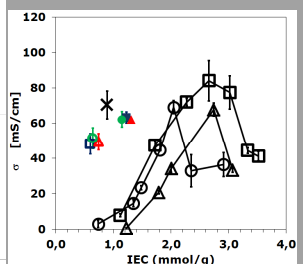




■ S ▲ M ● L ■ $SB_{40:60}$ ▲ $MB_{40:60}$ ● $LB_{40:60}$ □ $SB_{25:75}$ △ $MB_{25:75}$ ○ $LB_{25:75}$ ◇ $Graft_{40:60}$ × Nafion 117

Perspective

Proton conductivity of blends is higher than for equivalent IEC-value partially sulfonated P(VDF-*co*-CTFE)-*g*-SPS.



□ S △ M ○ L -partially sulfonated

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