Poly(organosiloxanes) Containing Crown Ether Functionalities

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ABSTRACT: A general method for the preparation of a range of crown ether functionalized methylsiloxane polymers of the type $Me_3Si(OSiMe_2)_a[\{OSiMe(CH_2)_x\}_y$-crown$]_bOSiMe_3$ ($a + b$ = 1 – ca. 600; $b/(a + b + 2)$ = 0.01 – 0.50; x = 6, y = 1, crown = 12-crown-4, 15-crown-5, 18-crown-6; x = 3, crown = monoaza-15-crown-5 or monoaza-18-crown-6; x = 3, y = 2, crown = diaza-18-crown-6) has been devised. The three crown ether derivatives $CH_2{=}CH(CH_2)_4$-crown (crown = 12-crown-4, 15-crown-5, and 18-crown-6) were synthesised from oct-7-ene-1,2-diol by reaction with the appropriate α,ω-disubstituted polyether derivative $X(CH_2)_2(OCH_2CH_2)_nX$, X = Cl or tosylate, n = 2, 3, or 4), using Li^+, Na^+, and K^+ ions, respectively, as templates. Their subsequent platinum-catalyzed hydrosilylation reaction with $Me_3Si(OSiMe)_a[OSi(H)Me]_bOSiMe_3$ yielded crown ether functionalized, linear siloxane polymers in quantitative yields. Monoaza- and diaza-crown containing polysiloxanes were prepared by an analogous procedure using *N*-allyl-substituted crowns. The spectroscopic properties of the fluid products have been determined.

Introduction

Linear poly(organosiloxanes) containing a range of pendant functional groups have attracted considerable recent interest,[1-6] because of the many applications for which such materials are suitable in view of their inherently flexible backbone, low glass transition temperature, and thermooxidative stability. The multitudinous applications of crown ethers and related ligand systems have also been well documented and acknowledged.[7-10] We considered it highly desirable to attempt to combine the useful properties of both classes of materials and explore the nature and applications of the resulting hybrid fluids.

Although the properties of solid-supported crowns have received considerable attention,[11-15] our recent publication, in which we showed that linear poly(dimethylsiloxane) modified with a low mole percentage of pendant 12-crown-4 receptor sites can be used as a highly specific liquid extractant,[16] is to our knowledge the first devoted to such a polymeric fluid supported crown ether. With other applications in mind, we wished to generate a general procedure that could be used to synthesize a range of crown ether functionalized polymers of this type, and in this paper we describe the preparation and characterisation of 12-crown-4, 15-crown-5, monoaza-15-crown-5, 18-crown-6, and mono- and diaza-18-crown-6, bonded via an alkyl spacer chain to a linear polysiloxane backbone to give products of the type $Me_3Si(OSiMe_2)_a[\{OSiMe(CH_2)_x\}_y$-crown$]_bOSiMe_3$.

Experimental Section

All work with air-sensitive materials was carried out in a dry, oxygen-free atmosphere using freshly distilled, deoxygenated solvents. IR spectra were measured on a Perkin-Elmer 599b spectrometer. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded with JEOL PS 100 and GX 270 instruments, using $CDCl_3$ as solvent unless otherwise stated. Data shifts are given in ppm downfield from internal $SiMe_4$. IR and NMR data are given in Table I. Mass spectra were recorded on a VG 70-70E spectrometer, equipped with a DS 2025 data system, which operated in the CI mode (isobutane). Analyses for carbon, hydrogen, and nitrogen were carried by the Analytical Services Unit, University of Bath, and gel permeation chromatographic studies were performed with a Knauer HPLC pump 64 together with a Knauer differential refractometer. Glass transition temperatures (T_g) were measured by using a Du Pont 990 DSC. Data were recorded on 5–6-mg samples with a heating rate of 5 °C/min. Analytical studies were on 30-cm PL-Gel 5-m mix and 10-m mix columns with toluene as solvent. The starting materials 1,11-dichloro-3,6,9-trioxaundecane, pentaethylene glycol, 1,4,7,10-tetraoxa-13-azacyclopentadiene, and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane were prepared by literature methods or simple extensions thereof.[17,18] Commercial samples of 1,7-octadiene, 1,8-dichloro-3,6-dioxaoctane, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, hexamethyldisiloxane, and cyclooctamethyltetrasiloxane were used as supplied.

