



Stimuli-responsive amphoteric ion exchange polymers bearing carboxylic and amine groups grafted to a cross-linkable silica network

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ABSTRACT

Stimuli-responsive hybrid organic-inorganic amphoteric ion exchange polymers were synthesized via a non-hydrolytic sol-gel process with carboxylic acid and amine groups in silica side chains. Structural characterization of samples with a ratio carboxylic acid/amine 1:2 (PSU-SiCA(1:2)) and 2:2 (PSU-SiCA(2:2)) showed a degree of functionalization of 0.5 in both cases. The ion exchange capacity, analysed by acid-base titration, elemental analysis and thermogravimetric analysis, was 1.8 meq/g for PSU-SiCA(1:2) and 1.2 meq/g for PSU-SiCA(2:2). pH-Dependent properties for acidic, basic and zwitterionic forms were studied including hydration isotherms, ionic conductivity and selective deposition on acidic and basic substrates. The water uptake and ionic conductivity of the acidic and basic forms were highest for PSU-SiCA(1:2), due to the higher IEC. The zwitterionic forms, which contain a minimum of mobile ions, showed the lowest water uptake and ionic conductivity. The acidic form deposited on basic Al_2O_3 substrates and the basic form on acidic SiO_2 , whereas the zwitterionic polymer was deposited on neither. The stimulus-dependent ionic conductivity and hydration and the selective deposition depending on interfacial charges are striking properties, which make these hybrid bio-friendly ionomers compelling for applications.

1. Introduction

Polyelectrolytes are a fascinating class of macromolecules with applications in different fields comprising biomedical and soft matter sciences [1,2]. Electrostatic interactions between charged groups and/or solvents lead to a considerably different behaviour compared to uncharged polymers given the dominant role played by Coulomb interactions [3].

Amphoteric ionomers are a particular class of polyelectrolytes containing both acidic and basic groups in their structure [4]. Typically, amphoteric polymers bear fixed positive and negative charges formed by weak basic and acidic moieties.

Among synthetic polyelectrolytes, amphoteric polymers are close to biological macromolecules. They may provide useful analogues of proteins and are important to model some properties and functions of biopolymers, such as protein folding and enzymatic activity. They are also relevant in separation technologies [5–8] and drug delivery [9–11], but also in electrochemical energy technologies, such as

polymer electrolyte membrane fuel cells [12,13] and redox flow batteries [14–16].

It was also reported that polymers with weak acid or basic groups can activate water splitting in bipolar membranes, considering that water splitting strongly depends on the interface characteristics [17–21]. Different polyelectrolytes were used for this aim: anion exchange membranes with secondary amine or tertiary ammonium groups or proton exchange polymers with weak acidic groups [19].

A peculiarity of amphoteric polymers is that the electrostatic interaction can be varied changing pH and ion concentrations modifying the kind and nature of the interfaces with surrounding phases. For example, their adsorption on charged surfaces was studied in depth in the last years [22,23].

Synthetic ampholytic ionomers are often prepared by polymerization of alkenyl moieties [24,25] or by blending acidic and basic polymers [26]. In the past, we synthesized amphoteric aromatic polymers starting by a chlorosulfonated synthon [27].

In this paper, we report the synthesis and the characterization of a

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Table 1

Degree of functionalization, molecular weight (MW) and ion exchange capacity (IEC) of hybrid amphoteric polymers.

Sample	Degree of functionalization	Calculated MW repeat unit g/mol	Calculated total IEC meq/g	Total IEC (titration) meq/g
PSU-SiCA(1:2)	0.5 (TGA)	612	1.64	1.80
PSU-SiCA(2:2)	0.5 (el. analysis)	686	1.45	1.20

novel class of amphoteric ionomers where the acidic and basic groups are part of an inorganic network forming ionic clusters grafted on a polymeric matrix.

These class II hybrids present covalent bonds among the organic and inorganic fragments [28]. Hybrid polymers represent a promising class of materials, which allow regulating a suitable ratio between hydrophilic and hydrophobic domains; the resulting ionomers intrinsically retain chemical and physical properties of both inorganic and organic components. Generally, expected improvements of ionomer properties by inorganic groups include an increased thermal and mechanical stability, the achievement of an interconnected porous network, or specific chemical properties.

We have prepared different class II hybrids, following several strategies [29–34]. The sol-gel process represents a versatile synthetic approach to tailor structures at a molecular level controlling the amount of different components with fine tuning of the inorganic clusters. The presence of functionalizable Si-OH groups in the hybrid ionomers synthesized in this work opens flexible and simple routes to tailor reticulation and mesoporosity, or to bond molecules modulating their chemical and biological properties.

