Preparation and saponification of vinyl siloxane–vinyl acetate copolymers

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Copolymerization of two vinyl siloxanes, n-butyldimethylsiloxydimethylvinyl silane (n-VSiO) and t-butyldimethylsiloxydimethylvinyl silane (t-VSiO), with vinyl acetate (VAc) has been carried out. Copolymerization parameters $r_1(\mathrm{VAc})=0.61$, $r_2(\text{n-VSiO})=0.68$ and $r_1(\mathrm{VAc})=0.72$, $r_2(\text{t-VSiO})=0.98$ were obtained. Treatment of both the VSiO–VAc copolymers with the usual saponification catalyst, NaOH in methanol, caused undesired scission of the siloxane bond in the VSiO units along with deacetylation of the VAc units. However, satisfactorily selective saponification of the VAc units in both the VSiO–VAc copolymers was attained when aqueous NaOH in tetrahydrofuran was used as catalyst with the addition of the appropriate amount of methanol. The type of alkyl substituent on the silicon did not affect the hydrolytic stability of the vinyl siloxane unit in these copolymers.

(Keywords: vinyl siloxane; vinyl acetate; vinyl alcohol; copolymerization; saponification)

INTRODUCTION

The siloxane bond (Si–O–Si) is characterized by high flexibility and high bond energy, conferring unique properties to siloxane-containing compounds[1]. As examples of polymer materials other than the well known silicone rubbers, methyl methacrylate derivatives with siloxane units were studied as possible candidates for soft contact lenses[2,3].

Although vinyl siloxane (VSiO) is regarded as a simple vinyl monomer containing a siloxane unit, there have been few studies on the polymerization behaviour of vinyl siloxanes[4], in contrast to the various examples of copolymerization of vinyl silane derivatives with conjugated monomers[5]. The copolymerization of vinyl silane derivatives containing a hydrolysable Si–OR function with vinyl acetate (VAc) has also been reported[6].

We have recently reported an easy preparation method for vinyl siloxanes and their homopolymerization using di-t-butylperoxide as initiator[7]. We have also described the synthesis of poly(dimethyl siloxane) with a vinyl silane end group (thus a vinyl siloxane end group) and its copolymerization with vinyl acetate, leading to poly(vinyl acetate)–poly(dimethyl siloxane) graft copolymer and subsequent saponification to poly(vinyl alcohol)–poly(dimethyl siloxane) graft copolymer[8].

As part of our studies on the polymerization behaviour of vinyl siloxane derivatives, the present paper describes the copolymerization of two types of vinyl siloxanes with VAc and the subsequent saponification of the resulting VSiO–VAc copolymers. The two vinyl siloxanes, namely n-butyldimethylsiloxydimethylvinyl silane (n-VSiO) and t-butyldimethylsiloxydimethylvinyl silane (t-VSiO), are used in this study to elucidate the effect of the substituent on silicon on copolymerization reactivity as well as on hydrolytic stability of the siloxane bond, since the hydrolytic stability of silyl ethers (C–O–Si) is known to be sensitive to the substituent on the silicon[9]. Besides, the properties of vinyl alcohol–vinyl siloxane copolymers will be of interest, since the combination of hydrophilic–hydrophobic, crystalline–amorphous nature of the monomer units may exhibit unique properties in the bulk as well as at the surface, as is already seen in ethylene–vinyl alcohol copolymers[10].

EXPERIMENTAL

Reagents

n-VSiO and t-VSiO were synthesized by the reaction of n- and t-butyllithium with hexamethylcyclotrisiloxane, followed by the addition of vinyldimethylchlorosilane. The details of the preparation procedure have been described elsewhere[7]. VAc was purified by distillation under reduced pressure in the presence of azoisobutyronitrile (AIBN). AIBN was recrystallized from methanol. Other reagents were purified by conventional methods.

Procedures

Copolymerization. Copolymerization of vinyl siloxanes with vinyl acetate was carried out in benzene solution at 60°C with AIBN as initiator. Copolymers were isolated by precipitation into petroleum ether (VSiO feed up to 25 wt%), into water/ethanol (1/3 by volume) mixture (VSiO feed up to 50 wt%) or into water/methanol (1/9 by volume) mixture (VSiO feed more than 50 wt%), and purified by reprecipitation with the corresponding solvent/non-solvent systems. Each comonomer ratio in the copolymer was determined by integrating the ^{1}H n.m.r. signal intensities of the corresponding monomer unit.

