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Synthesis and Modification of Silicon-Containing Polymers using Ultrasound

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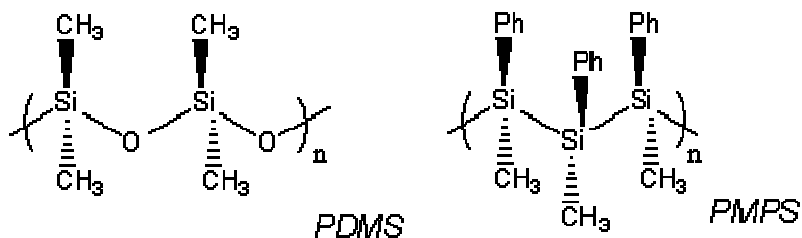
ABSTRACT

The application of high intensity ultrasound to silicon backbone polymers, particularly poly(dimethylsiloxane) and poly(organosilanes) is described. There is advantage in using ultrasound both in modifying the molecular weights or end-group structures of pre-formed polymers as well as accelerating the course of polymerization reactions.

KEYWORDS: Siloxane; poly(organosilane); sonochemistry; ultrasound.

INTRODUCTION

While most work in polymer science continues to involve organic materials, there continues to be an emerging interest in polymers whose backbones contain inorganic elements¹. After carbon, the element most often used is silicon, chiefly as polysiloxanes (silicones) but also as polysilazanes and polysilanes. Inorganic polymers offer a range of properties not found in wholly organic systems. For example, polysiloxanes², with their alternating Si – O backbone are, depending on the substituent, low Tg, low viscosity and surface energy fluids or elastomers. Poly(organosilanes)^{3,4}, are electro- and photoactive due to σ conjugation along the all Si backbone.



Scheme 1. Poly(dimethyl siloxane), PDMS and poly(methyl phenyl silane), PMPS, as examples of silicon containing polymers

The recent advances in developing synthetic methods⁵ such as RAFT and ATRP which allow precise control over chain structure and length in vinyl polymers has not been paralleled for inorganic materials. Some systems are amenable to anionic polymerization but in general, less control over structure, and hence properties, is available. In recent years, there has been growing interest in using high intensity ultrasound in chemistry, for which the term *sonochemistry* has been coined. Early chemical applications were in organic and organometallic synthesis^{6,7}, but more recently it has been used for the preparation of polymers⁸, nanoparticles⁹ and other materials¹⁰. High intensity (or *power*) ultrasound has a number of effects which may be used to control polymerization reactions or for post-synthesis modification and this mini-review will illustrate their use in silicon-containing polymer systems and related materials.

SONOCHEMICAL EFFECTS

Sonochemical effects can primarily be attributed to the generation in liquids of cavitation¹¹. If the rarefaction phase of the longitudinal acoustic wave generates a sufficiently negative pressure, bubble (or cavity) formation occurs. The bubbles grow to 50 – 100 μm in size before collapsing explosively as the sound wave propagates through the fluid. This can result in extreme conditions of temperature ($> 2000\text{ K}$) and pressure ($>500\text{ bar}$) being generated¹² in the bubbles although they last only on a microsecond timescale. Moderately high concentrations of reactive intermediates such as radicals can be formed, either from breakdown of solvent or of added reagents¹³. The region of liquid around the bubble has high gradients of temperature, pressure and strain. The motion of fluid around the bubbles is rapid resulting in very efficient mixing and the formation of liquid jets due to shock waves emitted after final collapse. This rapid motion can result in effective strain degradation of polymer chains in the vicinity of cavitation bubbles¹⁴ as long as they are over a certain molecular weight. Thus, there are a number of sonochemical effects, summarized in Figure 1, which may be exploited.

