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Realisation of siloxane ionomers by mild oxidation of alkylmercaptosiloxanes

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New siloxane polymers containing pendant mercaptopropyl and methyl groups have been synthesized by an acid-catalysed sol–gel reaction. The mercapto group was then oxidised to sulfonic acid using an excess of 3-chloroperoxybenzoic acid. This approach avoids the use of traditional strongly acidic sulfonating agents. Products with varying ratios of methyl and propanethiol/propanesulfonic acid constituents have been characterised by FT-infrared and NMR spectroscopies, elemental microanalyses, thermogravimetry and differential thermal analysis and ion exchange titrations.

Introduction

Many polymeric materials can be used for ion exchange and/or ion conductivity applications (ionomers). Most ionomers 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® (Fig. 1) and BAM 3G® (Fig. 2); sulfonated poly(vinylidene fluoride) (PVDF)[4] and sulfonated styrene-grafted PVDF systems;[5,6] and polybenzimidazole.[7]

Current interest lies in the development of materials that perform well in their respective roles at higher temperatures. Materials such as sulfonated polyphosphazene systems (P=N backbones)[8,9] and siloxane/perfluorosulfonated hybrid systems have been the emphasis of research studies.[10,11] Our work concerns the introduction of the sulfonic acid functionality into polysiloxanes; materials containing the siloxane Si–O backbone have the potential for high temperature stabilities.[12]

The direct sulfonation of aromatic-functionalised siloxanes with acid-based sulfonating reagents has been reported,[13,14] but the harsh acidic conditions used cause disruption of the siloxane backbone. Our current programme is concerned with minimising siloxane backbone disruption by utilising milder sulfonation methodologies. This paper describes the synthesis and characterisation of various siloxanes containing mercapto groups which are subsequently oxidised to sulfonic acid groups using a peroxyacid reagent.

Experimental

Infrared spectroscopy

Infrared spectra over the range 400–4000 cm^{-1} were recorded using a Nicolet Magna-IR 550 spectrometer. Solid samples were dispersed in potassium bromide discs and liquid samples pressed as thin films between sodium chloride plates.

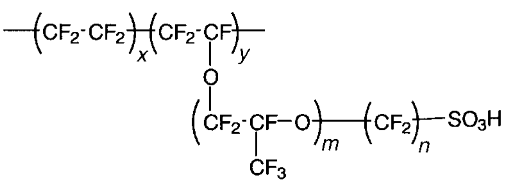


Fig. 1 Schematic structure of Flemion, Aciplex and Nafion.

NMR spectroscopy

Solution phase ^{1}H, ^{13}C-{^{1}H} and ^{29}Si-{^{1}H} NMR spectra were recorded using either a Bruker AC300 or AX400 spectrometer, with 5 mm sample tubes and a probe temperature of 20 °C. Spectra were determined in d^{1}-chloroform solution for the mercapto forms and in d^{4}-methanol for the sulfonic acid forms. All samples were referenced to internal TMS. The addition of chromium(III) acetylacetonate was used to aid the relaxation of the ^{29}Si nucleus.

Thermogravimetry and differential thermal analysis

Thermogravimetry and differential thermal analysis (TG-DTA) were performed under flowing air (50 cm^{3} min^{-1}) using a Stanton Redcroft STA-781 thermal analyser and a heating rate of 10 °C min^{-1}. Temperatures quoted in the text are sample temperatures measured with a Pt:Rh (13%) thermocouple referenced to 0 °C; differential thermal analyses were recorded with calcined α-alumina as reference.

Hydrolysis and polycondensation of (3-mercaptopropyl)trimethoxysilane and diethoxydimethylsilane (siloxane 1)

(3-Mercaptopropyl)trimethoxysilane (5.00 g, 4.81 cm^{3}, 0.0255 mol, Apollo Scientific), diethoxydimethylsilane (3.77 g, 4.36 cm^{3}, 0.026 mol, Aldrich), ethanol (11.73 g, 14.86 cm^{3}, 0.26 mol, Fisons), water (2.75 g, 2.75 cm^{3}, 0.15 mol) and hydrochloric acid (40.8 cm^{3}, 0.10 mol dm^{-3}, 0.026 mol) were mixed and heated at 50 °C for 3 h. The mixture was then heated at 80 °C under vacuum for 2 h to remove the solvent yielding a viscous colourless oil (4.59 g, 87% estimated yield). This experiment was repeated for other ratios of silane precursors (Table 1), producing siloxanes **2** and **3**. For materials **4–6**, diethoxydimethylsilane was replaced with (3-mercaptopropyl)-dimethoxymethylsilane (Table 1). For all materials the ratio of