Preparation of Oct-7-ene-1,2-diol (1). A stirred solution of octa-1,7-diene (34.1. g, 0.31 mol) dissolved in acetone (30 cm^3) was cooled to −10 °C and treated over a 5-h period with a solution of $KMnO_4$ (39.5 g, 0.25 mol) in 10% aqueous acetone (1100 cm^3). The reaction mixture was allowed to stand for 1 h and was then filtered and the filtrate saturated with CO_2 in order to precipitate $KHCO_3$. After removal of this salt the solvent was evaporated and the crude product distilled. Yield 13.5 g, 30%; bp 98 °C at 0.1 mmHg. Anal. Found: C, 66.3; H, 11.5. Calcd for $C_8H_{16}O_2$: C, 66.6; H, 11.1. MS calcd for **1** 144, found 144.

Preparation of 1,4,7,10-Tetraoxa-2-(1-hexen-6-yl)cyclododecane (2). This compound was prepared by an extension of the literature procedure,[19] using due precautions in the handling of organic materials in the presence of ionic perchlorates. Dried lithium perchlorate (12.2 g, 0.115 mol) was stirred with NaOH (11.6 g, 0.115 mol) in dimethyl sulfoxide (DMSO) (50 cm^3) for 0.3 h and then treated with a solution of **1** (7.2 g, 0.05 mol) in DSMO (10 cm^3). The mixture was held at 30 °C for 20 h before a solution of 1,8-dichloro-3,6-dioxaoctane (9.3 g, 0.05 mol) in DSMO (10 cm^3) was added dropwise. The reaction mixture was held at 110–115 °C for 3 days prior to filtration, the cooled filtrate was poured into water (300 cm^3), and the resultant clear solution was extracted four times with $CHCl_3$ (100 cm^3). The combined extracts were dried over $MgSO_4$ and the solvent was evaporated to yield a light brown oil. The crude product was purified by elution from a neutral alumina column, using $CHCl_3$–hexane, followed by distillation under reduced pressure. Yield 2.33 g, 18%; bp 145 °C at 0.1 mmHg. Anal. Found: C, 65.0; H, 10.1. Calcd for $C_{14}H_{26}O_4$: C, 65.1; H, 10.0. MS calcd for **2** 258, found 258.

Preparation of 1,4,7,10,13-Pentaoxa-2-(1-hexen-6-yl)-cyclopentadecane (3). This crown ether was prepared as above by the reaction of oct-7-ene-1,2-diol (14.4 g, 0.1 mol) with 1,11-dichloro-3,6,9-trioxaundecane (23.0 g, 0.1 mol) in the presence of sodium hydroxide (0.021 mol). The product was finally distilled at 220 °C (0.1 mmHg) using a Kugelrohr apparatus. Yield 9.0 g, 30%. Anal. Found: C, 63.8; H, 9.98. Calcd for $C_{16}H_{30}O_5$: C, 63.5; H, 9.93. MS calcd for **3** 302, found 302.

Preparation of 1,4,7,10,13,16-Hexaoxa-2-(1-hexen-6-yl)-cyclooctadecane (4). A mixture of oct-7-ene-1,2-diol (14.4 g, 0.1 mol) and metallic potassium (CARE) (7.8 g, 0.2 mol) in 1000 cm^3 of dry THF was stirred at room temperature to effect dissolution and then treated over a 2-h period with pentaethylene glycol ditosylate (54.6 g, 0.1 mol) dissolved in THF (200 cm^3). The resulting mixture was stirred for a further 62 h at 65 °C and then cooled and filtered. The precipitate was washed with CH_2Cl_2 and added to the filtrate which was evaporated to dryness leaving a brown oil. The crude product was eluted from a neutral alumina column using $CHCl_3/C_6H_6$ prior to distillation at 245–250 °C at 0.05 mmHg. Yield 7.9 g, 22.8%. Anal. Found: C, 62.3; H, 9.80. Calcd for $C_{18}H_{34}O_6$: C, 62.4; H, 9.82. MS calcd for **4** 346, found 346.

