Synthesis and reactions of silyl ketene acetal-modified polysiloxanes. Preparation and preliminary dielectric characterization of some new polysiloxanes

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A new route to the functionalization of polysiloxanes is described. Polysiloxanes having pendant silyl ketene acetals are synthesized through hydrosilation of poly(methylhydrosiloxane) with a terminal olefin bearing a silyl ketene acetal. The functionalized polysiloxanes can be reacted with electrophiles such as *p*-nitrobenzenesulphenyl chloride, affording derivatives having highly polar pendants. These materials have dielectric constants as high as 9 and dissipation factors as low as 0.02–0.06 at 100 kHz at room temperature. The temperature dependencies of the dielectric constants are a function of polar pendant group concentration.

(Keywords: synthesis; polysiloxanes; silicones; chemical modification; dielectric properties)

INTRODUCTION

Polysiloxanes, or silicones, have received much attention as speciality polymers since their commercial application in the 1940s and are by far the most important of the inorganic backbone polymers. Special interest in these systems has developed as a result of their unique properties, which include low glass transition temperatures (T_gs), good thermal and oxidative stability, low surface energies, excellent biocompatibility and high gas permeabilities[1,2].

The hydrosilation reaction, because of its typically high conversion, enjoys frequent utility as a route to functionalized silicones[2]. However, the range of materials which can be synthesized is often limited by the range of terminal olefins which can be purchased or easily prepared. We wish to report a variant of this approach which introduces silyl ketene acetal groups for subsequent reactions with a variety of electrophiles, preliminary accounts of which have appeared elsewhere[3,4]. The latter reaction, like hydrosilation, affords high yields with appropriately chosen substrates and is thus attractive as a polymer modification reaction. Silyl ketene acetals are important reagents in organic chemistry[5], and Webster *et al.* demonstrated that silyl ketene acetals are excellent initiators for the polymerization of methacrylates and related monomers[6,7]. They coined the term 'group transfer polymerization' (GTP) to describe the propagation step in which a silyl group is transferred to the monomer, generating a new silyl ketene acetal. The 'living' ends, bearing silyl ketene acetals, can be derivatized[7], a recent example being the introduction of phosphonic ester groups[8].

As indicated in *Scheme 1*, poly(methylhydrosiloxane) (PMHS) can be derivatized with silyl ketene acetal groups by one of two routes.

An ester bearing a terminal olefin, such as ethyl 2-methyl-4-pentenoate, can be first transformed into the corresponding silyl ketene acetal and then used for hydrosilation. Alternatively, hydrosilation with the ester can be accomplished first, followed by transformation to the silyl ketene acetal. The former approach is used exclusively in this paper. In addition, copolymers are readily prepared by hydrosilation with a mixture of the ketene acetal and ethyl 2-methyl-4-pentenoate. We also note that copolymers can in principle be prepared by partial hydrolysis or alcoholysis of the silyl ketene acetal-functionalized polymer.

We report here the details of the synthesis of the silyl ketene acetal-modified polysiloxanes and their reactions with selected electrophiles (*Scheme 2*) such as 4-nitrobenzenesulphenyl chloride. The resulting polysiloxanes have highly polar side groups and thus may have large dielectric constants over a broad frequency range. Preliminary results will be presented later which support this contention. Because the silyl ketene acetals are GTP initiators, the silyl ketene acetal-derivatized polysiloxanes may be employed as 'macroinitiators' for the preparation of new silicone graft and comb copolymers or, using cyclosiloxane oligomers or end-functionalized polydimethylsiloxanes, star and block copolymers, respectively[9]. This aspect however will be the subject of another paper.

