Synthesis of novel organosilicon-containing oligomers with reactive functional groups through anionic polycondensation reactions

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Through novel metallation reactions of active hydrogen compounds by lithium diisopropylamide, followed by coupling reactions between the carbanion and organosilyl chloride, new organosilicon-containing oligomers with reactive double bonds were synthesized. The silicon-containing oligomers obtained have ultra-violet (u.v.) crosslinking ability and can be expected as ultrathin films for gas separation membranes. Using 4-methylstyrene (MST) and/or allyltrimethylsilane (AS) as active hydrogen compounds, organosilicon-containing oligomers with reactive double bonds in the main chain and/or in the side chains were synthesized. By changing the molar ratio of MST/AS, it was found that the stiffness of the oligomers can be controlled. U.v. irradiation induced the crosslinking reactions of the organosilicon-containing oligomers with pendent vinyl groups.

(Keywords: silicon-containing oligomer; anionic polycondensation; photocrosslinking)

INTRODUCTION

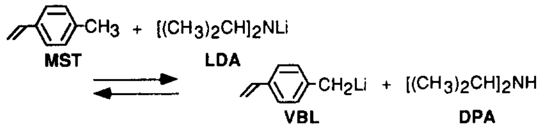
Gas separations through membranes are one of the most attractive fields for industries because of low energy needs, clean processes, ease of handling, etc.[1]. Polydimethylsiloxane (silicone) is well known to have one of the highest permeation coefficients for several gases. However, there are several problems for oxygen permselective membranes, such as low mechanical strength, low permselectivity in terms of oxygen against nitrogen, etc. There are several approaches to creating new gas separation membranes with high performance, such as high permeability coefficients, high permselectivities and high mechanical strengths. For these purposes, silicon-containing polymers such as poly(1-trimethylsilylpropyne)[2], polyfumarates[3], poly(trimethylvinylsilane)[4], etc., are promising materials.

In the past few years, we have been studying organosilicon-containing polystyrenes as oxygen permselective membranes[5]. In the course of our studies, we found that polymers with higher Si content showed higher oxygen solubility in membranes, and such polymers can be regarded as one candidate for high-performance gas separation membranes. Polystyrene homologues, however, are known to be brittle in general. To solve this problem, we synthesized new polystyrene derivatives with high Si content and crosslinkable double bonds as pendent groups[6]. Such polymers showed a fairly high oxygen permeability among polystyrene homologues and have the ability to form tough films by the crosslinking reaction.

One of the other needs for high-performance gas separation membranes is to get high flux through an ultrathin film technique. Reactive oligomers with organosilicon groups can be one suitable material for this purpose. For example, when an oligomer solution is coated onto the surface of hollow fibres, then crosslinked by certain stimuli such as temperature and light, an ultrathin film must be formed on the surface of the hollow fibres. If such an ultrathin film has a high permselectivity, the device can be used as a gas separation module with high flux.

Our strategy for creation of functional materials is to create polymers having a new structure using novel reaction routes, because such polymers with a new structure have many possibilities as materials.

We found previously that lithium diisopropylamide (LDA) induced a metallation reaction of 4-methylstyrene (MST) to form 4-vinylbenzyllithium (VBL) without any side reaction[7]:



(1)

VBL can be regarded as a unique carbanion having a reactive vinyl group and can be utilized as an

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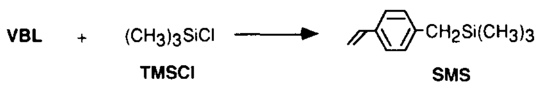
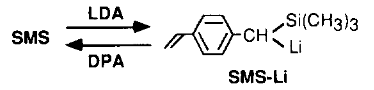
intermediate to synthesize new functional monomers. For example, when trimethylsilyl chloride (TMSCl) was dropped into the equilibrium system, TMSCl reacted predominantly with VBL to form 4-(trimethylsilylmethyl)styrene (SMS):

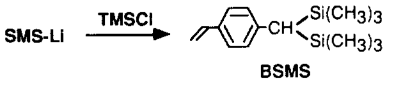


(2)

Further, SMS formed was metallated again by LDA, and finally, the metallated SMS reacted with TMSCl to form 4-[bis(trimethylsilyl)methyl]styrene (BSMS)[8]:



