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Two-step synthesis of polystyrene sulfonate based copolymers bearing pendant primary amines

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Highlights:

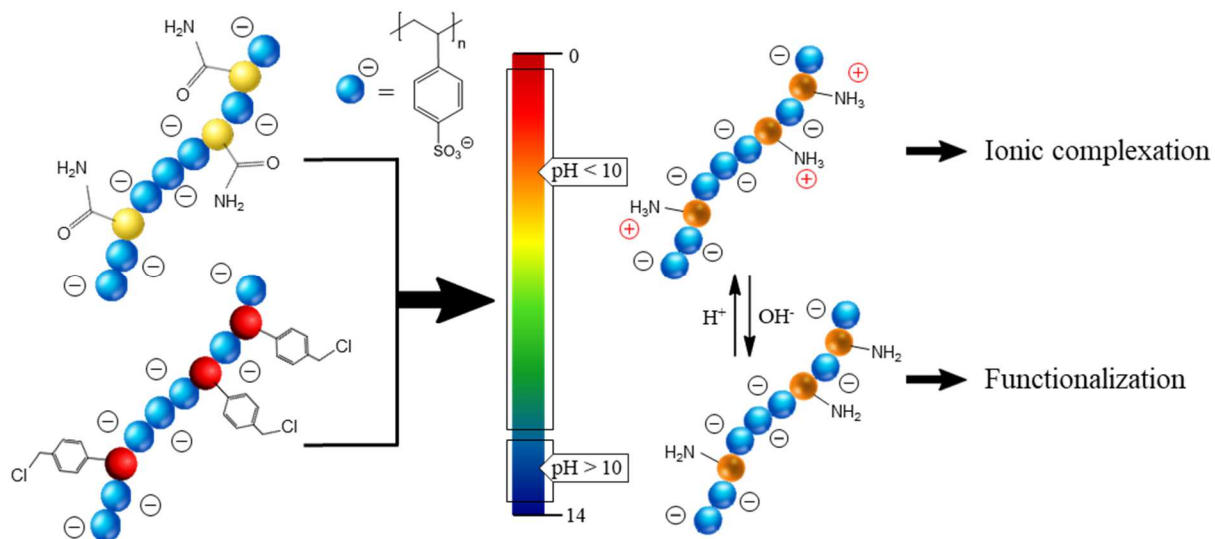
- Synthesis of P(SS-*co*-AAM) and P(SS-*co*-CMS) copolymers by free radical polymerization
- Post-polymerization modification of P(SS-*co*-AAM) into P(SS-*co*-VA) by Hofmann reaction, and P(SS-*co*-CMS) into P(SS-*co*-BA) by N-alkylation
- Evidences of the polyampholyte and reactive nature of the amino PSS copolymers

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Keywords: polyelectrolyte, free radical polymerization, random copolymers with pendant primary amines, styrene sulfonate, acrylamide, chloromethylstyrene,

For Table of Contents use only



Two-steps synthesis of polystyrene sulfonate based copolymers bearing pendant primary amines

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ABSTRACT

Polyelectrolytes are macromolecular building blocks which find numerous applications in the design of colloids, interfaces, gels and membranes. Herein, new polyelectrolytes copolymers with primary amines have been synthesized through the free radical polymerization of sodium p-styrene sulfonate (SS) and acrylamide (AAm) or chloromethylstyrene (CMS) followed by a post-polymerization modification. The first strategy relies on the use of the Hofmann reaction to convert polystyrene sulfonate-polyacrylamide (P(SS-*co*-AAm)) copolymers into polystyrene sulfonate-polyvinylamine (P(SS-*co*-VA)) copolymers. The second route includes the N-alkylation of polystyrene sulfonate-polychloromethylstyrene (P(SS-*co*-CMS)) copolymers with 1,8-diamino-3,6-dioxaoctane (DADO). It was observed that the chemical modification of P(SS-*co*-AAm) copolymers through the Hofmann reaction lead to some side reactions. In addition, P(SS-*co*-CMS) copolymers of several composition were prepared in anhydrous DMSO to prevent the early hydrolysis of the CMS units, and were then further quantitatively post-modified at RT with an excess of DADO. The resulting copolymers were soluble in both water and DMSO, and preliminary experiments on their properties evidenced both the reactivity of their amino group toward reductive amination (either performed with propanal or onto an oxidized nanocellulose), and their polyampholyte behavior at pH below the amine pKa.

1. INTRODUCTION

Polyelectrolytes represent a broad family of macromolecules whose ionized backbone provide them specific physico-chemical properties in solution. They are thus a unique tool to build a large number of structured assemblies either as colloids, at solid interfaces or in the bulk. It includes microgels [1] and surfaces [2, 3] with stimuli responsive swelling, coacervates and layer by layer assemblies driven by electrostatic complexation, [4] gels with peculiar mechanical properties [5] either from a brittle ionically crosslinked network, or from a tough polyampholyte network, and membrane and gels with specific ionic transport and exchange properties. [6] [7]

Among the large library of polyelectrolytes which can be extracted from natural resources or synthesized, [8] polystyrene sulfonate (PSS) is certainly the most commonly used anionic polyelectrolyte thanks to its strong electrolyte behavior and the easiness of its synthesis either by post sulfonation of polystyrene [9] or by radical polymerization. [10] The latter approaches also offer the possibility to prepare block or statistical copolymers to tailor the PSS physico-chemical properties in solution or in the bulk. The most usual example are amphiphilic copolymers of SS with styrene units, which are known as ionomers, and whose properties vary with the chain microstructure. [11] Fluorinated backbones with SS ionic graft copolymers can also be synthesized by ATRP from a poly(vinylidenedifluoride-*co*-chlorotrifluoroethylene) macroinitiator, while controlling the graft length and sulfonation degree in order to tune the phase separation behavior of the resulting amphiphilic copolymer. [12] Synthesis of N-isopropylacrylamide (NIPA) copolymers with sodium styrene sulfonate has also been reported through a free radical polymerization in water at 70°C, and it was demonstrated that their inter- and intra-molecular associations were temperature dependent. [13] As last examples, in order to improve the colloidal stability of poly(methacrylic acid), Charleux *et al.* [14] studied the effect of the presence of a small amount of styrene sulfonate

units in poly(methacrylic acid-*co*-sodium 4-styrene sulfonate) copolymers over a broad pH range, while Caruso *et al.* [15] prepared pH responsive films of poly(acrylic acid-*block*-styrene sulfonate) copolymers.

