JOURNAL OF
Materials
CHEMISTRY

Realisation of ORMOSIL ionomers by the crosslinking of propyl methacrylate siloxane and a protected styrenesulfonic acid

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Received 13th October 1999, Accepted 21st January 2000

1,2,3,4-Tetrahydro-1-naphthylideneamino styrene-*p*-sulfonate (NISS) and poly(propyl methacrylate siloxane) (PMS) were free-radically crosslinked, yielding insoluble copolymers in which the siloxane and NISS components appear well intermixed. These materials were then treated with ultraviolet radiation to deprotect the sulfonic acid functionality and give insoluble hydrophilic ionomers which are stable to temperatures greater than 150 °C. Materials were characterised, before and after ultraviolet deprotection, using FTIR and various NMR spectroscopies, thermogravimetry and differential thermal analysis.

Introduction

Many polymeric materials can be used for ion exchange and/or ion conductivity applications. Most of the best performance polymers for proton ion exchange and conductivity contain the sulfonic acid functionality.[1–3] Examples include: perfluorinated polymers containing pendant sulfonic acid capped sidegroups such as Flemion®, Axciplex®, Nafion®[2] and BAM 3G®, sulfonated poly(vinylidene difluoride) PVDF,[4] sulfonated styrene-grafted PVDF systems,[5,6] and sulfonated polybenzimidazole.[7]

Current interest lies in the development of materials that perform well in their respective roles at elevated temperatures. Materials such as sulfonated polyphosphazene systems (P=N backbones)[8,9] and siloxane/perfluorocarbon sulfonated hybrid inorganic–organic systems have been the emphasis of some studies.[10,11] Our work concentrates on the introduction of the sulfonic acid functionality into organically modified siloxanes (ORMOSILS). There are major benefits in the use of hybrid organic–inorganic materials; such materials can exhibit the properties of both the inorganic and organic components. The inorganic network can impart improved thermal stability,[12] while the organic networks enable the introduction of a large variety of functionality. ORMOSILS, with siloxane backbones, do suffer from some disadvantages; they are not resistant to strong acids or bases and when they are sulfonated with traditional sulfonating agents such as sulfuric acid and chlorosulfonic acid (to give polybenzyl sulfonic acid siloxane for example)[13,14] disruption of the siloxane backbone can occur.

Our current programme is concerned with minimising siloxane backbone disruption by investigating milder sulfonation methodologies. In a previous paper the introduction of sulfonic acid groups by the mild oxidation of thiol (SH) groups was investigated.[15] This study utilises a protected styrene sulfonic acid precursor, 1,2,3,4-tetrahydro-1-naphthylideneamino styrene-*p*-sulfonate (NISS),[16,17] which is soluble in organic solvents and hence can be used simply to form organic–inorganic hybrid materials (*e.g.* Scheme 1). Poly(propyl methacrylate siloxane) was chosen as the inorganic component as it is cheap, readily available, and undergoes facile free radical reactions. On ultraviolet irradiation ($\lambda = 254$ nm) the sulfonic acid groups are deprotected.

Experimental

All solvents were dried over sodium wire (with benzophenone indicator) under a dried nitrogen atmosphere.

Infrared spectroscopy

Samples for infrared analysis were prepared as potassium bromide discs for solids, or as pressed films between sodium chloride plates for liquids. Infrared spectra were collected over the range 400–4000 cm^{-1} using a Nicolet Magna-IR 550 spectrometer.

NMR analysis

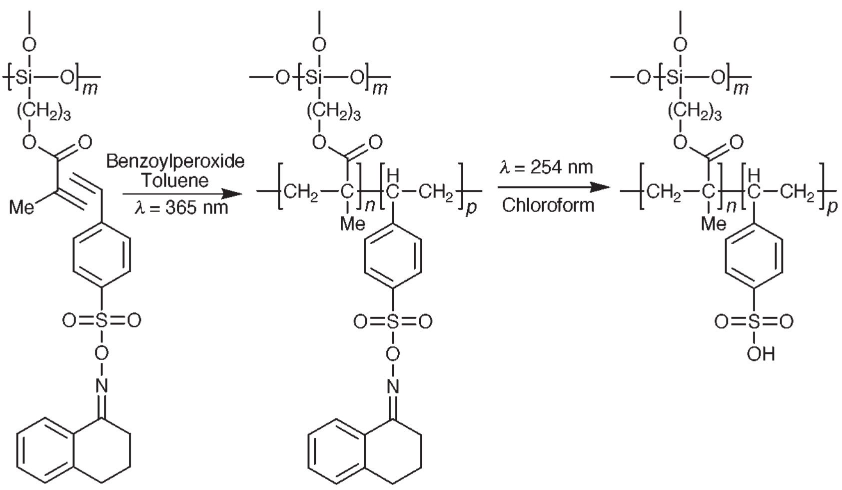
High resolution solution state ^{1}H, ^{13}C-{^{1}H} and ^{29}Si-{^{1}H} NMR spectra of precursor materials were recorded using either a Bruker AC300 or a Bruker AX400 spectrometer, with 5 mm sample tubes and a probe temperature of 20 °C. Samples were prepared in $CDCl_3$ solution with chromium(III) acetylacetonate added to aid relaxation of the ^{29}Si nuclei.

High resolution solid state ^{13}C and ^{29}Si data were collected at the EPSRC solid state service (Durham) on a Varian Unityplus 300 spectrometer. Carbon-13 spectra were normally recorded using cross polarisation (contact time of 1 ms) with a flip-back pulse after acquisition and a relaxation delay of 1 s. ^{29}Si spectra were recorded with cross polarisation (contact times of 3–4 ms) and flip-back. Direct polarisation experiments were carried out with some samples to compare with the cross polarisation experiments, and for more quantitative results. Rotor spin rates of 4–5 kHz were used throughout. Specialist experiments (*e.g.* WISE 2-D NMR experiments) are described in detail in the NMR results section.

Ultraviolet analysis

The ultraviolet spectrum of NISS (as a dilute solution in chloroform) was recorded on a Unicam UV4 spectrometer, with the sample in a sodium chloride cell. Spectra were also

DOI: 10.1039/a908218b



Scheme 1 The crosslinking of poly(propyl methacrylate siloxane) and NISS ($\lambda = 365$ nm), and the release of the tetralone oxime protecting group ($\lambda = 254$ nm). Note the sequential use of ultraviolet radiation of two different frequencies.

recorded as a function of duration of ultraviolet irradiation ($\lambda = 254$ nm).

Syntheses

1-Tetralone oxime. Tetralone (98%, Aldrich) and hydroxylamine hydrochloride (99%, Aldrich) were used without further purification. 1-Tetralone (3,4-dihydronaphthalen-1(2*H*)-one) (20.6 g, 0.14 mol) and hydroxylamine hydrochloride (15.7 g, 0.23 mol) were dissolved in a mixture of ethanol (55 cm^3, AR grade) and water (14 cm^3). Sodium hydroxide (28 g, 0.70 mol, powder) was slowly added as the mixture was stirred in an ice–water bath. The mixture was refluxed for 5 min, cooled to room temperature and then poured, with vigorous stirring, into a solution of concentrated hydrochloric acid (83 cm^3) in water (550 cm^3). The creamy solid that formed was recovered by filtration, washed with water and dried in a vacuum oven at 50 °C for 3 h. 1-Tetralone oxime was recovered as an off-white solid (20.6 g, 0.13 mol, 93% of theoretical yield): mp = 104–106 °C. ^{1}H NMR: δ 7.9 (1H, d, $^2J = 9$); 7.3–7.2 (3H, m); 2.9 (2H, t, $^2J = 6$); 2.8 (2H, t, $^2J = 6$); 1.9 (2H, m). ^{13}C NMR: δ 155.5 (*C*=N–OH) [literature value[18] δ 155]; 139.9(ar.), 130.5(ar.), 129.2(ar.), 128.7(ar.), 126.5(ar.), 124.1(ar.), 29.8(al.), 23.9(al.), 21.3(al.).