All components of the hybrid ionomers synthesized in this work, polysulfone (PSU), amine and carboxylic acid groups and silanol moieties are biocompatible and can be employed in the biological field. The acid-base interaction in the amphoteric polymers is very important for the ion transport and we paid particular attention to the stimuli-sensitive properties as a function of pH. An understanding of the physico-chemical properties of such polyampholytes can be relevant for many applications.

2. Experimental

2.1. Materials

Polysulfone (MW = 55,500 g/mol, PSU) was obtained from Solvay. 3-(2-aminoethylamino) propyldimethoxymethylsilane (AEAPS), 3-cyanopropyltrichlorosilane (CNSi) and all other chemicals were reagent grade and were used as received from Aldrich.

2.2. Synthesis of hybrid carboxylated and aminated PSU (PSU-SiCA)

2.2.1. Aminated PSU (PSU-CH₂AEAPS)

The chloromethylation of PSU was reported elsewhere [35–37]. PSU-CH₂Cl (degree of chloromethylation = 0.7; 1.08 meq) was dissolved in 50 mL of anhydrous THF at RT under N₂. Anhydrous sodium acetate and 20 mL of a solution of AEAPS in THF (eq_{PSU-CH₂Cl}:eq_{AcONa}:eq_{AEAPS} = 1:1:1) were added and the solution heated at reflux under stirring for 48 h. After this time, a sample was taken and directly dried for NMR and FTIR analyses (Supplementary Materials).

¹H NMR (Bruker AVANCE III spectrometer, 400 MHz, DMSO-*d*₆) δ 0.0 (CH₃-Si, 1.6H), δ 0.4 (–CH₂-Si, 0.9H); δ 1.2 (N-H, 2H); δ 1.4 (–CH₂CH₂-Si, 1.4H); δ 1.6 (CH₃-C, 6H); δ 6.5–8.3 (aromatic region PSU, 15.5H).

2.2.2. Carboxylated and aminated PSU (PSU-CH₂AEAPS-CNSi)

Glacial AcOH was added to the solution containing PSU-CH₂AEAPS and the reaction was kept at reflux for other 4 h under N₂. The solution was cooled to RT and CNSi (eq_{PSU-CH₂Cl}:eq_{AcOH}:eq_{CNSi} = 1:3:1) was directly added. The reaction was kept at reflux and left for 48 h under

stirring. A second batch was taken, dried, and analysed by FTIR (Supplementary Materials).

The muddy dark orange solution was precipitated in ethanol and washed several times with water. PSU-CH₂AEAPS-CNSi was hydrolysed with 0.1 M NaOH during 4 h at reflux. After this time, the powder was washed with water and dried at 60 °C for 3 days.

The reaction was repeated using PSU-CH₂Cl DCM = 0.5 and two moles of CNSi to balance the acid and base groups (eq_{PSU-CH₂Cl}:eq_{AcONa}:eq_{AEAPS}:eq_{AcOH}:eq_{CNSi} = 1:1:1:3:2). The two organic-inorganic amphoteric ionomers are in the following called PSU-SiCA(1:2) and PSU-SiCA(2:2), indicating the ratio between acid and basic groups.

2.3. Titration

The acid form of the two amphoteric ionomers was obtained by immersion under stirring in 2 M HCl during 24 h. Powders were filtered, repeatedly washed with water and then dried in the oven at 60 °C under vacuum and one week over P₂O₅. A weighed quantity of the dry samples was immersed in water and potentiometrically titrated with 0.022 M NaOH under nitrogen. The pH values were measured after equilibration of the mixture; this process can take up to 16 h. The titration gives the acid and base constants and the isoelectric point, as discussed in the results section.

The total ion exchange capacity (IEC) was determined by back titration. The basic form was obtained by immersion under stirring in NaOH 2 M during 24 h. After washing with water, the samples were placed in 5 mL of 0.1 M HCl for 24 h, and then the solution was back titrated with NaOH 0.02 M. The results are reported in Table 1.

2.4. Hydration measurements

The water uptake at 25 °C was determined by exposition of powders to saturated water vapour during 1 week. The sample mass (*m*_{wet}) was determined by rapid weighing in a closed vessel. The dry sample mass was measured after drying over P₂O₅ for 24 h (*m*_{dry}).

The water uptake WU was calculated from the equation:

$$WU/\% = 100 * \frac{(m_{wet} - m_{dry})}{m_{dry}} \quad (1)$$

The hydration isotherm was determined at 25 °C between 5 and 95% relative humidity (RH) using a thermogravimetric analyzer TA Q5000. The sample mass was about 7 mg; the sample was dried in situ 3 h at 80 °C before the measurements. RH was then changed by 10% increments during 3 h. The hysteresis was studied by measurements in the opposite direction, between 95 and 5% RH.