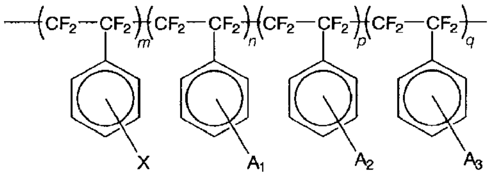
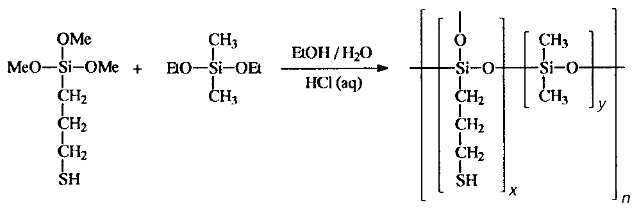
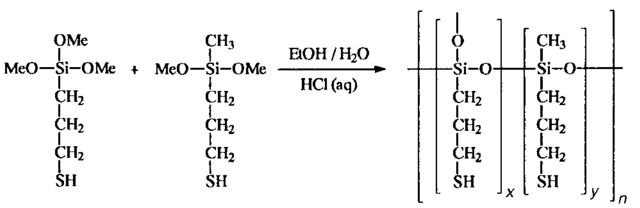


Fig. 2 Structure of BAM 3G, with X = SO_3H, PO_3H_2 or CO_2H and A_1, A_2, A_3 = alkyl, halide, OR or OH.



Scheme 1 Hydrolysis and polycondensation of (3-mercaptopropyl)-trimethoxysilane and diethoxydimethylsilane (siloxanes **1**, **2** and **3**).



Scheme 2 Hydrolysis and polycondensation of (3-mercaptopropyl)-trimethoxysilane and (3-mercaptopropyl)dimethoxymethylsilane (siloxanes **4**, **5** and **6**).

the total amount of monomers reacted to solvents and acid was kept constant.

Oxidation of the mercaptosiloxanes with 3-chloroperoxybenzoic acid

Siloxane **1** (2.5 g, 0.012 mol thiol units) was dissolved in dichloromethane (100 cm^3) and cooled using an ice bath. 3-Chloroperoxybenzoic acid[15] (9.06 g, 0.037 mol, 70% purity, Acros) was added slowly in small portions and the mixture allowed to warm to room temperature with stirring for 2 h. A fine white precipitate formed very quickly on addition of the peroxyacid, and was recovered by filtration (the dichloromethane extract contained unreacted peroxy acid as confirmed by infrared spectroscopy). The precipitate was then stirred in ethanol; some of the material was observed to dissolve. The insoluble residue (found by infrared analysis to be 3-chlorobenzoic acid) was removed by filtration. A white solid was obtained on removal of the solvent; this was stirred in water for several hours. The aqueous solution was collected (after filtration) and the water removed under vacuum, leaving the product material (a misty solid), which was then thoroughly dried at 50 °C in a vacuum oven.

The above procedure was repeated for siloxanes **2**, **3**, **4**, **5**, and **6**. Yields of the sulfonic acid forms were variable ($\approx$1–4 g) reflecting various amounts of trapped solvent, some materials containing lower loadings of oxidisable mercapto functions than others, and the partial insolubility of the mercapto forms of siloxanes **3** and **6**.†

Results and discussion

Methodology

The initial step of the synthesis of these hybrid materials is the sol–gel polymerisation[16] to form the siloxane network (Schemes 1 and 2). The siloxane materials have been synthesized with a range of ratios $x:y$ (Table 1) forming two classes of material that have the chemical formulae $\{OSiMe_2\}_y\{O_{3/2}SiCH_2CH_2CH_2SH\}_x$ (siloxanes **1**, **2**, and **3**) and $\{OSi(Me)CH_2CH_2CH_2SH\}_y\{O_{3/2}SiCH_2CH_2CH_2SH\}_x$ (siloxanes **4**, **5**, and **6**). The mercapto forms are all slightly misty, colourless oils. The sulfonic acid forms of the materials are white brittle solid products, which dissolve in water yielding acidic liquors (pH$\approx$2).

3-Chloroperoxybenzoic acid enables mild and clean oxidation to form sulfinic acids (SO_2H) when allowed to react slowly and stoichiometrically with the thiol-containing materials. When the reagent is used in excess (at least 3 times) sulfonic acids result.[17]

Characterisation by ^1H NMR spectroscopy

The ^1H NMR spectrum of siloxane **1** in both the mercapto and sulfonic acid forms is shown in Fig. 3. The peak at δ 1.3 in the spectrum of the mercapto form can be assigned to the mercapto (SH) exchangeable proton and, as expected, disappears upon oxidation; this is consistent with the infrared analysis, but deuterium exchange of the SH proton could also account for this. The signal at δ 0.1 corresponds to the Si–CH_3 group; this signal gains more fine structure and shifts to δ 0.2 on oxidation suggesting siloxane backbone disruption from the formation of sulfonic acid functions. Residual ethoxy signals are present in the spectrum of the sulfonic acid form (δ 1.2, 3.7) corresponding to trapped ethanol introduced in the work-up of the oxidation reaction; these signals decrease in intensity with vigorous drying. The low intensity broad signals at δ 3.0–4.0 and 1.4, observed especially in the spectra of the mercapto forms, arise from small quantities of residual methoxy and ethoxy groups. There is broadening of the spectral features for the sulfonic acid form. This may be because of hydrogen bonding introduced with the newly formed sulfonic acid groups (this restricts the motion of the ionomeric siloxanes) or the formation of cross-links from any side reaction that occurred.

