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Synthesis and characterisation of poly(sodium 4-styrenesulfonate) combs

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Abstract

A series of poly(sodium 4-styrenesulfonate) (NaPSS) combs has been synthesized. Architecturally and molecularly well-defined polystyrene combs were initially produced with the branch molecular mass fixed at 30,000 g/mol, the average number of branches being the major variable. Conditions were established whereby linear polystyrene (PS) synthesized via anionic polymerization was chloromethylated using zinc (II) chloride, side-reactions such as Friedel–Crafts alkylation being suppressed. An excess of diphenylethylene-capped polystyryllithium (PSLi) was then reacted with the functionalized backbone to yield materials having long chain branches. The polystyrene combs were then reacted with sulfuric acid to yield water-soluble poly(styrenesulfonic acid) combs and subsequently neutralized with sodium hydroxide to give the corresponding sodium 4-styrene sulfonate species. The extent of sulfonation was determined via titration and nuclear magnetic resonance spectroscopy (NMR). Aqueous triple-detector size exclusion chromatography (SEC) was used to characterize the sulfonated combs. Although the SEC traces were monomodal and the M_n values agreed well with the expected values, an increase in the polydispersity index compared to the polystyrene combs may reflect the susceptibility of the sulfonation reaction to cross-linking.

Keywords: Poly(4-styrene sulfonate); Long-chain branching; Biomimetic

1. Introduction

Despite the interest in polyelectrolytes, studies of synthetic materials have mainly been focused on the properties of linear polymers. For example, linear polystyrene has been sulfonated [1–3] to different degrees and the effects of charge density examined [4,5]. Also, block copolymers containing sulfonated polystyrene have been studied using rheological [6], X-ray scattering (SAXS) [7], mechanical [8] and solution measurements [9]. The mechanical behavior of an ABA triblock, where A is polystyrene and B is isobutylene, before and after sulfonation has also been reported [10].

The main method of polymerizing narrow molecular weight distribution polymers of specific architecture is via anionic polymerization. Well-defined polystyrene stars [11–13] and combs [14–31] have been synthesized by this technique. Mays [32] has synthesized many-armed polystyrene stars and then sulfonated them and has also synthesized star-block copolymers consisting of polystyrene and poly(4-*tert*-butylstyrene), the polystyrene then being selectively sulfonated [33]. One potential drawback of the sulfonation of branched polystyrenes has been linked to the limited stability of Si–C linkages to the sulfonation process, these being commonly present in stars and certain comb materials made via a combination of anionic polymerization and chlorosilane chemistry [32].

In this paper, we describe the synthesis and characterization of a series of sulfonated comb polystyrenes. To our knowledge, the materials are novel and furthermore they offer potential as model branched polyelectrolytes, the synthesis and properties of which have previously been centred on graft copolymers. The importance of synthesizing polystyrene sulfonates specifically of comb architecture is to provide materials having biomimetic properties [34]. Highly branched sulfate structures are found in aggrecan. Aggregan (aggregating chondroitin sulfate proteoglycan) is a major component of cartilage. It is thought to produce a high osmotic pressure plus strong intermolecular repulsions which allow articular joints to be subjected to compressional forces. A study comparing aggrecan to one of the combs produced in this study has recently been published [34]. By examining the role of

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the branching density in synthetic polyelectrolyte combs, it may increase our understanding of the behavior of highly complex biological comb and bottle–brush structures.

The present work is part of a larger study of the effects of small to moderate amounts of long-chain branching upon the properties of poly(styrene sulfonates), in particular the solution properties [35]. To this end, it was first necessary to re-visit the chloromethylation of linear polystyrene and establish a set of conditions offering good control whereby the extent of functionalization could be limited and cross-linking minimized for a (relatively) high molecular weight polystyrene backbone. Thereafter, optimum conditions needed to be determined for the coupling reaction of the chloromethylated polymer with living polystyrene in order to produce well-defined comb materials, particularly in the case of sparsely branched materials. Finally, the combs were sulfonated so as to render them fully water-soluble whilst ensuring their comb structure was retained.

2. Experimental

Styrene (Aldrich) was dried over CaH_2. Benzene (Aldrich) was distilled from sodium/potassium and dried over *n*-BuLi. *sec*-BuLi (Aldrich) was distilled over a short-path using a cold-finger, diluted with dry cyclohexane and the molarity of the resulting solution determined by titrating a known volume against standard HCl using phenolphthalein as an indicator. Dimethoxymethane, thionyl chloride, tin (IV) chloride and zinc (II) chloride (Aldrich) were used as received.

Anionic polymerization of styrene was performed using high vacuum techniques [36], reagents being transferred into a reactor via breakseals. *sec*-Butyllithium was used as the initiator and benzene as the solvent. The reactions were performed at room temperature overnight with a monomer concentration of approximately 10% v/v and a *sec*-BuLi concentration of between 0.5 and 10 mMol, dependent on the desired molar mass of the polymer. Degassed methanol was used to terminate the reactions.

