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Investigations of crystallinity and chain entanglement on sorption and conductivity of proton exchange membranes



Ami C.C. Yang^a, Rasoul Narimani^b, Barbara J. Frisken^b, Steven Holdcroft^{a,*}

^a Department of Chemistry, Simon Fraser University, Burnaby, Canada BC V5A 1S6

^b Department of Physics, Simon Fraser University, Burnaby, Canada BC V5A 1S6

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ABSTRACT

Proton-conducting hydrocarbon membranes often require an ion exchange capacity (IEC) in excess of 2 mmeq/g to achieve a conductivity sufficiently high for technological applications (typically > 50 mS/cm). Membranes with high IEC are often brittle when dry and swell excessively when fully hydrated. Increasing the crystallinity of hydrocarbon membranes is hypothesized to increase phase segregation thereby enhancing their mechanical integrity in water by reducing their propensity to swell excessively, and to provide an ionic network when water contents are reduced when RH < 100% and under elevated temperatures. In this work we examine the effect of increasing the crystallinity of highly sulfonated graft copolymer membranes by blending with polycrystalline poly(vinylidene difluoride) (PVDF). The addition of PVDF increases the crystallinity, reduces the ion exchange capacity, reduces swelling, yet does not deleteriously affect proton conductivity. The extent to which crystallinity increases and water swelling is reduced was found dependent on the molecular weight of the PVDF. The incorporation of high m. wt. PVDF enhanced crystallinity to a lesser degree than incorporating low m. wt. PVDF but swelling was reduced to a greater extent. This observation is explained by an increase in elastic forces of the membrane that oppose osmotic swelling due to an increase in physical connectivity of the PVDF crystallites via long PVDF polymer chains that span multiple crystallites. The addition of PVDF did not compromise proton mobility in the ionic phase and as a consequence of the much higher proton concentrations attained, proton conductivities were significantly enhanced. Finally, the properties of membranes containing different ratios of ionomer and high m. wt. PVDF are described. Optimal compositions of these components are found in membranes which possess minimal swelling in water and have proton conductivity that is less susceptible to large fluctuations in RH.

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1. Introduction

Research continues towards the development of proton exchange membranes (PEMs) capable of exhibiting high proton conductivity under reduced humidity (e.g., ≥ 0.1 S/cm, $\leq 50\%$ RH) [1], and limited swelling upon full hydration [2,3]. State-of-the-art PEMs are based on perfluorosulfonic acid (PFSA) ionomers for which it is established that a nanoscale phase-separated morphology provides contiguous hydrophilic channels for the transport of protons under reduced RH and water content [4–11]. Hydrocarbon-based ionomers, [12–21] partially fluorinated ionomers [22–24], and ionomer blends [25–32], are coming to the forefront because of their variable, controlled composition and microstructure. As with PFSA ionomers, the formation of a channel-supporting morphology is a requirement for facile proton transport under lower levels of hydration. The polymer

microstructure plays a large part in determining the membrane's morphology, which in turn affects water sorption, proton conductivity and mechanical integrity. However, the relation between microstructure and membrane properties is still poorly understood; the relationship in membranes prepared from polymer blends, even more so.

Block and graft copolymers are versatile model systems for elucidating structure-property relationships and can be designed to form specific nanostructures [33–35]. Previous work on fluorinated diblock and graft copolymers confirmed that the polymer architecture greatly impacts water sorption and proton transport [36]. Sulfonated block copolymers allow for the alteration of block length and the formation of relatively large lamella-like ionic domains which have the disadvantage of swelling excessively in water. Graft copolymer ionomers, on the other hand, form membranes consisting of an interconnected network of disordered, ionic nanoclusters (2–3 nm diam.) which afford high IEC membranes (> 2 mmol/g) that do not dissolve in water. Modifications to the graft copolymer architecture, including molecular weight,

* Corresponding author.