Surprisingly, PSS-based copolymers bearing primary amino groups have not been reported so far, although the introduction of such moiety would allow numerous possibilities of post-modification, [16] and would provide a polyampholyte character at a pH below the pKa of the corresponding amine. [17] This is most probably related to the radical scavenging abilities of primary amines, which induce unwanted transfer reactions during direct copolymerization. Consequently, the synthesis of polyvinylamine (PVA) and its copolymers is achieved in a two-step procedure, [16, 18-22] from polyacrylamide (PAAm) and subsequent Hofmann reaction, [23] from poly N-vinylacetamide (NVA) or N-vinyl formamide (NVF) followed by an hydrolysis reaction, or from poly N-vinylphthalimide (NVP) after a subsequent hydrazinolysis. Such two-step procedures have not been reported for PSS copolymers. Alternatively, a popular styrenic comonomer to introduce functionality is chloromethylstyrene (CMS), which is commonly N-alkylated with a tertiary amine to obtain a cationic group. Indeed, the copolymerization of styrene sulfonate with CMS and subsequent N-alkylation allowed for the preparation of polyampholytes despite the presence of both unhydrolyzed and hydrolyzed vinylbenzylchloride units. [24] Alternatively, Hillmyer employed a protected monomer to synthesize triblock copolymers consisting of poly(*n*-propylstyrene sulfonic ester), poly(4-chlorostyrene), and poly(vinylbenzylchloride) followed by their chemical functionalization through exposure to gaseous trimethylamine. [25]

Herein, we report two strategies to easily synthesize such PSS copolymers bearing primary amines groups by free radical polymerization of commercial monomers followed by their chemical modification. P(SS-*co*-AAm) copolymers have been synthesized and the post-

modification of AAm units into VA units was accomplished through the Hofmann reaction, while the second strategy was based on the N-alkylation of P(SS-*co*-CMS) copolymers.

2. EXPERIMENTAL

2.1. Materials

The monomers and other reagents were used without further purification. Acrylamide was purchased from TCI Chemicals, sodium styrene sulfonate (SS, $\geq 90\%$), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethyl acetate, α , α' -azobisisobutyronitrile (AIBN, 98%), as well as chloromethyl styrene (CMS) and 1,8-diamino-3,6-dioxaoctane (DADO, 98%) were purchased from Merck (Sigma-Aldrich). Sodium metabisulfite (SBS), sodium hypochlorite (NaOCl, 10-15wt.%) were obtained from Acros Organics. Anhydrous magnesium sulfate (MgSO₄), acetone, dimethyl sulfoxide (DMSO) were purchased from Carlo Erba. Dialysis membranes (Spectra/Por RC) were purchased from Fischer Scientific. Microfibrillated nanocellulose aqueous suspensions prepared by the mechanical homogenization of a never dried bisulfite pulp from birch, was purchased from the CTP. Sodium periodate (NaIO₄, purity $\geq 99.8\%$), hydroxylamine hydrochloride (NH₂OH.HCl, purity $\geq 99\%$), sodium cyanoborohydride (NaBH₃CN, purity $\geq 96\%$), and propanal were purchased from Sigma-Aldrich. Deionized water was used for experiments and samples preparation.

2.2. Copolymer synthesis & post-modification

*2.2.1. Synthesis of P(SS-*co*-AAm) copolymers.*

In a typical experiment, sodium styrene sulfonate (SS, 5.00 g, 24.2 mmol) was first solubilized in 162 ml of distilled water at a concentration of 0.15 mol.L⁻¹. Then, acrylamide (AAm, 0.515 g, 0.045 mol.L⁻¹, 7.24 mmol, 23 mol.%), potassium persulfate (KPS, 1.00 mol.%) and sodium metabisulfite (SBS, 0.7 mol.%) were added to the solution and the mixture was deoxygenated at room temperature for 1 h under argon. The copolymerization

was then carried out at 50°C for 6 hours. Finally, the obtained copolymer was purified by dialysis against distilled water (membrane cut-off 12-14 kDa). The dialysate was replaced twice daily with fresh distilled water until the conductivity reaches that of distilled water ($\sigma_{\text{distilled water}} = 2 \mu\text{S}\cdot\text{cm}^{-1}$). The resulting P(SS-co-AAm) solution was finally freeze-dried. In some cases, the P(SS-co-AAm) copolymer has been purified by precipitation in acetone before filtration on a glass filter. Finally, the copolymer was dried overnight under vacuum at 80°C and we obtained a mass yield of about 50% for all the experiments

2.2.2. Synthesis of P(SS-co-VA) copolymers from the chemical modification of P(SS-co-AAm) copolymers.

The post-modification of P(SS-co-VA) copolymers was conducted through a Hofmann reaction according to the experimental procedure previously reported by El Achari *et al.* [23]. The concentration of the NaOCl solution was evaluated by iodometric titration prior to reaction. The molar ratio $\alpha = n_{\text{NaOCl}}/n_{\text{AAm}}$ was varied between 1 and 2.5 depending on the experiment. In a typical experiment, the NaOCl solution ($\alpha=2$, 1.6 mol.L⁻¹, 5.04 ml) and the NaOH solution (1.0 mol.L⁻¹, 4.03 ml, $\beta = n_{\text{NaOH}}/n_{\text{AAm}}=1$) were mixed in 50 ml deionized water in a flask before being cooled at 0-5°C. In a separated flask, the P(SS-co-AAm) copolymer ($F_A=0.15$, 5.0 g) was solubilized in deionized water at a concentration of 100 mg.ml⁻¹ and the solution was also cooled to 0-5°C. Then, the NaOCl/NaOH solution was slowly added to the polymer solution and the mixture was stirred for 90 minutes at 0-5°C. After 90 minutes, a second solution of 10 M NaOH (10.5 ml, $n_{\text{NaOH}}/n_{\text{AAm}}=26$) was cooled to 0-5°C and added to the cold mixture. After 17 hours under stirring, the pH was adjusted to 2 by adding a few mL of concentrated 2 M HCl solution. The resulting P(SS-co-VA) copolymer was purified by dialysis against distilled water (membrane cut-off 12-14 kDa) and the dialysate was replaced twice daily with fresh distilled water until the conductivity was close to that of distilled water

(2 $\mu\text{S}\cdot\text{cm}^{-1}$). Finally, the P(SS-*co*-VA) copolymer was recovered in a powder form after freeze-drying.

2.2.3. Synthesis of P(SS-*co*-CMS) copolymers.

In a flask, SS (5.0 g, 24.2 mmol) was dissolved in 65 ml of DMSO and CMS (1.234 g, 25 mol.%, 8.08 mmol) and AIBN (2.0 mol.%) were added to the solution. The final monomer concentration was 0.5 mol.L⁻¹. The corresponding mixture was dried under anhydrous MgSO₄ (10% w/w) before use to avoid any hydrolysis of the CMS units. After filtration, the solution was degassed with argon for 1 h and heated to 70°C for 2 to 24 hours. The copolymer was first purified by precipitation in a cold mixture of acetone/methanol (75/25, v/v) or ethyl acetate/methanol (80/20, v/v). Next, the collected copolymer was solubilized in DMSO and finally stored at 5°C in the presence of MgSO₄.

2.2.4. Synthesis of P(SS-*co*-VBA) copolymers from the chemical modification of P(SS-*co*-AAM) copolymers.

The amine (40 eq NH₂/Cl, 8.143 g, 55 mmol) was solubilized in 107 ml of DMSO at room temperature before the dropwise addition of the P(SS-*co*-CMS) copolymer solution (31.91 g, F_{Cl}=0.18, C=0.094 g.g⁻¹, 3.0 g [P(SS-*co*-CMS) dry basis]). The final copolymer concentration was 20 mg.mL⁻¹. The resulting copolymer was isolated by precipitation in acetone and then collected and solubilized in water or DMSO before being stored at 5°C.