The CH_2 signals are located at δ 0.7, 1.7 and 2.5 (1 : 1 : 1 intensity ratio) [^1H combined rotation and multiple pulse spectroscopy (CRAMPS) solid state NMR:[18] δ 1.1, 1.9, 2.7] for the mercapto form. On oxidation these shift to higher frequency (to δ 0.8, 1.9 and 2.9 respectively). These shifts are too large to be explained as solvent shifts alone, and arise from the introduction of the SO_3H group. Increasing deshielding of the CH_2 protons leads to an increased signal shift on oxidation, *i.e.* the signal at δ 2.5 (next to the SH group) shifts 0.4 ppm to higher frequency on oxidation, while that at δ 0.7 (next to the Si) shifts only 0.1 ppm to higher frequency. The signal at δ 2.9

Table 1 Ratio of monomers in pre-reaction mixture (A = diethoxydimethylsilane, B = (3-mercaptopropyl)trimethoxysilane, C = (3-mercaptopropyl)dimethoxymethylsilane) and the composition of the final siloxanes in both the mercapto and sulfonic acid forms. Composition data are represented as mole percentages of each unit or monomer and are calculated from 300 MHz ^1H NMR spectra. Percentage yield data for mercapto forms are calculated from mass yields and mole percentage compositions

	% Monomers		% Composition in mercapto forms			% Composition in sulfonic acid forms	
Siloxane	A	B	Me_2SiO	$(C_3H_6SH)SiO_{3/2}$	% Yield of mercapto forms	Me_2SiO	$(C_3H_6SO_3H)SiO_{3/2}$
1	50	50	46	54	87	41	59
2	66.6	33.4	64	36	82	37	63
3	33.4	31	31	69	98	19	81
	C	B	$(C_3H_6SH)MeSiO$	$(C_3H_6SH)SiO_{3/2}$		$(C_3H_6SO_3H)MeSiO$	$(C_3H_6SO_3H)SiO_{3/2}$
4	50	50	49	51	95	54	46
5	66.6	33.4	65	45	98	69	31
6	33.4	66.6	32	68	97	43	57

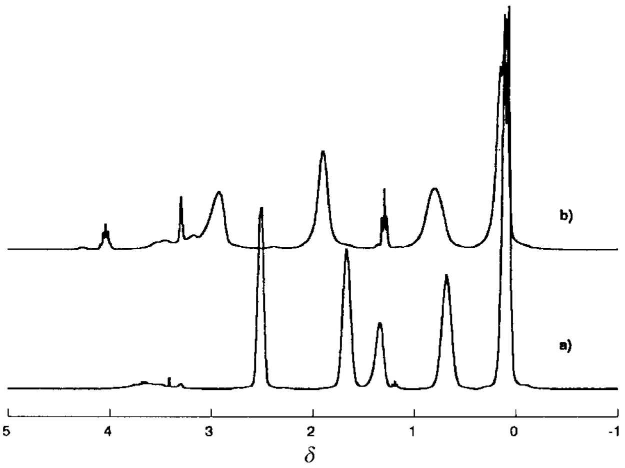


Fig. 3 The ^1H NMR spectra of siloxane **1** in (a) mercapto and (b) sulfonic acid forms.

for the sulfonic acid form is 33% lower in intensity than the signals at δ 0.8 and 1.9 (1 : 1 ratio). This indicates some of the CH_2SO_3H protons have been removed. A potential scenario is the abstraction of a fraction of these protons in the radical oxidation step, followed by reaction with other radical species during the oxidation (*e.g.* 3-$ClC_6H_4C(O)O^·$, $HO^·$). This could account for some very weak aromatic signals in the NMR spectrum of the sulfonic acid form. Proton abstraction would also aid cross-linking of the material leading to powder products as opposed to mercapto oils.

Siloxanes **2** and **3** in both mercapto and sulfonic acid forms show similar features to those of **1**; the only variations between the spectra of these materials are the relative signal intensities between the Si–CH_3 and CH_2 protons. Hence, the ^1H NMR spectra of siloxanes **1**, **2**, and **3** enabled determination of the ratio of monomer units incorporated in the mercapto and sulfonic acid forms of the siloxanes (Table 1). The ratios of the monomers before sol–gel polymerisation are very similar to those in the resulting mercapto forms of the siloxanes; this shows the composition of these materials can readily be tailored.

