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Interpolymer complexes of poly(sulfonic acid)s and poly(ethylene oxide): an unexpected association†

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The formation of novel interpolymer complexes (IPCs) between poly(sulfonic acid)s and poly(ethylene oxide) (PEO) is reported. The complexes were precipitated from polymer mixtures in aqueous solution and deposited on surfaces as layer-by-layer films. Based on evidence from infrared spectroscopy, the interpolymer association in poly(sulfonic acid)/PEO IPCs is ascribed to hydrogen bonding between the sulfonic acid and the ether in PEO. This interaction is not anticipated because sulfonic acids are fully dissociated in aqueous solutions due to their strong acidity. Theoretical calculations suggest that the unexpected association of PEO and poly(sulfonic acid)s results from the formation of very strong sulfonic-acid/ether hydrogen bonds, which increase the apparent pK_as of the poly(sulfonic acid)s and, therefore, decrease the net charge of these polymers. It is shown that while poly(styrene sulfonic acid) (PSSA) and Nafion form IPCs with PEO, poly(vinyl sulfonic acid) (PVSA) does not. This result is explained in terms of the hydrodrophobic nature of PSSA and Nafion, which stabilizes their IPCs, and the fact that hydrogen bonds in PSSA/PEO IPCs are predicted to be stronger than in PVSA/PEO IPCs.

Introduction

Hydrogen-bonded interpolymer complexes (IPCs)[1–3] have been widely studied due to their applications in drug formulation and delivery,[1,2,4] membranes,[5] emulsifiers,[6] solid-state electrolytes[7] and self-assembly.[8] The extensive literature on these complexes has explored several types of polymeric hydrogen acceptors, for example poly(ethylene oxide) (PEO),[4,7,9,10] poly(vinylpyrrolidone),[10] poly(*N*-isopropylacrylamide),[11] poly(acrylamide),[12] poly(4-vinylpyridine) (PVP)[13] and poly(*N*-vinylcaprolactam).[12] On the other hand, examples of hydrogen donors are mostly limited to different poly(carboxylic acid)s, with a few exceptions that include poly(phenol)s,[11,14,15] poly(alcohol)s,[13] and poly(aniline).[16]

The formation of IPCs between a poly(carboxylic acid) and a hydrogen poly(acceptor) requires an acidic pH for two reasons:[7,9,10] (i) the carboxylic group should be protonated to form the hydrogen bond, (ii) electrostatic repulsions among negative charges of deprotonated carboxylates destabilize the IPC. Therefore, IPCs of poly(carboxylic acid)s are stable only below a critical pH, which in most cases is smaller than the pK_a of a carboxylic acid.[7,9,10,17]

Sulfonic acids are very strong acids: the p$K_{a\,SO_3H}$ reported for CH_3SO_3H, $C_6H_5SO_3H$ and CF_3SO_3H is −1.5, −2.8 and −5.9, respectively.[18] Due to their acidity, sulfonic acids are fully dissociated even in the presence of small traces of water.[19,20] The formation of hydrogen-bonded IPCs between poly(sulfonic acid)s and hydrogen poly(acceptor)s from aqueous solutions is, therefore, unexpected. However, we show in this work that some poly(sulfonic acid)s can form IPCs with PEO both in solution and on surfaces. Infrared reflection absorption spectroscopy shows the emergence of new bands in the 3800–2500 cm^{-1} spectral region upon polymer complexation. These bands suggest important changes in the hydrogen-bond structure of the polymers following the formation of the interpolymer complex. The critical pHs of the novel IPCs of poly(sulfonic acid)s and PEO lie in the range of 0.5–1.0, which is considerably higher than the range of values reported for p$K_{a\,SO_3H}$. We performed DFT calculations on model molecules that suggest that the higher-than-expected stability of the IPCs results from a very strong hydrogen-bond interaction between protonated sulfonic acids and the ether in PEO. This interaction not only stabilizes the IPCs, but it also displaces the acid–base equilibrium of the sulfonic-acid/sulfonate groups toward the protonated species.

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† Electronic supplementary information (ESI) available: Assignments of FTIR bands for PSSA/PEO and Nafion/PEO, IRRAS spectrum of PAA/PEO LbL films, additional information for electronic structure calculations, coupled chemical equilibrium model, additional turbidity titration experiments and determination of film thickness with AFM. See DOI: 10.1039/c9sm01768b