2.2.5. Reductive amination between PSS amino copolymers and propanal or oxidized cellulose (OxCell)

2.2.5.1. Reductive amination of PSS-based copolymers with oxidized cellulose (OxCell)

The copolymer bearing pendant amino groups (1 eq $\text{NH}_2/\text{C}=\text{O}$, 0.453 g of P(SS-co-DADO)-0.25) was solubilized in 5 ml of DMSO. Oxidized nanocellulose (OxCell) bearing surface aldehyde functions was prepared and characterized following procedures detailed elsewhere [26] and the resulting aldehyde content reached $3.7 \text{ meq}\cdot\text{g}^{-1}$. The OxCell product was dispersed in DMSO (0.1 g in 5 ml) and mixed with the copolymer solution to reach a final OxCell concentration of 1.0 wt.%. The mixture was stirred for 1 h at room temperature, and 1 eq of NaBH_3CN per aldehyde (0.024 g, 0.38 mmol) was added to the suspension. After 24 hours at room temperature, the suspension was washed by successive centrifugations/redispersions with distilled water for 30 minutes at 15°C until the conductivity of the supernatant was close to that of distilled water ($2 \mu\text{S}\cdot\text{cm}^{-1}$). The resulting product was freeze-dried and we obtained a mass yield of 19% for the OxCell-P(SS-co-DADO)-0,25 coupling product.

2.2.5.2. Reductive amination of aminated PSS copolymers by propanal

The reaction, which was performed in a phosphate buffer solution ($\text{pH}=5,5$), followed the same procedure as previously described, with a copolymer bearing amino groups (0.200 g of P(SS-co-VA)-0.15), an excess of propanal (0.15 eq $\text{NH}_2/\text{C}=\text{O}$, 0.052 g) and NaBH_3CN (1 eq per aldehyde, 0.061 g). The resulting product was purified by dialysis against distilled water (membrane cut-off 2 kDa) and the dialysate was replaced twice a day with fresh distilled water until the conductivity was close to that of distilled water ($2 \mu\text{S}\cdot\text{cm}^{-1}$). Finally, the modified P(SS-co-VA) copolymer was recovered in a powder form after freeze-drying and the resulting mass yield reached 74% for the Pro-P(SS-co-VA)-0.15 product.

2.3.Characterization

2.3.1. NMR (^1H , ^{13}C , ^{13}C CP MAS)

^1H NMR spectra were recorded at 298K with a Bruker Advance III spectrometer (400 MHz) equipped with a 5 mm multinuclear broadband probe (BBFO+) with z-gradient coil. The samples (around 20 mg) were dissolved in D_2O (0.7 mL). Quantitative ^{13}C NMR analyses were recorded with Bruker Advance II spectrometer (400 MHz) equipped with a 10 mm ^1H - ^{13}C selective probe (SEX) with z-gradient coil at 100.6 MHz. The samples (around 300 mg) were dissolved in DMSO-d_6 (3 mL). Chemical shifts (δ , in ppm) are reported relative to internal 3-(Trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TSP- d_4 , $\delta = 0.00$ ppm). High-resolution solid state ^{13}C spectra were recorded at room temperature ($\sim 298\text{K}$) on a Bruker Advance III 500 MHz spectrometer equipped with a 4 mm ^{15}N - ^{31}P / ^1H probe, using magic angle rotation (MAS) and cross-polarization (CP) techniques. A minimum of 1000 scans were performed for each spectrum. The frequency was set to 125.7 MHz with a contact time of 2 ms and $D_1=10$ s for the CP-MAS. The chemical shifts were measured in agreement with the carbonyl signal of glycine set at 176.03 ppm. The samples were placed in a zirconium rotor with a rotation frequency fixed at a frequency of 10 kHz.

2.3.2. GPC

The copolymers were characterized at room temperature with an aqueous phase (0.1 M NaNO_3 , $\text{pH}=7$), using an elution rate of $0.500 \text{ ml}\cdot\text{min}^{-1}$. The SEC curves were obtained with two PSS SUPREMA 30A and 1000A columns equipped with a differential refractometer detector. Polymer samples at concentrations of 1 or $3 \text{ mg}\cdot\text{mL}^{-1}$ were analyzed after filtration through a $0.45 \mu\text{m}$ Millipore Methyl-Ethyl Cellulose (MEC) membrane. The data were processed on Astra 6.1 software (Wyatt technology). Molar mass calculations were obtained by conventional calibration with PSS equivalents. The P(SS-*co*-CMS) copolymers solutions ($2 \text{ mg}\cdot\text{mL}^{-1}$) were characterized at room temperature with a DMSO mobile phase (NaNO_3 $1 \text{ mg}\cdot\text{mL}^{-1}$) and using PSS GRAM columns. The molecular weights were calculated using a conventional PMMA equivalent calibration.

2.3.3. FTIR

KBr pellets containing 1% w/w of dry sample were prepared and their IR spectra recorded in transmission mode using a Thermo Scientific Nicolet iS-10 FTIR spectrometer in the 400-4000 cm^{-1} wavenumber range.

2.3.4. TGA

Thermogravimetric analyses were recorded with a TA Q500 apparatus under helium flow. The measurement was performed on 1-5 mg samples over a temperature range between 25 and 900°C at a rate of 10°C.min⁻¹.

3. RESULTS AND DISCUSSION

The synthesis of the PSS based polyelectrolytes was conducted according to the two strategies, illustrated in Figure 1. The first route relies on the synthesis of P(SS-*co*-AAm) prepolymers that can be subsequently modified into a P(SS-*co*-VA) copolymer through a Hofmann rearrangement (Fig. 1a). The second strategy involves the synthesis of a P(SS-*co*-CMS) copolymers followed by the N-alkylation of the CMS units in the presence of a primary diamine (Fig. 1b).