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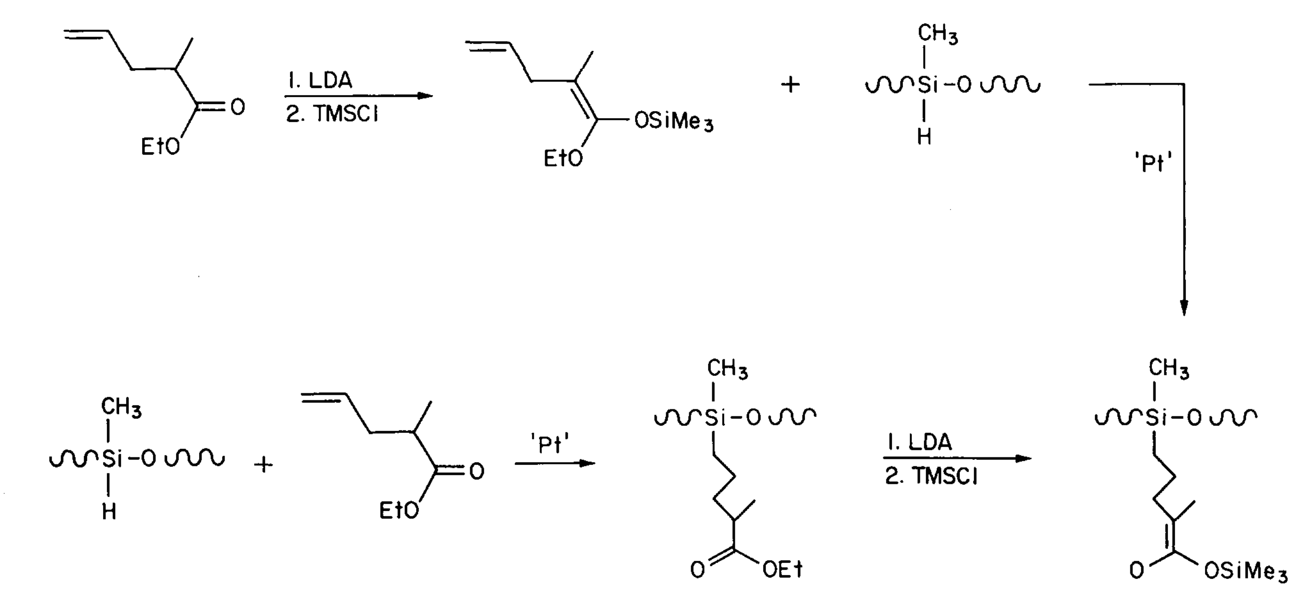
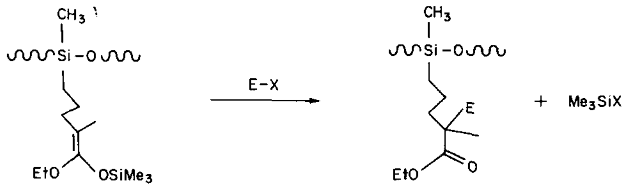


Scheme 1



Scheme 2

EXPERIMENTAL

Materials

PMHS was acquired from Petrarch, and had a number-average molecular weight of ~4500–5000 g mol^{-1} according to the supplier. Ethyl 2-methyl-4-pentenoate and methyl trimethylsilyl dimethylketene acetal (MTDA) were acquired from Aldrich and distilled prior to use. Chloroplatinic acid, 4-nitrobenzenesulphenyl chloride, 2,4-dinitrobenzenesulphenyl chloride and 4-nitrobenzoyl chloride were acquired from Aldrich, and stored in a refrigerator. Tetrahydrofuran (THF) and toluene were refluxed over sodium benzophenone radical anion and calcium hydride, respectively, and distilled just prior to use. Methylene chloride and diethyl ether were distilled prior to use. Trimethylsilylchloride was distilled prior to use.

Model reactions

The reaction of MTDA with 4-nitrobenzenesulphenyl chloride, 2,4-dinitrobenzenesulphenyl chloride and 4-nitrobenzoyl chloride as model systems were investigated. Representative conditions follow.

MTDA with 4-nitrobenzenesulphenyl chloride. To a solution of 4-nitrobenzenesulphenyl chloride (8.1 g, 42 mmol) in 100 ml dry ether, MTDA (8.5 ml, 42 mmol) was added. The mixture was refluxed under argon for 30 min. Ether was removed using a rotary evaporator and then the product was distilled at reduced pressure (b.p. 138–140°C/4 mm). The yield of methyl-2-methyl-2-(4-nitrothiophenoxy)propionate (MNTP) was 99%. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 8.16 (q, 2H, Ar), 7.56 (q, 2H, Ar), 3.68 (s, 3H, OCH_3), 1.54 (s, 6H, $2CH_3$).

MTDA with 2,4-dinitrobenzenesulphenyl chloride. To a solution of 2,4-dinitrobenzenesulphenyl chloride (2.3 g, 9.8 mmol) in 25 ml dry methylene chloride, MTDA (2 ml, 9.8 mmol) was added. The mixture was refluxed under argon for 40 min. Methylene chloride was removed under reduced pressure, and methyl-2-methyl-2-(2,4-dinitrothiophenoxy)propionate was obtained as yellow crystals (m.p. 82–86°C). The yield was 95%. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 8.89 (d, 1H, Ar), 8.33 (q, 1H, Ar), 7.63 (d, 1H, Ar), 3.75 (s, 3H, OCH_3), 1.68 (s, 6H, $2CH_3$).

