

Synthesis of Organopolysilanes using a Crown Ether

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The polymerization rate of organopolysilanes is successfully increased by adding 18-crown-6 to the reaction mixture, accompanied by a change in molecular weight distribution from bimodal to monomodal.

Organopolysilanes, which have silicon backbones, are usually synthesized by the condensation of dihalogeno-organosilanes with molten sodium metal as a catalyst.^{1,2} Prolonged polymerization times (over several hours) are generally necessary to obtain the polymers in high yields. A bimodal molecular

weight distribution is also frequently observed. This paper reports an increase in polymerization rate of organopolysilanes by adding a crown ether to the reaction mixture. The molecular weight distribution also changes from bimodal to monomodal.

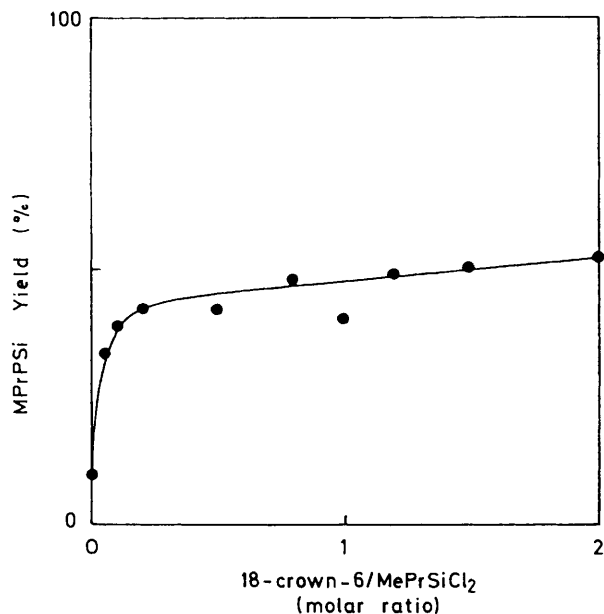


Figure 1. Polymerization yield of MPrPSi for various amounts of added 18-crown-6. Polymerization time 30 min.

The polymerization reaction is a Wurtz-type reaction and the rate is restricted by the reactivity of silyl anions. The crown ether would be expected to increase the reactivity of the silyl anions by forming a crown ether-sodium ion complex, resulting in a dramatic increase in the polymerization rate. We chose 18-crown-6 as a likely candidate because it has a large equilibrium constant for formation of such a complex. The crown ether was added to the reaction mixture of toluene, sodium, and the monomer in a molar ratio in the range 0–2.0 with respect to the monomer concentration.

Figure 1 shows the yield of methylpropylpolysilane (MPrPSi) for various amounts of additional 18-crown-6. The yield reached almost 40% with the addition of a 0.1 molar ratio of crown ether within the short polymerization time of 30 min. The yield gradually increased with increasing proportions of crown ether, reaching 52% at a molar ratio of 2.0. This yield is about five times larger than that obtained without the crown ether.

The molecular weight distribution was monomodal although bimodal distributions¹ are usually observed in the synthesis of alkylpolysilanes. The molecular weight distribution of MPrPSi is shown in Figure 2; it was 100 000 (M_w/M_n 2.2) with addition of a 0.05 molar ratio of crown ether. This M_w is intermediate between the high (~1 000 000) and low (~10 000) molecular weights of MPrPSi synthesized without crown ether. The distribution shifted to the lower molecular weight region when further crown ether was added. At 0.2 molar ratio, M_w was 52 000 (M_w/M_n 2.3) with an increase in low molecular weight polymers ($M_w \sim 10$ 000). A longer polymerization time also reduced the molecular weight. The reasons for this drastic molecular weight distribution change are not clear yet.

The same effect was observed in the synthesis of dihexylpolysilane (DHexPSi). Although the yield was only 0.05% for polymerization without crown ether, the yield was 17% within

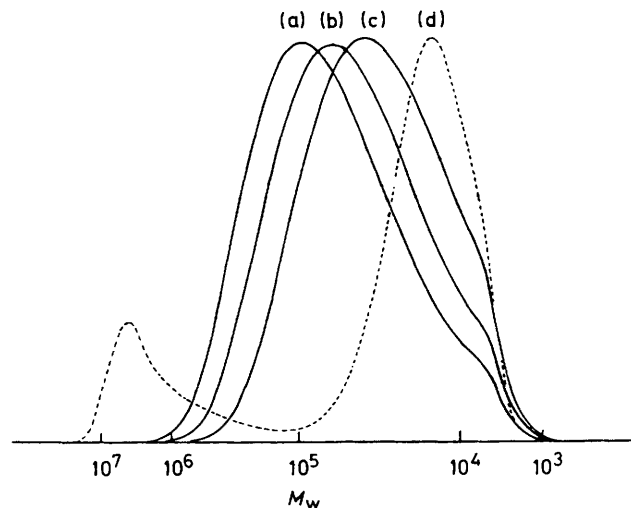


Figure 2. Gel permeation chromatography elution curves for MPrPSi in tetrahydrofuran. Solid lines: with 18-crown-6; broken lines: without crown ether. Molecular weights are relative to polystyrene standards. Molar ratio 18-crown-6 to MePrSiCl₂: (a) 0.05; (b) 0.1; (c) 0.2; (d) 0.

30 min when a 0.1 molar ratio of 18-crown-6 was added. The molecular weight was 130 000 (M_w/M_n 2.6; 91.8%) with a small amount of high molecular weight polymers (6 500 000, M_w/M_n 1.5; 8.2%).[†]

The polymerization procedure was carried out as follows. In a typical run, freshly cut sodium metal (1.76 g) and 18-crown-6 (0.84 g) in dry toluene (50 cm³) was refluxed with stirring under argon. Methylpropyldichlorosilane (5 g) was quickly injected into the mixture using a glass tube syringe. Stirring was continued for 30 min. The reaction was quenched by cooling, and unreacted sodium metal destroyed by adding ethanol (15 cm³). The polymer was precipitated by pouring the mixture into ethanol (700 cm³) dropwise, washed with water, and reprecipitated using toluene-methanol. Undissolved substances in toluene were removed with a 10 μ m filter. The polymer was identified by its i.r. spectrum. No significant amount of residual 18-crown-6 was observed in the polymer.

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References

- 1 See R. West, *J. Organomet. Chem.*, 1986, **300**, 327, for a review of organopolysilanes containing many references.
- 2 M. Fujino, N. Matsumoto, H. Ban, and K. Sukegawa, *J. Polym. Sci.: Part C: Polym. Lett.*, 1988, **26**, 109.

[†] The molecular weight distribution of DHe \times PSi produced in the absence of 18-crown-6 was bimodal: $M_w \sim 4$ 000 000, 80%; $M_w \sim 20$ 000, 20%.