2.5. Conductivity measurements

The ionic conductivity was determined by electrochemical impedance spectroscopy EIS (Parstat 4000) in fully humidified conditions using a Swagelok cell with cylindrical stainless steel electrodes of 6 mm diameter. The ac voltage amplitude was 20 mV and the frequency range was between 10 Hz and 6 MHz.

Sample powders were compressed to dense pellets under 1 MPa pressure at room temperature. The samples were cut in the middle part of the pellets in order to avoid thickness changes at the periphery. The through-plane resistance of the samples *R*_{mat} was determined from a non-linear least-square fitting of Nyquist plots using the Zfit program.

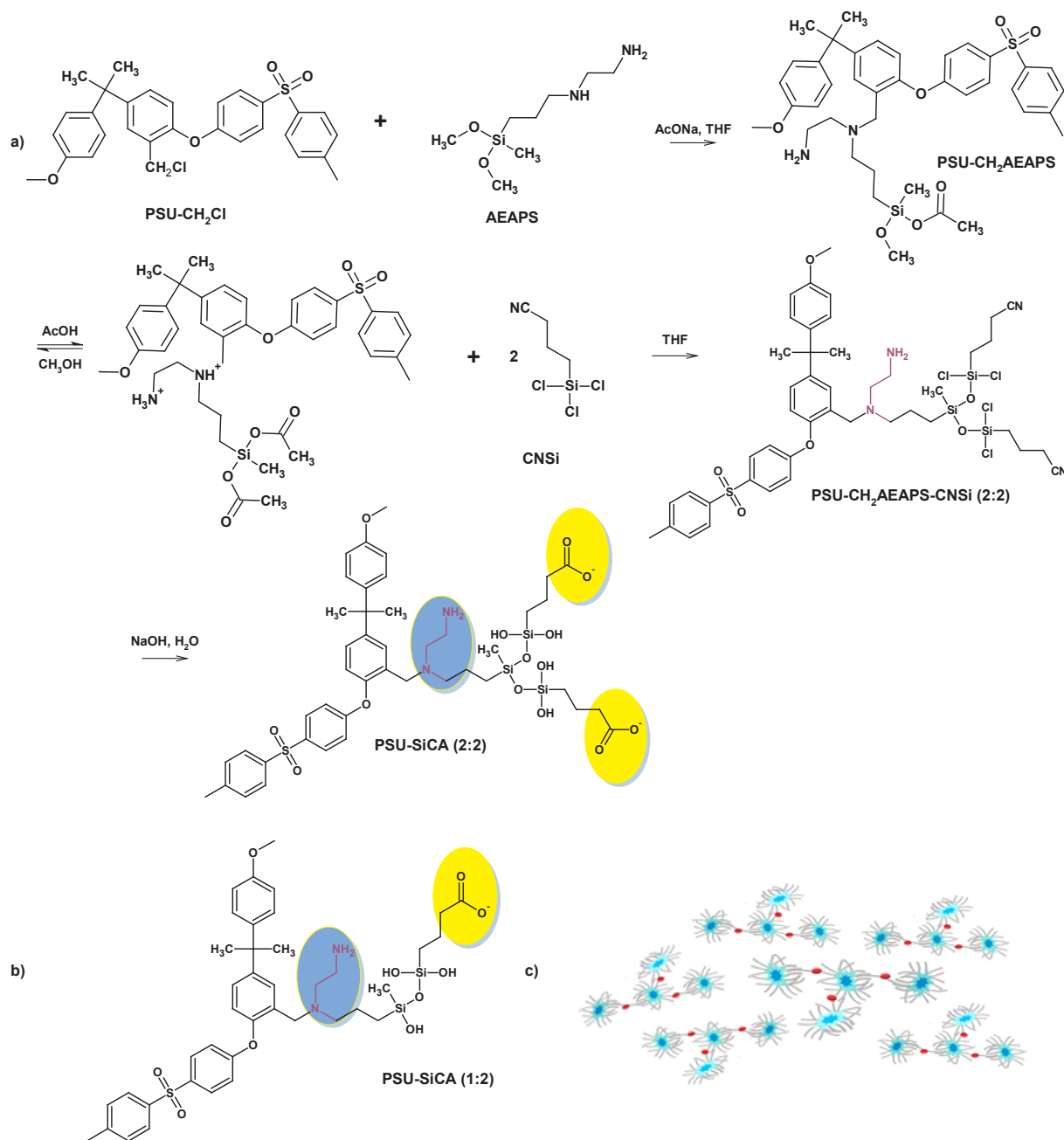


Fig. 1. (a) Reaction pathways for the synthesis of PSU-SiCA(2:2); (b) repeat unit of PSU-SiCA(1:2); (c) schematic of cross-linking between silica networks.

