

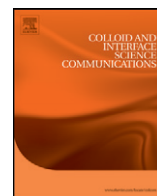
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## Rapid Communication

## Trivial and Non-Trivial Supramolecular Assemblies Based on Nafion

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## ABSTRACT

We demonstrate that Nafion, a perfluorosulfonic acid ionomer, undergoes synergistic mixing with non-ionic diblock copolymers in selective solvents. A range of experimental techniques (Quartz Crystal Microbalance, Dynamic Light Scattering, optical microscopy, TEM and SEM) was employed to gain insights on the evolution of ionomer–copolymer supramolecular assemblies. Depending on the copolymer architecture and the type of the suspension medium, spherical nanoparticles, micron-long tubular conformations or vesicular structures are formed. Those morphologies are dictated by localized interactions arising from Nafion's amphiphilicity. The effect has implications on the preparation of the technologically important ion conducting membranes.

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Molecular and supramolecular self-assemblies at various length scales underlie many physical phenomena, including crucial functions in biological systems such as the formation of phospholipid bilayers in living cells, the self-replication of DNA, the tissue architecture, and the folding and the misfolding of proteins [1,2]. Micellization is a well explored form of self-organization that is governed by the hydrophobic effect [3]. In the presence of a different type of amphiphilic molecule the thermodynamics and the mode of micellization are significantly altered to the extent that synergistic mixing might occur [4].

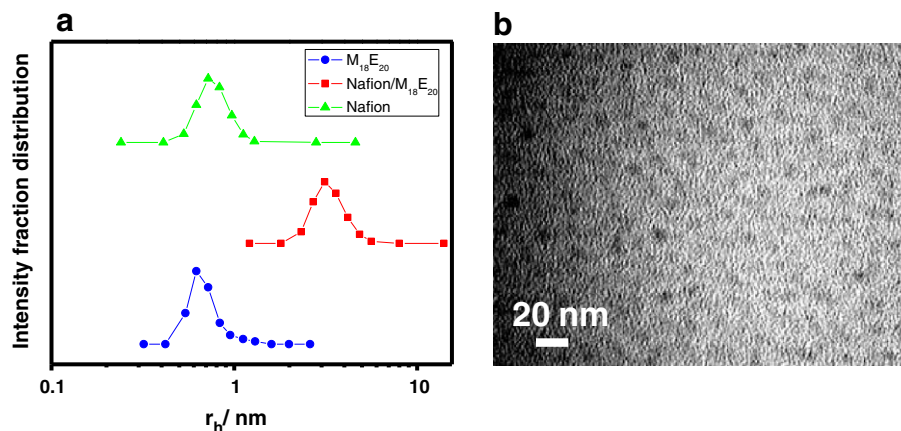
In this study we explore the interaction mechanism between the typical ionomer Nafion and two non-ionic block copolymers;  $M_{18}E_{20}$  (otherwise known as Brij 78) and  $E_{18}B_{10}$  that stand for  $C_{18}H_{37}(OCH_2CH_2)_{20}OH$  and  $(CH_2CH_2O)_{18}[OCH_2CH(C_2H_5)]_{10}OH$ , respectively. The two copolymers have comparable hydrophilic blocks, but the length and the composition of their hydrophobic blocks are very different so that  $E_{18}B_{10}$  exhibits a much stronger tendency for micellization. Both copolymers are easily dispersible in water, yielding well-defined spherical micelles comprised by an insoluble core surrounded by the solvent-swollen corona [5]. By virtue of their non-toxic and biocompatible nature they are widely applied in drug solubilization, cosmetics, printing inks and protective coatings.

Nafion is a highly ionically conductive polymer that is routinely used in fuel cell membranes, electrochemical convertors and biosensors. Its unmatched structural stability stems from the rigid Teflon-like backbone and its superior ion conducting properties arise from the presence of the pendant perfluoroether chains bearing terminal sulfonic acid groups. This macromolecular architecture results in microphase separation and the formation of hydrophilic nanochannels that expand reversibly to accommodate large quantities of water [6]. Despite the extensive investigations focusing on Nafion membranes, very limited information is available with respect to binding of colloidal Nafion with amphiphiles in selective solvents. We demonstrate here that Nafion not only forms stable complexes with non-ionic macromolecules, but it readily generates a rich variety of supramolecular architectures.