(3)



(4)

The poly(BSMS), the Si content of which is 21.4 wt%, showed a fairly high oxygen permselectivity against nitrogen (3.8), keeping a high oxygen permeation coefficient ($P_{O_2} = 50$ Barrer; Barrer denotes 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}). In equations (1) to (4), the methyl group in MST acted as a difunctional group in terms of the lithiation reaction by LDA. If a difunctional Si–Cl compound is used for the silylation reaction instead of TMSCl, a polycondensation reaction must take place. From our preliminary data, new silicon-containing oligomers were obtained when 1,2-bis(chlorodimethylsilyl)ethane (BSE) was used for the silylation reactions[9]. If true polycondensation occurred in the reaction, the oligomer formed must have both reactive vinyl groups as the pendant and organosilicon moieties in the main chain. Such reactive oligomers are promising in terms of gas separation technology.

This paper deals with the synthesis of new silicon-containing oligomers with reactive double bonds. Allyltrimethylsilane (AS), another monomer with acidic protons, was also examined for the anionic polycondensation reactions. The thermal and photocrosslinking properties of these Si-containing oligomers were also examined.

EXPERIMENTAL

Anionic polycondensation reactions were carried out under an argon (Ar) atmosphere to eliminate oxygen and moisture.

Materials

Commercial tetrahydrofuran (THF), diisopropylamine (DPA), 4-methylstyrene (MST), 1,2-bis(chlorodimethylsilyl)ethane (BSE) and allyltrimethylsilane (AS) were purified using the conventional methods[10]. Butyllithium was used as a hexane solution, the concentration of which was determined using Gilman's double titration method[11].

Polycondensation reactions of 4-methylstyrene (MST) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA)

A representative procedure for the anionic polycondensation reaction of MST with BSE is described. To a stirred THF solution (16.3 ml) of diisopropylamine (0.51 g, 5.0 mmol) was added a hexane solution of butyllithium (1.35 ml, 2.5 mmol, 1.85 mol dm^{-3}) in a two-necked 100 ml round-bottomed flask equipped with a three-way stopcock and an isobaric-type dropping funnel. After stirring for a few minutes to complete the formation of lithium diisopropylamide (LDA), MST (0.15 g, 1.25 mmol) was added by using a syringe. The colour of the mixture was observed to turn yellow immediately. Then, a THF solution (6.5 ml) of BSE (0.27 g, 1.25 mmol) was dropped from the isobaric-type dropping funnel into the mixture for 7 h at 20°C. Unreacted Si–Cl compounds were converted to Si–Et (Et, ethyl group) by adding a THF solution of ethylmagnesium bromide. After low-boiling materials were evaporated, the reaction mixture was dissolved in diethyl ether and washed with a two-fold excess of water. The organic extract was dried over Na_2SO_4, filtered and then dried *in vacuo* to remove the solvent employed.

Polycondensation reactions of allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA)

A representative procedure for the anionic polycondensation reaction of AS with BSE is described. A hexane solution of butyllithium (1.54 ml, 2.5 mmol, 1.62 mol dm^{-3}) was added at 20°C to THF solution (1.60 ml) of diisopropylamine (0.51 g, 5.0 mmol) in a two-necked 100 ml round-bottomed flask equipped with a three-way stopcock and an isobaric-type dropping funnel. After stirring for a few minutes to complete the formation of LDA, AS (0.14 g, 1.25 mmol) was added by using a syringe. Then, a THF solution (5.0 ml) of BSE (0.27 g, 1.25 mmol) was dropped from the isobaric-type dropping funnel into the mixture for 7 h at 20°C. Unreacted Si–Cl compounds were converted to Si–Et by adding a THF solution of ethylmagnesium bromide. After low-boiling materials were evaporated, the reaction mixture was dissolved in diethyl ether and washed with a two-fold excess of water. The organic extract was dried over Na_2SO_4, filtered and then poured into a large excess of methanol at −40°C. The precipitate was washed with cooled methanol and dried under reduced pressure. Products obtained were analysed by ^{1}H n.m.r. spectra.