The ion conductivity σ was calculated using the following equation:

$$\sigma = \frac{d}{R_{\text{mat}} \cdot A} \quad (2)$$

where d is the sample thickness and $A = 0.28 \text{ cm}^2$ the electrode area.

2.6. Scanning electron microscopy (SEM)

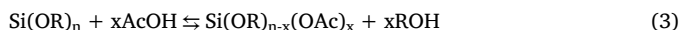
The scanning electron micrographs were recorded on a Hitachi S-2460N microscope, using an acceleration voltage of 20 kV and an emission current of 90 μA .

3. Results and discussion

3.1. Synthetic strategy and structural characterization

The reaction routes are reported in Fig. 1a. The synthesis was made in anhydrous THF, to avoid the sol-gel self-condensation of AEAPS. The first step of the amphoteric-PSU synthesis is the formation of the aminated derivative. The reaction is a nucleophilic bimolecular substitution (S_N2) where the N atom acts as nucleophile. Two different reaction centres are present in AEAPS: primary and secondary amine. The nucleophilic character of nitrogen depends on many factors, among them basicity, partial electrical charge, solvation, steric phenomena and polarizability. The parameter defined by Swain and Scott for nucleophilic attack upon saturated carbon atoms shows that the amine reactivity lies in the order tertiary > secondary > primary justifying the formation of the tertiary amine (Fig. 1) [38,39].

Acetic acid or acetate, added during the first step, can have an additional effect: some AcO groups can weakly bond to Si alkoxide via a fivefold coordination with silicon [40] forming an alcohol (Eq. (3)). This equilibrium is shifted towards the left and only few acetate groups are consumed, although heating the solution under reflux moves the equilibrium towards the right, because the reaction is endothermic [41].



The second step is a non-hydrolytic reaction between silicon alkoxides and silicon chlorides that is generally carried out around 100 °C or more and involves the elimination of alkyl halide [42]. In the case of metal acetates, the reaction is supposed to occur also at a lower temperature (Eq. (4)). In our case, to favour the reaction in THF and to protect amino groups, acetic acid was added before the reaction with CNSi to form Si-OAc.



The reaction is a nucleophilic substitution involving $\text{SiO}^{\delta-}\text{-Ac}^{\delta+}$ polarization leading to an acyl cation (CH_3CO^+). The last step of the synthesis of PSU-SiCA is the hydrolysis in basic condition of the cyano groups (Fig. 1a). This step leads also to the formation of some cross-links between the repeat units creating a silica network (Fig. 1c).

Two different molar ratios AEAPS:CNSi were used 1:1 and 1:2. In the first case, there is an excess of amine groups, in the second case, the quantity $\text{NH}/\text{CO}_2\text{H}$ is equal.

Based on the structures of PSU-SiCA(1:2) and PSU-SiCA(2:2) in Fig. 1, the compositional characteristics of the samples are reported in Table 1. The degrees of functionalization were assessed from elemental analysis and thermogravimetry (TGA, see below for discussion). The molecular weights were calculated according to Fig. 1 for a degree of functionalization of 0.5; however, the partial cross-linking of the silica network could not be taken into account in this simple calculation. The calculated total IEC is compared with data from acid-base titration.

The elemental analysis (mass%) performed on PSU-SiCA(2:2) gave results in good agreement with a degree of functionalization 0.5, corresponding to a formula $\text{C}_{34.5}\text{H}_{39.5}\text{NO}_9\text{SSi}_{1.5}$: C calculated 60.3, measured 62.1, N calculated 2.0, measured 2.2, Si calculated 6.1 measured 6.5.

The total ion exchange capacity of the two samples (Table 1) was obtained by back-titration with NaOH of the acidic form (made according to Eq. (5)). The obtained IEC are consistent with a degree of functionalization 0.5.



The insolubility of the two samples in organic solvents, also in acid form, containing 6.1% PSU-SiCA(2:2) and 4.5% PSU-SiCA(1:2) of Si respectively [43], can be attributed to the presence of cross-links between the silanol groups. The low IEC value measured by titration for the sample PSU-SiCA(2:2) (Table 1) can be related to this formation of a cross-linked polymeric network, evidently facilitated by the presence of another silanol group.