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Table I
Spectral Data[a]

infrared data		NMR data			
assignment	cm^{-1}	signal	^1H chem shift, ppm	intensity	^{13}C chem shift, ppm
		Oct-7-ene-1,2-diol (1)			
OH	3400 (s)	^{7}CH	5.80 (m)	1	138.6
$CH{=}CH_2$	1650 (m)	$^{8}CH_2$	4.95 (t)	2	114.3
		^{1}COH	4.16 (s)	1	66.5
		^{2}COH	4.27 (s)	1	72.1
		$^{1}CH_2$	3.61 (q)	2	
		^{2}CH	3.38 (q)	1	
		$^{6}CH_2$	2.05 (m)	2	32.77
		$^{3}CH_2$, $^{4}CH_2$, $^{5}CH_2$	1.40 (m)	6	25.0, 28.8, 33.5
		1,4,7,10-Tetraoxa-2-(1-hexen-6-yl)cyclododecane (2)			
$CH{=}CH_2$	1645 (m)	^{5}CH	5.72 (m)	1	138.9
OCH_2	1140 (s)	$^{6}CH_2$	4.90 (t)	2	114.5
		^{2}CH	3.68 (m*)	15	79.7
		$^{3}CH_2$, $^{9,8}CH_2$, $^{6,5}CH_2$, $^{12,11}CH_2$			74.2, 71.7, 70.7, 70.4, 70.2
		$^{4}CH_2$	2.09 (q)	2	33.7
		$^{1}CH_2$, $^{2}CH_2$, $^{3}CH_2$	1.40 (m)	6	31.9, 25.2, 29.1
		1,4,7,10,13-Pentaoxa-2-(1-hexen-6-yl)cyclooctadecane (3)			
$CH{=}CH_2$	1640 (m)	^{5}CH	5.80 (m)	1	138.4
OCH_2	1122 (s)	$^{6}CH_2$	4.92 (t)	2	114.0
		^{2}CH, $^{3}CH_2$, $^{12,11}CH_2$, $^{9,8}CH_2$ $^{6,5}CH_2$, $^{15,14}CH_2$	3.67 (m*)	19	79.4, 74.1, 71.7, 70.7, 70.2, 70.1
		$^{4}CH_2$	2.06 (q)	2	33.7
		$^{1}CH_2$, $^{2}CH_2$, $^{3}CH_2$	1.40 (m)	6	31.9, 24.6, 28.6
		1,4,7,10,13,16-Hexaoxa-2-(1-hexen-6-yl)cyclooctadecane (4)			
$CH{=}CH_2$	1645 (m)	^{5}CH	5.78 (m)	1	138.4
OCH_2	1140 (s)	$^{6}CH_2$	4.95 (t)	2	114.2
		^{2}CH, $^{3}CH_2$, $^{15,14}CH_2$, $^{12,11}CH_2$, $^{9,8}CH_2$, $^{6,5}CH_2$, $^{17,18}CH_2$	3.68 (m*)	23	79.4, 74.2, 70.6, 70.5, 70.4, 70.2, 69.3
		$^{4}CH_2$	2.05 (q)	2	33.8
		$^{1}CH_2$, $^{2}CH_2$, $^{3}CH_2$	1.40 (m)	6	31.3, 24.9, 31.3
		13-Allyl-1,4,7,10-tetraoxa-13-azacyclopentadecane (5)			
$CH{=}CH_2$	1645 (m)	^{2}CH	5.88 (m)	1	135.5
OCH_2	1120 (s)	$^{3}CH_2$	5.04 (t)	2	117.5
		$^{2,3}CH_2$, $^{5,6}CH_2$, $^{8,9}CH_2$, $^{11,15}CH_2$	3.63 (m*)	16	70.7, 70.1, 69.8, 69.7, 69.4
		$^{14,12}CH_2$	2.72 (t)	4	59.7
		$^{1}CH_2$	3.16 (d)	2	53.8
		16-Allyl-1,4,10,13-pentaoxa-16-azacyclooctendecane (6)			
$CH{=}CH_2$	1460 (m)	^{2}CH	5.87 (m)	1	135.5
OCH_2	1120 (s)	$^{3}CH_2$	5.08 (t)	2	116.4
		$^{2,3}CH_2$, $^{5,6}CH_2$, $^{8,9}CH_2$, $^{11,12}CH_2$, $^{14,18}CH_2$	3.64 (m)	20	70.2, 70.0, 69.8, 69.7, 69.6, 69.2
		$^{15,17}CH_2$	2.72 (t)	4	58.3
		$^{1}CH_2$	3.13	2	53.0
		7,16-Dialkyl-1,2,10,13-tetraoxa-7,16-diazacyclooctadecane (7)			
$CH{=}CH_2$	1640 (m)	^{2}CH	5.86 (m)	2	135.7
OCH_2	1140 (s)	$^{3}CH_2$	5.13 (t)	4	117.1
		$^{2,3}CH_2$, $^{11,12}CH_2$, $^{5,9}CH_2$, $^{14,18}CH_2$	3.62 (t)	16	70.5, 70.0, 69.8, 69.2
		$^{6,8}CH_2$, $^{15,17}CH_2$	2.7 (t)	8	58.8
		$^{1}CH_2$	3.16 (d)	4	53.4
		Copolymers Containing SiH Functionalities (9)			
SiH	2180 (m)	SiH	4.74		
$SiCH_3$	1260 (s)	$SiCH_3$	0.05–0.10		0.92–1.30
SiO	1070 (s)				
		Copolymers Containing Crown Ethers (11)			
$SiCH_3$	1260 (s)	OCH	3.65 (m)	15 (crown-4)	78.9
SiO, OCH_2	1060 (s)	$OCHCH_2O$	3.65 (m)	19 (crown-5)	74.2
		other ring CH_2	3.65 (m)	23 (crown-6)	70.8–70.1
		MeSi	0.05–0.08 (m)		0.8–1.6
		$SiCH_2$	0.46 (t)	2	17.5
		other side-arm CH_2	1.20–1.40 (m)	10	23.0–33.6
		$SiCHCH_3$	0.94 (d)		
		$SiCHCH_3$	0.80 (m)		