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Experimental methods

Materials

Poly(acrylic acid) sodium salt (NaPA) (35% in water M_w 100 000); sodium poly(styrene sulfonate) (PSS) (M_w 70 000); PSS (M_w 1 000 000); poly(ethylene imine) (PEI) (M_w 750 000); Nafion 117 (acid form, ~5% in a mixture of lower aliphatic alcohols and water); poly(ethylene oxide) (PEO) (M_w 100 000) and sodium poly(vinyl sulfonate) (PVS) were obtained from Sigma-Aldrich. Other reagents were of analytical grade and were used without further purification. Polyelectrolyte solutions were prepared with 18 MΩ Milli-Q (Millipore) deionized water and their pH was adjusted using 1 M or 10 M HCl. The glass electrode used to measure the pH in all solutions was calibrated with a pH 4.01 buffer and 1.0 M HCl (pH 0.1[21]) solution. It should be noted that the solutions of poly(styrene sulfonic acid) (PSSA), poly(vinyl sulfonic acid) (PVSA) and poly(acrylic acid) (PAA) were prepared by acidification of solutions of the commercially available sodium salts (PSS, PVS and NaPA, respectively) using HCl. The final solutions contain, therefore, a small concentration of Na^+ cations (which is equal to the concentration of polyacid monomers in solution, 10 mM) in addition to the polymer and excess HCl. This small amount of Na^+ ions is not expected to produce an important effect on the formation of IPCs (see discussion of the effect of ionic strength below and Fig. S4 in the ESI†).

Methods

Measurement of turbidity in solution. Turbidity due to the formation of IPCs was measured by recording the extinction of mixtures of solutions of the poly(sulfonic acid)s and PEO at λ = 400 nm using a Shimadzu UV-1601 spectrophotometer in a 1 cm cuvette. The extinction of the sample is ascribed to light scattering because neither PSSA nor PEO absorbs light at 400 nm. For the experiments in Fig. 2a (extinction *vs.* molar fraction of PEO), we mixed the aliquots of PEO and PSSA solutions required to achieve the target PEO molar fraction and a final volume of 2.0 mL. Both solutions were 10 mM in monomer units and had pH = 0.1. We measured the extinction of the solution immediately after mixing (the extinction of the sample was found to slowly decrease with time). Measurements were performed in duplicate. For the experiments in Fig. 2b (extinction *vs.* pH), we mixed equal volumes of 10 mM solutions of PEO and the poly(sulfonic acid) adjusted to pH 2. We recorded the extinction of the solution at decreasing values of pH, which was adjusted by further addition of 1 M or 10 M HCl. We corrected the measured extinctions to take into account the dilution effect due to the addition of HCl.

Layer-by-layer self-assembly. Multilayer films were prepared on silicon(100) substrates coated with a 200 nm gold layer on a 20 nm titanium and 20 nm palladium adhesion layer by thermal evaporation with an Edwards Auto 306 vacuum coating system at a pressure $<1 \times 10^{-8}$ bar. We first deposited a single PEI adhesion layer on the substrate by immersion in a 10 mM PEI solution for 15 min. After rinsing with Milli-Q water, we deposited a layer of the poly(acid) by immersion for 15 min in a 10 mM poly(acid) solution, rinsed the sample with pH-adjusted Milli-Q water and dried it with nitrogen. The same procedure was then repeated to deposit the PEO layer using a 10 mM PEO solution for the immersion step. The alternate assembly of the poly(acid) and PEO was repeated until the deposition of the desired number of layers was achieved. The solutions of poly(acid)s, PEO and the rinsing water were all adjusted to the same pH using 1 M or 10 M HCl.

Ellipsometry. The ellipsometric thickness of LbL films was determined using a Sentech SE400 ellipsometer equipped with a 632.8 nm laser as a polarized-light source. All measurements were performed at an incidence angle of 70.00° and avoiding any variations of the substrate position in order to keep the system alignment. The ellipsometric parameters, ψ and Δ, were collected on the dried sample after each adsorption step. These parameters were analyzed with a model that considers a homogeneous film of varying thickness and constant refractive index (n = 1.5) and extinction coefficient (k = 0.03) on a semi-infinite gold substrate.[22]

Atomic force microscopy. AFM imaging was performed in air using an Agilent 5500 scanning probe microscope (Agilent Technologies) isolated from vibrations, air turbulence and acoustic noise. Images were acquired using an insulating triangular Si tip PointProbe® Plus Non-Contact/Soft Tapping Mode (radius < 10 nm, force constant 48 N m^{-1}, and resonance frequency 309.1 kHz) in non-contact mode. In a typical experiment, the surface topography of the LbL film assembled onto a Au-coated silicon substrate was imaged with AFM. The images were analyzed and edited using Gwyddion®.

IRRAS infrared spectroscopy. The infrared reflection absorption spectroscopy (IRRAS) experiments were performed on a Thermo Nicolet 8700 (Nicolet) spectrometer equipped with a custom-made external table-top optical mount and a MCT-A detector (Nicolet). The angle of incidence was set at 80°. The background and sample spectra were acquired on a clean gold-coated silicon substrate and on the LbL or drop-casted polymer films deposited on gold-coated silicon surfaces, respectively. Typically, 1000 scans were acquired and the resolution was set to 4 cm^{-1}.