E-mail address: holdcrof@sfu.ca (S. Holdcroft).

graft length, graft number density, and degree of sulfonation confer subtle but impactful changes on the membrane's transport properties [37–42]. For instance, shorter graft side chains yield larger, but fewer, ionic-rich domains – which reduces swelling and allows for even greater proton conductivity [37]. Short graft ionomers bearing a lower graft number density allow for a longer sequence length between graft side chains, which, as a result of increased crystallinity of the fluorinated component, afford even higher IEC membranes (up to 3.3 mmol/g) that resist dissolution in water [38]. Moreover, because of the high IEC attainable, the hydrophilic volume fraction of the membranes remains large, even under reduced humidity, thus facilitating proton conductivity under reduced RH. The caveat of designing high IEC membranes is that they are brittle when dry. The solution to this paradox is to design membranes with an overall low IEC that possess highly localized ion clusters and channels that suppress excessive swelling of the ionic rich regions in the presence of water.

In this work, we investigate blending a hydrophobic fluorinated polymer with partially-fluorinated ionic graft copolymers in order to prepare and examine membranes that possess highly localized ion-rich channels exhibiting high proton conductivity under lower RH, improved mechanical properties when dry, and improved resistance to swelling when fully hydrated. We utilized poly(vinylidene difluoride) (PVDF) as the non-ionic polymer because of its chemical and thermal stability, commercial availability, and its tendency to form crystalline domains that impart enhanced mechanical strength [43–50]. Blending ionic and non-ionic fluorinated polymers has been previously observed to promote a phase-separated morphology and improve mechanical integrity [43]; however, several studies indicate that blending ionic and non-ionic polymer blends leads to a significant decrease in proton conductivity compared to the parent ionomer [51]. For example, Nafion®/PVDF blends possess reduced proton conductivity due to the hydrophobic nature of PVDF which limits water sorption [52,53]. In contrast, preliminary work on blends of a low molecular weight (m. wt.) PVDF ($M_n \sim 2000$ g/mol) with a partially sulfonated graft copolymer revealed that blend membranes were able to maintain high proton conduction despite a large reduction in ion content due to the formation of an interconnected network of ionic clusters [54]. To extend the work, we use the blending approach to prepare membranes from high IEC, sulfonated poly(vinylidenedifluoride-co-chlorotrifluoroethylene)-g-polystyrene, P[VDF-co-CTFE]-g-PS. These ionomers have been shown to have fluorinated domains embedded in a continuous phase of polystyrene (PS) domains [55], and possess small, highly interconnected ionic clusters that give rise to high proton conductivity under reduced RH (< 100% RH) [38]. In the first section, we report on blends of a highly sulfonated graft ionomer which exhibits high water swelling (λ , 211; water content, 92%) and two different molar masses of PVDF (~ 2000 g/mol and 270,000 g/mol) in order to distinguish the effect of induced crystallinity and/or entanglement from effects brought about solely by increasing crystallinity. A diagram illustrating the structure of the graft ionomer and schematic representations of the subsequent graft blends is shown in Scheme 1. In the second section, we investigate blend membranes based on different ratios of high m. wt. PVDF (270,000 g/mol) under reduced humidity and high temperatures and demonstrate promising proton conductivity from blend membranes in both fully water-saturated and reduced humidity conditions.

2. Results and discussion

2.1. Membrane preparation and characterization

The graft ionomer consists of a fluorinated P[VDF-co-CTFE] backbone and sulfonated polystyrene (PS) side chains. A fluorinated macroinitiator