Table I (Continued)

infrared data assignment	cm^{-1}	NMR data signal	^{1}H chem shift, ppm	intensity	^{13}C chem shift, ppm
		Copolymers Containing Monoaza-crowns (12)			
$SiCH_3$	1260	NCH_2	2.72 (t)	4	69.8
SiO, OCH_2	1060	other ring CH_2	3.62 (m)	16 (crown-5) 20 (crown-6)	70.1–71.0
		MeSi	0.04–0.06		0.45–1.00
		$CH_2CH_2CH_2Si$	2.47 (t)	2	54.5
		$CH_2CH_2CH_2Si$	1.46 (m)	2	20.6
		$CH_2CH_2CH_2Si$	0.45 (t)	2	14.9
		$SiCHCH_3$	0.93 (d)		
		$SiCHCH_3$	0.81 (m)		
		Copolymers Containing Diaza-crown-6 (13)			
$SiCH_3$	1260	NCH_2	2.74 (t)	8	59.5
SiO, OCH_2	1060	other ring CH_2	3.65 (m)	16	70.0–70.9
		$NCH_2CH_2CH_2$	2.49 (t)	4	54.0
		$NCH_2CH_2CH_2Si$	1.47 (m)	4	20.7
		$NCH_2CH_2CH_2Si$	0.46 (t)	4	15.1
		MeSi	0.04–0.06		0.60–0.90
		$SiCHCH_3$	0.93 (m)		
		$SiCHCH_3$	0.81 (d)		

[a] IR; s, strong; m, medium. NMR: s, single; d, doublet; t, triplet; q, quartet; m, multiplet; m*, singlet and multiplet superimposed. Numbering scheme: rings are numbered clockwise starting from the O atom nearest and the alkyl substituent. The spacer chain is numbered 1–6 from the ring toward Si.

