Pergamon

Tetrahedron Letters 40 (1999) 4123–4126

TETRAHEDRON
LETTERS

# New Neutral Carrier-type Ion Sensors.
# Crown Ether Derivatives of Poly(methylhydrosiloxane)

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Received 28 December 1998; revised 2 April 1999; accepted 5 April 1999

**Abstract:** A facile one step synthesis of poly(methylalkoxy-crownether)siloxanes has been achieved by dehydrogenative alkoholysis of PMHS (polymethylhydrosiloxane) catalyzed by a Rh(I) complex.

*Key Words: Polysiloxane, Crown Ether, Ion-Sensor, Catalysis, Dehydrogenative Oxidation*

Because of their high ion selectivities, neutral carrier-based ion sensors are widely used, especially in clinical ion assays. Most neutral-carrier-type ion sensing membranes are made by dispersing neutral carriers in plasticized poly(vinylchloride) (PVC). However, since special plasticizers are required for PVC-based ion-sensing membranes, exudation of the membrane plasticizers often causes sensor deterioration[1] and contamination of measuring samples.[2,3] It has also been observed that PVC membranes are not suitable candidates for ion-sensitive field effect transistors and ion-selective metal electrodes because of their poor adhesion to inorganic materials.[4]

On the other hand, silicones are promising candidates for ion sensing membranes because of their low toxicity, high bio-compatibility and high durability.[5,6,7] Kimura et al. demonstrated that sol-gel based glasses that encapsulate neutral carriers such as valinomycin and crown ethers can afford excellent ion sensing membranes for ion-selective field effect transistors.[4,8] However, these membranes were also found to suffer from the exudation of the encapsulated neutral carriers. Later, it was observed by the same researchers that immobilization of neutral carriers on membranes by chemical bonding is one of the best ways to prevent the extrusion of neutral carriers to improve the toxicity and durability of the membranes.[9, 10, 11]

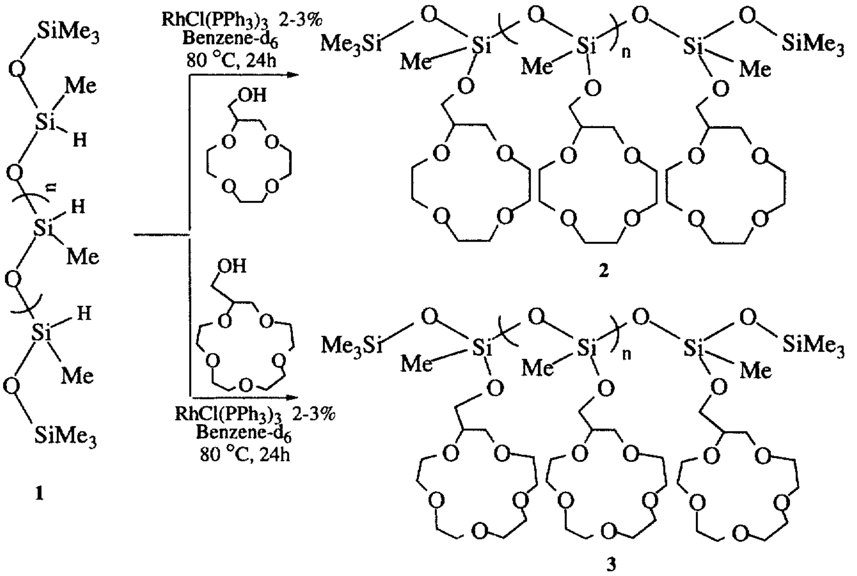
Recently, we reported an alternative to hydrosilylation as a route to achieve designer silicon polymers with multiple components built into one covalent network. This synthetic strategy employs Rh-catalyzed selective oxidation of poly(methylhydro)siloxane in the presence of alcohols[12,13] and thiols.[14] Our success with this methodology prompted us to investigate the possibility of incorporating neutral carriers into the silicon polymers. Herein, we describe a route to poly{methyl-(2-methoxy-12-crown-4)}siloxane and poly{methyl-(2-methoxy-15-crown-5)}siloxane polymers that is not only very efficient but also avoids the problem of redistribution.[15]

In a Schlenk tube, $RhCl(PPh_3)_3$ (0.04 mmol) was dissolved in 2.5 mL of benzene-$d_6$, followed by the addition of 2-(hydroxy)methyl-12-crown-4 (0.412 g, 2 mmol) and **1** (0.120 mL, 2 mmol). This mixture was degassed by 3-4 freeze pump-thaw cycles and heated in an oil bath at 78 °C, just below the refluxing temperature, under a constant flow of argon. The red color of the catalyst disappeared within 15 min of heating

*PII:* S0040-4039(99)00722-4

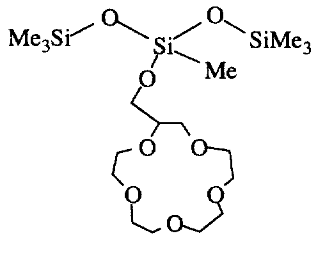
and the reaction mixture turned yellow and homogeneous. As the reaction proceeded, the yellow color turned orange and returned to red when the reaction was completed typically after 24 h. During the course of the reaction, evolution of a gas (presumably $H_2$) was observed. Polymer **2** was characterized by a combination of $^{29}$Si, $^{13}$C and $^{1}$H NMR techniques. The $^{29}$Si NMR displayed complete consumption of **1** {$^{29}$Si ∂ -34.16; -34.20; -34.26; +10.58 (terminal $OSiMe_3$)} and appearance of new resonances at {$^{29}$Si ∂ -56.72; -57.48; -57.69; +9.51 (terminal $OSiMe_3$)} reflecting the change in the electronic environment of the central -($MeSiHO_2$)- units to -($MeSiO_3$)- units. The $^{1}$H NMR of **2** revealed disappearance of the Si-H signal and Si-$CH_3$/O-$CH_2$ (crown ether) resonances in a ratio consistent with the assigned structure. Under identical reaction conditions and molar ratios, Rh-catalyzed oxidation of **1** in the presence of 2-(hydroxy)methyl-15-crown-5 produced polymer **3** in essentially quantitative yield after 24 h (Scheme).