Chloromethylation reactions (note: reaction performed with great caution in a well-ventilated fume-hood) were performed using the method of Wright et al. [37], whereby, chloromethyl methyl ether was formed by the in situ reaction of dimethoxy methane and thionyl chloride in the presence of a Lewis acid catalyst. In a typical preparation PS (2 g, 200,000 g/mol) was dissolved in dimethoxymethane (10 cm^3) and the flask sealed under nitrogen. The solution was cooled to 0 °C and thionyl chloride added (3.7 cm^3, 0.05 mol), the solution was stirred at room temperature and then the catalyst (0.08 mmol) was injected into the solution at 0 °C. After a set reaction time, the polymer was precipitated in methanol, redissolved in dichloromethane, precipitated once more then dried under vacuum. The reaction times and temperatures were varied in order to control the extent of chloromethylation.

The chloromethylated polystyrene was charged to a large ampoule fitted with a greaseless stopcock, then freeze–dried from benzene, dissolved in THF (<5% w/v) and attached to a reactor. Polystyryllithium was synthesized in the reactor as described above. Benzene was removed from the living polystyrene by distillation and replaced with dry THE. A three-fold molar excess of 1,1-diphenylethylene (DPE) was added to the PSLi, instantly turning the solution deep red. The temperature was lowered to −78 °C and the chloromethylated backbone gradually added to the PSLi and stirred, the process of addition taking around 30 min. An excess of living polystyrene was present throughout the reaction as evidenced by the retention of the red colour of DPE-capped polystyryllithium. Once addition was complete, the reaction temperature was raised to −50 °C and allowed to proceed for 2 h; it was then allowed to slowly reach room temperature and the reaction was then left stirring overnight. The residual polystyryllithium was terminated using degassed methanol and the comb and linear polymer was precipitated in a large excess of methanol. To remove the excess linear polystyrene, fractionation was performed by the addition of 60–80 petroleum ether to a 1% solution of polymer in toluene.

The polystyrene combs were sulfonated using the method of Vink [1]. Sulfuric acid (BDH), phosphorus pentoxide (Aldrich) and cyclohexane (Fisher) were used as received. PS (3 g) was dissolved in cyclohexane (150 cm^3) at 50 °C and then cooled to 40 °C. Phosphorus pentoxide (22 g) was slowly dissolved in sulfuric acid (100 cm^3) and the mixture equilibrated at 40 °C. The polystyrene solution was added slowly to the acid and stirred for 30 min, two phases becoming apparent. The mixture was allowed to stand at 40 °C for 1 h then cooled to 0 °C and 50 g of crushed ice was added to the mixture, inducing precipitation of the polyacid. The mixture was transferred to a separating funnel and the mineral acid drained away. Water (150 cm^3) was added to the cyclohexane/precipitated polyacid and the polyacid dissolved. Once the polyacid was fully dissolved it was separated from the cyclohexane and transferred into dialysis tubing (Visking, molecular weight cut off 12,000–14,000). The polyacid was thoroughly dialyzed with distilled water then isolated as a brittle, brown solid by removing the water by rotary evaporation. Sodium chloride saturated (aqueous) solutions of the polymer were titrated against 0.1 M sodium hydroxide solution, phenol phthalein being used as the indicator.

3. Characterization

^1H NMR spectroscopy was performed in $CDCl_3$ at 30 °C using a Bruker AC250 MHz spectrometer for the chloromethylated PS, and in D_2O for the NaPSS.

Size exclusion chromatography (SEC) analysis of polystyrene samples were obtained using a triple detection method (with angular correction) using a Viscotek 200 SEC apparatus fitted with two PLgel mixed C $300 \times 7.5\ mm^2$ columns running at 30 °C with a THF flow rate of 1 ml/min, having refractive index, viscometer, and right angle laser light scattering (RALLS) detectors, the wavelength of the laser being 670 nm. A d*n*/d*c* value of 0.185 ml/g was used for all the samples. The concentration of the PS samples varied from 0.25 to 1 mg/ml depending on their calculated molecular mass.

The poly(sodium 4-styrene sulfonate) samples were analysed by aqueous SEC using a triple detection method (with angular correction) and measurements were performed on a Viscotek TDA 301 triple detection SEC fitted with two (300×7.5 mm^2) GMPWxl methacrylate based mixed bed columns with an exclusion limit of 5×10^7 g/mol, having refractive index, viscometer and RALLS detectors. A mobile phase of 70% 0.1 M sodium nitrate/30% acetonitrile was used at a constant temperature of 30 °C and a flow rate of 1 ml/min. The NaPSS sample concentration varied between 0.06 and 0.37 mg/ml. The d*n*/d*c* value was determined to be 0.177 ml/g using samples of linear NaPSS obtained from polymer standards service.

