

Preparation of Poly(organosilanes) using High-intensity Ultrasound

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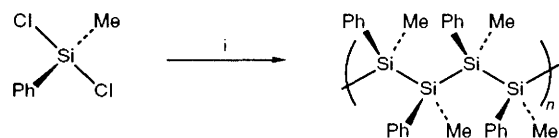
Poly(organosilanes) with controlled molecular weight distribution are prepared by Wurtz coupling reactions under varying ultrasound conditions.

There has been considerable recent interest in the synthesis of poly(organosilanes) with controlled structures, these materials having a range of potential applications.¹ For example, they are photoactive and photoconductive and are being investigated for use as photoresists, they have also been used as precursors to ceramic materials although have not fulfilled their early promise in this area.

The usual polymerization method^{2,3} uses molten sodium in refluxing toluene in a Wurtz-type coupling of diorganodichlorosilanes. However, the reactions are irreproducible and the yields are rather low, ~55% at best, depending on the nature of the substituents, and the polymers often have a very wide, usually bi- or tri-modal, molecular weight distribution. While this has been attributed to two concurrent polymerization mechanisms being involved, Jones *et al.* recently⁴ showed that the results could be explained in terms of the mechanism of Gauthier and Worsfold⁵ involving an anionic chain-growth mechanism and consideration of the solubility characteristics of the polymeric materials. To achieve commercial use, synthetic methods to produce polysilanes with controlled structure and preferably, monomodal molecular weight distributions are needed. These have been produced by carrying out the reaction in the presence of additives such as crown ethers.^{6,7}

Ultrasound has been found to be useful in promoting a range of chemical reactions, particularly those involving metal surfaces.^{8,9} However, few systematic studies of the effects of the ultrasound parameters have been reported. Ultrasound has been applied to poly(organosilane) synthesis but with conflicting results. Matyjaszewski *et al.*¹⁰ have prepared poly(methylphenylsilane) with a monomodal molecular weight distribution by carrying out the reaction in an ultrasound bath as well as with an ultrasonic horn system. However, Miller *et al.*¹¹ report that they obtained bimodal polymers using this method. While investigating applications of ultrasound in polymer chemistry we noticed effects that may explain the apparent anomalies in this reaction.

The reaction (Scheme 1) was performed by ultrasonically dispersing a 2.5-fold molar excess of sodium under nitrogen in a cooled reaction vessel attached to a 'MSE Soniprep 150' 22 kHz sonicator fitted with a 0.5 inch horn. After cooling to 25°C and adjusting the sonicator to the required setting, dichloromethylphenylsilane (Aldrich) was added from a syringe over *ca.* 5 min. After 1 h, the mixture was quenched with ethanol and the polymer was precipitated by pouring into ethanol-water, washed with water, and reprecipitated from toluene solution. Three polymerizations were carried out under identical conditions; only the intensity of ultrasound was varied. The molecular weight distributions of the resulting polymers, obtained by gel permeation chromatography, are shown in Fig. 1 and clearly demonstrate that the ultrasound properties play an important part in determining the course of the reaction. The intensities indicated were measured cal-



Scheme 1 Reagents and conditions: i, Na, toluene, reflux (110°C) or sonicate (25°C)

orimetrically and molecular weights indicated refer to polystyrene standard equivalent values.

Evidently, the use of higher intensity ultrasound results in a much narrower distribution of molecular weights and use of still higher intensities (not available on this apparatus) may well lead to a monomodal distribution. Many sonochemical reactions have been interpreted in terms of the preferential promotion of radical and single electron-transfer processes over those involving an ionic pathway.¹² However, there is no firm evidence of radical intermediates in this polymerization and the explanation of our results lies in the physical rather than chemical effects of ultrasound. The ultrasonic acceleration of heterogeneous reactions is usually attributed to the continual sweeping of the surface leading to a greater concentration and faster regeneration of reactive sites. In the present case, this would lead to a more homogeneous chain-growth process. In addition, once formed, low molecular weight polymer would still have reactive chloro end groups and the presence of more reactive sites on the sodium would mean that these could be involved in further growth, hence the increase in molecular weight under ultrasound of the low molecular weight fraction normally produced. However, the main effect shown in Fig. 1 is the reduction in the proportion of the high molecular weight material formed. This can be explained in two ways. First, the growing polymer is swept away from the metal surface by the action of the ultrasound before it has the opportunity to attain the very high molecular weights usually found in the conventional reaction. Secondly, any high molecular weight material formed is subjected to the degradation process owing to shear effects caused by the ultrasound. This process is known to be more efficient at high intensity¹³ and is also more efficient at higher molecular weights so that it leads to a reduction in polydispersity. Further work is underway to quantify these various effects.

Thus, it has been shown that the apparently anomalous results in the literature may be explained by changes in the reaction conditions. In addition, ultrasound can be used to prepare poly(organosilanes) with narrow and controlled molecular weight distributions under the correct conditions

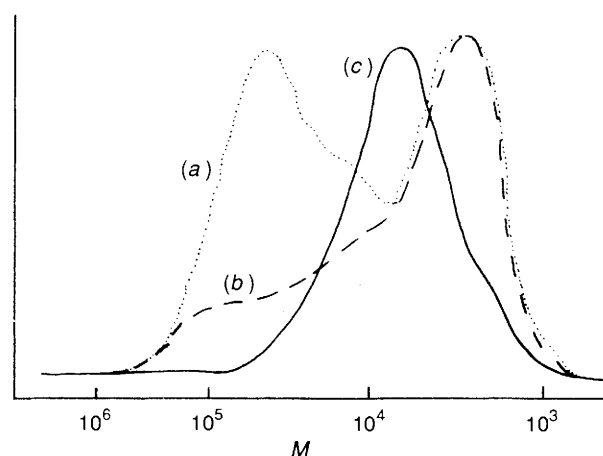


Fig. 1 Molecular weight distributions of sonochemically produced poly(methylphenylsilane) prepared using different ultrasound intensities. Intensities/W cm⁻² (a) 30 (b) 65 (c) 95.

and to prepare polymers with accurately controlled properties. The results also indicate that care should be taken to optimise and report the precise conditions used for sonochemical reactions if they are to be reproduced by other workers.

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