While ethanol is a good solvent for Nafion,  $M_{18}E_{20}$  precipitates out at low temperatures. Upon heating, 1 wt.%  $M_{18}E_{20}$  dispersion in ethanol undergoes a cloudy to clear transition at 15.6 °C, but this temperature systematically drops in the presence of Nafion approaching, for example, 8.2 °C for a 1 wt.% Nafion. This behavior points out to favorable ionomer–copolymer interactions within the given suspension medium. Dynamic Light Scattering (DLS) provides additional evidence for the formation of thermodynamically stable Nafion/ $M_{18}E_{20}$  complexes in ethanol with average  $r_h$  close to 3 nm, whereas only particles with  $r_h$  lower than 1 nm were detected in the corresponding single-solute systems (Fig. 1a). TEM imaging (Fig. 1b) of the dried Nafion–copolymer hybrids reveals the presence of spherical particles with dimensions in fair

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**Fig. 1.** (a) Intensity fraction distributions of apparent hydrodynamic radius ( $r_h$ ) ( $T = 25^\circ\text{C}$ ) for ethanol solutions of; 1 wt.% Nafion (top curve), 1 wt.%  $M_{18}E_{20}$  in the presence of 1 wt.% Nafion (middle curve) and 1 wt.%  $M_{18}E_{20}$  (bottom curve). For clarity the plots have been shifted in the ordinate. And (b) TEM image of the dried Nafion/ $M_{18}E_{20}$  complexes (1 to1 by weight) derived from ethanol dispersion.

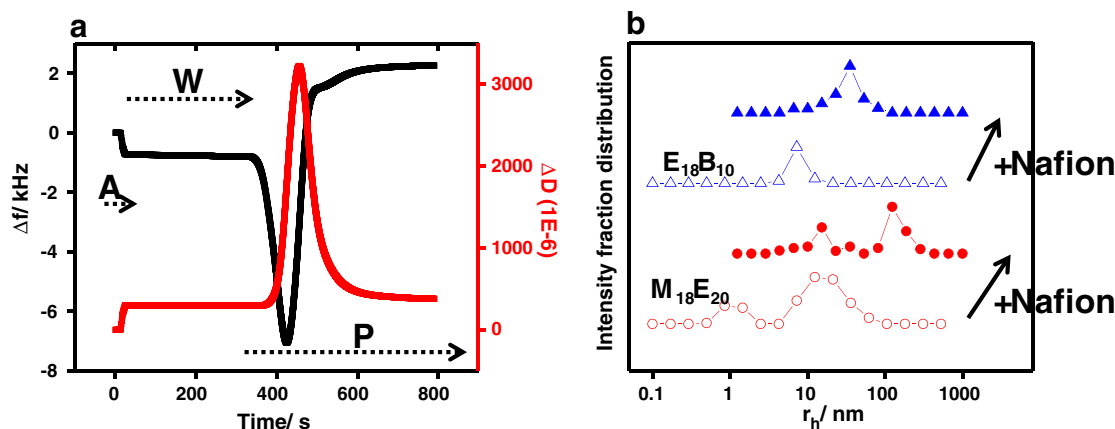
agreement to those found in solution. Overall, the two polymeric components appear to be compatible and are able to build together supramolecular assemblies that remain intact after the removal of ethanol.

The Quartz Crystal Microbalance (QCM) adsorption profile of  $M_{18}E_{20}$  to a Nafion-coated crystal resonator is shown in Fig. 2a and a very similar behavior was observed for  $E_{18}B_{10}$ . The sensogram includes an initial equilibrium step against air to determine the fundamental resonant frequency of the crystal (region marked A in Fig. 2a), followed by a second equilibrium step under flowing water to establish the baseline of the hydrated resonator (region marked W in Fig. 2a). The spontaneous hydration of the Nafion membrane is evident by the substantial and steep drop of the oscillating frequency ( $f$ ) and points to the ability of ionic domains of Nafion to accommodate large quantities of water. Notably, the stability of the W baseline rules out the dissolution of the Nafion under flowing water. Previous studies have shown that Nafion thin films cast on hydrophilic substrates (like the  $\text{SiO}_2$  crystal used here) show isotropic orientations of the polar channels in a manner that favors water sorption and swelling [7]. Moreover, exposure of a Nafion film to water causes major interface reorganization, as manifested by the large water contact angle hysteresis [8].