4. Results and discussion

4.1. Chloromethylation

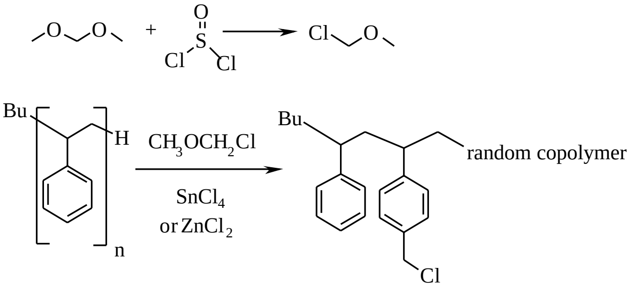
The chloromethylation method was based on that of Wright [37] as this offers a relatively safe and clean method of generating chloromethyl methyl ether and subsequently used to functionalize the polystyrene, the general reaction is shown in Scheme 1. However, their research indicates that the reaction of chloromethyl methyl ether with high molecular mass polystyrene in the presence of a Lewis acid is accompanied by side-reactions, for example, an insoluble gel was formed when using tin IV chloride at 40 °C. Although the paper investigated the extent of chloromethylation using $SnCl_4$ and $ZnCl_2$, neither SEC data nor traces were provided apart from a statement that the polydispersity index increased from 1.53 to 1.72 after 34% modification, using $ZnCl_2$.

Table 1
Results of the chloromethylation reactions

Catalyst	Reaction time (min)	Temperature (°C)	Extent of reaction (%)[a]
$SnCl_4$	5	30	<0.5%
$SnCl_4$	10	30	3.3
$SnCl_4$	20	30	7.5
$SnCl_4$	60	30	10
$SnCl_4$	60	0	<0.5%
$SnCl_4$	60	10	4.2
$SnCl_4$	60	20	4.9
$SnCl_4$	60	40	16.5
$ZnCl_2$	360	30	<0.5%
$ZnCl_2$	960	30	0.7
$ZnCl_2$	1440	30	1
$ZnCl_2$	2460	30	7

[a] The extent of reaction calculated from ^{1}H NMR for PS of 200,000 g/mol.

For this research, conditions were required, which minimised cross-linking, such high molecular mass species being potentially difficult to remove from the final comb product. A series of experiments was performed to determine the best conditions for the chloromethylation of monodisperse 200,000 g/mol PS. The extent of the reaction was calculated using ^{1}H NMR, the peak integrals of the $-CH_2$ protons adjacent to the chlorine resonating at δ4.5 ppm were used in conjunction with the aromatic protons at δ6.6 and δ7.15 to work out the ratio between chloromethylated and unchloromethylated styrene repeat units. The results can be seen in Table 1. The ^{1}H NMR result was subsequently used to calculate an approximate value for the number of chloromethyl groups per backbone chain and although the resonance due to the chloromethyl group was usually small compared to that of the aromatic protons it could be used to calculate the amount of polystyryllithium branch material required for the completion of the subsequent comb reaction.



Scheme 1. Chloromethylation of polystyrene.

The zinc (II) chloride catalyzed chloromethylation was found to be much slower that that of tin (IV) chloride and no reaction was detectable at a time of less than 6 h at 30 °C. However, the extent of chloromethylation gradually increased with time, the results were reproducible and cross-linking was virtually eliminated even at relatively high levels of chloromethylation i.e. up to 10%. However, tin (IV) chloride was found, under similar reaction conditions, to accelerate the reaction, a few minutes being sufficient for significant levels of chloromethylation but was also found to induce cross-linking. SEC data (from the refractive index detector response) in Fig. 1 can be used in conjunction with the results listed in Table 1 and illustrates that cross-linking increases with time and extent of the reaction for the tin (IV) catalysed reactions. Whereas, the

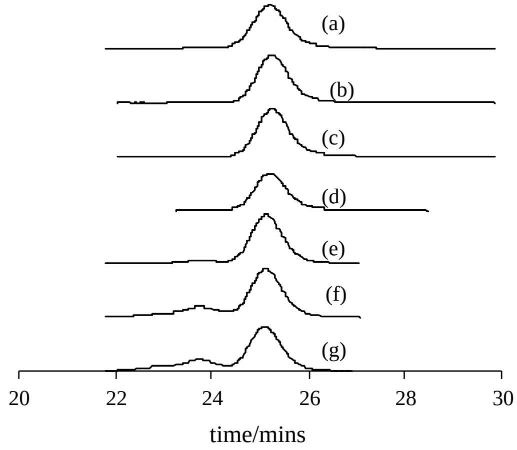


Fig. 1. SEC traces showing the extent of cross-linking with time for the chloromethylation of polystyrene (200,000 g/mol) performed at 30 °C (a) zinc(II) chloride catalysed reaction after 42 h (b) polystyrene prior to chloromethylation (c) tin(IV) chloride catalysed reaction after 1 min then (d) 5 min, (e) 10 min, (f) 20 min and finally (g) 60 min.

zinc (II) chloride catalysed reaction leaves the polystyrene unaffected as shown in SEC trace (a), trace (f) corresponding to the tin (IV) chloride catalysed reaction at a similar extent of chloromethylation (ca. 7%) exhibits significant cross-linking with additional peaks apparent at lower elution times. For the $SnCl_4$ catalysed reaction, a series of reactions was also performed where the reaction time was held constant (60 min); it was found that the reaction proceeded without signs of cross-linking only when the reaction temperature was lowered to 0 °C and at this temperature the reaction is slow and the extent of chloromethylation was less than 1%. In contrast, at 40 °C much of the product was insoluble.

