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The molecular weight distribution of polymerized iso-butylsilane and γ-methacryloxypropylsilane in aqueous solutions

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The condensation of iso-butyltrimethoxysilane and γ-methacryloxypropyltrimethoxysilane (γ-MPS) in aqueous solutions has been studied. The silanes were hydrolysed in acidic solutions followed by adjustment of the pH of the solutions to allow condensation at different pH conditions. The molecular weights of the polymer mixtures obtained were determined by using gel permeation chromatography (GPC) with a light scattering detector. The GPC results suggest that the polybutylsilsesquioxanes differ in molecular weight distribution to the polymethacryloxypropylsilsesquioxanes. In general, polymers with the highest molecular weight were obtained in mild alkaline conditions. Strongly acidic as well as strongly alkaline conditions gave low molecular weight oligomers. The effect of fluoride ions on polymer molecular weight was also investigated. The polymers from the hydrolysis and condensation of iso-butylsilane and γ-MPS were monodisperse when the condensation was catalysed by fluoride ion. The molecular weights of the polymers were lower than those from the analogous base-catalysed reactions and the molecular weights increased with an increase in fluoride concentration.

1. Introduction

The condensation of hydrolysed organofunctional silanes has been previously studied [1–4]. Early experiments involved the hydrolysis of alkylchlorosilanes or alkylalkoxysilanes in organic solvents. Silanes rather than the hydrolysis products were the major research interest. In the past 20 years, the silane coupling agents have gained particular research interest due to their wide industrial application in the modification of mineral particulates [5, 6]. In general, the study of silane coupling agents primarily focused on using the silane hydrolysis products (silanols) to promote adhesion between mineral particulate fillers and organic matrix resins in an effort to improve the strength and chemical resistance of the particulate-filled composites. The stability of silanol solutions has been reported to be decreased by traces of fluoride ions and to be strongly influenced by pH [7]. Ishida and Miller simulated the deposition of products from γ-MPS on mineral substrates by adjusting the pH of an aqueous alcohol solution of the silane in the absence of a substrate [8–10]. The molecular weight distribution of the polymeric or oligomeric siloxanes so-formed was determined by GPC. The authors concluded that the molecular weight of the polymer from γ-MPS obtained in aqueous alcohol was a function of the pH of the solution and decreased in the order neutral > alkaline ⩾ acidic. The focus of these studies was the condensation process in alcohol as the solvent rather than water, and the subsequent products.

The effect of fluoride ions on silane hydrolysis and condensation has been reported [11]. The fluoride ion was compared in its catalytic properties to the hydroxyl anion. Piana and Schubert tested several compounds including hydrogen fluoride for their ability to influence the molar mass distribution of the hydrolysis products of γ-MPS in aqueous alcohol [12]. They found that higher molecular weight polymers were formed only with strong base or with hydrogen fluoride as the catalyst. The effect of the fluoride ion on hydrolysed silane solutions was not reported.

Studies reporting the molecular weight distribution of the hydrolysis and condensation products of alkyltrialkoxysilanes are very limited. These studies were carried out at a time when the molecular weight of the polyalkylsilsesquioxane was not able to be determined due to the lack of effective analytical instruments. Andrianov and Izmaylov observed the products from hydrolytic polycondensation of higher and lower alkyltrichlorosilanes, and concluded that with increasing size of the alkyl group on silicon the condensation favoured cyclic products [13]. This conclusion was based on visual observation and no quantitative

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analysis was carried out. Without quantitative analysis, the molecular weight of the polyalkylsilsesquioxanes was unknown. It has been assumed that all trifunctional silanes behave similarly in condensation. However, due to the size and polarity difference between functional groups, such an assumption may not be valid and a molecular weight determination should be conducted.

