

Wurtz synthesis of a high-molecular-weight organostannane–organosilane copolymer

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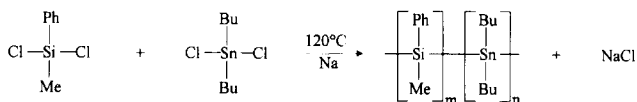
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An organosilane–organostannane copolymer of average molecular mass approaching 10 000 Daltons has been prepared by the reaction of dichloromethylphenylsilane and dichloro-*n*-butylstannane, in a 4 : 1 molar ratio, with sodium metal in the absence of a solvent. Its subsequent fractionation using hexane led to a product of $M_w = 15100$ with an almost normal distribution ($M_w/M_n = 2.3$) in 11% yield. Nuclear magnetic resonance spectroscopy indicates an Si : Sn molar ratio of 6.2 : 1. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Of the polymers of group IVb elements, high-molecular-weight polysilanes and polygermanes are prepared by the *Wurtz*-coupling technique in which diorganodichlorosilanes or diorganodichlorogermanes in a high boiling, refluxing solvent are reacted with molten sodium^{1,2}. This technique has also been used to prepare organosilane–organogermane copolymers^{3–5}. The preparation of polystannanes by the standard *Wurtz* coupling reaction has proved to be more difficult, but recently the synthesis of high-molecular-weight polystannanes from an *n*-Bu₂SnCl₂/Na/15-crown-5 mixture in a toluene/heptane solvent system⁶, and by the dehydropolymerization of *n*-Bu₂SnH₂ catalysed by CpCp[†]Zr[Si(SiMe₃)₃]Me have been reported^{7,8}. However, there are discrepancies between the quoted structural characteristics of what should be identical polymers prepared by these different methods. Matyjaszewski and co-workers^{9,10} have reported the preparation of organosilane–organostannane copolymers using an ultrasonic method, but these were of a relatively low molecular weight and have a broad distribution (typically $M_w = 4000$, $M_w/M_n = 3.7$). We report here the preparation of a relatively high molecular weight organosilane–organostannane copolymer prepared by the *Wurtz* coupling of dichloromethylphenylsilane with di-*n*-butyldichlorostannane in the absence of a solvent (see *Scheme 1*).



Scheme 1

Experimental

Di-*n*-butyldichlorostannane (1 molar equivalent) was dissolved in dichloromethylphenylsilane (4 molar equivalents) and added to a slight stoichiometric excess of sodium under argon at room temperature. This mixture, where the dichloromethylphenylsilane is in effect both solvent and reagent, was then heated to 120°C with rapid stirring. After 2 min at this temperature the blue colour characteristic of *Wurtz*-type reactions was evident but this rapidly changed to a grey/black colour. After 20 min the mixture was allowed to cool and dry methanol was added. The resultant precipitate was filtered, giving a largely insoluble grey powder and a black paste. Analysis of the paste by size exclusion chromatography (relative to polystyrene standards) revealed a sharp peak at about 460 which is thought to be a cyclic species, and a higher molecular mass fraction at about 1900, as shown in *Figure 1a*. The entire solid sample was then added to tetrahydrofuran, stirred vigorously and repeatedly filtered. Dropwise addition of the filtrate to methanol gave a white solid, $M_w = 9100$, $M_n = 4600$ and $M_w/M_n = 2.0$, in 20% yield. Soxhlet extraction for 1 h with hexane was carried out to remove the remaining low-molecular-weight material[†]. The size exclusion chromatogram of the remaining white powder, shown in *Figure 1b*, was of a high-molecular-weight copolymer (copolymer I) in 11% yield, for which $M_w = 15100$, $M_n = 6500$ and $M_w/M_n = 2.3$.

For the purposes of comparison, another copolymer (copolymer II) was also prepared by the conventional *Wurtz* coupling reaction of dichlorodi-*n*-butylstannane and dichloromethylphenylsilane with a molten sodium dispersion in refluxing toluene over 2.5 h. Following similar isolation procedures, the size exclusion chromatogram of this polymer gave molecular weight parameters $M_w = 3000$ and $M_w/M_n = 1.5$.

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† Denotes permethylated cyclopentadiene

† It became apparent during this extraction that a softening and/or melting of the solid occurred as globules of white solid were clearly visible outside the extraction thimble during the procedure

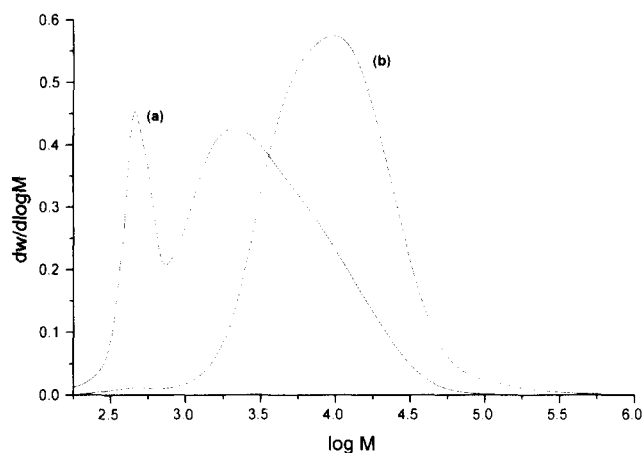


Figure 1 Size exclusion chromatograms of the organosilane/organostannane copolymer I: (a) as prepared and (b) after precipitation in methanol and fractionation with hexane