It can be concluded that because zinc (II) chloride is a milder Lewis acid, it is less likely to cause Friedel–Crafts reactions, which, in effect cause the aromatic rings to link together intermolecularly.

4.2. Comb formation

The synthetic route is displayed in Scheme 2. The conditions under which comb materials were formed had to be chosen carefully. Several side-reactions are known to accompany the grafting procedure between chloromethylated PS and PSLi, which can cause cross-linking, and indeed, such problems were initially encountered specifically with lightly branched combs. A set of three combs was made, which illustrate the very sensitive nature of the reaction. The chloromethylated polystyrene backbone employed for the different reactions varied in the number of functional groups, with one calculated to have five chloromethyl groups, the second 20 and the most functionalized having approximately 30 reactive sites per backbone. The SEC traces of the products are shown in Fig. 2. It can be seen that the lightly branched species is highly cross-linked whereas no cross-linking is seen for the comb having the most branches (175-35-28). The conditions for these particular reactions were such that the DPE end-capped polystyryllithium, in a 50:50 v/v mixture of THF and benzene, was added slowly from an ampoule into the chloromethylated PS solution in THF at –30 °C until the solution remained permanently red. The above conditions had initially proved successful in preliminary reactions but were modified in subsequent experiments to prevent the formation of super-macromolecular cross-linked species during the synthesis of lightly branched combs. Little work has been reported on combs bearing very few branches and so the additional difficulties faced due to intermolecular cross-linking have not been explicitly examined, although Takaki [23] notes that electron transfer and metal–halogen exchange could lead to intermolecular cross-linking in the absence of steric hindrance from existing branches during comb formation. Cross-linking was suppressed for the remaining reactions by performing the reactions in THF, the benzene being removed from the polystyryllithium branches and replaced in THF before further reaction; the solvent polarity may have a positive effect on the outcome of the reaction by reducing metal-halogen exchange [38]. The initial temperature of the reaction was low (−78 °C rising to − 50 °C) and this may help prevent the known side-reactions and improve the branching efficiency [39]. Another contributory factor to prevention of cross-linking could be the order of the addition of the reagents. It was found that a clean product was formed when the chloromethylated backbone was slowly added to an excess of polystyryllithium branch material rather than vice-versa. It is possible that the presence of excess PSLi allows a branched species to be quickly formed, the branches affording at least some steric barrier to the cross-linking of the nascent combs via radical or ionic species. It is important that the reaction goes to completion and a modest excess of PSLi branch is necessary to ensure this. DPE was added to end-cap the polystyryllithium;

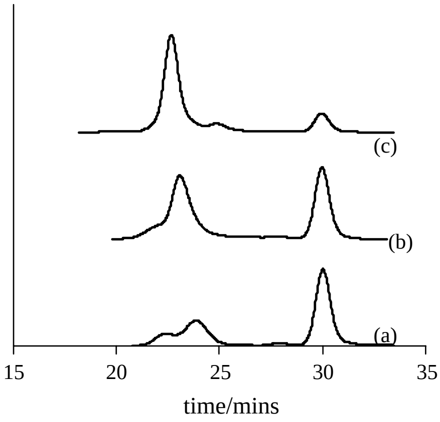
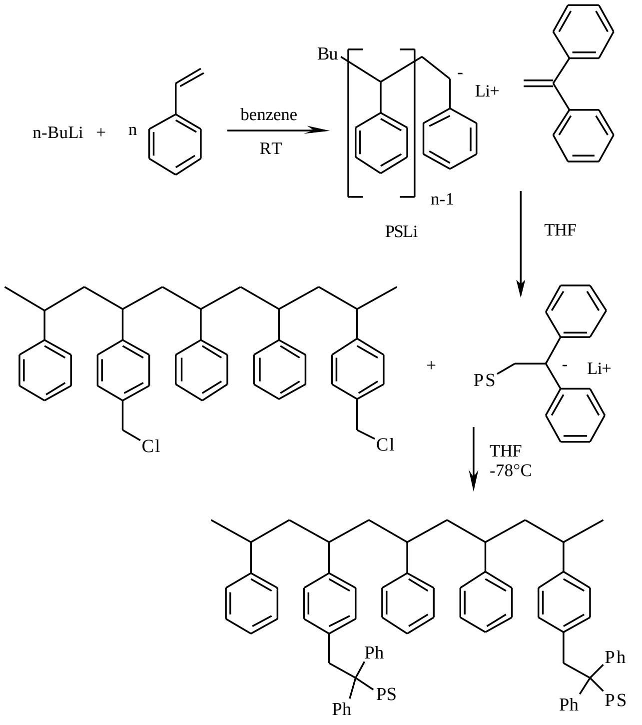


Fig. 2. SEC (R.I.) trace showing the final comb raw products where the chloromethylated PS starting material is (a) very lightly functionalised (b) slightly more functionalised and (c) most highly functionalised.