The commonly used detectors have difficulty in the detection of polymeric alkysilanes using GPC. Polyalkylsilsesquioxanes do not possess ultraviolet-sensitive functional groups so that a UV detector is not useful. The refractive index detector (RI) has the problems of poor sensitivity and temperature instability. In the determination of the molecular weight of polysilsesquioxanes herein, these problems were overcome by using an evaporative light scattering detector (ELSD). The ELSD has several advantages over the conventional RI detector. It is not sensitive to changes in ambient temperature and it is a 'universal detector'. The detector can detect any species having a lower volatility than the mobile phase. In addition, the ELSD is mass-responsive and can be used to obtain peak mass directly from the peak area. In this case the materials of major interest are polysilsesquioxanes which are low in volatility. The ELSD detector together with GPC enabled the molecular weight of oligomeric and polymeric silanes to be estimated quantitatively.

2. Experimental procedure

2.1 Materials

Iso-Butyltrimethoxysilane was purchased from Dynamit Nobel (U.K.) Ltd. and γ-methacryloxypropyltrimethoxysilane (γ-MPS, 97% purity) was purchased from Aldrich Chemical Company, Inc. and used without further purification. The aqueous silane solutions were prepared by stirring 5 ml of silane in 95 ml of dilute hydrochloric acid solution at pH 3.0 for 30 min until the hazy solutions became clear. The solution after hydrolysis of iso-butyltrimethoxysilane was clear and this solution was used in the experiments. However, the product from γ-MPS hydrolysis contained impurities which were insoluble in water. After the hydrolysis, the mixture was filtered through activated carbon so that the oil droplets were separated. The clear solution obtained after the filtration through activated carbon was used in the experiments.

The condensation of silanols in solutions under different pH conditions was investigated. The pH of the silanol solution was adjusted to produce solutions at pH 3.0, 5.0, 7.0, 9.0, 11.0, 12.0 and 13.0 by adding buffer solutions into the silanol solutions. The condensation products were collected by leaving the silanol solutions at room temperature until the precipitation ceased. The precipitates were dissolved in tetrahydrofuran (THF) and submitted to GPC analysis.

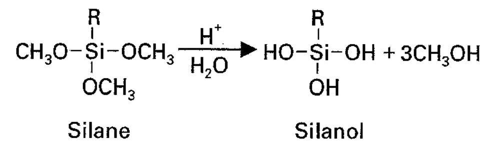
Fluoride influence on the molecular weight distribution was investigated by collecting the precipitate obtained in the solutions with the presence of fluoride. Ammonium fluoride as a source of fluoride ion was added to silanol solutions at trace levels. Before the addition of the fluoride, the pH of these solutions was adjusted to between 4 and 5 to minimize the effect of either acid or base on the condensation. Sodium dihydrogen phosphate was also incorporated at a concentration of 0.2% in the silanol solution to stabilize the pH of the solution.

2.2. Chromatography and detector

The sample injection volume was constant at 20 µl. Injected sample concentrations were between 0.1% and 0.2%. GPC was performed using HPLC grade THF as the mobile phase. The system consisted of a HPLC pump (Bio-Rad model 1330) and two independent series of packed columns. One series of columns utilizing Ultrastyragel 10^4 nm (10^5 Å) (Waters Associates) and Ultrastyragel 10^3 nm (10^4 Å) (Waters Associates) was used to separate high molecular weight components in the range between 10^6 to 10^3 g mol^{-1} polystyrene standards. A second series of columns was used to separate low molecular weight components of less than 10^4 g mol^{-1} polystyrene standard. It consisted of Ultrastyragel 50 nm (500 Å) (Water Associates) and Ultrastyragel 10 nm (100 Å) (Waters Associates). The flow rate of the mobile phase was maintained at 1.0 ml min^{-1}. A Varex MKIII ELSD purchased from Alltech Associates, Inc. was used. The temperature of the drift tube was 60 °C. The nitrogen gas flow rate was controlled at 2.5 standard litres per minute (SLPM). The molecular weight distribution of the polysilsesquioxane was expressed relative to a monodisperse polystyrene standard. An ultraviolet detector was used at 254 nm with GPC to produce chromatograms of the 6 monodisperse polystyrene and styrene standards with a molecular mass ranging from 104 to 35 000 (purchased from Aldrich Chemical Company, Inc.) so a calibration curve was obtained.