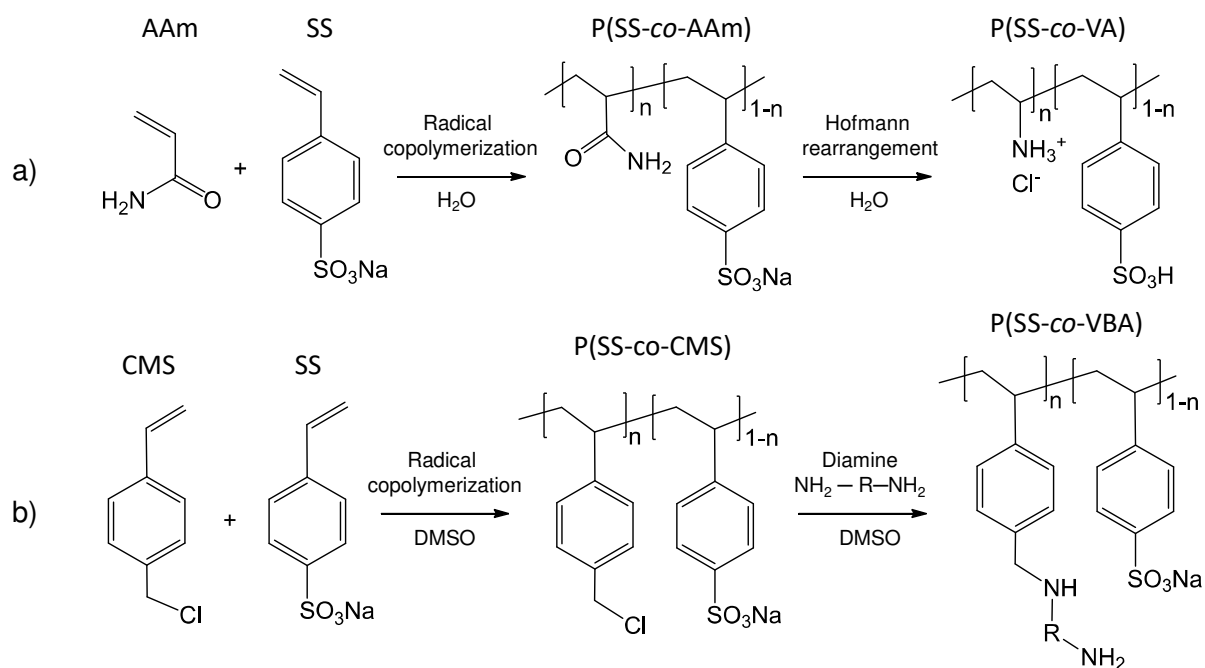


Figure 1: Synthetic strategies for the preparation of PSS copolymers bearing primary amines. a) through the Hofmann rearrangement of P(SS-co-AAm) copolymers. b) through the N-alkylation of P(SS-co-CMS) copolymers.

3.1. Synthesis of P(SS-co-VBA) copolymers through the chemical modification of P(SS-co-AAm) copolymers

This strategy involves the synthesis of PSS based copolymers bearing primary amines by free radical polymerization, and relies on the use of protected comonomers, namely NVF, NVA, NVPI and AAm, which are typically reported in the literature for the synthesis of PVA. [16] Nevertheless, among those candidates NVP is expensive, and preliminary experiments (data not shown) indicated that NVA do not copolymerize with SS, which is in agreement with the literature [16]. In contrast, the copolymerization of SS and AAm has been already reported, [27, 28] and using similar experimental conditions as ours (high conversion, no added salt), the authors calculated monomer reactivity ratios of $r_1=9.0$ for SS and $r_2=0.2$ for AAm, highlighting a statistical copolymerization.

3.1.1. Copolymerization of SS and AAm

Several copolymerization experiments were conducted while varying the monomer molar fraction in the feed (f). The related composition evolution was first qualitatively evidenced by FTIR (Fig SI-1a). It can be observed that the absorption bands located at 1650-1680 cm^{-1} and attributed to the C=O stretching $\nu(\text{C}=\text{O})$, as well as the amide N-H symmetric and asymmetric stretching $\nu(\text{N-H})$ at 3200 and 3350 cm^{-1} clearly indicate the increase in AAm units incorporation in the copolymer when increasing the feed comonomer ratio. The ^1H NMR analysis confirms the presence of both SS and AAm repetitive units in the copolymers as illustrated in Figure 2. Indeed, P(SS-*co*-AAm) copolymers display signals in the regions 6.5 ppm and 7.5 ppm which are characteristic for the aromatic hydrogen atoms (a, b, Fig. 2) whose intensities decrease as the AAm content in the copolymers increases. Moreover, AAm units are characterized by the signal belonging to the hydrogen atom near the amide group which appears in the chemical shift range 2.1-2.4 ppm (d, Fig. 2). The latter signal decreases as the AAm molar fraction in the copolymer decreases. The evolution of the copolymer composition as a function of the monomer molar fraction in the feed was also evidenced by ^{13}C NMR (Fig SI-2), with the presence of a characteristic signal of the C=O group at 183 ppm (C9), as well as other signals located at 43 and 36-39 ppm and attributed to C7 and C8 carbon atoms respectively. Once again, these signals are hardly visible for low AAm content because of aliphatic carbon signals overlapping.

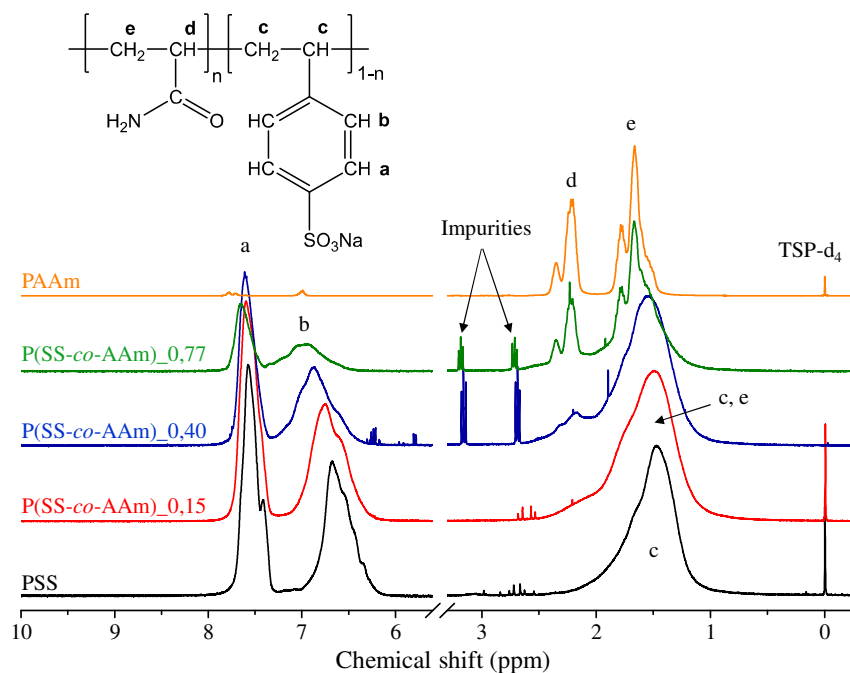


Figure 2: ^1H NMR spectra of P(SS-*co*-AAm) copolymers in D_2O .

The copolymer compositions are then easily calculated either from ^1H or ^{13}C NMR spectra and the AAm molar fraction in the copolymer (F_{AAm}) was then plotted as a function of the molar fraction in the feed (f_{AAm}) (Fig SI-3). As expected, from our experimental conditions and the related monomer reactivity ratios available in literature, [27, 28] F_{AAm} is smaller than f_{AAm} in the range of feed composition relevant to our study ($f_{\text{AAm}} < 0.5$). GPC of P(SS-*co*-AAm) copolymers was also performed to assess their molecular weight characteristics as well as their elution behaviors in water (Fig SI-4a). It can be observed that most of the molar mass distributions are monomodal, with an elution time that do not vary significantly with composition, but which is lower for the copolymers than for the PSS and PAAm homopolymers. Both the conformations of the copolymer chains and their corresponding hydrodynamic volumes may vary with increasing the AAm unit content which will dictate the results obtained from the GPC analysis. In addition, the thermal degradation of these copolymers was studied by TGA (Fig SI-5a). A typical water loss is observed in the temperature range 25-150°C, as expected for hydrophilic polymers. P(SS-*co*-AAm)

copolymers have a higher thermal stability than the PAAm homopolymer one, and a lower thermal stability than the PSS, while the thermal stability of the copolymers increases by decreasing the AAm unit content.