Theoretical methods

Electronic structure calculations

We performed electronic structure calculations on small model molecules to estimate the relative stability of the hydrogen bonds in poly(sulfonic acid)/PEO and poly(carboxylic acid)/PEO IPCs. MP2 calculations (which offer a good trade-off between accuracy and computational cost[23]) using aug-cc-pVDZ and 6-311++G(d,p) basis sets were performed with the General Atomic and Molecular Electronic Structure Software (GAMESS) package.[24,25] For comparison, we also performed DFT calculations with a B3LYP exchange–correlation functional (expected to be less accurate than MP2[23]) and the aug-cc-pVDZ basis set. All geometries were fully optimized up to a gradient smaller than 10^{-5} Hartree $Bohr^{-1}$. The Hessians were calculated at the optimized geometries in order to guarantee that all their eigenvalues are positive, and, therefore, the optimized structures

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correspond to energy minima. Table S4 in the ESI† shows the hydrogen bonding energies for the three complexes under study, which were calculated as the difference between the energy of the complex and the energies of the isolated ether and acid molecules. The values reported in the main text correspond to the MP2/aug-cc-pVDZ calculations, corrected by the zero-point energies (ZPEs) determined with the same method (see Table S5, ESI†).

Results and discussion

Formation of complexes of PEO and poly(sulfonic acid)s in solution

We observed that a mixture of PEO and PSSA (see polymer structures in Fig. 1a) in solution at $\text{pH} < 0.5$ (adjusted with HCl) produces a turbid suspension that we ascribe to the formation of an IPC. In order to quantify this process, we determined the turbidity of mixtures of PEO and PSSA by measuring the extinction at 400 nm. Fig. 2a shows that a plot of the extinction as a function of the composition of the solution has a maximum at a molar fraction of PEO (on a monomer basis) of $x_{\text{PEO}} \sim 0.5$–0.6. This result indicates that the formation of the IPCs is maximized for a 1 : 1 stoichiometry of PEO monomers to PSSA monomers as was previously observed for PAA/PEO mixtures.[9]

Fig. 2b shows the effect of pH on the turbidity for different poly(sulfonic acid)/PEO mixtures. PSSA/PEO mixtures display a steep increase in light scattering below pH ∼ 0.5. This critical pH is rather insensitive to the molecular weight of PSSA. Nafion/PEO mixtures show $\text{pH}_{\text{crit}} \sim 1$ and PVSA/PEO mixtures do not evidence IPC precipitation even at $\text{pH} < 0.0$. Interestingly, the formation of poly(carboxylic acid)/PEO IPCs in solution has critical pHs in the range of 2.0–4.5[9,17,26] (see also Fig. S5 in the ESI†), which is lower than the typical $\text{p}K_\text{a}$ of a carboxylic acid, $\text{p}K_{\text{a COOH}} = \sim 4.8$.[21] On the other hand, the critical pHs for PSSA/PEO and Nafion/PEO IPCs (0.5 and 1.0, respectively) are much higher than the $\text{p}K_\text{a}$ range reported for sulfonic acids, $\text{p}K_{\text{a SO}_3\text{H}} = -1.5$ to -5.9.[18]

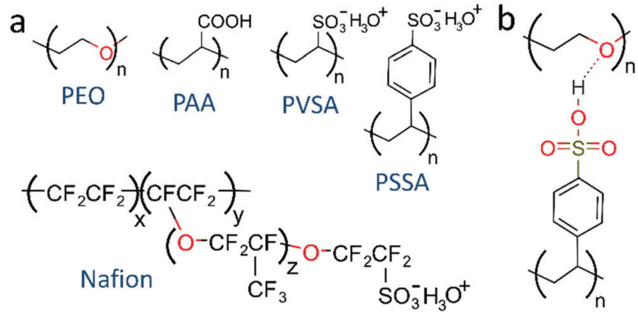

Fig. 1 (a) Structure of the polymers used in this work. PEO: poly(ethylene oxide), PAA: poly(acrylic acid), PVSA: poly(vinyl sulfonic acid), and PSSA: poly(styrene sulfonic acid). The PAA, PVSA and PSSA solutions contain sodium cations (same concentration as poly(acid) monomers) originating from the polyelectrolytes used to prepare the solutions (see Methods). (b) Proposed structure of the PSSA/PEO IPC.