Preparation of 13-Allyl-11,4,7,10-tetraoxa-13-azacyclopentadecane (5). A stirred mixture of $NaHCO_3$ (2.18 g, 0.026 mol) and 1,4,7,10-tetraoxa-13-azacyclopentadecane (4.38 g, 0.02 mol) in DMF (30 cm^3) was treated dropwise with a solution of allyl chloride (1.60 g, 0.21 mol) in DMF (5 cm^3) at room temperature. Stirring was then continued for a further 3 days at 50 °C before the mixture was poured into water (20 cm^3). The solution was extracted with 5 × 40 cm^3 of CH_2Cl_2, the combined extracts were dried over $MgSO_4$, and the solvent was removed to leave the crude product as a brown oil, which was purified by distillation at 125 °C (0.1 mmHg). Yield of **5** 4.7 g, 90%. Anal. Found: C, 60.1; H, 9.65; N, 5.42. Calcd for $C_{13}H_{25}NO_4$: C, 60.2; H, 9.65; N, 5.41. MS calcd for **5** 259, found 259. Both 16-allyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**6**) and 7,16-diallyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**7**) were prepared by similar procedures. The former was isolated as an oil of bp 225 °C at 0.1 mmHg, in a yield of 90%, 5.5 g. Anal. Found: C, 59.4; H, 9.60; N, 4.62. Calcd for $C_{15}H_{29}NO_5$: C, 59.4; H, 9.57, N, 4.62. MS calcd for **6** 303, found 303. The latter was isolated as a pale yellow solid of mp 45 °C following recrystallization from $CHCl_3$–petroleum ether. Yield 6.2 g, 90%. Anal. Found: C, 63.2; H, 9.95; N, 8.20. Calcd for $C_{18}H_{34}N_2O_4$: C, 63.1; H, 9.94; N, 8.18. MS calcd for **7** 342, found 342.

Synthesis of Linear Copolymers $Me_3Si(OSiMe_2)_a(OSi(H)Me)_bOSiMe_3$. Copolymers of this composition were prepared by equilibrating octamethylcyclotetrasiloxane with either the polymethylhydridosiloxane $Me_3Si[OSi(H)Me]_nOSiMe_3$ (n = ca. 40) or the decasiloxane $Me_3Si[OSiMe_2]_3[OSi(H)Me]_5OSiMe_3$ in the presence of hexamethyldisiloxane and 0.1% trifluoromethanesulfonic acid as catalyst. Before reaction $Me_3Si[OSi(H)Me]_nOSiMe_3$ was first purified by dissolution in a 3-fold excess of toluene, and the clear solution was stirred at ambient temperature for 1 h with a 6-fold excess of MeOH and then allowed to separate for 24 h before the lower toluene layer was removed and pumped in vacuo to recover the purified starting material. Equilibration with the required stoichiometric quantity of octamethylcyclotetrasiloxane and $Me_3SiOSiMe_3$ was carried out for 24 h at 70 °C, after which time dimethylformamide (50% of the weight of the added acid catalyst) was added and the mixture was stirred for a further 1 h and then cooled. A 3-fold excess of toluene was added and the solution extracted with an equal volume of water. The toluene layer was dried over $MgSO_4$ and stirred for 1 h with a 6-fold excess of methanol. After standing for a further 24 h the toluene layer was separated and the solvent evaporated in vacuo to leave the product as a colorless oil in yields in excess of 90%. In this way 10 polymers with different mole percentage SiH contents and/or chain lengths (degree of polymerization, DP) were prepared. Analytical data for these materials are given in Table II. The SiH content of each polymer was also determined by quantitative infrared measurements at 2180 cm^{-1} by the procedure outlined in ref 20.

Table II
Molecular Weight ($\bar{M}_n$) and Analytical Data on Poly(dimethylsiloxane-*co*-methylhydridosiloxane)

polymer mol % functionality	polymer deg of polymeriztn	$\bar{M}_n$ found	$\bar{M}_n$ expected	anal. (calcd, %) C	anal. (calcd, %) H
33.3	3			37.6 (37.8)	9.90 (9.90)
2	50	3560	3700	33.1 (32.7)	8.22 (8.21)
4	50	3740	3686	32.2 (32.5)	8.31 (8.19)
14	86	6150	6210	32.0 (31.3)	8.10 (8.01)
10	250	19050	18164	31.5 (31.5)	8.11 (8.01)
4	300	21850	22046	31.9 (32.0)	8.25 (8.35)
10	350	25500	25424	31.9 (31.4)	8.10 (8.00)
4	450	33060	33300	32.4 (32.0)	8.20 (8.07)
8	495	36100	36084	31.4 (31.6)	7.99 (7.92)
4	1000	73230	73454	31.9 (31.4)	8.11 (8.00)