Copolycondensation reactions of 4-methylstyrene (MST) and allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA)

A representative procedure for the anionic polycondensation reaction of MST and AS with BSE is described. To a stirred THF solution (15.6 ml) of diisopropylamine (2.04 g, 20.0 mmol) a hexane solution of butyllithium (6.17 ml, 10.0 mmol, 1.62 mol dm^{-3}) was added in a two-necked 100 ml round-bottomed flask equipped with a three-way stopcock and an isobaric-type dropping funnel. After stirring for a few minutes to complete the formation of lithium diisopropylamide (LDA), MST (0.15 g, 1.25 mmol) and AS (0.42 g, 3.75 mmol) were added by using a syringe. The colour of the mixture was observed to turn yellow immediately. Then, a THF solution (10.0 ml) of BSE (1.08 g, 5.0 mmol) was dropped from the isobaric-type dropping funnel into the mixture for 7 h at 20°C. Unreacted Si–Cl compounds were converted to Si–Et by adding a THF solution of ethylmagnesium bromide. After low-boiling materials were evaporated, the reaction mixture was dissolved in diethyl ether and washed with a two-fold excess of water. The yellow organic extract was dried over Na_2SO_4, filtered and then dried *in vacuo* to remove the solvent employed. The structures of the resulting oligomers and monomer compositions in the oligomers were analysed by ^1H n.m.r.

Photocrosslinking reactions of the reactive oligomers in the presence of 1,6-hexanedithiol

A representative procedure for the photocrosslinking reaction is described. On a Si wafer, a THF solution of the oligomer (10 wt%) containing 1,6-hexanedithiol and benzophenone was coated by using a spinner ($[\text{double bond}]_0/[\text{1,6-hexanedithiol}]_0/[\text{benzophenone}]_0 = 3/1/0.05$). U.v. irradiation of the oligomer film was carried out with a Xe lamp at 500 W. The resulting films were analysed by using i.r. spectrometry.

Measurements

^1H n.m.r. spectra were observed on a JEOL EX400 at room temperature, using a 5 mm glass tube containing a solution of the polymer sample in $CDCl_3$ (1.0 g dl^{-1}). $CHCl_3$ was used as the internal reference for the measurements ($\delta = 7.26$ ppm). For g.p.c. measurements, a Toyo Soda HCL-8020 and Shimadzu SCL-6A were used (column: TSK-Gel G4000H8 + G3000H8 + G2500H8). The glass transition temperatures of the oligomers were determined by using a differential scanning calorimeter (Mettler TA 4000 system) at a heating rate of 20°C min^{-1} from -150 to 100°C. U.v. irradiation was carried out using an Ushio UI-501C equipped with a 500 W Xe lamp (Ushio UXL-500D-0).

RESULTS AND DISCUSSION

Synthesis of novel organosilicon-containing oligomers with reactive vinyl groups in the side chain

In the metallation reaction shown in equation (1), there are two anionic species, viz. lithium diisopropylamide (LDA) and 4-vinylbenzyllithium (VBL). From the equilibrium constant ($K = 0.54$ at 20°C in THF[7]), the ratio of VBL/LDA is estimated to be 14/86 under the initial reaction conditions of $[LDA]_0/[DPA]_0/[MST]_0 = 0.1/0.1/0.1$ (mol dm^{-3}). When trimethylsilyl chloride (TMSCl) was dropped into the reaction system, TMSCl reacted preferentially with VBL to form silylated MST derivatives. This can be explained by the different coupling rates of TMSCl towards carbanion and amide anion[12]. By maintaining the concentration of TMSCl in the reaction system as low as possible, the selective reaction between TMSCl and VBL was achieved, viz. when TMSCl was dropped into the reaction system, VBL was consumed by the coupling reaction with TMSCl, then a rapid compensation of VBL took place, followed by the equilibrium constant.