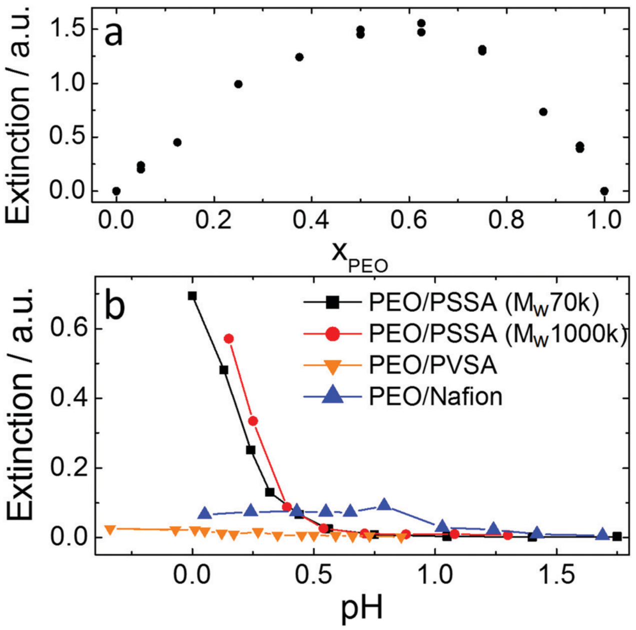

Fig. 2 (a) Turbidity of PEO/PSSA mixtures measured by the extinction at 400 nm as a function of the fraction of PEO monomers to total PEO + PSSA monomers in solution. The total monomer concentration was 10 mM and the pH was 0.1 (HCl 1.0 M). (b) Extinction of PEO/poly(sulfonic acid) mixtures, for $x_{\text{PEO}} = 0.5$, as a function of the solution pH. The concentration of PSSA, PVSA and PEO solutions was 10 mM, and the concentration of Nafion solution was 1 mg mL^{-1}.

Layer-by-layer deposition of complexes of PEO and poly(sulfonic acid)s

IPCs can be deposited as ultrathin polymer films by layer-by-layer (LbL) self-assembly.[27] We succeeded in depositing PSSA/PEO LbL films on a gold surface only when the polymer and rinsing solutions had $\text{pH} < 1.0$. Nafion/PEO deposition from solutions of pH = 0.1 was also successful (higher pH values were not explored). On the other hand, deposition of PVSA/PEO was unsuccessful even when the deposition solutions had pH = 0.1 (HCl 1.0 M), which agrees with the lack of precipitation of IPCs from PVSA/PEO mixtures in solution. Fig. 3a shows that the thickness of the PSSA/PEO LbL film (measured by ellipsometry) monotonically increases as a function of the number of deposited layers. The observed non-linear growth is similar to that previously observed for some poly(carboxylic acid)/PEO LbL films.[10,12]

Fig. 3b–d show AFM topographic images for PSSA/PEO, Nafion/PEO and PAA/PEO LbL films, respectively. The thicknesses of these films (measured by AFM by mechanically removing part of the films, see Fig. S3 in the ESI†) were (306 ± 15) nm, (1080 ± 80) nm and (535 ± 44) nm, respectively. Fig. 3e shows height profiles along selected lines for these three samples. Interestingly, the PSSA/PEO film was extremely flat (rms roughness of 1.3 nm), which may indicate the existence of an annealing process during preparation.[28] The rms roughness of Nafion/PEO was 159 nm. As a comparison, the roughness of a PAA/PEO LbL film (Fig. 3d) was 230 nm, which is consistent with previous reports.[7]

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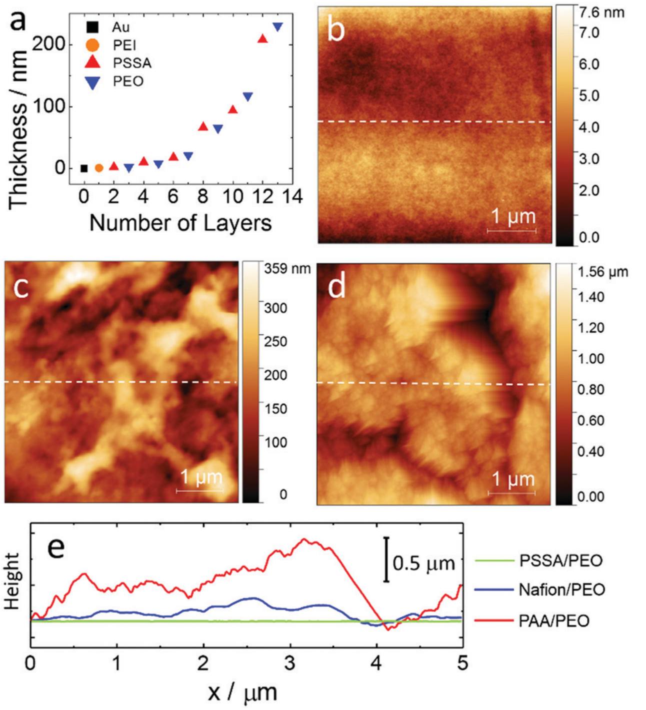

Fig. 3 (a) Ellipsometric thickness as a function of the number of adsorbed layers for the deposition of a PSSA/PEO film from pH 0.5 solutions. The substrate was a Au surface coated with a single PEI, poly(ethylene imine), adhesion layer. (b–d) Topographic AFM images of LbL films: (b) (PSSA/PEO)$_5$PSSA film deposited from pH 0.1 solutions, (c) (Nafion/PEO)$_{10}$ film deposited from pH 0.1 solutions and (d) (PAA/PEO)$_{10}$ film deposited from pH 2 solutions. (e) Height profiles along the white dashed lines in panels b–d.