Scheme 2. Formation of a polystyrene comb.

Table 2
Molecular characteristics of the polystyrene comb series

Comb[a]	$M_{w,\ PS\ backbone}$[b] (kg/mol)	$M_{w,\ PS\ branch}$[b] (kg/mol)	$M_{n,\ PS\ comb}$[b] (kg/mol)	$M_{w,\ comb}$[b] (kg/mol)	PD[b] PS comb	p[c]
170-21-31	167.5	31.4	758.4	797.9	1.05	21 (21)
175-35-28	175.9	27.9	1088	1157	1.06	33 (35)
105-27-30	104.9	30.0	852.6	906.1	1.06	26 (27)
105-13-35	103.9	34.5	505.2	541.0	1.07	12 (13)
190-15-35	191.3	34.6	684.5	715.3	1.04	15 (15)
190-23-33	191.3	32.8	909.5	949.0	1.04	22 (23)
190-160-30	191.3	30.0	[d]	[d]	[d]	160[e]

[a] The combs are labelled *xxx–yy–zz* where x is the M_w of the backbone, y is the number of branches and z the branch M_w in kg/mol.

[b] M_w, the weight average molecular weight and M_n, the number average molecular weight were determined using triple-detector SEC. The polydispersity of the component backbone and branch were less than 1.05 in all cases. PD is the polydispersity of the comb M_n/M_w.

[c] p, the average number of branches as calculated from the M_ns using Eq. (1) (the corresponding values calculated from M_ws are in brackets).

[d] Too large to be measured.

[e] Calculated from degree of functionalisation of the backbone using ^{1}H NMR.

the resultant delocalization reduces the basic nature of the anion and makes it less likely to abstract a proton from the chloromethyl group [39]. The combs were analysed by ^{1}H NMR to confirm the absence of chloromethyl groups although very small numbers of chloromethyl groups would not be detected on combs of high molecular mass. In order to ensure the absence of residual solvent in the products, the samples were heated to above the glass transition temperatures in a vacuum oven. No detectable change in the SEC trace was seen after 24 h at 130 °C; the thermal stability of the combs was examined in preparation for the study of the processing properties of the polymers [40], the original basis for the synthesis of the PS comb series.

The molecular weight data obtained by SEC analysis of the polystyrene combs are listed in Table 2. An example of the formation of a comb (105-27-30) is shown by the SEC traces in Fig. 3. The chloromethylation reaction was successfully scaled up and 5–10 g of chloromethylated high molecular mass backbone was used per comb reaction and thus the yield of the reaction amounted to at least 20 g. Typically, less than 5% of unlinked branch material would remain after a single fractionation step and this would be reduced to 1% or less after further step. It can be seen that by capping the polystyryllithium with DPE and adopting the above procedures, a product having a symmetrical molecular weight distribution and narrow polydispersity is attained even for relatively lightly branched polystyrenes. An average number of branches per comb, p, is calculated wing Eq. (1), the number average molecular mass M_n used in the calculations being obtained using the triple detection methodology. The M_w values can also be used to estimate p and the values are very close to those calculated by M_n as can be seen by the results in Table 2.

$$p = \frac{M_{n,comb} - M_{n,backbone}}{M_{n,branch}} \qquad (1)$$

It must be noted that there is a distribution (Poisson) in the number of branches per comb because of the random nature of the chloromethylation reaction. Because the polydispersity indices for the branches, backbone and the comb were all determined to be less than 1.1 in all instances, the above equation can be expected to yield a reasonable average for the number of branches in the comb. Work previously published on polybutadiene combs compares the number of branches calculated from the chemistry, i.e. using triple detector-SEC data, to the number of branches calculated from rheological measurements and the two values were found to be in good agreement [41].

4.3. Sulfonation

Although there are several different methods of polystyrene sulfonation, it is a reaction that is prone to cross-linking and degradation [2,3]. Certainly, for reactions which use concentrated sulfuric acid, a relatively low temperature is required in order to yield a fully water-soluble product. The reaction scheme is shown in Scheme 3. For the sulfonation of the polystyrene combs, a method was required which would afford a high level of sulfonation with the minimum amount of