**Scheme**: Rh-complex catalyzed selective synthesis of neutral carriers



To compare the spectroscopic properties model compounds were prepared. Thus, the addition of heptamethyltrisiloxane **4** and 2-(hydroxy)methyl-15-crown-5 to a benzene solution of $RhCl(PPh_3)_3$ (0.04 mmol) led to the formation of the desired 2-methoxy-15-crown-5-heptamethyltrisiloxane **5** after 24h of reaction at 78 °C. Similarly, the reaction of octamethyltetrasiloxane **6** with 2-(hydroxy)methyl-15-crown-5 furnished corresponding crown ether substituted siloxane **7** (Figure). The spectroscopic characteristics of these new oligomers are compared with analogous polymer **3** in the table. Interestingly, a closer look at the structures of these oligomers reveals that these molecules can also be used as precursors to sol-gel derived membranes incorporating crown ether carriers. Since in sol-gel preparation, silanol groups which are formed by acid or base-catalyzed hydrolysis of alkoxysilane are condensed with another alkoxysilane to yield highly crosslinked polysiloxanes.[9,10,16] It should be pointed out that Si-O-C bonds are more susceptible to acid or base catalyzed hydrolysis and may lead to loss of some of the crown ether pendant groups.

**Figure**: Model crown ether substituted siloxanes



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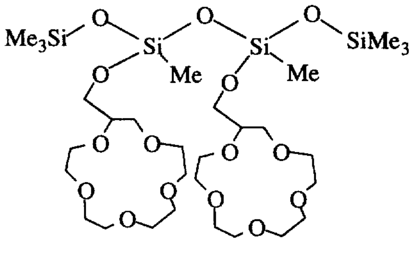

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The salient features of the present methodology are as follows: first, the reaction conditions are mild and lead to selective oxidation of Si-H bonds, without disproportionation and degradation of the backbone. Second, starting and resulting polymers have relatively high solubility in common organic solvents, which facilitates spectroscopic characterization by NMR, IR, and UV methods. Finally, the progress of the reaction can be monitored easily by NMR spectroscopy.

**Table. $^{29}$Si, and $^{1}$H NMR data for polysiloxanes and model compounds**

| Compound | $^{1}$H NMR (C$_6$D$_6$) | $^{29}$Si NMR (C$_6$D$_6$) |
|---|---|---|
| 1 | 0.11(s, OSiMe$_3$); 0.20(d, Si-CH$_3$); 4.71(q, Si-H) | -34.16; -34.20; -34.26 (SiMe), +10.58 ( terminal OSiMe$_3$) |
| 2 | 0.26(s, OSiMe$_3$); 0.45(s, broad, SiMe); 3.56 (m, broad, SiOC*H*$_2$ and OC*H*$_2$); 3.88 (t, OC*H*CH$_2$, broad) | -56.72; -57.48; -57.69 (SiMe), +9.51 (terminal OSiMe$_3$) |
| 3 | 0.16 (s, OSiMe$_3$); 0.35 (s,broad, SiMe); 3.47 (m, broad, SiOC*H*$_2$ and OC*H*$_2$); 3.72 (t, OC*H*CH$_2$, broad) | --56.41; 56.78; -57.55 (SiMe), +9.35 (terminal OSiMe$_3$) |
| 4 | 0.11(s, OSiMe$_3$); 0.20(d, SiMe); 4.71(q, Si-H) | -36.42 (SiMe); +9.73 (OSiMe$_3$) |
| 5 | 0.058 (s, OSiMe$_3$); 0.90 (s, SiMe); 3.40 (d, SiOC*H*$_2$); 3.43 (s, broad, OC*H*$_2$); 3.66 (t, OC*H*CH$_2$) | -56.25 (SiMe); +8.44 (OSiMe$_3$) |
| 6 | 0.14 (s, OSiMe$_3$); 0.16 (d, SiMe); 4.93(q, Si-H) | -35.60, -35.63 (SiMe); +10.13 (OSiMe$_3$) |
| 7 | 0.09, 0.10, 0.12, 0.15(s, OSiMe$_3$ and SiMe); 3.39(d, SiOC*H*$_2$); 3.42, 3.43 (s, broad, OC*H*$_2$); 3.66, 3.71 (t, OC*H*CH$_2$) | -56.53, -57.45 (SiMe); +9.02, +9.05 (OSiMe$_3$) |

In conclusion, these polymers are the first examples of selectively modified linear polysiloxane based materials.[7,8] Because they are highly soluble, processable and covalently bonded to neutral carriers, these PMHS derivatives are particularly interesting candidates for study as ion sensors. Furthermore, the methodology provides flexibility for systematic modification by varying the length of the tether and nature of the crown ethers. It is our hope that the generality of this synthetic method applies far beyond the development and optimization of sensing materials.

**Acknowledgements:** The financial support of the National Science Foundation through Grant No. OSR-9452892 and the Air Force Office of Scientific Research through Grant No.AFOSR 49620-929 J0431 is gratefully acknowledged.

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