3.2. Thermogravimetric analysis

The thermogravimetric curve of PSU-SiCA(1:2) (Fig. 2) shows two main mass loss peaks. The first one starting above 330 °C can be attributed to the loss of amine groups and the complete side chain. This is in accordance with the literature, reporting that aminated PSU loses the amine group around 330 °C [46]. The calculated mass loss corresponding to the loss of the branched side chain (MW = 338 g/mol, degree of functionalization = 0.5) is around 27%, in good agreement with the experiment. A remarkable effect of the inorganic component is the stabilization of the carboxylic groups, because in carboxylated PSU the degradation of CO_2H starts already around 290 °C [45]. The

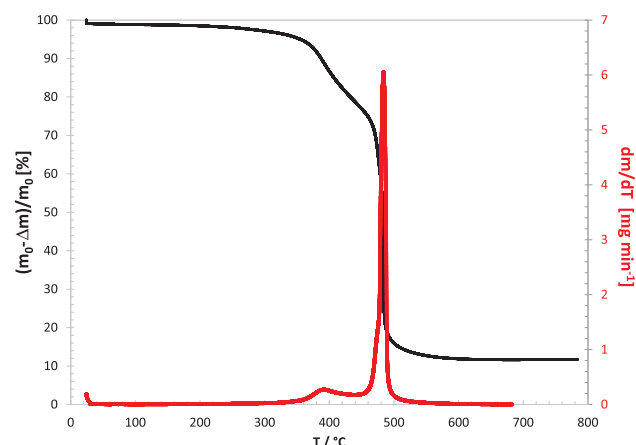


Fig. 2. Thermogravimetric curve of the decomposition of PSU-SiCA(1:2).

decomposition of the PSU main chain (MW = 442 g/mol) above 450 °C is in line with previous experiments. Finally, the residue above this temperature, which is formed by SiO_2 , should give a residual mass percentage of 10% ($\text{M}(\text{SiO}_2)/\text{M}(\text{repeat unit})$) in excellent agreement with the observation. Altogether, the thermogravimetric analysis confirms the composition of the hybrid sample [44].

3.3. Determination of the acid and base constants by titration

Ampholytic ionomers show many properties, such as ionic conductivity and swelling behaviour, which are strongly pH-dependent, because they are sensitive to the ionization of functional groups in the membrane matrix. In the isoelectric region, the membrane deswells in length and mass and the electric resistance increases. The ion selectivity is determined by the sign of fixed charges. If the charge is positive, the membrane is anion-selective; if the charge is negative, it is cation-selective. Therefore, the membrane is anion selective in acidic conditions, whereas it is cation selective in basic conditions. If both acidic and basic functional groups are ionized, the average distance between opposite charges is important.

Fig. 3 shows schematically the different forms of amphoteric polymers as a function of pH.

At low pH, the amino moieties have a positive charge while the carboxylic groups are essentially undissociated. Increasing the pH, the carboxylic acids start to dissociate due to their higher acid constants with respect to ammonium moieties (typically 10^{-5} vs 10^{-9}). When all carboxylic groups have lost their protons, the ammonium groups dissociate with further pH increase.

The following equation relates the isoelectric point (pI) to the acid constants when the number of acid (carboxylic) and basic (amine) groups is equal [3]:

$$\text{pI} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} \quad (6)$$

Here pK_{a1} is the acid constant of the carboxylic groups, whereas pK_{a2} is the acid constant of the ammonium groups.

From the potentiometric titration curve for PSU-SiCA(2:2) (Supplementary Materials) a pI = 5.7 can be estimated from the inflection point, which corresponds to the neutralization of the two carboxylic groups. The acid constant of the second carboxylic group can be calculated from the pH at half neutralization. From the titration curve, one can read $\text{pK}_{a1} = \text{pH} = 4.4$, which is realistic for a carboxylic acid. Using Eq. (6), one gets for the acid constant of the first ammonium group: $\text{pK}_{a2} = 7.0$, which corresponds to a basic constant $\text{pK}_{b2} = 7.0$ for the secondary amine group (conjugated base). This pK_{a2} value can be confronted with the value of the curve at half neutralization of the first ammonium group giving $\text{pK}_{a2} = 7.2$ in good agreement with the