3. Results and discussion

The hydrolysis of iso-butyltrimethoxysilane and γ-methacryloxypropyltrimethoxysilane in acidic solutions gave clear silanol solutions (Fig. 1). The silanols condense in the aqueous solutions to form polymers or oligomers which separate from the aqueous phase. The pH of the solution affects the condensation product considerably as the mechanisms of acid–catalysed and base–catalysed condensations are quite different [14]. The polysilsesquioxanes obtained from the acidic solution had a different appearance to those condensed from alkaline solutions. The precipitate in the acidic solution was an oily liquid at room temperature compared to the highly viscous or even solid precipitate obtained in alkaline solutions. The solubility of these polymers in THF was also different. The polybutylsilsesquioxane samples all dissolved completely in THF. However of the polymethacryloxypropylsilsesquioxanes, only the sample obtained in acidic solution dissolved in THF within 1 min. The elastic polymers obtained in neutral and alkaline solutions were very difficult to dissolve in THF. In particular, the sample obtained at pH 11.0 did not dissolve in



$$\mathrm{CH_3O{-}\overset{R}{\underset{OCH_3}{Si}}{-}OCH_3 \xrightarrow[H_2O]{H^+} HO{-}\overset{R}{\underset{OH}{Si}}{-}OH + 3CH_3OH}$$

Figure 1 The hydrolysis of iso-butyltrimethoxysilane or γ-methacryloxypropyltrimethoxysilane in an acidic solution (R denotes iso-butyl group or γ-methacryloxypropyl group).

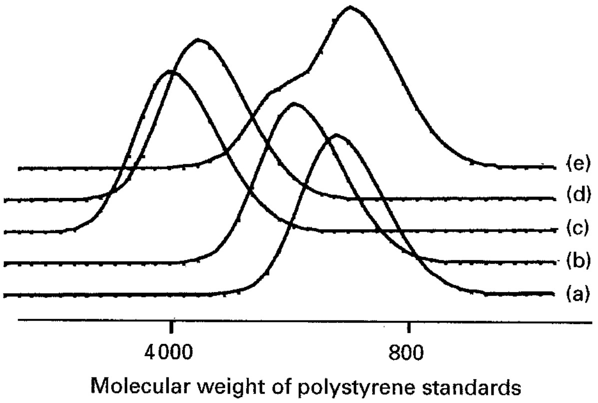


Figure 2 GPC chromatograms of polybutylsilsesquioxanes obtained in aqueous solutions at the pH conditions; (a) pH 3.0, (b) pH 5.0, (c) pH 9.0 and 11.0, (d) pH 7.0 and 12.0, and (e) pH 13.0.

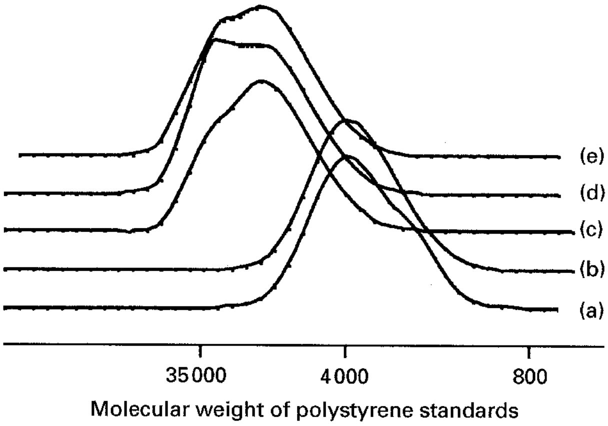


Figure 3 GPC chromatograms of polymethacryloxypropylsilsesquioxanes obtained in aqueous solutions at the pH conditions of; (a) pH 3.0, (b) pH 5.0, (c) pH 7.0, (d) pH 9.0 and (e) pH 11.0.

THF completely and a trace of residue remained even after considerable vigorous stirring. The solubilities of these samples in THF indicated the relative molecular weight of each sample. The polymer from γ-MPS obtained in neutral and alkaline conditions appeared to be of a relatively higher molecular weight.

