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Sacrificial Additives in the Wurtz Synthesis of Polysilanes

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High molecular weight substituted silane polymers have interesting electronic properties which have been attributed to extensive σ electron delocalization in the polymer backbone.[1,2] As a result, these materials have elicited significant scientific interest and a number of potential applications have arisen. In addition to earlier applications[2] such as ceramic precursors, photoconducting and hole transporting media, and materials for multilayer microlithography, more recently they have been auditioned as potential optical storage media,[3] active materials for xerographic multiduplication,[4] new electroluminescent polymers,[5] and materials with interesting nonlinear optical properties,[6–11] including the recent demonstration of fast photorefractive grating formation in a nonlinear optical (NLO) guest doped polysilane.[12]

The first polysilane derivatives were prepared in the 1920s by Kipping by the Wurtz-type coupling of aryl-substituted dichlorosilanes.[13] The explosion in interest in these materials over the last 15 years has led to the development of alternative synthetic procedures including transition-metal dehydrogenation of silanes,[14,15] anionic polymerization of masked disilanes,[16] and ring-opening polymerization of strained cyclosilanes.[17] In spite of this, the Wurtz-type polymerization remains the most generally useful synthetic approach to the preparation of high molecular weight, linear polysilanes.

The high-temperature Wurtz coupling, usually run in inert solvents boiling above the melting point of the metal reductant, is a complex, exothermic, heterogeneous reaction usually resulting in polymodal polymeric products which is sensitive to temperature, solvent, rate and order of reagent addition, stirring rates, etc.[1,2] As such, process control is marginal at best. The use of polar additives such as polyethers, crown ethers, cryptands, etc., often leads to improved polymer yields and dispersities but *always* at the expense of molecular weight.[1,2,18,19] This decrease in polymer molecular weights is particularly troublesome for reactive monomers such as diaryl- and alkylaryl-substituted dichlorosilanes.

We have recently described the improvement in process control and product polymer properties which is achievable using low-temperature polymerization techniques where the reaction temperature is maintained below the melting point of the metal reductant.[19,20] Other workers have also emphasized the advantages of low-temperature Wurtz polymerization conditions.[21–23] However, even at lower reaction temperatures, the use of dipolar additives always greatly decreases the molecular weight of the isolated products.[19,20] We report here the use of consumable (sacrificial) additives such as ethyl acetate which not only often significantly improves the polymer yields, but also leads to high molecular weight products even from reactive diaryl- and alkylaryl-substituted monomers.

We have tested a number of sacrificial additives in the Wurtz-type polymerization of dichlorosilanes with sodium. These include acetates and higher esters, alcohols, α-diketones, aryl ketones, α,ω-diesters, diaryl ketones, etc. Of these, acetate esters, in particular ethyl acetate, have produced the best results to date. Results for polymerizations run at 65 °C are shown in Table 1. In these studies, the sodium was dispersed at 100 °C in toluene and the reaction mixture cooled to 65 °C. The monomer in toluene (0.4 M) was added over 10 min (final monomer concentration 0.2 M) at 65–70 °C. The ethyl acetate was added 15–30 min after the monomer addition was comlplete. The reactions were run until no monomer was detectable by GLPC analysis (usually ca. ~2 h for dichloroarylalkylsilanes) and filtered after cooling. After washing the organic phase with water and drying, the polymer was precipitated with 2-propanol and dried under vacuum. A lower molecular weight fraction of cyclics and oligomers does not precipitate. In the examples studied, the mass balance was almost quantitative and no insoluble organic material was produced. Increases in the yield of high polymer come at the expense of the oligomer fraction. For those monomers which readily polymerize at 65 °C without additives (entries 1–3), the yield of isolated polymer increases significantly in the presence of EtOAc while the molecular weights are comparable to those runs without additives. Similar improvements are realized relative to polymerizations containing 15-crown-5. For those examples where the monomers are intrinsically unreactive at 65 °C (entries 4–6), the use of EtOAc results in the formation of high molecular weight polymer. For the specific example n-PrMeSiCl$_2$ (entry 6), the use of 15-crown-5 leads to a slightly higher product yield of significantly lower molecular weight material than was obtained using ethyl acetate. The improvement in polymer yield achieved by the use of ethyl acetate as an additive is more clearly shown by the bar graph in Figure 1.

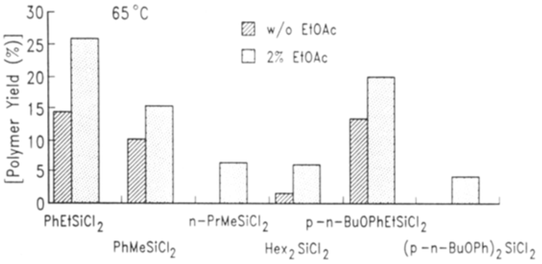

Figure 1. Effect of ethyl acetate on the Wurtz-type polymerization at 65 °C.