MTDA with 4-nitrobenzoyl chloride. To a solution of 4-nitrobenzoyl chloride (5.6 g, 30 mmol) in 80 ml dry ether, MTDA (6 ml, 30 mmol) was added. The mixture was refluxed under argon for 24 h. Ether was removed under reduced pressure, and 2-methyl-2-(4-nitrobenzoyl)-propionate was obtained as yellow crystals (m.p. 62–64°C). The yield was 95%. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 8.27 (d, 2H, Ar), 7.95 (d, 2H, Ar), 3.64 (s, 3H, OCH_3), 1.53 (s, 6H, $2CH_3$)

Synthesis of ethyl trimethylsilyl 2-methyl-2-allylketene acetal (ETMA)

A 500 ml three-necked round-bottomed flask was fitted with a reflux condenser, magnetic stirring bar, rubber septum and a gas inlet. The apparatus was connected through the gas inlet to an argon source and reflux condenser to a bubble. After the flask was flame-dried and flushed with argon, it was charged with 250 ml of THF and distilled diisopropylamine (30.2 ml, 214.9 mmol). The flask was immersed in an ice-salt bath and cooled to −10°C, and over a period of ~5 min, 2.5 M n-butyllithium in hexane (86.0 ml, 214.9 mmol) was added dropwise, with continuous stirring, with a syringe through the septum. After an additional 20 min of stirring, ethyl 2-methyl-4-pentenoate (35 ml, 214.9 mmol) was added dropwise through an additional funnel over a 10 min period, and the solution was stirred for an additional 30 min at 0°C. At this point, distilled trimethylsilylchloride (40.9 ml, 322.1 mmol) was rapidly introduced with a syringe through the septum. After the addition was complete (~30 s) the solution was stirred for an additional 1 h at room temperature. Solvent was removed using a rotary evaporator and the residue was treated with 200 ml of pentane. The slurry was filtered and the filtrate was concentrated on a rotary evaporator and then distilled at reduced pressure. The product, ethyl trimethylsilyl 2-methyl-2-allylketene acetal, was distilled at 79°C (15 mm). The yield was 97%. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 5.70 (m, 1H, allyl), 4.96 (m, 2H, allyl), 3.70 (m, 2H, $O\underline{CH_2}CH_3$), 2.68 (q, 2H, $-CH_2-$), 1.47 (d, 3H, CH_3), 1.19 (m, 3H, $OCH_2\underline{CH_3}$), 0.19 (d, 9H, $SiMe_3$).

Hydrosilation of PMHS with ETMA

To a mixture of PMHS (6 g, 100 mmol) and ETMA (21.4 g, 100 mmol) in 100 ml dry toluene, several drops of H_2PtCl_6 solution (40 mg in 0.5 ml isopropanol) were added. The mixture was refluxed under argon at 50°C for 18–24 h. The extent of reaction was followed by i.r. spectroscopy. After the Si-H peak in the i.r. spectrum disappeared, solvent and unreacted ETMA were removed with a rotary evaporator, and the resulting liquid was kept under high vacuum for 24 h. ^{1}H n.m.r. indicated that the extent of hydrosilation was >97%. The product, poly[(5-ethoxy-5-trimethylsiloxy-4-methylpentyl-4-ene)methylsiloxane] or PSi-SKA, was a colourless, viscous liquid. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 3.71 (m, 2H, $O\underline{CH_2}CH_3$), 1.90 (quintet, 2H, $SiCH_2\underline{CH_2}CH_2$), 1.48 (d, 3H, CH_3), 1.33 (m, 2H, $SiCH_2CH_2\underline{CH_2}$), 1.14 (m, 3H, $OCH_2\underline{CH_3}$), 0.43 (t, 2H, $Si\underline{CH_2}CH_2CH_2$), 0.15 (d, 9H, $\underline{SiMe_3}$), 0.02 [s, 3H, $Si(\underline{CH_3})O$]. The wholly pendant ester derivative, poly-[5-ethoxy-4-methylpentyl-5-one)methylsiloxane], was also prepared by hydrosilation of PMHS with ethyl 2-methyl-4-pentenoate under similar conditions; this is referred to as PSi-Ester. ^{1}H n.m.r. ($CDCl_3$) δ (in ppm from TMS): 4.09 (q, 2H, $O\underline{CH_2}CH_3$), 2.37 [m, 1H, $\underline{CH}(CH_3)$], 1.65 (m, 2H, $SiCH_2\underline{CH_2}CH_2$), 1.34 (m, 2H, $SiCH_2CH_2\underline{CH_2}$), 1.25 (t, 3H, $OCH_2\underline{CH_3}$), 1.17 [d, 3H, $CH(\underline{CH_3})$], 0.46 (t, 2H, $Si\underline{CH_2}CH_2CH_2$), 0.02 (s, 3H, $Si(\underline{CH_3})O$]. Copolymers containing various percentages of pendant silyl ketene acetal functionality, with the remainder the corresponding ester, were synthesized using the same procedure with appropriate ratios of ETMA and ethyl 2-methyl-4-pentenoate. These are termed PSi-SKA-*co*-Ester (x%), where x% is the percentage of silyl ketene acetal.