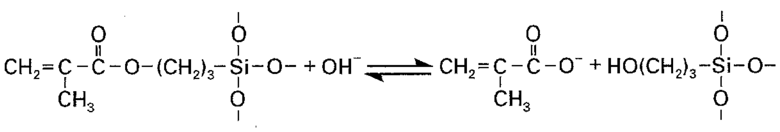
Figs 2 and 3 demonstrate the molecular weight distribution of polymeric iso-butylsilsesquioxanes and γ-methacryloxypropylsilsesquioxanes from the chromatograms. These samples were obtained at a wide range of solution pH. The GPC results suggest that the molecular weights of polysilsesquioxanes obtained in aqueous solution were strongly influenced by the pH of the solution. Strongly acidic solutions gave rise to low molecular weight products. As the pH was increased, the average molecular weight of the polysilsesquioxane increased accordingly. The increase in molecular weight shown on the chromatograms is consistent with the observed viscosity and the relative rate of dissolution in THF over the same range. High molecular weight samples exhibited high viscosities and low dissolution rates in organic solvents. With a rise in pH to 13.0, the molecular weight distribution of the polymers decreased markedly. It is evident that strongly alkaline conditions reduce the polymer chain propagation and this phenomena has been previously reported by Brown *et al.* to be as a result of the formation of cyclic products [15].

The chromatograms of the polymethacryloxypropylsilsesquioxanes from solutions at pH 12.0 and 13.0 are not illustrated in Fig. 3. The reactions of γ-MPS at pH 12.0 and 13.0 were affected by side reactions producing methacrylic acid as a result of the cleavage of the γ-methacryloxypropyl group under strongly alkaline conditions (Fig. 4). The cleavage of the γ-methacryloxypropyl group under high pH conditions has been reported by Ishida and Miller to be base–catalysed hydrolysis of the ester to an acid and an alcohol [9]. As a consequence, the chromatogram at high pH obtained in the present study was no longer representative of polymethacryloxypropylsilsesquioxanes.

The polymethacryloxypropylsilsesquioxanes obtained in aqueous solutions in general have a higher molecular weight than polybutylsilsesquioxanes obtained under the same conditions. Fig. 5 illustrates the average molecular weight ($\bar{M}_n$) of polybutylsilsesquioxanes and polymethacryloxypropylsilsesquioxanes obtained in aqueous solutions over a wide pH range. The surprising result is that the bulky γ-methacryloxypropyl functional groups attached to silicon did not impede growth of polymeric chains. In contrast, it has been reported that the molecular weight of polyalkysilsesquioxanes are strongly influenced by the size of the alkyl groups. Andrianov and Izmaylov have shown that the steric hindrance caused by the size of the alkyl group gives rise to the formation of low molecular weight cyclic oligomers and impede the intermolecular condensation [13].

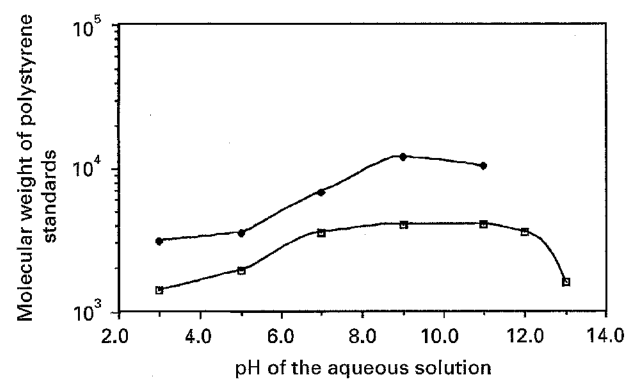
In addition to the difference in molecular weight, the chromatograms of polymethacryloxypropylsilsesquioxanes and polybutylsilsesquioxanes differ in peak shape. Polybutylsilsesquioxanes exhibited single peaks over the entire pH range indicating the polymers were monodisperse. The molecular weight of the polymer increased with the increase in pH and the highest molecular weight polymer formed was at a pH between 9.0 and 11.0. In contrast, the peaks of polymethacryloxypropylsilsesquioxane exhibited doublets on the chromatograms except at pH 5.0. The shape of the peaks suggest that the polymer obtained at pH 5.0 was monodisperse but the molecular weights of the polymers obtained in conditions other than this were in a bimodal distribution.