Styrene-*p*-sulfonyl chloride. Sodium styrene-*p*-sulfonate (Aldrich), quinol (99%, BDH) and phosphorus pentachloride (95%, Aldrich) were used without further purification. Synthesis of styrene-*p*-sulfonyl chloride was as reported by Iwakura *et al.*[19] Quinol (0.41 g, 0.037 mol) was added to a suspension of sodium styrene-*p*-sulfonate (36.4 g, 0.18 mol) in chloroform (180 cm^3). Phosphorus pentachloride (47 g, 0.23 mol) was then added slowly to the suspension (cooled in an ice–water bath). After heating the mixture for 2 h at 45–50 °C, the precipitate was removed by filtration and the chloroform removed under vacuum. The resulting yellow liquid was dissolved in diethyl ether (150 cm^3) and then, after cooling to 0 °C, washed carefully with ice-cold water (2×50 cm^3). The ethereal solution was dried over anhydrous calcium chloride and stored in a freezer overnight to minimise any polymerisation. After the ether was removed under vacuum, crude styrene-*p*-sulfonyl chloride was obtained as a yellow liquid (22.14 g, 0.11 mol, 63% of theoretical yield) and used immediately; no further purification was carried out as this leads to polymerisation of the product.[19]

1,2,3,4-Tetrahydro-1-naphthylideneamino styrene-*p*-sulfonate (NISS). Pyridine (AnalaR grade, BDH) was stored over activated molecular sieve (grade 5A). 1-Tetralone oxime (16.0 g, 0.099 mol) was dissolved in pyridine (37 cm^3), yielding a deep brown solution. Crude styrene-*p*-sulfonyl chloride (22.14 g, 0.11 mol) was added dropwise with stirring and cooling in an ice–water bath. The mixture was stirred at 15 °C for 3 h, and then poured into an ice-cold solution of concentrated hydrochloric acid (60 cm^3) in water (360 cm^3). The resulting red mixture was extracted into chloroform (3×150 cm^3), yielding a red organic solution which was washed with water (50 cm^3) and then dried over anhydrous potassium carbonate overnight. After filtration to remove the desiccant, the chloroform was removed under vacuum, leaving a thick red oil.

The product oil was continuously extracted with boiling heptane (5×20 cm^3). On cooling, a fluffy white precipitate formed. After recovery by filtration the white solid was recrystallised from toluene by slow addition of methanol. The 1,2,3,4-tetrahydro-1-naphthylideneamino styrene-*p*-sulfonate (NISS) (3.69 g, 0.011 mol, 11.3% of theoretical yield) [literature value:[20] 23% yield (the discrepancy arises from the rigorous purification of the product in this study)] was recovered as a brilliant, white fluffy powder; mp = 81–83 °C [literature value:[20] 80–82 °C]. ^{1}H NMR: δ 7.15–8.01 (8H, m); 6.75 (1H, dd); 5.45–5.90 (2H, dd); 2.83 (2H, t); 2.73 (2H, t); 1.84 (2H, m) [literature values:[20] δ 7.14–8.0 (8H, m); 6.77 (1H, dd); 5.45–5.9 (2H, dd); 2.84 (2H, t, $^2J = 6$); 2.73 (2H, t, $^2J = 6$); 1.85 (2H, m)]. ^{13}C NMR: δ 162.4 (*C*=N–O–S); 143.0 (ar.), 141.1 (ar.), 135.3 (ar.), 134.6 (ar.), 131.1 (ar.), 128.3 (ar.), 128.8 (ar.), 128.0 (ar.), 126.5 (ar.), 125.3 (ar.), 118.0 (ar.), 29.3 (al.), 25.4 (al.), 21.0 (al.). Infrared (see Table 3): 1369 and 1177 cm^{-1} (S=O str.) [literature values:[20] 1370, 1180 cm^{-1}]. Ultraviolet: $\lambda_{max} = 256$ nm, $\varepsilon = 24\,000$ dm^3 mol^{-1} cm^{-1} in chloroform.

Poly(propyl methacrylate siloxane) (PMS). 3-(Trimethoxysilyl)propyl methacrylate (97%, Aldrich) was used without further purification. 3-(Trimethoxysilyl)propyl methacrylate (10.01 g, 4.03×10^{-2} mol) was stirred with a mixture of ethanol (9.28 g, 0.20 mol), water (2.19 g, 0.12 mol) and hydrochloric acid (32.2 cm^3, 0.10 mol dm^{-3}, 3.2×10^{-3} mol) at 50 °C for 2.5 h. Low boiling temperature materials were removed under vacuum. The resulting thick colourless oil was dissolved in toluene and filtered to remove any insoluble material. The toluene was then removed under vacuum. Poly(propyl methacrylate siloxane) was recovered as a thick clear, colourless oil (6.85 g, 3.80×10^{-2} mol, 94% yield). Infrared (see Table 3): 3000–2890 (C–H str. sat., m); 1719 (C=O str., α,β-unsat. ester, m); 1637 (C=C str. α,β-unsat. ester, s); 1453 (CH_2 deformation); 1322; 1298 (C–O str. ester); 1167–1013 (Si–O–Si, s); 940 cm^{-1}. ^{1}H NMR: δ 6.04 and 5.49 (1H each, broad,

$\mathrm{C}H_2$=C); 4.05 (2H, broad, C(=O)O$\mathrm{C}H_2$$\mathrm{CH_2}$); 1.87 (3H, broad, $\mathrm{H_2C}$=C($\mathrm{C}H_3$)C(=O)O); 1.73 (2H, broad, $\mathrm{OCH_2C}H_2\mathrm{CH_2Si}$); 0.65 (2H, broad, $\mathrm{CH_2C}H_2\mathrm{Si}$). ^{13}C NMR: δ 167.4 (broad, *C*=O); 136.2 and 125.3 (broad, *C*=*C*); 66.4 (broad, C(=O)O*C*$\mathrm{H_2}$); 22.2 and 18.2 (broad, C(=O)C(*C*$\mathrm{H_3}$)=$\mathrm{CH_2}$ and $\mathrm{OCH_2}$*C*$\mathrm{H_2CH_2Si}$); 8.6 (broad, Si*C*$\mathrm{H_2}$).

Crosslinked PMS (for NMR comparison). Poly(propyl methacrylate siloxane) (0.45 g, 2.5×10^{-3} mol Si assuming $\mathrm{O_{3/2}SiCH_2CH_2CH_2OC(=O)C(CH_3)C{=}CH_2}$ as the formula of the repeat unit) and benzoyl peroxide (0.10 g, 4.1×10^{-4} mol) were dissolved in toluene (20 cm^3) in a thin-walled glass vessel. Nitrogen was bubbled through the solution to ensure the absence of any oxygen, and then the tube was sealed. The solution was then irradiated with ultraviolet light ($\lambda = 365$ nm, 4 mW cm^{-2}) with stirring for 20 h. The formation of a gel suspended in the solution was observed within the first 2 h. After recovery by filtration, the gel was washed with fresh toluene and then dried in a vacuum oven at 50 °C overnight. The product was recovered as a pure white powder (0.47 g). IR: 3000–2890 (C–H str. sat., m); 1734 (C=O str. sat. ester, s); 1200–1050 (O–Si–O, s).

Crosslinked poly(NISS-co-propyl methacrylate siloxane). Benzoyl peroxide (>97%, Fluka) was stored in a freezer at −25 °C and used without further purification. Poly(propyl methacrylate siloxane) (3.52 g, 0.0195 mol Si assuming $\mathrm{O_{3/2}SiCH_2CH_2CH_2OC(=O)C(CH_3)C{=}CH_2}$ as the formula for the repeat unit), NISS (6.36 g, 0.19 mol) and benzoyl peroxide (0.34 g, 0.014 mol) were dissolved in toluene (100 cm^3) in a thin-walled glass vessel. Nitrogen was bubbled through the solution to ensure the absence of any oxygen, and then the vessel was sealed. The solution was then irradiated with ultraviolet light ($\lambda = 365$ nm, 4 mW cm^{-2}) for 1 day with stirring. The formation of a gel (suspended in the solution) was observed within the first 2–4 h. After recovery by filtration, the gel was washed with fresh toluene, methanol and diethyl ether, and then dried in a vacuum oven at 50 °C overnight. The copolymer **I** was recovered as a pure white powder (6.89 g). The above procedure was repeated with various concentrations of initiator (**II** and **III**) and a lower NISS : siloxane ratio (**IV**) (see Table 1). A crosslinking reaction time of 1 day was chosen as, after this length of time, the composition of the insoluble solid was constant (confirmed with EDAX studies).