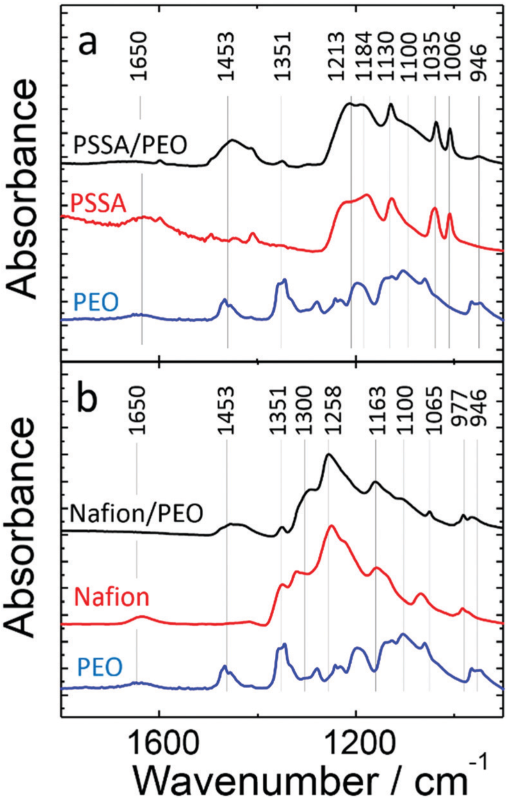

Fig. 4 Infrared (IRRAS) spectra in the 1800–900 cm^{-1} spectral region of LbL films (PSSA/PEO and Nafion/PEO, same films as in Fig. 3) and polymer films drop casted from pH 0.1 solutions (PSSA, PEO and Nafion).

Infrared spectroscopy shows the presence of hydrogen bonds within IPCs

We measured the IR spectra of the films prepared by LbL self-assembly and of nitrogen-dried samples of the polymers drop casted from pH 0.1 solutions using infrared reflection–absorption spectroscopy (IRRAS). The spectra of drop-casted PSSA and Nafion films in the 1800–900 cm^{-1} spectral region (see red lines in Fig. 4a and b, respectively) are consistent with that of the respective hydrated poly(acid)s,[29] which contain $SO_3^-H_3O^+$ groups, rather than the non-hydrated sulfonic-acid group, SO_3H. This result confirms that sulfonic acids are fully dissociated even in highly acidic water solutions. Black curves in Fig. 4a and b show the spectra of PSSA/PEO and Nafion/PEO films in the 1800–900 cm^{-1} spectral region, respectively. The spectrum of the PSSA/PEO film shows prominent PSSA bands at 1035 cm^{-1} (ascribed to the symmetric stretching of SO_3^- groups[19,30]), 1130 cm^{-1} (symmetric stretching of SO_2[19,20,30]), 1184 cm^{-1} and 1213 cm^{-1} (antisymmetric stretching of SO_3^- (ref. 19 and 30)), and PEO bands at 946 cm^{-1} (rocking of CH_2[31]), 1100 cm^{-1} (combination of symmetric and asymmetric COC stretching vibrations, and CC stretching and CH_2 rocking vibrations[32]), 1351 cm^{-1} (wagging of CH_2[31,33]) and 1453 cm^{-1} (scissor/deformation modes of CH_2[33]). The Nafion/PEO film exhibits the same bands attributed to PEO in the PSSA/PEO spectrum and the following IR bands ascribed to Nafion: 1163 cm^{-1} (CF_2 symmetric stretching[34]), 1258 cm^{-1} (CF_2 asymmetric stretching[34]) and 1300 cm^{-1} (CF_2 backbone vibrations). A comprehensive list of all IR bands in Fig. 4 and their tentative assignments are reported in Tables S1 and S2 in the ESI.†

The fact that the spectra of PSSA/PEO and Nafion/PEO films evidence bands both from PEO and the respective poly(sulfonic acid) confirms the presence of both components in the LbL films.