3.1.2. Modification of P(SS-co-AAm) copolymers into P(SS-co-VA).

The P(SS-co-AAm) copolymers with various AAm contents were then modified via an Hofmann reaction according to a procedure detailed in the literature for PAAm. [23] As the AAm moieties conversion to vinylamine (VA) groups is difficult to evidence by ^1H NMR due to the similarities between both P(SS-co-AAm) and P(SS-co-VA) spectra (Fig SI-6), the efficiency of the Hofmann rearrangement has been controlled by ^{13}C NMR (Fig. 3).

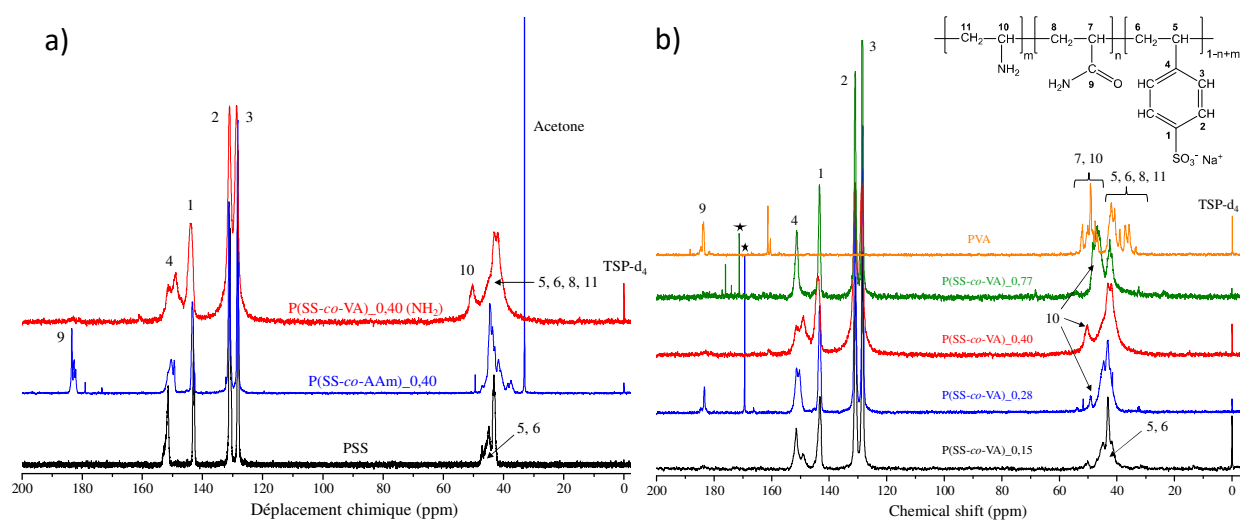


Figure 3: ^{13}C NMR spectra of P(SS-co-VA) copolymers in D_2O . a) comparison of the parent P(SS-co-AAm) and the modified P(SS-co-VA). b) composition variation of the P(SS-co-VA) copolymers.

The most striking features (Fig. 3a) are the disappearance of the carbonyl C9 located at 183 ppm, as well as the apparition of the C10 peak at 50 ppm, both corresponding to the AAm groups hydrolysis and to the successful formation of a VA repetitive unit, respectively. Moreover, the intensity of the signal attributed to the carbon atom C10 increases with the

AAm fraction in the parent P(SS-*co*-AAm) copolymers (Fig. 3b). In addition, depending on the experiments and on the composition of the P(SS-*co*-AAm) copolymer, some ^{13}C NMR spectra still contain signals above 160 ppm which may be assigned to remaining carbonyl groups at 183 ppm due to the presence of unmodified AAm units, and to side reactions which can lead to the formation of urea and/or carboxylic acid groups. [23] The qualitative modification of P(SS-*co*-AAm) into P(SS-*co*-VA) can also be observed through FTIR analysis (Fig. SI-1b) with the apparition of a new absorption band at 1520 cm^{-1} attributed to the presence of primary amines. In the case of protonated amines, the hydrohalides also display a large $\nu(\text{N-H}^+)$ absorption band between 2700 and 3350 cm^{-1} whose intensity also increases when increasing the initial molar fraction of AAm units in P(SS-*co*-AAm) copolymers. Regarding TGA thermograms (Fig. SI-5b), no significant evolution of the thermal decomposition behavior of the P(SS-*co*-VA) copolymers is observed after the chemical modification of P(SS-*co*-AAm) into P(SS-*co*-VA). At last, GPC measurements (Fig. SI-4b) indicate a change in polyelectrolytes chromatograms profiles after the Hofmann reaction, and higher elution times for the P(SS-*co*-VA) copolymers than for the P(SS-*co*-AAm) precursor ones. In addition, the multimodal profiles on Fig SI-4b suggest the presence of multiple populations of copolymers with different compositions. Such phenomenon could be related to chain scission phenomenons which have been discussed in earlier studies [23] and, or to the formation of $-\text{NH}_3^+$ groups in the P(SS-*co*-VA) copolymers which may induce interactions with the column or with the surrounding sulfonate functions as mentioned in section 3.3.

As we identified side products within the P(SS-*co*-VA) architectures, we further detail the quantitative analysis from ^1H and ^{13}C NMR spectra in Table 1. The total molar fraction of amine groups, unmodified acrylamide units and side products can be determined from both ^1H NMR and ^{13}C NMR using the peaks associated to the hydrogen atoms from the aliphatic

chain and the aromatic ring. The molar fraction of the VA units can then be determined from ^{13}C NMR after subtraction of unreacted and side products previously quantified with the carbonyl peak. When performing Hofmann rearrangement, the two important experimental parameters are the reagents molar ratios α and β (Table 1). $\alpha = \beta = 1$ were initially reported to be the optimal conditions to modify PAAm while limiting side products. [23] However, in our experiment on the homopolymer PAAm, only 75% of the AAm units were converted into VA units (product PVA in Table 1). In addition, in another experiment performed with $\alpha = \beta = 1$ on a copolymer containing a reduced amount of AAm units (P(SS-*co*-VA)-0.15*) only 50% of the AAm units were converted to VA. Nevertheless, when performing the modification with $\alpha = 2$ and $\beta = 1$, all the AAm units are efficiently modified for different compositions of P(SS-*co*-AAm), except for P(SS-*co*-VA)-0.28.