Ultraviolet treatment of the copolymers

I, **II**, **III** or **IV** (2.0 g) was suspended in $\mathrm{CHCl_3}$ (50 cm^3) and irradiated in a photolysis cell with intense (50 W) ultraviolet light ($\lambda = 254$ nm) and with stirring for 24 h. The solids were then recovered by filtration, washed with chloroform and dried in a vacuum oven at 50 °C. The resulting products were brown solids **UVI**, **UVII**, **UVIII** and **UVIV** (typically 1.5 g yield) and gave acidic solutions when suspended in water (pH ≈ 3).

Table 1 The concentrations (mol dm^{-3}) of reactants for ORMOSIL synthesis

	Amount/mol		
	Concentration/mol dm^{-3}		
Material	NISS	PMS	Initiator concentration/ mol dm^{-3}
I	*0.0194* 0.194	*0.0195* 0.195	0.014
II	*0.0194* 0.194	*0.0194* 0.195	0.021
III	*0.0194* 0.194	*0.0195* 0.195	0.005
IV	*0.0113* 0.130	*0.226* 0.260	0.014

Results and discussion

Ion exchange

Ion exchange titrations were carried out by stirring the insoluble materials **I** and **UVI–UVIV** in KCl solution (1 mol dm^{-3}) for a week and then titrating with aqueous KOH solution (0.1029 mol dm^{-3}) under a nitrogen atmosphere (to exclude $\mathrm{CO_2}$ contamination) until pH 7 was achieved. Unfortunately, side reactions (possibly with residual oxime functions) were encountered during the titrations; this was first evident when material **I** had a larger ion exchange capacity than material **UVI**. It was clear that ion exchange titrations of this type were of no quantitative use for this system.

UV data

To demonstrate the effect of ultraviolet light on NISS the following experiment was performed. A solution of NISS in chloroform (5×10^{-6} mol dm^{-3}) was irradiated for increasing periods of time with ultraviolet light at $\lambda = 254$ nm (Phillips Model UV-54 lamp). The ultraviolet spectrum of the solution was recorded after each period of irradiation. The results are shown in Fig. 1. The decay of the peak at $\lambda = 254$–256 nm (arising from the *C*=*N*–O–S– group) is clearly visible, along with the increased intensity above $\lambda = 290$ nm which results from one of the by-products of the decomposition (>C=N–N=C<). The by-products >C=O, $\mathrm{NH_3}$ and NO are also formed.[20]

EDAX data

The Si : S ratio was investigated by EDAX analysis (recorded using a Philips SEM 501B scanning electron microscope with samples coated with a conducting carbon film†) as this gives a quantification of the amounts of the siloxane (which contains Si) and NISS (which contains S) components in the copolymers (Table 2). The results confirm that varying the concentration of reactants varies the ratio of the different components in the final copolymers. An important observation is that the NISS polymerises faster than the PMS, *e.g.* a PMS : NISS reactant

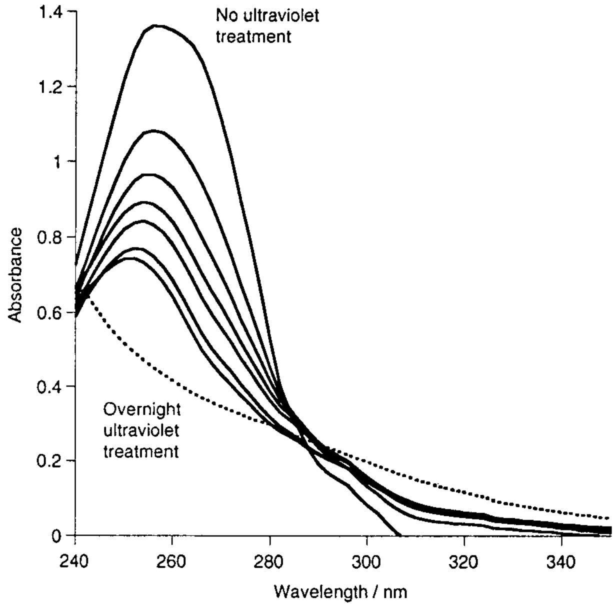


Fig. 1 The ultraviolet spectra of a solution of NISS in chloroform after various periods of ultraviolet treatment at $\lambda = 254$ nm (top to bottom: $t = 0$, 5, 10, 15, 20, 40, 60 min). The dotted line is the spectrum after overnight treatment (complete photolysis).

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†The usual gold coating could not be used as gold signals interfere with sulfur signals and quantitative results are less reliable.

Table 2 EDAX data for the ORMOSILS synthesized

Material	EDAX		Material	EDAX	
	% Si	% S		% Si	% S
I	37	63	**BUV1**	39	61
II	42	58	**BUV2**	38	62
III	41	59	**BUV3**	38	62
IV	50	50	**BUV4**	50	50

ratio of 2 : 1 produces a copolymer with a siloxane : NISS component ratio of 1 : 1.

Ultraviolet treatment ($\lambda = 254$ nm) does not significantly alter the siloxane : NISS ratio, indicating that the polymer remains substantially intact apart from the loss of the tetralone oxime protecting group. Varying the concentration of initiator has a very limited effect on the final composition; this is as expected as the initiator concentration would affect the molecular mass of linear polymers, but this system is crosslinked. The crosslinking reaction times are, as discussed above, sufficiently long that the composition is no longer changing in the copolymers.

NMR data[21]

^{13}C and ^{29}Si CP-MAS NMR.[22,23] To simplify the interpretation of the ^{13}C solid state NMR spectra of materials **B1**–**B4** the ^{13}C spectrum of PMS when crosslinked without NISS was initially examined (Fig. 2). The *C*=O signal in the spectrum of crosslinked PMS is located at δ 176.6; the weak signal at δ 167.0 is due to some residual uncrosslinked PMS *C*=O carbons. Clearly a small number of methacrylate side-groups remain unreacted as the weak signals at δ 137.0 and 125.5 arise from the $C(O)\mathit{C}(Me)=\mathit{C}H_2$ carbons. The signals at δ 66.5 ($-\mathit{C}H_2OC(O)-$), 22.5 ($-CH_2\mathit{C}H_2CH_2-$), 18.3 ($-C(O)C(\mathit{C}H_3)=CH_2$) and 9.0 ($O_{3/2}Si\mathit{C}H_2-$) are simply related to signals found in the solution state ^{13}C NMR of PMS. The signals at δ 128.7, 55.3, 45.9, however, are not found in the solution spectrum of poly(propyl methacrylate siloxane). They arise from the carbons formed when the vinyl function of the methacrylate group has been crosslinked. The signal at δ 128.7 corresponds to the $C(O)\mathit{C}(Me)$ carbon. Finally, the signals at δ 238 and 115 are spinning sidebands associated with the *C*=O signal at δ 176.6.

