Competitive Electrochemical Synthesis of Polydimethylsilane without Solvent

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Electrochemical reduction of dimethyldichlorosilane without solvent but in the presence of a small amount of complexing agent in an undivided cell fitted with a sacrificial aluminium anode and a stainless steel cathode, under constant current, was found to produce polydimethylsilane in very high faradaic yields.

The industrial interest in polydimethylsilane (PDMS) as a precursor to silicon carbide-based ceramics,[1] the publication of two papers on the electrochemical synthesis of polysilanes[2,3] and a recent patent from Dow Corning Corp.[4] in the area of polycarbosilanes, prompted us to report our most recent results in this field. This work extends a preliminary report[5] on the synthesis of PDMS from dimethyldichlorosilane by an electrosynthetic procedure using a single compartment cell fitted with a sacrificial aluminium anode, under constant current.[6,7] These reactions were carried out in tetrahydro-

Table 1 Electrochemical synthesis of PDMS without solvent[a]

				PDMS	
Run	Me_2SiCl_2 (Complexing agent)	Vol./ml	Electricity/F	Faradaic yield (%)[b]	Al (%)[c]
1	Me_2SiCl_2 alone		0.09	72 (grey)	>5
2	Me_2SiCl_2 (HMPA)	70 (13)	0.07	76	2.9
3	Me_2SiCl_2 (TDA-1, HMPA)	70 (15, 10)	0.18	84 (white)	0.1
4	Me_2SiCl_2 (TDA-1, HMPA)	70 (15, 10)	0.24	90 (white)	0.05

[a] Stainless steel cathode. [b] Faradaic yield of insoluble PDMS obtained after methanolysis, calculated with respect to electricity passed, according to a theoretical 2 F mol^{-1} process (Me_2SiCl_2 is both the substrate and the electrophile). [c] From elemental analysis.

furan (THF) in the presence of small amounts of hexamethylphosphoric triamide (HMPA) or tris(3,6-dioxaheptyl)amine (TDA-1),[8] but the yields of PDMS were limited (≈30%) owing to the ring opening of the THF leading to secondary reactions. The novelty of the present report consists in obtaining PDMS in almost quantitative faradaic yields without solvent but in the presence of a small amount of a complexing agent such as HMPA or TDA-1.

$$Me_2SiCl_2 \xrightarrow[\text{ii, methanolysis (24 h)}]{\text{i, } e^- \text{ (Al anode)}} \text{PDMS} \qquad (1)$$

The electroreduction occurs according to reaction (1). We used Bu_4NBr as the supporting electrolyte (3×10^{-3} mol dm^{-3}) in 70 ml of Me_2SiCl_2 and we verified that this mixture was sufficiently conducting to maintain 100 mA during more than one day (run 1). In the absence of the complexing agent, the PDMS was obtained in 72% faradaic yield, but it was grey owing to the presence of metallic aluminium resulting from reduction of $AlCl_3$. This was avoided by adding a small fraction of complexing agent(s) in order to shift the reduction potential of $AlCl_3$ towards more cathodic values (runs 2 and 3). Moreover, sonication (35 kHz) resulted in a further increase in the yield of PDMS (run 4). The results are summarized in Table 1.

Thus, our electrochemical synthesis of PDMS offers, besides the advantages of the electrosynthesis (replacement of sodium by aluminium and reactions carried out at room temperature), the possibility to avoid the use of a solvent and a significant increase in the yields (from 30 to 90%).

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