However, the amounts of the dimethylsiloxane units decrease when the mercapto forms have undergone oxidation; cyclic dimethylsiloxane oligomers are present in the mercapto forms of siloxane **1**, **2**, and **3** as synthesized (this is confirmed with thermal analysis data). These cyclic oligomers are lost in the oxidative work-up; they are soluble in dichloromethane and have no oxidisable mercapto functions and, hence, separate from the sulfonic acid siloxanes (which are insoluble in dichloromethane). This has implications for the synthesis of siloxanes with high dimethylsiloxane component loadings. Oxidation to the sulfonic acid form of siloxane **2**, where the initial sol–gel reaction mixture contained 66.6% dimethylsilane monomer, leads to a material with only 37% dimethylsiloxane component. This compares interestingly with siloxane **1**, synthesized initially with 50% diethoxydimethylsilane monomer, which contains 41% dimethylsiloxane component in the sulfonic acid form. It can be concluded that there is an optimum amount of dimethylsilane monomer precursor that can be used with this system; too much favours cylic dimethylsiloxane formation over copolymer formation, reducing the amount of dimethylsiloxane component in the final sulfonic acid form.

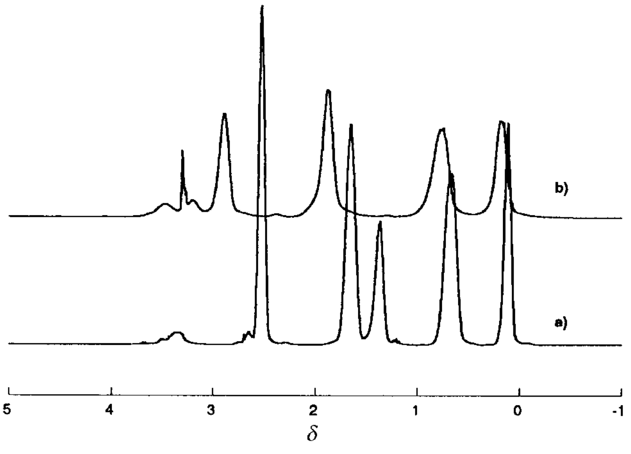


Fig. 4 The^1H NMR spectra of siloxane **4** in (a) mercapto and (b) sulfonic acid forms.

The ^1H NMR spectra for siloxanes **4**, **5**, and **6** (Fig. 4) in both forms show very similar features to those discussed above. When compared to siloxanes containing dimethylsiloxane components, the methyl(mercaptopropyl)siloxane units in siloxanes **4**, **5**, and **6** do not appear to cyclise as readily and higher loadings of methyl propanesulfonic acid siloxane in the final sulfonic acid forms are achievable.

^{13}C and ^{29}Si NMR spectra

The ^{13}C NMR spectra of the mercapto forms of siloxanes **1**, **2**, and **3** all show three broad signals at δ 1 (Si–CH_3), 12–13 ($SiCH_2CH_2$) and 28 (CH_2CH_2SH and $CH_2CH_2CH_2$) [^{13}C CP-MAS solid state NMR:[18] δ 12.6 and 28.7 for the CH_2 carbons]. The central signal is very broad in each case and all signals exhibit fine structure. Four signals were expected, but only three are observed because of overlap of the two signals at δ 28.

The ^{13}C NMR spectra of the sulfonic acid forms all show signals at δ 1 (Si–CH_3), 11 ($SiCH_2CH_2$), 18 ($CH_2CH_2CH_2$) and 54 ($CH_2CH_2SO_3H$). The signal at δ 11 is again very broad and all the signals exhibit less fine structure than for the mercapto forms. For the sulfonic acid form of siloxane **1** there are a number of minor signals present which relate to trapped solvents, residual OEt and OMe groups and benzoic acid contaminant. The spectra of the sulfonic acid forms of siloxane **1** and **3** also exhibit a weak unassignable signal at δ −3.

The ^{13}C NMR spectra of the mercapto forms of siloxanes **4**, **5**, and **6** exhibit four broad signals at δ 0 (Si–CH_3), 13 ($SiCH_2CH_2$), 16 ($MeSiCH_2CH_2$) and 28 (CH_2CH_2SH and

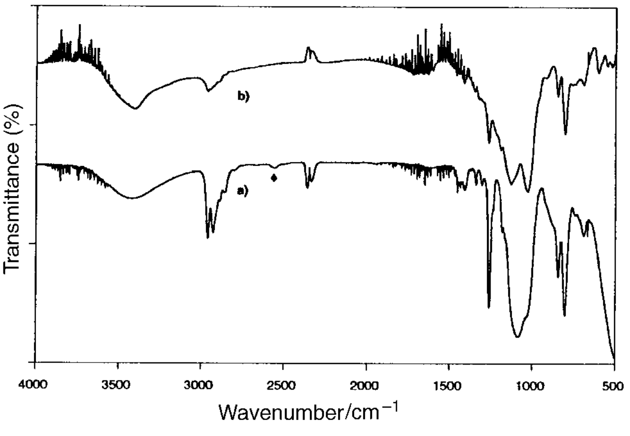


Fig. 5 The infrared spectra for siloxane **1** in mercapto form (a) and sulfonic acid form (b). The ◆ denotes the S–H band in the mercapto form.