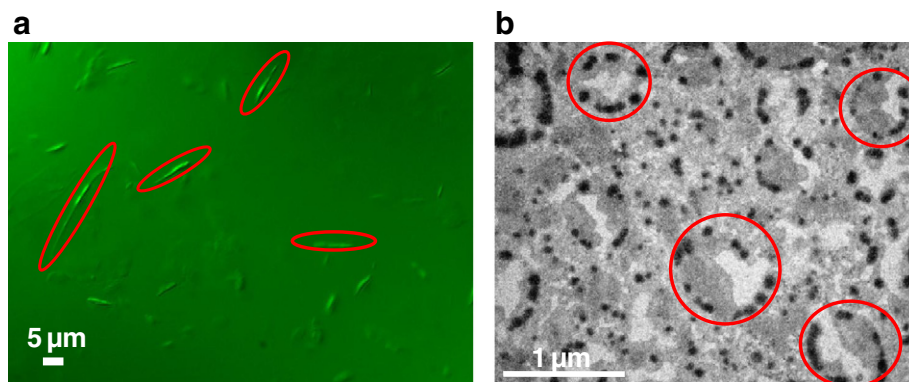
Upon injection of the copolymer solution (region marked P in Fig. 2a) the remarkable decrease in  $f$  suggests extensive adsorption of

the hydrated copolymer to the Nafion membrane. At the same time, the dissipation factor ( $D$ ) is increased dramatically given that the attached water molecules reduce the rigidity of the film. When the amount of the adsorbed copolymer exceeds a certain value,  $f$  undergoes a rapid and dramatic enhancement accompanied by a corresponding decrease in  $D$ . Those trends suggest the solubilization of the Nafion coating due to extensive Nafion-copolymer complexation. Typically, this behavior is understood in terms of the detergency efficiency of the flowing surfactant [9]. It has been supported that conventional surfactants such as sodium dodecyl sulfate and hexadecyltrimethylammonium bromide are massively adsorbed to the Nafion interface, but fail to solubilize Nafion [10].

The DLS curves plotted in Fig. 2b confirm the effective binding between Nafion and the block copolymers in water. We note that 1 wt.% colloidal particles of Nafion in water show a broad size distribution below 20 nm (data not shown here). The bimodal intensity distribution seen for the 1 wt.%  $M_{18}E_{20}$  aqueous solution implies a dynamic equilibrium between the unimers and the micelles. In the Nafion/ $M_{18}E_{20}$  mixed system the co-assembly of the macromolecular components leads to hybrid particles with  $r_h$  higher than 100 nm. Those aggregates rapidly grow and their size exceeds 500 nm within 24 h. Progressively the dispersion becomes cloudy and the presence of



**Fig. 2.** (a) QCM measurement using a Nafion-coated crystal resonator at  $25^\circ\text{C}$  (black points for the frequency and red points for the dissipation factor). The areas A, W and S indicate the equilibrium steps against air, flowing water and copolymer solution, respectively. And (b) Intensity fraction distributions of apparent hydrodynamic radius ( $r_h$ ) ( $T = 25^\circ\text{C}$ ) for aqueous solutions of; 1 wt.%  $M_{18}E_{20}$  in the absence (open circles) and in the presence (filled circles) of 1 wt.% Nafion and 1 wt.%  $E_{18}B_{10}$  in the absence (open triangles) and in the presence (filled triangles) of 1 wt.% Nafion. For clarity the plots have been shifted in the ordinate.