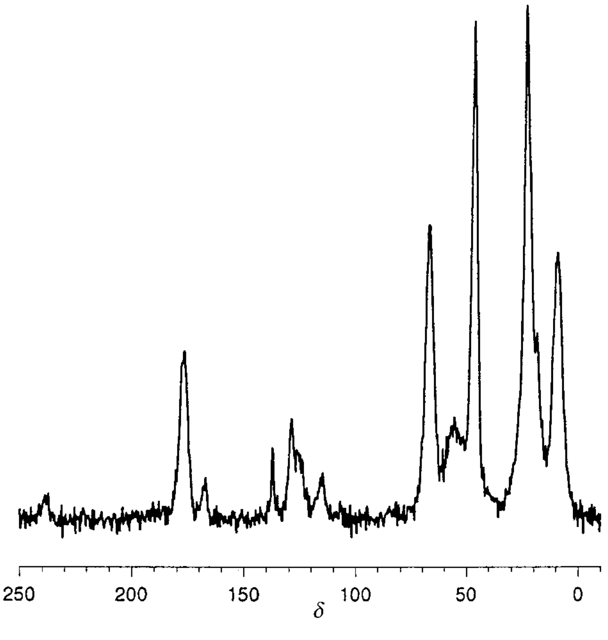

Fig. 2 The ^{13}C CP-MAS NMR of crosslinked poly(propyl methacrylate siloxane).

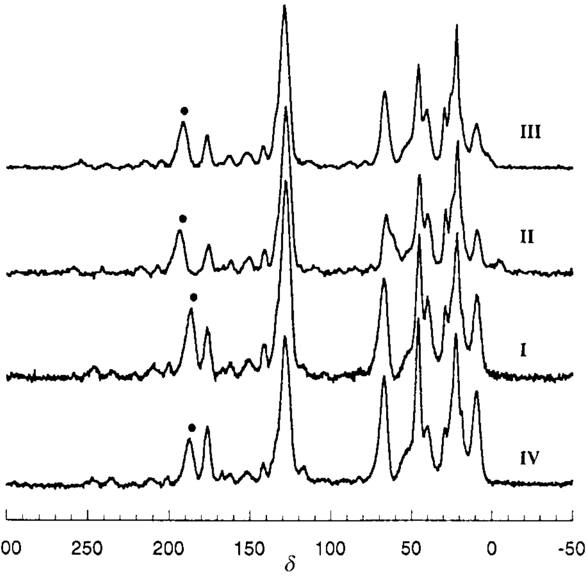

Fig. 3 The ^{13}C CP-MAS NMR spectra of copolymers **I**, **II**, **III** and **IV**. The signals marked ● are spinning sidebands (ssb) identified as such by varying the rotor spin rate. The spectra are stacked in the above order because, in the bulk of the text, **I** is first compared to **II** and **III**, and then **I** is compared to **IV**.

^{13}C CP-MAS NMR spectra for copolymers **I**–**IV** are shown in Fig. 3. Considering the spectrum of copolymer **I** in detail: the *C*=O signal of the siloxane has shifted to high frequency (δ 176.7 compared to 167.4 in the spectrum of PMS); the carbon is no longer conjugated. The *C*=N–O signal from the NISS component is at δ 162.9. Dipolar dephasing experiments[24] (with a 40 μs dephasing delay) were used to identify ^{13}C signals from non-protonated carbons. Subtraction of these signals from the full spectrum allowed signals from protonated carbons to be resolved. The large signal at δ 128 can be resolved into a signal at δ 127.9 corresponding to the aromatic *C*H carbons of the NISS component, an *ipso*‡ aromatic carbon signal at δ 134.4 and a signal due to the $C(O)\mathit{C}(Me)$ carbon at δ 128.4. The signals at δ 151.3, 141.8 and 116.4 account for the remaining three *ipso* aromatic carbons. The signal at δ 67.6 corresponds to the $C(O)O\mathit{C}H_2$ carbons and is also coincident with an overlapping spinning sideband (ssb) generated from the signal at δ 127.9.

In the range δ 0 to 60 the spectrum is more complex. The signals at δ 9.5 ($Si\mathit{C}H_2$), 21.9 (a cyclic $\mathit{C}H_2$ of the NISS component and an overlapping signal arising from the $CH_2\mathit{C}H_2CH_2$ of the siloxane component) and 29.3 (the remaining cyclic $\mathit{C}H_2$ of the NISS component) are simply assigned. The signals at δ 45.4 (protonated carbon), along with the broad hump to high frequency of this signal and the signal at δ 40.3 (protonated), are not present in the spectrum of either PMS or NISS. These signals correspond to the mixture of saturated carbons which is formed on radical crosslinking of the vinyl groups in NISS and PMS. A medium intensity overlapping quaternary aliphatic carbon signal at δ 45.4

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‡An aromatic carbon attached to a non-ring carbon.

remains unassigned and this indicates that the situation may not be as simple as suggested from other data.

Copolymer **IV** has twice as much siloxane as NISS in the reaction mixture, and the ^{13}C spectrum reflects this; all the carbon signals of the NISS component are decreased in intensity (in relation to the signals from the siloxane component) with respect to copolymer **I**. Copolymers **II** and **III**, synthesized with different initiator concentrations in the reaction mixture, give similar ^{13}C spectra to that of copolymer **I**, with only subtle variations in lineshapes. The principal variations are in the signals arising from the aliphatic carbons originating in the now crosslinked vinyl functions; the differing initiator concentrations have an effect on the structure of the crosslinking region but not on the macroscopic composition.

The ^{29}Si CP-MAS NMR spectra (Fig. 4) for materials **I**–**IV** each show two signals. The broad signal at δ −57 arises from Si–OH groups (silanol groups), while a signal at δ −66 arises from fully condensed $RSiO_3$ groups. The siloxane precursor used in the formation of **III** is not as extensively condensed as the siloxane precursors used in the other copolymers, even though consistent reaction conditions were used in the synthesis of PMS.

Comparing the ^{13}C CP-MAS spectrum (Fig. 5) of **UVI** to the spectrum of **I**, most of the carbon signals corresponding to the tetralone oxime protecting function of the NISS component have substantially decreased in intensity; this indicates protecting group removal by ultraviolet treatment. Two of the signals belonging to *ipso* aromatic carbons (δ 149.0 and 141.5) remain, as the benzene ring hosting the sulfonic acid group remains. The ^{13}C signals arising from the siloxane component appear mostly unaffected by ultraviolet irradiation and there is no evidence of the liberated sulfonic acid groups affecting the ester linkage in the methacrylate.

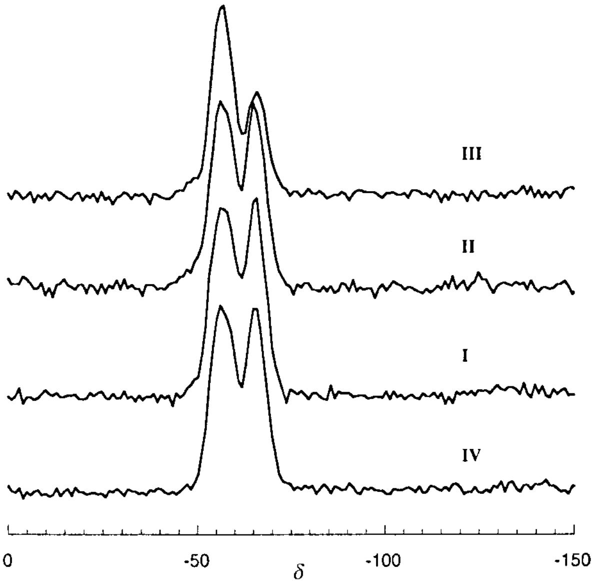

Fig. 4 The ^{29}Si CP-MAS NMR spectra of copolymers **I**, **II**, **III** and **IV**.

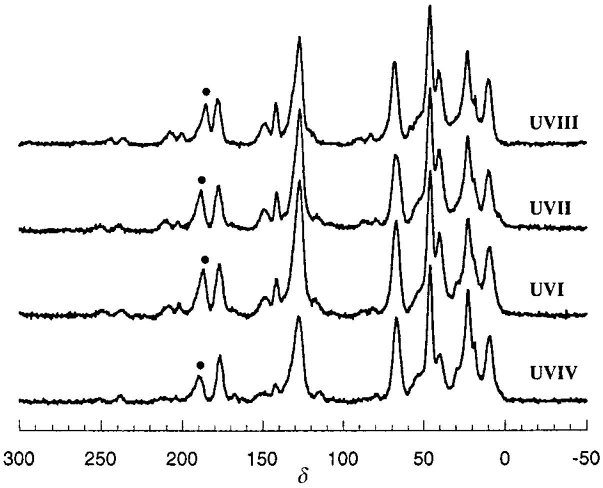

Fig. 5 The ^{13}C CP-MAS NMR spectra of copolymers **UVI**, **UVII**, **UVIII** and **UVIV**. The signals marked ● are ssb.

