sensitivity of double bond reactions to protonic catalysis may cover a very wide range of acid strength, depending upon the basicity of the substrate olefin. The formation of I accompanied by little or no ring-opening of 5-methylenenorbornene also indicates that any hydride or alkyl ligands are almost certainly polarized in the direction $[W]^{\delta-}-R^{\delta+}$, the tungsten ion being electron poor and drawing electron density away from the ligand R.

The ^{13}C n.m.r. positions characterizing the various types of $=CH(CH_2)_nCH=$ units are summarized in *Table 1*.

Acknowledgement

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Synthesis of novel siloxane block copolymers for use in photophysical studies

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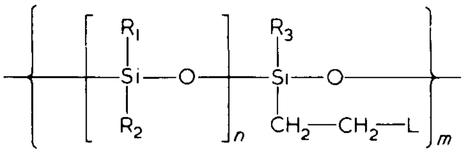
Introduction

In vivo chlorophyll (Chla) is tightly bound to natural proteins[1,2]. This forms so-called 'antenna chlorophyll' which allows efficient energy transfer to the active centre necessary for photosynthesis[1]. The concentration of chlorophyll in chloroplast is high, typically 0.1 M. Lower concentrations of Chla in solution exhibit strong quenching of fluorescence although in the absence of photoreactive centres, or at high dilution, Chla fluorescence can be intense. It has been proposed that the high activity of Chla in choroplasts is associated with a specific and regular organization of the Chla molecules induced by complexing to the protein. Attempts to model chloroplast activity in synthetic polymer systems must then include a photon collection and energy concentration facility corresponding to that exhibited by the Chla–protein–lipid combination, and it is as part progress to this objective that the syntheses described herein are directed.

A number of recent papers[3–9] describe the effect of polymeric species on the energy transfer characteristics of Chla solutions. The polymer used, poly(vinyl pyridine), interacts with the chlorophyll in a non-specific manner leading to a statistical distribution of non-oriented interacting sites along the polymer backbone and to little energy collection advantage. It is clear from these studies that use of a block copolymer with regularly spaced single interacting sites might offer a clear analogue to the *in vivo* collection and concentration system.

Regular or block copolymers can be synthesized by the anionic polymerization of vinyl monomers in the presence of difunctional reagents, usually dihaloalkanes. However, such syntheses do not lend themselves to the regular spacing of functional activity desired in this case. An alternative can be found in the condensation polymerization of siloxane derivates.

In this paper, the synthesis of a series of polymers with pendant groups capable of interacting with Chla is described. The polymers conform to the general structure:



$$\left[\left[-\mathrm{Si}(R_1)(R_2)-O- \right]_n -\mathrm{Si}(R_3)(CH_2-CH_2-L)-O- \right]_m$$

where L is a complexing ligand, separated by 'spacers' of different known lengths. The synthesis is achieved by the heterofunctional condensation of α,ω-difunctional (hydroxy or alkoxy functionality) siloxane oligomers with a difunctional silane containing the ligand groups attached to a silicon atom by means of an ethylene bridge. The critical step is the hydrosilation of the ligand–vinyl derivative:

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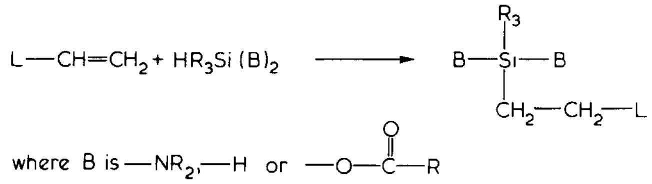
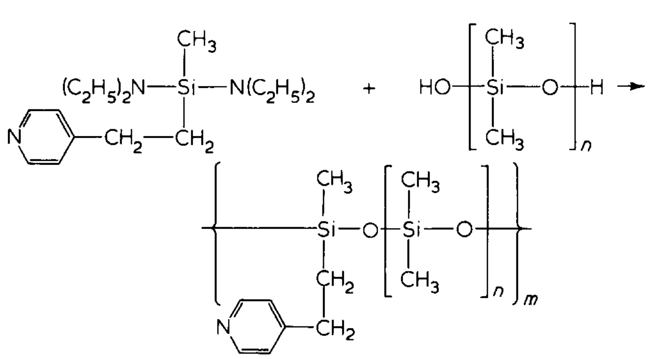


When the condensing functional groups are correctly chosen, the only side reaction possible is cyclization, and when the oligomer unit contains four or five siloxane groups this plays a minor role in the reaction.