Synthesis of Crown Ether Containing Polysiloxanes. $Me_3Si(OSiMe_2)_a[(OSiMe(CH_2)_xO)_y\text{-crown}]_bOSiMe_3$. Copolymers with up to 50 mol % crown ether functionality and molecular weights up to 75000 Da (daltons) were synthesized by the hydrosilylation of $CH_2{=}CH(CH_2)_{x-2}$-crown by using a platinum catalyst.[21] In a typical reaction, a mixture of $CH_2{=}CH(CH_2)_{x-2}$-crown (0.02 mol) and $Me_3Si(OSiMe_2)_a[OSi(H)Me]_bOSiMe_3$ (containing 0.02 mol of SiH) was added to dry toluene (1 cm^3). A stream of dry N_2 gas was passed through the solution for 0.5 h and a solution (0.1 cm^3) of either 0.001 M $H_2PtCl_6{\cdot}xH_2O$ in 2-propanol or dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) in dichloromethane added. The reaction vessel was then sealed and heated to 100 °C for 25 h, with stirring, after which time the vessel was cooled and opened while a further 0.1 cm^3 of the Pt catalyst solution was added, prior to completion of the reaction after a further 25 h under the conditions described above. Solvent was finally evaporated and the product washed several times with methanol (5 cm^3). After further evacuation, the fluid was centrifuged and decanted from any traces of solid catalyst residues. Analytical data on all crown-functionalized polysiloxanes are given in Table III.

Results and Discussion

In order to form polyorganosiloxanes functionalized with a spacer arm terminated by a crown ether unit, the following synthetic strategy was adopted: (a) formation of

Table III
Average Molecular Weight ($\bar{M}_n$) and Analytical Data on Functionalized Poly(organosiloxanes)

polymer			$\bar{M}_n$		anal. (calcd, %)		
mol % functionality	compd	deg of polymeriztn	found	expected	C	H	N
33.3	3				52.5 (52.6)	9.93 (9.92)	
33.3	5				50.2 (49.8)	9.18 (9.77)	2.82 (2.91)
50	2	10	1850	1970	52.6 (52.8)	9.41 (9.42)	
4	2	25	1950	2110	36.8 (37.0)	8.50 (8.58)	
4	7	25	4200	4040	35.0 (35.6)	8.00 (8.46)	0.55 (0.69)
2	2	50	3750	3960	34.0 (34.8)	8.23 (8.33)	
2	3	50	4306	4000	35.5 (35.0)	8.25 (8.34)	
2	4	50	4200	4040	35.5 (35.2)	8.30 (8.35)	
2	5	50	3750	3950	35.0 (34.5)	8.15 (8.30)	0.40 (0.35)
2	6	50	4300	4000	35.1 (34.7)	8.40 (8.31)	0.45 (0.34)
2	7	50	7100	7740	34.5 (34.0)	8.60 (8.33)	0.40 (0.36)
4	2	50	3950	4200	35.5 (36.5)	8.20 (8.42)	
4	3	50	3850	4290	35.3 (36.9)	8.30 (8.43)	
4	2	300	24500	25260	36.0 (36.4)	8.40 (8.28)	
4	5	300	24000	25150	34.0 (33.3)	8.20 (8.27)	0.70 (0.66)
4	7	300	46000	45030	33.8 (32.8)	7.90 (7.95)	0.25 (0.18)
10	2	250	24000	24630	39.0 (40.2)	7.90 (8.55)	
10	2	350	33500	34450	38.5 (40.2)	7.56 (8.55)	
4	2	450	37000	37710	34.8 (36.1)	7.50 (8.32)	

$CH_2{=}CH(CH_2)_{x-2}{-}CHOHCH_2OH$; (b) conversion of the diol to $CH_2{=}CH(CH_2)_{x-2}$-crown; (c) preparation of the copolymer $Me_3Si(OSiMe_2)_a[OSi(H)Me]_bOSiMe_3$; (d) attachment of the crown ether terminated alkene to the polymer backbone.