| Copolymer | $F_{\text{AAm}} (^{13}\text{C})$ | $\alpha = \frac{[\text{NaOCl}]}{[\text{Amide}]}$ | $\beta = \frac{[\text{NaOH}]}{[\text{Amide}]}$ | Post-polymerization yield (%) | $F_{\text{AAm+VA}} (^1\text{H}/^{13}\text{C})$ | F_{VA} |
|----------------------------|----------------------------------|--|--|-------------------------------|--|-----------------|
| P(SS- <i>co</i> -VA)-0.15* | 0.15 | 1.1 | 1.1 | 71 | 0.14/0.12 | 0.06 |
| P(SS- <i>co</i> -VA)-0.15 | 0.15 | 2.1 | 1.3 | 85 | 0.13/0.14 | 0.13 |
| P(SS- <i>co</i> -VA)-0.28 | 0.28 | 2.0 | 1.0 | 71 | 0.28/0.25 | 0.11 |
| P(SS- <i>co</i> -VA)-0.40 | 0.40 | 2.5 | 1.0 | 79 | 0.40/0.34 | 0.40 |
| P(SS- <i>co</i> -VA)-0.77 | 0.75 | 2.5 | 1.0 | 73 | 0.58/0.51 | 0.58 |
| PVA | 1.00 | 1.0 | 1.0 | 84 | 1.00/1.00 | 0.76 |

*The Hofmann reaction was performed on the same parent copolymer P(SS-*co*-AAm) ($F_{\text{AAm}}=0,15$) with a variation of the reaction parameter α .

Table 1: Composition of the P(SS-*co*-VA) copolymers determined from ^1H and ^{13}C NMR spectra. $F_{\text{AAm+VA}}$ stands for the total molar fraction of N containing units (AAm and VA) and F_{VA} for the molar fraction of units with primary amines obtained by subtracting F_{AAm} from the former, both after the Hofmann reaction.

In a nutshell, PSS statistical copolymers bearing pendant primary amines with a large range of compositions can be synthesized by free radical polymerization and subsequent modification of P(SS-*co*-AAm) under aqueous conditions with high yields. However, such approach is limited by the existence of side reactions inherent to the Hofmann reaction used to convert P(SS-*co*-AAm) into P(SS-*co*-VA). Finally, such strategy offers little flexibility in the choice of the amine substituent since it can only yield VA units. In order to overcome the aforementioned drawbacks, an alternative synthesis pathway based on the use of CMS as a styrenic comonomer should be more suitable as the post-modification can be easily performed by N-alkylation.

3.2. Synthesis of P(SS-*co*-VBA) copolymers through N-alkylation of P(SS-*co*-CMS) with amines

3.2.1. Synthesis of P(SS-*co*-CMS) copolymers

Considering that CMS is not soluble in water, the synthesis of P(SS-*co*-CMS) copolymers must be performed either in DMSO or in DMF/H₂O. [24] Nevertheless, the potential hydrolysis of the CMS units into vinyl benzyl alcohol groups can be observed even in the presence of a reduced amount of water. Such phenomenon was mentioned in the case of CMS free radical emulsion polymerization for which up to 25% of the reactive units were reported to be hydrolyzed. [29] After performing a copolymerization in the experimental conditions described in the literature, [24] we recovered a totally hydrolyzed copolymer, bearing only hydroxymethyl styrene units (HMS) which were evidenced by ¹H NMR analysis with a single peak at 4.4 ppm along with the SS units (spectrum P(SS-*co*-CMS)-0.30(H₂O) Fig. 4a).

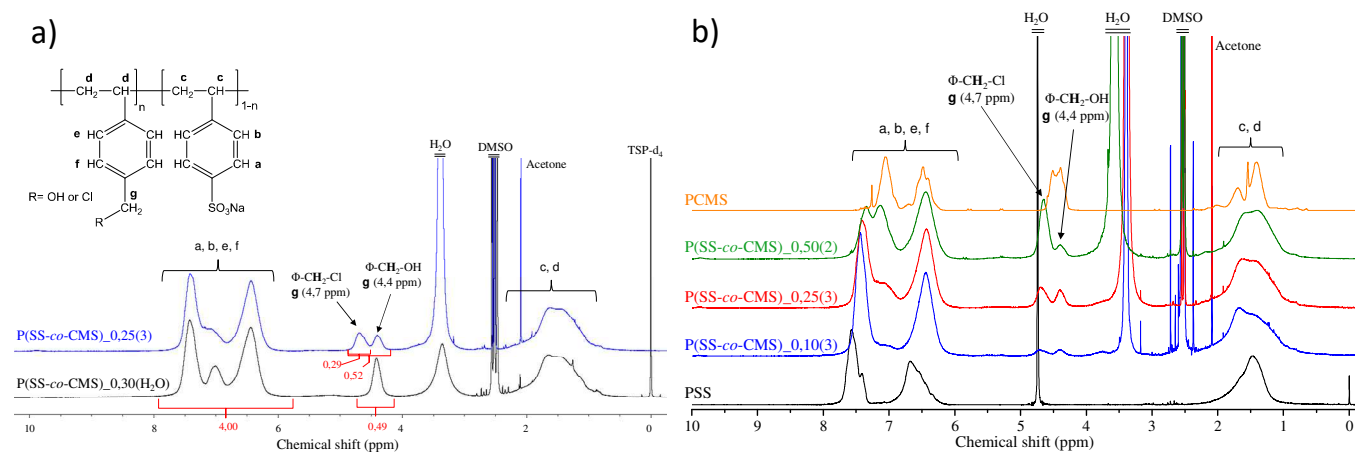


Figure 4: ^1H NMR spectra of P(SS-*co*-CMS) copolymers in DMSO- d_6 . a) synthesized in DMF/ H_2O or in DMSO (cf. Table 2), b) composition variation with optimized synthesis conditions in DMSO to prevent CMS hydrolysis. NB: PCMS reported here for comparison was synthesized with a protocol described elsewhere and analyzed in CDCl_3 . [30]

In contrast, performing the copolymerization in dry DMSO led to the appearance of a signal at 4.7 ppm, which is attributed to unhydrolyzed CMS moieties in the final copolymer, and which was not observed in the previous report of CMS/SS copolymerization. [24] We assume that even when dry DMSO is used, the hydrophilicity of the SS monomer can still lead to the hydrolysis of a portion of the CMS units by promoting the presence of physisorbed water. It's noteworthy that such hydrolyzed units are no longer observed when CMS is copolymerized with MMA [24] or with a protected styrene sulfonylester. [25] In order to optimize the synthesis conditions, we thus monitored the hydrolysis of the CMS in the presence of SS in dry DMSO (Fig. SI-8a). While no hydrolysis was observed after 2 days at room temperature, the signal assigned to HMS side product at 4.4 ppm is clearly observed after 6h at 70°C , while its intensity increases over time. Three P(SS-*co*-CMS) copolymers were then synthesized in dry DMSO while varying the reaction time from 3 to 24 h to investigate the influence of the reaction time on the hydrolysis. Figure SI-8b clearly shows the presence of a small amount of hydrolyzed CMS units after three hours while the characteristic signal of CMS units at 4.7