Reactions of ketene acetal-modified polysiloxane with electrophiles

The polysiloxanes having ketene acetal pendants can be reacted with various electrophiles. A procedure for reacting the copolymer containing ~70% pendant silyl ketene acetals with either 4-nitrobenzenesulphenyl chloride or 2,4-dinitrobenzenesulphenyl chloride is described here as a representative example.

To a solution of PSi-SKA-*co*-Ester (70%) (16.3 g, 64 mmol, in 250 ml dry ether), 4-nitrobenzenesulphenyl chloride (8.87 g, 46.8 mmol) or 2,4-dinitrobenzenesulphenyl chloride (10.98 g, 46.8 mmol) was added slowly. The mixture was stirred under argon at 40°C for 30 min. Then solvent and trimethylsilyl chloride were removed at reduced pressure. The residue was washed with ether several times in order to remove unreacted sulphenyl chloride. (For siloxanes containing < ~50% mono- or dinitrothiophenoxy groups, which are ether-soluble, unreacted sulphenyl chloride was removed on an aluminium oxide column with ether as eluant.) The products were dried under reduced pressure for 2 days. Both products were orange liquids, although the viscosity of the dinitrothiophenoxy derivative was visibly much higher.

Characterization

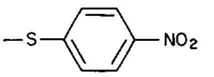
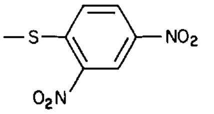
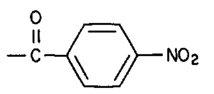
Elemental analyses were performed by Schwarzkopf Laboratory, Woodside, NY, USA. ^{1}H n.m.r. spectra were obtained on a Varian XL-200 spectrometer. I.r. spectra were obtained on a Perkin-Elmer 298 i.r. spectrophotometer. The concentrations of polar pendant groups were calculated from ^{1}H n.m.r. integrations and elemental analyses. G.p.c. was performed in THF using a Waters 600E chromatograph system equipped with a linear ultrastyrogel column and a Waters R401 differential refractometer operating at room temperature. Samples were ~1 wt% in THF. Number-average molecular weights were determined *versus* polystyrene standards (obtained from Tosoh Corp.). T_gs were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 20°C min^{-1}. Samples were dried overnight at 60°C prior to loading in the d.s.c. pans. The T_g was taken at the inflection point in the d.s.c. trace. Dielectric constants were measured at room temperature at 100 kHz using a Balsbaugh liquid cell and GenRad 1689M RLC bridge. Two measurements on water at 24–25°C afforded dielectric constants of 77.8 and 78.6; the dielectric constant of water is reported to be 78.5 at 25°C[10]. The silicones were loaded onto the bottom plate of the cell and any air bubbles were removed by maintaining the sample in a vacuum oven for as long as necessary (typically 2 h). For measurements of dielectric constants at elevated temperatures, a custom-built cell was employed which could be immersed in a constant-temperature bath. It was of a male–female type having a Teflon spacer and was constructed from stainless-steel. The capacity of the cell was ~1 ml. This cell provided less accurate but reasonable data. For example, the dielectric constant of nitrobenzene was ~30.5 at 24–25°C and decreased to ~27.4 at 50°C using this cell. For comparison, it has been reported that the dielectric constant of nitrobenzene is 34.4 at 25°C and 30.2 at 50°C[11].

RESULTS AND DISCUSSION

As a model system, we have investigated reactions of methyl trimethylsilyl dimethylketene acetal with various electrophiles. The extent of reaction as well as the time required to reach maximum conversion are collected in *Table 1*. The silyl ketene acetal readily reacts with the electrophiles shown (note that no catalyst is employed), and the yields are quite high. A longer reaction time was needed for 4-nitrobenzoyl chloride as compared with the sulphenyl chlorides. Incidentally, the highly polar liquid methyl-2-methyl-2-(4-nitrothiophenoxy)propionate has a dielectric constant of ~15 (0.1 kHz) which is invariant with frequency up to 100 kHz.