Saponification. Saponification of VSiO–VAc copolymers was carried out in methanol or THF solution. A measured amount of catalyst was added to the above solution and stirred for the desired period. The reaction system in methanol remained homogeneous throughout

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the reaction, whereas in the THF solution the reaction product precipitated out. The reaction product in methanol was isolated by precipitation into petroleum ether, washing with water until the washing became neutral and drying *in vacuo*. The reaction product obtained in THF was isolated by evaporating the solvent, rinsing with water until the washing became neutral and then drying *in vacuo*. The siloxane content and the degree of saponification were determined from ^{1}H n.m.r. spectral analysis.

Measurements

270 MHz ^{1}H n.m.r. spectra were taken on a JEOL GX-270 apparatus. VSiO–VAc copolymers were analysed in $CDCl_3$ solution at ambient temperature; the saponification products were analysed in DMSO-d_6 solution at 40°C. The proton of $CHCl_3$ (7.30 ppm) or DMSO (2.50 ppm) was used as internal standard for the chemical shift values. G.p.c. measurements were carried out using a Toyo Soda HLC 803C equipped with a G4000HXL column and THF as eluant. Viscosity measurements were performed with a conventional Ubbelohde viscometer in acetone solution at 30°C.

RESULTS AND DISCUSSION

Copolymerization of vinyl siloxanes with vinyl acetate

Radical copolymerization of VAc with n-VSiO and t-VSiO was carried out using AIBN as initiator at 60°C. The ^{1}H n.m.r. spectra of n-VSiO–VAc and t-VSiO–VAc copolymers are shown in *Figures 1a* and *b*, respectively. The signals for the VSiO unit as well as the VAc unit are observed, indicating the occurrence of the copolymerization reaction.

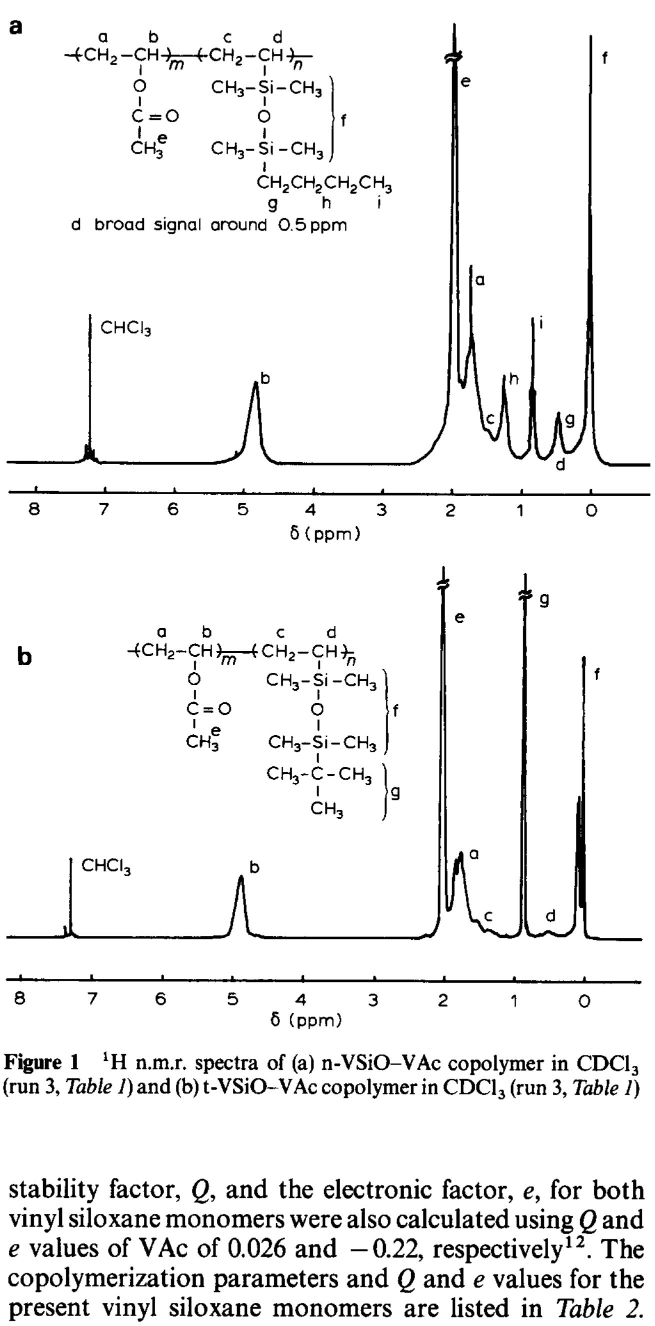


Figure 1 ^{1}H n.m.r. spectra of (a) n-VSiO–VAc copolymer in $CDCl_3$ (run 3, *Table 1*) and (b) t-VSiO–VAc copolymer in $CDCl_3$ (run 3, *Table 1*)