Experimental

The starting materials for the copolymer synthesis were (β,4-pyridyl ethyl) methyl bis(diethylamino) silane, and a series of siloxane–diol oligomers with n = 2,4,6. The copolymers were obtained by the reaction:



(Et–Py)MeSiCl$_2$ was synthesized by hydrosilation using a procedure described elsewhere[10,11]. The reaction was rather difficult and the yields (~15%) were considerably lower than reported. The product was distilled under vacuum (363K at 0.5 torr) and so separated from 4-vinyl pyridine (353K at 20 torr). The structure was confirmed by ^{1}H n.m.r. (shifts relative to TMS were: CH_3, τ = 0.1 ppm; CH_2, τ = 0.8 and 2.05 ppm; Py, τ = 6.33 and 7.22 ppm).

(Et–Py)MeSiN(Et)$_2$. Aminolysis of the dichloro derivative was performed in petroleum ether with excess of diethylamine (5 mol of amine to 1 mol dichlorosilane) at room temperature. The product of the reaction was washed with petroleum ether in air. During this process traces of the dichlorosilane were hydrolysed, releasing HCl which formed a salt with the amine and so assisting separation of the product. Absence of hydrolysis during the washing yields a product which contains traces of monosubstituted chlorosilane which is not separated by distillation. The desired product was distilled under vacuum (383K at 10^{-3} torr).

α,ω-HO(Si(Me)$_2$–O)$_n$H. The α,ω-dichlorosiloxanes were prepared by partial hydrolysis of dichlorodimethyl silane. The various oligomers were separated by fractional distillation on a column of approximately 20 theoretical plates. The purity of the fractions was determined by g.l.c. analysis and in all cases found to be higher than 99.5%. The siloxanediols were then obtained by direct hydrolysis of the corresponding dichlorosiloxanes. The 1,3-disiloxanediol was purified by recrystallization from n-hexane followed by sublimation. The 1,7-tetrasiloxanediol and 1,11-hexasiloxanediol were distilled under vacuum (368 and 399K at 1 torr, respectively).

Copolymers. The copolymers were prepared by reaction of 1 mol of (β,4-pyridyl ethyl) methyl bis(diethylamino)silane with 1 mol of siloxanediol under vacuum at approximately 353K for 10–20 h. As the reaction proceeds an increase in viscosity is observed, and a stoichiometric amount of diethylamine is evolved. The progress of the reaction was monitored by collection of the diethylamine in a graduated vessel. Traces of acid impurities increase the rate of polymerization, although their presence is not necessary for the reaction to occur. The resulting copolymers were carefully washed with water to eliminate acidic impurities, and were finally dried first using Na_2SO_4–ether solutions and then on the vacuum line at 406K for 5 h. They were viscous oils soluble in ether.

The pyridine containing homopolymer (n = 0) was obtained by hydrolysis of the dichlorosilane or its bis(diethylamine) derivative, and was purified using the method outlined above.

Characterization. The concentration of pyridyl groups was estimated using u.v. spectroscopy and found to correspond to the concentration predicted by the copolymer formulae. ^{1}H n.m.r. spectra confirmed the presence of the ethyl pyridyl group in the polymer, and a summary of the shift data is presented in *Table 1*.

The Si–CH_3 resonance is indicative of the extent to which the substituent influences the conformational structure of the backbone. The homopolymer in dioxane at room temperature exhibits a complex pyridyl spectrum indicating that the polymer backbone is relatively stiff, as a consequence of the strong interactions between the pendant pyridyl groups. The block copolymer shows differences in both the position and splitting of this resonance, as well as in the pyridyl resonances, indicating that the relative geometry of the pyridyl groups varies with the length of the spacer unit. Thus the objective of synthesizing polymers in which side group ligands can complex a chromophoric unit in different relative configurations is achieved.