As the slow reaction rate between LDA and TMSCl was mainly due to the steric factor[12], other Si-Cl compounds should be utilized for this synthetic method. Actually, several trialkylsilyl chlorides were examined, and corresponding organosilicon-containing monomers could be synthesized[13]. If difunctional silyl chloride can be utilized for this coupling reaction in the same manner, the opportunity for synthesis of organosilicon-containing materials will be expanded, not only monomer synthesis but also oligomer synthesis through polycondensation reactions because of the difunctional metallation ability of MST by LDA. When 1,2-bis(chlorodimethylsilyl)ethane (BSE) was used as a reactant instead of TMSCl under the condition of $[LDA]_0/[DPA]_0/[MST]_0/[BSE]_0 = 0.1/0.1/0.05/0.2$ (mol cm^{-3}), oligomeric mixtures were obtained[9]. *Figure 1* shows gel permeation chromatographic patterns of the oligomers produced as a function of time. As can be seen in the figure, in the initial stage of the dropping of BSE, the product was mainly the 1:2 condensate of MST and BSE shown in *Scheme 1*. With increasing reaction time with continuous dropping of BSE, the molecular weight of the product increased, indicating that actual polycondensation reactions took place between VBL and BSE. From ^1H n.m.r. measurements of the products obtained, the vinyl group in the MST moiety remained intact, which also supported the

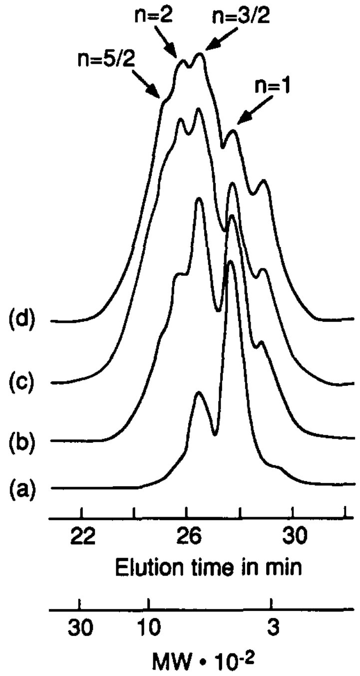
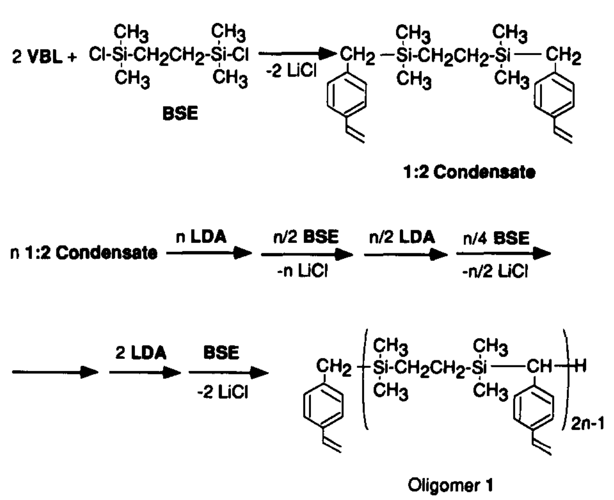


Figure 1 Change in the molecular weight of the oligomers in g.p.c. as a function of dropping time of 1,2-bis(chlorodimethylsilyl)ethane (BSE): (a) 1 h, (b) 3 h, (c) 7 h and (d) 10 h



Scheme 1

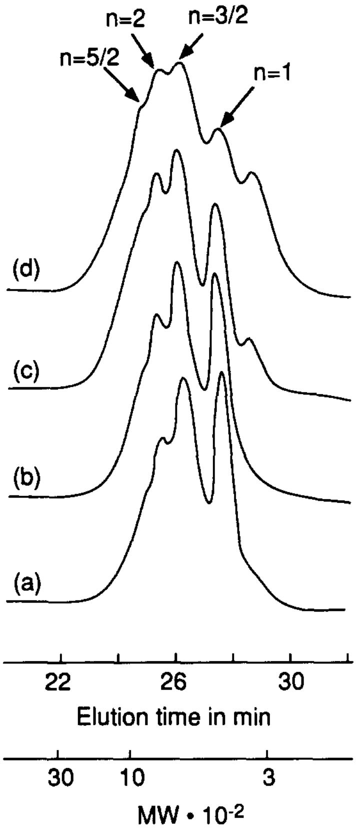


Figure 2 Effect of BSE dropping rate on the molecular weight of the oligomers in g.p.c.: (a) 7.0×10^{-3} mmol min^{-1}, (b) 4.2×10^{-3} mmol min^{-1}, (c) 3.0×10^{-3} mmol min^{-1}, and (d) 2.1×10^{-3} mmol min^{-1}; total amount of BSE is 1.25 mmol

suggestion that true polycondensation took place following *Scheme 1*.