Hydrosilation of PMHS with ETMA or ethyl 2-methyl-4-pentenoate proceeded in high yield as indicated by the absence of the Si-H stretch absorption at 2160 cm^{-1} in the i.r. and the Si-H resonance peak at

Table 1 Data from reactions of dimethylmethoxy(trimethylsilyl)ketene acetal with electrophiles E-X

E	Reaction time (h)	Conversion (%)	M_w (g mol^{-1}) theory/m.s.	m.p. or b.p. (°C)
	0.4	99	255.4/256	138–140/4 mm
	0.7	95	300.3/301	82–86 (m.p.)
	24	95	251.3/252	62–64 (m.p.)

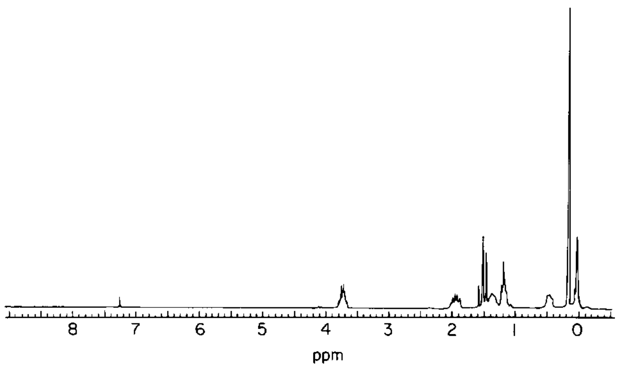


Figure 1 200 MHz ^{1}H n.m.r. spectrum of PSi-SKA (solvent: $CDCl_3$)

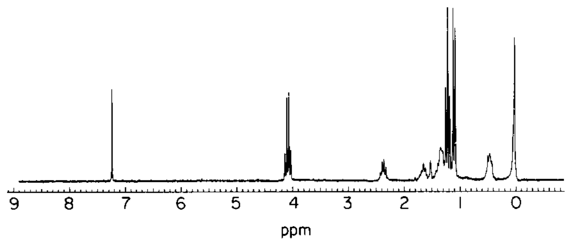


Figure 2 200 MHz ^{1}H n.m.r. spectrum of PSi-Ester (solvent: $CDCl_3$)

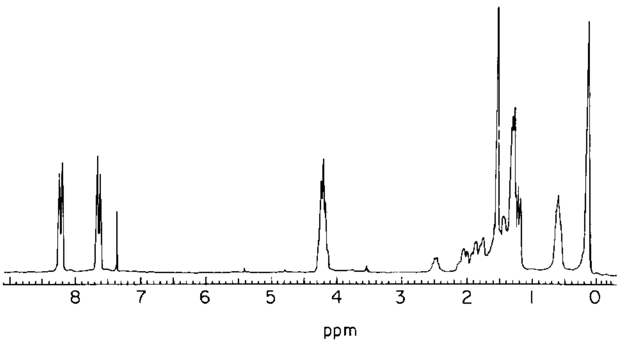


Figure 3 200 MHz ^{1}H n.m.r. spectrum of sample A3 (solvent: $CDCl_3$)

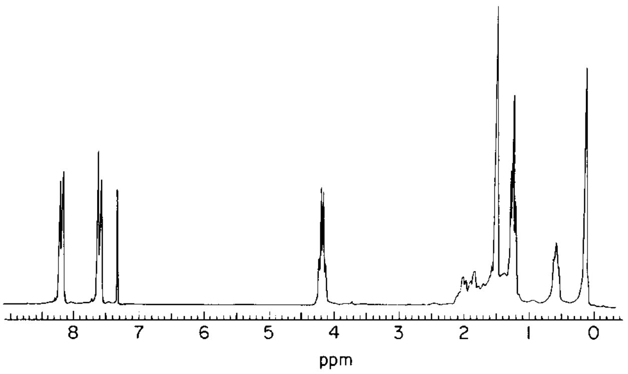


Figure 4 200 MHz ^{1}H n.m.r. spectrum of sample A4 (solvent: $CDCl_3$)

4.61 ppm in the ^{1}H n.m.r. spectra. *Figure 1* shows the ^{1}H n.m.r. spectrum of the product PSi-SKA. The resonances of the ethyl group at ~3.7 and 1.15 ppm are not well-defined due to the presence of *E–Z* isomers. The very small resonance at ~4.1 ppm is from the ethyl $-CH_2-$ of ester groups formed by protonation of a few silyl ketene acetals by methanol present in the hydrosilation catalyst (see below). An n.m.r. spectrum of PSi-Ester prepared by hydrosilation of PMHS with ethyl 2-methyl-4-pentenoate is shown in *Figure 2*.