In acidic solutions at pH 5.0, the polymethacryloxypropylsilsesquioxanes produced have a molecular weight around 3500. An increase in low molecular weight oligomers occurred with an increase in the acidity of the solutions. A significant molecular weight increase occurred when the solution changed from



$$CH_2{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_3{-}\underset{O}{\overset{O}{Si}}{-}O{-} + OH^- \rightleftharpoons CH_2{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}{-}O^- + HO(CH_2)_3{-}\underset{O}{\overset{O}{Si}}{-}O{-}$$

Figure 4 The cleavage of methacryloxypropylsilsesquioxane under the strongly alkaline conditions



pH	3.0	5.0	7.0	9.0	11.0	12.0	13.0
iso-butylsilane	1,410	1,910	3,500	4,000	4,000	3,500	1,560
γ-MPS	3,100	3,500	6,740	11,920	10,140		

Figure 5 The average molecular weights ($\bar{M}_n$) of (□) polybutylsilsesquioxanes and (◆) polymethacryloxypropylsilsesquioxanes from aqueous solutions at different pH conditions.

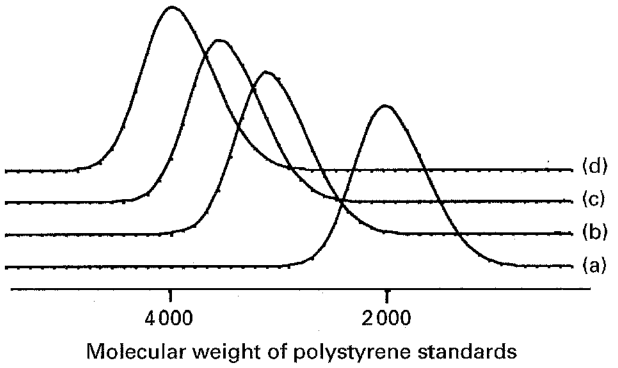


Figure 6 GPC chromatograms of polybutylsilsesquioxanes obtained in aqueous solutions influenced by fluoride ion at concentrations of (a) 2.5×10^{-7} M, (b) 5.0×10^{-7} M, (c) 1.0×10^{-6} M and (d) 2.5×10^{-6} M and 5.0×10^{-6} M.

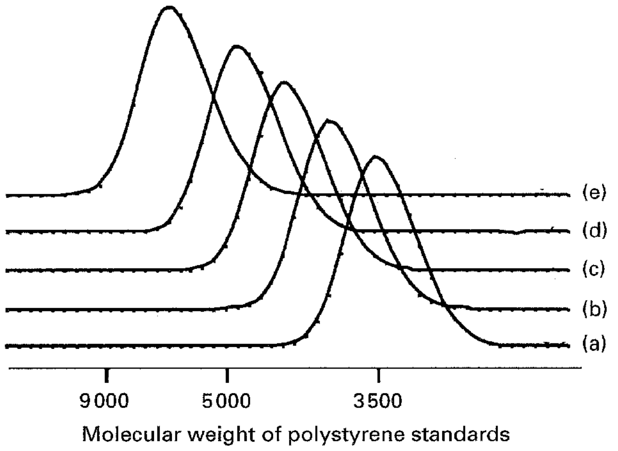
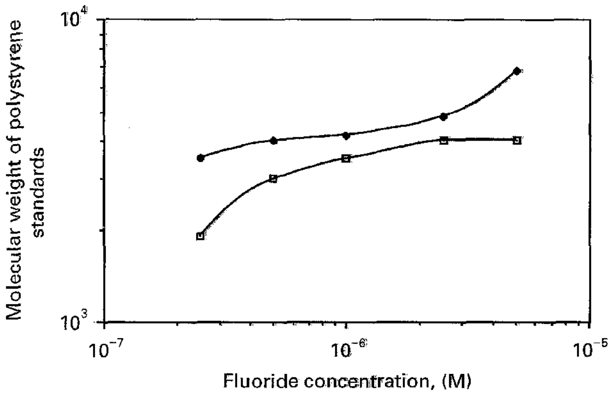