Other copolymerization data for n- and t-VSiO–VAc copolymers are collected in *Table 1*. Copolymers with up to ~30 mol% vinyl siloxane content with reasonably high molecular weight were obtained for these vinyl siloxanes, although the solution viscosity of the copolymer decreases with increase of the vinyl siloxane content. n-VSiO–VAc copolymers with more than 20 mol% VSiO content and t-VSiO–VAc copolymers with more than 30 mol% VSiO content were viscous, whereas powdery products were obtained with less VSiO monomer content.

The copolymerization parameters for n-VSiO–VAc as well as t-VSiO–VAc systems were obtained using the copolymerization data with less than 10% yield. *Figures 2a* and *b* show the Kelen–Tüdös plots[11] for n-VSiO–VAc and t-VSiO–VAc, respectively. Good linearity was obtained in both systems and the copolymerization parameters were obtained from these plots. The resonance stability factor, *Q*, and the electronic factor, *e*, for both vinyl siloxane monomers were also calculated using *Q* and *e* values of VAc of 0.026 and −0.22, respectively[12]. The copolymerization parameters and *Q* and *e* values for the present vinyl siloxane monomers are listed in *Table 2*. Both n-VSiO and t-VSiO monomers possess almost identical copolymerization reactivity with vinyl acetate, despite a considerable difference in the bulkiness of the substituent on silicon. Both vinyl siloxanes were regarded as scarcely conjugated and electrophilic monomers from the *Q* and *e* values.

Table 1 Copolymerization of n-VSiO (n-) and t-VSiO (t-) with VAc[a]

	Monomer feed (mol%)		Time (h)		Yield (%)		VSiO in copolymer (mol%)		$[\eta]^b$ (dl g^{-1})		$M\times10^{-4}$ (g.p.c.)[c]	
Run	VSiO	VAc	n-	t-	n-	t-	n-	t-	n-	t-	n-	t-
1	2.1	97.9	6	6	27.1	28.0	2.2	2.5	0.59	0.58	14.8	11.0
2	4.2	95.8	6	6	21.9	22.8	5.6	5.2	0.48	0.48	11.4	10.2
3	9.0	91.0	6	6	12.7	13.7	12.2	10.9	0.32	0.33	6.4	7.4
4	14.6	85.4	14	14	14.5	12.7	17.7	16.2	0.23	n.d.	n.d.	6.4
5	28.5	71.5	6	14	3.8	8.3	33.3	34.3	0.12	n.d.	n.d.	n.d.
6	48.2	51.8	6	14	0.9	3.3	49.4	50.4	n.d.	n.d.	n.d.	n.d.

[a] (VSiO + VAc)/Bz (solvent) = 1/1 (wt ratio); AIBN 0.17 wt%, 60°C
[b] In acetone at 30°C
[c] Calibrated by polystyrene standards