P[VDF-co-CTFE] ($M_n \sim 123,000$ g/mol) was first synthesized by emulsion polymerization and found to contain 2.6 ± 0.3 mol% CTFE. Atom transfer radical polymerization (ATRP) was used to grow PS graft chains, which were then post-sulfonated to different degrees of sulfonation (DS). A detailed synthetic description of the synthesis and characterization was reported previously and is included in the supporting information [38,54]. The average degree of polymerization (DP) of the PS graft chain was 79, which was sulfonated to a degree of 56 mol% to provide an ionomer possessing IEC ~ 2.91 mmol/g. Upon immersion in water, the membranes swelled 1060 wt% to a water content of 92 wt% (λ , 211). The ionomer was blended with two different m. wt. PVDF samples (~ 2000 and 270,000 g/mol) in a ratio of 70:30 wt%. The graft blend membranes are referred to as $G^{70\%}B_{2k}^{30\%}PVDF$ and $G^{70\%}B_{270k}^{30\%}PVDF$, respectively. The estimated volumetric fraction (vol%) of polystyrene sulfonic acid (PSSA) decreases from 50 vol% in the pure ionomer membranes to 38 vol% in the blend membranes.

2.2. Morphology

2.2.1. Degree of crystallinity

Wide-angle X-ray scattering (WAXS) spectra of the blend membranes are shown in Fig. 1. The X-ray spectra are characterized by a broad peak centered at $2\theta = 19^\circ$ and a sharper peak positioned at 20° corresponding to amorphous [56] and crystalline domains [57] PVDF. The crystalline peak for the graft ionomer is much less pronounced than for the graft blends. Three Gaussian curves were fit to each WAXS pattern and the degree of crystallinity extracted. An example of a WAXS spectrum showing the Gaussian peaks fitted to the data is shown in the Supporting information, Fig. S3, for determination of degree of crystallinity of samples. The pure graft ionomer membrane comprised 50 vol% PSSA, 30 vol% unsulfonated PS and 20 vol% fluorinated P[VDF-co-CTFE] matrix and possessed the lowest degree of crystallinity ($\sim 4.5 \pm 0.2\%$), which originates from the partially crystalline fluorinated backbone. The graft blends comprised 38 vol% PSSA, 22 vol% unsulfonated PS and 40 vol% fluorinated domains (backbone and introduced PVDF). The degree of crystallinity of the graft blend membranes was $15.0 \pm 0.2\%$ and $12.8 \pm 0.3\%$ for $G^{70\%}B_{2k}^{30\%}PVDF$ and $G^{70\%}B_{270k}^{30\%}PVDF$, respectively, noticeably higher than the pristine ionic membrane. Blending with low m. wt. PVDF (~ 2000 g/mol) provided a higher degree of crystallinity, consistent with its higher crystallinity [58]. Analysis using the Scherrer equation [59–61] indicates that the crystalline domains are similar in all samples, ~ 6 nm.

2.3. TEM

TEM micrographs (Fig. 2a) indicate that the pure ionomer possesses an ionic cluster morphology with ion-rich domains (dark regions) 3.7 ± 0.7 nm in size, randomly distributed throughout the brighter, fluorinated regions. $G^{70\%}B_{2k}^{30\%}PVDF$ possesses a similar phase-separated morphology (Fig. 2b) wherein ion-rich domains are also homogeneously distributed and have similar dimensions to the pure graft ionomer. Although the fluorinated regions are visibly sharper in $G^{70\%}B_{2k}^{30\%}PVDF$ there is no significant difference in the dimensions of the fluorinated domains. However, $G^{70\%}B_{270k}^{30\%}PVDF$ displays a distribution of morphologies including spherical clusters, similar to the pure ionomer, and regions where the fluorinated domains (bright) extend to form contiguous domains (see Fig. 2c). To illustrate this point, the distributions of ion-rich and fluorinated-rich domains for $G^{70\%}B_{270k}^{30\%}PVDF$ are highlighted in Fig. 3 (i, a and b) and illustrate fluorinated-rich (bright) and ionomer-rich (dark) phases, respectively. The fluorinated-rich phase is further illustrated in Fig. 3 (ii,a), and is presumed to consist of amorphous (ii, c) or crystalline PVDF homopolymer (ii,d). The

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