The ^{29}Si spectra in Fig. 6 show that the ratio of silanol Si atoms to fully condensed Si atoms varied on ultraviolet deprotection of copolymers **I**, **II**, **III** and **IV**, with fewer silanol groups being present after irradiation. All the copolymers now show similar degrees of condensation. This indicates that the removal of the protecting group, with the subsequent formation of sulfonic acid group, is partially disrupting the siloxane backbone, with the degree of condensation of silanol groups increasing.

Relaxation and ^1H solid state NMR studies. NMR studies can yield useful information on the morphological make-up of solid materials. The morphology is important as different chemical components could reside in segregated domains (*e.g.* for Nafion® the side chains form hydrophilic channels while the perfluoro backbone forms its own domains); a similar situation could exist with materials **UVI**–**UVIV** with the siloxane components forming separate zones within the material that are separated from the sulfonic acid/organic component.

Owing to the length of time it takes to record WISE spectra, it is often useful to look at the ^1H spectrum for any evidence of multi-component behaviour to assess if such a use of time is beneficial; for material **I** (Fig. 7) the bandshape is multi-component, with a narrow component and a broad component. A brief inversion-recovery T_1 (spin–lattice relaxation time) experiment over the whole sample gave a T_1 value of 0.7 s. Similar ^1H behaviour is observed for the other protected materials; the ^1H spectra of the ultraviolet deprotected materials also exhibited overlapping narrow and broad signals, though there was a greater differential between the linewidths compared with the protected materials (Fig. 8 shows the spectrum for **UVI**). There is clear evidence of multicomponent behaviour in the ^1H wideline spectra for all the materials and time intensive WISE experiments were justified.

WISE experiments[25] are ^1H–^nX correlation experiments ($^nX = {}^{13}C$ in this study), the feature of interest being the linewidth of the ^1H spectrum associated with each carbon signal. The ^{13}C WISE spectra were collected with a CP contact

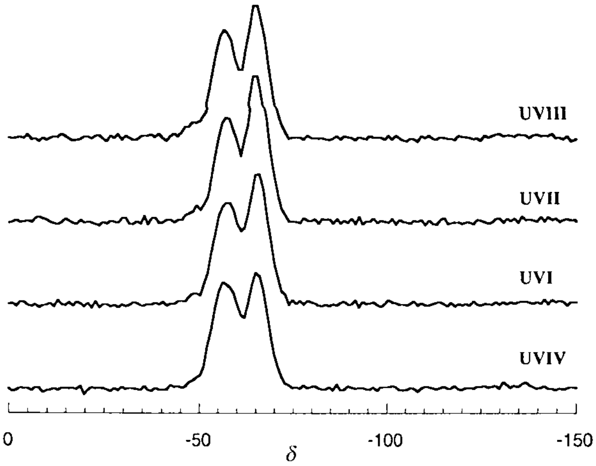

Fig. 6 The ^{29}Si CP-MAS NMR spectra of copolymers **UVI**, **UVII**, **UVIII** and **UVIV**.

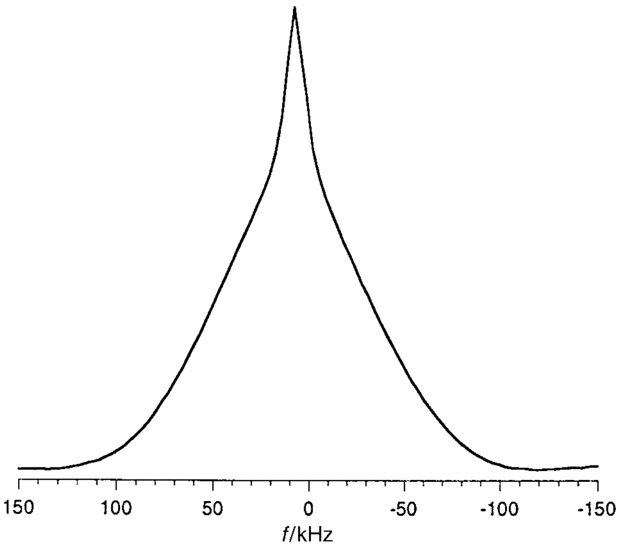

Fig. 7 The static ^{1}H NMR spectrum of copolymer **I**.

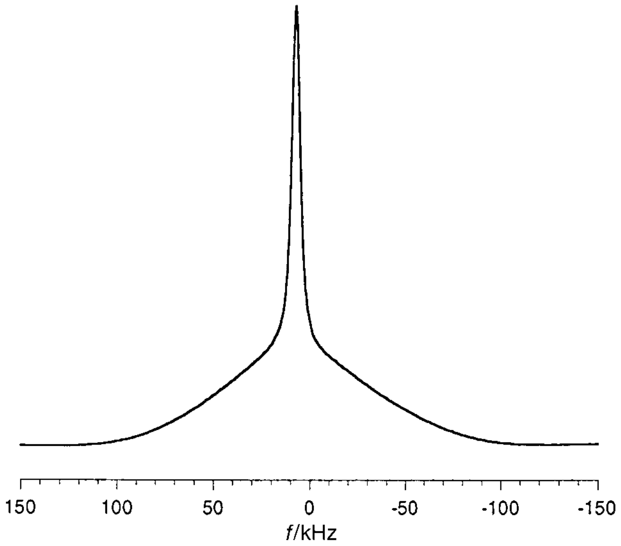

Fig. 8 The static ^{1}H NMR spectrum of copolymer **UVI**.

time of 0.2 ms and also with the TOSS (Total Suppression of Spinning Sidebands) pulse sequence to minimise the intensities of spinning sidebands. There is no evidence of the sharp bands from the original static ^{1}H spectrum in the WISE spectrum for material **I** (Fig. 9). The small differences in ^{1}H linewidths of the broad signal (between 32 and 46 kHz) in the ^{13}C–^{1}H WISE experiment can be explained with small variations in local motion and not macroscopic variation of composition within the sample. This poses the question of the origin of the narrow bands in the static ^{1}H spectrum.

The experiment was repeated with a mixing time (50 ms) added before CP contact (Fig. 10); this allows spin diffusion between any domains that might be present in the sample. With this added mixing time there is evidence of the narrower ^{1}H line superimposed on the original broad line in the WISE spectrum; this applies to all the signals in the carbon spectrum. Similar observations are made with the spectra of **IV**, **UVI** (Fig. 11) and **UVIV**. The spectra of the ultraviolet deprotected materials show a more obvious difference when recorded with and without the added mixing time; this is not surprising given that the narrow component in the ^{1}H spectrum was more prominent for these samples.

A T_2^{H}-filtered experiment was conducted where the CP could only take place from the narrow ^{1}H component. The result was a barely visible signal; this explains the lack of narrow signal in the WISE spectra without added mixing time. A short recycle time direct polarisation experiment was recorded which showed the signals not visible in the previous experiment; this proved that the failure to obtain a spectrum was due to inefficient cross polarisation. A further fast pulsing ^{13}C experiment showed no evidence for signals from a carbonaceous mobile phase or carbon-containing solvent which would both give narrow signals.