As stated above, a key point of this polycondensation reaction was to avoid the possible coupling reaction between LDA and BSE as much as possible. For this purpose, the effect of dropping rate of BSE on the polycondensation reactions was examined. With decreasing dropping rate of BSE, in other words 'increasing interval between each drop of BSE', the molecular weight of the products increased, as shown in *Figure 2*. This fact supports the above consideration, viz. at a low concentration of BSE in the reaction system, BSE reacted rapidly with two molecules of VBL to form the 1:2 condensate, avoiding possible coupling reaction between BSE and LDA. During the interval between each drop of BSE, the metallation reaction of MST and/or preformed oligomers took place according to the equilibrium constant to compensate the carbanion in an equilibrated amount. In this way, organosilicon-containing oligomers with reactive pendent groups (oligomer (**1**)) with molecular weight in the range of few hundred to 2000 were easily obtained by controlling the dropping rate of BSE.

Synthesis of organosilicon-containing oligomers with unsaturated double bonds in the main chain

Allyltrimethylsilane (AS) is known to have acidic proton(s) towards a strong base such as t-butyllithium[14]. Our previous study showed also that lithium diisopropylamide (LDA) had a metallation ability towards AS to form lithiated AS[15]. If AS can be utilized as a carbanion source instead of 4-methylstyrene (MST), another type of organosilicon-containing oligomer can be synthesized through polycondensation reactions with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of LDA.

After the reaction mixture was prepared using LDA and AS, as described in the Experimental section, a THF solution of BSE was dropped into the reaction mixture for 7 h. From g.p.c. analysis (*Figure 3*) of the reaction products after the low-boiling materials were evaporated, it was found that oligomeric products were formed, the molecular weights of which were in the range of 200 to 6000. It should be noted that AS has no anionic polymerization ability by LDA in THF even at ambient temperature. This led us to expect that anionic polycondensation took place between AS and BSE catalysed by LDA. Actually, the proton signals in the ^{1}H n.m.r. spectrum of the product were assignable when the products were formed through anionic polycondensation reactions shown in *Scheme 2* (oligomers (**2**)). In addition, the number-average molecular weight of the oligomers (M_n (n.m.r.) = 1700) determined from ^{1}H n.m.r. shown in *Figure 4*, using the terminal olefin protons (H2 and H3) and the olefin protons in the main chain (H6 and H7), agreed well with that from g.p.c. (M_n (g.p.c.) = 1800), using a calibration curve of polystyrene standard samples. These two results indicated that new anionic polycondensation reactions proceeded between AS and BSE to result in new organosilicon-containing oligomers with inner double bonds in the main chain shown in *Scheme 2*.

Synthesis of organosilicon-containing oligomers with unsaturated double bonds in both the main chain and side chain

When applications of silicon-containing oligomers are considered, every monomeric unit in the oligomers need not possess a reactive vinyl group. From these points of view, it is important to control the extent of the reactive groups in the oligomers. For this purpose, a mixture of 4-methylstyrene (MST) and allyltrimethylsilane (AS) was used as the carbanion source for the anionic polycondensation reactions with 1,2-bis(chlorodimethylsilyl)ethane