**Fig. 3.** (a) Optical microscope image of the Nafion/ $M_{18}E_{20}$  (1 to 1 by weight) aggregates in water after two week aging. And (b) TEM image of the anhydrous Nafion/ $M_{18}E_{20}$  complexes (1 to 1 by weight) derived from aqueous dispersion.

super-long worm-like structures can be directly observed in solution via an optical microscope (Fig. 3a). The large size of those aggregates suggests the self-assembly of an increasing number of ionomer and copolymer molecules, that ultimately lose their colloidal stability and precipitate. Nafion-rich extra-long tubes with high aspect ratio hold great promise for applications related to proton conduction.

TEM imaging (Fig. 3b) of the dried hybrids confirms the formation of stable complexes due to extensive Nafion- $M_{18}E_{20}$  binding. The structural details depicted in the SEM images for the anhydrous phase (Fig. 4), indicate that the elongated superstructures are probably formed by twisted ribbons. Non-conventional configurations with orientation ordering are expected to occur from the synergistic mixing of rigid rod-like amphiphile with flexible copolymers [11]. In this respect, we note that colloidal dispersion of Nafion possesses an intrinsic, highly rigid fibrillar structure [12]. Evidently, the flexible and relatively short copolymer chains follow the alignment of Nafion molecules, allowing the build-up of the supramolecular assemblies.

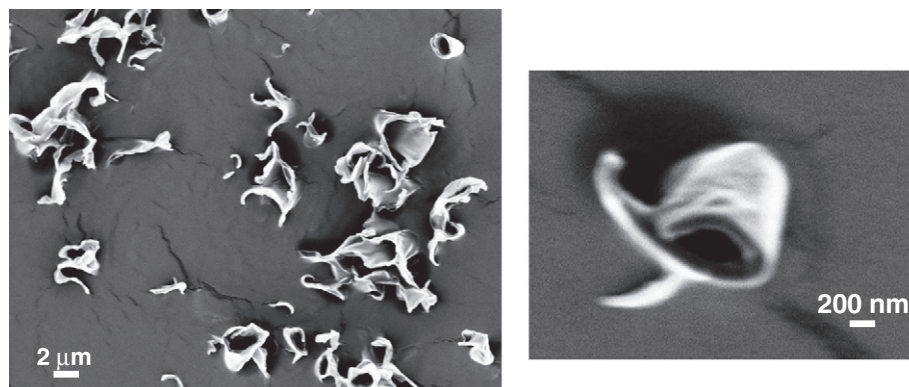
The apparent hydrodynamic radius of 1 wt.%  $E_{18}B_{10}$  is close to 7 nm (Fig. 2b), in agreement with previous studies [13]. The narrow size distribution of the micelles is characteristic for closed association where the absence of unimers is expected at concentrations far above the cmc ( $\text{cmc} = 0.06 \text{ g dm}^{-3}$  at  $30^\circ\text{C}$ ) [14]. In the mixed system, DLS plots reveals Nafion/ $E_{18}B_{10}$  hybrid particles with  $r_h$  higher than 50 nm, and their size increases with time, albeit in a slower rate compared to Nafion/ $M_{18}E_{20}$ . Optical microscopy provides further evidence that the initially formed relatively small particles (Fig. 5a) give rise to large structures with a wide size distribution after two week aging in water (Fig. 5b). TEM imaging of the anhydrous complexes indicates the evolution of vesicular conformations (Fig. 5c). In principle, vesicle formation reflects an interplay between the packing of the chains, the interfacial separation and curvature, while the presence of crystallizable

nanodomains can rigidify the membranes [15]. A large number of macromolecules have been shown to form vesicles under certain conditions, including the  $E_{18}B_{10}$  itself that generates vesicles upon complexation with anionic or cationic surfactants [13].

Previous studies have focused on polyelectrolyte complexation due to electrostatic attractions between the sulfonate groups of Nafion and oppositely charged molecules such as poly(oxyethylene) [16] and poly(oxypropylene) based diamines [17]. Systematic variation of the acid/base components results in stimuli responsive complexes with tuneable transfer properties [16].