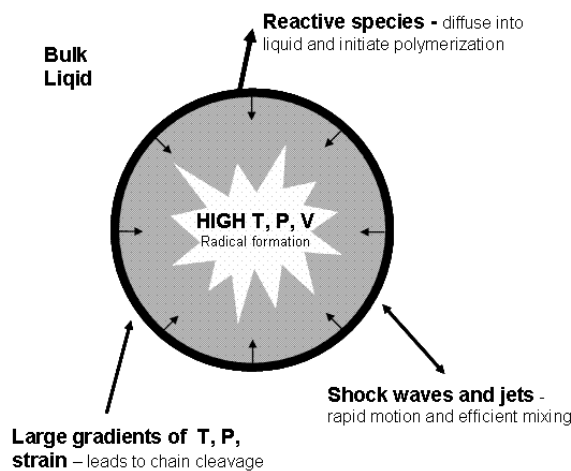


Figure 1. Schematic summary of sonochemical effects

The most familiar method for introducing ultrasound into a reaction is to immerse the reaction vessel into an ultrasonic cleaning bath. However, a better solution is to use a 'horn' system which uses a metal (usually titanium) rod to directly introduce vibrations from a transducer into the reaction¹⁵. Most apparatus of this type operates at frequencies

of 20 – 40 kHz. The intensity of ultrasound entering the system can be calculated by comparing the heating effect with a calibrated quantity of water.

The generation of radicals has led to ultrasound being used to initiate polymerization in vinyl monomers, both in bulk and in emulsion systems¹⁶⁻¹⁹, the latter taking advantage of the ready formation of emulsions and dispersions offered by ultrasound. Sonication can obviate the need for thermal initiators or emulsifiers and allows some control over the molecular weight, tacticity and polydispersity. In contrast, there has been relatively little work dealing with the use of ultrasound in step-growth polymerizations. Long²⁰ showed that temporal and spatial control over the synthesis of several polyurethane systems was possible and this was investigated in more detail by Price and coworkers²¹. There has also been some interest in ring-opening reactions. For example, Stoessel has also reported the use of ultrasound at very high intensities to promote the polymerisation of small cyclic polycarbonate oligomers²² while other work has investigated sonochemically enhanced polymerization of cyclic lactones²³ and caprolactam²⁴. In the latter, Ragaini *et al.* showed that ultrasound enhanced the ring opening of ϵ -caprolactam to form nylon-6, allowing a single step polymerization. Higher molecular weight materials with narrower distributions were formed in shorter reaction times than when using the conventional process.

SONOCHEMICAL PREPARATION OF POLYSILOXANES

Degradation of pre-formed polysiloxanes

One of the earliest sonochemical effects reported was the reduction in viscosity of polymer solutions. It is now apparent that this results from chain cleavage arising from strain when polymers are caught in the solvent flow around collapsing cavitation bubbles and/or in the resulting shock waves¹⁴. Ultrasonic degradation has many features of a mechanochemical process in contrast to thermal degradation, chiefly that it is not random but occurs preferentially at the middle of the chain. Thus, the molecular weight distribution is altered during sonication in a controlled, predictable manner^{25, 26}.

To exemplify the results for poly(dimethyl siloxane), PDMS, Figure 2 shows work from the author's laboratory demonstrating the change of molecular weight during sonication in toluene of a commercially available high viscosity (100000 cs) polymer,

end-blocked with trimethylsilyl groups ($M_n \sim 85\,000$, $\gamma \sim 1.8$). The characteristic reduction in M_n is seen, the rate of which slows as M_n falls until a limiting value is reached below which no further change is observed. As would be expected, higher intensities cause faster and a higher degree of degradation due to the formation of a larger number of bigger bubbles giving larger strain rates. All the features of the rate of degradation in terms of the effect of temperature and solvent were the same as with organic systems.

