Synthesis of α,ω-bis(*p*-hydroxyphenyl)polysiloxanes

Kimihiro Matsukawa and Hiroshi Inoue
Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan
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α,ω-Bis(*p*-allyloxyphenyl)polydimethylsiloxanes were synthesized by equilibrium polymerization of octamethylcyclotetrasiloxane (D_4) with 1,3-bis(*p*-allyloxyphenyl)-1,1,3,3-tetramethyldisiloxane in the presence of a base catalyst (Bu_4NOH). Cleavage of allyl groups from these polysiloxanes was performed by the use of palladium (II) catalyst and diethylamine, forming α,ω-bis(*p*-hydroxyphenyl)polydimethylsiloxanes in good yields.

(Keywords: α,ω-difunctional polysiloxanes; phenols; equilibrium polymerization; synthesis)

Introduction

Incorporation of polysiloxane chains into polymer materials is expected to afford some specific characteristics inherent in the polysiloxanes such as heat resistance, surface properties, water repellency, gas permeability, etc. Difunctional polysiloxanes are especially useful for the synthesis of new polymers having chemical bonds between siloxanes and other components. These polysiloxanes have been described as 'carbon-functional silicones' and their use in the preparation of some polymers has already been reported, e.g. poly(imide siloxane)s[1–3], poly(amide siloxane)s[4] and epoxy-polysiloxanes[5]. Most of these polymers have been derived from polysiloxanes containing amino, hydroxy, thiol, chloro and glycidoxy groups which are now commercially available.

Recently, we established the synthesis of 1,3-bis(*p*-hydroxyphenyl)-1,1,3,3-tetramethyldisiloxane **3**[6] via *p*-tetrahydropyranyloxyphenyldimethylsilanol and applied it to prepare poly(ester siloxane)s[7]. Further, the telechelic polysiloxanes containing hydroxyphenyl groups are useful for the synthesis of various polymer materials containing polysiloxane components. In this communication, we report a facile synthesis of α,ω-hydroxyphenyl-terminated polysiloxanes.

Experimental

All reagents were used as received. Tetrahydrofuran (THF) was dried over sodium and $LiAlH_4$, and distilled for a Grignard reaction. Fourier transform infra-red (*FT*i.r.) spectra were recorded on a Jeol JIR-FRX 3000. ^1H n.m.r. spectra were taken by a Hitachi NMR R-600. Mass spectra were recorded on a Jeol JMS-DX303H using an electric ionization method. Gel permeation chromatography (g.p.c.) was performed with a Waters 150-C using a RI detector, Shodex A80M, A80M and A802.5 as columns, and THF as an eluent. Ultraviolet spectra were measured by a Hitachi U-3210 spectrophotometer.

*Synthesis of 1,3-bis(*p*-allyloxyphenyl)-1,1,3,3-tetramethyldisiloxane* (**1**). A 900 ml THF solution of *p*-allyloxyphenylmagnesium bromide (2.5 mol) prepared from *p*-allyloxyphenyl bromide by a common Grignard preparative method was added dropwise to a 200 ml THF solution of 326 g (2.5 mol) of dimethyldichlorosilane and 511 g (5 mol) of triethylamine at 0–5°C under nitrogen atmosphere and the mixture was stirred for 1 h. After pouring the reaction mixture into chilled water, the solution was neutralized and the organic layer was extracted with diethylether. *p*-Allyloxyphenyldimethylsilanol was obtained in 54% yield (282 g) by distilling from the crude products (b.p. 105°C/$\sim$13 Pa). *FT*i.r. (cm^{-1}): 3302 (υ OH), 1649 (υ allyl C=C), 1595 (υ aromatic C=C), 1252 (υ_{as} C–O–C), 1024 (υ_s C–O–C), 926 (γ =C–H), 866 (υ Si–O). ^1H n.m.r. ($CDCl_3$): δ 7.51 (2H, d, $J = 8.6$ Hz, Ar–H), 6.92 (2H, d, $J = 8.6$ Hz, Ar–H), 6.38–5.72 (1H, m, =CH), 5.55–5.12 (2H, m, $=CH_2$), 4.52 (2H, d, $J = 5.2$ Hz, OCH_2), 1.90 (1H, s, OH), 0.36 (6H, s, Si–CH_3). Mass spectra (electron impact): *m/z* 208 (M^+). To 200 ml of 0.05% hydrochloric acid–isopropyl alcohol solution were added 104 g (0.5 mol) of the silanol, and the solution was stirred for 5 h at room temperature. The mixture was diluted with diethylether and washed with water, and the ether layer was dried over $MgSO_4$. After evaporating *in vacuo*, **1** was obtained in 92% yield (183 g). ^1H n.m.r. ($CDCl_3$): δ 7.44 (4H, d, $J = 8.4$ Hz, Ar–H), 6.87 (4H, d, $J = 8.4$ Hz, Ar–H), 6.38–5.72 (2H, m, CH=), 5.55–5.12 (4H, m, CH_2=), 4.52 (4H, d, $J = 5.8$ Hz, OCH_2), 0.27 (12H, s, Si–CH_3). Mass spectra (electron impact): *m/z* 398 (M^+).