Samples of PSi-SKA and copolymers with various concentrations of ketene acetal (PSi-SKA-*co*-Ester) were reacted with either 4-nitrobenzenesulphenyl chloride or 2,4-dinitrobenzenesulphenyl chloride. *Figures 3* and *4* show the ^{1}H n.m.r. spectra of a copolymer (~70% SKA) and PSi-SKA after each was treated with 4-nitrobenzenesulphenyl chloride. Again, the former exhibits poorly resolved ethyl resonances, but here it is due to two slightly different chemical shifts of the ethyl groups in the different repeat units. The highly derivatized polymer (~93% nitrothiophenoxy groups) shows single, well-resolved resonances of the ethyl group (*Figure 4*).

Elemental analysis and n.m.r. for PSi-SKA-*co*-Ester materials reacted with either 4-nitrobenzenesulphenyl chloride (mononitro series, labelled A) or 2,4-dinitrobenzenesulphenyl chloride (dinitro series, labelled B) are presented in *Table 2*. The ratio of peak areas of the aromatic protons to the $-CH_2-$ protons of the ethoxy groups was used to determine the mole fraction of mono- or dinitrothiophenoxy pendant groups. The percentages of pendants which were originally silyl ketene acetals are shown in parentheses in column 1 of *Table 2*. These were determined from the ratio of the $-CH_2-$ resonance of the ethoxy group of the ketene acetal (3.71 ppm) to that of the ester (4.09 ppm) in the PSi-SKA-*co*-Ester. These values are generally 4–5% lower than what is expected from the addition of ETMA (samples A1 and B1) or ETMA and ethyl 2-methyl-4-

pentenoate in the beginning of the reaction. This is probably due to protonation of silyl ketene acetals by the small amount of isopropanol present in the H_2PtCl_6 solution. (While this is not a particular problem here, other catalysts, such as the divinyl tetramethyldisiloxane Pt^0 complex in xylene, can be used in place of chloroplatinic acid in methanol.) The elemental analysis and n.m.r. data for all samples are in reasonably good agreement. Conversions to the mono- or dinitrothiophenoxy derivatives are generally high with the exception of the reaction between PSi-SKA and 2,4-dinitrobenzenesulphenyl chloride, which afforded only ~83% conversion to the dinitrothiophenoxy derivative.

Chloroplatinic acid is a quite common catalyst for the hydrosilation of siloxanes, although there may be some concern that its acidic nature can lead to cleavage of the polysiloxane backbone. However, this appears to be unlikely. First, the concentration of catalyst is very small ($\sim 10^{-4}$ M), and the actual proton concentration is likely to be far less. The platinum in the H_2PtCl_6 is presumably reduced to the zero-valent state with liberation of hydrogen[12], which is then stabilized and solubilized by olefins. Second, recent work supports the idea that Pt^0 colloids are the active catalytic species in hydrosilations with what have long been thought to be homogeneous catalysts (e.g. H_2PtCl_6)[13,14], hence the designation 'Pt' in *Scheme 1*. Our solutions become yellow and then light brown as hydrosilation proceeds, consistent with the suggestion that Pt^0 colloids are being formed. Third, our polymers have relative number-average molecular weights (M_ns) which are consistently higher than that of the starting material, PMHS, suggesting that chain cleavage during hydrosilation is not a significant problem. The M_n of PMHS is ~ 3500 g mol^{-1} by g.p.c., whereas PSi-SKA and PSi-Ester have relative M_ns of $\sim 1 \times 10^4$ g mol^{-1}. For polysiloxanes containing different concentrations of polar pendant groups, the relative M_ns range from 2×10^4 to 5×10^4 g mol^{-1}. Finally, a ^{29}Si n.m.r. spectrum of sample A4 reveals a single resonance at ~ -22.8 ppm *versus* TMS, suggestive of a linear polysiloxane.