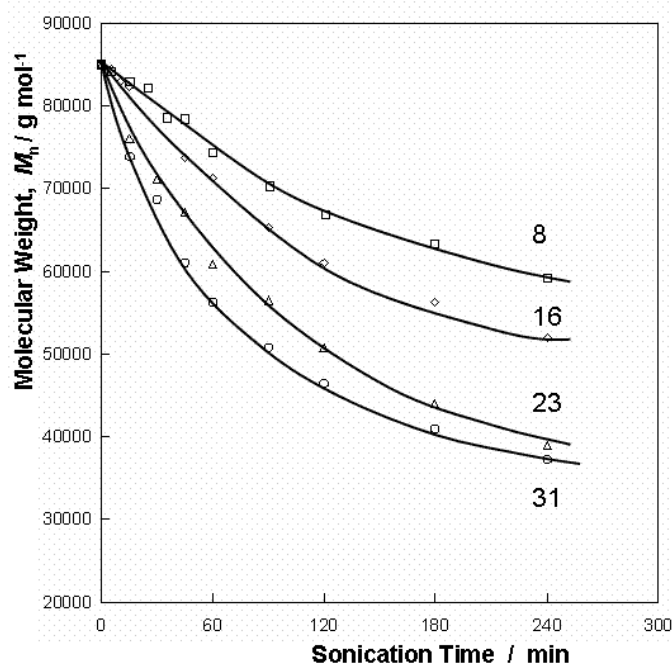


Figure 2. Sonochemical degradation of 1 % w/v solutions of PDMS in toluene at 30°C and the indicated ultrasound intensities in W cm^{-2}

The degradation will occur in any polymer solution. During a polymerization reaction therefore, it will occur concurrently with chain growth. To compare with the molecular weights obtained during synthesis of PDMS (see next section), we also investigated the degradation of PDMS in octamethylcyclotetrasiloxane, known as 'D₄'. The process is qualitatively the same as in other solvents as illustrated by Figure 3 which shows the degradation of PDMS in D₄ at different concentrations. As the concentration

is increased, the degradation is reduced due to increased solution viscosity and interchain entanglements. It has recently been shown that mechanochemical scission and hence polymer modification can also be caused in polymer melts by applying very high intensity ultrasound^{28, 29} during extrusion. With the equipment available to us, sonication of pure PDMS fluids resulted in no change in molecular weight; for low viscosity fluids, chain lengths were below the minimum in which degradation would be expected and in higher viscosity fluids, attenuation of the ultrasound caused only very rapid heating but no cavitation. One area where the effect has been exploited is in the work^{30, 31} of Isaev and coworkers who have used ultrasound enhanced extrusion of waste crosslinked rubbers including filled and unfilled silicone resins to recover usable materials for recycling.

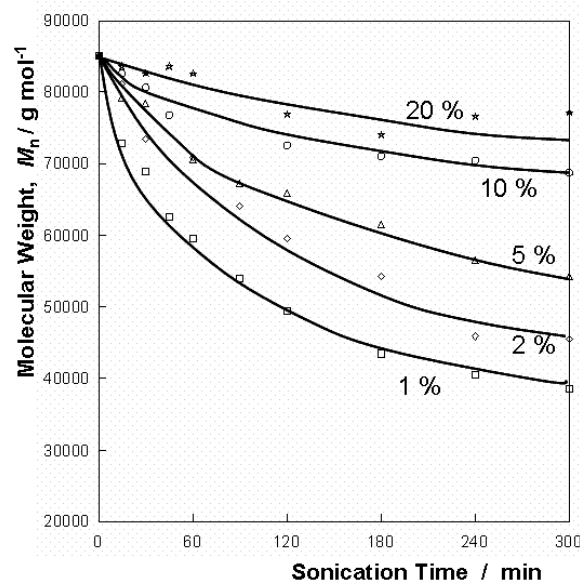


Figure 3. Sonochemical degradation of PDMS in D₄ at 40°C and 33 Wcm⁻² at the indicated solution concentrations in % w/v

When using D₄ as a solvent, the possibility exists of a re-equilibration between the linear PDMS and the D₄ rings. However, this did not occur and there was no change in

the proportions of the component during the reaction. Similarly sonication of D₄ in the absence of a catalyst caused no polymerization.

The change to polymer structure can be seen from Figure 4. As well as the change in average chain length, the polydispersity can be modified. While this method cannot produce polydispersities as low as, for example, anionic polymerization, lower values than those available from more common reaction types can be obtained.