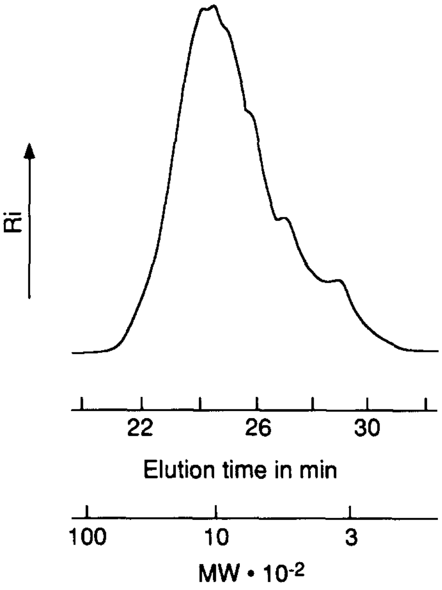
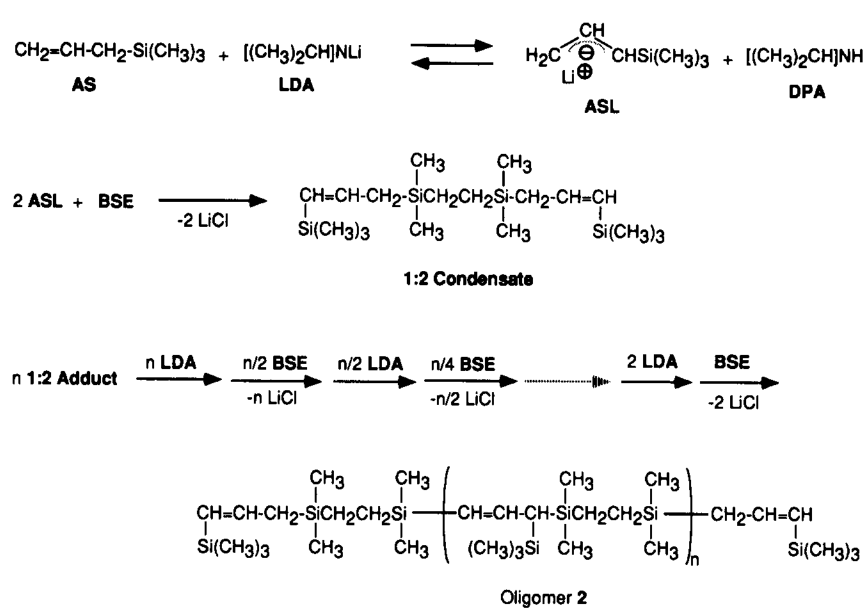


Figure 3 G.p.c. trace of the products formed by the anionic polycondensation of allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA) (total BSE dropping time was 7 h)



Scheme 2

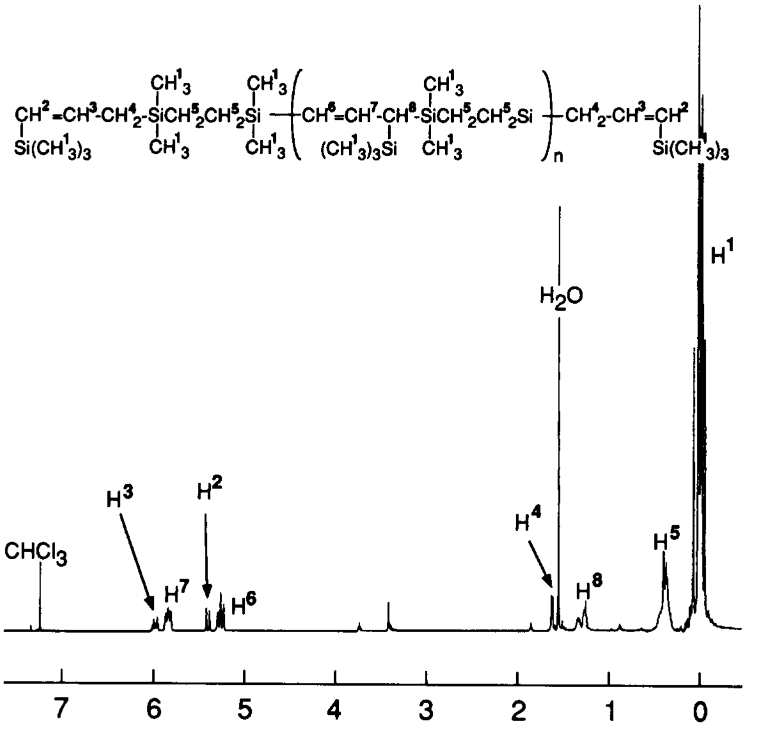


Figure 4 ^{1}H n.m.r. spectrum of products formed by the anionic polycondensation of allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA) (the same sample as in *Figure 3*)

(BSE) in the presence of lithium diisopropylamide (LDA) in THF (MST/AS = 1/3). The reactions were carried out according to the procedure described in the Experimental section, and the g.p.c. trace of the reaction products is shown in *Figure 5*. The chromatogram detected by u.v. absorption at 296 nm, which is a typical absorption band of vinylphenyl conjugation, showed an almost similar pattern to that of the *RI* detector, indicating vinylphenyl pendent groups to be distributed statistically into the oligomers, but not the mixture of two different oligomers (oligomers (**1**) and (**2**)). The molecular weight of the oligomers formed was found to be almost the same as that of oligomers (**1**) and (**2**). From ^{1}H n.m.r. analysis shown in *Figure 6*, both structural units, MST and AS, were introduced into the oligomers formed (oligomer (**3**)).

