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Synthesis and characterization of oligosiloxanes with hydroxyalkyl substituents

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Abstract

Three siloxanediols $HO(CH_2)_n[Si(CH_3)_2O]_xSi(CH_3)_2(CH_2)_nOH$ ($n = 3$, $x = 2$, 3 and $n = 11$, $x = 1$) have been prepared from the corresponding silicon hydrides, and characterized by ^{13}C and ^{29}Si NMR spectroscopy. The thermal behaviour of several oligosiloxanes containing hydroxyalkyl groups has been studied by differential scanning calorimetry (DSC) in the temperature range −173 to 37 °C.

Introduction

Recently, we described a simple two-step procedure for the preparation of disiloxanes containing hydroxyalkyl groups [1]. Using this method we have now synthesized three symmetrically-substituted oligosiloxanes $HO(CH_2)_n[Si(CH_3)_2O]_x$-$Si(CH_3)_2(CH_2)_nOH$ (IV) containing either long hydroxyalkyl groups (IVa: $x = 1$, $n = 11$) or elongated siloxane moieties (IVb: $x = 2$, $n = 3$; IVc: $x = 3$, $n = 3$). Such well defined α,ω-difunctionally terminated organosiloxanes are useful as starting materials in polymer chemistry [2,3]; e.g., we have utilized compounds IV for the preparation of polyesters with low transition temperatures [4]. The present account describes the synthesis of compounds IVa–IVc, and reports on the thermal properties of several siloxanes of type IV.

Results and discussion

In the first step of the synthesis the alkyl substituents were attached to the silicon by a hydrosilylation to yield compounds III (Scheme 1). Removal of the terminating trimethylsilyl groups under neutral conditions with an excess of methanol gave the required bis(ω-hydroxyalkyl)oligosiloxanes (IV). Physical properties and yields of siloxanes IIIa–IIIc and IVa–IVc are summarized in Table 1. Previous publications have often given markedly different physical data, possibly owing to the presence of impurities [5–7].

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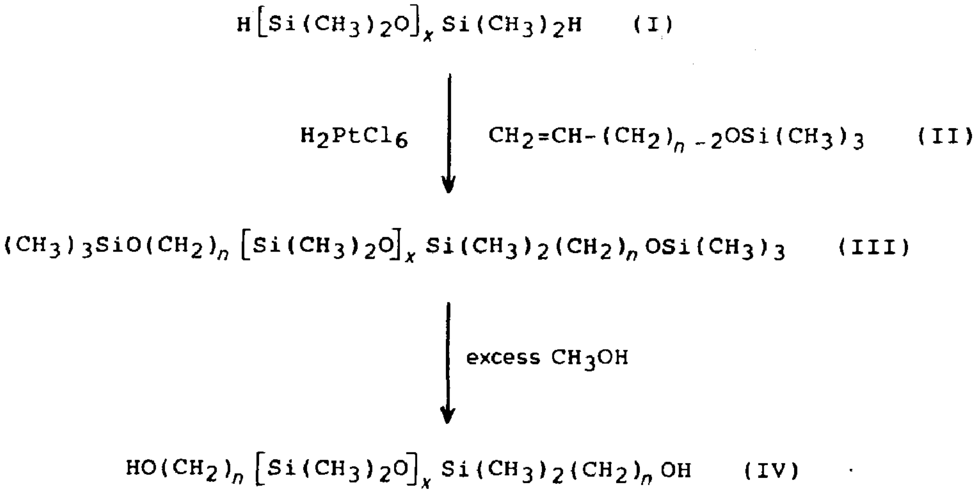

Scheme 1

Table 1

Physical properties and yields of compounds III and IV

Compound	*x*	*n*	B.p. (°C/hPa)	n_D (20 °C)	Yield (%)
IIIa	1	11	207–208/0.1	1.4444	52
IIIb	2	3	111–112/0.11	1.4224	71
IIIc	3	3	117–118/0.08	1.4205	63
IVa	1	11	215–216/0.15	1.4594 [a]	82
IVb	2	3	136–137/0.11	1.4393	67
IVc	3	3	141–142/0.08	1.4338	87

[a] Supercooled liquid (m.p. 22 °C).