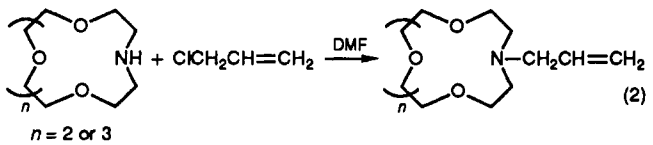
This route was chosen since both key steps (b) and (d) are well-defined processes in macrocyclic[8-10] and silicon chemistries,[22] respectively, and the procedure is very general and may be adopted for the preparation of polysiloxanes containing different sizes and types of crowns, various spacer arm lengths, and different mole percentage functionalities. Since SiH-containing siloxanes react readily with primary and secondary alcohols, step b, the conversion of the diol to an appropriate crown ether derivative was necessary before the hydrosilylation reaction (d) was attempted. Following the preparation of oct-7-ene-1,2-diol from 1,7-octadiene, the three crown ethers, 12-crown-4, 15-crown-5, and 18-crown-6, all containing alkyl chain spacer arms terminated by a terminal $CH{=}CH_2$ moiety, were readily prepared by the reaction of the diol with the appropriate α,ω-disubstituted polyether derivative (eq 1). By using Li^+, Na^+, and K^+ ions as

$$CH_2{=}CH(CH_2)_4CHOHCH_2OH + XCH_2CH_2(OCH_2CH_2)_nX \xrightarrow{\text{template}} CH_2{=}CH(CH_2)_4(CHCH_2O)(CH_2CH_2O)_n(CH_2CH_2O)$$

(X = Cl or tosylate; n = 2 (**2**), 3 (**3**), and 4 (**4**)) (1)

templates for the formation of 12-crown-4, 15-crown-5, and 18-crown-6 derivatives, respectively, yields of ca. 20–30% were obtained after workup, without applying high-dilution techniques. All three products were obtained as analytically pure, colorless oils following distillation at reduced pressure.

In order to introduce an aza-crown derivative onto the siloxane backbone, a more straightforward procedure was adopted in which the unsaturated side arm required for the hydrosilylation step (d) was introduced directly in high yield onto the N atom(s) of the aza- or diaza-crown by reaction with allyl chloride (cf. eq 2) in the presence of sodium bicarbonate.



(2)

Spectroscopic data for all alkenyl substituted crowns are summarized in Table I. Assignments are based on those reported for other C- and N-substituted analogues.[17-19,23]

Synthesis of Linear Copolymer Siloxanes. Unlike organic polymers, where unsaturated precursors may be readily polymerized to form a linear material, linear polysiloxanes are normally formed by ring-opening procedures[22] in the presence of end-blocking reagents. Thus by equilibration of octamethylcyclotetrasiloxane with either $Me_3Si[OSi(H)Me]_{40}OSiMe_3$ or the decasiloxane $Me_3Si(OSiMe_2)_3[OSi(H)Me]_5OSiMe_3$ and the appropriate quantity of $Me_3SiOSiMe_3$ in the presence of an acid catalyst, copolymers $Me_3Si(OSiMe_2)_a[OSi(H)Me]_bOSiMe_3$ containing from 2–50 mol % SiH functionalities [$b/(a + b + 2)$] and average molecular weights (M_n) up to 7500 Da were synthesized in a controlled manner, e.g.

$$x Me_3SiO[MeSi(H)O]_{40}SiMe_3 + y[Me_2SiO]_4 + z Me_3SiOSiMe_3 \rightarrow (x + z)Me_3Si(OSiMe_2)_a[OSi(H)Me]_bOSiMe_3 \quad (3)$$

where $a = (x + z)/4y$ and $b = 40x/(x + z)$. After purification, each polymer was characterized by infrared and NMR spectroscopies (Table I) as well as analysis, and its polydispersity and average molecular weight (M_n) were determined by GPC (Table II). All SiH-containing copolymers showed strong absorbances in their infrared spectra centered at 2180, 1260, and 1070 cm^{-1}, due to SiH, SiMe, and SiOSi stretching modes, respectively. The first of these modes was used for semiquantitative estimation of SiH content,[20] and data were compared with the ratio of ^1H signal intensities in the SiH (4.7 ppm) and SiMe (0.1 ppm) regions of their NMR spectra. In all cases these results give an SiH content within ±5% of the expected figure, and the copolymers were deemed suitable for use in the next stage of the reaction sequence.