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†Materials **3** and **6** 'as synthesized' were only partially soluble in dichloromethane (the siloxane backbone cured and cross−linked before the oxidation reaction could be carried out). The oxidation reactions were carried out with the insoluble materials in the reaction mixture. The insoluble components (oxidation was not detected in infrared spectra) were separated from the soluble oxidised material at the ethanol extraction phase of the work-up.

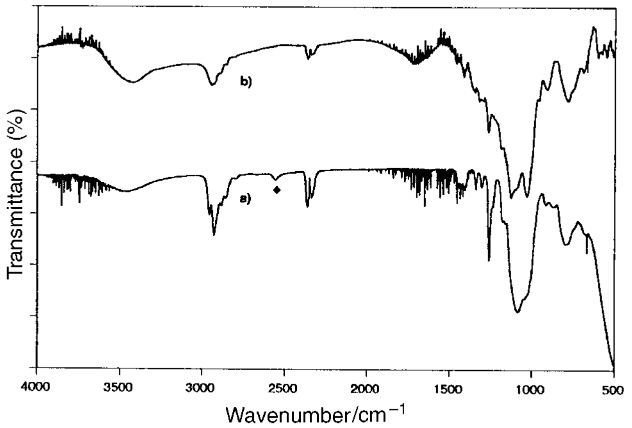


Fig. 6 The infrared spectra for siloxane **4** in mercapto form (a) and sulfonic acid form (b). The ◆ denotes the S–H band in the mercapto form.

$CH_2CH_2CH_2$), all of which show significant fine structure. Again in each case the signal at δ 13 is very broad. On oxidation the ^{13}C NMR spectra exhibit five signals at δ −2 (Si–CH_3), 11 (SiCH_2CH_2), 16 (MeSiCH_2CH_2), 18 ($CH_2CH_2CH_2$) and 54 ($CH_2CH_2SO_3H$).

There were considerable problems in obtaining good quality ^{29}Si NMR spectra, especially for the sulfonic acid forms. The spectra of all the siloxanes show a broad sub-structured signal at δ −18 to −22 (arising from R_2SiO_2 units with varying degrees of condensation of SiOH groups in the sol–gel polymerisation), a broad sub-structured signal at δ −57 to −60 (arising from $RSiO_3$ units with some residual SiOH groups present) and a broad sub-structured signal at δ −65 to −68 (arising from fully condensed $RSiO_3$ units). The ratios of the intensities arising from these groups varied, indicating the differing ratio of components and varying degrees of condensation of the siloxane backbone. The signal/noise (S/N) ratios of the spectra are not sufficient to allow quantitative analysis. The spectra of the sulfonic acid forms show similar groups of signals, but with even poorer S/N ratios.

Characterisation by infrared spectroscopy

The infrared spectra of siloxane **1** in mercapto and sulfonic acid forms are shown in Fig. 5. The weak band at 2550 cm^{-1} (◆) in the spectrum of the mercapto form is assigned to the S–H stretch and disappears upon oxidaton to the sulfonic acid form. The Si–O–Si band at 1000–1200 cm^{-1} is visible in the spectrum of both forms, but the bandshape changes on oxidation, indicating rearrangement or branching of the polymeric backbone. The fine structure on the high energy side of the Si–O–Si band in the spectrum of the sulfonic acid form is caused by overlapping of this band with the S=O stretches and the Si–Me band at 1260 cm^{-1}. Bands in the range 750–820 cm^{-1} can be assigned to various deformations and bends of the Si–Me groups. A change occurs in the O–H stretching band at 3100–3600 cm^{-1} on oxidation; the intensity of the band increases after oxidation, accompanying the increased water content (associated with the sulfonic acid function). The band also broadens due to increased hydrogen bonding (involving SO_3H functions and incorporated water). The water content is lost only on prolonged heating under vacuum at temperatures less than 60 °C (the materials discolour if heated above this). The infrared spectra for the remaining siloxanes (Fig. 6 shows the spectra of siloxane **4**) in both forms show similar features to that observed for siloxane **1**. The only variations between the spectra are in the ratios of intensities of the bands.