The data in Table 2 show the effect of adding ethyl acetate when the polymerization is run in refluxing toluene above the melting point of sodium (97 °C). These results suggest that there is generally little benefit achieved by adding ethyl acetate for the polymerization of monomers which are themselves already intrinsically quite reactive under the reaction conditions (entries 1 and 2). In these cases, even though the apparent yield of polymer increases with EtOAc, the molecular weight distributions are distinctly bimodal. However, for monomers of low or moderate reactivity (entries 3–5), the addition of EtOAc leads to improved yields of high molecular weight polymers. For example, although the yield from polymerization of the particularly unreactive, electron-rich monomer (3,5-dimethoxyphenyl)ethyldichlorosilane is less than 5% using EtOAc (entry 3b), there is no high polymer produced in the absence of the additive. In the case of n-PrMeSiCl$_2$, the yields using EtOAc are comparable to those obtained with crown ethers, although the molecular weight is slightly higher for the former. Surprisingly, the use of crown ether additives in the polymerization can add an additional complication, particularly in the polymerization of dichloroalkylarylsilanes. These polymeric products are somewhat unstable in the presence of crown ethers even at 65

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Table 1. Low-Temperature Wurtz-Type Polymerization: 65 °C

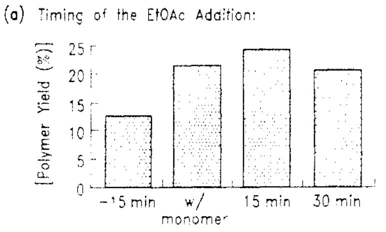
entry	monomer[a]	additive	polymer yield (%)	$M_w \times 10^{-3}$	M_w/M_n
1a	$PhMeSiCl_2$		10.2	422	2.5
1b	$PhMeSiCl_2$	2% EtOAc	15.3	337	3.3
1c	$PhMeSiCl_2$	2% 15-crown-5	14.2	17.3	2.3
2a	$PhEtSiCl_2$		14.5	756	2.4
2b	$PhEtSiCl_2$	2% EtOAc	26.0	922	2.8
2c	$PhEtSiCl_2$	2% 15-crown-5	9.4	40.7	3.8
3a	p-n-$BuOPhEtSiCl_2$		13.5	1130	3.3
3b	p-n-$BuOPhEtSiCl_2$	2% EtOAc	20.0	1260	3.1
4a	(p-n-$BuOPh)_2SiCl_2$			NR	
4b	(p-n-$BuOPh)_2SiCl_2$	2% EtOAc	4.0	2550	3.4
5a	n-Hex_2SiCl_2		1.6	1680	1.6
5b	n-Hex_2SiCl_2	2% EtOAc	6.3	1880	1.4
6a	n-$PrMeSiCl_2$			oligomers	
6b	n-$PrMeSiCl_2$	2% EtOAc	6.7	78.2	2.9
6c	n-$PrMeSiCl_2$	2% 15-crown-5	9.9	25.6	2.7

[a] Toluene solvent, 65 °C, 2.2 mol of sodium/mol of monomer.

Table 2. High-Temperature Wurtz-Type Polymerization: 110 °C

entry	monomer[a]	additive	polymer yield (%)	$M_w \times 10^{-3}$	M_w/M_n
1a	$MePhSiCl_2$		11.2	657(84), 11.0(16)	3.0/1.4
1b	$MePhSiCl_2$	2% EtOAc	16.1	431(43), 11.6(57)	2.1/2.0
1c	$MePhSiCl_2$	2% 15-crown-5	15.7	8.9	2.3
2a	$EtPhSiCl_2$		14.8	1000(55), 60(45)	2.5/1.5
2b	$EtPhSiCl_2$	2% EtOAc	17.3	1100(35), 14.4(65)	1.9/1.5
2c	$PhEtSiCl_2$	2% 15-crown-5	11.9	0.5	
3a	3,5-$Me_2OPhEtSiCl_2$				
3b	3,5-$Me_2OPhEtSiCl_2$	2% EtOAc	3.0	1150(85), 19.1(15)	2.4/1.4
4a	n-Hex_2SiCl_2		5.1	1434(93), 8.3(7)	2.2/1.3
4b	n-Hex_2SiCl_2	2% EtoAc	12.6	1300	1.8
5a	n-$PrMeSiCl_2$		5.8	137(32), 6.8(58) 0.41(8)	1.6/2.2
5b	n-$PrMeSiCl_2$	2% EtOAc	11.1	31.3	2.6
5c	n-$PrMeSiCl_2$	2% 15-crown-5	10.9	20.2	3.4

[a] Toluene solvent, 110 °C, 2.2 mol of sodium/mol of monomer.