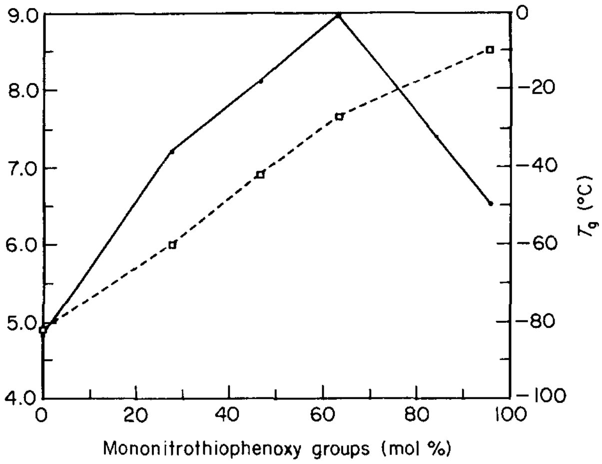


Figure 5 Change of dielectric constant (——) and T_g (- - -) with nitrothiophenoxy concentration for samples A1–A4

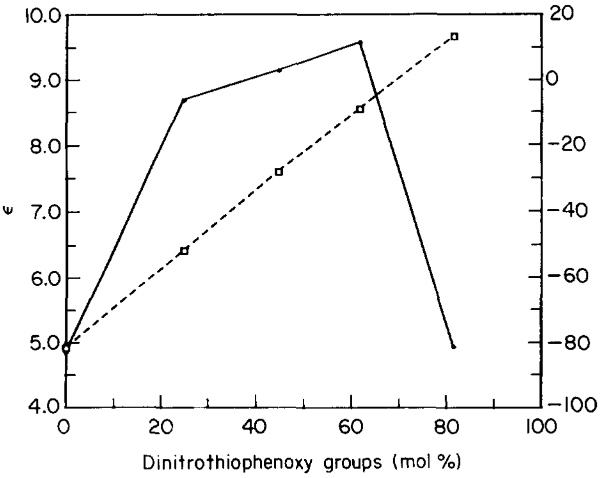
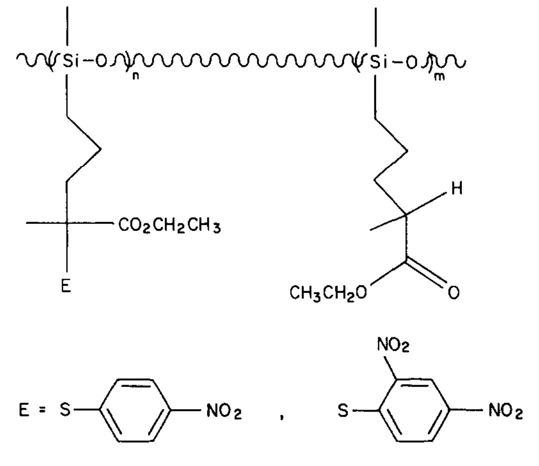


Figure 6 Change of dielectric constant (——) and T_g (- - -) with 2,4-dinitrothiophenoxy concentration for samples B1–B4

Table 2 ^{1}H n.m.r. and elemental analysis (EA) data for PSi-SKA and PSi-SKA-*co*-Ester reacted with either 4-nitrobenzenesulphenyl chloride (mononitro series, labelled A) or 2,4-dinitrobenzenesulphenyl chloride (dinitro series, labelled B)



Sample (SKA%)	$\frac{n}{n+m}$ % from n.m.r.	$\frac{n}{n+m}$ % from EA
A1 (32)	27.3	26.7
A2 (48)	46.4	47.0
A3 (69)	63.3	61.7
A4 (96)	95.5	92.7
B1 (31)	24.6	26.3
B2 (49)	44.5	44.5
B3 (69)	61.7	57.6
B4 (96)	81.8	83.8

Figures 5 and *6* summarize our d.s.c. and room temperature dielectric constant data (100 kHz) for the mononitro and dinitro copolymer series, respectively. Also included in these figures are data for Psi-Ester. The steady increase in T_g for both series as the number of mono- or dinitrothiophenoxy groups increases is principally the result of increased dipole–dipole interactions between siloxane chains. The T_gs of the dinitro series are higher than those of the mononitro series at a specific concentration of pendants, reflecting the higher polarity and/or larger molar volume of the dinitrothiophenoxy group. The highest dielectric constant (~9) is exhibited by sample A3. This is to be compared with two classes of silicones for which data are available, namely poly(β-cyanoethylmethylsiloxane)[15,16]* (~18 at 100 kHz, 25°C), and polymethyl-3,3,3-trifluoropropylsiloxane[17] (7.35 at 100 Hz, 25°C). These materials are liquids at room temperature, as are all samples in the present study.