Equilibrium polymerization of **1** *with* D_4. Compound **1** and octamethylcyclotetrasiloxane (D_4) with three different molar ratios were added to 1 wt% of Bu_4NOH, and the mixture was stirred under a nitrogen atmosphere at 85°C for 40–45 h. The reaction mixture was heated at 160°C for 3 h and for an additional 1 h *in vacuo*, and α,ω-bis(*p*-allyloxyphenyl)polysiloxanes were obtained after washing the residue with methanol.

Palladium-catalysed deallylation. To a mixture of **1**, 0.4 mol% of $PdCl_2(PPh_3)_2$ (ref. 8) and 2 mol% of PhONa was added 4 equivalents of diethylamine dropwise under a nitrogen atmosphere with stirring, and the mixture was maintained at 85°C for 1 h. After pouring

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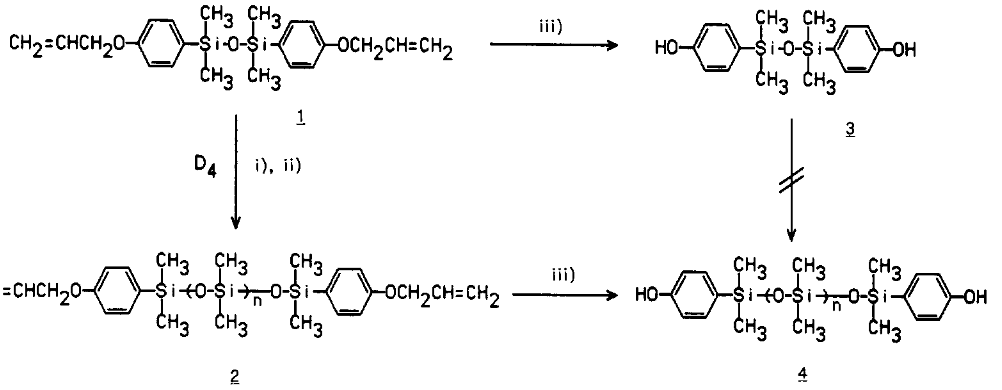
the reaction mixture into chilled water and then neutralizing, the organic layer was extracted with diethylether and washed with water. α,ω-Bis(*p*-hydroxyphenyl)polydimethylsiloxanes were obtained after evaporating the ether solution dried over $MgSO_4$ *in vacuo*.

Results and discussion

Siloxane chains of bis-aminopropyldisiloxanes were reported to be extended by equilibrium polymerization with D_4 using base catalysts[9]. However, the equilibrium polymerization of **3** with D_4 did not proceed successfully, because the cleavage of Si–aromatic carbon bonds occurred by the attack of base catalyst toward the hydroxyphenyl groups. In order to avoid this kind of cleavage reaction, both hydroxyphenyl groups must be protected. As the tetrahydropyranyl groups were eliminated during acid condensation of *p*-tetrahydropyranyloxyphenyldimethylsilanol[6], they did not act as protecting groups. Therefore, **1** was used for the polymerization with different amounts of D_4 in the presence of 1 wt% of Bu_4NOH as shown in *Scheme 1*. Contrary to the case of **3**, the polymerization proceeded without any decomposition and gave **2**. The results of the polymerization are summarized in *Table 1*.