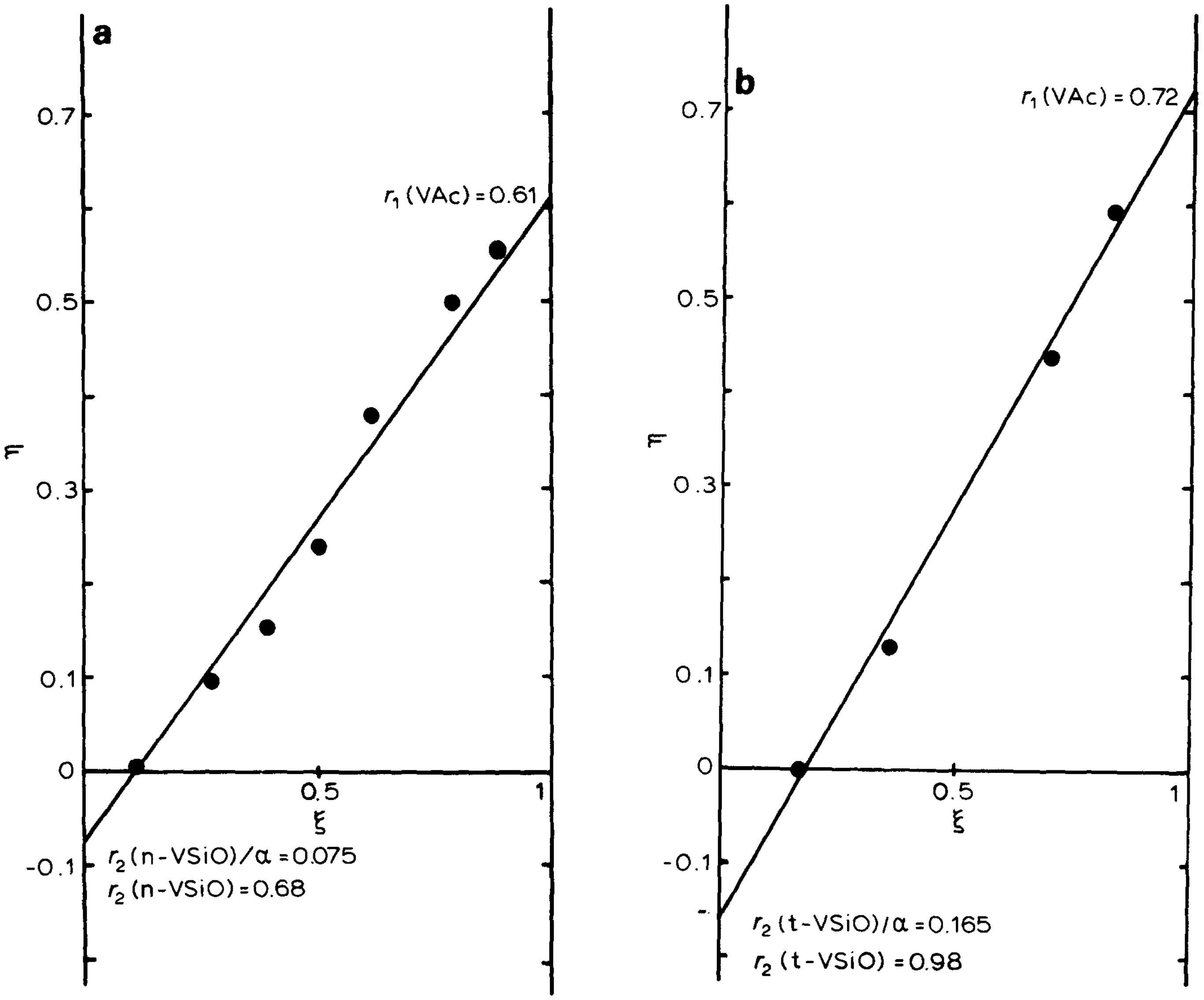


Figure 2 Kelen–Tüdös plots for (a) n-VSiO–VAc copolymerization and (b) t-VSiO–VAc copolymerization

Table 2 Copolymerization parameters of n-VSiO and t-VSiO[a]

M_1	M_2	r_1	r_2	Q_2	e_2
VAc	n-VSiO	0.61	0.68	0.035	0.72
VAc	t-VSiO	0.72	0.98	0.059	0.81

[a] Calculated by using Q and e values of VAc of 0.026 and −0.22, respectively[12]

Table 3 Saponification of n-VSiO–VAc and t-VSiO–VAc copolymers[a]

		Siloxane unit retained (%)	
Run	Catalyst	n-VSiO–VAc	t-VSiO–VAc
1	NaOH	9.0	13.5
2	CH_3ONa	6.3	14.4
3	K_2CO_3	7.2	21.2

[a] Sample: n-VSiO–VAc copolymer of 11.1 mol% VSiO unit; t-VSiO–VAc copolymer of 10.4 mol% VSiO unit. Run 1: NaOH, 6.25×10^{-1} mmol; CH_3OH, 7.1 ml. Run 2: CH_3ONa, 6.11×10^{-1} mmol; CH_3OH, 7.9 ml. Run 3: K_2CO_3, 2.39×10^{-1} mmol; CH_3OH, 6.5 ml. Copolymer, 0.1 g; 20°C; 9 h