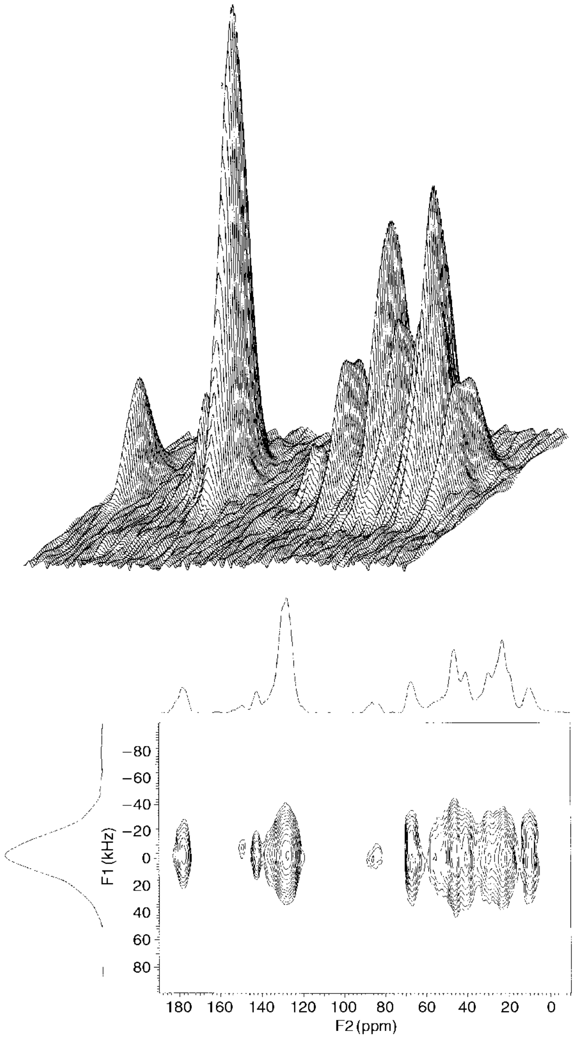

Fig. 9 ^{13}C–^{1}H WISE spectrum of copolymer **I** with no added pre-contact mixing time.

Delayed contact experiments are, in principal, sensitive to components in the spectrum that have different $T_{1\rho}{}^{\mathrm{H}}$; these relaxation times are in turn sensitive to the mobility of the local environment. For both samples **I** (Fig. 12) and **UVI**, ^{13}C CP-MAS NMR spectra were recorded with 0, 3 and 10 ms delays. Much of the signal has decayed away by 10 ms, hence the poorer signal to noise ratio level. No evidence that any constituent signal is behaving any differently from any other was observed. Finally, the standard CP spectrum for material **UVI** was recorded twice with short (0.2 ms) and long (15 ms) CP-contact times; the resulting spectra again appeared similar.

The WISE experiments did not detect separate phases of siloxane and NISS. This class of material presents a morphologically different scenario to that encountered with Nafion®, which consists of channels composed of the sulfonic acid containing side chains surrounded by a hydrophobic perfluorinated mass.[26] The mobile ^{1}H signal is assigned to water; this is consistent with the fast pulse ^{13}C result and with the difficulty of obtaining a CP spectrum for this component

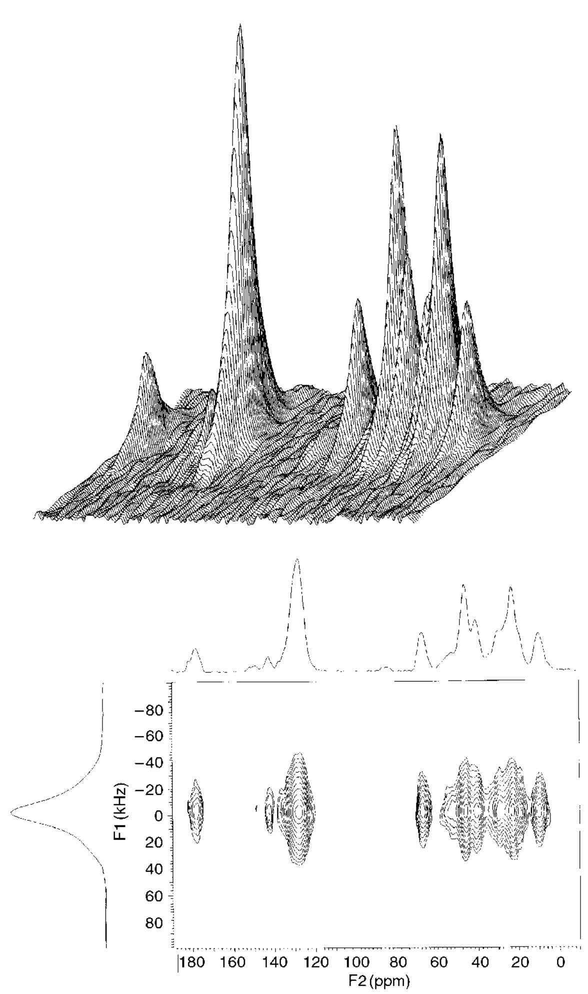

Fig. 10 ^{13}C–^{1}H WISE spectrum of copolymer **I** with 50 ms contact time added before CP contact, allowing spin diffusion within the sample.

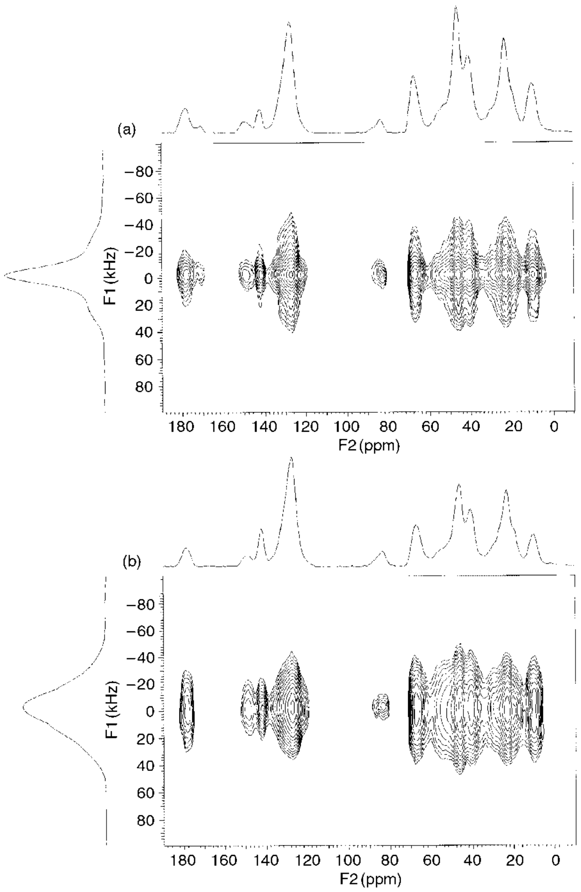

Fig. 11 The ^{13}C WISE NMR spectra of **UVI** (a) with 50 ms mixing time and (b) with no mixing time.

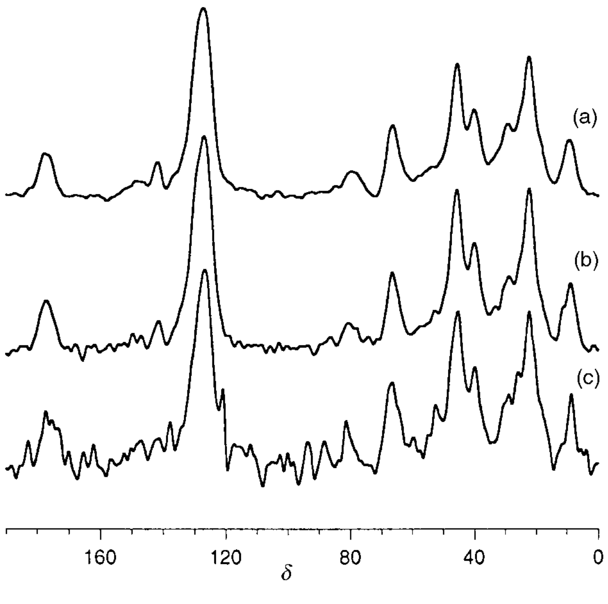

Fig. 12 The ^{13}C CP-MAS NMR of material **I** recorded with (a) 0, (b) 3 and (c) 10 ms delayed contact times.