Molecular weights (M_n and M_w) of **2** were determined by g.p.c. analysis using polystyrene standards and by calculation of ^1H n.m.r. spectra, in which signals of $Si–CH_3$ bonded with aromatic groups and siloxane $Si–CH_3$ of **2** appeared at 0.32 and 0.08 ppm, respectively. For example, the peak ratio of **2b** was $Ar–Si(CH_3)_2/Si(CH_3)_2O = \sim 1/12$, and the molecular weight calculated from the peak ratio was ~2200, if the structure of **2b** was presumed to be telechelic. The calculated molecular weight is in fair agreement with M_n (2000) from g.p.c. It is emphasized that the number (n) of dimethylsiloxy units in **2** approximately coincided with the feed ratio of D_4/**1**. The *FT*i.r. spectrum of **2b** showed the apparent absence of absorption bands based on Si–OH (3300 and 860 cm^{-1}) as shown in *Figure 1*. This also supports **2b** as having *p*-allyloxyphenyl groups as terminal groups. In order to determine the terminal functionalities, u.v. spectra of **2** were measured and the functionalities were calculated from ε_{max} due to two benzene rings of **1**. The λ_{max} of **1**, **2a**, **2b** and **2c** was 273.2 nm in n-heptane, and the functionalities of **2a**, **2b** and **2c** are shown in *Table 1*. It is considered that the slight discrepancy of functionalities of **2a** between two molecular weights (calculated from g.p.c. and n.m.r.) was caused by unavoidable errors due to several impurities in the resulting polymers; **2a** could not be sufficiently purified with methanol washing because of its high



i) 1 wt% Bu_4NOH, 85°C
ii) 160°C, 3 h, and 1 h *in vacuo*
iii) 0.4 mol% $PdCl_2(PPh_3)_2$, 2 mol% PhONa, and 4 eq $(C_2H_5)_2NH$, 85°C, 1 h.

Scheme 1

Table 1 Equilibrium polymerization of 1 with D_4[a]

Run	$1/D_4$[b]	Time (h)	2	Yield (g)	G.p.c.[c] M_n	M_w	n[d]	N.m.r.[e] M_n	n	Functionality F[f]	F[g]
1	2/2.9 (1/2)	45	**2a**	4.0	780	990	5.4	920	7.1	1.75	2.21
2	1/3.7 (1/5)	45	**2b**	3.0	2000	2500	21.6	2200	24.4	1.93	2.08
3	1/7.4 (1/10)	40	**2c**	6.9	3300	4900	39.2	3500	41.9	1.71	1.83

[a] Reaction conditions: stirring with 1 wt% Bu_4NOH at 85°C for the time shown, then at 160°C for 3 h and 1 h *in vacuo*
[b] Molar ratio of $1/D_4$ in parentheses
[c] Molecular weights were determined by using polystyrene calibration standards
[d] The number (n) of dimethylsiloxy units was evaluated from M_n
[e] M_n was determined from the calculation based on the peak ratio of CH_3Si at 0.32 and 0.08 ppm
[f] Functionality was estimated from the calculation of M_n from g.p.c. and u.v. data of 1 ($\lambda_{max} = 273.2$ nm, $\varepsilon_{max} = 2290$)
[g] The ε_{max} and M_n from n.m.r. were used