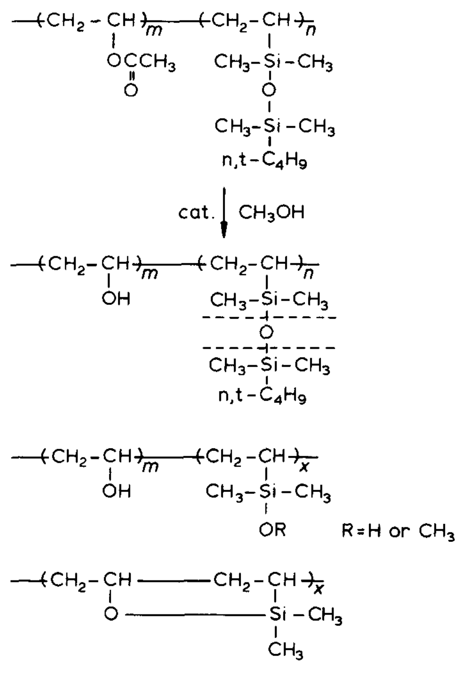
Saponification reactions of vinyl siloxane–vinyl acetate copolymers

Poly(vinyl acetate) is usually converted into poly(vinyl alcohol) with sodium hydroxide as the saponification catalyst in methanol solution. This saponification procedure was applied to the present VSiO–VAc copolymers, and significant scission of the siloxane bond in the VSiO unit was found to occur under reaction conditions in which the saponification of the VAc unit was completed. Other saponification catalysts, like sodium methoxide and K_2CO_3 in methanol, were then used, but the situation was scarcely improved as summarized in *Table 3*. This observation is in contrast to the case of saponification of poly(vinyl acetate)–poly(dimethyl siloxane) graft copolymers, where K_2CO_3 in methanol was an excellent catalyst for the selective saponification of the poly(vinyl acetate) segment[8]. It should be noted that the present reaction mixture remained clear throughout the reaction and no precipitation took place, contrary to the case of saponification of poly(vinyl acetate) in methanol.

Saponification of t-VSiO–VAc copolymer of about 10 mol% VSiO content was examined in methanol solution in more detail using K_2CO_3 as catalyst, with varying catalyst concentrations as well as reaction times. The results are collected in *Figure 3*. *Figure 3b* also shows the results of the saponification reaction of n-VSiO–VAc copolymer. The results obtained using sodium hydroxide as catalyst are also shown in *Figure 3c*. Under any reaction conditions examined, the saponification of VAc to vinyl alcohol was accompanied by scission of the siloxane bond in VSiO, although deacetylation of VAc proceeded more rapidly than the siloxane scission reaction. Little difference was observed with respect to the hydrolytic stability of the siloxane bond in n-VSiO and in t-VSiO in these reaction conditions.

A typical ^1H n.m.r. spectrum of the saponification product of t-VSiO–VAc copolymer is shown in *Figure 4*. A significant decrease of t-butyl signal at 0.84 ppm clearly indicates the occurrence of scission of the siloxane bond in VSiO during the saponification treatment mentioned above.

As commented before, in methanol, the reaction solution was clear throughout the saponification reaction, whereas after drying the isolated product was found to be no longer soluble in methanol (but soluble in DMSO). This product dissolved again in methanol on addition of a drop of hydrochloric acid into the medium. From these observations, an intramolecular condensation reaction as shown below: is believed to take place during the isolation of the reaction product. Similar intramolecular cyclization was observed in vinyl alcohol–acrylic acid copolymer system[13].



The reaction medium was changed from methanol to THF, and then an appropriate amount of methanol was added with sodium hydroxide as a catalyst. This time, precipitation of the reaction product from the medium was observed. As is shown in *Figure 5a*, fairly selective saponification of the VAc unit was achieved in this system. *Figures 5b* and *c* show the results of saponification of