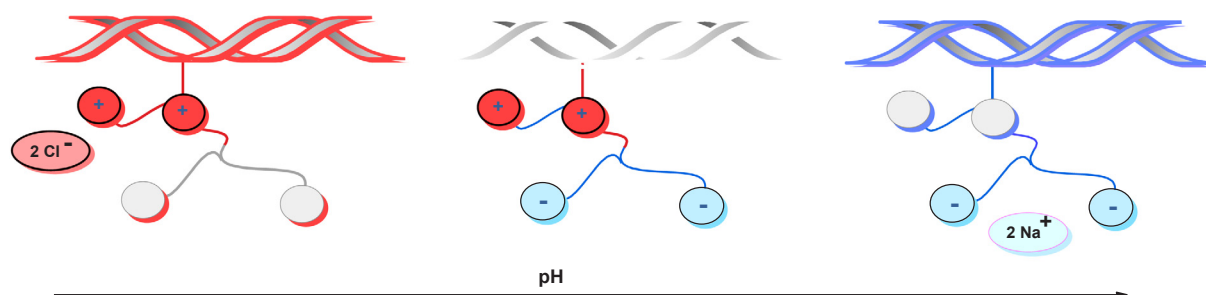


Fig. 3. Ion conduction in amphoteric ionomers as a function of pH (adjusted by HCl and NaOH). The zwitterionic form is observed at an intermediate pH.

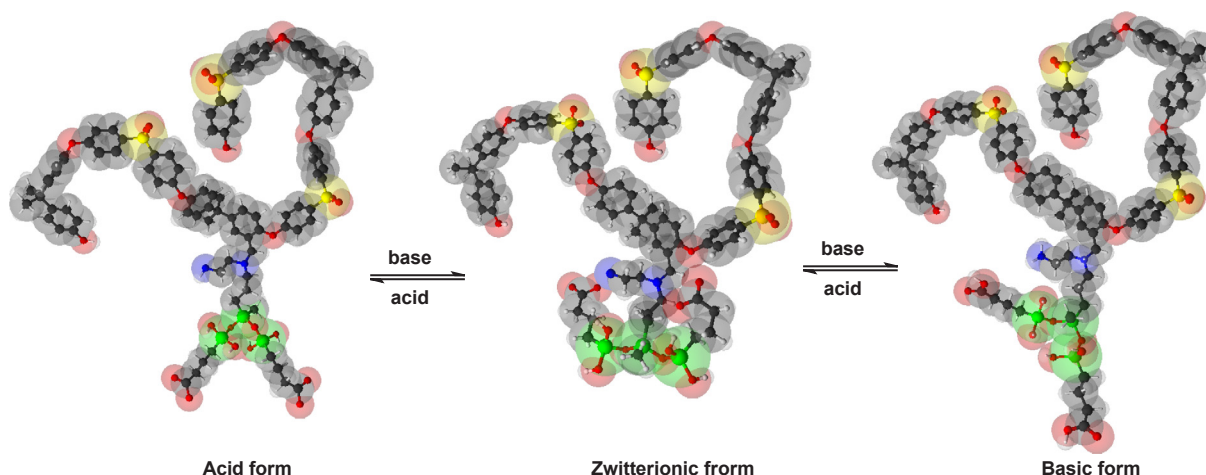


Fig. 4. Schematic representation of the swelling-deswelling behaviour of PSU-SiCA(2:2) as a function of pH. Color code: Si: green, O: red, N: blue, S: yellow, C: grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

above value. Finally, the pH value at half neutralization gives the acid constant of the second ammonium group: $pK_{a3} = 7.7$ corresponding to a basic constant $pK_{b3} = 6.3$ of the conjugated primary amine.

3.4. Water uptake

Fig. 4 shows the swelling-deswelling behaviour of ampholytic ionomers in different pH conditions. Polyampholyte chains assume a globular conformation and reduced solubility at $pH = pI$, which has been attributed to an intramolecular charge screening effect [3,47]. A minimum swelling value is observed at the isoelectric point. The swelling increases when the concentration of the grafted anions and cations is unbalanced.

The water uptake measured at 25 °C for the two compounds in acidic, basic and zwitterionic forms (Fig. 5) shows the lowest values for the zwitterionic form in agreement with the expectation. The generally low water uptake is probably related to the low dissociation of carboxylic acids, so that only few hydrophilic ionized groups are present in the macromolecule.

The acid forms, containing mobile chloride anions and grafted ammonium and carboxylic acid groups, present a higher water uptake than the basic forms, containing mobile sodium cations and grafted carboxylate and amine groups. The higher hydration observed for PSU-SiCA(1:2) is consistent with its higher IEC (Table 1).

The hydration isotherms of the two acidic forms are shown in Fig. 6. The water uptake is relatively low, below 10%, consistent with the data reported in Fig. 5.