Fig. 5a and b show the 3800–2500 cm^{-1} spectral regions of PSSA/PEO and Nafion/PEO LbL films, respectively, and the corresponding drop-casted polymers. In both LbL films, we observed a marked decrease (with respect to the drop-casted polymers) in the absorbance of the O–H stretching band due to adsorbed water at ~3450 cm^{-1}.[35] This decrease is consistent with the disappearance of the band at 1650 cm^{-1} (ascribed to the water bending mode[19,30,34,36]) in the LbL films, see Fig. 4a and b. Therefore, the bands at 1650 and 3450 cm^{-1} indicate that the LbL films are less hydrated than the drop-casted polymer films.

The PSSA/PEO and Nafion/PEO LbL films also show two new strong absorption bands at ~3190 cm^{-1} and ~3060 cm^{-1}, which indicate important changes in the hydrogen-bond interactions of the polymers upon the formation of the IPC. In poly(carboxylic acid)/poly(ether) IPCs, the O–H stretching band of hydrogen-bonded COOH/ether complexes is observed at ~3100 cm^{-1}.[37–39] The SO_3H/ether hydrogen bond is expected to be stronger than the COOH/ether one (see below); thus, the O–H stretching in a SO_3H/ether complex should occur

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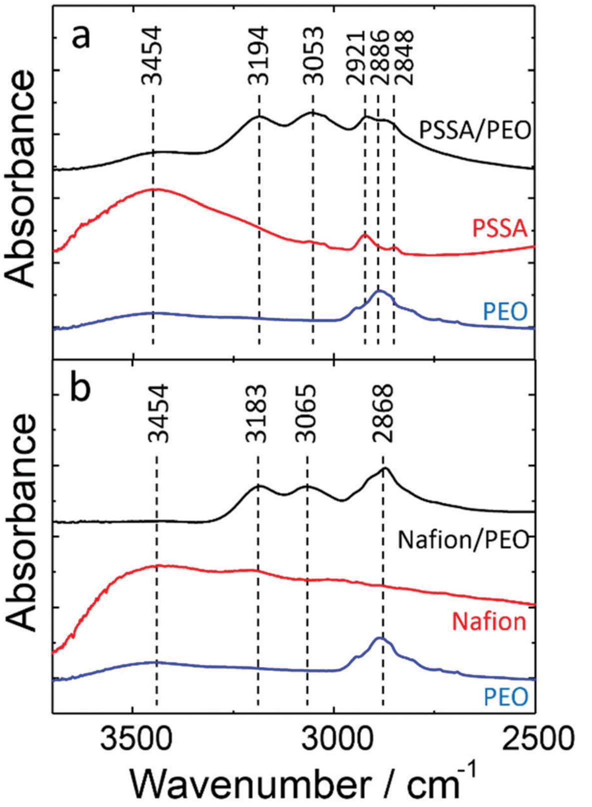

Fig. 5 Infrared (IRRAS) spectra in the 3800–2500 cm^{-1} spectral region of LbL films (PSSA/PEO and Nafion/PEO, same films as in Fig. 3) and polymer films drop casted from pH 0.1 solutions (PSSA, PEO and Nafion).

at $\nu < 3100\ cm^{-1}$.[40,41] Therefore, we tentatively assign the band at $\sim$3060 cm^{-1} in the spectra of PSSA/PEO and Nafion/PEO to the O–H stretching of the SO_3H/ether hydrogen-bonded pair. Note that pure Nafion completely lacks absorption bands at that wavenumber (Fig. 5b). The aromatic C–H stretching of PSSA appears in that region, but we believe that it cannot alone explain the band at 3053 cm^{-1} in the PSSA/PEO spectra due to its low intensity (see PSSA spectra as a red line in Fig. 5a). We do not have a clear assignment for the band at $\sim$3190 cm^{-1}, although a band at that wavenumber has been associated with hydrated H_3O^+ ions in the past.[36,42] Based on the spectroscopic evidence and the well-known structure of poly(carboxylic acid)/PEO IPCs,[1] we tentatively propose the structure in Fig. 1b for the poly(sulfonic acid)/PEO IPCs reported in this study. Some degree of proton transfer from the sulfonic acid to the ether can be expected;[43] note, however, that protonation of the ether groups in PEO in acidic aqueous solutions is not anticipated (the pK_a of protonated diethyl ether is reported to be −3.6[44]).

Comparative strength of hydrogen bonds in ether/sulfonic acid and ether/carboxylic acid complexes and its effect on the acid–base equilibrium

SO_3H groups are fully dissociated in aqueous solution due to their strong acidity, so it is intriguing how this group can exist in an IPC in the presence of water. A related question is why the critical pHs of PSSA/PEO and Nafion/PEO IPCs (0.5 and 1.0, respectively) are significantly higher than $\mathrm{p}K_{\mathrm{a\,SO_3H}}$, while the critical pHs of hydrogen-bonded IPCs of poly(carboxylic acid)s are smaller than the $\mathrm{p}K_{\mathrm{a\,COOH}}$.[7,9,10,17,26] We believe that the main factor that contributes to the stability of PSSA/PEO and Nafion/PEO IPCs is the strength of the SO_3H/ether hydrogen-bond interaction.