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* Wu *et al.*[16] report that a copolymer of (β-cyanoethylmethylsiloxane) (25%) and dimethylsiloxane has a dielectric constant of ~4 at room temperature

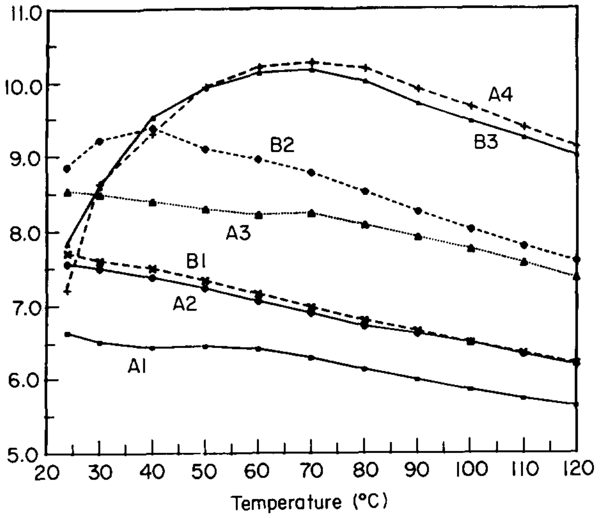

Figure 7 Temperature dependence of dielectric constant for all samples at 100 kHz

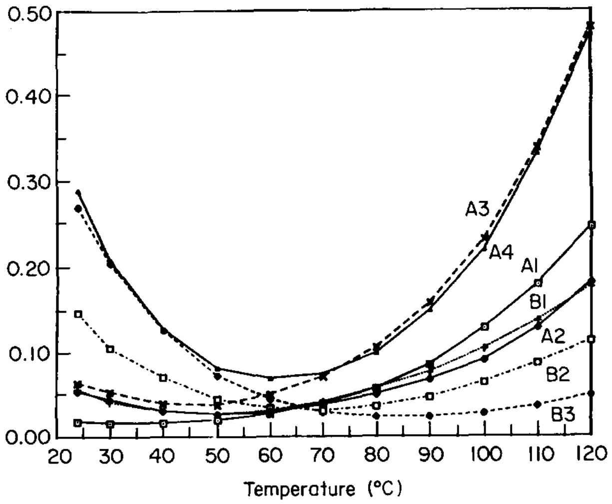

Figure 8 Dielectric dissipation factor (tan δ) for all samples at 100 kHz as a function of temperature

The room temperature dielectric constants also increase with polar pendant group concentration, as expected, but then decrease for the most highly derivatized samples. We note that samples A4 and B4 (*Table 2*) have the highest T_gs, and suggest that the dipoles cannot respond as effectively to the a.c. field at 100 kHz. An additional and probably dominant factor is dipole–dipole association in samples A4 and B4. It is well known, for example, that the dielectric constants of carboxylic acids are low at room temperature, due to dimer formation and subsequent cancellation of dipoles[18], but the dielectric constant increases with temperature as the dimers are dissociated[10]. The higher viscosity of the samples at lower temperatures may also assist dipole–dipole association. In order to address this point, we have examined the dielectric constants of all samples except B4 (due to its extremely high viscosity and difficulty in loading into the cell) as a function of temperature; the data are shown in *Figure 7*. Indeed, the dielectric constant of sample A4 initially rises with temperature, as would be expected if dipole–dipole association was being disrupted. Similar behaviour is exhibited by sample B3, and it it interesting to note that A4 and B3 have similar T_gs. The dielectric constants of A4 and B3 reach a maximum of ~10.2 at ~65°C, and then decrease with increasing temperature, implying a randomization of dipoles with increasing temperature. The remaining samples show a steady decrease in dielectric constant with increasing temperature in the range being studied. Apparently the concentration of nitro- or dinitrophenoxy groups in these is too low to promote dipole–dipole association. Cooling to room temperature in all cases restored the dielectric constants to their original values.

Dielectric loss tangents (tan δs or dissipation factors) of the samples at 100 kHz are shown in *Figure 8* as a function of temperature. No obvious correlation exists between the magnitude of the loss tangent and the composition at a given temperature. We do note, however, that loss tangents can be reasonably small (0.02–0.06) for selected samples.

CONCLUSIONS

Silyl ketene acetal-functionalized polysiloxanes are attractive intermediates for the synthesis of new classes of polysiloxanes. Reactions of silyl ketene acetal-modified silicones with 4-nitrobenzenesulphenyl chloride or 2,4-dinitrobenzenesulphenyl chloride afford new silicones with modest dielectric constants (5–10 at 100 kHz). The temperature dependencies of the dielectric constants are a function of polar pendant group concentration. It thus appears possible to design silicones with high dielectric constants as well as unique temperature dependencies.

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