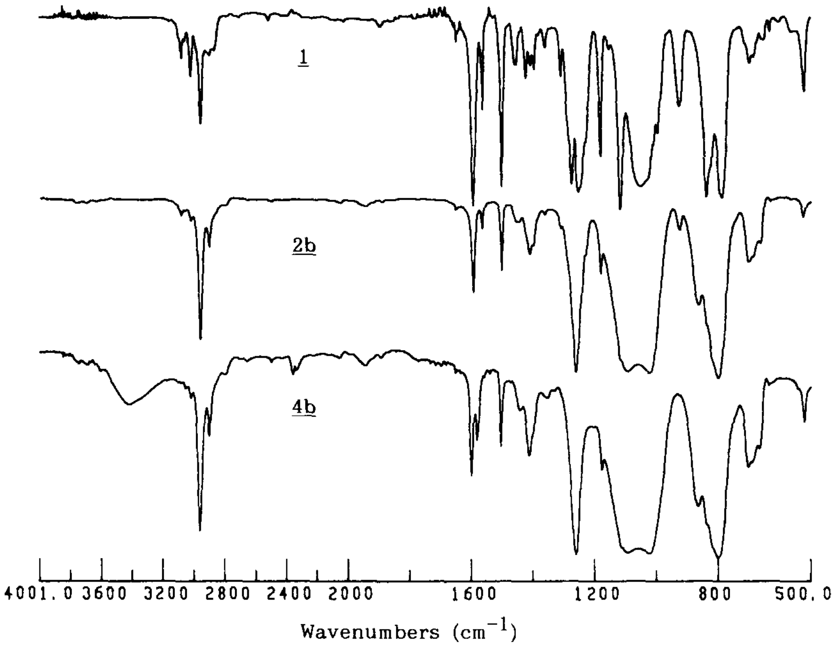


Figure 1 *FT*i.r. spectra of **1**, **2b** and **4b**

solubility. However, the functionalities of **2a**, **2b** and **2c** were 1.8–2.2, and from these results, the telechelic structure of polysiloxane **2** is almost established. Therefore, this polymerization was confirmed to proceed almost stoichiometrically to equilibrium and to form telechelic polysiloxanes.

The deallylation of **1** and **2** should be carried out under neutral or mild basic reaction conditions to prevent decomposition of the polysiloxane backbone. It was already known that the allyl exchange reaction from phenoxyallyl compounds proceeded through the use of a palladium(II) catalyst and an active hydrogen compound such as an amine under relatively mild conditions[10]. Also in this case, we performed palladium catalysed deallylation of **1** and **2**. It was found that deallylation of **1** proceeded successfully to produce **3** in 81% yield (after recrystallization), as shown in *Scheme 1*. Furthermore, allyldiethylamine as a by-product and excess diethylamine could be easily removed by neutralization of the reaction mixture. On the other hand, **3** could be also synthesized by an acid condensation of *p*-tetrahydropyranyloxyphenyldimethylsilanol as reported previously[6], but the tetrahydropyranyloxyethyl ether as a by-product of this reaction was very difficult to remove from **3**. Therefore, it was concluded that this synthetic procedure using palladium-catalysed deallylation of **1** was preferable for the synthesis of **3** compared to the previous method.

Palladium-catalysed deallylation of **2** was carried out in a similar manner as the conversion from **1** to **3**, and the results are summarized in *Table 2*. α,ω-Bis(*p*-hydroxyphenyl)polydimethylsiloxanes (**4**) were obtained in good yield from **2**, and a small change in molecular weight revealed that the polysiloxane bonds were quite stable under these reaction conditions. In the *FT*i.r. spectrum of **4b** (*Figure 1*), absorption bands based on allyloxy groups (922 cm^{-1} assigned to the $CH_2{=}CH$ deformation vibration) disappeared, and the phenol O–H stretching was observed at 3300 cm^{-1}. This spectrum indicates that the deallylation of **2** proceeded completely without any side reaction. The functionalities of **4** were also estimated from ε_{max} (2310) due to two benzene rings in the u.v. spectrum of **3**. For example, the functionalities of **4c** with a molecular weight of 3500 from n.m.r. were equal to 1.70 and 1.84 calculated from two M_n values based on g.p.c. and n.m.r., respectively. The good agreement between the functionalities of **2c** and **4c** suggests that the telechelic structure is maintained even after deallylation.

Table 2 Palladium-catalysed deallylation of **2**[a]

Run	2	4	Yield (%)	M_n[b]	M_w[b]
4	**2a**	**4a**	85	780	940
5	**2b**	**4b**	85	2000	2400
6	**2c**	**4c**	90	3200	5000

[a] Reaction conditions: stirring with 0.4 mol% $PdCl_2(PPh_3)_2$, 2 mol% PhONa and 4 equivalents $(C_2H_5)_2NH$ at 85°C for 1 h

[b] M_n and M_w determined from g.p.c. (calibrated with polystyrene standards)

Conclusions

Telechelic α,ω-bis(*p*-allyloxyphenyl and *p*-hydroxyphenyl)polysiloxanes have been synthesized using equilibrium polymerization and deallylation methods. For polysiloxanes having allyloxyphenyl and hydroxyphenyl in terminal groups, there are a lot of possibilities of applications as reactive siloxane polymers, and further investigations are now in progress.

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