Table 2

Chemical shifts [a] $\delta(^{13}C)$ and $\delta(^{29}Si)$ in ppm for compounds III and IV

	IIIa	IIIb	IIIc	IVa	IVb	IVc
δ(¹³C, ppm): $OSiC_3$	−0.34	−0.23	−0.31			
$OSiC_2O$		1.52	1.40		1.51	1.39
$OSi\mathit{C}_2C$	0.61	0.38	0.31	0.61	0.33	0.31
OC	62.63	65.41	65.36	62.52	65.29	65.21
OC*C*	33.90	27.09	27.03	33.89	26.89	26.85
$OSiC_2\mathit{C}$	18.83	14.46	14.40	18.79	14.35	14.35
$OSiC_2C\mathit{C}_9$	[b]					
δ(²⁹Si, ppm): $OSiC_3$	15.64	15.53	15.61			
$OSiC_2O$		−20.89	−21.33		−20.56	−21.22
$OSiC_2C$	7.68	7.98	8.22	7.62	8.13	8.26

[a] NMR spectra were measured in C_6D_6 at 27 °C using TMS (δ = 0 ppm) as internal standard. [b] 33.24, 30.11 (two carbons), 30.06, 29.90, 29.85, 26.32, 23.79. [c] 33.17, 30.15 (two carbons), 30.09, 29.97, 29.88, 26.28, 23.77.

Table 3

Glass transition temperatures [a] T_g for compounds $HO(CH_2)_n[Si(CH_3)_2O]_xSi(CH_3)_2(CH_2)_nOH$ (IV)

Compound	x	n	T_g (cooling) (°C)	T_g (heating) (°C)
IVa	1	11	[b]	[b]
IVb	2	3	−105	−98
IVc	3	3	−108	−100
IVd	1	3	−98	−93
IVe	1	4	−103	−97
IVf	1	5	−100	−94
IVg	1	6	−98	−93

[a] From successive cooling and heating runs (scan rate 20 °C/min). [b] Glass transition was not observed (m.p. 22 °C).

Compounds III and IV were characterized by ^{13}C and ^{29}Si NMR spectroscopy (Table 2). In the case of disiloxanes IIIa and IVa the ^{13}C NMR resonances could not be assigned unequivocally. Owing to the increased number of electronegative substituents, the ^{29}Si NMR signals from the $OSi(CH_3)_2O$ units appear at a lower field then those from $OSi(CH_3)_3$ groups [8].

As the compounds did not crystallize on storage at ambient temperature we used differential scanning calorimetry (DSC) in the temperature range −173 to 37 °C to determine the thermal transitions of IVa–IVc and the previously synthesized diols IVd–IVg ($x = 1$, $n = 3$–6) [1]. Except in the case of IVa (m.p. 22 °C), no crystallization was observed, even after slow cooling and long annealing periods. However, we noticed strong step changes in the baseline, indicating glass transitions. Table 3 lists glass transition temperatures (T_g) obtained from cooling and subsequent heating curves, each taken at a scan rate of 20 °C/min. Vitrification of IVa was not observed even at the highest cooling rate (320 °C/min).

Experimental

NMR spectra were recorded at 27 °C on a Bruker WM 300 and a Bruker CXP 300 with C_6D_6 as solvent and TMS ($\delta = 0$ ppm) as internal standard. Differential scanning calorimetry was performed with a Perkin–Elmer DSC-2 calorimeter. Cyclopentane and cyclohexane were used for temperature calibration. The glass transition temperature was taken as that point at which the change in heat capacity was one half of its maximum value.

Silicon hydrides I and 10-undecen-1-ol were obtained from commercial suppliers. (2-Propenyloxy)trimethylsilane (II, $n = 3$) was made as previously described [1]. A slightly different procedure (see below) yielded II ($n = 11$). Preparation and physical properties of disiloxanes IVd–IVg were described in an earlier paper [1].

Synthesis of (10-undecenyloxy)trimethylsilane (II, $n = 11$)

To a solution of 0.43 mole (47.1 g) of $(CH_3)_3SiCl$ and 0.43 mole (34.2 g) of pyridine in 250 ml of anhydrous THF, 0.4 mol (68.0 g) of 10-undecen-1-ol was added with vigorous stirring and cooling in an ice-bath. After 4 h refluxing the solution was filtered, and the filtrate was distilled after addition of a small amount of sodium to give 65.2 g (67%) $CH_2{=}CH(CH_2)_9OSi(CH_3)_3$ (II, $n = 11$). B.p. 132–134 °C/16 hPa; $n_D = 1.4318$ (25 °C) [9].

Synthesis of bis(ω-trimethylsiloxyalkyl)siloxanes (III)

The silicon hydride (I) (0.10 mole) was slowly added at 90 °C to 0.25 mole of (ω-alkenyloxy)trimethylsilane (II) containing a catalytic amount of H_2PtCl_6. After complete addition the mixture was stirred for 3 h at 120 °C, and then distilled in vacuo to yield compounds IIIa–IIIc. For physical properties see Table 1.

Synthesis of bis(ω-hydroxyalkyl)siloxanes (IV)

A mixture of 200 ml of methanol and 0.05 mole of the relevant compound III was vigorously stirred for 3 h at ambient temperature. After evaporation of methanol the residue was distilled under reduced pressure to give compounds IVa–IVc. For physical properties see Table 1.

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