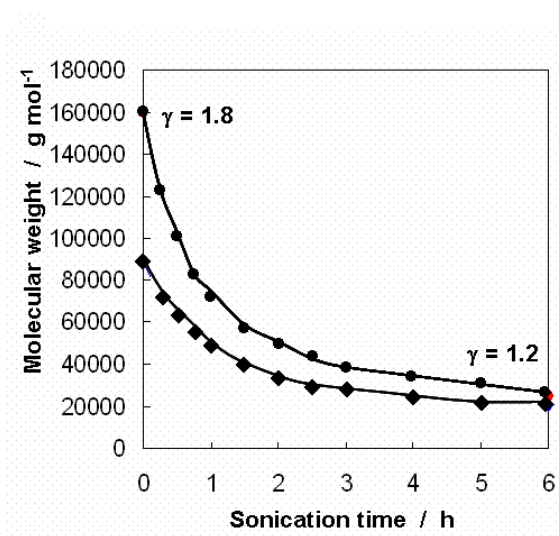


Figure 4. Change in molecular weight and polydispersity during sonication of 1 % w/v PDMS in D₄ at 30°C and 33 Wcm⁻²

Additional modification to structure can be achieved from reaction with the products of the chain cleavage. In wholly carbon (or wholly silicon) backboned polymers, chains undergo homolytic cleavage to form macroradicals¹³ which can react with other monomers to form block copolymers. However, in Si-O, cleavage is heterolytic. Thomas and de Vries some years ago suggested³² that an ion pair is formed in this case. Addition of styrene or methyl methacrylate to sonicated solutions of PDMS resulted in no subsequent reaction. Attempted trapping of intermediates and analysis by ESR gave no signal from PDMS, in contrast to polyisobutylene or poly(methyl phenylsilane) as shown in Figure 5. However, reaction in the presence of LiF yielded materials where some chains were terminated with fluorine while others were silanol terminated. Of more potential use was sonication in the presence of small amounts of

water (Scheme 2). Infrared and NMR analysis showed quantitative conversion to silanol terminated chains, giving a functionality appropriate for further elaboration.

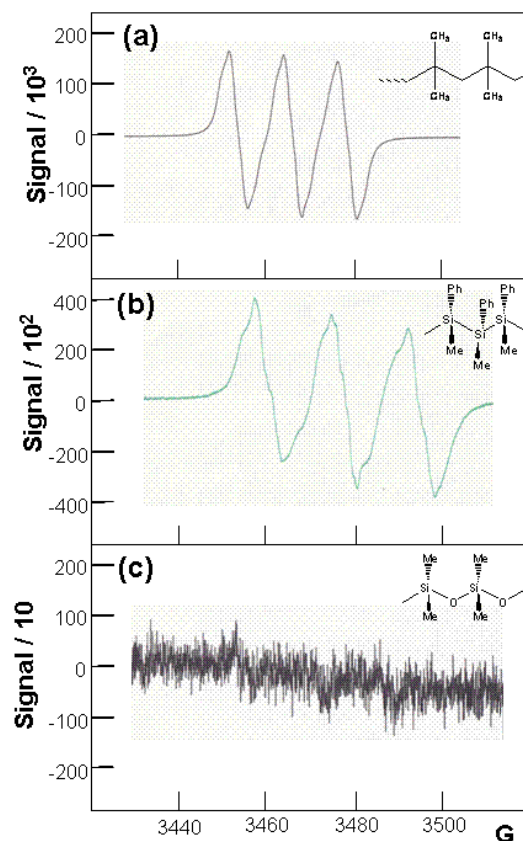
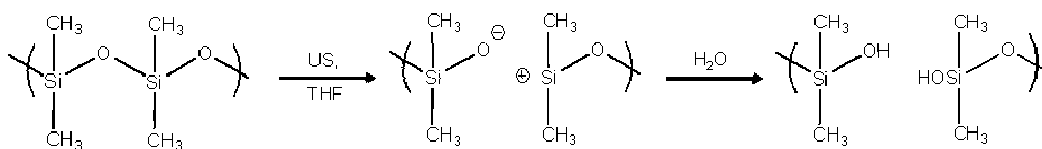


Figure 5. ESR spectra from sonochemical degradation of (a) polyisobutylene (b) poly(methyl phenyl silane) and (c) PDMS in toluene trapped with *t*-butyl phenyl nitron.