Results and discussion

The copolymers were characterized by Fourier transform infra-red (FTi.r.) spectroscopy, ultraviolet (u.v.) spectroscopy, proton (^1H), proton-decoupled carbon-13 ($^{13}\text{C}\{^1\text{H}\}$) and proton-decoupled silicon-29 ($^{29}\text{Si}\{^1\text{H}\}$) nuclear magnetic resonance (n.m.r.) spectroscopy and differential scanning calorimetry (d.s.c.). The ^1H n.m.r. spectrum of copolymer I showed a broad peak at about 7 ppm assignable to phenyl groups and a broad overlapping series of peaks from 1.2 to -1.2 ppm which are attributable to MeSi and the *n*-BuSn alkyl resonances. In the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum, in addition to the phenyl peaks at 135 and 127 ppm and those centred at -7 ppm attributable to the MeSi group, others were observed at 31, 27.5, 13 and 8 ppm. These can reasonably be attributed to the carbon atoms in the four distinct environments of an *n*-BuSn unit.

The $^{29}\text{Si}\{^1\text{H}\}$ spectrum of the polymer is shown in Figure 2 along with that for a poly(methylphenylsilane) (PMPS) sample prepared by a typical Wurtz coupling reaction. As well as showing the characteristic peaks at -39.3 , -39.7 and -41.1 ppm attributable to the heterotactic, syndiotactic and isotactic triads in PMPS^{11,12}, a peak at -31.8 ppm is evident. This is attributed to silicon atoms adjacent to tin units. This assignment does not distinguish between the several possible tin environments which might include isolated placements, short sequences and end-groups, but the evident downfield tail of the peak indicates a mixture of two or more structural environments. Whilst integration of the two groups of silicon resonances on the assumption that the peak at -31.8 ppm represents two silicon units adjacent to a single $-\text{SnBu}_2-$ segment reveals an Si:Sn molar ratio of 8.4:1, integration of the ^1H n.m.r. spectrum gives an Si:Sn molar ratio of 6.2:1. This supports a view that a significant portion of the -31.8 ppm resonance in the $^{29}\text{Si}\{^1\text{H}\}$ spectrum corresponds to Si units adjacent to Sn sequences and/or Sn end-groups. The latter would seem to be the more likely when the greater difficulty experienced in the homopolymerization of dichlorodiorganostannanes to give high polymers compared with that of dichloroorganosilanes is considered⁶⁻⁸.

Figure 2c is the $^{29}\text{Si}\{^1\text{H}\}$ spectrum of copolymer II and its size exclusion chromatogram is shown in Figure 3 alongside that for copolymer I. Whilst the molecular

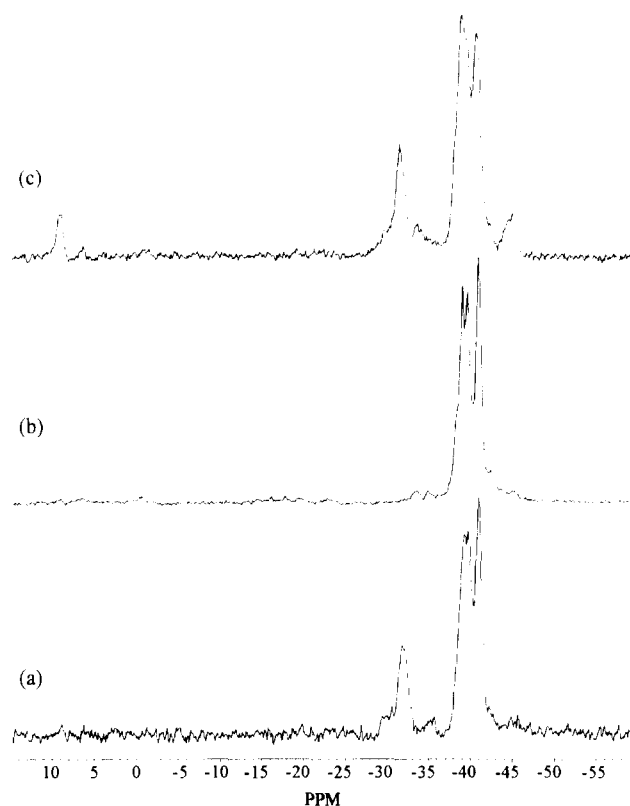


Figure 2 $^{29}\text{Si}\{^1\text{H}\}$ n.m.r. spectra of: (a) organosilane/organostannane copolymer I prepared by Wurtz-coupling in the absence of a solvent, (b) a PMPS sample prepared by the standard Wurtz reductive coupling in boiling diethyl ether, and (c) the organostannane/organosilane copolymer II prepared by Wurtz coupling in toluene solution