The relatively small amounts of polymer obtained limited the number of chracterization methods used. A comparison of viscosities and g.p.c. analyses indicated that the molecular weights, $\bar{M}_w$, lie in the range 100 000– 300 000. The $\bar{M}_w$ was estimated initially from a comparison of the viscosities derived from a comparison of the periods of rotation of a magnetic stirrer in the synthesized polymers and poly(dimethyl siloxanes) of varying molecular weight. These values were confirmed by use of a Waters Associates GPC operating with tetrahydrofuran as solvent and using a refractive index detector, poly(dimethyl siloxane) polymers of varying molecular weights being used as references. No attempt was made to correct for the difference in hydrodynamic interaction between the sample and the reference. Unlike poly(dimethyl siloxanes), these copolymers are in-

Table 1 N.m.r. shift data for the dimethylsiloxane-(4-pyridyl ethyl) methyl bis(diethylamino) silane copolymers

		Shift (ppm) relative to dioxane		
Polymer	Si–CH_3	Si–CH_2	CH_2–Py	Py
Homopolymer	–3.3 (doublet, split 0.5 ppm)	–2.60	–0.85	3.46, 4.78
Dimer (n = 2)	–3.35 (singlet)	–2.60	–0.85	3.54, 4.85
Tetramer (n = 4)	–3.72 (doublet, split 0.1 ppm)	–2.63	–0.80	3.52, 4.82
Hexamer (n = 6)	–3.40 (doublet split 0.1 ppm)	–2.66	–0.85	3.49, 4.83

soluble in aromatic and aliphatic solvents and in nitromethane, but are soluble in ether, dioxane and tetrahydrofuran.

The synthesis described above, although illustrated for the case of vinyl pyridine, is completely general and may be used for the addition of any vinyl monomer onto a siloxane backbone.

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An unsupported water soluble and heat sealable film from predominantly non-fossil raw materials

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The development of a polymeric film product with desirable properties, largely manufactured from renewable raw materials, will be viewed with considerable interest.

Poly(vinyl alcohol) film[1], and films based on combinations of poly(vinyl alcohol) with serum albumin[2] and poly(vinyl alcohol) with low molecular weight poly(ethylene glycol)[3] have been reported.

During the period of rapid development of man-made polymers based on cheap petrochemical raw materials, the potential use of materials incorporating natural products such as starch has been largely passed over, although starches which had been enzyme- or hypochlorite-converted have found extensive use as so-called film-forming starches, employed as pigment binders for paper coating. Such materials have not so far found widespread application as ingredients for unsupported film. For some years, I have been aware that modified starches and poly(vinyl alcohol) can be cosolubilized in water to provide a casting dope for film[4]. The system also makes it possible to impart a degree of water resistance by inclusion of liquid urea–formaldehyde resins which can further condense during the dehydration stage of the subsequent film casting procedure. More important still, the mechanical properties are decisively affected by the inclusion of up to 150 pph of polymers of suitable humectant plasticizers such as water-soluble mono- or oligomeric diols e.g. ethylene glycol, diethylene glycol (Digol) or glycerol. These not only have a plasticizing effect in their own right, but also ensure that the film, after drying, attracts quantities of moisture from the atmosphere which relate to the amount of humectant plasticizer included in the formulation.

The film products thus obtained are brittle in the anhydrous form (i.e. when freshly cast in the manner to be described when the plasticizer content is low). However, even with low plasticizer content, the film becomes tough after attracting its quota of equilibrium moisture. With high plasticizer content, the film shows distinctly elastomeric features, becomes increasingly pliable and clinging and yet maintains surprisingly high strength and elongation at break. Furthermore, all cast film so obtained readily heat-seals to itself, bonds paper to paper and adheres tenaciously to a variety of substrates including glass and certain polymers.

The actual proportions of poly(vinyl alcohol) and starch are not highly critical, within limits. For the present work a ratio of 50:50 by wt (including the equilibrium moisture present in air-dry converted starch – about 10%) was used and a small constant amount of urea and formaldehyde was added to form urea–formaldehyde resin *in situ*. After addition of humectant plasticizer, preparation of the film and storage at constant humidity and temperature, the moisture content was determined.

Materials

The starch was a hypochlorite-converted corn starch for paper coating (Flocote 64, Laing National) with an 'airdry' moisture content of 9–10%. The poly(vinyl alcohol) was an 88 ± 1% hydrolysed product with 19.5–22.7% of residual acetate and $MW \sim 125\,000$ (BDH Chemicals).

Film preparation

The casting dope was prepared in the following manner: 20 g each of airdry starch and poly(vinyl alcohol) powders were weighed into a 600 ml beaker fitted with a stirrer. 2 g urea were added and the mixed solids were wetted out by the addition of 40 ml IMS. This prevented lump formation during the subsequent solubilization. The beaker was then placed in a larger beaker filled with cold water, 10 ml formalin solution (40% w/v), 400 ml water and the pre-determined