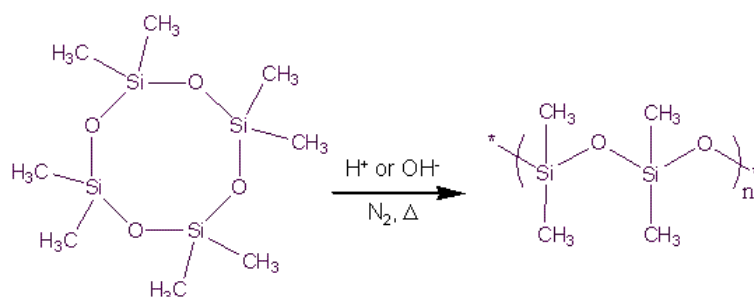


Scheme 2. Sonochemical degradation of PDMS in the presence of water

Ring opening polymerization

There are a number of methods available for preparing polysiloxanes³³. While polymers with low polydispersity can be obtained by living anionic reactions, it is more common to

use either the condensation of silanols or the ring-opening polymerization of small cyclics such as D₄. In a very brief report on the first study of sonochemical preparation of polysiloxanes, Kogan and Smirnov some time ago demonstrated³⁴ that reactions under ultrasound showed significant rate enhancements. Given the application of ultrasound to other ring-opening reactions described above, work in the author's laboratory investigated the ring opening route to PDMS, shown in Scheme 3.



Scheme 3. Ring opening polymerization of D₄ to PDMS

The reaction can be catalysed by either acid or alkali and Figure 6 shows that the acid catalysed reaction is not only accelerated by using ultrasound but gives higher molecular weight polymers with lower polydispersity³⁵. This was the case for a wide range of conditions. The results were interpreted by assuming that the mechanical effects of ultrasound in high rates of mixing lead to much better dispersion of the acid catalyst throughout the reaction as well as mixing with the immiscible D₄. The initial ring opening is thus more rapid than in the 'silent' case, leading to the faster kinetics. The 'initiation' also occurs more evenly through the system so that more chains are growing simultaneously at the same rate, hence giving lower polydispersity.

To further investigate the kinetics of the reaction, polymerisations under ultrasound were compared with that under 'silent' conditions over a range of temperatures at fixed acid concentration. Hexamethyldisiloxane (Me₃SiOSiMe₃) was employed as an end-blocker to control the molecular weight (M_n) to approximately 35 000 g mol⁻¹ to eliminate any effects due to large changes in viscosity. Temperature control in the sonochemical systems proved to be extremely difficult despite thermostating so that reactions had to be conducted over a range of temperatures. The

rate of sonochemical polymerization is much faster than the ‘silent’ case as shown in Figure 7. As an example, at 50 °C, the sonochemical reaction is essentially complete in around 45 min whereas the ‘silent’ conversion is only around 20%. Fitting the ‘silent’ data to an Arrhenius treatment of the first order rate constants gave an activation energy of $27 \pm 2 \text{ kJmol}^{-1}$. This compares well to the values of 24 - 27 kJmol^{-1} reported by Chojnowski et al. for the polymerisation of D_4 in dichloromethane³⁶ with triflic acid. The lack of control over the reaction temperature means that the uncertainties in sonochemical rate constants preclude any detailed comparison.

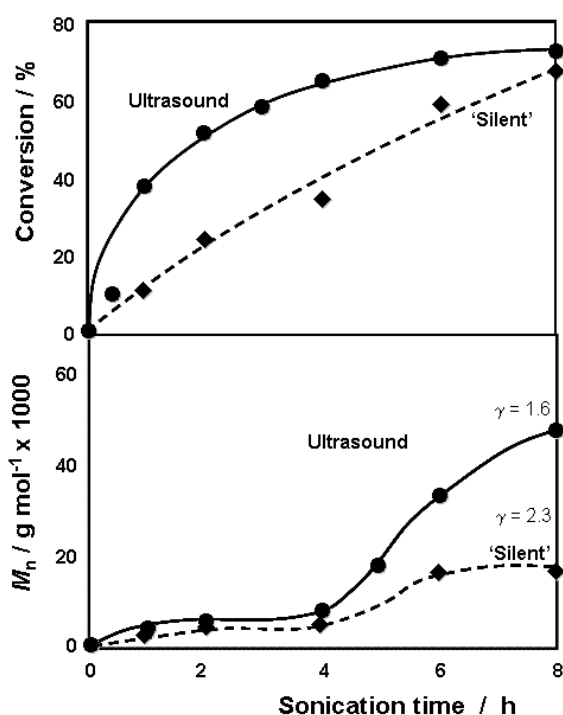


Figure 6. Acid catalysed polymerization of D_4 for at 30 °C. (a) conversion (b) number average molecular weight after 6 hr reaction.