ppm significantly increases for a copolymerization time of six hours. It was concluded that the key parameter to avoid too much hydrolysis of CMS units is the copolymerization time, which must be as short as possible. From the optimized experimental conditions (dry solvent, short polymerization time) we managed to synthesize P(SS-*co*-CMS) copolymers soluble in DMSO, and their composition could be easily followed from the variation of the peak intensity at 4.7 ppm and from the variation of the characteristic signals of the hydrogen atoms of the aromatic rings (Fig. 4b). The evolution of the molar fractions of CMS and HMS units in the copolymers can further be evidenced by ^{13}C NMR (Fig. SI-9a) through their respective chemical shift at 47 ppm and 64 ppm. FTIR analysis also provide useful insights regarding the evolution of the copolymer composition with the increase of the intensity of the absorption band located at 1515 cm^{-1} attributed to the CMS aromatic ring C=C stretching vibration (Fig. SI-10a). Chloromethyl groups also exhibit a characteristic band at 710 cm^{-1} and 1270 cm^{-1} assigned to the C-Cl deformation and $\text{CH}_2\text{-Cl}$ stretching vibrations, respectively. In addition, TGA thermograms (Fig. SI-11a) indicate that the thermal stability of P(SS-*co*-CMS) copolymers decreases as F_{CMS} increases. Finally, GPC analysis (Fig. SI-12) confirm the effective copolymerization through the presence of unimodal distributions, and further show that the elution time slightly increase with the CMS fraction. The P(SS-*co*-CMS) copolymer CMS molar fractions calculated from either ^1H or ^{13}C NMR are summarized in Table 2, and confirm that the CMS hydrolysis decreases from more than 60% to less than 20% by decreasing the copolymerization time from 24h to 3h in the case of an initial stoichiometric mixture of CMS and SS. In addition, the data suggest that the variation of F_{CMS} from 0.1 to 0.5 leads to rather constant hydrolysis rates in the resulting P(SS-*co*-CMS), with a F_{OH} value around 0.05.

| Copolymer | Reaction time (h) | Solvent | f_{CMS} | $F_{\text{CMS}} (^1\text{H})$ | | $F_{\text{CMS}} (^{13}\text{C})$ | Copolymerization yield (%) |
|-----------|-------------------|---------|------------------|-------------------------------|-----------------|----------------------------------|----------------------------|
| | | | | F_{Cl} | F_{OH} | | |

| | | | | | | | |
|--|----|----------------------|-------------|-------------|-------------|-------------|----|
| P(SS- <i>co</i> -CMS)-0.30(H ₂ O) | 24 | H ₂ O/DMF | 0.30 | 0 | 0.26 | - | 55 |
| P(SS- <i>co</i> -CMS)-0.50(24) | 24 | DMSO | 0.50 | 0.18 | 0.31 | - | 50 |
| P(SS- <i>co</i> -CMS)-0.50(6) | 6 | DMSO | 0.50 | 0.33 | 0.17 | - | 49 |
| P(SS- <i>co</i> -CMS)-0.50(3) | 3 | DMSO | 0.50 | 0.43 | 0.10 | - | 41 |
| P(SS- <i>co</i> -CMS)- 0.10 (3) | 3 | DMSO | 0.10 | 0.05 | 0.04 | 0.10 | 49 |
| P(SS- <i>co</i> -CMS)- 0.25 (3) | 3 | DMSO | 0.25 | 0.18 | 0.06 | 0.25 | 47 |
| P(SS- <i>co</i> -CMS)- 0.50 (2) | 2 | DMSO | 0.50 | 0.45 | 0.05 | 0.51 | 30 |

Table 2: Composition of the P(SS-*co*-CMS) copolymers from ¹H and ¹³C NMR spectra.

Finally, the plot of the composition of the total CMS units (hydrolyzed and unhydrolyzed) in the copolymer as a function of the feed composition (Fig. SI-7) indicates no deviation, and the copolymer composition can be easily tuned by adjusting the initial monomer feed molar ratio.

In order to obtain copolymers bearing pendant amine groups a post modification step of the CMS units is required. Different approaches have already been reported in the literature for the synthesis of polybenzylamine from PCMS through a Gabriel [31-33] or Staudinger [34] reaction. In contrast to these multi-steps approaches, we consider herein a simpler strategy, derived from the common N-alkylation with tertiary amine of CMS units, to introduce quaternary ammonium. [24, 25]

3.2.2. N-alkylation of P(SS-*co*-CMS) copolymers

We anticipate that using a difunctional primary amine in excess, we will easily produce a copolymer bearing pendant primary amine by forming a secondary amine through a nucleophilic substitution. The hydrophilic difunctional primary amine DADO was chosen to illustrate this approach. After a one-night reaction at room temperature in DMSO, the corresponding purified copolymers P(SS-*co*-DADO) no longer exhibit the characteristic signal of the chloromethyl group at 4.7 ppm in ¹H NMR spectra, while new resonances attributed to the DADO group are observed (Fig. 6a), thus confirming the quantitative

modification of the CMS units. The ^{13}C NMR analysis (Fig. 5b) also highlights the functionalization of the CMS units with the appearance of new peaks at 42, 72 and 75 ppm and attributed to aliphatic carbons from the DADO aliphatic groups. Although not detected by NMR, and despite the large excess of DADO used, intermolecular chain-chain coupling or intramolecular crosslinking in solution cannot be completely ruled out. Preliminary experiments with lower stoichiometry (data not shown) indeed resulted in the formation of a gel or aggregates, and additional characterizations currently in progress will be detailed in a follow-up paper focused on the copolymers solution properties.

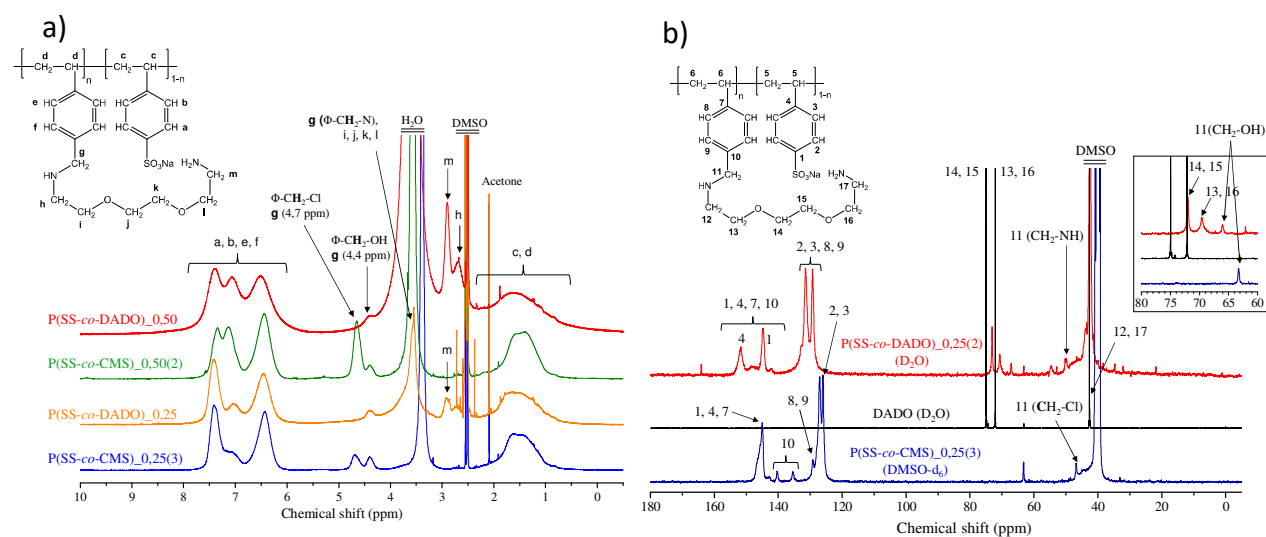


Figure 5: NMR spectra of P(SS-co-DADO) copolymers in DMSO- d_6 . a) ^1H NMR, b) ^{13}C NMR.