Further results on the co-oligomerizations of MST/AS with BSE under several reaction conditions are summarized in *Table 1*. As can be seen in the table, the extent of the pendent vinyl groups (MST extent) in the oligomers was almost the same as that in the feed. This fact indicated that it is easy to control the properties of the oligomers

Table 1 Syntheses of organosilicon-containing oligomers with reactive double bonds[a]

Sample No.	Mole fraction (%) In feed MST	In feed AS	In copolymer MST	In copolymer AS	Dropping time (h)	Yield (%)	$\bar{M}_w \times 10^{-2}$	T_g (°C)
1	100	0	100	0	5	63	6.9	−76
2	0	100	0	100	15	66	22.0	−48
3	25	75	33	67	7	64	11.7	n.d.
4	50	50	56	44	8	73	13.0	−61
5	75	25	71	29	7	71	9.2	n.d.

[a]Solvent, THF; temperature, 20°C; initial concentrations, $[\text{monomer}]_0 = 0.05$ mol dm^{-3}, $[\text{LDA}]_0 = [\text{DPA}]_0 = 0.10$ mol dm^{-3}, $[\text{BSE}]_0 = 0.2$–0.5 mol dm^{-3}; (total amount of Si–Cl)/(total amount of N–Li) = 1

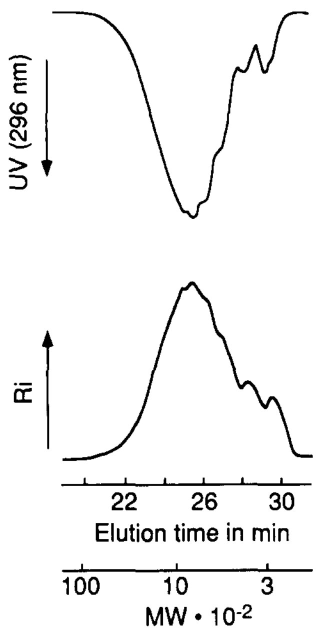


Figure 5 G.p.c. traces of the product formed by anionic copolycondensation of 4-methylstyrene (MST) and allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA) (total BSE dropping time was 7 h)

