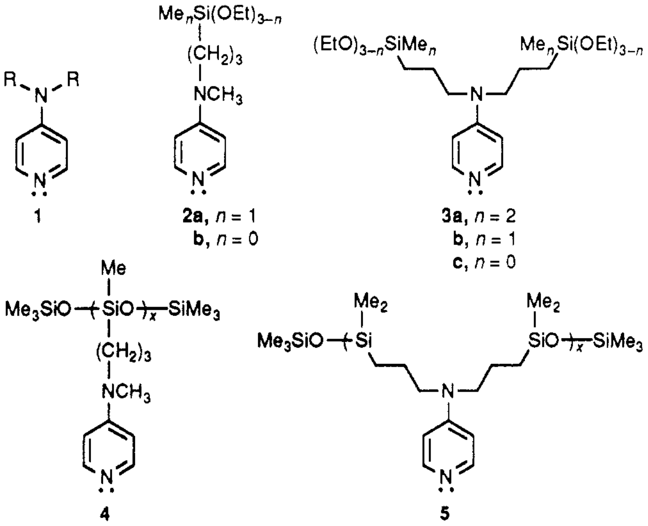
New Transacylation Catalysts: Silanes and Siloxanes Functionalized with 4-(Dialkylamino)pyridine Moieties

The high nucleophilicity of 4-(dialkylamino)pyridines (DAAP, 1; Chart I) has been well-established with a substantial number of monomolecular[1-3] and polymeric variants.[4-14] These species exhibit remarkable catalytic activity in acylation reactions of derivatives of carbon,[1-14] phosphorus,[15] and sulfur[16] acids and in silylation,[1,2,16,17] ester rearrangement,[6d] polymerization,[18] and redox[8] reactions. Polysiloxanes are well-known for their broadly applicable physical and dynamic-mechanical properties (e.g., flexibility, low-temperature elasticity, hydrophobicity, and thermooxidative stability). We have embarked on a program to combine the inherently useful properties of polysiloxanes with the catalytic (supernucleophilic[19,20]) properties of 1. We report the first-time synthesis and characterization of a variety of monomeric silanes (2 and 3) with the DAAP moiety. Since 2 may contain mono-, di-, or trifunctionality and 3 may contain di-, tetra-, or hexafunctionality (n = 2, 1, and 0, respectively), which is hydrolytically sensitive, the monomers can furnish (a) linear homopolymers 4 from **2a** with pendant DAAP functions and 5 from **3a** with intrachain DAAP functions and (b) a variety of cross-linked polymers with all residues having DAAP functions (e.g., 6 from **2b** and 7 and 8 from **3b** and **3c**, respectively).

The pendant DAAP diethoxysilane, **2a**, was prepared in 74% yield by hydrosilation of 4-(*N*-methylallylamino)pyridine (**9**), which is prepared by reaction of *N*-methylallylamine and 4-chloropyridine (**10**),[21] with diethoxymethylsilane in the presence of catalytic quantities of chloroplatinic acid in a sealed ampule at 130 °C for 10 h (Scheme I). Silane **2b** was obtained in 40% yield by the reaction of **9** with $(EtO)_3SiH$. Silane **3a** was obtained in a similar manner in 65% yield from dimethylethoxysilane and 4-(diallylamino)pyridine (**11**), which is prepared by the reaction of diallylamine and **10**.[21] Compounds **3b** and **3c** were obtained by reaction of **11** with $Me(EtO)_2SiH$ and $(EtO)_3SiH$ in 25% and 20% yield, respectively. Polymeric siloxane, **4**, was obtained in 65% yield by hydrolytic condensation polymerization of **2a** with 2 equiv of water and a catalytic amount of $Me_4N^+OH^-$ in THF/*i*-PrOH at room temperature for 12 h followed by trimethylsiloxy end blocking with bis(trimethylsilyl)acetamide (BSA) in CH_2Cl_2 at room temperature (Scheme I). Similar reactions were used to convert monomer **3a** to linear polymer **5** (90% yield). The tri- (**2b**), tetra- (**3b**), and hexa- (**3c**) functional monomers were converted to the corresponding polymers (**6**–**8**) by hydrolytic polycondensation in THF/*i*-PrOH at 60 °C for 12 h in the presence of catalytic quantities of Me_4NOH (Scheme II). Polymers **4** and **5** are pale yellow fluids, which are soluble in CH_2Cl_2, THF, and methanol. It is noteworthy that the polymer from monomer **2b** affords a yellow solid, **6**, which is soluble in CH_2Cl_2 and THF. The solubility characteristics of **6** suggest that the polymer may have either a ladderlike, polyhedral (cagelike), or oligomeric structure as opposed to a cross-linked network. Polymers **4**–**6** were characterized by IR and ^1H and ^{13}C NMR spectra and thermal degradative mass spectral analysis. Polymers **7** and **8** were characterized by IR and thermal analysis. The molecular weight of polymers **4** and **5** was determined by either end-group analysis using ^1H NMR when the average degree of polymerization (DP) was less than 10 (M_n > 2000) or size-exclusion chromatography in dimethylacetamide at 80 °C when the DP was larger than 10. For example, the largest number-average molecular weight for **5** was approximately 5000.