In order to compare the strengths of SO_3H/ether and COOH/ether hydrogen bonds, we performed electronic structure calculations at the MP2 level in small model molecules. We used dimethyl ether, $O(CH_3)_2$, as a small-molecule counterpart of PEO and acetic acid (CH_3COOH), methanesulfonic acid (CH_3SO_3H) and benzenesulfonic acid ($C_6H_6SO_3H$) as molecular models for PAA, PVSA and PSSA, respectively. Fig. 6 shows the converged structures for $CH_3COOH\cdots O(CH_3)_2$, $CH_3SO_3H\cdots O(CH_3)_2$ and $C_6H_6SO_3H\cdots O(CH_3)_2$ hydrogen-bonded complexes. The predicted formation energy for the hydrogen-bonded complex $CH_3COOH\cdots O(CH_3)_2$ is 38.5 kJ mol^{-1} ($15.5k_BT$ for $T = 298$ K). This complex is less stable than the complexes formed by dimethylether and the sulfonic acids: the formation energies for $CH_3SO_3H\cdots O(CH_3)_2$ and $C_6H_6SO_3H\cdots O(CH_3)_2$ are 54.9 kJ mol^{-1} ($22.2k_BT$) and 64.3 kJ mol^{-1} ($26.0k_BT$), respectively. The fact that $C_6H_6SO_3H$ forms a stronger hydrogen bond than CH_3SO_3H agrees with the observation that PSSA forms IPCs, but PVSA does not.

The strength of the hydrogen bond in IPCs is important not only because of its direct stabilizing effect, but also due to its indirect effect on the acid–base equilibrium of the poly(acid).[10] This effect originates in the coupling between the acid–base equilibrium of the sulfonic groups,

$$\mathrm{P{-}SO_3H} \overset{K_a}{\rightleftharpoons} \mathrm{P{-}SO_3^-} + \mathrm{H^+} \qquad (1)$$

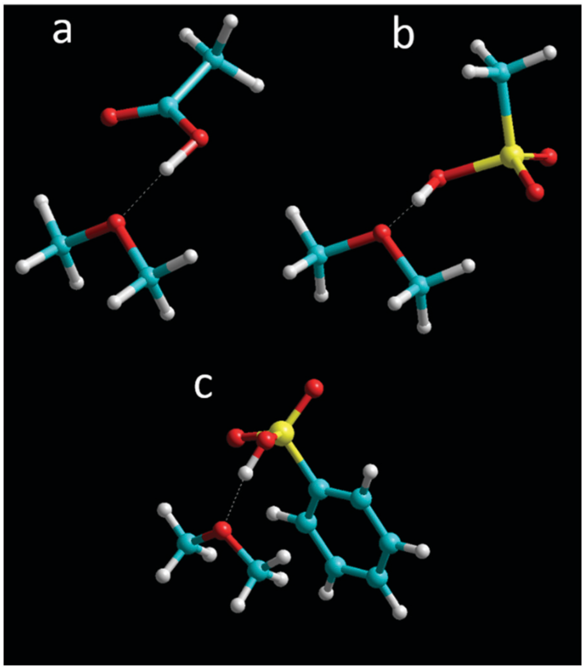

Fig. 6 Structures of: (a) $CH_3COOH\cdots O(CH_3)_2$, (b) $CH_3SO_3H\cdots O(CH_3)_2$ and (c) $C_6H_6SO_3H\cdots O(CH_3)_2$ optimized with MP2/aug-cc-pVDZ.

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and the hydrogen-bond formation equilibrium,

$$\mathrm{P{-}SO_3H + PEO \overset{K_f}{\rightleftharpoons} P{-}SO_3H\cdots PEO} \quad (2)$$

Increasing the strength of the hydrogen bond (*i.e.* increasing K_f) displaces eqn (2) toward the hydrogen-bonded complex and, therefore, displaces eqn (1) toward the protonated acid, which results in an increase in the apparent pK_a of the acid (the apparent pK_a is the pH where half of the groups are deprotonated). A simple model of coupled chemical equilibria presented in the ESI† indicates that a ten-fold increase in K_f produces an increase in the apparent pK_a of the polyacid of one unit (provided that the fraction of acid groups interacting with PEO *via* hydrogen bonds is larger than ~0.25). This effect operates on top of the well-known charge-regulation effect,[45,46] which also increases the apparent pK_a of the poly(acid)s in order to decrease electrostatic repulsions in the system. Assuming that the complexes $CH_3COOH\cdots O(CH_3)_2$ and $C_6H_6SO_3H\cdots O(CH_3)_2$ have similar entropies of formation, then the difference of $10.5k_BT$ in their energy of formation (determined from electronic structure calculations) indicates that the increase in pK_a due to hydrogen-bond formation for the sulfonic acid is 4.6 units larger than that for the carboxylic acid. This result supports the argument that the coupling of chemical equilibria in eqn (1) and (2) is responsible for the fact that IPCs of poly(carboxylic acid)s require $pH_{crit} < pK_{a\,COOH}$, while for poly(sulfonic acid)s, $pH_{crit} > pK_{a\,SO_3H}$.