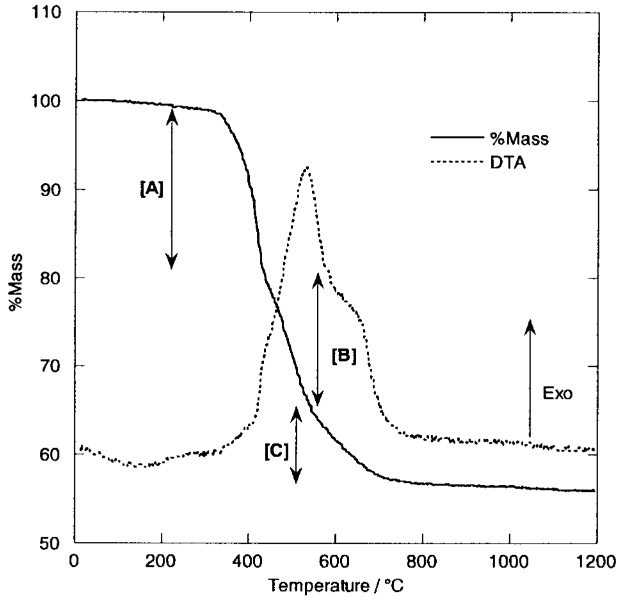
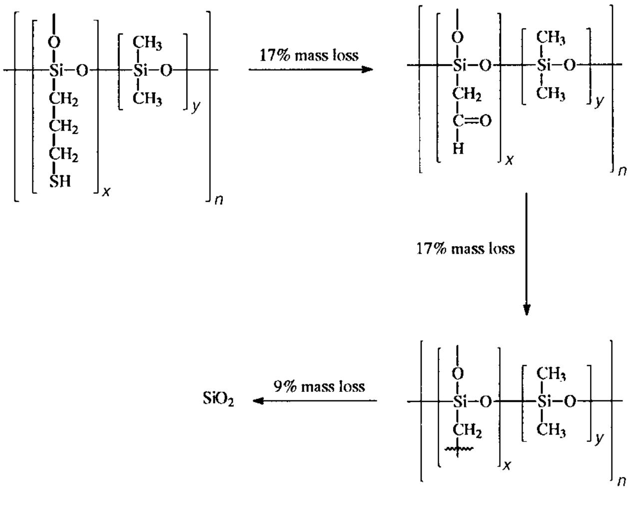


Fig. 7 The TG and DTA traces for siloxane **1** in the mercapto form. The single headed arrow indicates the exothermic direction in DTA; [A], [B] and [C] define three separate regions of mass loss in the TG trace (see Table 2).

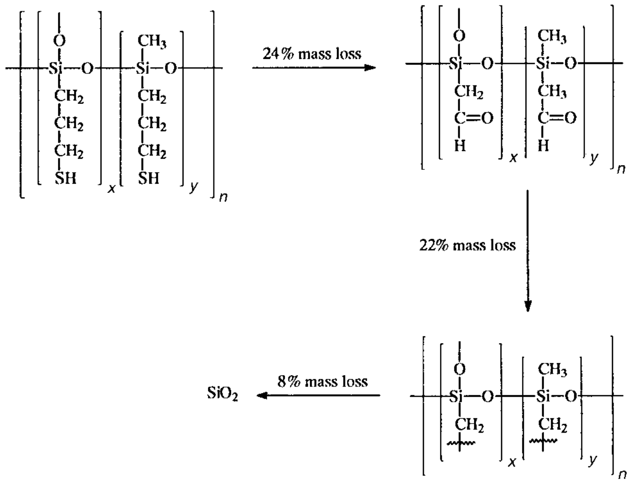
Thermal analysis

The temperature stabilities of the siloxanes synthesized were investigated using thermograivmetry (TG) and differential thermal analysis (DTA). The TG and DTA traces for the mercapto form of siloxane **1** are shown in Fig. 7. There is no significant mass loss until the sample reaches 286 °C. At this point there is a mass loss (with an increased weak exotherm) equivalent to the loss of methanethiol and subsequent oxidation of the remaining side-chain by atmospheric oxygen to form a ketone [calculated mass loss 17%, experimental 17%]. At 427 °C a strong exotherm is observed in the DTA trace, with a corresponding mass loss equivalent to carbonisation of the side group leaving a silicon methyl group or CH_2CH_2 cross-link [calculated mass loss 17%, observed 15%]. The final mass loss between 566 and 750 °C occurs alongside a small exotherm and arises from oxidation of the remaining organic mateiral to leave SiO_2. The overall total mass loss is 42% [calculated 43%] (Scheme 3). The final decomposition product was confirmed to be SiO_2 by powder X-ray diffraction.

The TG and DTA traces of siloxane **4** in the mercapto form are shown in Fig. 8. The thermal decomposition commences at



Scheme 3 The hypothetical decomposition pathway of siloxane **1**. The mass losses shown are the calculated values.



Scheme 4 The hypothetical decomposition pathway of siloxane **4**. The mass losses shown are the calculated values.