Crown Ether Functionalized Polysiloxanes. A series of crown ether functionalized poly(organosiloxanes) were obtained from the polymers listed in Table II and also from the trisiloxane $Me_3SiOSi(H)MeOSiMe_3$, by the standard Pt-catalyzed hydrosilylation reaction between a 1-alkene derivative and SiH-containing material (eq 4).

$$CH_2{=}CH(CH_2)_{x-2}\text{-crown} + Me_3Si(OSiMe_2)_a[OSi(H)Me]_bOSiMe_3 \xrightarrow{\text{Pt catalyst}} Me_3Si(OSiMe_2)_a[OSiMe(CH_2)_x\text{-crown}]_bOSiMe_3 \quad (4)$$

Although anti-Marknownikoff addition is normally favored in these reactions,[24] leading to an n-alkyl spacer chain, we

have shown that in some similar reactions up to 15% Marknownikoff addition may occur, leading to an SiCH(Me)$(CH_2)_{x-2}$ moiety.[21] In the reactions described above, NMR measurements confirmed that the required linear chain was formed in the major product, but weak ^1H NMR signals at 0.93 and 0.81 ppm, due to SiCH(*Me*) and SiC*H*(Me), respectively, were observed for most polymeric products, and their intensities indicated that less than 10% of the internal addition products were formed under the given experimental conditions. GPC measurements for crown ether polysiloxanes gave molecular weight data ($\bar{M}_n$) that were in general in good agreement with that expected on the basis of the reaction stoichiometries. The polydispersities of both the final products and their poly(dimethylsiloxane-*co*-methylhydridosiloxane) precursors were in the range 1.30–1.80. Crown ether containing polysiloxanes formed by using hydrated H_2PtCl_6 in 2-propanol as catalyst generally had polydispersities somewhat larger than those formed with Cp_2PtCl_2 in dichloromethane as catalyst. It seems likely that the hydroxyl functions present in the water or solvent used in the former catalyst system react to some degree with SiH groups, leading to polymer scission and redistribution as has been noted previously,[25] and although there was no analytical or NMR evidence which demonstrated unequivocally the incorporation of solvent residues, the latter catalyst system, which is devoid of OH-containing materials, is preferred for reactions of the type described above.

Properties of the Polymers. All crown ether containing polymers were isolated as fluids, whose solvent miscibility was dependent upon both the degree of functionality and the degree of polymerization. As expected, a high loading of hydrophilic crown ethers confers water miscibility, whereas low loaded polymers are readily miscible with chlorinated and hydrocarbon solvents. Glass transition temperatures were determined on a selection of the polymers containing crown-4 and crown-6, and these were found to vary relatively little (−108 to −128 °C) for materials with 25–300 degrees of polymerization and 2–4 mol % of either functionality. However, similar polymers with 10 mol % crown ether showed a second T_g at −50 to −70 °C. Although we have no information on the sequencing of the polymers, it seems likely from these observations that the more highly loaded linear polymers are block copolymers.

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Registry No. **1**, 85866-02-0; **2**, 115880-95-0; **3**, 121029-93-4; **4**, 121029-92-3; **5**, 69978-50-3; **6**, 69978-51-4; **7**, 93000-67-0; $CH_2=CH(CH_2)_4CH=CH_2$, 3710-30-3; $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$, 112-26-5; $Cl[(CH_2)_2O]_3CH_2CH_2Cl$, 638-56-2; Ts-$(OCH_2CH_2)_5OTs$, 41024-91-3; $ClCH_2CH=CH_2$, 107-05-1; 1,4,7,10-tetraoxa-13-azacyclopentadecane, 66943-05-3.

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