An alternative route to PDMS involves reacting D_4 over a basic catalyst, in this case powdered KOH. A comparison of sonochemical and ‘silent’ results is shown in Figure 8. While the sonochemical reaction is faster, the acceleration in this case is only of the order of 50 – 70%. An end-blocker was again used to control molecular weight to approximately 35 000. The reactions all obeyed first order kinetics after an induction

period which is more pronounced at lower temperatures. The activation energy was calculated as $85 \pm 6 \text{ kJmol}^{-1}$ which compares very well to the reported value³⁷ of the anionic polymerisation of $\sim 82 \text{ kJmol}^{-1}$. The corresponding value for the sonochemical case was $72 \pm 12 \text{ kJmol}^{-1}$, which is marginally lower but may not be significant. This suggests that there is no major change in mechanism and it seems likely that the rate acceleration stems from the enhanced mass transfer to reagents to the surface of the KOH in this heterogeneous system. Microjet and shockwave impacts at the surface of the KOH particles may also cause erosion and particle size reduction, leading to an increase in the surface area of the KOH. The net effect of these two processes is that initiation of the polymerisation will be faster under ultrasound, i.e. the induction period that is seen will be reduced, so that the polymerisation can then begin. Once polymerisation has begun, the rapid movement in the solution generated by cavitation collapse will enhance mass transport, resulting in the increase in rate of the ultrasonic polymerisations.

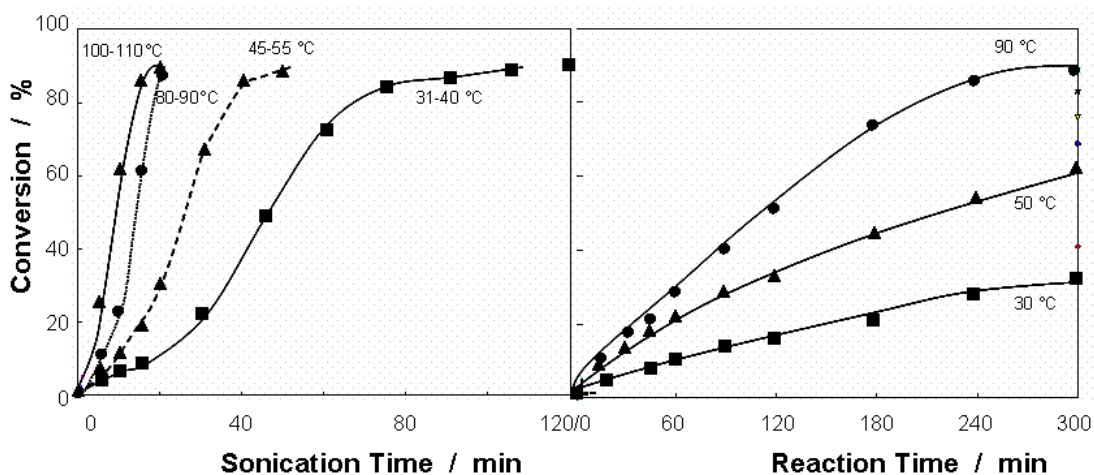


Figure 7. Conversion – time plots for (a) 'silent' and (b) sonochemical polymerization (22 Wcm^{-2}) of D_4 catalysed by H^+