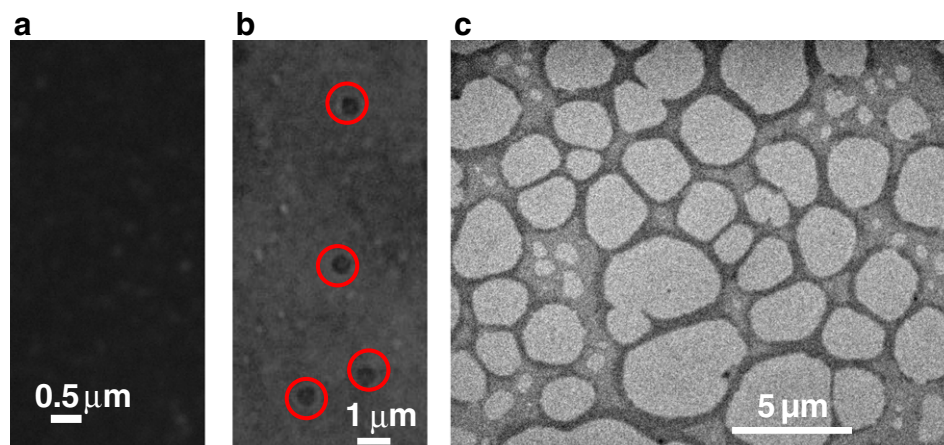
In the present study, the Nafion-copolymer complexation can be assigned to three distinct factors: hydrogen bonding, hydrophobic interactions and the structural matching between the polymeric partners. To that end, we note that spectroscopic data indicate the presence of H-bridging between the Nafion protons and the ether oxygen of the Pluronics (ethylene oxide/propylene oxide triblock copolymers), as a result of the electron donor capability of the ethylene oxide group [18]. QCM experiments using aqueous solutions of the poly(ethylene glycol) as the flowing phase have shown that the oligomer is strongly adsorbed to the Nafion substrate [10].

Incorporation of Nafion to aqueous solutions of  $E_{19}P_{69}E_{19}$  inhibits micellar growth as evident by the higher critical micelle temperatures and the reduced dye solubilization capability observed on the mixed systems [10]. Likewise, the Nafion- $E_{19}P_{69}E_{19}$  interaction phase diagram suggests that addition of small amounts of ionomer adversely impacts copolymer gelation as a consequence of the micellar suppression [10]. Following a Pluronic-templating strategy, highly ordered mesoporous Nafion membranes for fuel cells with improved water retention have been synthesized [18]. In another study, homogenous Nafion/Pluronic hybrid membranes were shown to exhibit improved proton conductivity under partially anhydrous conditions [19].



**Fig. 4.** SEM images of the anhydrous Nafion/ $M_{18}E_{20}$  complexes derived from aqueous dispersion.





**Fig. 5.** (a) Optical microscope images of the Nafion/E<sub>18</sub>B<sub>10</sub> aggregates in water after; (a) two day and (b) two week aging. And (c) TEM image of the anhydrous Nafion/E<sub>18</sub>B<sub>10</sub> complexes derived from aqueous dispersion.

In addition, we emphasize the architectural similarity between the side chains of Nafion ( $-\text{O}-\text{CF}_2-\text{CF}_2-$ ) and the hydrophilic ( $-\text{O}-\text{CH}_2-\text{CH}_2-$ ) block of the copolymers. Notably, the Nafion's backbone ( $-\text{CF}_2-\text{CF}_2-$ ) is structurally similar to the hydrophobic building block of M<sub>18</sub>E<sub>20</sub> ( $-\text{CH}_2-\text{CH}_2-$ ) but not to the E<sub>18</sub>B<sub>10</sub> ( $-\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)-$ ). Those compositional differences between the two copolymers might account for the very different morphologies detected in the mixed systems.

Capitalizing on Nafion-block copolymers synergistic mixing in selective solvents we were able to access supramolecular assemblies with trivial and non-trivial morphologies. Localized interactions (hydrogen bonding and the hydrophobic effect) coupled with the architectural ionomer/copolymer matching give rise to spherical, micron-long tubular and vesicular structures. The structural characteristics of those assemblies critically depend upon the type of the copolymer and the nature of the suspended medium.

## Appendix A. Supplementary data

Detailed description of the experimental section can be found in the on-line version of this article. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colcom.2014.06.005>.

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