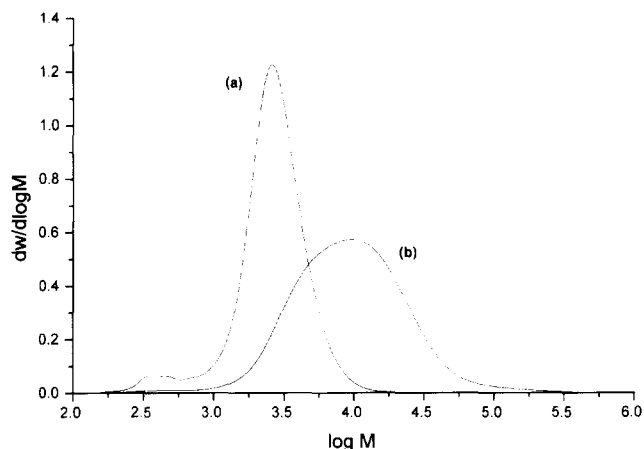


Figure 3 Overlaid size exclusion chromatograms of the organosilane/organostannane copolymers

weight parameters of copolymer II are similar to those reported for the organostannane-organosilane copolymer prepared by Matyjaszewski and co-workers^{9,10}, they are noticeably lower than those observed for the Wurtz coupling in the absence of solvent. It is worth noting that the dehydropolymerization of di-*n*-butylstannane in the absence of a solvent led similarly to a polymer of substantially higher molecular weight than one prepared in toluene^{7,8}. Thus it seems that the inclusion of solvent has a deleterious effect on organosilane/organostannane homo- or copolymerizations. This tenet is supported by closer analysis of the

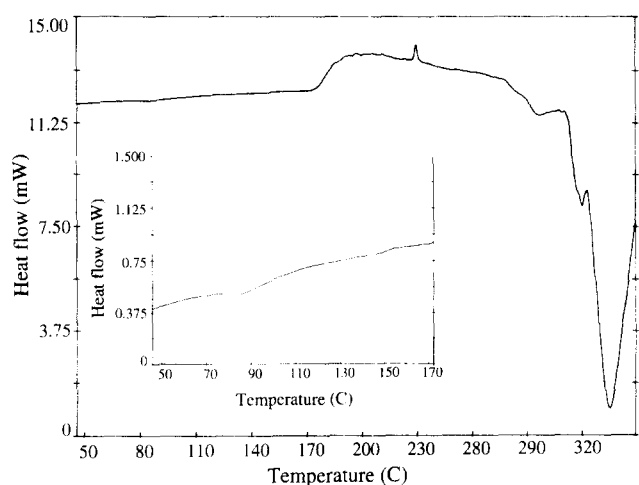


Figure 4 D.s.c. traces of the organosilane/organostannane copolymer I

$^{29}\text{Si}\{^1\text{H}\}$ spectrum of Figure 2c. In addition to the resonances seen in Figure 2a, new ones centered at -34 , -45 and 9 ppm are clearly evident. Those at -34 and -45 ppm have previously been assigned to silicon atoms at structural defects in the PMPS chain, i.e. the silicon atom at a branch point and three silicon atoms of the adjacent strained silane units, respectively¹³. Thus, a greater degree of branching appears to be present in copolymer II than is usually encountered in a PMPS prepared by the normal Wurtz-coupling reaction in the presence of a solvent. The remaining peak at 9 ppm is tentatively assigned to polymer chain end-groups or siloxane linkages (established during the isolation procedures), both of which would be expected to be more evident in this spectrum than in the spectrum of the corresponding unbranched, high-molecular-weight copolymer I.

U.v. spectroscopy of copolymer I revealed a λ_{max} at 342 nm. For comparison, PMPS samples prepared by the Wurtz method typically have λ_{max} at 338 nm, thus a slight redshift in the electronic absorption is observed. It is likely that incorporation of higher molar ratios of Sn will lead to further increases in λ_{max} as has been observed for the corresponding organosilane/organogermane copolymers³.

Of further interest is the thermal behaviour of copolymer I for which a typical d.s.c. trace is shown in Figure 4. A small but reproducible thermal event starting at about 70°C is just discernible (see inset) and this is tentatively assigned as a glass transition. The glass transition temperature (T_g) of PMPS appears as a very broad, molecular-weight-dependent transition in the

range 95 – 120°C and is not readily detected by d.s.c.^{14,15}. A lower value for the T_g of the copolymer is to be expected when the disruption to the PMPS chains resulting from the introduction of di-*n*-butylstannane units is considered. The broad endotherm starting at 190°C , which corresponds to the melting of the sample, appears to be overlapped by the decomposition exotherm observed at temperatures above 250°C .

Conclusion

It has been shown that relatively high molecular weight copolymers of di-*n*-butylstannane and methylphenylsilane can be prepared using the Wurtz coupling procedure. In addition to the synthesis of novel copolymers with potentially interesting physical properties, the continued study of such preparations by Wurtz coupling with and without solvent will lead to greater understanding of this method as it is applied to the synthesis of polymers of the group IVb elements, and in particular to the roles of comonomers and any solvents that might be used.

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