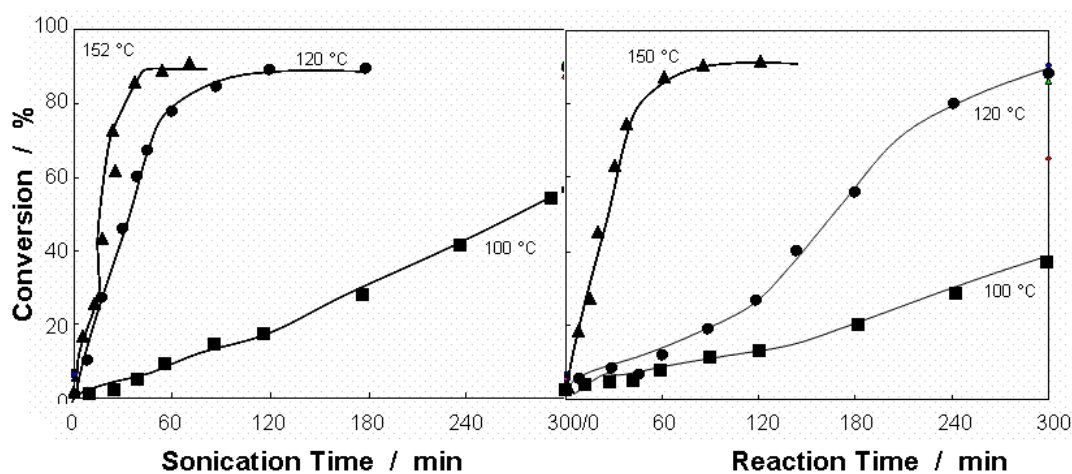
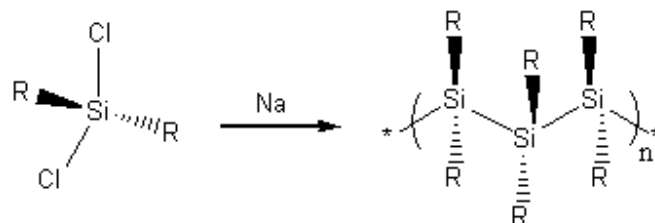


Figure 8. Conversion – time plots for (a) 'silent' and (b) sonochemical polymerization (17 W cm^{-2}) of D_4 catalysed by solid KOH

SONOCHEMICAL PREPARATION OF POLY(ORGANOSILANES)

Although there are a number of methods⁴ for synthesising poly(organosilanes), the most common remains that of Wurtz coupling over sodium (Scheme 4). Until recently, this reaction suffered from irreproducibly low yields, and a very wide bimodal or trimodal molecular weight distribution³⁸. Typically, the major fraction has a molecular weight in the region of $30000 - 4000 \text{ g mol}^{-1}$ along with a much higher molecular weight fraction together with oligomers which are readily removed during work up of the product. This was originally ascribed to competing polymerization mechanisms. However, the very careful characterization of the Wurtz reaction by Jones and co workers has shown that the bimodal distribution is due to the nature of the chain growth process at the surface of the sodium and the main fraction arises naturally from diffusion of conformational 'defects' or 'kinks' along the growing chain. They also showed⁴ that reproducible synthesis of single distribution polymers is at lower temperatures in solvents such as tetrahydrofuran.



Scheme 4. Wurtz coupling synthesis of poly(organosilanes)

The principle of applying ultrasound to the Wurtz reaction arises from the work of Boudjouk and Han³⁹ who demonstrated the facile sonochemical coupling of organosilanes, R_3SiCl , over alkali metals. Matyjaszewski et al.^{40, 41} and Price and Patel⁴² applied ultrasound to the reaction of dichloroorganosilanes and showed that narrower molecular weight distributions could be achieved. Bianconi and coworkers⁴³ as well as Matyjaszewski and Kim⁴⁴ showed that similar reactions could be applied to make soluble poly(silynes), $(RSi)_n$, by reaction of alkyl- or phenyl trichloro silanes.

Some dichloroorganosilanes such as the dimethyl or diphenyl compounds give highly crystalline intractable materials. Here, using ultrasound gives significantly higher yields and shorter reaction times although the difficulty in analysis means that little mechanistic insight can be gained. Longer alkyl substituents (e.g. butyl or hexyl) give soluble materials in higher yield under ultrasound, albeit the yields were still rather low. Work in the author's laboratory showed that higher yields and narrower distributions can be obtained at lower temperatures – a significant environmental impact in obviating the use of molten alkali metals. However, the “model” polysilane about which most mechanistic information is known is poly(methyl phenylsilane), PMPS.