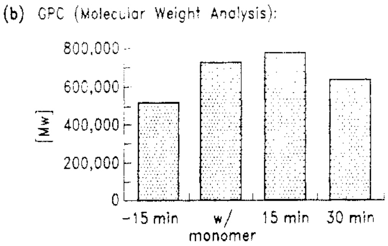


Figure 2. Effect of timing of the addition of ethyl acetate on the yield (a) and the polymer molecular weight (b) in the Wurtz-type polymerization of dichloroethylphenylsilane.

°C, and the molecular weights degrade with time. In control reactions, we observed that poly(ethylphenylsilane) was more susceptible to degradation than poly(methylphenylsilane), and this effect was exacerbated at 110 °C. For this reason, short reaction times (<2 h) are recommended for these monomers in the presence of crown ether additives.

Using the polymerization of dichloroethylphenylsilane as a typical model reaction, the effect of both the concentration of the ethyl acetate additive and timing of the addition was studied. The data are shown in bar graph form in Figure 2. Surprisingly, the additive is most effective when added subsequent to the monomer, after the polymerization has already proceeded to some extent. Typically we find that the optimal point for introduction varies with monomer, but for reactive monomers, the best results are achieved if it is added soon after the reaction mixture begins to assume the characteristic blue–purple color. Figure 2b shows that the molecular weight of the isolated polymer roughly tracks the polymer yields shown in Figure 2a.

The amount of additive incorporated also appears to be somewhat critical. For the example discussed, 2 mol % (based on sodium) appears to be about ideal. Much lower concentrations (e.g., 0.5 mol%) lead to no improvement in yield, while larger amounts (5–10%) not only reduce the isolated yield by factors ranging from 5 to 8 but also lead to a strongly bimodal polymer distribution.

The actual role of ethyl acetate in the Wurtz polymerization of dichlorosilanes is not well understood at this time. Earlier workers have reported using much larger quantities of this material in the coupling of pentamethyldisilyl chloride[24] and the formation of branched silyl anions[25] using sodium metal. Ethyl acetate was employed in these examples without comment, and use of this additive seems to have been largely ignored since then. At this time, we can only speculate on the role of this additive in the Wurtz-type polymerization based on certain empirical observations. First, it is generally observed that the use of this additive has relatively little effect on the molecular weight of the isolated polymer product. For those reactions where the yields are improved relative to no additive, the molecular weights are comparable in either case. It seems unlikely, therefore, that the role of the additive is chain extension of a preformed, but reactively functionalized, oligomeric or polymeric polysilane. Second, we have observed that there is relatively little change in the initial rate of disappearance of the aryl monomers either with or without the ethyl acetate. In either case, the rate of disappearance is quite rapid, even at 65 °C. Finally, the additive is most effective when added *after* the polymerization has initiated and proceeded to some extent (see Figure 2) and there is an optimal quantity (i.e., too little has no effect and too much is very detrimental). Based on circumstantial evidence at this point, it seems possible that the role of the additive may be to penetrate the coated (sodium chloride, oligomer, polymer, etc.) sodium particles and reactivate the surface toward continued polymerization.

The effectiveness of the ester additive also depends subtly on structure. Ethyl acetate is the most effective additive (poly(ethylphenylsilane), yield 26%), while ethyl isovalerate and diethyl succinate were much less so (polymer yields, 7–9%). The effect of ethyl propionate was intermediate (polymer yield, 16%). Interestingly, both ethyl acetate and ethyl propionate in concentrated solution react only slowly with sodium and give relatively poor yields of acyloin-type products.[26] The major products from these esters under the conditions are β-ketoesters. Higher esters, branched esters, and α,ω-diesters, on the other hand, react much more rapidly with sodium to yield acyloin products in higher yields with little condensation to produce β-ketoesters. The implication here is that esters which form acyloin-type products in high yields in concentrated solution are less effective additives for the Wurtz-type polymerization.

In summary, we report that certain sacrificial additives such as acetate esters (most preferably ethyl acetate) can significantly increase the polymer yields both at low and high temperatures (depending on monomer reactivity) without causing a substantial decrease in the molecular weight. While the technique is most effective for diaryl- and alkylaryl-substituted dichlorosilanes, under certain conditions advantages are realized for dialkyl derivatives as well.

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