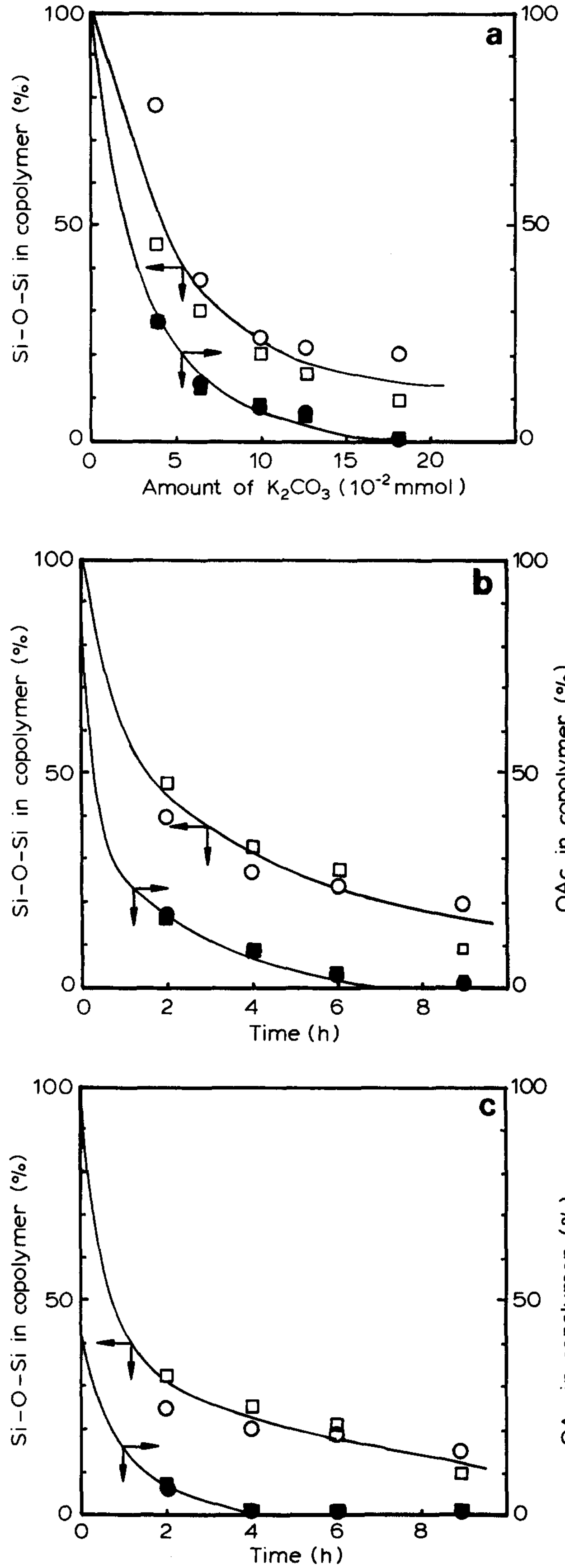


Figure 3 (a) Saponification of n-VSiO–VAc (□, ■) and t-VSiO–VAc (○, ●) copolymers at various K_2CO_3 concentrations: copolymer (run 3, *Table 1*), 0.1 g; methanol, 6.5 ml; 20°C; 9 h. (b) Saponification of n-VSiO–VAc (□, ■) and t-VSiO–VAc (○, ●) copolymers for various reaction times: copolymer (run 3, *Table 1*), 0.1 g; methanol, 6.5 ml; K_2CO_3, 33 mg; 20°C. (c) Saponification of n-VSiO–VAc (□, ■) and t-VSiO–VAc (○, ●) copolymers by NaOH catalyst: copolymer (run 3, *Table 1*), 0.1 g; methanol, 7.1 ml; NaOH, 25 mg; 20°C

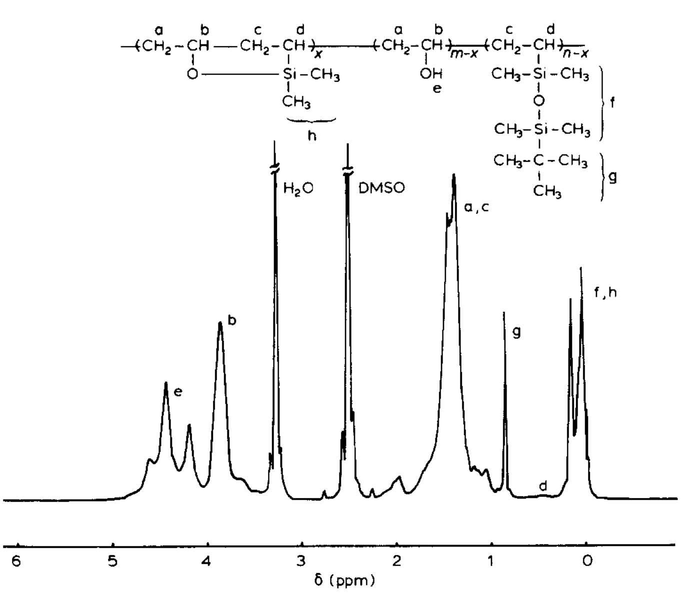


Figure 4 ^1H n.m.r. spectrum of the saponification product of t-VSiO–VAc copolymer in DMSO-d_6; 40°C; sample of *Figure 3b*; 9 h

VSiO–VAc copolymers by varying the catalyst concentration and the reaction time, respectively. Complete deacetylation of the VAc unit was attained while preserving as much as 70% of the siloxane units of the VSiO–VAc copolymer with 10mol% VSiO content. The amount of THF in the reaction medium and the use of a catalyst other than sodium hydroxide did not improve the selectivity of the saponification of VAc while keeping the siloxane bond in VSiO.