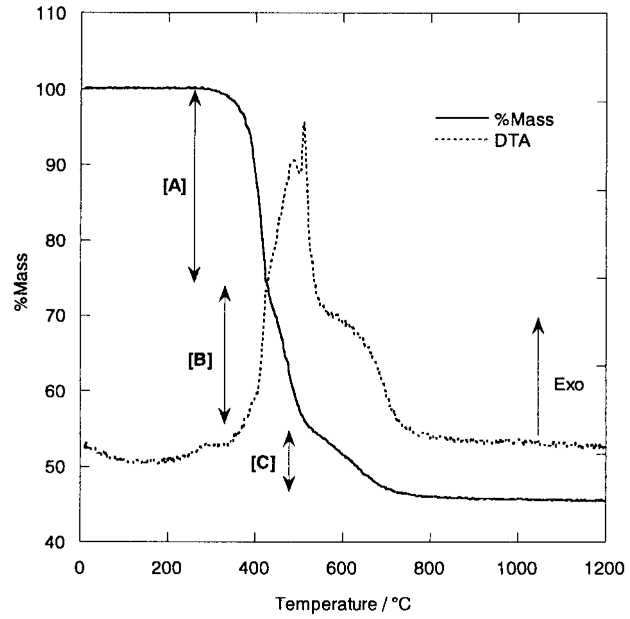


Fig. 8 The TG and DTA traces for siloxane **4** in the mercapto form. The single headed arrow indicates the exothermic direction in DTA; [A], [B] and [C] define three separate regions of mass loss in the TG trace (see Table 2).

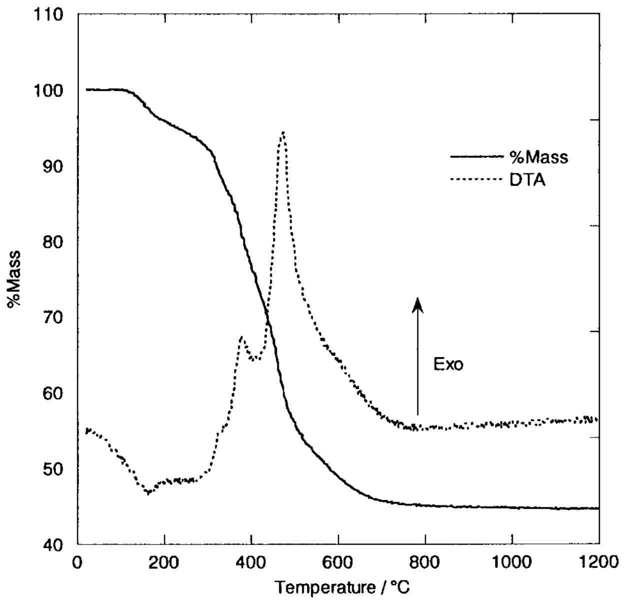


Fig. 9 The TG and DTA traces for siloxane **1** in the sulfonic acid form.

242 °C and ends at 750 °C. The mass losses differ from those of siloxane **1** in that both siloxane units contain propanethiol groups that decompose (Scheme 4). Table 2 summarises the TG data for the mercapto forms of all the siloxanes synthesized. The predicted mass losses are calculated based on Scheme 3 for siloxanes **1**, **2**, and **3** and on Scheme 4 for **4**, **5**, and **6**. The inconsistencies between the observed and calculated mass lsses for the mercapto form of siloxane **2** arise from the formation of cyclic dimethylsiloxane oligomers in the sol–gel synthetic step. These oligomers evaporate when heated in the thermal analyser (the boiling temperature for hexamethylcyclotrisiloxane is 134 °C and for octamethylcyclotetrasiloxane is 175 °C) leading to loss of silicon content from the sample. This discrepancy is not observed for the sulfonic acid form of siloxane **2**; the cyclics were removed in the work-up of the oxidation reaction. Cyclic siloxane formation is consistent with NMR spectroscopic observations.

The situation for the sulfonic acid forms is more complex (Figs. 9 and 10). The total mass losses observed for the sulfonic acid form siloxanes and the calculated mass losses predicted are shown in Table 3). The thermal stability of the sulfonic acid forms has greatly decreased in relation to the mercapto forms for siloxane **1**. No mass loss was observed in the TG trace of the mercapto form until 286 °C, whereas decomposition of the sulfonic acid form commences at 58 °C. For siloxane **4** the decomposition begins at 242 °C for the mercapto form and at 42 °C for the sulfonic acid form. Initial mass losses for the sulfonic acid forms could be due to solvent (water) loss, but the materials were thoroughly dried in a vacuum oven and the predicted total mass losses calculated from ^{1}H NMR data are consistent with observed values when assuming minimum

Table 2 The TG data for the mercapto forms of the siloxanes synthesized. Data in percentage mass loss. Obs. = observed and Calc. = calculated mass loss (based on compositions calculated from ^{1}H NMR data and assuming the decompositions are following Scheme 3 for materials **1**, **2** and **3** and Scheme 4 for **4**, **5** and **6**)

		Mass loss A		Mass loss B		Mass loss C		Total	
Siloxane	Temperature stability/°C	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	286	17	17	15	17	10	9	42	43
2[a]	139	12	13	13	13	22	11	50	37
3	253	21	20	17	18	8	8	46	46
4	247	25	24	21	22	8	8	54	54
5	261	27	24	20	22	9	8	56	54
6	250	26	25	18	22	10	7	54	54

[a] The discrepancy between the observed and calculated values for this sample arise from a detectable amount of low molecular weight cyclics formed in the initial sol–gel reaction, which evaporate on heating, resulting in a loss of silicon content. This also accounts for the lower onset temperature for mass loss A.