The higher water uptake observed for PSU-SiCA(1:2) is in agreement with the data in saturated water vapour. The aspect of the hydration isotherms is in line with previous experiments on proton-conducting ionomers [48] and corresponds to type 2 BET adsorption [49]. Whereas the initial part of the isotherms (up to about 70 %RH) can be

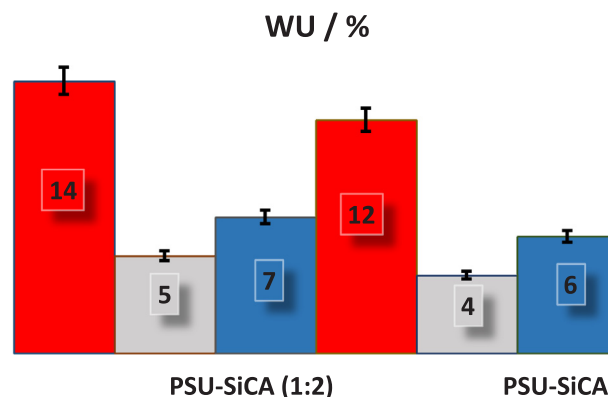


Fig. 5. Water uptake in saturated humidity (RH = 100%) at 25 °C of PSU-SiCA(1:2) and PSU-SiCA(2:2) in acidic (red), basic (blue) and zwitterionic (grey) forms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

attributed to formation of a monolayer of water molecules, the final part corresponds to multilayers of water in pores of the ionomers. The hysteresis of the desorption part is classical for a material with a large quantity of mesopores, due to the presence of the inorganic network. This opportunity can be further exploited for the synthesis of materials with controlled mesoporosity.

3.5. Ionic conductivity

At low and high pH (Fig. 4), polyampholytes can be considered as ionomers with mobile anions or cations, respectively. The behaviour at the pI depends on the distance between the grafted charged groups. If

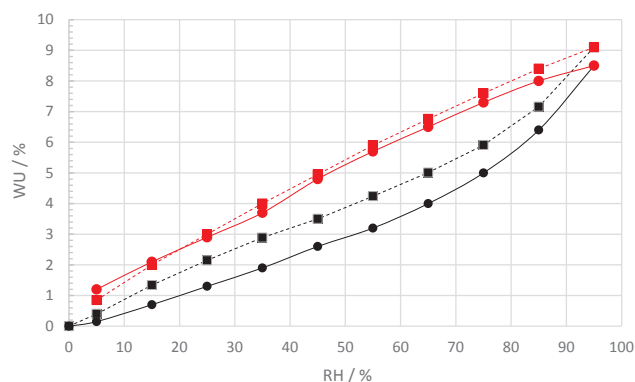


Fig. 6. Hydration isotherms of PSU-SiCA(1:2) (squares and dotted lines) and PSU-SiCA(2:2) (dots and full lines). The red curves correspond to water desorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the opposite ions are near enough (typically below the Bjerrum radius, i.e. around 0.7 nm) they neutralize each other (or form ion pairs) by Coulombic attraction and the ionic conductivity should present a minimum value. If the distance between charges is high, anions and cations might both contribute to the conductivity [50,51].

The ionic conductivity of PSU-SiCA(1:2) and PSU-SiCA(2:2) samples in acidic, basic and zwitterionic form at temperatures between 298 and 353 K is reported in Table 2.

The ionic conductivity of PSU-SiCA(1:2) is consistently higher than that of PSU-SiCA(2:2), due to a higher IEC of the former. In agreement with the expectation, the zwitterionic forms show the minimum of ionic conductivity; the highest ionic conductivity is observed for the acidic forms, where chloride ions conduct together with few protons from partially dissociated carboxylic acid groups. The variations of ionic conductivity are accompanied by differences in activation energies. The activation energy calculated from the data for the two acidic forms is (0.25 ± 0.02) eV, consistent with a predominant migration of chloride ions. Similar values were reported for other anion-conducting ionomers [52,53]. In the basic forms, sodium ions are the predominant ionic carriers and the activation energy calculated for the two basic forms is higher (0.37 ± 0.05) eV. Slightly lower values were reported for sodium ion transport in aqueous solution or in Nafion [53,54]. Finally, the activation energy is highest for the zwitterionic form: (0.44 ± 0.03) eV.

More than the absolute values of ionic conductivity, which remain modest, the versatility and the pH-stimulus dependence are of real interest.

To study the stability of these ampholytic polymers in alkaline solution, the PSU-SiCA(2:2) powder was treated with 2 M NaOH at 80 °C

Table 2

Ionic conductivity of PSU-SiCA(1:2) and PSU-SiCA(2:2) at temperatures between 298 and 353 K in acidic, basic and zwitterionic forms.