Figure 6 shows the ^1H n.m.r. spectrum of the t-VSiO–vinyl alcohol copolymer obtained by the above reaction system. By comparison with the spectrum in *Figure 4*, the increase of the signal at 0.84 ppm for t-butyl protons as well as that at −0.04 ppm for methyl protons on the external silicon atom in the siloxane bond is evidence to indicate the occurrence of selective saponification of VAc units in VSiO–VAc copolymer.

A series of n-VSiO–VAc and t-VSiO–VAc copolymers with various VSiO unit contents were treated in THF as described above. The results are summarized in *Figure 7*. Although considerable scission of the siloxane bond was observed in VSiO–VAc copolymers with small VSiO unit

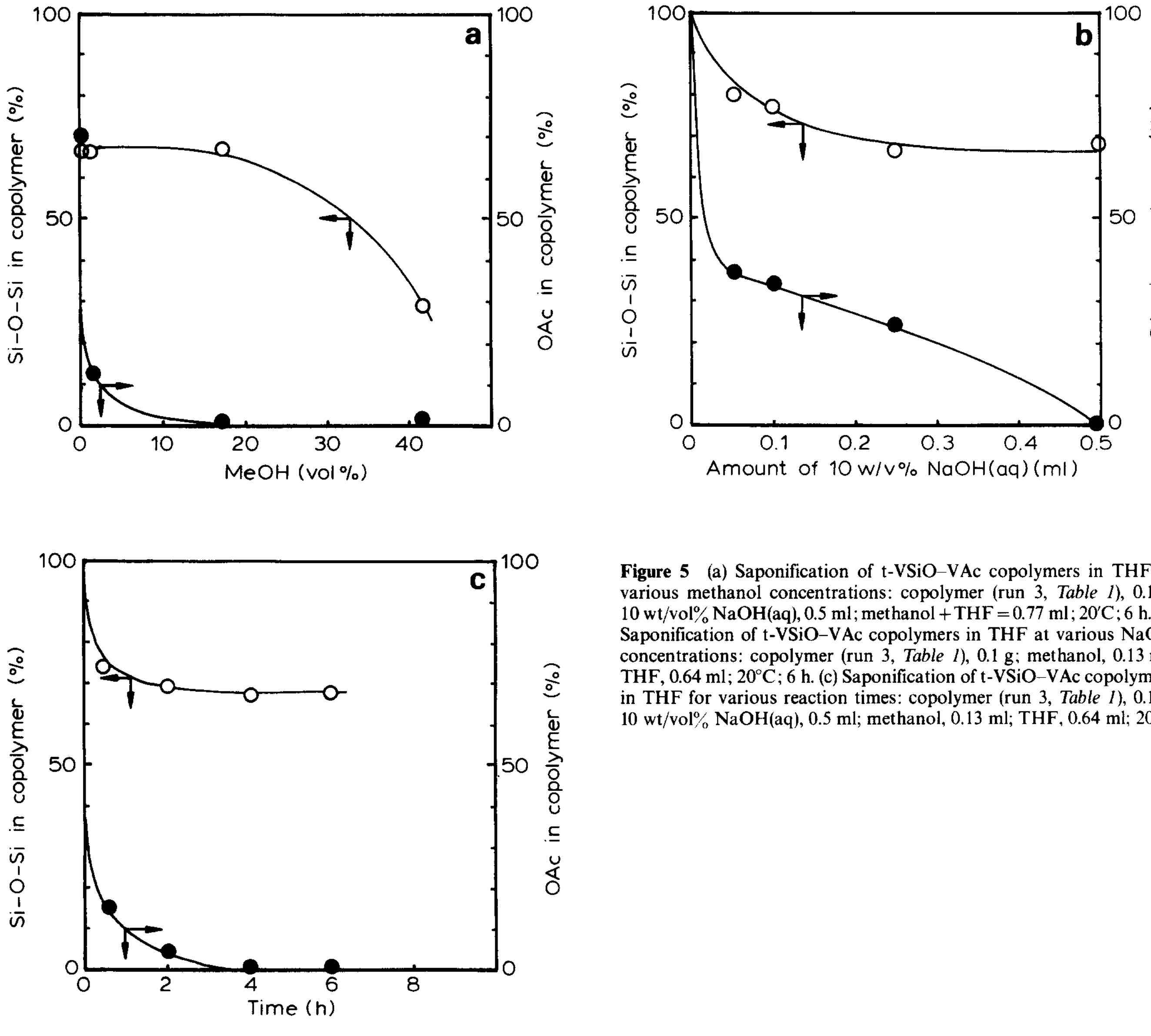


Figure 5 (a) Saponification of t-VSiO–VAc copolymers in THF at various methanol concentrations: copolymer (run 3, *Table 1*), 0.1 g; 10 wt/vol% NaOH(aq), 0.5 ml; methanol + THF = 0.77 ml; 20°C; 6 h. (b) Saponification of t-VSiO–VAc copolymers in THF at various NaOH concentrations: copolymer (run 3, *Table 1*), 0.1 g; methanol, 0.13 