In addition to the strength of the hydrogen bond between sulfonic acids and ethers, there are two factors that may contribute to the higher-than-expected stability of their IPCs. First, the hydrophobic properties of PSSA and Nafion may stabilize the complexes. This mechanism agrees with the fact that these two polymers are expected to be more hydrophobic than PVSA, which does not form IPCs. It also agrees with the literature reports of poly(carboxylic acid) IPCs that show that increasing the hydrophobicity of the poly(carboxylic acid)[7,9,17] or the hydrogen poly(acceptor)[46] results in an increase of the pH_{crit}. A second factor that contributes to the higher-than-expected stability of poly(sulfonic acid)/PEO IPCs is that these complexes are stable in solutions with pH < 1.0, which necessarily have high ionic strengths (>0.1 M). In IPCs of poly(carboxylic acids)/PEO, it has been shown that increasing the ionic strength leads to a higher pH_{crit} due to the screening effect of salt on electrostatic repulsions.[7,17] For PSSA/PEO, we observed that adding 500 mM NaCl to the polymer mixture increases the pH_{crit} (determined from solution turbidity) by approx. 0.1 pH units (see Fig. S4 in the ESI†).

We believe that the displacement of the apparent pK_a of sulfonic acids by the formation of the hydrogen bond may be relevant for other soft materials besides the IPC complexes. For example, poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) gels show a de-swelling transition at pH ~ 1 that has been ascribed to the protonation of the sulfonic groups in PAMPS and the formation of an intramolecular hydrogen bond with the carbonyl group of the amide.[47,48] The fact that the de-swelling transition occurs at $pH \gg pK_{a\,SO_3H}$ suggests that the coupling between acid–base and hydrogen-bonding equilibria may be a relevant mechanism for the collapse of PAMPS gels.

Conclusions

In summary, this work reports for the first time the formation of IPCs between poly(sulfonic acid)s and PEO. These complexes were precipitated from aqueous solutions and deposited on surfaces in a layer-by-layer assembly procedure. The experimental evidence supporting the formation of IPCs of poly(sulfonic acid)s and PEO is: (i) polymer precipitation is maximized for a 1 : 1 monomer stoichiometry (Fig. 2a) and (ii) the two polymers can be sequentially deposited as LbL films (Fig. 3), which require a complexation mechanism for assembly.[49] Furthermore, IRRAS experiments (Fig. 4 and 5) demonstrate the presence of both PEO and the poly(acid)s in the films.

The formation of IPCs with PEO was successful for PSSA and Nafion, but not for PVSA. We explain this result as the combination of two effects: (i) PSSA and Nafion are expected to be more hydrophobic than PVSA (hydrophobic interactions are known to stabilize IPCs) and (ii) hydrogen bonds in ether/aromatic-sulfonic-acid complexes (*i.e.* the bonds in PSSA/PEO) are predicted to be stronger than those in ether/aliphatic-sulfonic-acid complexes (bonds in PVSA/PEO).

The interpolymer bonding in PSSA/PEO and Nafion/PEO was tentatively proposed to result from hydrogen bonding between the non-dissociated sulfonic acid groups (SO_3H) and the ether in PEO because the spectra of poly(sulfonic acid)/PEO IPCs have an IR band at ~3060 cm^{-1} that is absent in the spectra of the pure polymers. The proposed interpolymer interaction is in principle unexpected because SO_3H species are known to be unstable in the presence of water due to their very strong acidic nature. We explained the unexpected formation of PSSA/PEO and Nafion/PEO IPCs in terms of the strength of the ether/sulfonic-acid hydrogen bond and the fact that its formation displaces the sulfonic-acid/sulfonate acid–base equilibrium toward the protonated SO_3H species. Nevertheless, further work is in progress to provide additional support to the proposed interpolymer interaction between PEO and the poly(sulfonic acid)s.

Complexes of poly(carboxylic acid)s and polymeric hydrogen acceptors have been exhaustively studied in the past in the form of blends and as thin layer-by-layer films. These complexes have found applications in medicine,[1,2,4] separation science,[5] and solid-state electrolytes for energy applications.[7] Due to the rich variety of potential uses for hydrogen-bonded IPCs, exploring the applications of the novel complexes of poly(sulfonic acid)s reported here emerges as an interesting future direction in soft-matter science.

Conflicts of interest

There are no conflicts to declare.

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