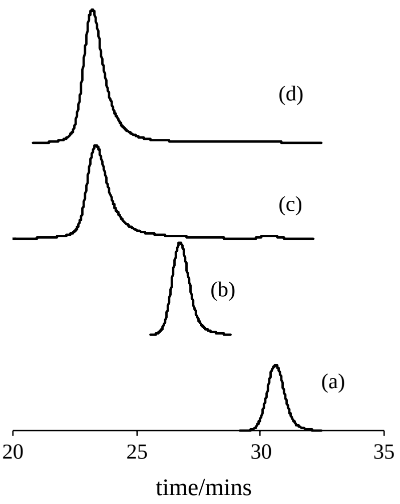
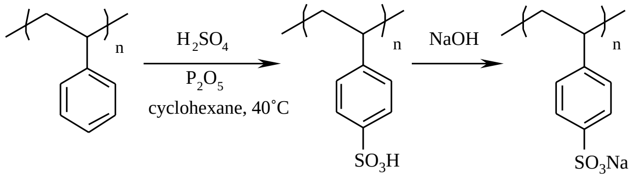


Fig. 3. SEC traces showing the formation of polystyrene comb 105-27-30 (a) the branch (b) the backbone (c) the unfractionated comb and (d) the comb after fractionation.



Scheme 3. Formation of poly(sodium 4-styrene sulfonate).

side-reactions. The Vink [1] method was reported to yield high levels of sulfonation (90–95%) for linear polymers of up to 860,000 g/mol, using viscometry to analyse the sulfonated products.

The results from the titration of the dialyzed acid with NaOH indicated that over 80% of the styrene units had undergone sulfonation for each of the comb samples as detailed in Table 3. NaCl saturated solutions were employed for the titration in order to help reduce the viscosity, allowing the chains to assume random coil conformations in solution. The neutralized (NaPSS) combs were subsequently used for further analysis. Although the ^{1}H NMR peaks for the sulfonated samples are very broad, the viscosity being very high in D_2O, the ^{1}H NMR spectra indicate a high level of sulfonation as can be observed in Fig. 4. The absence of any remaining peak at δ7.1 ppm, attributed to meta/para protons of polystyrene, after sulfonation indicates near-quantitative conversion to the sulfonate. The low-field shift of the meta protons from δ7.1 to δ7.6 ppm is due to the presence of the adjacent electron withdrawing sulfonate group [4].

Aqueous SEC of these materials is not straightforward and the data need to be considered with certain qualifications. The eluent used was chosen in reference to the work of Baigl [4]. The branched architecture renders any analysis by a conventional calibration purely qualitative, even if generated with well-defined linear standards of NaPSS. However, the use of a light scattering detector (as part of a triple detection SEC) allows the generation of more quantitative data. It should be noted though that the presented data was generated using a single angle (90°) light scattering detector and whilst a right angle detector has the optimum angle for minimizing the signal to noise ratio, a correction is required to take into account the angular assymmetry of light scattering. If the dimensions of the scattering molecules are much smaller than the wavelength of the incident light, the molecule behaves as point source of scattered light. This results in a symmetrical scattering pattern and R_θ (Rayleigh ratio at angle θ) approximates to R_0 without significant error. The accuracy of this approximation is dependent on the magnitude of the scattering angle θ and on the size of the macromolecule. Where θ is 90° as in the case of RALLS this is a good approximation for polymers with a radius of gyration <15 nm, which corresponds roughly to a M_w of 150,000 g/mol or less for polymers which adopt a random coil in solution. When the scattering molecules are comparable in size to the wavelength of the incident beam, the scattering radiation from different parts of the molecule may become out of phase. This phase mismatch increases with scattering angle and because of destructive radiation field interference, a lower scattering intensity is observed at larger scattering angles. Therefore, for large macromolecules exhibiting light scattering assymmetry, one must estimate R_0 from measurements of R_θ by carrying out a mathematical angular correction. A theoretical description of the triple detection SEC method with RALLS has been reported elsewhere [42,43].

In order to demonstrate the molecular weight range for which the angular correction is valid, a series of SEC experiments were carried out by Viscotek (SEC manufacturer). Data supplied by Viscotek, show that for a series of linear polystyrene standards with molecular weights in the range of 6000–3,000,000 g/mol, molecular weight data obtained by triple detection-RALLS using an angular correction show excellent agreement with both data provided by the supplier of the standards and SEC data obtained by Viscotek using a universal calibration method, The excellent agreement between the triple detection data and the universal calibration data implies that the angular correction works well for linear polymers of up to 3,000,000 g/mol.

We would, however, note that the potential errors associated with the angular correction do become larger when the size of the molecule becomes very large, and some of the NaPSS combs are very large molecules! Furthermore, in our analyses, the calibration constants (detector response) for the aqueous SEC system were determined using a solution of a narrow molecular weight distribution PEO of known molecular weight, solution concentration and intrinsic viscosity (M_w 43,000 g/mol,

Table 3
Molecular characteristics of the poly(sodium 4-styrene sulfonate) comb series

Comb[a]	% Conversion to sulfonate[b]	$M_{n\ \mathrm{comb\ theory}}$[c] (g/mol)	$M_{n\ \mathrm{SEC}}$[d] (g/mol)	$M_{w\ \mathrm{SEC}}$[d]$\times10^{-3}$ (g/mol)	PD[e] PS comb
Linear standard	–	–	114,000	153,000	1.34
S175-35-28	93	2,154,000	2,660,000	4,180,000	1.57
S105-27-30	82	1,688,000	1,890,000	3,440,000	1.82
S105-13-35	100	1,000,000	1,190,000	2,260,000	1.89
S190-15-35	83	1,355,000	1,170,000	2,400,000	2.09
S190-23-33	87	1,801,000	1,650,000	3,400,000	2.11

[a] S denotes sulfonated: the numbering protocol refers to the ‘parents’ polystyrene combs as explained in Table 2.