ml; THF, 0.64 ml; 20°C; 6 h. (c) Saponification of t-VSiO–VAc copolymers in THF for various reaction times: copolymer (run 3, *Table 1*), 0.1 g; 10 wt/vol% NaOH(aq), 0.5 ml; methanol, 0.13 ml; THF, 0.64 ml; 20°C

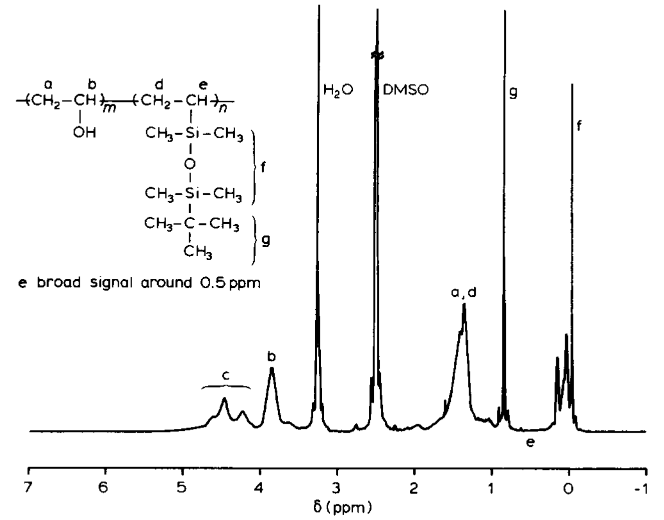


Figure 6 ^1H n.m.r. spectrum of the saponification product of t-VSiO–VAc copolymer in DMSO-d_6; 40°C; sample of *Figure 5c*; 6 h

content, the selectivity of saponification increased in the copolymer with higher VSiO unit content. The hydrolytic stability of the siloxane unit in n-VSiO and that in t-VSiO were found to be almost identical. This is in contrast to the hydrolytic stability of silyl ethers with C–O–Si bond[9], where the hydrolytic stability is heavily dependent on the type of substituent on silicon.

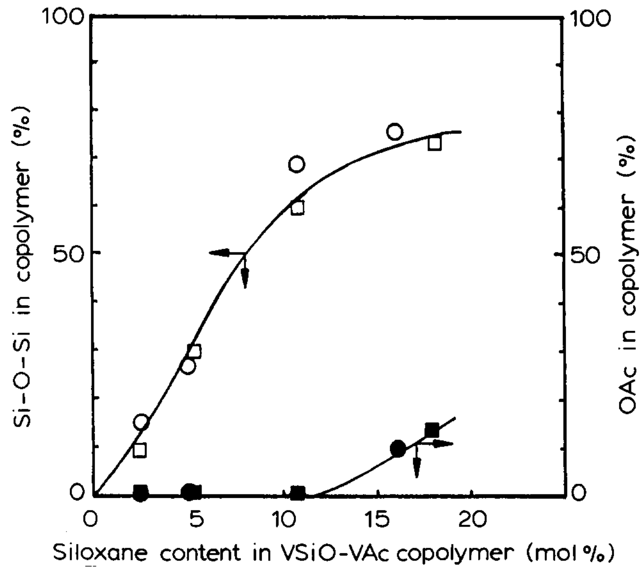


Figure 7 Saponification of n-VSiO–VAc (□, ■) and t-VSiO–VAc (○, ●) copolymers in THF; copolymer (runs 1, 2, 3, 4, *Table 1*), 0.1 g; 10 wt/vol% NaOH, 0.5 ml; methanol, 0.13 ml; THF, 0.64 ml; 20°C; 4 h

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