3.3. Properties of the synthesized PSS copolymers with pendant primary amines

In order to illustrate the interest of such new PSS based copolymers bearing primary amines to build macromolecular assemblies, their reactivities toward an aldehyde and the surface of oxidized cellulose by reductive amination were evaluated (Fig. 6). First, we performed the reductive amination of propanal as a model molecule whose chemical modification can be easily evidenced by ^1H NMR (Fig. 6a), through the appearance of a new signal in the region

0,5-0.8 ppm. Such reactivity could be thus easily adapted to form crosslinks with divalent aldehyde to obtain either hydrogel or microgels from those polymers. The same modification strategy was also be applied to graft those copolymers onto reactive surfaces, and we chose periodate oxidized nanocellulose with aldehyde moieties on their surface as an example. [26] The successful grafting was evidenced by ^{13}C CP MAS NMR with the appearance of new signals attributed to the aliphatic and aromatic carbons of the copolymer in the product (Fig. 6b). Ongoing experiments are devoted to the detailed investigation of this specific reactivity and will be reported in an upcoming paper.

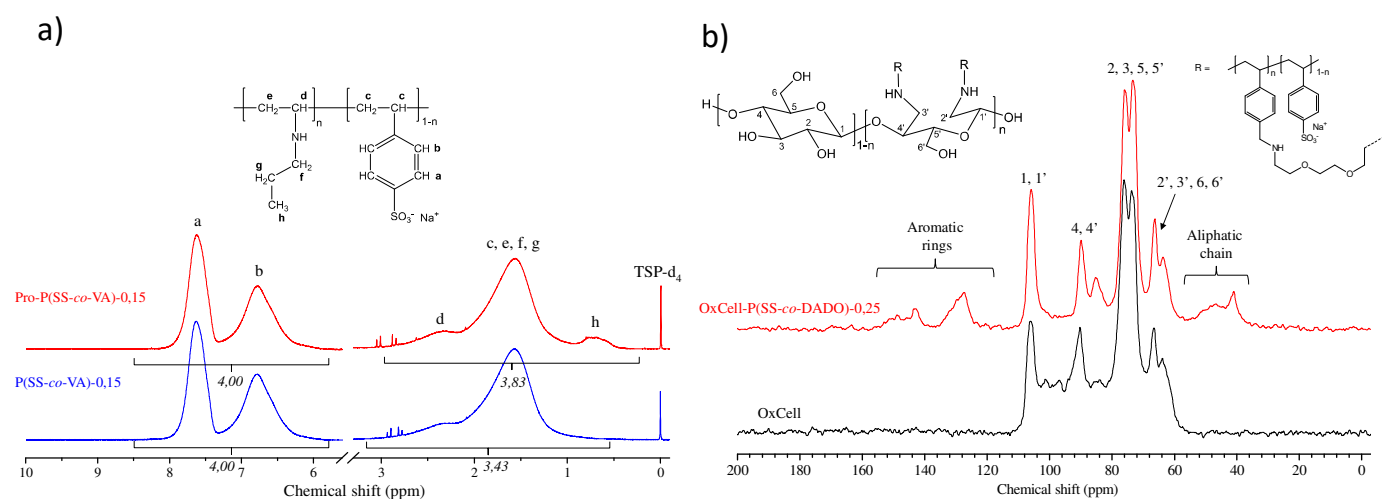


Figure 6: NMR analysis of aminated PSS-based copolymers modified by reductive amination. a) ^1H NMR in D_2O of $\text{P}(\text{SS-co-VA})\text{-0.15}$ reacted with propanal. b) ^{13}C CP/MAS NMR of periodate oxidized nanocellulose (OxCell) modified with $\text{P}(\text{SS-co-DADO})\text{-0.25}$.

Another key feature of those PSS copolymers is their characteristic acid-base nature, allowing amine/ammonium equilibrium in water, which shall yield to a polyampholyte behavior at pH below the pK_a of the amine. To illustrate this, we performed simple visual observations of aqueous solutions of the several copolymers synthesized in this report while varying the pH (Table SI-1). For copolymers containing less than 20% of amino units ($F_A < 0,20$), we observe that the solutions are translucent at all pH, suggesting that even if inter or intra-molecular

ionic interactions are formed between the sulfonate and ammonium groups, the excess of sulfonate groups prevents the formation of large aggregates. In contrast, for copolymers whose composition gets closer to the stoichiometry between ammonium and sulfonate ($F_A > 0,40$), opaque solutions are evidenced at $\text{pH} < 10$, which is in line with common values of pK_a for alkylamine. This behavior clearly evidences the formation of large aggregates through ionic complexation due to the polyampholyte nature of the P(SS-*co*-VA) et P(SS-*co*-VBA) copolymers.

CONCLUSION

In this report we detailed two indirect strategies to synthesize PSS copolymers bearing pendant primary amines. In the first one, P(SS-*co*-AAM) statistical copolymers were synthesized and subsequently modified through Hofmann rearrangement to obtain vinylamine units. Even if such approach can be performed in water with good yields, the copolymerization was non-ideal and the Hofmann rearrangement step tends to form a minority of side products. In contrast, the second approach based on the N-alkylation of P(SS-*co*-CMS) copolymers evidenced an ideal statistical copolymerization of SS and CMS and a quantitative post-modification of the CMS units with a primary amine in excess. The main constraint of such approach is to work in anhydrous polar solvent and at moderate temperature to respectively solubilize the CMS and prevent its early hydrolysis before modification. Apart from this, this approach appeared as a straightforward way to introduce a controlled amount of amine functions within the PSS chain. We expect that such building blocks will lead to numerous applications in the field of polyelectrolyte assemblies, thanks both to the several modification pathways available involving amines, and also by taking advantages of the acid-base properties of the amine, which confers a polyampholyte nature to the copolymer in the particular conditions where the pH is lower than the amine pK_a in water. As an illustration of this potential, we performed preliminary experiments which have

demonstrated that such copolymers can efficiently be modified by propanal and grafted onto the surface of oxidized cellulose, in both cases by reductive amination. Moreover, tuning the pH of the copolymers solution in water resulted in the formation of aggregates at pH < 10 for cation/anion composition close to the stoichiometry. Ongoing experiments are focused on the variation of the amine nature (and consequently its pKa) and the subsequent investigation of the copolymers physico-chemical properties, combining titration, light scattering and rheology to rationalize their assembly mechanisms.

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DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

The raw and processed data required to reproduce these findings are available on demand to the corresponding authors.

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