Table 3 The TG data for the sulfonic acid forms of the siloxanes synthesized. Data in percentage lass loss. Obs. = observed and Calc. = calculated mass loss (based on compositions calculated from ^{1}H NMR data and Schemes 3 and 4)

		Total mass loss	
Sulfonic acid form of siloxane	Temperature stability/°C	Obs.	Calc.
1	58	55	55
2	69	58	56
3	38	62	62
4	42	66	68
5	36	66	68
6	47	66	67

Table 4 The ion exchange capacities and C : S atom ratios acquired from elemental (C, H and S) analyses. The theoretical values are deduced using ^{1}H NMR data

		C : S atom ratio	
Sulfonic acid form of siloxane	Ion exchange capacity/mol g^{-1}	Elemental analyses	Theoretical
1	2.73×10^{-4}	4.6	4.4
2	3.36×10^{-4}	3.5	4.2
3	3.57×10^{-4}	3.0	3.5
4	3.48×10^{-4}	3.5	3.5
5	3.55×10^{-4}	3.4	3.7
6	3.70×10^{-4}	3.6	3.4

solvent incorporation; this indicates that the mass losses are truly due to polymer degradation.

For the sulfonic acid forms of the materials containing dimethylsiloxane units, the higher the proportion of methyl side groups, the higher the temperature of initial decomposition commences. The theoretical decomposition pathway for the mercapto siloxanes is simply defined and consistent with observed values; the presence of the sulfonic acid groups in oxidised forms has a marked effect on the shape of the thermal trace.

Elemental analyses and ion exchange

Elemental analysis (C and S) and ion exchange capacity determination was conducted for all materials, with the results summarised in Table 4. The ion-exchange capacities were calculated by titration of aqueous solutions of the oxidised materials (≈0.1 g powdered material dissolved in 150 cm^3 water) with aqueous KOH solution (0.1029 mol dm^{-3}). The ion exchange capacities compare well with those of Nafion®, which exhibits a capacity ≈1100 g mol^{-1} SO_3H.

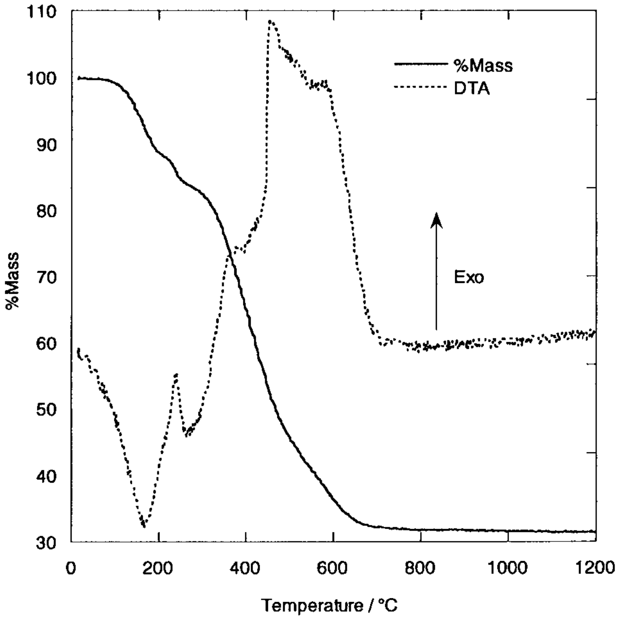


Fig. 10 The TG and DTA traces for siloxane **4** in the sulfonic acid form.

Empirical C : S ratos for the sulfonated forms are close to those calculated from ^{1}H NMR results, but agreement is least good for materials with dimethyl substituents (**2** and **3**). Materials used for elemental analysis had been stored for several months. Infrared spectroscopy of the sulfonated forms of **1** and **4** before and after storage showed clear changes; after storage the Si–O region displayed much sharper bands and there was an enhanced OH stretch at 3400 cm^{-1}. The materials thus appear to have limited long term stability in air.

Conclusion

Thermally stable siloxane copolymers contaning mercaptopropyl and methyl side groups have been synthesized. These were then oxidised using an excess of 3-chloroperoxybenzoic acid (this reagent was chosen for its mild oxidising properties) to form soluble hydrophilic siloxane ionomers containing a mixture of methyl and propanesulfonic acid pendant groups. Some disruption to the siloxane backbone was observed on liberation of the sulfonic acid functions. Varying ratios of methyl and propanesulfonic acid side chains can be incorporated by simple variation of the concentrations of the reagent monomers in the initial sol–gel polymerisation, though there is a limit to the amount of dimethylsiloxane units that can be included using this simple sol–gel methodology. These alkanesulfonic acids are of limited thermal stability and lack stability at ambient temperature in air over long periods of time, but demonstrate the validity of the concept of alternative routes to sulfonation of siloxanes. The use of thiols bound to aromatic rings and subsequent oxidation could lead to increased thermal stability. No commercial siloxanes containing aromatic bound thiols are available and their synthesis is the focus of ongoing research.

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