[b] Determined by titration of the acid with 0.1 M NaOH.

[c] $M_{n\ \mathrm{comb\ theory}}$ calculated from PS comb M_n results, assuming 100% conversion in the sulfonate.

[d] $M_{n\ \mathrm{SEC}}$, $M_{w\ \mathrm{SEC}}$, value from the triple detector SEC.

[e] PD is the polydispersity of the comb M_w/M_n.

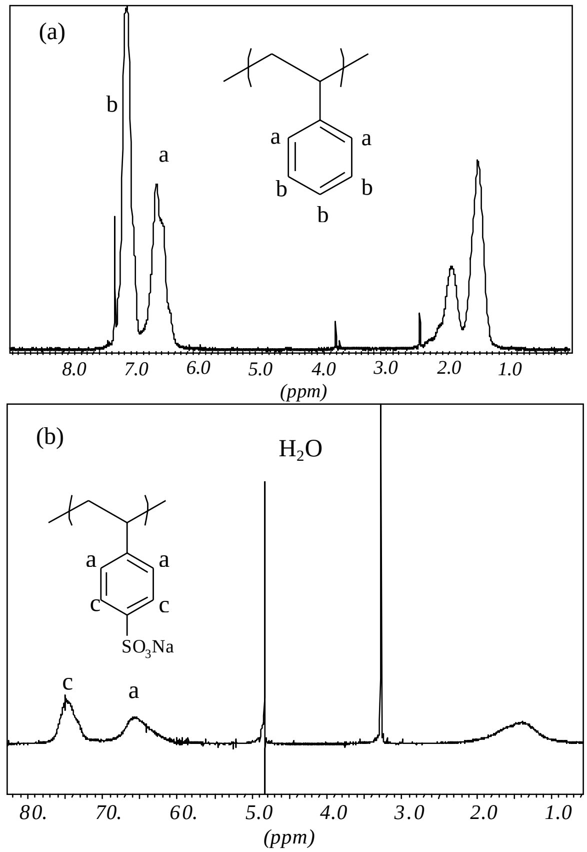


Fig. 4. (a) ^{1}H NMR of a polystyrene comb prior to sulfonation ($CDCl_3$) and (b) after sulfonation (D_2O).

d*n*/d*c* 0.135). This can introduce the possibility of further inaccuracies since the standard adopts a random coil conformation in solution whereas the samples of NaPSS combs to be analysed, being polyelectrolytes, tend to adopt an extended rod-like configuration of electrostatic blobs [44], the flexibility of the polymer chain being somewhat dependent on salt concentration. This introduces the possibility of further inaccuracies. In order to help understand the magnitude of some of these issues we first analysed two NaPSS linear ‘standards’ supplied by polymer standards service. These materials were prepared by the sulfonation of narrow polystyrene standards with molecular weights ($M_{\rm w}$) 43,500 and 77,500 g/mol, respectively, and polydispersities of 1.03 and 1.05, respectively. Data supplied by Polymer Standards Service indicated molecular weights ($M_{\rm w}$) for the sulfonated linear polymers of 81,800 and 145,000 g/mol, respectively, and polydispersities of <1.2. Using the aqueous SEC eluent as the solvent solutions of the linear NaPSS ‘standards’ were prepared in volumetric flasks for accurate solution concentrations, and a value for the d*n*/d*c* of NaPSS of 0.177 was calculated using the SEC triple detection method which had previously been calibrated (for detector response) with a narrow molecular weight distribution linear PEO standard. Using this value of 0.177 for the d*n*/d*c* of NaPSS the molecular weights ($M_{\rm w}$) obtained for the two linear NaPSS standards were 88,700 and 152,700 g/mol, in excellent agreement with the supplied values. The polydispersities were 1.20 and 1.34, respectively, which are higher than, but not dissimilar to, those provided by polymer standards service suggesting at least for linear samples of NaPSS the triple detection method (with angular correction), calibrated with PEO gives reasonably reliable data.

The difference in the polydispersity between the linear polystyrene precursors and the NaPSS comb samples may be due to a number of factors including a variable degree of sulfonation from molecule to molecule and from sample to sample which could affect the d*n*/d*c*, anomalies arising from the SEC analysis as alluded to above and traces of cross-linking/degradation, although evidence of the latter is not evident from the SEC chromatograms which are in the main reasonably symmetric.