(this would arise only if the water was tightly bound to the structure, which the narrow ^{1}H linewidth suggests is not the case). The increased prominence for this component in the deprotected materials (with liberated SO_3H functions) further supports this. The spin diffusion during the mixing time used shows close "contact" (by acid chemical exchange) of the water with the organic component.

Infrared spectra

The most prominent bands in the spectrum of NISS (Fig. 13, Table 3) are the S=O stretching modes (of the RSO_3–X group) at 1369 and 1177 cm^{-1}; these bands are clearly visible in the spectrum of copolymer **I** (Table 3). Also visible in the spectrum of **I** are various CH deformations which are observed in the spectra of NISS and PMS. The C=O (α,β-unsaturated ester) band at 1719 cm^{-1} for PMS is prominent in the spectrum of copolymer **I**, as is the Si–O band at 1113 cm^{-1} (though this band is sharper for **I**). The C=C stretch at 1637 cm^{-1} for PMS disappears on reaction with NISS; this confirms copolymerisation. The copolymer contains residual water and/or SiOH groups due to the presence of a broad OH stretch at 3475 cm^{-1}. The fingerprint region is complex, but the aromatic out of plane C–H deformations at 825 (*p*-disubstituted) and 764 cm^{-1} (*o*-disubstituted) are discernible.

The S=O stretches in the spectrum of copolymer **IV** are less intense than for **I**, which is consistent with the ^{13}C NMR data and with the higher siloxane containing composition for **IV**. The spectra of **II** and **III** are similar to that of **I**, again confirming the bulk composition of the copolymers is not dependent on the initiator concentration if reaction times of a day and longer are employed. On ultraviolet treatment of **I**, to give copolymer **UVI**, most of the bands assignable to the NISS component show a large drop in intensity, especially the S=O stretching bands and C–H deformation bands (Fig. 14). This is again consistent with the NMR data which indicates deprotection. Similar changes are seen on ultraviolet treatment of

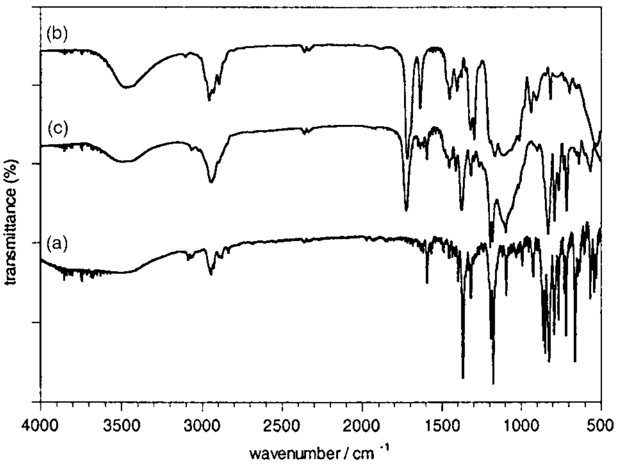

Fig. 13 The infrared spectra of (a) NISS, (b) poly(propyl methacrylate siloxane) and (c) copolymer **I**.

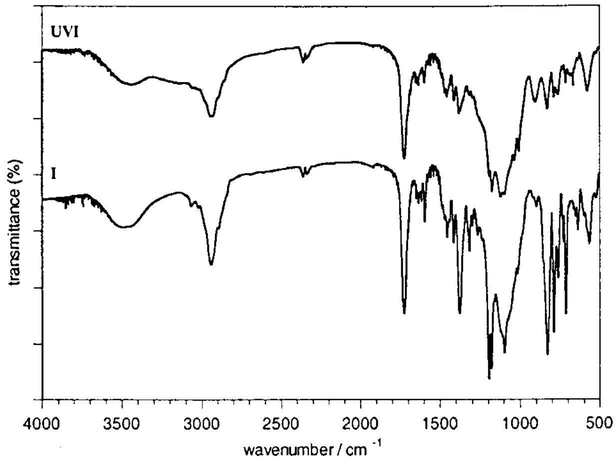

Fig. 14 The infrared spectra comparing copolymers **I** and **UVI**.

copolymers **II**, **III** and **IV**. The Si–O bands (1000–1200 cm^{-1}) change shape on ultraviolet treatment for all the materials, indicating the siloxane backbone is being partially disrupted due to the liberation of strong acid groups (confirming the deduction from ^{29}Si NMR spectra).

Thermal analysis (TG/DTA)

Thermogravimetry and differential thermal analysis (TG/DTA) were performed in flowing air (50 cm^3 min^{-1}) using a Stanton Redcroft STA-781 thermal analyser and a heating rate of 10 °C min^{-1}. All temperatures quoted in the text are sample temperatures measured with a Pt : Rh(13%) thermocouple. DTA used calcined α-alumina as reference.

For comparative studies, the TG/DTA of NISS and PMS were studied (Figs. 15 and 16). NISS is stable up to 254 °C and the initial loss of mass (42–44%) occurs with no detectable exotherm or endotherm. This corresponds to bond cleavage and loss of the protecting group, resulting in a styrene-*p*-sulfonic acid residue (calculated to be a 43.7% mass loss). This is a distinct feature in the thermal traces of all the oxime protected copolymers synthesized. Other features include the endotherm at 84 °C, which represents the melting temperature, and an exotherm at around 125 °C, which is due to the spontaneous polymerisation of NISS (no mass change evident).

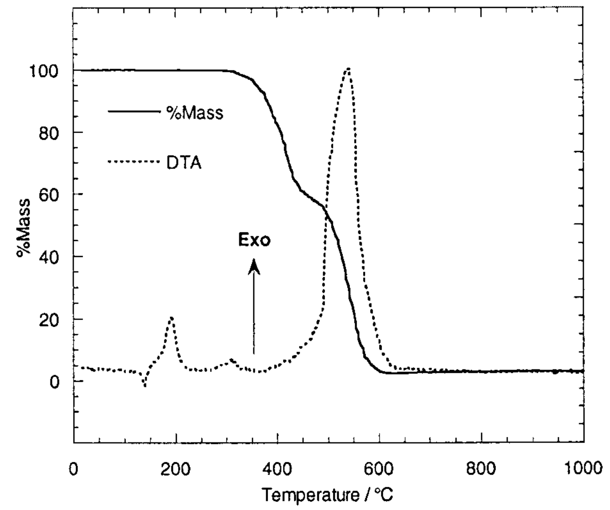

Fig. 15 The thermal analysis of NISS.

Fig. 16 shows the thermal analysis of poly(propyl methacrylate siloxane). The mass loss in the range 27–200 °C corresponds to loss of solvent incorporated in the siloxane. The 54.1% mass loss in the range 296–508 °C, with an associated

Table 3 The infrared spectra of poly(propyl methacrylate siloxane) (NaCl plates), NISS (KBr disk) and material **I** (KBr disk)

Wavenumber/cm^{-1}			
NISS	Poly(propyl methacrylate siloxane)	Material **I**	Assignment
—	3107w	—	C–H str.: C=CH$_2$ α–β unsat. ester
3090w	—	—	C–H str.: C=CH$_2$ conjugated
3071w	—	3072	C–H str.: ar.
2945m	2956	2944	C–H str.: al.
2929m	2924	2899	
2882w	2894		
2837w			
—	1719s	1725s	C=O str.: ester
—	1637m	—	C=C str.: conjugated to ar.
1595m	—	1595m	C=N str.: conjugated cyclic or Ar–H def.
—	1453m	1456w	C–H def.: –CH$_3$ and –CH$_2$–
—	1405m	1415w	C–H def.: –CH$_3$ sym. def.
1369s	—	1377s	S=O str.: R–O–SO$_2$R′
—	1321s	1318m	C–O str.: ester
1297s		1299w	
1194s	—	1197s	S=O str.: R–O–SO$_2$R′
1177s		1180s	
—	1168s	—	Si–(CH$_2$)$_3$O
—	1112s	1097s	O–Si–O broad
—	1012s	—	O–Si–O