Form	T/K	PSU-SiCA(1:2) S/cm	PSU-SiCA(2:2) S/cm
Acidic	298	$2.6 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$
	313	$4.4 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$
	333	–	$3.7 \cdot 10^{-5}$
	353	–	$7.1 \cdot 10^{-5}$
Basic	298	$7.8 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$
	313	$1.6 \cdot 10^{-5}$	$4.4 \cdot 10^{-6}$
	333	$3.3 \cdot 10^{-5}$	–
	353	$5.4 \cdot 10^{-5}$	–
Zwitterionic	298	$5.5 \cdot 10^{-7}$	$4.5 \cdot 10^{-7}$
	313	$1.5 \cdot 10^{-6}$	$4.7 \cdot 10^{-7}$
	333	$5.5 \cdot 10^{-6}$	$6.1 \cdot 10^{-7}$
	353	$8.8 \cdot 10^{-6}$	$6.5 \cdot 10^{-6}$

during one week. After this harsh treatment, the FTIR spectrum did not show appreciable differences. The IEC of treated samples was also measured by titration and the value found (1.2 meq/g) did not change. Both analysis techniques show an excellent alkaline stability, possibly related to the presence of silica networks in the samples.

3.6. Deposition on acidic and basic substrates: interface potential dependence

We tested the opportunity of preferred deposition on oxide substrates with basic or acidic properties; the interfacial variability is one of the most attractive features of amphoteric polymers. Fig. 7 shows SEM images of PSU-SiCA(2:2) deposited on SiO₂ and Al₂O₃ substrates. The appearance is typical of hybrid materials with an inorganic (silica) part. The basic compound is deposited only on the acidic substrate (SiO₂), while the acidic form is observed only on the basic substrate (Al₂O₃). This observation is consistent with the excess charge of the ionomers. The basic form presents an excess of grafted negative charges, due to the carboxylate anions, which are attracted by the surface protons of the acidic silica substrate. The acidic form contains an excess of positive charges due to the anchored ammonium cations, which are interacting with the hydroxide surface groups of the basic alumina substrate. The zwitterionic form does not deposit on both substrates, because it does not present excess charges and attractive and repulsive interactions are balanced (Fig. 7a). These experiments show impressively how the interface potential modifies the adsorption and the phase deposition of ampholytic polymers, which allows a controlled synthesis of complex material/material architectures.

4. Conclusions

We have synthesized hybrid organic-inorganic amphoteric ionomers by non-hydrolytic sol-gel chemistry. They include a silica-based inorganic side chain with grafted functional groups, which allows developing materials with controlled microporosity and pH-sensitivity. Thermogravimetric and elemental analysis confirmed the presence of the inorganic component and helped to assign the degree of functionalization. The isoelectric point and the various acid and base constants were determined by acid-base titration. The deposition on substrates with basic and acidic behaviour shows the influence of the interfacial potential on adsorption and phase deposition allowing the controlled design of complex architectures. The pH-dependent variations of various properties, such as hydration and ionic conductivity of acidic, basic and zwitterionic forms, gives the opportunity to tune and optimize these properties by an external stimulus.

5. Funding sources

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6. Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2019.01.003>.

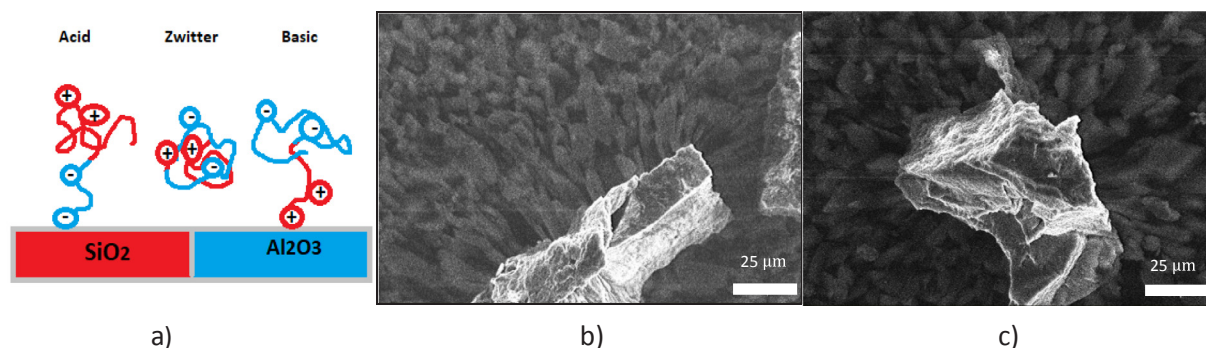


Fig. 7. (a) Schematic interface interaction; SEM micrographs of PSU-SiCA(2:2) deposited on (b) SiO₂ (basic form) and (c) Al₂O₃ (acid form).

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