The SEC chromatograms (refractive index detector) for all the sulfonated combs are shown in Fig. 5. It can be seen that all the traces are reasonably symmetrical except for S 105-13-35, which has a high molecular weight shoulder. The traces also suggest the presence of a low molecular weight peak at around 14.5 min, which can be attributed to the presence of approximately 1% residual branch material remaining after the fractionation of the PS comb. Additionally, Fig. 6 shows all the traces (refractive index, viscosity and RALLS) generated for the sample with the greatest apparent polydispersity S 190-23-33, and it can be seen that they are monomodal. The results from SEC analysis of the NaPSS combs are listed in Table 3. The measured values of $M_{\rm n}$ show reasonable agreement with the calculated values (which have been based on the assumption of quantitative sulfonation); the greatest discrepancy is found for sample S 190-23-33, which also happens to have the highest molecular weight and reflects the difficulties

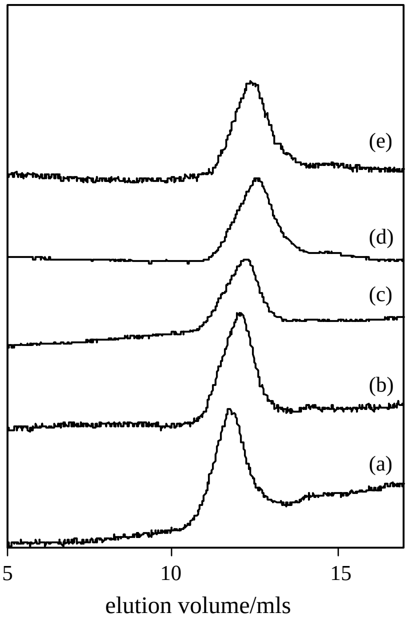


Fig. 5. Refractive index detector (SEC) traces from aqueous triple detector SEC (a) S175-35-28 (b)S105-27-30 (c) S105-13-35 (d) S190-15-35 (e) S190-23-33.

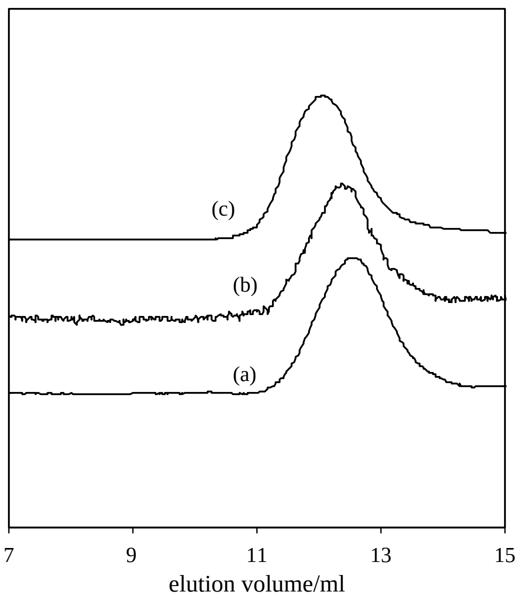


Fig. 6. SEC trace of S190-23-33 where (a) is the viscosity (b) the refractive index and (c) the light scattering response after normalization.

in obtaining accurate molecular weight data for high molecular weight polyelectrolytes. The values of M_w are higher than expected and the polydispersisties are higher than for the polystyrene comb precursors. To an extent this is to be expected given the data for the linear 'standards'. It is likely that the increase in polydispersity is due in some part to cross-linking occurring as a result of the sulfonation reaction, given that cross-linking reactions have a lesser effect on M_n than on M_w, and to the different (non-random coil) conformation of the sulfonated combs in solution. Other possible SEC anomalies such as interactions between the eluting polymers and the columns and polymer–polymer interactions have been minimized (but maybe not eradicated) by the choice of solvent and polymer solution concentration. It was observed in preliminary analyses of the sulfonated combs at solution concentrations in excess of 4.0 mg/ml that the chromatograms exhibited significant bimodality, this could be attributed to either column overloading or to aggregation. At much lower concentrations (less than 0.4 mg/ml) monomodal distributions have been observed. The monomodal SEC chromatograms also demonstrate that any cross-linking is limited and although the chromatograms are broad, the structure of the combs has been maintained.

5. Conclusions

The ability to control the extent of chloromethylation by employing a zinc (II) chloride catalyst permitted the synthesis of a series of polystyrene combs in which the branch lengths were all similar but the number of (randomly placed) branches varied. The combs were successfully sulfonated to yield polystyrene sulfonic acid combs and then neutralized to give a series of poly(sodiurn 4-styrene sulfonate) combs. The combs were analyzed by ^{1}H NMR and titration and thus shown to be highly sulfonated. Aqueous SEC, using a triple detection method with angular correction showed reasonable agreement between predicted and actual number average molecular weights and furthermore demonstrated the lack of significant cross-linking or degradation and the overall the preservation of the comb structure after sulfonation. The synthesis of a series of comb polyelectrolytes opens up the opportunity to examine the structure–property relationships of such materials and furthermore to compare them to biological molecules such as proteoglycans.

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