Figure 7 GPC chromatograms of polymethacryloxypropylsilsesquioxanes obtained in aqueous solutions influenced by fluoride ions at the concentrations (a) 2.5×10^{-7} M, (b) 5.0×10^{-7} M, (c) 1.0×10^{-6} M, (d) 2.5×10^{-6} M and (e) 5.0×10^{-6} M.

acidic to neutral. The peak started to split into two with a large peak corresponding to a molecular weight around 6000 together with a small peak corresponding to a molecular weight around 35 000. The small peak indicated the presence of high molecular weight polymer and apparently the presence of such high molecular weight polymer is high in the products obtained at pH 9.0. However, the chromatogram only provides information on products soluble in THF. The polymethacryloxypropylsilsesquioxane mixture obtained at pH 11.0 could not be completely dissolved in THF. The insoluble fraction was apparently a high molecular weight material. Therefore the relative proportion of high molecular weight polymer may be higher than the chromatogram suggested. In general, high molecular weight polymethacryloxypropylsilsesquioxane was formed under neutral and alkaline conditions. In particular, alkaline conditions produced a fraction with a much higher molecular weight. The pattern of molecular weight changes of polymethacryloxypropylsilsesquioxane as a function of pH is somewhat similar to that of polybutylsilsesquioxane. The molecular weights of the polybutylsilsesquioxanes and the polymethacryloxypropylsilsesquioxanes obtained in aqueous solutions decreased in the order alkaline $\geqslant$ neutral $>$ acidic (alkaline refers to mild alkaline conditions).

In addition to pH, the influence of fluoride on the molecular weight distribution of polymeric products from silanes was also investigated. The addition of fluoride ions in silanol solutions between pH 4 and 5 was carried out to reduce the catalytic effect caused by acid or base in the solution because at pH between 4 and 5 the silanol solution has maximum stability. The solution became hazy soon after the addition of fluoride. The polybutylsilsesquioxanes and polymethacryloxypropylsilsesquioxanes resulting from the addition of fluoride into the solutions were oily or viscous materials and were submitted to GPC analysis. Figs 6 and 7 illustrate the chromatograms of polybutylsilsesquioxanes and polymethacryloxypropylsilsesquioxanes obtained in the presence of fluoride ions in the solution. The molecular weights are all of monodisperse distribution and increase with the rise in fluoride ion concentration. The polymers formed by condensation under the influence of fluoride ion exhibit molecular weights of only a few thousand (Fig. 8). For the polymethacryloxypropylsilsesquioxanes in particular, the molecular weight is much lower than that of the comparable base-catalysed reaction.



Fluoride Conc. (M)	2.5×10^{-7}	5.0×10^{-7}	1.0×10^{-6}	2.5×10^{-6}	5.0×10^{-6}
iso-butylsilane	1,900	3,000	3,500	4,000	4,000
γ-MPS	3,500	4,000	4,180	4,790	6,760

Figure 8 The average molecular weights ($\bar{M}_n$) of (□) polybutylsilsesquioxanes and (◆) polymethacryloxypropylsilsesquioxanes influenced by fluoride ions in aqueous solutions.

4. Conclusions

The hydrolysis and condensation of organofunctional silanes in aqueous solutions produced polymers or oligomers with distinctive differences in molecular weight distribution. iso-Butyltrimethoxysilane formed monodisperse polymer with a molecular weight ranging from 1000–4000. In contrast, the polymer from γ-methacryloxypropyltrimethoxysilane exhibited a higher molecular weight and had a bimodal distribution. In alkaline solution in particular, the high molecular weight fraction can achieve a molecular weight as high as 35 000. In common with polymethacryloxypropylsilsesquioxanes, high molecular weight polybutylsilsesquioxanes were obtained in alkaline solution. In general polysilsesquioxanes formed from fluoride–catalysed condensation exhibited molecular weights of a few thousand and the molecular weight increased with the concentration of the fluoride ions. In comparison with acid or base catalysis, the molecular weight distribution of polybutylsilsesquioxanes formed under the influence of fluoride ion was somewhat similar to base–catalysed reaction whereas the molecular weight of polymethacryloxypropylsilsesquioxanes formed under the influence of fluoride ions are significantly less than the products formed from the base–catalysed reaction.

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