As an example of the rate enhancements that can occur, a conventional synthesis of PMPS in refluxing toluene gave a yield of ca. 15% after 1 hr. Using ultrasound at room temperature gave 43% conversion. In addition, the molecular weight distribution was markedly different in the sonochemical reaction⁴². One possible explanation for this is that polymer chains, once formed, undergo the type of mechanical degradation described above, a process known to occur in PMPS^{45,46}. Figure 9 shows how the molecular weight distribution changes during synthesis. It is clear that the amount of the high molecular weight fraction decreases relative to the main fraction. However, there is no major evidence for the sonochemical degradation as the high molecular weight

fraction increases in value. Some effect on the chain growth must be taking place. This is also suggested by Figure 10 which shows syntheses carried out while varying the ultrasound intensity⁴⁷. At low intensity, the usual bimodal polymer is obtained but as the sonochemical effects are increased, a monomodal (albeit quite wide) distribution is produced. This seems to arise from a reduction in the chain length of the longer fraction combined with an increase in length of the major fraction. The precise reason for these enhancements remains not completely clear. Partly they arise from the increased mass transfer of reagents and break-up of solid particles caused by cavitation in heterogeneous systems. There may also be an influence on the kink diffusion along chains that has been shown^{48,49} to be the major determinant on the molecular weight distribution. Using ultrasound allows a high rate of reaction to be achieved around ambient temperatures and, as suggested by Jones and Holder⁴ this slows down the conformational changes and kink diffusion that limit chain growth. Utilising the various effects that ultrasound can offer should lead to significant improvements along those already achieved in the synthesis of poly(organosilanes).

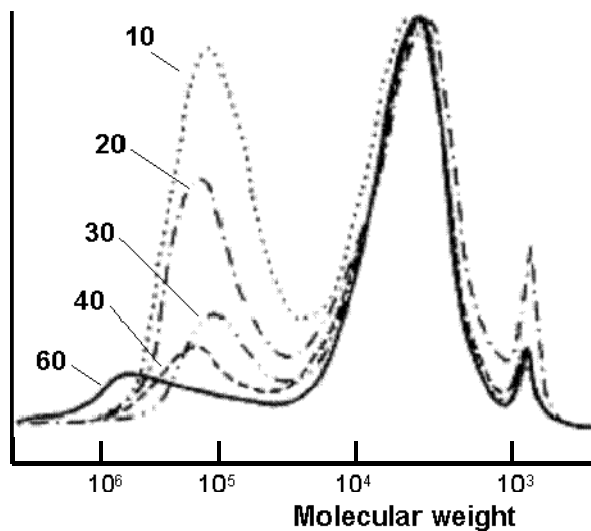


Figure 9. Molecular weight distributions at various times (min) of PMPS during sonochemical Wurtz synthesis at 25° C.

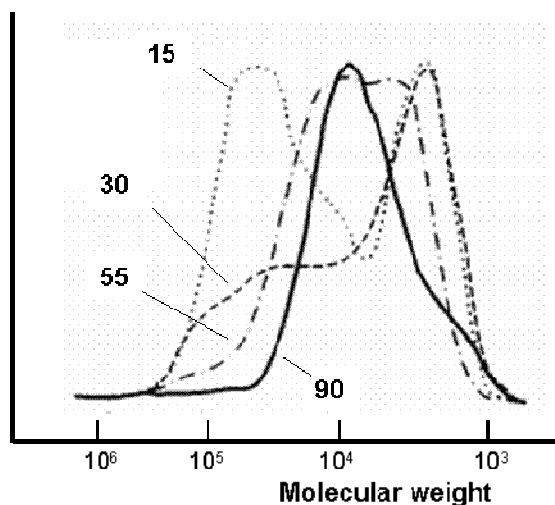


Figure 10. Effect of ultrasound intensity (Wcm^{-2}) on molecular weight distributions after 3 hr reaction during sonochemical Wurtz synthesis at 25°C .

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