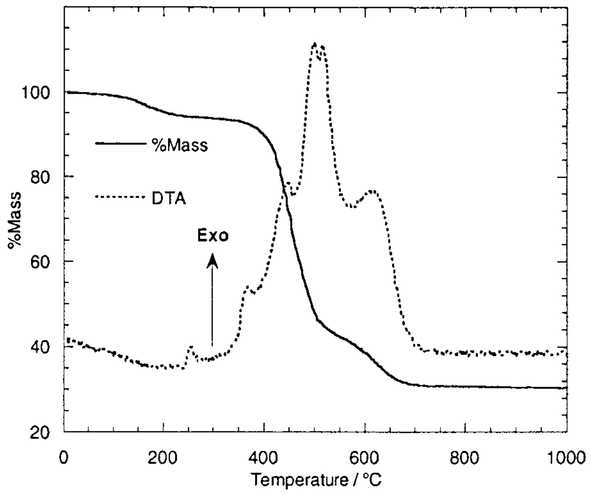

Fig. 16 The thermal analysis of poly(propyl methacrylate siloxane).

complex exotherm, is equivalent to the loss of a HCO-C(O)C(CH_3)=CH_2 unit (calculated to be a 54.7% mass loss) leaving the $O_{3/2}SiCH_2CH_3$ repeating fragment. The final mass loss of 13.0% corresponds to oxidation to leave SiO_2 (calculated to be an 11.8% mass loss). The residue was confirmed as SiO_2 by powder X-ray diffraction. The small discrepancies between observed and calculated mass losses are accounted for by noting the presence of uncondensed silanol groups.

For copolymer **I** (Fig. 17) the first significant mass loss ([A], 25.8%) begins at 225 °C and coincides with no noticeable thermal event (the 5.6% mass loss in the range 25–143 °C is due to solvent/water loss). At 351 °C the rate of mass loss increases, with a coincident large sharp exotherm, followed by an abrupt decrease in the rate of mass loss at 384 °C, after a 17.1% mass loss [B]. The final 43.4% mass loss [C] then continues up to 700 °C, with an associated broad exotherm. This pattern is also observed for **II**, **III** and **IV** (Table 4). The data clearly show that the different concentrations of initiator have some effect on the structure of the polymers; the values of the mass losses [A], [B] and [C] vary, but the total mass losses are similar (within experimental error $\approx 1\%$) because bulk compositions are not affected (as indicated by EDAX, NMR and infrared studies). An increased siloxane content of the copolymer results in the expected lowering of the total mass loss as can be seen for material **IV**.

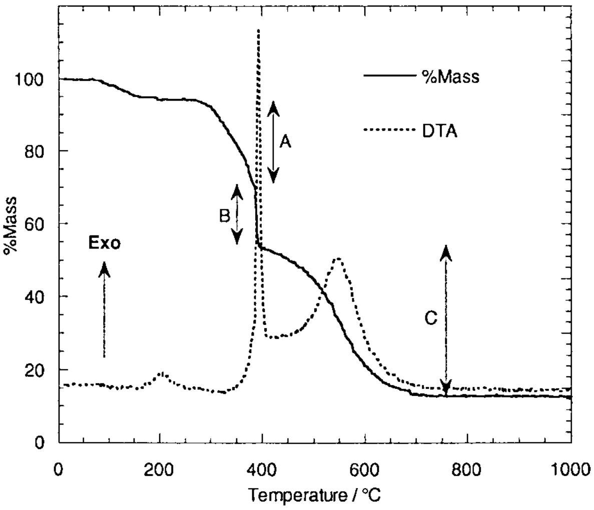

Fig. 17 The thermal analysis of copolymer **I**.

Table 4 The TG data for copolymers **I**–**IV** as percentage mass losses; [A], [B] and [C] are defined in Fig. 17. Temperature stabilities are estimated (±20 °C error) from the commencement of mass loss [A]

		Mass loss				
Material	Temperature stability/°C	[A]	[B]	[A]+[B]	[C]	Total
I	225	25.8	17.1	42.9	43.4	86.3
II	202	24.1	21.7	45.8	39.4	85.2
III	222	27.8	20.6	48.4	37.4	85.5
IV	227	25.1	21.0	46.1	35.4	81.5

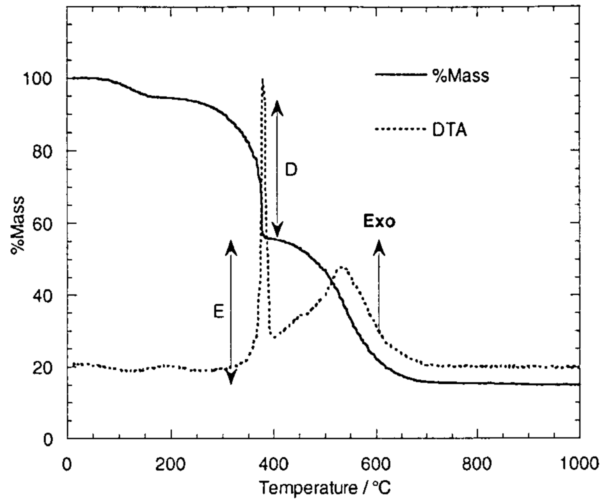

Fig. 18 The thermal analysis of copolymer **UVI**.

The TG/DTA traces for copolymer **UVI** (Fig. 18) are similar to those for **I**, but with important differences. The mass loss in the range 25–131 °C is again due to the loss of incorporated solvent/water. The 39.8% mass loss [D] in the range 159–377 °C is smaller than the corresponding 42.9% mass loss for **I** ([A]+[B]), confirming deprotection on ultraviolet treatment. The final 43.7% mass loss [E] is similar in magnitude to the equivalent mass loss for **I** ([C], 43.4%). Copolymers **UVII**, **UVIII** and **UVIV** behave similarly. Table 5 gives the short-term thermal stabilities of the deprotected materials; while these stabilities are lower than for the protected materials, they are stable at $T \leqslant 150$ °C (much higher than the short-term stabilities of siloxanes containing alkanesulfonic acid functions).[15]

Conclusion

1,2,3,4-Tetrahydro-1-naphthylideneamino styrene-*p*-sulfonate (NISS, a novel protected styrenesulfonic acid) and poly(propyl methacrylate siloxane) (PMS, a cheap and readily available siloxane precursor) can be free-radically copolymerised yielding insoluble materials. Chemically segregated domains (as found in Nafion®) could not be detected from WISE NMR data and were not anticipated from the synthetic methodology. These materials can then be treated with ultraviolet radiation ($\lambda = 254$ nm) to release the sulfonic acid functions, forming insoluble hydrophilic materials which exhibited short-term temperature stabilities to at least 150 °C.

Table 5 Temperature stabilities for materials **UVI**–**UVIV** estimated (±20 °C error) from the commencement of mass loss [D]

Material	Temperature stability/°C
UVI	183
UVII	181
UVIII	176
UVIV	171

Potential uses for these materials include ion exchange applications and applications where proton conducting membranes are utilised (*e.g.* in fuel cell applications). The siloxane : sulfonic acid ratio can be tailored by varying the amount and concentration of the reactants in the radical copolymerisation reaction. Varying the initiator concentration affects only the microstructure of the crosslinked region of the materials, but not the final bulk composition. There is evidence that the Si–O backbone of the siloxane component has partially been disrupted on deprotection and liberation of the sulfonic acid groups, but there is no evidence of the ester group of the methacrylate being affected. These materials demonstrate the viability of this methodology of introducing sulfonic acid groups in siloxane-containing materials, with the use of NISS as a novel protected styrene sulfonic acid.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council for funding this work (grant GR/K 58722) and for access to the national solid-state NMR Service at Durham. We also thank Drs David Evans (Beijing University of Chemical Technology) and Sara Flint (Exeter), for useful discussions, and the Earth Resources Centre at the University of Exeter, for access to SEM.

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Paper a908218b