Chart I



1

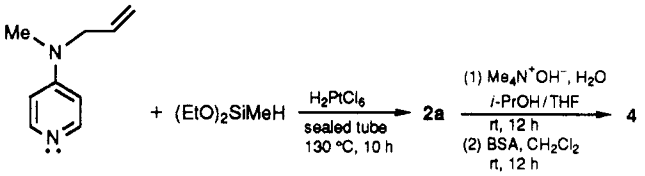
2a, n = 1
b, n = 0

3a, n = 2
b, n = 1
c, n = 0

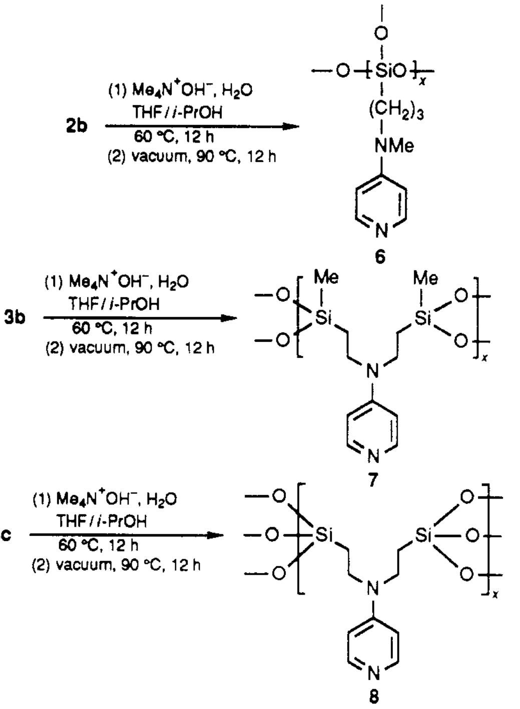
4

5

Scheme I



Scheme II



The two homopolymers, **4** and **5**, differ significantly in distribution between CH_2Cl_2/H_2O phases when titrated with hydrochloric acid. The water solubility of polymer **4**, which has DAAP units pendant to a siloxane chain, is directly proportional to the degree of protonation of the DAAP residues. This is consistent with conversion of an organic-soluble strong base to its water-soluble salt by neutralization with aqueous HCl. In contrast, the solubility of polymer **5**, which has DAAP residues that furnish a dialkylamino portion to the polymer backbone, in organic solvent goes through a minimum at an HCl/DAAP residue ratio of 1.0 with a small fraction of the residues protonated. Moreover, the solubility of **5** in water increases with the degree of protonation and reaches a maximum at 1.0

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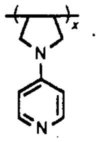
Table I
Relative Reactivity of 4-(Dialkylamino)pyridine Catalysts in Acetylation of 1-Methylcyclohexanol[a]

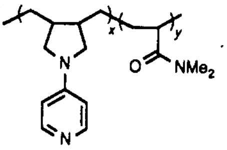
catalyst	relative reactivity (lit.)[b]
DMAP[c]	1.00
4-pyrrolidinopyridine	~1.00
PMVBAP[d]	(0.54)[10]
PMSPAP[e]	(0.77–0.95)[14]
poly[(diallylamino)pyridine][f,9]	0.12
poly(DAAP-*co*-DMAM)[g,9]	0.29
Reillex 404[23]	0.54
4	0.81
5	0.85
6	0.52

[a] The reaction mixture contained acetic anhydride (1 mL), 1-methylcyclohexanol (0.62 mL), triethylamine (1 mL), dodecane (0.2 mL, internal reference), and catalyst (0.10 mmol). The mixture was stirred at room temperature (24–26 °C) and sampled at 31 h for GLC analysis. [b] Relative reactivity = product yield (polymer catalyst)/product yield (DMAP). [c] 4-(Dimethylamino)pyridine. [d] Poly[[*N*-methyl-*N*-(4-vinylbenzyl)amino]pyridine]. [e] Poly[4-[*N*-methyl-*N*-(3-styrenylpropyl)amino]pyridine] cross-linked with divinylbenzene. A different assay method was used, which optimized for the catalysts.

[f]



[g]



equiv of added acid. At this point about 40% of the polymer is in the water layer with approximately half its DAAP residues protonated. With additional acid (i.e., up to 2.5 equiv), the solubility in water decreases. This fascinating and unusual difference in solubility behavior between 4 and 5 is worthy of further investigation since it may be related to the structure and conformation of the polymer chains and may provide a measure of control over the surfactant and/or catalytic properties of these materials.

Acetylation of 1-methylcyclohexanol (**12**) with acetic anhydride,[1,2,22] which is a widely accepted criterion for DAAP activity in transacylation reactions, was used to evaluate the catalytic behavior of polymers **4**–**6**. Comparison of them with vinyl-based polymeric catalysts, which were developed earlier by Menger,[10] Frechet,[14] Mathias,[9] and Reilly Industries,[23] and with 4-pyrrolidinopyridine (PPY)[2] and 4-(dimethylamino)pyridine (DMAP) confirmed the exceptional catalytic activity of the polymeric form of these new materials. The relative reactivity of the DAAP-functionalized polysiloxanes and other catalysts in acetylation of **12** is summarized in Table I. It is relevant that Klotz predicted, for high levels of catalytic group loading, a higher level of catalytic activity for polymers with intrachain sites than with pendant sites.[4c] Our results are consistent with Klotz's suggestion. Work is currently underway to prepare an extensive series of linear and cross-linked polymers and copolymers for examination of their catalytic effectiveness in a variety of transacylation reactions. Attention will be directed to the influence of polymer backbone (vinyl vs siloxane), mode of DAAP attachment (pendant vs intrachain), and microenvironmental structural constraints on catalytic activity.

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(23) Reillex 404, which was provided to us by Reilly Industries, is a cross-linked macroreticular resin with DAAP residues. It is comparable to the structure in Table I, footnote *f*.
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