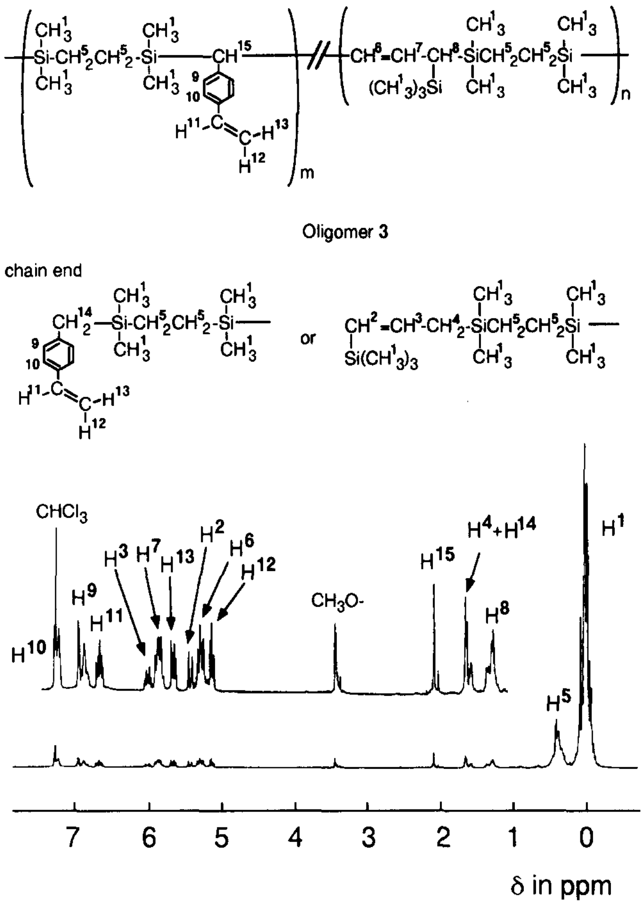


Figure 6 ^{1}H n.m.r. spectrum of the products formed by the anionic co-polycondensation of 4-methylstyrene (MST) and allyltrimethylsilane (AS) with 1,2-bis(chlorodimethylsilyl)ethane (BSE) in the presence of lithium diisopropylamide (LDA) (the same sample as in *Figure 5*)

such as stiffness and crosslinking ability by changing feed MST/AS ratios in the co-oligomerization reactions.

Thermal property and film formability of the reactive oligomers

As stated above, we were able to synthesize three different organosilicon-containing oligomers: (1) Si-containing oligomers with pendent vinyl groups, (2) Si-containing oligomers with inner double bonds in the main chain, and (3) Si-containing oligomers with both vinyl groups in the side chain and inner double bonds in the main chain. To estimate the properties of the oligomers, glass transition temperatures of these oligomers were determined by d.s.c. measurements, the results of which are listed in *Table 1* (sample Nos. 1, 2 and 4). As the molecular weights of these oligomers were low, the glass transition temperatures of the oligomers were quite low, even that of the oligomer possessing phenyl rings. For example, T_g of oligomer (**1**) was −76°C. It is rather surprising for us that T_g of oligomer (**2**) was much higher (−48°C) than that of oligomer (**1**). This may be explained by the low mobility of trimethylsilyl groups adjacent to the main chain. Actually, poly(trimethylvinylsilane) shows relative higher T_g (120°C)[16]. Trimethylsilyl groups branching as the side chain of oligomer (**2**) prevented the mobility of the oligomer chain, resulting in the high T_g even though the oligomer possessed repeating double bonds in the main chain. The glass transition temperature of oligomer (**3**) (MST/AS = 1/1) showed −61°C, the results of which indicated that the stiffness of the oligomers can easily be controlled by changing the initial molar ratios of MST/AS.

To estimate if an ultrathin film can be made by these oligomers, photocrosslinking reactions were examined.

Figure 7 I.r. spectra of the products formed by the photocrosslinking reactions between oligomer (**1**) and 1,6-hexanedithiol with u.v. irradiation time of (a) 0 min, (b) 3 min and (c) 10 min

Using 1,6-hexanedithiol and benzophenone as crosslinking agent and sensitizer, respectively, the photocrosslinking reactions were examined. In the case of oligomer (**1**), the oligomer film, which was made by the spin-coating method, was insoluble immediately in any solvents under u.v. irradiation. In the case of oligomer (**2**), however, the film was soluble in THF even after u.v. irradiation. No difference in molecular weight of the oligomer could be detected by g.p.c. before and after the u.v. irradiation of oligomer (**2**). This may be attributable to low reactivity of the inner olefins towards thiyl radicals mainly due to the steric factor of substituents around a double bond.

Figure 7 shows i.r. spectra of oligomer (**1**) film after u.v. irradiation. As can be seen in the figure, the asymmetrical bending vibrations of $-CH{=}CH_2$ at 991 and 903 cm^{-1} decreased with u.v. irradiation. This also supports the idea that effective crosslinking took place through the reaction between thiyl radicals and pendent vinyl groups in oligomer (**1**). The oligomer (**3**) possessing pendent vinyl groups also showed insolubilization after u.v. irradiation similar to that of the poly(**1**).

CONCLUSIONS

Utilizing the unique characteristics of lithium diisopropylamide (LDA), viz. (1) the strong basicity of LDA towards compounds with acidic hydrogens, (2) a low addition rate towards conjugated olefins, and (3) a slow coupling rate towards organosilyl chlorides owing to steric hindrance, a new synthetic route for organosilicon-containing oligomers with reactive double bonds in the side chains and/or in the main chain was established. The organosilicon-containing oligomers obtained have u.v. crosslinking ability, and can be anticipated as functional materials in several fields such as gas separation technologies and resist materials.

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